

Synthesis of Bismuth-based Nanocomposites for Hydrogen Generation and Degradation of Organic Pollutants

Thesis submitted for the award of degree of

Doctor of Philosophy

by

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Certificate

This is to certify that thesis entitled "Synthesis of Bismuth-based Nanocomposites for Hydrogen Generation and Degradation of Organic Pollutants", is being submitted by Ms. Shelly in fulfillment of the requirement for the award of the Degree of Doctor of Philosophy in the School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala, is a record of candidate's own independent and original research work carried out by her under my supervision and guidance. The matter presented in the thesis has not been submitted in part or full for the award of any degree in any other University or Institute.

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Candidate's Declaration

I, hereby declare that the present work in the thesis entitled “**Synthesis of Bismuth-based Nanocomposites for Hydrogen Generation and Degradation of Organic Pollutants**”, in the fulfillment of the requirement for the award of the Degree of Doctor of Philosophy in the School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my work carried out under the supervision of Dr. Soumen Basu, Professor, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala, India and Dr. Pooja Devi, Principal Scientist, CSIR-CSIO, Chandigarh. The matter embodied in the thesis has not been submitted in part or fully to any other University or Institute for the reward of any degree in India or Abroad.



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Shelly

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List of Abbreviations

AOP	Advanced Oxidation Process
Deg.	Degradation
BOD	Biological oxygen demand
PEC	Photoelectrocatalytic
PC	Photocatalyst
OP	Oxidation photocatalyst
RP	Reduction photocatalyst
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
COD	Chemical oxygen demand
TOC	Total carbon content
Conc.	Concentration
CB	Conduction band
VB	Valence band
DMSO	Dimethyl Sulfoxide
BQ	Benzoquinone
DRS	Diffuse reflectance spectroscopy
EDS	Energy dispersive X-ray spectroscopy
MB	Methylene blue
TC	Tetracycline
SEM	Scanning electron microscopy
pzc	Point of zero charge
XRD	X-ray diffraction
PL	Photoluminescence
XPS	X-ray photoelectron spectroscopy
JCPDS	Joint committee of powder diffraction standards

List of Symbols

%	Percentage
% Deg	Percent degradation or degradation efficiency
min ⁻¹	Per minute
kHz	Kilo hertz
% COD	Percent chemical oxygen demand
% TOC	Percent total carbon content
COD _i	Initial chemical oxygen demand
COD _t	Chemical oxygen demand at certain time
TOC _i	Initial total carbon content
TOC _t	Total carbon content at certain time
A ₀	Initial absorbance of pollutant
A _t	Absorbance of pollutant at a certain time
C ₀	Initial concentration of pollutant
C _t	Concentration of pollutant at a certain time
k	Rate constant
mmol	Millimole
Å	Angstrom
g	Gram
mg	Milligram
g/L	Gram per litre

μL	Microlitre
W/m^2	Watt per meter square
mW/cm^2	Milliwatt per centimeter square
nm	Nanometer
eV	Electron volts
ppm	Parts per million
cm^3/g	Centimeter cube per gram
m^2/g	Meter square per gram
E_g	Band gap energy
α	Absorption coefficient
h	Planck constant
λ	Wavelength
ν	Light frequency
M	Molar
mL	Millilitre
mL/min	Millilitre per minute
mM	Millimolar
Ω	Ohm
nm	Nanometer
$^\circ$	Degree
$^\circ\text{C}$	Degree Celsius
R	Synergy factor

>	Greater than
$\cdot\text{OH}$	Hydroxide radical
$\text{O}_2^{\cdot-}$	Superoxide radical
h^+	Holes
e^-	Electrons
O_2	Oxygen
E_e	Standard free energy on hydrogen scale
E_{VB}	Valence band energy
E_{CB}	Conduction band energy
χ	Mulliken electronegativity
H	Hysteresis Loop
t	Time, min
V	Volts
θ	Theta
mA/cm^2	Milliampere per centimeter square
$\mu\text{A}/\text{cm}^2$	Microampere per centimeter square
$\text{mmoles}/\text{cm}^2/\text{sec}$	Millimoles per centimeter square per sec
E_{fb}	Flat band potential
R_{ct}	Chare transfer resistance

Abstracts

Chapter 1

This chapter highlights the importance of heterojunction photocatalysts with narrow band gap, lower recombination rate, and higher visible light absorption capability. It discusses the negative impacts of modernization, particularly water pollution from various sources, and explores wastewater treatment techniques. It also elaborates the negative impact of the utilization of the fossil fuels and advantage of hydrogen. The significance of heterojunction photocatalysts is explained, and existing research on photodegradation of organic pollutants, and photoelectrocatalytic water splitting is presented. The chapter identifies research gaps and outlines the objectives of the current study.

Chapter 2

In this Chapter, BiVO₄/MoSe₂ (BMS) heterojunction material of various mole ratios was prepared via hydrothermal method. BMS photocatalyst is solar light active, has better charge separation, good surface area, lower recombination rate, and narrow band gap of ~1.5 eV as affirmed through different characterization techniques. The photocatalytic and photoelectrocatalytic experiments were conducted under solar light for tetracycline (TC) degradation and hydrogen production via water splitting, respectively to test out the efficiency of the photocatalyst. Under the illumination of sunlight for 150 min, the 3:1 BiVO₄:MoSe₂ (31BMS) had the maximum degradation efficiency of 91.9 % (rate constant 0.0147 min⁻¹). The GC-MS analysis was also conducted to examine the intermediates and products formed during the photocatalytic degradation of TC. Moreover, the photoelectrochemical hydrogen evolution experiment revealed a significantly improved photocurrent density of 0.433 mA/cm² for 31BMS at 1.23 V vs RHE, under simulated solar light in comparison to BiVO₄ (0.0045 mA/cm²) and MoSe₂ (0.0322 mA/cm²). No change in current density was found for ~330 minutes, thus confirming the stability of the electrode, with constant H₂ evolution rate of 3.59 mmol/cm². The reusability efficacy of the photocatalyst was tested for 7 cycles and the stability was confirmed by XRD, BET and FESEM after the reaction.

Chapter 3

A hydrothermal approach (environmentally safe route) was followed to synthesize eco-friendly, non-toxic, sunlight responsive $\text{BiVO}_4/\text{SnS}_2$ (BVSNS) nanocomposites with varying mole ratios in this Chapter. BVSNS exhibits favorable band gap, high charge carrier mobility, good surface area, lower recombining capability rendering it highly efficient photocatalyst. The superiority of photocatalysts was then tested for the degradation of pharmaceutical pollutants, ofloxacin (oflox) and tetracycline (TC), and PEC water splitting under sunlight illumination. The 1:3 $\text{BiVO}_4:\text{SnS}_2$ (13BVSNS) composite had highest decomposition efficiency of 93.7 and 80.8 % with rate constants of 0.0164 and 0.010 min^{-1} for oflox and TC-degradation, respectively. The GC-MS analysis was also conducted to examine the intermediates and products formed during the photocatalytic degradation of TC. The PEC water splitting experiments revealed that 13BVSNS photoanode exhibited highest photocurrent density of 0.21 mA/cm^2 at 1.23 V vs RHE. The Mott-Schottky experiments demonstrated flat band potential of -0.37 V at 1.23 V vs RHE for the 13BVSNS electrode. As a result, $\sim 21 \mu\text{mol cm}^{-2} \text{sec}^{-1}$ of H_2 was produced and electrode was stable for 6 h. Reusability studies (7 runs) were used to further examine the photocatalyst's efficacy, and post reaction characterization results justified that the materials are highly stable with a long life.

Chapter 4

This Chapter deals with heterojunction photocatalysts that have emerged as promising candidates for addressing significant global challenges related to energy and the environment. In this study, a series of $\text{BiVO}_4/\text{BiOBr}$ composites with varying mole ratios were successfully synthesized using a hydrothermal method. The in-situ synthesis strategy facilitated the formation of a close interfacial contact between BiVO_4 and BiOBr at the depletion zone, resulting in improved charge segregation, migration, and reduced charge recombination. Additionally, the $\text{BiVO}_4/\text{BiOBr}$ nanocomposite exhibited a narrow band gap, increased surface area, and enhanced light absorption capacity, enabling efficient utilization of a broad spectrum of solar energy. This study investigates the influence of different mole ratios of BiVO_4 and BiOBr in a $\text{BiVO}_4/\text{BiOBr}$ nanocomposite on the photocatalytic degradation of tetracycline (TC), a pharmaceutical pollutant, and photoelectrocatalytic water splitting (PEC) under solar light irradiation. Maximum decomposition efficiency of ~ 90.4 % (with a rate constant of 0.0159 min^{-1}) for TC was achieved

with 0.5 g/L of 3:1 BiVO₄ : BiOBr (31BVBI) photocatalyst within 140 min. The stability of the photocatalyst was demonstrated over seven cycles, with significant retention of degradation efficacy. The degraded compounds resulting from the TC abatement were analyzed using GC-MS. Furthermore, TC standards exhibited 78.2% and 87.7% removal of chemical oxygen demand (COD) and total organic carbon (TOC), respectively, while TC tablets showed 64.6% COD removal and 73.8% TOC removal. The PEC water splitting experiments demonstrated that the 31BVBI photoanode achieved the highest photocurrent density of approximately 0.2198 mA/cm² at 1.23 V vs RHE, resulting in the generation of approximately 1.864 mmolcm⁻²sec⁻¹ of hydrogen, while remaining stable for 21600 seconds. The stability of the photocatalyst was confirmed by post-degradation characterizations, which revealed intact crystalline planes, shape, and surface area. Comparisons with existing physicochemical methods used in industries indicate that the reported photocatalyst possesses strong surface catalytic properties and has the potential for application in industrial wastewater treatment and hydrogen generation, offering an advantageous alternative to costly and time-consuming processes.

Chapter 5

The coupling of different oxide materials in a nanohybrid enables the customization of their optical and charge transport properties, leading to improved interfacial charge segregation and migration. In this Chapter, BiVO₄/WO₃ (BVW), a sunlight driven photocatalyst with distinct mole ratios was synthesized via facile hydrothermal approach. The resultant catalyst exhibits a nanorods shape morphology decorated onto dendrite-like matrix, and is studied for photocatalytic elimination of tetracycline (TC) and photoelectrocatalytic (PEC) H₂ production. The effect of illumination time, solution pH, photocatalyst concentration, and mole ratios of BiVO₄ to WO₃ on the photocatalytic abatement of TC were tested sequentially as effective operating factors. Under optimal condition, 3:1 BiVO₄:WO₃ (31BVW) nanohybrid demonstrated a maximum degradation efficacy of 96.2 % (rate constant ~0.0241 min⁻¹), which is much better than its individual components and commercial TiO₂-P25 (50.9 %). The resultant by-products of TC decomposition were analyzed using GC-MS to explain the degradation mechanism. Moreover, as a photoanode, 31BVW showed a high photocurrent density of 0.64 mA/cm² at 1.23 V vs RHE and a steady photocurrent for ~6 h under chronoamperometry study at 1.23 V vs RHE. However, bare BiVO₄ and WO₃ exhibited the photocurrent density of 0.001 mA/cm², and 0.015

mA/cm², respectively at 1.23 V vs RHE. The Mott-Schottky analysis of 31BVW confirm their n-type behavior, with a calculated flat band potential of -0.067 V. The hydrogen production rate was theoretically calculated as 4.56 mmolcm⁻²sec⁻¹ from chronoamperometric measurements. The photocatalyst's efficacy in TC degradation was further established via its reusability upto 7 cycles. Post degradation characterization of catalyst confirm its stability in lieu of practical usage. Comparative studies with existing literature revealed the superiority of reported photocatalysts in both applications. Overall, the binary BVW photocatalyst shows great potential for removing detrimental contaminants as well as H₂ production via PEC water splitting due to efficient charge separation, reduced recombination, high surface area, and widen absorption window of the nanohybrid.

Chapter 6

Heterojunction photocatalysts (PC) with controllable compositions and in-built electric fields have attracted extensive research interest for remediation of environmental pollutants owing to supreme photocatalytic activity. Here, simple hydrothermal route synthesized different mole ratios of BiVO₄/Sb₂S₃ is reported as PC. Inclusion of Sb₂S₃ with BiVO₄ in BiVO₄/Sb₂S₃ composite possess ability to harvest wide spectrum of solar light, increased surface area, and effective charge separation of charge carriers. Efficacy of synthesized catalyst was gauged by photocatalytic abatement of recalcitrant pollutant, tetracycline. Highest decomposition efficacy of 88.7 % (rate constant 0.01557 min⁻¹) was achieved with 0.3 g/L of 1:3 BiVO₄:Sb₂S₃ photocatalyst for tetracycline under sunlight illumination for 120 min. Catalyst was found stable upto 5 cycle with significant retention of its efficacy. Post degradation characterizations revealed that photocatalyst is stable due to intactness of crystalline planes, morphology, and surface area. Further, GC-MS was done to study decomposed products formed by abatement of tetracycline. Moreover, % COD/ TOC removal of 80.9 and 85.4, %, respectively were observed for tetracycline standards, while for real samples, it was found to be 78.3 and 82.1 %, respectively. This signify that photocatalyst have good surface catalytic property in comparison to expensive and time-consuming existing physicochemical approaches in industries.

Chapter 1

Introduction and Literature

1.1 Introduction to nanotechnology and nanoscale

Nanotechnology is a fascinating field that operates at the nanoscale (1-100 nm) and harnesses the power of single atoms and molecules to fabricate structures with practical applications [1]. It encompasses the construction and utilization of systems (physical, chemical, and biological) that possess intricate features spanning from individual atoms to submicron dimensions [2]. This multidisciplinary field holds tremendous potential for developing a diverse range of functional materials with a wide range of applications.

1.2 Nanomaterials and their applications

Nanomaterials particularly nanoparticles, are defined as a group of atoms that are bonded together, typically comprising 10 to 10^5 atoms with an average radius ranging from 1 to 100 nm. Nanomaterials are revolutionizing the field of environmental science by offering innovative and eco-friendly solutions to some of the most pressing ecological challenges. These remarkable materials are making significant contributions, from addressing water scarcity and purification challenges to detecting and eliminating harmful contaminants. Nanoparticles, in particular, have emerged as a game-changing technology with a wide range of applications, including spanning solar energy, wastewater remediation, hydrogen production, catalysis, and much more. Rising energy crises and water pollution are the two most significant problems tackled by the use of nanoparticles, paving the way for a cleaner and sustainable future.

1.2.1 Water pollution

Water, the essence of life and a cherished jewel of nature, is an indispensable resource for the survival of all living beings [3]. However, the world is facing a grave water crisis characterized by a scarcity of safe, hygienic, and high-quality drinking water [4,5]. Rapid industrialization and urbanization have accelerated the emergence of water pollution as a critically pressing environmental issue, posing threats to both humans and the delicate organisms

that inhabit our ecosystems [6]. The quality of surface water has declined due to organic and inorganic pollutants in water bodies brought on by industrial activity [7]. These pollutants are introduced into water bodies, causing a detrimental impact. A range of organic compounds, including pharmaceutical disposable waste from animal husbandries and hospitals, vibrant dyes, and various agrochemicals such as pesticides, weedicides, insecticides, fungicides, and fertilizers, are among the major environmental contaminants [8,9]. These substances pose significant challenges to the health and sustainability of our water ecosystems, necessitating comprehensive efforts to mitigate their adverse effects and restore the pristine state of the surface water [10].

Over the past years, exploitation of synthetic organic dyes and pigments has witnessed a surge across various industries, ranging from food production to textiles, rubber, and printing inks [11,12]. Astonishingly, over 10,000 dyes and pigments find application each year, resulting in a staggering production volume of 7×10^5 tons [13]. Utilizing these dyes is an indispensable aspect of industrial operations, especially within the paper and textile sectors. However, the improper disposal of these vibrant substances, particularly by the industries, has cast a shadow of contamination over the water bodies. Among these industries, the textile sector stands out as the most significant contributor releasing a staggering 50,000 tons of synthetic dyes annually, which pollutes around 17-20 % of our precious water resources [14]. These dyes, with their low biodegradability, high chemical stability, aromaticity, and harmful properties, including carcinogenicity, mutagenicity, and toxicity, pose a significant threat to living organisms and the environment. They cause various health problems, including anemia due to hemolysis, irritations, and gastrointestinal problems [15]. The effluents from dye disposal exhibit high levels of suspended solids, pH, color, temperature, biological oxygen demand (BOD), metals, chemical oxygen demand (COD), and salt content [16]. Notably, synthetic azo dyes and their by-products are challenging to decompose due to the presence of $-N=N-$ linkages, intricate aromatic structures, and sulfonic acid groups [17]. These complex chemical dyes not only impede sunlight penetration thereby harming aquatic photosynthetic plants but also disrupt the overall water type and quality [18]. The need for comprehensive measures to mitigate the environmental impact of these intricate and hazardous substances has become imperative, paving the way for a more sustainable and ecologically responsible approach across these industries [19].

Pesticides are the potent substances employed to combat pests like insects, rodents, fungi, and weeds and possess inherent toxicity [20]. Recently, pesticides have been utilized in the fight against contagious diseases like dengue, malaria, and chikungunya. Similarly, herbicides are deployed to eliminate weeds and enhance agricultural productivity. However, the excessive use of pesticides elevates the risk of hazardous pesticide residues in the atmosphere, water, food, and soil. Shockingly, only 1 % of applied pesticides effectively target the intended species, while the remaining 99 % bioaccumulate throughout the food chain [21]. Regrettably, consumers are exposed to pesticide residues, albeit in relatively lower quantities, through the food they consume, as these chemicals find widespread use in agriculture and food production [22]. Prolonged pesticide exposure has been associated with the development of severe health conditions, including leukemia, Parkinson's disease, depression, asthma, anxiety, hyperactivity disorder, and non-Hodgkin's lymphoma. According to reputable sources such as the United Nations Environment Program and World Health Organization (WHO), a staggering 3 million farmers suffer from severe pesticide poisoning [23]. The escalating use of pesticides and inadequate wastewater disposal raises significant concerns for freshwater, coastal, and marine habitats. Consequently, the removal of toxic pesticides from water sources becomes an imperative task [24]. Some of the extremely poisonous substances known as chemical warfare agents, such as soman, and sarin are among the organophosphorus compounds which are predominantly utilized as agricultural pesticides. These compounds swiftly dissolve in water, air, and soil, perpetually posing a threat to living organisms and the environment. Prolonged exposure to organophosphorus chemicals can lead to adverse effects such as muscle paralysis, disruption of nerve impulse transmission, brain damage, and cholinergic crises [25].

Antibiotics have captivated widespread attention for their vital role in combating infectious diseases across various domains of human life and agricultural practices [26]. However, the prolonged, abusive, and excessive utilization of antibiotics has inflicted profound and lasting damage on the environment [27]. Due to their persistent nature and poor biodegradability, antibiotics are frequently detected in surface and groundwater, resulting from their excessive usage [28,29]. Even at concentrations as low as mg/L or even ng/L, residual antibiotics retain their potent drug resistance and toxicity, posing a long-term accumulation threat to human health, animals as well as to the stability of the ecosystems. The contamination

of water sources with residual antibiotics stems from multiple pathways, including wastewater discharge from hospitals, animal waste, including urine and feces, and leaching from manufacturing facilities [8,30]. Tetracycline (TC), widely employed in aquaculture and veterinary medicine due to its cost-effectiveness and potent antibacterial properties, emerges as the most frequently used antibiotic [31]. However, the presence of TC residues in irrigation or drinking water utilized for fruit and vegetable cultivation fosters the proliferation of antibiotic-resistant bacteria, thereby exerting a detrimental impact on human health [32].

1.2.1.1 Methods for remediation of organic pollutants present in wastewater

Over the years, various methodologies have been employed to eliminate harmful pollutants from water sources effectively. These methodologies encompass a range of approaches, including biological, physical, and chemical processes [33]. Biological processes offer a promising approach for the exclusion of organic detrimental pollutants from wastewater. These processes involve microbiological or enzymatic decomposition and biodegradation, harnessing the power of living organisms to break down and eliminate organic pollutants [34]. However, slow pace, limited controllability, and fluctuations in composition and volume render biological methods ineffective for photocatalytic deprivation of recalcitrant organic pollutants.

Traditional physical methods for instance reverse osmosis, adsorption, and ultrafiltration are commonly employed for pollutant elimination [35]. However, these conventional techniques essentially transfer the contaminants from one medium to another, producing secondary pollution [36]. Additionally, they necessitate additional steps for treating solid waste and regenerating the adsorbent, thereby adding to the overall cost of the process.

Various chemical processes, including chemical oxidation, chlorination, ozonation, precipitation, and chemical oxidation, are commonly used to eliminate the detrimental organic pollutants [37]. However, the formation of toxic and unstable metabolites can pose adverse effects on the well-being of both animals and humans [38].

In recent years, scientists have paid great attention to the oxidation process, particularly the advanced oxidation process (AOP) for treating wastewater. AOPs offer a powerful approach that enables the rapid and non-selective oxidation of contaminants present in water matrices [39]. The process of AOP includes the formation of highly active free radicals for oxidation and

destruction of organic pollutants. Amongst the AOPs, photocatalytic degradation stands out as an effective approach for the abatement of organic pollutants. This method offers the potential for the complete mineralization of pollutants and has the advantage of harnessing natural sunlight as an energy source [40].

1.2.2.2 Photocatalysis as a promising approach for wastewater remediation

Photocatalysis is a revolutionary technique that harnesses the power of solar energy for the abatement of refractory organic contaminants from an aquatic environment, as depicted in **Fig. 1.1** [41]. It has attracted a lot of interest because it is an affordable, non-toxic, eco-friendly, and very successful approach [42]. Also, the photocatalytic breakdown approach assists in completely eliminating refractory organic contaminants from wastewater by converting them to water and carbon dioxide [43]. However, the photocatalytic decomposition method necessitates the formation of an effective visible-light-driven photocatalyst [44].

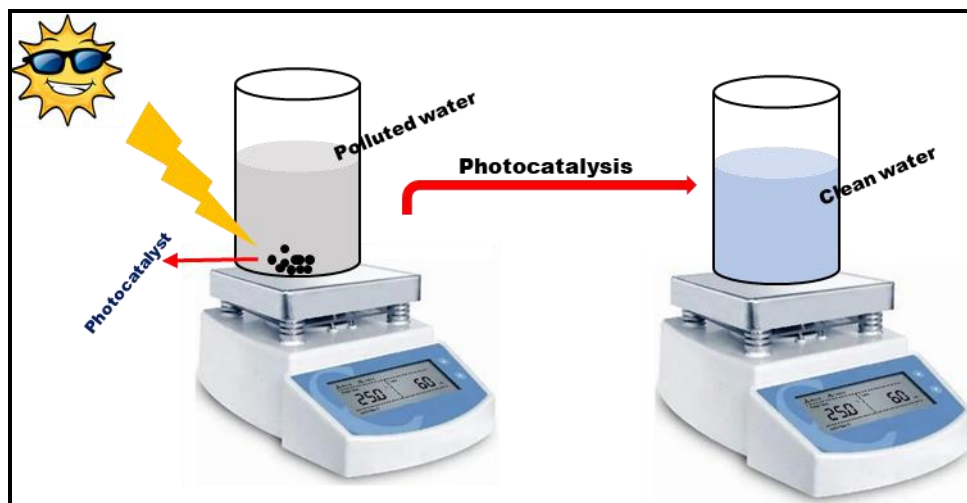


Fig. 1.1 Schematic representation of photocatalysis

1.2.2.3 Principle of photocatalysis

Photocatalysis is a process that involves the absorption of light by a semiconducting photocatalyst, leading to the generation of various reactive species [45]. At absolute zero, the high energy conduction band (CB) of photocatalyst is vacant, while lower energy valence band (VB) is fully occupied by electrons (e^-). However, when the semiconductor absorbs energy ($h\nu$) equal to or more than its band gap (E_g), the e^- present in the VB get excited to the CB, leaving

behind positively charged holes (h^+) as shown in **Eq. 1.1** [46]. This results in the simultaneous presence of e^- and h^+ in the CB and VB, respectively. Under the influence of the internal electric field, produced e^- and h^+ tend to segregate and migrate toward the surface of the particles. Both photogenerated h^+ and e^- have considerable oxidation and reduction capabilities, respectively. These charge carriers are capable of moving across the semiconductor surface, enabling them to engage in redox reactions with adsorbed contaminants [47]. However, when photons having energies lesser than the band gap are absorbed, the energy is typically dissipated as heat.



In a nutshell, photocatalytic reactions involve five major steps:

- a) Absorption of light by the semiconductor: The semiconducting material absorbs light energy, typically in ultraviolet or the visible range.
- b) Generation of charge carriers: The absorbed light energy promotes e^- from the VB to CB, creating e^- - h^+ pairs (charge carriers).
- c) Transportation and recombination of charges: The generated e^- and h^+ move within the semiconductor, often guided by internal electric fields. They may also recombine, leading to a loss of photocatalytic activity.
- d) Adsorption and desorption of reactants and products: The reactant molecules or contaminants in the surrounding environment adsorb onto the surface of the photocatalyst. As the photocatalytic reaction proceeds, the products are formed and eventually desorb from the surface.
- e) Occurrence of redox reactions: The photogenerated charge carriers, specifically the h^+ and e^- , exhibit oxidation and reduction capabilities, respectively. These charge carriers engage in redox reactions with the adsorbed reactants, leading to the desired transformations and the removal or conversion of pollutants.

Together, these steps define the photocatalytic process, enabling the harnessing of light energy to drive environmental purification and renewable energy applications.

1.2.2 Fossil fuels as a traditional energy source

The global energy demand has been relentlessly increasing over the past decades, along with environmental pollution owing to ever-increasing industrialization and urbanization [48]. Energy usage has been considered an important aspect of sustainable economic development and the prosperity of modern society [49]. Conventional fossil fuels such as petroleum, coal, natural gas, etc., have been widely explored to fulfil the energy demands. However, the burning of these fuels is accountable for the release of nearly 7.8 billion metric tons of CO₂ into the environment in addition to other detrimental gases such as CH₄, SO₂, NH₃, etc [50]. These gases pose grave issues to biodiversity and living beings as a result of global warming and acid rain. More than 70 % of CO₂ that is emitted in the environment causes the greenhouse effect. It is now realized that fossil fuels, being non-renewable, are getting exhausted, and hence it is necessary to conserve energy and explore advanced renewable energy sources [51]. The excessive exploitation of fossil fuels can be minimized by the development of renewable energy resources. These include hydro, wind, and solar energy which help to solve the challenges of global energy demand by releasing less harmful pollutants into the atmosphere. In efforts to focus on developing low CO₂ power resources, competent technologies for the production of energy, storage, and distribution are needed. Even the smallest accessibility of renewable energy is better than the boundless extent of fossil fuels. The implementation of renewable technologies may therefore be useful in controlling the immigration of people to urban areas by providing better job opportunities. This has prompted interest in the production of hydrogen energy which can be an alternative to fossil fuels [52].

1.2.2.1 Hydrogen as a cleaner fuel

Hydrogen is a potent non-carbon-based energy source that can substitute fossil fuels and is determined as an alternative fuel since it can be evolved from clean and green resources and has a higher energy content by weight (122 kJ/g) [53]. It is valued over the other fuels as the combustion products of water are easily regenerative, portable, and storable [54]. Moreover, the energy yield of hydrogen fuel is reportedly 2.75 folds greater in comparison to hydrocarbon fuels. It is considered to be an ultraclean source of energy as it does not release destructive gases such as CO₂ that can cause global warming because only water is generated as the product [55]. In addition, hydrogen has a high diffusion coefficient, low density, high combustion energy, and

high energy per unit weight ratio. Also, it is non-toxic, odorless, colorless, tasteless, and capable of converting into other forms of energy owing to its high heating value [56]. Hydrogen is used as a fuel in space shuttle engines as it is extensively flammable. It is also used in polymer industries, food, petrochemical, and microelectronics, besides metallurgical industries. Although initial installation for hydrogen production is expensive, but its maintenance is less expensive.

Hydrogen can be synthesized via conventional methods such as electrolysis of water, hydrocarbon steam reforming, auto thermal reforming, non-catalytic partial oxidation, and; it can also be synthesized via biological methods for example bio-photolysis, integrated fermentation, dark fermentation, photo-fermentation, and artificial photosynthesis [57]. Among the many approaches, photoelectrocatalytic (PEC) water splitting is one of the most convincing routes to convert water into hydrogen and O_2 using an effective semiconductor photocatalyst employed to harvest solar energy.

1.2.2.2 Photoelectrocatalytic water splitting for hydrogen generation

PEC is considered an effective and promising technique for the hydrogen generation owing to utilization of natural resources such as solar energy and water for green hydrogen production [58]. On illumination of light onto photoelectrodes, charge carriers are generated. Under external bias in PEC, electrons flows through the external circuit to carry out the reduction reaction also known as hydrogen evolution reaction, while holes are engaged in water oxidation or known as oxygen evolution reaction. Photoelectrodes are synthesized by the deposition of the photocatalyst for carrying out the water-splitting reaction. The external beam of sunlight is illuminated on PEC changes the energy of the photon into electrochemical energy, thereby decomposing H_2O into O_2 and hydrogen [59]. The scattered sunlight then gets rehabilitated into a form that can be stored.

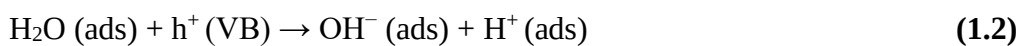
Hence, photocatalytic deprivation of the organic pollutants and PEC water splitting requires the usage of the competent visible-light-responsive photocatalyst.

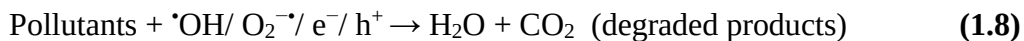
1.3 Optimum photocatalyst for photocatalysis and PEC application

A photocatalyst is a semiconducting material that, when exposed to light, can accelerate the chemical reaction without any modification. The photocatalytic/PEC activity of photocatalysts is known to be shape-dependent, with their morphology having a significant

influence [60]. The surface characteristics of the photocatalysts, such as the pore diameter, pore volume, and specific surface area have a significant influence on the photocatalytic/PEC activity since these factors affect adsorption. A high specific surface area provides more active sites for photocatalytic/PEC activity [61]. For the efficient transformation of organic contaminants and hydrogen evolution, photocatalytic performance heavily relies on the characteristics of semiconducting photocatalysts. Besides good surface characteristics, an ideal photocatalyst should possess specific properties like a low recombination rate, narrow band gap, high reusability, good stability, and cost-effectiveness. A low recombination rate prevents the loss of photoexcited charge carriers and promotes higher charge separation, which promotes efficient utilization of the photoexcited charges [62]. A narrow band gap is desirable to allow the absorption of a broader range of light, including visible light. Good stability ensures the longevity of the photocatalyst. Cost-effectiveness is essential for practical applications, and suitable band edge potentials facilitate the desired redox reactions.

The following redox reactions occur at the VB and CB edges of the photocatalyst, facilitating the degradation and hydrogen production. $\cdot\text{OH}$ radicals are formed by the reaction of surface bonded water or OH^- with the generated h^+ present in VB of the photocatalyst (**Eq. 1.2 - 1.3**). Whereas, $\text{O}_2^{\cdot-}$ is generated by the reduction of O_2 with the e^- present in the CB (**Eq. 1.4**). The resultant superoxide ($\text{O}_2^{\cdot-}$) undergoes protonation to form hydroperoxyl radical ($\text{HO}_2^{\cdot}$), followed by H_2O_2 , which further cleaves to form highly reactive hydroxyl radicals ($\cdot\text{OH}$) (**Eq. 1.5 - Eq. 1.7**). Thus, the $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, h^+ , and e^- react with the adsorbed organic pollutant and mineralizes it to form the lesser toxic decomposed products (**Eq. 1.8**). The most important step amongst them is the reduction of O_2 to produce $\text{O}_2^{\cdot-}$, which not only prevents the reintegration of charge carriers but also prolongs the lifespan of the h^+ [63]. Prompt quenching of the charge carriers immediately after photoexcitation is crucial to prevent their recombination at the photocatalyst's surface, as such recombination events can reduce the efficiency of photocatalytic degradation. Also, the adsorbed (ads) H^+ reacts with the e^- present in the CB of the semiconductor and tends to reduce to generate hydrogen (**Eq. 1.9**).





Therefore, different types of photocatalysts i.e., first, second, and third generation have been developed to carry out the photocatalysis and PEC.

1.3.1 Different types of photocatalysts

1.3.1.1 First-generation photocatalysts

First-generation photocatalysts correspond to the single component semiconductor i.e., sulphides, phosphates, oxides, nitrides, etc. For a single component photocatalyst, e^- excite to CB leaving behind the h^+ in the VB after the irradiation of light. Later, these e^- and h^+ can undergo reduction and oxidation reactions as represented in **Fig. 1.2(a)** [64]. OH^- gets oxidized in the presence of h^+ to form $\text{OH}^{\cdot}$, whereas the e^- tends to reduce O_2 , and H^+ to form $\text{O}_2^{\cdot-}$ and H_2 , respectively. As discussed earlier, a good semiconductor photocatalyst must exhibit higher carrier charge mobility, narrow band gap, lower recombination rate, and a propensity to absorb an ample amount of visible light. However, single-component photocatalysts exhibit certain flaws like a higher reintegration rate of the charge carriers and a wider band gap of > 3 eV, which allows it to absorb a small portion of visible light [65]. A variety of metal oxides, sulphides, phosphides, etc., have been appeared as single-component semiconductors. Amongst these, TiO_2 has been comprehensively studied owing to its inexpensive, high oxidizing, non-poisonous, good biocompatible, and highly sturdy nature [66]. However, its huge band gap (~ 3.2 eV), and ability to absorb just a small amount of visible light ($\sim 4\text{-}5\%$), renders it less effective [67].

1.3.1.2 Second-generation photocatalysts

To circumvent the bottlenecks of single-component photocatalysts, researchers have focused on developing second and third-generation photocatalysts. These include numerous approaches, including the formation of heterojunctions, decoration with noble metals,

heteroatom doping, coupling with carbon-based materials, and morphology tailoring. These approaches aim to enhance light absorption, increase the segregation and lifetime of the charge carriers, and improve overall photocatalytic/PEC activity. By advancing the design and engineering of photocatalytic semiconducting materials, it is possible to develop more efficient and versatile photocatalysts for applications in environmental remediation, water splitting, solar fuel production, and other areas of sustainable energy research.

1.3.1.2.1 Doping

Rate of evolution of the hydrogen and photocatalytic deterioration of the organic contaminants increases by doping the semiconductors with the metals like Pt or the non-metals such as carbon, oxygen, etc. Doping causes the segregation of the photogenerated charges and surges the absorption of visible light [68]. The electronic structure of the reactive sites of the semiconductors gets modulated with the increase in the impurities in the structure [69]. Formation of the donor level occurs above the VB and acceptor level underneath the CB, which helps to obtain the narrow band gap with increased photocatalytic/PEC activity with certain metal ions. The electronic structure of the semiconducting photocatalysts gap gets modified with the doping of the metal ions. Migration and the segregation of the charge carriers got intensified which tends to advance the photocatalytic/PEC performance. However, the metal ions should be doped in a considerable amount because doping exposes the active sites for the recombination of the charges. Owing to this, the photocatalytic/PEC activity gets reduced.

1.3.1.2.2 Cocatalyst engineering

The photocatalytic/PEC activity of the semiconductor can be heightened by linking it with the other cocatalyst. The e^- and the h^+ of the semiconductor are quenched by the cocatalyst and tend to reduce the overpotential. The cocatalyst also offers the effectual segregation and the promotion of the charges. Cocatalysts like Pd, Pt, Ru, Au, and Ag tend to quench the e^- of the semiconductor and serve as reaction sites, thus reducing the recombination rate as they have low Fermi levels compared to some semiconductors. However, the inexpensive nature of the cocatalysts renders the cocatalyst engineering less effective.

1.3.1.2.3 Heterojunction formation

One of the most effective approaches to achieve photogenerated carrier charge segregation is the development of heterojunction by coupling two diverse semiconductors (**Fig. 1.2(b)**). A heterojunction is defined as an interface in the two semiconductors with unequal band structures, which can result in the band alignments. A built-in electric field is anticipated to occur at heterojunction interface when two semiconductors have distinct Fermi energy levels or work functions owing to the spontaneous migration of the e^- from the higher Fermi energy level to lower one. On the illumination of the light, the charge carriers are compelled to migrate between two semiconductors, which prevents charge recombination, thus enhancing the efficacy of the heterojunction photocatalysts. Heterojunction photocatalysts possess certain advantages like a higher visible light response, narrow band gap, lower charge carrier recombination, etc.

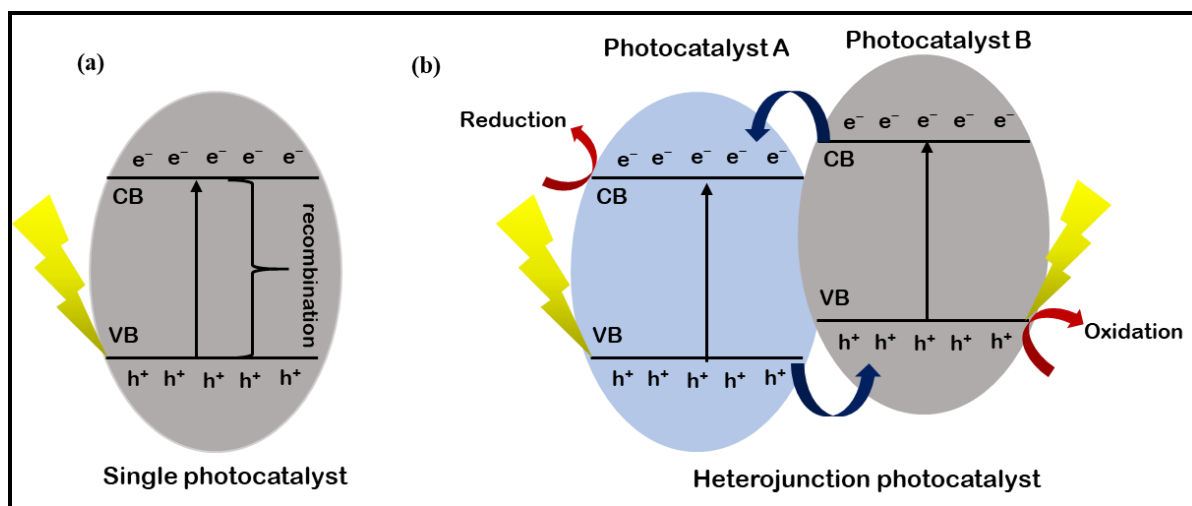


Fig. 1.2 Schematic depiction of single and heterojunction photocatalyst.

1.4 Conventional heterojunctions

There are three different kinds of conventional heterojunction photocatalysts: type-I, type-II, and type-III, which are distinguished by their straddling, staggered, and broken gaps, respectively.

1.4.1 Type-I heterojunction photocatalyst

For the type-I heterojunction photocatalyst VB and CB edge potential of the one semiconductor are lower and higher than the corresponding bands of other semiconductor,

respectively as shown in **Fig. 1.3(a)**. As a result, on the exposure of light, h^+ , and e^- will assemble at the VB and CB edges, respectively. However, in a type-I heterojunction, efficient separation of e^-h^+ pairs is challenging because both charges accumulate on the same semiconductor. This limitation hinders the photocatalytic/PEC performance as it reduces the possibility of charge transport to the other semiconductor and subsequent redox reactions at the interface. The redox capability of the type-I photocatalyst is also significantly diminished due to redox reactions occurring primarily on the photocatalyst with the lower redox potential. This type of heterojunction may still exhibit some photocatalytic/PEC activity, but its performance is generally lower compared to other types of heterojunctions. To overcome these limitations, researchers have explored type-II and other more favorable heterojunction configurations, where the spatial segregation of charges is achieved, allowing for efficient redox reactions and improved photocatalytic efficiency [70].

1.4.2 Type-II heterojunction photocatalyst

The VB and CB edge potentials of the one semiconductor are higher than the corresponding band potentials of other semiconductor for type-II heterojunction photocatalyst. As a result, when exposed to light, photogenerated e^- transport from the semiconductor with a higher CB potential (semiconductor A) to the semiconductor with a lower CB potential (semiconductor B). At the same time, photogenerated h^+ move from semiconductor B to semiconductor A owing to the higher VB potential of semiconductor A. This spatial segregation of the charges leads to efficient charge separation in type-II heterojunction. The lower CB potential of semiconductor B makes it a favorable site for reduction reactions since it has a more negative potential. Conversely, the higher VB potential of semiconductor A promotes oxidation reactions as it possesses a more positive potential (**Fig. 1.3(b)**). This spatial separation of charges and the associated difference in redox potentials facilitate efficient charge transfer and enable the occurrence of redox reactions at the respective band edges of each semiconductor [71].

1.4.3 Type-III heterojunction photocatalyst

In a type-III heterojunction photocatalyst, band gaps of the both semiconductors do not overlap due to a large energy offset between them, resulting in an extremely staggered gap as depicted in **Fig. 1.3(c)**. This configuration makes it challenging for efficient charge carrier

migration and segregation between the two semiconductors. Due to lack of band overlap, e^- transfer from one semiconductor to the other is highly restricted, and charge carrier separation is not effectively achieved. As a result, the type-III heterojunction is not suitable for improving the partition of e^- - h^+ pairs and enhancing the overall photocatalytic/PEC performance [72]. Therefore, the concept of a p-n junction photocatalyst was put forth.

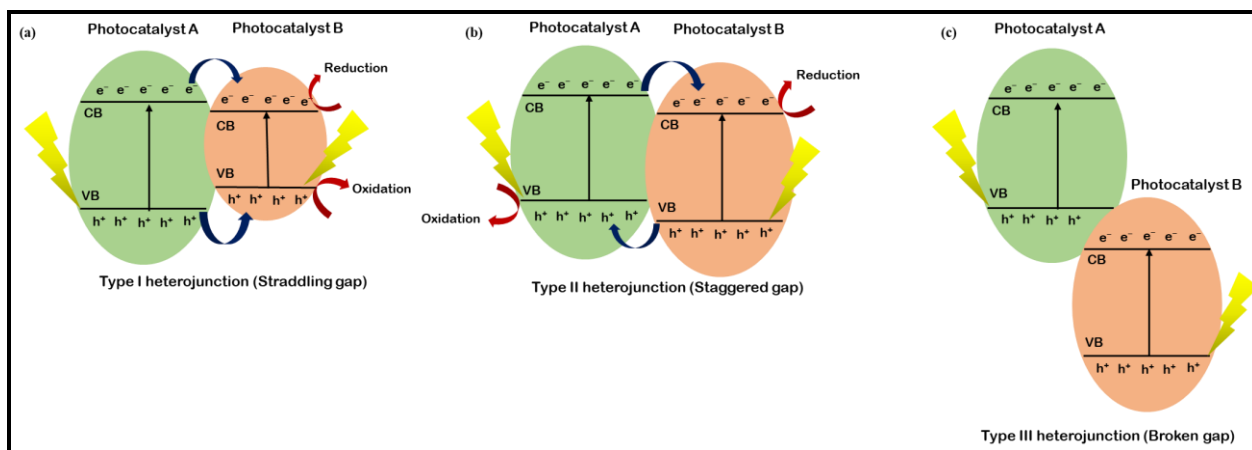


Fig. 1.3 Schematic diagrams of various types of conventional heterojunctions.

1.5 p-n heterojunction photocatalyst

Indeed, the issue of rapid recombination of e^- - h^+ pairs in type-II heterojunction photocatalysts can limit their overall photocatalytic/PEC efficiency. In order to address this challenge, the notion of p-n heterojunction photocatalysts was put forth, which utilizes an additional electric field to speed up the charge migration across the heterojunction. Particularly, p-type semiconductor and n-type semiconductor are combined to create a potent p-n heterojunction photocatalyst [73]. Prior to illumination, e^- present in vicinity of the p-n interface of n-type tend to diffuse to the p-type semiconductor, leaving behind h^+ . Conversely, negatively charged species are left behind as the h^+ near the p-n interface of the p-type semiconductor tends to migrate into the n-type semiconductor. The diffusion of the charges continues to occur till the equilibrium between the Fermi levels of both semiconductors is attained. Therefore, an internal electric field is created in the vicinity of p-n interface [74]. Upon absorption of light with energy equal to or more than the band gap, both the n-type and p-type semiconductors generate e^- - h^+ pairs. An internal electric field present in the p-n heterojunction causes the h^+ in the n-type semiconductor and the e^- in the p-type semiconductor to transfer to the VB of the p-type and the

CB of the n-type semiconductor, respectively (**Fig. 1.4**). Thus, spatial segregation of the e^- - h^+ charge pairs is facilitated by the difference in CB and VB potentials between the p-type and n-type photocatalysts. Additionally, since the CB and VB potentials in the p-type semiconductor are higher than those in the n-type photocatalyst, the charge partition process is thermodynamically feasible. The combination of band alignment and the internal electric field in p-n heterojunction photocatalysts facilitates faster charge separation compared to type-II heterojunction photocatalysts. The synergy between these factors contributes to the enhanced performance of p-n heterojunction photocatalysts, allowing for efficient charge separation and reducing the reintegration of e^- - h^+ pairs [75]. Even though all of the aforementioned heterojunction photocatalysts are effective at increasing charge carrier segregation, the redox ability of the heterojunction photocatalyst is reduced. This is owing to the existence of the oxidation and reduction reactions on the photocatalyst with the higher oxidation and lower reduction potential, respectively.

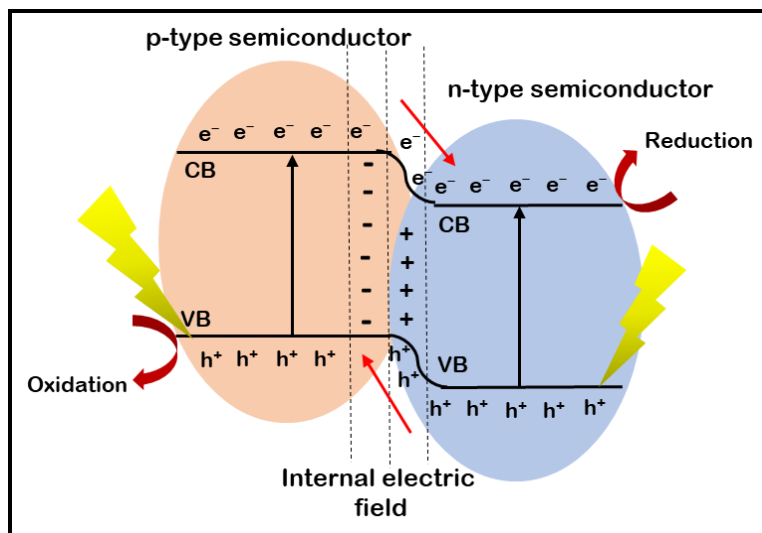


Fig. 1.4 Schematic illustration of p-n junction photocatalyst.

1.6 Conventional Z-scheme photocatalysts

In order to enhance the redox potential, a Z-scheme heterojunction is also proposed. The photocatalyst I (PC I) and photocatalyst II (PC II), as well as an acceptor/donor pair (A/D), all comprise of typical Z-scheme photocatalytic system. The following redox processes take place during the photocatalytic reaction as the e^- transport across an A/D pair from the CB of PC II to the VB of PC I:



Particularly, A reacts with the e^- present in CB edge of the PC II to form D. Then, h^+ present in VB edge of PC I tend to oxidize the D into A (**Eq. 1.10 – Eq. 1.11**). The segregation of charge carriers and an ideal redox ability can be obtained because e^- gather on PC I, having a greater reduction potential, and h^+ gathers on PC II, having a greater oxidation potential, as represented in **Fig. 1.5(a)** [76]. However, a significant bottleneck of conventional heterojunctions is the manifestation of backward reactions attributed to the use of reversible redox intermediates. Additionally, it is only effective in the liquid state, which leads to the development of a second-generation Z-scheme photocatalyst.

1.7 Second-generation Z-scheme photocatalyst

In the second generation Z-scheme photocatalyst, an e^- mediator (for e.g., Au, Pt, Ag, etc) is introduced as a bridge between the two different semiconductors, PC I and PC II [53]. The e^- mediator facilitates the transport of the e^- from the CB edge of PC II to the VB edge of PC I, thereby optimizing the redox potential and achieving spatial segregation of charges as illustrated in **Fig. 1.5(b)**. Then, these e^- get stimulated to the CB potential of PC I. Thus, the e^- and h^+ gather in PC I, having a larger reduction potential, and in PC II, having a higher oxidation potential, respectively. This causes the spatial segregation of the charges and the optimization of the redox potential [77]. The utilization of all-solid-state Z-scheme semiconductor photocatalysts, which operate in solid, gaseous, and solution environments, expands their potential applications in various photocatalytic processes. But, the large-scale applications of these photocatalysts is restricted by the high cost and scarcity of e^- mediators required to enhance the migration channel for e^- in the Z-scheme heterojunction. The need for these e^- mediators can present economic and practical challenges, hindering the widespread adoption of second-generation Z-scheme photocatalysts [78].

Ongoing research efforts focus on developing an alternative Z-scheme heterojunction to overcome this limitation and enable the practical implementation of Z-scheme photocatalysts in various applications.

1.8 Direct Z-scheme heterojunction

Direct Z-scheme heterojunction semiconductor photocatalysts offer several advantages over conventional Z-scheme photocatalysts. In direct Z-scheme photocatalysts, two different photocatalysts can be combined without the need for rare and expensive e^- mediators, as presented in **Fig. 1.5(c)** [79]. This eliminates the cost and scarcity associated with e^- mediators, making the synthesis of direct Z-scheme photocatalysts more affordable. Key advantage of direct Z-scheme semiconductor photocatalysts lies in an electrostatic interaction in the charge carriers. This facilitates the easy transportation of e^- from the CB edge of the PC II to the h^+ -rich VB potential of the PC I. The electrostatic interaction allows for efficient charge carrier segregation without relying on e^- mediators [80]. But, the formation of direct Z-scheme semiconductor photocatalysts requires certain considerations. The Fermi levels of the two photocatalysts need to be adjusted to ensure the appropriate alignment for efficient e^- transport. Additionally, a suitable pathway for e^- transport, the development of an in-built electric field, and band bending are necessary for the functioning of direct Z-scheme photocatalysts. Also, the built-in electric field cannot be formed when Fermi levels are the same because of the loss of the potential difference. This drawback has led to the development of alternative heterojunction photocatalysts known as step scheme (S-scheme) heterojunctions.

1.9 S-scheme heterojunction photocatalysts

S-scheme photocatalysts consist of two components: an oxidation photocatalyst (OP) and a reduction photocatalyst (RP). In this configuration, the e^- are useful in the RP, while the photogenerated h^+ are ineffective and need to be eliminated using sacrificial agents. Conversely, the photogenerated h^+ are effective in the OP. On the illumination of light, e^- got transferred to the CB of both semiconductors when both are visible active. The e^- from the RP instinctively diffuses to the OP when both semiconductors are in close proximity, forming an e^- accumulation layer and depletion layer close to an interface of RP and OP (**Fig. 1.5(d)**). This results in the construction of an internal electric field that directs e^- migration from the OP to the RP. Also, OP and RP should have aligned Fermi levels when both the photocatalysts come into contact. The Fermi levels of the OP and RP are subsequently shifted upward and downward, respectively. In addition to band bending, the Coulombic interaction in the h^+ in RP and e^- in OP aid in the charge migration. Whereas, the migration of e^- from CB of RP to CB of OP (directing the

transfer of h^+ from VB of OP to VB of RP) is hindered by band bending, Coulombic repulsion, and a built-in electric field. The S-scheme heterojunction semiconductor photocatalyst exhibits strong redox capability owing to the combined effects of charge separation and a strong redox capacity. This augments the overall photocatalytic performance of the system [81,82].

The S-scheme heterojunction photocatalyst configuration offers advantages in terms of improved charge separation and enhanced redox potential [83]. By leveraging these properties, S-scheme photocatalysts can achieve higher photocatalytic/PEC activity compared to other heterojunction configurations [84].

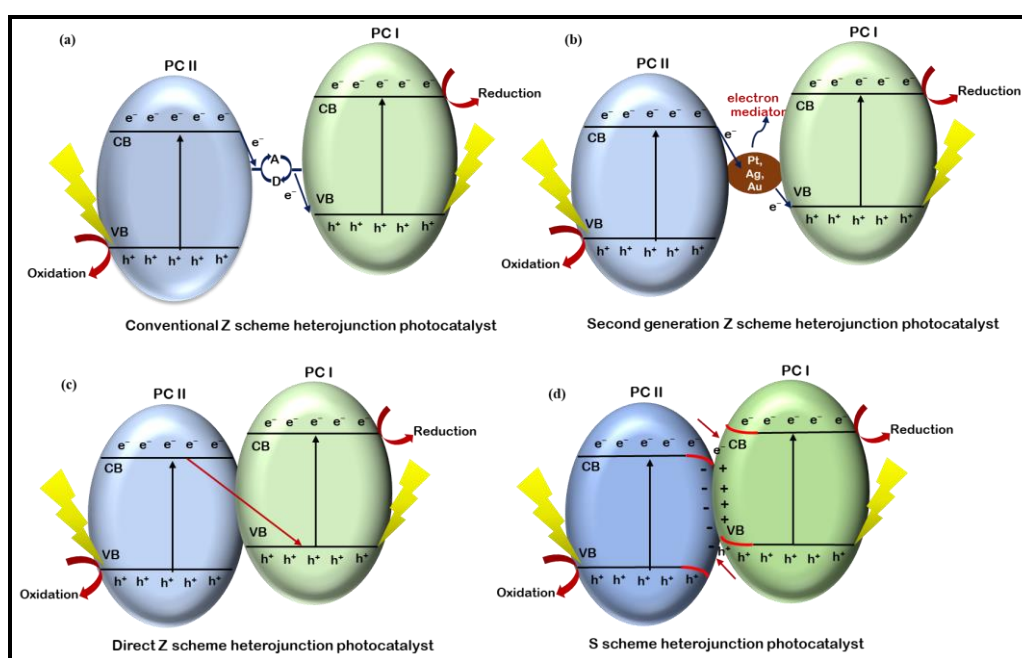


Fig. 1.5 Schematic diagram of different kinds of Z-scheme heterojunction photocatalysts and S-scheme photocatalysts.

1.10 Bismuth (Bi) based photocatalyst

Bi is the heaviest, most metallic, and fundamentally non-radioactive in the periodic table and has a half-life of 2.01×10^{19} years. It also possesses vast spin-orbit coupling and is non-toxic in nature. Additionally, Bi has a $6s^2$ lone pair that is stereo-chemically active, the ability to form compounds with a variation of nuclearities, possesses the wide range of coordination numbers and bonding modes, and the capacity to adopt all oxidized and reduced states from +5 to -3 in compounds with Bi-Bi, Bi-metal, and Bi-nonmetal interactions [85]. It has some intriguing properties like strong oxidation ability, high carrier migration, high specific gravity, low carrier

density, good photovoltaic and photoelectronic effects, and good photoluminescence [86]. It is the utmost diamagnetic material of its class. In addition to photocatalysis, Bi is also involved in medicine, sensing, therapy, and diagnosis, with an emphasis on infrared photocatalysis, flexible wearable sensing, and therapies [87].

1.10.1 Bismuth-derived nanoparticles

In the current state of material science, nanomaterials such as nanoparticles, nano-multilayers, and thin films have grown in significance. The quantum behavior generated by the size of nanostructured Bi materials has attracted a significant attention [86]. Due to unique shape and size-dependent magnetic, optical, and catalytic capabilities and potential uses in photonics, biolabeling, catalysis, and information storage [88]. These Bi-derived size-controlled, crystalline nanomaterials can be fabricated by colloidal chemistry, where Bi-based salts are utilized as precursors, together with surface enhancers and reducing agents.

1.10.2 Bismuth Vanadate (BiVO_4) a potential photocatalyst

BiVO_4 has gained attention owing to its capability to absorb an ample amount of visible light, the narrow band gap of ~ 2.4 eV, favorable VB potential, inexpensive nature, and good charge transport capability [89]. Also, the photochemical stability of BiVO_4 is outstanding, and the materials are environmentally safe [90]. Nonetheless, bare BiVO_4 has several drawbacks that have hampered the overall usefulness of this semiconductor material. It possesses a small surface area owing to which its capability of adsorption decreases [91]. Moreover, the photogenerated e^- and h^+ recombine at a faster rate, thereby decreasing its photocatalytic/PEC efficacy [92]. Therefore, hybridization of BiVO_4 with other semiconductor photocatalysts has become a popular choice as heterojunction formation reduces the recombination and prolongs the lifetime of photoinduced charges owing to the synergistic effect.

1.10.2.1 Heterojunction formation with BiVO_4

BiVO_4 can be hybridized with other semiconductor photocatalysts for e.g., MoSe_2 , SnS_2 , WO_3 , BiOBr , Sb_2S_3 , MoS_2 , $g\text{-C}_3\text{N}_4$, Sb_2Se_3 , WS_2 , etc in order to reduce its recombination rate and increase the lifetime of charge carriers.

1.10.2.1.1 Molybdenum Selenide (MoSe₂) as a cocatalyst

MoSe₂ is the p-type, graphene-like layered semiconductor photocatalyst capable to lessen the reintegration rate of the photogenerated excitons when combined with the other semiconductors [93]. It has a larger surface area of the contract with a porous network owing to which the heterojunction formation becomes easier [94]. Furthermore, MoSe₂ multilayer edge has a lot of surface-active sites capable of lowering the energy barrier for the conversion of H⁺ to hydrogen to carry out the hydrogen evolution reaction. Moreover, it has good electrical conductivity, non-poisonous nature, and a suitable band gap of ~ 1.4 eV- 1.7 eV allowing it to absorb the sunlight [95]. As optical transitions of MoSe₂ exist between nonbonding metal 'd' states, therefore it has good anti-photo corrosion stability [96].

1.10.2.1.2 Tin sulphide (SnS₂) as a cocatalyst

SnS₂, an n-type semiconductor, has a strong anisotropic optical feature, which could be useful in catalytic reactions along with several other applications like electrical switching, solar cells, etc [97]. The crystal structure of SnS₂ is hexagonal CdI₂-type, with one layer of Sn atom, sandwiched amongst two layers of S atom via in-plane covalent bonding and a weak Van der Waals force amid the neighboring layers [98]. SnS₂, additionally, is affordable, non-toxic, has good thermal stability, and possesses a band gap of 1.91-2.35 eV, which renders it a visible light-responsive. Moreover, it is stable in neutral as well as acid media, has high carrier mobility, and possesses a greater number of active sites; therefore, several efforts have been made to use this material [99].

1.10.2.1.3 Bismuth oxy bromide (BiOBr) as a cocatalyst

BiOBr is a typical p-type semiconductor photocatalyst and is the catalyst of choice for heterostructure due to its excellent stability, environmental friendliness, non-toxicity, and appropriate band gap [100]. It has a unique lamellar structure with [Bi₂O₂]²⁺ sheets interspersed with two-layer bromine atoms (tetragonal matlockite structure) [101]. This shape offers enough room to polarize the associated kernel and orbital, making it easier to separate photo-produced carriers for effective photocatalysis/PEC activity [102]. Also, the visible light activity of other semiconductors can be enhanced by coupling with BiOBr.

1.10.2.1.4 Tungsten trioxide (WO₃) as a cocatalyst

WO₃ has good semiconducting characteristics. Owing to non-toxic, cost-effective, and thermally stable characteristics, WO₃ is said to be a potent photocatalyst [103]. It exhibits good electron mobility, and high conductivity. Moreover, it possesses narrow band gap (~ 2.7 eV), has a higher VB edge potential, and absorbs solar light substantially (≤ 480 nm) [104]. Also, it has a high surface area and better surface permeability, rendering it ideal photocatalyst for a broad range of applications.

1.10.2.1.5 Antimony sulphide (Sb₂S₃) as a cocatalyst

Sb₂S₃ is thought to be a potential photocatalyst owing to its narrow band gap of ~ 1.84 eV, have its capability to absorb solar light, its non-carcinogenic, and its inexpensive nature [105]. Moreover, it possesses an outstanding photosensitive nature, a chain-like layered topology as well as higher thermoelectric power [106]. Also, Sb₂S₃ has extensive use in various thermoelectric microwave devices, rechargeable Na/Li-ion batteries, and solar cells [107].

Recently, the focus has been growing on the construction of new heterojunction photocatalysts, particularly those that can be driven by visible light. These novel photocatalysts have garnered significant attention due to their potential to achieve higher photocatalytic/PEC efficiencies. **Table 1.1**, and **Table 1.2** provides a summary of different literature reports that explore the utilization of diverse photocatalysts for the purpose of photocatalytic abatement of different organic contaminants and for the PEC hydrogen evolution via water splitting, respectively.

Table 1.1 Different kinds of photocatalysts for the photocatalytic remediation of various contaminants.

Photocatalyst	Pollutant	Concentration of photocatalyst	Reaction time	Light source	% degradation	Rate constant	Ref.
g-C ₃ N ₄ /CuWO ₄	Rhodamine B	1 g/L	150 min	Visible	93	0.0149 min ⁻¹	[108]

CaSb ₂ O ₆ /g-C ₃ N ₄	TC	20 mg/L	120 min	Visible	85	0.0138 min ⁻¹	[109]
ZnSnO ₃ /g-C ₃ N ₄	TC (10 ppm)	0.25 g/L	120 min	Visible	85	0.0131 min ⁻¹	[110]
WO ₃ /rGO	Rhodamine B	20 mg/L	120 min	Visible	94	0.0276 min ⁻¹	[111]
ZnO/g-C ₃ N ₄	Methylene Blue (50 mg/L)	0.1 g/L	180 min	Visible	75	0.0128 min ⁻¹	[112]
Bi ₂ S ₃ /ZnInS ₄	Methylene Blue (40 ppm)	0.5 g/L	300 min	Visible	95.4	-	[113]
Bi ₂ MoO ₆ /ZnO	Ofloxacin (10 ppm)	0.25 g/L	120 min	Visible	94	0.0179 min ⁻¹	[114]
MnWO ₄ /g-C ₃ N ₄	Ofloxacin	0.5 mg/L	70 min	Visible	90.4	0.0095 min ⁻¹	[115]
BiVO ₄ /CoO	TC (40 mg/L)	0.6 g/L	90 min	Visible	87.3	0.022964 min ⁻¹	[116]
Sb ₂ S ₃ /rGO	Thiamethoxam (5 ppm)	1 g/L	150 min	Solar light	64	0.0056 min ⁻¹	[107]
TiO ₂ /g-C ₃ N ₄ /cotton	Thiamethoxam (5 ppm)	-	150 min	Visible	80	-	[74]
Cu ₂ O/g-C ₃ N ₄	TC	0.2 g/L	90 min	Visible	90.7	0.0227 min ⁻¹	[117]

Table 1.2 Different types of photocatalysts for the PEC water splitting.

Photocatalyst	Electrolyte used	Hydrogen production rate	Photocurrent density	Light source	Type of anode	References
TiO ₂ nanotubes/CdS	0.1 mol/L Na ₂ S	22.4 $\mu\text{mol h}^{-1}\text{cm}^{-1}$	-	Solar light	Photoanode	[118]
WO ₃ /Sb ₂ S ₃	1 mol/L H ₂ SO ₄	-	1.79 mA/cm ² at 0.8 V vs RHE	Visible light	Photoanode	[119]
TiO ₂ nanotubes/Bi ₂ S ₃	0.35 M Na ₂ SO ₃ and 0.24 M Na ₂ S	28.58 $\mu\text{mol h}^{-1}\text{cm}^{-1}$	1.9 mA/cm ²	Visible light	Photoanode	[120]
MoSe ₂ /CdS/ZnO	0.12 M Na ₂ SO ₃ and 0.55M Na ₂ S	39.70 $\mu\text{mol h}^{-1}\text{cm}^{-1}$	2.4 mA/cm ² at 0.3 V vs RHE	Visible light	Photoanode	[121]
BiVO ₄ /Bi ₂ S ₃	0.2 M Na ₂ SO ₃	33.4 $\mu\text{mol h}^{-1}\text{cm}^{-1}$	-	Solar light	Photoanode	[91]
BiVO ₄ /g-C ₃ N ₄ /rGO	0.5 M Na ₂ SO ₄	63.5 mmol h ⁻¹ cm ⁻¹	14.44 mA/cm ² at -0.05 V vs Ag/AgCl	Visible light	Photoanode	[122]

Research gaps

Based on the comprehensive literature study, the current research work has successfully addressed and fulfilled the following research gaps:

1. Photo (electro) catalytic organic pollutant degradation/ hydrogen generation with heterojunction nanocomposites has received little attention.
2. Visible Light responsive binary/ternary photocatalysts haven't been explored much for removing colorless pollutants (pesticide, pharmaceutical pollutants, etc).
3. Comparison of the photo (electro) catalytic efficacy of hydrothermally synthesized photocatalysts with different mole ratios hasn't been done much.

Objectives

The main aim of this research work is to fabricate different heterojunction semiconductor photocatalysts for the efficient photocatalytic abatement of detrimental colourless organic contaminants, such as pesticides, and pharmaceutical compounds from aqueous solutions under natural sunlight irradiation and PEC water splitting. The specific objectives include:

1. Synthesis and characterization of bismuth-based (BiVO_4 , BiOBr) nanocomposites (transition metal dichalcogenides, metal oxides, nitrides, etc.).
2. Optimization of the reaction conditions for the photocatalytic degradation of the organic pollutants (tetracycline, ofloxacin, thiamethoxam, etc.).
3. To study the photoelectrochemical hydrogen generation with the optimized photocatalyst.

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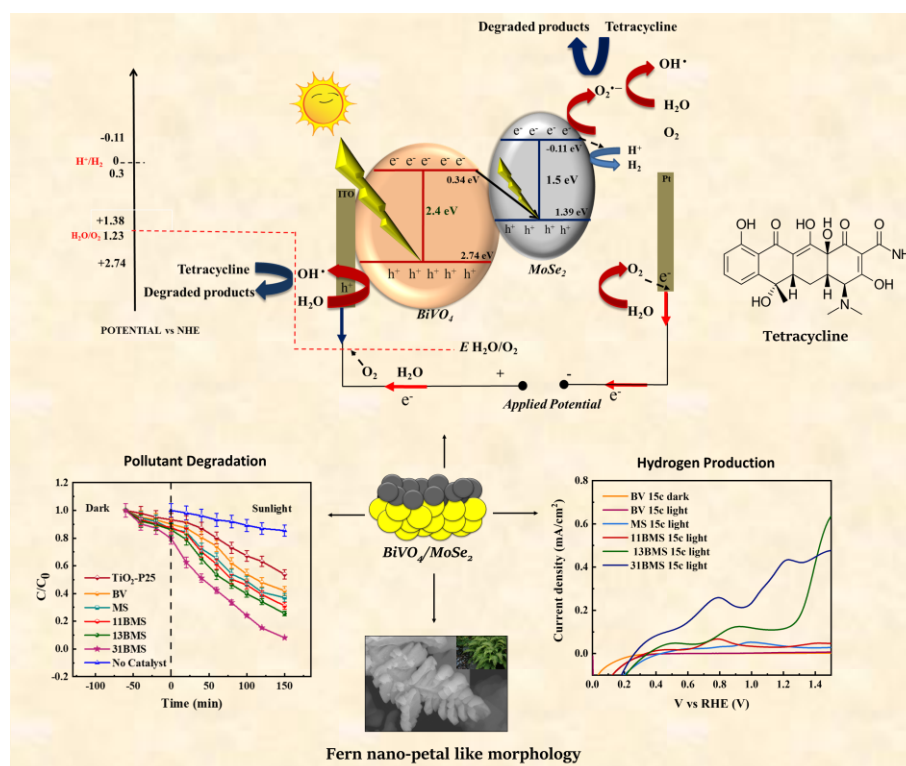
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Chapter 2

BiVO₄/MoSe₂ photocatalyst for photocatalytic abatement of tetracycline and photoelectrocatalytic water splitting



Highlights of the Chapter

- Fabrication of different mole ratios of BiVO₄/MoSe₂ nanocomposites was done via hydrothermal method.
- Photocatalysts efficacy was tested by carrying out photocatalytic degradation of pharmaceutical pollutant, tetracycline and photoelectrocatalytic hydrogen production via water splitting.
- Tetracycline efficiently got degraded to 91.9 % by the 3:1BiVO₄/MoSe₂ photocatalyst under the irradiation of natural sunlight for 150 min.
- Hydrogen production rate of 3.59 mmol/sec/cm² was calculated with optimum 3:1BiVO₄/MoSe₂ electrode.

2.1 Introduction

Environmental and energy challenges are gaining prominence on a global scale owing to a rapid expansion of the social economy and the effects of human activity [1,2]. Due to escalating industrialization and unnecessary use of human resources, water pollution has recently emerged as one of the most significant global environmental issues [3,4]. More than two billion people lack access to the clean drinking water, and millions contract illnesses from contaminated water each year, according to reports [5]. The release of pharmaceutical pollutants into natural resources such as sediments, surface waters, soil, ground waters, and even drinking water pose threat to marine, freshwater ecosystem, and people [6]. The indiscriminate use of antibiotics has caused their buildup and biotransformation in aquatic environments, which is a severe environmental problem. However, antibiotics can be removed as unmetabolized parent chemicals through urine and faeces if they are not adequately absorbed by living beings [7]. Tetracycline (TC) has been widely used as a broad-spectrum antibiotic medication in human medicine, animal farming, and agriculture to prevent and treat diseases caused by bacterial infections [8]. However, TC residues present in the water offer major harm to humans, animals, plants, and microorganisms and also disrupt the ecological balance [9]. People often consume water laced with TC, which can alter the composition of their gut flora and greatly increase the risk of developing noxious diseases including fatty liver, metabolic syndrome, autism, and other neurological disorders [10].

As a result, numerous processing methods, such as membrane filtration, adsorption, microwave catalysis, the electro-Fenton process have been developed to remediate organic pollutants from the wastewater [8]. However, due to limited biodegradability, stable structure, and higher toxicity, TC cannot be completely removed by conventional water treatment methods [11]. Moreover, these methods lead to the production of secondary pollutants at last stage of treatment. Hence, it is necessary to find out the effective method to eliminate TC from the water completely [12]. In this context, photocatalysis based on the direct exploitation of solar energy for the total mineralization of refractory organic pollutants in an aquatic environment is regarded as a promising technique since it is safe, non-toxic, energy-saving, and very effective [13]. Additionally, the photocatalytic remediation approach assists in eliminating refractory organic contaminants from the water completely by converting them to carbon dioxide and water [14].

Apart from environmental pollution, the energy crisis issues brought on by the excessive use of fossil fuels is also one of most significant obstacles preventing human society from expanding [15]. The burning of fossil fuels releases hazardous gases into the environment, such as ammonia, carbon dioxide, methane, etc [16]. Additionally, because fossil fuels are exhaustible, their supply is becoming scarce. Many scientific experts are concentrating on discovering ecologically acceptable and renewable energy alternatives to replace fossil energy sources [17]. Since hydrogen is a clean, affordable, and durable energy source, it is frequently viewed as the most suitable alternative energy carrier [18]. A low-cost, high-efficiency method of water splitting is becoming more and more in demand in order to produce long-term hydrogen [19]. Therefore, PEC water splitting has been proposed as a viable and most effective method to evolve hydrogen due to its tendency to utilize plentiful water resource and solar light, and the fact that the process is devoid of secondary pollution [20].

However, the photocatalytic degradation of organic pollutants and PEC water splitting involves the use of suitable visible light responsive photocatalyst [21]. Therefore, numerous inorganic semiconductors have been explored and exploited in numerous applications including the splitting of water to produce hydrogen and O₂, photo-decomposition of hazardous compounds, etc. In this context, binary metal oxides, phosphides, sulphides, etc., have sparked considerable interest for use in photocatalytic/PEC reactions. Owing to high stability, good resistance towards corrosion, inexpensive, durable, and non-toxic nature, a lot of work has gone into researching TiO₂-based materials for various photocatalytic/ PEC reactions [22]. However, TiO₂ has a few significant flaws, including the lower absorption capability of solar light besides having a higher reintegration rate of the photogenerated charges as it has a wide band gap [23]. As a result, semiconducting materials possessing a narrow band gap are the potential photocatalysts for overcoming light absorption limitations and maximizing solar energy consumption [24]. Recently, BiVO₄ has gained attention owing to its capability to absorb an ample amount of visible light, the narrow band gap of ~ 2.4 eV, favorable valence band edge potential, and good charge transport capability [25]. Also, the photochemical stability of BiVO₄ is outstanding, and the materials are environmentally safe [26]. Nonetheless, bare BiVO₄ has some drawbacks that have hampered the overall usefulness of this semiconductor material. It possess a small surface area owing to which its capability of adsorption decreases [27].

Moreover, the photogenerated electrons and holes recombine at a faster rate, thereby decreasing its photo(electro)catalytic efficacy.

Several strategies including doping with metals and non-metals, heterojunction formation, and morphological tuning are studied to enhance the efficacy of BiVO₄ [28]. Amongst these strategies, coupling of BiVO₄ with other semiconductors having appropriate band edge potentials in order to form the heterojunction is demonstrated as the most proficient method for improving its efficiency [28,29]. The coupling of BiVO₄ with MoSe₂ is a good choice as MoSe₂ has good semiconducting properties. MoSe₂ is a p-type, graphene-like layered semiconductor capable to lessen the recombination of the photogenerated excitons when combined with the other semiconductors [30]. It has a larger surface area of the contact with a porous network owing to which the heterojunction formation becomes easier [31]. Furthermore, MoSe₂'s multilayer edge has a lot of surface-active sites capable of lowering the energy barrier for the conversion of H⁺ to hydrogen in order to carry out the hydrogen evolution reaction. Moreover, it has a good electrical conductivity, non-poisonous nature, and a suitable band gap of ~ 1.4 eV- 1.7 eV allowing it to absorb the sunlight [32]. As optical transitions of MoSe₂ exist between nonbonding metal 'd' states, it has been mentioned that it has good anti-photo corrosion stability [25]. Luo et. al decomposed the glyphosate with BiVO₄/MoSe₂ nanocomposite under the illumination of visible light and reported a degradation efficacy of 86.1% [33]. Photodegradation efficiency of 89 %, 86 %, and 91.5 % was reported when the degradation of triclosan, ciprofloxacin antibiotic, and methyl orange was carried under visible light for 120 min, 10 min, and 180 min by BiVO₄/rGO and Ag₃PO₄/g-C₃N₄/MoSe₂, and ZnO/ZnSe/MoSe₂ photocatalyst, respectively [34–36]. However, there is no literature reported till date for the decomposition of pharmaceutical contaminant as well as PEC hydrogen production activity using different mole ratios of BiVO₄/MoSe₂ under the illumination of sunlight. At a certain compositional ration, it is found to be the optimum photocatalyst for the degradation of the TC for its conversion to CO₂ and H₂O.

In this Chapter, hydrothermally synthesized fern petal-like BiVO₄/MoSe₂ nanocomposites of varying mole ratios are studied. The efficiency of the fabricated photocatalysts was manifested by carrying out PEC hydrogen production as well as the photocatalytic elimination of the hazardous pollutant, TC under the illumination of the solar light. Various experiments like linear

sweep voltammetry (LSV), chronoamperometry, Mott-Schottky, kinetic studies, pH, scavenger studies were done to evaluate the efficiency of the as-prepared photocatalyst. Gas chromatography-Mass spectrometry (GC-MS) was done to assess the degraded products produced after carrying out photocatalytic degradation. Mineralization experiments were conducted. Reusability studies were performed for the 7 cycles to determine the reusability of the synthesized photocatalyst. Stability study was carried out for 5.5 h to evaluate the stability of the fabricated electrode.

2.2 Experimental section

This part includes materials, methods and the synthesis techniques followed to fabricate the different photocatalysts.

2.2.1 Materials and methods

Merck provided sodium hydroxide pellets (NaOH) 97%, nitric acid (HNO₃) 69%, and ethanol were utilized as such without any further purification. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and ammonium metavanadate (NH₄VO₃) were procured from Spectrochem. Sodium dodecyl benzene sulphonate (C₁₈H₂₉NaO₃S) and anhydrous sodium sulphate (Na₂SO₄) were purchased from Loba Chemie, India. Sigma Aldrich provided ammonium molybdate dihydrate ((NH₄)₆Mo₇O₂₄·2H₂O), ethylene glycol, selenous acid as well as TC. Analytical-grade chemicals were utilized in an uncontaminated manner without additional refining.

2.2.2 Syntheses

2.2.2.1 Synthesis of BiVO₄ powder

About 5 mmol of Bi(NO₃)₃·5H₂O was dispersed in 10 mL of 4 M HNO₃. Similarly, 5mmol of NH₄VO₃ was dissolved in 10 mL of 2 M NaOH. Under vigorous stirring for 30 min, 0.25 g of C₁₈H₂₉NaO₃S was added to both of the produced solutions. Then, both solutions were combined together, and the acidity of the solution was neutralized with 2 M NaOH while vigorously swirling. The resulting mixture was heated at 200°C for 1.5 h in a 50 mL Teflon-lined stainless-steel autoclave. The mixture was rinsed 4-5 times with double-distilled (DI) water and ethanol before being dried in a hot air oven at about 60°C. Eventually, a yellowish BiVO₄ powder was obtained and was named as BV.

2.2.2.2 Synthesis protocol of BiVO₄/MoSe₂ hybrids

The BiVO₄/MoSe₂ hybrids of varied mole ratios were prepared using the hydrothermal method. Initially, 1.619 g of BV (5 mmol) was dispersed in 30 mL ethylene glycol followed by sonication for 30 min to acquire a uniform solution. The in-situ production of MoSe₂ (MS) was then done by dissolving 5 mmol of (NH₄)₆Mo₇O₂₄·2H₂O and 10 mmol of selenous acid in the prepared mixture under vigorous agitation. The entire mixture was agitated for 1 h before being heated at 200°C for 12 h in a 50 mL Teflon-lined stainless-steel autoclave to create a homogenous solution. After 4-5 washes with DI water followed by ethanol, the mixture was dried at 60°C. Hence, 11 BMS (1:1 BiVO₄:MoSe₂) was the name given to the black-colored powdered material that resulted. Similarly, the amount of chemicals needed to synthesize the various mole ratios (1:3 and 3:1) were computed and labeled as 13BMS and 31BMS, respectively.

In order to compare, black colored raw MoSe₂ was synthesized under identical conditions without the addition of BV [37].

2.2.3 Characterization methods

PAN analytical X' Pert-Pro X-ray diffractometer instrument possessing the radiation of Cu K α , operated at 45 kV with a scan range of 10-80°, step size 0.026°, and wavelength = 1.5406 was utilized to assess the materials' X-ray diffraction analysis (XRD). The nitrogen sorption scrutiny was performed using a Microtrac Belsorp Mini-II (Bel, Japan, Inc.) surface area analyzer. Prior to the evaluation, the fabricated samples were pre-treated in a nitrogen atmosphere at 100°C for 5 h to prevent the trapping of undesirable pollutants and gases. The Brunner-Emmet-Teller (BET) method and Barrett Joyner Halenda's (BJH) approach was utilized to inspect the pore size distribution and surface area curves, respectively. The pH was evaluated via pH meter from Eutech (Singapore), model cyber scan pH 1100. The kinetics of samples were analyzed by photocatalytic remediation of organic pollutants under sunshine by Analytik Jena spectrophotometer. The 75 W Xenon lamp (Shilpent, $\lambda < 400$ nm) was used as an ultraviolet light source for carrying out degradation. A 65 W CFL lamp (Phillips, $\lambda > 400$ nm) with intensity of 125 W/m² was used for supplying visible light for all the photocatalytic reactions. UV-Vis diffuse reflectance spectroscopy (DRS) were examined by a Shimadzu UV 2600

spectrophotometer in diffused absorbance mode. At the excitation wavelength of 325 nm and slit width of 5-10 nm of fabricated catalyst, photoluminescence (PL) spectroscopic experiments were performed using the Perkin Elmer LS-55, USA PL spectrometer. The oxidation states of metal oxides were evaluated using the PHI5200 X-ray photoelectron spectroscopy (XPS) system, which included an Omicron ESCA apparatus and a monochromatic Al K X-ray source (1486.7 eV). Carl-Zeiss Sigma 500 equipped with Gemini 1 column and Bruker EDS to assess the morphological studies of as-prepared catalyst along with color mapping images. Energy dispersive X-ray spectroscopy (EDS) was done to inspect the color spectra and elemental distribution of the composite. Total organic carbon (TOC) was measured using a TOC analyzer of Model: Multi N/C 2100 BU, Analytik Jena AG Corporation.

2.2.4 Photocatalytic abatement of recalcitrant organic contaminants

The pharmaceutical contaminant, TC was decomposed in the natural sunlight to scrutinize the photocatalytic activity of the synthesized photocatalyst. Initially, to achieve adsorption-desorption equilibrium, 10 ppm solution of TC containing 0.3 g/L catalyst was swirled in the dark for 60 min. After that, the prepared solution was agitated for 150 min in natural sunlight to carry out photocatalysis. The experiments were carried out in October and the intensity of solar light was found to be 600-700 W/m² which was measured by Pyranometer (LICOR). The trials were repeated thrice times, and the plots are displayed with error bars with a data source error of 5 %. After the separation of the catalyst at the regular intervals, UV visible spectrophotometer was utilized to examine the absorbance spectra ($\lambda_{\text{max}} = 360 \text{ nm}$) of the TC. The degradation efficacy (% Deg) is represented in the **Eq. 2.1** where Ab_0 , Ab_t , C_0 , C_t designates initial absorbance and absorbance at time t, initial concentration, and concentration at time t, respectively [38].

$$\% \text{ Deg} = \{(Ab_0 - Ab_t) / Ab_0\} \times 100 = \{(C_0 - C_t) / C_0\} \times 100 \quad (2.1)$$

A 200 mL solution containing 60 mg of 31BMS photocatalyst was exposed to sunlight for 150 minutes prior to the analysis. The COD was determined through titration, while TOC elimination was used to calculate mineralization. The percentage of COD and TOC removal was computed using **Eq. 2.2** and **2.3**, respectively. This approach provided valuable insights into the effectiveness of the photocatalytic treatment for TC.

$$\% \text{ COD} = \{(COD_i - COD_f) / COD_i\} \times 100 \quad (2.2)$$

$$\% \text{ TOC} = \{(TOC_i - TOC_f) / TOC_i\} \times 100 \quad (2.3)$$

Here, COD_i, COD_f, TOC_i, and TOC_f, designates initial and final COD, and TOC, respectively.

GC-MS technique was carried out to analyze the products produced after the decomposition of TC by 31BMS photocatalyst. The aqueous reaction mixture was gathered after the separation of the photocatalyst and the photocatalytic reaction. The residue was dispersed in dichloromethane and by drying at 37°C, the solvent was removed. Shimadzu GCMS QP-2010 plus ultra instrument equipped with a split/split less injector was utilized. Conditions - split mode injector, helium carrier gas with flow rate = 1.21 mL/min, an injection volume = 1 µL, injector temperature = 260°C, ion source temperature = 220°C. The initial oven temperature was 100°C for 2 min grip time, this was increased to 300°C for 18 min hold time. Mass spectra were conquered at a range m/z = 40–650, number of scans = 3333.

2.2.5 PEC measurements

The PEC analysis was conducted in the typical three-electrode configuration and a potentiostat (Autolab, Metrohm). A solar simulator (LOT Quantum design) equipped with AM 1.5 G filter (intensity = 100 mW/cm²) was used for carrying out LSV, transient photocurrent response, and an electrochemical impedance spectroscopy (EIS) studies under dark and light conditions. Pt-wire and Ag/AgCl acted as the counter and the reference electrode, respectively, while synthesized samples spray-coated onto ITO glass were utilized as a working electrode i.e. photoanode. For electrode fabrication, samples BV, MS, 11BMS, 13BMS, and 31BMS were dissolved in DI water (1 mg/ml) and optimized in terms of spray coating layers i.e. 5, 10, and 15 times. The 0.5 M Na₂SO₄ was used as the supporting electrolyte for all PEC analysis. Mott-Schottky measurements were carried out in frequency-potential scan mode at 10 kHz.

2.3 Results and Discussions

2.3.1 XPS analysis

XPS was done to examine the local electronic environment of composites, including chemical state and composition. The occurrence of Bi, V, O, Mo, and Se at the respective binding energies can be seen in survey spectra as represented in **Fig. 2.1(a)**. Due to the existence

of adventitious carbon in the instrument, an extra peak appeared at 284.5 eV when all peaks were calibrated using the C 1s. De-convoluted peaks of Bi^{3+} found at the binding energies of 159.0, and 164.3 eV, respectively correlate to $4f_{7/2}$, and $4f_{5/2}$ state [39] (**Fig. 2.1(b)**).

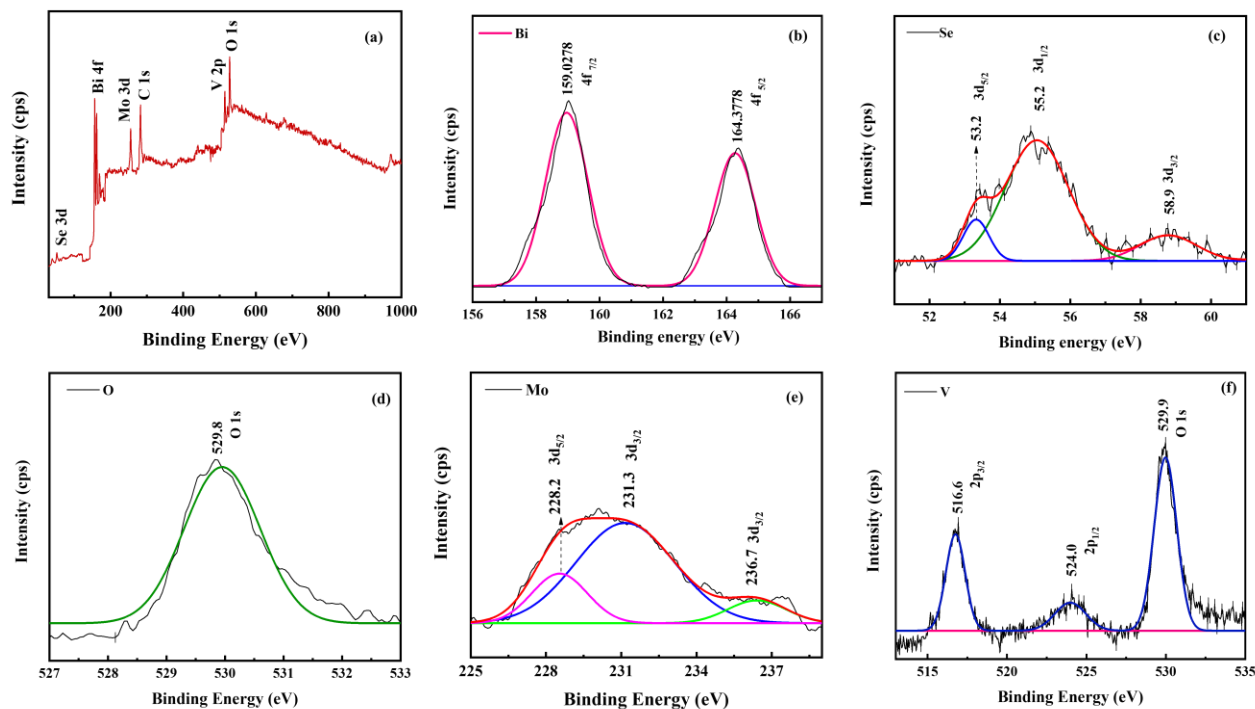


Fig. 2.1 XPS plot of 31BMS, (a) the survey spectra, (b) Bi 4f, (c) V 2p, (d) O 1s, (e) Mo 3d, and (f) Se 3d.

Binding energies of 516.9 and 524.0 eV correspond to three peaks in V^{5+} 2p spectra, credited to V $2p_{3/2}$ [40] and $2p_{1/2}$ [41]. The O 1s of V^{5+} was ascribed to the peak at 529.9 eV [42] (**Fig. 2.1(c)**). The O 1s XPS pattern displayed in **Fig. 2.1(d)** entails the deconvoluted asymmetric peak with binding energy 529.8 eV, attributed to the O^{2-} oxidation state [43]. The peak at 231.3 and 228.2 eV which were accredited to the Mo $3d_{3/2}$ [44] and $3d_{5/2}$ [45] suggest the +4 oxidation state of molybdenum in MS. However, the existence of a peak at 236.7 eV corresponds to Mo^{+6} oxidation state which might be owing to the formation of MoO_3 species in the composite as the sample was exposed to air [46](**Fig. 2.1(e)**). The peaks at 53.2, 55.2, and 58.9 eV were credited to the Se $3d_{5/2}$ [47], $3d_{1/2}$ [48], $3d_{3/2}$ [49] respectively, conclude the +2 valence state of Se, as illustrated in **Fig. 2.1(f)**.

2.3.2 XRD analysis

To examine the purity, as well as the formation of structure, XRD analysis of the fabricated BV, MS, 11BMS, 13BMS, and 31BMS photocatalysts was done as indicated in **Fig. 2.2**. Peaks in the XRD of BV was found at 18.9° (011), 24.4° (102), 28.9° (112), 30.7° (004), 34.9° (200), 35.3° (020), 39.8° (211), 46.0° (123), 46.8° (204), 47.3° (024), 50.2° (220), 53.3° (301), 58.2° (303) which correspond to its standard JCPDS file 83-1699. Also, the diffraction peaks indexed to the planes (022), (004), (006), (102), (111), (201), (110), and (103) found at 23.4° , 29.7° , 41.3° , 43.7° , 45.5° , 51.7° , 56.0° , and 61.4° , respectively confirms the successful formation of MS (JCPDS 77-1715) [48].

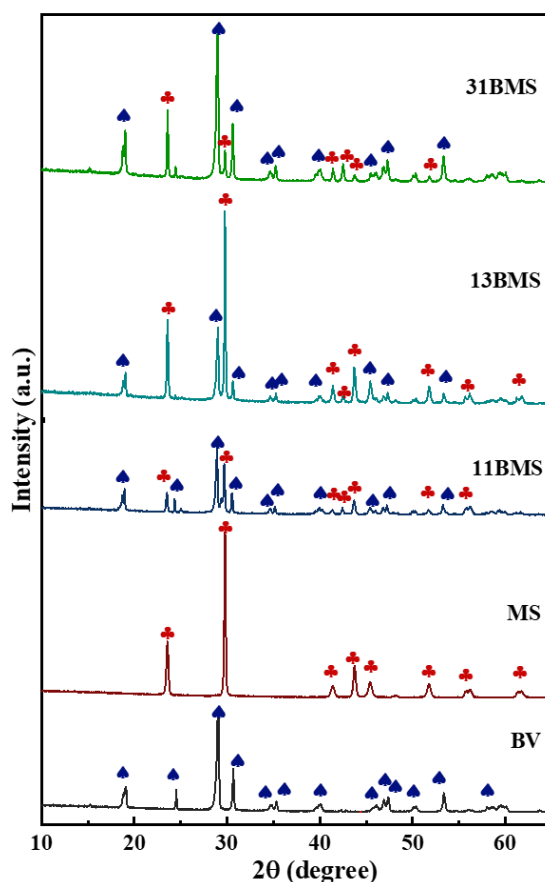


Fig. 2.2 XRD graph of prepared BV, MS, 11BMS, 13BMS, and 31BMS photocatalysts.

The crystalline nature of the composites was proved by the presence of sharp peaks [50]. The presence of both types of peaks approves the efficacious synthesis of composites. Also, the peak intensity is dependent on the proportion of BV and MS in the composites. The XRD pattern of

the composites also revealed an absence of impurity peaks, confirming the purity of the composites [51].

2.3.3 PL study

Recombining capability, migration, and the transfer of the excitons was determined by the PL analysis. The photocatalytic performance of the composites is correspondent with the PL intensity, i.e., a lower PL intensity indicates that charge carriers are less prone to rapid reintegration, allowing for better photocatalytic performance [52]. The emission peak at 447 nm was observed for all the photocatalysts as indicated in **Fig. 2.3**. The following order of intensity of the photocatalysts was observed: 31BMS<13BMS<11BMS < MS <BV

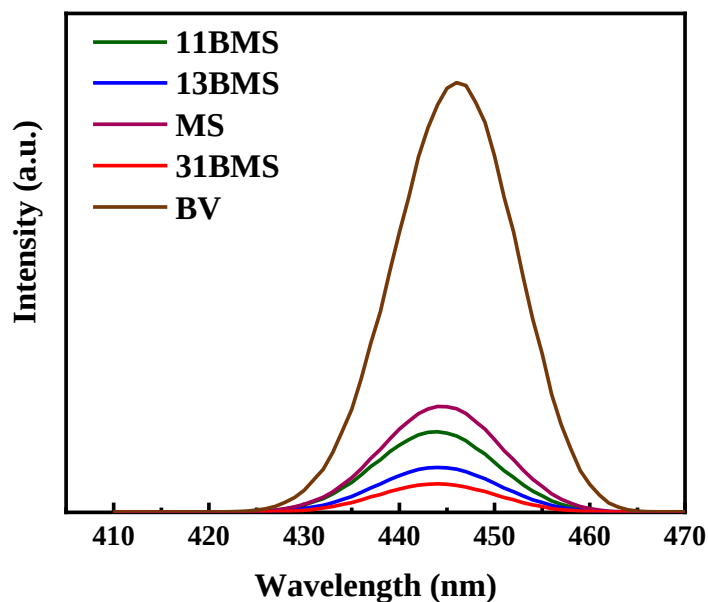


Fig. 2.3 PL spectra of the fabricated photocatalysts.

The 31BMS sample has the lowest PL intensity compared to the other samples while pristine BV has the highest intensity. These results showed that 31BMS has a good charge separation, allowing for a significant augmentation in the photo(electro)catalytic performance. The recombination rate of the charges gets lowered as sunlight exhibits the potential to excite the electrons allowing the segregation of the charge carriers which may be owing to the formation of the heterojunction between BV and MS. Therefore, 31BMS has a favorable photo(electro)catalytic performance under sunlight.

2.3.4 Nitrogen adsorption/desorption study

Porosity and surface area characteristics of the BV, MS, 11BMS, 13BMS, and 31BMS was evaluated using the nitrogen sorption analysis as depicted in **Fig. 2.4(a)**. An average pore diameter and the total pore volume were scrutinized by BJH method as represented in **Fig. 2.4(b)**. The procured isotherms of the photocatalysts were classified as Langmuir's type 3, according to the IUPAC classification with H1 hysteresis loop which reveals the occurrence of mesopores [53]. The specific surface area, pore volume, and mean pore diameter of the samples are represented in **Table 2.1**. Thus, it can be predicted that the surface area of the composites enhanced with the augmentation in the concentration of BV.

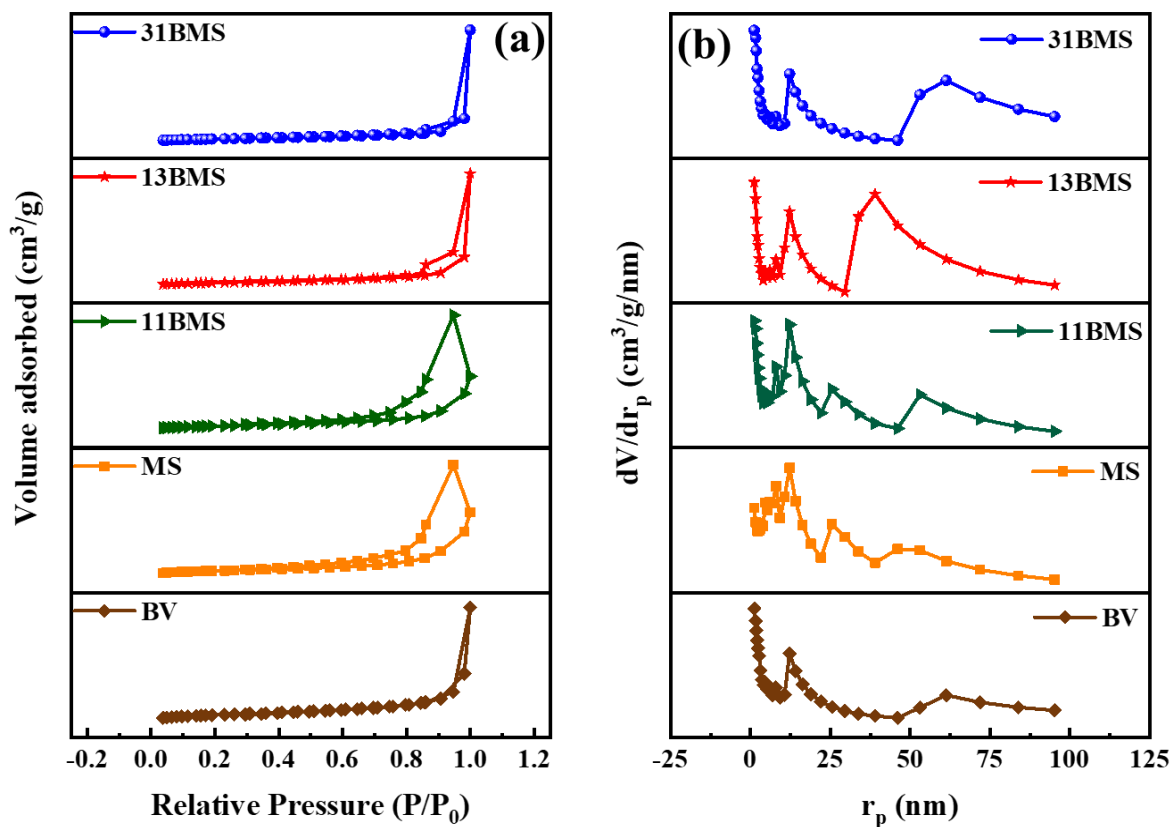


Fig. 2.4(a) BET specific surface area isotherm of prepared photocatalysts, and **(b)** BJH plot. Hence, an increment in the photo(electro)catalytic activity was observed owing to the increased surface area as a large specific surface area provides more surface-active sites for the photocatalytic decomposition of the organic contaminants and production of hydrogen by water splitting.

Table 2.1 The specific surface area, mean pore volume, and the pore diameter of the photocatalysts.

Sample	Specific surface area (m^2/g)	Mean pore volume (cm^3/g)	Pore diameter (nm)
BV	31	0.521	13.21
MS	36	0.587	14.72
11BMS	54	0.662	16.10
13BMS	57	0.681	20.44
31BMS	59	0.672	22.70

2.3.5 UV- visible DRS study

Lower recombination, higher migration rate, good segregation of the photogenerated excitons, and ability to absorb the optimum amount of light in addition to narrow band gap are some of the properties of the efficacious photocatalyst [54].

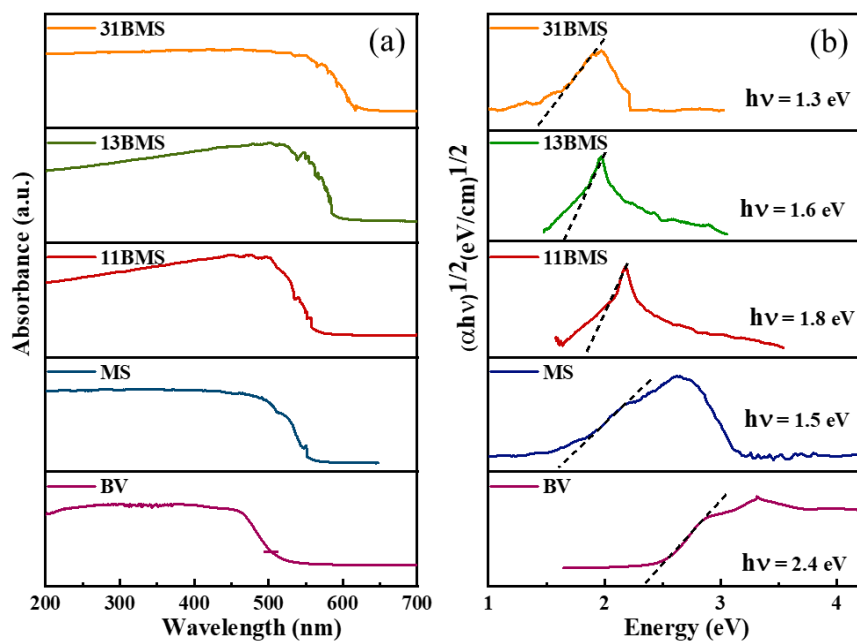


Fig. 2.5(a) absorbance spectra, **(b)** Band gap energies of synthesized BV, MS, 11BMS, 13BMS, and 31BMS photocatalysts.

Band gap and the absorption range of the nano-composites was manifested by UV-visible DRS. The absorbance spectrum of the fabricated photocatalysts are exemplified in **Fig. 2.5(a)**. The Tauc's relation represented in **Eq. 2.4** was utilized to evaluate the band gap energies of the composites and bare BV, MS respectively [55].

$$(\alpha h\nu)^{1/2} = h\nu - E_g \quad (2.4)$$

where frequency of light, an absorption coefficient, the Planck's constant, and the band gap energy are symbolized by ν , α , h , and E_g respectively. The band gap energies of bare BV and MS were calculated to be 2.4 and 1.5 eV, respectively as depicted in **Fig. 2.5(b)**. Band gap energies of 11BMS, 13BMS, and 31BMS were found to be 1.8, 1.6, and 1.3 eV, respectively. Thus, it can be manifested that the synthesized composite possesses narrow band gap in comparison to the bare BV, and MS. As a result, the band gap range is in the visible region, making it the ideal photocatalyst for the photocatalytic deterioration of the organic contaminants and PEC water splitting.

2.3.6 FESEM analysis

FESEM was done to analyze surface morphology of the 31BMS composite at different magnifications.

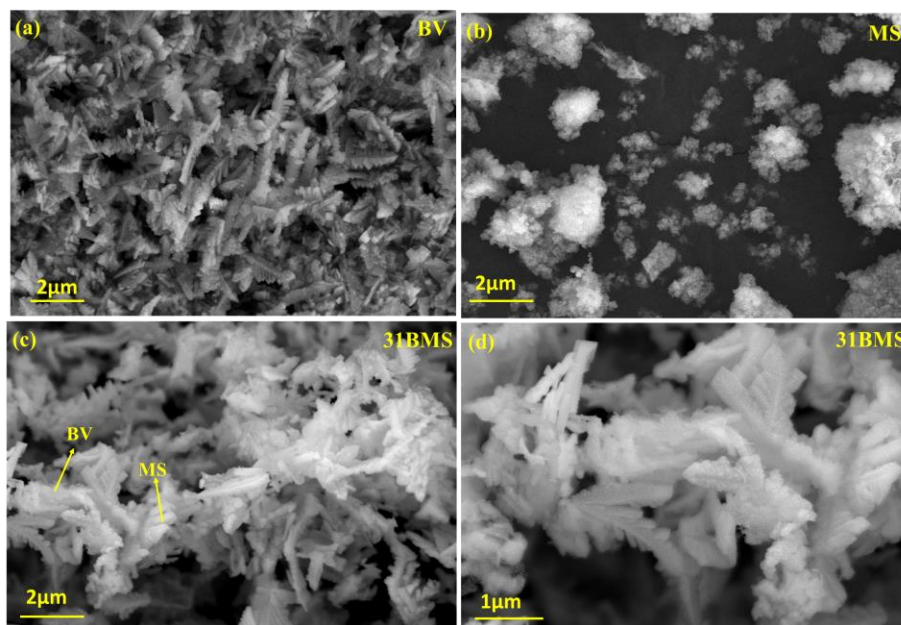


Fig. 2.6 The FESEM images of (a) BV, (b) MS, and (c, d) 31BMS nanocomposite at different magnifications.

It was assessed that BV has a resemblance with fern-petal-like structure whereas, MS has wool shaped morphology (**Fig. 2.6(a, and b)**). It was analyzed that the composite has a resemblance with a both types structure as depicted in **Fig. 2.6(c, and d)**. Wool loaded onto fern-petals were observed in the composite. The occurrence of both type of structures confirmed the efficient formation of the heterojunction between BV and MS. Hence, the photo(electro)catalytic activity of the composite got enhanced owing to the interfacial intimate contact in BV and MS.

2.3.7 EDS, and Elemental Mapping

The elemental composition, purity, and the distribution of 31BMS nanocomposite was investigated using EDS as represented in **Fig. 2.7(a)**.

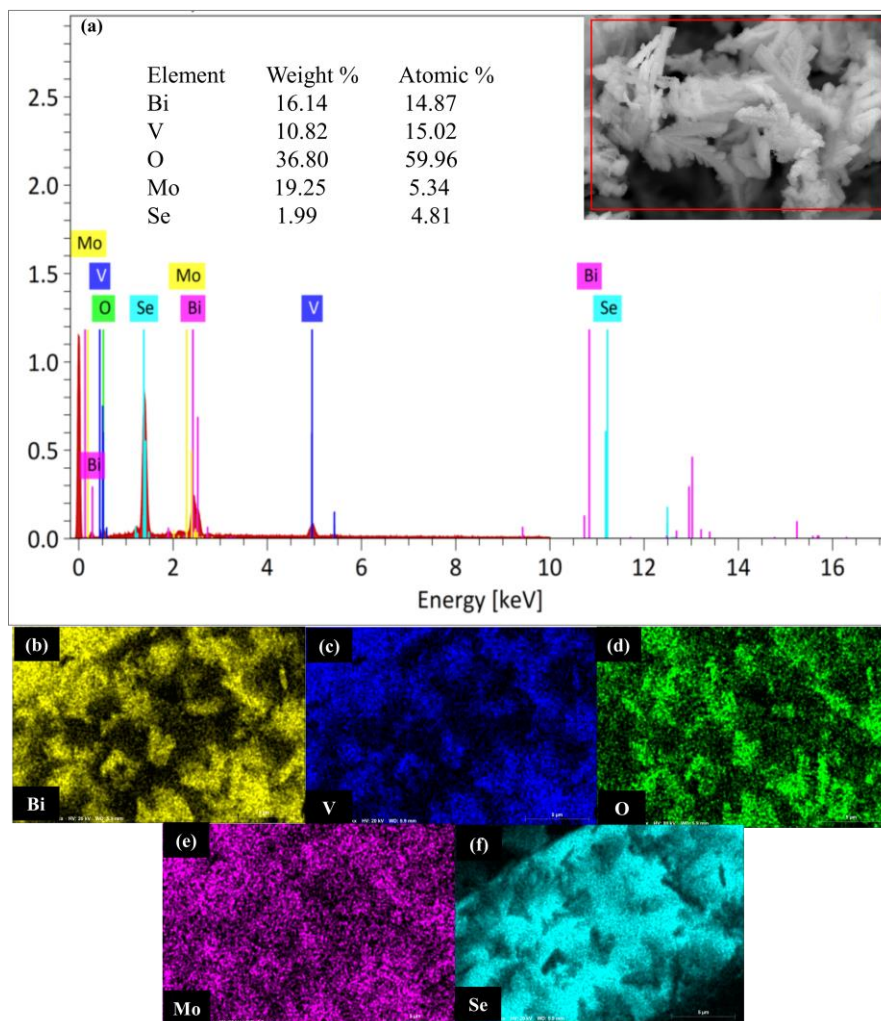


Fig. 2.7(a) EDS spectrum with FESEM image micrograph, **(b-f)** color mapping of the 31BMS nanocomposite.

The EDS spectra show a significant signal of Bi, Mo, V, Se, and O. The absence of any extra elemental peak in the spectrum indicates that there were no contaminants on the surface of the synthesized composite, indicating that the successful synthesis of the material. Elemental mapping affirms that the elements (Bi, V, O, Mo, Se) were evenly scattered, demonstrating the uniform distribution of MS and BV throughout the composite (**Fig. 2.7(b-f)**).

2.3.8 Photocatalytic study

Decontamination of colorless antibiotic TC was carried out under natural sunlight to assess the performance of prepared photocatalysts. Firstly, 20 mL of 10 ppm TC in the absence of the catalyst was illuminated in sunlight for 150 min to carry out a photolysis experiment as a result of which 15 % of TC degraded. After carrying out the photocatalytic degradation experiment, bare BV and MS decomposed maximum up-to 58, and 68 %, respectively. While 31BMS exhibited a high photocatalytic degradation rate of 91.9 % among all the photocatalysts. This may be most likely due to the formation of interfacial contact in two photocatalysts. In contrast, the degradation efficacy of the photocatalysts was compared by conducting the degradation experiment with commercial TiO₂-P25 under similar conditions. For TiO₂-P25 the highest decomposition efficiency of 46.2 % was attained. The photocatalytic procedure followed the pseudo-first-order kinetics. The rate constant was figured out by **Eq. 2.5** where C₀ is the concentration of the model pollutant at the time (t=0), C is the concentration at any time (t) respectively, and k is the rate constant [55].

$$\ln (C/C_0) = -kt \quad (2.5)$$

The rate constant of 0.0147 min⁻¹ and 0.0037 min⁻¹ was attained by 31BMS and TiO₂-P25, respectively. Kinetic analysis of the photocatalysts is described in **Fig. 2.8(a, b)**. Synergy factor (R) was computed using **Eq. 2.6** for the calculation of extent of synergistic effect of the different composites.

$$R = \frac{k_{BV}/k_{MS}}{k_{BV} + k_{MS}} \quad (2.6)$$

Here, k_{BV}/k_{MS}, k_{BV}, and k_{MS} stand for the rate constant of coupled BV and MS, bare BV, and MS, respectively. The R factor for the 31BMS composite was the highest (1.26). This was due to

the increased synergistic effect of BV and MS, it had the best efficiency of all the fabricated materials. **Table 2.2** lists the degrading efficacy, rate constant, and synergistic constant value of the various photocatalysts.

Table 2.2 Rate constant, the decomposition efficiency of TC, and the synergy factor of the prepared photocatalysts.

Catalyst	Rate constant (min^{-1})	Degradation efficacy (%)	R factor
TiO ₂ -P25	0.0037	46.2	-
BV	0.0054	58.0	-
MS	0.0062	63.0	-
11BMS	0.0071	68.8	0.61
13BMS	0.0081	74.4	0.69
31BMS	0.0147	91.9	1.26
No catalyst	0.0011	15.0	-

2.3.8.1 Concentration effect of catalyst

The analogous experiment was conducted with varied catalyst concentrations (0.05, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35 g/L) to scrutinize the impact of concentration of the synthesized photocatalyst on the photodecomposition process. The increase in concentration from 0.05 to 0.30 g/L, resulted in enhanced photodegradation efficacy. However, a drop in removal efficacy was noticed after that, which was accredited due to the opaqueness of the solution which hindered the light absorption of the catalyst [56]. As represented in **Fig. 2.8(c)**, with 0.3 g/L of catalyst, the highest degrading efficacy of 91.9 % was accomplished.

2.3.8.2 Effect of different light sources

To further explore the effectiveness of the 31BMS photocatalyst, a similar experiment was performed under different light sources (UV and visible light) under optimal conditions for

comparison. As shown in **Fig. 2.8(d)**, TC was degraded to 60.4 % under UV light and 77.1 % under the visible light. Interestingly, the highest degradation rate of 91.9 % was achieved under natural sunlight when using the 31BMS photocatalyst. These results indicate that natural sunlight alone is sufficient for the effective degradation of pollutants by the synthesized photocatalyst, outperforming the UV and visible light sources tested.

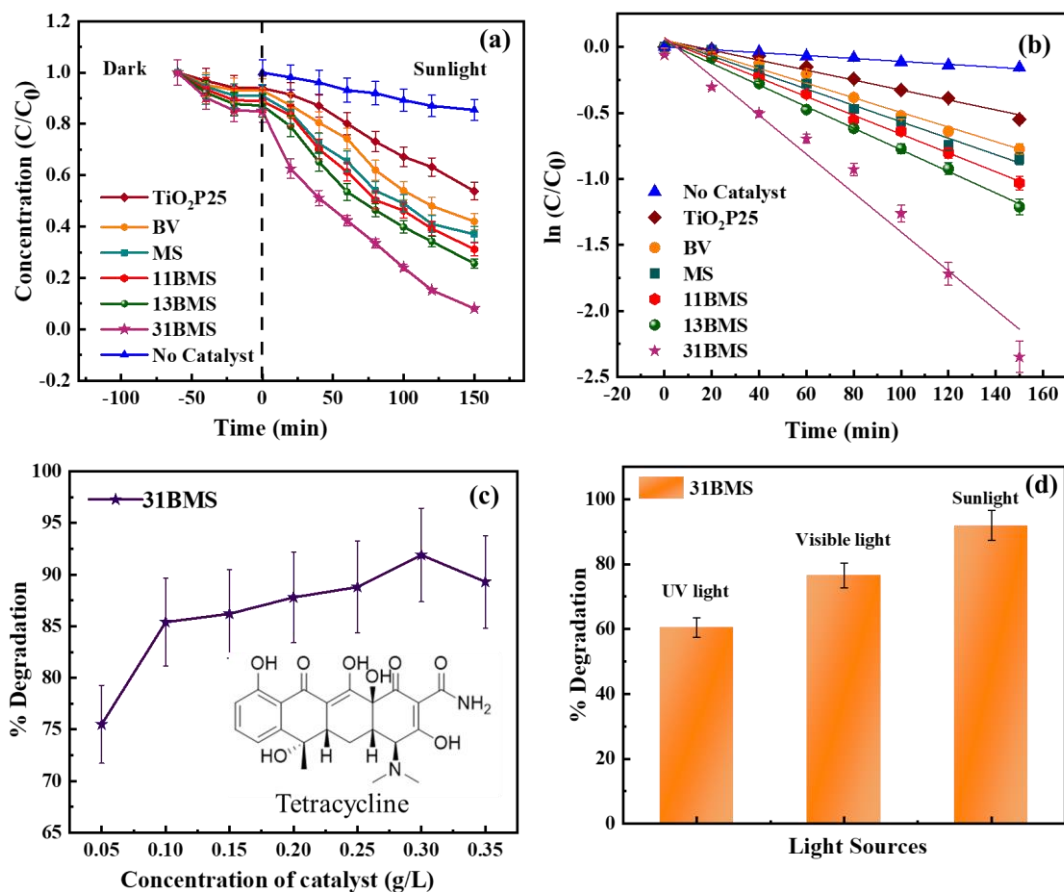


Fig. 2.8(a, b) Kinetic studies for the decomposition of the pharmaceutical pollutant, TC utilizing the various prepared photocatalysts with standard deviation of 24.25, **(c)** concentration impact of 31BMS photocatalyst on the degradation, and **(d)** comparative study of the degradation efficacy in different light sources.

2.3.8.3 Impact of pH

A series of batch experiments were conducted at the various pH to find out the impact of pH on the degrading efficacy of the catalyst [57]. Surface characteristics, charge of photocatalyst, dissociation, and structure of pollutant are affected by the change in pH.

Therefore, differential pH values such as 1, 3, 5, 7, 9, 11 were obtained by adding NaOH or HCl to analyze its effect in a solution of 0.3 g/L of catalyst dissolved in 10 ppm of TC solution. The dimethyl ammonium group possesses the tendency to get protonated at $\text{pH} < 4$, leaving the TC positively charged (TCH^+). At the expense of the proton from the diketone group of phenol, TC exists in the zwitterionic form ($\text{TCH}^\pm$) at pH between 3.3-7. However, the abstraction of the electron from the proton diketone group of phenol and carbonyl group leaves the TC negatively charged ($\text{TCH}^-/\text{TC}^{2-}$) at $\text{pH} > 7$. **Fig. 2.9(a)** reveals that pzc of the 31BMS composite was evaluated to be 5.6. It clearly states that when the $\text{pH} > \text{pzc}$ and $\text{pH} < \text{pzc}$, the surface of the catalyst becomes negatively and positively charged respectively. Owing to the repulsion of anionic contaminant due to the presence of M-O^- species on the catalyst's surface, the catalyst's tendency to interact with the pollutant gets minimized at the basic pH, therefore the efficacy of degradation decreases. Furthermore, the presence of M-OH_2^+ species at $\text{pH} < \text{pzc}$ leads to the repulsion of the catalyst with the cationic pollutant causing a decrease in the degradation efficacy. However, the decomposition of the model pollutant was found to be maximum at pH 6 owing to the electrostatic interactions taking place between the zwitterionic form of the pollutant and the anionic form of the catalyst as represented in **Fig. 2.9(b)** [58]. The efficiency towards degradation increases with the augmentation in pH, determined to be maximum at pH 6, and further decreases with the increase in pH.

2.3.8.4 Scavenger study

The scavenger analysis was carried out with the frequently utilized quenchers to manifest the role of active radical species in the breakdown of TC in photocatalytic processes. With the addition of methanol, DMSO, and ascorbic acid (AA), the role of holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), and superoxide ions ($\text{O}_2^{\cdot-}$) was investigated [59]. The inclusion of methanol greatly hindered the photocatalytic performance of 31BMS composite, as seen in **Fig. 2.9(c)**, which was expected given that h^+ were typically the primary species accountable for pollutant decomposition. The presence of methanol in the reaction mixture suppresses all h^+ -dependent activities, including the generation of $\cdot\text{OH}$, and the direct oxidation of molecules on the photocatalyst's surface. DMSO, a radical scavenger for $\cdot\text{OH}$, also delayed the process, albeit to a less amount which suggests that $\cdot\text{OH}$ has a role in the degrading process, but it is little as the degradation efficiency got decreased to 62.7 %. It was also observed that AA also slowed down

the process though to a very lesser extent, demonstrating that $O_2^{\cdot-}$ plays a little part in the decomposition process (the degradation efficiency drops down to 75.2 %). The experiment results revealed the methanol's extensive activity as the inclusion of little amount of h^+ affects the decomposition of TC. These results reveal the vulnerability of the reactive species to the photocatalytic elimination of TC with the nanocomposite.

2.3.8.5 Mineralization experiment

In the quest to assess the mineralization potential of the 31BMS photocatalyst on TC, a TOC experiment was conducted. The presence of a significant amount of organic substances in the pollutant was initially established by elevated levels of TOC and COD.

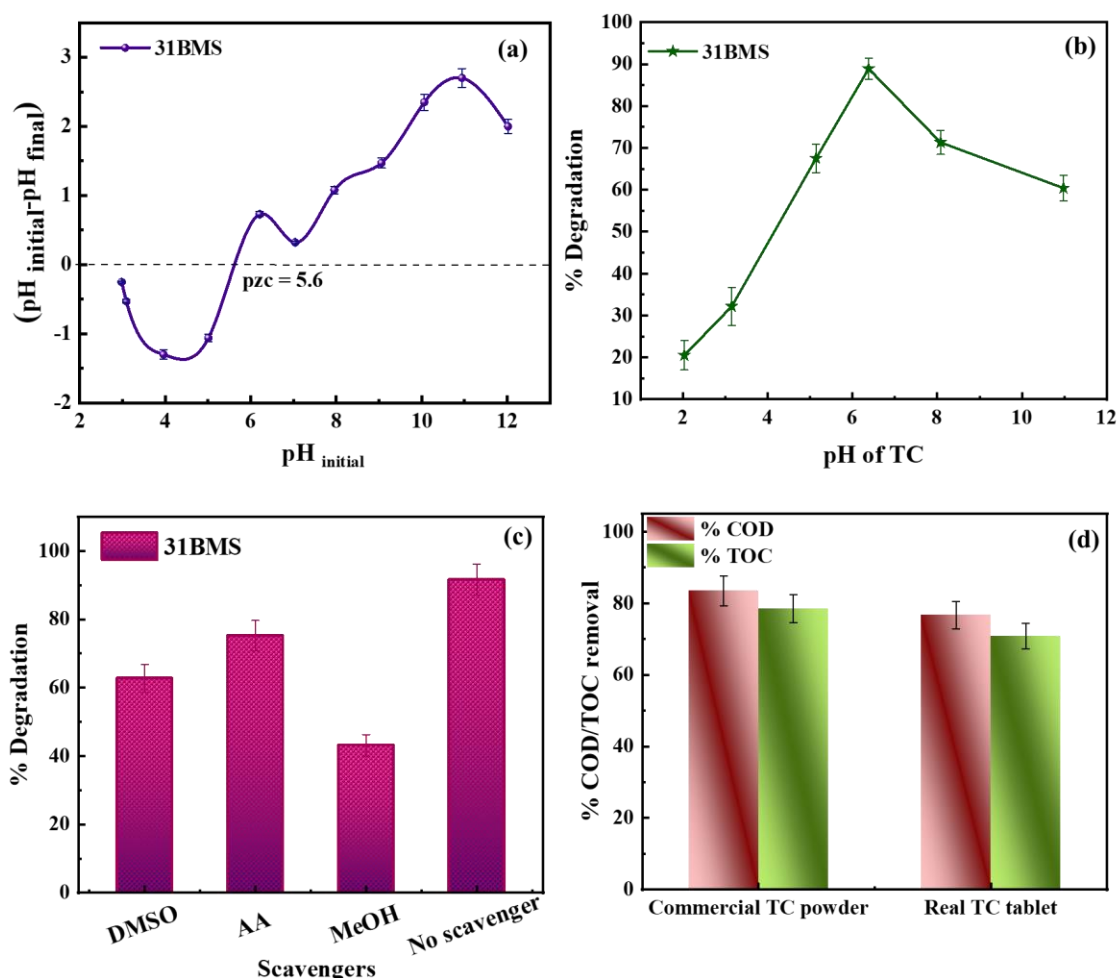


Fig. 2.9(a) pzc of the 31BMS photocatalyst, and **(b)** the impact of pH on the degradation of TC, **(c)** effect of the different quenchers on the photocatalytic decomposition of TC, **(d)** % COD/TOC examination of commercial powder of TC, and real TC pill.

Under natural sunlight for 150 minutes, the photocatalytic treatment using 31BMS resulted in a remarkable reduction of 83.4 % and 78.4 % in COD and TOC, respectively (**Fig. 2.9(d)**). However, the percentage of TOC removal was lower than that of degradation due to the formation of intermediate organic compounds during the process before complete breakdown of TC to simpler products and carbon dioxide. It is worth noting that a rapid degradation rate in aqueous conditions does not necessarily imply extensive mineralization and complete destruction of organic compounds. Unfortunately, ethical considerations limit the feasibility of conducting experiments with actual medical/pharmaceutical wastewater. Nevertheless, to validate the efficacy of the 31BMS photocatalyst, COD and TOC analyses were conducted on a real TC tablet (Abbott, Tetracycline capsules I.P. Rستهcline 250 with a concentration of 250 mg). The results showed an impressive reduction of 76.6 % and 70.8 % in COD and TOC, respectively, highlighting the excellent surface catalytic property of the photocatalyst compared to the conventional and time-consuming physicochemical methods used in industries.

2.3.8.6 Reusability experiment

To examine the stability of the 31BMS photocatalyst for TC decomposition, the experiments were repeated many times for each of the tested photocatalysts (7 runs) as depicted in **Fig. 2.10(a)**. Due to the features of the heterogeneous catalyst, the recycling process went off without a hitch. One of the benefits of utilizing this type of catalyst is that it is simple to separate the spent catalyst from the examined solvent as it adsorbed organic pollutants physically only [60]. It is only needed to be washed and dried in the oven before being used again, rendering it to be easily recoverable. The little loss of photocatalyst in the sedimentation and allocation results in a slight decline in photocatalytic activity. XRD, BET, and SEM analyses were carried out to assess the stability of 31BMS photocatalyst post the degradation studies. Post the reusability studies, the XRD pattern of the nanocomposite exhibited no distinct changes (**Fig. 2.10(b)**). The peak intensity and the positions of MS and BV were unchanged. No new diffraction peak corresponding to crystalline impurities was observed. The BET analysis performed after the reusability studies validated that the photocatalyst had pore diameter (15.4 nm), mean pore volume (0.436 cm³/g), and specific surface area (45m²/g) as presented in **Fig. 2.10(c, d)**. Although the specific surface area got decreased but it was still enough to carry out photocatalytic remediation of TC. Further, FESEM analysis was done at the same magnification

to compare the morphology of the composite before and after the degradation experiments. It was observed that the wool loaded onto fern-petal morphology of the composite remained intact before and after the experiments, thereby, confirming the stability of the synthesized composite (**Fig. 2.10(e)**). Hence, the prepared 31BMS photocatalyst is stable, reusable, and can be utilized for practical applications.

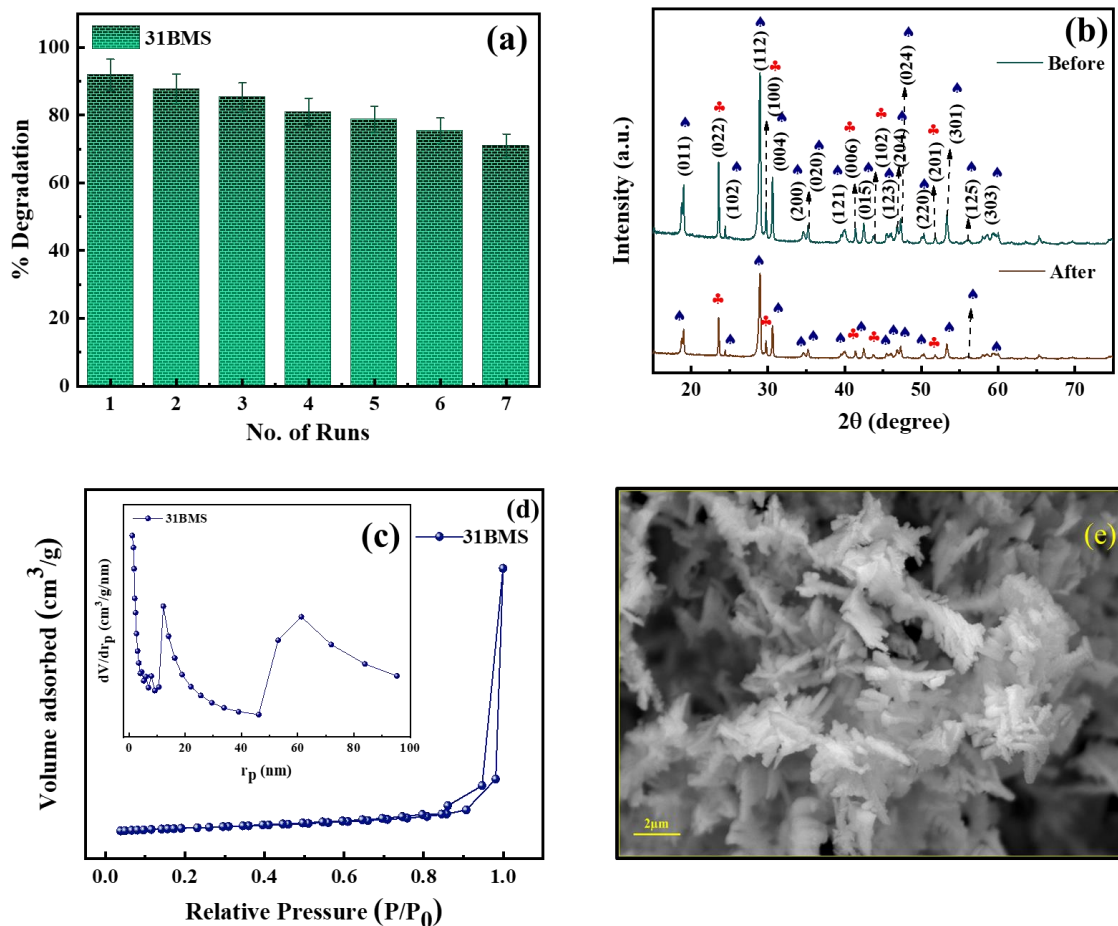


Fig. 2.10(a) recyclability studies on the decomposition of TC using 31BMS, **(b)** XRD graph post the photocatalytic degradation, **(c, d)** BET plot after degradation with inset having BJH graph, **(e)** SEM image after the degradation experiments.

2.3.9 Comparison with the literature

A comparative analysis of the fabricated BMS catalyst was done with the other reported BV and MS dependent photocatalysts for the photocatalytic deterioration of various model pollutants as tabularized in **Table 2.3**. In accordance with the table, even in the presence of little

amount of the BMS photocatalyst harmful contaminants can be eliminated in the sunlight at ambient temperature.

Table 2.3 Comparative study of BV and MS-dependent catalysts for the decomposition of the model pollutants.

Photocatalyst	Contaminant's concentration (ppm)	Time of the reaction (min)	Source of light	Rate constant k	Decomposition efficiency (%)	Ref.
BiVO ₄ /NiFe ₂ O ₄	Methylene Blue (10 ppm)	180	Sunlight	-	80	[61]
BiVO ₄ /Fe ₃ O ₄ /CdS	TC (10ppm)	90	Visible Light	0.0232 min ⁻¹	87.37	[62]
MoSe ₂ /Ag ₃ PO ₄ /g-C ₃ N ₄	TC	10	Visible Light	0.0123 min ⁻¹	69	[63]
BiVO ₄ / MoSe ₂	Glycophosphate	180	Visible Light	-	86.1	[33]
MoS ₂ /MoSe ₂	Fipronil (600 ppm)	80	Visible Light	0.016 min ⁻¹	80	[48]
31BMS	TC (10 ppm)	150	Sunlight	0.0206 min ⁻¹	91.9	Present work

2.4 GC-MS analysis

A GC–MS analysis was done to gauge all the intermediates and the products in the photocatalytic decomposition process of the TC. **Fig. 2.11(a, b)** represent the GC chromatogram and mass spectra of TC, respectively. As depicted in **Fig. 2.12**, the degradation pathway may follow two pathways. In the first route, initially, 3,6,10,12,12a-pentahydroxy-6-methyl-4-(methyldiamino)-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide, 3,6,10,12,12a-pentahydroxy-6-methyl-5a,6-dihydrotetracene-1,11(5H,12aH)-dione, 6,10,12,12a-tetrahydroxy-6-methyl-5a,6-dihydrotetracene-1,11(5H,12aH)-dione were formed by the abstraction of the electron from the organic moiety by the h⁺. Indirect substitution or the addition

of $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ resulted in the formation of the intermediate structure, (Z)-4,8-dihydroxy-3,4-dimethyl-2-(1,2,2-trihydroxyethylidene)-3,4-dihydronaphthalen-1(2H)-one. Further, the h^+ gets oxidized to form (Z)-4,8-dihydroxy-2-(hydroxymethylene)-3-methyl-3,4-dihydronaphthalen-1(2H)-one and 4,8-dihydroxy-2-methylene-3,4-dihydronaphthalen-1(2H)-one. The hydroxylation reaction resulted in the formation of 3-vinylbenzene-1,2-diol [64].

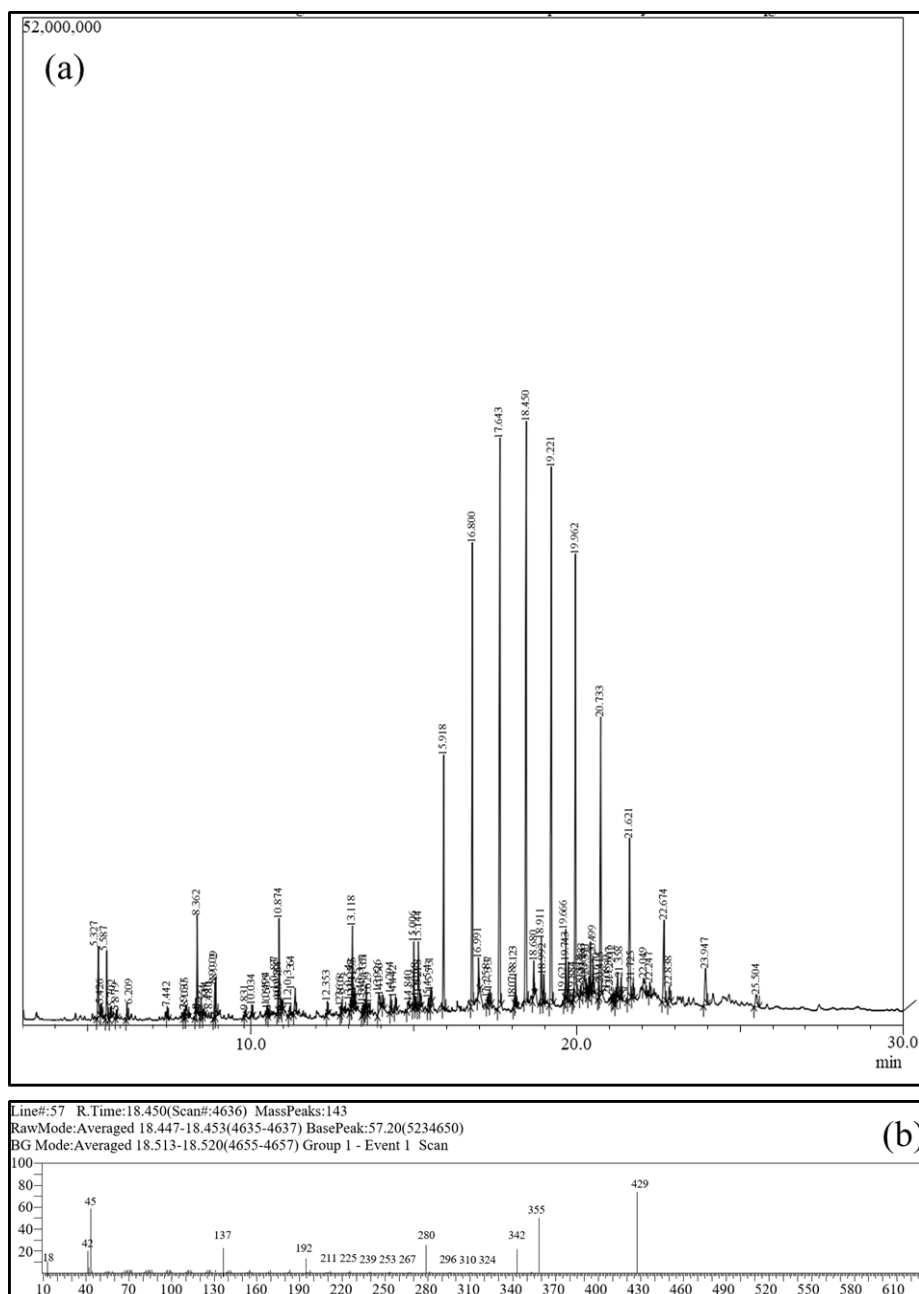


Fig. 2.11(a) Gas chromatogram, **(b)** Mass spectra of products formed post the degradation of TC by 31BMS photocatalyst.

In the second pathway, 3,6,10,12,12a-pentahydroxy-6-methyl-4-(methylamino)-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carbaldehyde, and 6,10,12,12a-tetrahydroxy-6-methyl-4-(methylamino)-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carbaldehyde was formed by the oxidation of h^+ ions. After that, a ring cleavage occurred and methanediimine was formed as a result. Finally, the fragmentation resulted in amine, carbon dioxide, and water as the byproducts [65].

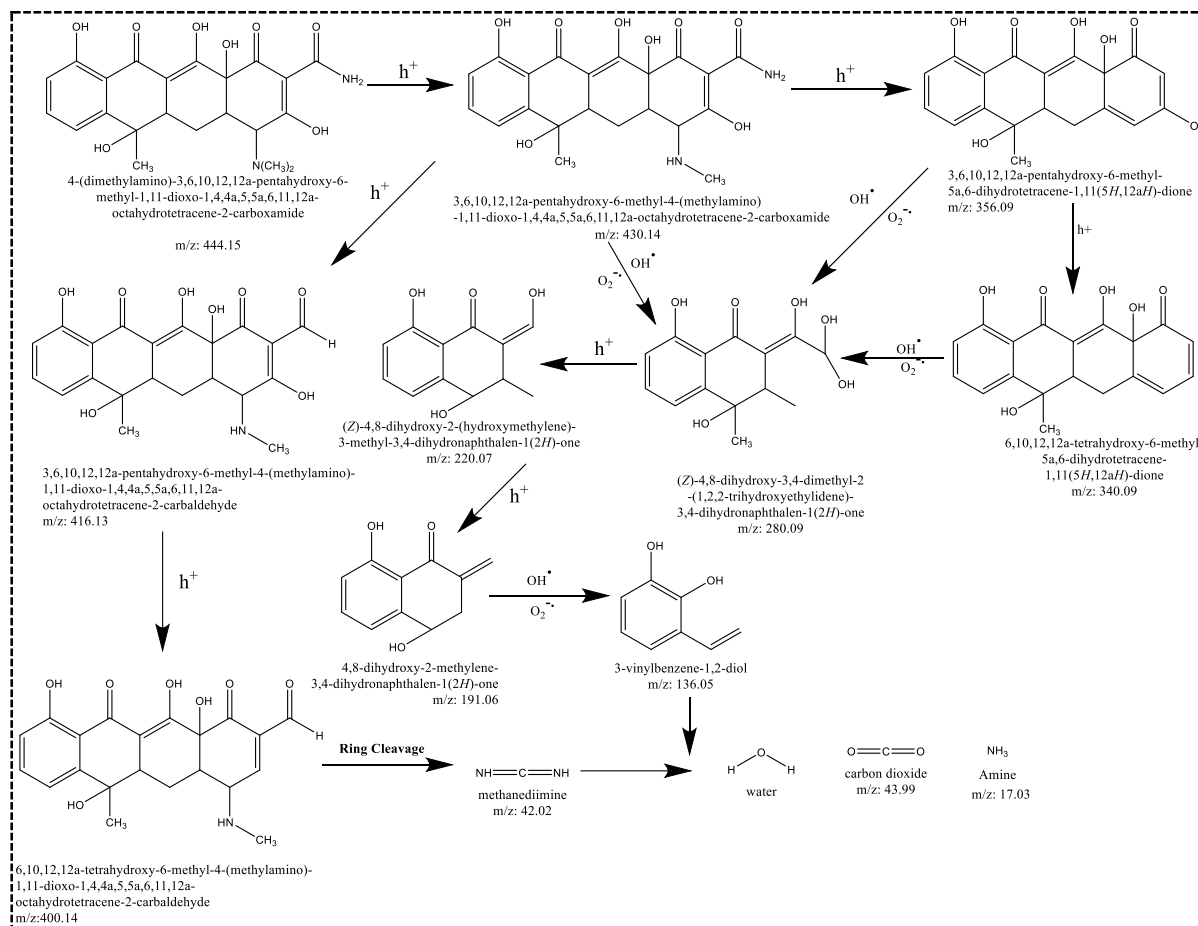


Fig. 2.12 Proposed degradation route of TC by 31BMS nanocomposite.

2.5 PEC measurements

The PEC studies of individual catalysts (BV, MS) and as-synthesized hybrids (11BMS, 13BMS, and 31BMS) with different coating layers were performed to investigate their photo response as well as PEC water splitting performance. LSV studies revealed that the electrodes showed an increase in current with applied bias with an onset potential of 0.26 V vs RHE in case of 31BMS

electrode (**Fig. 2.13(e)**). The appearance of an oxidation peak in LSV graph of MS, 11BMS, 13BMS, and 31BMS can be attributed to MoO_3 (the same is observed in XPS analysis). Further, the LSV corresponding to the coating layer optimization (**Fig. 2.13(a-e)**) showed that photocurrent response in the case of 15 layer coated sample was higher (0.43 mA/cm^2) as compared to 5c (0.24 mA/cm^2) and 10 layer (0.37 mA/cm^2) coatings LSV of the optimized electrode i.e. 15c of BV, MS, 11BMS, 13BMS, and 31BMS shows the significant difference in dark and light condition, thus revealing their photo responsive behavior (**Fig. 2.15(a)**). The photocurrent densities were calculated at 1.23 V vs RHE and were scrutinized to be 0.0044 , 0.032 , 0.031 , 0.121 , and 0.43 mA/cm^2 for BV, MS, 11BMS, 13BMS, and 31BMS respectively.

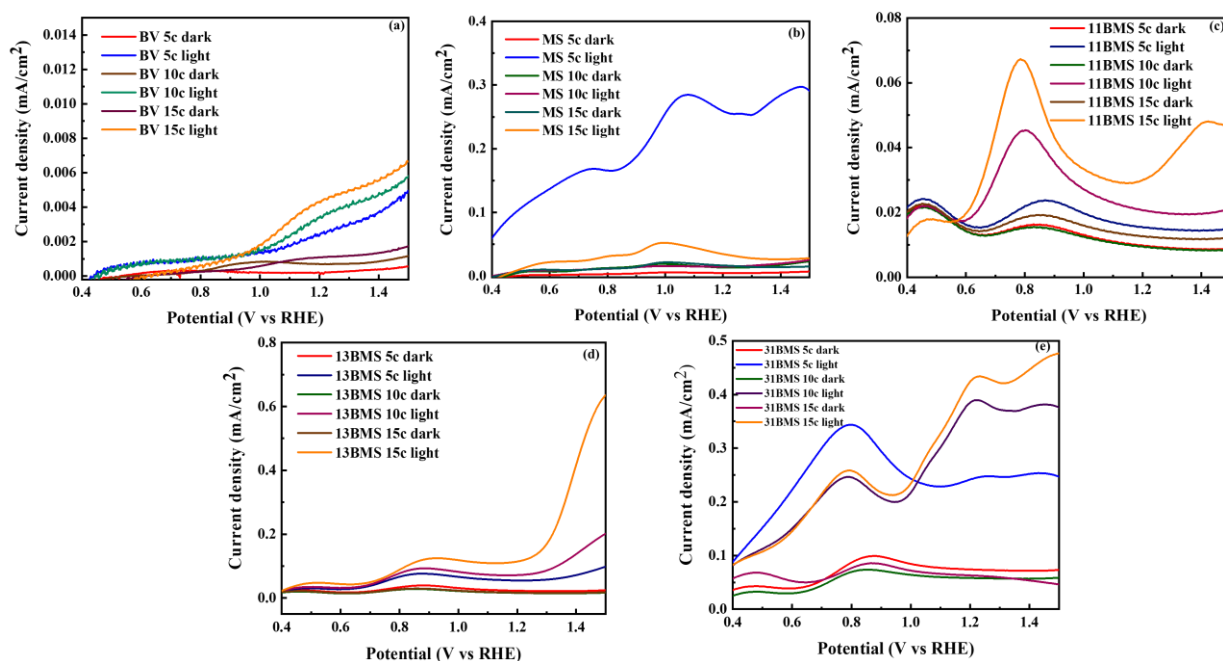


Fig. 2.13 LSV of different coating layers of (a) BV, (b) MS, (c) 11BMS, (d) 13BMS, and (e) 31BMS in dark & light condition.

To manifest the charge transfer characteristics at electrode/electrolyte interface of fabricated electrodes, EIS measurements were also carried out in dark and light. It can be seen from the Nyquist plot (**Fig. 2.14(a-e)**) that the 31BMS has the smallest semi-circle associated with the charge transfer resistance (R_{ct}) thus indicating better charge transfer than other electrodes, which could be assigned to the heterostructure of BV and MS, thus enabling excellent charge generation, separation, and channelization. The R_{ct} was calculated from the Randel's equivalent circuit and

was found to be 991Ω (**Fig. 2.15(b)**) in the case of 31BMS, which otherwise was $284k\Omega$ and $58.1k\Omega$ for BV and MS, respectively.

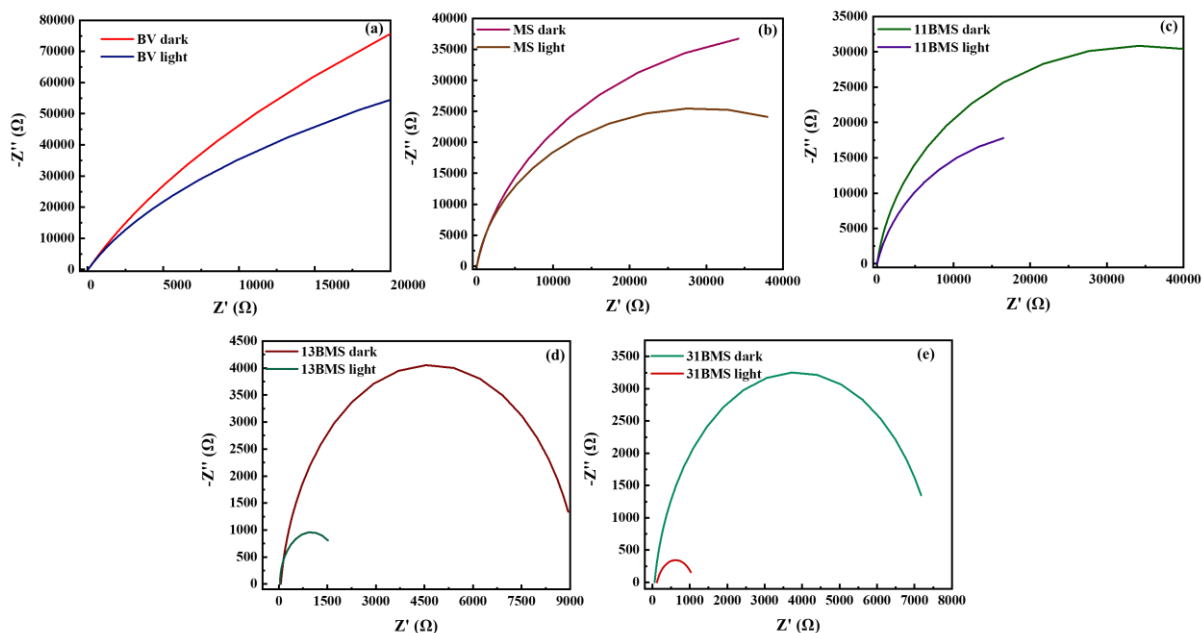


Fig. 2.14 Nyquist plot of 15 coatings of (a) BV, (b) MS, (c) 11 BMS, (d) 13 BMS, and (e) 31 BMS in dark & light condition.

The semiconducting nature of the fabricated hybrid electrode was analyzed from the Mott-Schottky analysis. The positive slope in MS analysis (**Fig. 2.15(c)**) specified that the 31BMS electrode is a n-type semiconductor and acted as a photoanode. The flat band potential (E_{fb}) was calculated and manifested to be 0.13 V. The charge carrier density for 31BMS electrode was calculated as 1.49×10^5 .

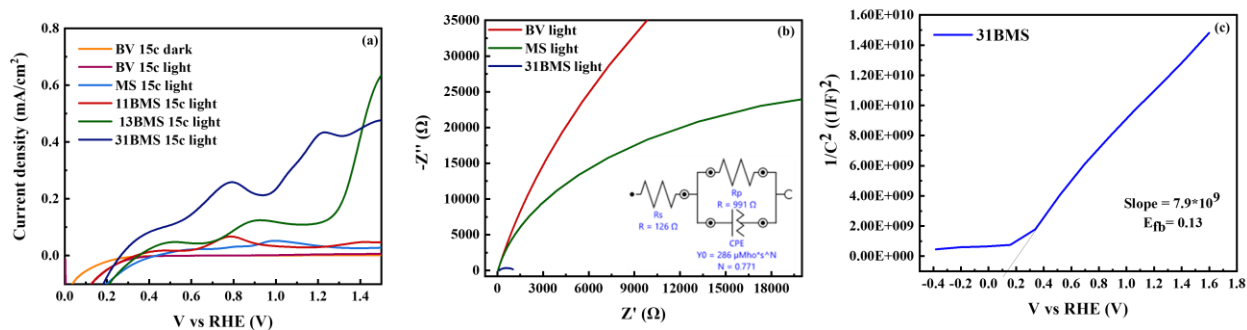


Fig. 2.15(a) LSV of BV (15c), MS, 11BMS, 13BMS, and 31BMS in dark & light conditions, (b) Nyquist plot of BV, MS, 31BMS in light conditions, and (c) Mott Schottky of 31BMS hybrid.

Fig. 2.16(a) indicates the transient photocurrent response of BV, MS, and 31BMS at a constant voltage of 1.2 V vs RHE under the chopped light conditions with 50 sec time intervals. The fast switching behavior shows the fast charge kinetic of 31BMS electrode. It indicates the effectual segregation of charges.

To understand the stability of the fabricated electrode, chronoamperometric measurements were done 18000 sec (5.5 h) at 1.23 V vs RHE under light condition. The photocurrent was found to be stable, and only a small decrease in current density was observed as seen in **Fig. 2.16(b)**. The **Eq. 2.7** was used to calculate the amount of hydrogen produced theoretically from the stability study data and the hydrogen produced was found to be 3.59 mmol/cm².

$$\text{No. of moles of Hydrogens produced} = \frac{\text{Faradic efficiency} * \text{Charge}}{2 * \text{Faradic constant}} \quad (2.7)$$

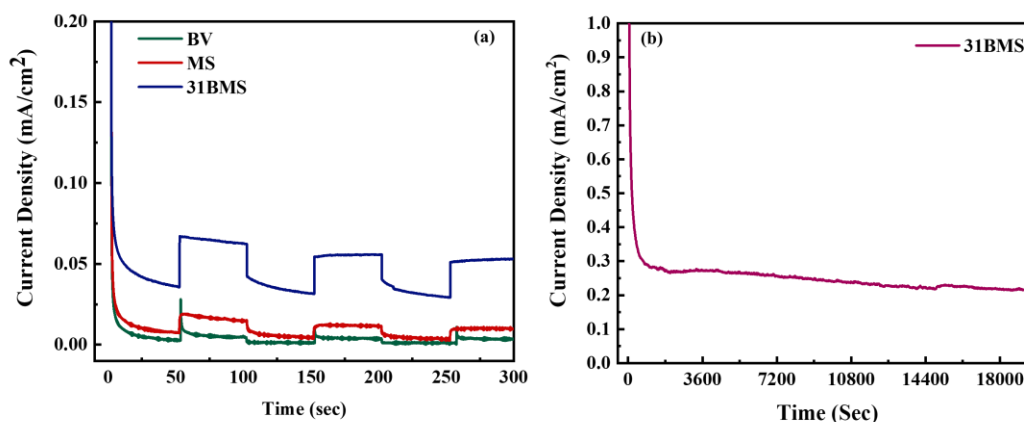


Fig. 2.16(a) Transient current density of BV, MS, and 31 BMS at 1 V vs RHE with 50 sec time intervals, and **(b)** Stability study of 31 BMS hybrid electrode for 5.5 h.

2.5.1 Comparison with the literature

The 31BMS exhibited the highest PEC activity amongst the fabricated hybrid electrodes. The higher loading of MS onto BV reduced its photocurrent as well as exhibited poor stability due to oxidation of MS in anodic window. It also showed the enhanced photo response over BV and MS alone, thus confirming the role of interface formation to enhance the charge generation as well as separation. The interfacing allowed maximum photo absorption of light. Comparison of the PEC performance of the fabricated electrodes in terms of current density and no. of moles of hydrogen over previously published literature is summarized in **Table 2.4**. Hence, it can be inferred that 31BMS electrode with 15c is efficient for evolving the hydrogen via PEC water splitting.

Table 2.4 PEC performance comparison of 31BMS with previously published literature.

S.No.	Photocatalyst	Electrolyte	Electrode type	Photocurrent	No. of moles of Hydrogen	Reference
1.	Au-doped BiVO ₄	0.1 M KOH	Photoanode	0.24 mA/cm ²	-	[66]
2.	BiVO ₄	0.5 M Na ₂ SO ₄	Photoanode	50 μA/cm ²	-	[67]
3.	BiVO ₄ Nanowire	0.1 M potassium Phosphate buffer	Photoanode	9.3 μA/cm ²	-	[68]
4.	g-C ₃ N ₄ /Ag/AgCl/BiVO ₄	Sewage wastewater	Photoanode	0.1-0.2 mA/cm ²	178 μmol/cm ²	[69]
5.	31BMS	0.5 M Na ₂ SO ₄	Photoanode	0.43 mA/cm ²	3.59 mmol/cm ²	Current Work

2.6 The proposed mechanism

To better understand the charge migration mechanism in the composite BMS, the location of the VB and CB were determined using Mulliken's electronegativity value (**Eq. 2.8, and 2.9**).

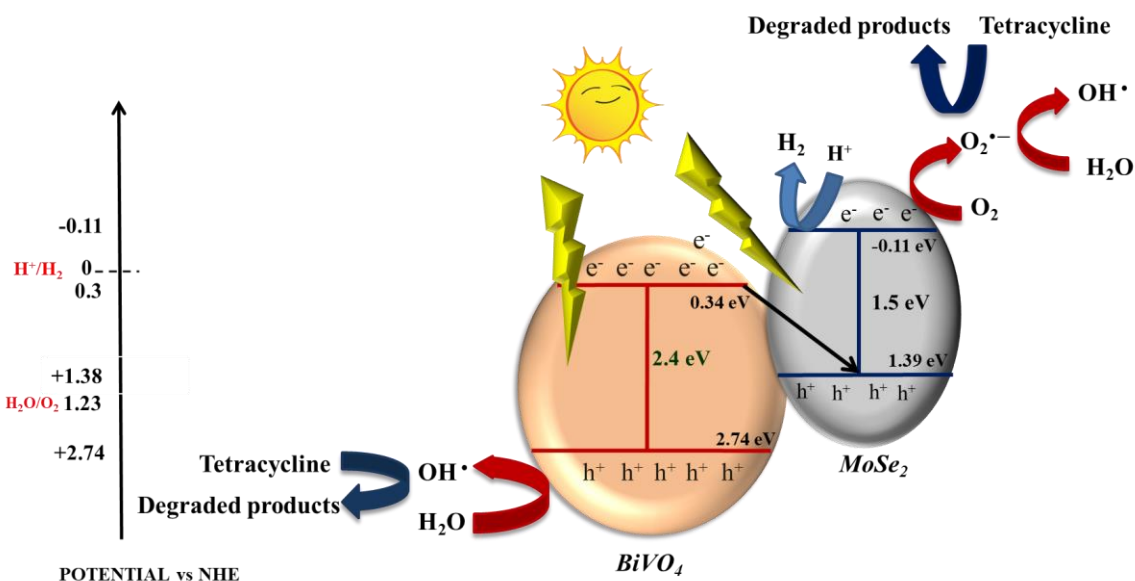
$$E_{VB} = \chi - E_e + 1/2E_g \quad (2.8)$$

$$E_{CB} = E_{VB} - E_g \quad (2.9)$$

Maximum VB oxidation potential, minimum CB reduction potential values, and Mulliken electronegativity are denoted by as, E_{VB} , E_{CB} , and χ respectively. E_e and E_g stand for the free-electron energy on the hydrogen scale (4.5 eV) and the band gap value, respectively. As a

consequence, the E_{VB} values for BV and MS were 2.74 and 1.39 eV, respectively, whereas the E_{CB} values were 0.34 and -0.11 eV, respectively [70,71].

The probable interface electron transport behavior of 31BMS in the illumination of the sunlight is hypothesized based on all the above experiments and an alignment of their energy levels. The e^- migrate to the CB of BV and MS from their respective VB on the illumination of solar light. Even after continuous illumination, the high recombining capability of photogenerated charges in BV prevents the extraction and buildup of e^- . To prevent the reintegration of the charges in BV, the e^- in BV with the higher CB potential tend to migrate to MS with lower VB potential owing to the existence of a large driving force that originates from a high potential difference, and thus the e^- in BV with a higher oxidation capacity will reintegrate with the h^+ in MS with a higher reduction capability. Thus, MS works as an e^- sink to minimize carrier charge recombination and provide a large number of reactive sites for hydrogen production. Hence, H^+ ions can be reduced to evolve the hydrogen. Also, the redox reactions could result from the accumulated e^- reacting with dissolved oxygen molecules to produce $O_2^{\cdot-}$.



Scheme 2.1 Photo(electro)catalytic pathway of BMS photocatalyst for the production of hydrogen and breakdown of TC.

The $OH^{\cdot}$ produced from water by the reaction with $O_2^{\cdot-}$ which resulted from the reaction of e^- at the CB of MS possesses the tendency to decompose the contaminants or directly oxidize and

break them. Also, after the interaction of h^+ from VB of the BV with water to form $OH^\bullet$, refractory substances can be converted to lesser harmful molecules. Thus, the heterojunction photocatalyst follows Z scheme mechanism. The mechanistic photo(electro)catalytic pathway for the decomposition of the pharmaceutical pollutant, TC besides the production of hydrogen via splitting of water is demonstrated in **schematic diagram 2.1**.

2.7 Conclusions

Finally, various mole ratios of BMS was successfully fabricated by the hydrothermal approach. After that, the photocatalysts were employed to decompose the pharmaceutical pollutant, TC, and the photoelectrochemical evolution of hydrogen via splitting of water under sunlight. The concentration of catalyst, pH of the solution, scavenger study, LSV, chronoamperometry, Mott-Schottky were all investigated. It was analyzed that the degradation besides current density was changed when the mole ratio of BV to MS was varied. Under the sunlight, even at a lesser catalyst dose, the decomposition, as well as photoelectrochemical hydrogen production activity, was quite effective. The presence of favorable optical properties, good surface area rendered the photocatalysts effectual. Various characterization techniques, for e.g., XPS, XRD, EDS, FESEM were done to ensure the successful formation of the photocatalysts. After seven testing runs, the good performance of the 31BMS demonstrates its reusability for photocatalytic removal of hazardous model contaminants. The 31BMS composite was stable for even after 5 h which was tested out by carrying out the stability study. The morphological aspects, crystallinity, besides surface properties of the material were virtually unaffected following the photocatalytic process, according to FESEM, BET, and XRD testing. The products and intermediates of the photodegradation experiments were studied using GC-MS analysis. Hence, for large-scale applications, 31BMS can work as an efficient photocatalyst.

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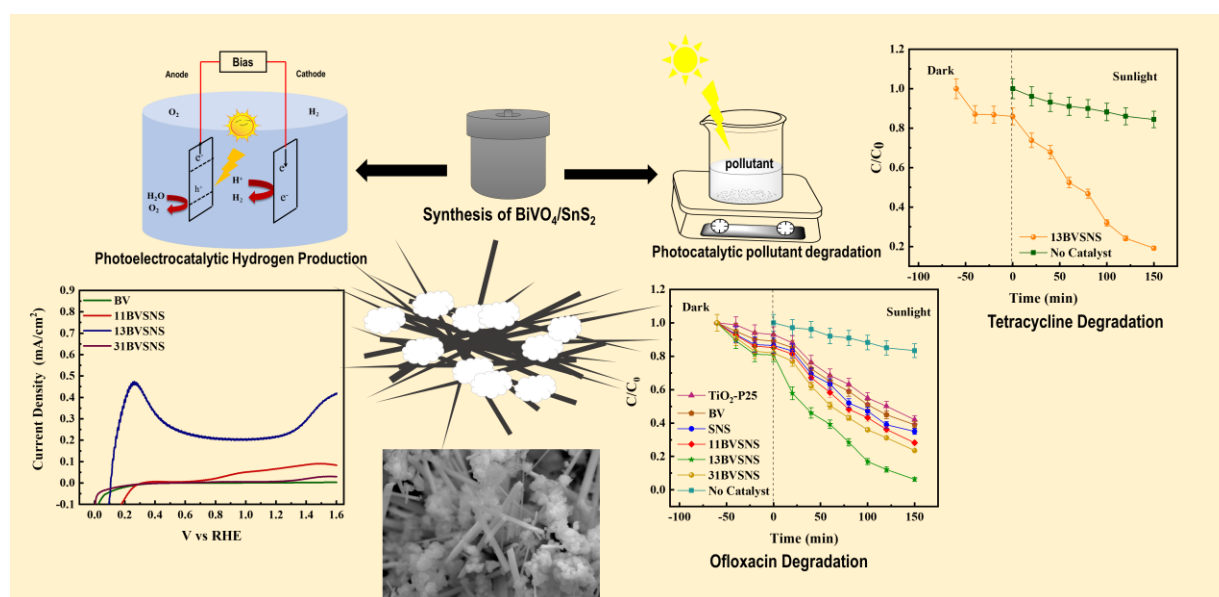
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Chapter 3

Solar light responsive $\text{BiVO}_4/\text{SnS}_2$ nanocomposite for photocatalytic elimination of recalcitrant antibiotics and photoelectrocatalytic water splitting



Highlights of the Chapter

- In-situ hydrothermal preparation of various mole ratios of $\text{BiVO}_4/\text{SnS}_2$ nanocomposites was done.
- Photocatalytic elimination of the pharmaceutical contaminants, oflox and TC and photoelectrocatalytic water splitting was carried out to manifest the proficiency of photocatalysts.
- Degradation efficacy of 93.7 % and 80.8 % was observed for oflox and TC, respectively in the irradiation of natural sunlight for 150 min with 1:3 $\text{BiVO}_4/\text{SnS}_2$ photocatalyst.
- The 1:3 $\text{BiVO}_4/\text{SnS}_2$ photoanode produced $\sim 21\mu\text{molcm}^{-2}\text{sec}^{-1}$ of hydrogen at 1.23 V vs RHE and fabricated electrode remained stable for 6 h.

3.1 Introduction

Photocatalytic elimination of the detrimental pollutants, and PEC water splitting to evolve the hydrogen was done to test out the efficiency of the fabricated photocatalysts. As described in the **Chapter 2**, photocatalytic decomposition possesses the enormous potential to use natural sunshine and the ability to eliminate hazardous pollutants entirely after complete degradation by changing them to H_2O and CO_2 . Along with TC, photocatalytic abatement of the another hazardous antibiotic ofloxacin (oflox) was done in this chapter. Oflox, a fluoroquinolone antibiotic, has been found in copious amount in surface water as high as 31.7 gL^{-1} [1]. Likewise, TC level was found to be $5.4 - 8.1 \text{ ngL}^{-1}$ in ground and surface water [2]. These antibiotics can have negative impact on the environment as their presence can lead to the formation of antibiotic-resistant bacteria, and could cause other ecotoxicological impacts [3,4]. Also, people often consume water laced with TC, which can alter the composition of their gut flora [5] and greatly increase the risk of developing noxious diseases including fatty liver, metabolic syndrome, autism, and other neurological disorders. Therefore, in order to ensure a safe and pollution-free environment; decomposition and separation of these organic waste products have taken precedence [6,7]. As a result, it is critical to focus on the development of effective photocatalysts for the removal of these lethal pollutants in order to protect flora and fauna [8].

Recently, BiVO_4 (BV) is attracting widespread interest as a photocatalyst ascribing to appealing properties like non-toxic and eco-friendly nature, and excellent band position. However, more than 60 % of photogenerated charges carriers reintegrate easily before reaching the interfaces due to the reduced lifetime of the charge carriers of BV [9]. Furthermore, the electrons (e^-) on the conduction band (CB) of BV are unable to combine with oxygen to create superoxide radicals ($\text{O}_2^{\cdot-}$), resulting in a lower number of reactive species participating in the photocatalytic process resulting in decreased activity [10]. In order to improve light absorption efficiency and prevent the reintegration of the charges, hybridization of BV with other photocatalysts to form the heterojunction has become a popular choice. This is because the in-built electric field created by uneven Fermi levels between two components can aid spatial segregation of e^- - h^+ pairs and boost interfacial charge transfer efficiency [11]. For example, $\text{BiVO}_4/\text{g-C}_3\text{N}_4/\text{carbon}$ nanotubes composite, $\text{BiVO}_4/\text{Ag}_3\text{PO}_4/\text{PANI}$, $\text{Bi}/\text{BiVO}_4/\text{CdS}$ is successfully demonstrated for the photocatalytic decomposition of phenol, ciprofloxacin,

tetracycline hydrochloride under the illumination of sunlight. The photodegradation efficiency of 80.6 %, 84.5 %, 85.5 % was achieved within 120, 70, 30 min, respectively [12–14] .

On the other hand, SnS_2 (SNS), an n-type semiconductor photocatalyst is thought to be potential photocatalyst as it has a strong anisotropic optical feature, which could be useful in catalytic reactions along with several other applications like electrical switching, solar cells, etc. [15]. The crystal structure of SNS is hexagonal CdI_2 -type, with one layer of Sn atom sandwiched amid two layers of S atom by an in-plane covalent bonding and a weak Van der Waals force amongst the neighboring layers [16]. SNS, additionally, is affordable, non-toxic, has good thermal stability, and possesses a band gap of 1.91-2.35 eV which renders it a visible light-responsive. Moreover, it is stable in neutral as well as acid media, has high carrier mobility, and possesses the larger number of active sites, therefore, several efforts have been made to use this material [17]. For instance, hydrothermally synthesized $\text{SnS}_2/\text{MoS}_2$ is shown for photocatalytic degradation of methylene blue under the visible light with a photodegradation efficacy of 96.5 % and rate constant of 0.079 min^{-1} [18] In an another work, photocatalytic elimination efficacy of 94.8 % was reported for the decomposition of rhodamine B within 60 min in the illumination of visible light utilizing $\text{SnS}_2/\text{g-C}_3\text{N}_4$ photocatalyst [19].

$\text{BiVO}_4/\text{SnS}_2$ (BVSNS) is also investigated as a proficient catalyst for the photocatalytic remediation of the organic contaminants and PEC hydrogen production via water splitting in lieu of its band straddling with water redox potential. Although, many photodegradation and PEC water splitting experiments have been reported in literature with different composites of BV, and SNS separately [20–22], the BVSNS heterojunction has never been investigated employed for this purpose to the best of authors' knowledge.

This Chapter deals with the synthesis of various mole ratios of BVSNS nanocomposite using a hydrothermal procedure to obtain optimal combination of catalyst and to investigate same for photo(electro)catalytic water splitting as well as photocatalytic degradation of pharmaceutical pollutants, oflox and TC. The concentration, scavenger, pH, reusability, LSV, chronoamperometry, Mott-Schottky, and stability experiments were all conducted to evaluate the performance and efficiency of the prepared photocatalyst. The degrading and hydrogen production efficacy of the catalyst was also compared to that of the literature to support its superiority over existing catalysts.

3.2 Experimental section

This section pertains to the synthesis of catalysts, including the chemicals, materials, and methodologies utilized in the process.

3.2.1 Materials and methods

Acetic acid was procured from Merck. Thioacetamide (CH_3CSNH_2 , Sigma Aldrich), and tin tetrachloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Lobal chemie, India) were used for the catalyst synthesis. Antibiotics including, TC and oflox were procured from Sigma Aldrich. DI water ($18 \text{ M}\Omega\text{cm}^{-1}$) was employed to prepare all the solutions. Analytical-grade (AR) chemicals were utilized in an unadulterated form and without further refinement.

3.2.2 Syntheses

3.2.2.1 Synthesis of BiVO_4 powder

BV was synthesized as per the protocol discussed in the **Chapter 2 (section 2.2.2.1)**.

3.3.3.2 Synthesis of $\text{BiVO}_4/\text{SnS}_2$ composite

The hydrothermal synthesis approach was used to create ($\text{BiVO}_4/\text{SnS}_2$) BVSNS hybrids with various mole ratios. To obtain a homogeneous solution, 1.615 g of BiVO_4 (5 mmol) was dissolved in the 80 mL of 5% V/V acetic acid and sonicated for 30 min. Under vigorous stirring, 1.753 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (5 mmol), and 0.751 g of CH_3CSNH_2 (10 mmol) were dissolved in the prepared mixture to produce SnS_2 (SNS). To make a homogeneous solution, the entire mixture was agitated for 1 h before being heated at 150°C for 12 h in the 100 mL Teflon-lined stainless-steel autoclave. The mixture was dried at 60°C after 3-4 washes with DI water and the ethanol. The resultant greenish-colored powdered substance formed was given the name 11BVSNS. Likewise, the chemical quantities required to synthesize the different mole ratios (1:3 and 3:1) were calculated and labeled as 13BVSNS and 31BVSNS, respectively.

Raw SnS_2 was synthesized under comparable conditions without the addition of BiVO_4 . The orangish-colored powder obtained was named as SNS.

3.2.3 Methods of characterization

Methods of the characterization are elaborated in **Chapter 2 (section 2.2.3)**.

3.2.4 Photocatalytic degradation of organic contaminants

To gauge the photocatalytic efficacy of photocatalyst, photocatalytic degradation of oflox and TC (pharmaceutical impurities) was carried out under natural sunlight. Around 10 ppm oflox and TC solution containing 0.2 g/L catalyst was agitated in the dark for 60 min to achieve adsorption-desorption equilibrium. For carrying out degradation, solutions were then kept under the sunlight for 150 min. The studies were carried out in the month of March, and the solar light intensity was found to be 700 W/m^2 , as measured by Pyranometer (LICOR). The experiments were carried out in triplicates, and the graphs were presented with error bars representing a 5 % data source error. The samples were collected at regular interval and studied for their absorbance characteristics after the removal of catalyst. The degradation was monitored by monitoring absorbance intensity at $\lambda_{\text{max}} = 380 \text{ nm}$, and 360 nm for oflox and TC, respectively and the degradation efficacy (% Deg) is represented according to **Eq. 2.1** provided in the **Chapter 2**.

The photocatalytic treatments pharmaceutical pollutants, TC and OF were assessed using TOC and COD analysis. A 200 mL of oflox and TC solution containing 40 mg of 13BVSNS was illuminated in sunlight for 150 min prior to the analysis. The mineralization was calculated using TOC removal, while the COD was calculated using the titration method. **Eq. 2.2, and 2.3** given in the **Chapter 2** were followed in order to calculate the % TOC and COD removal.

The decomposed intermediates and the products attained after photocatalytic abatement of the deleterious pollutant, TC by 13BVSNS nanocomposite were scrutinized using GC-MS. Methods followed to fabricate the samples for the GC-MS study are provided in **Chapter 2**.

3.2.5 PEC studies

For PEC studies, an electrochemical workstation (AUTOLAB, Metrohm) equipped with the solar simulator (LOT Quantum design) and a typical three-electrode arrangement was used to examine the photo-activity of the fabricated electrodes under one-sun irradiation. BiVO_4 , SnS_2 , 11BVSNS, 13BVSNS, and 31BVSNS were spray-coated on an Indium Tin Oxide (ITO) and employed as photoanodes (working electrodes), Pt wire as the counter electrode, and Ag/AgCl as a reference electrodes. Coating of the catalyst was optimized in terms of coating layers as 5, 10, and 15 layers w.r.t their photo-response behavior. As a supporting electrolyte, 0.5M Na_2SO_4 (pH = 7) was used. An illumination intensity 100 mW/cm^2 photo response studies i.e. LSV,

impedance, transient photocurrent, and chrono-amperometry were carried out. Impedance spectra were recorded at an open circuit potential (ocp) with an AC perturbation signal of 10 mV in both dark and light conditions. The fabricated electrodes were also subjected to Mott-Schottky measurements at frequency-potential scan mode at 100 kHz. The Ag/AgCl reference electrode was utilized to measure all potentials, and the Nernst equation was used to convert them to the RHE reference scale. The photo electrodes' stability was characterized by XRD analysis post-PEC studies.

3.3 Results and discussions

3.3.1 XPS analysis

XPS analysis was done to scrutinize the binding state of the elements in the prepared composite. The survey spectra of binary composite BVSNS is depicted in **Fig. 3.1(a)**, which confirms the occurrence of Bi, V, O, Sn, and S at their constituent binding energies. The additional peak of C1s that appeared at 284.4 eV is accredited to the adventitious carbon of the instrument as C1s was used as reference.

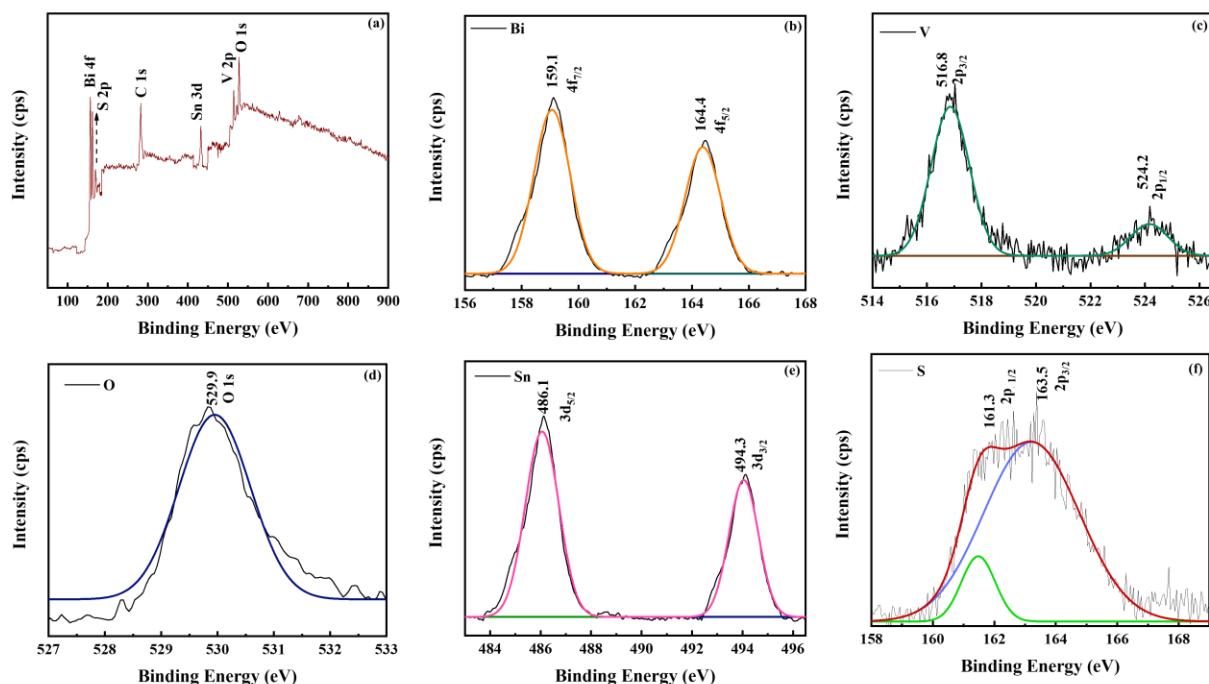


Fig. 3.1 XPS spectrum of the 13BVSNS, (a) the survey spectra, (b) Bi 4f, (c) V 2p, (d) O 1s, (e) Sn 3d, and (f) S 2p.

Further core level spectrum is recorded for Bi, V, Sn, O, and S. In deconvolution of Bi 4f doublet spectra (**Fig. 3.1(b)**), the peak $4f_{7/2}$ and $4f_{5/2}$ were found at a binding energy of 159.1 and 164.4 eV, respectively were ascribed to Bi^{3+} oxidation state in the composite [23]. Deconvolution of V was done considering V^{5+} spin-orbit doublet coupling. The $2p_{3/2}$ and $2p_{1/2}$ peaks of V^{5+} were positioned at 516.8 and 524.2 eV [24,25], respectively (**Fig. 3.1(c)**). In the deconvoluted spectra of O 1s, shown in **Fig. 3.1(d)**, the asymmetric peak at 529.9 eV corresponds to O^{2-} oxidation state [26]. Core level analysis of Sn and S, shows the peaks at 486.1, 494.3 eV (**Fig. 3.1(e)**), 161.3, and 163.5 eV (**Fig. 3.1(f)**), which corresponds to Sn $2p_{5/2}$ and Sn $2p_{3/2}$, S $2p_{1/2}$, S $2p_{3/2}$, respectively, thus suggest +4 oxidation state of Sn and -2 oxidation state of S in the synthesized SNS onto BV [27–30].

3.3.2 XRD analysis

Fig. 3.2 signifies the XRD diffractogram of the photocatalysts. The characteristic peaks of BV corresponding to 2θ at 18.9° , 24.4° , 28.9° , 30.7° , 34.9° , 35.3° , 39.8° , 46.0° , 46.8° , 47.3° , 50.2° , 53.3° , and 58.2° can be indexed to (011), (102), (112), (004), (200), (020), (211), (123), (204), (024), (220), (301), and (303) planes, respectively (JCPDS file 83-1699).

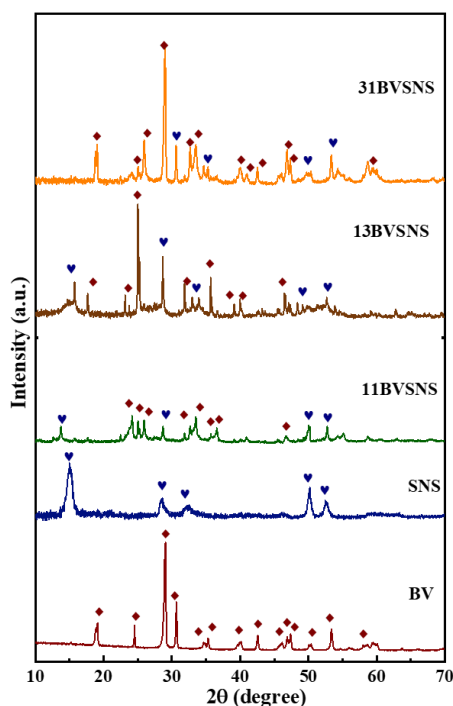


Fig. 3.2 XRD plot of fabricated BV, SNS, 11BVSNS, 13BVSNS, and 31BVSNS photocatalysts.

The peaks of SNS indexed to 14.8° (001), 28.4° (100), 32.2° (101), 49.6° (110), 52.5° (111) are correspondent to the JCPDS file 00-023-0677. Formation of the composite was thus confirmed by the incidence of both kinds of peaks. The crystalline nature of the photocatalysts was observed owing to the occurrence of sharp peaks. The augmentation in the intensity was observed with the enhancement in the proportion of BV and SNS in the composite. There were no impurities discovered in any of the samples, and the patterns exhibited well-defined peaks, which confirms the formation and purity of the composites.

3.3.3 PL measurements

The PL analysis determines the excitons' reintegration ability, migration, and transfer. The lower reintegration rate of the charge carriers is indicated by the lower fluorescence emission intensity, implying a higher photogenerated charge segregation efficacy [31,32]. All of the fabricated samples exhibited broad emission peaks, as seen in **Fig. 3.3**, and the inherent luminescence in e^- and h^+ of BV and SNS is responsible for the highest emission peaks between 460 and 490 nm.

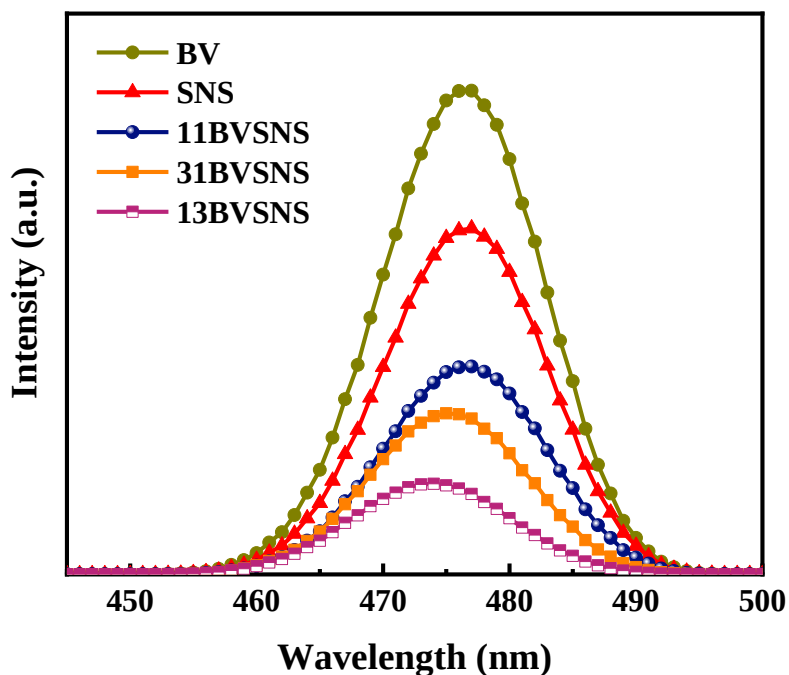


Fig. 3.3 PL spectra of the synthesized photocatalysts.

The 13BVSNS have a lower PL emission intensity than other samples, indicating that the 13BVSNS can effectively limit photogenerated e^- - h^+ pair recombination. This stimulates effective segregation of generated charge carriers that could be attributed to the establishment of the heterojunction between BV and SNS, which is beneficial to photo(electro)catalytic function.

3.3.4 Nitrogen sorption analysis

Nitrogen sorption experiments were performed to further investigate the structural characteristics for e.g., specific surface area, porosity, etc., of composites. The BJH method was used to determine the total volume as well as the average diameter of the pores. The nitrogen sorption and pore size distribution curve are revealed in **Fig. 3.4(a, b)**, respectively, and the extracted parameters are presented in the **Table 3.1** [33].

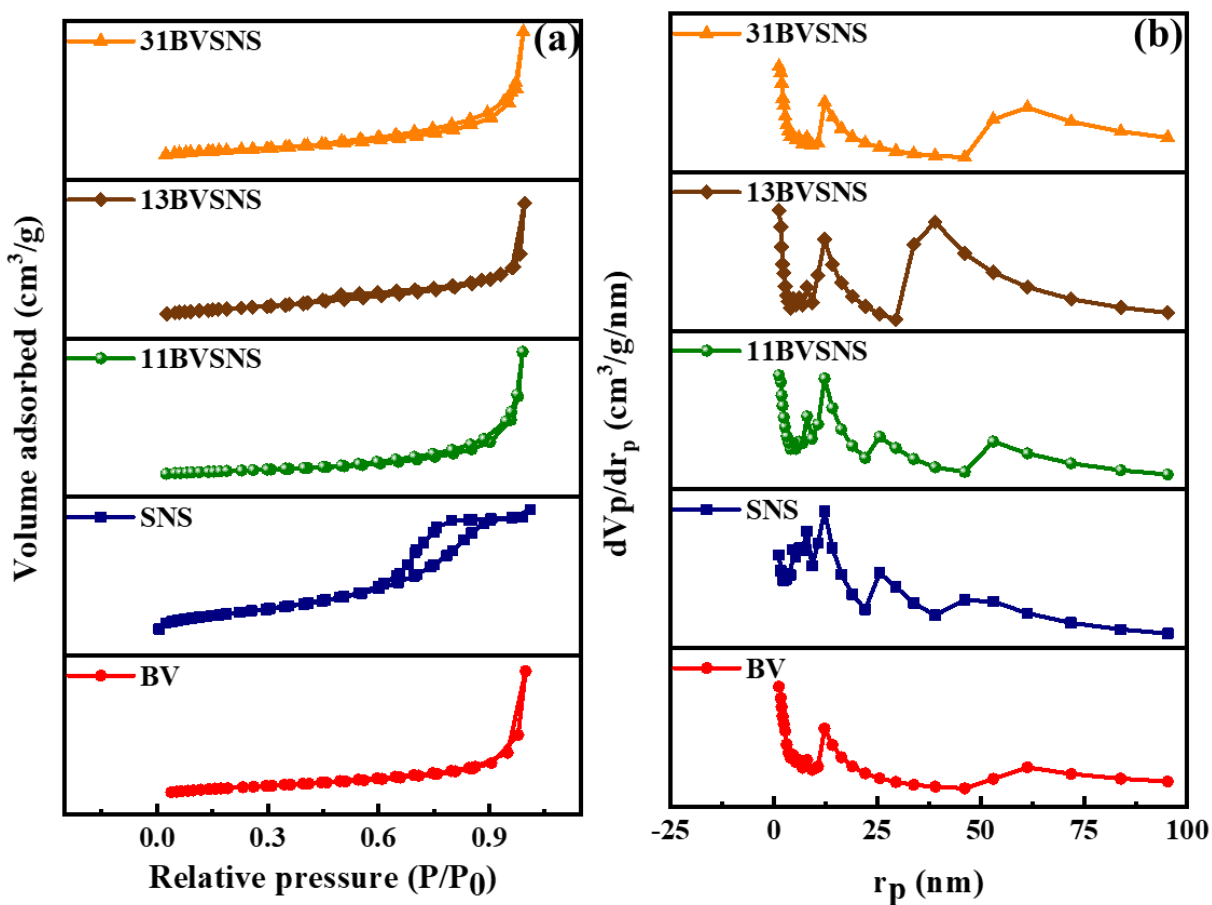


Fig. 3.4(a) BET surface area isotherm of the fabricated photocatalysts, and **(b)** BJH graph.

According to IUPAC categorization, the isotherm was type IV with a H2 hysteresis loop for SNS and large H3 type hysteresis loop for BV, 11BVSNS, 13BVSNS, and 31BVSNS ascribed to the existence of the mesopores. The specific surface area of composites increases noticeably when BV and SNS are combined. It is generally known that a higher surface area on the surface of a photocatalyst might give more active sites, facilitating the reaction's occurrence. It is thus expected to have higher activity for the composite catalyst over bare BV and SNS.

Table 3.1 Surface properties of the as-prepared photocatalysts.

Sample	Mean pore volume (cm ³ /g)	Specific surface area (m ² /g)	Pore diameter (nm)
BV	0.534	32	13.61
SNS	0.457	26	11.24
11BVSNS	0.587	48	18.93
13BVSNS	0.697	58	22.40
31BVSNS	0.634	52	20.37

3.3.5 UV- visible DRS study

The photocatalyst's ability to absorb light influences its photo(electro)catalytic activity significantly. To assess the optical absorbance of composites, UV-vis DRS was performed and results are represented in **Fig. 3.5(a)**. It can be noticed that the composite possesses the ability to absorb light in a wide wavelength range of 470-600 nm. The band gap of synthesized semiconductors was further calculated using the **Eq. 2.4** provided in **Chapter 2**.

Band gap energies of BV, SNS, 11BVSNS, and 31BMS were found to be 2.4, 2.3, and 2.2, and 2.0 eV, respectively. The 13BVSNS exhibits the narrow band gap of ~1.9 eV amongst all the fabricated photocatalysts which renders it the sunlight-responsive photocatalyst as demonstrated in **Fig. 3.5(b)**. According to the results of the UV-vis DRS investigation, composites have substantial visible light absorption capability, which provides a solid foundation for their high solar light photo(electro)catalytic activity.

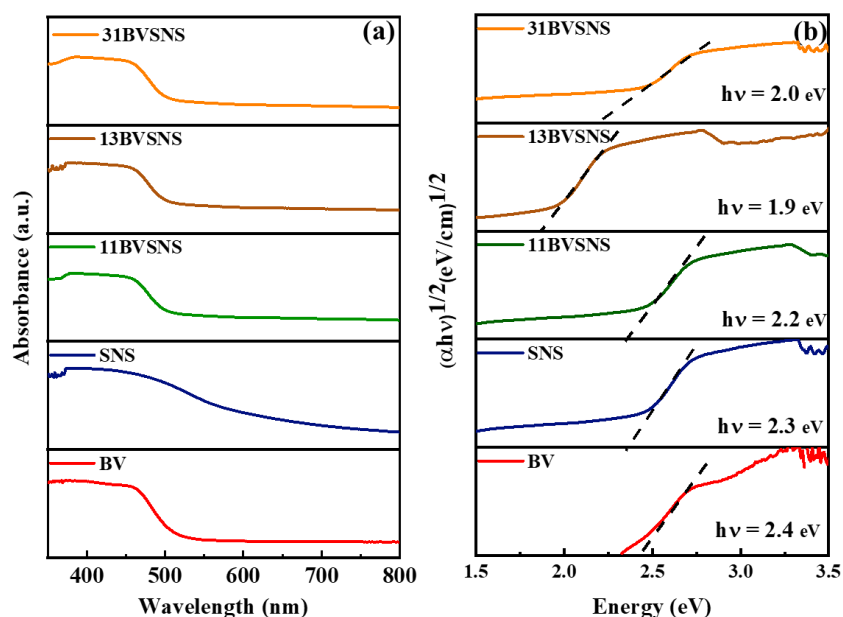


Fig. 3.5(a) DRS spectrum, and **(b)** the band gap energies of the as-synthesized materials.

3.3.6 SEM analysis

SEM was done to scrutinize the morphology of the BV, SNS and 13BVSNS composite (Fig. 3.6(a-d)).

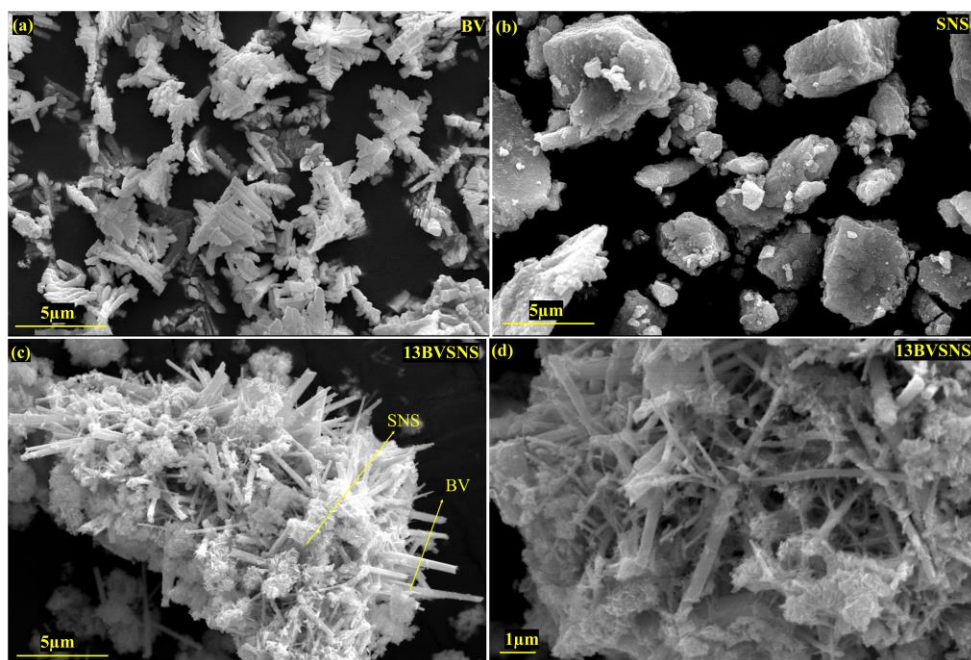


Fig. 3.6 SEM images of **(a)** BV, **(b)** SNS, and **(c,d)** 13BVSNS composite with different magnification.

It can be analyzed that BV comprises of fern petal shape structures (**Fig. 3.6(a)**), while SNS exists as the cotton candy like structures (**Fig. 3.6(b)**). As observed in **Fig. 3.6(c and d)** both kinds of structures were present in the composite 13BVSNS where cotton candy was deposited onto the nano-needles, therefore results revealed that due to the closed proximity of the two materials lot of heterojunctions are created. This improved the charge separation and may have contributed to the enhanced photo(electro)catalytic activity. Also, the presence of both kinds of morphology in the composite reveals its successful formation.

3.3.7 EDS and elemental mapping

The composition, distribution, besides purity of the elements of the prepared composite can be assessed from EDS analysis.

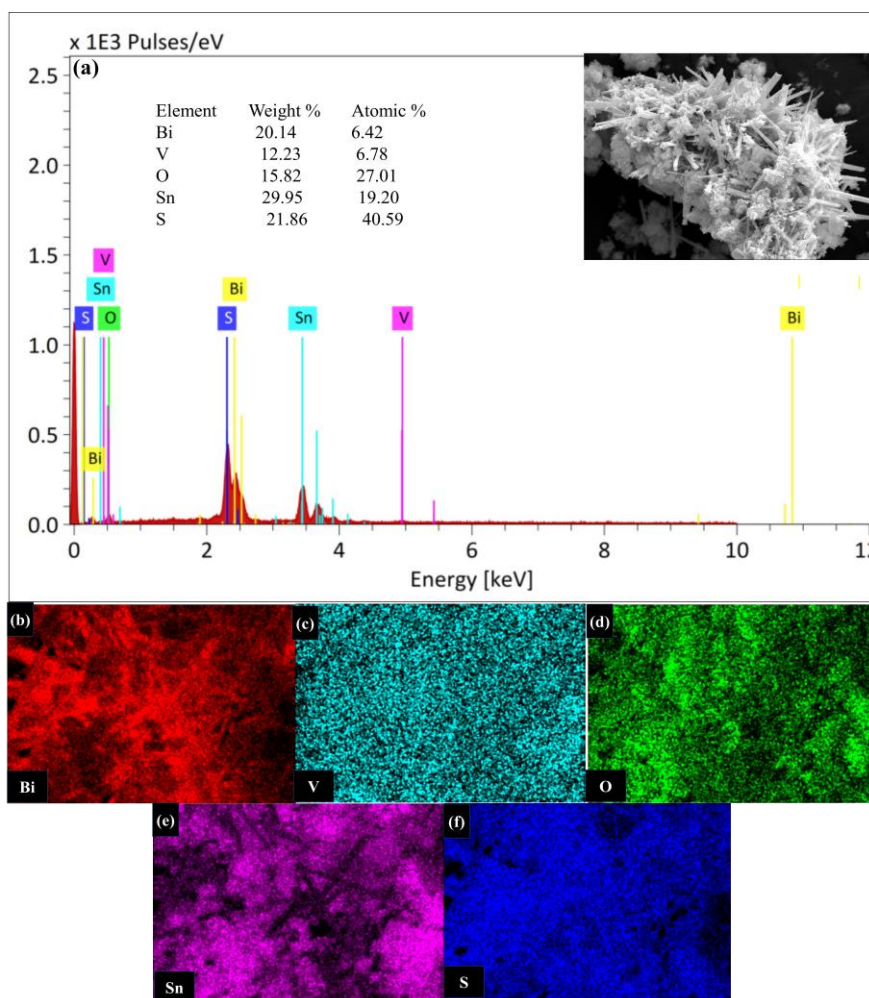


Fig. 3.7(a) EDS spectra of the 13BVSNS photocatalyst with the corresponding SEM micrograph and **(b-f)** elemental mapping of the 13BVSNS composite.

The weight percent of each constituent in the 13BVSNS composite was examined and results are shown in **Fig. 3.7(a)**. Based on EDS and elemental mapping analysis, uniform distribution and concurrence of all elements i.e., Bi, V, O, Sn, and S in the BVSNS composite was observed (**Fig. 3.7(b-f)**).

3.3.8 Photocatalytic degradation studies for the pollutant, oflox

To scrutinize the photocatalytic activity of the photocatalysts, decomposition of the pharmaceutical pollutant, oflox was carried out under the illumination of the natural sunlight. To begin, a photolysis experiment was conducted by exposing 20 mL of 10 ppm oflox solution under sunlight for 150 min in the absence of a catalyst. About 16.6 % of the decomposition of oflox was observed as a result. Photodegradation experiments of different photocatalysts were then carried out under the identical conditions and by comparing the decomposition efficacy of the photocatalysts to that of TiO₂-P25 under identical conditions, the efficiency was determined. The apparent pseudo-first-order model provided by **Eq. 2.5** given in **Chapter 2**. was followed to quantitatively analyze the photocatalytic decomposition of oflox based on the Langmuir-Hinshelwood kinetics model [34].

Fig. 3.8(a, b) shows the kinetics studies of photocatalytic degradation with studied catalysts. Without the addition of catalyst, TC degraded to 16.6 % (rate constant 0.0012 min⁻¹). Amongst all, 13BVSNS exhibited the maximum photodecomposition efficacy of 93.7 % with a rate constant of 0.0164 min⁻¹. Degradation efficacy of the physical mixture of BV and SNS was observed to be 68 % which was more than pure BV and SNS while lesser than the in-situ composites. Further, R factor was used to calculate synergy obtained by the coupling of BV and SNS can be obtained from the **Eq. 3.1**.

$$(R) = \frac{k_{BV}/k_{SNS}}{k_{BV} + k_{SNS}} \quad (3.1)$$

Here, k_{BV}/k_{SNS} , k_{BV} , and k_{SNS} stands for rate constant of hybrid BV and SNS, bare BV, and SNS, respectively. R factor for 13BVSNS composite was found to be 1.33. The decomposition efficiency, rate constant, and the R value for the different photocatalysts are summarized in the **Table 3.2**. Thus, from the table, it can be manifested that the 13BVSNS had the highest synergy factor confirming that it has the highest efficacy amongst the prepared photocatalysts.

Table 3.2 Rate constant, degradation efficiency, and synergy factor of oflox by various photocatalysts.

Catalyst	Rate constant (min ⁻¹)	Decomposition efficacy (%)	Synergy factor (R)
No catalyst	0.0012	16.6	-
TiO ₂ -P25	0.0054	58.0	-
BV	0.0058	61.0	-
SNS	0.0065	65.0	-
11BVSNS	0.0075	71.8	0.60
13BVSNS	0.0164	94.0	1.33
31BVSNS	0.0085	76.4	0.69

3.3.8.1 Effect of concentration of photocatalyst

The impact of catalyst dose was examined to optimize the simulated sunshine-driven photocatalytic decomposition reaction of pharmaceutical pollutant oflox. The concentration was varied from 0.1 g/L to 0.3 g/L (**Fig. 3.8(c)**). Based on these findings, the decomposition efficacy of oflox was noticed to be 77.2 % and rose to 84.4 % with the increase in the photocatalyst dosage in the illumination of the sunlight. The maximum degradation efficiency was observed to be 93.7 % at a concentration of 0.2 g/L of photocatalyst in 10 ppm of oflox solution, which was chosen as the optimum for further photocatalytic studies. When utilizing a huge dose of catalysts, it is simple to comprehend that more exposed surface areas are available for the adsorption of oflox molecules as well as absorption of incident photons, resulting in enhanced efficacy. The decline in the degradation efficiency was noticed when the concentration of the photocatalyst was further augmented to 0.25 g/L. The decline in decomposition efficacy with an augmentation in catalyst content could be due to an opaqueness of the solution. Furthermore, lesser penetration and increased scattering of light caused by nanoparticle turbidity, and failure to maintain homogenous conditions in the solution due to particle agglomeration could be the main reasons for the lowered decomposition with increasing catalyst concentration beyond a certain amount [35].

3.3.8.2 Impact of different light sources

An analogous experiment was carried out using different light sources (UV light and visible light) under optimal conditions to draw a comparison. From **Fig. 3.8(d)** it can be observed that oflox degraded to 67.4 % in UV light and 83.5 % in visible light. However, the highest degradation rate of 93.7 % was observed under natural sunlight with the 13BVSNS photocatalyst. Thus, sunlight is sufficient for the degradation of the oflox using the synthesized photocatalysts.

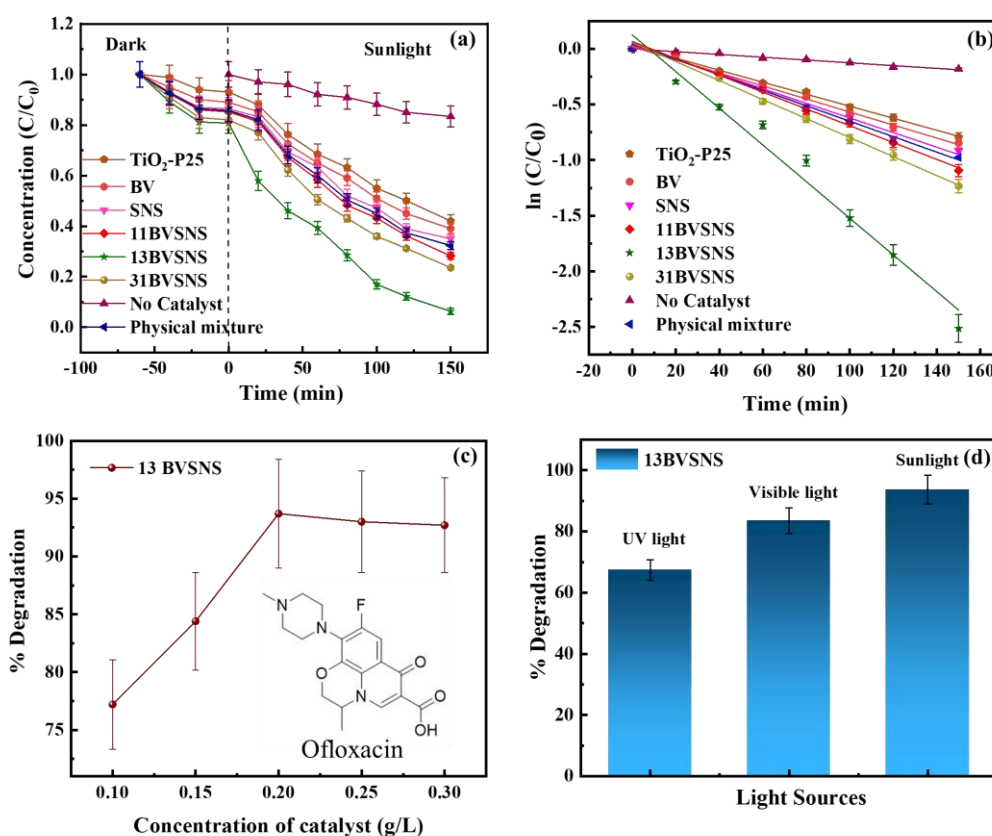


Fig. 3.8(a, b) Kinetic analysis of the different photocatalysts for the degradation of oflox having standard deviation 23.85, **(c)** impact of concentration of the 13BVSNS photocatalyst on the decomposition of the contaminant, and **(d)** comparative analysis of the degradation efficacy under different light sources.

3.3.8.3 Impact of pH

Structural changes in organic compounds, catalyst characteristics, as well as the formation of the oxidative species, can be caused by the pH of the solution, resulting in

significant alterations during organic pollutant breakdown. Thus, we studied effect of pH on oflox degradation in the differential pH values of 1, 3, 5, 7, 9, 11. At a pH of 3, 7, and 11, oflox exists in cationic (OFH^+), zwitterionic ($\text{OFH}^\pm$), and anionic (OFH^-) forms, respectively. Fig. **3.9(a)** suggests that the point of zero charge (pzc) of the composite 13BVSNS was 5.3. This indicates that for pH 3 and 11, the catalyst and the pollutant (oflox) surfaces both bear either positive or negative charges, respectively. Owing to the electrostatic repulsion, there may be less adsorption of oflox on the surface of 13BVSNS photocatalyst in acidic or alkaline pH. However, at the pH of 7, the efficiency towards the breakdown of oflox was found to be maximum due to the existence of a zwitterionic form of oflox. The effectiveness of decomposition elevates with augmentation in pH, reaching a maximum at pH 7, and then decreases with increasing pH as represented in **Fig. 3.9(b)** [36].

3.3.8.4 Scavenger study

In general, the photodegradation process is driven by reactive oxygen species or the photogenerated radicles for the photocatalytic breakdown of an organic compounds. The formation of reactive oxygen species is fueled by the capture of photogenerated charge carriers by several species present in the solution, primarily dissolved oxygen, hydroxyl ions, and water molecules [37]. Thus, to understand the role of the active species in the decomposition of oflox, scavenger study was carried out using methanol, DMSO, and benzoquinone (BQ) as scavenger for holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), and superoxide ions ($\text{O}_2^{\cdot-}$), respectively. In presence of methanol, DMSO, and BQ scavenger, the decomposition of oflox dropped from 93.7 % to 68.1, 40.7, and 77.2 %, respectively, indicating that $\cdot\text{OH}$ is the primary reactive species (**Fig. 3.9(c)**). While the contribution by h^+ and $\text{O}_2^{\cdot-}$ in the degradation process is relatively less.

3.3.8.5 Mineralization experiments

Recalcitrant contaminant OF along with the TC was treated to scrutinize the efficacy of the photocatalyst. The % TOC and % COD analysis of the contaminant, OF is depicted in the **Fig. 3.9(d)**. The presence of the considerable quantity of the organic matter in the pollutants, OF was proved by the higher TOC and COD values initially. About 76.4 % and 82.1 % reduction in TOC and COD for OF was recorded when the experiments were conducted using 13BVSNS photocatalyst in the illumination of the natural sunlight for 150 min. The difference between the % removal of TOC and % degradation was observable for OF which may be due to the

formation of intermediates [38]. This suggests the incomplete mineralization of the pharmaceutical contaminants. The rapid deterioration in the aquatic conditions does not always imply to widespread mineralization and total loss of organic molecules. Unfortunately, ethical concerns make studies using genuine medical/pharmaceutical effluent impractical. Nonetheless, COD and TOC studies were performed on a real oflox pill (Cipla, Ofloxacin tablets I.P. Floxavin 200) to validate the efficacy of the 13BVSNS photocatalyst. The results indicated the reduction in COD and TOC of 74.6 % and 69.8 %, respectively, illustrating the photocatalyst's superior surface catalytic property when compared to the conventional and time-consuming physicochemical methods employed in industries.

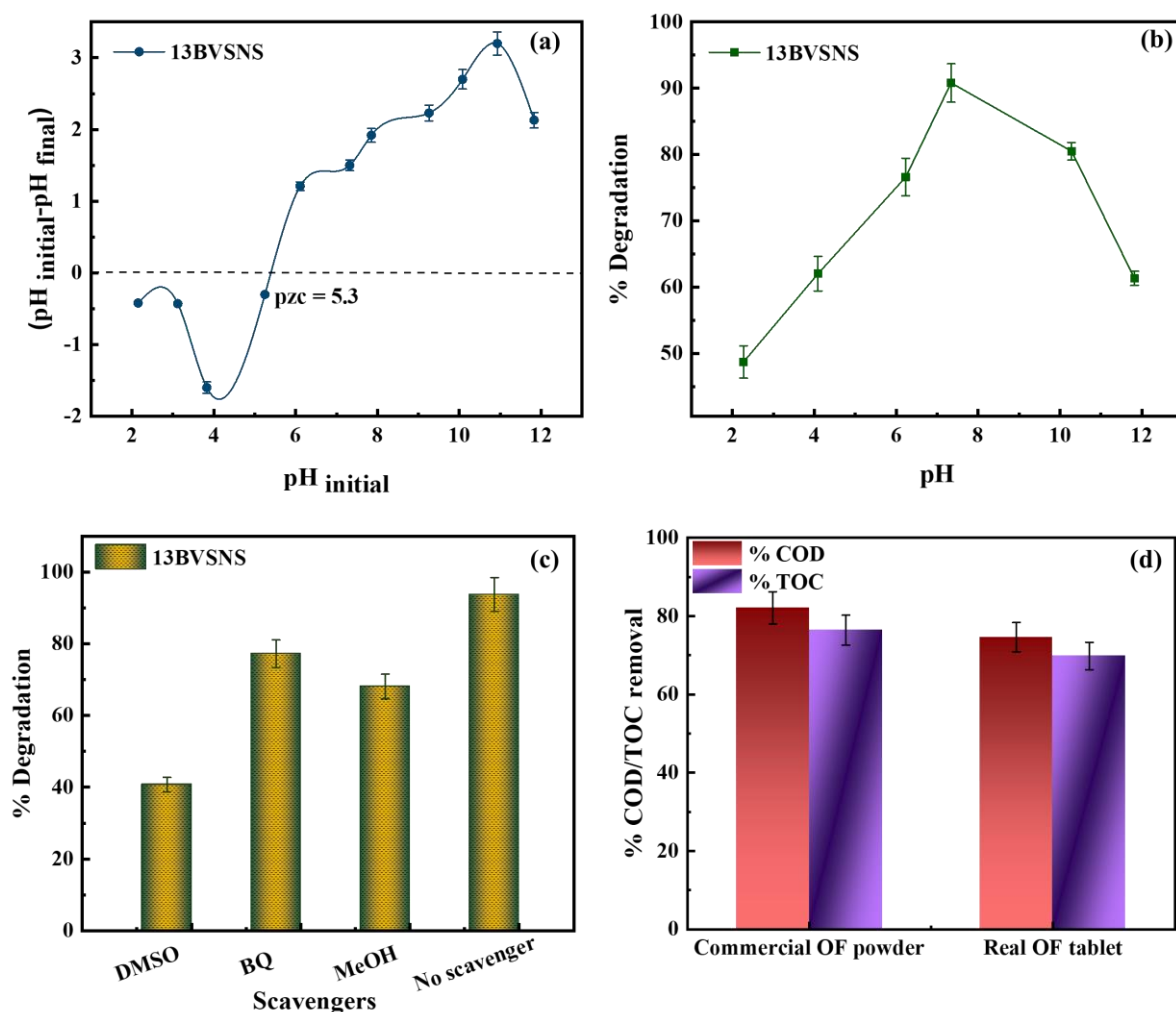


Fig. 3.9 (a) pzc of the 13BVSNS photocatalyst, (b) impact of the pH on the % degradation, (c) impact of various quenchers on the photocatalytic elimination of oflox, (d) % COD/TOC analysis of commercial oflox powder, and real oflox pill.

3.3.8.6 Reusability experiment

Both recyclability and durability are critical factors for determining the cost-effectiveness and applicability of a catalyst in real-world applications. To determine the catalyst's stability and effectiveness, the reusability of the spent 13BVSNS composite for oflox decomposition was examined. The recycling process went off without hindrance because of the heterogeneous catalyst's properties. One of the advantages of using this sort of catalyst is that because it is just physically adsorbed, it is easy to separate the spent catalyst from the investigated solvent. It merely needs to be washed and dried in the oven before being reused, making it very easy to recover. **Fig. 3.10(a)** indicates that after the seven cycles, the photocatalytic activity of the 13BVSNS decreases to a lesser amount (66.9 %), which could be due to photocatalyst loss during the washing and drying processes involved in the catalyst recovery after each cycle. Furthermore, after seven cycle reactions, the pore diameter (11.34 nm), specific surface area (38 m²/g), and mean pore volume (0.342 cm³/g) of the spent catalyst was comparable with the unused one as confirmed by the BET and BJH plot (**Fig. 3.10(b, and c)**). In addition, SEM analysis at the same magnification was performed to examine the morphology of the composite after the decomposition experiments. The cotton candy like structure loaded onto nano-needles like morphology in the composite remained intact before and after the trials, showing the stability of the synthesized composite (**Fig. 3.10(d)**). Thus, the reported 13BVSNS catalyst is proposed as one of the most efficient, stable, and reusable photocatalyst for the decomposition of oflox, a pharmaceutical pollutant.

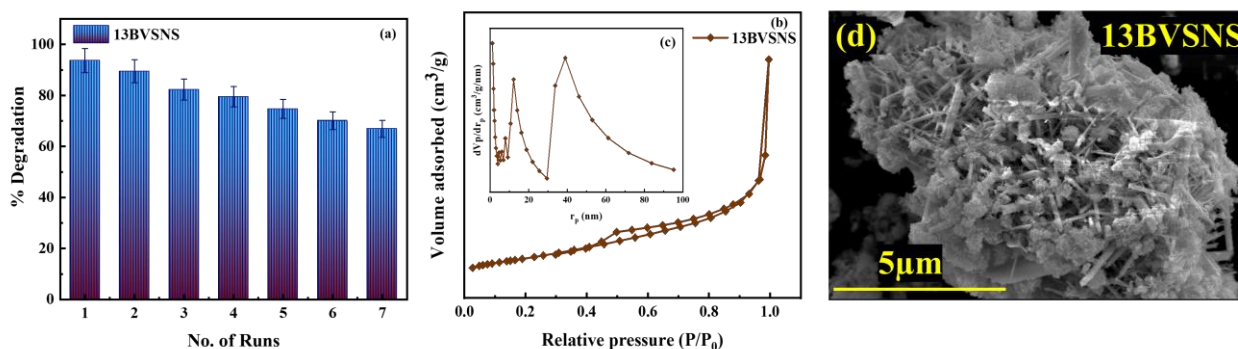


Fig. 3.10(a) Reusability studies of 13BVSNS photocatalyst, **(b, c)** BET plot after the degradation experiment along with the inset containing BJH plot, and **(d)** SEM image after the degradation studies.

3.3.9 Photocatalytic activity of TC

To test 13BVSNS's ability to decompose other categories of colorless pharmaceutical pollutant, photocatalytic decomposition of TC was also performed under optimized conditions. By swirling around 4 mg of photocatalyst in 20 mL TC solution (10 ppm) in the dark for 60 min before illuminating it in sunlight for 150 min, the adsorption-desorption equilibrium was achieved and the subjected to sunlight exposure. Under optimal condition, the highest degradation efficacy of 80.8 % was achieved with the rate constant of 0.010 min^{-1} . The kinetic analysis of 13BVSNS photocatalyst is shown in **Fig. 3.11(a, and b)**. Thus, 13BVSNS is the effectual photocatalyst for the decomposition of the other similar model pollutants as well.

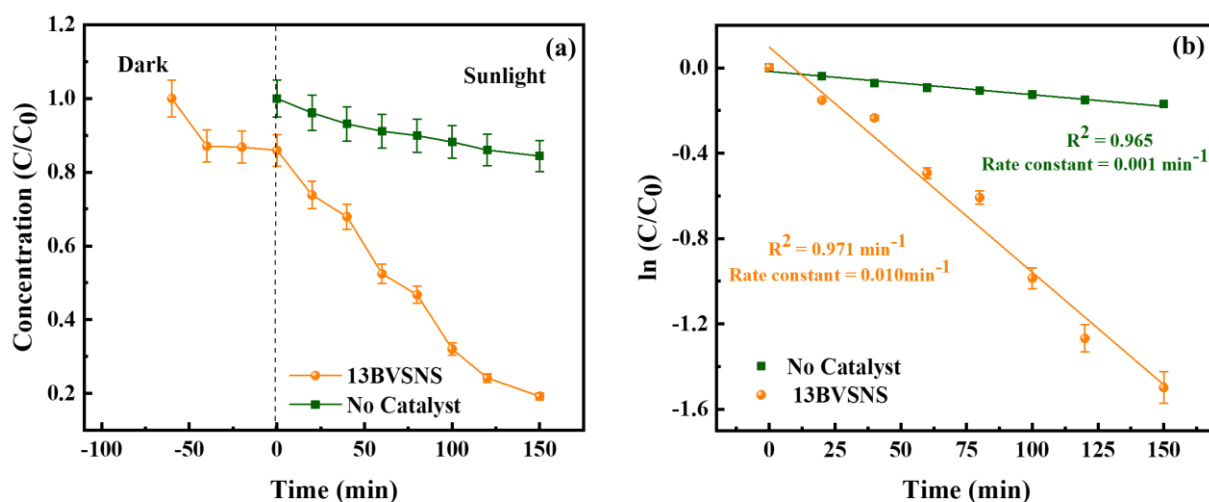


Fig. 3.11(a, b) Kinetic analysis of the photocatalytic degradation of the pharmaceutical pollutant, TC with and without 13BVSNS photocatalyst.

3.3.10 Comparison with the existing literature

The produced BVSNS photocatalyst was related to other published heterojunction photocatalysts for the photocatalytic deterioration of model pollutants, oflox and TC as shown in **Table 3.3**. According to the table, hazardous pollutants, oflox and TC can be photocatalytically removed in the illumination of the natural sunlight at room temperature even in the occurrence of a little amount of the fabricated BVSNS photocatalyst. Hence, BVSNS is the efficient photocatalyst for the elimination of hazardous contaminants from the waste water.

Table 3.3 Comparative study of various photocatalysts for the decomposition of the model pollutants, oflox and TC.

Photocatalyst	Contaminant's concentration (ppm)	Time of the reaction (min)	Source of light	Rate constant k	Decomposition efficiency (%)	Ref.
CdS/TiO ₂	oflox (10 ppm)	180	Visible light	-	86	[39]
AgBr/WO ₃	oflox (10ppm)	240	Solar light	0.0057 min ⁻¹	68	[40]
MoSe ₂ /CdS/ZnO	oflox (10 ppm)	90	Visible light	0.024 min ⁻¹	89	[41]
BiVO ₄ /Bi ₂ SiO ₅	TC (10 ppm)	120	Visible light	0.0072 min ⁻¹	72.2	[42]
BiVO ₄ /Cu /g-C ₃ N ₄	TC	120	Visible Light	0.011 min ⁻¹	69	[43]
SnS ₂ /LaFeO ₃	TC	120	Visible light	0.0028 min ⁻¹	28.8	[44]
BVSNS	oflox (10 ppm)	150	Sunlight	0.0085 min ⁻¹	93.7	Present work
BVSNS	TC (10 ppm)	150	Sunlight	0.010 min ⁻¹	80.8	Present work

3.4 GC-MS analysis

A GC–MS study was carried out to scrutinize an intermediates and products formed by the photocatalytic remediation of TC by BVSNS photocatalyst. **Fig. 3.12(a, b)** represent the GC chromatogram and the mass spectrum of TC, respectively. The degradation pathway may follow three routes (**Fig. 3.13**). In the first pathway, 4-amino-3,6,10,11a,12a-pentahydroxy-6-methyl-

1,11,12-trioxo-1,2,3,4,4a,5,5a,6,11,11a,12,12a-dodecahydrotetracene-2-carboxamide was formed owing to the addition of h^+ and $\cdot\text{OH}$ to $\text{C}=\text{C}$ bond as well as the loss of N-methyl group. Dehydroxylation of 4-amino-3,6,10,11a,12a-pentahydroxy-6-methyl-1,11,12-trioxo-1,2,3,4,4a,5,5a,6,11,11a,12,12a-dodecahydrotetracene-2-carboxamide resulted in the formation of 4-amino-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,2,3,4,4a,5,5a,6,11,11a,12,12a-dodecahydrotetracene-2-carboxamide.

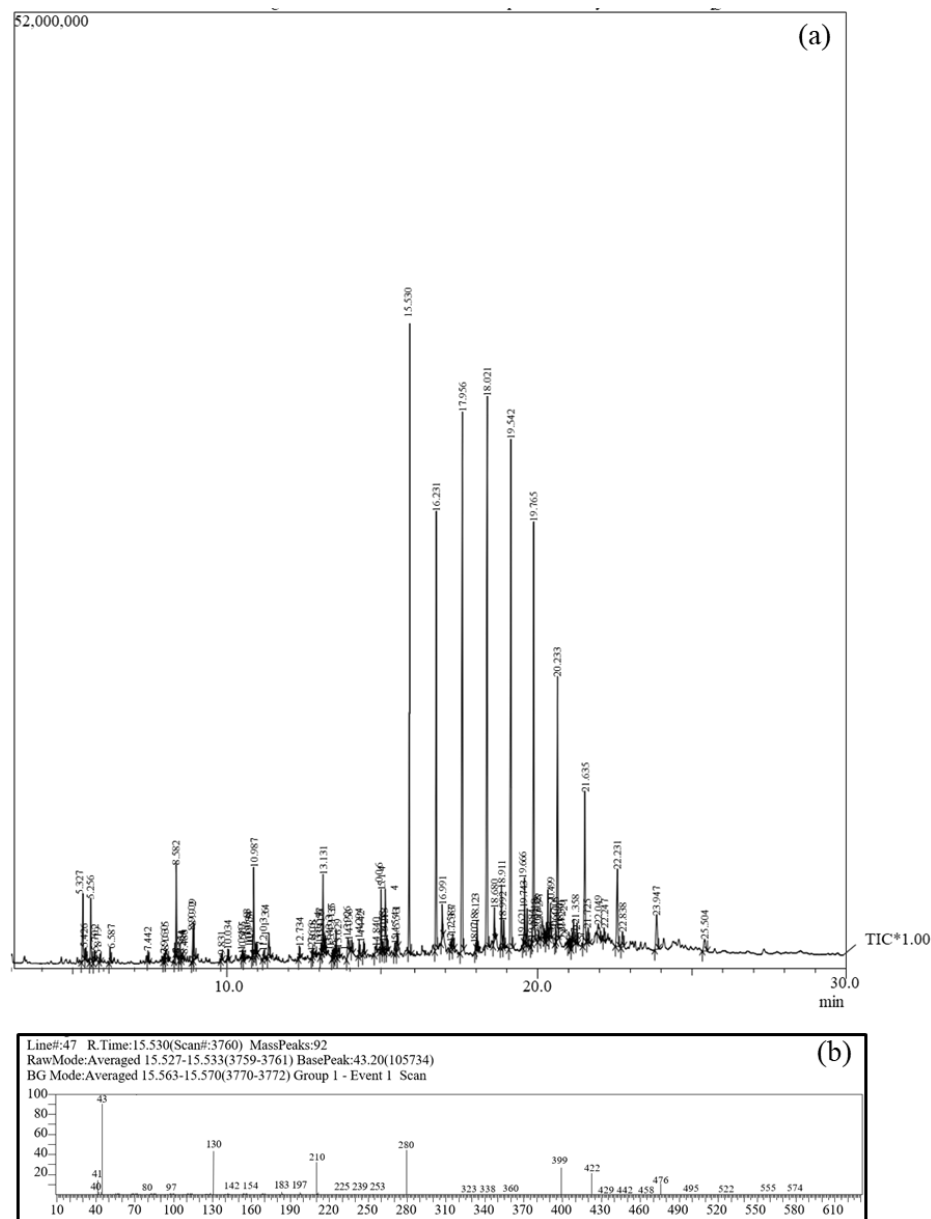


Fig. 3.12(a) Gas chromatogram and **(b)** mass spectra of the products after the degradation of TC by 13BVSNS photocatalyst.

octahydrotetracene-2-carbaldehyde. After that, a ring cleavage occurred and methanediimine was formed. Lastly, the fragmentation resulted in the formation of amine, carbon dioxide and water as the byproducts [48].

3.5 PEC measurements

To manifest the performance of the prepared catalysts (BV, SNS, 11BVSNS, 13BVSNS, and 31BVSNS) towards PEC hydrogen production, LSV measurements with 5, 10, 15 layer coating (5c, 10c, 15c) were carried out with all the fabricated electrodes and results are shown in **Fig. 3.14(a-e)**. The 15c was optimized to be the best amongst others as the higher current density of 0.21 mA/cm^2 was noticed in 15c amongst other photocatalysts. The 15c-13BVSNS, 31BVSNS, 11BVSNS exhibited higher current densities of 0.21, 0.01, and 0.07 mA/cm^2 respectively in comparison to bare BV (0.001 mA/cm^2) at 1.23 V vs RHE. LSV spectra of the synthesized composites with an optimal coating is presented in **Fig. 3.16(a)**.

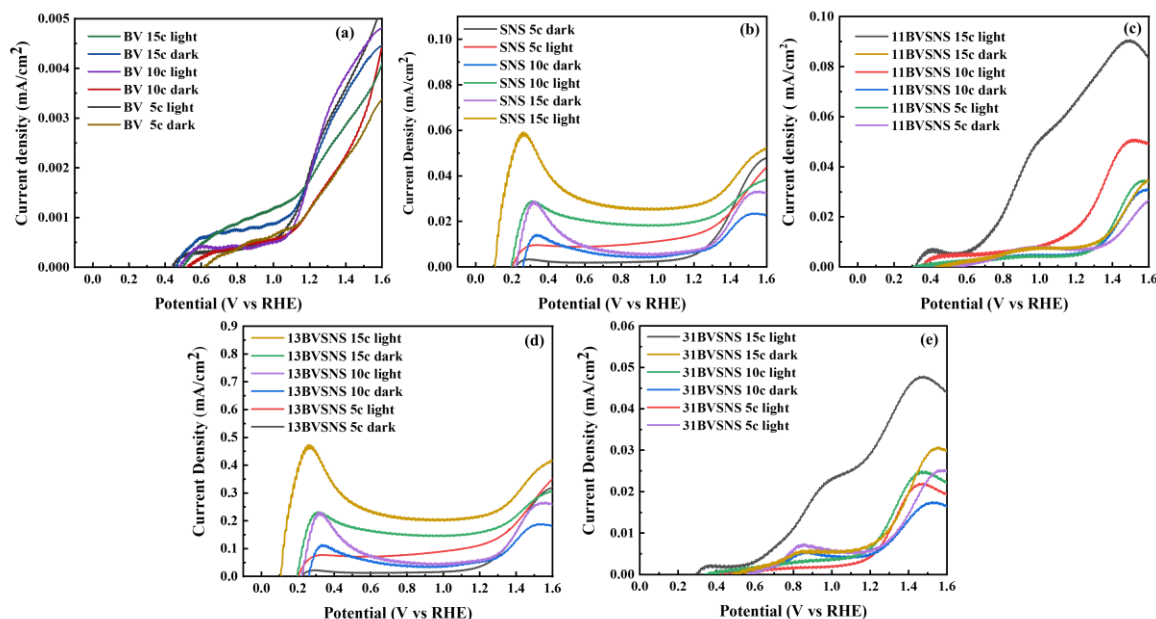


Fig. 3.14 LSV plot of 5, 10, and 15c layers of (a) BV, (b) SNS, (c) 11BVSNS, (d) 13BVSNS, and (e) 31BVSNS in dark & light condition.

The results suggest that a composition 13BVSNS with 15c showed the highest photocurrent amongst all the composites. However, the oxidation peak at 0.2 V may be due to the oxidation of SNS owing to the presence of atmospheric oxygen as the experiments were not conducted in an inert environment [49].

To further scrutinize the charge transport characteristic at the electrode/electrolyte interface under the dark and light in fabricated electrodes, the impedance spectra was recorded and results are depicted in **Fig. 3.15(a-e)**. In line with LSV results, 15c was recorded to be the optimal coating amongst all the composites as it exhibits lower resistance. The BV electrode has a substantially higher impedance than the 13BVSNS electrode with optimum coating, as indicated by Nyquist plots in **Fig. 3.16(b)**. This reveals that the hybrid 13BVSNS electrode had higher electrical conductivity than the bare one.

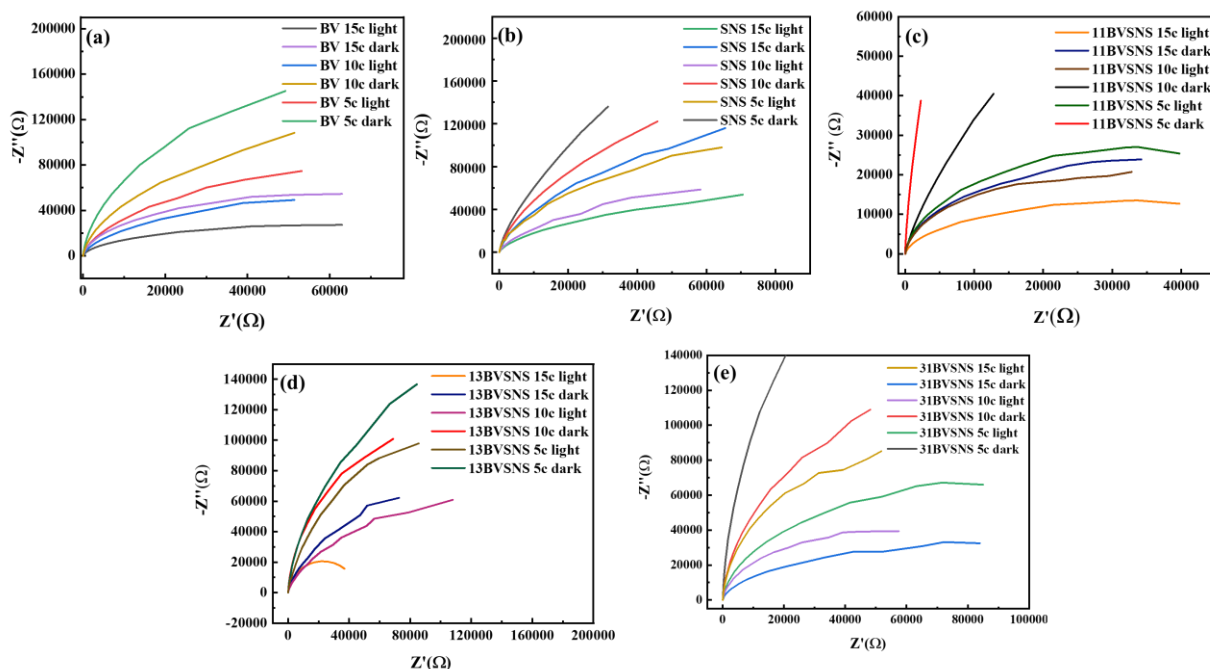


Fig. 3.15 Nyquist plot of 5, 10, and 15c layer of **(a)** BV, **(b)** SNS, **(c)** 11BVSNS, **(d)** 13BVSNS, and **(e)** 31BVSNS in dark & light condition.

In addition, the results were thoroughly examined by fitting an equivalent circuit model. The R_{ct} of BV and 13BVSNS electrode with the optimized coating was found to be 190 and 45.6 kΩ under the light illumination. A decline in R_{ct} value was observed under the light compared to dark conditions for all the fabricated photo-electrodes. The 13BVSNS exhibited the least R_{ct} value under the sunlight irradiation confirming higher migration of the photogenerated e^- under light illumination compared to other photocatalysts.

The fabricated electrode semiconductor's characteristics were measured by Mott-Schottky analysis in dark condition. It also enabled to calculate the flat band potential of

synthesized composite. Flat band potential of 13BVSNS was observed to be -0.37 V at 1.23 V vs RHE (**Fig. 3.16(c)**). The presence of a positive slope confirmed n-type nature of semiconductor. Moreover, n-type semiconductors possess the conduction band edge close to flat band potential [50].

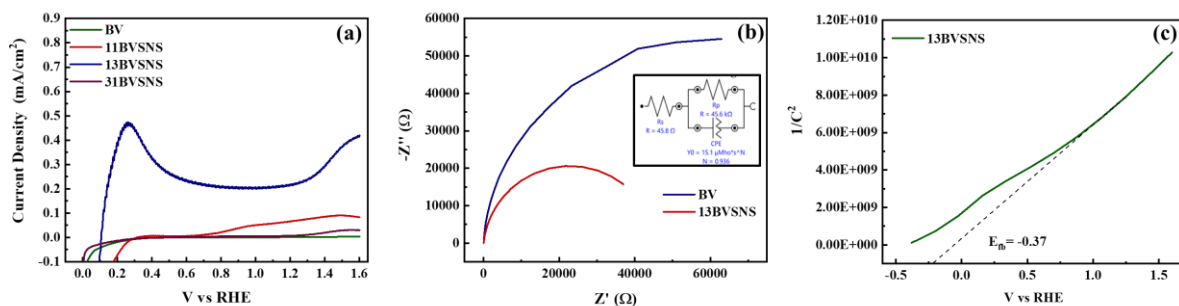


Fig. 3.16(a) LSV plot of 15c- BV, 11BVSNS, 13BVSNS, and 31BVSNS, **(b)** Nyquist plot of 15c-BV, and 13BVSNS, and **(c)** Mott-Schottky plot of 13BVSNS.

Chopped LSV experiments were performed further under the light and dark conditions to investigate the photo-response of 13BVSNS, and BV photocatalyst at 1.23V vs RHE. From **Fig. 3.17(a)** it can be inferred that the fabricated electrodes exhibit instantaneous increase in current to a steady-state in the light, and a return to background level once the light is shut off. The highest current density of 0.019 mA/cm² was achieved for 13BVSNS over BV (0.0011mA/cm²).

The slow oxidation stage on the photoanode usually controls the overall process of PEC water splitting to hydrogen and O₂. As a result, the photoanode's PEC performance can be measured by the evolution of either hydrogen (from a cathode) or O₂ (from an anode).

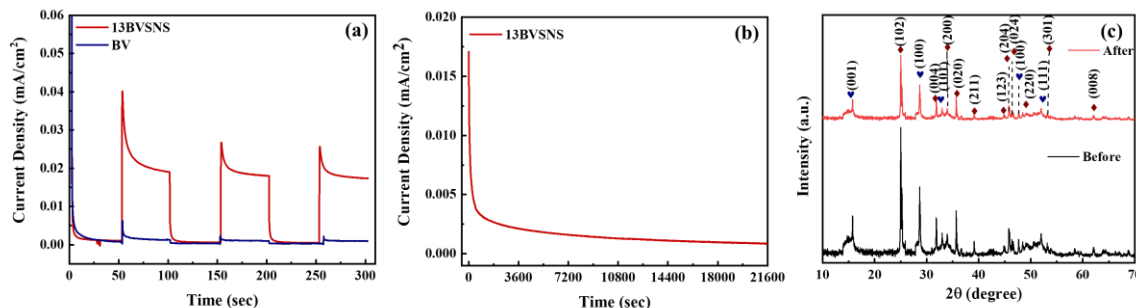


Fig. 3.17(a) Chronoamperometry plot of 13BVSNS composite, **(b)** stability study of 13BVSNS, and **(c)** XRD post the PEC studies.

So, a stability study of the 13BVSNS electrode for 6 h was carried out and the amount of hydrogen evolved was quantified. It is observed that the photocurrent was nearly stable after 6 h and a minimal decline was noticed (**Fig. 3.17(b)**). The 13BVSNS photoanode produced $\sim 21 \mu\text{molcm}^{-2}\text{sec}^{-1}$ of hydrogen at 1.23 V vs RHE which was calculated theoretically from **Eq. 2.7** given in **Chapter 2**. XRD was done post-PEC experiments to evaluate the stability of the electrode as presented in **Fig. 3.17(c)**. It was analyzed that the binary composite 13BVSNS possesses similar peaks as the un-utilized catalyst which suggested its stability as the nature of the composite did not change after the studies.

3.5.1 Comparison with the existing literature

Table 3.4 tabulates the comparative PEC performance of BVSNS with earlier reported literature. Hence, it can be scrutinized that PEC water splitting haven't been studied using BVSNS nanocomposite. Also, ideal amount of hydrogen was evolved using optimum 13BVSNS.

Table 3.4 Evaluation of PEC performance of 13BVSNS photocatalyst with the previously reported literature.

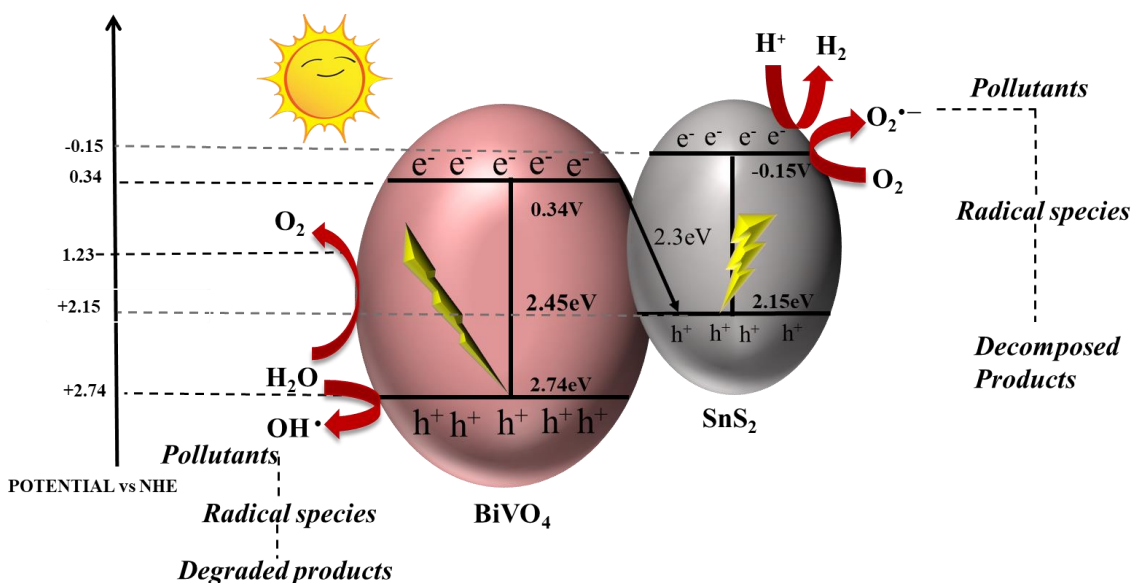
Photocatalyst	Electrolyte	H ₂ production rate	Potential	Electrode	Ref.
Bi ₂ S ₃ /BiVO ₄	0.2 M Na ₂ SO ₃	0.0092 $\mu\text{molcm}^{-2}\text{s}^{-1}$	0.45 V vs RHE	Photoanode	[51]
BiVO ₄ /GQD/ g-C ₃ N ₄	-	17.6 $\mu\text{molcm}^{-2}\text{s}^{-1}$	19.2 mA/cm ² at 1.0 V vs Ag/AgCl	Photoanode	[52]
BiVO ₄ /g- C ₃ N ₄	0.5 M Na ₂ SO ₄	5.94 $\mu\text{molcm}^{-2}\text{s}^{-1}$	9.68 mA/cm ² at 1.0 V vs Ag/AgCl	-	[53]
BiVO ₄ /ZnO	0.1 M Na ₂ SO ₄	-	-	Photoanode	[54]
13BVSNS	0.5 M Na ₂ SO ₄	21 $\mu\text{molcm}^{-2}\text{s}^{-1}$	1.23 V vs RHE	Photoanode	Present work

3.6 Photo(electro)catalytic mechanism

To better understand the charge migration process in the BVSNS couple, the location of the VB and CB were estimated using Mulliken's electronegativity value (**Eq. 2.8 and 2.9**) as detailed in **Chapter 2**.

E_{VB} values for BV and SNS were calculated as 2.74 and 2.15 eV, respectively, and further E_{CB} were assessed to be 0.34 and -0.15 eV, respectively.

On absorption of light energy, the e^- and h^+ are produced in both BV and SNS as both are sunlight active and the e^- in the VB are stimulated to CB level of BV, leaving behind the h^+ . The heterojunction formation reduces the reintegration rate and permits the e^- to migrate from BV to SNS. The rapid integration of the charge carriers is prevented by the generation of the Z scheme heterojunction by coupling both semiconductors. The $O_2^{\bullet-}$ radicals formed by the reaction of e^- in CB of SNS with molecular oxygen cause breakdown of contaminants. Also, because of the more negative CB of SNS, H^+ ions can be reduced to evolve hydrogen as SNS offers the reaction sites for the H^+ ions. The $\bullet OH$ radicals formed by reaction of the H_2O with the h^+ produced in VB of BV can further degrade contaminants to CO_2 and H_2O or comparably simpler compounds. **Scheme 3.1** contains a photo(electro)catalytic mechanism for the decomposition of the model pollutants and PEC water splitting.



Scheme 3.1 The illustrative photo(electro)catalytic mechanism.

3.7 Conclusions

Different mole ratios of BVSNS photocatalysts were prepared hydrothermally. The successful synthesis of the fabricated photocatalysts was scrutinized by XRD, SEM, XPS, BET,

and EDS. The composites possess good optical properties and optimum surface area for the effectual photo(electro)catalytic performance. The pharmaceutical pollutants, oflox and TC were eliminated to gauge the photocatalytic decomposition efficacy of the photocatalyst. Altering the mole ratio of BV and SNS, resulted in a change in decomposition efficacy apart from the influence of catalyst dose, pollutant-pH, etc. Amongst the prepared photocatalysts, 13BVSNS had the highest degrading efficiency along with the highest rate constant. As evidenced by scavenger trials, hydroxyl radicals were found to play significant influence in the degrading activity. The remarkable efficacy of 13BVSNS hybrid after seven testing runs illustrated its reusability for photocatalytic elimination of refractory pharmaceutical pollutants. BET analysis carried out after the photocatalytic process revealed that the surface characteristics of the material were essentially unchanged. Higher % COD and TOC removal of pollutants suggested that the photocatalyst is efficient. The products and intermediates of the photodegradation experiments were studied using GC-MS analysis. The PEC hydrogen production efficiency was discovered through LSV, chronoamperometry, and Mott-Schottky experiments. Alike photocatalysis, the 13BVSNS catalyst exhibited the maximum PEC efficiency with a highest current density of $\sim 0.21 \text{ mA/cm}^2$ at 1.23V vs RHE. The prepared 13BVSNS electrode was stable for up to 6 h as confirmed through stability experiments. Also, the XRD data after PEC experiments confirmed the unchanged nature of electrode before and after the experiments. As a result, this benign photocatalyst has a lot of potential for environmental sustainability.

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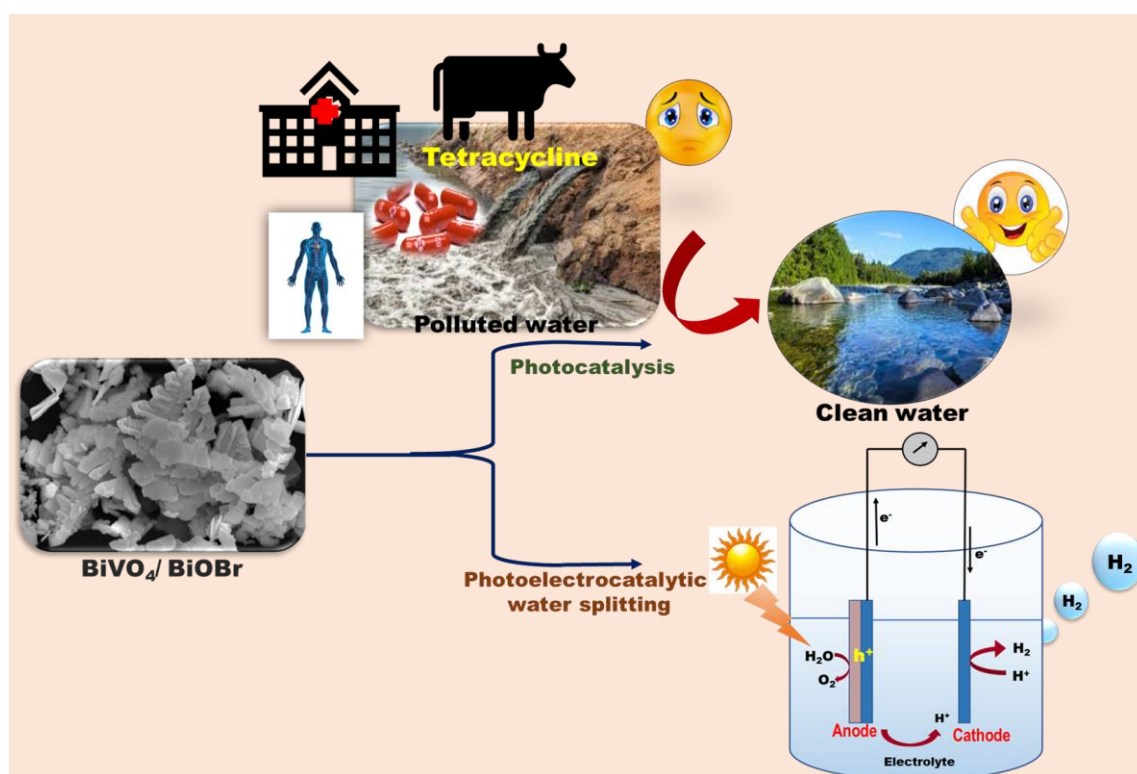
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Chapter 4

Unraveling the influence of $\text{BiVO}_4/\text{BiOBr}$ photocatalyst on solar-powered photocatalytic removal of tetracycline and photoelectrocatalytic water splitting



Highlights of the Chapter

- Fabrication of different mole ratios of $\text{BiVO}_4/\text{BiOBr}$ nanocomposite was done.
- The 3:1BVBI composite exhibited discs loaded onto fern nano-petal morphology.
- Proficiency of the prepared photocatalysts was tested by the photocatalytic remediation of tetracycline and photoelectrocatalytic water splitting under solar light.
- Photocatalytic elimination 90.4 % for tetracycline and hydrogen production rate of $1.864 \text{ mmolcm}^{-2}\text{sec}^{-1}$ was calculated with 31BVBI photocatalyst under solar light.

4.1 Introduction

Ecological and energy challenges are attracting widespread interest on a global scale because of a fast growth of the social economy and an impact of human activity [1,2]. To assess the efficacy of the synthesized photocatalyst, photocatalytic elimination of the hazardous pollutant, TC and PEC water splitting to evolve hydrogen was done in the illumination of solar light. The harmful effect of TC, need for the production of hydrogen, superiority of the photocatalysis and PEC technique over the other conventional methods has also been discussed in **Chapter 2**.

The efficient photocatalytic decomposition of organic contaminants and PEC water splitting requires the suitable design of visible light-active photocatalysts [3]. Numerous inorganic semiconductors have been explored and exploited in these directions [4,5]. Amongst these, BiVO_4 has generated significant attention owing to its chemical stability, easier preparation, low cost, and environmental friendliness [6]. Also, it has visible light absorption capacity and possesses a narrow band gap. However, its practical applicability is constrained by the poor charge transfer rate and quick recombination of photogenerated charge carriers [7]. In order to ameliorate these issues, BiVO_4 should be hybridized with another semiconductor photocatalyst as the heterojunction formation increases the lifetime of the charges owing to the synergistic effect [8]. Utilizing this approach, about 86.7 % of degradation of ciprofloxacin was observed with CuS/BiVO_4 under visible light irradiation within 90 min [9]. Likewise, for PEC water splitting, $\text{BiVO}_4/\text{WO}_3$ photoanode is reported to exhibit a photocurrent density of 0.002 mA/cm^2 at 1.23 V vs Ag/AgCl [6]. BiOBr is a typical p-type semiconductor photocatalyst is the catalyst of choice for heterostructure due to its excellent stability, environmental friendliness, non-toxicity, and appropriate band gap. It has a unique lamellar structure with $[\text{Bi}_2\text{O}_2]^{2+}$ sheets interspersed with two-layer bromine atoms (tetragonal matlockite structure) [10]. This shape offers enough room to polarize the associated kernel and orbital, making it easier to separate photo-produced carriers for effective PEC activity [9,11,12]. Also, the visible light activity of other semiconductors can be enhanced by coupling with BiOBr . WS_2/BiOBr , $\text{CuBi}_2\text{O}_4/\text{Bi/BiOBr}$ exhibited 85 % of degradation of metronidazole, and 81 % for ciprofloxacin under visible light [11,12].

Although, many photocatalytic remediation experiments using pure BiVO₄, BiOBr, and BiVO₄/ BiOBr couple and PEC experiments with BiVO₄, BiOBr and their hybridization with the other semiconductors have been published in the literature. However, the impact of different mole ratios of BiVO₄ and BiOBr has not been discovered for the photocatalytic abatement of the noxious pollutant, TC under natural sunlight and PEC water splitting under solar light simultaneously. Also, the degradation efficiency of the BiVO₄/BiOBr photocatalyst has not been compared under different light sources and with the commercial TiO₂-P25 photocatalyst.

This chapter is focused on synthesizing different mole ratios of the BiVO₄/BiOBr couple via hydrothermal method. Thereafter, the performance of the synthesized photocatalyst has been tested for the photocatalytic abatement TC in the natural sunlight as well as for PEC water splitting. Numerous experiments like the impact of photocatalyst concentration, scavenger studies, kinetic studies, the impact of pH, Mott-Schottky, LSV, reusability, chronoamperometry, and stability studies have been carried out. Mineralization studies with commercial TC and real TC tablet have also been done. Degraded products have been scrutinized by GC-MS. Additionally, based on all the experiments, the catalytic mechanism has been proposed.

4.2 Experimental part

This part encompasses the chemicals, methods and the materials used for the fabrication of the used photocatalysts.

4.2.1 Materials and methods

Acetic acid was bought from Spectrochem. From Loba Chemie, potassium bromide (KBr) was procured.

4.2.2 Syntheses

4.2.2.1 Synthesis of BV

BV was prepared as per the procedure discussed in the **Chapter 2 (section 2.2.2.1)**.

4.2.2.2 Fabrication of BiVO₄/BiOBr hybrid

Hydrothermal synthesis was followed to fabricate a BiVO₄/BiOBr (BVBI) couple with various mole ratios. Bi(NO₃)₃.5H₂O (0.005 mol) was dissolved into 7.5 mL of acetic acid. In

other flask, KBr (0.005 mol) was dissolved into 75 mL of DI water under vigorous stirring. Both the solutions were blended together and BV (0.005 mol) was dissolved into the resultant solution, and then it was subjected to sonication for 30 min. The solution was heated at 120°C for 5 h in a Teflon line autoclave. The resultant suspension was dried at 70°C in hot air oven after 3-4 washes with DI water and ethanol. The obtained pale yellowish powder was named as 1:1BiVO₄:BiOBr (11BVBI). Likewise, BVBI with different molar ratios (1:3 and 3:1) were synthesized and were designated as 13BVBI and 31BVBI.

For the comparison, white-colored bare BiOBr was prepared analogously without the addition of BV and was considered as BI [9].

4.2.3 Characterization techniques

Characterization procedures are detailed in the **Chapter 2 (section 2.2.3)**.

4.2.4 Photocatalytic remediation of TC

The refractory pharmaceutical pollutant, TC was decomposed in the existence of natural sunlight photocatalytically to gauge the activity of the prepared photocatalysts. A 5 mg of the photocatalyst was dispersed into 10 mL of 10 ppm solution of TC. The mixture was magnetically agitated in the dark for 80 minutes prior to irradiation to accomplish adsorption-desorption equilibrium between the pollutant and photocatalyst. Finally, the photocatalytic decomposition was initiated by illuminating the reaction mixture under sunlight for 140 min. The experiments were performed in September-October, and the LICOR Pyranometer determined that the sunlight intensity ranged between 700-760 W/m² during this time. About, 1.5 mL aliquots of the solutions were centrifuged to extract the photocatalyst at predetermined intervals. The experiments were repeated three times, and the graphs are plotted with error bars showing ~5 % data source error. A UV-visible spectrophotometer was employed to record changes in the absorption band of TC at a characteristic wavelength ($\lambda_{\text{max}} = 360 \text{ nm}$) in order to evaluate the filtrates and to determine the concentration of the pollutant. The decomposition performance can be assessed by the **Eq. 2.1** given in **Chapter 2**.

The effectiveness of the photocatalytic remediation of TC was also evaluated using COD and TOC analyses. Before the analyses, a 200 mL solution of TC containing 100 mg of 31BVBI

photocatalyst was illuminated under sunlight for 140 min. COD was gauged by the titration method, while the mineralization was estimated using TOC eradication. **Eq. 2.2, and 2.3** provided in the **Chapter 2** were used to compute the % COD and TOC elimination.

The degraded products obtained after photocatalytic reduction of the hazardous pollutant, TC by 31BVBI photocatalyst were examined using GC-MS. Methodology followed to prepare the samples for the GC-MS analysis is given in **Chapter 2**.

4.2.5 PEC studies

In order to conduct PEC investigations, the electrochemical workstation (AUTOLAB, Metrohm) outfitted with a standard three-electrode configuration and the solar simulator (LOT Quantum design) was utilized to test out PEC activity of the prepared electrodes under one sun illumination. Spray-coated BV, BI, 11BVBI, 13BVBI, and 31BVBI onto Indium Tin Oxide (ITO) were utilized as photoanodes (working electrodes), Pt wire (counter electrode), and Ag/AgCl (reference electrode). According to the photo-response behavior, the coating of the photocatalyst was optimized for 5, 10, and 15 layers. 0.5 M Na₂SO₄ solution (pH = 7) was utilized as a supporting electrolyte. The solar light intensity of 100 mW/cm² was used for performing photo-response tests which included LSV, electric impedance spectroscopy (EIS), chronoamperometry, and transient photocurrent. In both dark and light environments, impedance spectra were recorded at open circuit potential (ocp) with an AC perturbation signal of 10 mV. Additionally, Mott-Schottky measurements were performed on the constructed electrodes in a frequency-potential scan mode of 100 kHz. All the potentials were analyzed using the Ag/AgCl as a reference electrode, and their conversion to the RHE scale was done using the Nernst equation. Lastly, the stability study was carried out for 21600 sec (6 h) to evaluate the stability of the fabricated electrode.

4.3 Results and discussions

4.3.1 XPS analysis

The XPS analyses was performed to scrutinize the local electronic environment of the composite along with the binding energy, an oxidation state, and the chemical composition of the elements. **Fig. 4.1(a)** representing the survey spectrum of 31BVBI nanocomposite specifies the existence of Bi, O, V, and Br at corresponding binding energies. Supplementary peak of the

adventitious carbon at a binding energy of 284.5 eV was seen as all peaks were calibrated concerning to the C 1s. Deconvolution was done according to the least square Gaussian-fit model to fit the peaks. In the core level spectra of Bi, and V, the existence of peaks at the binding energies of 159.2, 164.3, and 166.1 eV (**Fig. 4.1(b)**), 516.7, and 524.3 eV (**Fig. 4.1(c)**) correspond to Bi 4f_{7/2} and 4f_{5/2}, V 2p_{3/2} and 2p_{1/2} attribute to +3, and +5 oxidation state of Bi, and V, respectively [13–15]. The peak at the binding energy of 166.1 eV of Bi attribute to Bi-O band of the 31BVBI photocatalyst [16]. O 1s XPS spectra consist of a dual peak with binding energy 529.7, and 531.6 eV, which is accredited to Bi-O and Bi-O-Bi band of BVBI nanocomposite, respectively (**Fig. 4.1(d)**) [16]. The dual peak of Br at binding energy 68.5 and 69.6 eV correspondent with energy states 3d_{5/2} and 3d_{3/2} were ascribed to -1 oxidation state as depicted in **Fig. 4.1(e)** [17,18]. Thus, the XPS spectrum manifested the successful fabrication of the hetero-composite.

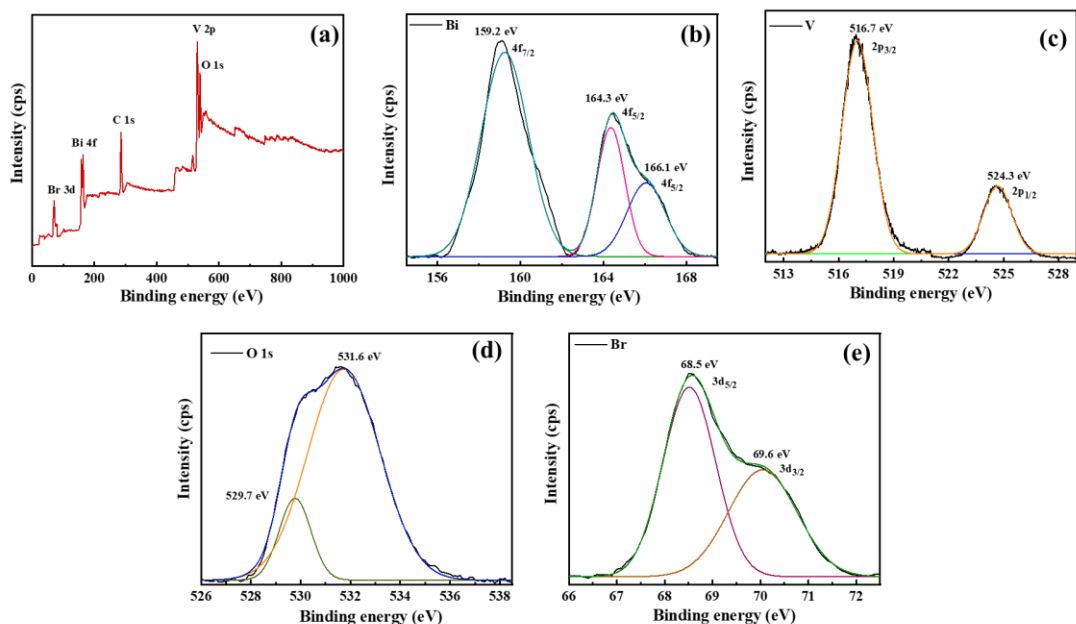


Fig. 4.1 XPS spectra of 31BVBI nanocomposite, (a) the survey spectrum, (b) Bi 4f, (c) V 2p, (d) O 1s, and (e) Br 3d.

4.3.2 XRD analysis

The XRD was performed to validate the successful fabrication, crystallite phase, purity, and structural analysis of the fabricated photocatalysts [19]. **Fig. 4.2** represents the XRD pattern of BV, BI, 11BVBI, 13BVBI, and 31BVBI photocatalyst. The crystallinity of monoclinic BV

was emphasized by the presence of sharp peaks indexed to 2θ values at 19.0° , 24.5° , 28.8° , 30.6° , 34.8° , 35.2° , 40.0° , 42.6° , 46.1° , 46.9° , 47.4° , 50.1° , 53.2° , and 58.3° attributing to the crystal planes (011), (102), (112), (004), (200), (020), (211), (015), (123), (204), (024), (220), (301), and (303), respectively (JCPDS card-83-1699). The efficient fabrication of tetragonal BI was confirmed by the presence of peaks indexed at crystal planes (001), (002), (101), (102), (003), (112), (004), (201), (104), (114), (203), (105), (204), (006), (214), (106), and (116) agrees to 2θ value of 10.9° , 21.9° , 25.1° , 31.7° , 33.1° , 39.3° , 44.6° , 47.6° , 50.6° , 56.1° , 58.0° , 61.8° , 66.2° , 69.5° , 71.0° , 74.1° , and 78.7° , respectively (JCPDS-01-078-0348). The existence of sharp peaks confirms the crystal nature of the fabricated photocatalysts. The incidence of both types of diffraction peaks certified the efficacious fabrication of the nanocomposite (BVBI) without the presence of any impurities.

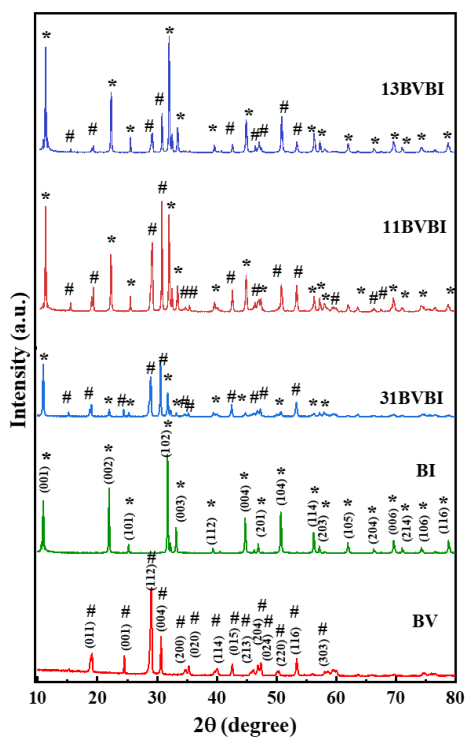


Fig. 4.2 XRD plot of BV, BI, 11BVBI, 13BVBI, and 31BVBI photocatalyst # and * denote peaks of BV, and BI, respectively.

4.3.3 PL study

The PL study was done to investigate the separation, allocation, and reintegration rate of the photogenerated charges. A lower recombination rate, more carrier charge migration capacity,

and effective charge separation are all necessary for an efficacious photocatalyst [20]. Lower PL signal intensity of photocatalyst results in less photoexcited carrier recombination and higher charge migration efficacy, which is beneficial for the PEC performance of the photocatalyst [21]. **Fig. 4.3** represents the PL spectra of the synthesized photocatalysts. The 31BVBI photocatalyst exhibited weaker PL emission intensity amongst the fabricated photocatalysts indicating a lower recombination rate while bare BI and BV exhibited the strongest PL signal. Due to the synergetic effect between both semiconductors, 31BVBI can significantly enhance the number of charge capture sites with the addition of BI, hence boosting the charge separation efficiency.

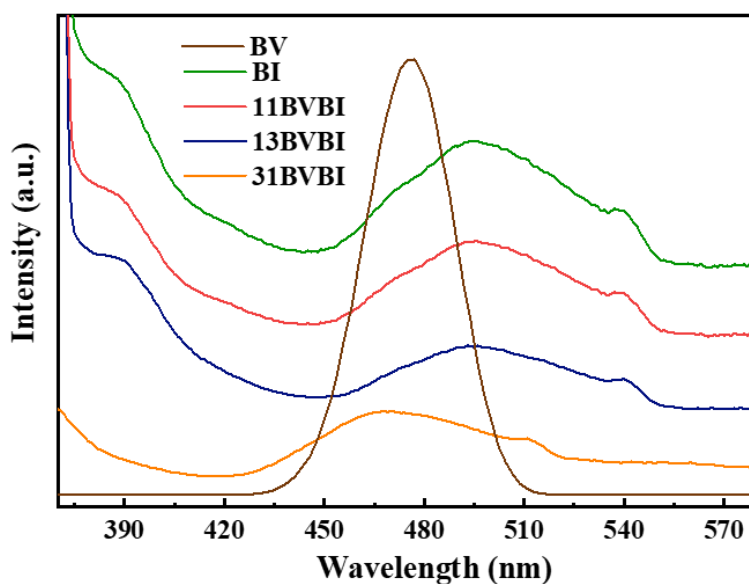


Fig. 4.3 PL spectra of fabricated photocatalysts.

4.3.4 Surface area analyses

Surface area analyses is one of the important parameters for PEC/photocatalysis [22]. The concept of monolayer formation of the nitrogen gas molecules on a solid surface was employed to calculate the precise surface area. BJH process was done to monitor the pore size distribution. The fabricated photocatalysts have a type-IV N_2 adsorption curve together with H3 hysteresis regression loop, signifying the mesoporous nature (**Fig. 4.4(a), (b)**). Mean pore diameter, pore volume, and surface area results are tabularized in **Table 4.1**. These results suggest that surface area was highest for 31BVBI nanocomposite owing to the formation of heterojunction amongst all the fabricated photocatalysts. Higher surface area facilitates a greater

number of surface-active sites [23]. Also, mesopores offer effective pathways for mass transport and improve the interfacial contact between the pollutant and the surface of the catalyst, therefore higher photocatalytic degradation activity [24]. Additionally, the H₂ production rate also increases with the intensification in the specific surface area of the photocatalyst.

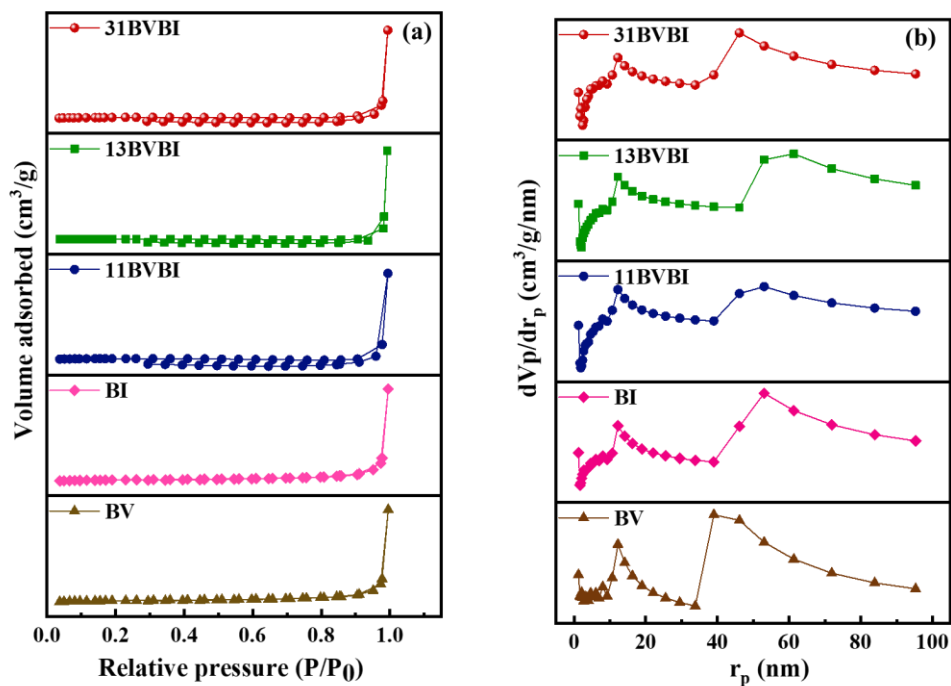


Fig. 4.4(a) Nitrogen sorption isotherms, **(b)** BJH plot.

Table 4.1 The specific surface area, mean pore volume, and the pore diameter of fabricated BVBI catalysts.

Sample	Specific surface area (m ² /g)	Mean pore volume (cm ³ /g)	Pore diameter (nm)
BV	32	0.551	13.62
BI	28	0.520	12.72
11BVBI	50	0.572	16.37
13BVBI	54	0.661	19.14
31BVBI	63	0.686	21.46

4.3.5 Absorption studies

DRS was performed to assess an optical absorption property of the as-synthesized nanocomposites. On absorbing a photon of energy greater than the band gap of the photocatalyst, the excitation of the e^- occurs from its VB to the CB [25]. The transition of the electron, therefore, results in the sharp rise in the absorbance tendency of the photocatalyst to the wavelength ascribing to the band gap energy. **Fig. 4.5(a)** validates that nanocomposites possess better visible light absorption intensity than pristine BV and BI. Enhanced light absorption may be owing to the synergistic effect of both semiconductors. Tauc plot equation (**Eq. 2.4**) given in **Chapter 2** was used to assess the band gap of the prepared photocatalysts. The band gap can be assessed by extrapolating the linear area of curve to the energy axis. E_g values for BV, BI, 11BVBI, 13BVBI, and 31BVBI were determined to be 2.4, 2.7, 2.2, 2.0, and 1.8 eV as represented in **Fig. 4.5(b)**. These findings suggest that 31BVBI nanocomposite offers a narrow band gap and an extensive visible light absorption capability among the synthesized catalysts. The electronic properties caused by a successful interface between both photocatalysts are responsible for the narrow band gap, which is essential for boosting PEC/photocatalytic activity.

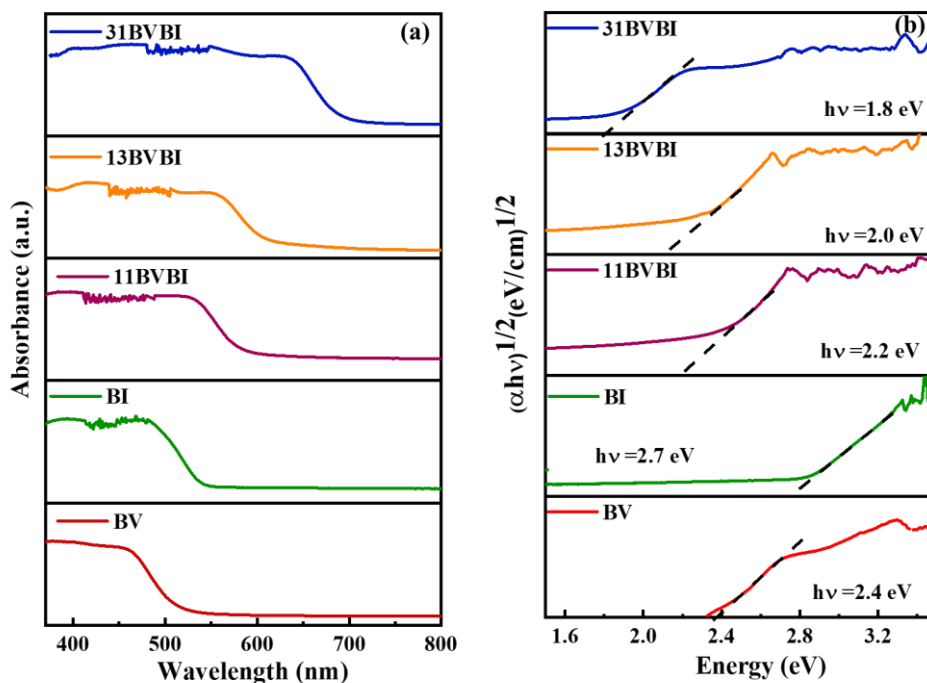


Fig. 4.5(a) Absorbance spectrum, and **(b)** band gap energies of the prepared photocatalysts.

4.3.6 SEM analysis

SEM was performed to ascertain the surface morphology of the 31BVBI nanocomposite. The outcomes revealed that BV possesses fern-petal-like morphology while BI has disc-shaped morphology (**Fig. 4.6(a, b)**). As revealed in the **Fig. 4.6(c, d)**, 31BVBI photocatalyst possess discs decorated onto fern petals. The efficacious formation of the 31BVBI nanocomposite was thus confirmed by the existence of both type of structures. Additionally, these results show an excellent distribution of BI onto BV, which is advantageous for a heterojunction photocatalyst.

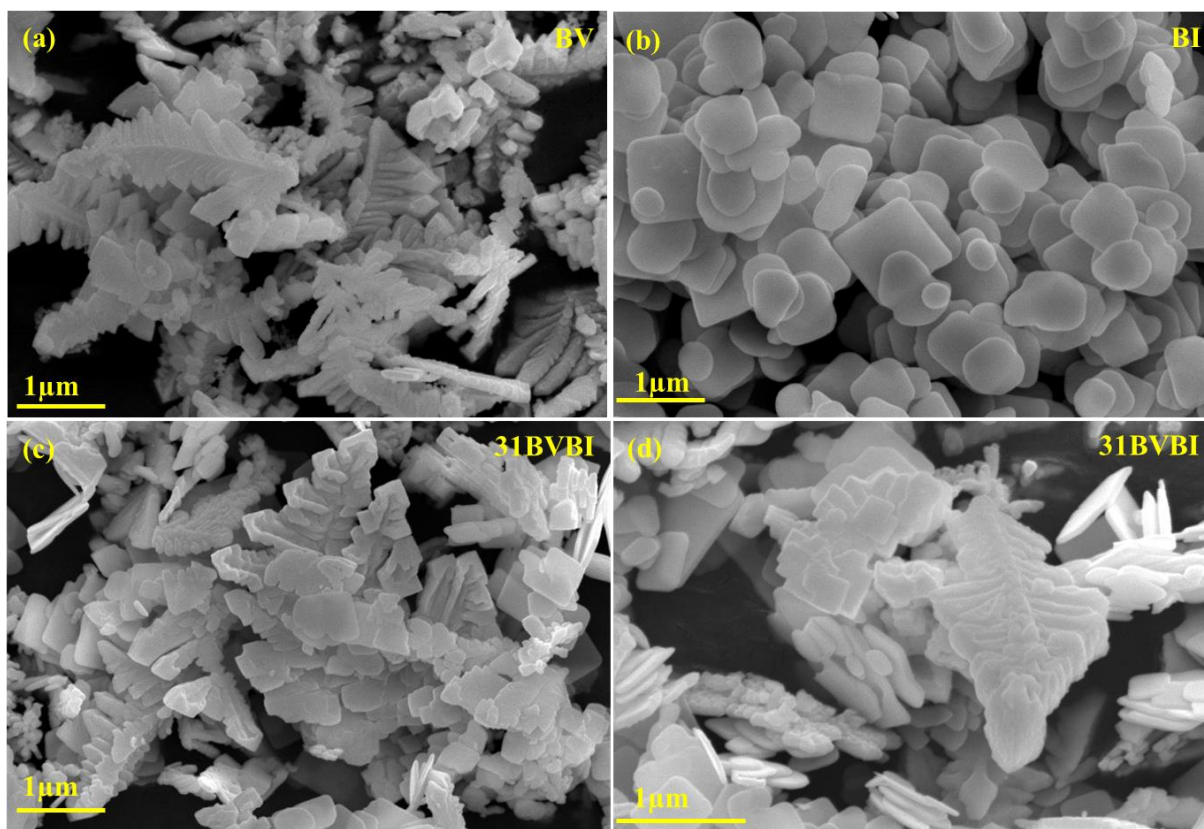


Fig. 4.6 The SEM images of (a) BV, (b) BI, and (c, d) 31BVBI nanocomposite at different magnifications.

4.3.7 EDS and elemental mapping

EDS was done to evaluate an elemental composition, distribution, and purity of the photocatalyst. The EDS spectra exhibit a strong signal of Bi, Br, V, and O, all of which were embedded inside the selected regions of 31BVBI photocatalyst as represented in **Fig. 4.7(a)**. The absence of any additional elemental peak in the spectrum implies that there were no impurities on the surface of the synthesized composite, supporting the successful synthesis of the material

[26]. Elemental mapping reveals that all the elements were uniformly dispersed and their distribution agrees well with the SEM image of the composite which is advantageous for a heterojunction nanocomposite (**Fig. 4.7(b-e)**).

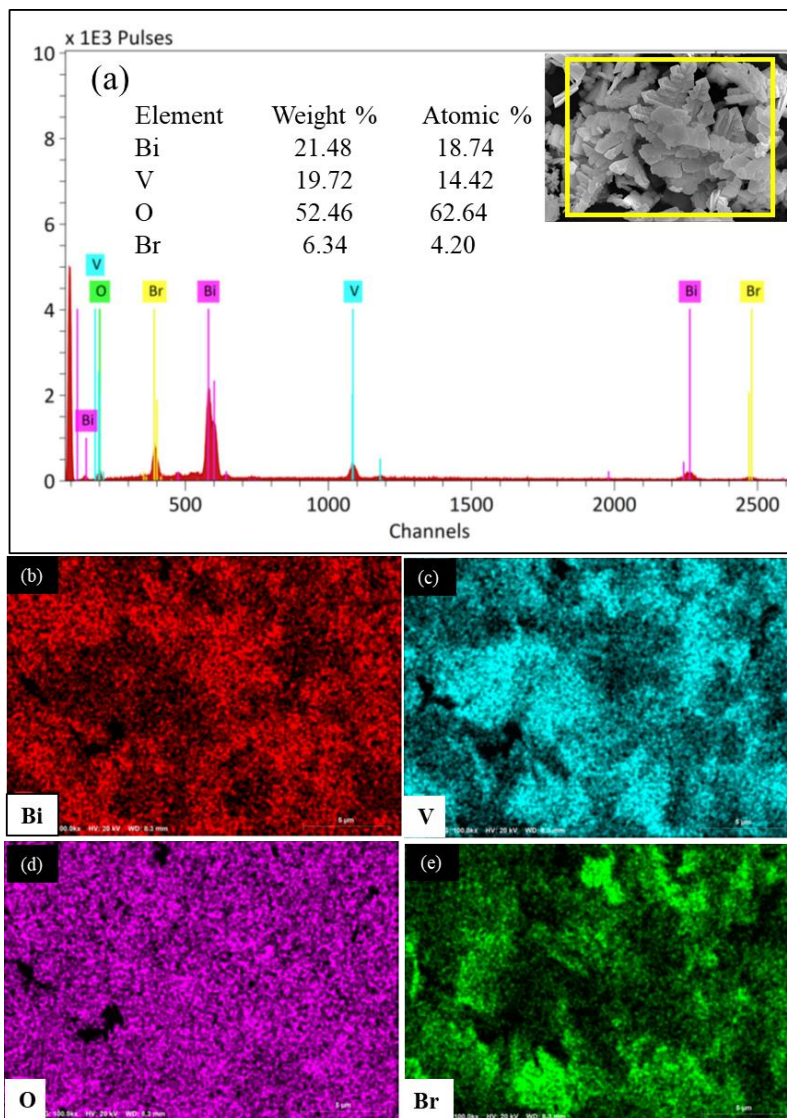


Fig. 4.7(a) EDS spectrum of 31BVBI with the corresponding SEM micrograph, and **(b-e)** elemental mapping.

4.3.8 Photocatalytic abatement studies

The activity of the photocatalysts was gauged by the photocatalytic deterioration of TC in the illumination of sunlight for 140 min. **Fig. 4.8(a, and b)** depicts the photocatalytic abatement results of the detrimental TC. Little change in the concentration of TC was observed without the photocatalyst, indicating that self-degradation of the pollutant (9 %) is less under sunlight owing

to its stable nature. However, the highest decomposition of TC was observed to be 90.4 % in the existence of 0.5 g/L of the 31BVBI photocatalyst. Two major factors attribute to the increased photocatalytic performance of the 31BVBI composite. Before the degradation through photocatalysis, TC should be thoroughly adsorbed on the surface of the nanocomposite. Higher adsorption of pollutant occurs due to electrostatic interaction between negatively charged surface of BI (due to Br^- layer) and positively charged surface of TC (due to the cationic moiety of TCH_3^+ and TCH_2^+). Also, the unique structure of BI promotes the segregation of the charge carriers in BV. However, the capacity of the holes and electrons to oxidize and reduce may be deprived owing to the excess amount of BI present in the composite, which might also prevent electron transport and push the conduction band of BV to a more positive position [27]. Therefore, the highest degradation efficacy of 90.4 % was observed for 31BVBI nanocomposite. Pristine BV and BI exhibited the least photocatalytic performance of 58.4 %, and 68.4 %, respectively. The photocatalytic performance of commercial TiO_2 -P25 powder was also evaluated in comparison to synthesized catalysts and was found to have 50.8 %. The wide band gap of TiO_2 -P25, which renders it receptive to UV light only, may be the cause of its reduced performance. Hence, it is evident that the produced photocatalysts show higher photocatalytic performance over TiO_2 -P25 photocatalyst. **Eq. 2.5** given in the **Chapter 2** was used to compute the rate constant for the observed catalytic performance. The reaction followed Langmuir-Hinshelwood kinetics model or pseudo-first-order kinetics as validated in **Fig. 4.8(b)** because the lines were well fitted linearly with $R^2 > 98.5$ %. The 31BVBI composite possesses the maximum rate constant of $\sim 0.0159 \text{ min}^{-1}$ owing to the formation of the heterojunction. However, for TiO_2 -P25 powder, the rate constant was discovered to be 0.0042 min^{-1} which was the lowest of all the photocatalysts illustrating the superiority of the fabricated materials.

The R factor was used to quantify the degree of a synergistic effect of the nanocomposites (**Eq. 4.1**).

$$R = \frac{k_{BV}/k_{BI}}{k_{BV} + k_{BI}} \quad (4.1)$$

Here, k_{BV}/k_{BI} , k_{BV} , and k_{BI} stand for the rate constant of coupled BV and BI, bare BV, and BI, respectively. R value for the 11BVBI, 13BVBI, and 31BVBI nanocomposite was found to be

0.68, 0.79, and 1.34, respectively. Thus, it was gauged that 31BVBI had the highest R-value owing to the interfacial contact between BV and BI, and therefore higher photocatalytic performance. The decomposition efficiency, the value of rate constant, and synergistic constant of the synthesized photocatalysts are tabulated in **Table 4.2**.

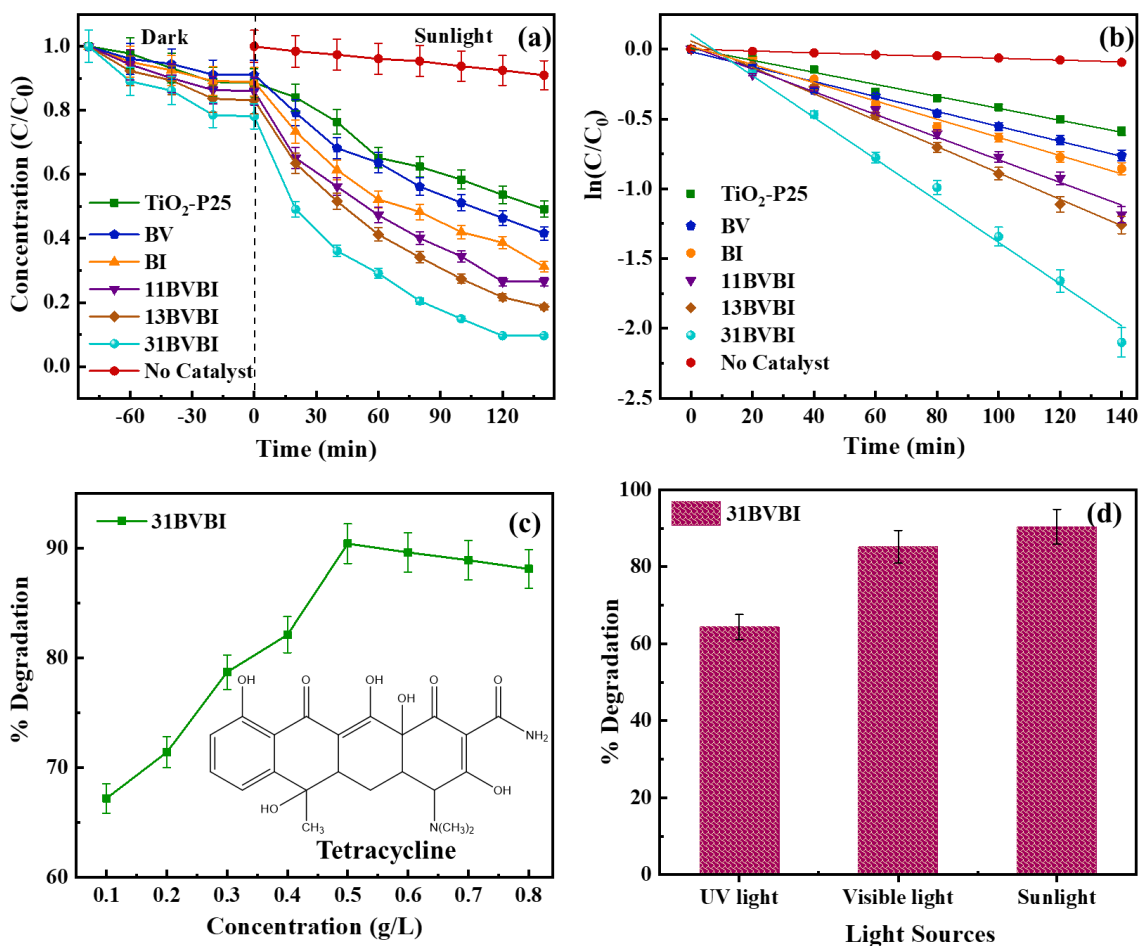


Fig. 4.8(a, b) The kinetic analyses of the different photocatalysts for the deterioration of the TC having standard deviation 26.77, **(c)** influence of the photocatalyst's concentration on removal of the TC pollutant, **(d)** impact of the different light sources.

4.3.8.1 Impact of the catalyst amount

The decomposition efficacy is also dependent on the usage of the optimal amount of the photocatalyst for the degradation of the pollutant. **Fig. 4.8(c)** depicts that the rate of deterioration of the pollutant initially increases from 67.2 % to 90.4 % as the catalysts concentration augment from 0.1 g/L to 0.5 g/L. This could be owing to the increment in the number of active centres on

the surface of the catalyst. However, the reduction efficiency of the photocatalyst gets decreased by further increasing the catalyst amount to 0.6 g/L. The main factor responsible for decreasing the decomposition efficacy is the reduction in the ability of the photocatalyst to absorb light owing to the agglomeration of the particles with the augmentation in the catalyst amount. Additionally, the agglomerations may hinder the photons from penetrating the inner layers of the photocatalyst. As a result, the minimal number of particles get activated, which ultimately results in the generation of fewer holes (h^+), hydroxyl ($\cdot OH$), electrons (e^-), and superoxide radicals ($O_2^{\cdot -}$) [28]. Consequently, as the catalyst dose rises, the degradation rate tends to decrease. So, based on reduction efficiency, a dose of 0.5 g/L of the photocatalyst was selected as an optimal dosage for the subsequent studies. Hence, it can be concluded that even a small amount of 31BVBI is sufficient for the photocatalytic abatement of TC under exposure to sunlight.

Table 4.2 Degradation efficacy, rate constant, and synergistic factor of the prepared photocatalysts.

Photocatalyst	Degradation (%)	Rate constant (min^{-1})	R factor
TiO ₂ -P25	50.8	0.0042	-
BV	58.4	0.0053	-
BI	68.4	0.0065	-
11BVBI	73.5	0.0081	0.68
13BVBI	81.4	0.0094	1.79
31BVBI	90.4	0.0159	1.34
No catalyst	9.01	0.00069	-

4.3.8.2 Effect of different light sources

A comparable experiment was carried out in ideal conditions using UV light and visible light as the light sources. According to **Fig. 4.8(d)**, TC deteriorated to 64.4, and 85.2 % in UV, and visible light, respectively. However, the 31BVBI photocatalyst manifested the highest

degradation rate of 90.4 % when exposed to sunlight. As a result, the fabricated photocatalysts possess the ability to deteriorate refractory pollutants in the illumination of the natural sunlight. Therefore, the synthesized photocatalysts are efficient.

4.3.8.3 Influence of pH

The pH is the significant factor governing the degradation efficiency of the photocatalyst. The variation in pH affects the adsorption capacity, electric surface charge distribution, and ionization state of the photocatalyst [29]. The point zero charge (pzc) of the photocatalyst was validated to be 6.02 (**Fig. 4.9(a)**). Therefore, at $\text{pH} > 6.02$ and $\text{pH} < 6.02$, the surface of the nanocomposite is negatively and positively charged, respectively. TC exists in the amphoteric state with 4 different pKa values (3.3, 7.7, 9.7, and 10.7). As a result, TC occurs as a positively charged molecule (TCH_3^+ and TCH_2^+) in $\text{pH} < 3$ owing to the protonation of dimethyl ammonium group. It occurs as an anionic molecule (TC_2^- and TCH^-) at $\text{pH} > 7.7$ due to deprotonation of diketone or tricarbon of phenol. While it exists in isoelectric form ($\text{TCH}^\pm$) in pH between 3.3-7.7 owing to the subtraction of proton from the phenolic diketone group [30]. Due to repulsions developing between the anionic and cationic forms of TC and the negatively and positively charged surface of photocatalyst, respectively, the degradation efficiency of TC by 31BVBI photocatalyst got reduced in both acidic and alkaline environments. However, the zwitterionic form of TC and the negatively charged catalyst had an electrostatic affinity that improved the degradation ability of TC. Due to the affinity of TC for the surface of the photocatalyst, TC removal by the 31BVBI composite was therefore maximum at pH 7 (90.4 %) and was greater in alkaline than in an acidic environment as depicted in **Fig. 4.9(b)**.

4.3.8.4 Scavenger experiment

Photocatalytic degradation of TC involves a series of complex reactions driven by photogenerated radicals, or reactive oxygen species (ROS). Various species, mostly dissolved hydroxyl ions, oxygen, and water present in the solution capture photogenerated electrons and the holes to generate ROS i.e., h^+ , $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, etc [31]. Therefore, different scavengers e.g., methanol as h^+ , dimethyl sulfoxide (DMSO) as $\cdot\text{OH}$, and benzoquinone (BQ) as $\text{O}_2^{\cdot-}$ quencher were utilized to examine the role ROS responsible for the photocatalytic experiment. From **Fig. 4.9(c)**, it can be inferred that the highest decomposition efficacy of 90.4 % was observed for TC

in the absence of any scavenging agent. The decomposition efficacy of TC by 31BVBI nanocomposite significantly gets quenched from 90.4 % to 46.2 % in the presence of BQ. This indicates that the $O_2^{\cdot-}$ is the major ROS responsible for the remediation of TC. DMSO had a comparable (60 %), but less significant impact on the degradation process, indicating that $\cdot OH$ plays a little but crucial function in the removal of antibiotic. These results specify that the $O_2^{\cdot-}$ is the main reactive species for removal of TC by the 31BVBI nanocomposite.

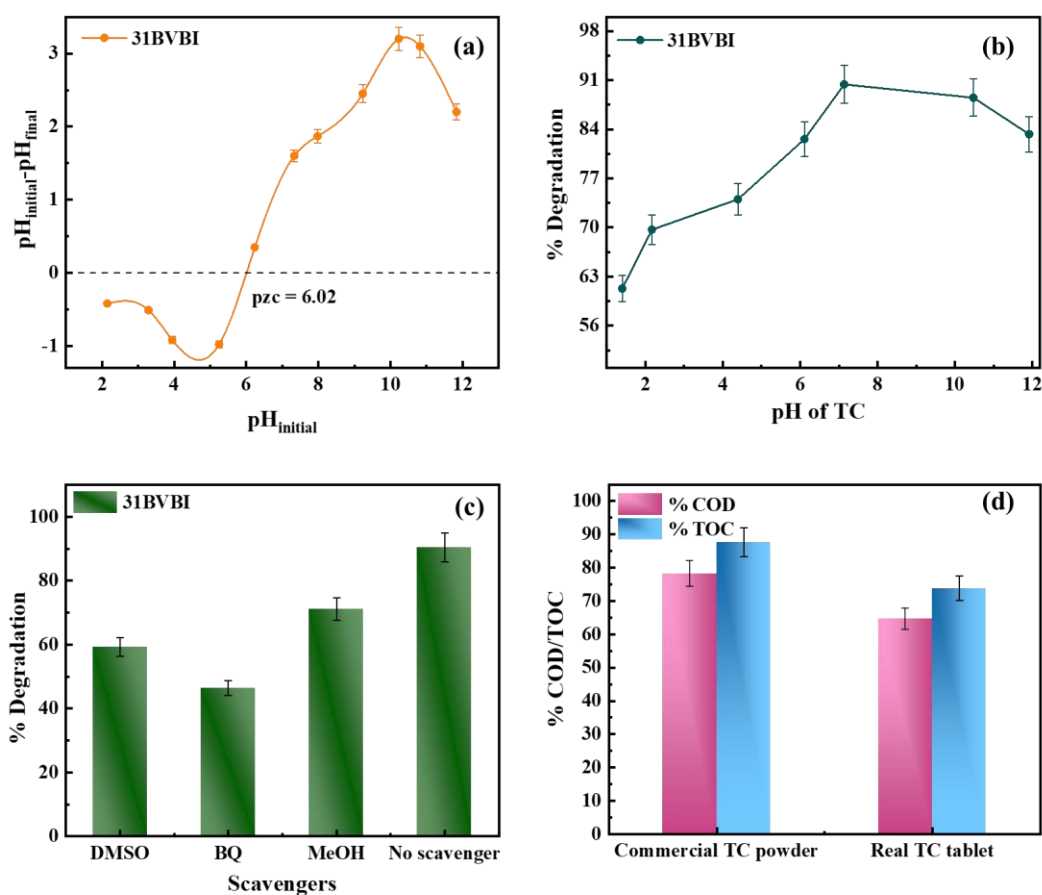


Fig. 4.9(a) pzc of the 31BVBI photocatalyst, **(b)** influence of pH on the degradation efficacy, **(c)** impact of different quenchers on the photocatalytic degradation of TC, **(d)** % COD/TOC analysis of commercial powder of TC, and real TC tablet.

4.3.8.5 Mineralization study

Evaluation of the degree of mineralization of the organic matter along with the degradation of the organic pollutants is important. To determine the amount of mineralization of TC, TOC, and COD was carried out [32] (**Fig. 4.9(d)**). Elevated COD and TOC readings

suggested that the antibiotic, TC contained a significant amount of organic matter. After carrying out photocatalytic treatment for 140 min under the irradiation of sunlight, % COD removal of 78.2 and 64.6 % were observed for commercial TC solution and real TC tablet. Whereas, the % TOC removal was observed to be 87.7, and 73.8 %, respectively. The great effectiveness of the as-prepared photocatalyst can be validated by high COD and TOC removal efficacies. The successive organic intermediates that were formed during the process before the complete breakdown of TC to carbon dioxide and other simpler products caused the % TOC removal to be lower than % degradation [33]. Hence, the fabricated photocatalyst appears to be more effective in removing COD and TOC than the industrial physicochemical treatment.

4.3.8.6 Reusability study

Reusability and the optical stability of the photocatalyst are the key components for its practical use. The stability and the recyclability of the 31BVBI photocatalyst for the photocatalytic abatement of the TC were checked over 7 cycles and the outcomes are demonstrated in **Fig. 4.10(a)**. The photocatalyst was washed, filtered, and dried in an oven at 80°C for 14 h before being used for the subsequent cycle. According to the results, the photocatalytic effectiveness of the 31BVBI photocatalyst has decreased roughly by 20.2 %. This may be due to the loss of the photocatalyst during washing and drying procedure, which could lower the surface catalytic property of the photocatalyst. Also, aggregation of the nanocomposites may occur which could result in the reduced effective surface area and the number of reactive sites, thereby decreasing activity. Additionally, due to the occlusion of the pores and active sites of photocatalyst by TC and its intermediates after each cycle, the adsorptive surface activity of 31BVBI steadily diminishes [34]. However, the decrease in the photocatalytic activity was not significant even after 7 long runs. This validates that the photocatalyst is reusable and is potent for photocatalytic applications. XRD, SEM, and BET analyses were done to determine the stability of 31BVBI photocatalyst after the degradation studies. Post the reusability studies, the XRD pattern of the nanocomposite displayed no discernible changes (**Fig. 4.10(b)**). The peak positions and peak intensity of BI and BV were unaltered. No new diffraction peak corresponding to crystalline impurities was seen. Also, the BET physisorption analysis after the reusability studies validated that the photocatalyst had the mean pore diameter (17.26 nm), the specific surface area (57 m²/g), and the mean pore volume

(0.521 nm), respectively as represented in **Fig. 4.10(c, d)**. Even though the surface area got reduced but it was still sufficient to carry out photocatalytic decomposition. SEM done after the recycling studies revealed that the morphology of the photocatalyst doesn't change (**Fig. 4.10(e)**). Hence, the synthesized 31BVBI nanocomposite is stable, reusable, and can be utilized for practical applications.

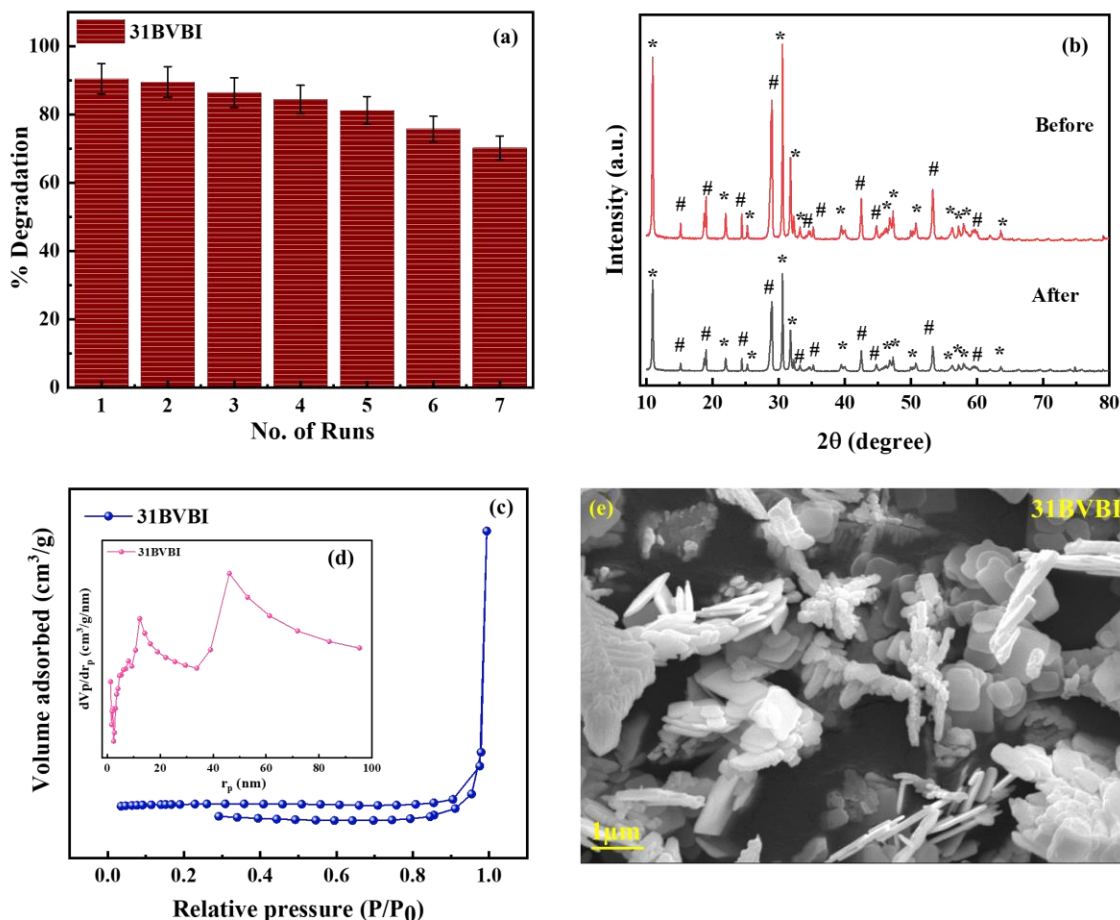


Fig. 4.10(a) Impact of different quenchers on the photocatalytic degradation of TC, **(b)** XRD, **(c, d)** BET plot along with the inset having BJH graph, and **(e)** SEM image of used photocatalyst post degradation studies.

4.3.9 Comparison with the existing literature

A comparative study of the fabricated BVBI nanocomposite was carried out with the different reported BV and BI based composites and other catalysts for the photocatalytic elimination of TC under different light sources as tabulated in **Table 4.3**. It is clear from

literature that decomposition of deleterious antibiotic, TC was not studied earlier by BVBI photocatalyst under illumination of natural sunlight. Thus, it can be assessed that highest decomposition efficacy was attained by the fabricated 31BVBI nanocomposite by employing a little amount of produced photocatalyst under the irradiation of natural sunlight and in the ideal reaction conditions in comparison to the current literature.

Table 4.3 Comparison of different photocatalysts for the photocatalytic reduction of TC.

Photocatalyst	Contaminant's concentration (ppm)	Time of the reaction (min)	Source of light	Rate constant k	Decomposition efficiency (%)	Ref.
BiVO ₄ /MoS ₂	TC (20 ppm)	120	Visible light	-	68.83	[35]
BiVO ₄ /Fe ₃ O ₄ /CdS	TC (10ppm)	90	Visible light	0.0232 min ⁻¹	87.37	[36]
BiVO ₄ /Cu /g-C ₃ N ₄	TC	120	Visible light	0.011 min ⁻¹	69	[37]
BiOBr/carbon fibre /g-C ₃ N ₄	TC (10ppm)	120	Visible light	0.015 min ⁻¹	86.1	[38]
CuInS ₂ /Bi ₂ MoO ₆	TC (10 ppm)	120	Visible light	0.015 min ⁻¹	84.7	[39]
MnTiO ₃ /Ag /g-C ₃ N ₄	TC	120	Visible light	-	61	[40]
31BVBI	TC (10 ppm)	140	Sunlight	0.0159 min ⁻¹	90.4	current work

4.4 GC-MS study

A GC–MS analyses was done to investigate the products and the intermediates generated during the photocatalytic remediation of TC by 31BVBI nanocomposite. **Fig. 4.11(a, and b)** illustrates Gas chromatogram and mass spectrum, respectively. As represented in **Fig. 4.12**, the

In the second route dihydroxylation leads to the formation of 3,10,12,12a-tetrahydroxy-6-methyl-3,4,4a,5a,6,12a-hexahydrotetracene-1,11(2H,5H)-dione followed by the abstraction of NCH₃ group from 4-(dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide. The 1-hydroxyanthracen-9(10H)-one was formed by the cleavage of ethyl, acetyl, hydroxyl group, and ring-opening reactions.

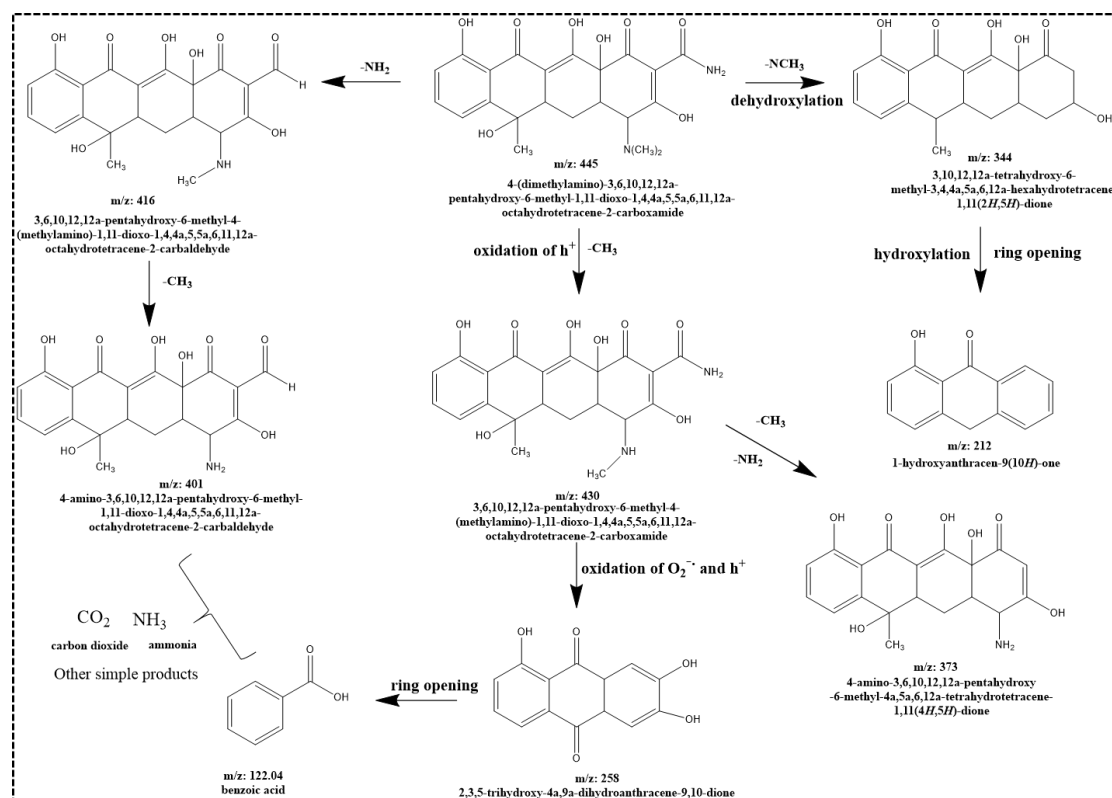


Fig. 4.12 Proposed photocatalytic decomposition route of TC by 31BVBI nanocomposite.

In the third decomposition route, formation of 3,6,10,12,12a-pentahydroxy-6-methyl-4-(methylamino)-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide occurred by the demethylation of 4-(dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide. Deduction of amide group and demethylation further lead to the formation of 4-amino-3,6,10,12,12a-pentahydroxy-6-methyl-4a,5a,6,12a-tetrahydrotetracene-1,11(4H,5H)-dione. Whereas, oxidation of h⁺ and O₂⁻ lead to the formation of 2,3,5-trihydroxy-4a,9a-dihydroanthracene-9,10-dione. The polarization resulting from the intense adsorption of h⁺ to the electrons surrounding the benzene ring caused the stable benzene ring to break down and produce benzoic acid. Later got degraded to give CO₂, NH₃, and other simple products.

4.5 PEC measurements

LSV analyses with 5, 10, and 15 layer coating (5c, 10c, and 15c) were conducted to assess the performance of the fabricated photocatalysts towards PEC hydrogen generation and to investigate the photo-response as presented in **Fig. 4.13(a-e)**. Due to its higher photocurrent density of 0.2198 mA/cm² compared to other photocatalysts, the 15c was designed to be the best among the others. 15c -11BVBI, 13BVBI, and 31BVBI unveiled greater photocurrent densities of 0.0139, 0.1130, and 0.2198 mA/cm², respectively at 1.23 V vs RHE than bare BV (0.0015 mA/cm²) and BI (0.0052 mA/cm²). **Fig. 4.15(a)** displays the LSV spectra of the fabricated 15c photocatalysts in light. The results imply that among all the composites, 15c-31BVBI composition had the maximum photocurrent density.

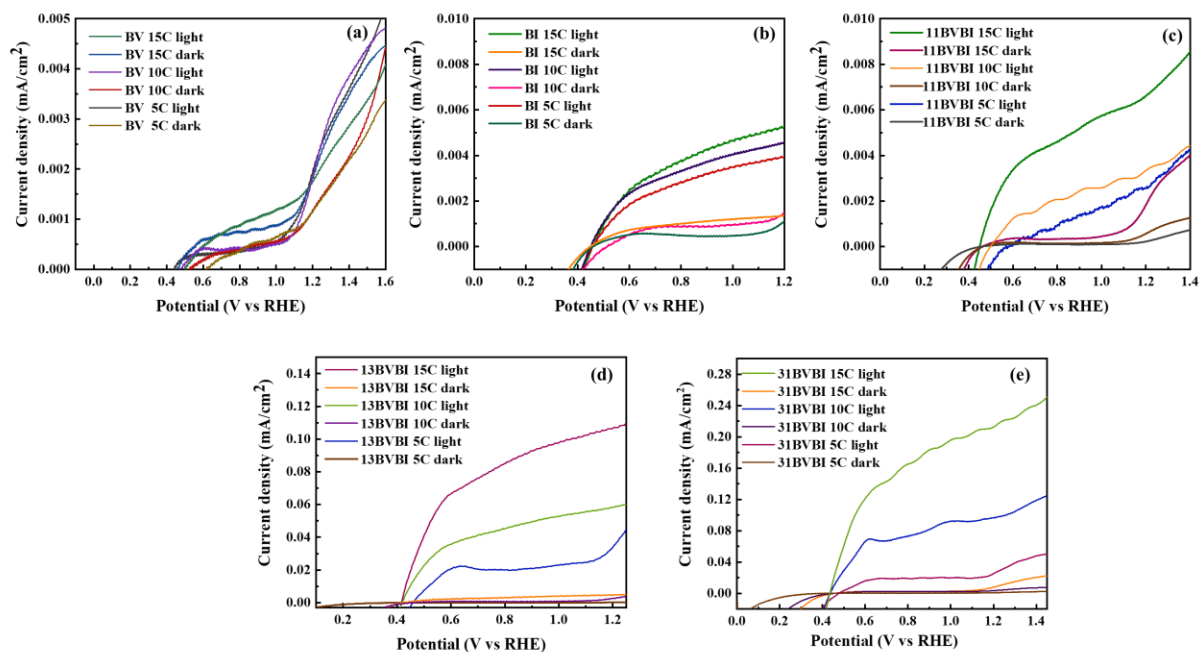


Fig. 4.13 LSV of different coating layers of (a) BV, (b) BI, (c) 11BVBI, (d) 13BVBI, and (e) 31BVBI in dark and light condition.

To scrutinize the kinetics of the interfacial photogenerated charge migration of the fabricated photocatalysts in both light and dark at the electrode/electrolyte interface, EIS was performed and results are as illustrated in **Fig. 4.14(a-e)** [40]. Nyquist plots reveal that the controlled BV and BI electrode has a significantly greater charge transfer resistance (R_{ct}) than

the 31BVBI electrode with the optimal coating as represented in **Fig. 4.15(b)**. Results are in agreement with LSV observation.

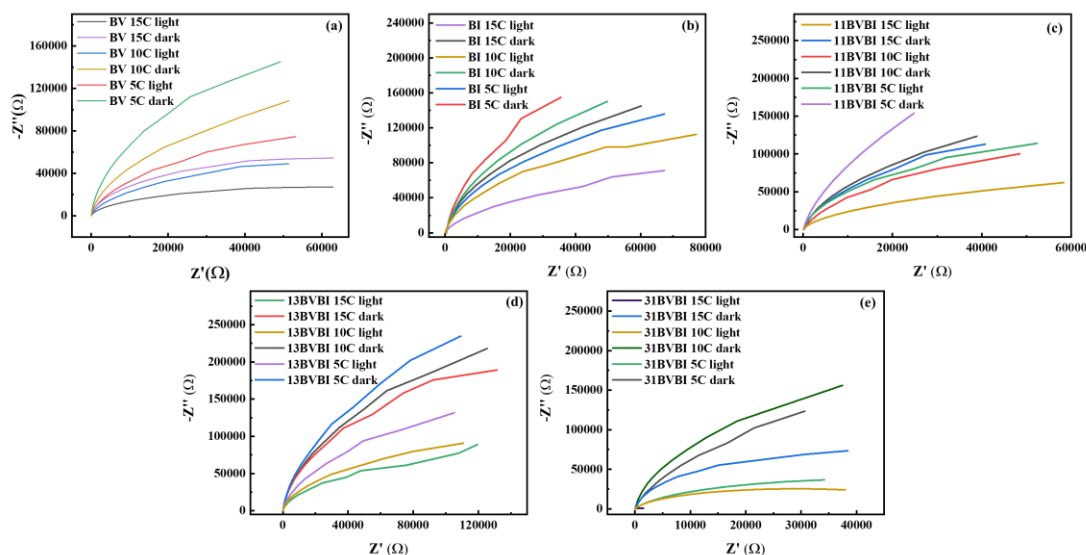


Fig. 4.14 Nyquist plot of 15 coatings of (a) BV, (b) BI, (c) 11BVBI, (d) 13BVBI, and (e) 31BVBI in dark and light condition.

For all of the prepared photoelectrodes, a decrease in R_{ct} value was detected in the light compared to the dark. The R_{ct} value of the 31BVBI electrode was found to be 83.3 k Ω , which otherwise was 388 and 294 k Ω for BV and BI, respectively under the of solar light.

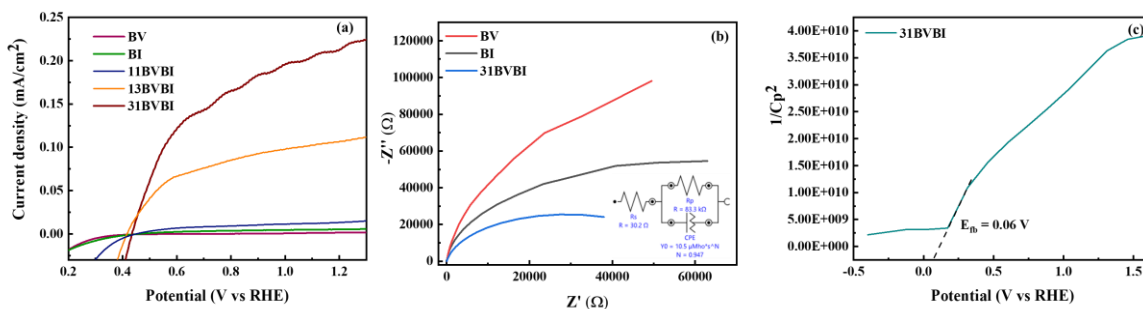


Fig. 4.15 LSV of 15c- BV, BI, 11BVBI, 13BVBI, and 31BVBI in solar light, (b) Nyquist study of BV, BI, and 31BVBI in light condition, and (c) Mott-Schottky graph of 31BVBI composite.

The flat band potential (E_{fb}) of 31BVBI electrode was further calculated using the Mott-Schottky measurements to comprehend the charge transfer mechanism. It was observed that 31BVBI had a positive slope, indicating that the photocatalyst exhibit n-type semiconductor

properties and behaves as a photoanode [41]. The x intercept of the Mott-Schottky plot can be used to estimate the flat band potential and it was validated to be 0.06 V as shown in **Fig. 4.15(c)**.

Chopped LSV experiments under 50 sec pulse time in both solar light and dark were done to investigate the photo-response behavior of the fabricated BV, BI, and 31BVBI photocatalyst at 1.23V vs RHE (**Fig. 14.16(a)**). The produced electrodes manifest an instant increase in current in the light to a steady state, followed by a return to ground on when the light was switched off [42]. Their photocurrent values were consistently steady during all light-switching processes, demonstrating that they are consistently stable when exposed to light. The 31BVBI exhibited a higher current density of 0.011 mA/cm², therefore, confirming, high charge separation and transport efficiency over BV (0.00049 mA/cm²), and BI (0.0011 mA/cm²).

Chronoamperometry measurements were carried out for 21600 sec (6 h) to assess the stability of fabricated 31BVBI electrode. As illustrated in **Fig. 4.16(b)**, after 6 h, photocurrent was seen to be almost steady, and just a slight drop was gauged indicating that the fabricated electrode was stable. The amount of hydrogen evolved was also measured theoretically from the **Eq. 2.7** provided in **Chapter 2** during 6 h stability study of the 31BVBI electrode and found to be 1.864 mmolcm⁻²sec⁻¹ at 1.23 V versus RHE.

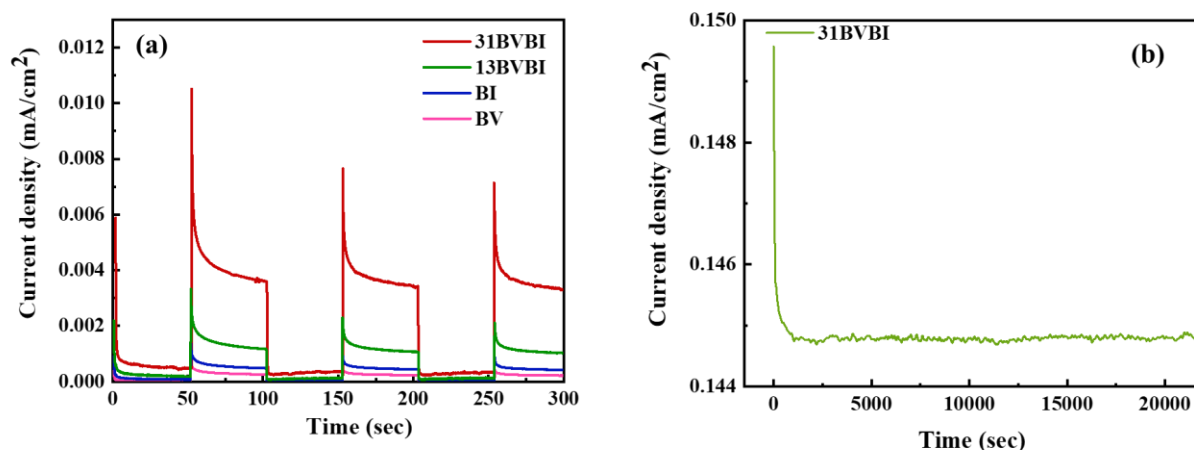


Fig. 14.16(a) Transient current density graph of the fabricated BV, BI, 13BVBI, and 31BVBI electrodes at 1.23 V vs RHE with 50 sec time intervals, and **(b)** Stability examination of 31BVBI electrode for 21600 sec.

4.5.1 Comparison with the existing literature

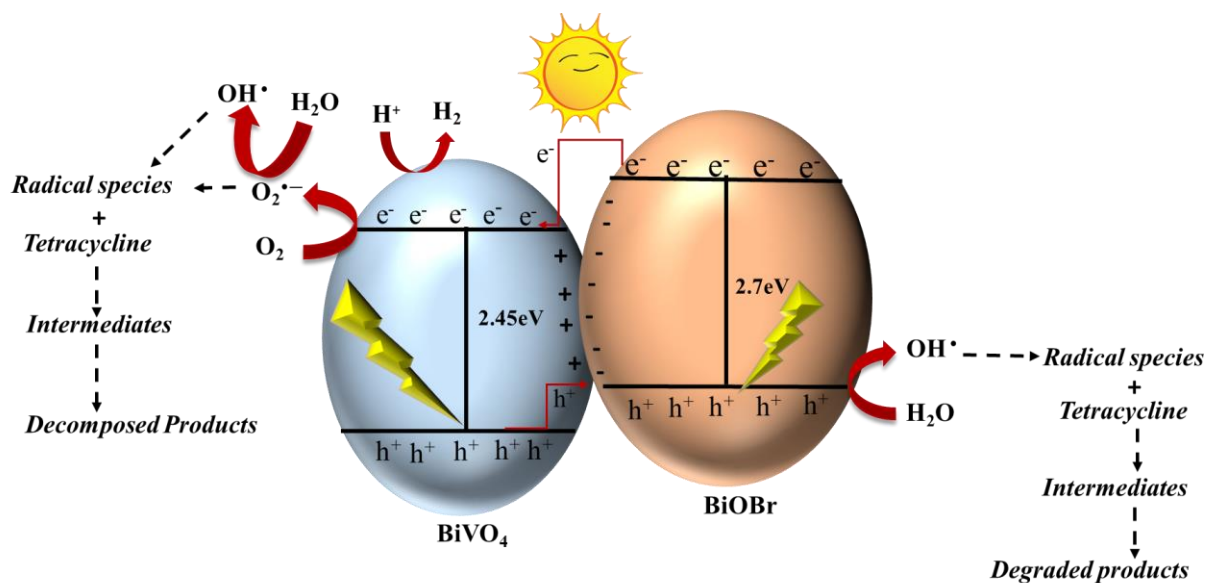
Table 4.4 summarizes PEC activity of different photocatalysts in comparison to the fabricated 31BVBI photocatalyst. Thus, from the literature it can be manifested that until now PEC water splitting to evolve hydrogen haven't been studied using BVBI nanocomposite. Also, optimum amount of hydrogen was produced and good photocurrent density was achieved.

Table 4.4 Comparison of PEC activity of 31BVBI with the reported literature.

S.No.	Photocatalysts	Electrolyte	Electrode type	Photocurrent density	Moles of H ₂ produced	References
1.	BiOBr nanosheet arrays	0.1 M Na ₂ SO ₄	Photoanode	0.0069 mA/cm ² at 0.9 V vs RHE	-	[43]
2.	Bi ₂ S ₃ /BiOBr/TiO ₂	0.5 M Na ₂ SO ₄	Photoanode	0.00911 mA/cm ² at 1.2 V vs RHE	0.0047 $\mu\text{molcm}^{-2}\text{sec}^{-1}$	[44]
3.	BiVO ₄ Nanowire	0.1 M potassium phosphate buffer	Photoanode	0.0093 $\mu\text{A}/\text{cm}^2$ at 1.2 V vs RHE	-	[45]
4.	g-C ₃ N ₄ /BiVO ₄	Lake wastewater	Photoanode	9.68 mA/cm ² at 1.0 V vs Ag/AgCl	0.0059 $\mu\text{molcm}^{-2}\text{sec}^{-1}$	[46]
5.	BiVO ₄ /BiOBr	0.5 M Na ₂ SO ₄	Photoanode	0.2198 mA/cm ² at 1.23 V vs RHE	1.864 mmolcm ⁻² sec ⁻¹	Current Work

4.6 Photo(electro)catalytic mechanism

Photogenerated charge transport mechanism for a photo(electro)catalytic performance of the fabricated photocatalyst is provided in **Schematic 4.1**. The Fermi level of BV (n-type semiconductor) is positioned slightly below its CB while, Fermi level of BI (p-type semiconductor) is just above its VB.



Scheme 4.1 Proposed photo(electro)catalytic route of BVBI photocatalyst for the reduction of pollutant, and the evolution of hydrogen by water splitting.

On the construction of heterojunction, the Fermi levels of BV and BI will gradually migrate closer one another, eventually attaining the same potential value. BV has a greater negative Fermi level than BI resulting in the movement of the Fermi level of BV to a positive and BI to negative direction until the equilibrium is obtained. The CB and VB potential of BV will change positively in response to the positive migration of its Fermi level. These bands will therefore incline upward. At the interface of BV and BI an electric field will be created directing from BV to BI. The e^- existing in the VB edge potential of BV and BI get excited to their respective CB when illuminated by solar light. Occurrence of electric field at the interface of the semiconductors will cause the e^- to migrate to the CB of BV from that of BI. Thus, the photogenerated h^+ present in the VB edge of BI forms a h^+ -rich layer, while the e^- in the CB edge of BV forms an e^- -rich layer. Heterojunction formation can significantly increase the charge separation efficiency, thereby promoting photocatalytic TC degradation and PEC hydrogen

production by effectively inhibiting the secondary recombination of the charges. For the degradation of TC, electrons present in CB of BV can interact with O_2 to form $O_2^{\cdot-}$ and later react with H_2O to produce $OH^{\cdot}$. This $OH^{\cdot}$ radical can directly oxidize and reduce the organic contaminant. Additionally, the h^+ present in the VB of BI can combine with water to produce $OH^{\cdot}$, which can further oxidize harmful pollutants into less dangerous byproducts. For the PEC water splitting, H^+ ions can be reduced to form hydrogen at the counter electrode.

4.7 Conclusions

Fabrication of efficient and reliable photocatalysts is crucial to clean the polluted water and to evolve hydrogen by the water splitting. By using the hydrothermal process, various mole ratios of $BiVO_4/BiOBr$ heterojunction photocatalysts were prepared. The characterization studies revealed that the hetero composite had a lower rate of recombination of charges, large surface area, and narrow band gap which is crucial for both photocatalysis and PEC. The photocatalytic remediation of recalcitrant antibiotic, TC, and PEC water splitting to evolve the hydrogen was conducted under solar light to evaluate the photo(electro)catalytic performance of the manufactured photocatalysts. The impact of different mole ratios on photocatalytic degradation of TC and PEC water splitting has been studied. Various studies, including photocatalyst concentration, the pH effect, kinetic studies, the influence of the light sources, scavenger studies, reusability, LSV, Mott-Schottky, EIS, Chronoamperometry, stability were studied. Amongst the synthesized photocatalysts, 31BVBI was most effective in decomposing the pharmaceutical pollutant, TC photocatalytically. The $O_2^{\cdot-}$ radicals were the primary quenching species accountable for the decomposition experiment. According to the reusability experiment, synthesized photocatalysts were easily recoverable and reusable after seven cycles. The results of the post-degradation investigations using BET, SEM, and XRD depicted that the surface area properties, morphology, and crystallinity of the nanocomposites remain unchanged. Using GC-MS, the products and intermediates formed during the decomposition of the TC were verified. High COD and TOC values for the mineralization of TC confirm that the prepared composite is effective for removing harmful antibiotic. The 31BVBI nanocomposite unveiled the highest PEC efficacy with the photocurrent density $\sim 0.2198 \text{ mA/cm}^2$ at 1.23V vs RHE. As a result, the BVBI photocatalyst provides enormous potential for the degradation of harmful contaminants and PEC water splitting.

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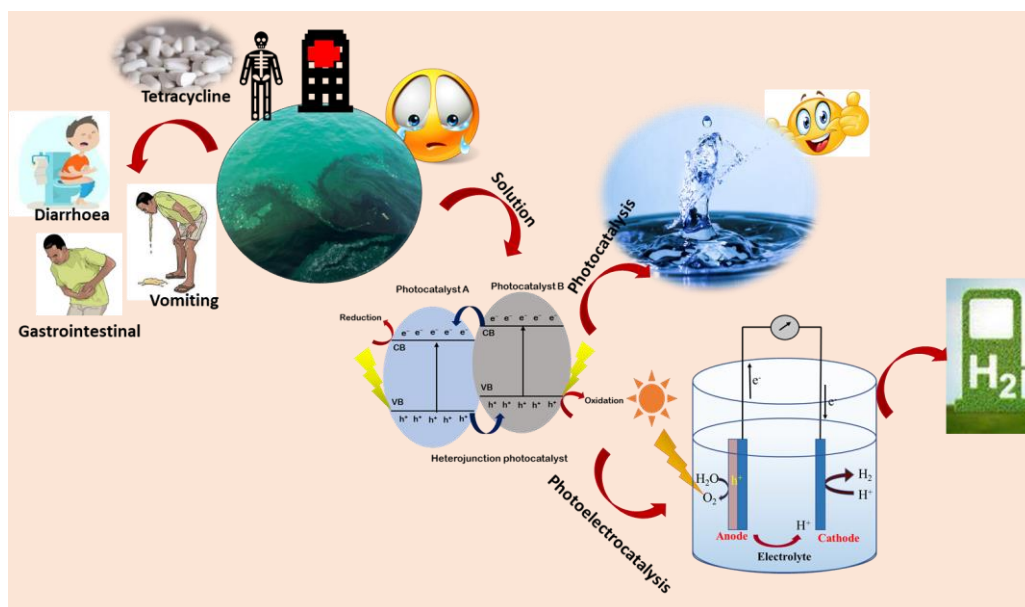
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WO₃ nanorods decorated onto BiVO₄ dendrites for tetracycline detoxification and water splitting



Highlights of the Chapter

- Fabrication of different mole ratios of sunlight-active BiVO₄/WO₃ was carried out via hydrothermal approach.
- Activity of the prepared photocatalysts as tested by carrying out photocatalytic deterioration of tetracycline and photoelectrocatalytic water splitting under solar light.
- 3:1BiVO₄/WO₃ exhibited highest degradation efficacy of 96.2 % for tetracycline removal (rate constant $\sim 0.02557 \text{ min}^{-1}$) under the irradiation of sunlight.
- GC-MS and TOC analysis was done to identify degraded products formed by the elimination of TC and mineralization, respectively.
- 3:1BiVO₄/WO₃ electrode produced $4.56 \text{ mmol cm}^{-2} \text{ sec}^{-1}$ of hydrogen via water splitting and the electrode remained stable for 6 h.

5.1 Introduction

The two most significant difficulties facing humanity in the coming decades will undoubtedly be the rising energy crises and environment pollution [1,2]. Photocatalytic reduction of the hazardous pharmaceutical pollutant, TC and PEC water splitting has been carried out to manifest the proficiency of the synthesized photocatalysts. In the **Chapter 2**, the detrimental impact of the pollutant, TC, and necessity for the evolution of hydrogen via water splitting, superiority of the photocatalysis and PEC method over the other traditional techniques has been explained in detail.

Various photocatalysts are being developed having dual functionality for carrying out the photocatalytic decomposition of the organic contaminants as well as PEC hydrogen production in a broad solar absorption spectrum. BiVO_4 as a semiconductor photocatalyst exhibit high capacity to absorb visible light, good charge promotion ability, narrow band gap (~ 2.4 eV), high photochemical stability, and an environment-friendly nature [3]. But its photocatalytic activity gets reduced owing to the higher carrier charge recombination[4]. The proficiency of BiVO_4 can be enhanced by coupling it with other visible light responsive semiconductor possessing suitable band edge potentials to form heterojunction such as $\text{BiVO}_4/\text{g-C}_3\text{N}_4/\text{GO}$, $\text{BiVO}_4/\text{g-C}_3\text{N}_4/\text{Cu}$, CuS/BiVO_4 , etc. [5]. These heterostructure are shown to degrade the organic pollutants with a degradation efficiency of 85 %, 78.4 %, and 86.7 %, respectively under visible light illumination [6–8]. Likewise, BiVO_4 heterostructure with WO_3 is shown to enhance the hydrogen production rate to $52.6 \mu\text{mol cm}^{-2} \text{h}^{-1}$ [9]. WO_3 has good semiconducting characteristics, tuning BiVO_4 with it is an excellent choice owing to non-toxic, cost-effective, and thermally stable characteristics[10]. It possesses a narrow band gap (~ 2.7 eV), has a high VB potential, and absorbs solar light substantially (≤ 480 nm) [11]. The reintegration of the photogenerated excitons in BiVO_4 gets reduced owing to the development of interfacial contact in two semiconductors with almost equal band gap energies [12]. Utilizing this basis, $\text{BiVO}_4/\text{WO}_3$ composite is designed for the photodecomposition of 2-chlorophenol and sulfasalazine drug with an efficacy of 92.1 and 91.02 % under visible light [13,14]. Similarly, $\text{WO}_3/\text{Bi}_2\text{MoO}_6$ hybrid is shown to degrade TC as well up to 85.9 % [15].

Although various photocatalytic decomposition experiments have been reported previously with the bare BiVO_4 , WO_3 , and $\text{BiVO}_4/\text{WO}_3$ hybrid. However, there is always a

chance to engineer the hybrid with respect to size, shape, and surface area, and understand the properties to design an efficient photocatalyst. In lieu of prior state of art on BiVO₄/WO₃ hybrid as a multifunctional system, we have chosen to study this w.r.t different molar ratios of precursor and their effect on the catalytic properties. The photocatalytic efficacy of synthesized photocatalysts under different light sources and the degraded products formed after the degradation have not been evaluated previously. Furthermore, the decomposed products formed after the photocatalytic deterioration of the pollutant haven't been analyzed. Also, photocatalytic detoxification of the TC and PEC water splitting utilizing BiVO₄/WO₃ composite has not been done concurrently.

Thus, motivated by above facts, the present work in this Chapter reports the synthesis of BiVO₄/WO₃ nanohybrid by optimizing the mole ratio in hydrothermal process. The efficacy of the prepared photocatalysts was examined by photocatalytic decomposition of TC under natural sunlight and the activity was compared with commercial TiO₂-P25 photocatalyst. The different parameters viz; impact of dose of the catalyst, influence of pH, effect of quenchers, reusability, were studied. Degraded products formed were also gauged by the GC-MS. COD and TOC examination was done to determine the rate of mineralization. XRD, SEM, and BET post experiments were also done to scrutinize the stability of photocatalyst. The photocatalysts efficacy was further tested out for PEC hydrogen production. Chronoamperometry, Mott-Schottky, LSV, and stability experiments were manifested to establish optimized catalyst utility in PEC hydrogen generation.

5.2 Experimental section

This section comprises of the chemicals, methodologies and the materials utilized for the preparation of the photocatalysts.

5.2.1 Materials and methodology

Hydrochloric acid (HCl) (35 %), and the nitric acid (HNO₃) 67 % were all supplied by Merck. From Loba Chemie, anhydrous sodium sulphate (Na₂SO₄), and sodium tungstate dihydrate (Na₂WO₄·2H₂O), were purchased. For the preparation of the solutions, DI water was utilized. Analytical-grade (AR) chemicals were utilized in an unadulterated form and without further refinement.

5.2.2 Synthesis

5.2.2.1 Synthesis methodology of BV

BV was synthesized as per the method provided in the **Chapter 2 (section 2.2.2.1)**.

5.2.2.2 Synthesis of BiVO₄: WO₃ (BVW) nanohybrids

Hydrothermal in-situ synthesis was carried out to fabricate the different mole ratios of BVW hybrids. About 0.01 mol of pre-synthesized BV was dispersed in the 70 mL of DI water under continuous agitation followed by an addition of 0.01 mol Na₂WO₄·2H₂O and 0.02 mol NaCl. The pH of the resultant mixture was maintained to 1.5 with HCl (4 M). Thereafter, the obtained solution was heated at 180°C for 48 h in the 100 mL Teflon-lined autoclave. The obtained compound was washed 4-5 times with DI water followed ethanol washing and was dried in an oven at 50°C. The resultant yellowish tinge powder was named as 11BVW (1:1 BVW). In the similar way, different molar ration of BVW i.e., 1:3 and 3:1BVW were synthesized by varying the precursor molar concentration.

As a control, WO₃ (pale white powder) was also synthesized without addition of BV, and was termed as WO.

5.2.3 Characterization procedures

Characterization procedures are explicated in the **Chapter 2 (section 2.2.3)**.

5.2.4 Photocatalytic reduction of TC

Detoxification of the hazardous antibiotic, TC was performed in the irradiation of natural sunlight to manifest the photocatalytic performance of the prepared photocatalysts. Photolysis, adsorption, and the photocatalysis all comprise the degradation reaction. First and foremost, 0.2 g/L of the catalyst was dispersed in 10 ppm of TC. The prepared solution was agitated in the dark condition for 30 min to accomplish the adsorption-desorption equilibrium and then under sunlight for 120 min to perform decomposition. Photocatalysis was done in March between 10:00 a.m. to 3:30 p.m. on bright sunny days with an average sunlight intensity of 600-900 W/m² (monitored by the LICOR Pyranometer). After the partition of catalyst at regular times, the absorbance spectra of the TC were examined using a UV-visible spectrophotometer with respect to $\lambda_{\text{max}} = 360$ nm. The investigations were conducted thrice, and the plots are represented with

error bars showing a 5 % inaccuracy in the data source. The photocatalytic abatement efficacy was determined using **Eq. 2.1** provided in the **Chapter 2**.

COD and TOC studies were done to scrutinize the photocatalytic activity of the 31BVW photocatalyst for TC. Initially, 200 mL TC solution containing 40 mg of BVW nanohybrid was irradiated under sunlight for 120 min. The COD was computed by titration method; however, the mineralization was assessed by TOC reduction. To calculate the % COD/TOC elimination, **Eq. 2.2, and 2.3 given** in the **Chapter 2** were utilized.

GC-MS was done to assess the decomposed products attained after the photocatalytic remediation of detrimental contaminant, TC. The protocol followed to fabricate the samples for the GC-MS study is detailed in **Chapter 2**.

5.2.5 PEC Studies

The photo-activity of the prepared electrodes were studied under one-sun irradiation using an electrochemical workstation (AUTOLAB, Metrohm) fitted with a solar simulator (LOT Quantum design) and a standard three-electrode setup. Indium Tin Oxide (ITO) spray coated with BV, WO, 11BVW, 13BVW, and 31BVW photocatalyst served as the photoanodes (working electrodes), Pt wire as the counter electrode and Ag/AgCl as reference electrodes. According to the photo-response performance, the coating of the catalyst was optimized in terms of coating layers as 5, 10, and 15. LSV, transient photocurrent, impedance, and chrono-amperometry measurements were done to investigate the photo response of the electrode using 0.5 M Na₂SO₄ solution electrolyte under 100 mW/cm² solar light intensity. In both dark and light situations, impedance spectra were measured at open circuit potential (ocp) possessing a 10 mV AC perturbation signal. The Mott-Schottky analysis were scrutinized with the potential scan operating at frequency of 100 kHz. All potentials were calculated using the Ag/ AgCl reference electrode, and were converted to the RHE reference scale using the Nernst equation.

5.3 Results and discussions

5.3.1 XPS analysis

The XPS examination was done to determine the oxidation state, an elemental composition, and the binding state of elements in the photocatalyst. The occurrence of tungsten,

bismuth, oxygen, and vanadium at the particular binding energies was observed in the survey spectra of the 31BVW nanohybrid (**Fig. 5.1(a)**). As all peaks were calibrated using the C 1s at 284.2 eV, an additional peak was noticed due to the incidence of adventitious carbon in the sensor. For the deconvolution, least square Gaussian-fit model was utilized to fit all the peaks. Bi 4f spectrum consists of dual peak at binding energy 159.1 and 164.2 eV ascribes to $4f_{7/2}$ and $4f_{5/2}$ and corresponds to +3 oxidation state of Bi [16] (**Fig. 5.1(b)**). V 2p_{3/2} and 2p_{1/2} have doublet peaks focused at binding energies of 516.7 and 524.2 eV, indicates +5 oxidation state of V as represented in **Fig. 1(c)** [16]. Peak at binding energies of 529.3 eV (**Fig. 5.1(d)**), 35.4, and 37.5 eV (**Fig. 5.1(e)**) attribute to O 1s [17] and W 4f_{7/2}, and W 4f_{5/2} [18], respectively ascribes to -2, and +6 oxidation states of O and W, respectively. Therefore, the XPS spectrum validated the successful preparation of 31BVW nanohybrid.

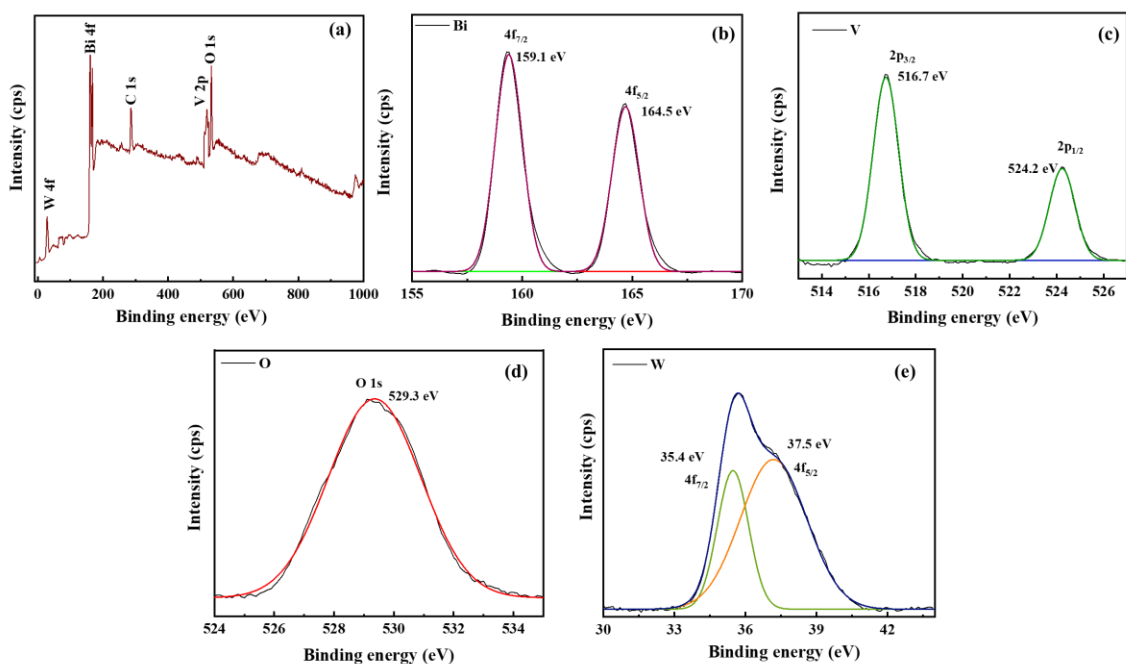


Fig. 5.1 XPS spectra of 31BVW nanohybrid, **(a)** the survey spectra, **(b)** Bi 4f, **(c)** V 2p, **(d)** O 1s, **(e)** W 4f.

5.3.2. XRD analysis

XRD studies were carried out to gauge the crystallographic structure, purity, and efficacious fabrication of the prepared photocatalysts [19]. XRD pattern of the designed photocatalysts is depicted in the **Fig. 5.2**. The crystalline nature of monoclinic BV was affirmed

by the occurrence of sharp peaks at 19.0° (011), 24.5° (102), 28.8° (112), 30.6° (004), 34.8° (200), 35.2° (020), 40.0° (211), 42.6° (015), 46.1° (123), 46.9° (204), 47.4° (024), 50.1° (220), 53.2° (301), 58.3° (303), which attribute to the JCPDS card no. 83-1699. The XRD peaks of WO present at 14.0° (100), 22.7° (002), 24.3° (110), 26.7° (102), 28.1° (200), 33.5° (112), 36.4° (202), 44.3° (212), 49.8° (220), 55.3° (222), 58.2° (400), and 63.1° (402) correspond to JCPDS file 85-2460 affirmed its successful formation. The efficacious fabrication of the different ratios of the nanohybrids was confirmed by the occurrence of both types of peaks deprived of any contamination as well as little bit peak shifting. Also, with the increment in the concentration of WO and BV, the augmentation in the peak intensity was detected. The existence of sharp peaks emphasizes the crystalline nature of the fabricated photocatalysts.

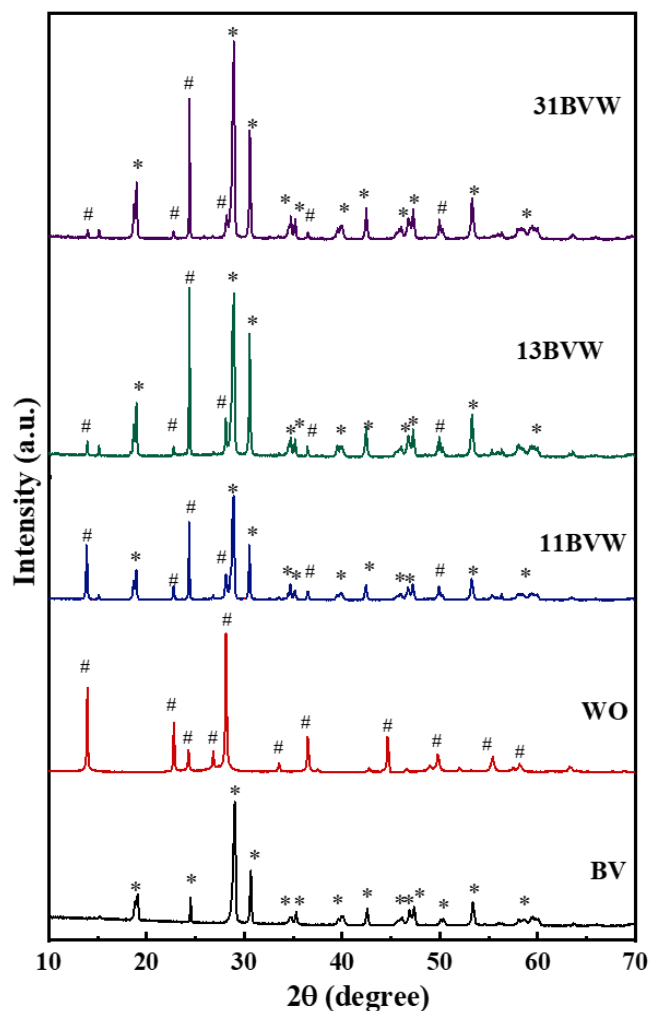


Fig. 5.2 XRD graph of fabricated photocatalysts.

5.3.3 PL analysis

An effectual photocatalyst must have a lower carrier charge recombination rate, higher migration capacity, and efficient separation. [20]. The lower PL intensity ascribes to the lower reintegration rate, higher charge separation and migration, thereby higher photo(electro)catalytic activity. The PL spectra was recorded at an excitation wavelength of 325 nm. Bare BV and WO exhibited higher reintegration rate of the charge carriers as indicated by the presence of the emission peaks of the higher intensity as depicted in **Fig. 5.3**. However, by hybridizing both semiconductors, the PL intensity got reduced significantly. This may be due to interfacial contact between both photocatalysts, thereby allowing the better migration of the charges, lowering the recombination rate as the separation efficacy got enhanced owing to longer lifetime of the excitons [21]. Amongst the coupled photocatalysts, 31BVW unveiled the lowest PL intensity, which could be advantageous for photocatalytic and PEC activities.

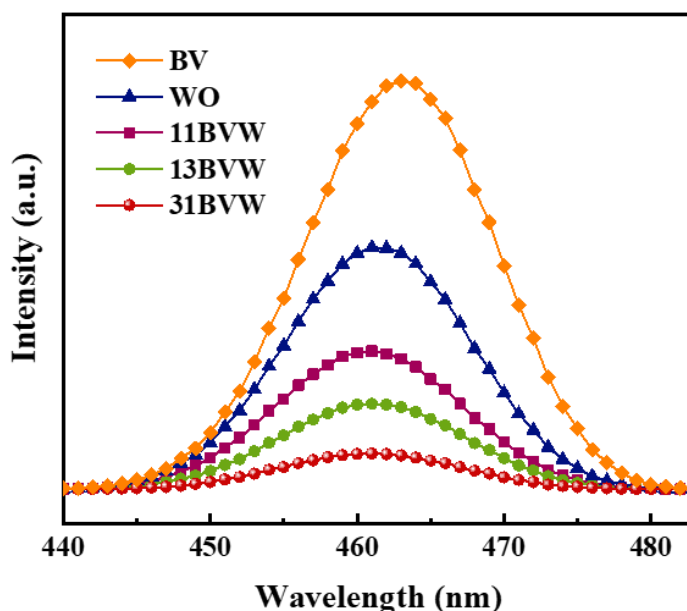


Fig. 5.3 PL spectra of synthesized BV, WO, 11BVW, 13BVW, and 31BVW photocatalysts.

5.3.4 Nitrogen adsorption/desorption study

Nitrogen sorption isotherm was utilized to assess pore size distribution as well as the specific surface area of synthesized BV, WO, 11BVW, 13BVW, and 31BVW. BJH method was

done to examine the pore size distribution [22]. **Fig. 5.4(a, and b)** suggest that the photocatalysts unveiled the features of a type IV isotherm specifying the typical mesoporous nature.

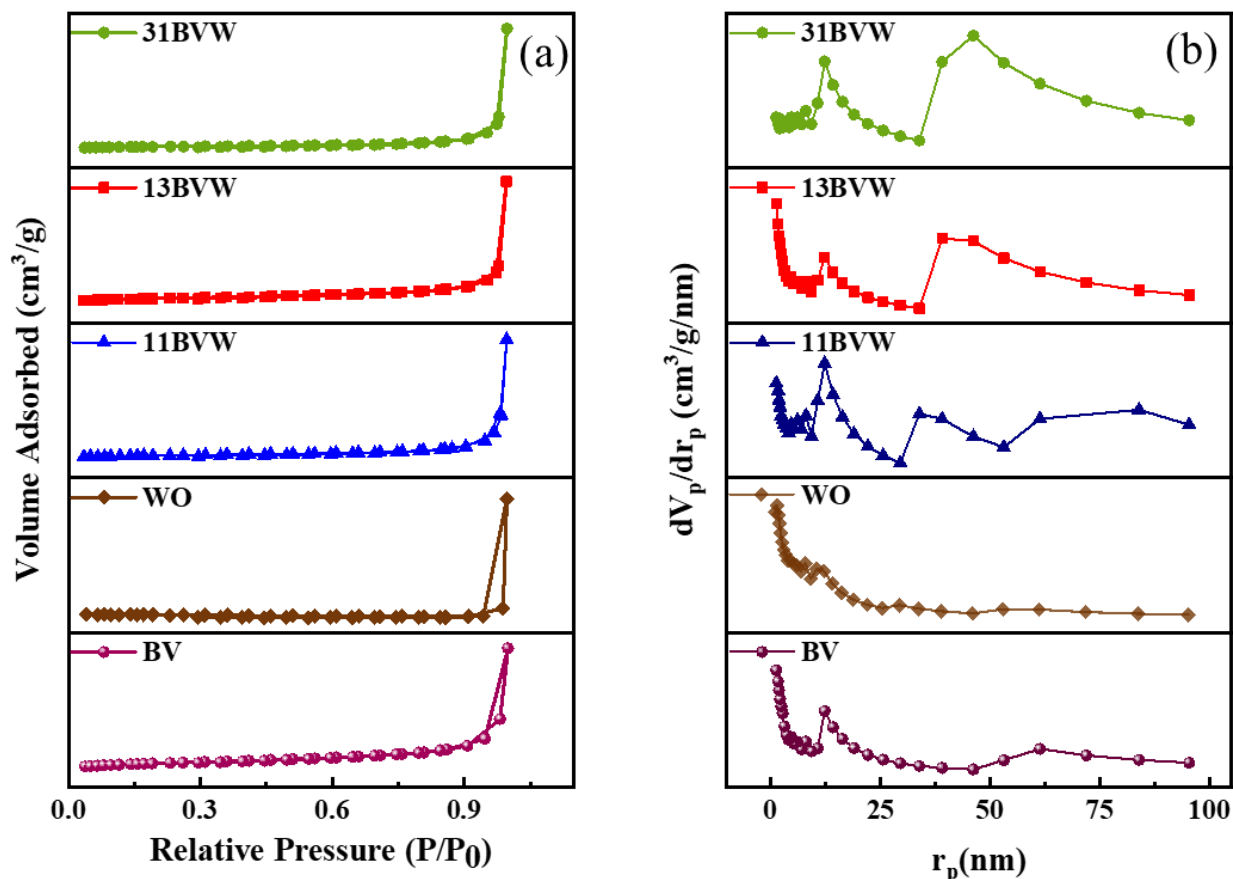


Fig. 5.4(a) BET plot of different designed catalysts, **(b)** BJH plot.

Mesopores present in all the photocatalysts supplied the pore volumes, offer the effective channels for the mass transport thereby, improving the interfacial contact between the photocatalyst surface and contaminant [23]. The mean pore diameter, specific surface area, and pore volume acquired from BET and BJH plot for the prepared photocatalysts is summarized in **Table 5.1**. It was gauged that the 31BVW hetero-composite have the largest specific surface area and it got enhanced on increasing the concentration of BV. The large surface area allows for increased synergic contact between the two semiconductors. This may increase the photoinduced charge transport and exposed surface-reactive sites to adsorb more pollutant, which could improve photo(electro)catalytic activity [24].

Table 5.1 The surface area characteristics of the designed BVW photocatalysts.

Sample	Specific surface area (m^2/g)	Mean pore volume (cm^3/g)	Pore diameter (nm)
BV	34	0.549	13.73
WO	39	0.630	15.12
11BVW	52	0.689	15.98
13BVW	57	0.721	16.83
31BVW	68	0.874	16.27

5.3.5 DRS study

The absorbance characteristics and the alignment of the band gaps of bare and coupled photocatalysts were investigated using UV–vis DRS [25].

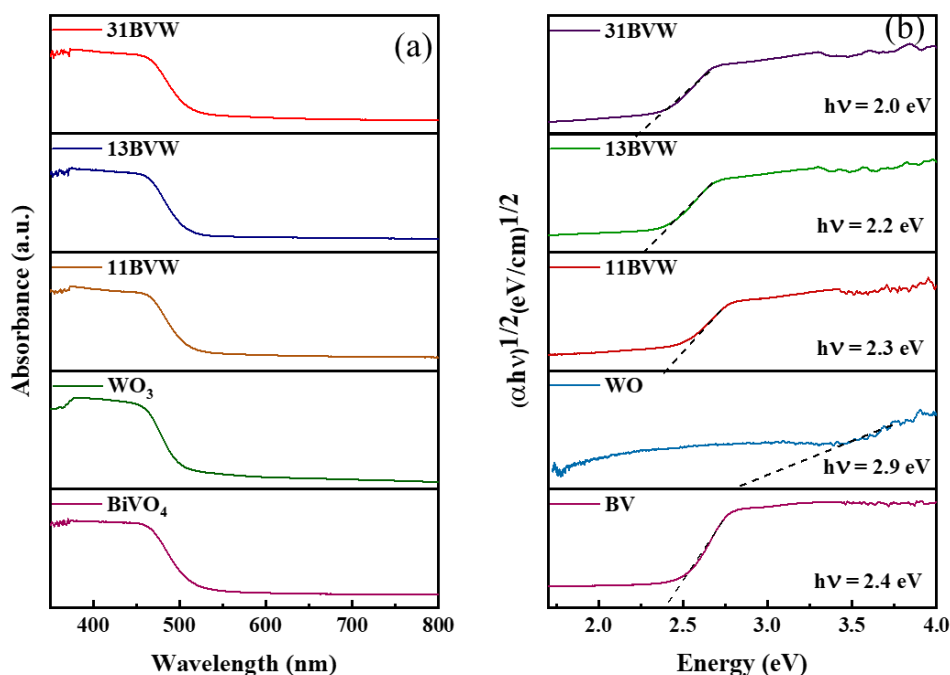


Fig. 5.5(a) The absorbance spectrum, and **(b)** the band gap energies of fabricated photocatalysts.

The absorption edge of the nanohybrids and bare photocatalysts was found in the range of 450–800 nm as depicted in **Fig. 5.5(a)**. It was inspected that compared to pure BV, and WO, the

11BVW, 13BVW, and 31BVW nanohybrids had a higher absorption potential in the visible-light range. This characteristic facilitates more effective light usage due to the generation of additional photons for carrying out photocatalytic degradation and PEC water splitting. The red shift in the absorption band of hybrids may attribute to the interfacial contact between both the semiconductors, which is beneficial for the photo(electro)catalysis. Additionally, the band gap energies of the designed photocatalysts were evaluated by the Tauc's relation as expressed in **Eq. 2.4** provided in **Chapter 2**. As represented in **Fig. 5.5(b)** band gap of the BV, WO, 11BVW, 13BVW, and 31BVW was observed to be 2.4, 2.9, 2.3, 2.2 2.0 eV, respectively. The 31BVW photocatalyst had a marginally reduced band gap value, favoring the formation of more photoexcited charge-carriers and thereby, enhancing its photo(electro)catalytic capability. Also, the narrow band gap of the 31BVW renders it the ideal solar light harvesting photocatalyst.

5.3.6 Morphological study

The surface morphology of the fabricated photocatalysts (BV, WO, and 31BVW) was scrutinized by SEM analysis at the different scales.

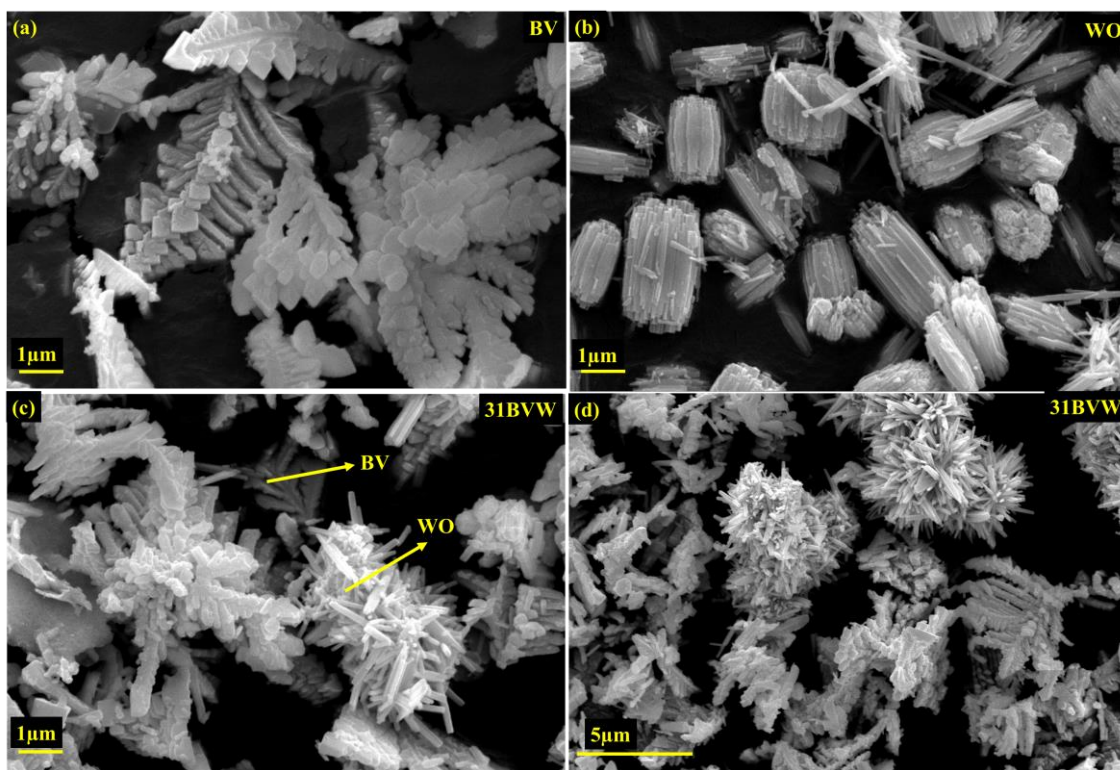


Fig. 5.6 SEM micrograph of (a) BV, (b) WO, and (c, d) 31BVW catalyst at differential magnifications.

From the **Fig. 5.6(a, and b)**, it was inspected that BV exhibited the dendrite like structure whereas, WO displays stacked and clustered nano-rods like morphology. However, 31BVW nanohybrids exhibited clustered nano-rods anchored onto the dendrite like morphology as represented in **Fig. 5.6(c, and d)**. The existence of both types of morphology supported the successful synthesis of the in-situ nanohybrids. Also, the results supported strong association of BV and WO.

5.3.7 EDS, and elemental mapping

EDS was done to study the purity, the composition, and the distribution of the elements in the as-prepared hybrids.

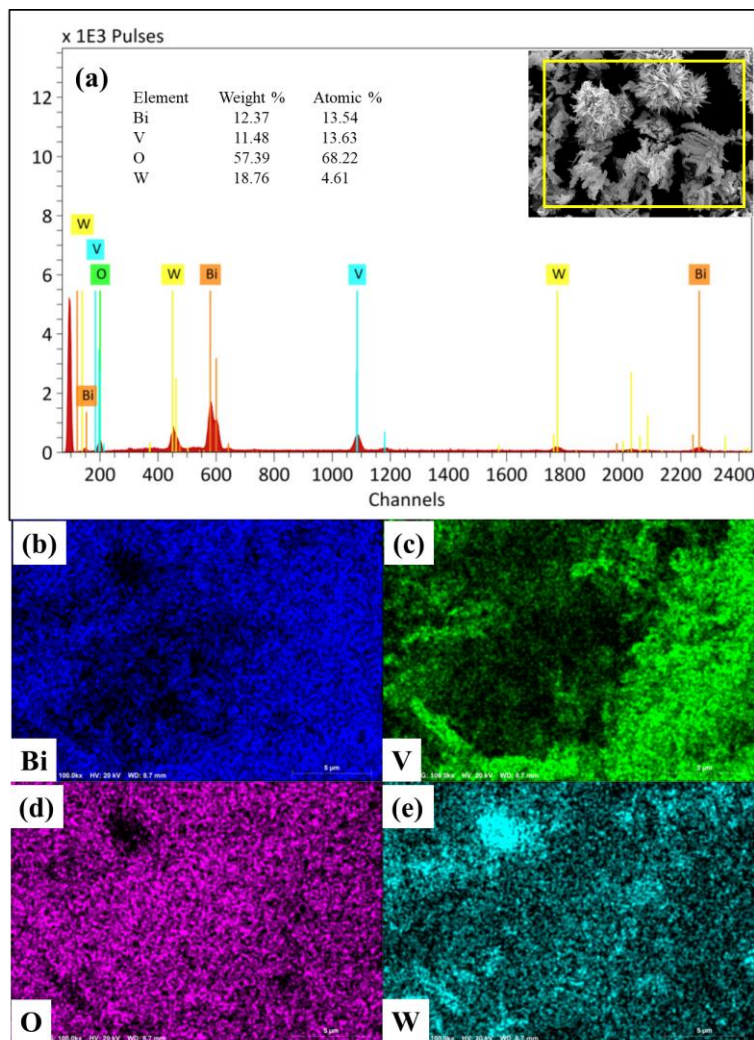


Fig. 5.7(a) The EDS spectrum with the SEM micrograph, **(b-e)** an elemental mapping of the 31BVW nanohybrid.

The EDS spectra of 31BVW exhibits a strong signal of Bi, V, O, and W as indicated in **Fig. 5.7(a)** illustrating the excellent purity of the samples and the precision of the synthesis protocol followed to prepare the samples [26]. According to **Fig. 5.7(b-e)**, the elements (Bi, V, W, O) were homogeneously scattered demonstrating the uniform dispersion of BV as well as WO. These outcomes show an excellent dispersal of WO onto BV, which is advantageous for a heterojunction photocatalyst.

5.3.8 Kinetic analysis

Remediation of the detrimental pollutant, TC was monitored under the sunlight to analyze the photocatalytic performance of the designed photocatalysts. Since TC is a stable molecule, so it degrades at a low rate (11.1 %) when exposed under the sunlight for 120 min without the photocatalyst. The highest photocatalytic abatement of 96.2 % was achieved by the 0.2 g/L of 31BVW photocatalyst. Additionally, the fabricated photocatalysts displayed the higher photocatalytic activity compared to commercial TiO₂-P25 under same conditions. The elimination efficiency of only 50.9 % was achieved with commercial TiO₂-P25 photocatalyst. The wider band gap of TiO₂-P25, which renders it receptive to UV light only, may be the cause of the reduced performance. **Fig. 5.8(a, b)** represents the kinetic studies of the different photocatalysts. After the kinetic analysis, the rate constants were assessed by the **Eq. 2.5** provided in the **Chapter 2**.

The reaction obeys pseudo-first order kinetics. Among the fabricated hybrids, 31BVW unveiled the maximum rate constant of 0.02557 min⁻¹. However, pure BV and WO had rate constants of 0.00597 min⁻¹ and 0.00672 min⁻¹. Rate constant of commercial TiO₂-P25 was examined as well and found to be the lowest (0.00552 min⁻¹) of all the photocatalysts demonstrating the superiority of the prepared photocatalysts. The synergy attained from hybridization of BV and WO can be calculated by the R factor given in the **Eq. 5.1**.

$$(R) = \frac{k_{BV}/k_{WO}}{k_{BV} + k_{WO}} \quad (5.1)$$

Where, k_{BiVO_4}/k_{WO_3} , k_{BiVO_4} , and k_{WO_3} is the rate constant of coupled BV and WO, controlled BV, and WO, respectively. **Table 5.2** symbolizes the decomposition efficacy, rate constant of the

synthesized photocatalysts as well the R factor. Since, 31BVW had the highest R value approving that it had the maximum efficiency among the synthesized photocatalysts owing to the interfacial contact among BV and WO.

Table 5.2 Rate constant, R factor, and the reduction efficiency of TC by as-synthesized photocatalysts.

Catalyst	Rate constant (min^{-1})	Degradation efficacy (%)	R factor
TiO ₂ -P25	0.00552	50.9	-
BV	0.00597	57.9	-
WO	0.00672	62.8	-
11BVW	0.00831	71.1	0.65
13BVW	0.00974	76.5	0.76
31BVW	0.02557	96.2	2.01
No catalyst	0.00152	11.1	-

5.3.8.1 Impact of the catalyst's concentration

A catalyst levels ranging from 0.10 to 0.3 g/L were investigated to understand the impact of concentration of catalyst on the degradation of TC. It was perceived that with augmentation in photocatalyst concentration from 0.1 to 0.2 g/L, the rate of deterioration of TC got increased from 75.4 to 96.2 %. This may be attributable to the increase in number of reactive sites on the surface of the photocatalyst. As a result, the generation of the amount of hydroxyl ($\cdot\text{OH}$), superoxide radicals ($\text{O}_2^{\cdot-}$) on the surface of the photocatalyst got enhanced, therefore the degradation rate got enhanced [27]. However, on increasing the catalyst amount from 0.2 g/L, the reduction efficacy got decreased marginally. The solution becomes turbid on increasing the catalyst amount which may disperse the light and lessen its influence on the solution. Thus, the light prevents from penetrating and the generation of photogenerated excitons gets minimized. Hence, formation of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals gets lowered, thereby, lowering the degradation

efficiency of the pollutant [28]. So, based on reduction efficacy, a concentration of 0.2 g/L was selected as the optimum for subsequent studies as shown in **Fig. 5.8(c)**. Thus, a slight amount of photocatalyst is enough to carry out photocatalytic degradation of noxious pollutant.

5.3.8.2 Impact of different light sources

To make a comparison, an analogous experiment was carried out under ideal circumstances using UV light and visible light sources. According to **Fig. 5.8(d)**, TC deteriorated to only 66.4, and 89.2 % in UV and visible light, respectively with 31BVW photocatalyst. Nevertheless, the highest decomposition rate of 96.2 % was scrutinized when the solution was exposed to natural sunlight. So, sunlight is sufficient for the synthetic photocatalysts to decompose the pollutants.

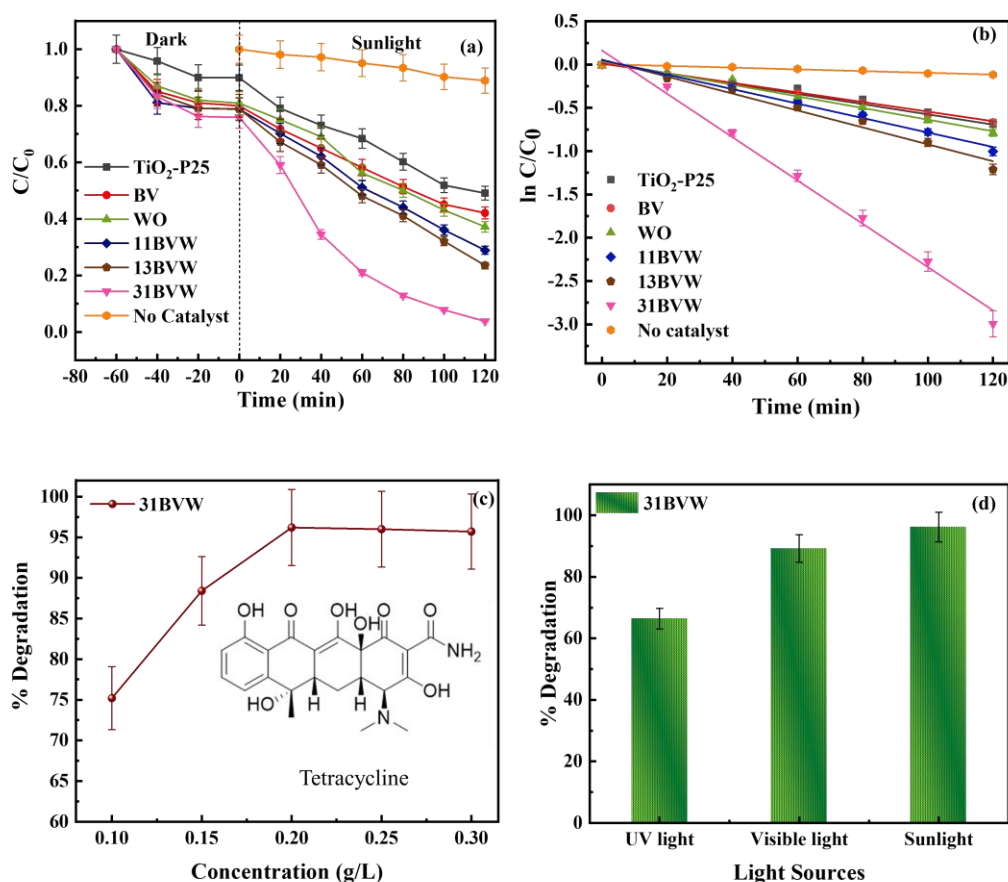


Fig. 5.8(a, b) Kinetic analysis of the different fabricated catalysts for the remediation of TC with standard deviation 26.41, **(c)** concentration's effect on the elimination of the pollutant, **(d)** impact of different light sources on the decomposition efficacy of TC.

5.3.8.3 Effect of pH

The decomposition of the targeted pollutant, TC using BVW photocatalyst is also influenced by pH. The characteristics of the charges present on the surface of a photocatalyst, ability of adsorption, and columbic forces occurring between the photocatalyst and the pollutant are influenced with the variation in pH. Therefore, to study the influence of pH on the elimination efficacy of the catalyst, experiments were conducted under optimum conditions with the pH ranging from 2 to 12. The pzc of the 31BVW photocatalyst was calculated to be 5.0, as depicted in **Fig. 5.9(a)** [29]. Negatively charged surface of the photocatalyst exists when pH is greater than pzc while positively charged surface exists when the pH value is smaller than pzc. Owing to the protonation of the dimethyl ammonium, TCH_2 and TCH_3^+ are the major TC species at $\text{pH} < 3.3$. Therefore, the decomposition efficiency of the TC decreases due to repulsion of positively charged surface (presence of M-OH_2^+ species) of photocatalyst with the cationic pollutant. TCH^- and TC^{2-} are the dominating TC species at $\text{pH} > 7.7$ due to deprotonation of ketonic or tricarbonyl group of phenol [30]. So, existence of M-O^- on the surface of nanohybrid causes the repulsion of anionic pollutant, thereby reducing the decomposition efficacy [31]. However, zwitterionic form of TC interacts with anionic form of photocatalyst at pH 7 due to electrostatic interactions resulting in the highest decomposition of the pollutant. Therefore, the effectiveness of degradation increases as the pH rises, reaching maximum at pH 7, and then gradually lowers with further increase in pH (**Fig. 5.9(b)**).

5.3.8.4 Quenching experiment

Reactive oxygen species (ROS) trigger the series of reactions involved in the photocatalytic deterioration of TC. Many species existing in the solution mainly water, dissolved oxygen, and hydroxyl ions capture photogenerated excitons to drive the formation of ROS, for e.g., holes (h^+), $\text{O}_2^{\cdot-}$, and $\cdot\text{OH}$ [32]. The photogenerated excitons and ROS get quenched by the different reagents used as scavengers. Therefore, in-situ quenching experiments with the different scavengers viz., methanol (h^+), BQ ($\text{O}_2^{\cdot-}$), and DMSO ($\cdot\text{OH}$) having concentration of 1 mM were carried out. The photocatalytic decomposition of TC typically got retarded from 96.2 % to 40.2 % in the presence of DMSO demonstrating that $\cdot\text{OH}$ were majorly responsible species for the elimination of refractory pollutant. Inclusion of $\text{O}_2^{\cdot-}$ in the solution of TC also affected the photocatalytic activity but to the lesser amount as the decomposition got retarded to 62.2 %.

Therefore, the occurrence of little amount of DMSO in the solution of TC containing 0.2 g/L of the catalyst causes the acceleration of photocatalytic abatement of the pollutant as shown in the Fig. 5.9(c).

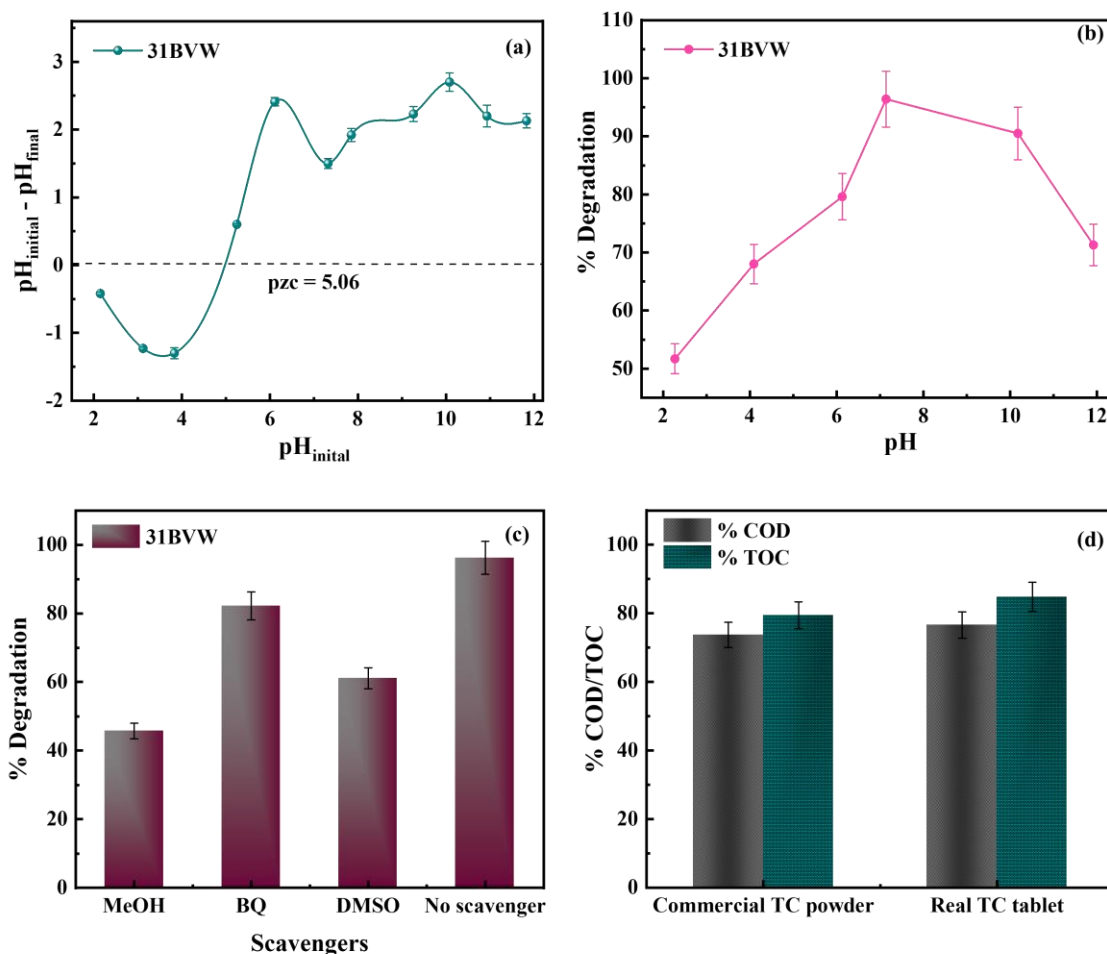


Fig. 5.9(a) pzc on the surface of 31BVW photocatalyst, **(b)** the influence of pH on the decomposition, **(c)** impact of different quenching species on the photocatalytic abatement of pollutant, and **(d)** % COD/TOC investigation of commercial pollutant, TC and real TC pill.

5.3.8.5 Mineralization studies

The degree of mineralization of an organic pollutant, TC was manifested by COD and TOC measurements. Higher initial TOC and COD levels indicated the presence of extensive amount of organic matter in the pollutant [33]. About 76.7 and 84.4 % reduction in COD and TOC was observed during the mineralization studies using 31BVW nanohybrid under illumination of sunlight for 120 min (**Fig. 5.9(d)**). % mineralization was lower than %

decomposition due to the formation of non-toxic HCOO^- , CH_3COO^- , and organic mineral salts before complete reduction of TC into CO_2 and other simple products [34]. Real pharmaceutical waste water cannot be used in studies due to ethical approval concerns. Therefore, the COD/TOC analysis of a real TC pill (TC pills I.P. Restecline 250 with a 250 mg concentration, manufacturer Abbott, India) was performed to test the mineralization efficacy of the 31BVW photocatalyst and it was assessed to be 73.6 % and 79.8 %, respectively. Therefore, it may be perceived that the fabricated 31BVW photocatalyst exhibits higher mineralization efficacy compared to the currently used expensive and laborious physicochemical methods used in industries.

5.3.8.6 Reusability study

For a selection of inexpensive and viable catalyst, recovery and reusability are critical parameters. The reusability of the optimum nanohybrid (31BVW) was studied for 7 cycles for the photocatalytic deterioration of TC. After the photocatalytic abatement reaction, the photocatalyst was carefully rinsed with DI water and then dried in oven at 50°C . The activity of 31BVW photocatalyst got retarded from 96.2 % to 73.9 % after 7 successive rounds as indicated in **Fig. 5.10(a)**). 31BVW is the potent photocatalyst due to its easy separable nature as the pollutant is merely physically adsorbed on the surface of catalyst. The following factors may have contributed to the small drop in photocatalysis activity: The loss of catalyst may occur during recovery step (washing as well as drying), resulted in a lower dosage in the next cycle, thereby, lowering the catalytic activity of surface and reducing the activity. Also, after each cycle, the adsorptive surface activity of the catalyst steadily diminished owing to the blockage of active sites of photocatalyst by TC [35]. The surface area analysis, surface morphology, and XRD after the photocatalytic decomposition (7 cycles) were analyzed to gauge the stability of the 31BVW nanohybrid. After the reaction, the XRD peaks in the reused catalyst were essentially unchanged as represented in **Fig. 5.10(b)**. Position and the intensity of the peaks were intact. The surface area isotherms confirmed that the hierarchical character of the material was preserved post the reaction, and the specific surface area got reduced from 68 to $56 \text{ m}^2/\text{g}$ (**Fig. 5.10(c, d)**). The decreased surface area was enough to carry out the photocatalytic reactions efficiently. As presented in **Fig. 5.10(e)**, the morphology of the nanohybrid remained unchanged

after the photocatalytic reaction. The outcomes suggested the reusability efficacy of the 31BVW and hence, proved that it is potential photocatalyst for industrial scale applications.

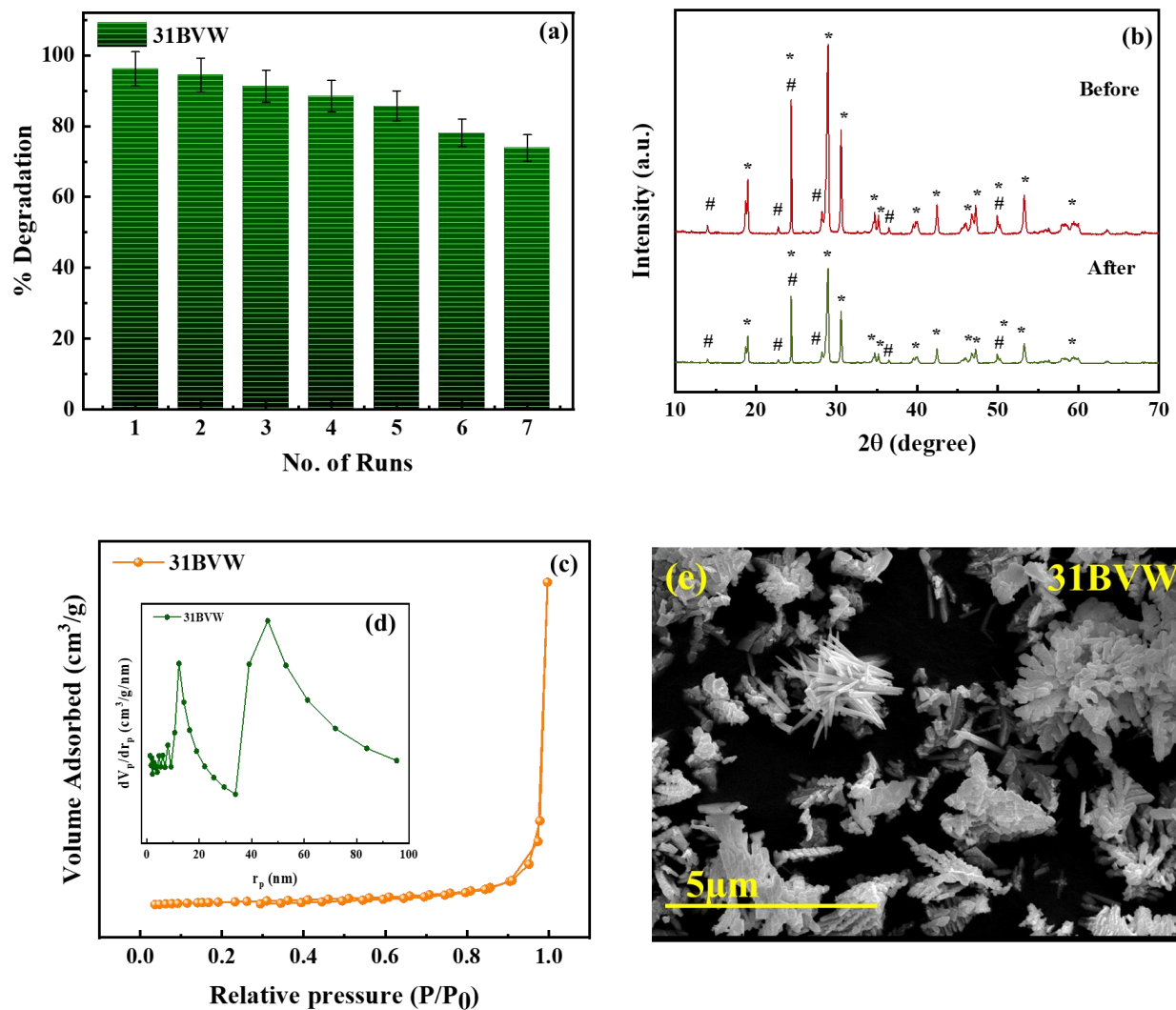


Fig. 5.10(a) Reusability analysis, **(b)** post- degradation XRD plot of 31BVW photocatalyst, **(c, d)** BET sorption isotherm along with the inset having BJH plot after the experiments, **(e)** SEM micrograph of 31BVW photocatalyst after the degradation studies.

5.3.9 Comparison with the literature

Table 5.3 summarizes a review of the literature on several photocatalysts for the photodegradation of TC. From the table it can be manifested that the refractory contaminants can be eliminated in the sunlight even if only a small amount of the catalyst is present and in the optimum reaction conditions in comparison to the literature.

Table 5.3 Comparative study of the diverse catalysts used for the elimination of the TC.

Photocatalyst	Contaminant's concentration (ppm)	Time of the reaction (min)	Source of light	Rate constant k	Decomposition efficiency (%)	Ref.
BiVO ₄ /g-C ₃ N ₄	TC (10 ppm)	120	Visible	0.01174 min ⁻¹	89	[36]
CuBi ₂ O ₄ /MoS ₂	TC (10 ppm)	120	Visible	0.0095 min ⁻¹	76	[37]
Ag ₃ PO ₄ /g-C ₃ N ₄ /ZnO	TC (30 ppm)	180	Visible	-	88.48	[38]
WO ₃ /Bi ₂ MoO ₆	TC	180	Visible	0.00899 min ⁻¹	85.9	[15]
LaFeO ₂ /SnS ₂	TC (10 ppm)	120	Visible	0.0028 min ⁻¹	28.8	[39]
BVW	TC (10 ppm)	120	Sunlight	0.0241 min ⁻¹	96.2	Current work

5.4 GC-MS analysis

Products and the intermediates produced during the remediation of TC by 31BVW photocatalyst were measured using GC-MS analysis. The GC chromatogram and mass spectrum, respectively, are elucidated in **Fig. 5.11(a, and b)**. The photocatalytic decomposition process follows three different paths as shown in **Fig. 5.12**. In the first route, 4-(dimethylamino)-2,6,10,11a,12a-pentahydroxy-6-methyl-1,3,11,12-tetraoxo-1,2,3,4,4a,5,5a,6,11,11a,12,12a-dodecahydrotetracene-2-carboxamide was formed by the hydroxylation of 4-(dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide. Attack of hydroxyl radical at the methyl of amino group of the former leads to the formation of 2,6,10,11a,12a-pentahydroxy-6-methyl-4-(N-methylformamido)-1,3,11,12-tetraoxo-1,2,3,4,4a,5,5a,6,11,11a,12,12a-dodecahydrotetracene-2-carboxamide. Ring cleavage and addition of hydroxyl radical leads to the formation of 2-methylbenzoic acid and oxalic acid

[40]. Lastly, the ring opening of aromatic group occurred and CO₂, NH₃, and other simple compounds were formed as a result.

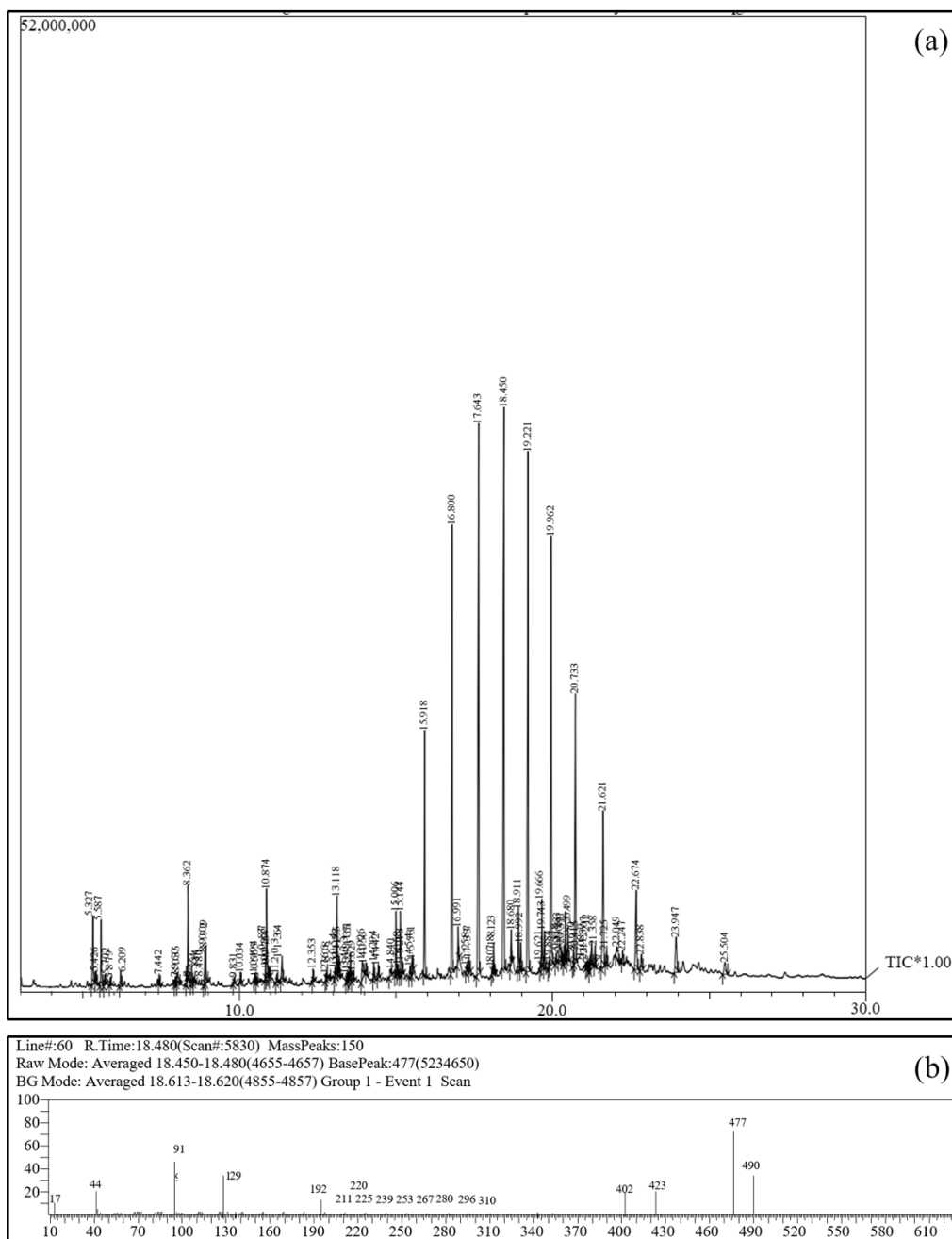


Fig. 5.11(a) Gas chromatogram, **(b)** the mass spectra of the degraded products formed after the photocatalytic degradation of TC by 31BVW photocatalyst.

Second route involves the formation of 4-amino-3,6,10,11a,12a-pentahydroxy-6-methyl-1,11,12-trioxo-1,2,3,4,4a,5,5a,6,11,11a,12,12a-dodecahydrotetracene-2-carboxamide by the

addition of hydroxyl group and abstraction of N-methyl group from 4-(dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide. Further, dihydroxylation lead to the formation of 4-amino-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,2,3,4,4a,5,5a,6,11,11a,12,12a-dodecahydrotetracene-2-carboxamide. Ring opening and reduction of some functional moiety leads to the production of 5-aminocyclohex-3-ene-1,2-diol. CO₂, NH₃, and other simple compounds were ultimately formed via ring cleavage [41].

In the third pathway, loss of methyl group and addition of hydroxyl radical generated 4-amino-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide. Hydroxylation lead to the formation of 4-amino-6,10,12,12a-tetrahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide [42].

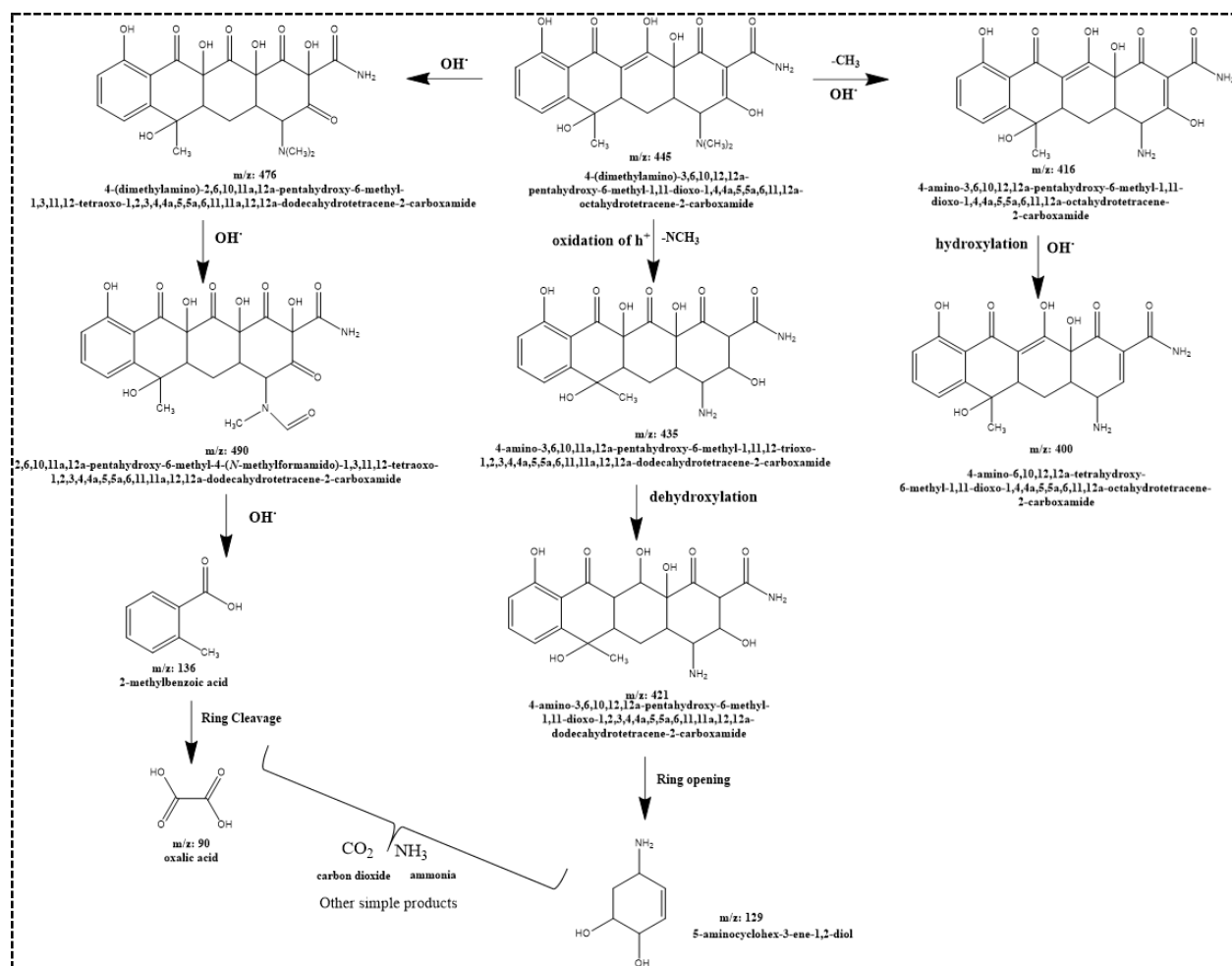


Fig. 5.12. Proposed photocatalytic abatement route of TC by 31BVW nanohybrid.

5.5 PEC studies

LSV experiments with 5, 10, and 15 layers coating (5c, 10c, 15c) were done to emphasize the PEC H_2 evolution efficacy of the synthesized nanohybrids (BV, WO, 11BVW, 13BVW, and 31BVW) as depicted in **Fig. 5.13(a-e)**. The 15c was chosen as the optimal among the other prepared electrodes because of lower onset potential and the higher current density of 0.64 mA/cm^2 at 1.23 V vs RHE. As compared to controlled BV (0.001 mA/cm^2) and WO (0.015 mA/cm^2), the 15c-11BVW, 13BVW, and 31BVW exhibited the high current densities of 0.10, 0.12, and 0.64 mA/cm^2 , respectively as presented in **Fig. 5.15(a)**. The results indicate that of all the hybrids, the 31BVW with 15c composition had the maximum photo-response.

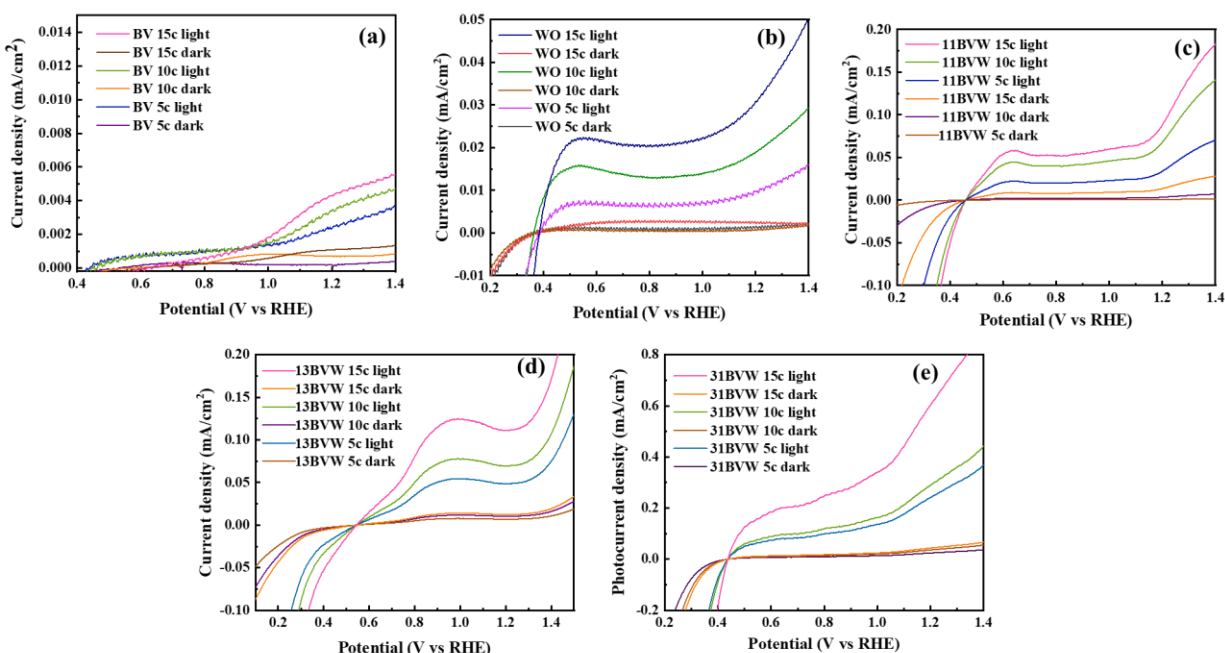


Fig. 5.13 LSV of different coating layers of (a) BV, (b) WO, (c) 11BVW, (d) 13BVW, and (e) 31BVW in dark and light condition.

Impedance measurements were to inspect the photogenerated charge transfer resistance (R_{ct}) at the semiconductor/electrolyte interface, that can be determined from the diameter of semicircle in Nyquist plots [43]. A narrower radius indicates a lower R_{ct} value and as a result a faster charge transfer rate. EIS spectrum of 5, 10, and 15 coating layers of all the fabricated electrodes in both light and dark is presented in **Fig. 5.14(a-e)**. In accordance with the LSV data, 15c was found to exhibit lowest charge transfer resistance. Nyquist plots of the EIS spectra of optimal coating of BV, WO, and 31BVW photocatalyst is presented in **Fig. 5.15(b)**. The

fabricated photo-electrodes showed a decrease in R_{ct} value when exposed to light compared to dark circumstances. Under the illumination of light, the R_{ct} of BV, WO, and 31BVW electrodes with the optimum coating were determined to be 195, 181, and 43.3 k Ω , respectively.

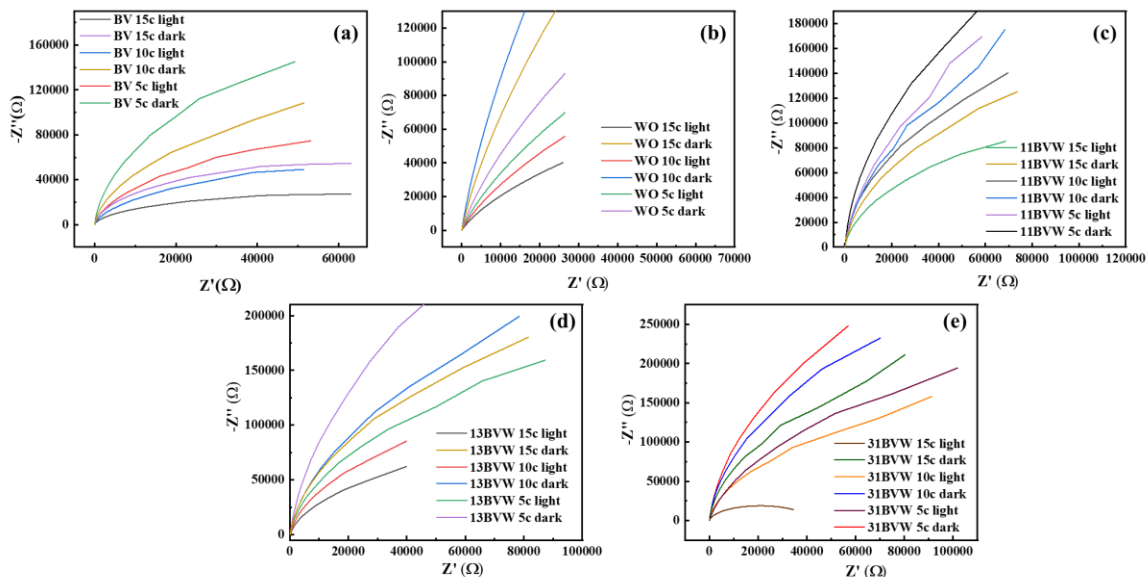


Fig. 5.14 Nyquist plot of 15 coatings of (a) BV, (b) WO, (c) 11BVW, (d) 13BVW, and (e) 31BVW in dark and light condition.

Therefore, BV and WO electrode has a significantly greater impedance than the 31BVW electrode with optimal coating under sunlight. As a result, the 31BVW electrode had a greater electrical conductivity proving that it exhibits greater PEC activity. Under solar light illumination, the 31BVW had the lowest R_{ct} value, indicating that the photogenerated electrons migrates more under light illumination than other photocatalysts.

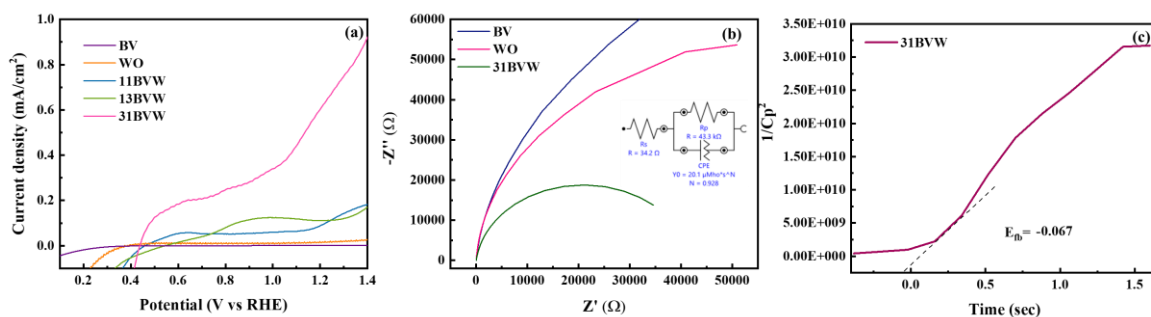


Fig. 5.15(a) LSV plot of 15c- BV, WO, 11BVW, 13BVW, and 31BVW under solar light, (b) Nyquist graph of BV, WO, and 31BVW photocatalysts in solar light, and (c) Mott-Schottky graph of 31BVW nanohybrid.

The Mott-Schottky examination was performed to assess the charge transport properties and flat band potential of fabricated 31BVW electrode. The flat band potential of 31BVW electrode was manifested to be -0.067 V (**Fig. 5.15(c)**). The positive slope of the measurements indicated that the n type behavior of BVW electrode [44]. The negative flat band potential values indicate that charge carriers are easily segregated on the surface of a semiconductor when exposed to solar radiation. It also implies that the PEC reaction for the conversion of H^+ to hydrogen can be driven by a reduced external bias.

To examine the photo-response of the 31BVW and pristine BV and WO photocatalyst at 1.23V against RHE, chopped LSV experiments were carried out in both light and dark under pulse size of 50 sec. The electrodes showed instantaneous increment in current to a steady-state in the light, and a return back to ground level once the solar light was turned off as shown in **Fig. 5.16(a)**. The photocurrent values remained constant during all light-switching procedures, proving that they are dependably stable in the presence of light [45]. Over BV ($0.01\text{mA}/\text{cm}^2$), and WO ($0.029\text{ mA}/\text{cm}^2$), 31BVW attained the maximum current density of $0.10\text{ mA}/\text{cm}^2$. Thus, it can be analyzed that owing to the formation of the heterojunction, the recombining capacity of the photogenerated excitons got reduced in 31BVW nanohybrid.

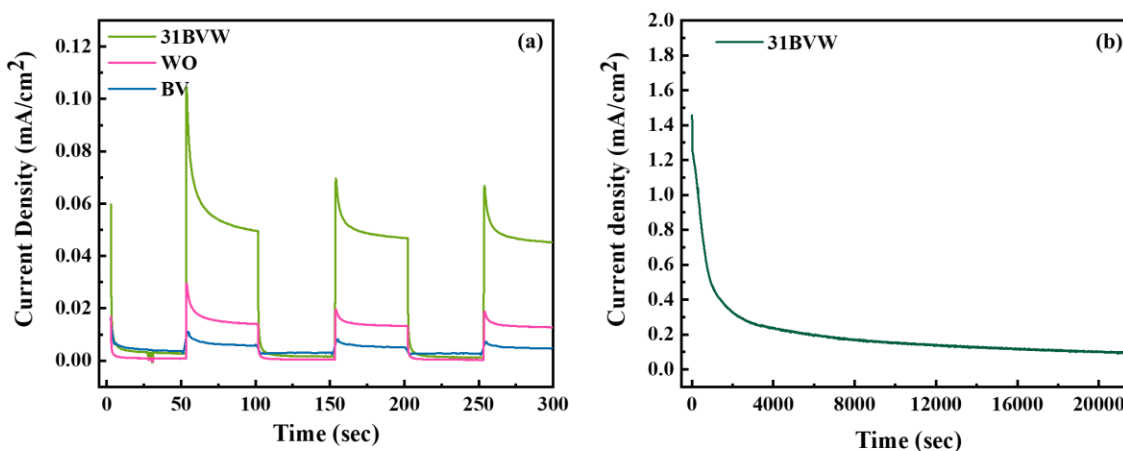


Fig. 5.16(a) Transient current density of BV, WO, and 31BVW electrode at 1.23 V vs RHE with 50 sec intervals, and **(b)** Stability analysis of 31BVW electrode for 21600 sec.

For PEC, the stability of the photoelectrode is also the important index. As a result, a 6 h stability analysis of the 31BVW electrode was conducted. After 6 h, the photocurrent was essentially steady with only a minor decrease (**Fig. 5.16(b)**). The amount of evolution of hydrogen was used to determine the PEC activity of the constructed electrodes. Therefore,

quantity of hydrogen evolved was calculated theoretically from the **Eq. 2.7** provided in **Chapter 2**. The 31BVW photoanode produced $4.56 \text{ mmolcm}^{-2}\text{sec}^{-1}$ of hydrogen at 1.23 V vs RHE.

5.5.1 Comparison with the current literature

Table 5.4 tabulates PEC performance of various reported photocatalysts in comparison to 31BVW nanohybrid. Thus, it can be analyzed that higher hydrogen production rate was achieved with the fabricated BVW photocatalyst.

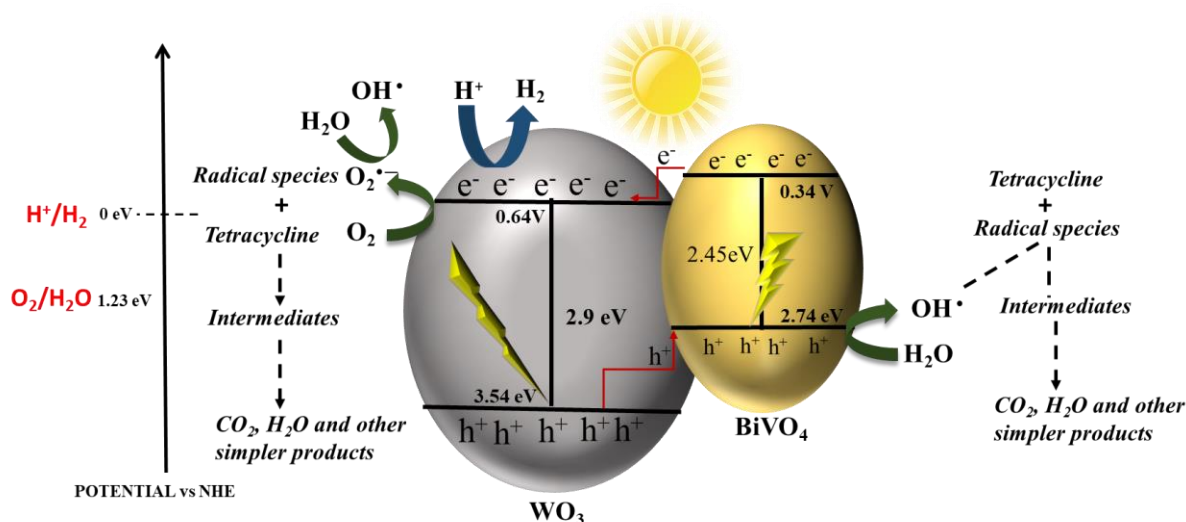
Table 5.4 PEC performance of various reported photocatalysts in comparison to 31BVW nanohybrid.

Photocatalyst	Electrolyte	H ₂ production rate	Potential	Electrode	Source	Ref.
Bi/BiVO ₄	Na ₂ SO ₄	10.6 $\mu\text{molcm}^{-2}\text{h}^{-1}$	2.0 V vs RHE	Photoanode	Visible light	[46]
WO ₃ /Sb ₂ S ₃	H ₂ SO ₄	-	1.79 mA/cm ² at 0.8 V vs RHE	Photoanode	Visible light	[47]
WO ₃ /TiO ₂	0.5 M NaClO ₄	4.4 $\mu\text{molcm}^{-2}\text{min}^{-1}$	0.42 mA/cm ² at 1.6 V vs Ag/AgCl	Photoanode	Visible light	[48]
Bi ₂ S ₃ /BiVO ₄	0.2 M Na ₂ SO ₄	33.4 $\mu\text{molcm}^{-2}\text{h}^{-1}$	-	Photoanode	Visible light	[3]
BVW	0.5 M Na ₂ SO ₄	4.56 $\text{mmolcm}^{-2}\text{sec}^{-1}$	0.64 mA/cm ² at 1.23 V vs RHE	Photoanode	Solar light	Present work

5.6 The schematic mechanism

The band edge positions were scrutinized by Mulliken's electronegativity to analyze the process of charge transfer in 31BVW photocatalyst using **Eq. 2.8 and 2.9** given in **Chapter 2**. BV possess E_{VB} and E_{CB} of 2.74 and 0.34 eV, respectively while WO possess E_{VB} and E_{CB} of 3.54 and 0.64 eV, respectively. The e^- in the VB edge of BV and WO drift to their respective CB on

the absorption of light while h^+ are left behind. To reduce the reintegration rate of the charges in BV, the interfacial contact occurs between both the semiconductors owing to the comparable band potentials. Hence, promotion of the holes occurs from the VB of WO to BV owing to the more positive VB potential of WO. However, due to more negative CB potential of BV, e^- transport from the CB of BV to WO (**Schematic diagram 5.1**). The adsorbed O_2 reacts with the e^- of the WO and results in the formation of $O_2^{\bullet -}$ radicals. These e^- can be externally biased to the counter electrode to generate hydrogen via proton reduction. Similarly, holes accumulated in VB of BV generates $\cdot OH$ species by the oxidation of H_2O . $O_2^{\bullet -}$ and $\cdot OH$ are potent reducing and oxidizing agents that can eliminate TC separately or $O_2^{\bullet -}$ can also form $\cdot OH$ by reacting with H_2O in conduction band of WO to further degrade the pollutant to form H_2O , CO_2 and other simple compounds.



Schematic diagram 5.1 Proposed photo(electro)catalytic mechanism of the BVW photocatalyst.

5.7 Conclusions

In conclusion, the hydrothermal synthesis of BVW nanohybrids with varying mole ratios proved to be highly effective. The resulting hetero-composite exhibited several advantageous properties, including a higher surface area, reduced recombination rate, enhanced charge migration, and a narrow band gap that enables absorption across a wide spectrum of solar light. Extensive investigations were conducted to manifest the catalyst's performance, including photocatalytic decomposition of the antibiotic TC, as well as PEC water splitting under solar light. Various factors such as the catalyst concentration, pH of the contaminant, kinetics, light

sources, quenching experiments, and reusability were thoroughly examined. The results demonstrated that modifying the BV and WO mole ratio had a significant impact on the pollutant degradation efficiency. Among the prepared photocatalysts, the 31BVW nanohybrid displayed the highest degradation efficiency, rate constant, and synergistic effect. The photocatalyst's effectiveness in TC removal was primarily attributed to the generation of $\cdot\text{OH}$ radicals. Impressively, even after seven cycles, the 31BVW hybrid maintained its efficient photocatalytic performance and demonstrated excellent reusability for the removal of persistent pollutant TC. Surface characterization techniques such as SEM, BET, and XRD analysis confirmed that the material's surface features, morphology, and crystallinity remained largely unaffected after the photocatalytic process. The identification of TC degradation products and intermediates was confirmed through GC-MS analysis. Additionally, chrono-amperometry, LSV, and Mott-Schottky analyses were conducted to investigate the PEC hydrogen evolution activity. The 31BVW electrode exhibited a noteworthy hydrogen production rate and demonstrated stability over a six-hour testing period. The formation of a heterojunction in the BVW photocatalyst played a crucial role in effective segregation of photogenerated excitons, leading to a significantly enhanced photo(electro)catalytic efficiency. In conclusion, the BVW nanohybrid holds great promise for mitigating organic pollutants that pose a serious threat to the environment, as well as for efficient hydrogen production through water splitting. Its remarkable performance and stability make it a compelling candidate for environmental remediation and sustainable energy applications.

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6.1 Introduction

In this Chapter, TC was used as model pollutant for testing out photocatalytic efficacy of $\text{BiVO}_4/\text{Sb}_2\text{S}_3$ (BVSBS) photocatalyst. The detrimental impact of TC, and advantages of the photocatalysis technique over the other conventional wastewater treatment methods has also been discussed in the previous chapters. BiVO_4 (BV) has emerged as a promising option as it possesses many exciting properties as described earlier. However, pure BV has poor photocatalytic performance since it possesses a higher recombination rate of photogenerated charges [1,2]. The hybridization of BV with other semiconductor photocatalysts has become a popular choice, as the heterojunction formation reduces recombination and prolongs the lifetime of photoinduced charges owing to its synergistic effect [3]. About 80.6 %, 90.3 %, and 86.7 % degradation of phenol, norfloxacin, and ciprofloxacin was attained with $\text{BiVO}_4/\text{g-C}_3\text{N}_4/\text{carbon nanotubes}$, BiVO_4/LDH , and CuS/BiVO_4 , respectively, under the illumination of solar light for 120 min and the visible light for 90 min [4–6].

Sb_2S_3 (SBS) is thought to be a potential photocatalyst due to its narrow band gap of ~ 1.84 eV, its capability to absorb solar light, its non-carcinogenicity, and its inexpensiveness [7]. Therefore, the hybridization of SBS with BV tends to boost the photocatalytic performance of the latter by reducing the reintegration rate of charge carriers. $\text{Sb}_2\text{S}_3/\text{rGO}$, $\text{Sb}_2\text{S}_3/\alpha\text{Ag}_2\text{WO}_4$ was synthesized and 89 % of rhodamine B and 91.23 % of methylene blue were degraded under solar light and the visible light for 150 min and 120 min, respectively [8,9].

Several photocatalytic degradation experiments have been reported in the literature with pristine BV and SBS [26]. Although BVSBS composites have been previously synthesized [10], but the different mole ratios of BVSBS composites have not yet been synthesized. In addition, the impact of different mole ratios on photodegradation experiments with the colorless pollutant under natural sunlight has not yet, to the author's knowledge, been reported. A comparison of the synthesized heterojunction photocatalyst with the commercial $\text{TiO}_2\text{-P25}$ under different light sources has not been conducted.

In this Chapter, different mole ratios of BVSBS nanocomposite have been prepared using the hydrothermal method. The performance of the fabricated photocatalyst was tested using the photocatalytic decomposition of the noxious colorless pollutant, TC, under the irradiation of natural sunlight. Different experiments, including the concentration of the photocatalyst, kinetic studies, the impact of pH, reusability, and scavenger studies, were all conducted. In addition, the

superiority of the synthesized photocatalysts was tested by comparing the elimination efficacy with that of commercial TiO_2 -P25. GC–MS was performed to analyze the decomposed products which were produced. Mineralization studies were also carried out.

6.2 Experimental part

This section involves all the chemicals, materials and the methods followed for the synthesis of photocatalysts.

6.2.1 Materials and methods

Antimony chloride (SbCl_3) was procured from Spectrochem. Thioacetamide (CH_3CSNH_2) and Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) were purchased from Loba Chemie.

6.2.2 Syntheses

6.2.2.1 Synthesis protocol of BV

BV was fabricated as per protocol discussed in the **Chapter 2 (section 2.2.2.1)**.

6.2.2.2 Synthesis method of the $\text{BiVO}_4/\text{Sb}_2\text{S}_3$ hybrid

The BV/SBS couple with different mole ratios was fabricated using the hydrothermal synthesis method. Initially, BV (0.0016 mol) was dissolved in 80 mL of distilled water to obtain a uniform solution. In this mixture, SbCl_3 (0.0016 mol), $\text{C}_4\text{H}_6\text{O}_6$ (0.010 mol), and CH_3CSNH_2 (0.0032 mol) were slowly added under vigorous stirring, followed by sonication for 1 h. The solution was heated at 180 °C for 8 h in a Teflon-lined stainless-steel autoclave. After 3–4 washes with DI water and ethanol, the mixture was dried at 60 °C in a hot air oven. The resulting purplish powdery material was named 11BV/SBS. The quantity of the chemicals needed to fabricate the various mole ratios (1:3, 3:1, and 1:5) were computed and named 13BV/SBS, 31BV/SBS, and 15BV/SBS, respectively.

For comparison purposes, the purple-colored bare SBS was similarly synthesized without the addition of BV, and was labeled SBS.

6.2.3 Methods of characterization

Characterization methods are explained in the **Chapter 2 (section 2.2.3)**.

6.2.4 Photocatalytic elimination of TC

The decomposition of the recalcitrant antibiotic, TC, was performed under natural sunlight to manifest the photocatalytic efficacy of the fabricated photocatalysts. About 6 mg of the photocatalyst was inoculated into 20 mL of 10 ppm of TC (0.3 g/L). Before the illumination, the solution was stirred at 900 rpm in the dark for 60 min to achieve an absorption–desorption equilibrium. Eventually, it was stirred under natural sunlight for 120 min to carry out degradation, by placing the test tubes vertically towards the sun. About 3 mL of solution was taken out at regular intervals and monitored by a UV-vis spectrophotometer after separating the catalyst using centrifugation. The experiments were conducted in July–August, and the sunlight intensity was 800–830 W/m² during these months as measured with the LICOR Pyranometer. The studies were carried out three times, and the plots are displayed with the error bars displaying a ~5 % data source error. To monitor the degradation of the TC, the absorbance intensity of a UV-visible spectrophotometer was scrutinized at $\lambda_{\text{max}} = 360$ nm. The degradation efficacy was determined by using **Eq. 2.1** as provided in **Chapter 2 (section 2.2.4)**.

COD and TOC analyses were used to assess the photocatalytic treatments for TC. Prior to the analysis, a 200 mL solution containing 60 mg of the 13BVSBS photocatalyst was illuminated with sunlight for 120 min. The COD was estimated via titration method, whereas the mineralization was computed using a TOC elimination. **Eq. 2.2, and 2.3** discussed in **Chapter 2** were used to compute the % COD and TOC eradication.

GC-MS was done to analyze the degraded products and the intermediates formed by the photocatalytic elimination of TC by 13BVSBS photocatalyst. The method followed for the fabrication of the samples for the GC-MS analysis is explicated in **Chapter 2**.

6.3 Results and discussions

6.3.1 XPS study

The elemental composition, binding energy of the core electrons, and oxidation state of the elements were examined using XPS analysis. The XPS can distinguish between the spin-orbit splitting of metal ions into two conceivable states, i.e., when they have different binding energies. The survey spectra of the as-prepared composite are represented in **Fig. 6.1(a)**. The peaks specify that antimony, sulfur, oxygen, bismuth, and vanadium are the main elements in the 13BVSBS composite. The presence of C 1s may be accredited to the adventitious carbon of the

instrument. The least-square Gaussian-fit model was used to deconvolute. In the core level spectra of Bi, V, and O, the presence of deconvoluted peaks at binding energies of 159.3 and 164.7 eV (**Fig. 6.1(b)**), 516.9 and 524.6 eV (**Fig. 6.1(c)**), and 530.1 eV (**Fig. 6.1(d)**) can be ascribed to Bi $4f_{7/2}$ and $4f_{5/2}$, V $2p_{3/2}$ and $2p_{1/2}$, and O $1s$ attributes to the +3, +5, and -2 oxidation states of Bi, V, and O, respectively. This confirms the successful synthesis of BV in the composite [11–14]. As depicted in **Fig. 6.1(e)**, the doublet peak centered at a binding energy of 529.8 and 539.2 eV corresponds to Sb $3d_{5/2}$ and $3d_{3/2}$, respectively, and suggests the +3 oxidation state of Sb [15]. The doublet peak of S at a binding energy of 161.3 and 163.1 eV, related to S $2p_{1/2}$ and S $2p_{3/2}$ due to spin-orbit coupling, were credited to the -2 oxidation state as represented in **Fig. 6.1(f)** [15].

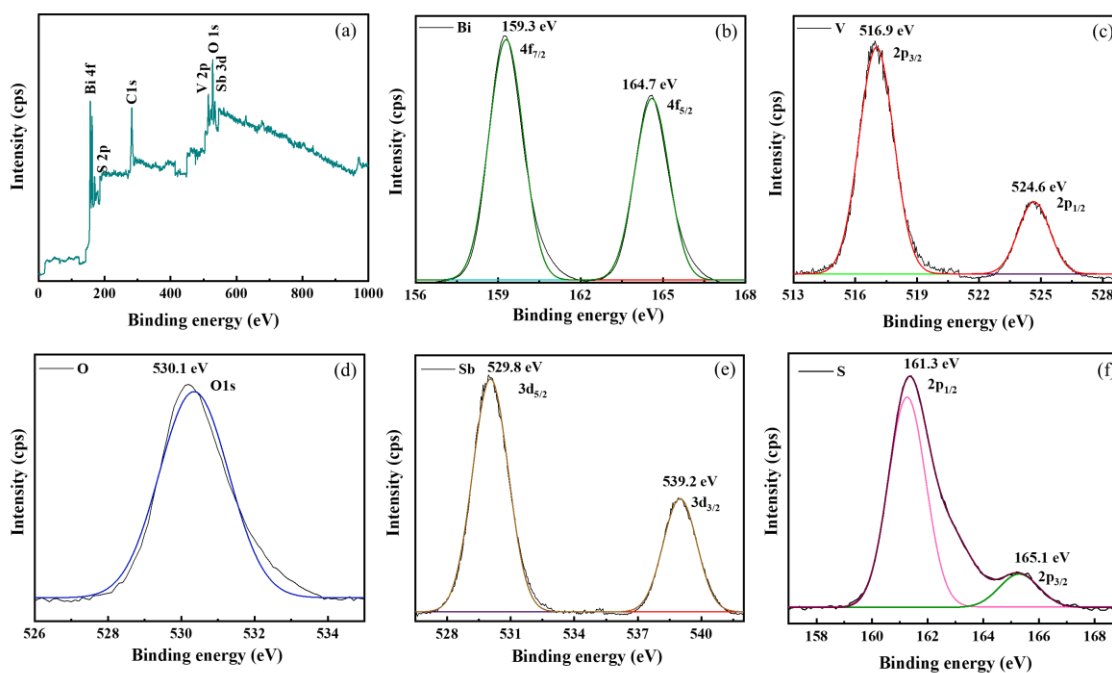


Fig. 6.1 XPS spectrum of 13BVSBS photocatalyst: **(a)** survey spectra, **(b)** Bi 4f, **(c)** V 2p, **(d)** O 1s, **(e)** Sb 3d, and **(f)** S 2p.

6.3.2 XRD analysis

The crystallite phase, structural analyses, and purity of the photocatalysts were analyzed using XRD [16]. The XRD pattern of the prepared photocatalysts is provided in the **Fig. 6.2**. The successful formation of monoclinic BV was confirmed by the existence of peaks at 19.0° (011), 24.5° (102), 28.8° (112), 30.6° (004), 34.8° (200), 35.2° (020), 40.0° (211), 42.6° (015), 46.1° (123), 46.9° (204), 47.4° (024), 50.1° (220), 53.2° (301), and 58.3° (303), which matches the

standard JCPDS card 83–1699 of BV. The diffraction peaks indexed at planes (110), (020), (120), (220), (130), (111), (230), (211), (221), (301), (311), (240), (231), (041), (141), (520), (440), (501), (531), and (132) corresponds to the 2θ value of 11.01° , 15.7° , 17.5° , 22.2° , 24.9° , 25.8° , 28.4° , 29.0° , 32.3° , 33.5° , 34.4° , 35.6° , 37.0° , 39.4° , 40.6° , 43.1° , 45.3° , 46.8° , 53.1° , and 54.2° , respectively, which matches well with the JCPDS card 00-006-0474, and confirms the efficacious formation of orthorhombic SBS. The synthesized BVSBS composites lack any impurity peaks. Further, little peak shifting was observed, indicating that the binary photocatalysts were of excellent purity and had a two-phase composition [17]. Additionally, the intensity of the peaks became stronger by increasing the concentration of SBS in the composite.

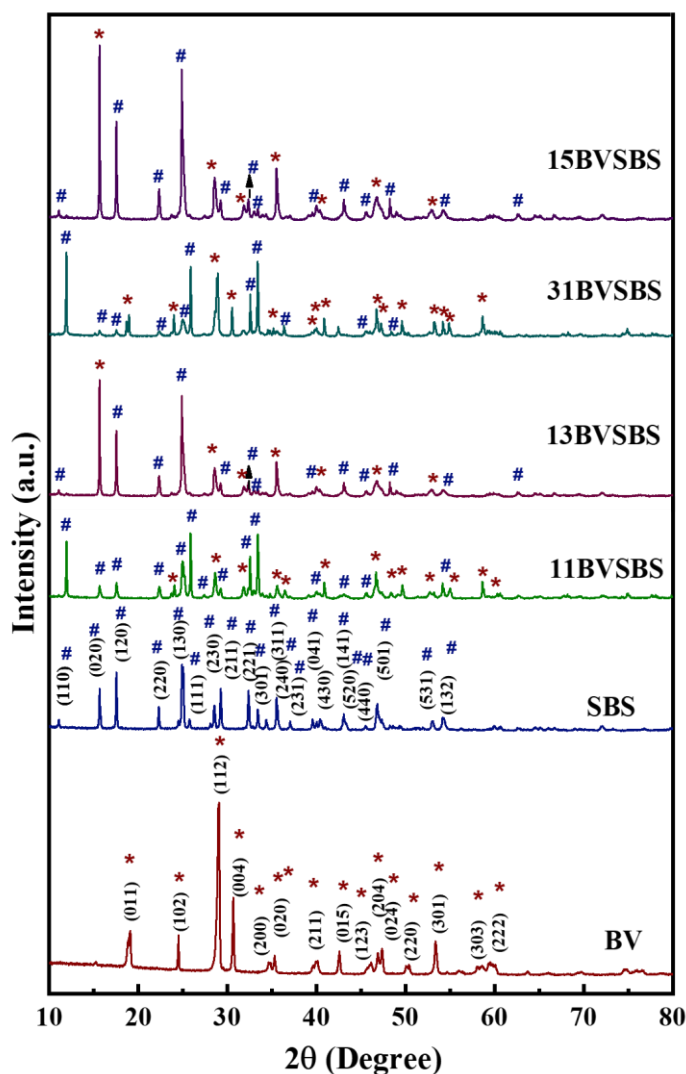


Fig. 6.2 XRD plot of the fabricated photocatalysts where * and # denote peaks of BV, and SBS, respectively.

6.3.3 PL study

The migration, segregation, and the recombination of the charge carriers can be examined using the PL spectra [10]. An efficacious photocatalyst should possess a low recombination rate, high carrier charge transport ability, and efficient separation of the charges [18]. The intensity of the PL signal is directly correlated to the reintegration rate of the photogenerated excitons. The lower the PL emission intensity of a photocatalyst is, the less the recombination ability of the photoexcited carriers is, and thus the better the charge transfer efficiency is, which is advantageous for the photocatalytic performance of the photocatalyst [19].

An excitation wavelength of 325 nm was utilized to record the PL spectra. Pristine BV and SBS have the highest PL intensity, while the 13BVSBS and 15BVSBS photocatalysts have an analogous, and the lowest, PL intensity amongst all the photocatalysts, signifying the lowest recombination rate, good charge separation, and higher charge transport ability, as shown in **Fig. 6.3**. This might be due to the formation of a heterojunction between BV and SBS, and the increased electron transport aids in decreasing the recombination rate of charges [20]. It was also analyzed that by increasing the amount of SBS in the composite, the PL intensity was considerably reduced.

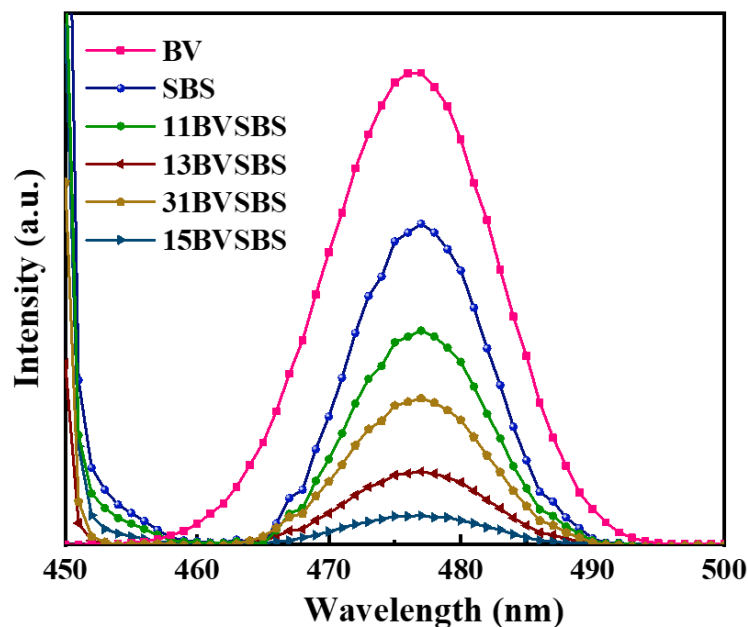


Fig. 6.3 PL plot of the synthesized BV, SBS, 11BVSBS, 13BVSBS, 31BVSBS, and 15BVSBS photocatalysts.

6.3.4 Surface area analyses

The surface area of the photocatalysts is crucial parameter in the field of photocatalysis. Nitrogen physisorption experiments were carried out to evaluate the surface area characteristics and pore size distribution of the fabricated materials. The photocatalysts exhibit a type-IV N_2 adsorption curve, specifying that they possess a mesoporous nature (**Fig. 6.4(a, b)**). The pore size distribution was determined utilizing the BJH plot. **Table 6.1** summarizes the specific surface area results, and the mean pore diameter along with the pore volume calculated from the BJH plot.

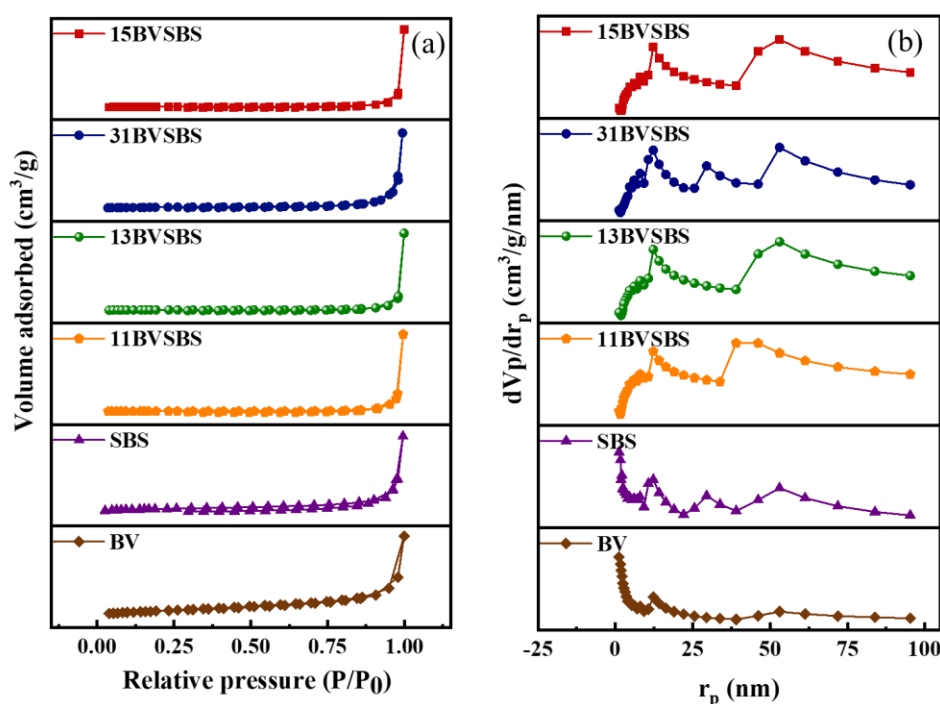


Figure 6.4(a) BET surface area isotherm, and **(c)** BJH graph.

It was detected that the specific surface area and the pore volume of the 13BVSBS and 15BVSBS hetero-composites are comparable and the highest among the prepared photocatalysts. The larger surface area of the heterojunction photocatalysts facilitates greater interfacial contact between both components for photoinduced charge migration and provides abundantly exposed surface-active sites to adsorb more pollutant, thereby improving photocatalytic activity [21]. The 13BVSBS and 15BVSBS catalyst composites exhibit the highest value among the various compositions of the synthesized photocatalyst.

Table 6.1 The surface area characteristics of the BV SBS photocatalysts.

Sample	Specific surface area (m^2/g)	Mean pore volume (cm^3/g)	Mean pore diameter (nm)
BV	33	0.582	13.81
SBS	12	0.187	9.72
11BVSBS	38	0.242	11.10
13BVSBS	42	0.481	14.52
31BVSBS	39	0.372	11.70
15BVSBS	43	0.521	14.96

6.3.5 Absorption studies

An optimum light absorption capability and a narrow band gap are the key features of a good photocatalyst. The absorption characteristics were measured using DRS to scrutinize the absorption range as well as the band gap of the synthesized photocatalysts.

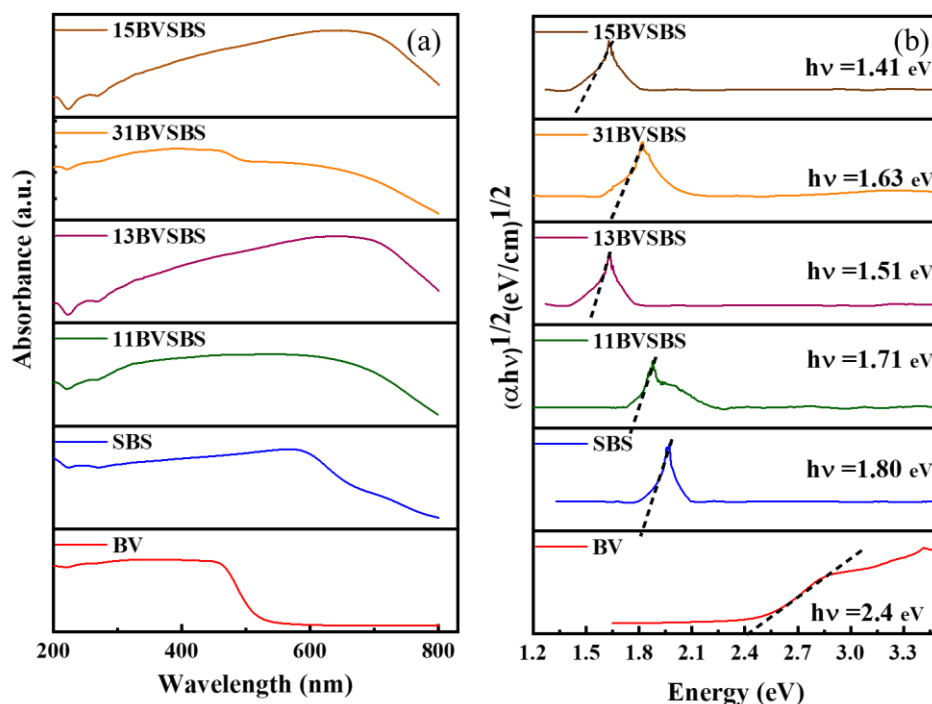


Fig. 6.5(a) Absorption spectrum, and **(b)** band gap potential of the used photocatalysts.

From **Fig. 6.5(a)**, it can be seen that they display a significant visible light absorption capacity in the absorption range of 400–800 nm. A Tauc plot was used to calculate the band gap of the semiconductors according to **Eq. 2.4** as given in **Chapter 2**. Therefore, the band gaps of BV, SBS, 11BVSBS, 13BVSBS, 31BVSBS, and 15BVSBS were calculated to be 2.40, 1.80, 1.71, 1.51, 1.63, and 1.41 eV, respectively (**Fig. 6.5(b)**). These results demonstrate that the 13BVSBS and 15BVSBS composites exhibit narrow band gap, and the widest visible light absorption capacity among the synthesized catalysts.

6.3.6 SEM analysis

The surface morphology of the BV, SBS, and 13BVSBS composites was examined using SEM at a differential magnification. According to the analysis, BV possesses a nano-rod-like structure, whereas SBS has a nano-sphere-like morphology (**Fig. 6.6(a, b)**). The 13BVSBS composite features nano-spheres deposited onto a nano-rod-like structure, as shown in the (**Fig. 6.6(c, d)**).

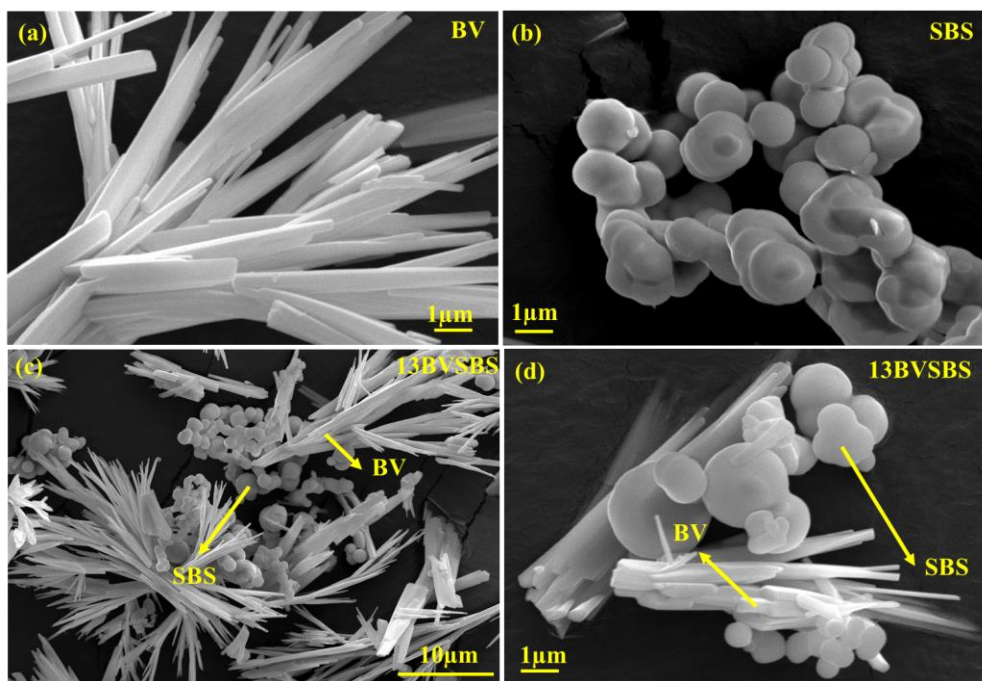


Fig. 6.6. SEM images of (a) BV, (b) SBS, and (c, d) 13BVSBS photocatalyst with different magnification.

Hence, the successful fabrication of the composite was validated due to the presence of both kinds of morphology. In addition, this type of morphology provides an ample number of active sites, therefore promoting more photocatalytic activity.

6.3.7 EDS and elemental mapping

EDS was performed to gauge an elemental distribution, composition, and purity of photocatalyst [22]. The EDS spectrum displays a significant signal from Bi, V, O, Sb, and S, all of which were effectively embedded inside the chosen regions of the 13BVSBS composite, as represented in **Fig. 6.7(a)**.

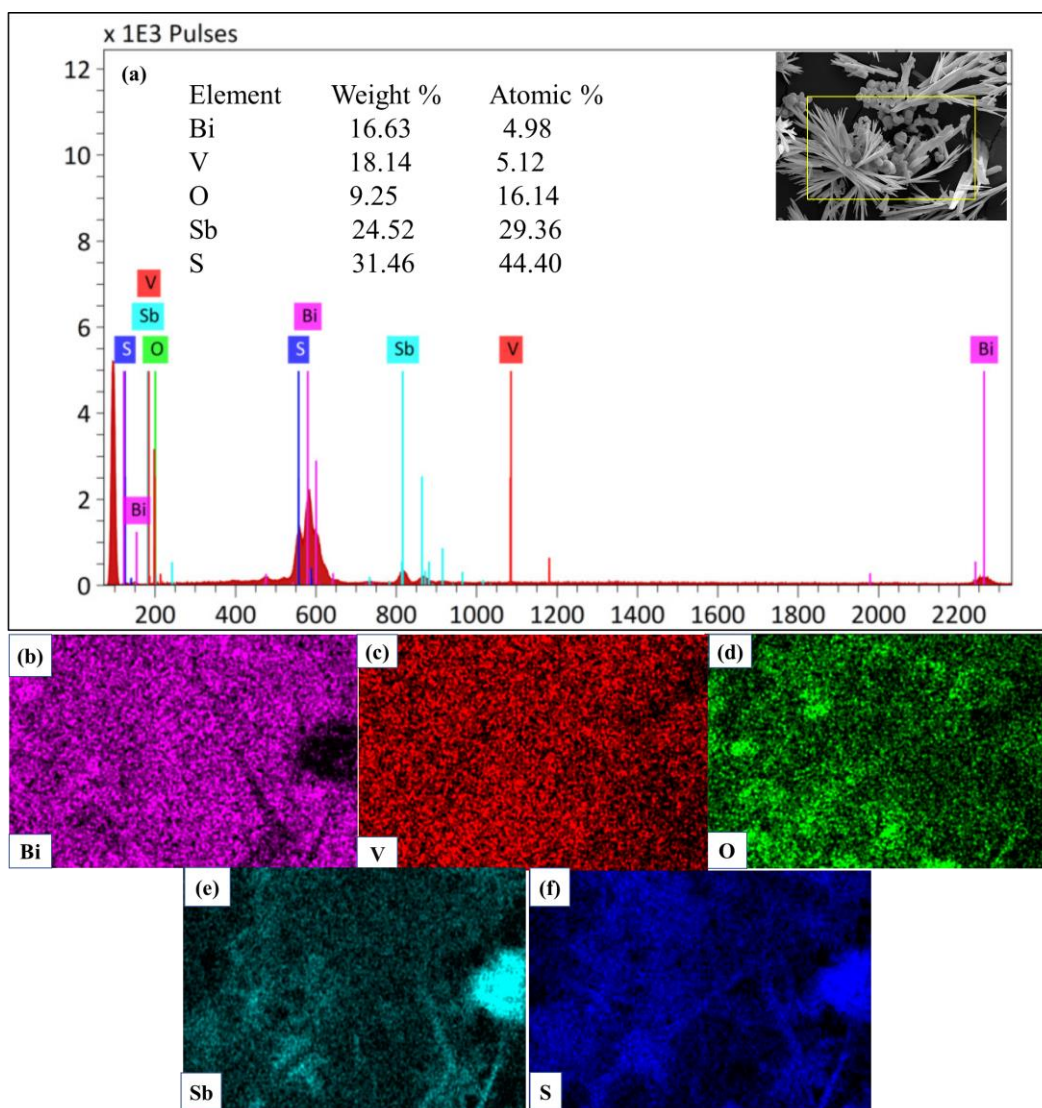


Fig. 6.7(a) EDS spectrum of the 13BVSBS photocatalyst with the corresponding SEM image and **(b–f)** elemental mapping of the 13BVSBS composite.

The lack of any other elemental peaks in the EDS spectrum suggests that the surface of the synthesized composite is devoid of any impurities, confirming its successful formation. The spatial distribution of Bi, V, O, Sb, and S agrees well with the SEM of the composite, indicating

that all the elements were uniformly dispersed (**Fig. 6.7(b-f)**). These results demonstrate an excellent distribution of SBS onto BV, which is favorable for a heterojunction photocatalyst.

6.3.8 Photocatalytic studies

A kinetic analysis of the photocatalytic deterioration of TC is represented in **Fig. 6.8(a, b)**. The colorless pollutant, TC, was decomposed under sunlight to gauge the performance of the photocatalysts. When exposed to sunlight for 120 min, a 20 mL solution of TC decomposes at a low rate (8.9 %) in the absence of a photocatalyst, as TC is a stable molecule. However, in the occurrence of 0.3 g/L of the 13BVSBS and 15BVSBS photocatalysts, up to 88.7 % and 89.6 % degradation of the TC was achieved, respectively. The photocatalytic performance of commercial TiO₂-P25 powder was also compared to the synthesized catalysts and was found to exhibit a photoactivity of 47.0 %. The lower performance of TiO₂-P25 could be due to its wide band gap, thus rendering it responsive to UV light only. Therefore, the study revealed that the prepared photocatalysts exhibited superior photocatalytic activity over commercial TiO₂-P25. The rate constant for the observed catalytic activity was determined using **Eq. 2.5** as mentioned in **Chapter 2**, where k , C_0 , and C are the rate constant, initial concentration of the pollutant, and concentration at any time (t), respectively, and the outcomes are represented in **Fig. 6.8(b)**. It can be seen from **Fig. 6.8(b)** that the reaction followed pseudo-first-order kinetics, i.e., the Langmuir–Hinshelwood kinetic model, owing to the good linear fitting of the lines ($R^2 > 98.5\%$) [23].

The 13BVSBS and 15BVSBS nanocomposites had the highest and analogous rate constants of 0.01557 min⁻¹ and 0.01655 min⁻¹, respectively, among the prepared composites; meanwhile, the pristine BV and SBS exhibited rate constants of 0.00419 min⁻¹ and 0.00447 min⁻¹, respectively. The rate constant of commercial TiO₂-P25 powder was also evaluated and found to be 0.00413 min⁻¹, which was the lowest among all the photocatalysts, revealing the superiority of the synthesized materials. Detailed photocatalytic studies were further carried out using 13BVSBS, since it was more efficient and cost-effective than 15BVSBS. The 15BVSBS exhibits similar activity but entails the use of a larger amount of SBS (the precursor salt of SBS is more expensive than BV).

For the quantification of the degree of the synergistic effect of the composites, the R factor was calculated using **Eq. 6.1**.

$$R = \frac{k_{BV}/k_{SBS}}{k_{BV} + k_{SBS}} \quad (6.1)$$

Here, k , k_{BV}/k_{SBS} , k_{BV} , and k_{SBS} stand for the rate constant, the rate constant of hybrid BV and SBS, the bare BV, and SBS, respectively. The 13BVSBS had the highest R factor (1.75). This indicates that it had the highest efficiency amongst all the prepared materials owing to its higher synergistic effect on BV and SBS. The degradation efficacy, rate constant, and the value of the synergistic constant of the different photocatalysts are also tabularized in **Table 6.2**.

Table 6.2 Degradation efficacy, rate constant, and synergistic factor of the prepared photocatalysts.

Photocatalyst	Degradation (%)	Rate constant (min^{-1})	Synergy factor
TiO ₂ -P25	47.0	0.00413	-
BV	49.1	0.00419	-
SBS	51.2	0.00447	-
11BVSBS	58.9	0.00559	0.64
13BVSBS	88.7	0.01557	1.75
31BVSBS	66.5	0.00674	0.77
15BVSBS	89.6	0.01655	1.91
No catalyst	8.90	0.00079	-

6.3.8.1 Impact of the amount of catalyst loading

The ideal amount of catalyst used is the most important parameters affecting the degradation efficacy of the photocatalytic process. The use of the optimum amount of catalyst is crucial to avoid its excess use, which may promote the agglomeration of the particles, as well as to ensure the maximal absorption of photons for efficient photodecomposition [24]. As represented in **Fig. 6.8(c)**, the degree of abatement of the TC was enhanced from 76.8 % to 88.7 % with an increase in the amount of the catalyst from 0.1 to 0.3 g/L, due to the increase in the sum of reaction sites. However, the decomposition efficacy declined slightly with a further rise in the amount of catalyst to 0.4 g/L. This is because when more of the catalyst is added to the solution, the turbidity of the solution increases, which disperses the light and reduces its impact on the solution [25]. In addition, the emergence of the active species is reduced as precipitation of the photocatalyst occurs. Therefore, for the subsequent experiments, a photocatalyst dose of

0.3 g/L was chosen as best dosage based on the removal efficiency [26]. Thus, it can be inferred that even a little dose of the photocatalyst is enough for the photocatalytic abatement of TC under natural sunlight.

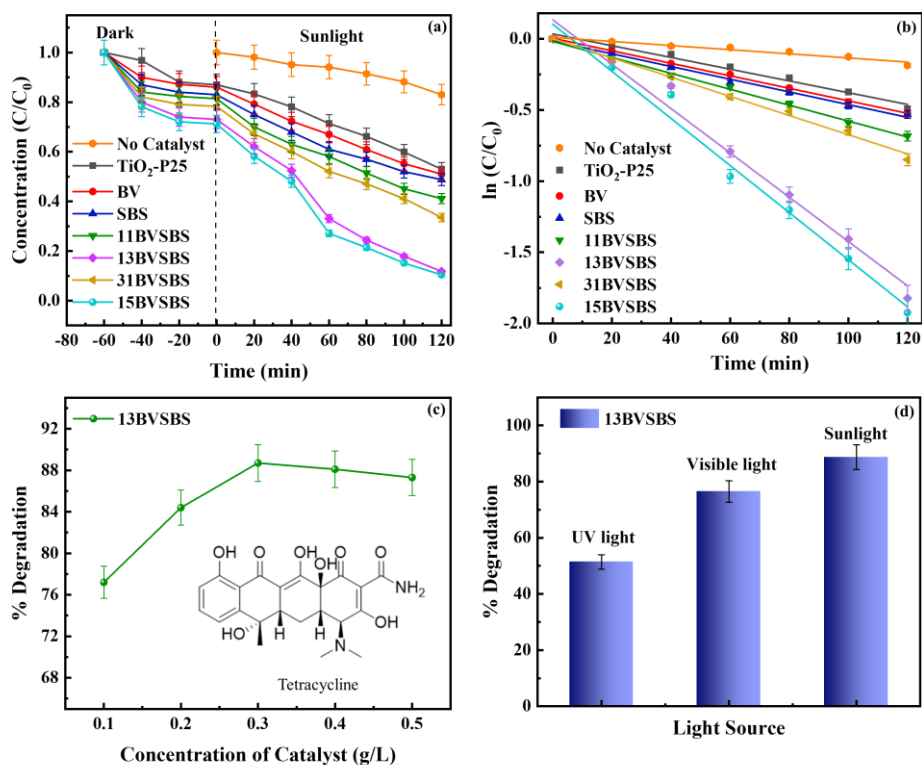


Fig.6.8(a, b) Kinetic studies of the fabricated photocatalysts for the detoxification of TC having standard deviation 18.12, **(c)** concentration impact of the 13BVSBS photocatalyst, and **(d)** the influence of different light sources on the decomposition efficiency of TC using the 13BVSBS photocatalyst.

6.3.8.2 Effect of light sources

A similar experiment was conducted using different light sources (UV light and visible light) under optimum conditions to draw a comparison. From **Fig. 6.8(d)** it can be seen that TC degraded to 51.4 % in UV light and 76.5 % in visible light. However, the highest degradation rate of 88.7 % was observed under natural sunlight with the 13BVSBS photocatalyst. Thus, sunlight is sufficient for the degradation of the pollutant using the synthesized photocatalysts.

6.3.8.3 Impact of pH

The pH is the significant parameter in the photocatalytic decomposition process because it affects the capability of adsorption, the distribution of electric charges over the surface of the

photocatalyst, and the degradation of the targeted organic contaminant by altering the surface charge properties of the photocatalyst, as well as varying the ionization state [27]. Thus, experiments were done with varying pH values ranging from 2 to 12 to determine the influence of pH on the degrading efficacy of the TC. It was determined that with a rise in the pH of the solution, the degradation efficiency was first increased and then decreased, i.e., the composite's ability to degrade the TC was lower in an acidic environment than in an alkaline. A maximum decomposition efficiency of 88.7 % was observed at pH 7. The point of zero charge (pzc) of the photocatalyst was determined to be 5.8 (**Fig. 6.9(a)**). TC is an amphoteric molecule and has three different acidic constants ($\text{pK}_{\text{a}1} = 3.30$, $\text{pK}_{\text{a}2} = 7.7$, and $\text{pK}_{\text{a}3} = 9.80$). At different pH values, the different ionizing functional groups of TC have different pKa values. TC exists as a cationic molecule (TCH_3^+ and TCH_2^+), because of the protonation of the dimethyl ammonium group, at $\text{pH} < 3.3$. It exists as an anionic species (TC_2^- and TCH^-), owing to the deprotonation of the tricarbon or diketone group of phenol, at $\text{pH} > 7.7$. However, it exists as an amphoteric form ($\text{TCH}^\pm$) when the pH ranges from 3.3 to 7.7, due to the abstraction of a proton from the diketone group of phenol [28]. The removal efficacy of TC using the 13BVSBS photocatalyst was decreased in acidic and alkaline environments due to the repulsive electrostatic forces emerging between the cationic and anionic forms of TC, and the surface of the positively and negatively charged photocatalyst, respectively. However, the electrostatic attraction amid the negatively charged catalyst and the zwitterionic form of the pollutant enhanced the degradation efficiency of the pharmaceutical pollutant, TC. Hence, TC removal using the 13BVSBS composite was maximized at pH 7 and was higher in an alkaline than in an acidic environment, owing to the affinity of TC for the surface of the photocatalyst, as revealed in **Fig. 6.9(b)**.

6.3.8.4 Scavenger studies

To scrutinize the role of the active radical species which are responsible for the photocatalytic elimination of TC, a trapping experiment was performed with commonly used quenchers. The chemical quenchers methanol, DMSO, and BQ, each of 1 mM concentration, were utilized to investigate the role of h^+ , $\cdot\text{OH}$ radicals, and $\text{O}_2^{\cdot-}$ radicals, respectively, in the photocatalytic experiments [29]. In the absence of any trapping agent, a maximum degradation of the TC (88.7 %) was observed. The inclusion of the above-mentioned scavengers in the reaction media efficiently quenched the photocatalytic decomposition of the TC. As shown in **Fig. 6.9(c)**, the addition of DMSO expressively reduced the photocatalytic performance (32.4 %)

of the 13BVSBS composite, indicating that $\cdot\text{OH}$ is the major species responsible for pollutant decomposition. The decomposition process was similarly affected by BQ (54.2 %), albeit by a smaller amount, suggesting that $\text{O}_2^{\cdot-}$ plays a small but important role in the antibiotic elimination process. These findings demonstrate the susceptibility of $\cdot\text{OH}$ as the active species responsible for the photocatalytic elimination of TC in the existence of the 13BVSBS nanocomposite.

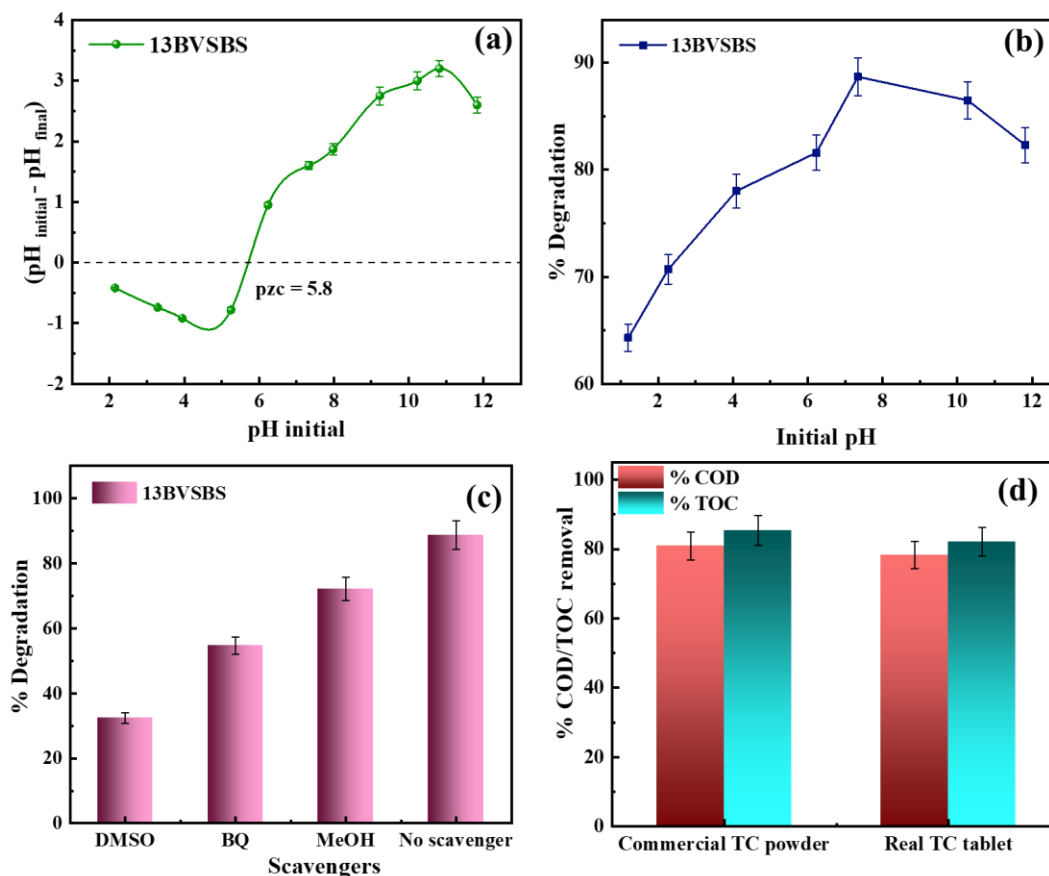


Fig. 6.9(a) pzc of the 13BVSBS nanocomposite, (b) impact of pH on the degradation efficacy of the 13BVSBS photocatalyst, (c) impact of different scavengers on the removal efficacy of the TC, and (d) COD and TOC analysis of a commercial sample of TC.

6.3.8.5 Mineralization experiment

TOC experiment was conducted to calculate the amount of TC mineralized by the 13BVSBS photocatalyst. The existence of a substantial amount of organic substances in the pollutant, TC, was initially demonstrated by a higher TOC and COD levels. When the experiment was conducted utilizing the 13BVSBS photocatalyst under natural sunlight for 120

min, there was a 80.9 % and 85.4 % reduction in COD and TOC, respectively (**Fig. 6.9(d)**). The % TOC removal was lower than the % degradation owing to the generation of sequential organic intermediates during the process before the complete breakdown of TC into carbon dioxide and other simpler products. In an aqueous solution, the degradation rate does not always imply extensive mineralization and the full destruction of organic compounds [7]. Due to ethical permission issues, experiments with real medical/pharmaceutical waste water cannot be performed. Therefore, the degradation efficacy of the 13BVSBS photocatalyst was tested by carrying out a COD and TOC analysis of a TC tablet (company name Abbott, TC capsules, I.P. Restecline 250, having a concentration of 250 mg) and was found to be 78.3 % and 82.1 %, respectively. This verifies that the fabricated photocatalyst has a good surface catalytic property in comparison to industries' existing expensive and time-consuming physicochemical approaches.

6.3.8.6 Reusability studies

Photocatalytic materials must be stable and reusable in order to be used in real-world applications. Therefore, a reusability experiment was performed for five cycles to determine the usefulness and stability of the photocatalyst for the photocatalytic degradation of TC [30]. 13BVSBS was chosen as the potential photocatalyst because it is easily separable, as the pollutant is physically adsorbed on its surface. The photocatalyst was centrifuged and rinsed with DI water before being dried at 50°C for 10 h and reused for the next cycle. Following the fourth cycle, the decomposition of TC declined to 71.9 %, in comparison to 88.7 %, as depicted in **Fig. 6.10(a)**. Loss of the photocatalyst may occur during the washing and the drying processes. Hence, the 13BVSBS nanocomposite is advantageous for use as a photocatalysis as it is reusable. In addition, the XRD pattern of the photocatalyst after carrying out reusability studies revealed no significant variations. Furthermore, the intensities and locations of all the diffraction peaks of BV and SBS remained intact after the reaction. No additional diffraction peaks, attributed to crystalline impurities formed after the recycling process, were observed (**Fig. 6.10(b)**). In addition, a BET analysis performed after the recycling experiment confirmed that the photocatalyst had a specific surface area of 37 m²/g, a mean pore diameter of 11.22 nm, and a pore volume of 0.231 nm, respectively, as shown in **Fig. 6.10(c, d)**. Although the surface area decreased, it was enough to proceed with the photocatalytic decomposition. As demonstrated in

Fig. 6.10(e), the morphology of the 13BVSBS photocatalyst post-degradation experiment remained intact. Thus, it can be confirmed that the 13BVSBS photocatalyst had good recycling photocatalytic stability.

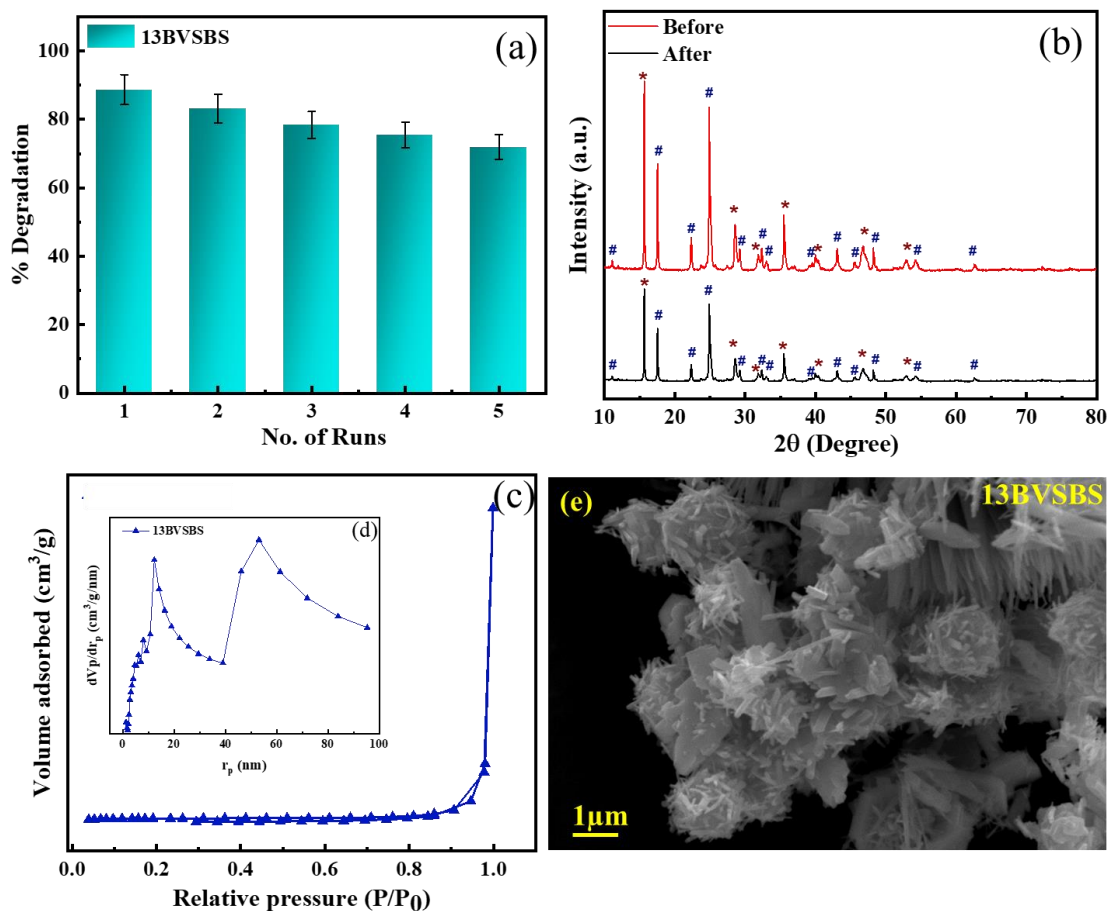


Fig. 6.10(a) The reusability graph, **(b)** XRD of 13BVSBS composite post degradation studies, **(c)**, **(d)** BET with inset showing BJH graph, and **(e)** SEM image of the used catalyst's post degradation studies.

6.3.9 Comparison with the literature

A comparison study of the synthesized BVSBS nanocomposite was done with the various reported BV and SBS based photocatalysts and other catalysts for the photocatalytic remediation of TC as summarized in **Table 6.3**. Decomposition of TC was not studied earlier by BVSBS photocatalyst under irradiation of sunlight as apparent from literature. It can be manifested that, in comparison to the existing literature, highest degradation efficacy can be

achieved by using the small amount of the 13BVSBS photocatalyst under the natural sunlight under the optimum reaction conditions such as pH and catalyst loading amount.

Table 6.3 Comparison of different photocatalysts for the photocatalytic abatement of colorless pollutant, TC.

Photocatalyst	Concentration of pollutant	Reaction time (min)	Light source	Rate constant k	Degradation efficiency (%)	Ref.
BiVO ₄ /BiOI	10 ppm	60	Visible light	0.0133 min ⁻¹	69.57	[31]
BiVO ₄ /Bi ₂ SiO ₅	10 ppm	120	Visible light	0.0072 min ⁻¹	72.2	[32]
ZnInS ₄ /Sb ₂ S ₃	10 ppm	140	Visible light	0.009 min ⁻¹	85.36	[33]
Ag ₂ WO ₄ /Sb ₂ S ₃	10 ppm	180	Visible light	0.0041 min ⁻¹	53.06	[9]
BiOBr/g-C ₃ N ₄ /carbon nanofibres	-	120	Visible light	0.015 min ⁻¹	86.1	[34]
BVSBS	10 ppm	120	Sunlight	0.01557 min ⁻¹	88.7	Current work

6.4 GC–MS Analysis

A GC–MS study was carried out to scrutinize the products and the intermediates produced in the photocatalytic breakdown process of TC. **Fig. 6.11(a, b)** depicts the GC chromatogram and mass spectra, respectively. As represented in **Fig. 6.12**, the photocatalytic decomposition follows three pathways. In the first route, deamination, ring opening, and demethylation of 4-(dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide resulted in the formation of 1-(2-(2-hydroxy-3-(propylamino) propoxy) phenyl)-3-phenylpropan-1-one. Further, 3,4-dimethylbenzaldehyde and 2,4-di-tert-butylphenol were

formed by the addition of $O_2^{\bullet -}$ and $\bullet OH$ to 1-(2-(2-hydroxy-3-(propylamino) propoxy) phenyl)-3-phenylpropan-1-one. Oxidation of the intermediate species, the addition of $\bullet OH$, and the ring opening of 3,4-dimethylbenzaldehyde and 2,4-di-tert-butylphenol resulted in the formation of 2-ethylhexan-1-ol. Lastly, H_2O , CO_2 , and the simpler products were formed as a result of the abstraction of $\bullet OH$ and bond cleavage [35].

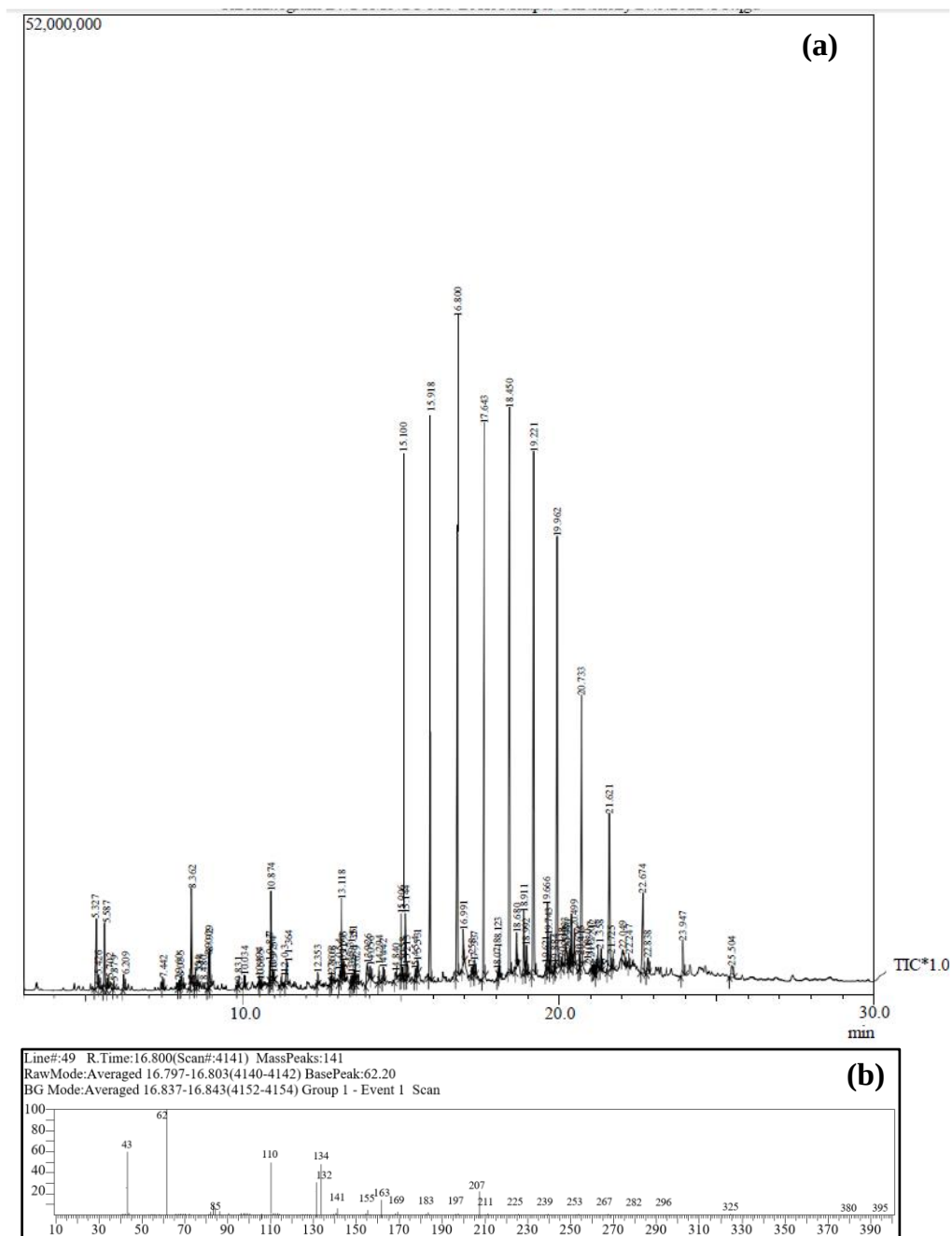


Fig. 6.11(a) Gas chromatogram, and **(b)** mass spectra of the products after the degradation of TC by 13BVSBS photocatalyst.

The second degradation route involved the formation of 5-hydroxy-2-phenyl-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione by the abstraction of the electron from the organic moiety by the h^+ from 4-(dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide. The addition or substitution of $\cdot\text{OH}$ and ring cleavage led to the formation of 1,2,3,4-tetrahydronaphthalene. Furthermore, oxidation and ring cleavage resulted in the formation of o-cresol and ethane-1,2-diol, respectively [36].

In the third route, the indirect addition or substitution of $\cdot\text{OH}$ and the ring opening of 4-(dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide led to the production of two intermediate structures, 4-hydroxy-2,5-dimethylfuran-3(2H)-one and 3-(methoxycarbonyl)benzoic acid. After that, oxidation of these intermediate structures occurred and 3-hydroxybutanoic acid was formed. Finally, water and carbon dioxide were formed as products by fragmentation [37].

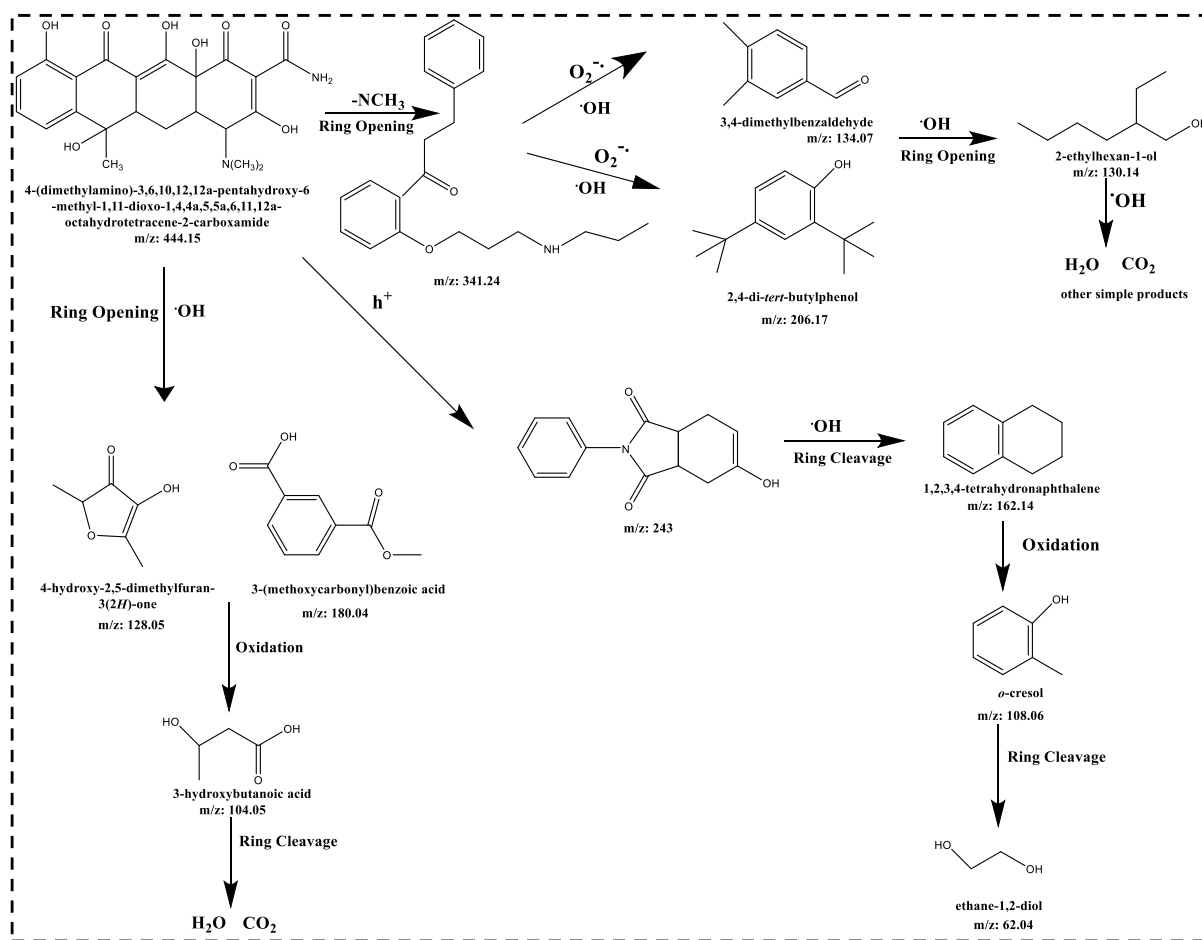
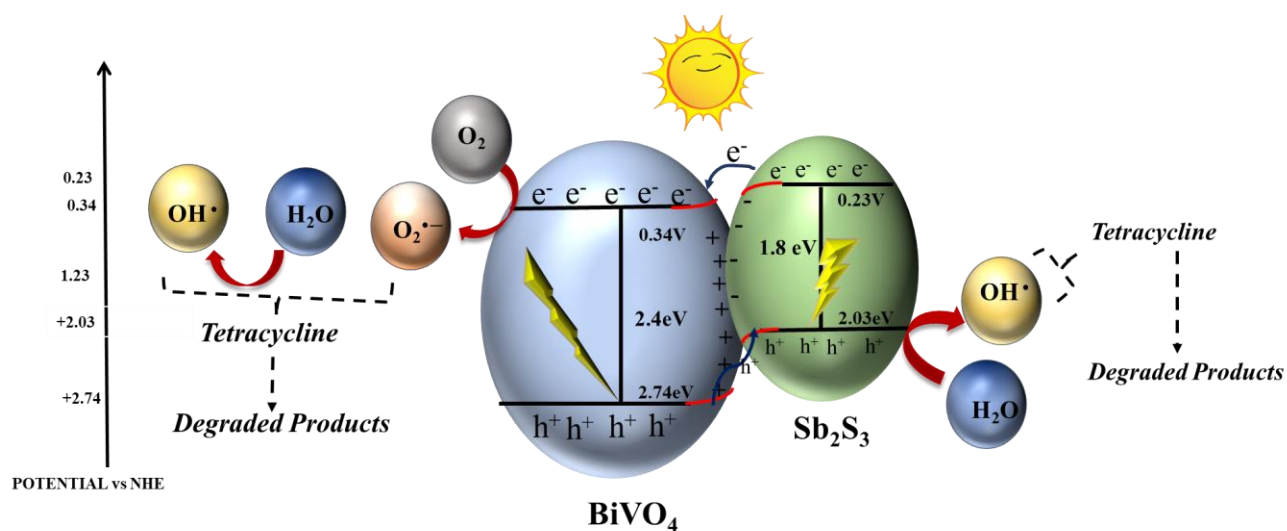


Fig. 6.12 The deteriorated intermediate products formed by the photocatalytic remediation of TC by the 13BVSBS composite.

6.5 Photocatalytic degradation mechanism

To understand the photocatalytic abatement of TC and the charge transport mechanism for photoactivity, the VB and the CB potential of the fabricated catalyst were gauged with Mulliken's **Eq. 2.8 and 2.9** as provided in **Chapter 2**.

The E_{CB} potential values for BV and SBS were 0.34 and 0.23 eV, while the E_{VB} potential values were 2.74 and 2.03 eV, respectively [38]. Even after a longer period of illumination of the light, the accumulation of e^- is prevented due to the higher reintegration rate of the charge carriers of BV. During the illumination of light, e^- were transferred to the CB of both semiconductors as both are activated by sunlight.



Scheme 6.1 The proposed photocatalytic mechanism of BV/SBS photocatalyst for the photocatalytic degradation of TC.

To avoid the reintegration rate of the photogenerated charge carriers of BV, e^- from the BV instinctively diffuse to the SBS when both semiconductors are in close proximity, forming an e^- accumulation layer and depletion layer close to the interface of BV and SBS. An internal electric field that flows from BV to SBS is formed, accelerating the migration of e^- from SBS to BV. In addition, the e^- in the CB of SBS and the h^+ in the VB of BV are urged to reintegrate at the interface region by band bending. Thus, e^- present in the CB of SBS have the ability to react with $O_2^{\bullet-}$ and later have the potential to react with water to form $OH^\bullet$. This $OH^\bullet$ radical can either directly oxidize and decompose the organic pollutants, or produce decomposed products from the oxidation of hazardous pollutants. In addition, the h^+ present in the VB of BV has the ability to react with water to form $OH^\bullet$, which can further oxidize the detrimental pollutant to less toxic

and simpler products. As depicted the **Scheme 6.1**, the photocatalysts follow a S-scheme heterojunction. Then the photocatalytic performance of the catalyst was compared to existing reports.

6.6 Conclusions

In this Chapter, various mole ratios of the novel heterojunction BVSBS photocatalysts were fabricated using the environmentally friendly hydrothermal method. The characterization studies revealed that the binary composite possesses a high surface area and a low reintegration rate, which is significant for the degradation of the detrimental pollutant. In addition, the composite had a narrow band gap allowing it to cover the broad range of solar light. The 13BVSBS composite had a nano-sphere-like morphology deposited onto nano-rods. To gauge the photocatalytic performance of the fabricated photocatalysts, the photocatalytic remediation of the recalcitrant antibiotic, TC, was performed under natural sunlight. Different experiments, including the concentration of the photocatalyst, the pH impact of the detrimental pollutant, kinetic studies, effect of the light source, a scavenger study, and a reusability experiment were carried out. It was observed that with an increase in the concentration of SBS, the decomposition efficacy increased. The 13BVSBS and 15BVSBS exhibited the highest photocatalytic elimination efficacies among the synthesized photocatalysts, of 88.7% and 89.6%, respectively. However, owing to its cost-effectiveness, 13BVSBS was considered to be the more efficacious photocatalyst. The decomposition efficacy of the synthesized nanocomposites was also compared to commercial $\text{TiO}_2\text{-P25}$ to test the superiority of the prepared nanocomposites. The trapping studies confirmed that $\text{OH}^\bullet$ radicals were the major scavenging agent in the decomposition experiment. The reusability experiment suggested that the synthesized photocatalysts are reusable and easily recoverable even after five cycles. The BET, SEM, and XRD post degradation experiments demonstrated that the surface area characteristics, morphology, and crystallinity of the material did not change after photocatalysis. GC–MS was carried out to validate the intermediates and the products generated during the breakdown of the TC. High % COD and % TOC values for the mineralization of TC confirmed that the synthesized composite is an excellent choice for the photocatalytic remediation of the detrimental antibiotic. Therefore, the BVSBS photocatalyst offers huge possibilities for the decomposition of detrimental pollutants.

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Conclusions and Future Perspectives

This present thesis work includes the fabrication of various mole ratios of 5 different sunlight driven photocatalysts i.e., BiVO₄/MoSe₂, BiVO₄/SnS₂, BiVO₄/BiOBr, BiVO₄/WO₃, and BiVO₄/Sb₂S₃ by hydrothermal route. The synthesized heterojunction photocatalysts possessed a high surface area, narrow band gap, lower recombination rate and good carrier charge transport ability than their bare components. One of the important characteristics of these photocatalysts is their good reusability and high stability. Thus, these photocatalysts can be effectively used multiple times without significant deterioration in their performance. The performance of the fabricated photocatalysts was gauged by conducting the photocatalytic degradation studies for the different pharmaceutical contaminants, and PEC water splitting. The impact of pH of the solution, concentration of the photocatalyst, influence of different light sources was all studied for the photodegradation process. Quenching experiment was also performed to understand the role of active radical species responsible for the degradation of the pollutant. The reusability studies were conducted of the synthesized photocatalysts to establish their practical utility. Also, post degradation XRD, SEM, and BET were carried out to know the stability of the photocatalysts. For the PEC water splitting studies different experiments for e.g., LSV, EIS, chronoamperometry, and Mott-Schottky were carried out. Lastly stability study was conducted to assess the stability of the electrode and quantify hydrogen evolution rate. The outcomes revealed that the heterojunction photocatalysts exhibited good efficiency compared to the corresponding bare ones. This can be attributed to their higher surface area, increased number of active sites, lower recombination rate, and good charge migration ability to promote high reaction kinetics. The fabricated heterojunction photocatalysts can be efficiently utilized for the decomposition of the various organic pollutants present in the wastewater and for PEC water splitting to evolve the hydrogen.

Among the prepared photocatalysts compared in **Table 7.1**, the BiVO₄/WO₃ photocatalyst outperforms the others, exhibiting the highest removal efficiency (96.2 %) under optimal conditions and possess the highest current density of 0.64 mAcm⁻² at 1.23 V vs RHE with highest hydrogen production rate of 4.56 mmolcm⁻²sec⁻¹. This could be due to its high

surface area, and lower reintegration rate of the charge carriers. Hence, it the most effective catalyst for the photodegradation of the hazardous pollutant, TC and for the production of hydrogen via water splitting.

The future opportunities for this work primarily focus on wastewater purification and simultaneous hydrogen production. The photocatalysts used in this research hold enormous potential for further exploration in processes such as CO₂ reduction and ammonia reduction. owing to their easy synthesis, low production cost, and the feasibility of mass production.

Table 7.1 Comparison of fabricated photocatalysts for the photocatalytic abatement of TC and PEC hydrogen production.

Photocatalyst	Catalyst concentration (g/L)	Pollutant (10 ppm)	Reaction time (min)	Degradation efficacy (%)	H ₂ generation rate/onset potential
BiVO ₄ /MoSe ₂	0.2	TC	120	80.2	3.59 mmolcm ⁻² sec ⁻¹ / 0.40 mAcm ⁻²
BiVO ₄ /SnS ₂	0.2	TC	120	76.4	21 μmolcm ⁻² sec ⁻¹ / 0.21 mAcm ⁻²
BiVO ₄ /BiOBr	0.2	TC	120	68.8	1.86 mmolcm ⁻² sec ⁻¹ / 0.219 mAcm ⁻²
BiVO ₄ /WO ₃	0.2	TC	120	96.2	4.56mmolcm ⁻² sec ⁻¹ / 0.64 mAcm ⁻²
BiVO ₄ /Sb ₂ S ₃	0.2	TC	120	84.4	-

List of Publications

1.1 Related to Ph.D. work (objectives)

- i. **Shelly Singla**, Pooja Singh, Soumen Basu, Pooja Devi, BiVO₄/MoSe₂ Photocatalyst for the photocatalytic Abatement of tetracycline and photoelectrocatalytic water splitting, 295 (2023) 127111. *Materials Chemistry and Physics* (IF: 4.6).
- ii. **Shelly Singla**, Soumen Basu, Pooja Devi, Solar light responsive BiVO₄/SnS₂ for the photocatalytic elimination of recalcitrant antibiotics and photoelectrocatalytic water splitting with high performance, 118 (2023) 119-131. *Journal of Industrial and Engineering Chemistry* (IF: 6.1).
- iii. **Shelly Singla**, Pooja Devi, Soumen Basu, Highly Effectual Photocatalytic Remediation of Tetracycline under the Broad Spectrum of Sunlight by Novel BiVO₄/Sb₂S₃ Nanocomposite, 13 (2023), 731. *Catalysts* (IF: 3.9)
- iv. **Shelly Singla**, Pooja Devi, Soumen Basu, Revolutionizing the Role of Solar Light Responsive BiVO₄/BiOBr Heterojunction Photocatalyst for the Photocatalytic Deterioration of Tetracycline and Photoelectrocatalytic Water Splitting, 16 (2023) 5661. *Materials* (IF: 3.4)
- v. **Shelly Singla**, Pooja Devi, Soumen Basu, Unleashing the power of solar light: WO₃ nanorods decorated onto BiVO₄ fern-petals for tetracycline detoxification and water splitting. *Environmental Science and Pollution Research* (IF: 5.8) (Accepted).

1.2 Review Articles

- i. **Shelly Singla**, Surbhi Sharma, Soumen Basu, Nagaraj P. Shetti, Kakarla Raghava Reddy, Graphene/graphitic carbon nitride-based ternary nanohybrids: Synthesis methods, properties, and applications for photocatalytic hydrogen production, 24 (2020) 100200. *FlatChem* (IF: 6.2).
- ii. **Shelly Singla**, Surbhi Sharma, Soumen Basu, Nagaraj P Shetti, Tejraj M Aminabhavi, Photocatalytic water splitting hydrogen production via environmental benign carbon

based nanomaterials, 46 (2021) 33696-33717. *International Journal of Hydrogen Energy* (IF: 7.2).

- iii. **Shelly Singla**, Soumen Basu, Nagraj P. Shetti, Kunal Mondal, Tejraj M Aminabhavi, Hydrogen Production Technologies - Membrane Based Separation, Storage and Challenges, 302 (2022) 113963. *Journal of Environmental Management* (IF: 8.7).
- iv. **Shelly Singla**, Nagraj P. Shetti, Soumen Basu, Mallikarjuna N Nadagouda, Tejraj M Aminabhavi, Mineralization/Degradation of PFAS using Different Techniques. *Chemosphere* (IF: 8.8) (Revision submitted).

1.3 Other Publications

- i. **Shelly Singla**, Surbhi Sharma, Soumen Basu, MoS₂/WO₃ heterojunction with the intensified photocatalytic performance for decomposition of organic pollutants under the broad array of solar light, 324 (2021) 129290. *Journal of Cleaner Production* (IF: 11.1).
- ii. Charu Maggu[†], **Shelly Singla**[†], Soumen Basu, Unleashing the power of sunlight: Bi₂O₃/Sb₂S₃ photocatalysis for sustainable wastewater remediation of tetracycline and rhodamine-B. *Journal of Environmental Management* (IF: 8.7) (Revision submitted)

([†] equal contribution)

1.4 Book Chapter

- I. **Shelly Singla**, Soumen Basu, Pooja Devi. Possible ways for CO₂ Reduction into Hydrocarbons, (2022), 169-186. *Wiley Book Entitled- Materials Advances for Sustainable Environment and Energy: Theory, Status, and Challenges*.

Conferences and Workshops

1. Oral Presentation on “**Solar light active BiVO₄/SnS₂ nanocomposite for the photocatalytic degradation of antibiotics and photoelectrocatalytic water splitting**” at International Conference on Emerging Materials for Sustainable Development held in CSIR-CSIO, Chandigarh on October 2022.
2. Students project proposal entitled “**Fabrication of sunlight responsive hybrid semiconductors for photocatalytic abatement of organic pollutants and photoelectrocatalytic water splitting**” got accepted by Materials Research Society of India (MRSI) (presented as a speaker at IUMRS-ICA at IIT Jodhpur on 23rd December 2022).
3. Attended an International conference on Beyond the Contemporary Sciences, November 2022.