

Sukhandeep Kaur Thesis

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Introduction and literature review

1.1 Introduction

In the wake of ever-increasing environmental issues, including contamination of freshwater sources, overexploitation of earth's non-renewable energy sources, deteriorating air quality, and global heating of the planet, the primary anticipation about photocatalysis is undoubtedly rooted in the need for energy conservation and environmental remediation. Photocatalysis is modeled after the natural process of photosynthesis, which employs optical energy to propel chemical reactions. Thus, photocatalysis utilizes light-energy-induced redox reactions to provide practical, sustainable solutions through cleaner energy sources and improved environmental health.[1] The essence of this technology lies in developing neoteric photocatalysts capable of capturing both visible and ultraviolet (UV) radiations, which are the key constituents of solar light, a renewable energy resource.

1.1.1 Semiconductor Photocatalysis

Photocatalysis essentially comprises four fundamental steps: (i) absorption of light by the photocatalyst to produce excitons (e^-h^+ pairs), (ii) charge separation, (iii) transport of charges to the photocatalysts' surface, (iv) redox reactions mediated by the e^- s and h^+ s at the surface.[2] Typically, a photocatalyst absorbs light photons possessing energy ($h\nu$) higher than its band gap (E_g).[3] When a photocatalyst is placed in the field of a light source with photons of required energy, the electrons (e^- s) from the valence band (VB) of the semiconductor get excited to the conduction band (CB), creating positively charged holes (h^+) in the VB.[4] In heterogeneous photocatalysis, the various organic pollutant materials can be adsorbed at the semiconductor material's surface and degraded into minor, non-toxic by-products like (CO_2 and H_2O) by undergoing oxidation and reduction reactions initiated by the e^- s and h^+ s.[5] In addition, the charges formed also undergo recombination at the surface as well as in the bulk of the photocatalyst. This process releases heat or light energy and is detrimental to the overall photocatalytic ability of the semiconductor material.[6]

1.1.2 Wastewater remediation

Deterioration of environmental resources, lack of clean air and water, and the depletion of the earth's energy reserves are the significant crises of today's generation. The rapid rise in global population and unregulated industrial expansion have led to the overconsumption of energy. Concurrently, the unabashed discharge of untreated industrial and chemical waste into the air and water bodies has caused epidemics, global warming, and the seeping of poisonous chemicals into our food chain. Thus, our objective should be to look for environmentally and ecologically safe solutions for energy production and treating toxic industrial effluents. Some prominent water pollutants include pesticides, pharmaceuticals, personal care products, and industrial dyes. The persistence of these contaminants in the water bodies adversely impacts human and aquatic life. Pharmaceutical drugs like antibiotics and analgesics have often been found in high amounts, either untreated or in forms of various metabolites. Unchecked exposure to medicaments like tetracycline, amoxicillin, and paracetamol can cause antibacterial resistance, liver dysfunctions, skin irritations, and anemia.[7–9]

Advanced oxidation processes (AOPs), like semiconductor photocatalysis, which harnesses abundant, clean, and safe light energy, are an elegant solution for treating this contaminated water. Semiconductor photocatalysis is advantageous over other water treatment methods owing to its low cost, reusability, non-toxicity, and optimal cost.[10] This process involves the formation of reactive oxygen species (ROS) like $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ upon the redox reactions of O_2 and H_2O molecules with the photoexcited charge carriers (e^- - h^+). The redox potentials of most organic toxicants fall between $-1\text{eV} - 2\text{eV}$, which is well within the redox capacity of the ROS formed. A defining characteristic of AOPs is their ability to produce highly reactive ROS ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$) whose oxidative power surpasses even ozone and hydrogen peroxide. These reactive species will oxidize or reduce a majority of contaminants to less toxic by-products, CO_2 , H_2O , and other simpler compounds. Thus, in recent years, AOPs have substituted most water treatment methods.

1.1.3 ZnO and TiO_2 as photocatalysts

Numerous photocatalysts have been extensively explored in the literature, for example, metal-oxides, metal-nitrides, and metal-sulfides; however, the primary focus of this study is two conventional semiconductor-oxides, namely, ZnO and TiO_2 . Both these materials are suitable candidates for photocatalysis due to their wide band gaps ($E_g(\text{ZnO}) \sim 3.2\text{ eV}$ [11], and $E_g(\text{TiO}_2) \sim$

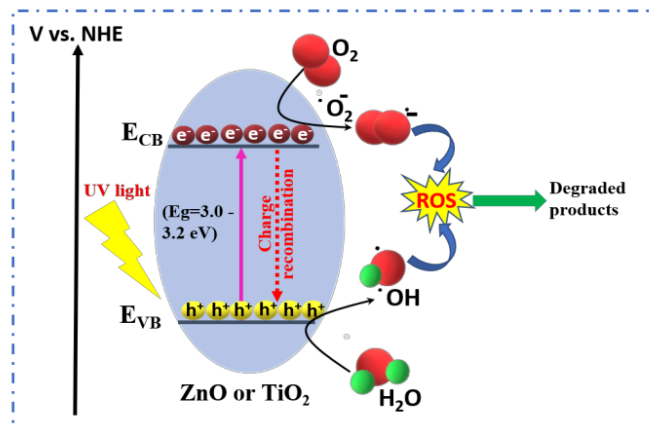
3.0 for rutile phase, and 3.2 for anatase phase[12]), chemical stability[13], non-toxic properties, lower cost, and higher photostability.[14] A very early report by Markham et al. described the UV-light-induced photocatalytic oxidation of organic compounds by some metal-oxides, including TiO₂ and ZnO.[15] After this, numerous researchers have exploited the photocatalytic abilities of these two metal oxides for wastewater remediation, hydrogen production, and self-cleaning materials (shown in **Table 1.1**). These photocatalysts fall under the heterogeneous category of AOPs. Semiconductor-mediated heterogeneous catalysis has an edge over homogeneous catalysis because it harnesses air as an oxidizing agent and performs effectively under ambient temperature and pressure conditions. ZnO and TiO₂ metal oxides have gained popularity as photocatalytic materials owing to their optical absorption properties, chemical and physical stability, and low cost. Although the specific photocatalytic degradation mechanism is unique for each pollutant, the primary process involves the abovementioned four fundamental steps. It is often crucial to understand the formation, relaxation, transfer, and recombination of the photogenerated excitons to decode the entire photocatalytic process.

Table 1.1 Summary of the photocatalytic performances of bare ZnO and TiO₂ catalysts.

S.No.	Photocatalyst used	Pollutant	Irradiation	Degradation efficiency	Ref.
1	ZnO	Phenol, O-Cresol	180 min Sunlight	51%, 52%	[16]
2	ZnO	Methyl orange	420 min UV light	87%	[17]
3	ZnO	Methylene blue	10 min Visible light	31%	[18]
4	ZnO	Methyl orange	30 min UV light	99.7%	[19]
5	P25 TiO ₂	Rhodamine B	120 min UV light	55%	[20]
6	TiO ₂	Methylene blue	180 min UV light	97.5%	[21]
7	TiO ₂	Orange II	2000 min UV light	89.5%	[22]

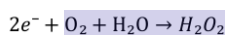
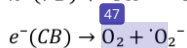
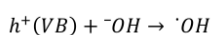
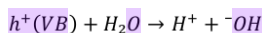
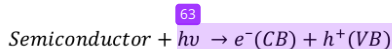
Before delving into the photocatalytic processes at the surface of ZnO and TiO₂ succeeding light exposure, it is imperative to grasp the situation prior to illumination. The bulk of organic molecules surrounding the surface of the photocatalytic material can form bonds with the surface atoms. This process is labeled as dark adsorption, and if the reactant or any intermediate molecule forms strong chemical bonds with the exposed surface sites of the photocatalyst, photocatalysis would not be possible. Conversely, if the ⁷⁷interactions between the organic molecules and the surface atoms are

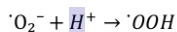
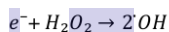
weak, the reaction intermediates can easily be desorbed, thus forming various degradation by-products.[10,23]



Scheme 1.1 A schematic illustration of the photocatalytic mechanism of ZnO and TiO₂.

When the ZnO or TiO₂ materials are exposed to ultra bandgap irradiations, the e^- from the valence band (VB) gets excited to the conduction band (CB), leaving behind h^+ in the VB. After their formation, the fate of the photogenerated charge carriers can either be their rapid recombination or the surface redox reactions with electron and hole acceptors.[10] The excess e^- in CB reduces the dissolved O_2 to produce O_2^- , and the h^+ in the VB produce $^{\bullet}OH$ upon oxidation of H_2O and ^-OH . Both these ROS have the ability to mineralize a wide variety of organic contaminants. The organic pollutants can eventually be converted into simple molecules like CO_2 , H_2O , and other non-toxic by-products (shown in **Scheme 1.1**). The following equations demonstrate the sequential redox reactions involved in the photocatalytic degradation process:



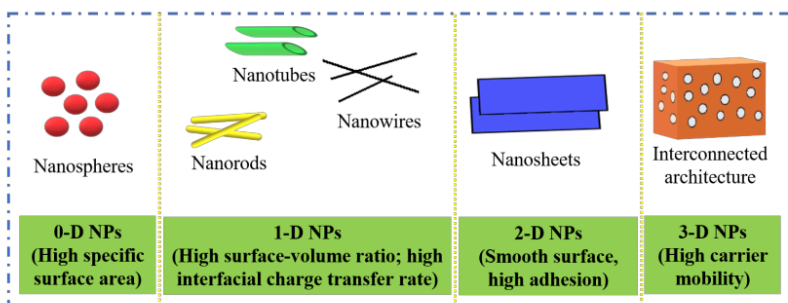


Organic pollutants $\rightarrow CO_2 + H_2O + \text{other degradation products}$

1.1.4 Morphologies of nanoparticles

Nanotechnology implies producing objects of a size in the nanoscale range, i.e., ~ 1-100 nm, and nanoparticles are the most significant products of it. Nanoparticles are important in heterogeneous catalysis because by reducing the size of particles to the nanoscale, their surface-to-volume ratio increases, and their catalytic properties are significantly altered.[24] The nanoparticles can be classified based on their morphologies as follows:

- i) Zero-dimensional nanoparticle (0-D): All three dimensions of these nanoparticles are in the nanoscale. Examples are nanospheres and quantum dots.
- ii) One-dimensional nanoparticles (1-D): One of the dimensions of nanoparticles is outside the nanoscale. These include nanorods, nanowires, and nanotubes.
- iii) Two-dimensional nanoparticles (2-D): In this class of nanoparticles, two dimensions are outside the nanoscale. Examples are nanofibers and nanosheets.
- iv) Three-dimensional nanoparticles (3-D): The nanoparticles are not confined to the nanoscale in any dimension. These include nanoflowers, bulk powders, and arrays of 1-D particles.[25]



Scheme 1.2 Illustration of various morphologies of nanoparticles.

The photocatalytic properties of these nanomaterials are highly dependent upon the morphological parameters of the NPs, including their aspect ratio, surface area, and crystallographic orientations. The morphological changes of NPs can highly affect their surface-to-volume ratios and electron transfer properties, eventually impacting their photoabilities. The unique properties of different morphologies are shown in **Scheme 1.2**.

1.1.5 Limitations of ZnO and TiO₂ photocatalysis

The photocatalytic efficiency (η) is often assessed as the rate of formation of products divided by the number of incident photons. Unfortunately, this is relatively low (<10%) with pristine ZnO and TiO₂. This low efficiency is primarily caused by the rapid recombination of the photoexcited charge carriers (e^-h^+), which leads to a lower concentration of ROS that are ultimately responsible for the deterioration of contaminants.[26] Further, the wide band gaps of TiO₂ and ZnO make them active only towards UV light, therefore possessing a limited photo-response. Moreover, the organic pollutants are hydrophobic; thus, they tend to have a lower affinity towards these semiconductor photocatalysts. This repulsion decreases the chances of an effective interaction between the pollutant molecules and the surface of photocatalysts.[27] Thus, studies need to be conducted to improve these photocatalysts' optical and electronic parameters, sensitize them to visible light, and improve the lifetime of excitons.

1.1.6 Strategies for improvement of photocatalysis

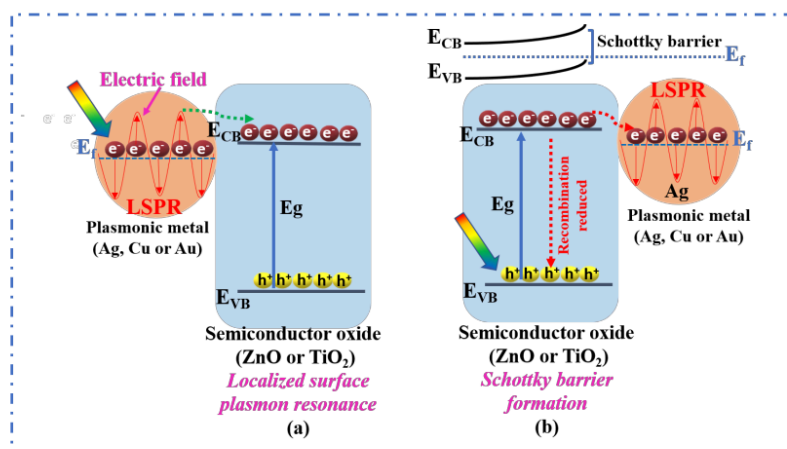
Several strategies have been employed to enhance the photocatalytic ability of semiconductor oxides, ZnO, and TiO₂, including heterojunction formation, metal deposition, metal doping, introduction of carbon materials, and transition metal doping. However, out of these techniques, the surface photodeposition of plasmonic noble metals has emerged as an outstanding choice.

Photodeposition of noble metals

Noble metal photodeposition is a widely studied strategy for modifying the band gap and extending the absorption range of semiconductor materials to higher wavelengths in the solar spectrum. The photodeposition of noble metals like Ag, Cu, and Au on the semiconductor surface can suppress the rejoining of photogenerated excitons and increase the concentration of charge carriers, thereby enhancing their photocatalytic activity. Unlike doping, the noble metal's Fermi level differs from ZnO and TiO₂. Upon contact, due to energy instability, electrons transfer from the material with

the higher Fermi level to the one with the lower Fermi level. As a result, the formed space charge layer increases the number of active sites, extends the lifetime of e^-h^+ pairs, increases the interval available for redox reactions, and promotes the generation of additional excitons.[28] The introduction of plasmonic metals at the surface of semiconductors induces dual benefits: (i) visible light activation due to the surface plasmonic resonance (LSPR) effect and (ii) electron trapping due to Schottky barrier formation (Scheme 1.3).

Localized surface plasmon resonance (LSPR) arises when the valence electrons in plasmonic metal nanoparticles undergo synergic oscillations due to the influence of an external light-induced electric field. This effect enhances light absorption and significantly strengthens the localized electric fields near the metal–semiconductor interface. In surface plasmon resonance, metal nanoparticles primarily serve as optical antennas, facilitating the conversion of incident light into confined electric fields, eventually dissipating, generating high-energy hot electrons. These hot electrons can multiply the photocatalytic activity many folds.[29,30] Electrons can transfer through the semiconductor-metal interface when a semiconductor oxide is in close contact with a metal of higher work function (ϕ). This diffusion of electrons will lead to an equilibrium between the fermi levels of both materials.[31]

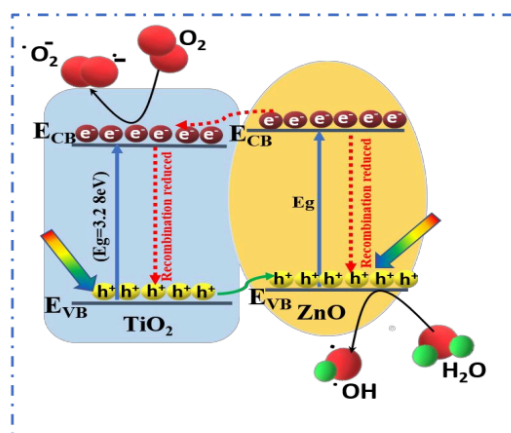


Scheme 1.3 Schematic illustration of (a) surface plasmonic resonance effect of noble metals and (b) Schottky barrier formation.

Thus, a deformation of the conduction band of the semiconductor oxide occurs, forming a 'Schottky barrier.' The Schottky barrier will act as an e^- sink that can entrap these charge carriers. The confined e^- s move toward the catalyst's surface to induce the redox reactions. The Schottky barrier prevents the backflow of diffusing electrons to the conduction band of ZnO or TiO₂, thereby reducing e^-h^+ recombination. Consequently, the photocatalytic reaction rate is improved, as the active charge carriers on both the semiconductor oxide and noble metal surfaces can independently participate in redox reactions.[32]

Formation of ZnO-TiO₂ nanohybrids

Variations in bandgap positions and redox potentials among semiconductors make it possible to engineer interfaces that enhance electron mobility while limiting the recombination of charge carriers. Therefore, establishing a well-matched heterojunction is essential, primarily governed by the relative positioning of the semiconductor band positions and the uniformity of their interfacial contact. A ZnO-TiO₂ combination is well-suited for forming a type II heterojunction via direct surface coupling, enabling effective charge separation (Scheme 1.4).[33,34]



Scheme 1.4 Schematic illustration of the formation of a ZnO-TiO₂ heterojunction.

These semiconductor-semiconductor nanohybrids are especially promising in photocatalytic and photoelectrochemical contexts due to their substantial bandgaps (~3.2 eV) and notable

photoactivity. The type II heterojunction created between ZnO and TiO₂ consequently suppresses rapid electron-hole recombination, making it highly effective for energy conversion and environmental applications.[35]

Incorporating these modifications into pristine ZnO and TiO₂, several research groups have fabricated efficient materials for environmental applications. Raji et al. synthesized ZnO:Ag plasmonic nanostructures via the co-precipitation method.[36] The ZnO:Ag nanostructures were highly effective in the sunlight-induced photocatalytic degradation of sulforhodamine B. The exceptional photocatalytic performance of these nanostructures was primarily due to Ag's ability to capture electrons owing to its high electronegativity, improved solar energy absorption via plasmonic effects, the expanded surface area of ZnO:Ag nanostructures, and the formation of a Schottky barrier at the Ag-ZnO interface. Lu et al. designed Ag nanocubes/ZnO microspheres to remove ionic liquids efficiently.[37] An Ag content of 1.12% could degrade 90% of ionic liquids within 7 hours. Zia Shahabi et al. developed a novel Ag/ZnO hybrid nanostructure demonstrating high-efficiency photocatalytic degradation of methylene blue under visible light and without illumination.[38] It was found that the hybrid nanostructure's absorption edge shifted into the visible spectrum, driven by the combined influence of Ag's plasmonic effect and defects in ZnO. Thus, this study offers valuable guidance for designing a robust plasmonic-metal oxide nanocomposite capable of efficiently degrading dyes, with and without light. In addition to dyes, pharmaceutical drugs have emerged as top-class pollutants in recent years. Onkani et al. conducted a comparative study on the photodegradation of ciprofloxacin (CPF) and tetracycline (TC) using a ZnO photocatalyst and its Ag-doped variants (2.5%, 5%, and 7.5%).[39] While Ag doping had minimal impact on the ZnO crystal structure, it significantly increased the specific surface area, enlarged pore size, and reduced band gap energy. Among the tested compositions, 2.5 wt% Ag-ZnO exhibited the most favorable properties, achieving a 50% and 43% improvement in CPF and TC degradation, respectively, compared to pristine ZnO. Veziroglu et al. focused on the photodeposition of Au nanoclusters onto TiO₂ thin films, resulting in improved photocatalytic degradation of dyes.[40] The Au-modified TiO₂ exhibited enhanced activity towards methyl orange under visible light due to the SPR effect of Au nanoparticles. Optimal photodeposition time and Au content were critical to achieving peak performance. Dvoranová et al. synthesized TiO₂ NPs modified with varying molar ratios of Ag and CuO using an aqueous sol-gel method.[41] The modified samples were tested for the degradation of nitrogen oxides, removal of benzene, and

hydrogen production. It was found that the TiO₂ modified with an Ag:Cu molar ratio of 1:1 (Ag 0.50 wt%/Cu 0.50 wt%) exhibited the most effective performance across all tested applications. It is also crucial to explore how different plasmonic metals (Ag, Cu, and Au) differ in enhancing the photocatalytic properties of ZnO and TiO₂. Nyamukamba et al. coated thin layers of copper and silver on fused silica using the thermal evaporation method.[42] Subsequently, a 100 nm titanium dioxide (TiO₂) film was deposited over the plasmonic metal layers through sputter coating. The photodegradation applications were explored employing methyl blue as a model pollutant. Silver demonstrated superior plasmonic performance compared to copper in enhancing the photocatalytic activity of TiO₂ under UV light. Copper exhibited better performance when placed beneath the TiO₂ film, whereas silver was more effective when deposited on top of the TiO₂ photocatalyst layer. Moreover, the photodeposition of the same metal upon ZnO and TiO₂ could have different impacts, even though both the semiconductors possess a comparable band gap. Zheng et al. compared Au-sensitized TiO₂ and ZnO nanoparticles for degrading pharmaceuticals under UV and visible light.[43] Au loading enhanced photocatalytic efficiency by broadening the light absorption range and improving charge separation. The materials showed strong potential for water purification, particularly against persistent pharmaceutical pollutants, namely, chloroquine phosphate (CLQ), paracetamol (PAR), diclofenac sodium (DCF), and ciprofloxacin (CIP). Exceptional degradation rates were achieved with all four pollutants, and the differences in photoactivity were seen as a function of pollutants. Additionally, using bimetallic layers further improved the photocatalytic efficiency of TiO₂ compared to single-metal layers. Several research groups have also explored the possibility of ZnO/TiO₂ hybrid formation to understand if these semiconductor oxides can provide better photoactivity when combined. Song et al. presented the highly efficient and selective photo-oxidation of methane to ethane using dioxygen in a flow reactor facilitated by an Au nanoparticle-loaded ZnO/TiO₂ hybrid catalyst.[44] Detailed studies were carried out to establish the role of the TiO₂/ZnO interface in the augmentation of photocatalytic ability. The results demonstrated that the synergy between ZnO, TiO₂, and Au enhanced the photocatalytic oxidation and reduction capabilities.

These findings by various research groups establish the role of plasmonic noble metals (Ag, Cu, and Au) in augmenting the photocatalytic efficiency of the UV-active ZnO and TiO₂ NPs under visible illumination.

1.2 Research Gaps

After an extensive literature review, it was found that although the ZnO and TiO₂-based photocatalysis has been well documented, a few sub-sections need further exploration. The role of plasmonic metals in enhancing photoactivity is widely known; however, the study of the effect of varied concentrations of the plasmonic metal loading upon different morphologies of the ZnO and TiO₂ nanoparticles was less common. It would be interesting to investigate how altering the amount of the metal photo deposited at the surface of the semiconductor could affect the enhancements in the photocatalytic activities. Additionally, it is crucial to find an optimum loading percentage of noble metals so that the overall cost of the photocatalysts produced is economically viable. Further, ZnO and TiO₂ have comparable band gaps (~3.0 – 3.2 eV), but assessing whether they have the same photocatalytic ability under similar reaction conditions is crucial. However, fewer reports present a contrast in the photocatalytic degradation efficiencies of these two conventional semiconductors. Moreover, the comparative effects of plasmonic-metal loading upon these photocatalytic materials have not been investigated. Determining whether coinage metals like Ag, Cu, and Au induce the same photocatalytic prowess in both semiconductor materials is imperative. Moreover, ZnO and TiO₂ are primarily investigated for their photocatalytic applications; however, these nanostructures could also act as adsorbents owing to their high surface areas. The synergic adsorption-photocatalytic mechanisms of removing pollutants by these nanocatalysts have also been explored less.

The enhancement of ZnO and TiO₂ using various techniques like composite formation, doping of plasmonic metals, and modifications with non-metals have been investigated by several groups. However, a semiconductor-semiconductor interface formation between ZnO and TiO₂ could also have some exciting outcomes. Only quite a few research groups have scrutinized this possibility, and there is room for further research. Moreover, the formation of ZnO-TiO₂ heterojunctions employing nanoparticles of distinct morphologies could augment the photocatalytic activity by enhancing both the adsorption and degradation processes. Additional modification of these nanohybrids with plasmonic metals could lead to the formation of superior photocatalysts for the much-needed environmental remediation. These types of ternary nanohybrids could not be found in any reports. Moreover, some non-conventional pollutants or pollutants causing indirect

pollution should also be examined, in addition to run-of-the-mill pollutants like dyes, drugs, and pesticides.

1.3 Objectives

1. Preparation and structural characterization of ZnO and TiO₂ nanostructures.
2. Influence of photo deposition of Cu, Ag, and Au onto as prepared ZnO and TiO₂ nanostructures for photocatalytic properties.
3. Study of adsorption properties and photocatalytic degradation of organic pollutants by as prepared nanostructures under visible light irradiation.

1.4 Characterization Techniques

Distinct chemical procedures were employed for the fabrication of different morphologies of pristine ZnO and TiO₂ nanostructures (NSs), coinage-metal (Ag, Cu, and Au) loaded ZnO and TiO₂ NSs, and binary (TiO₂/ZnO) and ternary (metal@TiO₂/ZnO) nanohybrids (details of each are discussed in respective chapters). The numerous characterization techniques employed for the rigorous assessment of the structural, morphological, optical, and electrical properties of these materials are discussed below:

1.4.1 X-ray powder diffraction (XRD)

The crystalline structure, phase purity, and diffraction patterns of all the synthesized materials were analyzed via X-ray powder diffraction technique. The measurements were done with 2θ ranging between 20° - 80° using an X'pert PRO powder diffractometer (PANalytical) fitted with a Cu-K alpha radiation source having $\lambda = 1.544 \text{ \AA}$. The readings were obtained at a step size of 0.02°.

1.4.2 Morphological analysis

The morphological analysis of the various fabricated nanostructures was carried out by employing field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The FE-SEM analysis was carried out using the Carl Zeiss Sigma 500 electron microscope, possessing a resolution of 0.8 nm @ 15 kV and 1.4 nm @ 1kV. This microscope was fitted with Bruker, QUANTAX 200 energy-dispersive X-ray spectrometer (EDS), which was further utilized for elemental composition analysis. The HR-TEM images were acquired using a JEM-2100 (JEOL) 200kV analytical electron microscope.

1.4.3 Electrokinetic analysis

Zeta potential analysis and the dynamic light scattering approach were used to illustrate the electrokinetic characteristics of the fabricated materials. The analyses were performed on a Zetasizer Nano ZS (Light source: He: Ne laser) system using a disposable cuvette (for DLS analysis) and folded capillary cell (for zeta). The dispersions of the prepared nanostructures were prepared in distilled water, with 2 mg catalyst in 10 mL DI water.

1.4.4 Surface area and porosity determination

The surface area, pore volume, and pore diameter of the prepared nanocatalysts were assessed by studying the N₂ adsorption-desorption curves (Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models) obtained using a Quanta Chrome Nova 2200 Surface area analyzer.

1.4.5 Optical and electrical analysis

The optical absorption characteristics of each powder sample were obtained by employing a JASCO V-750 UV-visible spectrophotometer equipped with an integrating sphere. The measurements were done over a 200 – 800 nm wavelength range using BaSO₄ as a reference. The spatial separation and the lifetime of photogenerated excitons (e⁻ and h⁺) in various photocatalytic materials were determined by analyzing their room-temperature photoluminescence (PL) spectra. The measurements were recorded using a SHIMADZU RF-6000 spectrofluorometer at various excitation wavelengths selected according to the respective materials. For this examination, the dispersions of the various photocatalysts were made in DI water.

1.4.6 X-ray photoelectron spectroscopy (XPS)

The oxidation states and elemental configuration of the fabrication photocatalysts were elucidated using X-ray photoelectron spectroscopy (XPS) analysis. The measurements were performed employing a Thermo Fischer ESCALAB QXi Microprobe using a micro-focussed Al K α source.

1.4.7 Raman spectroscopy

A Labram HR, a Horiba Raman spectrometer equipped with a 532 nm excitation laser, was used to perform Raman spectral studies.

1.5 Adsorption and Photocatalytic activity

The photocatalytic efficiency of the prepared plasmonic-metal modified ZnO and TiO₂-based nanostructures was assessed based on their abilities towards the removal of organic pollutants. The removal of pollutants consists of two steps:

1.5.1 Adsorption studies

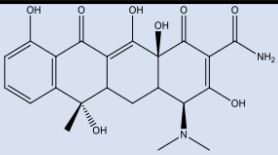
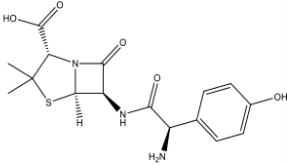
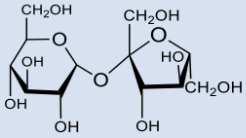
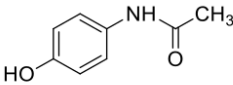
The adsorption of various organic pollutants upon the fabricated photocatalysts was assessed under dark conditions. A required amount of photocatalyst was added to different test tubes containing the aqueous pollutant solutions. These dispersions were stirred under dark conditions, and the solutions were collected after fixed time intervals and ultracentrifuged to separate the photocatalyst. The remaining pollutant concentrations were assessed using a UV-visible spectrophotometer (JASCO V-750) to measure the changes in absorption spectra before and after the adsorption process. The fitting of reaction parameters into the Langmuir and Freundlich models was examined for insights into the adsorption mechanism. Pseudo-first and second-order kinetic models were implemented to forecast the reaction kinetics. The corresponding chapters provide a detailed explanation of the intricate processes and formulas.

1.5.2 Photocatalytic degradation studies

The photocatalytic degradation studies of various pollutants (listed in Table 1.2) were performed using separate test tubes containing a fixed amount of photocatalysts dispersed in 5-10 mL of aqueous solutions of the toxicants. Before subjecting these test tubes to visible irradiation, these dispersions were stirred under dark conditions until the adsorption-desorption equilibria were reached between the photocatalyst and the pollutant. These solutions were then exposed to visible LED light (50W, WIPRO Garnett B22, intensity ~ 100 Watt/m², $\lambda > 365$ nm) installed inside a wooden chamber. After fixed time intervals, the solutions from the test tubes were collected, and the catalysts were separated from the dispersions via ultracentrifugation. The changes in concentration of the residual solutions of the pollutants were analyzed using UV-visible spectroscopy. The photodegradation efficiencies and reaction kinetics of various photocatalytic materials were assessed using the equations mentioned in the following chapters. Furthermore, the extent of mineralization of various toxicants by the prepared materials was assessed by TOC (total

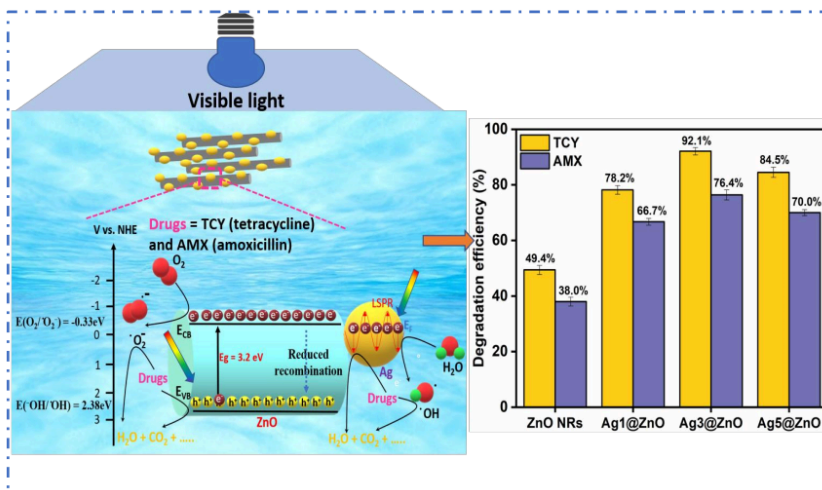
organic carbon) studies using titration techniques. Lastly, the reaction intermediates and by-products were identified using a high-resolution mass spectrometer (Waters QTOF with UPLC).

Table 1.2 Model pollutants chosen for the photocatalytic degradation studies using the fabricated nanostructures.

Chosen organic pollutant	Chemical formula	Chemical structure	Detrimental impacts
Tetracycline	C ₂₂ H ₂₄ N ₂ O ₈		Antimicrobial resistance, aquatic ecosystem disruption, bioaccumulation[45]
Amoxicillin	C ₁₆ H ₁₉ N ₃ O ₅ S		Ecotoxicity, antimicrobial resistance, and endocrine disruption[46]
Sucrose	C ₁₂ H ₂₂ O ₁₁		Eutrophication, sucrose-contaminated water becomes a habitat of pathogens, has high BOD and COD, and reduced light penetration[47]
Acetaminophen or Paracetamol	C ₈ H ₉ NO ₂		Oxidative stress in aquatic life, limited degradation, embryonic abnormalities, bioaccumulation[48]



Influence of Ag-photodeposition on ZnO nanorods for the enhanced visible-light-induced degradation of tetracycline and amoxicillin



Schematic summary

2.1 Introduction

Antibiotic use for treating bacterial infections is at an all-time high due to advancements in the medical care system.[1,2] Tetracycline (TCY) and amoxicillin (AMX) are two common drugs that pharmaceutical industries supply. Tetracycline is a broad-spectrum naphthacene antibiotic used to cure bacterial infections in humans, livestock, and poultry.[3] Amoxicillin is a penicillin antibiotic containing a β -lactam ring and is a high-priority human and animal drug.[4,5] Due to their incomplete metabolism, these drugs are often discharged into the environment in unmodified forms.[6] Hospital and industrial effluents contain high amounts of TCY ($\sim 2 \text{ ppm}$) and AMX ($\sim 30 \text{ ppm}$).[7,8] These antibiotics form very stable and non-biodegradable water-soluble complexes, thus contaminating drinkable water.[9] High concentrations of these medicaments in surface water

and groundwater increase antimicrobial resistance in living beings and produce other toxic by-products.[10,11] Various processes to remove these recalcitrant drugs include coagulation-flocculation, adsorption, membrane filtration, and advanced oxidation processes.[12] Among these, photocatalysis is emerging as a low-cost solution due to its ambient reaction conditions and non-toxic by-products like water and carbon dioxide production. However, photocatalysis suffers drawbacks like fast recombination of photogenerated charge carriers and lower visible light harnessing ability.[13] In recent years, semiconductor photocatalysts (ZnO and TiO₂) have emerged as an elegant solution due to their ³⁵chemical stability, non-toxicity, high band gap, and low cost.[14–17] Although TiO₂ and ZnO have similar band gaps, ZnO is emerging as a better photocatalyst due to its higher electron mobility and swift electron transfer, exhibiting augmented absorption ability over a broader range of the solar spectrum.[18,19] Recently, Jin et al. reported ZnO nanorods/K-doped g-C₃N₄ nanosheets nanocomposites with varying concentrations of K-CN (K-CN_x), which demonstrated high tetracycline degradation efficiency (90% in 2 hours) under simulated sunlight.[3] Lai et al. loaded CeO₂ nanoparticles onto carbonate-doped Bi₂O₂CO₃ via hydrothermal method followed by calcination for degradation of tetracycline (79.5%) under visible light.[20] Giam et al. fabricated Mn-doped Cu₂O and degraded 92% amoxicillin (15 ppm) under sunlight with a photocatalyst dosage of 1 gL⁻¹. [21] Jia et al. synthesized CdS/ZnO heterocomposites displaying 94.4% degradation of tetracycline (at pH=7) in 120 minutes under visible light irradiation.[22] Y. Li et al. synthesized coral-like BiVO₄ particles decorated on ZnO nanorods for the effective photoelectrodegradation of tetracycline up to 84.5% under visible light.[23] Z. Zheng et al. fabricated a core-shell quaternary ZnO/ZnS/CdSe/MoS₂ film for complete photoelectrodegradation of 10 ppm amoxicillin in 30 minutes. The hierarchical composites displayed high surface area and facilitated electron transfer pathways resulting in superior activity.[24] Y. Tang et al. used CdS-MoS₂ coating on a vertical ZnO core for enhanced photoelectrochemical activity. The enhanced charge transfer and visible light absorption led to 94% degradation of 20 ppm amoxicillin in just 60 minutes.[25] M. Yu et al. doped BiVO₄ films with Mo to alleviate its high charge carrier recombination rate and poor conductivity. Thus, the developed Mo-doped-BiVO₄ films displayed 70% phenol degradation in 120 minutes.[26] It is seen that a high catalyst dosage and lower antibiotic concentration are commonly used to improve photocatalytic degradation efficiency. However, this higher catalyst amount cannot be used for large-scale wastewater treatment prospects.

Overcoming the abovementioned limitations is crucial in fabricating a superior photocatalyst. Incredibly, 1-Dimensional (1-D) ZnO nanorods (NRs), due to their shape anisotropy, possess higher surface area, large aspect ratios, high interfacial charge-carrier transfer, and higher e^-h^+ lifetime, thus giving them an edge over 0-Dimensional (0-D) spherical ZnO nanoparticles (NPs).[27–29] Additionally, the existence of certain surface defects and high aspect ratios could exhibit higher photocatalytic abilities.[30] However, ZnO is a semiconductor oxide with a high direct band gap of ~ 3.3 eV, demonstrating UV-lasing at room temperature.[18] But UV light constitutes only 3% of the solar spectrum. In contrast, a significant portion (44%) is contributed by visible light. As a result, a substantial amount of light goes unutilized.[31] Modifying the semiconductor oxide with a noble metal is a sophisticated route to subdue this challenge.[32,33] Noble metals like Ag display a localized surface plasmon resonance (LSPR) effect, and a resonant absorption band is obtained when visible radiation interacts with their electrons.[34,35] In addition, the Fermi-level of Ag is lower than the conduction band of ZnO, aiding the transfer of e^- s from the surface of the semiconductor to the noble metal.[36] Consequently, Ag-loading improves the photocatalytic degradation efficiency of the catalyst in two ways: spatial separation of charge carriers due to the formation of a Schottky barrier at the ZnO-Ag junction and expansion of the photoresponse of ZnO to the visible region due to the LSPR effect of Ag.[37,38] Out of many methods to achieve the modification of ZnO, like wet impregnation, chemical deposition, etc., photodeposition is a facile route due to its simplistic reaction conditions and typically has an enhancement factor (ratio of photocatalytic activity of modified catalyst to bare catalyst) of 2–4.[39,40]

In this study, Ag NPs (1wt%, 3wt%, and 5wt%) loaded ZnO nanorods (NRs) are synthesized via a solvothermal followed by reduction of Ag on their surface via a photodeposition process. Various techniques studied the prepared materials' morphological and photocatalytic properties to establish their exceptional efficiency. Also, a low catalyst dosage (0.25 gL^{-1}) was used for the removal of high concentrations (50 ppm) of antibiotics (TCY and AMX). So far, no reports have been found on the effects of the concentration of Ag (wt%) loading onto ZnO nanorods for the removal efficiencies of such a high dosage of commercial pharmaceuticals. Thus, we systematically study the same for fabricated materials in this report.

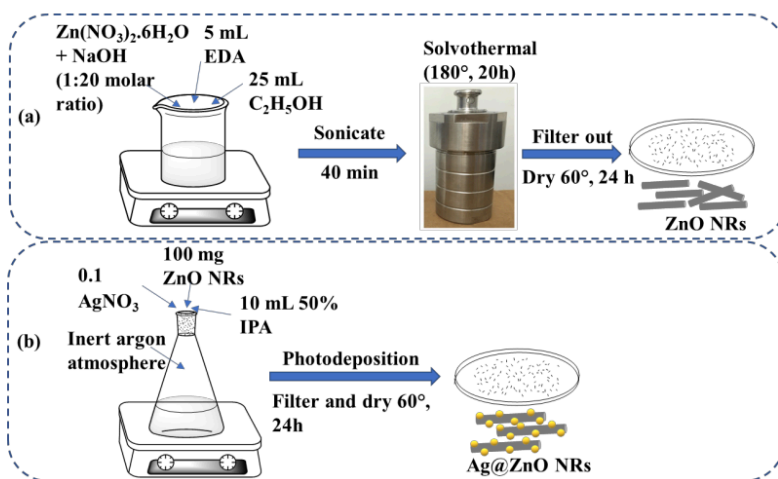
2.2 Experimental section

2.2.1 Chemicals and materials

Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], sodium hydroxide (NaOH), ethylenediamine EDA ($\text{C}_2\text{H}_4(\text{NH}_2)_2$), isopropyl alcohol (IPA) were purchased in high purity from Loba Chemie, India. Silver nitrate (AgNO_3) was bought from Sigma Aldrich, India. Ethanol was obtained from SD Fine Ltd. Triple distilled deionized (DI) water was purchased from Organo Biotech Laboratories Pvt. Ltd., India. All chemicals were of analytical grade and, therefore, used without further purification.

2.2.2 Synthesis of ZnO nanorods

ZnO nanorods were synthesized via a solvothermal process reported by Liu et al. (shown in Scheme 2.1(a)).[41]



Scheme 2.1 Schematic representation of the procedure for Synthesis of (a) bare ZnO NRs and (b) Ag@ZnO NRs.

Typically, an alkali solution was prepared by adding $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH in DI water, achieving the molar ratio $\text{Zn}^{+2}:\text{OH}^- = 1:20$. 3 mL of this solution was mixed with 0.5 mL DI water,

5-15 mL ethanol, and 0-5 mL EDA (ethylenediamine, $C_2H_4(NH_2)_2$) and pre-treated in an ultrasonication bath for about 35 minutes. Finally, the solution was transferred to a Teflon-lined autoclave and kept in a muffle furnace at 180° for 20 hours. After completion of the reaction, the white crystalline particles were harvested by ultracentrifugation and washed several times with deionized water. These particles were kept for drying in an electric oven at 80° for 12 hours to obtain a white powder.

2.2.3 Metal photodeposition

100 mg of as-prepared nanostructures are dispersed in 50% by-volume IPA solution. Then, according to the desired wt% loading required, different volumes of 0.01 M $AgNO_3$ (935-4675 μ L or 1.58-7.91 mg $AgNO_3$, corresponding to 1, 3, and 5 wt%) are added. This resultant solution was purged with argon gas for 20 minutes to achieve an inert atmosphere and kept under UV light irradiation (mercury arc lamp, power: 125W, intensity: 10.4 mW/cm^2) with magnetic stirring for up to 2 hours in a photochemical reactor. The resulting suspension was ultracentrifuged, and the obtained particles were washed several times with DI water and ethanol and dried at 50° for 8 hours. Thus fabricated nano-photocatalysts i.e., $Ag(1\text{wt\%})@ZnO$ NRs, $Ag(3\text{wt\%})@ZnO$ NRs, and $Ag(5\text{wt\%})@ZnO$ NRs have been abbreviated as $Ag_1@ZnO$ NRs, $Ag_3@ZnO$ NRs, and $Ag_5@ZnO$ NRs, respectively.

2.2.4 Photocatalytic activity analysis

The photocatalytic efficiency of each material was assessed as mentioned in Chapter 1, Section 1.5.2. Firstly, 1 mg of photocatalyst (0.2 g L^{-1}) was dispersed into 5 mL antibiotic solutions of 50 ppm concentration (0.05 g L^{-1}) contained in different test tubes. These suspensions were magnetically stirred for 40 minutes to achieve adsorption-desorption equilibrium. These suspensions are then exposed to visible light for 90 minutes. After regular intervals of 15 minutes each, solution from different test tubes were taken out one by one, centrifuged, and UV-VIS absorption spectra were recorded for TCY. The degradation of AMX was studied using a Thermo Fischer UHPLC equipped with a UV-detector and a C8 column. A gradient method of 10 minutes with methanol:water as a mobile phase with a flow rate of 1 mL/min was used. Initially, the methanol:water ratio remained at 30:70 for 2 minutes, followed by 40:60 for the next 2 minutes and 50:50 for the following 2 minutes. Afterward, the ratio changed to 70:30 for 2 minutes,

followed by 50:50 for 1 minute and 30:70 for the last minute. The efficiency of photocatalytic degradation was calculated by using the following formula:

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

(where η is the photocatalytic degradation efficiency (%), C_0 and C_t are the antibiotic concentration at the initial time ($t=0$ min) and at irradiation time ' t ' (min)). The reaction kinetics for the degradation of both pollutants were evaluated via the Langmuir-Hinshelwood model for a pseudo-first-order reaction:

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

(where k is the reaction rate constant (min^{-1}))

Active species involved in the process were determined using trapping experiments. The trapping process was performed the same way as photocatalytic degradation but with the addition of scavengers $\text{K}_2\text{Cr}_2\text{O}_7$, ascorbic acid (AA), IPA, and methanol initially. These act as agents to trap e^- , O_2^- , $\text{OH}^\cdot$, and h^+ , respectively. Further, to evaluate nanocatalysts' photocatalytic stability, the suspension was centrifuged after the degradation run, and the powdered sample was dried. This sample was then used in consecutive photocatalytic runs under the same conditions.

2.3 Results and Discussion

2.3.1 Structural analysis

X-ray diffraction patterns

The XRD patterns reveal high crystallinity and a wurtzite-type symmetry (hexagonal phase, space group: $\text{P6}_3\text{mc}$) for the ZnO NRs with lattice parameters $a_0 = 3.2495 \text{ \AA}$ and $c_0 = 5.2069 \text{ \AA}$. Fig. 2.1(a) shows peaks at $2\theta = 31.7^\circ, 34.4^\circ, 36.2^\circ, 47.5^\circ, 56.6^\circ, 62.9^\circ, 66.3^\circ$, and 68.9° corresponding to diffraction planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. Further, new peaks appear upon Ag loading at $2\theta = 37.9^\circ, 44.1^\circ$ and 64.3° corresponding to planes (111), (200), and (220) of cubic phase silver. The intensity of these peaks of silver increases with an increase in wt% of Ag (1-5%). Parallel to the rise in the concentration of Ag (1-5%), it is perceived that the intensity of the characteristic peaks of ZnO decreases. In addition, as shown in Fig. 2.1(b), the diffraction peaks of ZnO also shift to higher 2θ values upon Ag-loading, indicating the replacement of Zn^{+2} from its lattice sites by Ag^+ .

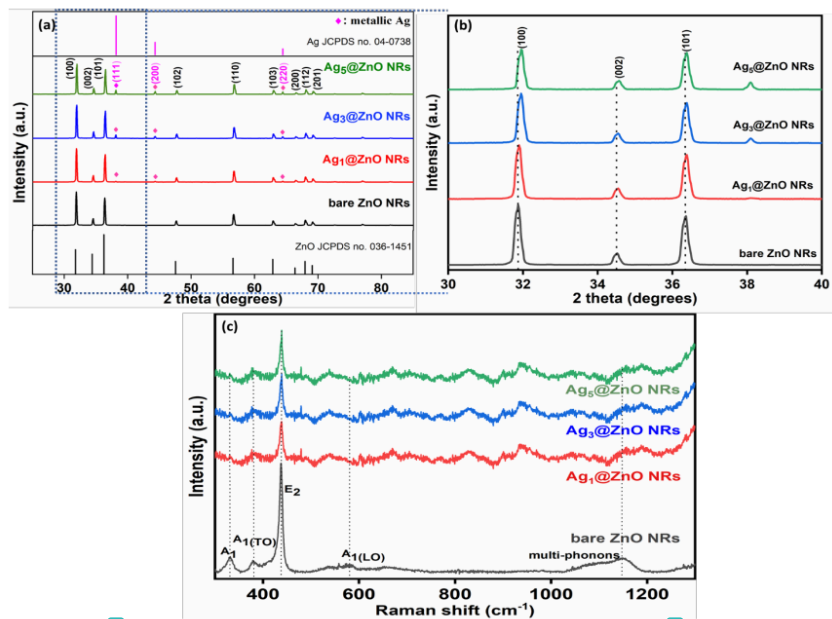


Fig. 2.1 (a) XRD patterns of bare ZnO NRs and its Ag-loaded counterparts, (b) Shift in the position of diffraction peaks (100), (002), and (101) ensuing 1, 3, and 5 wt% Ag- loading, and (c) Raman spectra of bare and Ag-loaded ZnO NRs.

But Ag^+ only partially occupies a few lattice sites due to its higher ionic radii (126 ppm) than ZnO (74 ppm). [43] The changes in the position of diffraction peaks, FWHM (full width at half maxima), and lattice parameters a_0 and c_0 are studied using two high-intensity peaks (100) and (101) of modified and pristine ZnO NRs (Table 2.1). As Ag-concentration increases, the FWHM increases, whereas lattice parameters of ZnO NRs gradually decrease, indicating a minute decline in crystallinity and crystallite size. Additionally, the crystallite size is calculated using the Debye-Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

(where D is the crystallite size, K is Scherrer constant having a value of 0.9, β is the full width at half maxima (FWHM), λ (1.54 Å) is the wavelength of X-Rays used, and θ is Bragg's diffraction

angle).[44] The computed values of ³crystallite sizes from the diffraction peak (100) are 47.65 nm, 47.40 nm, 47.14 nm, and 46.63 nm. This slight decrease in crystallite size upon Ag loading could be caused by the densification of particles by Ag.[45] The dislocation density (δ), which is a measure of the defects in a crystal system, was calculated by the following formula[46]:

$$\delta = \frac{1}{D^2} \quad (4)$$

(where D is ²the crystallite size). The microstrain of the lattice was calculated according to the William-Hall equation[46]:

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \quad (5)$$

(where D is the crystallite size, β is the FWHM, ϵ is the microstrain). The calculated values of δ and ϵ are listed in **Table 2.1**. A minuscule but gradual increase in crystal defects is observed with the increasing Ag density. The increase in dislocation density and micro strain are reported to augment the photocatalytic activity by causing a decline in recombination rates of spatial charge carriers.[47]

Table 2.1 Position (2 θ), FWHM, and lattice parameters for pristine and Ag-doped ZnO NRs using Rietveld refinement.

Amount of Ag (wt%)	2 θ and FWHM of peak (100) (deg)	2 θ and FWHM of peak (101) (deg)	Lattice parameters ($\text{\AA}$)		Dislocation density (δ) and microstrain (ϵ)	χ^2
			a_0	c_0		
0	31.8654 (0.1812)	36.3432 (0.195)	3.2492	5.2064	0.000440, 0.1320	3.77
1	31.8823 (0.1822)	36.3613 (0.198)	3.2489	5.2062	0.000445, 0.1326	3.54
3	31.9105 (0.1834)	36.3719 (0.201)	3.2487	5.2061	0.000450, 0.1332	3.26
5	31.9522 (0.1851)	36.3932 (0.226)	3.2483	5.2058	0.000459, 0.1348	3.81

The cell parameters and FWHM of the samples with increasing Ag-concentration were refined using Rietveld refinement by Fullprof software using P6₃mc symmetry. The peak shapes were fitted using the pseudo-Voigt function. The refinement of XRD data has been ⁵⁹shown in (Fig. 2.2). The refined parameters are shown in **Table 2.1**. A small decrease in lattice parameters is observed upon increasing Ag-concentration. This decrease could be caused by a minimal incorporation of

Ag into the ZnO lattice. However, this decrease is slight; thus, the maximum density of Ag must be deposited at the surface of ZnO nanorods.

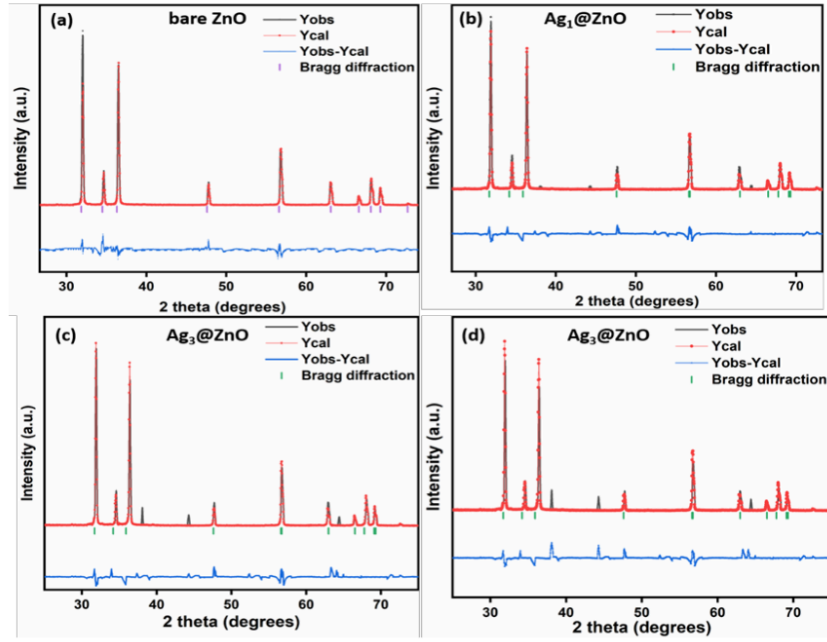


Fig. 2.2 Rietveld analysis of bare and Ag-loaded ZnO NRs.

Raman spectra analysis

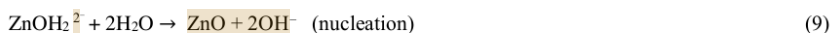
Raman spectroscopy was performed for further insights into materials' structural and morphological properties. In a typical Raman spectrum of ZnO, eight modes are observed: $1A_1 + 2B_1 + 1E_1 + 2E_2$ near the center of the Brillouin zone.[48] For ZnO NRs, five peaks are obtained at 332 cm^{-1} , 381 cm^{-1} , 437 cm^{-1} , 581 cm^{-1} , and 1145 cm^{-1} corresponding to A_1 , $A_1(\text{TO})$, E_2 , $A_1(\text{LO})$, and multi-phonons process (Fig. 2.1(c)). A_1 is a polar mode, whereas E_2 is a non-polar mode linked with vibrations of the oxygen atoms alone.[49] The Raman spectra for Ag-modified samples have $A_1(\text{TO})$ and $A_1(\text{LO})$ located at 379 cm^{-1} and 535 cm^{-1} , respectively, for all Ag concentrations. Upon Ag-decoration, a slight peak broadening and shift of 46 cm^{-1} are observed for $A_1(\text{LO})$ mode,

which could be assigned to scattering contributions outside the Brillouin zone. Moreover, the E₂ peak centered at 437 cm⁻¹ significantly decreases in intensity as the concentration of Ag NPs increases (1-5 wt%), further confirming the decline in crystallinity of ZnO nanostructures upon Ag-loading.[48]

2.3.2 Morphological analysis

FE-SEM, EDS, and HR-TEM analysis

The FE-SEM patterns and EDX spectra of bare and Ag₃@ZnO nanocatalysts are compared in Fig. 2.3 (a-f). The images clearly show the fabrication of rod-like structures with a calculated average diameter and length of 120.56 nm (population standard deviation, $\sigma = 25.09$ nm) and 1.356 μ m (population standard deviation, $\sigma = 0.619$ μ m), respectively (Fig. 2.4). Additionally, the FE-SEM images and EDX patterns of Ag₁@ZnO and Ag₅@ZnO are shown in Fig. 2.5(a,c). Thus, nanorods of a high aspect ratio of 9-14 are achieved. The nanorods have a uniform diameter throughout the length, and no further branching is observed. This indicates growth anisotropy along the c-axis.[41] The unidirectional growth of ZnO particles might be attributed to the addition of ethylenediamine, a known structure-directing agent. The following reactions possibly occur under high temperature and pressure conditions of the solvothermal process are:



The white precipitates of Zn(OH)₂ formed in Eq. 6 immediately react with excess OH⁻ to give a clear solution of Zn(OH)₄²⁻ ions (Eq. 7). Formation of ZnO nuclei spontaneously ensues in a supersaturated zinc and hydroxyl ions solution (Eq. 9).[50] The ethylenediamine present acts as a chelating agent, adsorbing to the zinc cations on the prismatic side planes of wurtzite ZnO, thus preventing growth of the rods in the radial direction.[41] Further, on the photodeposition of different wt% of Ag, the morphology of the catalyst remains unchanged. Still, small spherical particles are seen deposited on the surface of the rods, which might be Ag nanoparticles. The density of these tiny particles distributed on the rods is perceived to increase parallel to the growing

concentration of Ag NPs. The EDX spectra were performed for bare and Ag-loaded nanorods to confirm this.

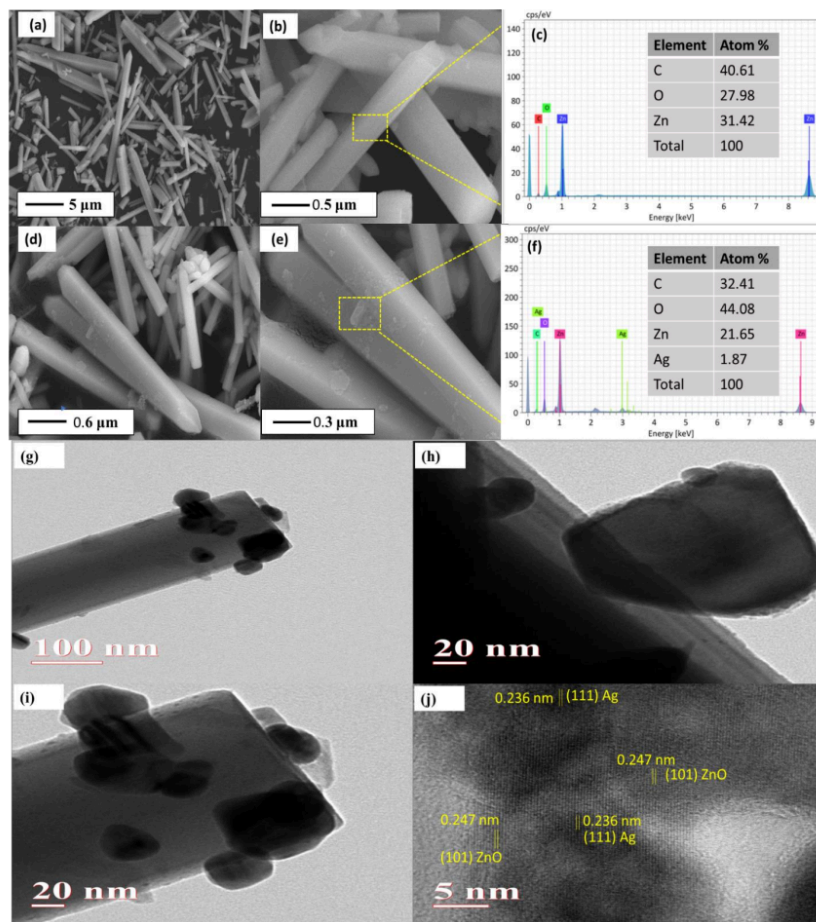


Fig. 2.3 FE-SEM images for (a–b) bare ZnO NRs, (d–e) Ag₃@ZnO NRs, and EDX line spectra for (c) bare ZnO NRs, and (f) Ag₃@ZnO NRs; HRTEM images of Ag₃@ZnO NRs at different scales: (g) 100 nm, (h–i) 20 nm, and (j) 5 nm.

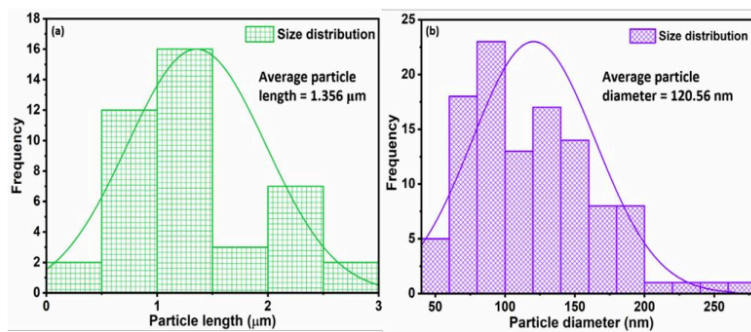


Fig. 2.4 (a) Average particle length and (b) diameter of ZnO NRs.

The obtained elemental wt% of Ag in $\text{Ag}_3@\text{ZnO}$ NRs is 1.87 (**Fig. 2.3(f)**), less than the added 3 wt%. In addition, for $\text{Ag}_1@\text{ZnO}$ and $\text{Ag}_5@\text{ZnO}$, the obtained wt% is 0.39 and 3.01 (**Fig. 2.5(b,d)**). This difference desired and obtained elemental wt% might be due to the scanning of only a particular area of the catalyst and the inevitable loss of some wt % of Ag during the washing of the catalyst.

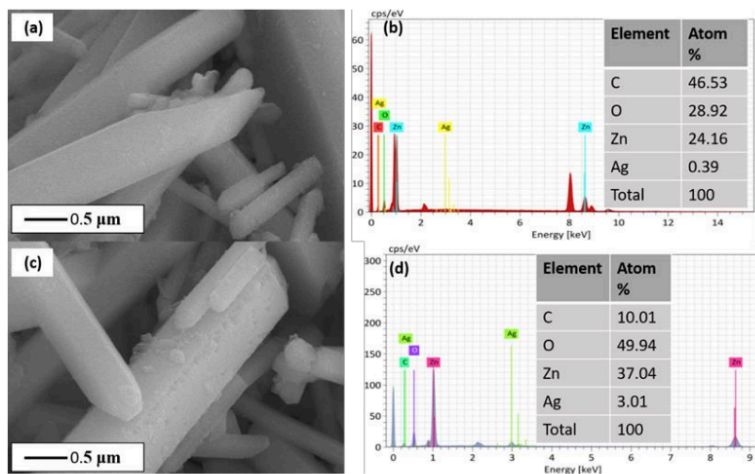


Fig. 2.5 FE-SEM images for (a) $\text{Ag}_1@\text{ZnO}$ NRs, (c) $\text{Ag}_5@\text{ZnO}$ NRs, and EDX line spectra for (b) $\text{Ag}_1@\text{ZnO}$ NRs, and (d) $\text{Ag}_5@\text{ZnO}$ NRs.

Further, HR-TEM studies are performed for $\text{Ag}_3@\text{ZnO}$ NRs, showing the presence of spherical Ag particles on the surface of rods (Fig. 2.3(g-j)). It can be noted that all the Ag particles are well distributed on the surface of nanorods and do not form separate aggregations. In Ag-loaded nanorods, the Ag particles appear as dark black particles embedded on the surface of the rods. The density of the dark spots will depend upon wt % of Ag loaded. The calculated lattice fringe spacing of 0.247nm and 0.236nm can be indexed to planes (101) of ZnO and (111) of Ag.[51]

2.3.3 Optical and charge transfer analysis

Diffuse reflectance spectra studies

The diffuse-reflectance spectra studies were performed to investigate the comparative photo-absorption abilities of bare and Ag-deposited ZnO NRs. Bare ZnO has an absorption edge at about 401 nm and no absorbance in the visible region due to its wide band gap. As observed in Fig. 2.6(a), upon Ag loading, a broad absorption band covering the visible region can be observed in the region 400-600 nm, which may be labeled as the LSPR band of plasmonic metal – Ag. The increased absorbance in the visible region was also supported by the color change from white to grey upon incremental Ag deposition.[52]

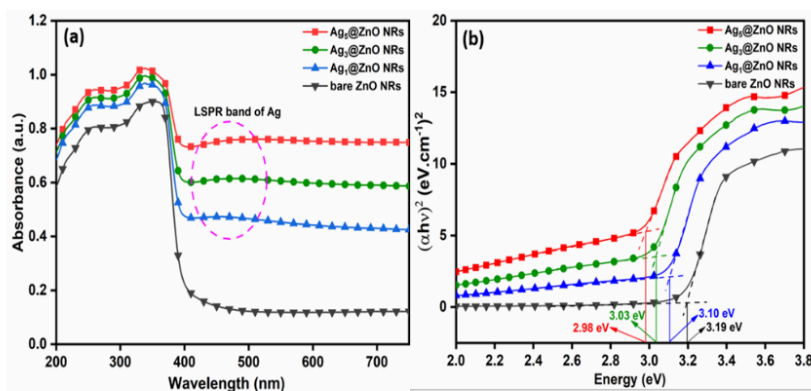


Fig. 2.6 (a) Diffuse reflectance spectra, and (b) Tauc plots of different materials.

The Ag NPs are solely responsible for the absorption of visible light by the prepared catalysts due to the charge transfer from d-electronic states of metal to CB of ZnO.[16] Upon the gradual growth

of Ag NPs (1-5 wt%), plasmon bands show a slight red shift and increased intensity confirms improved visible light absorption compared to pristine ZnO.[53,54] The band gap (E_g) of materials was computed using Tauc's relation: $(\alpha h\nu)^2 = A(h\nu - E_g)$, (where α is the optical absorption coefficient, $h\nu$ is the energy of photons, and E_g is the direct band gap). The band gap of various photocatalysts was calculated by applying a baseline approach for modified samples to Tauc's plot[51,55], as seen in **Fig. 2.6(b)**, giving values of $E_g = 3.19$ eV, 3.10 eV, 3.03 eV, and 2.98 eV for bare ZnO, Ag₁@ZnO, Ag₃@ZnO, and Ag₅@ZnO, respectively. Therefore, a gradual band-narrowing is perceived with increasing wt% loading of Ag, confirming the role of Ag in the band-gap engineering of ZnO. This synergistic effect between Ag-ZnO is responsible for enhanced light absorption by the photocatalyst.

The position of the valence band (E_{VB}) and conduction band (E_{CB}) edge for the photocatalyst could be calculated from the band gap values obtained by using the Mulliken electronegativity formulae:

$$E_{VB} = \chi - E^e + 0.5E_g \quad (10)$$

$$E_{CB} = E_{VB} - E_g \quad (11)$$

(where E_{VB} and E_{CB} are the valence band and conduction band edge potentials, χ represents the absolute electronegativity of the material, E^e is the free electron energy on the hydrogen scale (~4.50 eV), and E_g is the band gap energy of the semiconductor. The value of χ for ZnO is reported to be 5.76.[56] Substituting the values returns the E_{VB} and E_{CB} potentials for ZnO as 2.85 eV and -0.33 eV, v/s NHE. Thus, the electrons from the CB of ZnO NRs can readily reduce the adsorbed oxygen molecules at its surface to superoxide radicals ($E(O_2/O_2^-) = -0.33$ eV). Concurrently, the $^{\cdot}OH/OH$ redox potential is less positive (2.38 eV v/s NHE) than the holes in VB leading to increased production of hydroxide radicals.[51,57] Here, the role of Ag metal is to act as a charge carrier trapping site, thus increasing the lifetime of e^- and h^+ in CB and VB, respectively.

Photoluminescence spectra studies

The PL spectra are studied to investigate the semiconductor material's defects and photogenerated e^-/h^+ recombination rates. The spectra were recorded at room temperature (excitation wavelength = 325 nm). They showed two broad bands: in the UV region (3.25 eV) and the visible region (2.23 eV) (**Fig. 2.7**). The peak in the UV region is consistent with the absorption edge in UV-visible

absorption spectra of ZnO, which can be ascribed to the near band edge (NBE) emission originating from e^-/h^+ recombination.[51,53,58]

The visible emission peak can be attributed to crystal defects such as vacancies and interstitials.[59] The spectra for Ag-modified catalysts show identical peaks but both of decreased intensities, indicating the diminishing charge carrier recombination rates and defect emission.[60,61] All Ag counterparts (1-5 wt%) show decreased intensities for both peaks, but the lowest intensity is seen in the PL spectra of $Ag_3@ZnO$.

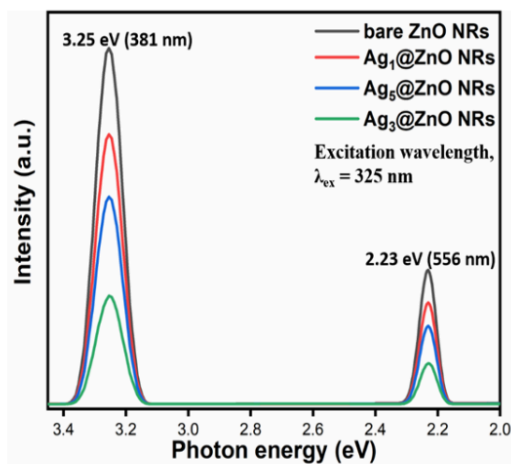


Fig. 2.7 Photoluminescence spectra of various photocatalysts.

This indicates that 3 wt% is the optimum percentage for the suppression of $e^- - h^+$ recombination, and a further increase in Ag concentration might lead to the formation of new recombination routes, which is not favorable for the separation of charge carriers and, thus, photocatalytic activity.[62] The emission peak in the UV region (photon energy ~ 3.25 eV) is congruous with the band gap calculated from the diffuse reflectance spectra of ZnO NRs. The emission peak at photon energy ~ 2.23 eV could be indexed to the mono-ionized oxygen vacancy ($V_O^\cdot$) created by the substitution of doubly ionized Zn^{+2} by Ag^+ in the lattice sites.[63] The suppression of emission intensity in the visible region (~ 2.23 eV) further confirms the e^- transfer between ZnO NRs and Ag NPs, thereby suppressing the defect emission. This outcome supports the desired role of Ag in improving the photocatalytic activity of ZnO NRs.

2.3.4 Electrokinetic analysis

The zeta potentials of fabricated powders were analyzed to decode the changes in the surface potential of samples ensuing Ag modifications. The zeta potential (ζ) for pristine ZnO is -6.46 ± 0.06 mV. Upon adding Ag, the zeta potential values shift towards higher negative, i.e., -9.7 ± 0.40

mV, -10.3 ± 0.14 mV, and -11.0 ± 0.4 mV for 1, 3 and 5 wt% Ag, respectively. The higher negative charges are associated with increased stability and better dispersion of NPs due to negative-negative repulsions.[64]

2.3.5 Surface area and porosity analysis

To investigate the surface area and porosity of the catalysts, Brunauer-Emmett-Teller (BET) isotherms were recorded. The N_2 adsorption-desorption isotherms for bare and $Ag_3@ZnO$ NRs can be seen in Fig. 2.8. According to the IUPAC convention, the curves match the Type IV isotherm and the H3 hysteresis loop of mesopores.

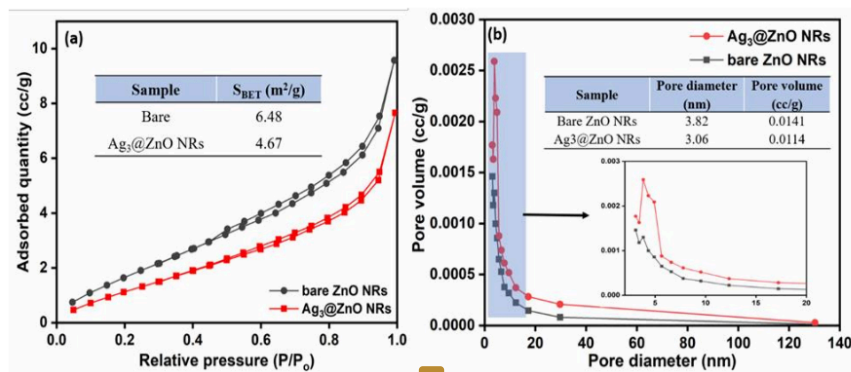


Fig. 2.8 (a) N_2 adsorption-desorption isotherms for bare ZnO NRs and $Ag_3@ZnO$ NRs, and (b) corresponding pore diameter and pore volume distributions.

The BET surface area (S_{BET}) of bare ZnO NRs and $Ag_3@ZnO$ were found to be $6.48 m^2/g$ and $4.67 m^2/g$. This slight decrease in the surface area might be observed due to Ag NPs occupying the pores of mesoporous ZnO. Nevertheless, this slight shrinkage of the surface area may not have diminished the photocatalytic activity, which is also dependent on several other factors like the band gap of materials, e^- transfer between plasmonic Ag and ZnO, and suppression of e^-h^+ recombination.[65]

Further, the pore size and pore diameter were calculated from the BJH (Barrett-Joyner-Halenda) model. The computed pore diameter values for bare ZnO NRs and $Ag_3@ZnO$ NRs are 3.82 nm

and 3.06 nm, respectively, and pore volumes are 0.0141 cc/g and 0.0114 cc/g. This decrease in pore diameter and volume further suggests the embedding of silver on the surface of nanorods.

2.4 Photocatalytic activity

2.4.1 Photocatalytic degradation reaction

To assess the photocatalytic efficiency of as-prepared catalysts, photocatalytic degradation of two antibiotics, TCY and AMX, was performed under visible light for 90 minutes. A blank sample without adding any photocatalyst was studied to check the photostability of pollutants. Before illumination, the suspensions of pollutants and catalysts were kept in the dark for 40 minutes to reach adsorption-desorption equilibrium. After 40 minutes, no significant increase in adsorption is observed (Fig. 2.9).

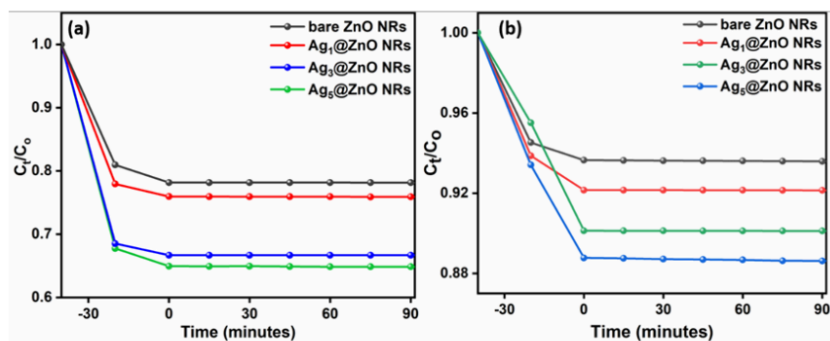


Fig. 2.9 Time course dark-adsorption spectra in of (a) TCY, and (b) AMX in 90 minutes.

The characteristic absorption peak of tetracycline at 357 nm is studied for degradation. As shown in Fig. 2.10(a-b), this absorption peak shows a bathochromic shift after reaching adsorption-desorption equilibria. This shift could be accounted for by the possible increased conjugation of pi-electron cloud resulting from interactions between oxygen vacancies in ZnO NRs and -OH groups of TCY adsorbed on its surface.[3] Tetracycline is insignificantly degraded in the absence of photocatalysts, suggesting it is highly photostable under visible light. After adsorption in the dark for 40 minutes, the removal rates of tetracycline over ZnO, Ag₁@ZnO, Ag₃@ZnO, and Ag₅@ZnO are 21.8%, 24%, 33.3%, and 35%. Dispersion forces and electrostatic affinities are the

major factors responsible for the adsorptive removal of pollutants. However, BET analyses suggest that the surface area of bare ZnO is higher than Ag₃@ZnO, hinting the surface area is not the sole factor for the adsorptive removal of tetracycline.

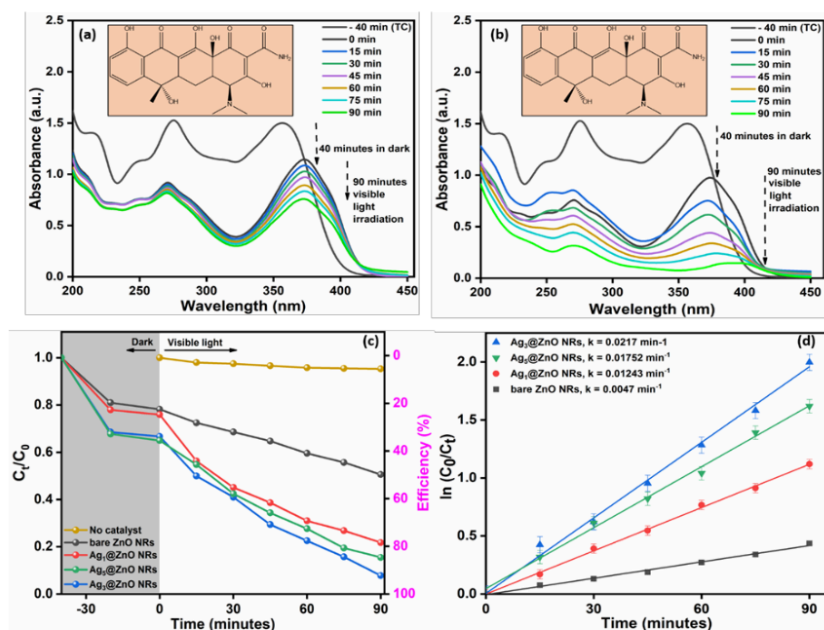


Fig. 2.10 Absorption spectra of time-dependent degradation of TCY in the presence of (a) bare ZnO NRs and (b) Ag₃@ZnO NRs under visible light (insets show the chemical structure of TCY), (c) the time-course degradation efficiency TCY under visible light, and (d) corresponding degradation kinetics.

AMX and TCY are zwitterionic species in the pH range of ~6.7-7.7.[66,67] The photodegradation studies were performed at a neutral pH of ~7.2. The surface potential of ZnO is computed to be -6.46 eV, which increases to a higher negative value (-9.7 to -11.0 eV) upon Ag-loading (1-5wt%). The red shift in the absorption peak of TCY due to interactions between oxygen vacancies of ZnO and hydroxyl groups remains unchanged in Ag-modified ZnO NRs. Thus, in the case of these zwitterions, positive charge localization on the amine groups might play a role in their

adsorption.[68] Further, for bare ZnO NRs, the degradation efficiency after 90 minutes is found to be 49.4%. This result is consistent with the fact that ZnO has a wide band gap of ~3.2 eV and has an absorption edge at ~401 nm, which makes it photoactive in the UV and near-visible region only. However, as confirmed by PL analysis, ZnO is known to have certain defect energy levels due to oxygen vacancies and interstitial Zn, which lie lower than E_{cb} . These defect levels may trap electrons and reduce the charge carrier recombination, thus improving photoactivity.[51]

Furthermore, the degradation efficiencies of photocatalysts were found to be 78.2%, 92.1%, and 84.5% for $Ag_1@ZnO$, $Ag_3@ZnO$, and $Ag_5@ZnO$, respectively, which are 1.6, 1.9, and 1.7 times higher than bare ZnO (Fig. 2.10(c)). The improved degradation for $Ag@ZnO$ nanorods is expected as DRS spectra confirmed a band contraction from 3.19-2.98 eV upon 1-5 wt% Ag-decoration. Moreover, the higher photoactivity can also be explained by the LSPR effect of Ag, which lies in the visible region and thus produces high-energy electrons, which aids the degradation process.[57]

The degradation studies of AMX were performed by HPLC analysis. The retention time (RT) of AMX is 6.02 minutes (Fig. 2.11(a)). The peak at RT = 4.7 corresponds to the potassium clavulanate salt present with AMX.[69] With the progress of the reaction, the concentration of AMX is perceived to decline. The photodegradation of AMX with bare ZnO for 90 minutes is shown in Fig. 2.11(a-d). The highest decline is observed for $Ag_3@ZnO$ NRs after 90 minutes, where the peaks (AMX and potassium clavulanate) almost disappear (Fig. 2.11(e-h)). Further, the appearance of new peaks indicates the formation of certain reaction fragments that have been analyzed successfully using HRMS analyses. The photolysis of the antibiotic was found to be insignificant ~ 5% under visible light in 90 minutes, revealing a high photostability. The photocatalysts show similar degradation trends, i.e., $Ag_3@ZnO > Ag_5@ZnO > Ag_1@ZnO > bare ZnO$, with an efficiency of 76.4%, 70%, 66.7%, and 38%, respectively (Fig. 2.11(i)).

A higher photocatalytic activity is often associated with higher aspect ratios of nanorods and crystal defects. In one-dimensional nanoparticles, growth along one direction promotes the delocalization of photogenerated e^- s along the crystal length. Simultaneously, the holes in the valence band become more populated. The presence of surface defects further aids in trapping e^- s and h^+ s, facilitating their separation. Consequently, a higher number of charge carriers are present at the surface of nanorods than zero-dimensional NPs.[30]

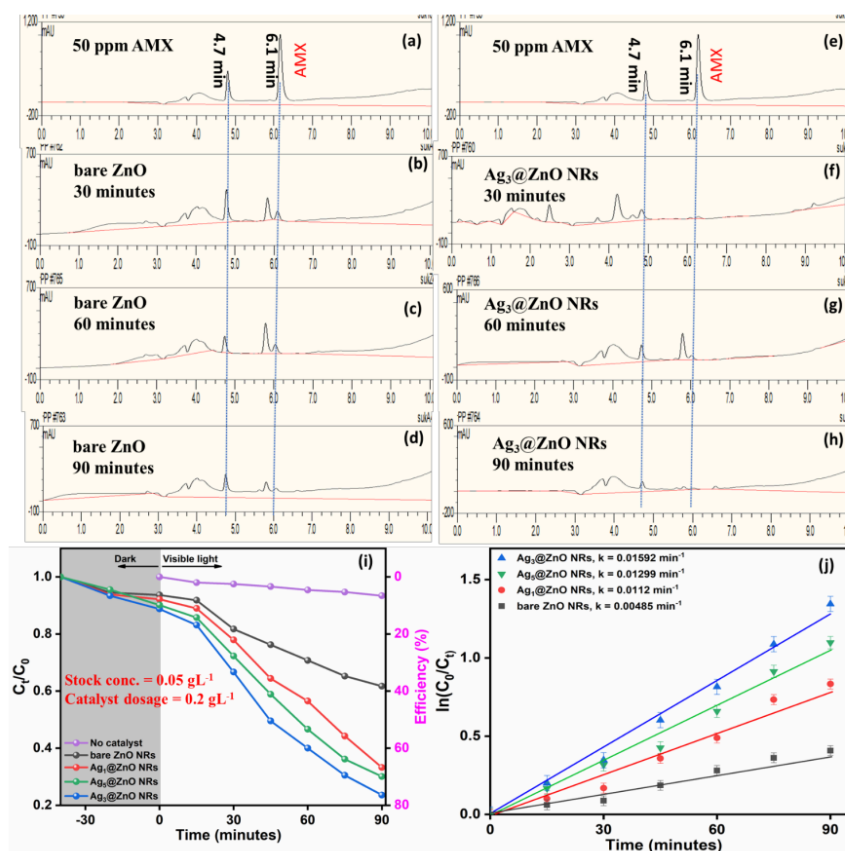


Fig. 2.11 HPLC chromatograms of time-dependent degradation of AMX in the presence of (a–d) bare ZnO NRs and (e–h) Ag₃@ZnO NRs under visible light, (i) the time-course degradation efficiency AMX under visible light, and (j) corresponding degradation kinetics.

Ag₃@ZnO NRs demonstrate the highest activity amongst the Ag (wt%), which could be explained based on their narrow band gap (3.02 eV) and most increased spatial charge carrier separation as seen from the PL spectra. Ag₅@ZnO NRs has a band gap lower than all Ag-concentrations; however, the slight decrease in degradation efficiency from 92.1% to 84.5% could plausibly be

due to the blocking of the surface of nanorods by silver, preventing the interaction between ZnO and tetracycline. Further, new e^-h^+ recombination paths are formed upon higher concentration loadings. Comparative photodegradation efficiencies of $Ag_3@ZnO$ NRs towards the decomposition of TCY and AMX are shown in Fig. 2.12(a).

The reaction kinetics for the degradation of both pollutants were evaluated using Eq. 2 for pseudo-first-order reaction. Fig. 2.10(d) shows the computed rate constant (k) for degradation of TCY is highest over $Ag_3@ZnO$ NRs (0.0217 min^{-1}), approximately five folds higher than pristine ZnO NRs (0.0047 min^{-1}). Comparably, the rate constant for removing AMX (0.0159 min^{-1}) is ~ 3.3 times higher than bare ZnO NRs (0.00485 min^{-1}) (Fig. 2.11(j)). Thus, $Ag_3@ZnO$ is an excellent visible-light active photocatalyst for the removal of pharmaceuticals.

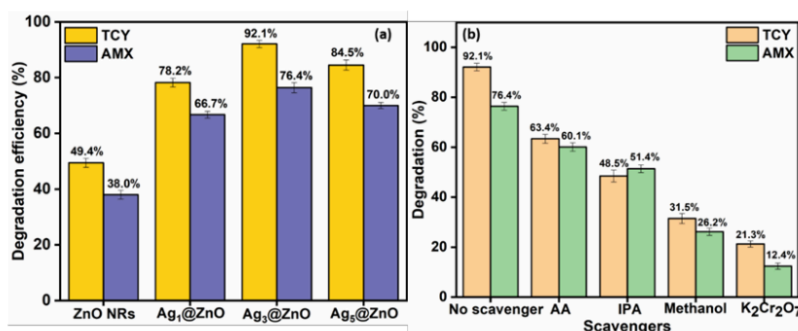


Fig. 2.12 (a) Comparative photodegradation efficiencies of materials towards AMX and TCY and (b) suppression of degradation ability of $Ag_3@ZnO$ NRs in the presence of scavengers.

2.4.2 Pollutant mineralization studies

Degradation of a pollutant does not necessarily mean complete mineralization to CO_2 and H_2O . TOC (total organic carbon) measurements reveal the proper amount of organic material present in a solution, and its decline toward the end of the degradation process divulges the actual degree of mineralization. The TOC was assessed by titration method with dichromate and sulfuric acid. The TOC (mg/L) measurements were performed for stock and photocatalyst-treated solutions. The mineralization (%) was evaluated by using the following formula:

$$\text{Mineralization}(\%) = \frac{TOC(\text{initial}) - TOC(\text{final})}{TOC(\text{initial})} \times 100 \quad (12)$$

TOC values for tetracycline declined from 31.6 mg/L to 18.7 mg/L. Thus, 42.7% mineralization is achieved after 90 minutes of visible light illumination. Whereas upon degradation with bare ZnO NRs, the TOC values declined insignificantly to 26.4 mg/L, bringing about a 16.4% mineralization. Following a similar procedure for amoxicillin, the TOC values decreased from 18.5 mg/L to 12.7 mg/L, revealing a mineralization of 31.35% (Fig. 2.13(a)). Further, pristine ZnO exhibited a mineralization of just 9.2%, with a decline of TOC to 16.8 mg/L. The higher mineralization in Ag₃@ZnO NRs in the visible light region due to the plasmonic effects of noble metal Ag. It can be noted here that mineralization is much lower than the degradation efficiencies calculated from absorption spectra. The formation of intermediates during the degradation process could be held responsible for this incomplete mineralization. Further decline in organic content might be possible by prolonged UV or visible light exposure, but the same has not been studied here.

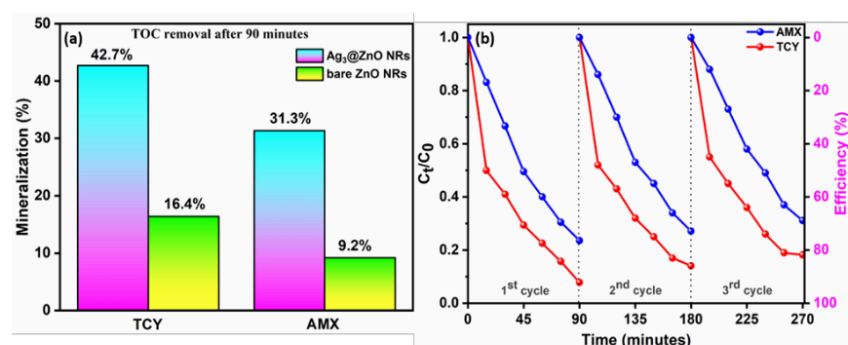


Fig. 2.13 (a) TOC removal of TCY and AMX by Ag₃@ZnO NRs and bare ZnO NRs after 90 minutes of visible light irradiation, and (b) recyclability tests for visible-light-induced photocatalytic degradation of TCY and AMX over Ag₃@ZnO.

2.4.3 Proposed photocatalytic degradation mechanism

For a deep insight into the degradation mechanism of both antibiotics, the role of reactive oxygen species (ROS) is investigated by trapping experiments. Reactive species are generated by photoinduced e⁻-h⁺ pairs by reacting with O₂ and H₂O molecules present in the reaction mixture. These ROS play a vital role in the degradation of pollutants through redox pathways. Scavengers

like $K_2Cr_2O_7$, methanol, IPA, and AA were added to trap e^- , h^+ , $^{\bullet}OH$, and $^{\bullet}O_2^-$. **Fig. 2.12(b)** shows the corresponding removal rates for TCY and AMX in the presence of these scavengers. The degradation efficiency of TCY over $Ag_3@ZnO$ declined from 92.1% to 21.3% in the presence of $K_2Cr_2O_7$ (approximately a 4-fold decrease). A lesser but notable decline in photocatalytic degradation of $Ag_3@ZnO$ NRs was also noticed with remaining scavengers (92.1% to 63.4%, 48.5%, and 31.5% in the presence of AA, IPA, and methanol, respectively). Comparably, the removal efficiency of amoxicillin fell from 76.4% to 12.4% while using $K_2Cr_2O_7$ to trap e^- . Moreover, a decrease in degradation efficiency from 76.4% to 60.1%, 51.4%, and 26.2% is noticed by adding AA, IPA, and methanol, respectively. The time-dependent photo-degradation of TCY and AMX over $Ag_3@ZnO$ NRs in the presence of these scavengers is demonstrated in **Fig. 2.14**. The trapping experiments reveal that photogenerated e^- are the primary species in the degradation of both antibiotics. Also, significant suppression in photocatalytic efficiencies is obtained with methanol as h^+ scavenger. This outcome is further reflected in the $^{\bullet}OH$ trapping trials as h^+ produces $^{\bullet}OH$ by reacting with H_2O .

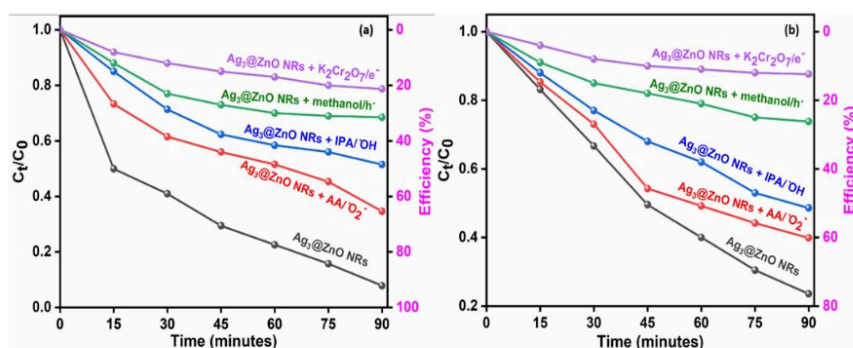
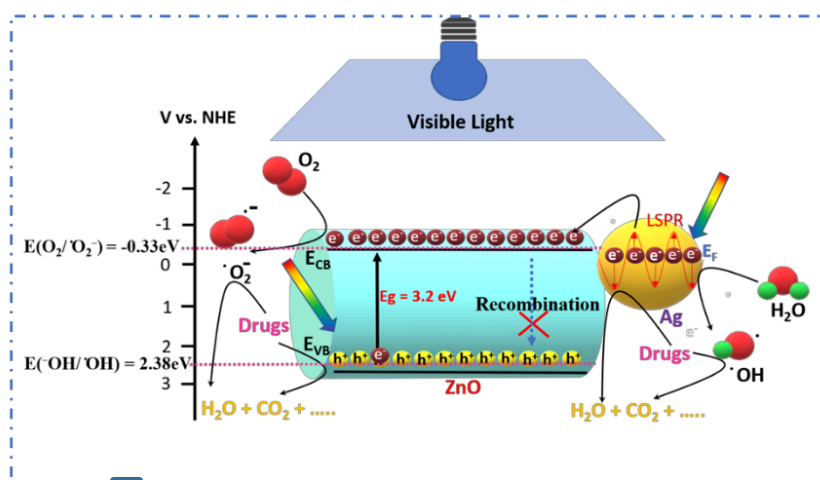


Fig. 2.14 Time-course photodegradation ability of materials under visible-light irradiation for (a) TCY and (b) AMX in the presence of active species' scavengers.

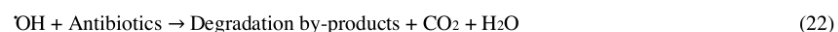
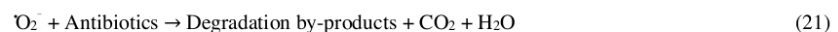
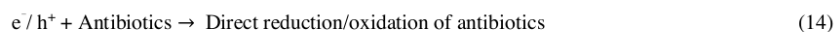
Based on the above experimental outcomes, the photocatalytic degradation mechanism for the decomposition of both antibiotics over $Ag_3@ZnO$ NRs is proposed (**Scheme 2.2**). Upon visible light illumination of $Ag_3@ZnO$ NRs with photons of suitable energy, the e^- present in the VB of ZnO gets excited to the CB while generating positively charged holes (h^+) in the VB. These electrons in the CB might recombine with h^+ , but this phenomenon is somewhat suppressed by the

trapping of electrons in various defect levels of ZnO.[57] Moreover, the LSPR band of Ag falls in the visible region, and thus hot electrons are generated through excitation in Ag, which can be donated back to the CB of ZnO. Through this mechanism, the LSPR effect of Ag appreciably reduces the e^-h^+ recombination in ZnO. As a result, excess e^- and h^+ are generated in the CB and VB of ZnO, respectively.

The excess e^- and h^+ produced can directly reduce and oxidize the pollutants adsorbed at the surface of the photocatalyst.[57] The electrons e^- in CB of ZnO ($E = 2.85$ eV vs. NHE) can further reduce H_2O or $\cdot OH$ molecules to yield $\cdot OH$ ($E(\cdot OH/\cdot OH) = 2.38$ eV vs. NHE). Simultaneously, the h^+ in VB of ZnO (-0.33 eV vs. NHE) have the suitable potential for production of $\cdot O_2^-$ ($E(O_2/\cdot O_2^-) = -0.33$ eV vs. NHE) from O_2 adsorbed at the surface of ZnO. Further, the plasmonic e^- of Ag can reduce O_2 to $\cdot O_2^-$, which further reacts with H_2O present in the solution to produce other ROS through a series of reactions. Eventually, these active species may decompose the pharmaceuticals into simple degradation by-products like CO_2 and H_2O (Eq. 13-22). However, in this work, we have not studied the complete mineralization of pollutants to carbon dioxide, and water.



Scheme 2.2 Schematic illustration of the proposed photocatalytic mechanism for the degradation of drugs (TCY and AMX) over Ag₃@ZnO NRs through visible-light illumination.



2.4.4 Photocatalytic degradation pathway

TOC results reveal only partial mineralization for TCY (42.7%) and AMX (31.35%). Thus, it was imperative to carry out the HRMS analysis to identify the reaction intermediates and by-products formed. For TCY, as shown in **Fig. 2.15(a-b)**, several fragments with m/z values 124, 129, 145, 149, 158, 177, 202, 217, 229, 245, 252, 275, 301, 327, 341, 351, 371, 393, 417, 461, 475, and 477 are obtained. It is known that TCY contains i) amine group, ii) amide group, and iii) keto-phenol group, which are prone to susceptible to dehydration, deamination, and decomposition reactions.[70] Herein, three potential pathways for the degradation of TCY are proposed (**Fig. 2.16**).

The first pathway involves the attack of h^+ on the high electron density dimethylamine group of TCY ($m/z = 445$), inducing N-demethylation to form an intermediate with $m/z = 417$. [71] Further attack of holes produces fragments of m/z ratios 400 and 274 via loss of hydroxyl and amine groups and opening of naphthalene ring. [72] Pathways II also involves the formation of fragments $m/z = 399$ and $m/z = 340$ through deamination and formation of a keto group. [73] The third pathway proceeds via the attack of hydroxy radicals on different sites of TCY, forming two possible structures with $m/z = 461$. Further attack of $\cdot\text{OH}$ leads to the formation of fragments with $m/z = 465$ and the oxidation of N-methyl to N-aldehyde, yielding product $m/z = 477$. [71,72] As the degradation proceeds, by-products of lower molecular masses ($m/z = 301, 245, 202, 124, 149$) are formed by further oxidative ring opening and functional group dissociation. [20,74] **Fig. 2.15(c-d)**

shows the AMX m/z fragments obtained upon its photo-degradation in visible light. The proposed degradation pathways of AMX ($m/z = 366.11$) are shown in **Fig. 2.17**. [75,76] In pathway I, the hydrolysis of AMX produces the fragment $m/z = 384$ upon the breakage of the β -lactam ring.[75,77]

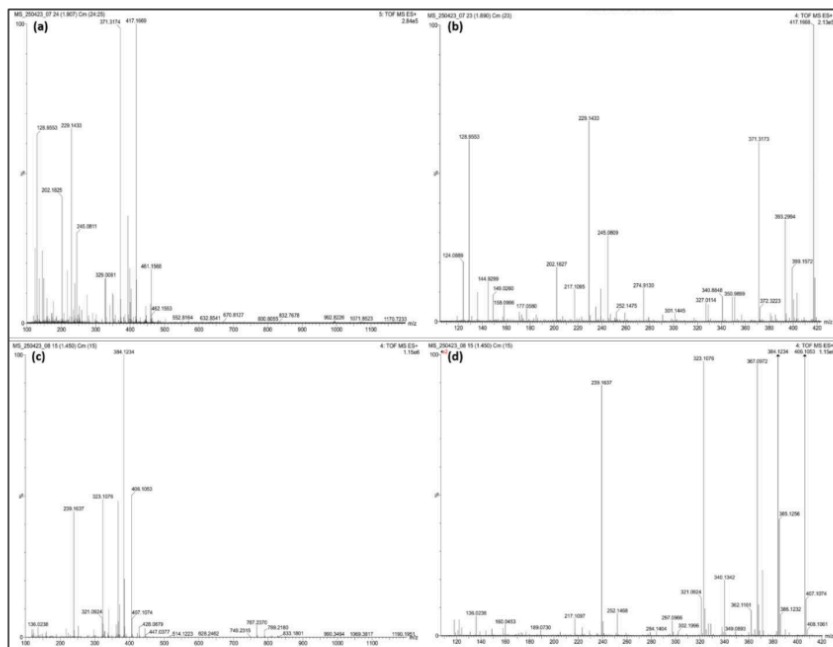


Fig. 2.15 HR-MS chromatograms and intermediates formed during photocatalytic degradation of (a-b) TCY and (c-d) AMX over $\text{Ag}_3\text{@ZnO}$ NRs under visible light.

Subsequent decarboxylation forms the product with $m/z = 340$, while hydroxylation at different sites forms the product at $m/z = 160$. A further electrophilic attack by $\cdot\text{OH}$ radical at the amino group gives the intermediate at $m/z = 189$. [78] The second pathway proceeds via the deamination process yielding a product at $m/z = 349$, which upon further fragmentation, produces a small molecular mass product at $m/z = 136$. [76] The complete mineralization of these fragments of TCY and AMX into CO_2 and H_2O , and other simple molecules might take longer than the degradation studied here.

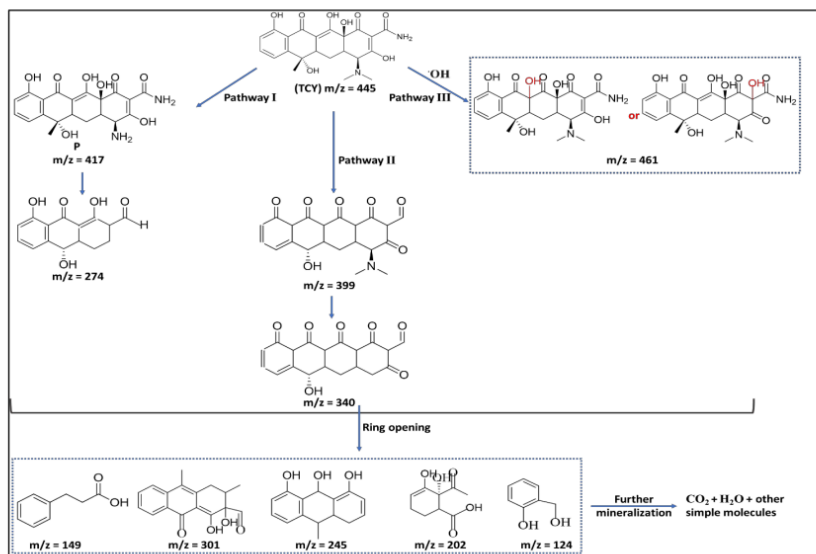


Fig. 2.16 Proposed visible-light-induced degradation route for TCY over $\text{Ag}_3\text{@ZnO}$ NRs.

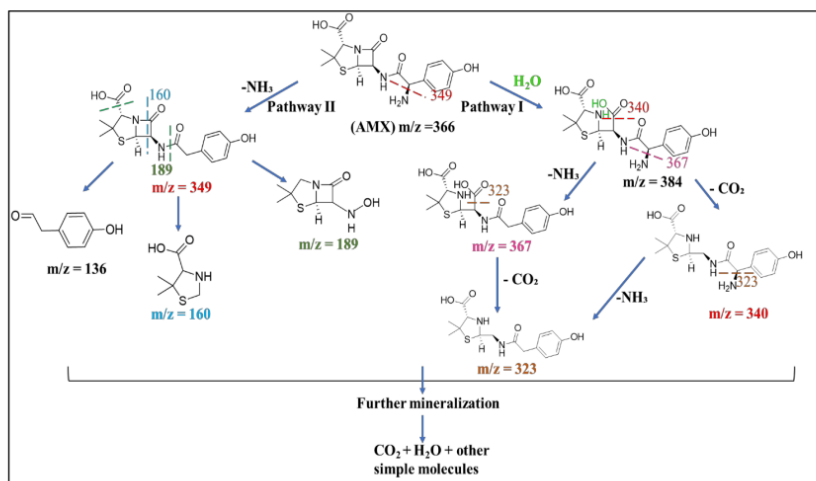


Fig. 2.17 Proposed visible-light-induced degradation route for AMX over $\text{Ag}_3\text{@ZnO}$ NRs.

2.4.5 Recyclability studies

The catalyst's stability and reusability parameters were also analyzed for practical applicability. The recycling experiments were performed, and the degradation efficiencies of the photocatalyst were only inconsequentially decreased after three runs for both TCY (92.1% to 82%) and AMX (76.4% to 69%) (**Fig. 2.13(b)**).

Further, the XRD spectra were recorded after recycling tests to analyze any structural changes in the photocatalyst after reusing several times. The XRD spectra clearly show that characteristic peaks found in the spectra of $\text{Ag}_3\text{@ZnO}$ NRs remain unchanged after three cycles (**Fig. 2.18**). The DRS spectra of $\text{Ag}_3\text{@ZnO}$ NRs after three photocatalytic runs with AMX show a negligible band gap change (**Fig. 2.19**). The decrease in absorbance after recycling tests could be accounted for by the adsorption of AMX on the catalysts, thus hindering light absorption by the photocatalyst. The same is reflected by the decreased activity after three runs (76.5% to 69%). A comparison of some ZnO-based photocatalysts with the one synthesized herein

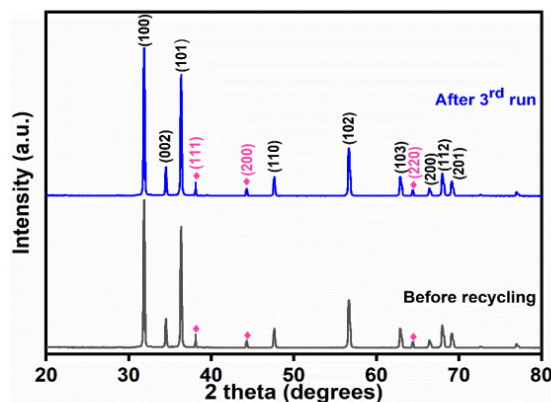


Fig. 2.18 XRD spectra of $\text{Ag}_3\text{@ZnO}$ NRs before and after 3 recycling runs.

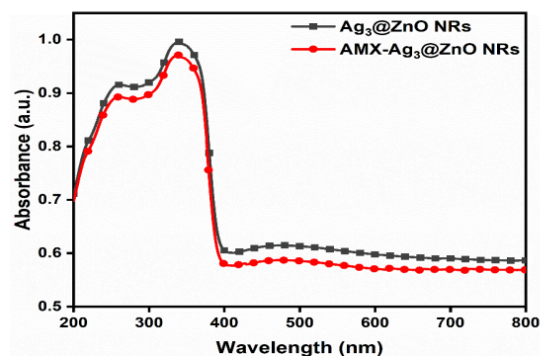


Fig. 2.19 DRS spectra of $\text{Ag}_3\text{@ZnO}$ NRs before and after three recycling runs with AMX.

towards the photo-degradation of organic pollutants is shown in Table 2.2.

Table 2.2 A comparison of ZnO-based photocatalysts toward the degradation of TCY and AMX.

Photocatalyst used	Pollutant	Pollutant conc. (mgL ⁻¹)	Catalyst dosage (gL ⁻¹)	Irradiation time (min)	Efficiency (%)	Ref.
ZnO/K-CN0.5/sunlight	TCY	50	0.5	60	90	[2]
Ag/g-C ₃ N ₄ /ZnO NRs/visible light	AMX	40	0.08	180	41	[40]
ZnO/ γ -Fe ₂ O ₃	TCY	30	0.5	150	88	[46]
MIL-53(Al)/ZnO/visible light	AMX	50	1	60	89	[47]
Ag/ZnO@Biochar / UV light	TCY	50	0.01	120	76	[48]
Ag ₃ @ZnO NRs/visible light	TCY and AMX	50	0.25	120	TCY - 92 AMX - 76	This work

It can be deduced from these trials that the prepared photocatalyst is highly stable under visible light irradiation and aqueous medium and hence have immense practicability for pharmaceutical waste treatment at reasonable expenses.

Conclusion

To summarize, the photocatalytic activity of the ZnO nanorods under visible light was greatly enhanced by loading with various wt% of plasmonic Ag metal. The photoreduction of Ag significantly improves the lifetime and separation of photogenerated charge carriers on the ZnO surface by acting as an electron sink. Further, the plasmonic effect of Ag allows UV-active ZnO to harness visible light, which is essential for fabricating a green and environmentally safe photocatalyst. For practical purposes, the catalyst was highly stable and recyclable and displayed excellent degradation efficiencies after three trials. Considering the economic aspect, only a small amount of Ag (3wt%) is required to demonstrate superior photo-degradation of a high concentration of antibiotics. The mineralization and HRMS studies confirmed the decomposition

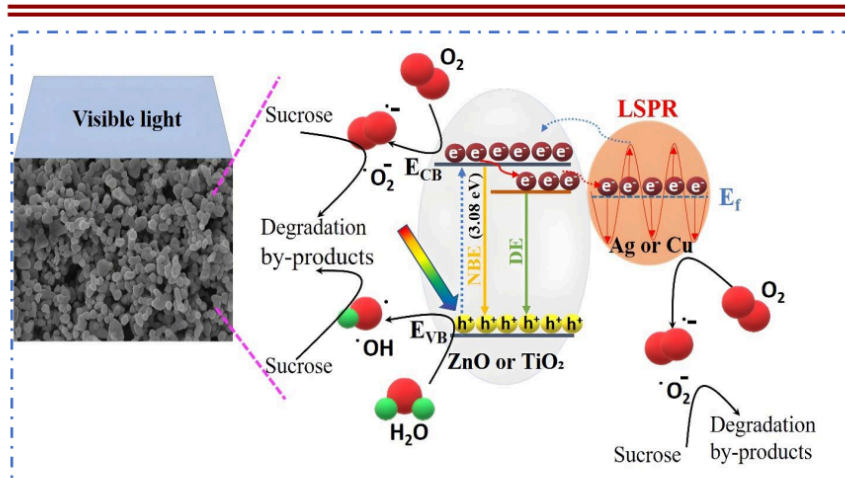
of chosen pollutants. Thus, the said photocatalyst could be a potential candidate for pharmaceutical wastewater treatment prospects.

Significance of this work: i) High-aspect ratio nanorods for improved photocatalytic activity towards antibiotics; ii) Assessing the role of varying Ag-concentrations towards physiochemical and photocatalytic properties of catalysts; iii) Illustration of the mechanistic pathway for the degradation of antibiotics by Ag-loaded-ZnO NRs.

For future studies, the complete degradation of contaminants may be explored. Moreover, the degradation of a mixture of drugs may be studied to establish the further role of this catalyst for the nanoremediation of pharmaceutical wastewater.

Chapter-3

Synergic adsorptive-photocatalytic removal of sucrose under visible light induced by plasmonic metal (Ag and Cu) loaded ZnO and TiO₂ nanoparticles



Schematic summary

3.1 Introduction

The extensive sugar usage has generated a substantial demand in domestic and foreign markets. In the sugar industry, the wastewater produced after condensation of sugars is often contaminated by high doses of sucrose (~ 50 ppm). Although non-toxic, sucrose accumulation may occur when this sugary water is dumped into the environment, becoming a habitat for pathogenic microorganisms. These pathogens affect the well-being of various life forms by causing diseases like diarrhea, pneumonia, skin and tissue infection, and many more.[1] Further, even reusing this sucrose-contaminated water for industrial purposes requires water treatment to remove sucrose.[2] This wastewater is typically characterized by high biological and chemical oxygen demands (BOD and COD) and poses a threat of environmental pollution. The biological methods for degrading sugars often require large areas and extended periods. Also, these methods do not entirely remove the organic matter and require additional post-treatment.[3,4] Here, photocatalysis may be a promising solution for removing these organic pollutants from water.

ZnO and TiO₂ are the most practical photocatalysts available due to their lower cost, non-toxicity, chemically inert properties, production of environmentally harmless by-products, and ambient reaction conditions. With wide band gaps of 3.2 and 3.3 eV, both TiO₂ and ZnO are activated by UV irradiations. However, their photoactivity suffers due to their rapid recombination rates of charge carriers.[5] Further, they have minimal absorption capacities in the visible region. An elegant solution to overcome these limitations is loading noble metal nanoparticles (NPs) such as Ag and Cu onto the surface of these semiconductors.[6,7] In recent years, several investigations have focused on visible-light active photocatalysts supported by plasmonic noble metals. Depositing a single or dual noble metal(s) atop a semiconductor spinal has been shown to induce localized surface plasmon resonance (LSPR), resulting in improved visible light photoactivity. A plasmon band arises from the collective oscillations of conduction band electrons caused by the interactions with incident electromagnetic radiations. This plasmon band can potentially increase the lifetime of photogenerated electron-hole (e⁻-h⁺) pairs while shifting the semiconductor oxide's photo response toward the visible region.[5,8–10]

Many research groups have achieved excellent results based on the abovementioned capabilities of noble metal loading. F. Jandaghian et al. compared the photodegradation performance of Ag-loaded ZnO and TiO₂ towards levofloxacin under UV-visible light. It was reported that a nominal

5 wt% Ag loading displayed 99% and 91% removal of levofloxacin by Ag@ZnO and Ag@TiO₂, respectively.[11] S. Kaur et al. synthesized visible light active Ag-decorated ZnO nanorods for the superior degradation of antibiotics. Ag (3 wt%) demonstrated the highest photodegradation ability towards the antibiotics tetracycline (92%) and amoxicillin (76%).[5] L. Buengkitcharoen et al. fabricated Ag/ZnO nanocomposites by sol-gel methods, showing a 90% removal of sucrose under visible light within 90 minutes.[2] B. A. Berehe et al. prepared a ZnO/Cu-Diphenylamine (ZnO/Cu-DPA) nanocomposite for wastewater purification. Among various compositions, the 20% Cu-DPA modified catalyst revealed the highest photodegradation rates for methylene blue dye in 80 minutes.[12] Experiments by S. Thakur et al. found that Ag loading on TiO₂ highly increased the photodegradation rates of various carbohydrates under UV irradiation.[1] B. D. Bhuskute et al. studied the sequential photodeposition of dual noble metals (Au and Ag) onto TiO₂ for their photocatalytic properties. Ag-shell-Au-core@TiO₂, where Au was deposited first, followed by Ag, showed the best photodegradation of methylene blue under solar irradiation.[13] S. Bhardwaj et al. investigated the influence of Ag-Cu binary metal loading on TiO₂ NPs for their adsorption and photocatalytic properties. The efficiency of Ag-Cu@TiO₂ composite in degrading methylene blue and salicylic acid was significantly greater than that of pristine TiO₂. [14] Furthermore, noble metal-loaded materials have gained popularity as antimicrobial agents. However, in contrast to the conventional Ag or Au-modified materials, C. Yang et al. coupled ZnO with ZPS to design ZnO/P-g-C₃N₄/Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ material for antimicrobial ceramic uses. The fabricated materials achieved an exceptional suppression of ~ 100% towards *E. coli* and *S. aureus* bacteria.[15] C. Yang et al. prepared a composite photocatalyst, a P-gC₃N₄/Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ (P-g-C₃N₄/SMSO), and its performance in degrading methyl orange (MO) is assessed, focusing on the effects of phosphorus doping and the SMSO composite. The antibacterial activity against *E. coli* and *S. aureus* on ceramic surfaces was also investigated. The day-night catalyst incorporating P-g-C₃N₄(0.01%)/SMSO(35.9%) with antimicrobial ceramics resulted in 100% inactivation of both *S. aureus* and *E. coli* within 60 minutes of exposure to LED light.[16] F. Yi et al., employing decomposition methods, fabricated a dual S-scheme g-C₃N₄/Ag₃PO₄/g-C₃N₅ heterojunction, exhibiting enhanced tetracycline hydrochloride degradation and ideal stability in various water substrates. This study offers a new avenue for exploring the design and mechanistic analysis of dual S-scheme photocatalysts.[17]

Several synthesis strategies have been employed to harness the unique abilities of noble metal-supported photocatalysts, including wet impregnation, electrochemical deposition, and photodeposition. However, the photoreduction method has proven superior to others due to its high deposition ratio, simplistic reaction conditions, low aggregation, and higher photoactivity enhancement factor (~3-4).[18,19] The authors found no reports showing the synergetic adsorptive-photocatalytic removal of sucrose, a potential environmental pollutant, using Ag and Cu-decorated ZnO and TiO₂ NPs. Hence, in the present work, we synthesize Ag and Cu photo-deposited ZnO and TiO₂ to study their relative photodegradation rates towards sucrose (100 ppm). The synthesized NPs were characterized using various techniques to establish the rationale for their high efficiencies. Thus, this report aims to (i) address the comparative degradation efficiencies of two photocatalysts (ZnO and TiO₂) with very similar band gaps and (ii) study the effect of different noble metals (Ag and Cu) loading on each of these catalysts.

3.2 Experimental Section

3.2.1 Chemicals and materials

Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O], potassium hydroxide (KOH), and isopropyl alcohol (IPA) of analytical grade were acquired from Loba Chemie, India. Titanium tetraisopropoxide (TTIP), cupric nitrate (Cu(NO₃)₂·3H₂O), and silver nitrate (AgNO₃) were acquired from Sigma Aldrich, India. Ethanol was purchased from SD. Fine Ltd. Organo Biotech Laboratories Pvt. Ltd., an Indian company, supplied the triple-distilled deionized (DI) water. All the chemicals were of high purity and used as such.

3.2.2 Synthesis of ZnO and TiO₂ nanoparticles

ZnO NPs were fabricated using a wet chemical technique adapted from Kuriakose et al.[20] A typical synthesis involved the preparation of aqueous solutions of 200 mL of 0.1 molar Zn(NO₃)₂·6H₂O and 100 mL of 2 molar KOH, each agitated separately until they turned transparent. The zinc nitrate solution was stirred continuously while the KOH solution was added drop-wise until a pH of approximately 12 was reached. The white precipitates obtained were agitated for two hours and aged overnight at ambient conditions. The white residues were separated by ultracentrifuged, followed by several washings with DI water. Finally, the powdered sample was obtained by drying the precipitates at 80 °C overnight.

TiO₂ NPs were synthesized via a sol-gel technique using titanium tetraisopropoxide (TTIP) as a starting material.[21] In a standard procedure, 3.7 mL of TTIP was mixed with 40 mL methanol. After further addition of 40 mL methanol and 20 mL deionized water, this reaction mixture was continuously stirred while maintaining the temperature at 60 °C. The white products obtained are harnessed by ultracentrifugation and kept at 40 °C for drying. Finally, to harvest the desired crystalline TiO₂ NPs, the synthesized powder was heated up to 400 °C for two hours.

3.2.3 Metal photodeposition

Noble metals Ag and Cu were deposited onto the as-prepared ZnO and TiO₂ NPs via the photodeposition route. For this, suspensions of ZnO and TiO₂ in 50% v/v IPA solution are maintained under an inert argon atmosphere. Computed amounts of metal precursors AgNO₃ and Cu(NO₃)₂ are added to these solutions to obtain the desired loading of 1 wt% of Ag and Cu. Photochemical deposition of Ag and Cu is then performed under a UV lamp (mercury arc lamp with an intensity of 104 W/m²) for two hours. Later, the powdered NPs were recovered by ultracentrifugation and dried at 85 °C overnight. The metal-decorated samples were labeled Ag@ZnO, Cu@ZnO, Ag@TiO₂, and Cu@TiO₂, representing 1 wt% loading of Ag and Cu on ZnO and TiO₂, respectively.

3.2.4 Adsorption studies

This study used the batch method to investigate the adsorption characteristics of the above-synthesized photocatalysts towards sucrose. In a typical adsorption setup, 2 mg of various catalysts were added to 5 mL of 100 ppm sucrose solutions in separate test tubes. These suspensions were agitated continuously in the dark for 60 min. The concentration of sucrose remaining in the solutions after adsorption was estimated by UV-visible spectroscopy using the colorimetric method.[22] 2 mL of sucrose solution was pipetted from the test tube, ultracentrifuged to separate the powder catalyst, and stored in a glass vial. To this solution, 1 mL of 5% w/w aqueous phenol solution and 5 mL of conc. sulfuric acid was added swiftly, directing it toward the liquid rather than the sides of the vial. A vibrant orange-colored solution is formed if sucrose is present in the solution. The λ_{max} of this organic solution was centered at a wavelength of 490 nm. The amount of dye adsorbed onto the photocatalysts (q_e) was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where C_0 and C_e were the concentrations of sucrose (mg L^{-1}) at time $t = 0$ min, and equilibrium, respectively, V (mL) is the volume of sucrose solution, and M (g) is the mass of the photocatalyst used. This data was used to draw the adsorption isotherms and kinetic analysis. Finally, the adsorption efficiency (AE) was calculated as:

$$AE(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

3.2.6 Photocatalytic activity analysis

The efficiency of prepared materials as photocatalysts was assessed for the removal of sucrose, employing the standard procedure of adsorption followed by photocatalysis. Firstly, 2 mg of various catalysts were added to separate test tubes, each carrying 5 mL of sucrose solution with a concentration of 100 ppm. Each solution was stirred continuously under dark conditions for 30 min. This step allows the catalyst and adsorbent to reach adsorption-desorption equilibrium.

Secondly, after 30 minutes, the sucrose solutions were exposed to visible light irradiation for 25 minutes using an LED lamp (Power: 50 W, intensity: 100 W/m^2) while stirring continuously. After every 5 minutes, solutions from the different test tubes were taken and centrifuged to separate the catalyst. The concentration of sucrose left in the solution after each time interval was then analyzed by UV-visible spectroscopy using the abovementioned method. The obtained data were fitted into the Langmuir-Hinshelwood model for a pseudo-first-order reaction:

$$\ln(C_0/C_t) = -kt \quad (3)$$

where C_0 and C_t were the concentration of sucrose (mg L^{-1}) initially and at the time 't' min, k is the rate constant in min^{-1} , and t is the time.

Finally, the degradation efficiency (DE) of various photocatalysts is calculated as:

$$DE(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (4)$$

3.3 Results and discussion

3.3.1 Structural analysis

X-ray diffraction patterns

The XRD spectra of various ZnO NPs presented in Fig. 3.1(a) show a high crystallinity and hexagonal wurtzite structure matching ICDD card no. 036-1451. The diffraction peaks were

observed at 31.86°, 34.5°, 36.34°, 47.62°, 56.7°, 62.92°, 66.48°, 68.02°, and 69.22°, which can be indexed to diffraction planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. The crystallite size was determined using Scherrer's equation, $D = (K\lambda) / (\beta \cos \theta)$, where K (Scherrer's constant) = 0.9, λ is the wavelength of Cu – K α radiation used in X-ray diffractometer (1.540598 Å), β is the FWHM (full-width at half-maxima), and θ is the position of the diffraction peak and the various computed values are presented in Table 3.1. The average crystallite size of ZnO, Cu@ZnO, and Ag@ZnO is 11.08 nm, 12.10 nm, and 13.225 nm, respectively. The increase in crystallite size could be due to the successful decoration of Cu and Ag particles at the ZnO NPs. The diffraction patterns of the synthesized TiO₂ NPs presented in Fig. 3.1(b) coincide with the anatase phase of TiO₂ (ICDD card no. 211276).

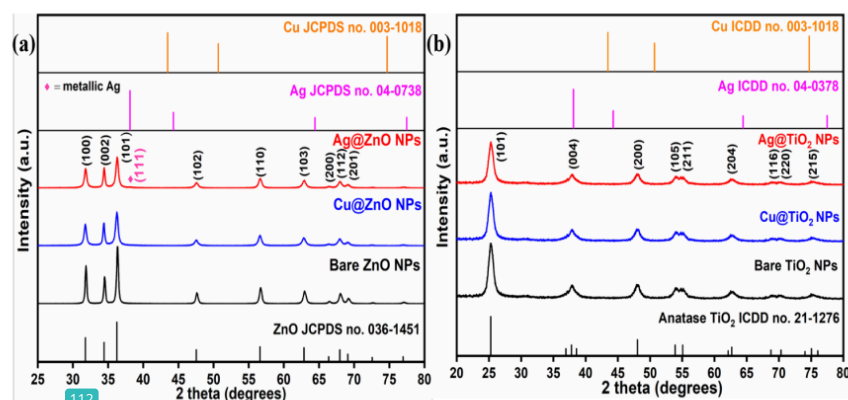


Fig. 3.1 X-ray diffraction patterns of (a) ZnO NPs and their Ag and Cu-loaded counterparts, (b) bare and modified anatase TiO₂ NPs.

The diffraction patterns were observed at 25.5°, 37.92°, 48.24°, 54.1°, 55.26°, 62.7°, 68.86°, 70.5°, and 75.22° corresponding to planes (101), (004), (200), (105), (211), (204), (116), (220), and (215) of anatase phase TiO₂, respectively. The calculated average crystallite size for TiO₂, Cu@TiO₂, and Ag@TiO₂ is 9.952 nm, 9.970 nm, and 9.972 nm, respectively. Thus, a very minuscule increase in crystallite size upon Cu and Ag loading is observed. Furthermore, in both photocatalysts, it is observed that upon 1 wt% Ag and Cu loading, no defined characteristic peaks for cubic phase Ag and Cu are obtained, plausibly due to the smaller size and lower concentration of these metallic NPs. However, upon metal loading, the height of the peaks declines due to a slight disturbance in

the crystalline structure of ZnO and TiO₂ NPs caused by the deposition of Ag and Cu at their surfaces. Nevertheless, no peak shifting of ZnO and TiO₂ peaks is observed, indicating no replacement of the semiconductor cations by Ag⁺ and Cu²⁺ in the lattice backbone of these NPs. The significant concentration of these metallic ions undergoes photoreduction and gets decorated at the outer planes of ZnO and TiO₂.

3.3.2 Morphological analysis

FE-SEM, EDS, and HR-TEM analysis

The FE-SEM images and EDS spectra of unmodified, Cu, and Ag-loaded ZnO and TiO₂ are shown in Fig. 3.2. Fig. 3.2(a-c) show almost spherical-like particles of ZnO, Ag@ZnO and Cu@ZnO. The calculated average size (Fig. 3.3(a)) of the NPs is 33.6 ± 12.3 nm. Fig. 3.2(g-i) shows spherical-like NPs of bare and modified TiO₂ NPs, with an average size of 28 ± 8 nm (Fig. 3.3(b)).

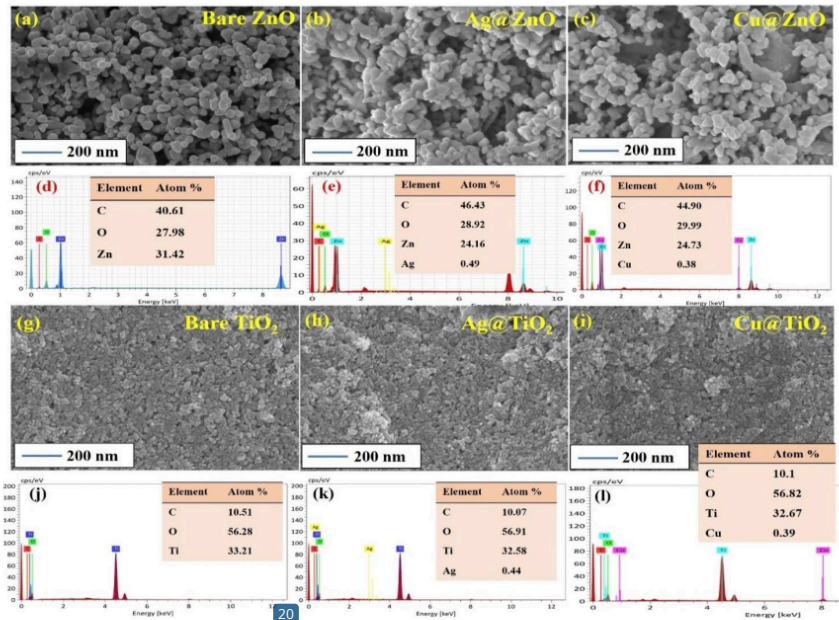


Fig. 3.2 FE-SEM micrographs of (a) bare ZnO, (b) Ag@ZnO, (c) Cu@ZnO, (g) bare TiO₂, (h) Ag@TiO₂, and (i) Cu@TiO₂, and EDS line spectra of bare, Ag, and Cu modified (d-f) ZnO, (j-l) TiO₂.

The EDS spectra confirmed the presence of Cu and Ag on ZnO and TiO₂ NPs (Fig. 3.2(d-f, j-l)), with the detected amounts less than the targeted 1 wt% due to the inevitable loss of these metal NPs during the washing of photocatalysts.

HRTEM analyses are conducted for better resolution. The dark spots in Fig. 3.4(a, c) relate to the silver particles deposited atop the ZnO and TiO₂ NPs. The computed lattice fringes in Fig. 3.4(b, d) for ZnO and TiO₂, respectively, conclude the presence of Ag in these materials. In Fig. 3.4(a), agglomeration of the ZnO base can be seen, which could be the reason for its larger particle size. Further, Ag NPs are clumped together at the surface of these ZnO NPs.

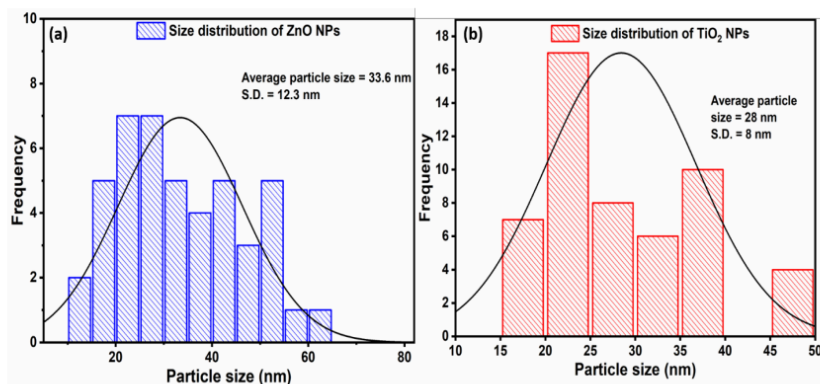


Fig. 3.3 Average particle size of (a) ZnO NPs and (b) TiO₂ NPs.

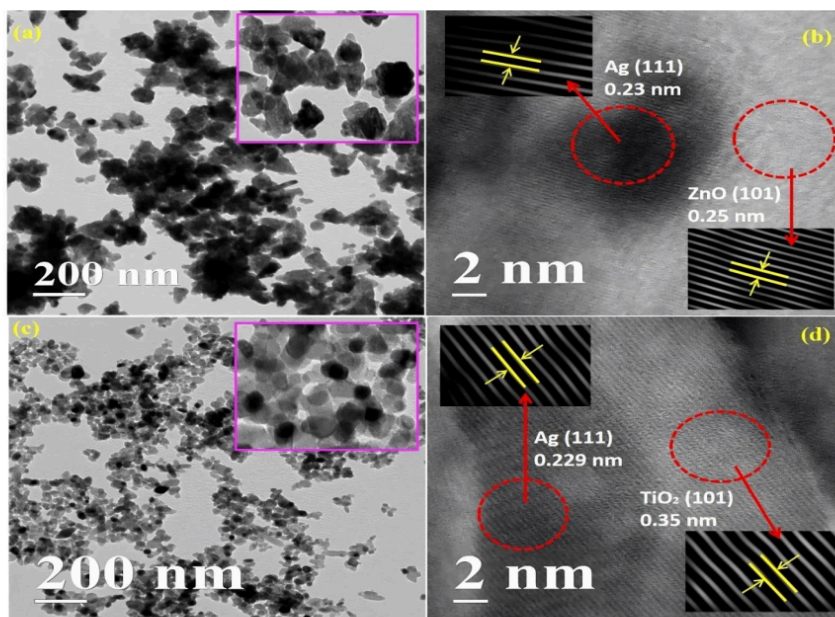


Fig. 3.4 TEM and HRTEM images of (a-b) Ag@ZnO NPs and (c-d) Ag@TiO₂ NPs. The respective lattice fringes are shown in inset (b) and (d).

In contrast, the TiO₂ base is seen as small spherical NPs with well-dispersed Ag-NPs at their surface. ZnO's greater particle size than TiO₂ is confirmed by both the FE-SEM and HR-TEM graphs.

3.3.3 X-ray photoelectron spectroscopy (XPS) elemental analysis

The XPS analyses examined the chemical states, composition, and charge-transfer properties of photocatalysts Ag@ZnO, Cu@ZnO, Ag@TiO₂, and Cu@TiO₂. The survey spectra shown in Fig. 3.5(g) validate the presence of carbon (C), oxygen (O), zinc (Zn), and silver (Ag) atoms in Ag@ZnO. Further, C, O, Ti, and Ag atoms are witnessed in Ag@TiO₂ NPs (Fig. 3.5(h)). The presence of Cu was confirmed in the survey spectra of Cu-loaded ZnO and TiO₂ materials, as shown in Fig. 3.6(g-h). These findings back the XRD and EDS results of these NPs. The absence of any other impurity provides further evidence of the excellent purity of fabricated photocatalysts.

The carbon peaks at a binding energy (BE) of 284.74 eV (Ag@ZnO), 283.5 (Cu@ZnO), 284.54 eV (Ag@TiO₂), and 284.2 eV (Cu@TiO₂) were primarily attributed to the residuary carbon in the samples and the hydrocarbons originating from the photoelectron spectroscopy instrument.[23]

The high-resolution spectra of Zn 2p, O 1s, and Ag 3d are shown in Fig. 3.5(a-c). As shown in Fig. 3.5(a), there are two peaks for Zn; the peak centered at 1021.8 eV corresponds to the Zn 2p_{3/2} energy level, and the second peak at 1044.8 eV corresponds to the BE of Zn 2p_{1/2}. These peaks indicate the presence of Zn²⁺ in a normal state in the Ag@ZnO NPs. Ti (2p) spectrum exhibits two identifiable peaks at 458.7 eV and 464.4 eV, attributed to Ti 2p_{3/2} and Ti 2p_{1/2} binding signals, respectively (Fig. 3.5(d)). The measured disparity in the binding energies (BE) of these two peaks was 5.7 eV, indicating the presence of titanium in the +4 (Ti⁺⁴) chemical state.[24] The O 1s spectra (refer to Fig. 3.5(b) and 3.6(e)) could be deconvoluted into two distinct peaks for both Ag@ZnO and Ag@TiO₂ NPs: 532.0 eV (O_I) and 530.6 eV (O_{II}) in Ag@ZnO, and 531.5 eV (O_I) and 530.0 eV (O_{II}) in Ag@TiO₂. In both cases, the higher BE (O_I) peak is associated with adsorbed oxygen or hydroxide attached to the surface of the nanocatalysts. The lower BE peak (O_{II}) is ascribed to the lattice Zn-O and Ti-O binding, respectively. This surface hydroxyl group plays a crucial role in heterogeneous photocatalysis.

The high-resolution spectra of Ag 3d (Ag@ZnO NPs), shown in Fig. 3.5(e), deconvoluted into two peaks centered at 373.9 eV and 368.07 eV. Similarly, in Ag@TiO₂, two distinct peaks are observed for Ag 3d (Fig. 3.5(f)), positioned at 373.9 eV and 367.8 eV. The peaks at higher BE correspond to Ag 3d_{3/2}, and those at lower BE are attributed to Ag 3d_{5/2} states of silver in the metallic state (Ag⁰), confirming the accomplishment of the photoreduction of Ag⁺ to Ag⁰ at the surface of the photocatalysts. Further, no peaks for Ag⁺ are obtained in either case.

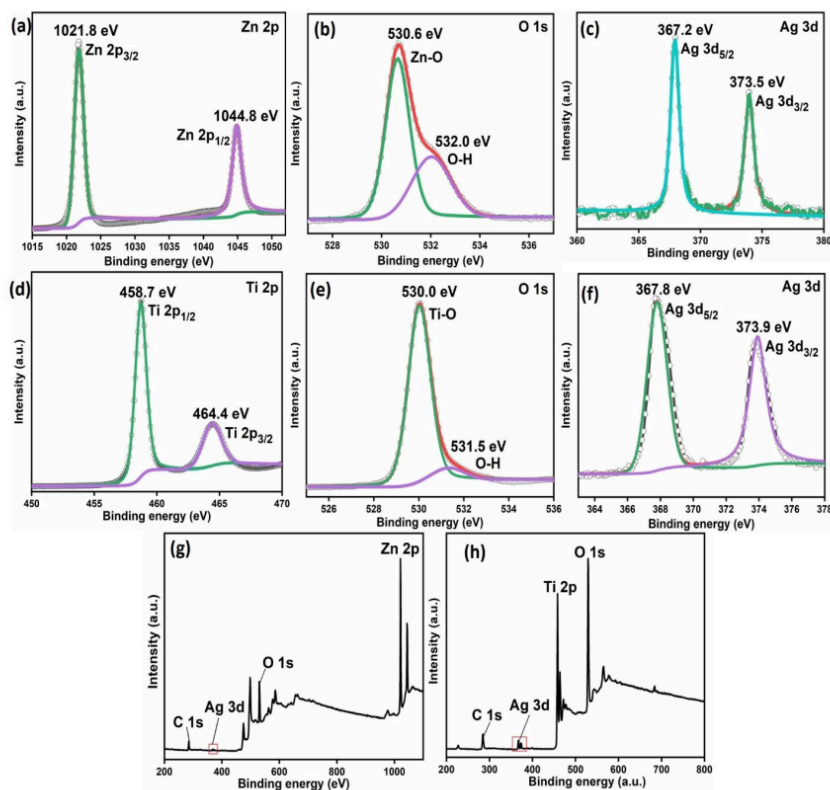


Fig. 3.5 XPS spectra (a-c) Ag@ZnO NPs, and (d-f) Ag@TiO₂ NPs. Survey scan of (g) Ag@ZnO, and (h) Ag@TiO₂.

Here, a subtle deviation in BE is seen compared to BE of chemical states of bulk Ag (374.2 eV and 368.2 eV). The slight shift towards lower BE reveals the strong interactions between Ag-ZnO and Ag-TiO₂.^[25] This interaction is further responsible for the redshift obtained in DRS results discussed in the next section. Further, this decrease is more in the case of Ag@ZnO, which could imply a stronger Ag-ZnO binding than Ag-TiO₂. Two peaks are obtained in the XPS spectra of both Cu-loaded materials (Fig. 3.6(c,f)), Cu@ZnO (933.28 eV and 952.5 eV) and Cu@TiO₂

(933.52 eV and 952.32 eV). The peaks at higher BE may be attributed to Cu 2p_{1/2} energy levels, and the peaks centered at lower BE could be indexed as Cu 2p_{3/2} chemical states.[26]

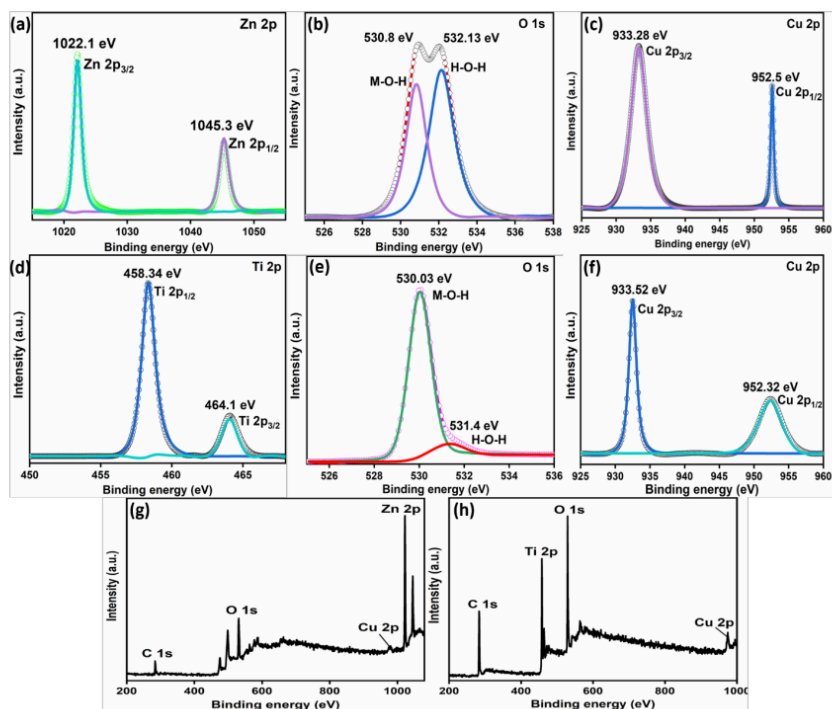


Fig. 3.6 XPS spectra (a-c) Cu@ZnO NPs, and (d-f) Cu@TiO₂ NPs. Survey scan of (g) Cu@ZnO, and (h) Cu@TiO₂.

3.3.4 Optical and charge transfer analysis

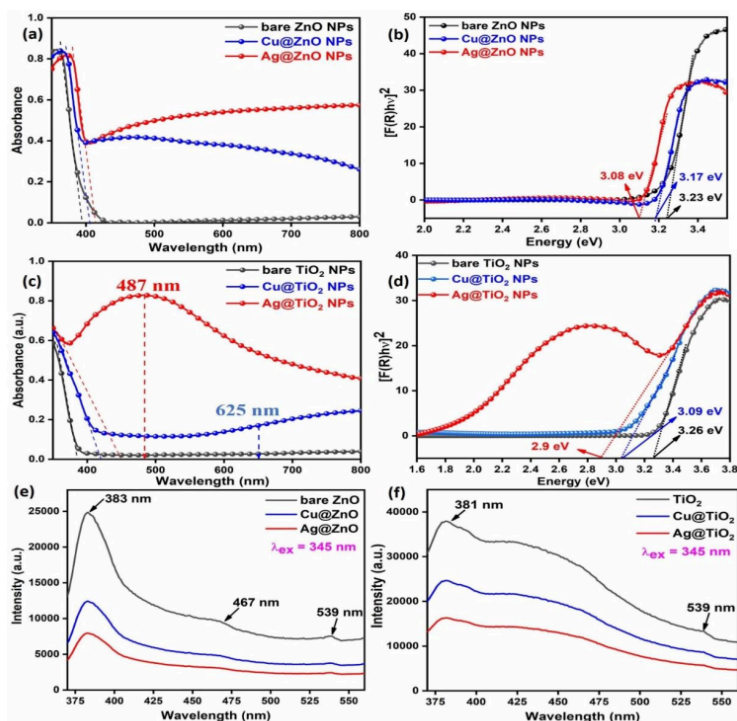
Diffuse reflectance spectra studies

The light absorbance and optical band gaps of pure and metal-deposited ZnO and TiO₂ samples were determined by analyzing the UV-Vis DRS spectra (shown in Fig. 3.7(a-d)). Pristine ZnO exhibits a prominent absorption edge at 394 nm in the ultraviolet (UV) region, which shifts towards the visible regions upon Cu (406 nm) and Ag (415 nm) loading (as shown in Fig. 3.7(a)). The presence of metallic Cu and Ag NPs in Cu@ZnO and Ag@ZnO samples is indicated by the

emergence of a broad band in the region 450-750 nm, corresponding to these metals' distinctive surface plasmon resonance (SPR). Further, the increase in absorption in the visible region is more significant in Ag than in Cu. In TiO₂, the edge of the absorption band is obtained at 384 nm (UV-active), which exhibits a red shift upon Cu and Ag loading to 419 nm and 450 nm, respectively (Fig. 3.7(c)). Further, an increased absorbance is seen in the visible region upon Cu deposition, with an edge at 625 nm. Additionally, in Ag@TiO₂, a strong absorption peak is obtained at 487 nm. Pristine ZnO and TiO₂ show no absorbance in the region 400-750 nm; therefore, the capturing of visible light by the synthesized photocatalysts is wholly attributed to the LSPR effect of Cu and Ag NPs, as they facilitate charge transfer from the d-electronic states of the metal to the conduction band (CB) of these semiconductor oxides. Also, it is reported that the absorption edge of plasmonic metals depends upon the number of free electrons in the metal.[27] The electron density of metal has an inverse relationship with the wavelength of plasmonic absorption. Thus, a red shift in the absorption edge of plasmonic metal-modified ZnO and TiO₂ would mean transferring the electron density between plasmonic metals (Cu and Ag) and the semiconductor oxides (ZnO and TiO₂). The Tauc plots in Fig. 3.7(b) and 3.7(d) were obtained using the Kubelka-Munk function, $(F(R_{\infty})/h\nu)^2 = B(h\nu - E_g)$, where h represents the photon energy, ν is the frequency of the photon, E_g is the direct band gap of the material, B is a constant, and R_{∞} is the reflectance of a specimen with infinite thickness and is equal to $R_{\text{sample}}/R_{\text{standard}}$. [28] The calculated band gaps for ZnO materials are 3.23 eV, 3.17 eV, and 3.08 eV for bare, Cu@ZnO and Ag@ZnO NPs. The observed band gaps for TiO₂, Cu@TiO₂, and Ag@TiO₂ are 3.26 eV, 3.09 eV, and 2.9 eV, respectively. Thus, a perceivable band contraction is obtained upon metal deposition, which is higher in the case of Ag in both photocatalysts. This contraction confirms the role of noble metals Cu and Ag in the band gap modification of semiconductor oxides ZnO and TiO₂ for their superior photoactivity under visible light irradiation.

Photoluminescence (PL) spectra studies

The room-temperature PL spectra of the fabricated materials were performed at $\lambda_{\text{ex}} = 345$ nm. In Fig. 3.7(e,f), respectively, ZnO and TiO₂ show emission peaks in the UV region at 383 nm and 381 nm.



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Fig. 3.7 UV-visible diffuse reflectance spectra (a, c) and Tauc plots (b, d) of various ZnO and TiO₂ materials. Room temperature photoluminescence spectra of various ZnO (e) and TiO₂ (f) materials at $\lambda_{\text{ex}} = 345$ nm.

These high-energy emission bands originate from the recombination of the photogenerated charge carriers. These UV emissions are centered near the absorption edge of ZnO and TiO₂ (observed in DRS spectra), referred to as a near-band edge emission (NBE). The PL spectra of ZnO also comprise two weak emissions in the visible region centered at 467 nm, and 539 nm. Similarly, weak visible emissions are observed in the spectra of TiO₂ between 410–480 nm, which have been linked to d-d transitions of localized states of Ti³⁺. [29] Additionally, in case of TiO₂ materials, a small peak is also observed at 539 nm. These emission peaks in the visible region can be linked to e⁻ transitions and deep-level emissions origination due to various crystal defects (DE). [14,30–32]

The visible region emissions are contingent upon the synthesis procedure, shape, and surface flaws of ZnO and TiO₂. These emissions occur when excited e⁻s move to defect levels with lower energy and combine with h⁺s in the VB.[33] The presence of Cu and Ag on the semiconductor surface appreciably reduced the intensity of all emission peaks. The quenching of all emissions can be attributed to the movement of photoexcited e⁻ from the CB of the ZnO and TiO₂ material to Cu and Ag NPs, as well as the injection of hot electrons from LSPR of Cu and Ag NPs when exposed to radiation. These results are consistent with the DRS and XPS results. Furthermore, the maximum suppression is seen in Ag@ZnO, which implies the least recombination rate and maximum spatial separation of charge carriers. Thus, a higher degree of interaction exists between Ag and ZnO than other metal-semiconductor combinations, which also manifested in the XPS binding energies.

3.3.5 Electrokinetic analysis

The influence of surface charge on the adsorption efficiency of the catalyst is widely recognized. The zeta potentials (ζ) of prepared ZnO and TiO₂ samples were determined under varying pH conditions by dynamic light scattering (DLS) studies. As depicted in **Fig. 3.8(a)**, ZnO NPs had a hydrodynamic size of 306 nm, which increased to 451 nm and 628 nm upon Cu and Ag loadings, respectively. The TiO₂ materials followed a similar fashion and possessed a hydrodynamic size of 1107 nm, 1280 nm, and 1652 nm for bare, Ag@TiO₂, and Cu@TiO₂, respectively (**Fig. 3.8(b)**). Further, the hydrodynamic size of TiO₂ materials was higher than ZnO, agreeing with the size calculation from XRD and FE-SEM data. The surface zeta potentials of all photocatalysts were determined by averaging ten values. The tests revealed that all the fabricated photocatalysts' surfaces were negatively charged at neutral pH. At pH=7, ZnO materials displayed a -ve zeta potential of -2.56 mV, -6.26 mV, and -7.46 mV for bare, Cu, and Ag-modified catalysts, respectively.

In contrast, TiO₂ materials showed higher negative values at neutral pH with zeta potentials -6.78 mV for bare TiO₂, -10.3 mV for Cu@TiO₂, and -13.9 mV for Ag@TiO₂, sequentially. Further, the zeta potential aqueous suspensions of nanoparticles can be influenced by various parameters, such as the pH of the solution.[34] The zeta potentials decreased upon increased pH, and the surface charge became +vely charged upon decreasing the pH. However, in extreme acidic or basic

conditions, ZnO dissolution occurs.[35] Thus, the zeta potential studies were performed at pH=5, 7, and 9. The ζ of all materials with varying pH are shown in Fig. 3.8(c).

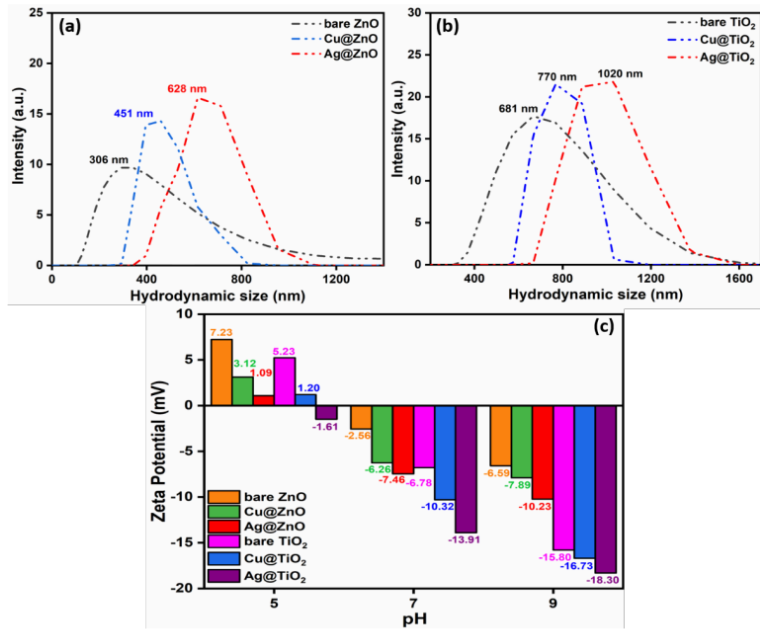


Fig. 3.8 Electrokinetic studies of various photocatalysts.

3.3.6 Surface area analysis

The agglomeration of Ag on the ZnO surface could block its active sites, manifested in the Brunaur-Emmett-Teller (BET) surface area analyses of these NPs. Fig. 3.9 reveals the N_2 adsorption-desorption curves for various materials. The S_{BET} (BET surface area) of various fabricated materials is shown in Table 3.1. It is noted that upon Cu and Ag loading, the S_{BET} of bare ZnO NPs declines from 8.331 m²/g to 5.92 m²/g and 4.89 m²/g, respectively. The TiO₂ NPs had a slightly higher surface area of 12.41 m²/g, which showed a very slight decrease to 12.20 m²/g upon Cu loading and 12.04 m²/g upon Ag loading. This trend could be explained by the uniformly distributed metal NPs at the surface of TiO₂ materials (as shown in the case of HRTEM images, Fig. 3.4(c)).

Table 3.1 Parameters analyzed using Scherrer method and BET analyses.

Photocatalyst	Crystallite size (nm)	S_{BET} (m ² /g)
Bare ZnO	11.08	8.331
Cu@ZnO	12.10	5.92
Ag@ZnO	13.225	4.89
Bare TiO ₂	9.952	12.41
Cu@TiO ₂	9.970	12.20
Ag@TiO ₂	9.972	12.04

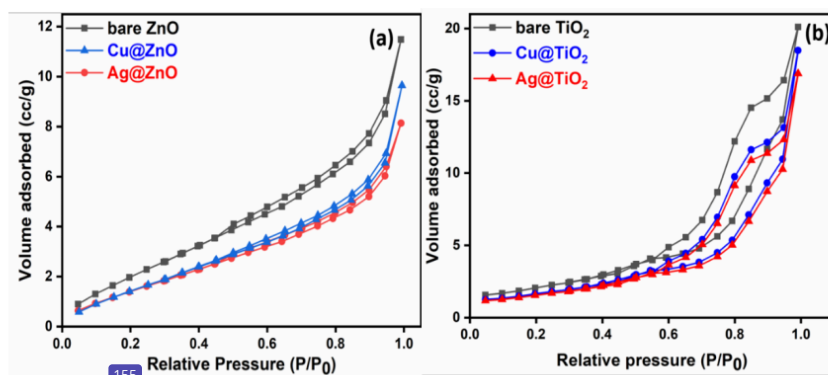


Fig. 3.9 (a) N₂ adsorption-desorption isotherms of (a) bare ZnO, Ag@ZnO, and Cu@ZnO; (b) bare TiO₂, Ag@TiO₂, and Cu@TiO₂.

3.4 Adsorption and photocatalytic activity

3.4.1 Influence of pH

Understanding the influence of pH change is crucial for studying pollutant adsorption. The initial pH of the reaction mixture can significantly impact the adsorption studies. For this study, we performed the adsorption studies in a pH range of 5.0 to 9.0, using initial concentrations of 100 ppm for sucrose. **Fig. 3.11(a)** displays the absorbance responses for sucrose at pH values of 5.0, 7.0, and 9.0. This pH range (5.0–9.0) was chosen for two reasons. Firstly, it was observed that if

pH falls below 5, the ZnO dissolves in the solution. This dissolution occurs due to surface hydrolysis, followed by the diffusion of Zn^{2+} ions into the bulk solution.[36,37] Secondly, sucrose is converted to invert sugar in acidic and alkaline solutions. This sucrose conversion is undesirable in sucrose treatment processes as it leads to sucrose loss and the formation of colorants with high molecular masses.

The maximum stability of sucrose is observed at a pH of 8.2.[38,39] For the adsorption of sucrose, it was noted that for both ZnO and TiO_2 -based materials, their AE increased with an increase in pH. The highest AE was observed at pH = 9, which was then singled out as the optimum pH for the subsequent sucrose removal studies. The maximum AE was shown by TiO_2 NPs, which depends upon two factors: surface area and surface charge. TiO_2 has the highest surface area and a less -ve surface charge than its metal-loaded counterparts. The -OH groups in the sucrose molecule also possess a partial negative charge due to the high electronegativity of the O atom. Thus, the sucrose molecule would feel the least repulsion towards TiO_2 NPs ($\zeta = -15.8$ mV) compared to Cu@TiO_2 ($\zeta = -16.73$ mV) and Ag@TiO_2 ($\zeta = -18.30$ mV).

3.4.2 Influence of contact time

The interaction duration between the adsorbate and adsorbent is a crucial aspect of the adsorption process, as the adsorption intensifies with extended contact periods until equilibrium is attained.

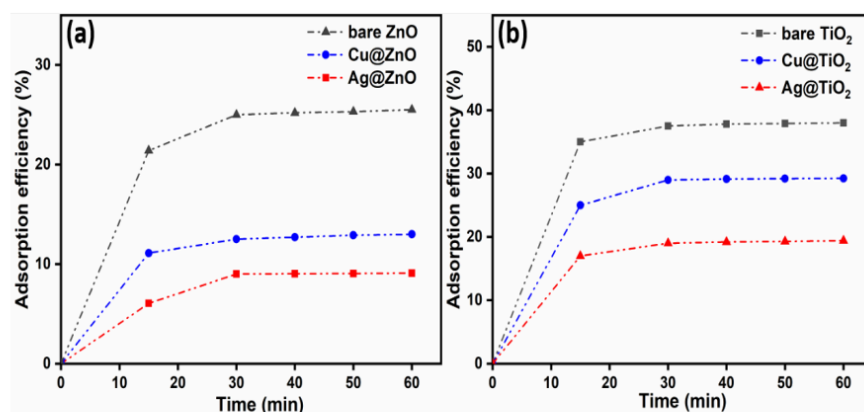


Fig. 3.10 Influence of contact time upon the adsorption of sucrose by (a) bare and metal loaded ZnO, and (b) bare and metal loaded TiO_2 .

It can be seen in **Fig. 3.10** that in both ZnO and TiO₂ materials, the adsorption rate increases almost linearly in the first 15 minutes. After which, the adsorption increase slowed and reached equilibrium in 30 minutes. This sharp increase might be due to high interactions between the adsorbate and adsorbent initially, which fall off as a significant amount of sucrose molecules gradually cover the surface of the adsorbents (pristine and metal-loaded ZnO and TiO₂). After 30 minutes, the increase in adsorption was insignificant; hence, 30 minutes was selected as the optimum time for adsorption experiments.

3.4.3 Assessment of adsorption isotherms

At the optimized pH and contact time conditions, adsorption studies were carried out to study the impact of changes in the initial sucrose concentration (C_0) from 10 – 100 ppm. The adsorption performances of various fabricated materials were assessed via Langmuir and Freundlich isotherms using the following formulae:

$$C_e/q_e = C_e/q_m + 1/K_L \cdot q_m \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

where the K_L denotes the Langmuir equilibrium constant, K_F denotes the Freundlich equilibrium constant, and the constant 'n' is associated with the Freundlich adsorption intensity. $1/n = 0$ indicates an irreversible isotherm, $1/n < 1$ indicates a favorable isotherm, and $1/n > 1$ indicates an unfavorable isotherm. For a favorable adsorption process, the value of n must lie between 0 and 10. [40] C_e represents the equilibrium sucrose concentration, and q_e and q_{max} are the photocatalysts' equilibrium and maximum adsorption capabilities, respectively. It can be observed in **Fig. 3.11(b)** that the amount of sucrose adsorbed q_e increases almost linearly upon an increase in C_0 of sucrose from 5 ppm to 80 ppm, after which the increase diminishes slowly at higher concentrations (80 ppm to 110 ppm). The maximum adsorption was observed at 100 ppm, which marked the saturation of the adsorption sites. Langmuir and Freundlich's adsorption isotherms characterized the adsorption equilibria upon various materials, presented in **Fig. 3.11(c-d)**. The Langmuir and Freundlich data fitting was done, and the corresponding fitting parameters of ZnO and TiO₂ materials are summed up in **Table 3.2**. The adsorption equilibrium data fitting into the Langmuir model provided a higher R^2 factor than the Freundlich isotherm for all six adsorbents. Thus, it can be concluded that sucrose adsorption on bare, Cu, and Ag-loaded ZnO and TiO₂ materials occurs

via monolayer formation. Further, the Langmuir adsorption model implies that molecules are adsorbed in a uniform manner. Therefore, it can be inferred that the synthesized materials are relatively homogeneous, with Cu and Ag metals decorated evenly on their surfaces.

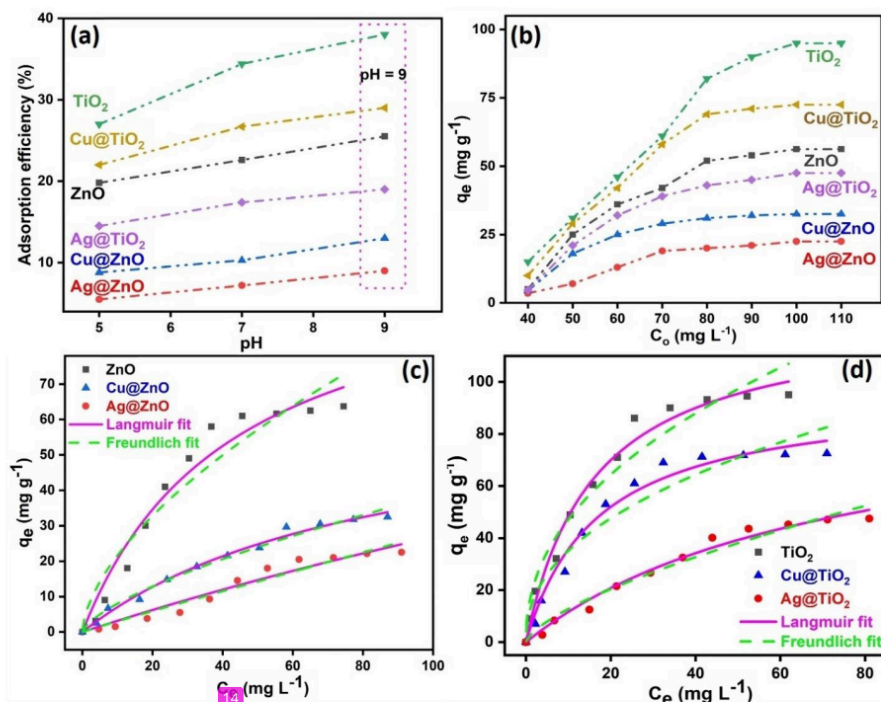


Fig. 3.11 (a) Adsorption responses at different pH values, (b) adsorption capacities of sucrose on various materials, Langmuir and Freundlich isotherm fit of adsorption of sucrose by (c) ZnO materials, and (d) TiO₂ materials.

Further, the $q_{\max}$ was the highest, i.e., 156.099 mg g⁻¹ for bare TiO₂, demonstrating the highest adsorption capability amongst all the synthesized materials, which could be due to its highest surface area and uniformly distributed nanoparticles. The q_m for bare TiO₂ was ~1.5 times higher than bare ZnO ($q_m = 109.074$ mg g⁻¹), which has a lower surface area, possibly due to the agglomeration of nanoparticles.

Table 3.2 Comparison of Langmuir and Freundlich model parameters for the adsorption of sucrose by various adsorbents.

Adsorbent	Langmuir model			Freundlich model		
	$q_{\max}$ (mg g ⁻¹)	K_L	R^2	K_F	$1/n$	R^2
ZnO	109.1	0.02323	0.96	5.3568	0.6058	0.89
Cu@ZnO	95.7	0.01175	0.99	1.6694	0.6810	0.96
Ag@ZnO	66.9	0.00207	0.95	0.3325	0.9611	0.93
TiO ₂	156.1	0.06223	0.98	16.801	0.4485	0.93
Cu@TiO ₂	126.1	0.05935	0.98	12.898	0.4355	0.89
Ag@TiO ₂	96.8	0.01363	0.98	2.6585	0.6802	0.95

3.4.4 Assessment of adsorption kinetics

Studying the rate at which a pollutant is eliminated is crucial for determining the most effective operational parameters in real-world systems.[41] Typically, adsorption is a two-step process: diffusion and absorption. Two kinetic models were employed to analyze the sucrose adsorption mechanism upon our fabricated materials. In the diffusion step, it is assumed that numerous sucrose molecules drift toward the surface of the adsorbent material due to a concentration gradient separating the bulk solution and adsorbate-adsorbent boundary. In this process, the diffusion rate is determined by the initial sucrose concentration and the adsorption positions available on bare and modified ZnO and TiO₂ materials. Therefore, pseudo-second-order kinetic calculations are employed to analyze the diffusion process. For the absorption step, the electrostatic contact plays a role between the sucrose molecules and the adsorbents. For this step, the number of vacant adsorption positions influenced the rate of adsorption. The rate constants of adsorption for pseudo-first-order and pseudo-second-order models, sequentially, are given below:

$$t/q_t = 1/(k_d q_e^2) + t/q_e \quad (7)$$

$$\ln(q_e - q_t) = \ln q_e - k_a t \quad (8)$$

where q_e and q_t are the amounts of sucrose adsorbed in mg g⁻¹ at equilibrium and time = t min, k_d and k_a are the rate constants for the diffusion and absorption process, respectively.[42] The values

of q_e , rate constants, and correlation coefficients (R^2) calculated by fitting experimental data into the above equations are presented in Fig. 3.12, and the computed values are shown in Table 3.3. It is observed that the correlation coefficients are higher (~ 1) for the pseudo-second-order model in all adsorbents. However, the R^2 values are also fairly high for the pseudo-first-order kinetics model. Thus, it was deduced that the adsorption of sucrose upon bare, Cu, and Ag-modified ZnO and TiO₂ catalysts could follow both kinetics. The adsorption would depend on the sucrose concentration gradient between the bulk of the solution and the adsorbate-adsorbent interface, as well as the availability of adsorption sites.[43]

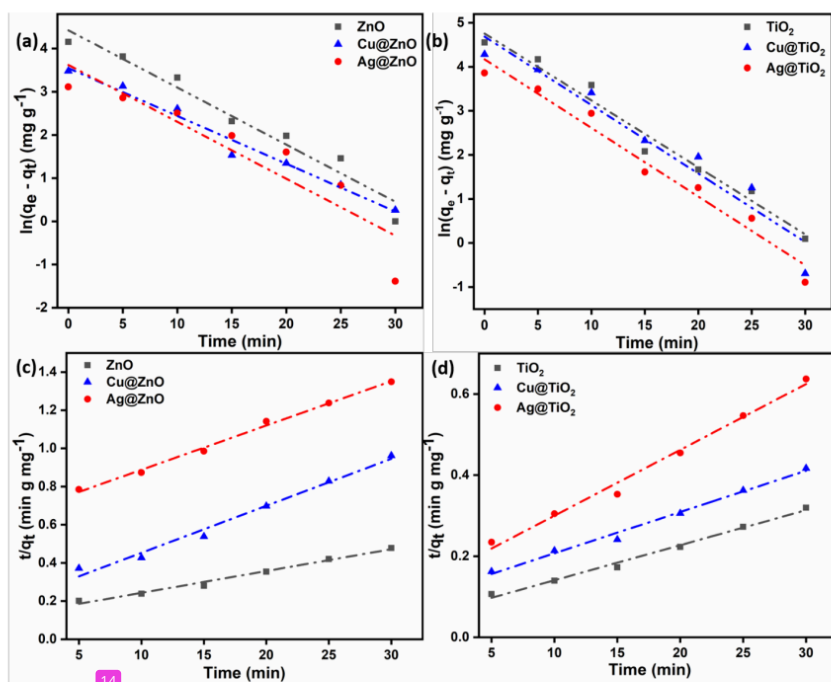


Fig. 3.12 (a) Kinetic psuedo-first order and (c) psuedo-second order models for bare and metal loaded ZnO. (b) Kinetic psuedo-first order and (d) psuedo-second-order models for bare and metal loaded TiO₂.

The adsorbent's surface area influences the first factor, whereas the surface potentials of adsorbent materials and the charge conditions of sucrose at various pHs influence the second. Thus, it is

observed that TiO₂ shows the highest AE of 38.2 %, which is higher than Cu@TiO₂ (29.5 %) and Ag@TiO₂ (19.1 %). The S_{BET} of these materials is comparable; however, upon Cu and Ag loading, the zeta potentials shift towards higher negative values (**Fig. 3.8(c)**). This increase in negative potential at the surface of the adsorbent materials might hinder the adsorption of sucrose molecules, which carry a partial negative charge centered at their oxygen molecules.[44] Further, in ZnO materials, the order of AE was found to be ZnO>Cu@ZnO>Ag@ZnO. Finally, the AE of TiO₂ is ~ 1.5 times higher than ZnO (AE = 25.4%), as the S_{BET} of TiO₂ is ~ 1.6 times higher than bare ZnO NPs.

Table 3.3 Comparison of pseudo-first-order and pseudo-second-order models of the adsorption of sucrose by various adsorbents

Adsorbent	pseudo-first-order kinetics			pseudo-second-order kinetics model		
	model (absorption)			(diffusion)		
	q _e (mg g ⁻¹)	K _a (min ⁻¹)	R ²	q _e (mg g ⁻¹)	K _d (g mg ⁻¹ min ⁻¹)	R ²
ZnO	83.096	0.13229	0.95	87.336	0.00202	0.99
Cu@ZnO	37.376	0.13178	0.95	43.066	0.00161	0.98
Ag@ZnO	34.639	0.11059	0.90	40.048	0.00095	0.99
TiO ₂	116.248	0.15199	0.97	115.60	0.00137	0.99
Cu@TiO ₂	108.251	0.15541	0.93	98.231	0.00098	0.99
Ag@TiO ₂	64.651	0.15558	0.96	61.652	0.00191	0.98

3.4.5 Photocatalytic degradation reaction

Before conducting the photocatalytic degradation experiment, the adsorption capacities of the synthesized bare and plasmonic metal (Cu and Ag) loaded ZnO and TiO₂ were examined without visible light for 30 minutes. Additionally, the photodegradation process was examined by varying the duration of irradiation in the absence of the photocatalyst. Subsequently, photocatalytic degradation was initiated after exposure to visible lamp radiation. The UV-visible absorption studies of sucrose photodegradation by Ag-loaded photocatalysts are depicted in **Fig. 3.14(a-b)**, and bare ZnO and TiO₂ are shown in **Fig. 3.13(a-b)**. The time-course photodegradation studies of sucrose in **Fig. 3.14(c-d)** demonstrated that Cu and Ag metal-loading led to a higher removal %

of sucrose than the unmodified semiconductor oxide NPs in both cases. In ZnO-catalysts, following a 25-minute exposure to visible light, the sucrose removal efficiencies are 100%, 89%, and 62% in Ag@ZnO NPs, Cu@ZnO NPs, and bare ZnO NPs. The removal % of sucrose achieved with bare TiO₂ NPs, Cu@TiO₂, and Ag@TiO₂ NPs is 58%, 72%, and 86%, respectively. These outcomes align with the observations from DRS spectra; ZnO possesses a broad energy gap of around 3.23 eV and an absorption edge at ~402 nm, whereas TiO₂ has a band gap of 3.26 eV and an absorption edge at ~395 nm. Consequently, ZnO and TiO₂ demonstrate photoactivity only in the ultraviolet (UV) and near-visible range.

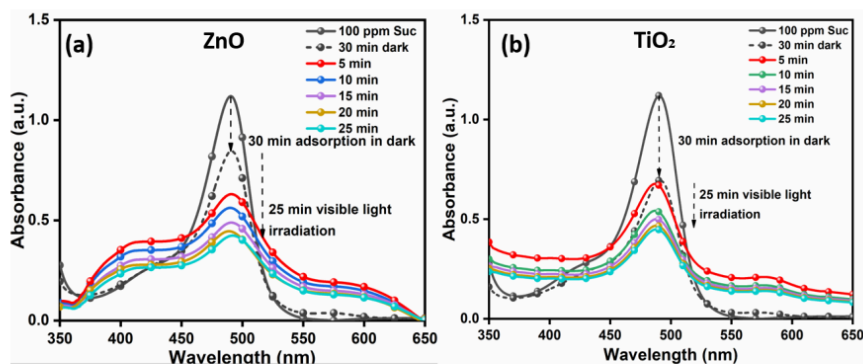


Fig. 3.13 Time-dependent UV-visible absorption spectra of photodegradation of sucrose by (a) ZnO and (b) TiO₂.

This band gap contracts upon loading plasmonic metals Cu and Ag, and the absorption response of semiconductor oxides moves towards the visible region. The plasmonic effects of Cu and Ag metals solely cause the high photoactivities in the visible range. ZnO-photocatalysts exhibit superior photocatalytic degradation, as they possess higher electron mobility (200–300 cm²/Vs) than TiO₂ (0.1–0.4 cm²/Vs), instrumental to a higher quantum efficiency.[45] Further, in both semiconductor oxides, Cu-loaded catalysts demonstrated slightly lower activities than Ag-loaded analogs, even though the DRS spectra reveal a high visible-light response for both noble metals. This gap possibly exists because the Ag materials possess a superior ability to trap electrons due to their higher reduction potential of + 0.79 eV as opposed to + 0.34 eV for Cu.

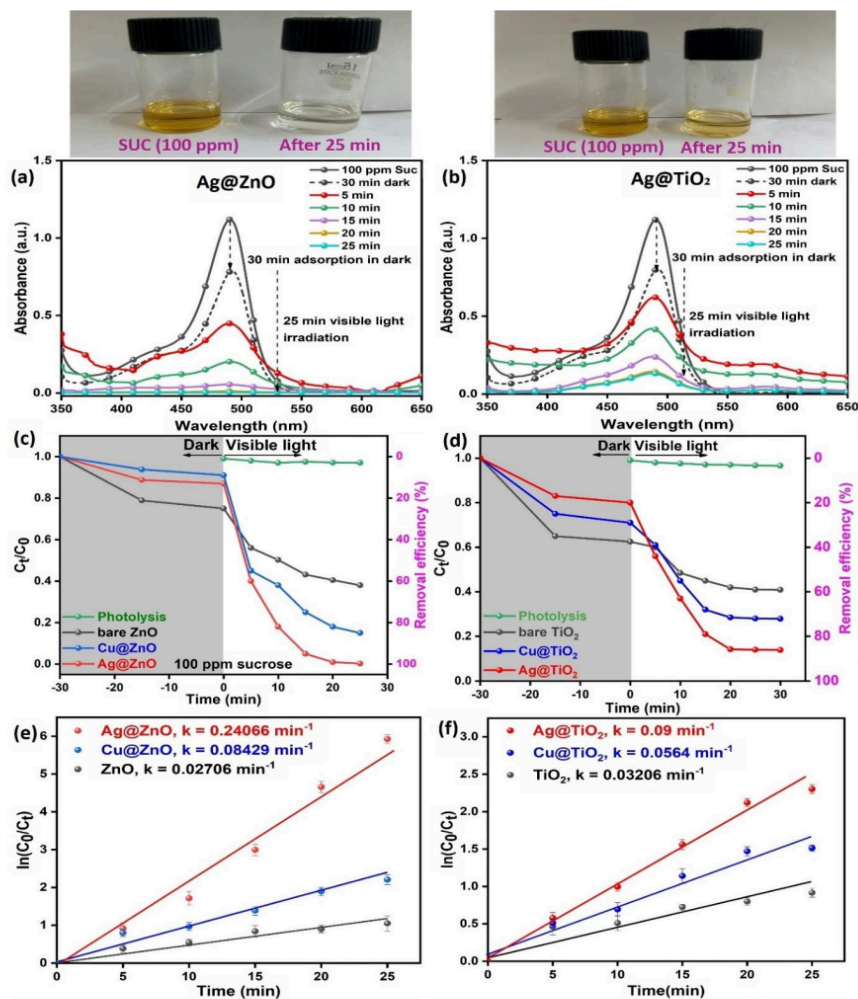


Fig. 3.14 UV-visible absorption spectra of photodegradation of sucrose by (a) Ag@ZnO and (b) Ag@TiO₂. Time-course photodegradation studies of 100 ppm sucrose by (c) ZnO and (d) TiO₂ photocatalysts. Pseudo-first order degradation kinetics of 100 ppm sucrose by (e) ZnO materials and (f) TiO₂ materials.

The order of prepared photocatalysts in terms of decreasing photocatalytic efficiency was found to be $\text{Ag@ZnO} > \text{Ag@TiO}_2 > \text{Cu@ZnO} > \text{Cu@TiO}_2 > \text{ZnO} > \text{TiO}_2$. However, the DE of Cu@ZnO is comparable to Ag@TiO_2 . Thus, it is aptly inferred that the plasmonic effects of both Ag and Cu are more pronounced in ZnO than in TiO_2 . The abovementioned outcomes indicate that even though Ag@ZnO has the least adsorption ability, the combined adsorption and photocatalytic degradation of Ag@ZnO NPs have a more effective synergistic impact on sucrose than other materials. The kinetics of sucrose's photodegradation were examined using eq. 3 for a pseudo-first-order reaction. The linear curves depicted in Fig. 3.14(e-f) confirm that the photocatalytic degradation of sucrose by all synthesized catalysts follows a pseudo-first-order reaction kinetics. The plasmonically modified catalysts showed a higher sucrose degradation rate than bare semiconductor oxides. The kinetic rate constant for the Ag@ZnO NPs was 0.24066 min^{-1} , approximately 12 times higher than pristine ZnO NPs and was the highest among all the catalysts. Furthermore, the rate constant for Ag@ZnO is ~ 3 times higher than Ag@TiO_2 NPs. The rate constants of other materials followed the trend $\text{Ag@ZnO}(0.24066 \text{ min}^{-1}) > \text{Ag@TiO}_2(0.09 \text{ min}^{-1}) > \text{Cu@ZnO}(0.08429 \text{ min}^{-1}) > \text{Cu@TiO}_2(0.0564 \text{ min}^{-1}) > \text{TiO}_2(0.03206 \text{ min}^{-1}) > \text{ZnO}(0.02706 \text{ min}^{-1})$. The reaction kinetics further establish the superiority of Ag@ZnO NPs towards the removal of sucrose from the solution.

3.5.3 Pollutant mineralization studies

The total organic carbon (TOC) removal calculations provide the precise quantity of organic carbon in a reaction mixture, and its decrease after the photocatalytic removal experiments reveals the exact extent of mineralization. The degree of mineralization for sucrose and its derivatives under 25 minutes of visible light was

Assessed using the formula:

$$\text{Mineralization (\%)} = ((\text{TOC}(\text{initial}) - \text{TOC}(\text{final})) / \text{TOC}(\text{initial})) \times (100).$$

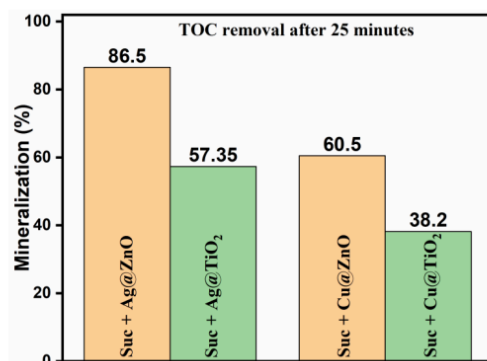


Fig. 3.15 (a) TOC removal studies of sucrose by Ag@ZnO and Ag@TiO_2

The TOC levels of sucrose decreased by 86.7% with Ag@ZnO. Meanwhile, % mineralization efficiency of 57.5% is attained with Ag@TiO₂ NPs (Fig. 3.15). In Cu-loaded counterparts, the TOC removal was computed at 60.5% and 38.2% by Cu@ZnO and Cu@TiO₂, respectively.

The photodegradation reaction of carbohydrates can also be confirmed by analyzing the change in the optical rotation of plane-polarized light passing through the solution.[39] The change in optical rotation of sucrose with different materials was observed before and after their photocatalytic reactions. The optical rotation of sucrose remained unchanged over time when not treated with any photocatalyst. However, it was observed that the optical rotation ($[\alpha]_D^{25}$) of sucrose declined from $[\alpha]_D^{25} = 55.2^\circ$ to zero upon treatment with Ag@ZnO NPs under visible light irradiation of 30-40 minutes. It implied the complete loss of chirality due to the degradation of sucrose to smaller optically inactive fragments.

3.5.4 Proposed photocatalytic degradation mechanism

Reactive oxygen species (ROS) are generated in photocatalytic processes when $e^- - h^+$ pairs react with the dissolved O₂ and H₂O molecules that get adsorbed at the surface of the photocatalytic material. These ROS facilitate the degradation of organic pollutants via oxidation and reduction processes. To shed light on the photocatalytic mechanism involved in the degradation of sucrose by our materials, trapping experiments were carried out by adding AgNO₃, potassium iodide (KI), methanol (MeOH), and benzoquinone (BQ) to capture e^- , h^+ , $\cdot OH$, and $\cdot O_2^-$, respectively. Fig. 3.16(a) shows that the photodegradation efficiency of Ag@ZnO decreases from 100% to 25%, 42%, 50%, and 58% upon trapping of e^- , h^+ , $\cdot O_2^-$, and $\cdot OH$, respectively. Thus, it could be seen that the addition of AgNO₃ to trap e^- significantly decreases the photoactivity (~ 4 times) of Ag@ZnO NPs. A similar trend is also observed for Cu@ZnO NPs (Fig. 3.16(b)). Thus, e^- s are the primary species in Ag@ZnO and Cu@ZnO photocatalysis towards sucrose, possibly due to the LSPR effects of Ag and Cu and the interfacial- e^- -transfer processes, leading to a higher density and longer lifetime of e^- s at the surface of the photocatalyst, as seen in the XPS and PL spectra. However, for Ag@TiO₂ NPs, it was observed that adding MeOH significantly diminishes the photoactivity (86% to 24%), followed by KI (86% to 49%), AgNO₃ (86% to 53%), and BQ (86% to 66%). (Fig. 3.16(c)) Thus, it was concluded that $\cdot OH$ is the primary species involved in Ag@TiO₂ and Cu@TiO₂ (MeOH: 72% to 33%, KI: 72% to 41%, AgNO₃: 72% to 48%, and BQ: 72% to 54%) photocatalysis (Fig. 3.16(d)). The photoinduced e^- s and h^+ s are produced when the

TiO₂ surface is irradiated by visible light. The photogenerated e⁻s and h⁺s are separated by the movement of e⁻s from the CB of TiO₂ towards metallic Ag or Cu NPs. Then, the holes oxidize the surrounding H₂O molecules to produce [•]OH radicals. A higher degree of charge carrier separation is achieved in Ag@TiO₂ compared to Cu@TiO₂ (as seen in PL studies), leading to its higher photocatalytic ability. However, the lowest PL intensity out of the six prepared materials is observed in Ag@ZnO NPs, plausibly causing its exception photodegradation capability towards sucrose.

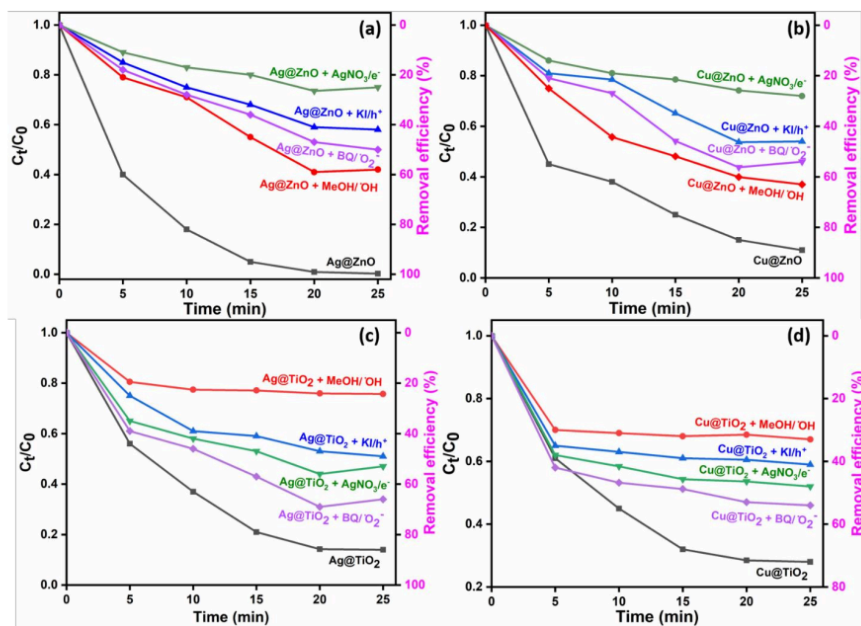


Fig. 3.16 Time-course sucrose photodegradation ability of various materials under visible-light irradiation in the presence of active species' scavengers.

Using these results, the photodegradation mechanism of sucrose over Ag@ZnO NPs was proposed (Scheme 3.1). When Ag@ZnO NPs are exposed to visible light, the excitons are generated in the CB and VB, whose recombination is partially inhibited due to the capture of e⁻s in defect levels of ZnO.[46] Additionally, when Ag absorbs visible light, it produces hot electrons that can be

transferred to the CB of ZnO, as concluded from XPS and PL studies. Consequently, an abundance of e⁻s and h⁺ are produced in the CB and VB of ZnO, respectively. These excitons can catalyze the redox reactions of sucrose at the surface of the photocatalyst.

The position of CB and VB of Ag@ZnO (E_{VB} and E_{CB}) was computed using the Mulliken electronegativity formulas:

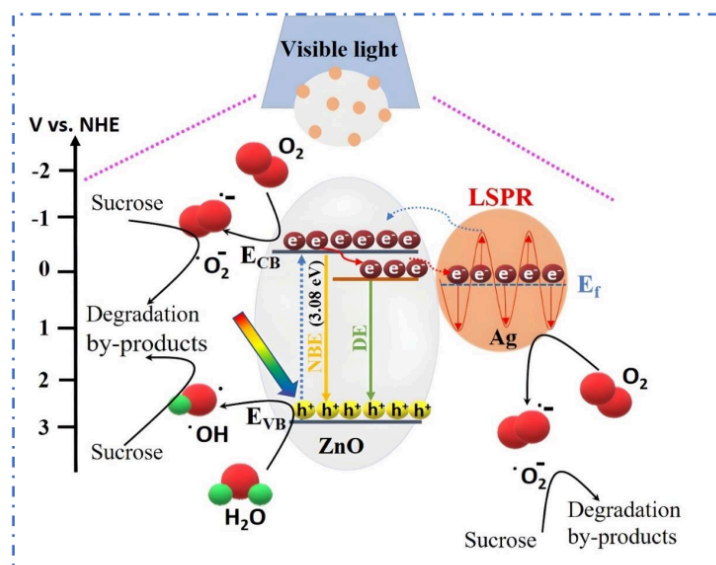
$$E_{VB} = \chi - E^e + 0.5E_g \quad (9)$$

$$E_{CB} = E_{VB} - E_g \quad (10)$$

The eq. (9) represents the relationship between the valence band energy (E_{VB}), the electron affinity (χ), the band gap of the photocatalyst as computed from the DRS analysis (E_g), and the energy of free e⁻ on the hydrogen scale (E^e = 4.50 eV). Eq. (10) represents the relationship between the CB energy (E_{CB}), the VB energy (E_{VB}), and the band gap (E_g). The stated χ value for ZnO is 5.89.[47] By substituting the numbers, E_{VB} and E_{CB} for Ag@ZnO are evaluated at 2.93 eV and -0.15 eV, respectively, relative to the Normal Hydrogen Electrode (NHE). Therefore, the photoexcited e⁻s in the CB of Ag@ZnO NPs can easily bring about the reduction of the O₂ molecules to superoxide radicals (E(O₂•O₂⁻) = -0.046 eV) at the photocatalyst surface. Simultaneously, the redox potential of •OH/•OH is lower (2.38 eV v/s NHE) than the h⁺s in the VB, resulting in an enhanced generation of hydroxide radicals. The purpose of the Ag NPs is to trap the photogenerated e⁻s, thus prolonging the lifespan of e⁻s in the CB and h⁺s in the VB. In addition, the plasmonic e⁻s of Ag have the ability to convert O₂ into •O₂⁻.

The ROS generated in these redox reactions are the primary species in the decomposition of sucrose as per the following equations.





Scheme 3.1 Schematic illustration of the proposed photocatalytic mechanism for sucrose degradation by Ag@ZnO NPs upon visible-light irradiation.

This work used metallic Ag and Cu NPs to alter the surface of two common semiconductor oxides (ZnO and TiO₂), thus increasing their photocatalytic activity. The goal of Cu and Ag deposition on the photocatalysts' surface is to manipulate the band gap and the interfacial charge-transfer process. As illustrated in Scheme 1, when the semiconductor oxide (ZnO or TiO₂) interacts with visible radiation, photoexcited e⁻s and h⁺s are generated in the CB and the VB, respectively. The secondary reactions of these photogenerated e⁻s and h⁺s generate hydroxyl and superoxide radicals, the key reactive species in the photocatalytic process.[48–50] However, as discussed in the introduction, only a tiny percentage of these excitons can complete the photodegradation process due to their shorter lifetimes. The Fermi levels of noble metals Ag and Cu lie close to the CBs of

ZnO and TiO₂. [27,51] This small gap facilitates the transport of photoexcited e⁻s from the surface of the semiconductors to the Fermi levels of noble metals. This electron transfer pathway is confirmed by dampening the photoluminescence intensity in the Cu and Ag-modified materials compared to bare materials (**Fig. 3.7(e-f)**). In addition, Cu and Ag NPs produce active species by reducing dissolved O₂ to O₂⁻ radicals. The photocatalytic degradation mechanism of sucrose by Ag-decorated-ZnO NPs is illustrated in Scheme 1. Other materials (i.e., Cu@ZnO, Ag@TiO₂, and Cu@TiO₂) follow a similar mechanism. Thus, the LSPR effects of noble metals highly augment the photocatalytic activities of bare ZnO and TiO₂.

3.5.5 Photocatalytic degradation pathway

The HR-MS chromatogram of the degraded sucrose solution, shown in **Fig. 3.17**, was examined to gain insight into the various by-products of the photodegradation process by Ag@ZnO NPs. The peak at $m/z = 365$ is the [M+Na]⁺ peak of sucrose. It was observed that several fragments of smaller m/z ([M+Na]⁺) ratios were obtained, which could be formed by breaking up the bulkier sucrose molecule.

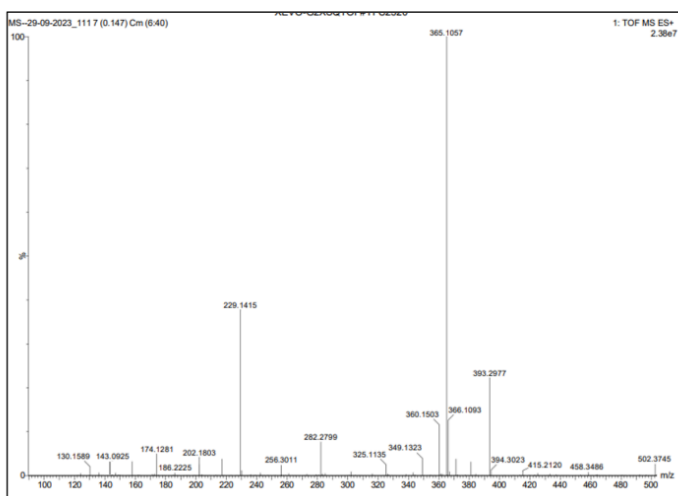


Fig. 3.17 HR-MS chromatogram and intermediates formed during photocatalytic degradation sucrose by Ag@ZnO under visible light irradiation.

The photooxidation of sucrose primarily gives glucose ($m/z = 202$) and fructose ($m/z = 202$), which further decomposes to 2,3-dihydroxy tetrahydro-furan-2-olate ($m/z = 143$) (Fig. 3.18). The decomposition reaction specifically affects the 1,2-glycosidic bond in sucrose.[1,2] These smaller fragments can further decompose to H_2CO_3 , CO_2 , and H_2O if the photodegradation is carried out for prolonged periods.

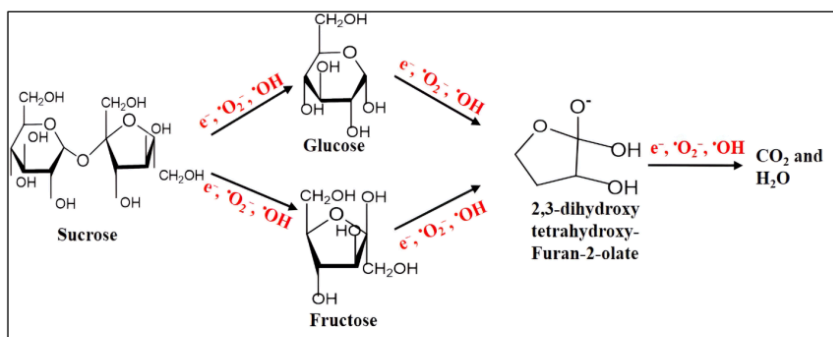


Fig. 3.18 Proposed visible-light-induced degradation route for SUC over Ag@ZnO NPs.

3.5.6 Recyclability studies and environmental application

Fig. 3.19 shows the recyclability tests of Ag@ZnO and Ag@TiO₂ towards sucrose. It was seen that the photocatalytic abilities of Ag@ZnO and Ag@TiO₂ declined from 100% and 86% to 93% and 78%. Thus, it was observed that the fabricated catalysts were highly stable and reusable for up to five cycles.

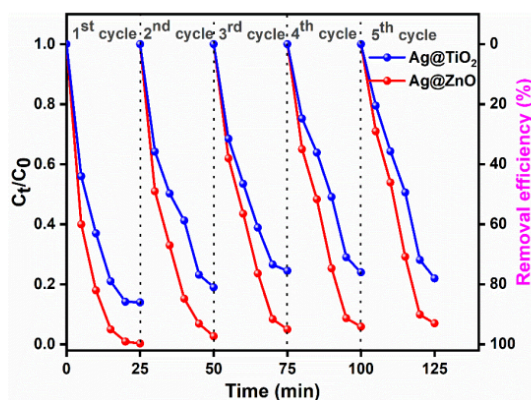


Fig. 3.19 The recyclability tests of Ag@ZnO and Ag@TiO₂.

The Ag@ZnO photocatalyst was used for practical applications to degrade the sucrose-contaminated wastewater collected from a jaggery manufacturing plant via an adsorption-photodegradation synergy under 60 minutes of solar light (solar light consisting of ~ 43% visible light). The UV-visible absorbance spectra of sucrose wastewater and pure sucrose (100 ppm) are shown in **Fig. 3.20(a)**. Pure sucrose has no absorbance in the UV-visible region, but the wastewater (containing sucrose, fibers like cellulose, and some dissolved solids) sample displayed a sharp peak at 271 nm. The initial sucrose concentration in the wastewater was determined using the phenol-sulfuric acid method approach described above and was found to be around 45 ppm. The sucrose removal tests were performed under solar irradiation in Patiala, India, during June 2024 (02-06-2024 to 10-06-2024). The wastewater samples were placed in sealed test tubes in sunlight from 12 pm to 1 pm, with an average solar radiation intensity of approximately 800 W/m² and a temperature of around 41 °C.

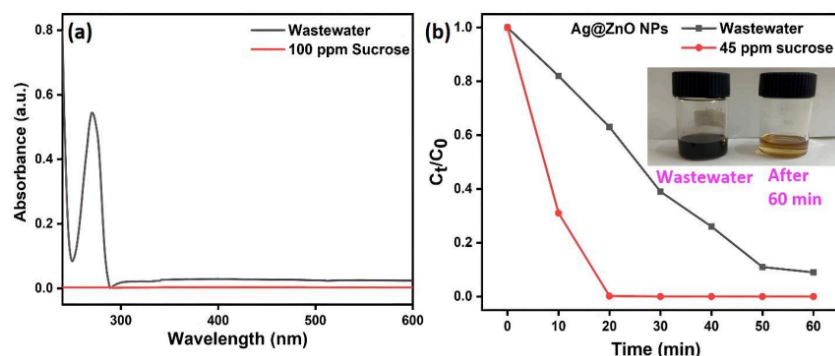


Fig. 3.20 (a) UV-visible absorption spectra of sucrose-contaminated wastewater, (b) time-course adsorptive-photocatalytic removal of sucrose from contaminated water by Ag@ZnO NPs under 60 minutes sunlight irradiation.

Fig. 3.20(b) shows that Ag@ZnO NPs demonstrated an exceptional ability to decompose sucrose in the wastewater, achieving a removal (through adsorption-photodegradation synergy) rate of ~ 91% within 60 minutes of solar irradiation. The 11% of residuals that persisted in the wastewater were due to other complex molecules, such as fibers or soluble solids, that are challenging to break down. These dissolved solids might interfere with the light-absorption process by the Ag@ZnO NPs. TOC removal studies revealed a mineralization of 75%, slightly lower than pure sucrose due

to other residual organic contaminants. Further degradation might require prolonged exposure to visible or UV light. **Table 3.4** compares the photocatalyst synthesized in this study and other photocatalysts to degrade sucrose and other sweeteners.

Table 3.4 A comparison of various photocatalysts towards the degradation of sucrose and other sweeteners.

Photocatalyst used	Pollutant used	Pollutant conc. (ppm)	Catalyst dosage (g L ⁻¹)	Irradiation source and time (min)	Efficiency (%)	Ref.
Ag(10%)/ZnO	Sucrose	100	1.35	UV-C, 105	100%	[2]
TiO₂	Sucralose	200	0.3	UV, 30	89%	[52]
TiO₂	Sodium saccharin	20	-	UV-A, 60	99%	[53]
Ag/TiO₂	Sucrose	800	1	UV, 120	100%	[1]
Cu-BiOI	Sucrose	450	4	Visible, 60	93%	[54]
TiO₂	Sucralose	100	4	UV, 30	84%	[55]
Ag(1%)/ZnO	Sucrose	100 ppm	0.4	Visible, 25	100%	This work

The results reveal that the prepared photocatalyst is notably stable under visible light and in aqueous solutions, offering great practicality for treating sucrose-contaminated wastewater at a reasonable cost, lower catalyst dosage, and shorter irradiation times.

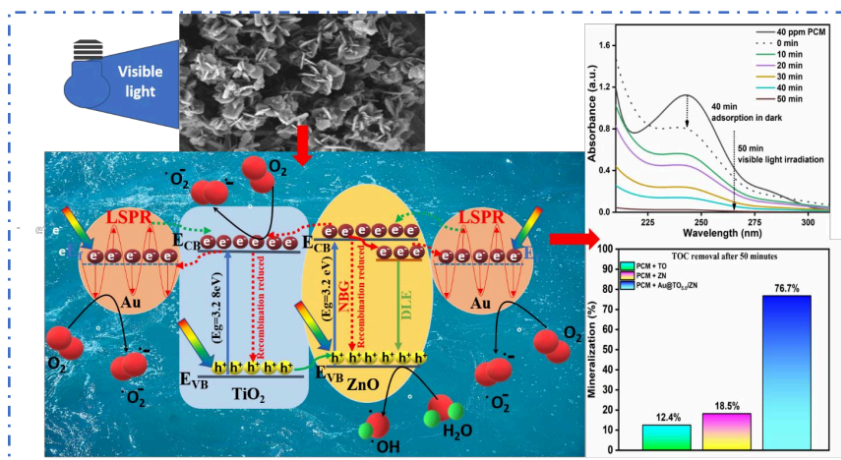
Conclusion

In summary, plasmonic metals Ag and Cu-modified ZnO and TiO₂ were investigated for their photocatalytic and adsorptive capabilities toward removing sucrose under visible light irradiation. The modification was achieved by decorating 1 wt% Cu and Ag noble metals at the ZnO and TiO₂ surface. The photoreduction process of plasmonic metals Cu and Ag greatly enhances the duration and spatial separation of photogenerated excitons at the surface of ZnO and TiO₂ by serving as an electron reservoir. However, they decrease the active surface areas of these semiconductor photocatalysts. Thus, bare TiO₂ displayed $q_{\max} = 156.099 \text{ mg g}^{-1}$ due to its highest surface area and fine-structured NPs. The adsorption ability of TiO₂ was ~1.5 times higher than the bare ZnO NPs, which had a lower surface area and agglomerated particles. However, the photodegradation ability

was highest for Ag@ZnO NPs due to the LSPR effects and effective interfacial charge transfer due to Ag. The sucrose removal efficiency of Ag@ZnO NPs (100%) was ~1.2 times higher than Ag@TiO₂ (86%), in which Ag NPs did not lower the PL emissions as efficiently as in ZnO. Furthermore, the Ag@ZnO photocatalyst exhibited exceptional stability and recyclability in up to five experiments. Ag@ZnO NPs were then employed for the removal of sucrose from a wastewater sample collected from a jaggery plant, where it successfully decomposed sucrose up to 91% under 60 minutes of sunlight exposure.

Significance of this work: i) A meager % (1 wt%) of Ag was required for 100% removal of high concentrations of sucrose; ii) Assessing the comparative role of Cu and Ag-loadings upon ZnO and TiO₂ towards adsorptive and photocatalytic properties of these catalysts; iii) Application of the synthesized photocatalyst for an environment-friendly wastewater treatment method of sucrose by employing the solar energy. Thus, as per our findings, Ag@ZnO has the potential to be an excellent catalyst for the treatment and remediation of sucrose-contaminated wastewater.

Fabrication of plasmonic Au-loaded TiO_2/ZnO -nanohybrids for the superior photocatalytic degradation of paracetamol under visible irradiation



Schematic summary

4.1 Introduction

Of late, untreated pharmaceutical compounds in wastewater have become a primary environmental concern, affecting aquatic and human life. A wide variety of drugs, such as antibiotics, disinfectants, antiseptics, and analgesics, are disposed of in the environment by chemical industries, hospitals, and domestic households.[1] One of the predominantly consumed drugs, a well-known antipyretic and analgesic, paracetamol (PCM) (or acetaminophen), has been found frequently in wastewater with 0.01–0.03 mg/L, which supports the status of an unsafe drug. PCM is a constituent of more than a hundred pharmaceutical drugs.[2] The effects of this contaminant can be fatal for both humans and animals.[3] In order to mitigate this problem, it is imperative to degrade paracetamol into non-toxic products before dumping it in wastelands or water bodies.

Advanced oxidation processes (AOP) are efficient techniques for administering further accumulation of pollutants by employing reactive intermediates like $\cdot\text{OH}$ to decompose these contaminants in water.[4–6] The photocatalytic degradation of organic pollutants is a crucial AOP, in which semiconductor catalysts, like ZnO and TiO_2 , undergo a surface phenomenon creating electron-hole (e^-h^+) pairs upon interaction with UV-visible light. These e^- s and h^+ s are highly reactive and initiate the reduction-oxidation reactions at the photocatalysts' surface.[7–9]

However, the photocatalytic degradation ability of ZnO and TiO_2 suffers due to the inability to interact with visible light and the quick recombination of excitons (e^-h^+).[10] Nevertheless, in contrast to the single-compound catalyst, the photocatalytic activity of the linked ZnO/ TiO_2 composite is significantly enhanced due to the effective spatial separation of the charge carriers.[11] Gasparotto et al. successfully fabricated ZnO- TiO_2 nanocomposite (NC) photoanodes, displaying a remarkable performance enhancement towards solar-driven water-splitting compared to single-phase ZnO or TiO_2 . [12] Qin et al. synthesized hierarchical nanostructures by hydrothermally modifying TiO_2 nanotubes with ZnO nanosheets to improve electron mobility for the photodegradation of rhodamine B.[13] Singh et al. reported that the synthesis of TiO_2 nanoparticles modified ZnO nanoflakes displayed an exceptional detoxifying capacity for the solutions of methylene blue, rhodamine 6G, and oxytetracycline molecules in water.[14] Wang et al. enhanced the photogenerated charge carrier separation efficiency by developing a semiconductor heterojunction through the embedding of ZnO particles in the TiO_2 array.[15]

Moreover, the morphologies of NPs are crucial for developing efficient photocatalysts for environmental applications since they dictate the active surface area, heterojunctions, crystal facets, and charge carrier recombination, all of which impact the photocatalyst's performance.[16] NMs are categorized as 0D, 1D, 2D, and 3D based on their dimensionality. The dimensional features and the structure of particles affect their properties. Consequently, NMs' morphology and size, which significantly impact the electron mobility at the surface, can be used to determine their efficacy.[17] 0D NMs comprise charges entrapped in a zero-dimensional space. On the other hand, the e^- s in 1D NMs can flow along an axial direction, while in 2D and 3D NMs, they can delocalize along a plane and in all three directions, respectively. A review of the literature by A. K. Ganguli et al. revealed that the most effective TiO_2 materials are the 1-D NSs, which provide exceptional

photocatalytic efficacy and require little time for contaminant destruction. Its large surface area guarantees easy access to the active areas during photocatalysis. When similar criteria were applied to ZnO materials, the nanoflower morphology emerged as the top performer compared to reported materials of other morphologies.[16] Thus, we have chosen these two morphologies for our study to devise an overlapping metal oxide/metal oxide nanohybrid photocatalyst with outstanding performance under visible light.

To further counter the limited absorption response and higher charge recombination rates of ZnO and TiO₂, a noble metal Au is introduced to the nanohybrid structure. Noble metals are well known for their advantageous characteristics, which include chemical stability, biological affinity, surface plasmon resonance, and ease of reduction.[18] Among these, gold (Au) nanoparticles are renowned for their superior SPR capabilities and capacity to store charges. The Schottky barrier formed at the Au-ZnO interface aids in efficiently separating the photogenerated charge.[19,20] The metal component's ability to trap photoinduced charge carriers in metal-loaded semiconductors promotes the interfacial charge-transfer processes.[8,21,22]

F. Zheng et al. fabricated Au-enhanced TiO₂ and ZnO NPs and computed their photocatalytic efficacies under UV and visible irradiation. The synthesized materials displayed excellent degradation abilities towards the four chosen organic pollutants; however, Au-sensitization enhanced the visible light-mediated photodegradation more.[23]

Thus, this report delves into the production of Au (0.5 weight percent) sensitized elongated-TiO₂/ZnO-nanoflower hybrid nanomaterials employing solvothermal techniques. As far as we know, no other reports have designed a 1-D/3-D heterojunction between TiO₂/ZnO, although these two morphologies have been reported to possess the highest photocatalytic activities. These overlapping TiO₂/ZnO nanostructures are highly photoactive compared to their physical mixtures of the same ratios. Further, a range of methods were utilized to examine the materials' morphological and photocatalytic characteristics to verify their exceptional effectiveness.

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4.2 Experimental section

4.2.1 Chemicals and materials

Analytical grade sodium hydroxide (NaOH), ammonium fluoride (NH₄F), isopropyl alcohol (IPA), and zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] were purchased from Loba Chemie, India. We purchased auric chloride (AuCl₃) and titanium tetraisopropoxide (TTIP) from Sigma Aldrich,

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India. We bought ethanol from SD Fine Ltd. The triple-distilled deionized (DI) water was acquired from an Indian company named Organo Biotech Laboratories Pvt. Ltd. All chemicals used were purchased in high purity and used without further treatment.

4.2.2 ⁵⁴ Synthesis of $\text{TiO}_2(\text{x})/\text{ZnO}$ nanohybrids

The synthesis of $\text{TiO}_2(\text{x})/\text{ZnO}$ nanohybrids consists of three steps: (i) Preparation of ZnO nanoflowers: In a typical synthesis, the precursor solution involved the mixing ¹⁶ 5 mmol of $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ with 30 mmol of NH_4F , followed by the addition 40 mmol of NaOH .^[25] Initially, white precipitates were formed upon adding a minute quantity of NaOH , which dissolved partly upon increasing the concentration of the base. The solution was stirred continuously at ambient conditions, turning turbid.²⁸ The reaction mixture was further treated at 75°C for 10 h in a Teflon-lined stainless-steel autoclave. White precipitates were harvested by centrifugation,⁴³ washed repeatedly with ethanol and deionized water, and dried overnight at 60°C . (ii) Preparation of 1-D elongated TiO_2 structures: The anatase TiO_2 NPs were synthesized using titanium tetraisopropoxide (TTIP) as a precursor.^[26] Furthermore, 500 mg of anatase TiO_2 NPs and 5 M aqueous NaOH solution were reacted hydrothermally for 12 h at 150°C . The resultant crystalline products were harvested by ultracentrifugation. The white catalyst formed was washed several times with HCl (1 M) and DI water. The obtained catalysts were calcined at 300°C for 2 hours. (iii) Preparation of $\text{TiO}_2(\text{x})/\text{ZnO}$ nanohybrids: The TiO_2 powders obtained in step (ii) were added to the final resultant solution from step (i) in different weight percentages ($x = 1.0\%, 3.0\%, 5.0\%$, and 10.0%). The mixture was sonicated for 60 mins. The solutions were kept hydrothermally at 180°C for 24 hours.^[27] The TiO_2/ZnO nanohybrids were harvested via ultracentrifugation and⁵ washed repeatedly with DI water and ethanol. The obtained samples were labeled as¹¹ $\text{TiO}_2(1.0)/\text{ZnO}$, $\text{TiO}_2(3.0)/\text{ZnO}$, $\text{TiO}_2(5.0)/\text{ZnO}$, and $\text{TiO}_2(10.0)/\text{ZnO}$ corresponding to the 1.0, 3.0, 5.0, and 10.0 wt% loading of TiO_2 , respectively.

4.2.3 Metal Photodeposition

Using the photodeposition approach, noble metal Au was decorated on the above-synthesized photocatalysts. $\text{TiO}_2(\text{x})/\text{ZnO}$ suspensions in 50% v/v IPA solution were sealed under an inert argon atmosphere.²⁴ To achieve the required loading of 0.5 weight percent (wt%) of Au, the calculated amount of the metal precursor, AuCl_3 , was added to these solutions. Following this, Au was photochemically reduced at the surface of $\text{TiO}_2(\text{x})/\text{ZnO}$ nanohybrids for two hours under

a UV lamp (a mercury arc lamp with an intensity of 104 W/m²). The resultant NSs were then recovered by ultracentrifugation and left to dry overnight at 80 °C. The metal-decorated NSs were labeled as Au@TiO₂(x)/ZnO.

4.2.4 Photocatalytic activity analysis

The photocatalytic performances of pristine and Au-loaded ZnO, TiO₂, and their nanohybrids (TiO₂(x)/ZnO) were evaluated through the degradation of a pharmaceutical drug, PCM (acetaminophen), a non-opioid analgesic and antipyretic drug, under LED visible-light irradiation. Prior to photodegradation, tests for photolysis and dark adsorption were conducted. The photodegradation studies were conducted through the batch method, using individual test tubes for each photocatalyst. Usually, 1.5 milligrams of photocatalytic materials were evenly distributed into individual test tubes filled with 5 milliliters of 40 ppm aqueous PCM solution. Before the visible light exposure, the suspensions were stirred for 40 minutes in the absence of light to establish a condition of adsorption-desorption equilibrium between the photocatalyst and PCM molecules. Further, the test tubes were exposed to a 50-W LED lamp (Wipro Garnet B22, with an intensity of about 100 W/m²) for 50 minutes. Periodically, the photocatalyst was extracted from the solutions by ultracentrifugation at 9000 revolutions per minute for 8 minutes to eliminate any remaining solid particles. Further analysis of the supernatant was conducted using UV-visible spectroscopy. Changes in the PCM levels were tracked by analyzing variations in the primary absorption peak of PCM at $\lambda_{\text{max}} = 243 \text{ nm}$ during various time intervals. The PCM degradation efficiency (DE) was determined using the following equation:

$$DE(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t represent the concentrations of PCM at an initial stage at time '0' and following exposure to light irradiation at a time 't,' respectively.

The kinetics of the photocatalytic degradation of PCM were quantitatively assessed by fitting the experimental data to a pseudo-first-order rate equation described below:

$$\ln \frac{C_0}{C_t} = -kt \quad (2)$$

Total organic carbon (TOC) evaluation experiments were conducted using the titrimetric method to assess the mineralization potential of the ternary nanohybrid Au@TiO₂(x)/ZnO. The TOC value was determined using the following equation:

$$TOC \text{ (mg/L)} = \frac{(\text{Blank} - \text{Sample}) \times \text{Normality of FAS} \times 12000}{\text{Sample volume} \times 4} \quad (3)$$

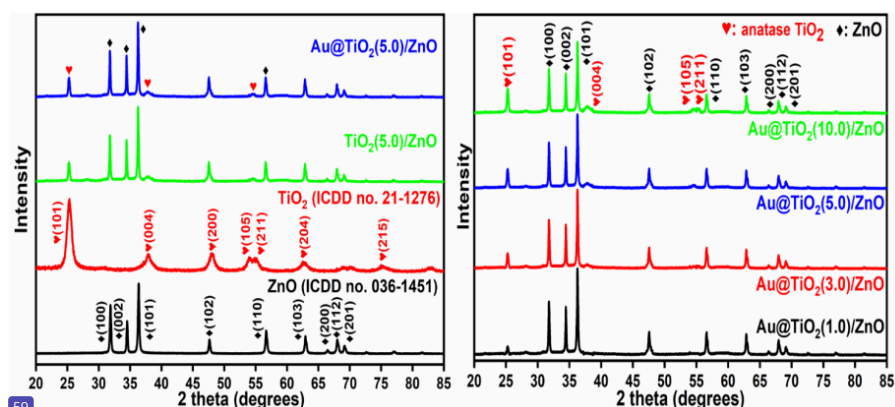
Here, distilled water served as a blank, and the sample used was the final degraded PCM solution after being exposed to 40 minutes of dark adsorption and 50 minutes of visible light irradiation.

76 4.3 Results and discussion

143 4.3.1 Structural analysis

X-ray diffraction patterns

Fig. 4.1(a) reveals the XRD patterns of the prepared ZnO, TiO₂, TiO₂/ZnO, and Au@TiO₂(x)/ZnO catalysts. The presence of wurtzite ZnO is evidenced in all diffraction patterns with lattice parameters $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$. The diffraction peaks of ZnO centered at 31.8°, 33.56°, 36.38°, 47.6°, 56.6°, 62.9°, 66.5°, and 69.2° can be indexed to the diffraction planes (100), (002), (101), (102), (110), (103), (200), and (112), respectively.



59 Fig. 4.1 (a) X-ray diffraction patterns of pristine ZnO nanoflowers, anatase TiO₂ NSs, their binary nanohybrid TiO₂(5.0)/ZnO, and the ternary Au@TiO₂(5.0)/ZnO NSs, (b) X-ray diffraction of the binary TiO₂(x)/ZnO nanohybrids with the increasing wt% of TiO₂.

Further, the XRD patterns of TiO₂ reveal the appearance of diffraction peaks at 2 θ values 25.3, 37.8, 48.0, 54.1, 54.9, and 62.75, corresponding to the planes (101), (004), (200), (105), (211), and (204), of anatase TiO₂, respectively. Further, in the ZnO samples containing 1.0 – 10.0% of TiO₂, the prominent diffraction peaks of ZnO were observed in addition to the TiO₂ peaks, whose intensity rises upon an increase in the concentration of TiO₂ (Fig. 4.1(b)). Further, no diffraction peaks of additional phases were observed in TiO₂(x)/ZnO materials, demonstrating the high phase purity of the fabricated materials. Moreover, no significant shift in the diffraction peaks was observed upon the nanohybrid formation (Table 4.1). Thus, the XRD patterns confirmed that the TiO₂ was deposited at the surface of the ZnO flowers and did not disturb its lattice structure. The lengthy TiO₂ NSs might get entrapped in the petals of the ZnO flower-like materials. Au NPs (0.5 wt%) were decorated onto TiO₂(x)/ZnO hybrids, forming Au@TiO₂(x)/ZnO NMs. The small size of the Au NPs and their high dispersion on TiO₂(x)/ZnO (as seen in Fig. 4.4) may be the reason for the absence of notable Au diffraction peaks in the XRD pattern of this sample. However, the surface plasmon resonance (SPR) of Au NPs was demonstrated by UV-vis absorption spectroscopy, which revealed an absorption band in the visible region (530–670 nm) with a peak at 575 nm (as shown in Fig. 4.6(a)).

Table 4.1 Changes observed in the position of three major diffraction peaks of ZnO upon consecutive TiO₂ and Au loading.

Sample	Peak (100) 2 θ	Peak (002) 2 θ	Peak (101) 2 θ
ZnO	31.88	33.56	36.38
TiO ₂ (5.0)/ZnO	31.87	33.58	36.36
Au@TiO ₂ (5.0)/ZnO	31.87	33.58	36.36

4.3.2 Morphological analysis

FE-SEM, EDS, and HR-TEM analysis

The morphologies of the prepared TiO₂ and ZnO NSs were investigated by employing FE-SEM and HR-TEM analyses. Fig. 4.2(a,b) displays the 1-D elongated structures of anatase TiO₂. The corresponding EDX (Energy dispersive X-ray) spectra confirm the presence of Ti and O elements. The flower-like assemblies of ZnO are shown in Fig. 4.2(d,e).

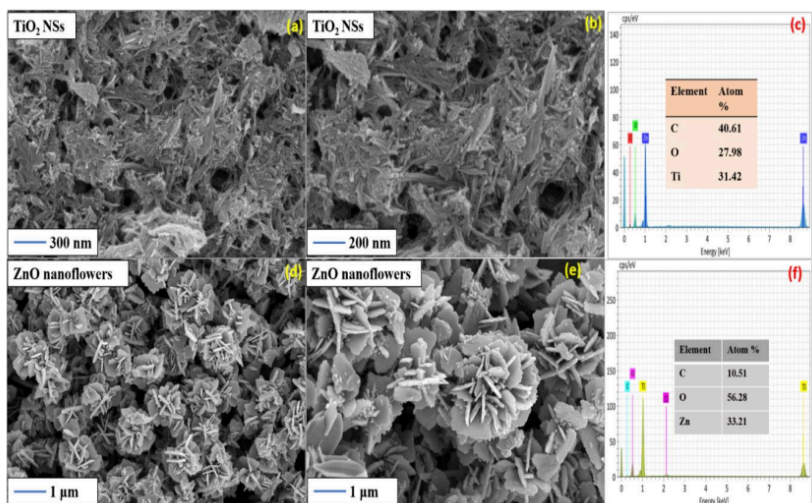


Fig. 4.2 FE-SEM micrographs of (a,b) lengthy TiO₂ NSs, (d,e) ZnO flowers, and (c,f) their corresponding EDX line spectra.

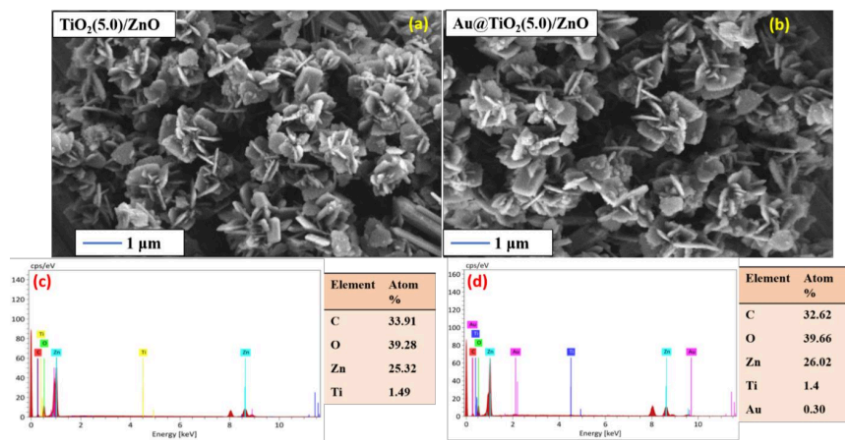


Fig. 4.3 FE-SEM micrographs of (a) TiO₂(5.0)/ZnO NSs, (b) Au@TiO₂(5.0)/ZnO NSs, and (c,d) their corresponding EDX spectra.

Further, in the case of $\text{TiO}_2(\text{x})/\text{ZnO}$ and $\text{AuTiO}_2(\text{x})/\text{ZnO}$, the different morphologies of NSs in the nanohybrids could not be distinguished by the FE-SEM micrographs (**Fig. 4.3**). However, the presence of the elements Zn, O, Ti, and Au was supported by the EDX spectra (**Fig. 4.2(c,f)**). The amount of Au loading achieved was slightly lower than the targeted concentration, possibly due to the inevitable loss of Au during the washing of the photocatalyst.

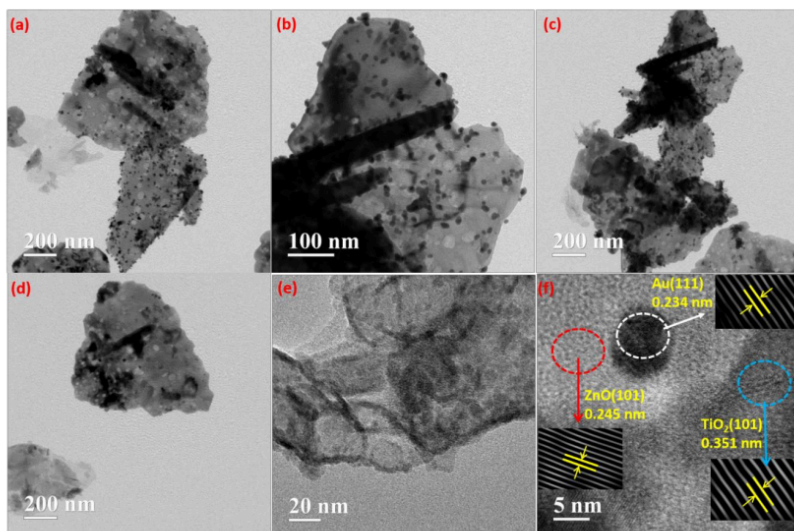


Fig. 4.4 TEM and HRTEM images of (a-f) $\text{Au@TiO}_2(5.0)/\text{ZnO}$ nanohybrids. The respective lattice fringes are shown in the inset in (f).

Additionally, the HR-TEM analysis was performed for the $\text{Au@TiO}_2(5.0)/\text{ZnO}$ NSs (shown in **Fig. 4.4(a-e)**). The micrographs of the nanohybrids display the presence of both flower-like ZnO and elongated rod-like TiO_2 , thus confirming the formation of a 1-D/3-D heterojunction. Further, it was observed that a highly uniform distribution of almost spherical Au NPs with an average particle size of 15.04 ± 3.5 nm was achieved at the surface of both ZnO flowers and elongated TiO_2 structures (**Fig. 4.5**). The lattice fringes obtained in **Fig. 4.4(f)** correspond to the diffraction patterns of ZnO, Au, and TiO_2 , thus confirming the presence of these three heterojunctions.

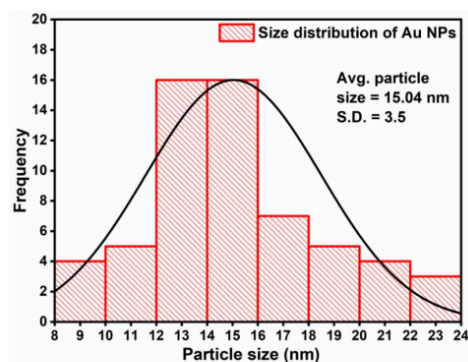


Fig. 4.5 Average particle size distribution of Au NPs.

4.3.3 Optical and charge transfer analysis

Diffuse reflectance spectra studies

Diffuse reflectance spectroscopy was used to assess the light absorption, or optical characteristics, of the as-fabricated samples. Fig. 4.6(a) shows that pure ZnO and TiO₂ absorb strongly in the UV region, displaying an absorption edge at $\lambda = 405$ and 390 nm, respectively. In the case of ZnO NSs, this absorption could be attributed to the electronic transition from the valence band (O 2p orbital) to the CB (Zn 4s orbital).[28] However, in TiO₂ materials, observed absorption is ascribed to the transition of e⁻s from the O 2p orbital of the valence band (VB) to the Ti 3d orbital of the conduction band (CB).[29,30] Compared to the restricted light absorption of unmodified ZnO and TiO₂, the four binary hybrids (TiO₂(1.0)/ZnO, TiO₂(3.0)/ZnO, TiO₂(5.0)/ZnO, and TiO₂(10.0)/ZnO) exhibited a modest red shift in the absorption edges to 416 nm, 419 nm, 421 nm, and 424 nm, respectively. This change in absorption corroborates the formation of a TiO₂-ZnO heterojunction.[31,32] The redshift is highest in the Au-loaded sample (Au@TiO₂(x)/ZnO), i.e., the absorption edge extends up to 442 nm. Furthermore, an additional absorption band appears in the visible region extending from 530 – 670 nm in the Au-modified sample. This peak could be described as the plasmonic band of noble metal Au and is responsible for the visible light activation of UV-responsive ZnO and TiO₂ materials. Here, Au islands augment the photoactivity by accepting electrons from the conduction band (CB) of TiO₂/ZnO nanohybrid materials by acting as e⁻ sinks, thus lengthening the lifetime of photogenerated excitons.[33,34]

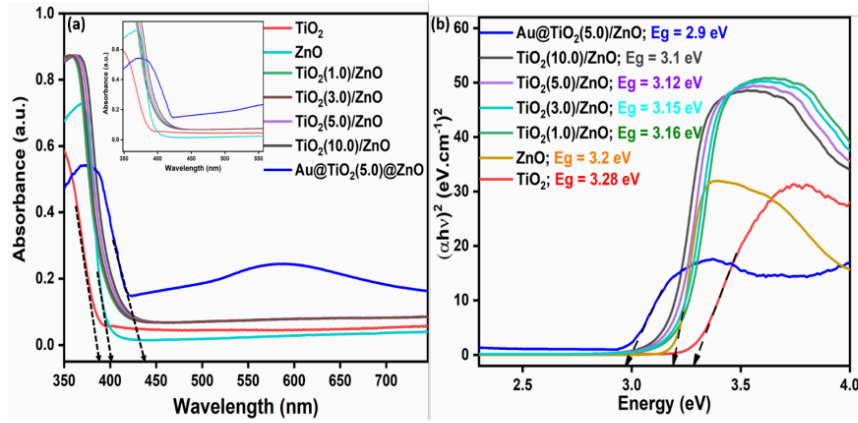


Fig. 4.6 (a) UV-visible diffuse reflectance spectra and (b) Tauc plots of the various bare and modified ZnO materials. The inset in (a) shows the changes in the absorption onset of the materials upon increasing the concentration of TiO₂ NSs.

Upon incorporating both TiO₂ and Au upon ZnO, the resulting hybrid demonstrates an enhancement in light absorption intensity and a significantly broader absorption band throughout the visible spectrum. Additionally, the band gap energies (E_g) of each photocatalytic material were evaluated using the Tauc's relation for direct band gap:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (4)$$

In this context, α , h , ν , A , and E_g denote the absorption coefficient, Planck's constant, frequency of incident light, proportionality constant, and bandgap energies, respectively. **Fig. 4.6(b)** illustrates that the ternary photocatalyst Au@TiO₂(x)/ZnO possesses the narrowest optical bandgap energy ($E_g = 2.9$ eV) compared to the more considerable bandgap energies of bare anatase TiO₂ ($E_g = 3.28$ eV), bare ZnO ($E_g = 3.2$ eV), TiO₂(1.0)/ZnO ($E_g = 3.16$ eV), TiO₂(3.0)/ZnO ($E_g = 3.15$ eV), TiO₂(5.0)/ZnO ($E_g = 3.12$ eV), and TiO₂(10.0)/ZnO ($E_g = 3.10$ eV). This band gap narrowing indicates that lesser energy will be needed to promote electrons from the valence band (VB) to the conduction band (CB) in the ternary Au@TiO₂(5.0)/ZnO nanohybrid. Thus, it became evident from these outcomes that the consecutive modification of ZnO with both TiO₂ and Au NPs was

crucial in narrowing the band gap and effectively harnessing the visible light response of the ZnO backbone in more extended wavelength regions. Therefore, it is anticipated that the newly created Au@TiO₂(5.0)/ZnO ternary hybrid with the best visible-light harvesting capacity will be able to absorb a multitude of photons, producing a large number of high lifetime excitons and thus possessing superior photoactivity.

Photoluminescence spectra studies

The room temperature PL spectra were explored to investigate the effectiveness of charge separation possessed by the produced nanomaterials, as this is a crucial aspect of a promising photocatalyst (Fig. 4.7). Thus, the excitation, transfer routes, and recombination rates of e⁻-h⁺ pairs were studied using the PL spectral technique at

an excitation wavelength of $\lambda_{\text{max}} = 355$ nm. The enhanced lifetime of excitons

often manifests as lower PL intensities.[8,35,36] In bare ZnO flowers, a sharp emission peak is obtained in the near-UV region at 400 nm. This peak could be ascribed to the near-band gap (NBG) emissions owing to the fast rejoining of photoexcited e⁻-h⁺ pairs. Further, a broad PL emission peak is observed in the visible region (550-660 nm) due to deep-level emissions (DLE) from various defect levels, i.e., interstitial atoms and oxygen vacancies.[37] In TiO₂-loaded ZnO counterparts, the shape of PL spectra was identical; however, upon an increase in TiO₂ concentration, the emission intensity declined. Interestingly, the lowest intensity emission peak was obtained in the TiO₂(5.0)/ZnO nanohybrid. Upon further increase in the TiO₂ concentration, the intensity of the emission peak was observed to increase, hinting that the TiO₂(5.0)/ZnO has the optimum amount of TiO₂ loading for efficient charge separation. When the concentration of TiO₂ is increased beyond the optimum ratio, newer centers could be formed, offering additional recombination pathways for the excitons.[38] Further, upon Au loading, no additional emission peaks were observed; however, the intensity of both the emission peaks, i.e., NBG and DLE, was

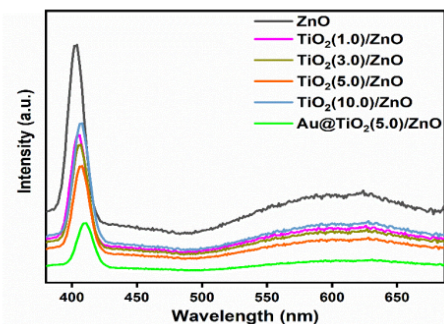


Fig. 4.7 Room temperature photoluminescence spectra of various materials at $\lambda_{\text{ex}} = 355$ nm.

found to be the lowest. This decline suggests that the direct recombination of charge carriers and defect emissions are suppressed upon the photodeposition of a minute amount of noble metal Au. The plausible mechanism for this trend could be explained by the stimulation of the CB e^- s of the $\text{TiO}_2(5.0)/\text{ZnO}$ hybrid to the Fermi level of the photodeposited Au islands. Thus, the Au centers act as an e^- sink and prevent the rapid rejoining of excitons.[20]

4.3.4 Surface area analysis

Further, determining the fabricated photocatalysts' surface area is crucial in decoding the catalytic ability. The calculated nitrogen adsorption-desorption curves of bare and ternary nanohybrid are shown in Fig. 4.8. The Brunar-Emmett-Teller (BET) surface area rises upon the 5.0 wt% loading of lengthy TiO_2 nanostructures upon bare ZnO flowers from 95.25 cc/g to 122.33 cc/g. This rise in the surface

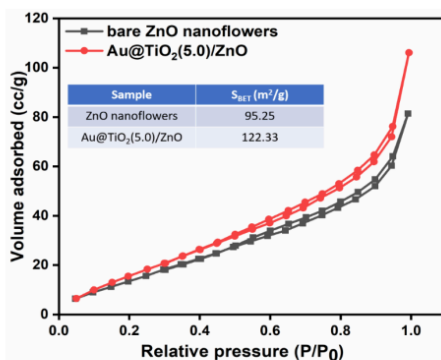


Fig. 4.8 N_2 adsorption-desorption isotherms of bare and

ternary hybrid of ZnO nanoflowers.

the nanohybrid by providing a greater active area for the heterogeneous catalytic action.

4.4 Photocatalytic activity

4.4.1 Photocatalytic degradation reaction

Fig. 4.9(e) illustrates that photolysis, conducted without catalysts, was ineffective for the removal of PCM, resulting in only a ~5% reduction in absorbance after 50 minutes of LED light exposure. The minimal photodegradation upon direct light exposure substantiates that PCM is relatively stable under visible light. At the adsorption-desorption equilibrium, reached after 40 min treatment in dark conditions, approximately 31.5% of PCM molecules were adsorbed on the $\text{Au@TiO}_2(5.0)/\text{ZnO}$ material. In comparison, the adsorption percentages for TiO_2 , ZnO, $\text{TiO}_2(1.0)/\text{ZnO}$, $\text{TiO}_2(3.0)/\text{ZnO}$, $\text{TiO}_2(5.0)/\text{ZnO}$, and $\text{TiO}_2(10.0)/\text{ZnO}$ samples were 19%, 22%, 28%, 31%, 33%, and 29%, respectively. Here, the binary heterostructure $\text{TiO}_2(5.0)/\text{ZnO}$ displayed an adsorption capability superior to all other modified and unmodified samples. This results from

incorporating TiO₂ nanostructures onto the surface of ZnO nanoflowers, which increases the BET surface area and provides numerous PCM adsorption sites. Upon Au photodeposition, a minute decline in adsorption capability is observed, which could result from blocking the active surface sites of the TiO₂(5.0)/ZnO photocatalyst. However, this decrease is negligible as a meager 0.5% of Au is loaded at the surface of this photocatalyst. The deterioration was initiated with visible light illumination for further removal of PCM. After 50 minutes of exposure to LED light, the synthesized photocatalysts demonstrated the following catalytic performance: TiO₂(32%) < ZnO(45%) < TiO₂(1.0)/ZnO(54%) < TiO₂(10.0)/ZnO(57%) < TiO₂(3.0)/ZnO(59%) < TiO₂(5.0)/ZnO(65%) < Au@TiO₂(5.0)/ZnO(98%). The study found that unmodified TiO₂ and ZnO have a restricted ability to degrade PCM owing to their limited visible light absorption, poor specific surface area, and rapid recombination of photoinduced excitons. Further, physically mixing ZnO and TiO₂ NSs in the same ratios as the nanohybrids does not enhance their photocatalytic efficiencies (**Fig. 4.10**). Modifying ZnO flowers with TiO₂ elongated structures is shown to augment its performance. Although all of the TiO₂(x)/ZnO heterostructures demonstrated increased photocatalytic activity compared to single-component samples, the degree of deterioration is particularly influenced by the quantity of TiO₂ loaded. As the TiO₂ content in the nanohybrids increases, their removal efficiency gradually rises before eventually declining.

Among the various TiO₂-deposited ZnO structures, the TiO₂(5.0)/ZnO nanohybrid, containing 5% TiO₂, demonstrated the highest efficiency in degrading PCM. However, upon increasing the TiO₂ content to 10%, a slight decrease in the PCM removal effectiveness was obtained. This behavior can be attributed to two critical factors. When the TiO₂ content is too low (1-3%), the photogenerated charge carriers may suffer from rapid recombination, thus providing limited active photodegradation sites at the catalyst's surface and poor photodegradability. An excess of TiO₂ can partly clog the ZnO surface, hindering the active reaction sites and obstructing the incident light, which impedes the photogeneration of excitons in both ZnO and TiO₂.

Additionally, new recombination centers for the photogenerated excitons could be formed, diminishing the efficiency of the photocatalytic process. Consequently, an optimum loading of TiO₂ species is instrumental in achieving the most favorable synergy between TiO₂ and ZnO.

Further modification of the optimal $\text{TiO}_2(5.0)/\text{ZnO}$ heterostructure by Au photodeposition resulted in an additional amplification of the photocatalytic activity.

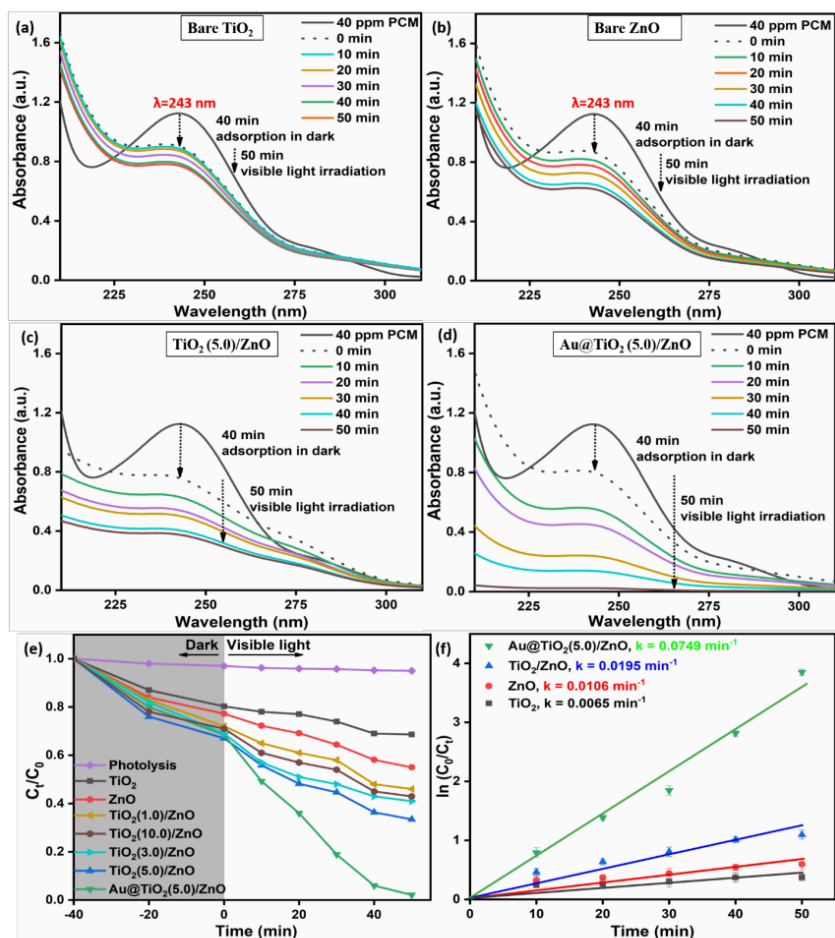


Fig. 4.9 UV-visible absorption spectra of photodegradation of PCM by (a) bare TiO_2 , (b) bare ZnO , (c) $\text{TiO}_2(5.0)/\text{ZnO}$, and (d) $\text{Au@TiO}_2(5.0)/\text{ZnO}$ NSs under 50 minutes visible illumination. (e) Time-course photodegradation studies of 40 ppm PCM by various photocatalysts, and (f) their corresponding pseudo-first order degradation kinetics.

This boost in the photodegradation ability of Au@TiO₂(5.0)/ZnO was attributed to a narrower band gap, improved light-harnessing capacity, expanded photo-response region, minimal exciton (e⁻ and h⁺) recombination, and the LSPR effects of noble metal Au. Furthermore, the kinetics of the photocatalytic degradation of PCM was investigated quantitatively using a pseudo-first-order rate equation (eqn. 2).

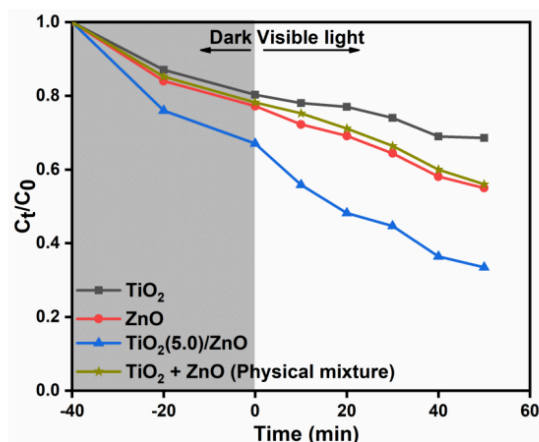


Fig. 4.10 The comparative time-course photodegradation studies of PCM with bare TiO₂, bare ZnO, binary nanohybrid of TiO₂(5.0)/ZnO, and the physical mixture of TiO₂ + ZnO.

Fig. 4.9(f) shows the linear connection between $\ln(C_0/C_t)$ and reaction time for the as-synthesized samples. In harmony with the photodegradation ability, the rate constant (k) of Au@TiO₂(5.0)/ZnO is the highest (0.0749 min⁻¹), which is approximately 3.8, 7.0, and 11.5 times greater than those of TiO₂(5.0)/ZnO (0.0195 min⁻¹), ZnO (0.0106 min⁻¹), and TiO₂ (0.0065 min⁻¹). Thus, the Au@TiO₂(5.0)/ZnO sample exhibited remarkable photocatalytic capacity, indicating that the combination of anchoring TiO₂ species and noble metal Au enhances ZnO's photocatalytic response tremendously under visible light. The temporal fluctuations in the UV-visible absorption spectra of PCM upon treatment with pristine ZnO and TiO₂, the binary TiO₂(5.0)/ZnO material, and the ternary Au@TiO₂(5.0)/ZnO catalysts were recorded during the degradation process. The results are shown in Fig. 4.9(a-d). The photodegradation graphs indicate that under prolonged light exposure, the intensity of the absorption maxima of PCM (λ_{max} = 243 nm) falls off with all the

materials. However, the complete flattening out of the absorption profile of PCM achieved by Au@TiO₂(5.0)/ZnO establishes its superiority as a photocatalytic material over other samples.

4.4.2 Pollutant mineraliation studies

A key objective of photocatalytic procedures is mineralizing the targeted organic pollutant. Subsequently, TOC analysis was utilized to assess the degree of mineralization of PCM achieved after being treated with our photocatalyst. The TOC value typically denotes the organic carbon concentration dissolved in the aqueous solutions. Moreover, a decline in TOC concentration after the conclusion of the reaction indicates the degree of mineralization of the organic matter.[39] Thus, in order to evaluate the degree of mineralization of PCM over the constructed heterostructure (Au@TiO₂(5.0)/ZnO) photocatalyst, the TOC of the aqueous solution was determined prior to and following the photodegradation process (Fig. 4.11).

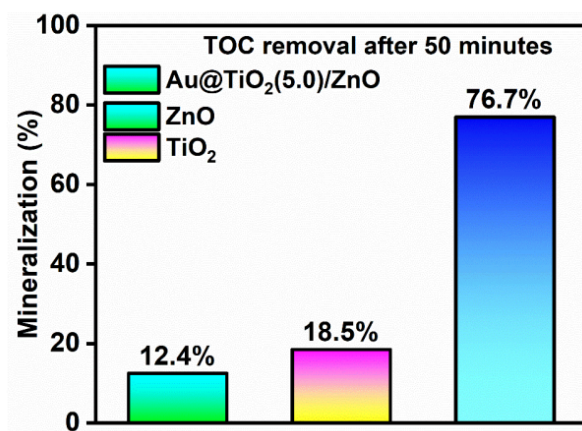


Fig. 4.11 TOC removal analysis of PCM by the bare TiO₂ NSs, bare ZnO flowers, and their ternary nanohybrid Au@TiO₂(5.0)/ZnO.

After 50 minutes of exposure to visible LED light, the mineralization ability reached 72%, suggesting that Au@TiO₂(5.0)/ZnO can mineralize a majority of the PCM molecules, which is sufficient to eliminate the toxicity of this drug and its detrimental effects on the ecosystem. Additionally, the aromatic ring structure of the PCM molecule and the production of intermediates accompanying the degradation process contribute to the solution's TOC, resulting in a lower

percentage of mineralization in comparison to the photodegradation capacity. It is, therefore, challenging to obtain complete organic pollutant mineralization. However, full mineralization of PCM from aqueous solutions is anticipated after extended treatment under UV or visible irradiation.

4.4.3 Proposed photocatalytic degradation mechanism ¹⁴⁶

In order to get deeper insights into the mechanism of Au@TiO₂(5.0)/ZnO mediated photodegradation of PCM, the role of reactive species was studied using radical scavenging experiments. The reactions were performed in the same manner as photocatalytic reactions described above but with the addition of scavengers AgNO₃, KI, methanol, and BQ in the reaction mixture to trap e⁻, h⁺, [•]OH, and, [•]O₂⁻ respectively.

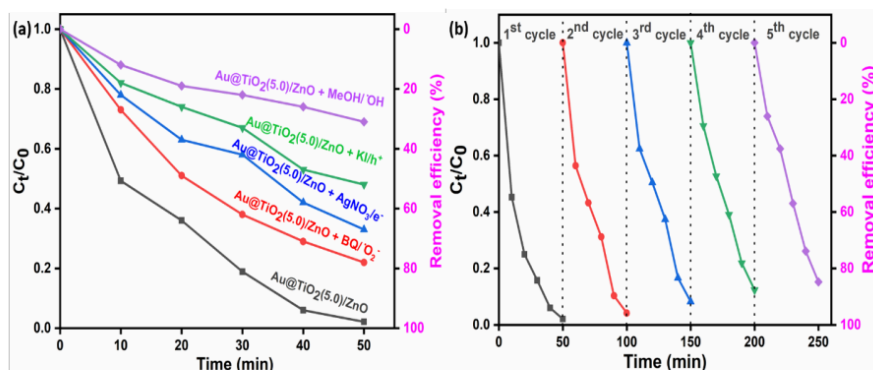


Fig. 4.12 (a) Time-course PCM photodegradation ability of various materials under visible-light irradiation in the presence of active species' scavengers, and (b) the reusability studies of Au@TiO₂(5.0)/ZnO photocatalyst. ⁹⁸

Fig. 4.12(a) illustrates that acute suppression of photoactivity was attained with MeOH followed by KI, indicating that [•]OH are the primary active species involved in the degradation of PCM. Further, the transfer of e⁻s from the surface of ZnO to the adjoining TiO₂ plasmonic Au extended lifetimes produced h⁺ in the VB of the photocatalyst to oxidize H₂O to [•]OH. [40,41] This mechanism is in agreement with the fact that quenching of h⁺ radicals leads to a sharp decline in photoactivity as well. The photoactivity is affected only marginally by suppression of e⁻ and [•]O₂⁻, ¹⁴⁷

thus pointing out their secondary role. Thus, it was deduced that the photodegradation of PCM using Au@TiO₂(5.0)/ZnO was primarily accomplished by [•]OH radicals.

In order to unravel the complete photocatalytic action, it is imperative to assess the transport channels for photoinduced charge carriers through the band-edge potentials of the photoactive material in question. Accordingly, the following formulas were used to determine the CB and VB locations of Au@TiO₂(5.0)/ZnO:

$$E_{CB} = \chi - E_e - \frac{1}{2} E_g \quad (5)$$

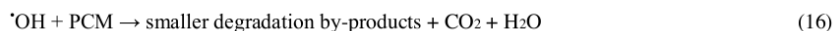
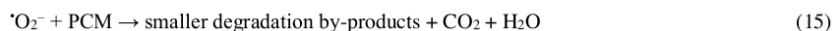
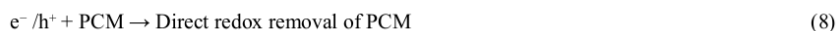
$$E_{VB} = \chi - E_e + \frac{1}{2} E_g \quad (6)$$

Here, E_e is the energy of free electrons on the H₂ scale (4.50 eV vs. NHE), χ represents the absolute electro-negativity of ZnO (5.79) and TiO₂ (5.86), and E_{CB} and E_{VB} are their CB and VB locations, and E_g denotes the calculated band gaps of ZnO (3.2 eV) and TiO₂ (3.28 eV). Thus, the calculated VB and CB positions are $E_{CB}(\text{ZnO}) = -0.31$ eV, $E_{VB}(\text{ZnO}) = 2.89$ eV, $E_{CB}(\text{TiO}_2) = -0.28$ eV, $E_{VB}(\text{TiO}_2) = 3.0$ eV for ZnO and TiO₂, respectively. Despite the comparable band gap energies of ZnO and TiO₂ (3.2 and 3.28 eV), the band gap potentials for both these materials are slightly different. Upon visible light exposure, the excited e⁻s in the CB of ZnO can flow to the CB of TiO₂, whereas the h⁺s can migrate from the VB of TiO₂ to that of ZnO to maintain the potential equilibrium.[42] Crucially, the formation of a TiO₂-ZnO heterojunction acts as a potential barrier, significantly minimizing the recombination of exciton pairs generated by the visible light excitation.

Furthermore, in the ternary composite, the photoexcited e⁻s demonstrates extended delocalization from CB of TiO₂ to Fermi levels of Au NPs. With their lower Fermi energy, Au NPs serve as e⁻ sinks, ensuring efficient charge separation. The separated e⁻s are then captured by molecular oxygen, either dissolved or adsorbed on the surface, forming the reactive superoxide ([•]O₂⁻) and hydroxyl ([•]OH) radicals. Concurrently, the h⁺s in the VB of ZnO could oxidize H₂O molecules, producing additional hydroxyl radicals ([•]OH), collectively contributing to the degradation of the chosen organic pollutant, PCM. Additionally, the e⁻s from the CB of ZnO could migrate to the Fermi levels of Au NPs decorated at its surface. Thus, this dual flow of e⁻s from the CB of ZnO reduces the charge recombination significantly, as evidenced by the PL spectra of the ternary Au@TiO₂(x)/ZnO materials. Notably, the as-prepared 3D ZnO flowers enable rapid flow of

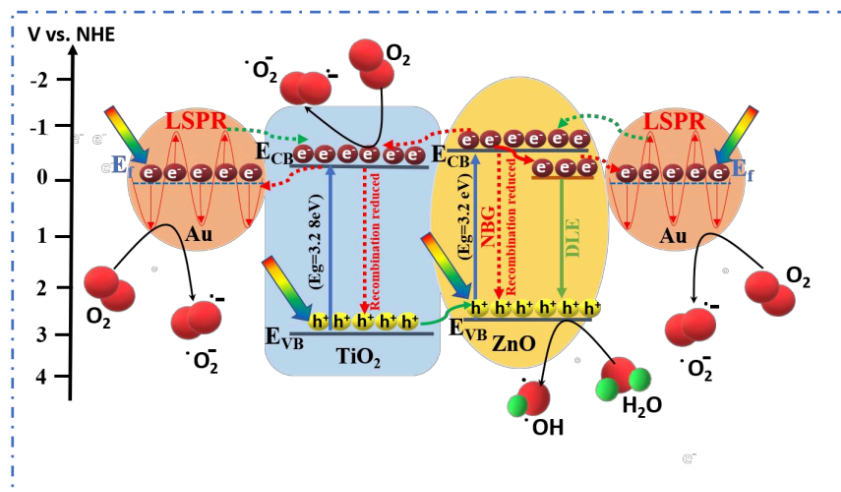
photoexcited e⁻s to the etched Au NPs via the TiO₂ layer, while h⁺s accumulate at their surface, promoting efficient photocatalytic degradation of PCM (as shown in **Scheme 4.1**). Consequently, the well-structured morphology of the photocatalyst, along with its optimized band structure, explains the remarkable improvement in photocatalytic.

Thus, the photodegradation mechanism of PCM upon Au@TiO₂(5.0)/ZnO could be proposed via the following equations:



In this work, we assessed the role of the photodeposition of a meager 0.5 wt% Au NPs upon TiO₂/ZnO NSs for achieving an exceptional photocatalytic removal of a prominent drug, PCM, under visible irradiation. As seen in the HR-TEM images (**Fig. 4.4**), a highly uniform deposition of Au NPs is accomplished upon the TiO₂ and ZnO NSs. As established by the DRS studies, the deposition of Au NPs induces a red shift in the absorption spectra of UV-active ZnO, thus sensitizing it toward visible light. Further, as depicted in **Scheme 4.1**, the interaction of the semiconductor oxides (ZnO or TiO₂) with visible light results in the excitation of electrons (e⁻) to the conduction band (CB) and the formation of holes (h⁺) in the valence band (VB). These photogenerated charge carriers subsequently undergo secondary reactions, forming hydroxyl and superoxide radicals—crucial reactive species in photocatalysis. However, only a tiny fraction of these excitons persist long enough to complete the photodegradation process due to their brief

lifetimes. Here, the role of co-catalyst Au comes into play. The Fermi level of Au NPs can trap e^- s from the CB of both ZnO and TiO_2 , thus acting as an e^- sink to increase the lifetime of these excitons. The e^- transfer synergy is evidenced by the PL spectra of the $\text{Au}@\text{TiO}_2(5.0)/\text{ZnO}$ NSs, which possess the least charge-recombination rates. Further, the LSPR effects of plasmonic Au NPs produce hot e^- s that assist in the photocatalytic mechanism for removing PCM. The role of diffusion of e^- is also established in the scavenger studies, where they were found to be responsible for the production of the primary active species ($\cdot\text{OH}$) involved in the photocatalytic degradation process. Thus, the dual role of Au NPs is imperative in producing a highly efficient visible-light active photocatalytic material for treating organic contaminants in wastewater.



Scheme 4.1 Schematics of the proposed photocatalytic mechanism for PCM degradation by $\text{Au}@\text{TiO}_2(5.0)/\text{ZnO}$ nanohybrids induced by visible-light irradiation.

4.4.4 Photocatalytic degradation pathway

The corresponding reaction intermediates of the photodegradation of PCM were determined using HR-MS analysis after a reaction time of 50 minutes (**Fig. 4.13**). At least five degradation products were identified from the m/z ratios, and the structures of the intermediates and two proposed degradation pathways are displayed in **Fig. 4.14**.

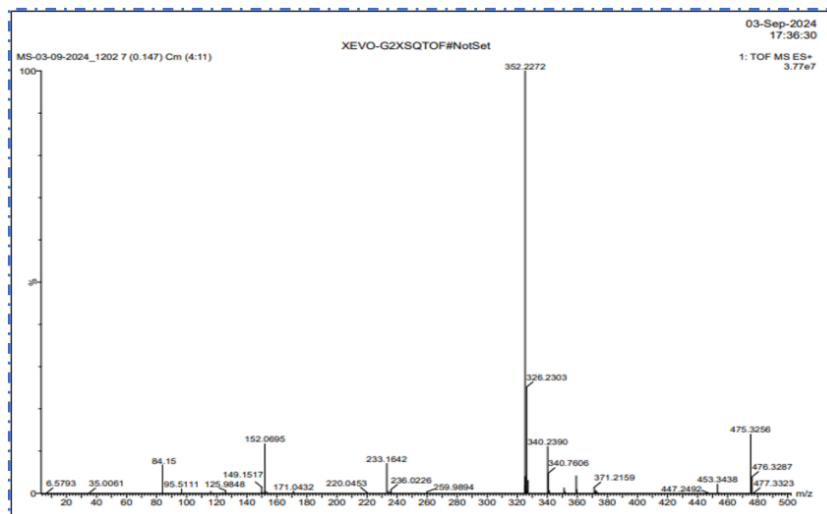


Fig. 4.13 HR-MS chromatogram of the photo catalytically degraded solution of PCM by Au@TiO₂(5.0)/ZnO under 50 minutes of visible light irradiation.

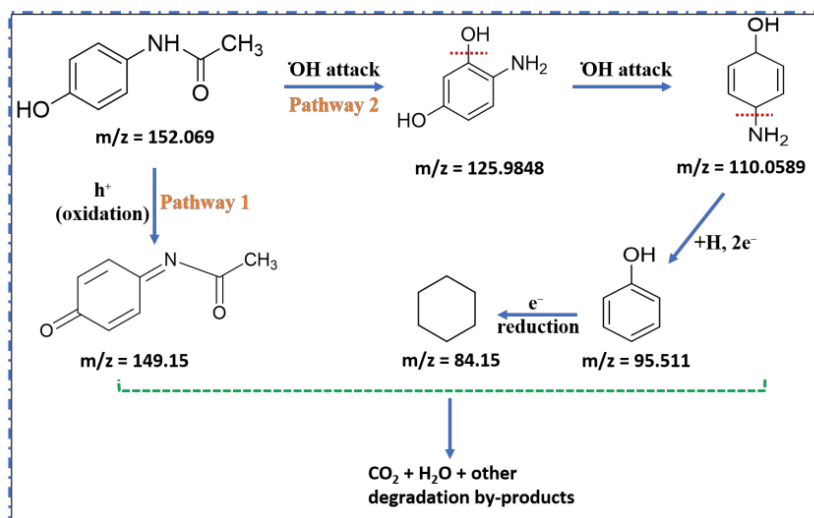


Fig. 4.14 Proposed photocatalytic degradation routes for PCM over Au@TiO₂(5.0)/ZnO NSs

The First pathway suggests the formation of the oxidation product NAPQI (N-acetyl-p-benzoquinone imine), which could be formed by the oxidation of PCM by the excess h^+ in the CB of ZnO material.[1] The second degradation pathway proceeded by removing the CH_3CO- group and attack of $\cdot OH$, forming the intermediate with $m/z = 125$. The crucial role of $\cdot OH$ radicals have also been established in the radical scavenging experiments. Further fission of the $-OH$ group led to the formation of 4-aminophenol ($m/z = 110$). Lastly, the amine group is eliminated, leaving the phenol intermediate ($m/z=95$) behind. Further, upon reduction by e^- s, cyclohexane ($m/z = 84$) is formed.[43] These smaller intermediates can eventually convert to CO_2 , H_2O , and other non-toxic by-products upon elongated UV-visible irradiations.

4.4.5 Recyclability studies

To assess the stability of photocatalytic activity under visible light irradiation, $Au@TiO_2(5.0)/ZnO$ was employed to degrade PCM across five repeated cycles, with the findings illustrated in Fig. 4.12(b). Following five cycles, the photocatalytic efficiency of this catalyst exhibits a minor decline (98% to 85%), indicating that the $Au@TiO_2(5.0)/ZnO$ heterostructures have a commendable capacity for the repeated photodegradation of PCM in aqueous solution under visible-light irradiation. The 13% decline in removal efficiency can be ascribed to the catalyst's inevitable loss during recovery. Furthermore, during the reusability cycles, certain reaction intermediates may have adhered to the catalyst's surface, obstructing active sites and pores, thereby diminishing its effectiveness.

After five cycles, the catalyst $Au@TiO_2(5.0)/ZnO$ was assessed by XRD analysis for its structural stability (Fig. 4.15). The photocatalyst's crystal structure was retained even after five cycles of usage, as evidenced by the reused sample's XRD pattern, which revealed that the positions of distinctive diffraction peaks stayed constant and that no significant change in the position or intensity of diffraction peaks was obtained. Further, the before and after degradation EDX spectra (Fig. 4.16) revealed the wt% of Au to be nearly similar, ruling out the possibility of Au leaching and thus preventing secondary water pollution. The findings indicate that the designed $Au@TiO_2(5.0)/ZnO$ heterostructure exhibits exceptional stability and regeneration capability, making it a reliable photocatalyst that may be used in various photocatalytic reactions over repeated runs.

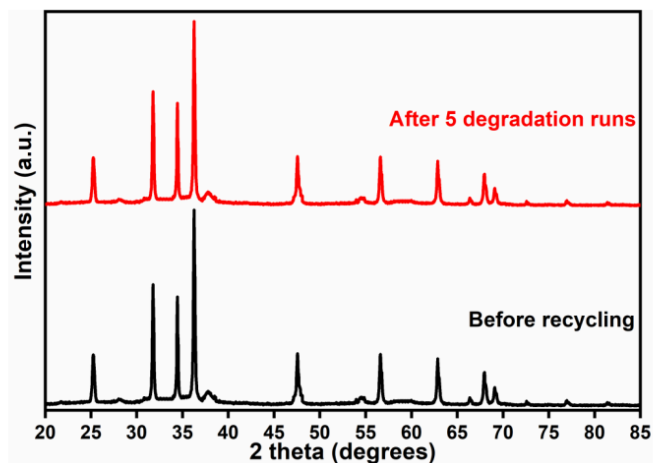


Fig. 4.15 XRD diffraction patterns of Au@TiO₂(5.0)/ZnO nanohybrids before and after five photodegradation cycles.

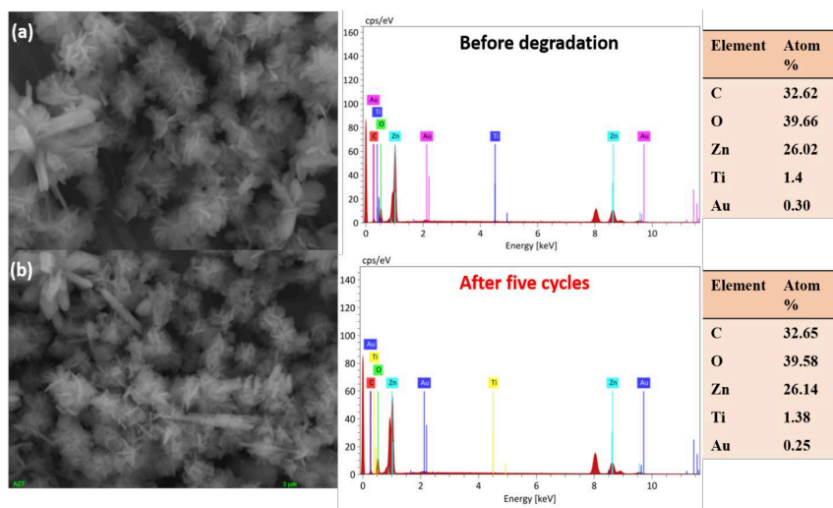


Fig. 4.16 EDX spectra of Au@TiO₂(5.0)/ZnO nanohybrids before and after five photodegradation cycles.

Conclusions

The ternary Au@TiO₂(5.0)/ZnO NSs have stood out as an outstanding photocatalyst for effectively removing the widespread pharmaceutical pollutant paracetamol (PCM). A meager 0.5% Au loading was effective in providing optimum visible light sensitization and reduced charge carrier recombination to the otherwise UV-active ZnO and TiO₂ materials. The TiO₂/ZnO heterojunction formation successfully increased the photocatalytic response of pristine ZnO from 45% to 65% (~ 1.5 times) towards the removal of PCM upon a surface modification with just 5% TiO₂ concentration. Upon formation of the ternary nanohybrid after incorporating Au, the degradation efficiency shot up to 98% after just 50 minutes of visible light illumination. The total organic content of 40 ppm PCM vanished up to 72%, resulting in the decomposition of more than half of the toxic species resulting from the redox reactions of PCM. Thus, the prepared catalyst demonstrated outstanding stability, with negligible leaching observed after five continuous treatment cycles. Overall, our results indicate that Au@TiO₂(5.0)/ZnO is a highly efficient, cost-effective, and non-toxic solution for pharmaceutical-based wastewater remediation.

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