

Plasmonic metal-TiO₂ nanocatalysts for water splitting under visible light irradiation

Thesis submitted in fulfillment of the requirement for the degree of

Doctor of Philosophy

by

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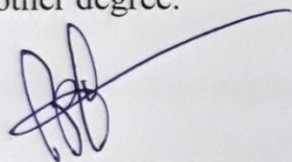
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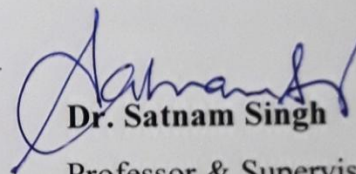
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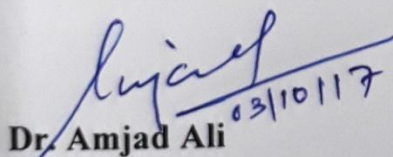
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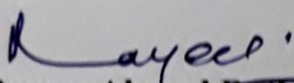
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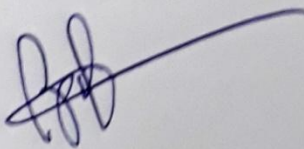
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Candidate's Declaration

I, hereby declare that the work presented in the thesis entitled "**Plasmonic metal-TiO₂ nanocatalysts for water splitting under visible light irradiation**" in partial fulfillment of the requirement for the award of the Degree of Doctor of Philosophy, School of Chemistry and Biochemistry, Thapar University, Patiala, is an authentic record of my own work carried out under the supervision of Dr. Bonamali Pal (Professor), and Dr. Satnam Singh (Professor), School of Chemistry and Biochemistry, Thapar University, Patiala, India. The matter embodied in this thesis has not been submitted in part or full to any other University or Institute for the award of any other degree.

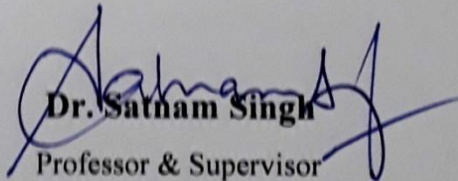

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Dedicated
To My
Grandmother & Parents

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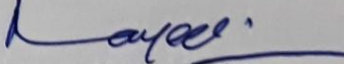

Rayees Ahmad Rather

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List of abbreviations

AQE	Acquired quantum efficiency
a.u.	Arbitrary unit
BET	Brunauer Emmett Teller
BJH	Barrett-Joyner-Halenda
c.a.	Calculated amount
CB/E _{CB}	Conduction band/Electronic conduction band
CTA	C ₃ N ₄ -Au-TiO ₂
DI	Deionizer
DRS	Diffuse reflectance spectroscopy
ESR	Electron spin resonance
FESEM	Field emission scanning electron microscopy
GC	Gas chromatography
GO	Graphene oxide
HPLC	High pressure liquid chromatography
HRTEM	High resolution transmission electron microscopy
ITO	Indium tin oxide
I-V	Potential-Voltage
JCPDS	Joint committee on powder diffraction standards
L	Length
M	Metal
mL	Milli-litre
mM	Milli molar
mol	Mole
mpTiO ₂	Mesoporous-TiO ₂
NHE	Normal hydrogen electrode
nm	Nanometre
NP	Nanoparticle

PEC	Photoelectrochemical cell
PHE	Photocatalytic hydrogen evolution
PL	Photoluminescence
P25-TiO ₂	Commercially available P25-TiO ₂
SAED	Selected area electron diffraction
SC	Semiconductor
SP	Surface Plasmon
SPR	Surface plasmon resonance
STH	Solar to hydrogen
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TNR	Titania nanorods
TNS	Titania nanospheres
TNST	Titania nanosheets
TNT	Titania nanotubes
UV	Ultraviolet
VB/E _{VB}	Valence band/Electronic valence band
Vis	Visible
vol%	Volume percentage
W	Width
wt%	Weight percentage
XPS	X ray photoelectron spectroscopy
XRD	X-ray diffraction
1D	One dimensional
μL	Micro-litre
μM	Micro molar

List of symbols

e^-	Electron
h^+	Hole
$OH^\cdot$	Hydroxyl radical
E_g	Band gap
$\text{\AA}$	Angstrom
α	Absorption coefficient
A	Absorbance
$^\circ$	Degree
λ	Wavelength
$\%$	Percentage
μ	Micro
Θ	Theta
τ_{av}	Average lifetime
H	Hour
Φ	Work function
E^0	Electrode potential
m	Meter
g	Gram
mg	Milligram
E_f	Fermi energy
V	Volt
d	Distance
s	Second
C	Concentration
ν	Frequency
μmol	Micromol

Abstracts

Chapter 1

This chapter elaborates the basis of semiconductor based water splitting reaction with a specific discussion on titanium dioxide (TiO_2). The properties, limitations and the measures to improve the photocatalytic activity of TiO_2 have been briefly discussed. Moreover, the methodology used in the fulfillment of the proposed objectives has been discussed.

Chapter 2

Hydrogen formation from water decomposition is being studied over the years by suitably designed catalysts exhibiting favorable interfacial band energetic under light irradiation. This study deals with the improved photocatalytic activity for hydrogen production from water photolysis by graphene oxide (GO) based core-shell $\text{Au-TiO}_2@\text{GO}$ nanocomposite under different light irradiation sources. Both TiO_2 and $\text{Au-TiO}_2@\text{GO}$ were synthesized by microwave hydrothermal technique. Optical absorption spectra exhibits a precise onset at 550 nm ascribed to characteristic plasmonic resonance of Au, the structural and morphological study revealed that a thin shell (~ 2.5 nm) of graphene oxide is uniformly coated over anatase polymorph of Au-TiO_2 core exhibiting higher specific surface area of $\text{Au-TiO}_2@\text{GO}$ ($\sim 100 \text{ m}^2\text{g}^{-1}$) than both the Au-TiO_2 ($\sim 71 \text{ m}^2\text{g}^{-1}$) and TiO_2 ($\sim 88 \text{ m}^2\text{g}^{-1}$) catalysts. Raman spectra revealed characteristic bands at 400 cm^{-1} (B_{1g}), 517 cm^{-1} (A_{1g}) and 638 cm^{-1} (E_g) of anatase phase of TiO_2 , after coating two new bands G band (1593 cm^{-1}) and D band (1317 cm^{-1}) of GO were observed. The current-voltage (I-V) characteristic shows that the interfacial property of nanocomposite depicted an exponential increase in current with applied voltage, and time resolved fluorescence decay also showing extended electron decay for $\text{Au-TiO}_2@\text{GO}$ nanocomposite. Au loading changed the optical response of nanocomposite because of plasmonic effect and easy transfer from conduction band (E_{CB}) of TiO_2 to GO surface resulting in its prominent hydrogen production activity ($\sim 114 \mu\text{mol}$) as compared to Au-TiO_2 ($\sim 45 \mu\text{mol}$) and TiO_2 ($0 \mu\text{mol}$) under UV-visible light irradiation. In this reaction, oxygen evolution was found in trace amounts, not in a stoichiometric ratio with H_2 , maybe because of anatase crystal structure, as earlier reports suggest anatase phase as a poor surface for oxygen evolution reaction.

Chapter 3

This chapter signifies the synthesis of TiO₂ nanorods (TNR ~ 79 nm) and nanospheres (TNS ~ 19 nm) and their Ag loaded counterparts AgTNR and AgTNS for the photocatalytic hydrogen production from water under monochromatic visible and direct sunlight irradiation. The Ag-TNR nano hybrid junction was sensitized at a matching monochromatic wavelength of 457 nm and sunlight to produce ~90 μmol and 105 μmol of gas respectively, increase in the efficiency is explained due to the surface plasmon (SPR) effect of Ag nanoparticles and is also correlated to fluorescence quenching (due to better charge distribution along larger nano-interface), crystal structure and surface area ($146 \text{ m}^2\text{g}^{-1}$) of fabricated AgTNR nanocomposite. The elongated morphology of AgTNR led to the effective distribution of charge along larger interface resulting in the increase of photocurrent density (0.01 mA/cm^2) which boosts the reaction rate. Plasmonic metal (Ag) activated with matching wavelength to SPR produces an electric field and the TiO₂ present in the proximity encounters these effects resulting in the formation of Schottky barrier, the SPR effect being more towards Ag-TiO₂ interface results in the ejection of electron towards the conduction band of TNR.

Chapter 4

In context to the recent advances in the development of sunlight active nanocomposites for the renewable H₂ production from water, a C₃N₄-Au-TiO₂ tubular nanocomposite (NC) has been prepared by a facile one pot hydrothermal method. Structural and morphological studies revealed the elongated anatase TiO₂ nanotubes (200-250 nm long, $d = 12 \text{ nm}$) embedded in a thin layer of graphitic C₃N₄ (1-3 nm) and dispersed Au (7-12 nm) nanoparticles. The bulk C₃N₄ turned into monolayer due to the self exfoliation process confirmed by Raman (G band = 1545 cm^{-1}) and X ray photoelectron spectroscopy analysis. The potential voltage (I-V) characteristics revealed the non ohmic properties of the heterojunction with a good current response ($1.385 \times 10^{-4} \text{ A}$). The C₃N₄-Au-TiO₂ showed an efficient photocatalytic activity with the production of $\sim 88 \mu\text{molh}^{-1}$ (*calculated* = $2933 \mu\text{molh}^{-1}\text{g}^{-1}$) of H₂ gas under direct sunlight irradiation using methanol as a hole scavenger. The C₃N₄ is activated under sunlight and simultaneously sensitized by Au due to its plasmonic effect. The band potential of C₃N₄ (-1.21 eV Vs NHE for E_{CB}) is more negative than TiO₂ ($E_{\text{CB}} = -0.29 \text{ Vs NHE}$) enabling photoinduced electrons to easily pass the interface into the E_{CB} of TiO₂ which promotes the charge carrier separation and enhance the photocatalytic activity for H₂ production.

Chapter 5

The rational design of a hybrid nanocatalyst for the water photodecomposition to hydrogen (H_2) is highly desired for greener energy needs. In this context, this chapter describes the synthesis of a novel sunlight responsive mesoporous Cu^{+1}/Cu^0 - TiO_2 (Cu-mp TiO_2) photocatalyst for the H_2 production from water. Structural analysis revealed the anatase polymorph of TiO_2 with mesoporous characteristics and an average particle size of ~ 32 nm. The mesoporous TiO_2 was observed of possessing high surface area ($188\text{ m}^2\text{g}^{-1}$) and pore size (0.32 nm) that decreased after Cu impregnation. HRTEM studies suggested the deposition of Cu in Cu^0 and Cu^{+1} oxidation states with three distinct lattice fringes of 0.21, 0.25 and 0.35 nm for Cu, Cu_2O and TiO_2 respectively, that was also confirmed by XPS analysis. Cu-mp TiO_2 produced 1000 μmol of H_2 (AQE = 11.39%) under sunlight irradiation which is several folds than obtained with Cu impregnated on commercial Cu- TiO_2 (P25). Moreover, the photostability of the Cu-mp TiO_2 increased after recycling, XPS analysis of recycled catalyst revealed that the excess Cu^{+1} (binding energy = 533.5 eV) is reduced to Cu^0 (533.3 eV) and the excess holes in the valence band of Cu_2O oxidize Cu^0 to Cu^{+1} helps to make a photostable ternary nanocomposite. The excited electrons in Cu_2O are transferred to the E_{CB} of TiO_2 via Cu due to its lower Fermi level resulting in the reduction of H^+ and at the same time, positively charged holes are expected to oxidize CH_3OH to $HCOOH$ to prevent e^-/h^+ recombination and also helped in making a balanced ternary (Cu^{+1}/Cu^0 - TiO_2) hybrid composite.

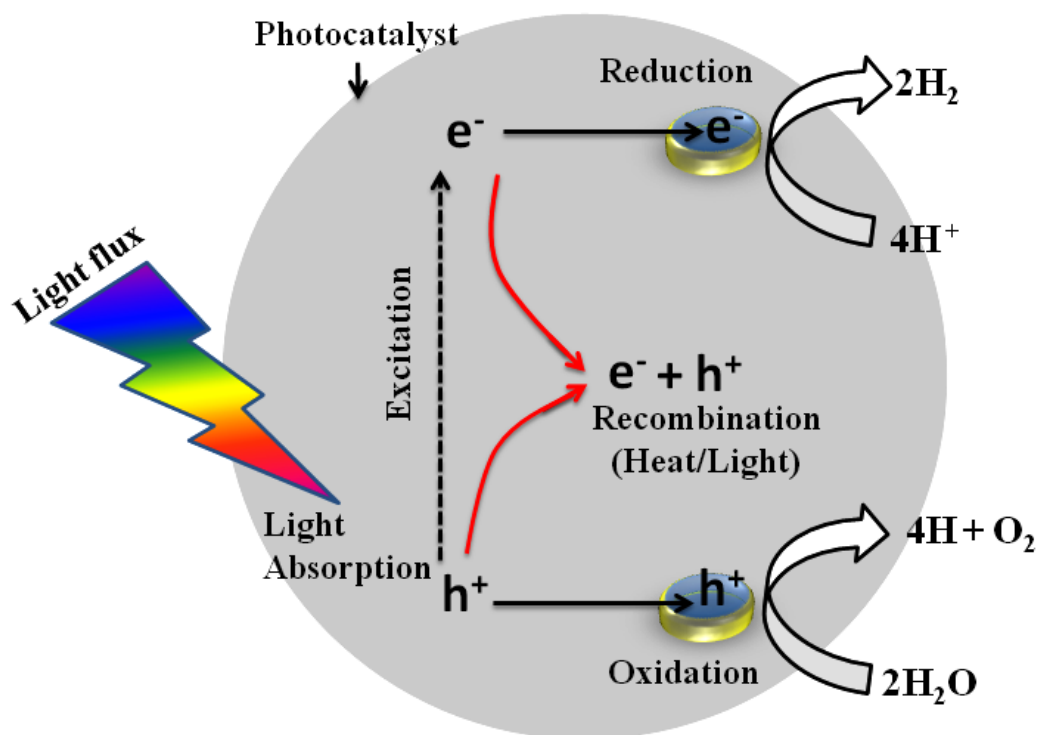
Chapter 6

The performance of TiO_2 for photocatalytic water splitting is vastly endorsed and recently the facet dependence upon the overall activity has achieved a lot of interest due to its better role for effective photoreduction. In this regard, this study demonstrates the synthesis of TiO_2 nanosheets (TNST) with a high percentage of (001) facet followed by co-deposition Au and Pt loading (Au/Pt-TNST) and its application for the photoreduction of water using different alcohols as hole scavengers. Structural and morphological studies revealed well defined sheet type morphology of TNST with a uniform rectangular morphology and an average size 55nm x 46 nm (length x breadth). The TEM micrograph shows the lattice spacing of 0.34 nm and the 0.23 nm lattice spacing was observed corresponding to (101) and (001) facets of anatase TiO_2 . The presence of Au and Pt was confirmed by the UV, XPS and EDS studies, and the characteristic plasmonic absorption was observed and found to be dependent on the amount of Au loading. The 0.4 wt%

and 0.75 wt% of Au and Pt were found to be optimized for better activity. The nanocomposite showed brilliant activity for H₂ production under direct sunlight (8 h) by producing 1150 μmol of H₂ using C₂H₅OH as a hole scavenger. Moreover, the time course study discloses the production of ~143 μmolh⁻¹. The rate of H₂ production decreased with the increase of carbon chain length of hole scavengers. The same photocatalyst showed brilliant photoelectrochemical (PEC) efficiency with highest current density in Au_{0.4}/Pt_{0.75}-TNST nanocomposite.

CHAPTER 1

INTRODUCTION AND METHODOLOGY



Schematic representation of photocatalysis and basis of photocatalytic water splitting reaction

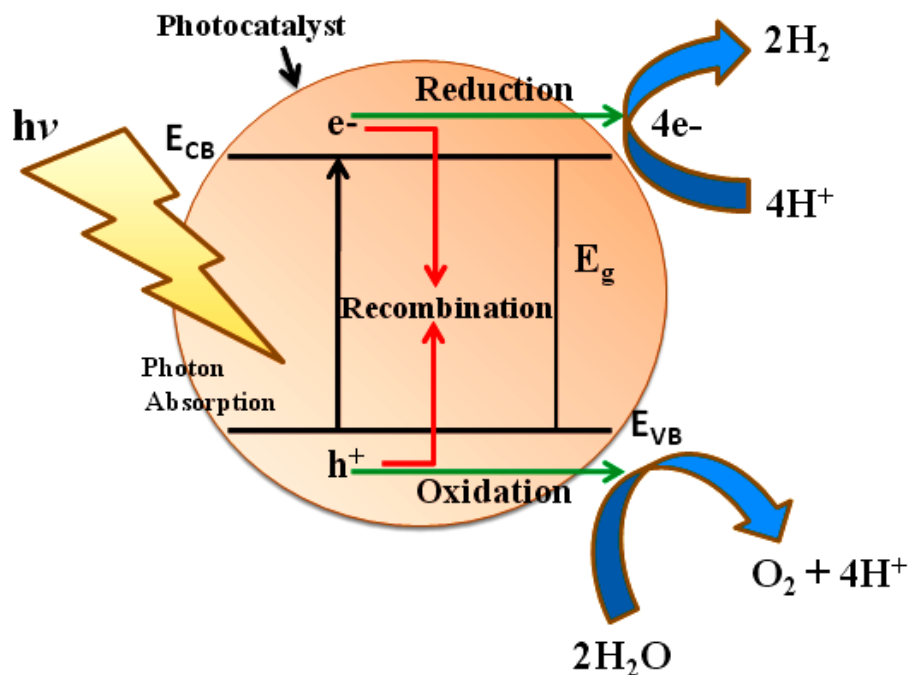
1.1. Introduction and literature survey

Energy and environment related issues are important topics of the current research considering the sustainable development. The total global energy need in 2014 was 15 TW and is expected to reach 30 TW in 2050 and currently 80 % of the total energy is coming from the fossil fuels [1]. A major thrust in research is provided globally to switch towards the renewable energy sources and among these hydrogen (H_2) is considered as an ideal candidate because of its clean, zero carbon emission and high energy output value [2-4]. Hydrogen is considered as the future fuel and could be produced by clean and renewable resources like water using solar and wind energy. However the total renewable production is approximately 5 % and the rest 95 % is produced by using the non renewable fossil fuels like coal reforming or gasification [5], but the limited fossil fuel resources will not be able to meet all our energy needs. The solar energy can go a long way to meet this formidable challenge, solar H_2 production is by far considered to be the best alternative. The most straight forward method to produce H_2 from water and sunlight is by coupling a semiconductor photocatalyst to a solar cell array.

1.1.1 Photocatalysis and the basis of water splitting

Photocatalysis is a catalytic reaction initiated by photons of light having energy equal to or greater than band gap (E_g) of a semiconductor (SC) photocatalyst. As shown in **Scheme 1.1** these light photons excite an electron (e^-) from valance band (E_{VB}) of SC to conduction band (E_{CB}) by leaving a positive hole (h^+). These charge carriers (e^-/h^+) can either produce heat by recombination in the bulk or perform different redox reactions on the surface of SC with donor or acceptor chemical species [6].

Since the discovery of infamous photoelectrochemical H_2 production by Honda and Fujishima [7] on the surface of titanium dioxide (TiO_2) the science of SC based photocatalysis has got a vivid attention and subsequently this field has grown significantly. Several SC like TiO_2 , Zinc Oxide (ZnO), tungsten trioxide (WO_3), cadmium selenide ($CdSe$), cadmium sulphide (CdS), iron oxide (Fe_2O_3) etc. [8-13] have been vastly employed for the photocatalytic water splitting but the photo corrosion, stability, and efficiency have retarded their application.

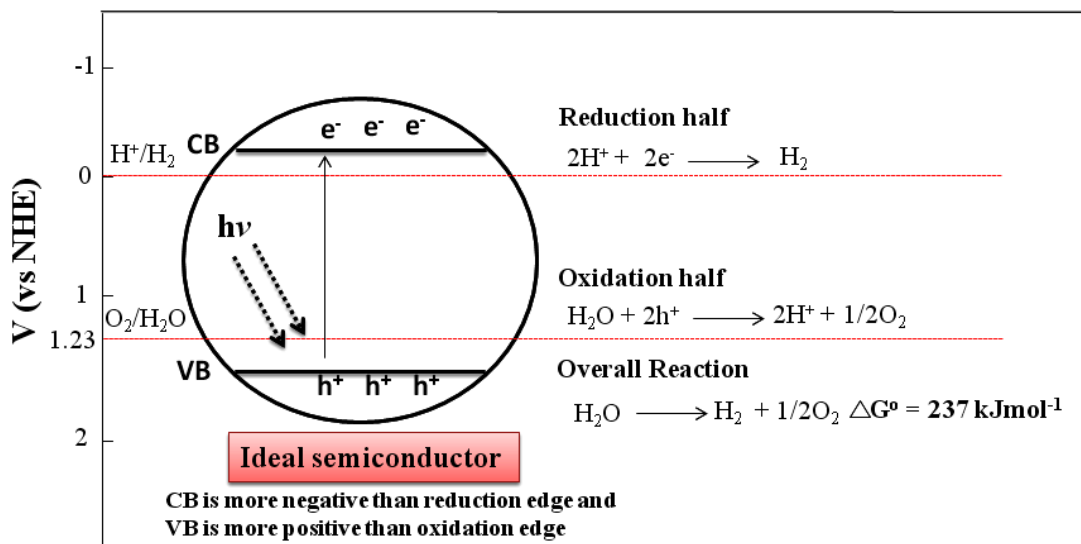


Scheme 1.1: Schematic representation of the process of photocatalysis.

The overall water splitting takes place as per the chemical equations are shown in **Scheme 1.2**. The photocatalytic water splitting also called as artificial photosynthesis is an uphill reaction that proceeds through difficult four electron reduction and needs enough energy to overcome the large positive Gibbs free energy change (237 kJ/mol) [14, 15]. During the photocatalytic water splitting the semiconductor converts the photon energy into chemical energy and the minimal band gap of 1.23 eV in compliance to the reduction potential of water vs NHE is required to split the water molecule [16].

Usually, the photocatalytic water splitting is achieved by two main approaches as illustrated in **Scheme 1.3**. First is by using a single light responsive powder sample with reliable thermodynamic potential having a suitable E_g and must be stable in an aqueous medium. The single photocatalyst is also supposed to be active in visible light that constitutes maximum portion (43 %) of total solar irradiance. In this category there are only a few semiconductors like Ge_3N_4 , Ta_3N_5 etc. [17, 18] but their performance for providing the required quantum yield is still very low. The second type is by making a nanocomposite of two semiconductors in a Z scheme manner to meet the thermodynamic potential for water splitting, this is influenced by the natural photosynthesis occurring in the plants and here the Gibbs free energy can be reduced more as

compared to single system photocatalyst [19, 20]. So, it can be concluded that the photocatalytic H₂ production is strongly dependent on the optical, electrical and physicochemical properties of the photocatalyst.

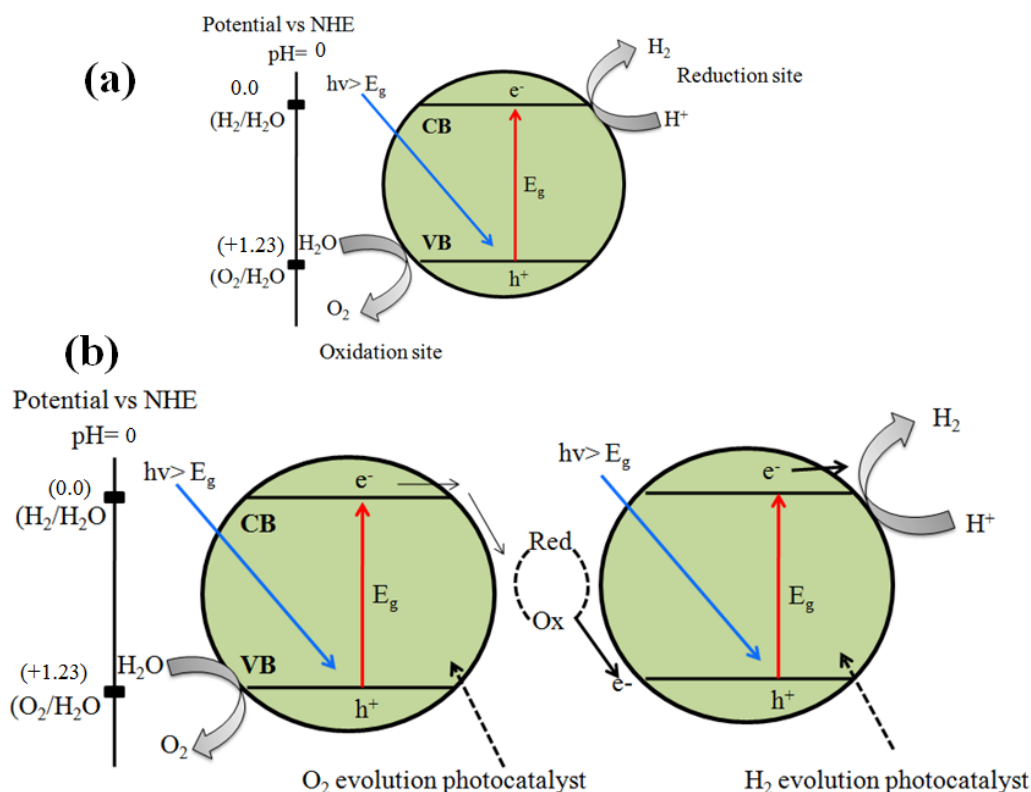


Scheme 1.2: Mechanistic representation of photocatalytic water splitting mechanism over an ideal semiconductor.

1.1.2. Semiconductors as photocatalysts for hydrogen production from water

During last several decades, large numbers of semiconductors including metal oxides, sulfides and nitrides have been employed as photocatalysts for the H₂ production from the half or overall water splitting [21-23]. As shown in **Fig. 1.1**, semiconductors like ZnO, WO₃, Fe₂O₃, CdS, CdSe, ZnS, TiN etc have been extensively studied for the water photocatalysis but various reasons have retarded their practical applicability. The primary condition of an ideal semiconductor is that the position of the conduction band (E_{CB}) and valence band (E_{VB}) must straddle within the limits of water-splitting reaction in accordance with the normal hydrogen electrode (NHE), the E_{CB} has to be more negative than the redox potential H^+/H_2 (0 V vs NHE) and E_{VB} has to be more positive than the redox potential of water O_2/H_2O (1.23 V vs NHE) [24] but none of the semiconductors fulfill this criterion (**Fig. 1.1**), other drawbacks include the photocorrosion (CdS, ZnO) [25], less stability in aqueous media (Fe₂O₃) [26] and absorption and activation under strong UV irradiation that constitutes a small amount (4 %) of the solar

spectrum. Out of this SC photocatalyst TiO_2 is considered as an ideal candidate because of its matching redox potential for the half reduction (H^+/H_2) [27].



Scheme 1.3: Schematic energy diagram of photocatalytic water splitting (a) One Step (b) Z Scheme.

1.1.3. Titanium dioxide (TiO_2) as a photocatalyst for H_2 production from water

Titanium dioxide (TiO_2) is one of the most widely studied photocatalyst since the discovery of pioneer Honda Fujishima effect. The brilliant properties of this material like photostability, cost effectiveness, abundance, low toxicity and strong optical and electrical properties gives it an edge over another metal oxide SC [28, 29]. The TiO_2 has been studied for the photovoltaics [30], photocatalytic water splitting [31], and harmful pollutant detoxification due to the strong oxidizing power of the holes from its E_{VB} and thermodynamically viable position of E_{CB} for redox reactions [16]. The TiO_2 normally consists of a metal cation (Ti^{+4}) with d^0 configuration constituting its E_{CB} and the E_{VB} is made of 2p orbitals of oxygen. The E_{VB} or O 2p orbital's has the potential of about 3 eV (vs NHE) while as E_{CB} is more negative (0 eV) making TiO_2 active in ultraviolet (UV) light only [16]. Considerable numbers of research reports are available discussing the fundamentals of TiO_2 photocatalysis for water splitting under UV light irradiation

[9, 32, 33]. Though large progress has been made in this field still the primary deficiencies retard its commercial activity. The major deficiencies in TiO_2 are the lesser interfacial charge transfer in bulk state or the fast recombination of charge carriers (electrons and holes), low surface area,

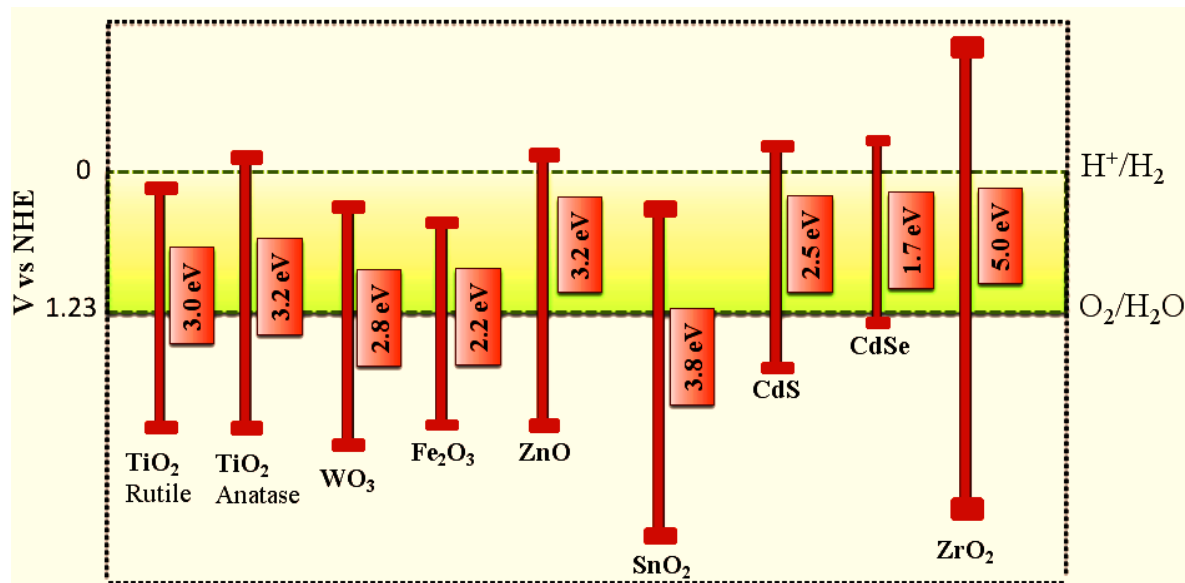


Fig. 1.1: The Band energetic profile of various semiconductors vs NHE.

and activation in UV light that constitutes only a small portion (4 %) of the solar spectrum [34]. So, numbers of groups have focused on modification of this material to overcome these limitations. Modifications like colloidal SC [35], SC-SC nanocomposite [36], quantum size effect, metal loading [37, 38] and addition of sacrificial reagents [39] to enhance the life time of charge carriers, and to improve the visible light sensitivity (44 % of total solar irradiance) in order to boost the reaction rate.

1.1.4. Strategies for the improvement of photocatalytic activity

The major strategies for the development of efficient photocatalyst are being described as follows:

(a) Nanosize and quantum confinement effect

The fundamental reasons for the development of nanosize material are to increase the surface area and the quantum confinement effect. The decrease in the size led to the increase of the surface area and also changes the optoelectronic properties of the material in comparison to the bulk [40]. The nanosize gives birth to the quantum confinement effect where discrete energy level particles are made with the exclusion of forbidden energy levels. Furthermore, when the

particle size decreases below 3 nm it has almost 50 % on its surface to go for the catalytic activity [40]. Our group has reported [41] the considerable enhancement in the photocatalytic activity of TiO_2 and by decreasing the size from 9 nm to 3 nm of metallic nanoparticles. So, the control over size is important in designing a photoactive material for the water splitting based H_2 production.

(b) Tailoring the morphology, polymorphism and facet design of TiO_2

The control over charge recombination is pivotal in determining the overall photocatalytic activity of the material. Careful design of the material can be effective in the charge separation and easy reach of these carriers to surface of the atom. The designs of TiO_2 have been modified by several ways like polymorphism [42], specific facet design [37], fabrication of core-shell structure [43] and formation of one dimensional nanostructure [44].

Chen et al. [45] have successfully synthesized a black TiO_2 that showed a good response in the visible region, the black TiO_2 consists of crystalline cores and the authors also calculated the mid gap states that contributed to the activation under visible light. Similarly, ZuO et al. [46] performed the self doping of TiO_2 with Ti^{+3} resulting in the band alignment of TiO_2 that was found beneficial for the H_2 production. The exposed facets of the TiO_2 are also prominent in determining the rate of the photocatalytic reaction. The fabrication of the specific facets of TiO_2 predominantly can be decisive for a specific reaction; Liu et al. [47] have fabricated the nanosheets with exposed (001) from TiN precursor. The N doping was also carried out that resulted in the absorption of the sample in visible light and showed the H_2 evolution from the alcoholic mixture under visible light. Similarly, Gordon et al. [48] prepared a well defined shape of TiO_2 with control over the formation of (101) and (001) facets of TiO_2 by using precursors like TiCl_4 and TiF_4 resulting in good activity for the methanol reforming.

Another most attractive strategy is the design of the core-shell type nanostructures. Such category shows a synergistic property of both the core and the shell and in this way, the electrons and the holes can be effectively separated due to the interfacial charge transfer [49]. Gombac et al. [50] designed a $\text{CuO}_x@ \text{TiO}_2$ core-shell structure by the hydrolysis of titanium butoxide with simultaneous embedment of CuO_x , this design showed a good H_2 production activity from ethanol and glycerol based aqueous solutions. Similarly, the nanocomposite formation of TiO_2 with other low bandgap semiconductors have been reported to enhance the rate of different photocatalytic processes [51, 52]. The small band gap (E_g) semiconductor is able to sensitize the

large E_g semiconductor due to electron injection into its E_{CB} . It has been previously reported [53] that the composite of CdS-TiO₂ is able to produce H₂ under visible light; electrons excited to the E_{CB} of CdS are injected into the E_{CB} of TiO₂ avoiding the rate of recombination and helping to reduce H₂O into H₂. Similarly, Doong et al. [54] coupled CdS with TiO₂ for the degradation of chlorophenol, So et al. [55] reported the same composite for the photocatalytic H₂ production. Similarly, large number of other SC-SC nanocomposites like Fe₂O₃-TiO₂ [56], WO₃-TiO₂ [57] etc. has been reported for several photocatalytic reactions with efficient results.

The one dimensional nanostructures of TiO₂ like nanorods (NR), nanotubes (NT) etc. have got a



Fig. 1.2: Efficiency of 1D nanostructures over bulk and spherical particles due to axial electron transport.

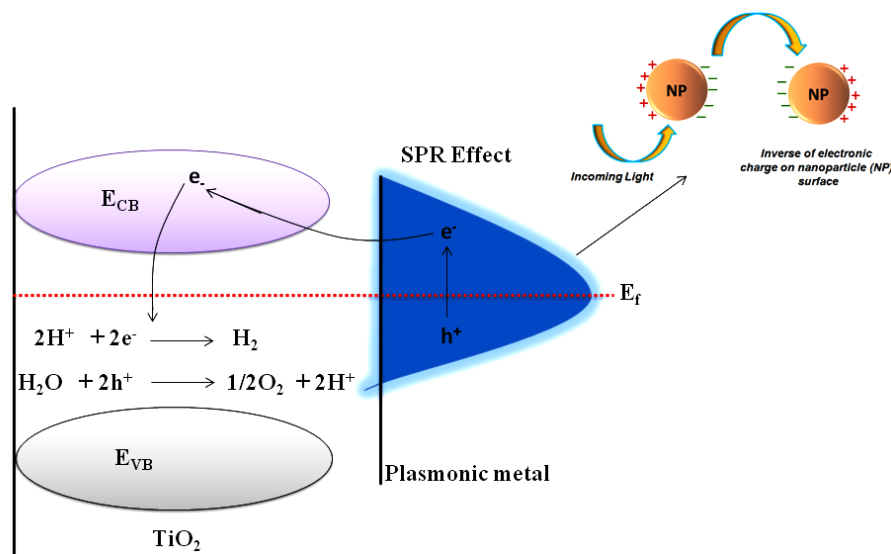
noted attention due to their brilliant surface and electronic properties, this modification results in the large aspect ratio, easy charge transport and collection, and good photoluminescence properties [58]. The change to 1D morphology resulted in the effective charge delocalization and distribution along larger interface boosting the rate of the reaction. As shown in **Fig. 1.2** in case of bulk material it is difficult for the electrons to reach the surface reaction site due to fast recombination of charge carriers, in spherical nanoparticles the excitons have to cross a number of grain boundaries leading to their recombination while as in the case of 1D nanostructures the effective distribution of the electrons can help them to easily reach the respective reduction site due to axial charge transport. Cho et al. [59] have reported the branched TiO₂ NR with good current density for the photoelectrochemical H₂ production from water. The 1D nanostructure has also been found to be effective for several other photocatalytic processes like photovoltaics, sensor, environmental remediation etc. [60, 61].

So, these methodologies have been adopted to enhance the interfacial charge transfer, lower the rate of recombination and sensitize the TiO₂ under visible and sunlight irradiation and these can prove fruitful in designing a specific nanocomposite for the H₂ production from water.

(c) Noble metal loading for the activation of TiO₂ and co catalysis

The two major limitation of TiO₂ are larger E_g making it active in UV region only and fast recombination of the charge carriers. To overcome these drawbacks the noble metal (Au, Cu, Ag & Rh) loading is reported to be very effective for the enhancement of its photocatalytic activity [31, 62-65]. As the Fermi levels of these noble metals are lower than that of TiO₂, photoexcited electrons are transferred from E_{CB} of metal nanoparticles to E_{CB} of TiO₂ until Fermi level of both the systems is equilibrated. Metal doping greatly reduces the possibility of electron-hole recombination, resulting in efficient separation and stronger photocatalytic reactions.

Noble metals like Au, Ag and Cu possess a strong absorption in visible region because of surface plasmon resonance (SPR) mechanism [66] as shown in **Scheme 1.4**. Plasmonic resonance is a columbic restoring force established when the charge density coherently oscillates, also called



Scheme 1.4: Surface plasmon resonance (SPR) effect shown by noble metals on TiO₂ surface for H₂ production.

localized surface plasmon resonance (LSPR). Significant progress has been made in the synthesis and assembly of plasmonic nanostructures and their application for the H₂ generation. Murdoch et al. [67] have reported that the gold-TiO₂ nanoparticles improved the efficiency by the interfacial charge-transfer process; similarly, Sadhana et al. [68] studied the effect of

photodeposition on different metal oxides including TiO_2 for efficient H_2 production from water splitting reaction. Several other reports [69-73] are available discussing the role of metal NP's like Ag and Cu for the sensitization and enhancement of interfacial charge transfer for the respective photon induced redox reaction. Some of the reports have also discussed that the noble metal atoms can act as the reduction sites for the half water splitting reaction suggesting the ejection of hot electrons from the E_{CB} of TiO_2 towards the metal NP surface. Anpo et al. [74] have reported the electron transfer from the TiO_2 towards Pt surface using the electron spin resonance (ESR) technique; similarly, Bamwanda et al. [75] have revealed the half reduction of water using Au and Pt deposited photocatalysts and ethanol as a sacrificial agent. Lee et al. reported [76] enhancement in the photoconductance by impregnating non percolating Au on a thin film of TiO_2 nanorods and also reported 20 fold higher efficiency in H_2 production by electrodepositing Au-NR.

In case of photocatalytic water splitting, the control over charge carriers (e^- and h^+) is very important to determine the final chemical transformation. One dimensional metal oxide nanostructure like nanorods, nanotubes, and nanowires can act as best alternative in terms of efficiency over their spherical counterparts for various photocatalytic reactions and when sensitized with the noble metal (Au, Ag & Pt) NP's these elongated structures with anisotropic interfaces provide a path to reduce electron hole recombination and increase in rate of final transformation [62, 77, 78]. So, photocatalytic H_2 production via water splitting process can be modified by loading these plasmonic NP's on TiO_2 surface.

(d) Role of Sacrificial agents for the water splitting

As discussed earlier not a single semiconductor so far meets the criteria for the overall water splitting process due to unsuitable band energetic, so it is difficult to achieve the same on a single SC. Adding the electron donors or hole scavengers is reported [31] to enhance the photocatalytic activity by avoiding the recombination and boosting the half reduction or oxidation. A number of sacrificial agents like EDTA, MeOH, $\text{C}_2\text{H}_5\text{OH}$, CN^- etc. has been reported [79-81] to be effective for the H_2 production. Nada et al. [82] qualitatively studied the role of different hole scavenging reagents and determined the effectiveness of EDTA, MeOH, and $\text{C}_2\text{H}_5\text{OH}$ for half reduction of water. Li et al. [83] have used formic acid and oxalic acid as hole scavengers and similarly other inorganic salts like sulfates and carbonates have been studied [84] and proved efficient for the H_2 production from water.

The photogenerated holes are consumed by these sacrificial reagents to form other intermediates and prove beneficial for the effective separation of electron/holes and instead of efficient results in the H₂ production, the mechanism still needs to be explored.

1.2. Research gaps

The literature review revealed that the photocatalytic activity of TiO₂ for the H₂ production from water can be modified by taking certain specific points into consideration.

The metal-semiconductor and semiconductor-semiconductor interface is an important architecture for the effective charge collection and separation. Literature reveals that the geometrical morphology and the alignment of the TiO₂ nanostructure plays an important role in photocatalysis and it has been found that the activity of one dimensional elongated nanostructures increased while performing photo redox reactions in comparison to spherical-spherical and other conventional counterparts. Other aspects like changing the surface area and synthesis of certain specific facets can be fruitful for the water splitting reaction. Furthermore, to satisfy the thermodynamic viability for the water splitting reaction the nanocomposite formation with some selective small bandgap semiconductors can also prove beneficial to shift the absorption edge of TiO₂ into the visible region and will operate in a Z schematic manner as in natural photosynthesis, thus making an energetically favorable photocatalytic nanostructure.

Loading of plasmonic metals (Au and Ag) and other coinage metals (Pt and Cu) on modified TiO₂ is also an important parameter needed to be studied for the overall photocatalytic activity. Plasmonic effects of coinage metals make them important co-catalysts and sensitizers for TiO₂ in visible light because of their coherent oscillation in visible light (SPR effect). So, SPR mediated water splitting by co-catalysts may prove effective in terms of quantum yield.

To find out a selective and a suitable hole scavenger in order to execute the half reduction of water molecules and to find out a plausible mechanism for the reaction to occur is also least studied. Using various spectroscopic and optical techniques can help in determining the path of half reduction. So, the choice of hole scavenger was also a preference to perform the photocatalytic H₂ evolution from the water.

1.3. Objectives

1. Synthesis and characterization of coinage M -TiO₂ (M = Au, Ag and Cu) nanocomposites for different morphologies.
2. Study of photo efficiency, current-voltage (IV) characteristics and interfacial properties of M-TiO₂ heterojunction.
3. Study of photocatalytic water splitting efficiency of M-TiO₂ in powder and thin film form by constructing a suitable photoelectrochemical cell under visible and sunlight irradiation.

1.4. Characterization techniques

Several modified and self designed synthetic protocols were followed for the fabrication of desired nanostructures (details are given in respective chapters). The as prepared nanocomposites were critically characterized by using various structural, optical and morphology determining techniques. The detailed description of characterization techniques are discussed as under:

1.4.1. UV-Vis spectroscopy

The preliminary absorption properties of nanoparticles were done both in dispersed and in the solid phase. The analysis of dispersed and liquid samples was carried out on Analytikjena Specord 205 (Germany) spectrophotometer (spectral range, 190-1100 nm). The analysis of solid samples was done on Avantes diffuse reflectance spectrophotometer (DRS) using BaSO₄ as an internal standard. Furthermore, the band gap (E_g) was calculated using the following Tauc equation:

$$\alpha h\nu = A (h\nu - E_g)^n$$

Where

α = Absorption coefficient

h = Planck's constant ($6.626 \times 10^{-34} \text{ m}^2\text{kg/s}$)

ν = Frequency of light

E_g = Band gap of the material

n = characteristic transition type for direct ($n = 1/2$) and indirect ($n = 2$) transitions.

1.4.2. X-ray diffraction analysis (XRD)

The phase structural, facet design, polymorphism and unit cell properties were studied by X-ray diffraction with PANalytical Xpert Pro (Almelo, Netherlands) with Cu K α at 1.54 Å⁰ operating at

45 kV and the diffraction angle was set between 10-80° with 5°/min rise. The samples for the XRD were finely grinded in mortar pestle before analysis.

1.4.3. Electron microscopy

Electron microscopy techniques like transmission electron microscopy (TEM), high resolution-TEM (HRTEM), and scanning electron microscopy (SEM) were done for the elucidation of morphological characters like the shape and statistical distribution of particle size. Moreover, the elemental ratio of the nanocomposite was determined by SEM-energy dispersive spectroscopy (SEM-EDS).

The TEM analysis was carried out on the Hitachi, 7500 model (Japan), operating at the voltage of 50-200 kV with the resolution of 2.4 Å. The HRTEM analysis was carried out using Technie G2- (FEI) S-Twin instrument, operating at 200 kV. The SEM, SEM-EDS was done using JEOL, JSM-7600 F, 01 operating at 30 kV and field emission-SEM (FESEM) on SU8-180 (Tokyo Japan) respectively.

1.4.5. Time resolved spectroscopy (TRS)

The time resolved spectroscopy was done in order to study the dynamics and lifetime of charge carriers (electrons and holes). The whole spectrum was recorded by using the nitrogen laser excited at 390 nm coupled with an oscilloscope (Tektronix TDS-1012). The solid mass sample (50 mg) was kept vertically and pulsed with the laser. Furthermore, the average lifetime was calculated either with a tangent (where Y axis approaches to zero value) or comparatively by using the following equation:

$$\tau_{av} = (a_1 \tau_1 + a_2 \tau_2) / a_1 + a_2$$

1.4.6. X-ray photoelectron spectroscopy (XPS)

The surface chemistry, quantitative elemental composition and oxidation state was studied by XPS technique. The XPS was recorded by using KRATOS Axis 165 (Shimadzu, UK) with Mg K α radiation (1252.6 eV at 75 W) and on commercial Omicron EA 125, source Al-K α 126 radiation at 1486.6 eV.

1.4.7. Surface area and porosity characteristics

The N₂ adsorption-desorption based Brunner-Emmet-Teller (BET) equation and BEL mini-II, Micro Trac Corp. Pvt. Ltd (Tokyo, Japan) instrument was used for the determination of surface area of the nanocatalysts. The sample was degassed at 150 °C to remove the adsorbed water and gas molecules. The analysis was done at cryogenic temperature (-190 °C) using liquid nitrogen.

The pore size distribution and pore volume were determined from the same experiment using Barret-Joyer-Halenda (BJH) curve that is based on the modified Kelvin equation in calculating the amount of adsorbate removed from the pores of the nanomaterial.

1.4.8. Raman spectroscopy

The structural parameters of the photocatalysts were elucidated by Raman spectroscopy recorded on the Renishaw system 2000 ($100\text{--}800\text{ cm}^{-1}$) using a He–Ne laser (514.5 nm) and Airix (STR500) spectrometers.

1.4.9. Potential voltage (I-V) characteristics

The interfacial potential voltage (I-V) characteristics of the metal-TiO₂ heterojunction were recorded on KEITHLEY (4200-SCS) with ZYVEX S100 nanomanipulator with variable potential (-5V to +5V).

The electrochemical current voltage characteristics of the photocatalysts were carried out on the three electrode potentiostat (Digi-IVY, D2300). The experiment was performed using Pt as a counter electrode, Ag/AgCl as a reference electrode and thin film (2.5 cm x 0.5 cm) of the photocatalyst on ITO support as a working electrode and KCl (0.5 M) was used as an electrolyte. The scan range was set between +2.5 to -2.5V and scan rate 1mV/s-100mV/s. For the *i-t* study, the potential was kept constant at -2.5 V.

1.4.10. Fourier transform infrared spectroscopy (FTIR)

The FTIR was done by using FTIR, Carry 660 Agilent Technologies (USA) with the spectral range of $400\text{ to }4000\text{ cm}^{-1}$ and slit resolution of 2.

1.4.11. Photoluminescence spectroscopy (PL)

The Perkin-Elmer (LS55) was used for the analysis of PL spectral properties of the nanomaterials. The analysis was carried at room temperature, excited with a xenon lamp (315 & 320 nm) and the sample was made as an ethanol suspension.

1.4.12. Gas chromatography (GC)

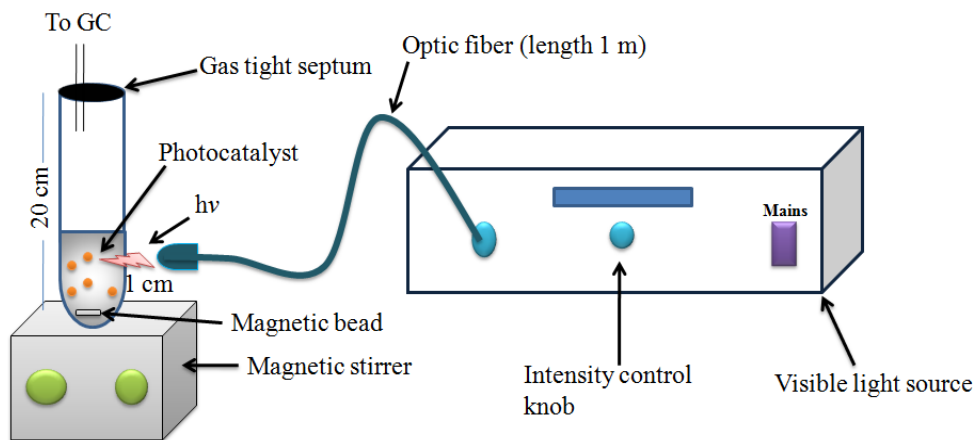
The quantification of H₂ evolved during the reaction was done by gas chromatography (GC, Nucon Ltd, India) with thermal conductivity detector (TCD) and molecular sieve column (5X A, 1m). The temperature of oven, injector, and detector was set at room and the sample injection was done manually by a gas tight syringe (Hamilton, 5 mL), the quantification of the evolved gas was done in comparison to standard 180 ppm (N₂ balanced) H₂ standard (Sigma gases, India).

1.5. Photocatalytic activity

Two different procedures were adopted for the study of the photocatalytic activity of coinage metal-TiO₂ nanostructures. One is by simple powder method and second by thin film assembly or photoelectrochemical cell (PEC) method.

1.5.1. Powder method

In case of powder method, the photocatalytic activity of as-synthesized metal-TiO₂ nanostructures was evaluated at room temperature under visible and sunlight irradiation. For visible light, a 125 W xenon lamp served as the light source to provide visible light within a range of 400–1100 nm. As shown in **Scheme 1.5** the source setup was extended with a thin fiber probe of length 1 m and diameter 1.4 cm terminated with an attachment of a lens (0.6 cm diameter) for the passage of light. The gas tight Pyrex test tube containing water and sacrificial agent and the optimized amount (details are given in respective chapters) of photocatalyst was

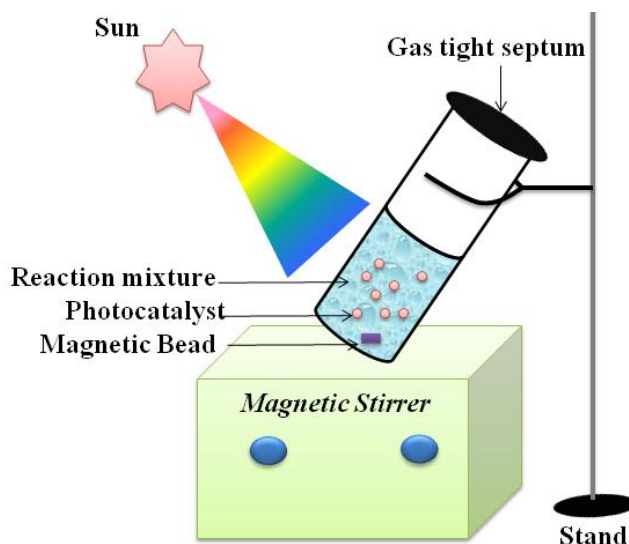


Scheme 1.5: Visible light set up for the photocatalytic H₂ production

irradiated along one dimension under continuous stirring. The experiment under sunlight was performed in a similar manner but under direct solar irradiation and the reaction tube was kept in the direct path of the sunlight as given schematically in **Scheme 1.6**. The sunlight irradiance (Wm⁻²) data was obtained from the Pollution Monitoring Laboratory at Thapar University and the role of sunlight irradiance is also discussed in the respective chapters.

The UV setup comprises a UV source (125 W) of low pressure mercury vapor lamp with the intensity of 10.4 mW/cm². The whole reactor is encapsulated with a water jacket with continuous circulation of cold water for cooling purposes. Some experiments were also carried under

different monochromatic Ar ion lasers (Stellar-Pro, MODU LASER) with 10-15 W intensity and the wavelengths emitted by the laser are 458 nm, 488 nm, 511nm and 314 nm.



Scheme 1.6: Sunlight based reaction set up for H₂ evolution

1.5.2. Electrochemical and photoelectrochemical (PEC) studies:

An interfaced Autolab (Metrohm) electrochemical workstation was used to carry out all electrochemical and photo-electrochemical measurements. Cyclic voltammetric (CV) and impedance behavior of the materials was studied by coating 10 μ l of respective nanocomposite (5 mg/ml) onto glassy carbon working electrode, which was air dried. Platinum (Pt) and Ag/AgCl were used as counter and reference and electrode, whereas 5 mM ferri/ferro containing 0.1 M KCl was used as redox electrolyte. Impedance spectra were recorded with frequency response analyzer at open circuit potential in the 0.1 to 10⁵ frequency range under 10 mV ac perturbation signal. The obtained Nyquist plot was analyzed with Z_{view} software to fit equivalent circuit. A solar simulator equipped with 300 W Xe lamp and AM 1.5 filter was used as light source and the intensity of the source was calibrated and controlled at 100mW/cm².

Photo-electrochemical (PEC) experiments were performed in three electrode configuration, where nanocomposite coated ITO was used as a working electrode in isolated experiments. The PEC chamber was air cooled, keeping the electrolyte temperature at 25 °C and purged with nitrogen to remove dissolved oxygen. Linear sweep voltammeter (LSV) measurements were recorded at a scan rate of 10 mV/s in the dark and light experiments in 0.1 M NaOH.

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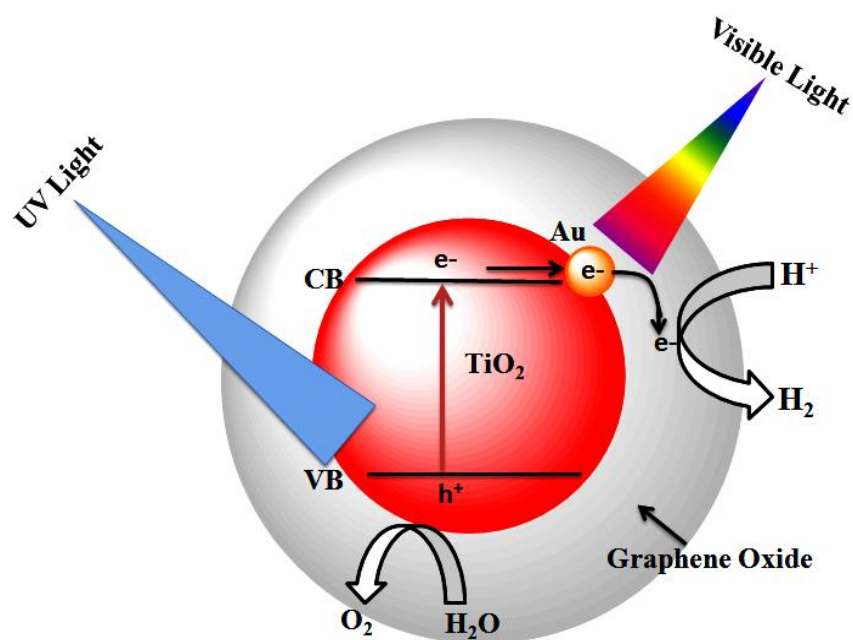
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CHAPTER 2

CORE-SHELL Au-TiO₂@GRAPHENE OXIDE NANOCOMPOSITE FOR HYDROGEN PRODUCTION FROM WATER SPLITTING



Schematic summary

A thin shell of graphene oxide (GO) coated over Au-TiO₂ core exhibited better hydrogen production efficiency from water than bare Au-TiO₂ catalyst under combined UV and visible light irradiation. The lower reduction potential of GO than TiO₂ facilitates the decrease in recombination rate of charge carriers whereas Au loading increases the sensitization of TiO₂ in the visible light resulting in an increase of solar to hydrogen conversion efficiency as compared to TiO₂ and Au-TiO₂.

2.1. Introduction:

In respect to the fast growing interest in the development of a viable semiconductor material for sustainable hydrogen (H_2) production, a large number of photocatalysts have been reported since it was firstly reported in the early seventies [1-5]. Among these, titanium dioxide (TiO_2) has been extensively studied [6-8] as an effective photocatalyst due to its excellent properties and high photocatalytic activity. Specifically for H_2 production from water TiO_2 has been found effective [9, 10] but the efficiency remains limited due to the low interfacial charge transfer of photogenerated electrons (e^-) and holes (h^+). Secondly, the band gap of TiO_2 (3.2 eV) primarily makes it inactive for water splitting under the visible light as band edge does not straddle within the thermodynamic limits of water splitting reaction. Efforts have been made to modify TiO_2 based nanocomposites for effective separation of charge carriers by loading of noble metal nanoparticles [11, 12], these act as electron storage and transport units. Metals like Au, Ag, and Cu have been widely used to enhance the rate of photoreaction [13, 14] as they act as electron trappers thereby inhibiting the recombination of excitons. Moreover, stability in aqueous media, strong response to visible light and increase in the photoinduced optical response of these plasmonic metals helped in enhancing the rate of a reaction [15, 16].

Furthermore, to achieve the requirement for water splitting reaction, the coating on TiO_2 with some electron rich transport materials and other semiconductors is favored [17, 18]. The composites of TiO_2 with carbon rich materials like carbon nanotubes (CNT), graphene and graphene oxide have got a vivid attention during last few years. Hoffman et al. [19] suggested CNT as an electron transfer site upon loading with TiO_2 , electrons are easily transferred to CNT surface thereby helping the retardation of recombination rate. Similarly, graphene, a carbon composite with sp^2 hybridization with brilliant properties has been said to be a good transporter of electrons [20], Kamat et al. [21] reported that electrons can be transferred to graphene oxide (GO) surface from the conduction band (CB) of TiO_2 . Few other reports have also suggested the effective role of carbon based materials for enhanced photocatalytic activity [22, 23]. In addition to this, changing the morphology to core-shell design of TiO_2 has also been investigated [24] as an effective measure for a wide range of applications like hydrogen production and solar cells. In comparison to other heterocomposites core shells structures act as a hybrid showing the synergistic property of inner core and outer shell, which is versatile and conducive for some photocatalytic reactions. Hence, a good electron transport shell like graphene or graphene oxide

over TiO₂ core can be effective owing to high conductance, specific surface area and shell layer acting as a reservoir for electron storage and transport.

In this respect, this chapter presents the production of H₂ from water, using a core shell Au-TiO₂@GO nanocomposite. Role of Au loading (plasmonic effect) and graphene oxide shell (as transport for electrons) has been elaborated under different irradiation sources for the evolution of H₂ from the water. The reduction of water is explained by the fact that the excited electrons are transferred to GO surface because of its lower reduction potential whereas the plasmonic effect of Au is able to increase the energy of trapped electrons resulting in efficient hydrogen generation from water photolysis.

2.2. Materials and methods

2.2.1. Chemicals and reagents

Titanium tetrachloride (TiCl₄) and hydrogen tetrachloroaurate(III) hydrate (HAuCl₄.3H₂O) were purchased from Loba Chemicals. Ethylene glycol, polyethylene glycol (PEG, MW 5000-7000) hydrochloric acid (HCl), hydrazine (N₂H₄), acetone (CH₃COCH₃), ammonium hydroxide (NH₄OH), natural graphite powder were purchased from SD Fine Chemicals Ltd. All the chemicals were used without further purification. Deionized water was obtained using Milli-Q (Milipore) an ultrafiltration system with a measured conductivity of 35 mho cm⁻¹ at 25 °C.

2.2.2. Synthesis of graphene oxide

Graphene oxide was prepared from natural graphite powder as per reported method [25] with little modification. In a typical method, 100 mL of graphite dispersion (1 mg/mL) was mixed with hydrazine monohydrate (1 mL), NaOH was added for adjusting pH =10 and the mixture was stirred at 80 °C for 24 h. The mixture was washed several times with DI water and 0.01 M H₂SO₄ to attain pH =7 followed by addition of concentrated H₂SO₄ (12 mL) and heating again at 80 °C for 4 h. The product was filtered, washed repeatedly with deionized (DI) water and finally dried at 60 °C for 24 h.

2.2.3. Synthesis of TiO₂ nanoparticles and Au photodeposition

The TiO₂ nanoparticles were synthesized by a modification of microwave assisted method using titanium chloride (TiCl₄) as a precursor. In a typical procedure, polyethylene glycol (PEG, 0.99 g) was dissolved in HCl (20.5 mL, 0.5 M) and stirred vigorously for 30 min till the solution turns transparent. In another beaker, TiCl₄ (3.2 mL) was dissolved in HCl (8 mL 0.5 M) and stirred for 30 min resulting in a pale yellow solution that was transferred to the first solution. The pH was

adjusted to 7 by NH_4OH , the suspension was stirred further for 2 h, centrifuged and rinsed several times with distilled water. The gel was irradiated under high power microwave irradiation (7 W, 80 °C) for 1 h, rinsed with distilled water and was calcined at 400 °C for 3h.

The photodeposition of Au was carried out in a sealed test tube containing 50 mg of TiO_2 suspended in 50 % aqueous solution of isopropanol and 1 wt% of Au (0.01 M, HAuCl_4) followed by Ar purging (10 min) and irradiation with UV light for 2 h with continuous stirring. The suspension was centrifuged, washed repeatedly with distilled water and then by ethanol, dried at 50 °C for 30 min.

2.2.4. Synthesis of Au-TiO₂@GO nanocomposite

The core-shell Au-TiO₂@GO nanostructure was fabricated by hydrothermal based microwave method. Graphene oxide (0.01 g) was dispersed in a mixture of water and ethanol (2:1) and was sonicated for 1 h. Photo deposited Au-TiO₂ (0.1 g) was added to above suspension followed by sonication for 5 min. The homogenous solution was transferred into microwave reaction vial (20 mL) and was kept at 180 °C and 19 bar for 1 h. The nanocomposite was washed with distilled water and ethanol by several cycles of centrifugation and dried at 60 °C. Hui Liu et al. [26] have reported that the core-shell formation is due to simple chemical bonding reaction involving van der Waals forces or dehydration reaction.

2.2.5. Characterization

The characterization of the photocatalysts has been carried as per discussion in section 1.4 (Chapter 1).

2.2.6. Photocatalytic activity

The photocatalytic activity of the nanocomposite was carried out in a sealed test tube (20 mL) containing catalyst (0.050 g) and 5 mL water. The pH of the water was adjusted to 2.5 by H_3PO_4 . Before irradiating, the solution was purged with argon for 30 min. The reaction mixture was irradiated with UV (125 W Hg arc) and visible light (Xenon lamp 125 W, 400-1100 nm). The experiment was also carried out in direct sunlight on 11th June 2015 (temperature, 41 °C). The solar to hydrogen conversion (STH) was calculated as per the following formula

$$\text{STH (\%)} = \frac{r\text{H}_2 * \Delta G}{\text{Solar flux} * \text{Surface area of Reactor}}$$

$r\text{H}_2$ = rate of hydrogen production, ΔG = 237 kJ/mol

2.3. Results and discussion

2.3.1. Optical and structural properties

The optical spectra of TiO_2 , Au-TiO_2 , and $\text{Au-TiO}_2@\text{GO}$ photocatalysts is presented in **Fig.2.1**. Surface plasmon absorption arising from collective oscillation of Au^0 on the surface of TiO_2 induced by an electromagnetic wave of matching wavelength in Au-TiO_2 and $\text{Au-TiO}_2@\text{GO}$ appears at 550 nm. Furthermore, there was no shift observed in the absorption edge of TiO_2 after composite formation. These results are in agreement to those reported earlier [27]. The appearance SPR band in the $\text{Au-TiO}_2@\text{GO}$ suggested that the core-shell formation is not uniform making it absorb in visible region that was later confirmed by HRTEM analysis.

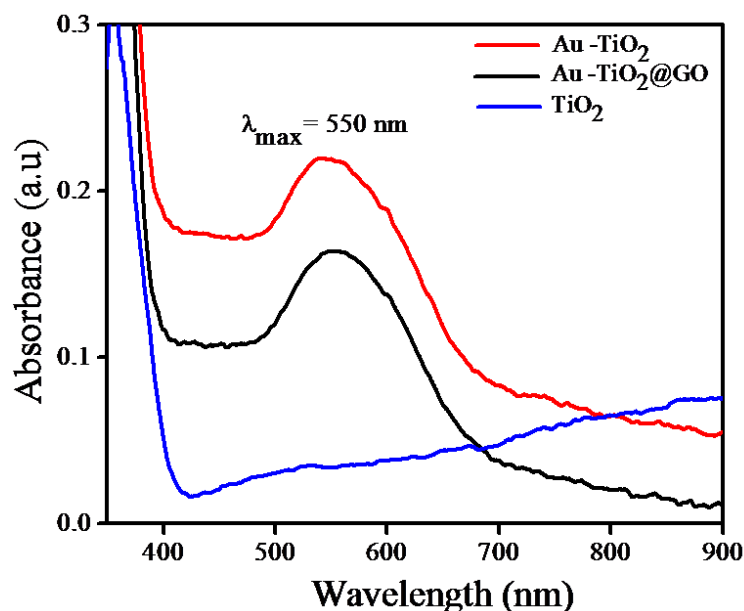


Fig. 2.1: Optical absorption spectra of TiO_2 , Au-TiO_2 and $\text{Au-TiO}_2@\text{GO}$ photocatalysts.

As shown in **Fig. 2.2** the XRD diffraction pattern of the as synthesized TiO_2 showed the predominant anatase and a small rutile phase (21:4, JCPDS Card no. 73-1764). The Au-TiO_2 showed a similar pattern and there was no characteristic Au peak due to its low content ($< 1 \text{ wt } \% \text{ Au}$) which is also supported by earlier findings [28] however increase in the intensity of the peak at 38.2° is attributed to the presence of Au. The TiO_2 and Au-TiO_2 photocatalysts possess tetragonal structure of the TiO_2 unit cell with edge length $a = 3.7$, $b = 3.7$ and $c = 9.5$ and angle $\alpha = \beta = \gamma = 90^\circ$. A similar pattern was also observed in $\text{Au-TiO}_2@\text{GO}$ except additional peak

appearing at 27° corresponding to 002 plane of carbon due to the formation of a shell of GO over the lattice of the Au-TiO₂ core. An earlier report [25] also showed similar pattern without the appearance of a peak at 27° in the graphene based TiO₂ composite. The crystallite size of TiO₂, Au-TiO₂, and Au-TiO₂@GO by Scherrer equation was 19, 20 and 7 nm, respectively. The Smaller size in Au-TiO₂@GO resulted from high microwave irradiation during coating of GO resulting in the breakdown of larger crystals into smaller ones.

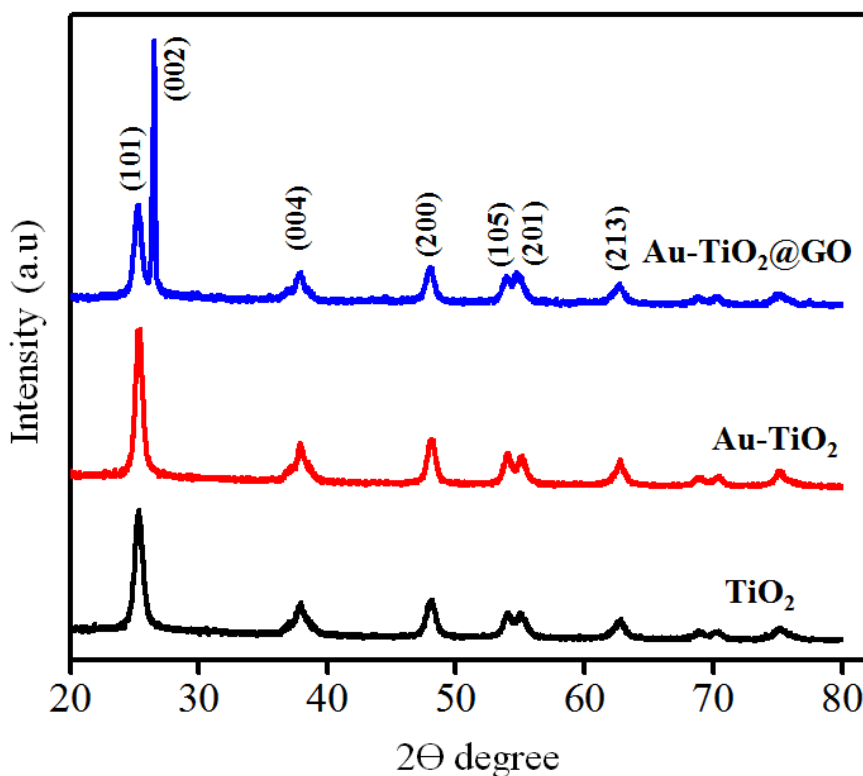
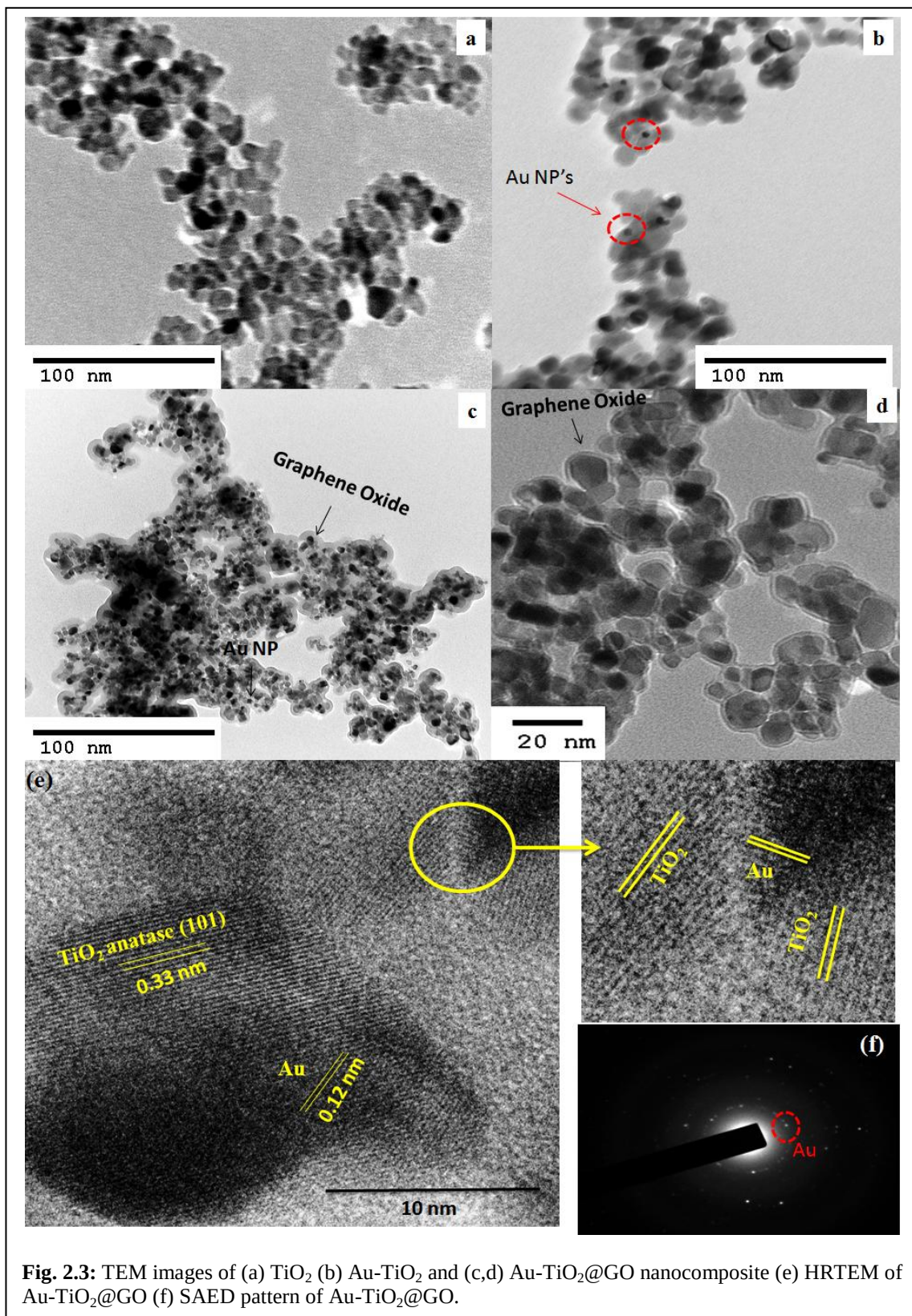


Fig. 2.2 : X-ray diffraction pattern of TiO₂, Au-TiO₂ and Au-TiO₂@GO photocatalysts.

The TEM micrographs of photocatalysts (**Fig. 2.3**) revealed a smooth and uniform coating of GO shell (~2.5 nm) over Au-TiO₂. The average particle sizes of the photocatalysts were obtained by particle size distribution histogram (**Fig. 2.4**) that was plotted by taking into consideration the size of 20-25 particles present on TEM micrographs disclosing the average particle size of ~11, ~12 and ~15 nm for TiO₂, Au-TiO₂ and Au-TiO₂@GO respectively. The smaller particle size of TiO₂ in all the three photocatalysts is due to higher microwave irradiation. HRTEM with SAED pattern of Au-TiO₂@GO has been provided as Fig 2.4 which revealed lattice fringes with

interplanar distance of 0.33 nm corresponding to the 101 plane (anatase phase) of TiO_2 and interplanar distance of 0.12 nm representing the diffraction of Au because of its polycrystalline nature. The lattice fringes of GO are not clear though it is clearly visible in TEM.



The energy dispersive spectroscopy (EDS) confirms the presence of Ti, O, Au and C elements (**Fig. 2.5**). The expected loading content was 1 % and 10 wt% of Au and C but the observed values were 0.68 % and 12.07 %. The higher percentage of C seems due to the interference of carbon present on a grid of SEM-EDX while the lower amount of Au is due to selective area selection for EDX and dispersion of Au on TiO₂ surface. As shown in **Fig. 2.6 (a)** the Brunauer-Emmett-Teller (BET) surface area of Au-TiO₂@GO ($\sim 100 \text{ m}^2\text{g}^{-1}$) was highest in comparison to Au-TiO₂ ($\sim 71 \text{ m}^2\text{g}^{-1}$) and TiO₂ ($\sim 88 \text{ m}^2\text{g}^{-1}$). The coating of GO resulted in the increase in surface area of Au-TiO₂@GO nanocomposite ascribed to its mesoporous nature. Porosity studies as per Barrett-Joyner-Halenda (BJH) curve (**Fig. 2.6 (b)**) showed that the nanocomposite possesses a large pore volume ($0.10 \text{ cm}^3\text{g}^{-1}$). In relevance to BJH studies, the water molecules can easily adsorb and diffuse into the nanocomposite which results in the enhanced efficiency in H₂ production. In comparison to TiO₂, the decrease in surface area of Au-TiO₂ is due to the accumulation of small AuNP's in the pores of TiO₂.

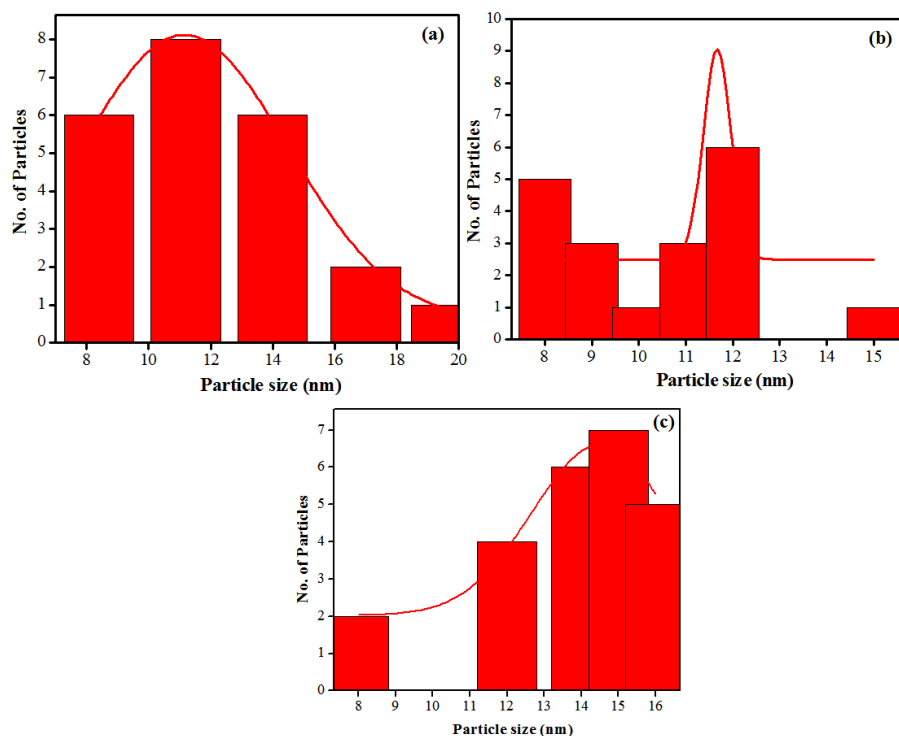


Fig 2.4: Particle size distribution of (a) TiO₂ (b) Au-TiO₂ (c) Au-TiO₂@GO photocatalysts.

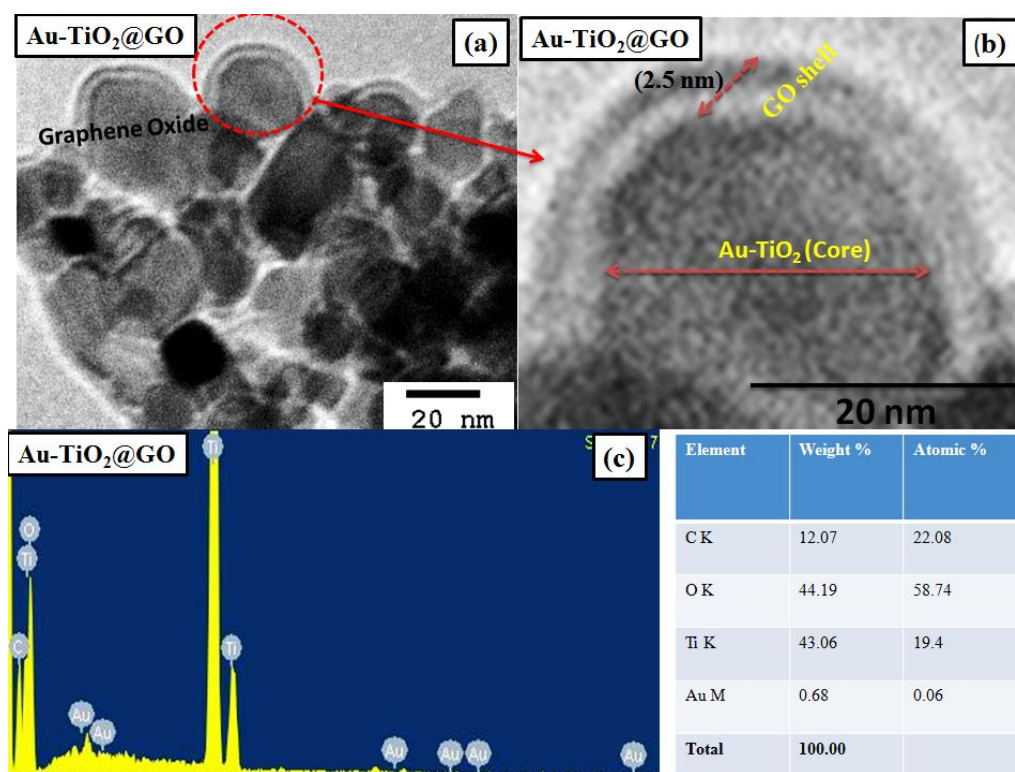


Fig. 2.5: (a, b) TEM micrographs of core shell morphology of Au-TiO₂@GO nanocomposite (c) EDS data of core shell Au-TiO₂@GO nanocomposite.

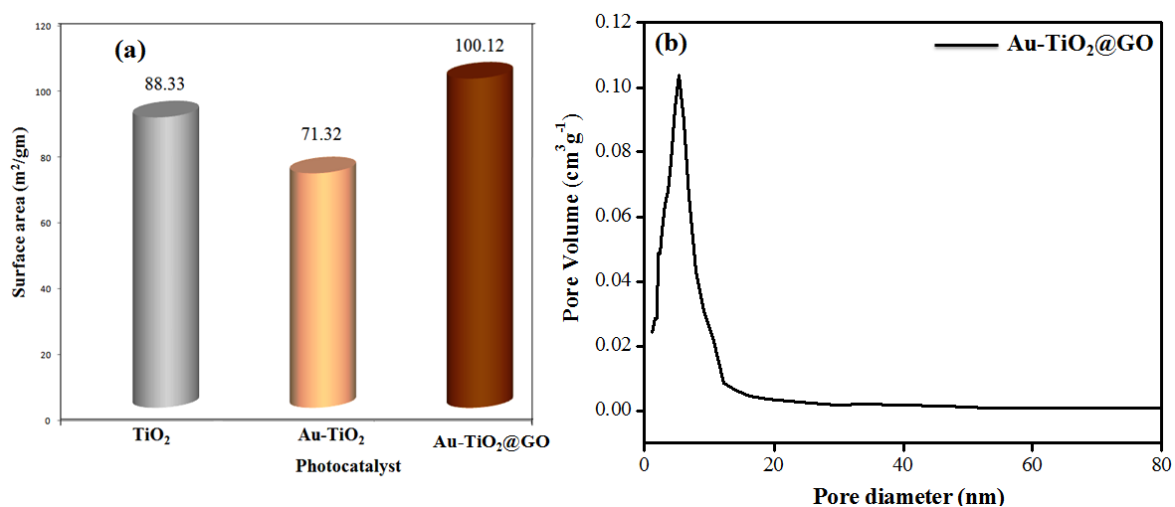


Fig. 2.6: (a) Specific surface area of different photocatalysts measured by BET analysis and (b) Barrett-Joyner-Halenda curve of Au-TiO₂@GO nanocomposite.

Raman spectra of TiO_2 , Au-TiO_2 , and $\text{Au-TiO}_2@\text{GO}$ (**Fig. 2.6**) showed the characteristic B_{1g} , A_{1g} and E_g modes at 400 cm^{-1} , 517 cm^{-1} and 638 cm^{-1} respectively, corresponding to the anatase phase of TiO_2 . Furthermore, $\text{Au-TiO}_2@\text{GO}$ showed two additional bands at 1593 cm^{-1} (primary stretching (sp^2) of G mode) and 1317 cm^{-1} (D band) of GO. The softening and lower intensity of G band results from the thickness of GO layer, the G band was not visible in natural graphite because it has been widely accepted that the higher disorder in graphite leads to broader sp^2 stretching. Another possibility of less intensity or absence of G band is the amorphous nature of graphite which contains certain fractions of sp^3 hybridized carbon [29]. The broadening of D band is ascribed to the oxygen defects on the surface of the ring. These bands were absent in TiO_2 and Au-TiO_2 .

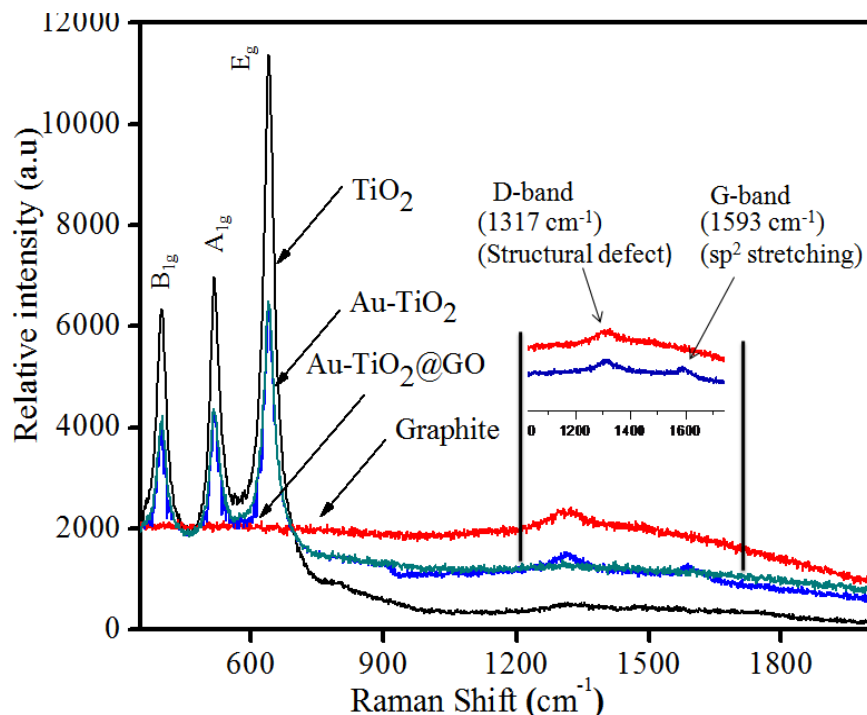


Fig. 2.6: Raman spectra of graphite and different photocatalysts, and appearance of D and G band after GO coating (enlarged panel).

2.3.2. Interfacial properties

The current (I) and voltage (V) curves of TiO_2 , Au-TiO_2 , and $\text{Au-TiO}_2@\text{GO}$ (**Fig. 2.7**) showed an exponential increase in I with applied V. The highest conduction was observed for the core-shell nanocomposite ($\text{Au-TiO}_2@\text{GO}$) heterojunction in comparison to TiO_2 and Au-TiO_2 . All the three photocatalysts showed a rectifying bias at 0 V which is against Ohm's law. The increase in

conductance in Au-TiO₂ and Au-TiO₂@GO is attributed to the high electron mobility on GO surface.

The decay/lifetime curves (**Fig. 2.8**) showed the average lifetime of 2.85, 2.88 and 2.94 ns for TiO₂, Au-TiO₂, and Au-TiO₂@GO nanostructures. The better delocalization of e⁻/h⁺ pairs from conduction band (CB) of TiO₂ to GO in core-shell nanocomposite resulted in higher lifetime for

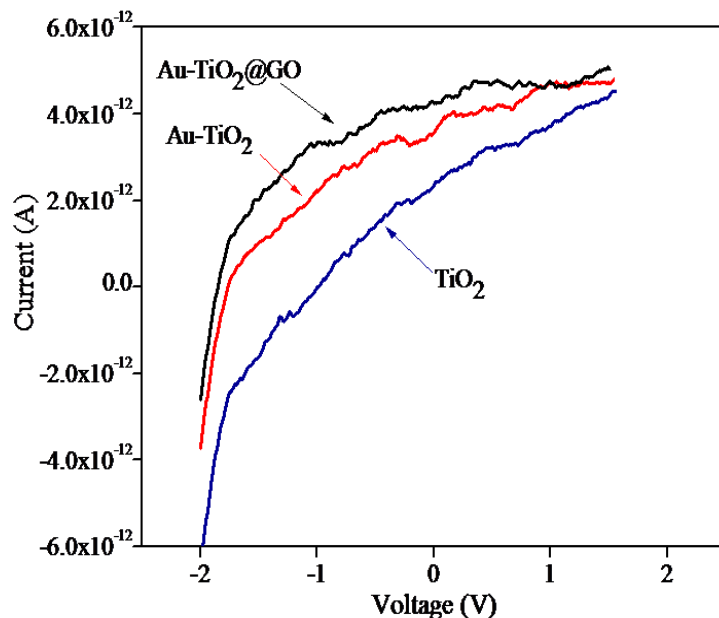


Fig. 2.7: I-V characteristic curve showing comparative increase in I flow through TiO₂ and Au nanocomposites with applied V.

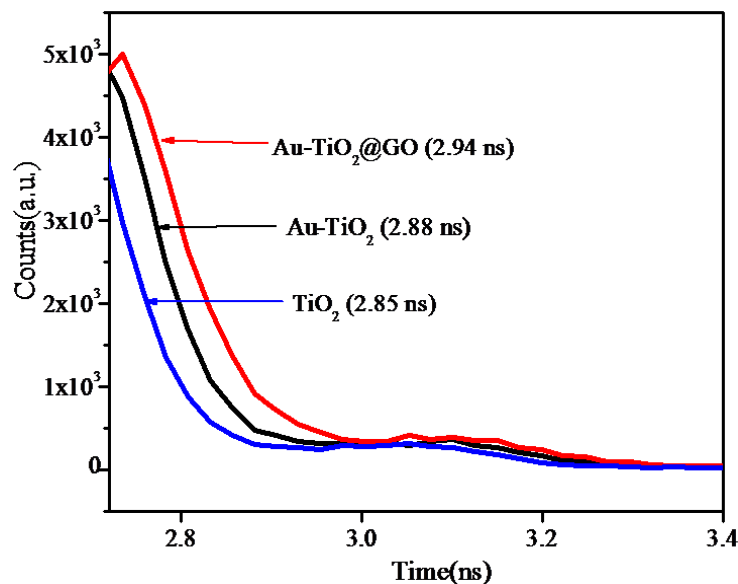


Fig. 2.8: Time resolved spectra of TiO₂, Au-TiO₂ and Au-TiO₂@GO nanocatalysts.

Au-TiO₂@GO. Similar results have been reported earlier [30] in graphene TiO₂ nanotube composite.

2.3.3. Photocatalytic activity

The photocatalytic activity of synthesized TiO₂ and Au nanocomposites was evaluated under different light sources i.e direct sunlight, visible light and under combined UV and visible light (UV-Vis) and is presented in **Fig. 2.9**. Hydrogen evolution was not observed with bare TiO₂ in different light sources under study due to thermodynamic potential and band edge of TiO₂ for water splitting. However, by the use of Au-TiO₂@GO, the highest amount of H₂ (19 μ mol, 40 μ mol, and 114 μ mol) was produced when the reaction was carried out under direct sunlight, visible light and combined UV-Vis light in comparison to Au-TiO₂ (7 μ mol, 38 μ mol, and 45.23 μ mol). The enhanced activity of Au-TiO₂ occurs due to surface plasmonic resonance at 550 nm, sensitization and co-catalytic properties of Au. The coating of GO over Au-TiO₂ in core-shell structure of Au-TiO₂@GO resulted in an abrupt increase in the rate of H₂ evolution, the GO acting as reservoir and transmission source of electrons, enabling good sites for hydrogen production. These findings are further supported by higher specific surface area of Au-TiO₂@GO, I-V analysis and time resolved spectroscopy showing a decrease in recombination rate of e⁻/h⁺ pair with larger decay time.

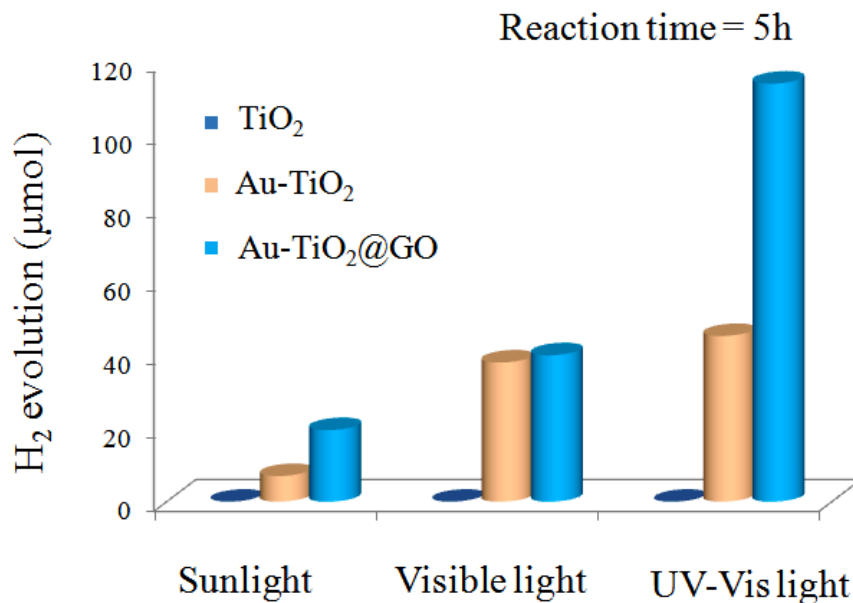
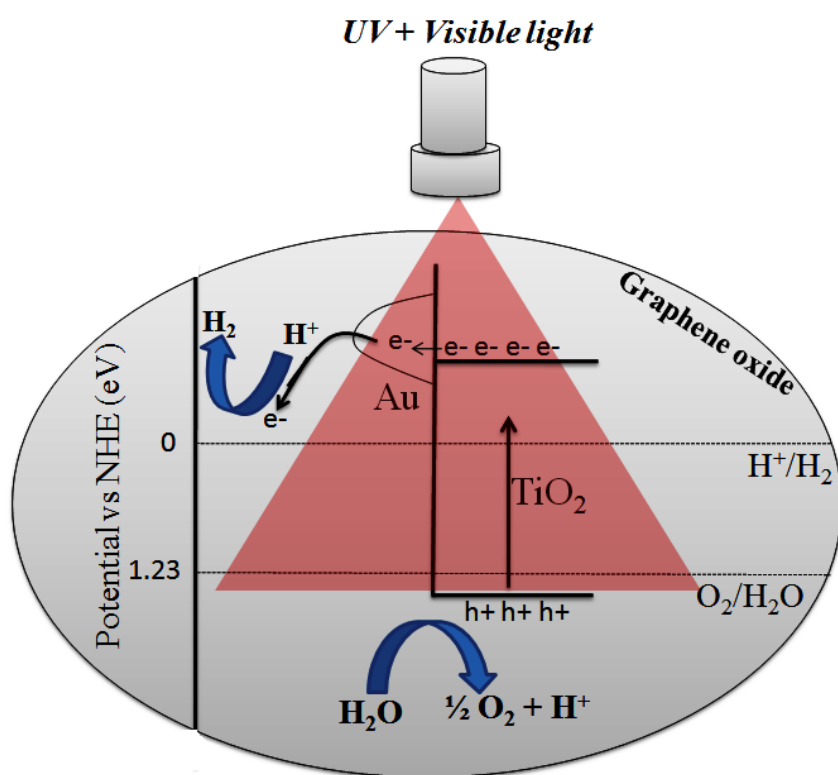


Fig. 2.9: Photocatalytic hydrogen production under different illumination sources.

The mechanism for the higher photocatalytic activity of Au-TiO₂@GO has been proposed in **Scheme 2.1**. Under combined UV-Vis irradiation, Au resonates under the visible light because of SPR effect and electrons of TiO₂ are excited to CB under UV irradiation. Hot electrons are ejected to the surface of GO due to its lower reduction potential (-0.08 eV) than TiO₂ (-0.24 eV). Earlier reports showed either the transfer of electrons to Au surface [31] or to the graphene [32]. The higher conduction of GO increases the mobility of these transferred electrons on the surface, reducing the recombination rate and resulting in the reduction of H₂O to H₂. Under combined UV and visible light, Au particles act as electron trappers and helped in the creation of reduction sites for water splitting.



Scheme 2.1: Proposed mechanism for hydrogen evolution under UV-Vis light irradiation using Au-TiO₂@GO nanocomposite.

The pH of the reaction was maintained acidic (pH = 2.5) using 0.01mmol H₃PO₄ and it remains constant during the reaction. The H₃PO₄ acted as a source for H⁺ transportation. The amount of H₃PO₄ added corresponds to the production of ~0.07 μmol of H₂. Hence, the amount of H₂ (114 μmol) being produced is merely by the reduction of water.

Throughout the reaction, oxygen (O_2) was detected only in trace amounts. Sodium periodate was used as an electron scavenger to mask the reduction reaction for observing the total amount of oxygen evolved during the course of the reaction. After 5 h UV-Vis irradiation, 41.2 μmol of O_2 gas was also observed which is lower than the actual stoichiometric ratio (57 μmol) of 2:1 ($H_2:O_2$), ascribed to the anatase phase of TiO_2 which is a poor surface for O_2 evolution. Rengui Li et al. [33] showed that anatase phase of TiO_2 results in the negligible amount of O_2 production upon prolonged UV light irradiation as kinetically anatase favors the formation of hydroxyl radicals inhibiting the oxygen evolution.

The time course study of H_2 evolution by different photocatalysts is illustrated in **Fig. 2.10**. The maximum rate of H_2 evolution was observed in the $Au-TiO_2@GO$ nanocomposite, the rate of H_2 evolution increased with time for 3 hours (110 μmol) and then the rate of H_2 evolution increases slowly due to the blockage of certain active sites and after the washing of the recovered photocatalyst the same reaction rate was observed for the second cycle. The maximum rate of H_2 evolution of 22.8 μmolh^{-1} was observed for the core-shell structure of $Au-TiO_2@GO$. The highest value of STH was also observed for $Au-TiO_2@GO$ (1.9 %) followed by $Au-TiO_2$ (0.68 %) of combined UV-Vis irradiation (**Fig. 2.11**). Thus $Au-TiO_2@GO$ shows a highest photocatalytic performance towards water splitting than bare TiO_2 and $Au-TiO_2$. The hydrogen production can further be enhanced by coating with graphene, changing the crystal polymorph of TiO_2 and with 1D metal nanoparticle loading.

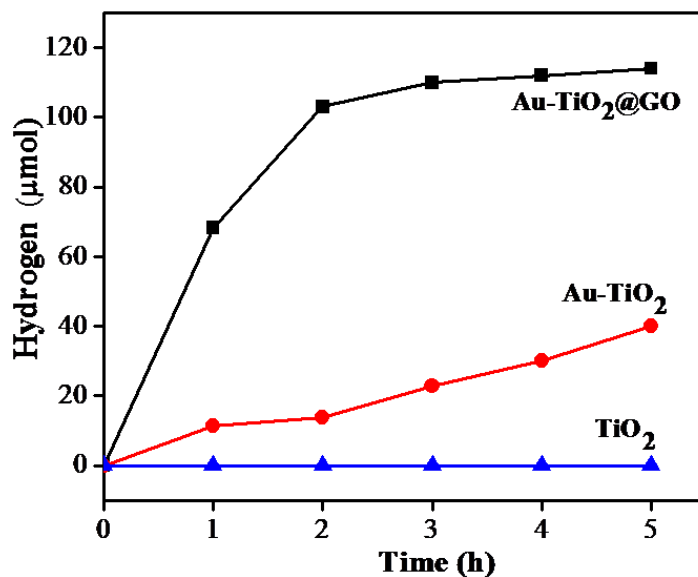


Fig. 2.10: Time course study of hydrogen evolution by different catalysts under UV-Vis irradiation.

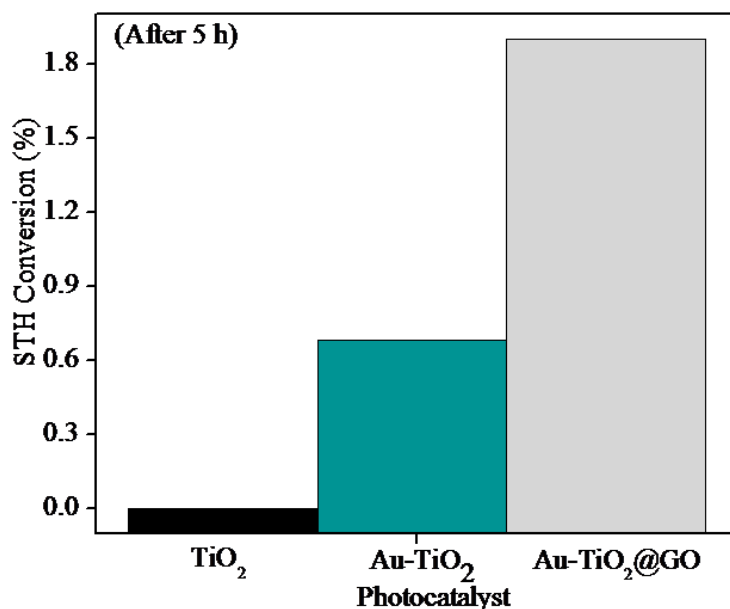


Fig. 2.11: Solar to hydrogen conversion efficiency of TiO₂, Au-TiO₂ and Au-TiO₂@GO photocatalysts under UV-Vis light irradiation.

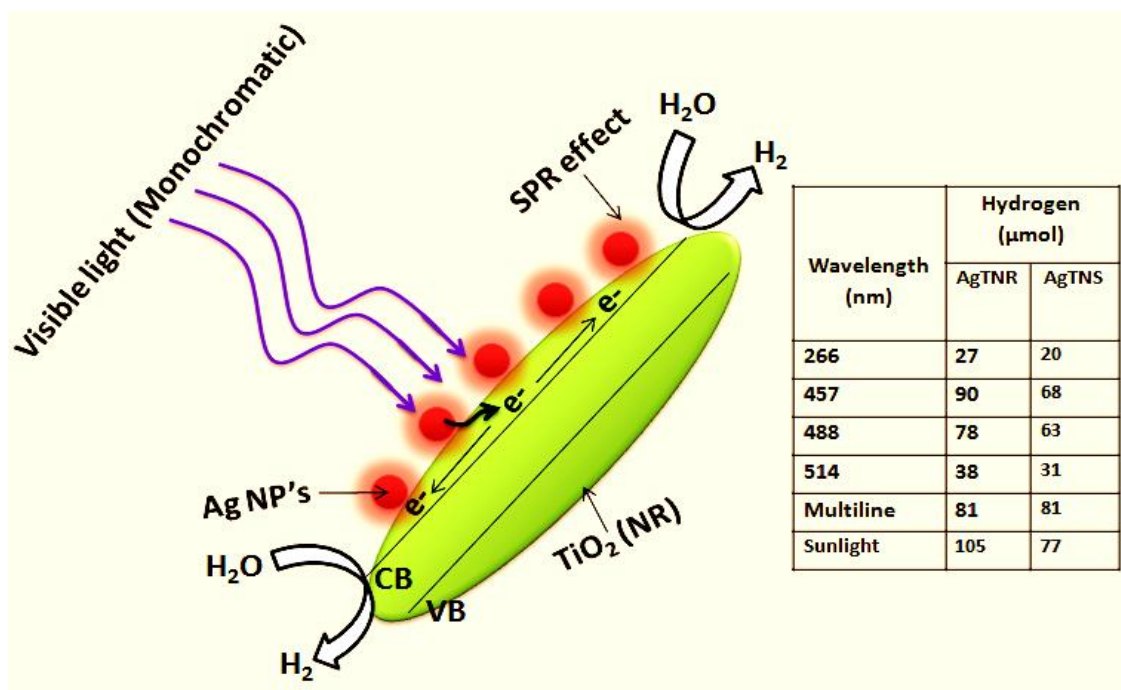
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CHAPTER 3

PLASMONIC Ag-TiO₂ NANORODS FOR HYDROGEN PRODUCTION FROM WATER PHOTOCATALYSIS



Schematic summary

This study demonstrated that Ag nanoparticles loaded lengthy TiO₂ nanorods (~79 nm) exhibited highly improved H₂ production (90 μmol) from water relative to TiO₂ nanospheres (~19 nm) due to the plasmonic effect at 457 nm light irradiation that also exhibited better H₂ production (105 μmol) rate under direct sunlight exposure.

3.1. Introduction

In the category of metal oxide semiconductors, titanium dioxide (TiO_2) based nanostructures are both theoretically and technologically relevant for hydrogen (H_2) production from water due to its brilliant optical and electrical properties [1-3]. This multifunctional material has been widely used for energy conversion processes such as photovoltaics, photocatalysis, and photoelectrocatalysis [4-7]. Some advanced TiO_2 based electrodes have been reported since the discovery of photovoltaic cell by O'Regan and Grätzel in 1991 [8]. Federico Bella et al. have reported [9-11] several polymer based flexible and vertically aligned TiO_2 nanotubes as the effective electrodes to avoid recombination, the quasi-1D TiO_2 showed superior charge transport and effective photoconversion efficiency. Similarly, Masoud Faraji et al. [12] have developed a binder-free PANi-g-MWCNT/ TiO_2 NTs/Ti electrode material for the potential application in supercapacitors.

As we know that the performance of TiO_2 is highly dependent on its morphology and dimensionality, previous reports suggest that 1D nanostructures like nanotubes, nanorods etc. can be more useful [13-16] as the solar conversion efficiency is usually determined by the competition of electron transport towards the reaction site and recombination of electrons with holes, and these 1D structures provide larger interface for better charge distribution. Still, the deficiencies like the optical absorption of TiO_2 [17] which is in UV region due to its larger energy gap ($E_g \sim 3.2$ eV) limits its efficiency. To overcome this drawback, doping and synthesis of nanodiodes with plasmonic metals like Ag and Au are used to sensitize it in visible light [18-21]. Reports reveal that doping of metals like Ag and Au leads to the formation of Schottky barrier which is further coined as Schottky nanodiodes [22, 23]. These Schottky nanodiodes convert photon energy into electrical energy [24] and can be effective for photolysis of water. The metal doping of TiO_2 with Ag and Au is effective in two ways, by helping to sensitize it in visible light region due to the surface plasmon resonance (SPR) effect [25-27] and are also helpful in generating the high kinetic energy hot electrons under photon irradiation because of low electron heat capacity of metals permitting easy and nonadiabatic energy transfer [28]. These hot electrons emitted by the deposited metal are prompted towards the metal-semiconductor interface. When the energy of the electron is high enough to cross over the Schottky barrier they easily transfer to semiconductor conduction band (CB) [29] and are redistributed along the elongated interface of nanorods, nanotubes etc. Previous reports investigated the use of modified

TiO₂ surface with Ag and Au for optimum photocatalytic activity for H₂ production [30, 31]. These two modifications related to TiO₂, i.e., loading with noble metals Ag /Au and transformation into 1D morphology have also been effective in several other photocatalytic processes like sensors, photovoltaics and environmental cleaning [32-37]. Certainly, in the case of bulk material, it is difficult for the electrons to reach the reaction site due to fast recombination of charge carriers. Similarly, in the case of spherical nanoparticles they have to cross a number of grain boundaries which again led to their recombination but in the case of 1D nanostructures, the effective distribution of the electrons can help them to easily reach the respective reduction site.

So, this chapter presents a study on the roles of the morphology of TiO₂ and Ag loading for H₂ production from water using different monochromatic and sunlight illumination sources. The photocatalytic activity was performed under different monochromatic beams and sunlight.

3.2. Experimental section

3.2.1. Chemicals and reagents

All the analytic grade chemicals like titanium butoxide (Ti(OBu)₄, 98%, Sigma-Aldrich), silver nitrate (AgNO₃, 99% Loba Chemie Ltd), sodium hydroxide (NaOH, 99 %, SD Fine Ltd), sodium sulphide (Na₂S, 98% SD fine Ltd), nitric acid (HNO₃, 99%, Spectrochem Ltd), ethylene glycol (MW = 4000, Loba Chemie), acetone (99%, Sigma-Aldrich) were used as received without any further purification. All solutions were made using DI water obtained from Milli-Q (Millipore) an ultrafiltration system (35 mho cm⁻¹ at 25 °C).

3.2.2. Synthesis of TiO₂ nanorods (TNR), nanospheres (TNS) and photodeposition of silver (Ag)

The titanium dioxide nanorods (TNR) were synthesized by the hydrothermal synthetic method. The commercially available TiO₂ (P25, Degussa Germany) have been used as a precursor for the synthesis of TNR. In a typical experiment, a mixture of 2.5 g of TiO₂ (P25) was mixed with 35 mL NaOH (10 mol/L), and heated at 130 °C in a Teflon-lined autoclave for 20 h. The filtered mixture was washed several times with HNO₃ (0.1 mol/L) to adjust the pH at 7. The 50 mL of this suspension (pH = 7) was treated hydrothermally in an autoclave at 150 °C for 48 h. The resulting slurry was then washed several times with DI water and dried at 100 °C to harvest the TNR.

The nanospheres (TNS) were synthesized by template synthesis approach reported earlier [38]. A mixture of $\text{Ti}(\text{OBu})_4$ (1 mL) and ethylene glycol (22.2 mL) was stirred vigorously for 8 h. The mixture was poured quickly in 100 mL acetone containing 1.5 mL DI water and acetic acid (0.4 mL), and was further stirred at room temperature for 3 h to form titanium glycolate spheres. These spheres were stirred at 70 °C for 8 h to produce TNS and were washed several times with DI water and dried at 100 °C.

The metal (Ag) photo deposition [39] was done in a sealed reaction tubes (20 mL, Pyrex). The respective TiO_2 powder (100 mg) of TNS/TNR were suspended in the reaction mixture containing DI water and isopropyl alcohol as hole scavenger (4 mL each), The respective amount of AgNO_3 (0.1 mol/L) corresponding to different wt% (1, 2, 3 and 5 wt%) was added to these suspension and purged with Ar for 20 min to create an inert atmosphere and was irradiated with UV (125 W, Hg arc) for 3 h under continuous stirring. The photocatalysts were washed several times with DI water and ethanol under several cycles of centrifugation and then dried at of 40 °C. The Ag loaded samples were abbreviated as AgTNR (nanorods) and AgTNS (nanospheres).

3.2.3. Characterization

The characterization of the photocatalysts was done by the procedures discussed in section 1.4 (Chapter 1).

3.2.4. Photoelectrochemical studies

The current voltage characteristics of the photocatalysts were carried out by a three electrode potentiostat (Digi-IVY, D2300). The experiment was performed using Pt as a counter electrode, Ag/AgCl as a reference electrode and thin film (2.5 cm x 0.5 cm) of the photocatalyst on ITO support as a working electrode and KCl (0.5 M) used as an electrolyte. The scan range was set between +2.5 to -2.5V and scan rate is 1 mV/s-100 mV/s. The working electrode (thin film) was prepared by blending photocatalyst powder (0.5 g) with poly ethylene glycol (MW = 5000-7000, 0.25 g) and 1.5 mL of DI water. After 10 min of blending the film was made on ITO glass (2.5 cm x 0.5 cm) by doctor blade method. Drained in the air for 30 min, the film was pressed with another glass under hydraulic press (50 kg/cm^3) for 30 s. The film was dried at room temperature overnight. The *I-V* experiment was carried both in dark conditions and by irradiating the above said thin film with multi wavelengths (457, 488, and 514 nm).

The stability of the photocurrent was measured by amperometric *i-t* titration method keeping the concentration of the electrolyte constant (KCl, 0.5 M). The potential was also kept constant at

-2.5 V. The stability curve was observed by simultaneously irradiating the photoanode with visible light.

3.2.5. Photocatalytic activity

The photocatalytic activity of the as-prepared photocatalysts (TNR, AgTNR, TNS, and AgTNS) was carried in a reaction tube (20 cm³, pyrex) containing 0.040 g photocatalyst and 5 mL water, 200 μ L of Na₂S (0.1 M) was added to the reaction mixture to act as hole scavengers. Before irradiation, the reaction mixture was purged with Ar (20 min) to create an inert atmosphere for the reduction. The reaction samples were irradiated (Modu laser-Steller Pro-L, line frequency 50 Hz-60 Hz, Intensity 300 mW) separately with several monochromatic wavelengths like 457 nm, 487 nm, 514 nm, the reaction was also carried out under multiline (457+487+ 514 nm), UV (266 nm, 125 W Hg arc lamp, Philips) and sunlight (9th May 2016, Patiala, India, temperature 38 °C, 298.78 Wm⁻²) irradiation for 8 h, H₂ was measured as per procedure discussed in chapter 1.

3.3. Results and discussion

3.3.1. Optical and morphological properties

The optimized 2 wt % Silver (Ag) was deposited on the two different morphologies of TiO₂ i.e. nanorods (TNR) and nanospheres (TNS) by photodeposition. The absorption spectra of these photocatalysts shown in **Fig. 3.1** showing a typical absorption edge in between 360-400 nm due to the geometry of TiO₂, after the Ag loading the rise of surface plasmon resonance (SPR) band (457 nm both for AgTNR and AgTNS, respectively) is observed due to coherent oscillation of Ag nanoparticles with identical frequency.

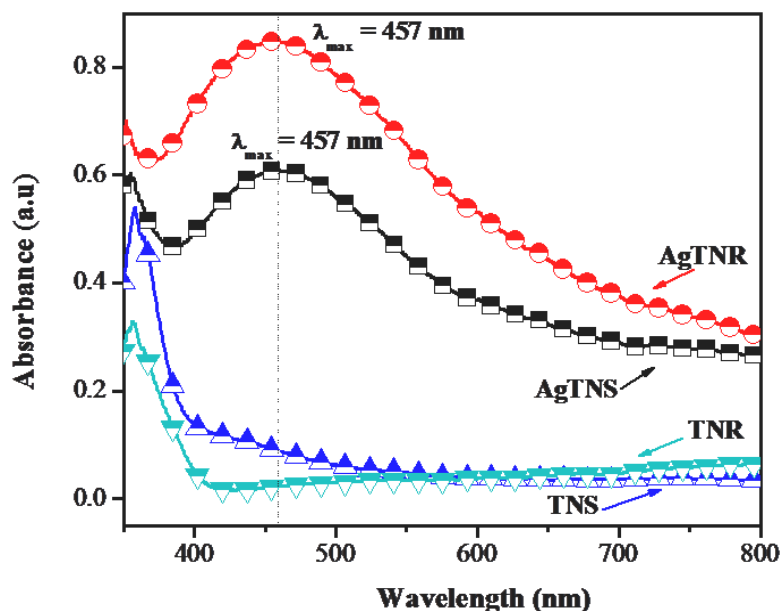


Fig. 3.1: Optical absorption spectra of different photocatalysts.

The polymorphism and crystal properties of as-synthesized photocatalysts were determined by X-ray diffraction studies (**Fig. 3.2**). The diffraction pattern of TNR and TNS displayed a typical

anatase phase properties with edge length ($a = 3.7$, $b = 3.7$ and $c = 9.4$) showing the tetragonal crystal system and calculated density of 3.92 g/cm^3 . The pattern of TNR displayed a relatively intense and narrow peak (101 plane, 25.4°) attributed to 1D growth direction, and 101 plane is also considered as the thermodynamically most stable facet of anatase polymorph. In the case of TNS after Ag loading the crystallinity is also modified and another peak was observed to rise at 45° corresponding to 200 plane of Ag. FESEM and TEM micrographs of the photocatalysts are shown in **Fig. 3.3** and **Fig. 3.4**, respectively. The hydrothermally synthesized TNR consists of rice grain shaped elongated particles with an average length of 79 nm and was found to be 19 nm in the case of TNS. The average diameter of TNR was calculated as 33 nm. There is no size or shape deformation after metal photodeposition and Ag particles were also seen deposited on TNR and TNS with an average size below $\sim 5 \text{ nm}$.

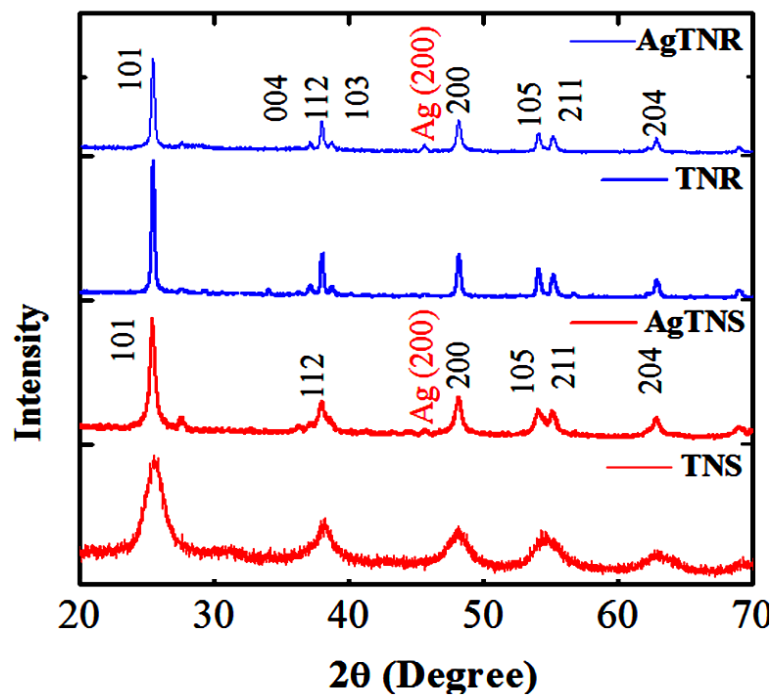


Fig. 3.2: X-Ray diffraction pattern of various photocatalysts.

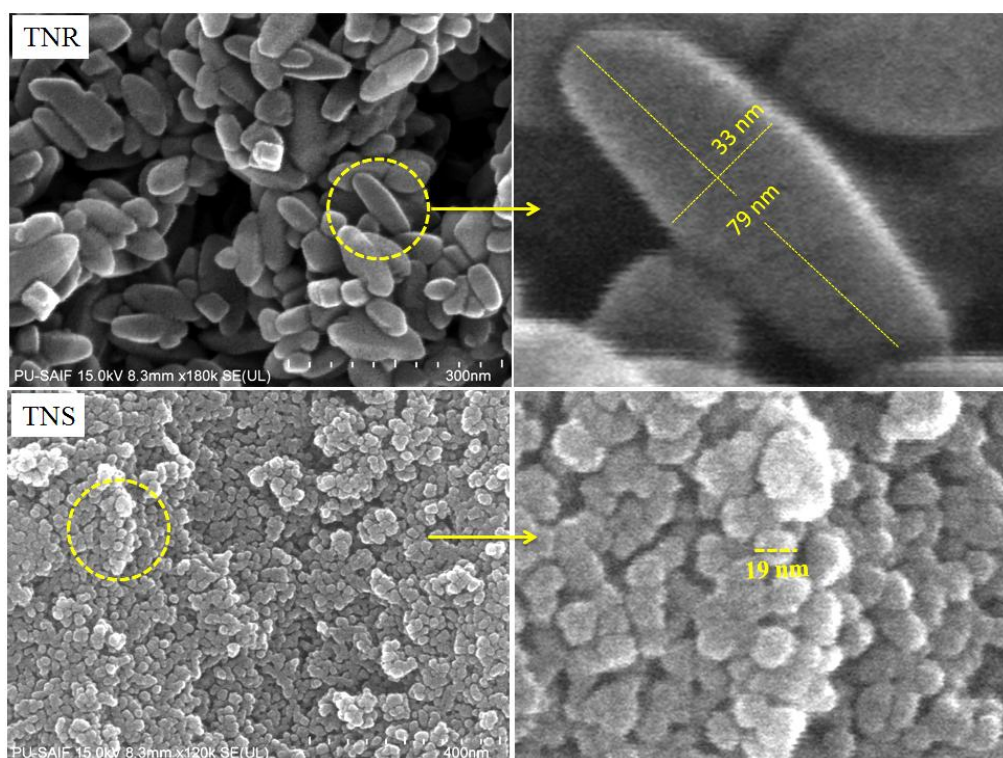


Fig. 3.3: FESEM micrographs of TNR and TNS photocatalysts.

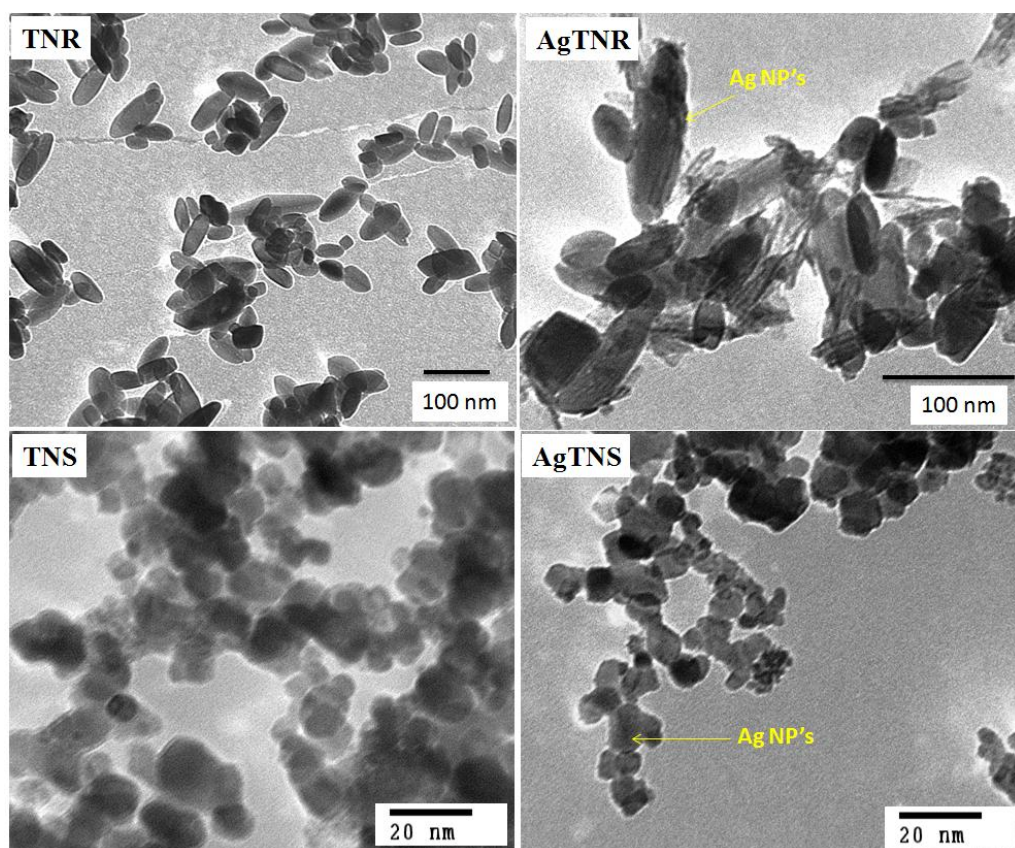


Fig. 3.4: TEM images of bare and Ag loaded TiO₂ of different morphologies.

3.3.2. Porosity and surface area analysis

Nitrogen (N₂) adsorption-desorption based Brunauer Emmet and Teller (BET) study revealed some interesting results. The isotherms of all the photocatalysts exhibit characteristics of type IV Langmuir isotherm [40] which is the specialty of porous materials (**Fig. 3.5**). Furthermore, as shown in Table 1, TNS exhibited highest surface area (181 m²/g) and was highly porous in nature, the average pore diameter and pore volume of TNS were observed to be 5.7 nm and 0.49

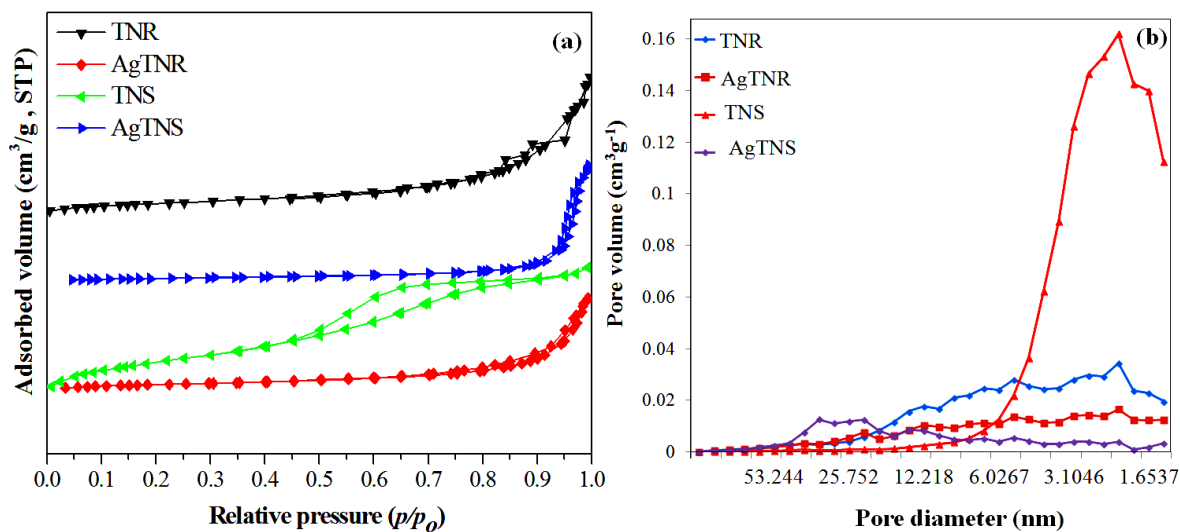


Fig. 3.5: Surface area and porosity study (a) Nitrogen adsorption desorption isotherm (b) BJH curve of different photocatalysts.

Table 3.1: Comparative porosity and surface area study of TNR, TNS, and Ag loaded photocatalysts.

Catalysts	Surface Area (m^2/g^{-1})	Mean Pore diameter (nm)	Pore Volume ($\text{cm}^3/\text{g}^{-1}$)
TNR	146.0	14.31	0.52
AgTNR	72.90	19.20	0.35
TNS	181.0	5.70	0.49
AgTNS	45.60	38.42	0.43

cm^3g^{-1} respectively. The surface area of TNS rapidly decreased to $45.6 \text{ m}^2\text{g}^{-1}$ after Ag loading ascribed to the incorporation of Ag NP's into the pores of the TNS whereas the increase in pore diameter (38.42 nm) is due to the internal pore strain or this large pore diameter can also be due to the stacking of nanoparticles forming small voids, and as expected after Ag loading, pore volume decreases to $0.43 \text{ cm}^3\text{g}^{-1}$. The similar result is observed in the case of TNR where surface area decreased after Ag loading from 146 to $72.9 \text{ m}^2\text{g}^{-1}$ and the change is observed in pore diameter (14.31 to 19.20 nm) and pore volume which decreased to $0.35 \text{ cm}^3\text{g}^{-1}$ from initial of $0.52 \text{ cm}^3\text{g}^{-1}$.

3.3.3. Interfacial properties

Photoluminescence (PL) spectroscopy (**Fig. 3.6**) revealed a number of emission bands from 350 nm to 600 nm for TNR and TNS indicating the presence of surface defects. In agreement with earlier results [41], emission bands at 423, 448 and 462 nm correspond to trap sites near the absorption, while bands at 486 and 530 nm are credited to trap site far from absorption edge of

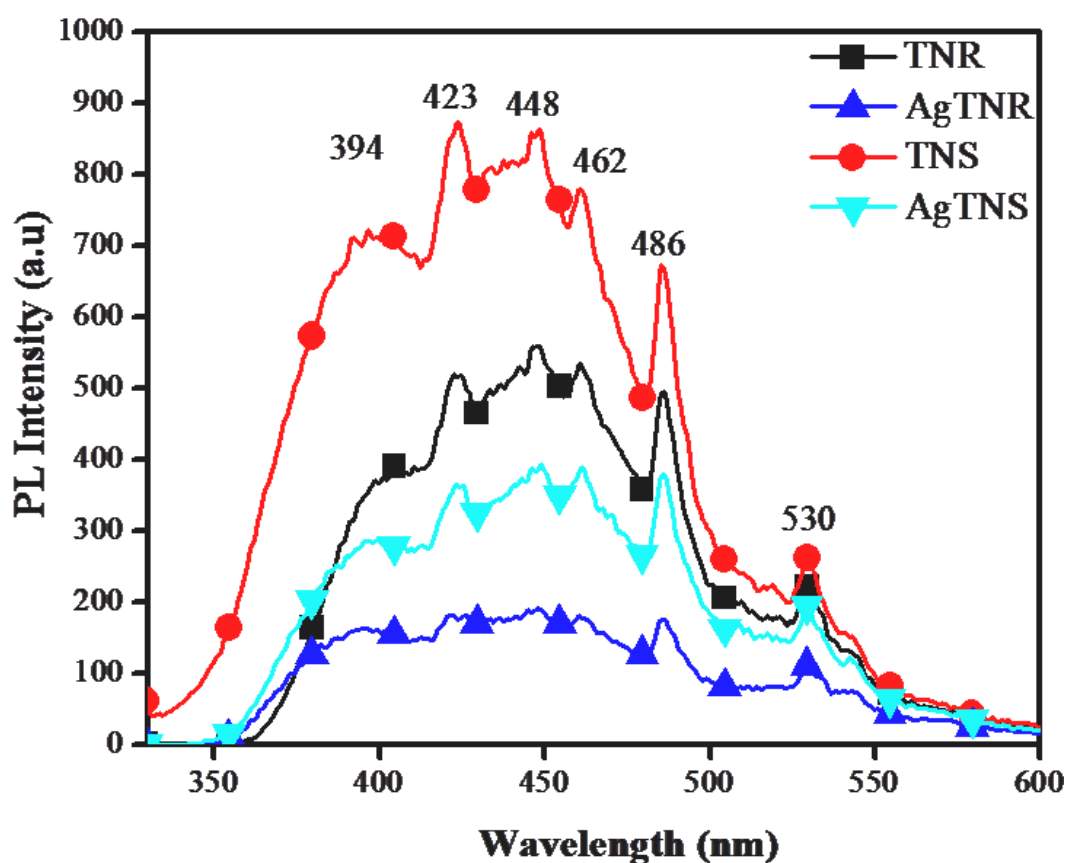


Fig. 3. 6: Comparative photoluminescence spectra of different photocatalysts.

TiO₂, the emission band at 394 nm is due to the recombination of excitons (electrons and holes). These trap sites for charge carriers are due to the presence of surface oxygen and hydroxyl defects. Comparatively, low intensity and lower number of these bands are observed in the case of TNR due to its more crystalline and less defective surface. Photoluminescence quenching is observed in the case of AgTNR and AgTNS due to effective shuttling of electrons from CB of TiO₂ to Ag enabling the separation of charge carriers and also preventing the recombination of electrons and holes. The quenching is higher in the case of AgTNR due to its dimensionality that helps in redistribution of electrons along larger interface directly enhancing the lifetime of charge carriers.

The behavior of current (I), upon application of a voltage (V) of all these synthesized photocatalysts, was evaluated using a prepared photoanode. As shown in **Fig. 3.7** the different *I*-*V* scans were recorded both in dark and upon illumination with multiline wavelength, tiny

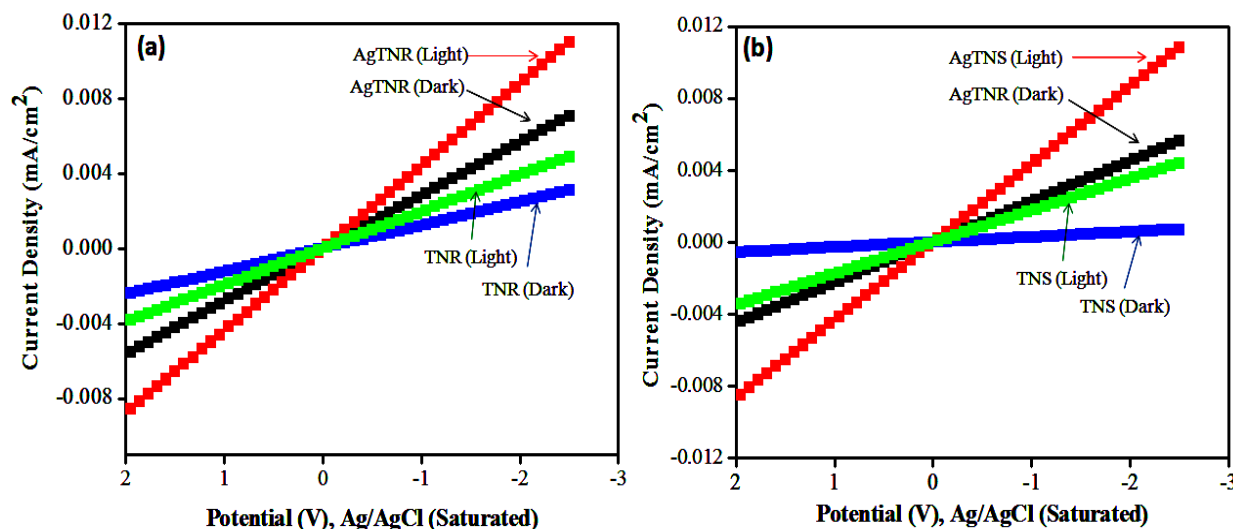


Fig. 3.7: I-V characteristics curves of (a) TNR and AgTNR (b) TNS and AgTNS under dark and visible light illumination conditions.

current was recorded in dark at an applied potential, in contrast under visible multiline irradiation. A sudden increase of photocurrent was observed at more negative potentials, the current density of AgTNR was highest as compared to other nanocomposites but overall all currents monotonically increase as functions of voltage. The Ohmic properties shown by the photocatalysts is due to the formation of the depletion region and Schottky barrier which is characteristics of photovoltaic materials. The larger photocurrent observed in the case of AgTNR and AgTNS could be explained due to more efficient electron injection at TNR electrolyte

interface. When the AgTNR and AgTNS photoanodes were irradiated with visible irradiation (multiline wavelength), the electrons are ejected towards the E_{CB} of TNR/TNS due to the lower Fermi level and SPR effect of Ag NP's. These electrons are efficiently injected towards semiconductor-electrolyte interface resulting in the enhancement of number of collected electrons by the substrate (ITO glass). Moreover, the stability of current through AgTNR photodiode was measured by I-t curve measurements (**Fig. 3.8**). The current density was recorded by continuous irradiation of working electrode (AgTNR) under multiline illumination, the potential was kept constant (-2.5 V) to observe the stability of current for 2 min, a stable oscillating current wave observed was credited to the effective generation of charge carriers. The oscillations are supposed to occur due to the interaction of light with photoanode and also interaction of AgTNR-electrolyte interface with the FTO glass, the oscillation of current has previously also reported [42].

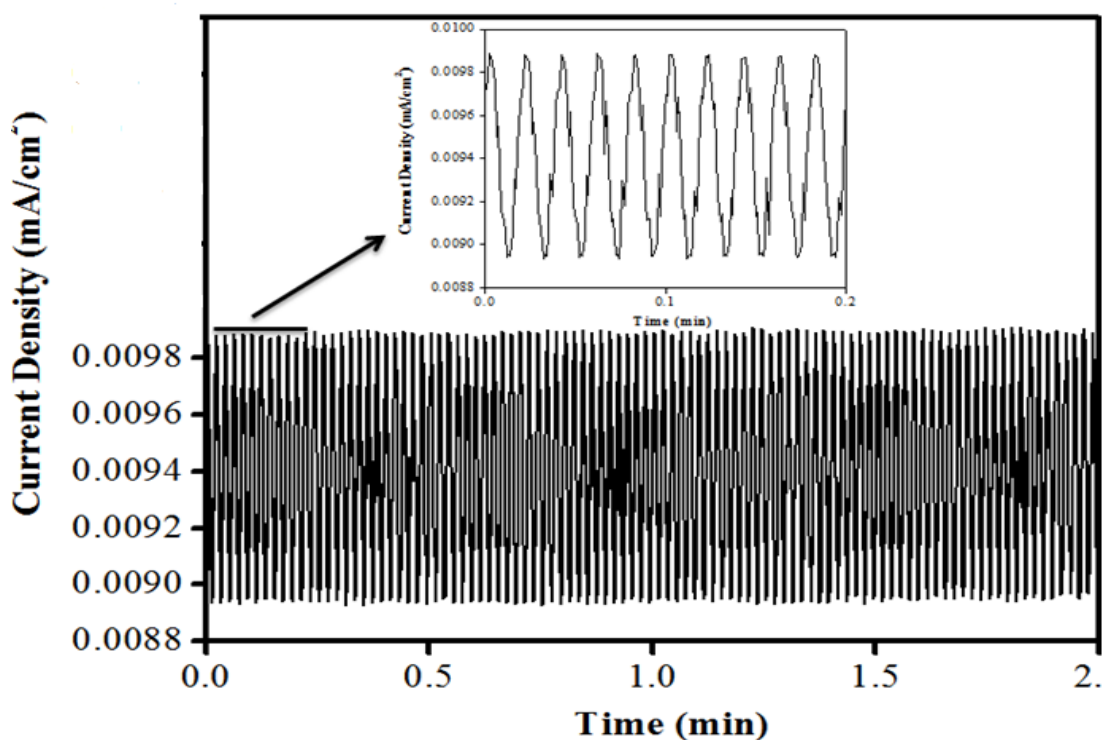


Fig. 3.8: Amperometric I-t Curve of AgTNR photocatalyst showing stability of current for 15 min under continuous multiline wavelength irradiation.

3.4. Photocatalytic activity

Amount of Ag loading for better efficiency was optimized by varying the Ag (%) content, 2 wt% and 3 wt% of Ag resulted in efficient results as compared to 1, 4 and 5 wt% (**Fig. 3.9(a)**), the result is consistent both in the AgTNR, AgTNS samples. The lower rate of H₂ production with higher metal content is due to aggregation and dispersion of metal NP's (Fig. 3.9(a) inset),

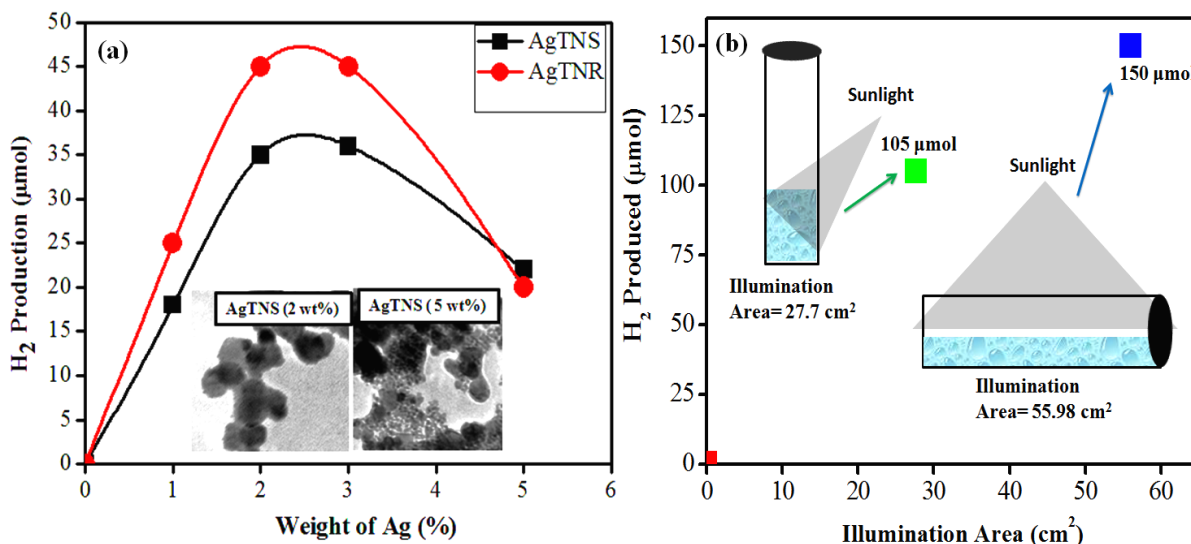


Fig. 3.9: (a) Effect of metal loading on H₂ production under multiline wavelength (b) Effect of surface area of the reactor (illumination area) on H₂ production using AgTNR under sunlight.

enabling them to act as recombination centers for charge carriers. The optimized elemental ratio (2 wt%) was further confirmed by SEM-EDX analysis (**Fig. 3.10**). The role of reactor surface area (total illumination area) was studied under sunlight conditions using AgTNR as a photocatalyst (**Fig 3.9(b)**). It was observed that the H₂ evolution rate increased to 1.5 times by increasing the illumination area (area of reactor occupied by reaction mixture and exposed to irradiation source) of the reactor 2 times.

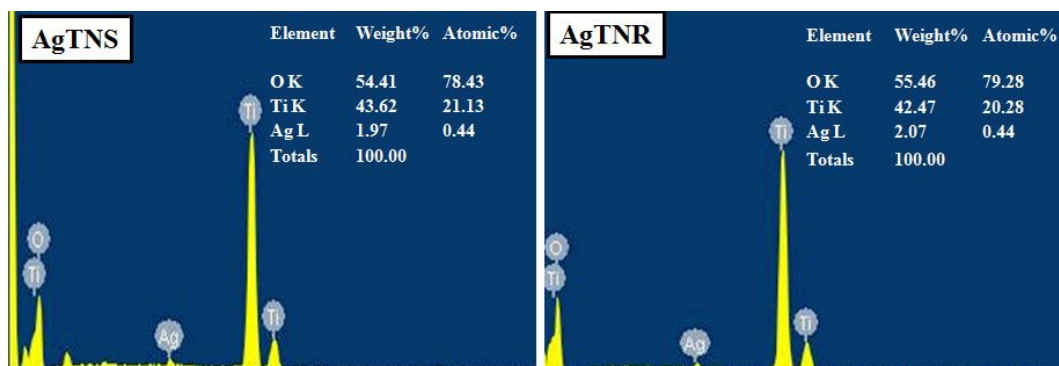
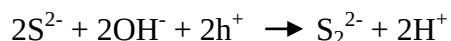
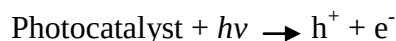


Fig. 3.10: EDS spectra of AgTNS and AgTNR photocatalysts.

Sodium sulfide (0.1 M) was used as a hole scavenger to calculate the amount of H₂ produced during the reaction under different illumination sources because sulfide (S²⁻) acts both as a hole scavenger and sacrificial agent and it is also reported to be more effective sacrificial reagent than sulfite (SO₃²⁻) [43]. The proposed mechanism for hole scavenging process of S²⁻ and H₂ production is as follows:



The S₂²⁻ produced in the reaction compete with the reduction of the proton. But it has been reported [43] that the presence of S²⁻ anions stabilizes the catalyst surface. So, in order to restrain the formation of disulfide the reaction mixture was purged with Ar.

The comparative rate of H₂ production from water under different monochromatic wavelengths by different photocatalysts is presented in **Fig. 3.11** the H₂ evolution was not witnessed in the absence of photocatalyst (photochemical reaction) and in absence of visible light (dark reaction).

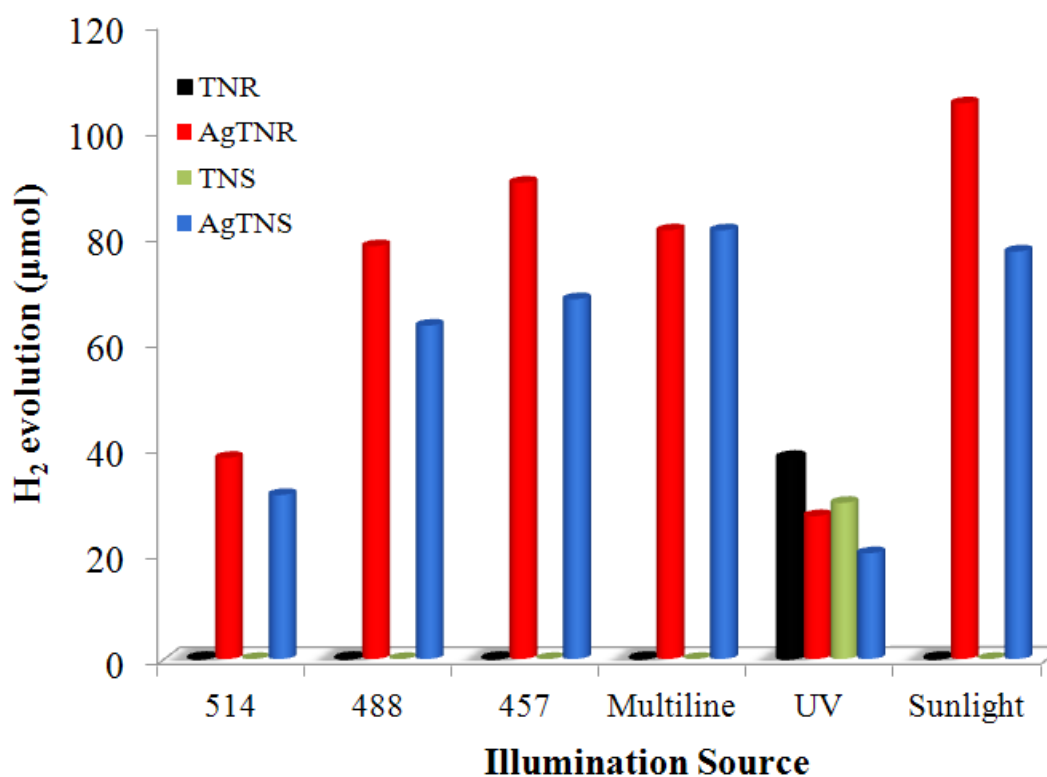
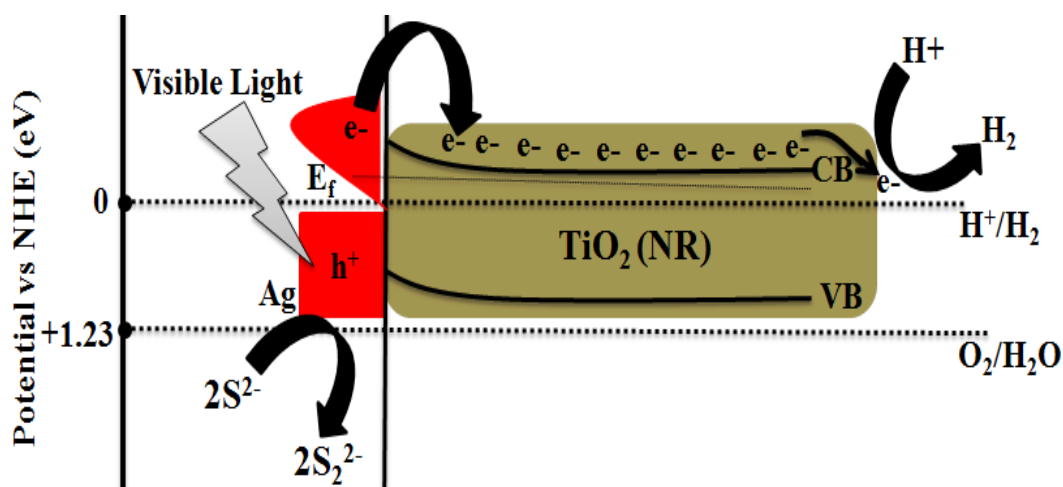


Fig. 3.11: Hydrogen evolution under different monochromatic and UV wavelengths by different photocatalysts

In comparison to other photocatalysts, the photocurrent density of AgTNR was increased under visible light illumination, the variation of current density under visible light is a function of Ag NP's loading comparing the same effect with bare TNR. The Ag NP's enhanced the photoresponse of TiO_2 , suggesting that the enhanced photocurrent of AgTNR is due to SPR effect of Ag NP's deposited on TNR, which is also supported by earlier reports [44].

Upon illumination, with different wavelengths (266 nm, 457 nm, 400 nm, 514 nm and multiline) it was observed that the photocurrent is proportional to the rate of H_2 production. In the case of the AgTNR highest rate for H_2 production (90 and 105 μmol) was observed after 8 h at 457 nm and under sunlight. The 457 nm is the characteristic SPR absorption band of Ag, showing that the enhancement depends strongly on the plasmonic properties of Ag loaded on TiO_2 . This mechanism is further supported by comparison of H_2 production by nanocomposites of other morphologies like AgTNS and bare TNR and TNS. Due to SPR, the local electric field in the neighborhood is increased and TiO_2 present in the proximity encounters these effects. Another aspect is that these SPR based effects are more on the TiO_2 attachment side (Ag- TiO_2 interface). So, as shown in **Scheme 3.1** when the nanostructure is irradiated with the matching SPR wavelength (457 nm or sunlight) the Ag NP's are activated, which shift their local electric field effect towards the TNR interface resulting in the ejection of electrons towards the E_{CB} of TNR, due to the formation of Schottky barrier [45]. The fundamental mechanism for the better efficiency of elongated AgTNR is also due to its unique surface and high aspect ratio, comparatively the specific surface area of bare TNR (181 m^2g^{-1}) is smaller than TNS (146 m^2g^{-1})



Scheme 3.1: Proposed mechanism of hydrogen evolution from water using elongated AgTNR photocatalyst.

but after Ag loading the surface area of AgTNR ($72.9 \text{ m}^2\text{g}^{-1}$) remains larger than AgTNS ($45.6 \text{ m}^2\text{g}^{-1}$), the high surface area is proficient for its better photocatalytic efficiency. Similarly, the XRD results displayed relatively an intense peak at 25.5° for TNR and AgTNR attributed to one dimensional growth of 101 facets and previously 101 plane has been reported [46] to be active for the better activity. In compliance with earlier reports [47] the 1D TiO_2 has superior charge transport through a one dimensional direction, which decreases the rate charge recombination and promotes the photocatalytic efficiency. Na_2S was used as a hole scavenger to mask oxidation reaction and also to prevent recombination of excitons. Other aspects like the less defective surface of TNR and PL quenching after Ag loading also support the higher activity of AgTNR. The huge surface area and porous nature of TNR and TNS are capable of providing enough surfaces for the diffusion and reduction of water molecules. Furthermore, the results were several folds when compared to commercial TiO_2 (P25) and Ag TiO_2 (P25) which produced below $30 \mu\text{mol}$ of gas. Highest H_2 production was recorded in case of elongated AgTNR followed by AgTNS. The sunlight and 457 nm wavelength were able to produce the highest amount of H_2 followed by rest illumination sources. TNR and TNS do not show H_2 evolution under sunlight because of the fast recombination of charge carriers (electrons and holes). The least charge separation ability of TNR and TNS was determined by photoluminescence (PL) and current voltage (IV) studies. The PL (Fig. 6) studies revealed large number of trap sites near the absorption edge of both TNR and TNS which disables them to shuttle the excited electrons for the photoreduction of water, while as in case of AgTNR and AgTNS the effective shuttling of electrons towards Ag resulted in PL quenching and higher photocatalytic activity. These results are supported by the IV studies where the low current was observed for both TNR and TNS compared to AgTNR and AgTNS. So, this study reveals that due to better charge delocalization and larger interface the elongated TiO_2 nanostructures are most efficient to produce H_2 under visible and sunlight irradiation.

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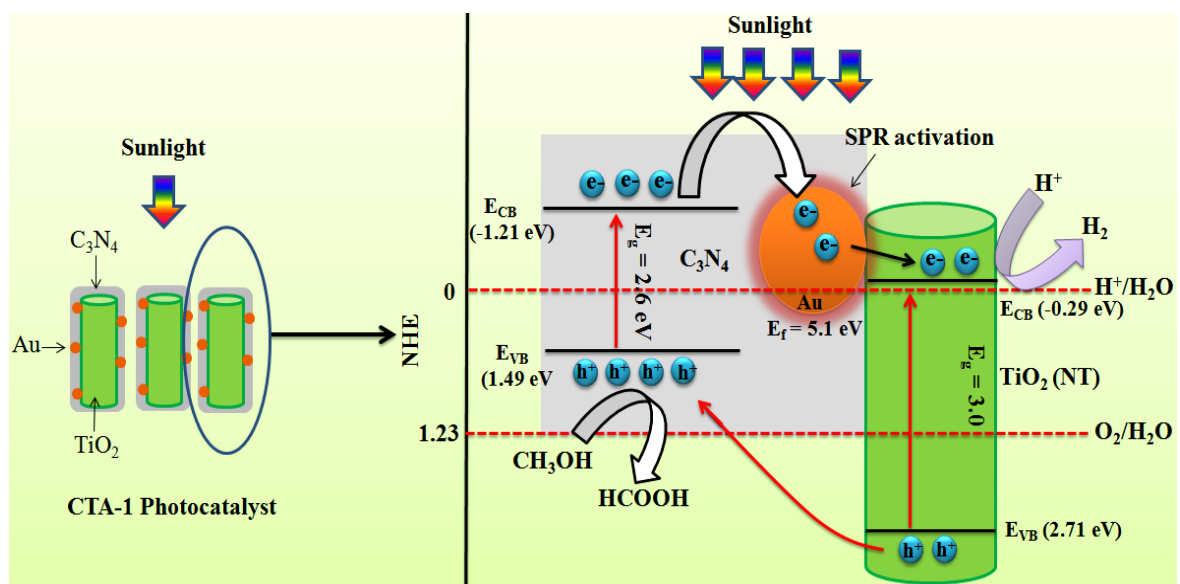
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CHAPTER 4

PHOTOCATALYTIC HYDROGEN PRODUCTION FROM WATER BY CARBON NITRIDE PASSIVATED Au-TiO₂ TUBULAR NANOSTRUCTURE



Schematic summary

This chapter presents the facile one pot hydrothermal synthesis of tubular C₃N₄-Au-TiO₂ nanostructures. The nanocomposite is formed due to self exfoliation of C₃N₄ leading to the formation of a uniform monolayer over TiO₂ possessing non ohmic properties with a good current response and showing efficient H₂ evolution of $\sim 88 \mu\text{mol h}^{-1}$ (*calculated* = $2933 \mu\text{mol h}^{-1} \text{g}^{-1}$) under sunlight irradiation.

4.1. Introduction

The pollution menace and huge energy demand has made solar driven hydrogen production from water splitting as a best future energy option ascribed to its zero carbon emission nature and to tackle the exponentially increasing energy demand [1]. However, the major challenge is finding a suitable photoactive, photostable and thermodynamically viable material to harvest the solar energy efficiently. As we know that water splitting is an uphill reaction needing 237 kJ/mol of energy thermodynamically involving a difficult four electron reduction process [2]. To satisfy this condition, the photocatalyst must possess suitable conduction band potential/position, high charge separation efficiency (electrons and holes) and enough time for these to take part in the interface water reduction reaction [3, 4].

Titanium dioxide (TiO_2) being an ideal candidate [5-7] due to its feasible reduction potential along normal hydrogen electrode (NHE) possesses some deficiencies in terms of its large band gap ($E_g = 3.2$ eV) and low charge separation efficiency [8]. The variations like increasing the specific surface area [9] and modification of nanosize geometries, in particular, the nanorods [10] and nanotubes [11] have been reported to be in a higher control of chemical and physical behavior. The electronic properties change drastically by changing the morphology due to the strong influence of surface curvature helping the TiO_2 to act in a more effective way. Secondly, the formation of composite system with other semiconductors like C_3N_4 had been reported [12, 13] to enhance the photocatalytic hydrogen evolution that is also associated with the effective charge transfer. The (carbon nitride) C_3N_4 is well known to build an electric field at the heterojunction with TiO_2 that helps to divert the electrons and holes in contrary directions owing to reduce their unfavorable recombination [14]. By building a heterojunction of different optical response (C_3N_4 and TiO_2) is also supposed to make the nanocomposite active in both UV and visible light.

Incorporation of noble metal like gold (Au) nanoparticles can also act as an electron trap aiding the charge separation and also sensitize the TiO_2 in visible light due to the localized surface plasmon resonance (LSPR) effect [15, 16]. Li et al. (2014) have previously reported [17] that addition of Au nanoparticles between two semiconductors (CdS-TiO_2) is able to reduce the trap state Auger rate and partially compensates the negative effects of the surface trap sites resulting in the improved photoconversion efficiency. The Au nanoparticles are also supposed to provide efficiency for the transport of electrons between two semiconductors. Several reports have already suggested the effective photocatalytic activity of the $\text{C}_3\text{N}_4\text{-TiO}_2$ [18-20] nanocomposite

but the role of morphology alteration of TiO_2 into elongated nanotubes and its composite formation with C_3N_4 and simultaneous Au loading is least studied, the synthetic protocols for the same are too tedious and less efficient.

In this chapter, we have explored a facile and one step hydrothermal route for the synthesis of C_3N_4 passivated Au- TiO_2 tubular nanocomposite (CTA) exhibiting the brilliant optoelectronic and structural properties. The nanocatalyst has been designed to minimize the drawbacks of TiO_2 . The C_3N_4 was chosen to sensitize the TiO_2 (nanotubes, NT) and Au nanoparticles can act both as sensitizers and transporter of electrons. This ternary NC has shown brilliant performance for the photoreduction of water in presence of methanol as hole scavenger.

4.2. Experimental section

4.2.1. Chemicals and reagents

All the analytical grade chemicals were used as received, urea (99.5 %, Loba Chemie Ltd), sodium hydroxide (NaOH, 97%, SD Fine Ltd), cetyl trimethyl ammonium bromide (CTAB, 98%, Spectrochem Pvt. Ltd.), L-ascorbic acid (99 %, Loba Chemie Ltd.), chloroauric acid (HAuCl_4 , 49% Sigma Aldrich), Ethanol (99.9 %, Jingsu Huaxi International China), titanium dioxide (TiO_2 -P25, 50% Evonik Industries). Deionized (DI) water from Millipore (Milli-Q an ultrafiltration system with 40 mho cm^{-1} at 25°C conductivity) was used throughout the experiment.

4.2.2. Preparation of carbon nitride (C_3N_4) and C_3N_4 passivated Au- TiO_2 (CTA) nanocomposite

The C_3N_4 was prepared under ambient conditions of temperature and pressure by the pyrolysis of the urea. In a typical procedure, urea (5 g) was put in a covered crucible and heated in an oven at 550°C for 3 h to obtain a yellow colored C_3N_4 .

The tubular C_3N_4 passivated Au- TiO_2 nanostructure has been synthesized by a single facile hydrothermal method. 0.9 g of CTAB was dissolved in NaOH (35 mL, 10 M) and stirred till a clear solution was obtained. In another beaker TiO_2 -P25 (2.5 g) and C_3N_4 (variable ratio with TiO_2 -P25) was mixed with a glass rod, the mixture was added to the CTAB solution and stirred further for 10 min. The required amount of HAuCl_4 solution (0.01 M, corresponding to different weight percent ratios with TiO_2) and 0.6 g of ascorbic acid (1 M) was added and stirred vigorously for next 20 min. The mixture was hydrothermally treated in an autoclave (80 mL) at 130°C for 24 h, the final composite was cooled at room temperature and separated under several

washings of HNO₃ (0.1 M) until pH = 7 was achieved. The composite was washed with ethanol and dried at 70 °C for further analysis.

The formation of the TiO₂ nanotubes is ascribed to the one dimensional growth and exfoliation process of the TiO₂ (P25) precursor, previously it had been reported that the growth occurs through the formation of sodium titanate nanotubes [21]. Moreover, in the same strong basic medium ascorbic acid gets easily hydrolyzed to ascorbate to reduce Au⁺⁴ to Au⁰ and CTAB helped in the stabilization of as formed Au⁰ nanoparticles. The exfoliation of TiO₂ and C₃N₄ took place simultaneously to form a tubular CTA nanostructure. Later the Na⁺ is removed by washing the nanocomposite several times with the HNO₃. The ratio of Au and C₃N₄ was changed to study the overall activity for the photoreduction of water, the different photocatalysts were abbreviated as CTA-1 (Au 0.75 wt%, C₃N₄:TiO₂ 1:10), CTA-2 (Au 0.50 wt% , C₃N₄:TiO₂ 1:10), CTA-3 (Au 0.25 wt%, C₃N₄:TiO₂ 1:10), CTA-4 (Au 0.75 wt%, C₃N₄:TiO₂ 3:10) and CTA-5 (Au 0.75 wt%, C₃N₄:TiO₂ 5:10).

4.2.3. Photocatalytic activity

The photocatalytic activity was carried out in a Pyrex tube (20 mL), containing the reaction mixture (water: MeOH, 4:1) and 0.03 g of photocatalyst under direct sunlight with intermittent stirring. Methanol was chosen to act as a sacrificial agent and hole scavenger. The mixture was purged before with argon gas for 20 min to create an inert atmosphere and irradiated under direct solar irradiation with an average solar flux of (330-750 Wm⁻²) and average 25 °C temperature. The analysis of gases has been done by the GC-TCD method, discussed in section 1.4 (Chapter 1).

4.3. Results and discussion

4.3.1. Structural and morphological characteristics

The X-ray diffraction studies of the as prepared photocatalysts displayed the presence of anataseTiO₂ passivated with a layer of C₃N₄. As shown in **Fig. 4.1** the samples give the clear signals for the C₃N₄ and TiO₂ (anatase) without the presence of any trace impurity. The C₃N₄ displayed a characteristic peak around 27.3° attributed to 002 plane of carbon (JCPDS card No. 75-1621) which reflects the formation of layer of C₃N₄ over TiO₂ nanotubes due to interlayer stacking of aromatic rings [22], it can be concluded preliminarily that the bulk C₃N₄ has been exfoliated as a single thin layer coating over TiO₂ (NT) that was later confirmed by Raman spectroscopy. The diffraction pattern of the TiO₂ showed several peaks assigned to different

planes of anatase polymorph, predominantly the formation of peak at 25.3° corresponding to (101) plane and several other peaks like 38.2° (112), 48° (200), 53.9° (105), 62.1° (612) and 70.3° (220) (JCPDS card No. 73-1764). The particle size of the tubular nanostructure was found to be larger in case of CTA-4, CTA-5 ascribed to the increase in C_3N_4 content resulting in the particle agglomeration. Moreover, the separate diffraction peak for the Au was not witnessed in the pattern though increase in the intensity of 38.2° peak can be attributed to the presence of Au (JCPDS card No.01-1172) and the low response to diffraction intensity can be due to its lower content of Au (< 1 wt %) in all the samples [23, 24].

The HRTEM results shown in **Fig. 4.2** and **Fig. 4.3** disclosed the 1D tubular type geometrical morphology of TiO_2 encapsulated by a monolayer of C_3N_4 . The nanostructures are open ended having an average diameter of 12 nm and length 200-235 nm, the thickness of C_3N_4 layer is variable between 1-3 nm. Moreover, the Au nanoparticles are seen deposited on the surface of TiO_2 and also sandwiched in between C_3N_4 and TiO_2 . The lattice fringes (d spacing) of CTA-1 photocatalyst have been measured to be 0.35 nm that is in consistency with the d spacing of 101

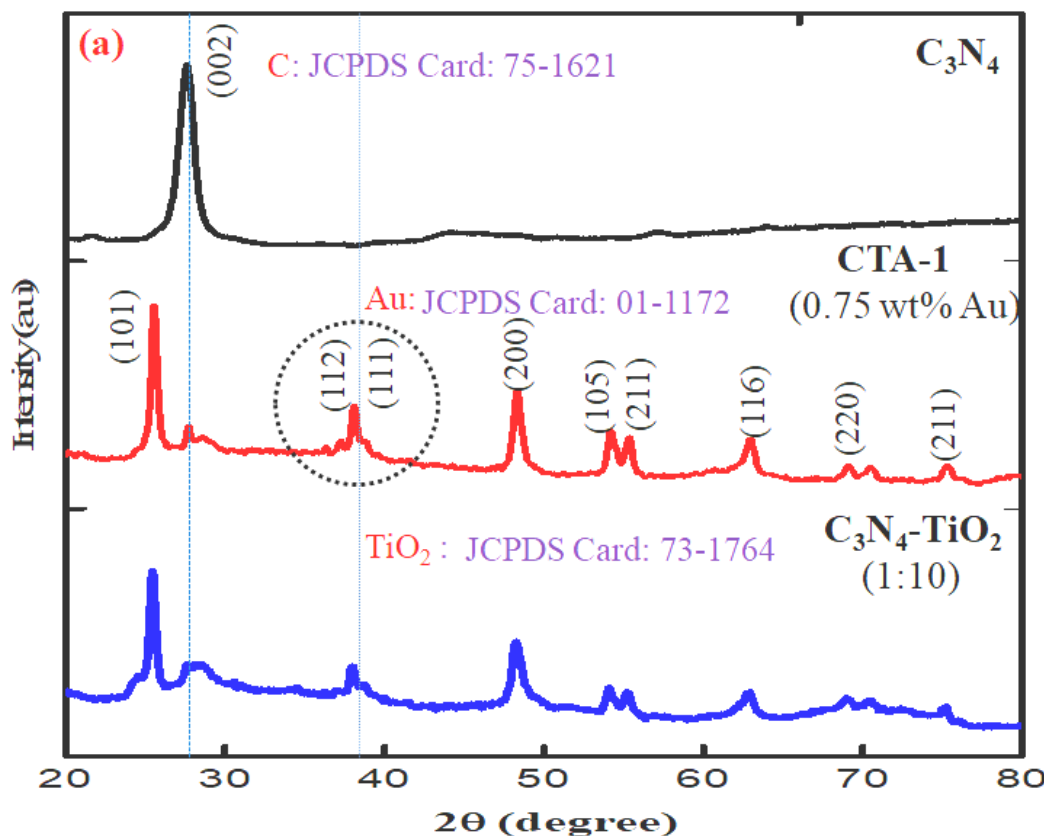


Fig. 4.1: X ray diffraction pattern of different photocatalysts

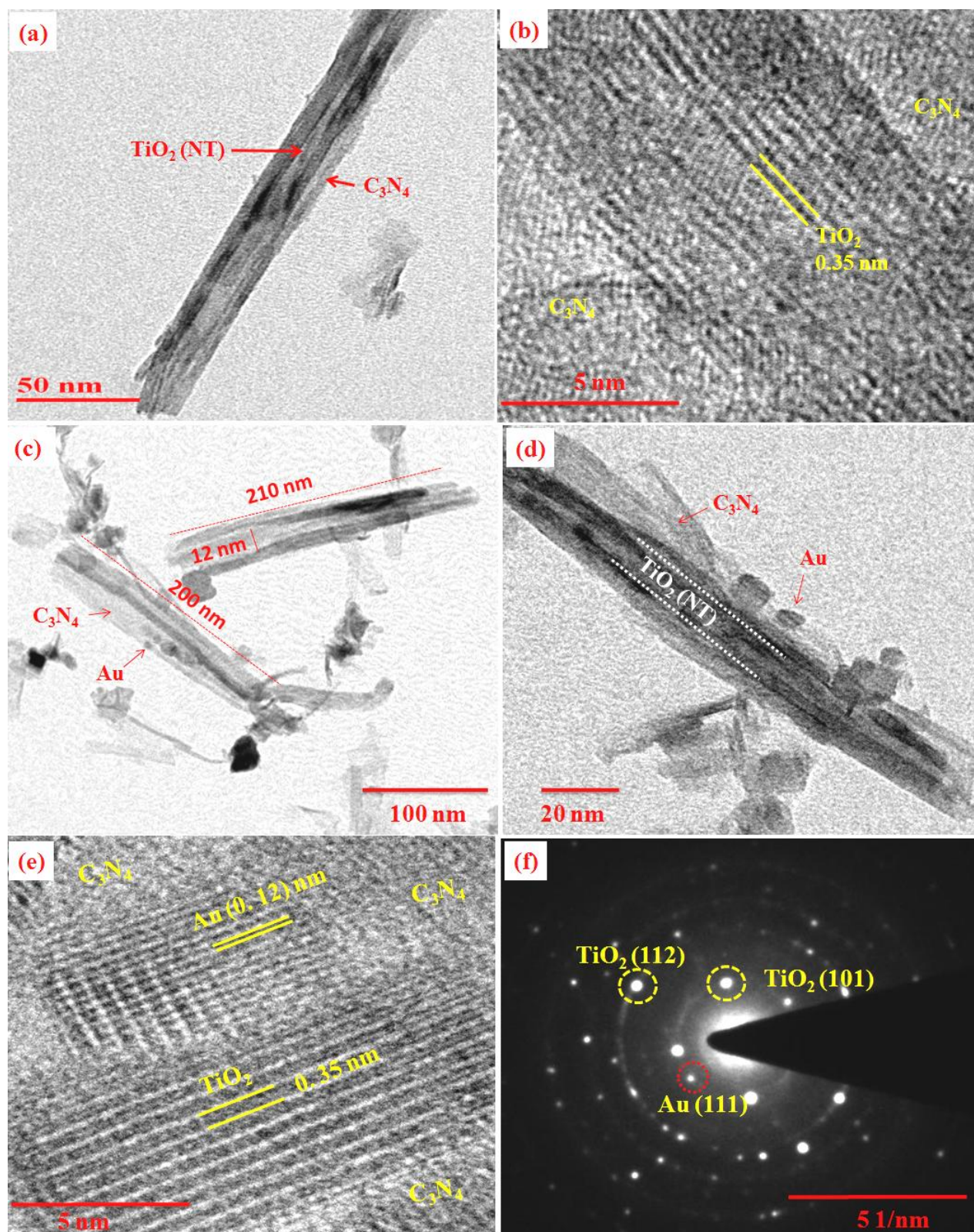


Fig. 4.2: HRTEM analysis of (a, b) C₃N₄-TiO₂ and (c, d, e) CTA-1 (Au, 0.75 wt%, C₃N₄:TiO₂ 1:10) photocatalysts (e) SAED pattern of CTA-1 photocatalysts.

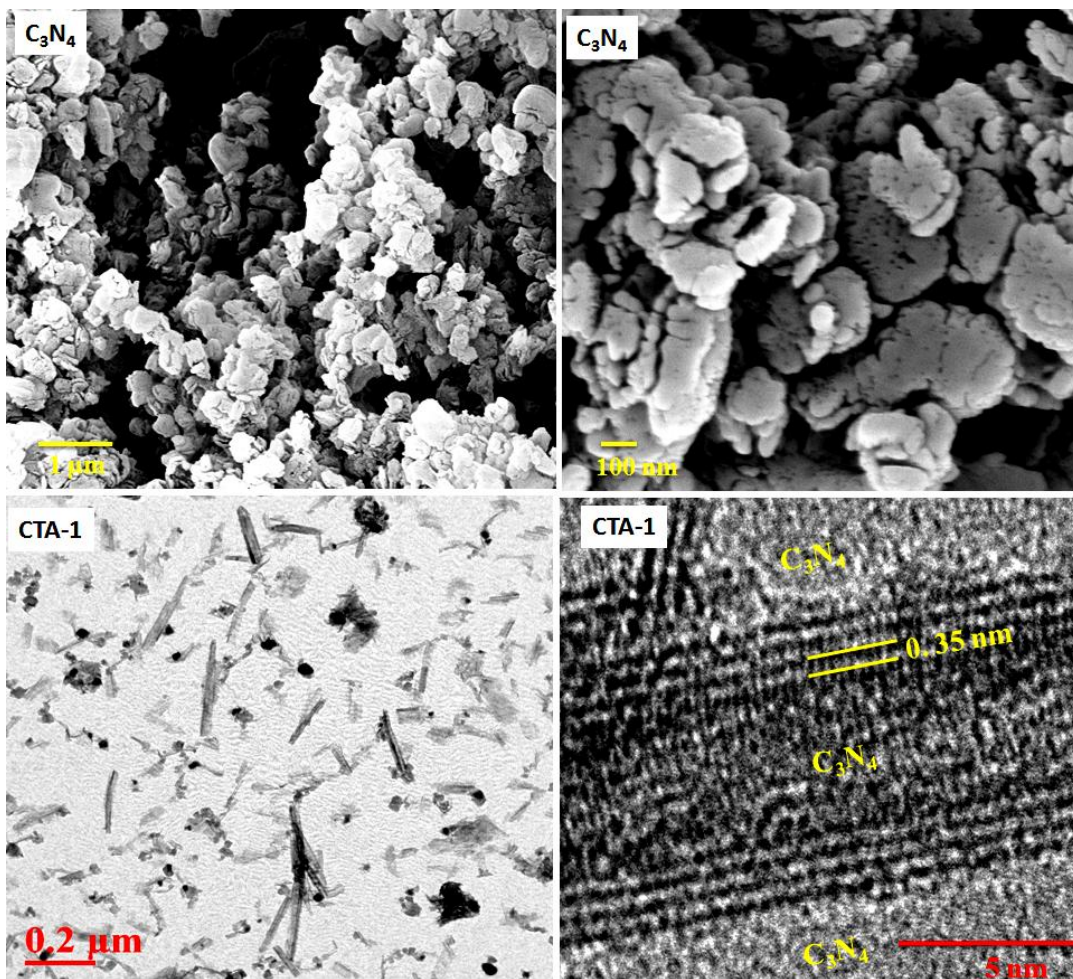


Fig. 4.3: FESEM and HRTEM micrographs of C_3N_4 and CTA-1 photocatalyst.

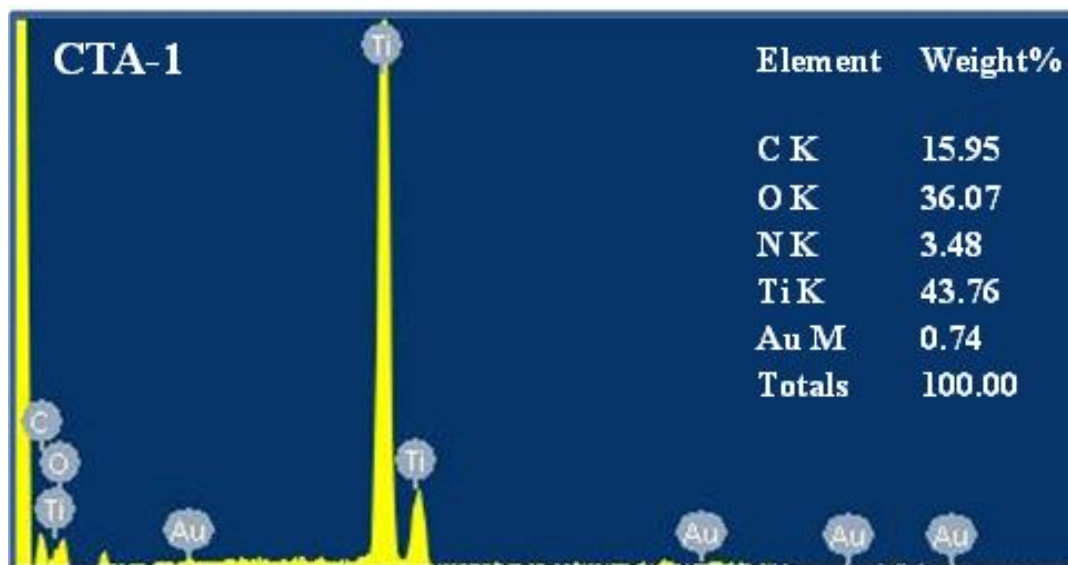


Fig. 4.4: EDX spectra of CTA-1 (0.75 wt% Au, C_3N_4 - TiO_2 1:10) photocatalyst.

(101) plane of TiO_2 . The SAED pattern is also in consonance with the XRD and TEM results showing the tetragonal structure of TiO_2 unit cell and little amorphous nature after passivation with C_3N_4 . The elemental ratio (**Fig. 4.4**) was found to be 0.74 wt%, which is in compliance with the expected ratio (0.75 wt%) and all the elements are spatially distributed as confirmed by elemental mapping (**Fig. 4.5**).

Raman scattering (**Fig. 4.6**) was specifically done to analyze the microstructures of the CTA-1 hybrid nanostructure showing the characteristics of anatase polymorph of TiO_2 and small shift in

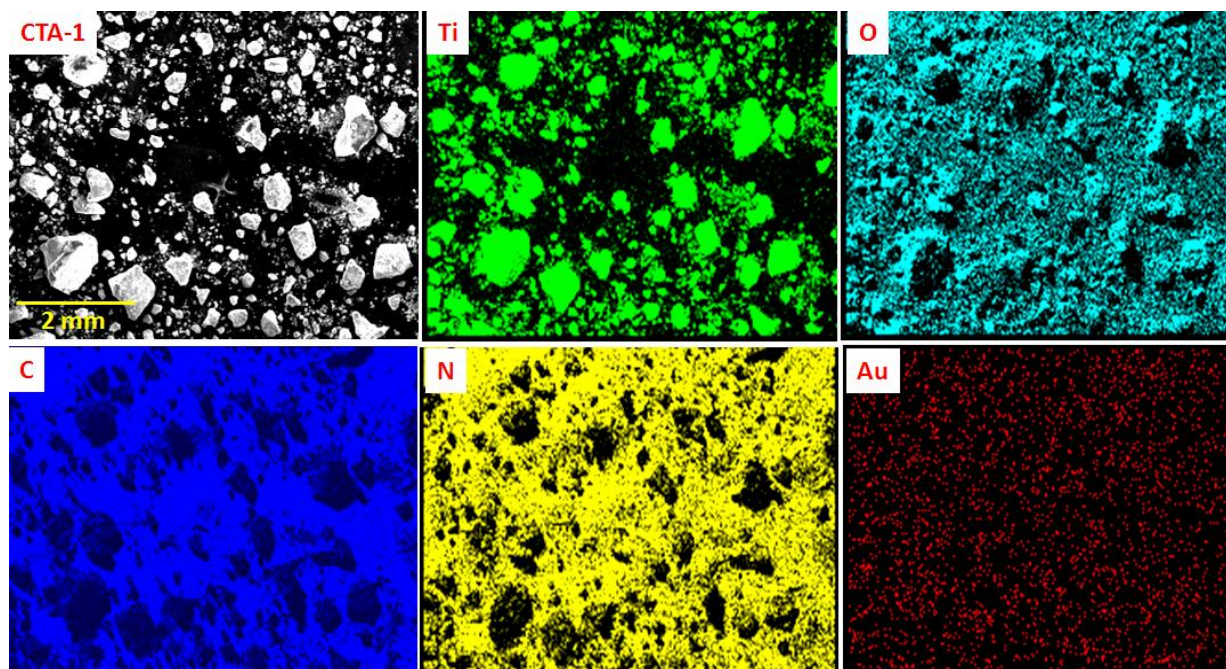


Fig. 4.5: EDS mapping of different elements present in CTA-1 (Au, 0.75 wt% and $\text{C}_3\text{N}_4\text{:TiO}_2$ 1:10) photocatalyst.

the intensity was observed after Au loading, peaks were observed around 106 cm^{-1} , 147 cm^{-1} (E_g), 398 cm^{-1} (B_{1g}), 473 cm^{-1} (B_{1g}) for both the $\text{C}_3\text{N}_4\text{-TiO}_2$ and CTA-1 related to the tetragonal structure of anatase TiO_2 with D_{4h} space group [25]. The band at 607 cm^{-1} is due to the Ti-O stretching vibration and the appearance of the G band at 1545 cm^{-1} is due to the uniform coating of C_3N_4 on TiO_2 , the formation of this band is ascribed to the formation of C_3N_4 layer and due to symmetric sp^2 stretching which imparts a graphitic nature to CTA-1. A significant increase in the intensity of a band around 235 cm^{-1} is due to the interaction of Au with $\text{C}_3\text{N}_4\text{-TiO}_2$, earlier findings showed the similar change and related it to the basis for high electron transfer [26].

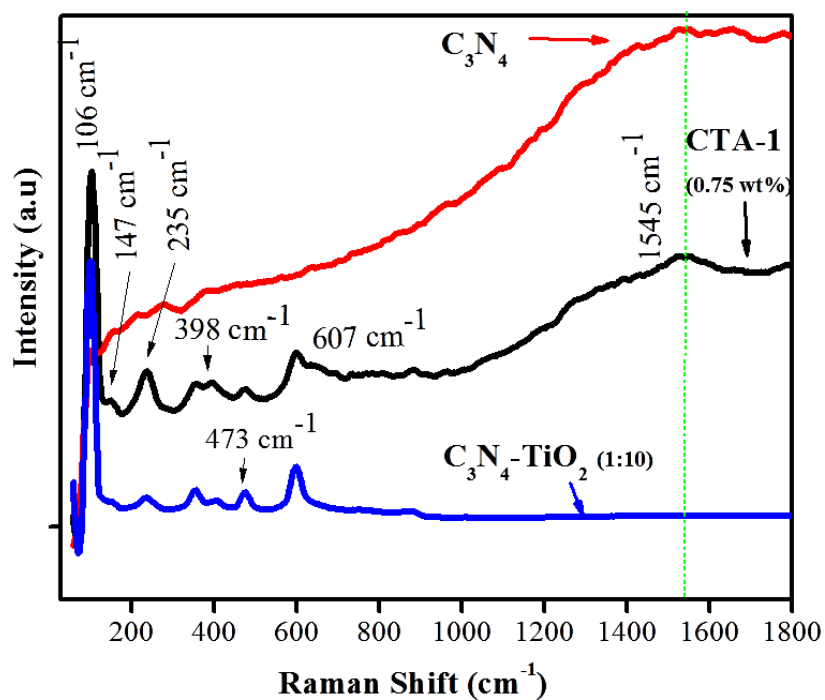


Fig. 4.6: Raman spectra of different photocatalysts.

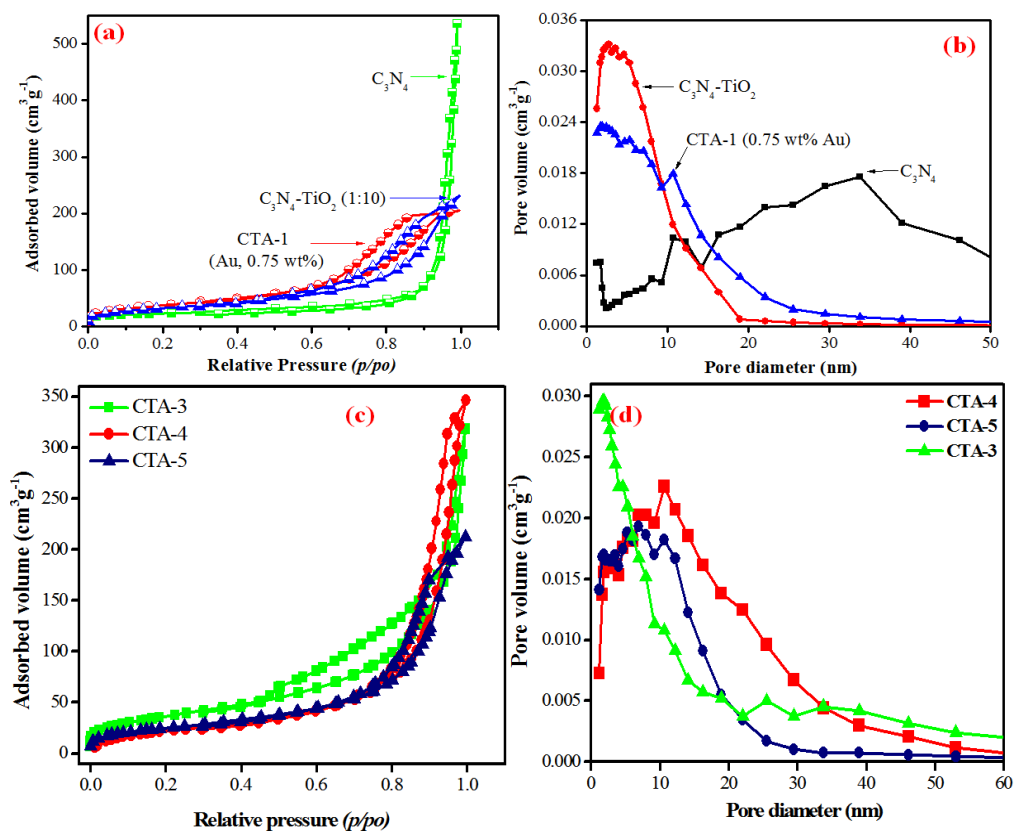


Fig. 4.7: N₂ adsorption-desorption and BJH curves of different photocatalysts.

Fig. 4.7 represents the BET (Brunner-Emmet-Teller) based N₂ adsorption and desorption curves of the nanocatalysts, all the isotherms are typical type IV Langmuir due to the porous nature of the nanocomposites [27]. The C₃N₄ possessed a small surface area (81 m²g⁻¹) and a huge pore diameter (80 nm) credited to the multilayer structure of C₃N₄ (FESEM, Fig. 4.3) and the pore distribution was non-uniform. As shown in the BJH curve (Barrett-Joyner-Halenda) this non distribution turns out into uniform after tubular composite formation with TiO₂ attributed to the self exfoliation process of C₃N₄. As shown in **Table 4.1** the C₃N₄-TiO₂ possess highest surface area (139 m²g⁻¹) that decreased after Au addition and was found to be 121 m²g⁻¹ due to the accumulation of Au particles into the pores of TiO₂ (NT) which also resulted in a little change in the pore volume (0.24 cm³g⁻¹ and 0.31 cm³g⁻¹ for CTA-1 and C₃N₄-TiO₂ respectively), in compliance to this the pore diameter decreased from 2.71 nm to 1.85 nm after Au loading. Furthermore, the specific surface area effectively decreased with the increase of C₃N₄ content due to aggregation of nanoparticles, the surface area of CTA-4 and CTA-5 was found to be 80.4 and 86.4 m²g⁻¹ respectively.

Table 4.1: Comparative porosity and surface area analysis of different photocatalysts.

Photocatalyst	BET (m ² g ⁻¹)	Pore diameter (nm)	Pore Volume (cm ³ g ⁻¹)
C ₃ N ₄	81	33.81	0.81
C ₃ N ₄ -TiO ₂	139	2.71	0.31
CTA-1	121	1.85	0.24
CTA-2	131.5	1.87	0.30
CTA-3	135	1.85	0.45
CTA-4	80.4	10.65	0.52
CTA-5	86.4	6.95	0.32

4.3.2. Optical and thermal characteristics

The optical properties of the photocatalysts were studied by UV-vis absorption spectroscopy (**Fig. 4.8**). It is evident that the as synthesized C_3N_4 showed strong response to visible light (440 nm) due to its lower band gap (2.6 eV), after its encapsulation on TiO_2 and simultaneous Au loading the NC's showed a blue shift, the absorption edge of $C_3N_4-TiO_2$ and CTA-1 was observed at 417 and 411 nm respectively. The expected blue shift is credited to the charge transfer from the C_3N_4 towards the E_{CB} of TiO_2 and quantum confinement effect. Moreover, the bare Au nanoparticles (Au NP's) showed a strong absorption maximum at 525 nm due to the surface plasmon resonance (SPR) effect [28], the band shifted to little higher λ_{max} (550 nm) after the incorporation of Au on $C_3N_4-TiO_2$. The band gap (E_g) calculated as per Tauc equation was found to be 2.6, 2.9 and 3.0 eV for C_3N_4 , $C_3N_4-TiO_2$, and CTA-1 photocatalyst respectively. There was little change in absorption maximum of the NC by changing the C_3N_4 ratio (CTA-4, and CTA-5) while as the intensity of SPR band was found to be dependent on the weight ratio of Au (**Fig. 4.9**), a low intensity SPR absorption band was observed in case of 0.25 wt% Au (CTA-3) that increased respectively for 0.50 wt% (CTA-2) and 0.75 wt % (CTA-1).

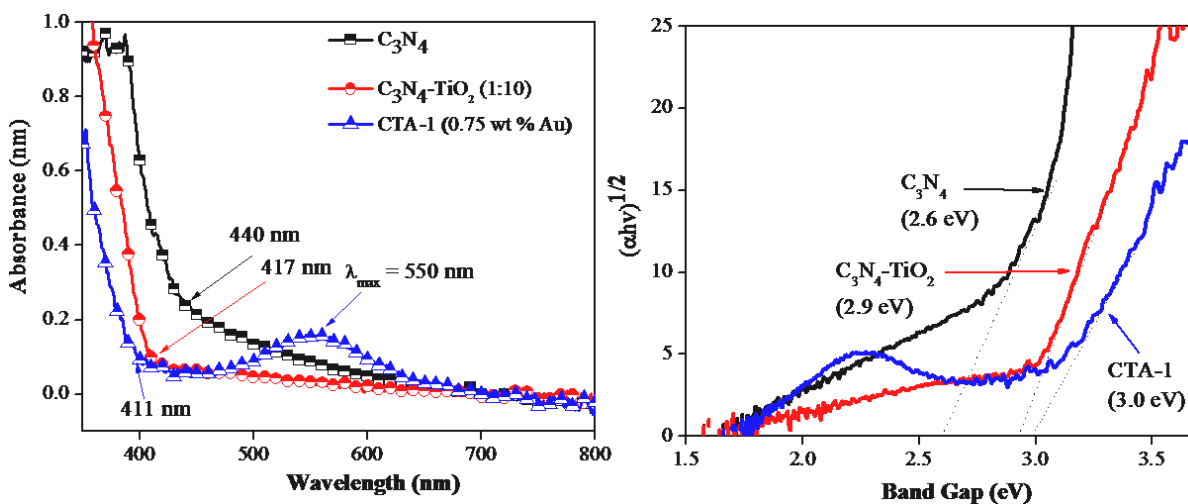


Fig. 4.8: Optical absorption spectra and band gap (E_g) calculated by Tauc equation of different photocatalysts.

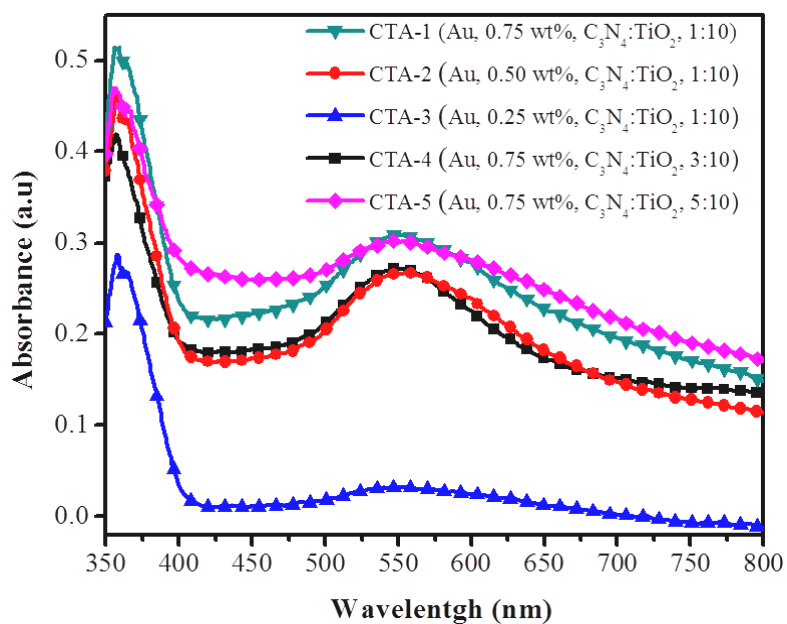


Fig. 4.9: Optical absorption spectra of different photocatalysts.

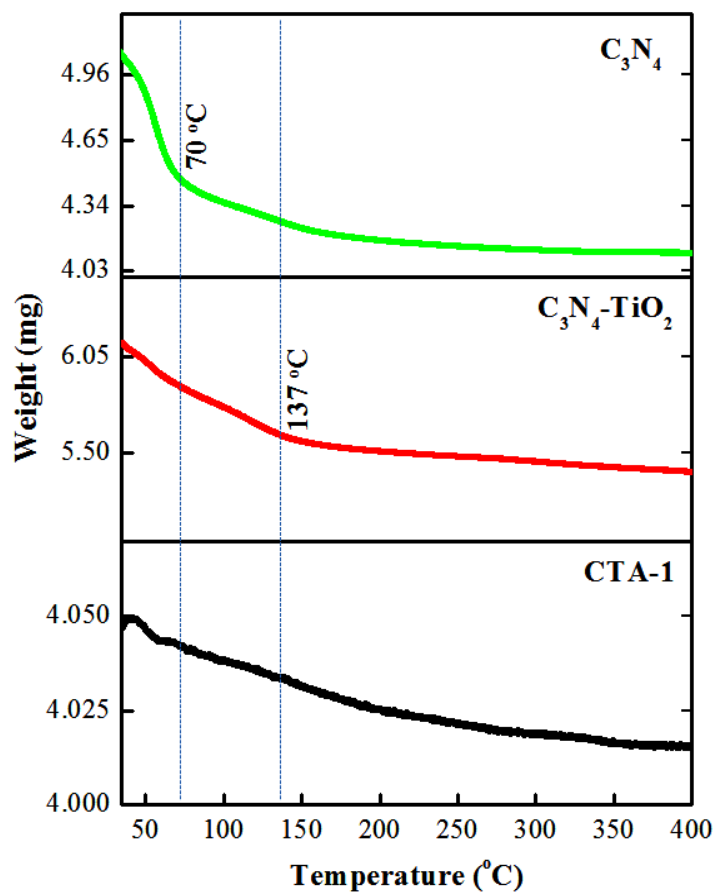


Fig. 4.10: Thermal stability of different photocatalysts analyzed by TGA.

The thermal gravimetric analysis (TGA) analysis revealed a good thermal stability of the photocatalysts (**Fig. 4.10**). It was observed that in comparison to bare C_3N_4 there was a negligible weight loss in C_3N_4 - TiO_2 and CTA-1 nanocatalysts up to 400 °C under N_2 atmosphere. Two breaks were observed in the TGA curve at 70 °C and 137 °C due to moisture loss and exclusion of adsorbed gases respectively. This result is in consonance with the earlier results showing the thermal stability of C_3N_4 - TiO_2 NC up to 500 °C [14].

4.3.3. X ray photoelectron spectroscopy (XPS) and potential voltage (I-V) characteristics

The survey spectrum of CTA-1 (**Fig. 4.11(a)**) showed that the hybrid tubular nanocomposite is composed of elements like C, N, Ti, O and Au. In C1s spectrum, two separate peaks were observed at 284.8 eV and 287 eV. The main peak around 287 eV is assigned to C-N-C and the C-(N)₃ group of C_3N_4 (Fig. 4.11(d)) and the other deconvoluted peak at 284.8 eV is assigned to C-C sp² hybridization [30]. The high resolution N1s spectra (Fig. 4.11(e)) is also fitted into two

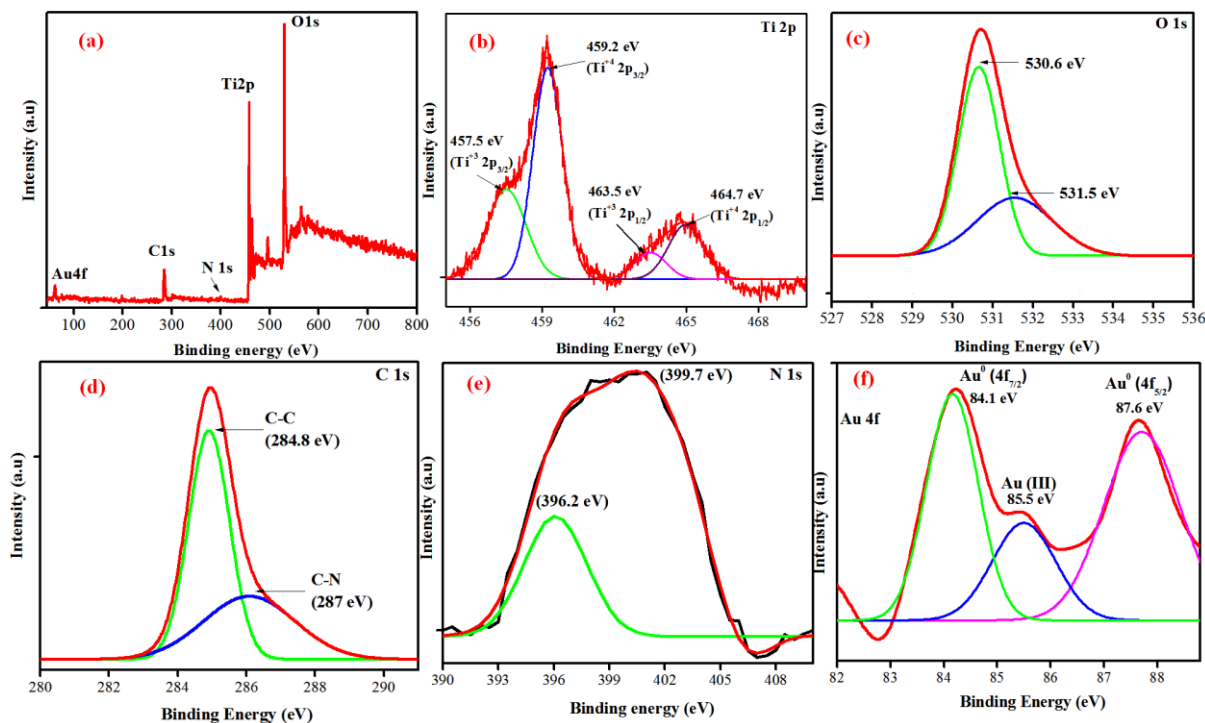


Fig. 4.11: XPS analysis of the tubular C_3N_4 -Au- TiO_2 photocatalyst (a) Survey Spectrum (b) Ti 2p (c) O 1s (d) C 1s (e) N 1s (f) Au 4f.

peaks of the binding energy 399.7 eV and 396.2 eV credited to C(N)₃ and C-N-C respectively. The O1s spectrum is fitted in two deconvoluted peaks with binding energy values at 530.6 eV and 531.5 eV which are directly ascribed to the TiO_2 and H_2O respectively, supported by earlier

finding [29]. In case of Ti 2p two binding energy values are recorded at 459.2 eV and 464.2 eV assigned to two typical states of Ti^{+4} ($2p_{3/2}$ and $2p_{1/2}$ respectively). Moreover, an interesting satellite peak was observed at a binding energy value (457.2 eV) of $\text{Ti}^{+3} 2p_{3/2}$ and at 463.5 eV for $\text{Ti}^{+3} 2p_{1/2}$ respectively and these peaks are ascribed to the possible formation of some Ti^{+3} ($2p_{3/2}$) species. This finding is in compliance to earlier finding [20, 30], Liyan Shen et al. reported [30] that the presence of reducing agent in the same mixture reduces some of the Ti^{+4} species to Ti^{+3} and in the current synthesis the mixture contains ascorbic acid that might have helped in the formation of some Ti^{+3} species giving rise to a shoulder peaks (457.5 eV and 463.5 eV). The XPS spectrum of Au is fitted into two major peaks at 84.1 eV and 87.6 eV assigned to typical $4f_{5/2}$ and $4f_{7/2}$ of elemental Au and a small peak at 85.5 eV is assigned to Au (III) oxidation state. The electric properties of the C_3N_4 , $\text{C}_3\text{N}_4\text{-TiO}_2$, and CTA-1 are presented in **Fig. 4.12** signifying the typical semiconductor nature of the nanocatalysts. With the applied voltage the CTA-1 heterojunction showed the higher conductivity (1.385×10^{-4} A) in comparison to $\text{C}_3\text{N}_4\text{-TiO}_2$ (8.04×10^{-5} A) and C_3N_4 (2.65×10^{-9} A). It has been observed that the apparent curve of C_3N_4 (**Fig. 4.12 inset**) is showing an ohmic behavior while as after composite formation the non-ohmic properties developed and the junction showed higher current efficiency due to the effective transfer and enhanced lifetime of electrons along the inbuilt junction [31]. An asymmetrical rectifying response has been observed indicating the existence of Schottky barrier in the heterojunction. In case of CTA-1 the ternary junction develops little ohmic properties compared to $\text{C}_3\text{N}_4\text{-TiO}_2$ due to effective quenching of electrons towards Au surface.

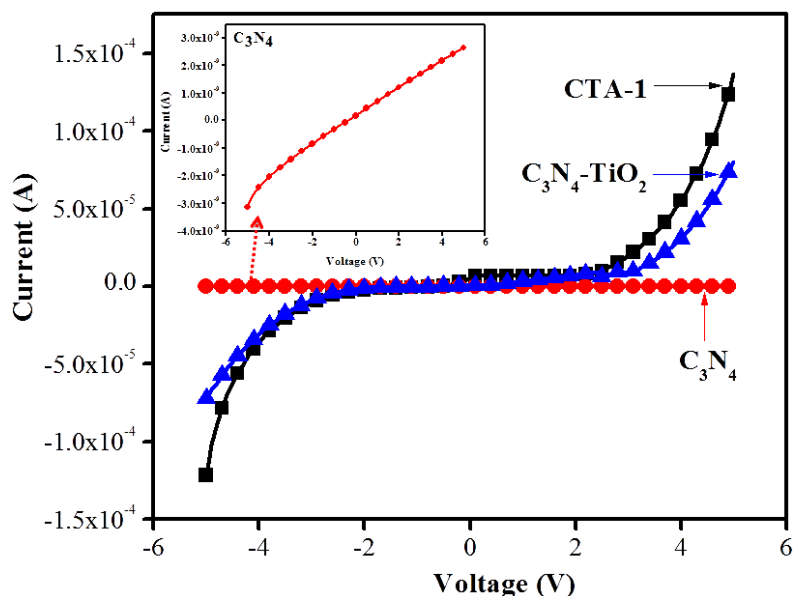


Fig. 4.12: Potential voltage (I-V) characteristics of the nanostructures.

4.4. Photocatalytic activity

Before studying the photocatalytic hydrogen evolution under sunlight several control experiments were performed for the optimization of reaction conditions. Photolysis (without the catalyst) and dark experiments showed no traces of H₂ evolution indicating that H₂ evolution is merely due to the photocatalysis process. The content of Au loading (wt %) was optimized by the photoluminescence (PL) studies (**Fig. 4.13(a)**). It has been observed that 0.75 wt% of Au loaded on C₃N₄-TiO₂ showed the maximum quenching followed by 0.50 wt% and 0.25 wt%. The

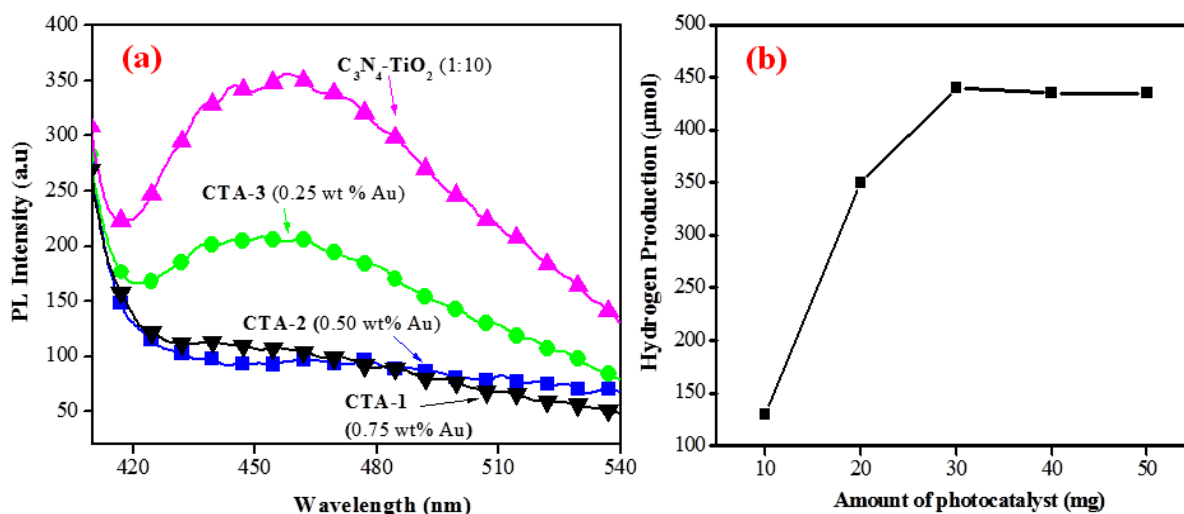


Fig. 4.13: (a) PL quenching due to Au loading on C₃N₄-TiO₂ (b) Amount of CTA-1 (mg/5mL) for the photocatalytic hydrogen production.

quenching is attributed to the effective separation of charge carriers, caused due to shuttling of electrons towards metal atoms [32]. So, 0.75 wt% of Au was considered as an optimized amount for the effective H₂ evolution. Furthermore, in compliance with our earlier report [33] here, it was also observed that 0.006 g/mL of the catalyst dispersed in the reaction mixture showed the highest H₂ evolution (**Fig. 4.13(b)**).

As presented in **Fig. 4.14** several hole scavenging/sacrificial donors were used to check the better compatibility regarding the performance of the nanocatalysts for the half reduction of H₂O. Methanol (CH₃OH) has been found to be effective for the H₂ evolution in comparison to Na₂CO₃, Na₂SO₄, and EDTA. Moreover, it is also found that after 5 h of sunlight irradiation using CH₃OH (5 mL) produced 250 μmol of H₂ while as a mixture (H₂O:CH₃OH 4:1) the H₂ evolution rate increases, mainly due to the reason that CH₃OH not only acts as a hole scavenger

but also as a sacrificial donor resulting in the formation of intermediates like formic acid (HCOOH) or formaldehyde (HCHO) [34] who are indirectly involved in the photocatalytic reduction of H^+ produced during water splitting reaction.

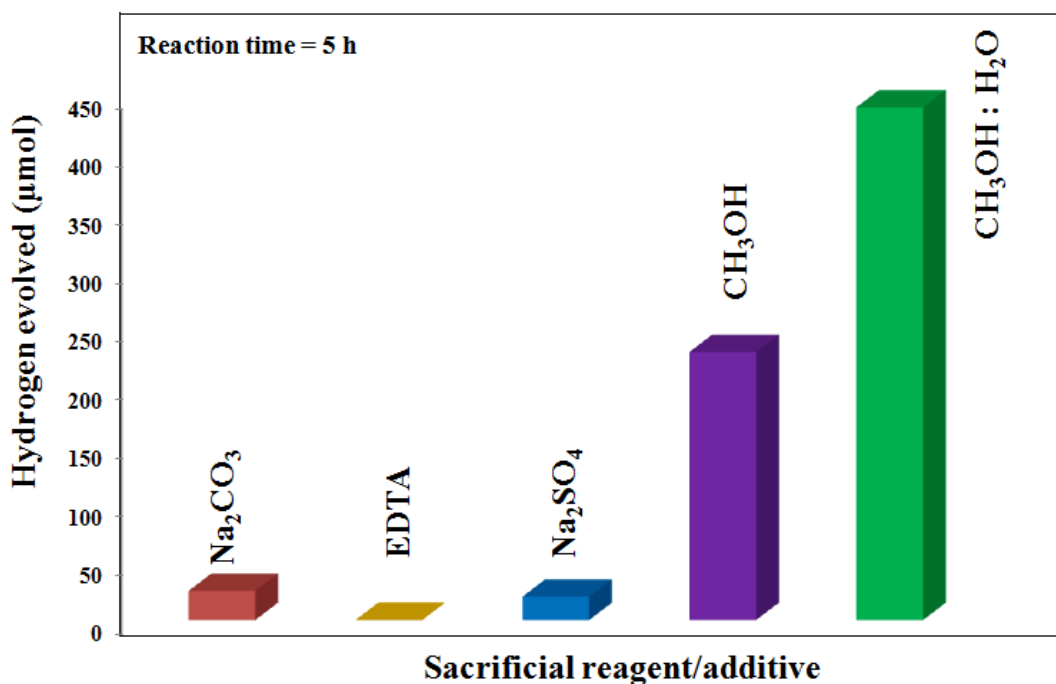


Fig. 4.14: Effect of different sacrificial reagents on the photocatalytic hydrogen evolution using CTA-1 photocatalyst

The H_2 evolution reaction rates with different photocatalysts are shown in **Fig. 4.15 (a)**, the bare C_3N_4 do not show any response to H_2 evolution due to its ineffectiveness for the separation of charge carriers (e^-/h^+) [35]. Compared to TiO_2 the C_3N_4 possess more negative reduction potential (vs normal hydrogen electrode, NHE) [29] due to which the transfer of electrons takes place from of C_3N_4 (E_{CB}) to TiO_2 (E_{CB}) and the nanocomposite (C_3N_4 - TiO_2) becomes active for the H_2 evolution resulting in the evolution of 35 μ mol of gas under direct sunlight (5 h). In case of the bare Au NP's little H_2 (39 μ mol) evolution was also observed. After the incorporation of Au, the rate of H_2 production increased and it was observed that the CTA-1 photocatalyst produced almost 450 μ mol of H_2 , showing a decrease in case of CTA-2 (170 μ mol) and CTA-3 (45 μ mol) due to lower Au content, in accordance to the PL results the higher activity of CTA-1 is directly related to the effective separation of charge carriers due to shuttling of the electrons in

three component system (CTA), also complies with the earlier results [36] and further correlated to the surface plasmon resonance (SPR) effect of Au leading to the activation of Au atoms, so Au acts both as a sensitizing agent for TiO_2 and also acts as a co-catalyst and helps in the

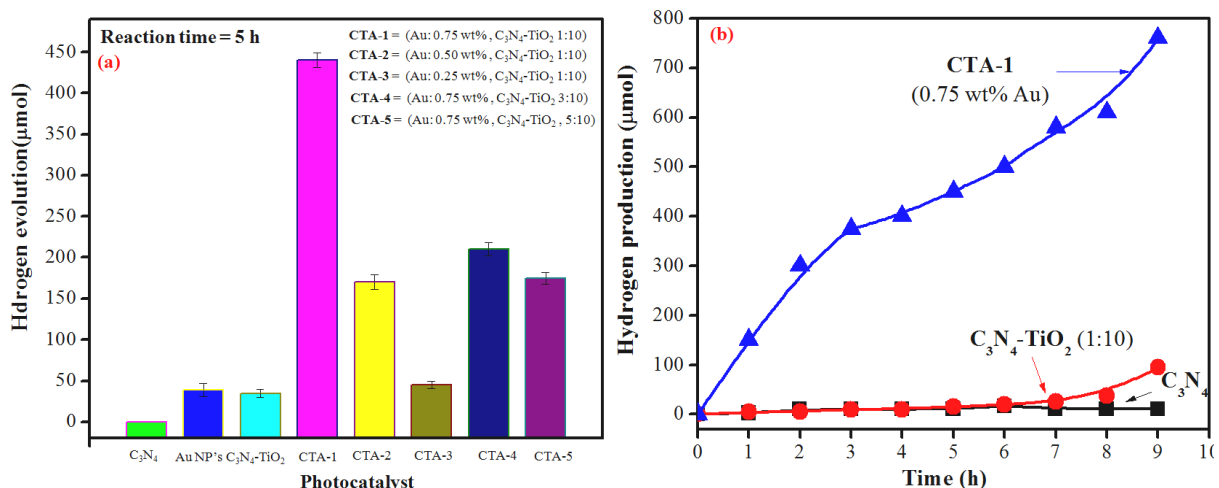


Fig. 4.15: (a) Photocatalytic H_2 production from water by different photocatalysts under sunlight irradiation (b) Time course photocatalytic hydrogen production by different photocatalysts.

transport of electrons. The H_2 evolution was witnessed to decrease by keeping the Au content constant (0.75 wt%) and varying the ratio of C_3N_4 . It is observed that CTA-4 and CTA-5 produced 210 μmol s and 175 μmol s of H_2 respectively. The decrease in the activity with the increase of C_3N_4 content is expected due to agglomeration of the nanoparticles resulting in the decrease of their specific surface area (Table 4.1). The time course study of CTA-1 (**Fig. 4.15(b)**) up to 9 hours showed an exponential increase in the H_2 production (88 μmolh^{-1}). Furthermore, the role of sunlight flux (Wm^{-1}) was also studied (**Fig. 4.16**) and it was found that the solar irradiance has the least effect on H_2 production up to 400 Wm^{-1} . It has been reported earlier [33] that the rate of reaction slowed down when the solar irradiance flux goes below 300 Wm^{-1} .

The higher photocatalytic activity of CTA over $\text{C}_3\text{N}_4\text{-TiO}_2$ and bare C_3N_4 is mainly due to two reasons; one is the synergistic effect of Au and second is the perfect band alignment after the formation of ternary heterojunction. Under direct solar light irradiation which constitutes 45 % of the visible light portion, Au is activated due to its SPR effect and simultaneously C_3N_4 is also activated because of its lower E_g (2.7 eV). The reduction of H^+ is expected to take place on the TiO_2 (NT) surface due to its matching E_{CB} potential (-0.29 Vs NHE) to the half reduction of

water splitting reaction [13]. Furthermore, in order to explore the intrinsic role of different components the photocatalytic reaction was carried under several monochromatic wavelengths like 514 nm, 457 nm, 488 nm and 314 nm and it was observed that the 457 nm wavelength produces highest amount of H_2 (112 μmol) followed by 488 nm (62 μmol) and 514 nm (32.25 μmol) and little response was also observed under 314 nm (31 μmol) wavelength. These results disclose the activation of C_3N_4 occurs under visible light due to its lower band energy and is more dominating in order to sensitize the TiO_2 compared to Au, similarly it was observed that the TiO_2 itself is also activated under UV light with a low response to the H_2 production.

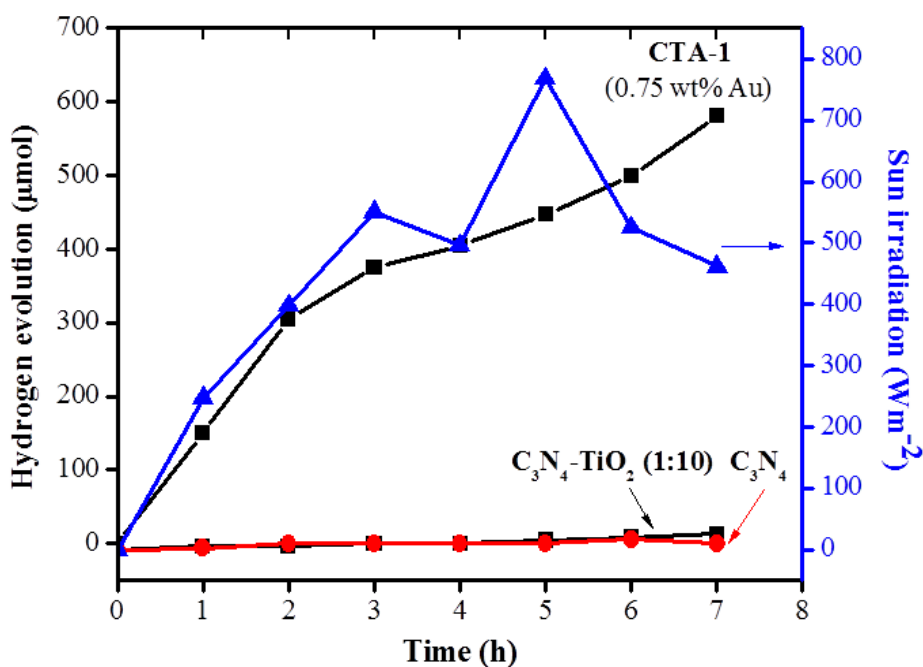
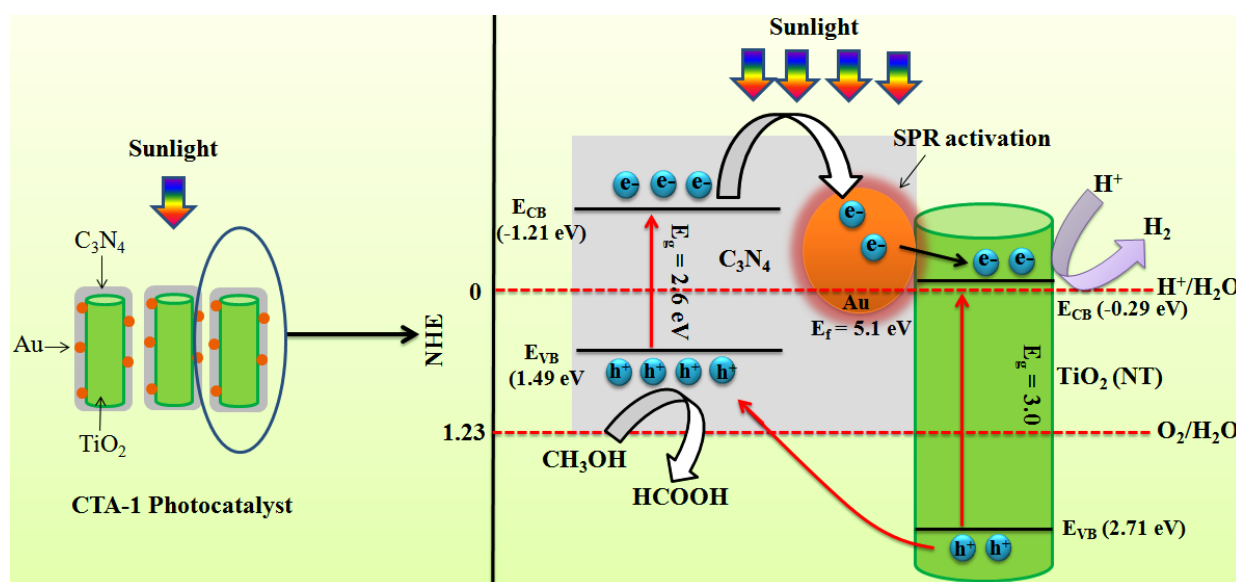


Fig. 4.16: Effect of total sunlight irradiance on hydrogen production using different photocatalysts.

As shown in **Scheme 4.1** when the NC is irradiated under sunlight irradiation, the electrons from E_{VB} (valence band) of C_3N_4 and TiO_2 are excited to their respective E_{CB} and simultaneously due to SPR effect Au nanoparticles are also activated. The I-V characteristics suggested the non ohmic properties of the heterojunction and in accordance with the HRTEM analysis, it is presumed that the comparative work function of C_3N_4 (4.31), Au (5.1) and TiO_2 (4.9) causes the

Fermi level equilibration between Au-TiO₂. So, at C₃N₄-TiO₂ interface the electrons move easily towards the E_{CB} of TiO₂ via Au, this mechanism is also supported by earlier studies reported by Yanfeng Chen et al [13]. Secondly, the band potential of C₃N₄ (-1.12 eV Vs NHE for E_{CB}) is more negative than TiO₂ (E_{CB}= -0.29 Vs NHE), the photoinduced electrons easily pass the interface and are transferred to the E_{CB} of TiO₂, simultaneously the holes produced in the TiO₂ under UV excitation are transferred to E_{VB} of C₃N₄ promoting the charge carrier separation and enhance the photocatalytic activity for H₂ production. Moreover, the presence of Ti⁺³ in the CTA-1 nanostructure due to the expected reduction of fewer Ti⁺⁴ are able to enhance the rate of the photocatalytic reaction [20, 30].



Scheme 4.1: Proposed mechanism for the H₂ production from water by C₃N₄-Au-TiO₂ (CTA-1) photocatalyst.

Methanol scavenges the holes and gets oxidized to formic acid or formaldehyde, which by indirect means boosts the half reduction of H₂O molecule to produce H₂. Furthermore, the rate of H₂ produced vs surface area has been normalized and presented in **Fig 4.17**, it was observed that the CTA-1 nanocomposite produced 24.2 $\mu\text{molh}^{-1}\text{m}^{-2}$ of H₂ followed by CTA-4 (17.42 $\mu\text{molh}^{-1}\text{m}^{-2}$) and CTA-5 (13.51 $\mu\text{molh}^{-1}\text{m}^{-2}$). The higher photocatalytic hydrogen production by CTA-1 photocatalyst is credited to better charge delocalization due to its high specific surface area and its mesoporous nature that enhances the binding ability of the reactants and also helps in efficient ionic transport along the elongated 1D surface with high aspect ratio.

The stability of the CTA-1 photocatalyst has been observed by doing the recycling for 3 consecutive cycles with a minimum loss (< 1 %) in overall activity (**Fig. 4.18**). The optical absorption analysis of the recycled photocatalyst didn't show any major destabilization confirming the photostability and long term applicability of the material.

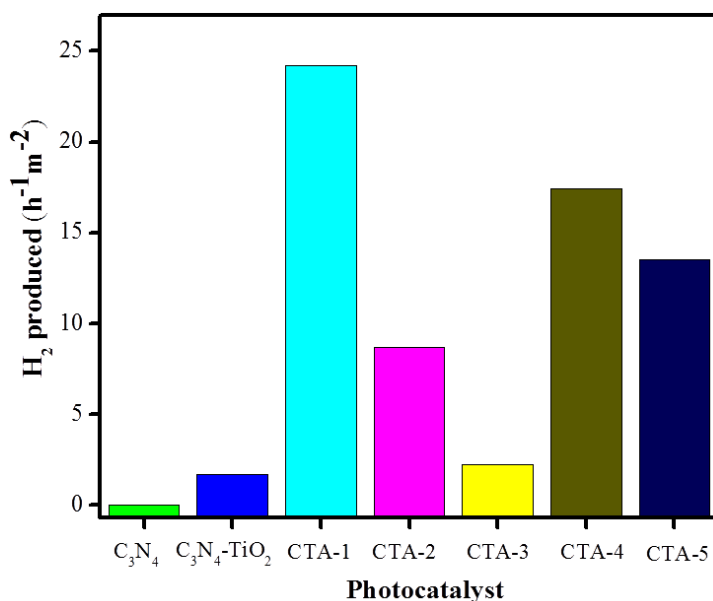


Fig. 4.17: Normalized H₂ production vs surface area

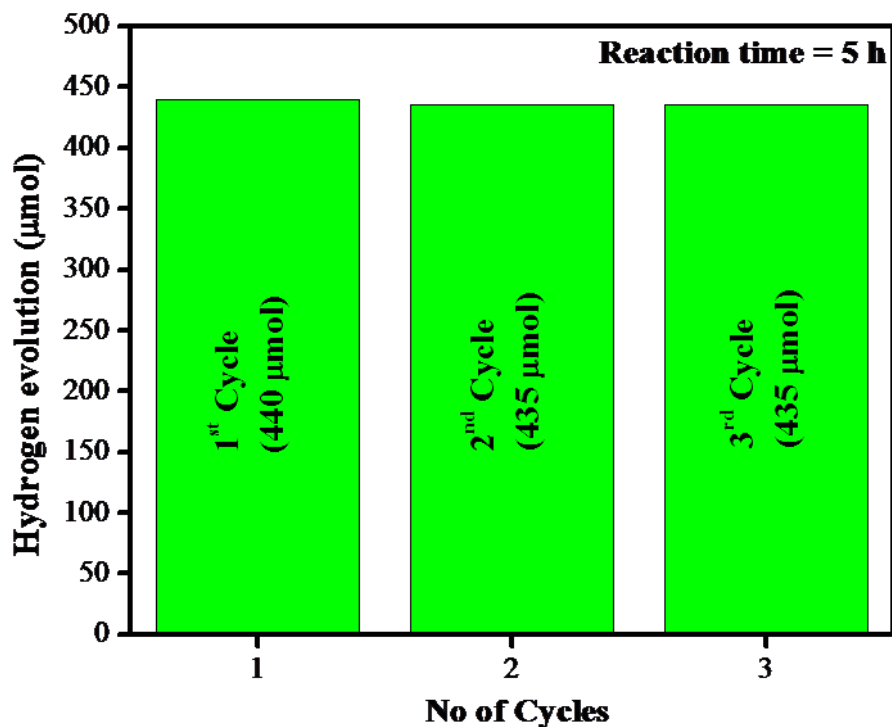


Fig. 4.18: Photostability of CTA-1 photocatalyst for three consecutive cycles

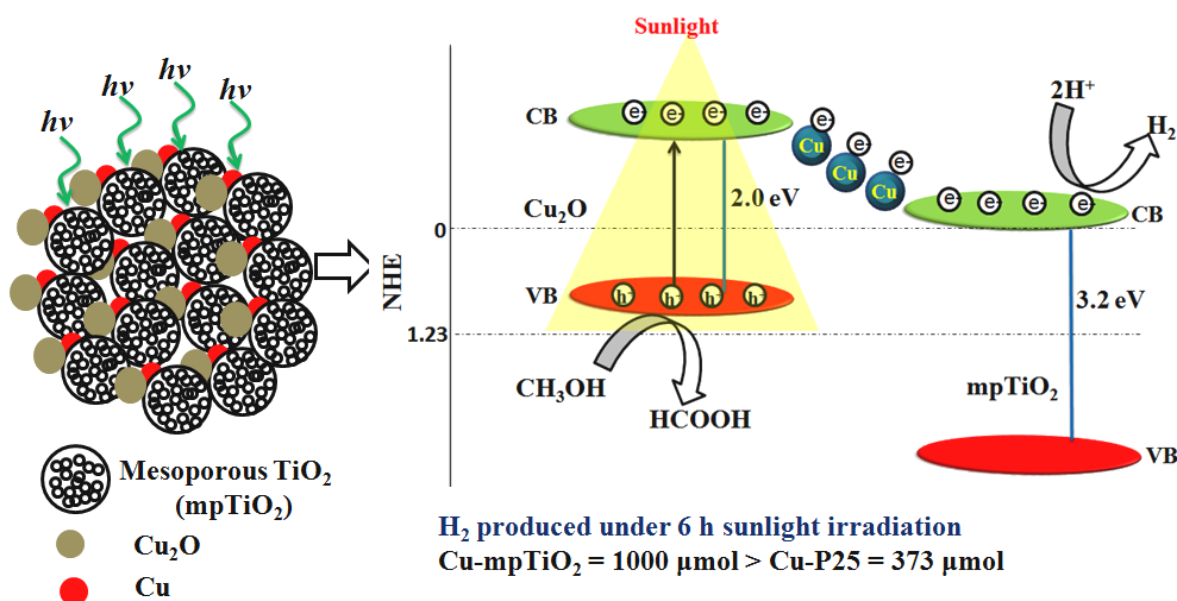
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CHAPTER 5

VARIABLE OXIDATION STATES OF Cu LOADED MESOPOROUS TiO₂ FOR H₂ PRODUCTION FROM WATER SPLITTING



Schematic summary

The Mesoporous TiO₂ exhibited better surface area of 188 m²g⁻¹ and structural properties. Wet impregnation of Cu led to the formation of the photostable Cu⁺/Cu-TiO₂ ternary hybrid photocatalyst. The photocatalyst showed good results for water splitting under direct sunlight irradiation using methanol as h⁺ scavenger. The apparent quantum yield (AQE) of Cu-mpTiO₂ for H₂ evolution was reported to be 11.39 %, and the nanocomposite also showed efficient photostability and recyclability for several cycles.

5.1. Introduction

As discussed in previous chapters after the discovery of Honda Fujishima effect [1] titanium dioxide (TiO_2) is most explored semiconductor for the photocatalytic water splitting. Modification always happens to conventional TiO_2 (P25) to eradicate its limitations [2-4] like low surface area, fast electron/hole recombination, absorption in UV region due to large band gap (E_g). Among these several effective structural and optical modifications have been reported [5, 6]. Characteristically mesoporous TiO_2 [7, 8] has recently emerged as the best alternative to be an effective material due to its excellent structural and electrical properties, high porosity, large surface area that results in effective charge transfer for promoting the quantum yield of several photocatalytic reactions like photocatalytic water splitting [9, 10]. Efforts are being made to increase the solar to hydrogen conversion efficiency by manipulating its band energetic [11] and light absorption ability [12]. Still, hydrogen generation from water over bare mesoporous TiO_2 is very low due to its inability to sensitize in sunlight/visible light and fast charge carrier recombination, in this regard noble metal (Au, Ag and Pt) loading has proven to be very effective [13-15]. Alternatively doping with transition metal like Cu, Fe, Co and Ni have recently turned to be a cheaper option [16-18], several other reports have also revealed the effectiveness of Cu in photocatalytic activity over noble metals [19, 20]. The complete mechanism is still less explored due to simultaneous formation of other active Cu species like Cu_2O and CuO . Copper is supposed to be in elemental (Cu^0) or oxide forms (Cu^{+1} or Cu^{+2}), some earlier reports [21-23] reveal that Cu_2O species are responsible for enhanced photocatalytic activity to generate hydrogen from water, few reports [24, 25] also suggested CuO is responsible for separation of charge carriers (electrons and holes). The Cu_2O (2.1-2.2 eV) [26] is also an important transition metal oxide (p-type) that has the capacity to work under sunlight irradiation and it is expected to form the p-n junction with n-type TiO_2 to enhance the lifetime of charge carriers.

Ampelli and co-workers [27] studied the effect of impregnation of copper oxide on TiO_2 for enhancement in photocatalytic activity similarly Korzhak et al. [28] reported the hydrogen production on Cu-doped TiO_2 nanocomposite and concluded that when Cu species are loaded on TiO_2 the expected stabilization of Cu and Cu oxides against photocorrosion results in the enhancement of photocatalytic efficiency. Hence, synthesis of mesoporous TiO_2 and its modification by the formation of heterocomposite and metal loading is done to eliminate the

drawbacks of commercial TiO₂ (P25) like low surface area, charge separation, and low quantum efficiency.

This chapter presents an elaborative study for the fabrication of recyclable Cu-mesoporous TiO₂ photocatalyst (Cu-mpTiO₂) for photocatalytic hydrogen evolution (PHE) from the water. This design increases the surface area of TiO₂ and impregnation of Cu in variable oxidation state especially the sunlight active Cu (I) state helps in sensitization of mpTiO₂. Cu in different oxidation states acts as a sensitizer and co-catalyst for TiO₂ and also maintains a balance of Cu⁺¹ and Cu⁰ due to reversible oxidation and reduction on Cu₂O by excess electrons and holes in the conduction band (E_{CB}) and valence band (E_{VB}) respectively.

5.2. Experimental section

5.2.1. Chemicals and reagents

All the analytic grade chemicals were used as received, titanium butoxide ((Ti(OBu)₄, 97 %, Sigma-Aldrich), cupric acetate (Cu(CH₃COO)₂, 99 % Loba Chemie Ltd), methanol and ethanol (99 %, SD Fine Ltd), Ethylene glycol (MW= 4000, Loba Chemie Ltd), Acetone (99%, Sigma-Aldrich). During the whole experiment, DI water obtained from Milli-Q (Millipore) an ultrafiltration system, (conductivity = 35 mho cm⁻¹ at 25°C).

5.2.2. Synthesis and characterization of photocatalysts

Mesoporous TiO₂ (mpTiO₂) was prepared by template synthesis approach, 2 mL of titanium butoxide [Ti(OBu)₄] was added to the ethylene glycol (44.4 mL) and stirred for 8 h at room temperature. The mixture was poured in 200 mL acetone containing 3 mL DI H₂O and 0.8 mL acetic acid and further stirred at 35 °C for 3 h resulting in the formation of mesoporous titanium glycolate precipitate. This titanium glycolate precipitate was stirred at 80-100 °C for 8 h to produce mpTiO₂ which was further washed with DI water and ethanol, dried at 100 °C and further calcined at 250 °C for 5 h to get an effective surface area and pore structure.

Copper nanoparticles (Cu NP's) were synthesized separately by a gelatin-sugar based green synthesis method. Gelatin was dissolved in distilled H₂O (30 mg/10 mL) in a 50 mL flask and vigorously stirred until the formation of a clear solution. In another flask, 5 mL NaOH (0.5 M) was added dropwise to the (CH₃COO)₂Cu solution (5 mL 0.2 M). This solution was quickly poured into the gelatin solution until a deep blue color is formed. The reduction was carried out by 5 mL (1 M) glucose and the solution was sonicated until the formation of brown color

indicating the formation of Cu NP's. The as-prepared Cu NP's were washed under several cycles of centrifugation with DI water and ethanol.

The fabrication of Cu-mpTiO₂ nanocomposites was done by wet impregnation method. The mpTiO₂ (100 mg) was suspended in DI water (10 mL) in a 50 mL beaker and sonicated for 10 min. The required amount (1-10 wt %) of Cu NP's was added to this suspension and stirred at room temperature for 24 h. The nanocomposite (Cu-mpTiO₂) was separated by centrifugation and dried at room temperature for further analysis.

5.2.3. Photocatalytic activity

The photocatalytic activity of different photocatalysts was carried in a Pyrex reaction tube (20 cm³), placed horizontally to sunlight and containing 30 mg photocatalyst and 5 mL reaction mixture (4:1, water: methanol), methanol was used to act both as sacrificial agent and hole scavenger. The reaction mixture was purged with argon for (10 min) and irradiated under direct sunlight during the month of May 2016 (06th-11th and 19th-21st) and August 2016 (27th), with an average sun radiation of ~637 W/m² and ~34.8 °C temperature. Moreover, the apparent quantum efficiency (AQE %) of the photocatalyst was calculated as per following equation [29].

$$AQE (\%) = \frac{n * \Delta G}{W * S * T} * 100$$

Where 'n' denotes the moles of H₂ produced (moles/L), 'ΔG' is total free energy change for water splitting reaction (237 kJ/mol), 'W' represents the sun radiation (W/m²), S is the surface area of the reaction tube (m²) and 't' is the time of the reaction (sec). The recycling experiments were performed by separating the photocatalyst from the earlier reaction mixture and before next cycle were washed several times with DI water and dried at room temperature. The analysis of gases has been done by the GC-TCD method, discussed in section 1.4 (Chapter 1).

5.3. Result and discussion

5.3.1. Optical and structural properties

Optical absorption analysis revealed (**Fig. 5.1**) that mpTiO₂ and Cu-mpTiO₂ photocatalysts exhibited absorption edges at ~418 nm and ~512 nm respectively. The red shift in Cu-mpTiO₂ along the formation of a new band around λ_{max} = 741 nm is ascribed to the good visible response of Cu and its oxide species (Cu₂O) on TiO₂ surface [22] and also due to charge transfer from Cu₂O to E_{CB} of TiO₂. The red shift shows the presence of impregnated of Cu⁰ and Cu₂O species which are later confirmed by XRD and HRTEM analysis.

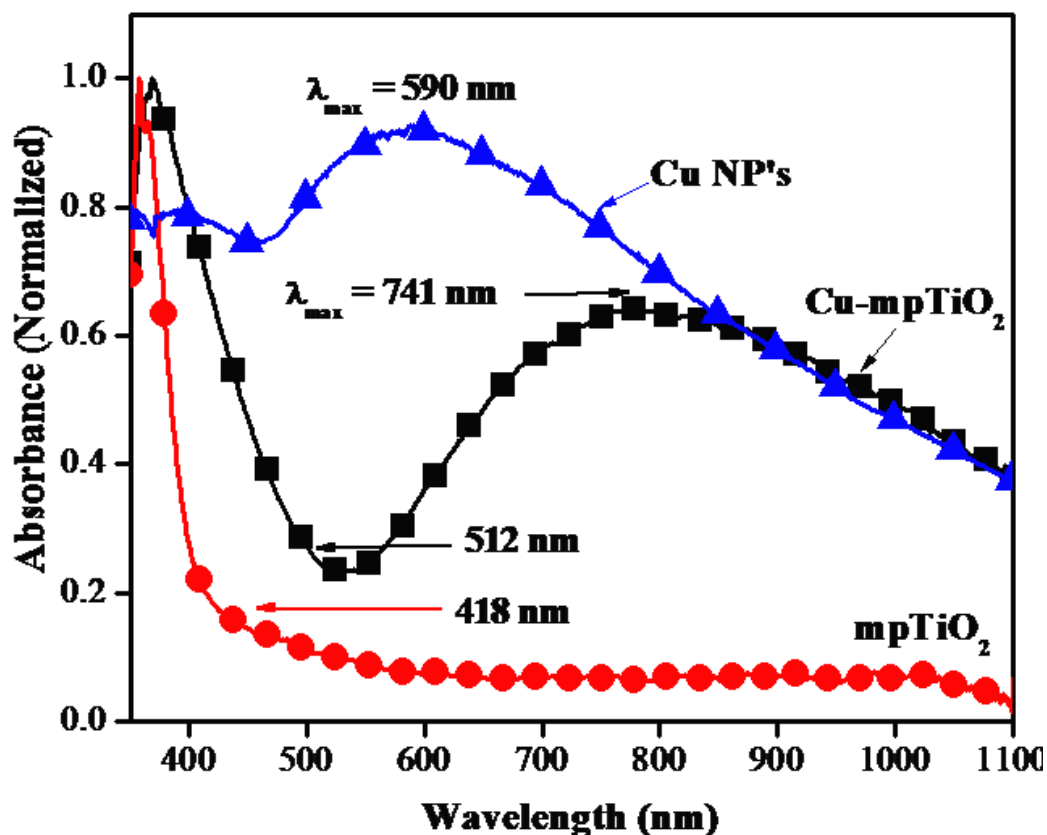


Fig. 5.1: Normalized optical absorption spectra of different photocatalyst.

The XRD pattern of fabricated mpTiO₂ (Fig. 5.2) matches with the anatase phase of TiO₂ (JCPDS card No. 21-1272), besides a strong diffraction peak around 25.2° (101 plane) some low intensity peaks were also observed via 38.5° (112), 48.0° (200), 55.0° (211) and 62.6° (204). The effect of temperature (up to 350 °C) on the crystal growth was also observed showing a small change in the sharpness of peaks and growth of 204 plane. After the impregnation of Cu on mpTiO₂, new small diffraction peaks were observed around 30.0°, 36.7°, 54.8° and 61.7° corresponding to Cu₂O (JCPDS card No. 78-2076), a small diffraction around 50.4° is for metallic Cu (JCPDS card No. 04-0836). These results confirm that the photocatalyst (Cu-mpTiO₂) consist of TiO₂ (anatase, tetragonal geometry) and Cu (both Cu₂O cubic form and Cu metallic state).

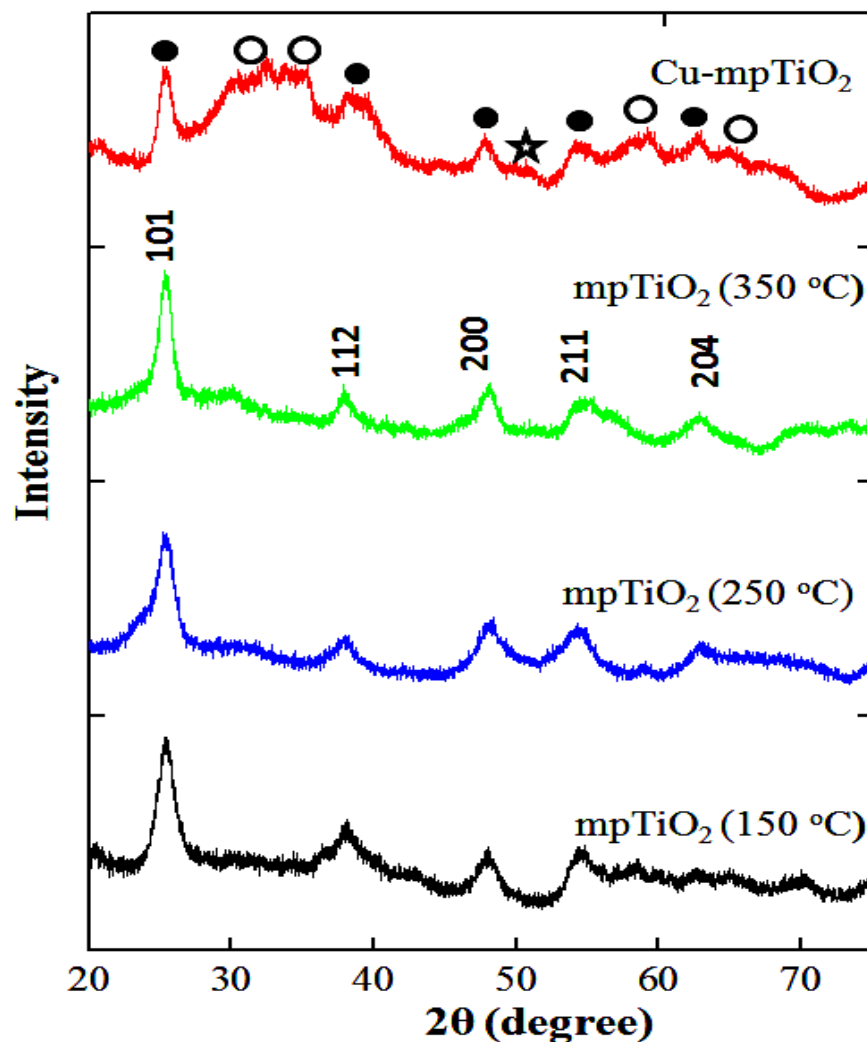


Fig. 5.2: XRD Pattern of mpTiO₂ (calcined at different temperatures) and Cu-mpTiO₂ (Dark circles represent mpTiO₂, hollow circles represent Cu₂O and star is for Cu⁰).

The XRD results were further supported by HRTEM (**Fig. 5.3**) suggesting that the Cu-mpTiO₂ consists of three distinct lattice planes corresponding to TiO₂, Cu₂O, and Cu with the interplanar distance of ~0.35 nm, ~0.25 nm, and ~0.21 nm respectively. As shown in SAED pattern, interplanar distance of Cu⁺¹ and Cu is attributed to (111) and (110) planes respectively, while for TiO₂ it is related to (101) planes. The mpTiO₂ possesses an average particle size of ~32 nm and the structural morphology also describes the presence of Cu/Cu₂O as small islands or surface

deposition on TiO_2 , as it is apparent in the **Fig. 5.3** and **Fig. 5.5**. The diameter of Cu NP's is $\sim 25\text{-}30\text{ nm}$, which is comparably little smaller than mpTiO₂ ($\sim 32\text{ nm}$). In order to clarify the elemental distribution, the FESEM and elemental mapping of Cu-mpTiO₂ were done. This analysis discloses spherical shape of mpTiO₂ nanoparticles (**Fig. 5.4**) and the dot color mapping revealed the spatial uniform distribution of Ti, O and Cu elements in mpTiO₂. Moreover, mpTiO₂ was further verified by EDS analysis for the confirmation of atomic ratio of dopant and it was found that Cu constitutes the expected ~ 3 atomic weight percent (wt%, **Fig. 5.6**).

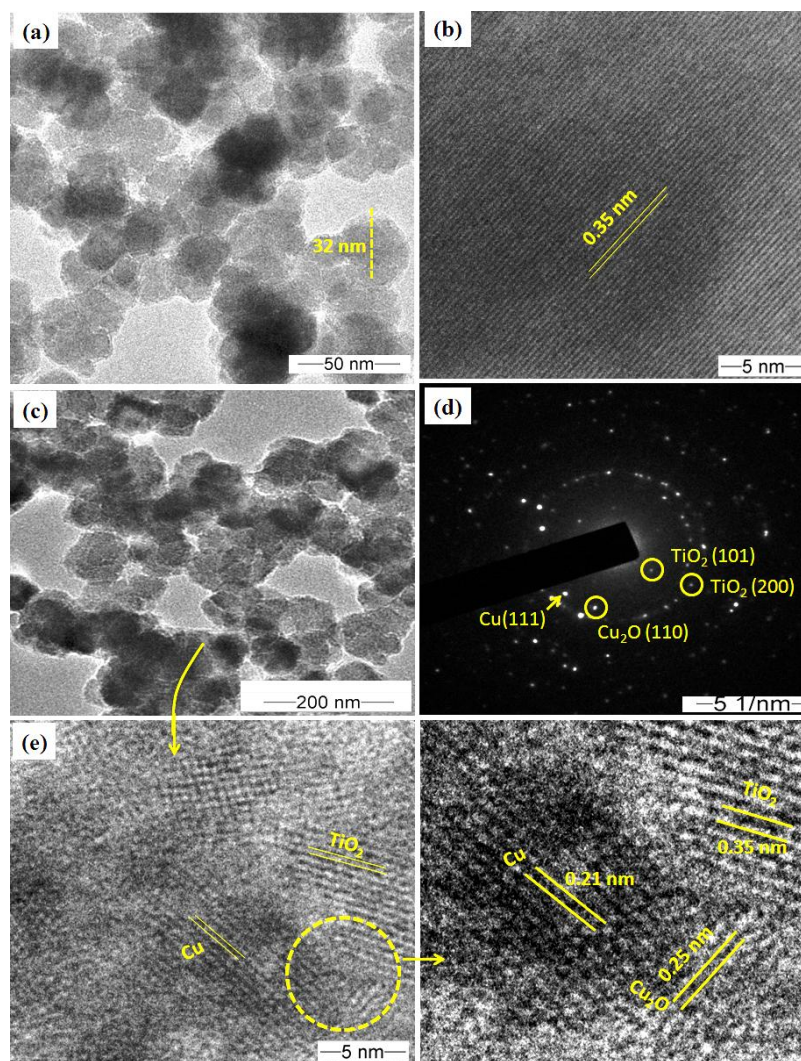


Fig. 5.3: HRTEM micrographs of (a) mpTiO₂, (b) lattice fringes of mpTiO₂, (c) Cu-mpTiO₂ (d and e) SAED pattern and lattice fringes of Cu-mpTiO₂.

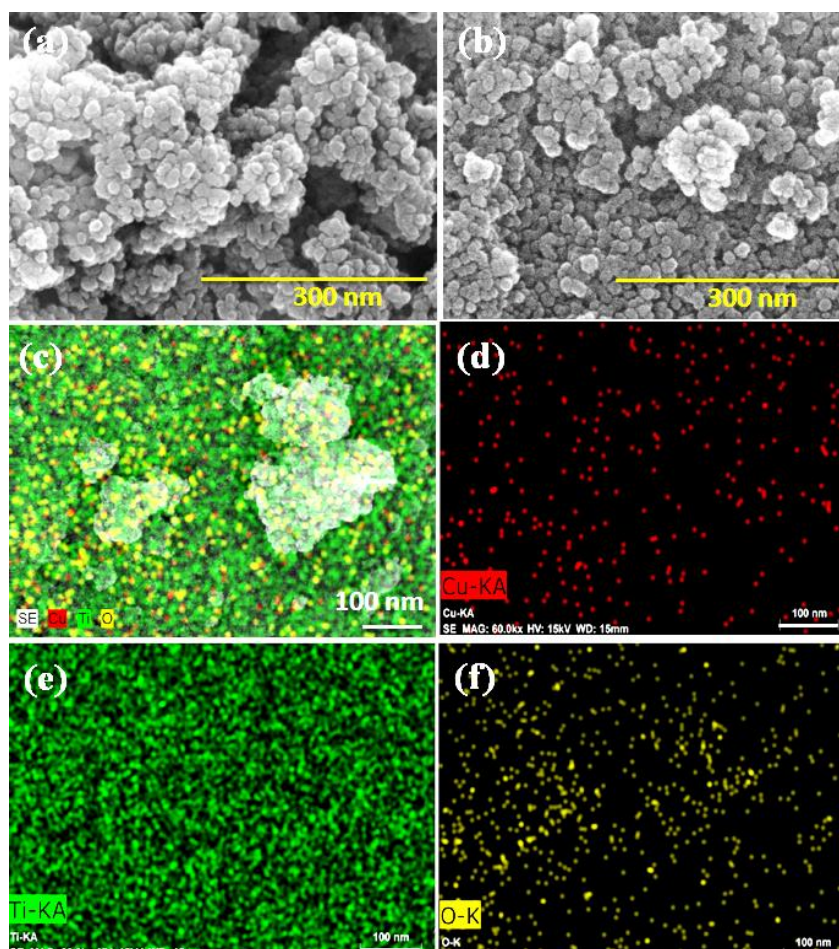


Fig. 5.4: FESEM images of (a) mpTiO₂ (b) Cu-mpTiO₂ (c) elemental mapping of Cu-mpTiO₂ (d) Red color for “Cu” (e) Green color for “Ti” (f) Yellow color for “O”.

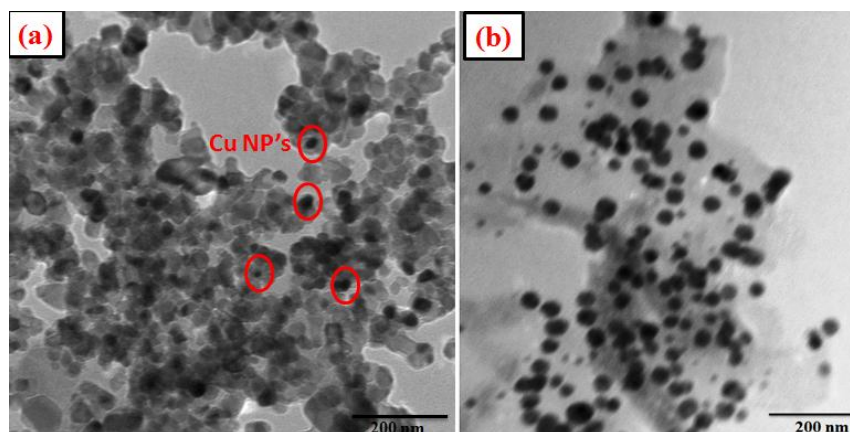


Fig. 5.5: TEM micrograph of (a) Cu-mpTiO₂ (b) bare Cu nanoparticles.

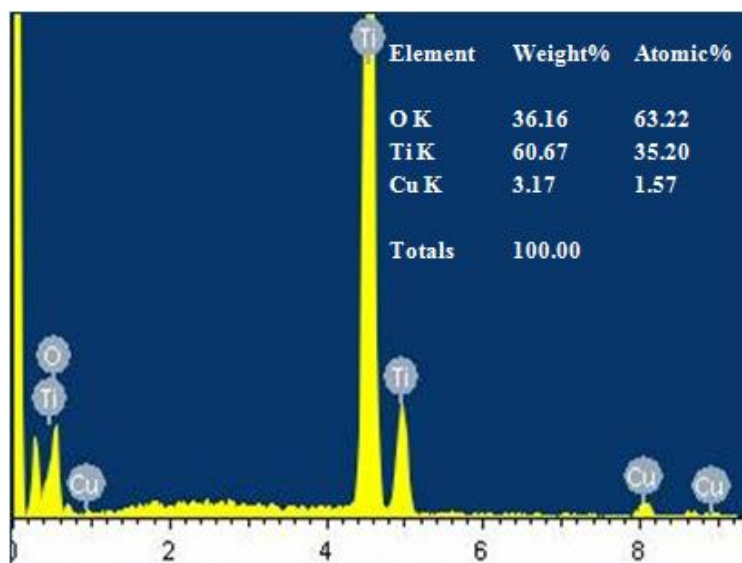


Fig. 5.6: EDS analysis of Cu-mpTiO₂ photocatalyst.

5.3.2. Surface area and porosity study

The Fig. 5.7 represents the nitrogen adsorption-desorption based Brunauer-Emmet and Teller (BET) analysis of the mpTiO₂ photocatalyst at different calcination temperatures. The adsorption isotherm exhibited type IV Langmuir characteristics [30] which are the specialty of mesoporous materials. It was observed that both the surface area and pore diameter are sensitive to the

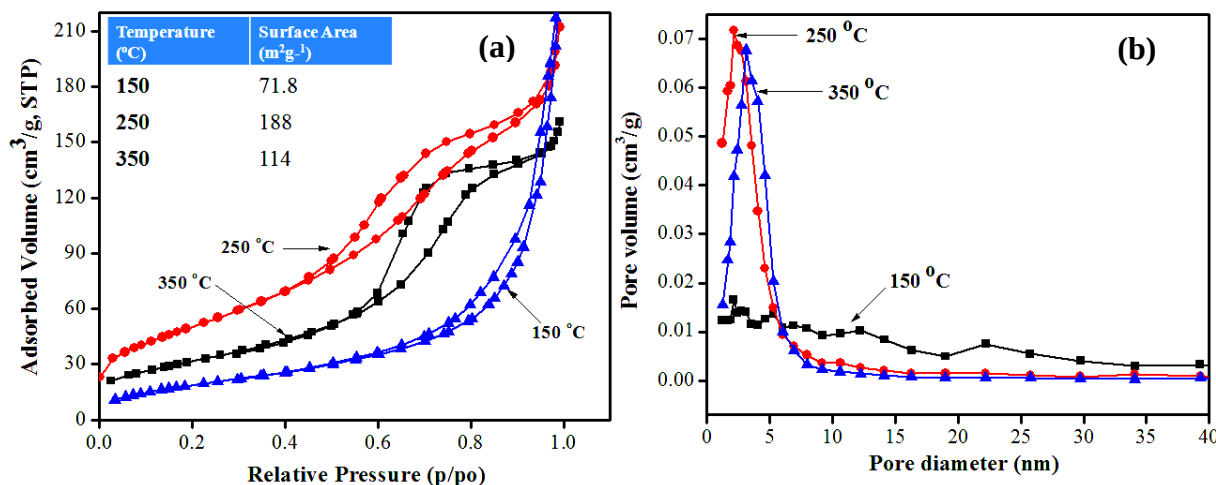


Fig. 5.7: (a) Effect of temperature on the surface area and (b) pore size of mpTiO₂ photocatalyst.

change of temperatures. The results revealed a small surface area 71.8 m²g⁻¹ and pore size 0.35 cm³g⁻¹ respectively for as prepared mpTiO₂ treated thermally at 150 °C. The surface area increased abruptly to 188 m²/g with the increase in the calcination temperature to 250 °C due to

the removal of adsorbed gasses and surfactant a good pore structure is developed, but further increase in the calcination temperature to 350 °C resulted in the decrease of the surface area ($114 \text{ m}^2\text{g}^{-1}$). This change is caused due to the internal pore strain or pore rupture that is confirmed by thermal gravimetric analysis (TGA, **Fig. 5.8**), a strain around 350 °C resulting in the decrease of pore size to $0.24 \text{ cm}^2\text{g}^{-1}$. As presented in **Fig. 5.9** and also elucidated in **Table 5.1**, the surface area $188 \text{ m}^2\text{g}^{-1}$ and pore size $0.32 \text{ cm}^3\text{g}^{-1}$ of mpTiO_2 are decreased to $74.6 \text{ m}^2\text{g}^{-1}$ and $0.25 \text{ cm}^3\text{g}^{-1}$ respectively, and after Cu impregnation the decrease is because of incorporation of small Cu particles into the pores of mpTiO_2 that also changed the pore diameter (13.5 nm) due to internal pore strain.

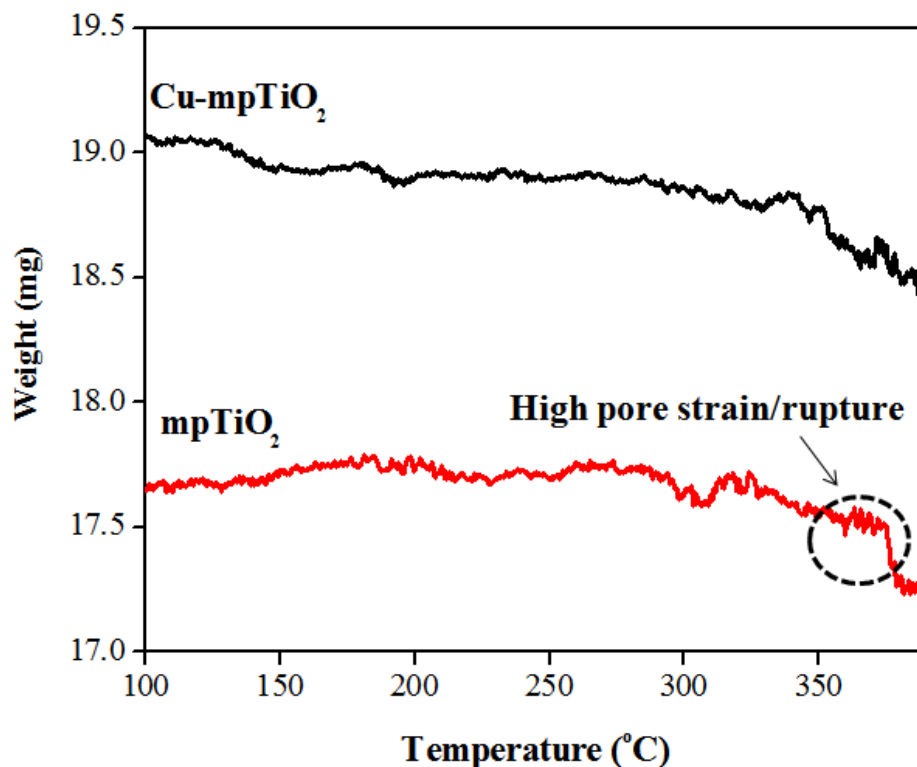


Fig. 5.8: Thermogravimetric analysis (TGA) of mpTiO_2 and Cu-mpTiO_2 photocatalyst.

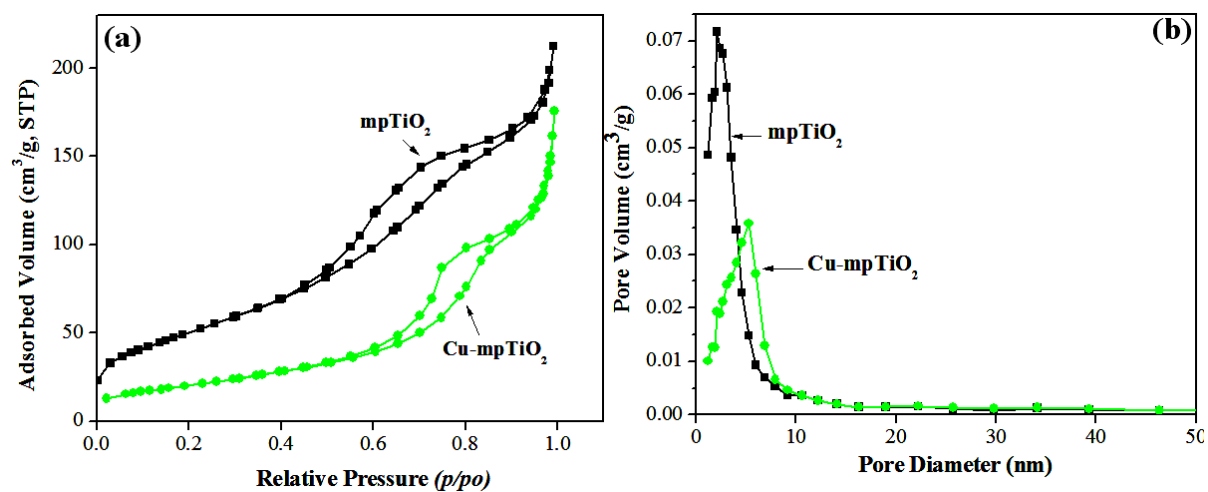


Fig. 5.9: (a) N_2 adsorption desorption curve (b) BJH Curve of $mpTiO_2$ and $Cu-mpTiO_2$.

Table 5.1: Effect of temperature and Cu loading on surface area and porosity of $mpTiO_2$

Photocatalyst	Temperature	Surface Area (m^2/g)	Pore Diameter (nm)	Pore Size (cm^3/g)
$mpTiO_2$	150 $^{\circ}C$	71.8	19.4	0.35
	250 $^{\circ}C$	188	6.8	0.32
	350 $^{\circ}C$	114	8.5	0.24
$Cu-mpTiO_2$		74.6	13.5	0.25

5.3.3. X-ray photoelectron spectroscopy (XPS) analysis

Information related to elemental composition and oxidation state of fabricated Cu-mpTiO₂ before and after sunlight reaction was analyzed by XPS. **Fig. 5.10** shows the XPS survey spectra of Cu-mpTiO₂ before and after the first cycle, showing the presence of Cu, Ti, and O which is in consonance with the obtained FESEM-EDS results. The detailed high resolution XPS results of

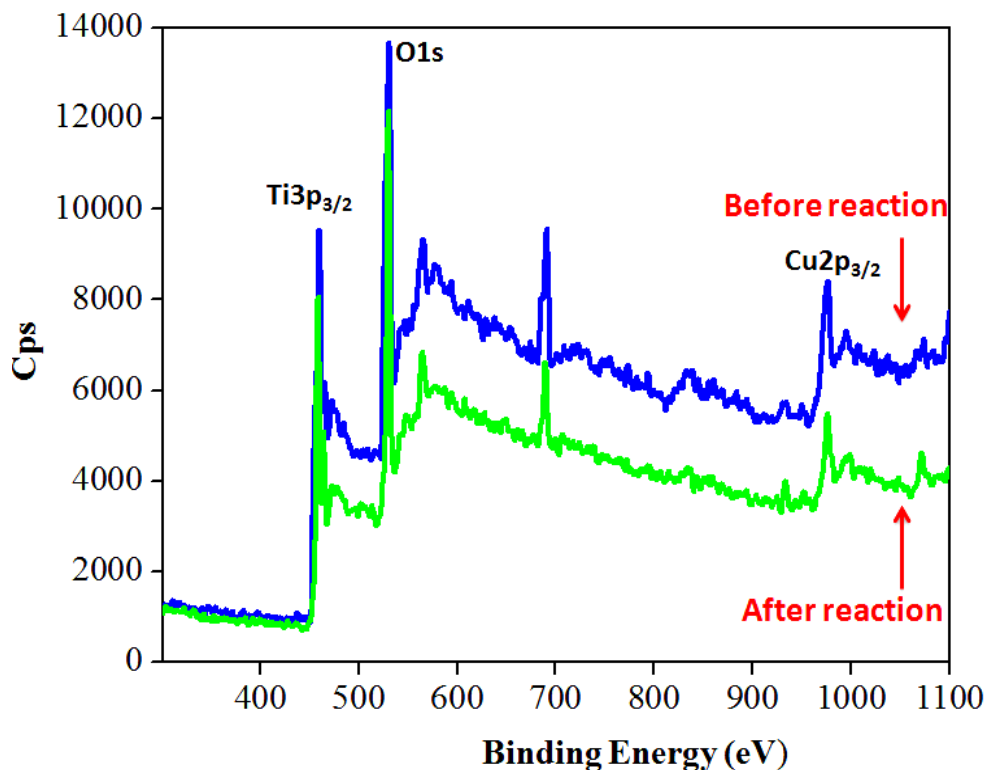


Fig. 5.10: XPS of Cu-mpTiO₂ photocatalyst before and after photoreaction with sunlight.

Cu2p, Ti2p, and O1s are presented in **Fig. 5.11** the peaks of Cu2p at 933.5 eV (binding energy) and 953.3 eV [31] and a satellite peak at 947.8 eV before irradiation is credited to Cu⁺¹ (Cu₂O), while after the irradiation of the same sample for 6 h a small downshift in binding energy (933.3 eV) was observed and a small shift was also observed in the peak at 947.8 eV to 947.2 eV suggesting the formation of more Cu⁰ nanoparticles that form a balanced ternary (Cu⁺¹/Cu-TiO₂) heterocomposite. In case of Ti2p before reaction two characteristic peaks at 459 eV and 464.7 eV were witnessed for Ti2p_{3/2} and Ti2p_{1/2} spin states suggesting the presence of Ti⁺⁴, similarly in case of oxygen a characteristic peak at 529.5 eV is assigned to binding of O with Ti and Cu whereas after the reaction in sunlight some interesting results were obtained. The Ti2p_{3/2} and Ti2p_{1/2} shifted to higher binding energies (459.8 eV and 465.5 eV respectively) with the

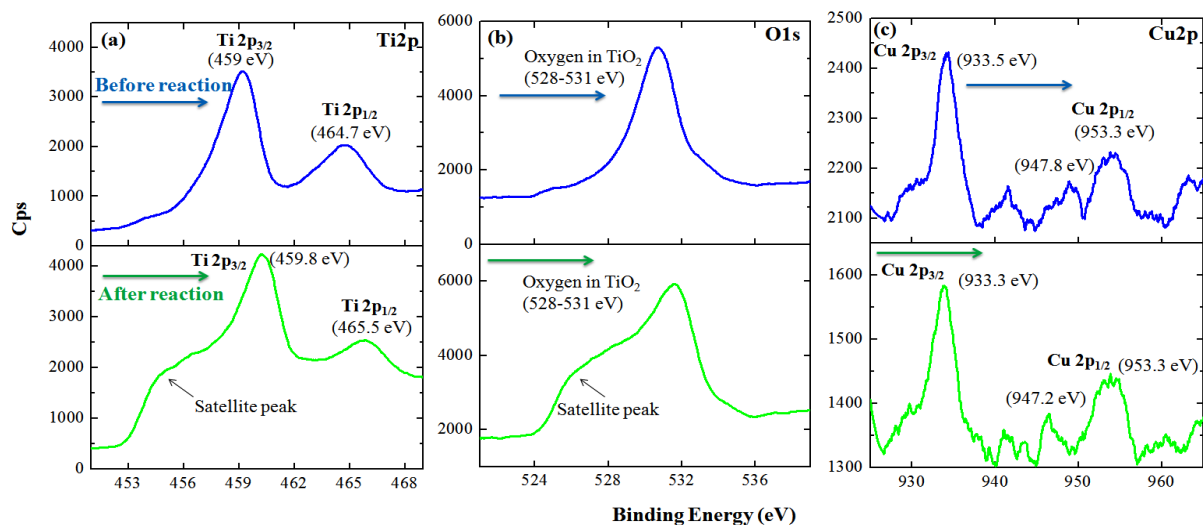


Fig. 5.11: XPS analysis of Cu-mpTiO₂, (a) Ti (b) O (c) Cu before and after photoreaction under sunlight.

formation of a shakedown satellite peak at 454.1 eV, the similar chemical shift was observed in the case of O1s where the main peak was shifted to 531.5 eV and formation of the little shakedown peak at 526 eV. The chemical shift is possibly due to the transfer of an electron from O to Ti resulting in the formation of Ti⁺³ in between T⁺⁴. The presence of characteristic shake up the satellite in case of Cu inferred the presence of Cu in both Cu⁰ and Cu⁺¹ oxidation state.

5.4. Photocatalytic hydrogen evolution

Photochemical and dark condition based control experiments showed that no hydrogen was evolved either in presence of sunlight (without catalyst) or in absence of sunlight (only with catalyst), which means that the H₂ produced during the reaction is by photocatalysis. Content of Cu loading (wt %) on TiO₂ and amount of photocatalyst (mg/5 mL) were optimized before the reaction, indicating 3 wt % of Cu NP's as optimum amount for the higher catalytic activity (**Fig. 5.12**), credited to the homo dispersion of Cu⁰ and it was witnessed that higher Cu content decreased the photocatalytic hydrogen evolution (PHE) because addition of percentage larger than optimum results in opposite effect on overall activity [32]. Furthermore, 6 mg/mL of Cu-mpTiO₂ photocatalyst was optimized to be the effective amount for the higher efficiency.

The PHE from water using methanol as the sacrificial agent was carried under sunlight illumination. As shown in **Fig. 5.13(a)** under continuous sunlight irradiation Cu-mpTiO₂ photocatalyst produced 1000 μmol of H₂ gas in presence of methanol and 118 μmol in absence of methanol, the results obtained were very high in comparison to Cu loaded on commercial Cu-

TiO₂ (P25), Cu NP's and bare mpTiO₂. The AQE (**Fig. 5.13(b)**) of Cu-mpTiO₂ was also higher (11.39 %) which is several folds than that of commercial Cu-TiO₂ (P25, 4.1 %) and bare mpTiO₂ (0 %)

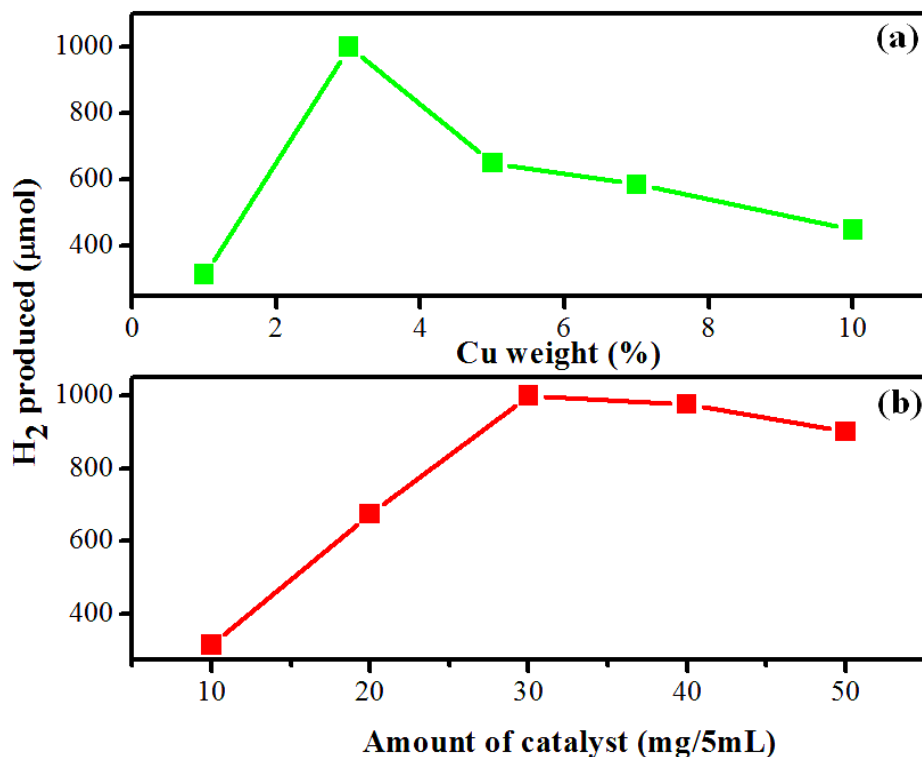


Fig. 5.12: Effect of (a) Cu loading (wt %) on mpTiO₂ (b) Amount of photocatalyst (Cu-mpTiO₂ (mg/5mL) on overall H₂ production.

To examine the role of sacrificial agent the reaction was also carried out in absence of methanol and it was observed that the Cu-mpTiO₂ showed higher photocatalytic activity ascribed to effective charge separation; however, the oxygen was not detected in this reaction. The less response to oxygen evolution reaction is mainly due to the crystal structure of mpTiO₂ as earlier reports [33, 34] suggested that anatase polymorph is less responsive for oxygen evolution reaction in water splitting.

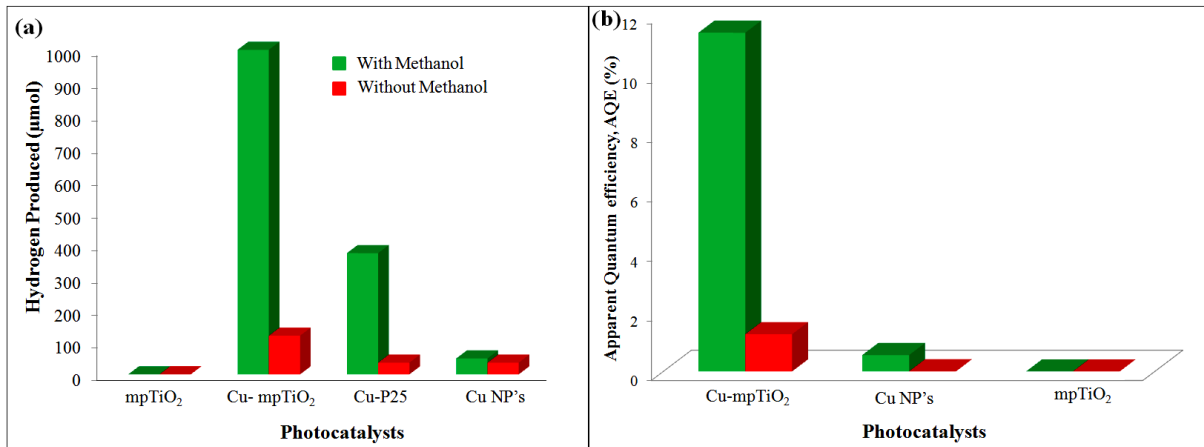


Fig. 5.13: (a) H₂ evolution by Cu-mpTiO₂ relative to Cu-TiO₂ (P25) and bare Cu NP's after 6 h sunlight irradiation (b) Apparent quantum efficiency (AQE %) of different photocatalysts for H₂ production.

The time course study (**Fig. 5.14**) reveals an exponential increase in PHE with time for continuous 6 h. The influence of total solar radiation and surface area on the overall reaction rate was also studied, as illustrated in **Fig. 5.15** the time course influence of solar radiation revealed that the rate of PHE enhanced with the increase of solar flux for first 5 h (1100-1600h IST) while during the last two hours of the reaction there was an abrupt decrease in the flux and the PHE rate also decreased instantly during last hour of irradiation. On the basis of action spectra, the

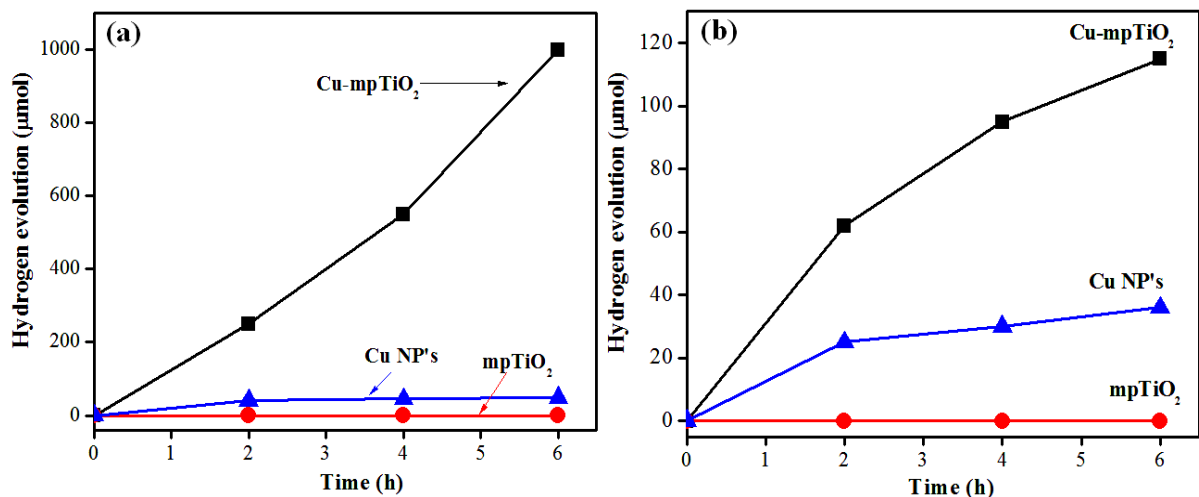


Fig. 5.14: Time course study of H₂ evolution by various photocatalysts in (a) presence of methanol (b) absence of methanol.

average intensity of solar radiation for efficient PHE was calculated to $\sim 637 \text{ W/m}^2$ (mean average of first six hours). Similarly, it was observed that by increasing the total effective

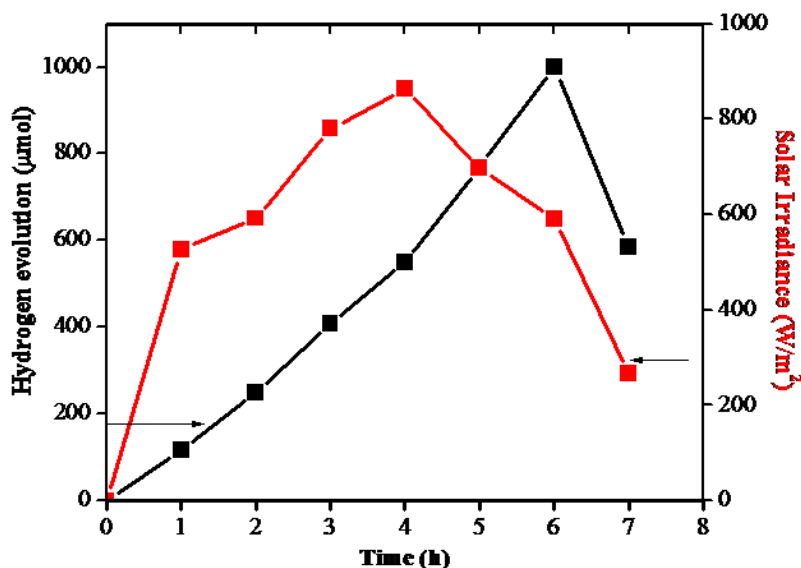
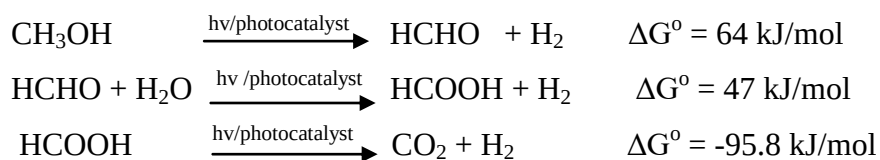


Fig. 5.15: Effect of solar irradiance (W/m^2) on hydrogen production from water.

illumination area the rate of PHE also increases several folds (**Fig. 5.16**), it was observed that by increasing the illumination area ~ 2 times the rate of PHE enhanced ~ 5 times.

The FTIR analysis (**Fig. 5.17**) showed the presence of HCOOH intermediate during the time course of the reaction (3 h). Hence, the reaction for PHE carried out in presence of methanol (CH_3OH) is supposed to take place as per following chemical equations.



This mechanism is favored because of the formation of HCOOH intermediate which leads to the spontaneous H_2 production due to its negative free energy value ($\Delta G^\circ = -95.8 \text{ kJ/mol}$) this mechanism is also supported by earlier findings [35].

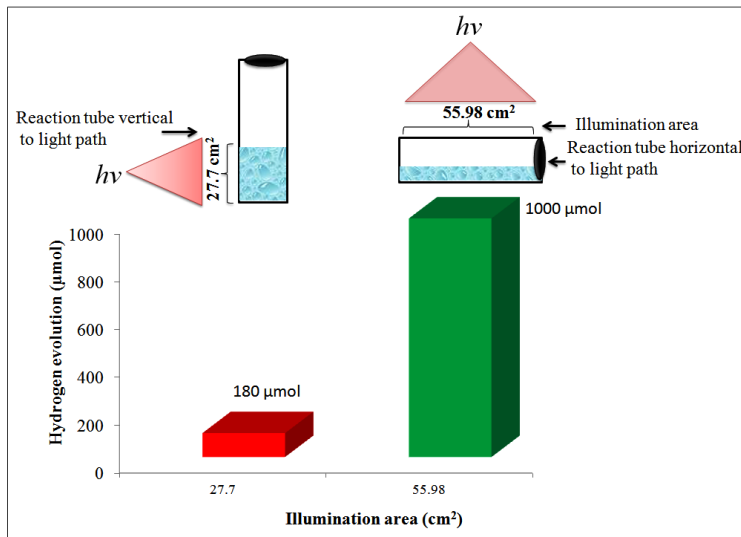


Fig. 5.16: Effect of illumination area on hydrogen production efficiency using Cu-mpTiO₂ photocatalyst.

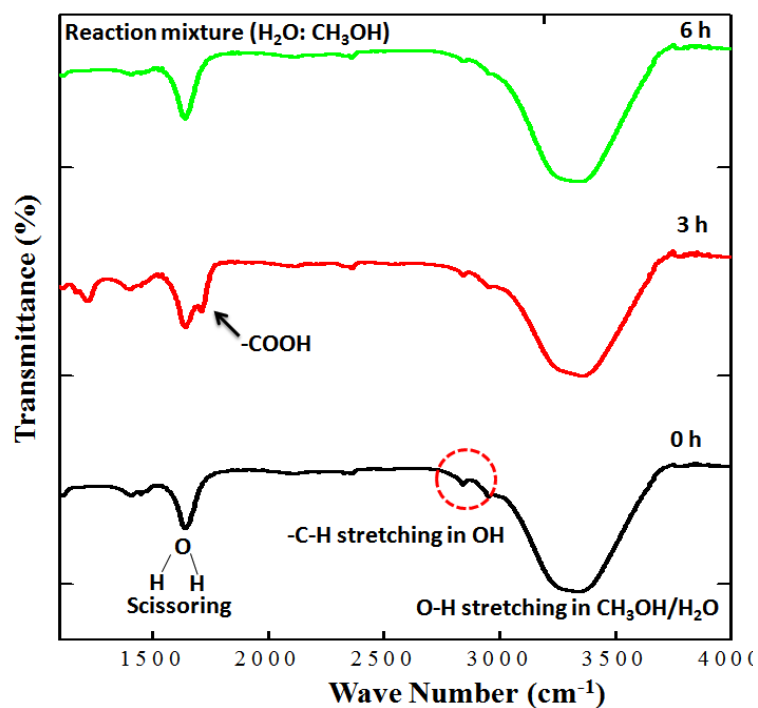


Fig. 5.17: FTIR spectra obtained during the course of reaction (3h) suggesting the photodecomposition of H₂O via formation of HCOOH.

The photocatalytic stability of Cu-mpTiO₂ was analyzed by its reusability for a maximum number of reaction cycles; here it has been analyzed for 3 consecutive cycles with some unexpected and interesting results. It was observed (**Fig. 5.18**) that the photocatalytic efficiency of the same photocatalyst for 2nd and the 3rd cycle was more than 1st cycle. This increase is ascribed to the photostability of Cu-mpTiO₂, which means that after first cycle the photocatalyst is more stable for PHE. Preliminary DRS analysis of the recycled photocatalyst (**Fig. 5.19**) showed a little

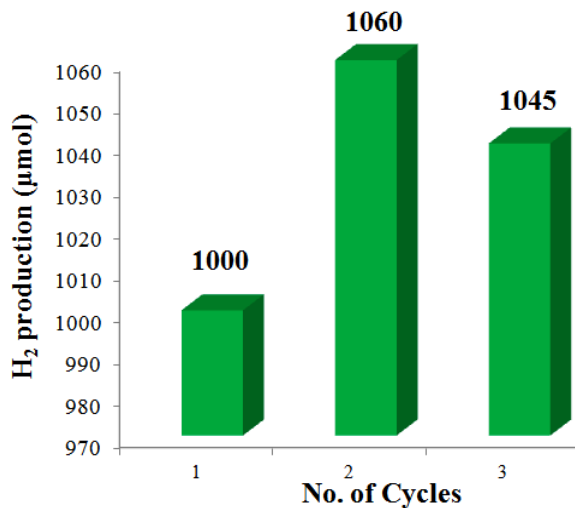


Fig. 5.18: Recyclability of Cu-mpTiO₂ photocatalysts for 3 consecutive cycles.

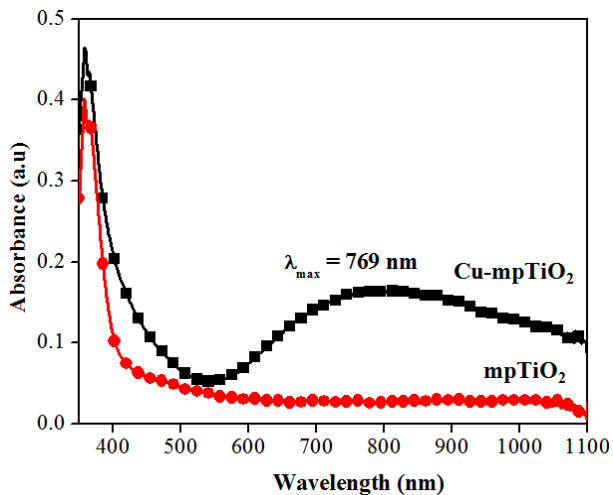
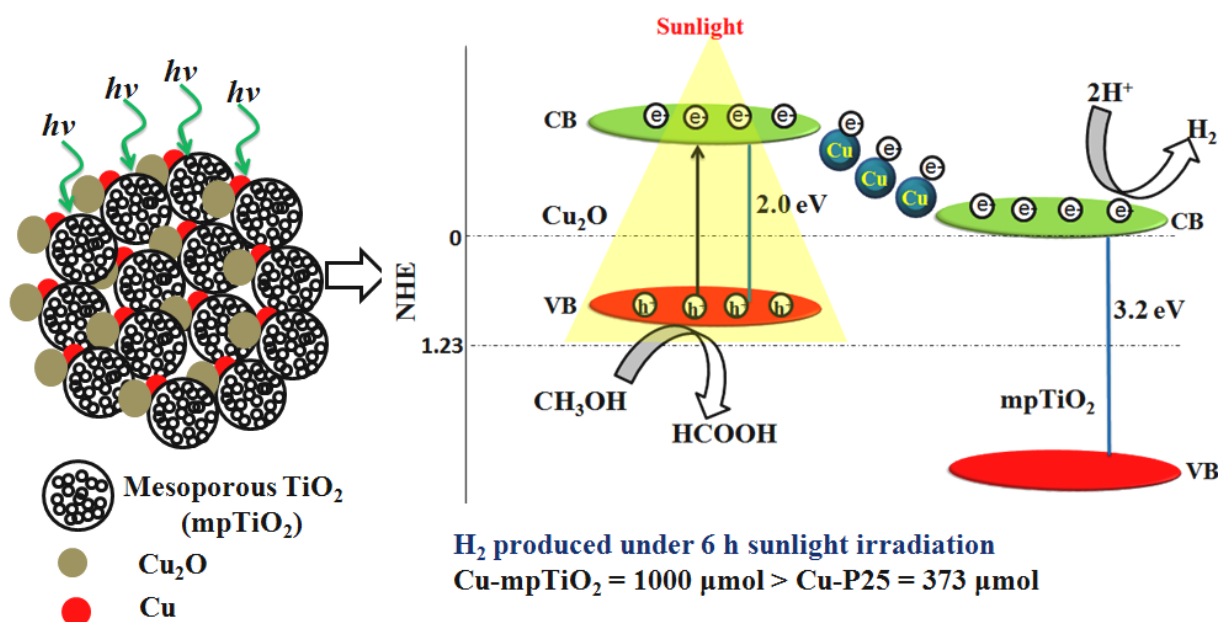


Fig. 5.19: DRS of the recycled photocatalysts.

red shift and increase in absorption intensity credited to the formation of more Cu^0 species due to the reduction of Cu_2O under prolonged sunlight irradiation. This was further proved by XPS and HRTEM studies, showing the presence of Cu_2O and Cu with TiO_2 , in such type of ternary hetrocomposite, Cu and Cu_2O both acts as a co-catalyst and sensitizers for TiO_2 . As illustrated in **Scheme 5.1** when the Cu-mpTiO_2 nanocomposite is irradiated with sunlight the electrons are excited to the conduction band (E_{CB}) of Cu_2O while as holes are accumulated in its valence band (E_{VB}), the photogenerated electrons are transferred from Cu_2O to E_{CB} of TiO_2 due to its much positive potential, in this way the recombination of electrons and holes is avoided [36]. Moreover, Cu_2O is not able to reduce H^+ alone due to its more positive potential than NHE (H^+/H_2). As the sunlight irradiation is continuous for prolonged time photoreduction of Cu_2O to Cu^0 take place because of large electron accumulation in the E_{CB} of Cu_2O , forming a more stable ternary hybrid. The result is also supported by in XPS, where a shift in the binding energy was



Scheme 5.1: Schematic representation of the mechanism for the H_2 evolution from water by Cu-mpTiO_2 photocatalyst.

observed. This ternary system ($\text{Cu}_2\text{O}/\text{Cu-mpTiO}_2$) follows the reaction pathway similar to that expected for a Z-scheme photocatalytic system. During the sunlight irradiation the electrons excited in Cu_2O are transferred to the E_{CB} of TiO_2 via Cu due to its lower Fermi level resulting in the reduction of H^+ [21] and at the same time holes produced in the E_{VB} oxidize CH_3OH to HCOOH , excess positively charged holes are also expected to oxidize few of Cu to Cu_2O in order to establish a balanced ternary system ($\text{Cu}_2\text{O}/\text{Cu-mpTiO}_2$). In summary, the Cu-mpTiO_2

mesoporous ternary structure is useful to suppress the charge recombination and also improves the interfacial electron transport resulting in the enhanced PHE.

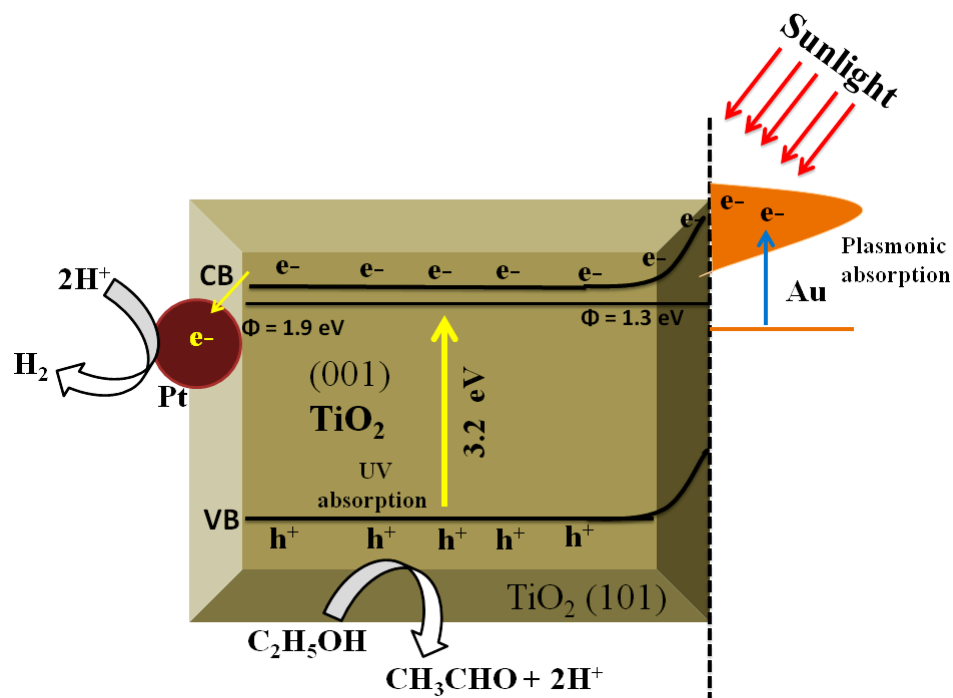
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CHAPTER 6

PHOTOCATALYTIC AND PHOTOELECTROCHEMICAL WATER SPLITTING BY THE (001) FACETED TiO_2 NANOSHEETS CO-DEPOSITED WITH Au AND Pt



Schematic Summary

Fabrication of (001) and (101) faceted TiO_2 and co-deposited with Au and Pt possessing brilliant morphological, structural and optical properties. The nanocomposite showed good photocurrent density and transient current under visible light due to SPR effect. Effective H_2 production by photocatalytic and photoelectrochemical water splitting was reported using ethanol as a hole scavenger.

6.1. Introduction

Numerous efforts have been made to change the morphology, shape, crystal design, surface area etc. of the titanium dioxide (TiO_2) in order to make it viable for the solar water splitting reaction [1-3]. Recently, the design and fabrication of specific faceted morphology have been commonly employed, the mechanism of this enhancement is due to suitable configuration and coordination of surface atoms which directly determines the efficiency of the metal or semiconductor photocatalysts [4, 5]. The vastly employed TiO_2 possesses several stable facets with variable activity, for example, the (001) facet of anatase phase is considered as more reactive compared to other facets including (101). Typically the anatase polymorph of TiO_2 is dominated with thermodynamically stable (101) facet but comparatively the surface energy of (101) facet (0.44 J/m^2) is very low then (001) facet (0.90 J/m^2) [6-8]. For this reason, the fabrication of controllable (001) faceted nanostructures with high surface energy is highly desirable for the enhancement of the rate of the photocatalytic hydrogen production.

Moreover, the TiO_2 is being treated as a promising photoactive material for the H_2 production from water due to its strong thermodynamic, electric and optical properties [9, 10]. But its photocatalytic activity is limited due to several well known reasons like fast recombination of excitons credited to defective crystalline structure, absorption in UV region due to higher band gap energy (3.2 eV) etc. [11, 12]. To resolve these problems in recent years, the design of highly energetic and reactive (001) facet in high percentage has attention [13]. Earlier reports [14, 15] have suggested that the surface energy of (001) facet is effective for the dissociative adsorption of reactant molecules and another reason is that in disparity to the most stable (101) facet, the (001) possesses 100 % Ti_{5c} surface atoms that is important for effectiveness in charge transport [16]. Other reports have suggested that the water molecules are able to physically absorb on (101) facet but can be chemically dissociated on (001) energetic surface resulting in higher photocatalytic efficiency of (001) facet [17-19].

Moreover, to sensitize TiO_2 in visible light the noble metal like Au loading has been preferred due to its characteristic surface plasmon resonance property [20, 21]. This enables TiO_2 to visible light active and also provides the co catalytic property. Other than plasmonic metals, Pt has also been extensively reported [22] as a suitable metal for water splitting reaction. The mechanism for its high reduction ability has been ascribed due to Schottky junction formation resulting in the increase of barrier height that directly reduces the electron hole recombination. Though Pt does

not absorb the visible light the co-deposition with Au and Pt on (001) faceted TiO_2 can be an effective strategy for the half reduction of water to produce H_2 .

In this regard, current study outlines the design and fabrication of high percentage (001) faceted TiO_2 nanosheets and followed by the photodeposition of Au and Pt. This nanostructure is proposed to be effective for water splitting reaction under direct sunlight. In this study, the role of Pt and Au loading, sacrificial reagents, sunlight intensity and surface area and was investigated with good results in overall water splitting reaction. The photoelectrochemical performance was also analyzed using a conventional PEC cell.

6.2: Experimental section

6.2.1: Chemicals and reagents

Titanium Butoxide, ($\text{Ti}(\text{OBu})_4$, 98%, Sigma Aldrich), Hydrogen Flouride (HF, 43%, Aventor Performance Materials Ltd.), chloroauric acid (HAuCl_4 , 49%, Sigma Aldrich), platinum chloride ($\text{H}_2\text{PtCl}_5 \cdot x\text{H}_2\text{O}$, 48%, Loba Chemie Ltd.), methanol, ethanol, propanol, butanol, pentanol, hexanol (98-99%, SD Fine Chemicals Ltd.) were used as received without any further purification. The deionized water used throughout the experiment was obtained from the Milipore ultrafiltration system with a conductivity of 40 mho cm^{-1} at 30°C .

6.2.2: Fabrication of TiO_2 nanosheets (TNST) with larger percentage of (001) facets and photodeposition of Au and Pt

The fabrication of TNST was done by using the $\text{Ti}(\text{OBu})_4$ as a precursor of TiO_2 , in a typical procedure 20 mL of $\text{Ti}(\text{OBu})_4$ and 3.2 mL of HF solutions were mixed directly in a Teflon lined autoclave (80 mL). The solution was kept at 200°C for 24 h. The solution was cooled at room temperature and the precipitate of as fabricated TNST was separated by high speed (8000 rpm) centrifugation and washed several times with distilled water and ethanol. The synthesis of TiO_2 nanosheets took place in two steps (i) Dissolution of titanium butoxide (ii) Recrystallization of TiO_2 . HF has a key role in the dissolution of $\text{Ti}(\text{OCH}_3)_4$ to form TiF_6^- that helps in the formation of TiO_2 nanosheets.

The photodeposition of variable weight percent ratios (wt %) of Au and Pt was done by a modified method reported earlier [23]. In a typical experiment, 100 mg of TNST powder was dispersed in a mixture containing isopropyl alcohol and water in 1:1 ratio. The respective amount of HAuCl_4 (0.01 mmol L^{-1}) and H_2PtCl_5 (0.01 mmol L^{-1}) corresponding to different weight ratio was added to the TNST dispersion and purged with Ar for 15 minutes. The sealed reaction tube

was irradiated under UV (125 mW) for 4 h. The photo-deposited TNST powder was separated, washed by DI water and ethanol under several cycles of centrifugation. The subscript in the symbols of Au and Pt represents the wt% of the respective metals loaded on TNST.

6.2.3: Characterization and photocatalytic activity

The characterization of the photocatalysts was done by the technique discussed in chapter 1 (Section 1.4). The photocatalytic activity was performed in a Pyrex reaction tube (20 mL) containing the reaction mixture and sacrificial agent (water: sacrificial agent, 4:1) and optimized 0.020 g of the photocatalyst. The reaction mixture was purged with Ar (10 min) to create an inert atmosphere for photoreduction followed by direct sunlight irradiation (average intensity 430 Wm^{-2}) for different time intervals under continuous stirring.

The quantification of the gas produced during the reaction was done by gas chromatography (GC, Nucon, India) attached with a thermal conductivity detector. The column used for the same is molecular sieve (5X A). The temperature of the injector, oven, and detector was programmed at 30°C each. The quantification of the gas produced during the reaction was done using a 180 ppm standard of N_2 balanced H_2 provided by Sigma gases New Delhi India.

6.2.4: Electrochemical characterization:

Cyclic voltammetric (CV) and impedance behavior of the materials was studied by coating 10 μL of TNST, Au/TNST, Pt/TNST and Au/Pt-TNST (5 mg/mL) on a glassy carbon working electrode, which was air dried. Platinum (Pt) and Ag/AgCl were used as counter and reference electrodes whereas 5 mM ferri/ferro containing 0.1 M KCl was used as redox electrolyte. Impedance spectra were recorded with frequency response analyzer at open circuit potential in the 0.1 to 10^5 frequency range under 10 mV ac perturbation signal. The obtained Nyquist plot was analysed with Z_{view} software to fit equivalent circuit. A solar simulator equipped with 300 W Xe lamp and AM 1.5 filter was used as light source and the intensity of the source was calibrated and controlled at 100 mW/cm^2 . Photo-electrochemical (PEC) experiments were performed in three electrode configuration, where TNST, Au/TNST, Pt/TNST and Au/Pt-TNST coated ITO was used as a working electrode in isolated experiments. The PEC chamber was air cooled, keeping the electrolyte temperature at 25°C and purged with nitrogen to remove dissolved oxygen. Linear sweep voltammeter (LSV) measurements were recorded at a scan rate of 10 mV/s in the dark and light experiments in 0.1 M NaOH.

6.3: Results and discussion

6.3.1: Morphological, structural and surface properties

The optimization of the photocatalysts suggested the 0.4 wt% of Au and 0.75 wt% of Pt ($\text{Au}_{0.4}/\text{Pt}_{0.75}$ -TNST) as an optimum amount for the efficient photoactivity. The HRTEM micrographs (**Fig. 6.1**) of as synthesized TNST and $\text{Au}_{0.4}/\text{Pt}_{0.75}$ -TNST consists of well defined sheet type and a uniform rectangular morphology. The side view of the TEM micrograph shows the lattice spacing of 0.34 nm and horizontally the 0.23 nm lattice spacing observed was corresponding to (101) and (001) facets of anatase TiO_2 . The presence of (001) is confirmed by the observed plane along the particle surface, study by XRD also confirms the presence of broad (004) plane which is a direct evidence for the presence of (001) facet. The other observed lattice spacing of 0.14 nm and 0.12 nm is credited to the Au and Pt respectively. The average length x breadth of the as synthesized nanosheets has been observed to be 55 nm x 46 nm (this calculation was done manually by taking 20 particles in counting, ignoring the interference of fewer larger particles).

The XRD patterns of the TNST, Au-TNST, Pt-TNST and Au/Pt-TNST (**Fig. 6.2**) showed several diffraction peaks at 25.4° , 37.8° , 48.0° , 55.2° and 62.8° indexed to (101), (004), (200), (105) and (116) planes of anatase TiO_2 (JCPDS card No. 73-1764). The increases in the diffraction peak of

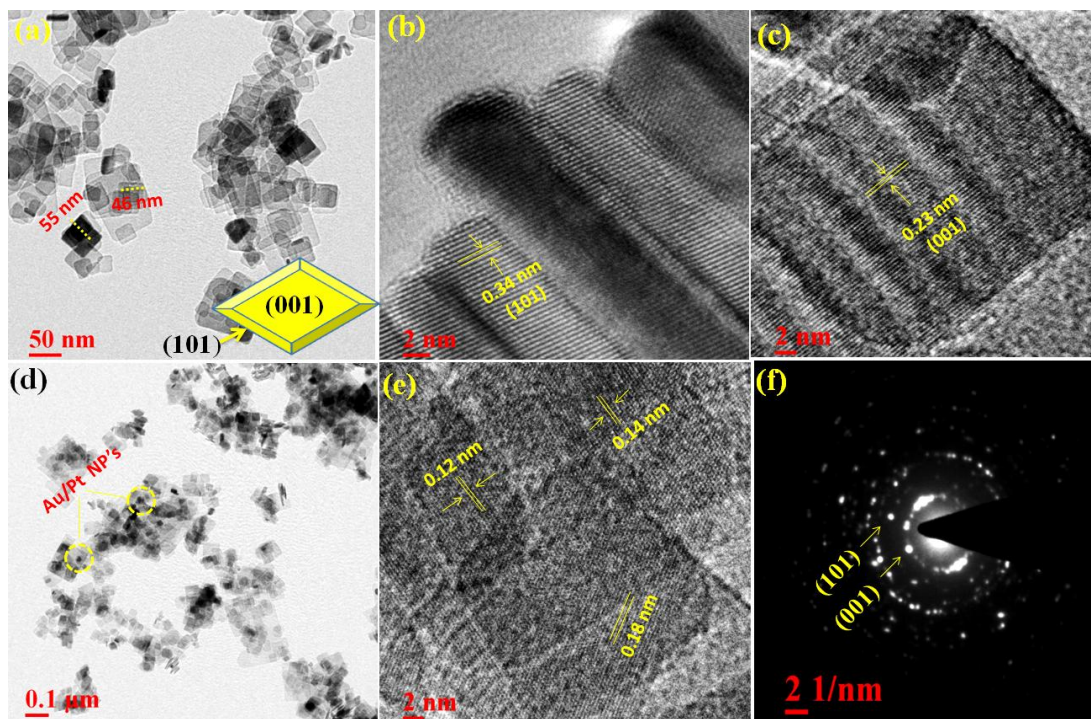


Fig. 6.1: The HRTEM micrographs of (a-c) TNST (d-e) $\text{Au}_{0.4}/\text{Pt}_{0.75}$ -TNST (f) SAED pattern of $\text{Au}_{0.4}/\text{Pt}_{0.75}$ -TNST.

(101) indicates the growth of TiO_2 at 200 °C, the peak of (004) plane suggests the presence of (001) facets as favored by earlier report [24], the value of structural factor for TiO_2 is zero disabling the presence of (001) peak. The sharpness of (101) peak and slight broadness of (004) is due to preferred exposure of respective planes after the removal of F^- by washing. The EDS studies confirm the absence of any traces of F^- . No separate diffraction peaks were observed in case of Au-TNST, Pt-TNST or Au/Pt-TNST ascribed to the lower content and larger diffraction angle (5° min^{-1}) for the analysis. The (001) plane is absent from the XRD pattern because the structure factor for the tetragonal body centered unit cell is zero.

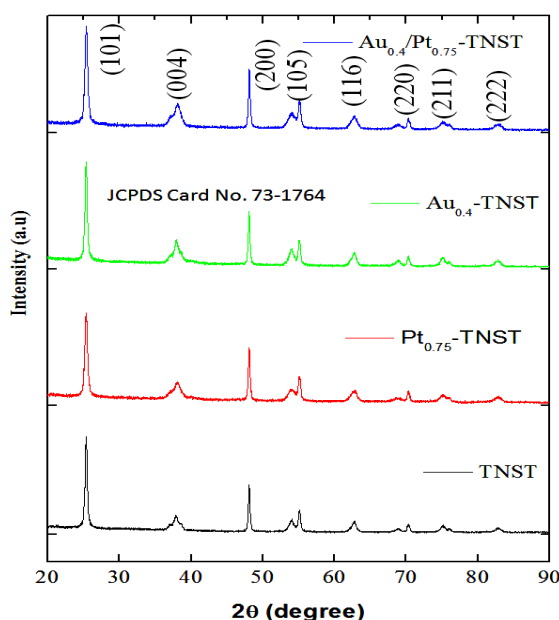


Fig. 6.2: X ray diffraction pattern of the photocatalysts .

Raman spectroscopy is usually used to determine the percentage of (001) facets, It can be noticed in the Raman spectra (**Fig. 6.3**) that as the exposure of (001) facets increases, the intensity of E_g peak reduces gradually, while the intensity of B_{1g} peak and A_{1g} peak increases. Basically E_g peak mainly originates due to the stretching vibration of O–Ti–O while as the B_{1g} peak is due to the symmetric bending vibration of O–Ti–O similarly A_{1g} peak is mainly due to antisymmetric bending vibration of O–Ti–O. As the percentage of exposed (001) facets increases the less number of stretching vibration modes of O–Ti–O are observed, and consequently the intensity of E_g peak decreases. On the other hand, when the exposed (001) facets lower the number of symmetric bending vibrations and the antisymmetric bending vibrations of O–Ti–O increases.

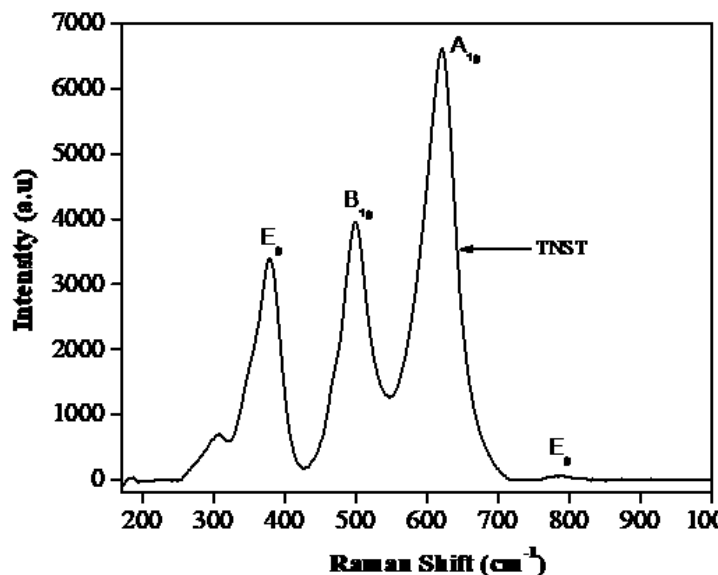


Fig. 6.3: Raman spectra of TNST photocatalyst.

The surface area depicted by Brunauer-Emmett-Teller (BET) analysis (**Fig. 6.4**) via N₂ adsorption-desorption method at cryogenic temperature revealed that the photocatalysts are mesoporous and multilayered in nature as witnessed by typical type IV Langmuir adsorption isotherms [25]. There was no larger variation observed in the specific surface area of the photocatalysts after metal loading, it was observed that TNST possesses 69.0 m²g⁻¹ of the surface area which got increased to 81.8 m²g⁻¹ for Au_{0.4}/Pt_{0.75}-TNST nanostructure, the increase in the surface area shows that both Au and Pt are deposited on the surface of TNST. In case of pore structure determined by the BJH curve method (**Fig. 6.5**), it was observed that the Au/Pt-TNST has got a smooth pore structure compared to bare Au-TNST and Pt-TNST.

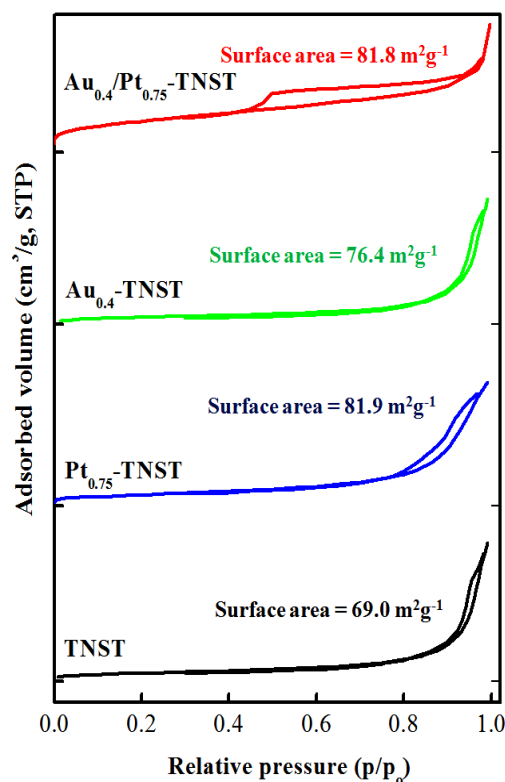


Fig. 6.4: The N₂ Adsorption-desorption curves of different photocatalysts.

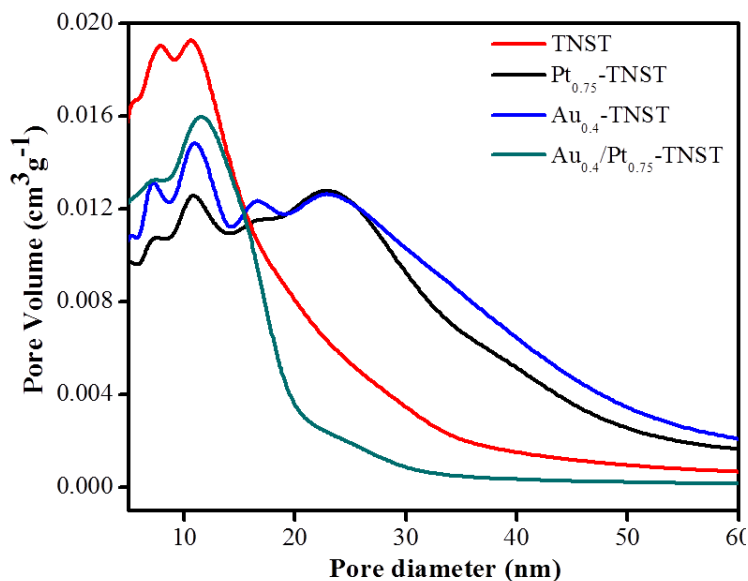


Fig. 6. 5: Barrett-Joyner-Halenda (BJH) curves of the different photocatalysts.

6.3.2: XPS and optical characteristics

The XPS analysis of the Au/Pt-TNST was done to reveal the surface composition and oxidation state of the elements. The survey spectra showed the presence of expected elements like Ti, O, Pt and Au (**Fig. 6.6**). Moreover, the deconvoluted spectra (**Fig. 6.7**) reveal the typical binding energy values at 459 eV and 464 eV for Ti 2p assigned to Ti^{+4} oxidation state with spin quantum state of $2p_{3/2}$ and $2p_{1/2}$ respectively, while a small peak was observed at 458.3 eV is ascribed to fewer Ti^{+3} species present in the same mixture. The fitted spectra of O1s also show two peaks at 530.3 eV and 531.3 eV credited to the interaction of oxygen with TiO_2 and H_2O respectively [26]. In case of Au two separate peaks were observed at 83.0 eV and 87.5 eV respectively credited to $4f_{5/2}$ and $4f_{7/2}$ spin states of Au^0 , similarly, in case of Pt, two smoothly fitted peaks at 70.5 eV and 73.9 eV are due to the presence of metallic Pt^0 [27].

The optical absorption spectra of different

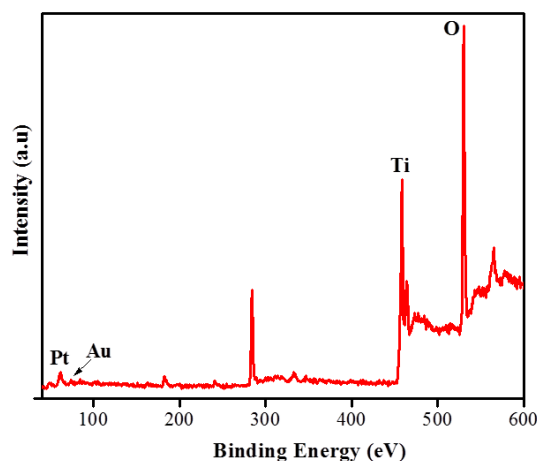


Fig. 6. 6: X-ray photon (XPS) survey spectra of $\text{Au}_{0.4}/\text{Pt}_{0.75}$ -TNST photocatalyst.

photocatalysts are presented in **Fig. 6.8**, it was observed that after metal loading there was no shift observed in the typical absorption edge of TNST (377-396 nm) due to the rectangular uniform geometry, while after the metal loading i.e., Pt and Au separately, a strong absorption maximum was observed at 577 nm due to the coherent oscillation of surface electrons with the matching incoming frequency or surface plasmon resonance (SPR) effect [28], while a no such property is revealed by Pt. Moreover, it was also observed that with the increase in the amount of Au the intensity of SPR band also increased, the little shift observed after increasing the amount of Au due to the influence and little variation of particle size.

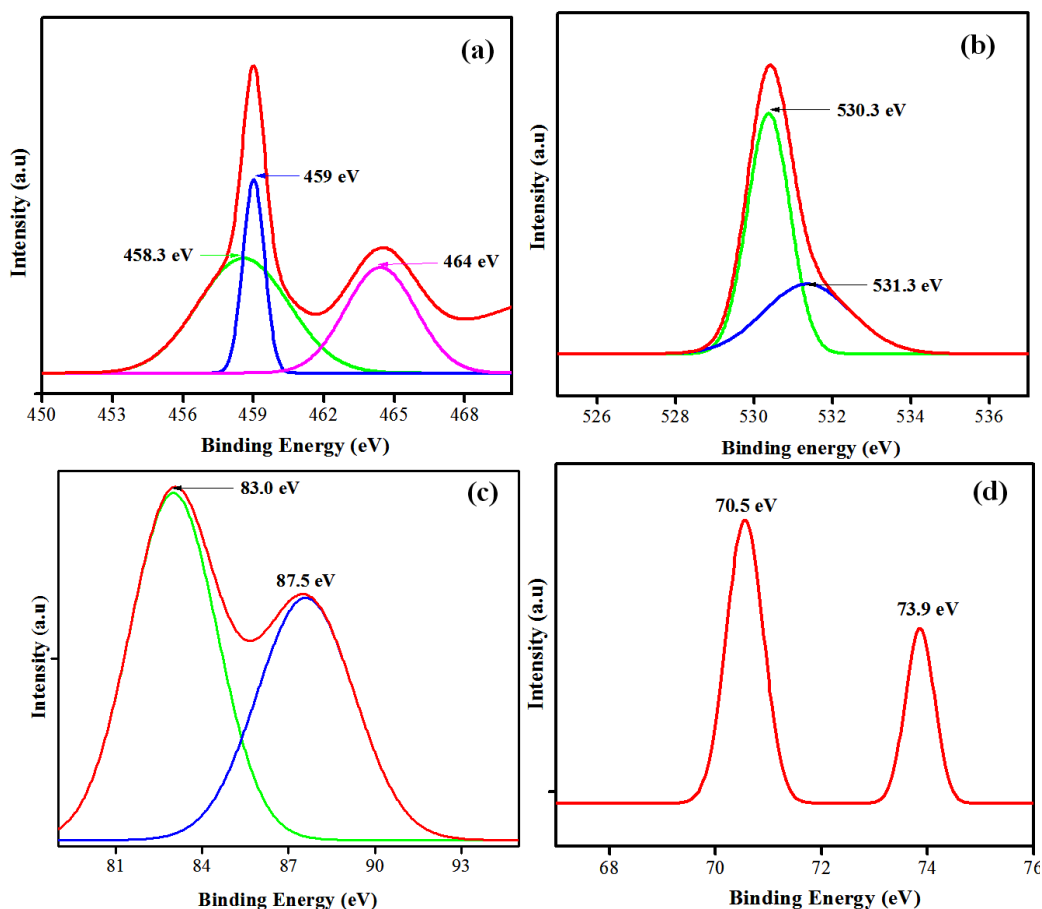


Fig. 6.7: Deconvoluted XPS spectra of $\text{Au}_{0.4}/\text{Pt}_{0.75}$ -TNST (a) Ti 2p (b) O 1s (c) Au 4f (d) Pt 4f.

6.3.3: Electrochemical and photoelectrochemical (PEC) studies

The **Fig. 6.9** (a-c) are associated with CV characteristic of TNST, Au/TNST, Pt/TNST and Au_{0.4}/Pt_{0.75}-TNST modified GC electrodes in Fe (CN)₆^{3-/4-} redox system. The Fe (CN)₆^{3-/4-} redox probe is used to characterize the fabricated modified electrodes owing to the dependence of their voltammetric characteristic on electrode/electrolyte surface interface. The changes in the peak current and separation of peaks of electrodes can be related to the electron transfer rate constant of the modified electrodes.

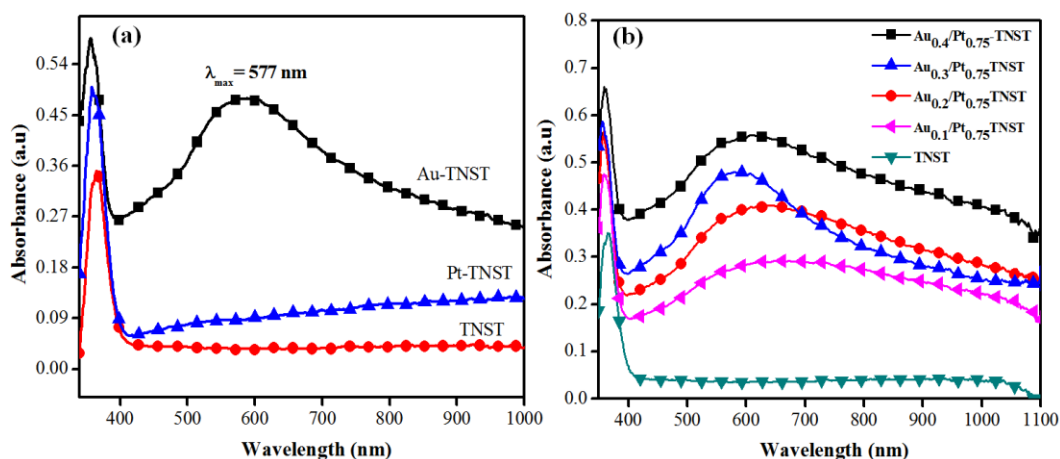


Fig. 6. 8: Optical absorption spectra of the (a) as synthesized photocatalysts (b) Effect of Au loading on SPR absorption.

It can be observed from **Fig. 6.9** (a), the anodic and cathodic peak current density associated with redox process of Fe²⁺/Fe³⁺ species, the peak current I_{pa} and I_{pc} , increases with loading of Au and Pt onto TNST (inset Fig. 6.7(a)), wherein the Au/Pt-TNST modified electrodes showed 8 % enhanced current characteristic than TNST electrodes (inset Fig. 6.7 (a)). This could be assigned to a conductive characteristic of Au NPs as well as catalytic properties of Pt loaded onto TiO₂ nanosheets. Further, the ratio of peak current, i_a/i_c is calculated to be ~ 1 for Au_{0.4}/Pt_{0.75}-TNST electrode surface indicating a nearly reversible oxidation/reduction process of the Fe²⁺/Fe³⁺ species . The capacitance, faradic current and formal potential were found to be 3.73 mF, 3.73×10^{-5} , 0.26 V, respectively. The number of electrons involved in an electrochemical reaction for a redox mediated is calculated via $\Delta E = 0.059/n$, where ΔE is the peak to peak separation and is found 0.53. The diffusion coefficient for the charge carriers was calculated to be 1.44×10^{-12} cm²/sec using Randles–Sevcik equation for Au_{0.4}/Pt_{0.75}-TNST modified electrodes [29]. The effect of scan rate on the electrochemical characteristic of Au_{0.4}/Pt_{0.75}-TNST modified electrode

was studied by recording CV as a function of scan rate (10-100 mV/sec), shown in Fig 6.9 (b). It is observed that redox peak current (I_{pc} & I_{pa}) increases linearly with the square root of scan rate ($v^{1/2}$) for the Fe^{2+}/Fe^{3+} system (Fig. 6.9(c)) indicating a diffusion controlled process [30, 31]. The slopes and intercepts can be estimated using equation 1 for anodic peak current:

$$i_{pa} = 9.39 \times 10^{-6} \times v^{1/2} + 1.3 \times 10^{-5} \dots \dots (1)$$

The current coefficient ($i_{pa}/v^{1/2}$), which is another indicator for reversible electron transfer has also been found constant at different scan rate ($10.5 \times 10^{-6} \text{ AmV}^{-1/2} \text{ sec}^{1/2}$) for $Au_{0.4}/Pt_{0.75}$ -TNST modified electrode, which clearly reveals that electron transfer at these electrodes is fast enough to maintain the equilibrium ratio between oxidized and reduced species of redox couple [32]. Likewise, impedance analysis of all the fabricated electrode in the studied frequency range also supported the cyclic voltammetric results. In impedance analysis, Nyquist plot presents the imaginary part of the impedance as a function of its real part. Further, the value of the charge

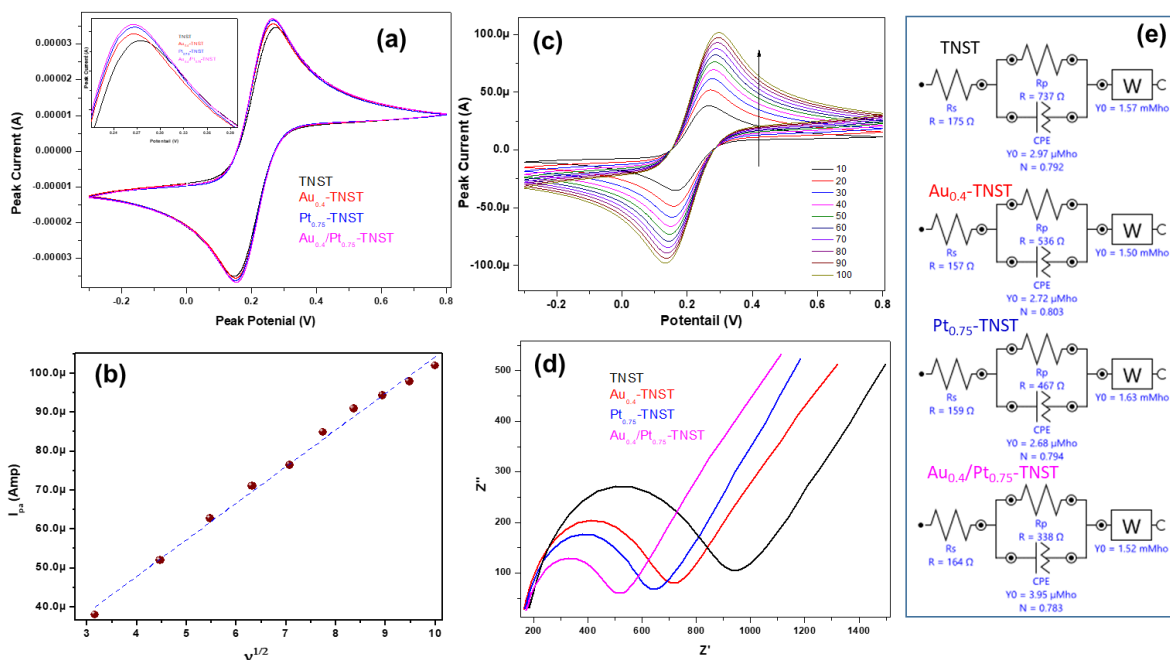


Fig. 6. 9: Electrochemical properties of the as prepared photocatalysts.

transfer resistance (R_p) depends on the dielectric and insulating features at the electrode/electrolyte interface. It is found from Fig 6.7 (d) & (e) that R_p value obtained for TNST modified electrodes equivalent circuit is 737Ω , which is reduced to 536Ω , 467Ω and 338Ω for

Au/TNST, Pt/TNST and Au_{0.4}/Pt_{0.75}-TNST modified electrodes, respectively, which could be again understood in terms of excellent electron transfer channelization due to presence of conductive Au and catalytic Pt in TNST sheets. The electrochemical characterization therefore revealed the potential of Au_{0.4}/Pt_{0.75}-TNST material as an excellent electroactive and charge carrier, which is a required characteristic for a photocatalytic and photo-electrochemical activity. The PEC performance of fabricated photoanodes were first investigated by linear sweep voltammetry (LSV) under dark and white light illumination conditions at a scan rate of 10 mV s⁻¹ and is shown in **Fig. 6.10**. In the dark, the current is negligible in the potential range from -0.6 to 0.65 V. Under illumination the current increases to 2 mA at 0.5 V and reaches 4.5 mA at 0.65 V for Au/Pt/TNST photo electrodes, which otherwise is 1.24 mA, 0.56 mA and 0.15 mA for Pt/TNST, Au/TNST and TNST photo electrodes, respectively. The photocurrent for Au_{0.4}/Pt_{0.75}-TNST is 30 fold higher than TNST alone and could be catalyzed by the presence of Au and Pt as observed from the photocurrent associated with them and electrochemical characterizations discussed earlier. The onset potential for photoanode Au_{0.4}/Pt_{0.75}-TNST is observed to be -0.35 V. The photocurrent versus time (I-t) properties for an externally applied bias of 0.5 V versus the Pt counter electrode for both photoanodes with 50 sec. light on/off cycles are shown in **Fig. 6.10** (b). Under dark condition, the fabricated photo electrodes (PEs) show a negligible current response, while upon illumination, the photocurrent increases rapidly and reaches steady state values. It can be concluded very clearly that Au_{0.4}/Pt_{0.75}-TNST PEs exhibit very good photo-switching performance over other PEs.

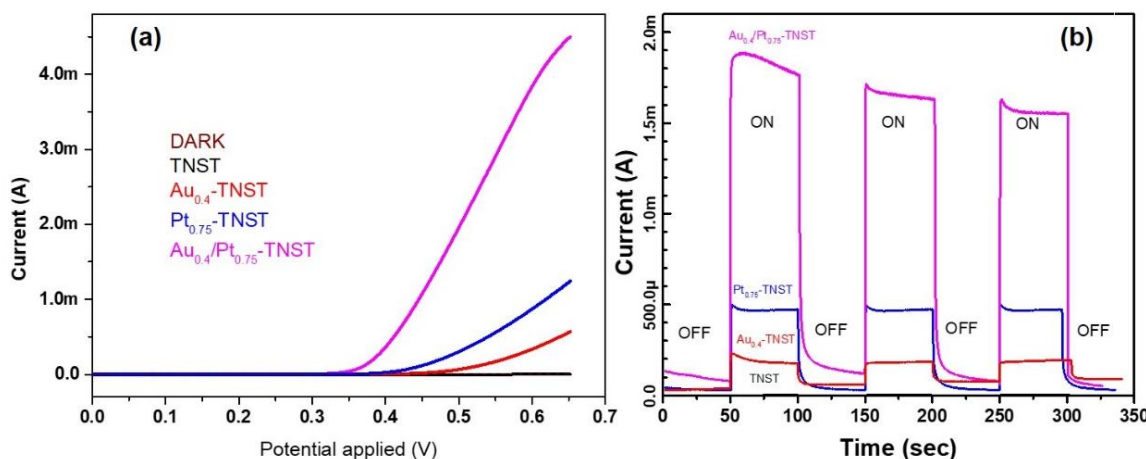


Fig. 6. 10: Photoelectrochemical properties of the different photocatalysts.

6.3.4: Photocatalytic activity for the hydrogen production under direct sunlight

Several controlled experiments were carried to optimize the reaction parameters before studying the overall photocatalytic activity for water splitting. Dark and photochemical (without catalyst) experiments were carried showing no response to the H_2 evolution. Similarly, before the fabrication of Au/Pt-TNST, the amounts of Au and Pt for loading on TNST were optimized using ethanol as a sacrificial reagent. As shown in **Fig. 6.11(a)** with the increase in Au content from 0.1 wt% to 0.4 wt% the rate of H_2 evolution increases and it was observed that $Au_{0.4}$ -TNST produced $\sim 200 \mu\text{mol}$ of gas after 8 h sunlight irradiation, this amount was fixed as the optimum

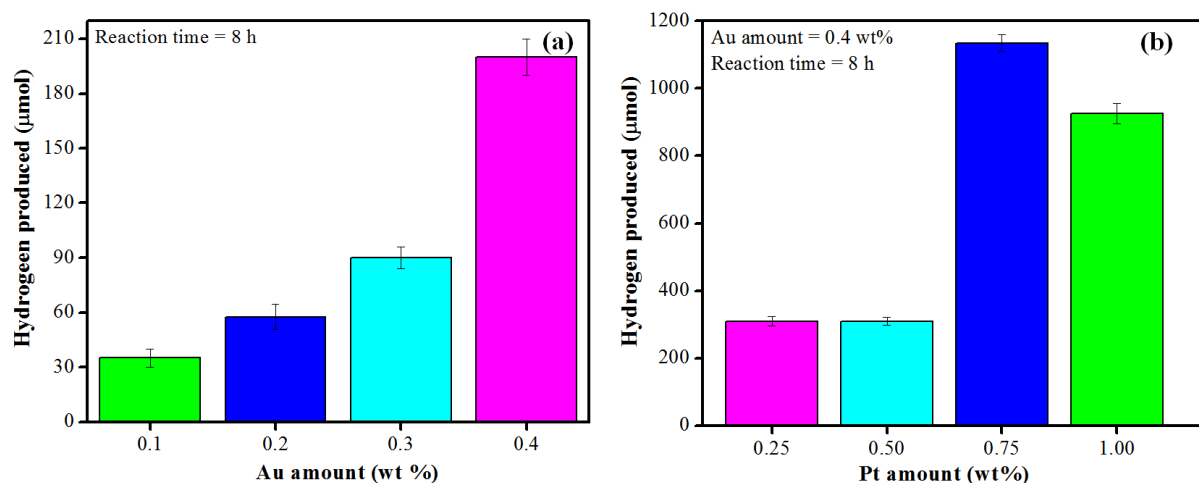


Fig. 6.11: Optimization of metal loading for the hydrogen production (a) Au content (b) Keeping Au content constant and varying Pt content.

amount followed by loading of different weight ratios of Pt that showed some interesting results, With the increase in Pt content from 0.25 to 0.75 wt% the H_2 evolution increases and when the amount of Pt was increased further to 1wt% a decrease was observed in overall hydrogen production due to overcrowding of active sites leading to recombination of charge carriers. So, it has been concluded that the optimized amount of Au and Pt is 0.4 wt% and 0.75wt% respectively ($Au_{0.4}/Pt_{0.75}$ -TNST), this ratio was used for the study of overall hydrogen production activity. The expected ratio was further confirmed by the EDS analysis (**Fig. 6.12**) showing the overall loading amount of 0.68 wt% for Pt and 0.47 wt% for Au, the little variation from the theoretical ratio is due to the selective portion analysis on EDS grid.

As shown in Fig. 6.13 the role of different alcohols as sacrificial agents have been studied for the half reduction of water splitting reaction. It has been observed that with the increase in hydrocarbon chain length, the rate of H₂ evolution decreases. Under the direct sunlight irradiation for continuous 8 h,

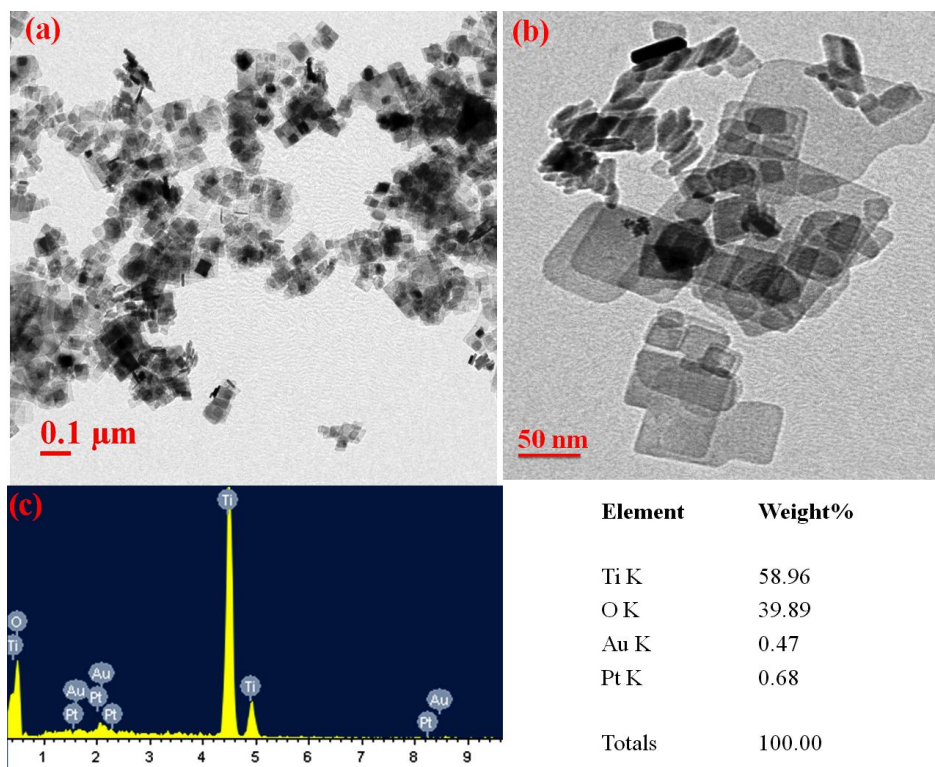


Fig. 6.12: The HRTEM micrographs with EDS analysis.

the highest amount of H₂ evolution of ~1150 μmol was observed in case of C₂H₅OH:H₂O mixture (1:4) followed by prop-1-ol (~550 μmol), prop-2-ol (~325 μmol) and methanol (~212 μmol) while lesser amount was observed in larger hydrocarbon chain alcohols like butanol, pentanol, and hexanol. The reason for the variation in photocatalytic activity is credited to the polarity and miscibility of the alcohols with water [33], the higher H₂ evolution in ethanol: water mixture is due to its strong miscibility and comparable polarity with water.

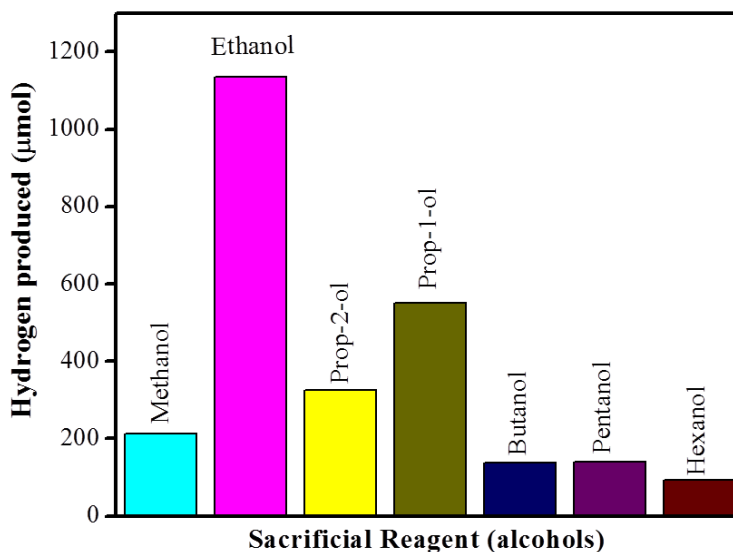


Fig. 6.13: Effect of different sacrificial reagents (alcohols) for the hydrogen production using Au_{0.4}/Pt_{0.75}-TNST photocatalyst.

The overall photocatalytic activity for the H₂ evolution of the different photocatalysts is presented in **Fig. 6.14(a)**, taking into account the with the optimized conditions it was observed that under the direct sunlight irradiation small amount of H₂ was observed in case of TNST due to its non viable band potential for activation under sunlight and fast recombination of charge carriers. After the monometallic loading with Au and Pt there was an abrupt increase in H₂ evolution, ~950 μmol of gas was detected in Pt_{0.75}-TNST followed by ~200 μmol by Au_{0.40}-TNST. The highest amount of ~1150 μmol was detected in case of co-deposited Au_{0.40}/Pt_{0.75}-TNST nanocomposite showing its better performance compared to monometallics. Moreover, the time course study (**Fig. 6.14(b)**) depicted an exponential increase in the hydrogen production up to 8 h the kinetic study showed the average ~143 μmolh^{-1} of H₂ evolution. Furthermore, the rate of H₂ evolution with respect to the surface area was also calculated and the highest amount of H₂ (m^{-1}) evolution was also observed in case of Au_{0.4}/Pt_{0.75}-TNST (**Fig. 6.15**).

Based on the results obtained a mechanism for the H₂ evolution from water using alcohols as sacrificial reagents is shown in **Scheme 6.1**. The H₂ evolution on the (001) facets was witnessed to be effective due to its high surface energy value (0.90 J/m²). After irradiation under sunlight, the two possible excitations took place, the activation of Au due to its strong SPR response and another is on the surface of TNST where electrons are excited to its conduction band (CB) leaving behind the positively charged holes. This is followed by the charge separation due to the formation of a Schottky barrier between Au and TNST, these excited electrons are transported towards Pt which acts as a storage unit for the reduction of water molecules. As reported earlier, the Schottky barrier height for this type of both metals lays between 1.3 eV (Au) and 1.9 eV (Pt) [34, 35] when the metals are present on TiO₂ surface, Fermi level equilibration took place in the nanostructure due to the photodeposition of both the metals making the SPR state of Au, E_{CB} of TNST and Fermi level of Pt electronically equilibrated making the charge transfer and separation easier at the interface [36]. The holes produced during the photoexcitation are quenched by the sacrificial reagent (alcohols) and itself gets oxidized to respective carbonyl or carboxyl species [37] that indirectly supports the overall H₂ production, we have previously also reported [25] the indirect role of sacrificial reagent for H₂ evolution via formation of some oxidized intermediates. So, the combination of Au, Pt co deposited TiO₂ with a high percentage of (001) facets show a brilliant performance for the H₂ production from water.

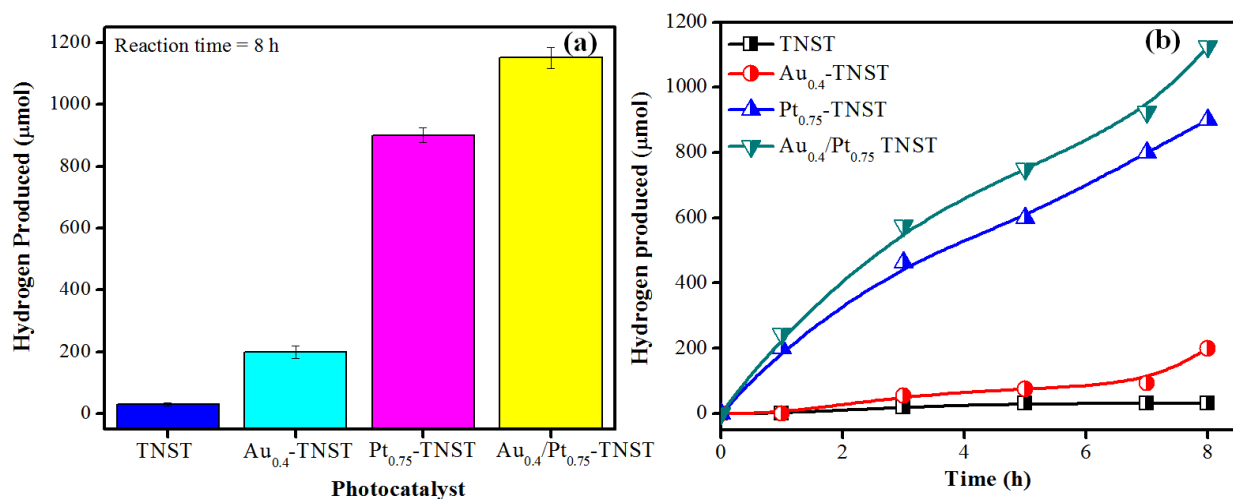


Fig. 6. 14: The photocatalytic activity (a) Different photocatalysts for hydrogen production under direct sunlight (b) Time course study of H_2 evolution

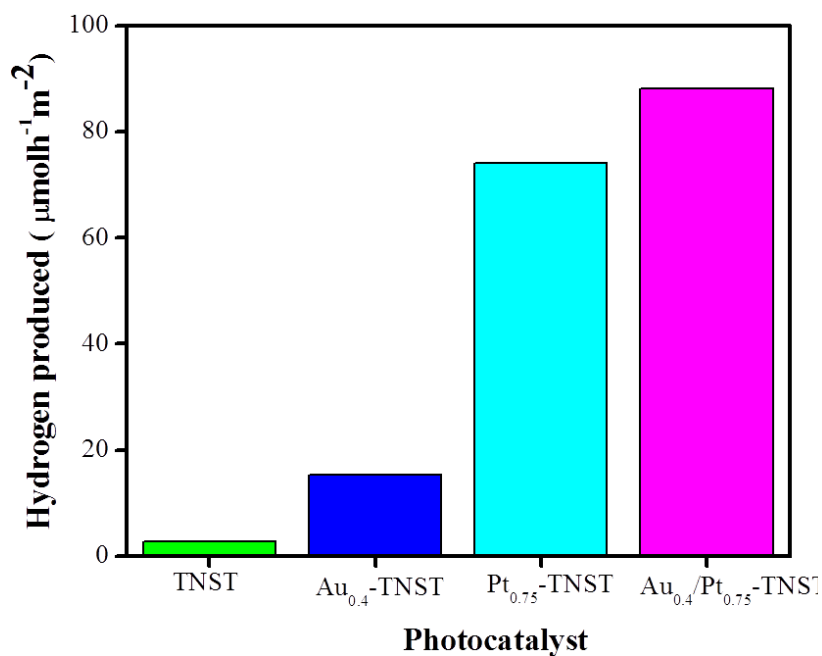
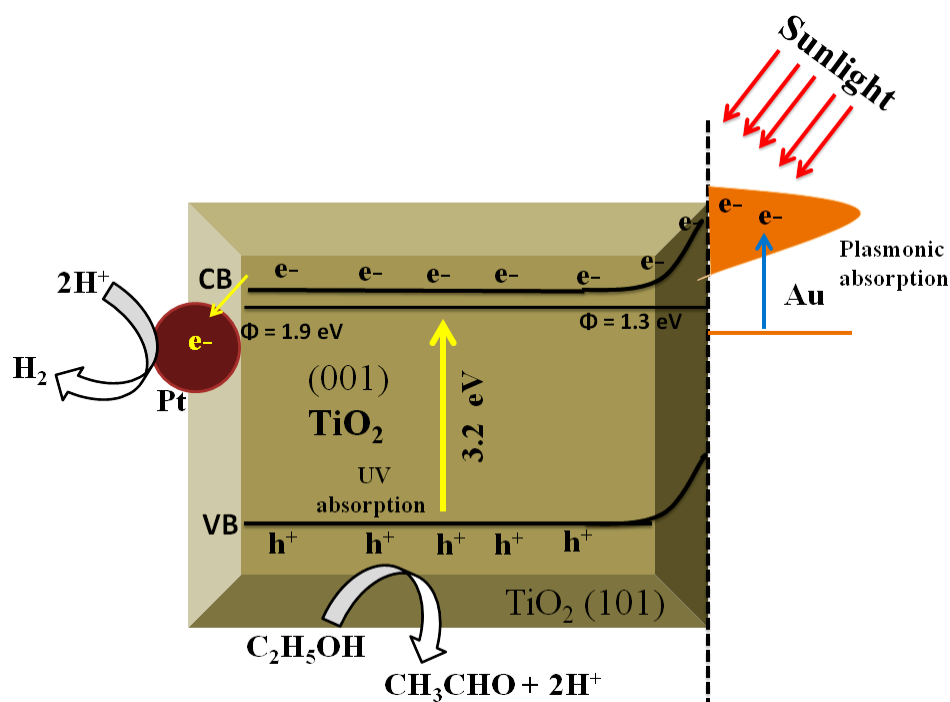


Fig. 6.15: The calculated H_2 produced vs specific surface area.



Scheme 6.1: Plausible mechanism of hydrogen production using Au/Pt-TNST nanostructure under direct sunlight irradiation.

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CONCLUSIONS AND FUTURE OUTLOOK

Chapter 1: Covers the brief background, basis and mechanism of water splitting reaction. The role of semiconductors in general and TiO_2 in specific for the photocatalytic water splitting has been elaborated in terms of recent research accounts published on this subject. The effect and role of nanosize, crystal design, morphology, metal loading, heterocomposite formation and sacrificial reagents for the water-splitting reaction has been briefly discussed.

Furthermore, the detailed accounts of the techniques used for the characterization of nanocatalysts like Optical absorption spectroscopy, X-ray diffraction, electron microscopy, Brunauer-Emmet-Teller (BET) analysis, Gas chromatography, etc. has been presented in detail. The procedures for the overall photocatalytic activity both by powder method and photoelectrochemical (PEC) method have been presented.

Chapter 2: Describes the microwave assisted synthesis of TiO_2 nanoparticles followed by its fabrication into a graphene oxide coated and Au deposited core-shell nanocomposite ($\text{Au-TiO}_2@\text{GO}$). The $\text{Au-TiO}_2@\text{GO}$ nanocomposite has been used successfully for the hydrogen production from water under different light irradiation sources. The Au loading boosts the visible light response of TiO_2 whereas GO shell delays the recombination of charge carriers (e^-/h^+). Further, GO acts as a reservoir to store and transport the electrons on its surface thereby helping in reduction of H^+ from water to produce H_2 . During the time course, oxygen evolution was in trace quantities, as a future perspective, the rate of oxygen evolution can be improved towards quantitatively balanced water splitting reaction.

Chapter 3: This chapter discloses that the morphology and surface plasmon resonance (SPR) effect of Ag- TiO_2 as the decisive factors for the enhancement of H_2 production from water. The rice grain shaped TiO_2 nanorods were synthesized by the hydrothermal method. The plasmonic frequency was found to be effective for the interfacial electron transfer from Ag to E_{CB} of TiO_2 , thereby altering several physicochemical and interfacial properties like fluorescence, current density and enhanced the rate of reaction. It was found that total illumination area of the reactor is also responsible for the effective H_2 production. The experimental evidence and results were in compliance with the objectives set for this study.

Chapter 4: In this chapter, the procedures for the synthesis and application of an Au-TiO₂ heterocomposite embedded in a thin layer of graphitic C₃N₄ has been elaborated. In summary, the C₃N₄ surface passivated Au-TiO₂ tubular nanostructure was found active in direct solar light for the efficient H₂ production from half water splitting reaction. The embedment of TiO₂ (nanotubes, NT) by a thin monolayer C₃N₄ causes the heterogeneous nucleation and the simultaneous Au loading resulted in the formation of an efficient sunlight activated nanocomposite (NC). The Au sensitizes the NC and also shows some co-catalytic activity. Sunlight activates both the C₃N₄ and Au and the formation of non ohmic heterojunction helps in the electron transfer along C₃N₄/Au-TiO₂ interface, simultaneously due to more negative reduction potential of C₃N₄ (E_{CB}), electrons are transferred to E_{CB} of TiO₂ (NT) resulting in the efficient charge separation with a remarkable photocatalytic H₂ evolution.

Chapter 5: In summary, this chapter elaborates the fabrication of a Cu₂O/Cu based ternary TiO₂ hybrid. The role of a photostable mesoporous Cu-mpTiO₂ nanocomposite for the efficient hydrogen evolution from the water. It is revealed that the efficiency of Cu-mpTiO₂ can be enhanced on the basis of the presence of a balanced amount of co-catalysts (Cu and Cu₂O). The Cu₂O is capable of harvesting sunlight while as Cu helps for the transport of excited electrons towards E_{CB} of TiO₂. Moreover, specific surface area, pore distribution, and oxidation state are found to have a profound effect on overall photocatalytic activity. The formation of an efficient p-n junction between Cu₂O and TiO₂ and the role of Cu⁰ as an electron bridge gives a novelty for water photodecomposition.

Chapter 6: This chapter presents the synthesis of (001) faceted TiO₂ nanosheets and its co-deposited composite with Au and Pt. These as prepared Au/Pt-TiO₂ nanosheets were utilized as a brilliant photocatalyst for the photocatalytic and photoelectrochemical H₂ production from water. The optimized Au_{0.4}/Pt_{0.75}-TNST exhibited good optoelectronic and surface properties; moreover it also showed a brilliant PEC performance. The Au helped in TiO₂ activation not only as a sensitizer due to SPR effect but also by acting as a co-catalyst, the Pt helped in the formation of certain reduction sites for transporting, separating and storing the excited electrons. The nanocatalyst proved efficient under direct sunlight for the H₂ evolution making it desirable for further analysis and application.

In summary, the work done in this thesis demonstrates some viable strategies for the modification of TiO_2 based materials in order to improve the efficiency of photocatalytic water splitting reaction. Here, it has been demonstrated that the photocatalytic efficiency of titania can be improved by modifying it into elongated, tubular or core-shell design. In order to sensitize TiO_2 in sunlight or visible light the heterocomposites with the coinage metals and some small bandgap semiconductors like Cu_2O and C_3N_4 has been studied in detail. These plasmonic metals and low bandgap semiconductors not only improved the lifetime of the charge carriers but also greatly activated TiO_2 in direct sunlight resulting in higher photocatalytic efficiency. Though the results obtained were good but the improvement is needed in terms of following points as an extension of this research work.

In this thesis with the help of differently modified nanocomposites like Cu-mptiO_2 , $\text{C}_3\text{N}_4\text{-Au-TiO}_2$ etc we have performed half reduction reaction of water splitting by using hole scavengers, so as an extension to this research we need to develop a photocatalyst for overall water splitting that can be capable of producing H_2 and O_2 separately. Although in a couple of reaction we have reported the evolution of oxygen and people have done this before by photoelectrochemical means using the nefion proton exchanger, but the stoichiometry and lifetime and cost of proton exchangers is still a hurdle. So, designing a photocatalyst that can work similar to the natural photosynthesis of plants can prove efficient by using some oxygen evolving catalysts and hydrogen evolution catalyst and their shape variation in a z schematic manner will be interesting. Another aspect is that during this thesis work we have mainly employed the (101) phase dominated anatase polymorph of Titania and in some cases also altered its shape to rods and tubes. The work needs an extension in terms of the development of one dimensional energetic and single faceted morphology of titania and simultaneously we need to change the morphology of metal nanoparticles to enhance their plasmonic capability and interfacial contact. The semiconductor-organic framework can also be a suitable option in future to increase the overall quantum yield of the water splitting reaction.

LIST OF PUBLICATIONS

1. **Rayees Ahmad Rather**, Satnam Singh and Bonamali Pal, A C_3N_4 surface passivated highly photoactive Au-TiO₂ tubular nanostructure for the efficient H₂ production from water under sunlight irradiation. *J. Appl. Catal. B-Environ.* 213 (2017) 9-17. **(IF = 9.44)**
2. **Rayees Ahmad Rather**, Satnam Singh, and Bonamali Pal, A Cu^{+1}/Cu^0 -TiO₂ mesoporous nanocomposite exhibits improved H₂ production from H₂O under direct solar irradiation *J. Catal.* 2 (2017) 1-9. **(IF =6.82)**
3. **Rayees Ahmad Rather**, Satnam Singh, and Bonamali Pal, Visible and direct sunlight induced H₂ production from water by plasmonic Ag-TiO₂ nanorods hybrid interface *Sol. Energy Mater Sol. cells* 160 (2017) 463-469. **(IF =4.73)**
4. **Rayees Ahmad Rather**, Satnam Singh, and Bonamali Pal, Core-shell morphology of Au-TiO₂@ graphene oxide nanocomposite exhibiting enhanced hydrogen production from water *J. Ind. Eng. Chem.* 37 (2016) 288-294. **(IF =4.44)**
5. **Rayees Ahmad Rather**, Pooja D, Parveen Kumar, Satnam Singh and Bonamali Pal, The photocatalytic and photoelectrochemical performance of the (001) faceted TiO₂ nanosheets co-deposited with Au and Pt for the water splitting reaction. **(Under Review)**.

Other Publications

1. Anila Monga, **Rayees Ahmad Rather**, Bonamali Pal, Enhanced co-catalytic effect of Cu-Ag bimetallic core-shell nanocomposites imparted to TiO₂ under visible light illumination *Sol. Energy Mater. Sol. Cells* 172 (2017) 285-292 **(IF= 4.73)**
2. **Rayees Ahmad Rather**, Satnam Singh and Bonamali Pal, Photocatalytic Degradation of Methylene Blue by Plasmonic Metal-TiO₂ Nanocatalysts Under Visible Light Irradiation *J. Nanosci. Nanotechnol.* 17 (2017) 1210-1216. **(IF =1.43)**
3. Ranjana Prakash, **Rayees Ahmad Rather**, Manpreet Kaur, Bonamali Pal. Oxidative degradation of aliphatic carboxylic acids by photocatalysis with bare and Ag-loaded TiO₂ under UV light irradiation *Particulate Sci. Tec.* (2016) 1-5. **(IF =0.9)**
4. **Rayees Ahmad Rather**, Ramandeep Kaur Sarwara, Niranjana Das and Bonamali Pal, Impact of reducing and capping effect of carbohydrates for the growth of Ag and Cu nanostructures and their antimicrobial activity. *Particuology* **(Under Review)**.

CONFERENCES AND WORKSHOPS

1. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, International conference on nano for energy and water & Indo French workshop on water monitoring, University of Petroleum Dehradun 22-24 Feb 2017 (*Oral talk*).
2. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Participated in national workshop on hydrogen energy at National institute of solar energy Gurugram, Haryana , 23-24 Jan 2017.
3. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Photocatalytic hydrogen production from water by variable oxidation state based Cu impregnated TiO₂ under sunlight irradiation, HETIS held at Punjab University Chandigarh 29th- 30th Sep 2016 (*Oral talk*).
4. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Enhanced hydrogen production from water by core-shell Au-TiO₂ @graphene oxide nanocomposite under Visible light irradiation. International Conference on Nanotechnology for better living (NIT Srinagar and IITKanpur) held at NIT Srinagar 25-29 May 2016 (*Oral talk*).
5. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Rice Grain like TiO₂ and Ag-TiO₂ Nanorods for Efficient Hydrogen Production From Water. NanoBio Interface (International Conference) held at JNU New Delhi 18-20 Mar 2016 (*Poster, Best paper award*).
6. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Second conference on microscopy in material science (AMST), Thapar University Patiala. 25-27 Feb 2016 (*Poster*).
7. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal , Hydrogen production from water by core-shell Au-TiO₂ @graphene oxide nanocomposite under sunlight irradiation. 8th seminar on NPICS : SAP-2016 held at Punjabi University Patiala, 04-05 Feb 2016 (*Poster, Best paper Award*).
8. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Participated in workshop on electrochemical technologies in hydrogen production and utilization for electrical energy at IIT Delhi 8-9th Dec 2015.
9. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Participated in national workshop on advanced techniques for surface characterization at Thapar University Patiala.

10. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Photocatalytic degradation of methylene blue by plasmonic Ag-TiO₂ nanocatalyst under Visible light irradiation. The 7th national seminar SACOS-2015 at Punjabi University Patiala 19-20, Feb 2015(*Poster*).
11. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Participated in workshop on X-Ray diffractometry held at Delhi University 25-26th Sep. 2014.
12. **Rayees Ahmad Rather**, Satnam Singh, Bonamali Pal, Photocatalytic degradation of methylene blue by Au-TiO₂ nanocomposite under visible light irradiation. 1st national conference NFCS-01 held at Khalsa College Patiala, 15 Nov 2014 (*Oral talk*).



Feature Article

A C₃N₄ surface passivated highly photoactive Au-TiO₂ tubular nanostructure for the efficient H₂ production from water under sunlight irradiation



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ABSTRACT

In context to the recent advances in the development of sunlight active nanocomposites for the renewable H₂ production from water, a C₃N₄ passivated Au-TiO₂ tubular nanocomposite (CTA) has been prepared by a facile one pot hydrothermal method. Structural and morphological studies revealed the elongated anatase TiO₂ nanotubes (200–250 nm long, d = 12 nm) embedded in a thin layer of graphitic C₃N₄ (1–3 nm) and dispersed Au (7–12 nm) nanoparticles. The bulk C₃N₄ turned into monolayer due to the self exfoliation process confirmed by Raman (G band = 1545 cm⁻¹). The potential voltage (I–V) characteristics revealed the non ohmic properties of the heterojunction with a good current response (1.385 × 10⁻⁴ A). The nanocomposite showed efficient photocatalytic activity with the production of ~88 μmolh⁻¹ (calculated = 2933 μmolh⁻¹g⁻¹) of H₂ gas under direct sunlight irradiation using methanol as hole scavenger. The C₃N₄ is activated under sunlight and simultaneously sensitized by Au due to its plasmonic effect. The band potential of C₃N₄ (-1.21 eV vs NHE for E_{CB}) is more negative than TiO₂ (E_{CB} = -0.29 Vs NHE) enabling photo induced electrons to easily pass the interface into the E_{CB} of TiO₂ which promotes the charge carrier separation and enhance the photocatalytic activity for H₂ production.

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1. Introduction

Solar driven hydrogen production from water splitting is considered as the zero carbon emission process to tackle the exponentially increasing energy demand [1]. But the major challenge remains in finding a suitable photoactive, photostable and thermodynamically viable material to harvest the solar energy efficiently. Water splitting is an uphill reaction needing 237 kJ/mol of energy thermodynamically and also involves a difficult four electron reduction process [2]. To satisfy this condition the semiconductor photocatalyst should possess suitable conduction band potential/position, high charge separation efficiency (electrons and holes) and enough time for these to take part in the interface water reduction reaction [3,4].

In this regard titanium dioxide (TiO₂) is considered as an ideal candidate [5–7] due to its feasible reduction potential along normal hydrogen electrode (NHE), photostability and cost effectiveness but still deficiencies prevail in terms of its absorption in the UV region due to its large band gap (E_g = 3.2 eV) and low charge separation

efficiency [8]. The variations like maximizing the specific surface area [9] and modification of nanosize geometries, in particular the nanorods [10] and nanotubes [11] have been reported to be in a higher control of chemical and physical behavior. The electronic properties changes drastically by changing the morphology due to the strong influence of surface curvature helping the TiO₂ to act in a more effective way. Secondly the formation of composite system with other semiconductors like C₃N₄ had been reported [12,13] to enhance the photocatalytic hydrogen evolution that is also associated with the effective charge transfer. The C₃N₄ is well known to build an electric field at the heterojunction with TiO₂ that helps to divert the electrons and holes in contrary directions owing to reduce their unfavorable recombination [14]. By building a heterojunction of different optical response (C₃N₄ and TiO₂) is also supposed to make the nanocomposite active in both UV and visible light. Incorporation of noble metal like gold (Au) nanoparticles can also act as an electron trap aiding the charge separation and also sensitizing the TiO₂ in visible light due to the localized surface plasmon resonance (LSPR) effect [15,16]. Li et al. have previously reported [17] that addition of Au nanoparticles between two semiconductors (CdS-TiO₂) is able to reduce the trap state Auger rate and partially compensates the negative effects of the surface trap sites resulting in the improved photoconversion effi-

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A Cu⁺/Cu⁰-TiO₂ mesoporous nanocomposite exhibits improved H₂ production from H₂O under direct solar irradiation



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ABSTRACT

A photostable sunlight-responsive mesoporous Cu⁺/Cu⁰-TiO₂ (Cu-mpTiO₂) photocatalyst has been fabricated for the H₂ production from water. Structural analysis revealed the anatase polymorph of TiO₂ with mesoporous characteristics and an average particle size of ~32 nm. Mesoporous TiO₂ was observed to possess high surface area (188 m² g⁻¹) and pore size (0.32 nm). HRTEM studies suggested the deposition of Cu in Cu⁰ and Cu⁺ oxidation states with three distinct lattice fringes of 0.21, 0.25, and 0.35 nm for Cu, Cu₂O, and TiO₂ respectively. Cu-mpTiO₂ produced 1000 μmol of H₂ (AQE = 11.39%) under sunlight irradiation, which is severalfold more than obtained with Cu impregnated on commercial Cu-TiO₂ (P25). The photostability of the Cu-mpTiO₂ increased after recycling because the excess Cu⁺ (binding energy = 533.5 eV) is reduced to Cu⁰ (533.3 eV) and the excess holes in the valance band of Cu₂O oxidize Cu⁰ to Cu⁺.

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1. Introduction

Titanium dioxide (TiO₂) is considered one of the promising candidates for photocatalytic water splitting after the discovery of the Honda Fujishima effect [1] during the early seventies. However, conventional TiO₂ (P25) has several limitations [2–4] such as low surface area, fast electron/hole recombination, an absorption in the UV region due to a large bandgap (E_g). Many effective structural and optical modifications have been adopted [5,6] to overcome these hindrances. Characteristically mesoporous TiO₂ [7,8] has recently emerged as the best alternative to be an effective material due to its excellent structural and electrical properties, high porosity, and large surface area, which results in effective charge transfer for promoting the quantum yield of several photocatalytic reactions such as photocatalytic water splitting [9,10]. Further efforts are being made to increase the solar-to-hydrogen conversion efficiency by manipulating its band energetic [11] and light absorption ability [12]. Still, hydrogen generation from water over bare mesoporous TiO₂ is very low due to its inability to respond to sunlight/visible light and fast charge carrier recombination. In this regard, noble metal (Au, Ag, and Pt) loading has proven to be very effective [13–15]. Alternatively, doping with transition metals such as Cu, Fe, Co, and Ni has recently turned out to be a cheaper option [16–18]. Several other reports have also revealed the effectiveness

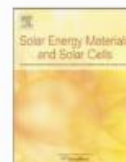
of Cu in photocatalytic activity over noble metals [19,20]. The complete mechanism is still less explored due to simultaneous formation of other active Cu species such as Cu₂O and CuO. Copper is supposed to be in elemental (Cu⁰) or oxide forms (Cu⁺ or Cu²⁺). Some earlier reports [21–23] reveal that Cu₂O species are responsible for enhanced photocatalytic activity to generate hydrogen from water. A few reports [24,25] also suggest that CuO is responsible for separation of charge carriers (electrons and holes). Cu₂O (2.1–2.2 eV) [26] is also an important transition metal oxide (p-type) that has the capacity to work under sunlight irradiation, and it is expected to form a p-n junction with n-type TiO₂ to enhance the lifetime of charge carriers.

Ampelli [27] and co-workers studied the effect of impregnation of copper oxide on TiO₂ for enhancement in photocatalytic activity. Similarly, Korzhak et al. [28] reported the hydrogen production on Cu-doped TiO₂ nanocomposite and concluded that when Cu species are loaded onto TiO₂, the expected stabilization of Cu and Cu oxides against photocorrosion results in the enhancement of photocatalytic efficiency. Hence, synthesis of mesoporous TiO₂ and its modification by formation of heterocomposites and metal loading are done to eliminate the drawbacks of commercial TiO₂ (P25), such as low surface area, charge separation, and low quantum efficiency.

This study demonstrates the fabrication of recyclable Cu-mesoporous TiO₂ nanocatalysts (Cu-mpTiO₂) for photocatalytic hydrogen evolution (PHE) from water. This design may increase the surface area of TiO₂ and impregnated Cu in variable

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Visible and direct sunlight induced H₂ production from water by plasmonic Ag-TiO₂ nanorods hybrid interface



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ABSTRACT

This report signifies the synthesis of TiO₂ nanorods (TNR ~79 nm) and nanospheres (TNS ~19 nm) and their Ag loaded counterparts AgTNR and AgTNS for the photocatalytic hydrogen production from water under monochromatic visible and direct sunlight. The Ag-TNR nanohybrid junction was sensitized at a matching monochromatic wavelength of 457 nm and sunlight to produce ~90 μmol and 105 μmol of gas, respectively, increase in the efficiency is explained due to the surface plasmon (SPR) effect of Ag nanoparticles and is also correlated to fluorescence quenching (due to better charge distribution along larger nano-interface), crystal structure and surface area (146 m² g⁻¹) of fabricated AgTNR nanocomposite. The elongated morphology of AgTNR led to the effective distribution of charge along larger interface resulting in the increase of photocurrent density (0.01 mA/cm²) which boosts the reaction rate. Plasmonic metal (Ag) activated with matching wavelength to SPR produces an electric field and the TiO₂ present in the proximity encounters these effects results in the formation of Schottky barrier, the SPR effect is also more towards Ag-TiO₂ interface which results in the ejection of electron towards the conduction band of TNR.

This study demonstrated that Ag nanoparticles loaded lengthy TiO₂ nanorods (~79 nm) exhibited highly improved H₂ production (90 μmol) from water relative to TiO₂ nanospheres (~19 nm) due to the plasmonic effect at 457 nm light irradiation that also exhibited better H₂ production (105 μmol) rate under direct sun light (8 h) exposure.

1. Introduction

Titanium dioxide (TiO₂) based semiconductor nanostructures are both theoretically and technologically relevant for hydrogen production from water due to its stability, efficiency, availability and brilliant optical and electrical properties [1–3]. TiO₂ is a multifunctional material widely used for energy conversion processes such as photovoltaics, photocatalysis, and photoelectrocatalysis [4–7]. Several advanced and modified TiO₂ based electrodes have been reported since the discovery of photovoltaic cell by O'Regan and Grätzel in 1991 [8]. Federico Bella et al. have reported [9–11] several polymer based flexible and vertically aligned TiO₂ nanotubes as the effective electrodes to avoid recombination, the quasi-1D TiO₂ showed superior charge transport and effective photoconversion efficiency, similarly Masoud Faraji et al. [12] have developed a Binder-free PANI-g-MWCNT/TiO₂NTs/Ti electrode material for the potential application in supercapacitors.

The photocatalytic performance of TiO₂ is strongly dependent on morphology and dimensionality; previous reports suggest that 1D

nanostructures like nanotubes, nanorods etc, can be more useful [13–16] as the solar conversion efficiency is usually determined by the competition of electron transport towards the reaction site and recombination of electrons with holes, and these 1D structures provide larger interface for better charge distribution. Still the deficiencies like the optical absorption of TiO₂ [17] which is in UV region due to its larger energy gap ($E_g \sim 3.2$ eV) limits its efficiency, to overcome this drawback, doping and synthesis of nanodiodes with plasmonic metals like Ag and Au is used to sensitize it in visible light [18–21]. Reports reveal that doping of metals like Ag and Au leads to the formation of Schottky barrier which is further coined as Schottky nanodiodes [22,23]. These Schottky nanodiodes convert photon energy into electrical energy [24] and can be effective for photolysis of water. The metal doping of TiO₂ with Ag and Au is effective in two ways, by helping to sensitize it in visible light region due to the surface plasmon resonance (SPR) effect [25–27] and are also helpful in generating the high kinetic energy hot electrons under photon irradiation because of low electron heat capacity of metals permitting easy and nonadiabatic energy transfer [28]. These hot electrons emitted by the deposited

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Core-shell morphology of Au-TiO₂@graphene oxide nanocomposite exhibiting enhanced hydrogen production from water



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Hydrogen production

ABSTRACT

The core-shell morphology of graphene oxide (GO) coated Au-TiO₂ (Au-TiO₂@GO) nanocatalysts has displayed enhanced photocatalytic activity for hydrogen production from water. The structural morphology of Au-TiO₂@GO revealed a thin layer (~2.5 nm) of GO shell over Au-TiO₂ core, possessing higher specific surface area (~100 m² g⁻¹). Raman spectroscopy revealed bands at 1593 cm⁻¹ and 1317 cm⁻¹ corresponding to G and D lines. GO facilitates decreases in the rate of e⁻/h⁺ recombination due to its reduction potential and Au loading increase sensitization of TiO₂ in the visible light resulting in the increased activity for H₂ production (~114 μmol) from the water.

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Introduction

There is a growing interest in the development of a suitable semiconductor photocatalyst for sustainable hydrogen (H₂) generation from water since the discovery of Honda-Fujishima effect [1]. A large number of semiconductor photocatalysts [2–5] have been reported to catalyze the photolysis of water. Among these, titanium dioxide (TiO₂) has been extensively studied [6–8] as an effective photocatalyst due to its excellent properties and high photocatalytic activity. Though TiO₂ has been found to be effective for hydrogen production from water [9–11], the efficiency remains limited due to fast recombination of photogenerated electrons (e⁻) and holes (h⁺). Secondly, the band gap of TiO₂ (3.2 eV) primarily makes it inactive for water splitting under the visible light as band edge does not straddle within the thermodynamics of water splitting reaction. Efforts have been made to modify TiO₂ based nanocomposites for effective separation of charge carriers by loading of noble metal nanoparticles [12,13] that act as electron storage and transport units. Metals like Au, Ag, and Cu are usually used to enhance the rate of photoreaction [14–16] as they act as electron trappers, thereby inhibiting the recombination of excitons. Stability in aqueous media, strong response to visible light and increase in the photo-induced

optical response of these plasmonic metals helped in enhancing the rate of a reaction [17,18].

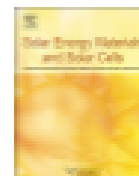
Furthermore, to achieve the requirement for water splitting reaction, the coating on TiO₂ with some electron rich transport materials and other semiconductors are favored [19–21]. The composites of TiO₂ with carbon-rich materials like carbon nanotubes (CNT), graphene and graphene oxide have got a vivid attention during last few years. Hoffman et al. [22] suggested CNT as an electron transfer site upon loading with TiO₂, electrons are easily transferred to CNT surface thereby helping the retardation of recombination rate. Similarly, graphene, a carbon composite with sp² hybridization with brilliant properties has been said to be a good transporter of electrons [23]. Kamat et al. [24] reported that electrons can be transferred to GO surface from conduction band of TiO₂. Few other reports have also suggested the effective role of carbon based materials for enhanced photocatalytic activity [25–28]. In addition to this, changing the morphology to the core-shell design of TiO₂ have also been investigated [29] as an effective for a wide range of applications like hydrogen production and solar cells. In comparison to other heterocomposites core shells structures act as a hybrid showing the synergistic property of inner core and outer shell, which is versatile and conducive for some photocatalytic reactions. Hence, a good electron transport shell like graphene or graphene oxide over TiO₂ core can be effective owing to high conductance, specific surface area and shell layer acting as a reservoir for electron storage and transport.

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journal homepage: www.elsevier.com/locate/solmatEnhanced co-catalytic effect of Cu-Ag bimetallic core-shell nanocomposites imparted to TiO₂ under visible light illuminationAnila Monga, Rayees Ahmad Rather, Bonamali Pal^{*}

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ABSTRACT

This paper signifies that the bimetallic (BM) core-shell metal NCs deposited on TiO₂ possess the ability to absorb visible light in a wide wavelength range and are also expected to display the new properties due to synergy between two distinct metals. As a result, they reveal highest level of activity than the monometallics deposited on TiO₂. In this respect, the core@shell (Cu@Ag), inverse core@shell (Ag@Cu) BM NCs and their monometallic modified TiO₂ have been relatively investigated for the optical absorption, emission, charge carrier dynamics, surface structural morphology and photocatalytic activity under visible light irradiation. A significant blue-shift in the SP band of Cu@Ag and a red-shift in Ag@Cu with notable color change were observed due to their composition change and morphology. Further, the TEM analysis also revealed the formation of concentric core-shell Cu@Ag and uniform core@shell Ag@Cu BM NCs which were deposited on TiO₂, evidenced by diffuse reflectance spectroscopy, EEX, photoluminescence and time resolved spectroscopy. The visible light irradiation on core@shell BM-TiO₂ promoted ~ 3 times higher reduction of 3-nitroacetophenone and 1-chloro-3-nitrobenzene and ~2 times higher degradation of salicylic acid as compared to monometallic-TiO₂. This can be attributed to the decrease in work function of resulting Cu-Ag BM NCs (ca. 3.8–4.6 eV) relative to their individual particles (4.3–5.3 eV) that lower the height of Schottky barrier created at the core@shell BM-TiO₂ heterojunction. As a result, this led to the efficient electron transfer from the BM NCs to TiO₂, resulting in enhanced photocatalytic activity than the monometallic-TiO₂.

1. Introduction

Titania (TiO₂)-metal nanocomposites have been widely employed for different photocatalytic applications, the metal in contact with TiO₂ enhances the interfacial charge-transfer process [1–4] resulting in the improvement of overall photocatalytic efficiency. Many reports are available for the preparation of Au/TiO₂, Ag/TiO₂, Pt/TiO₂, and Cu/TiO₂ nanocomposites (NCs) [5–9] with different morphological forms, which are progressively increasing with focus on enhancing the photocatalytic efficiency in oxidation and reduction processes. This not only results in improved photo-conversion, quantum yield, but also extends the absorption of UV-light active TiO₂ semiconductor in the visible light. For example, Zheng et al. [8] reported the photocatalytic properties of noble-metal photocatalysts, M@TiO₂ (M = Au, Pt, Ag) for the oxidation of benzene to phenol under visible light. The plasmonic nanoparticles (NPs) i.e., Au, Ag and Cu have the strong ability to absorb visible light due to their surface plasmon resonance (SPR) [10,11] effects. As a result, they act as an antenna to concentrate light and convert it to heat, that enables them to serve for photovoltaic,

photochromic, surface-enhanced Raman spectroscopy, photocatalysis, etc. [7,8,12–22]. Therefore, the deposition of plasmonic nanomaterials onto TiO₂ exhibits an effective transfer of the photoexcited electrons (*e*⁻) from the surface of metal NPs to the conduction band (CB) of TiO₂ [23–27] under visible light. As a result, the metals become *e*⁻ deficient and TiO₂ turn out to be *e*⁻ enriched, leading to the occurrence of photo-oxidation reaction on the surface of metal NPs rather than on TiO₂. The fast transference of *e*⁻ (less than 240 fs) was reported [28–30] into the TiO₂ support in the presence of Au NPs. However, the use of bimetallic (BM) nanostructures composed of two different metals can further enhance the photocatalytic performance [31–35], particularly with respect to activity and selectivity as compared to their monometallic counterparts. BM NPs deposited on TiO₂ are expected to display not only the combination of the properties associated with two individual metals, but also the new properties due to synergy between two metals. But, there are only few reports on TiO₂ modified with BM NPs. Recently, bimetalization of Pt with Au on TiO₂ has been reported to improve the catalytic activity of Pt clusters for visible light-induced hydrogen generation and degradation of organic dyes or phenol [36]. In

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Photocatalytic Degradation of Methylene Blue by Plasmonic Metal-TiO₂ Nanocatalysts Under Visible Light Irradiation

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This study demonstrates photocatalytic activity of 1 wt% plasmonic metal (Au, Ag and Cu)-TiO₂ nanocatalysts prepared via photodeposition method for the photo oxidative decomposition of methylene blue (MB 0.01 mM) under visible light (50 mWcm⁻²) irradiation. Plasmonic metal loaded-TiO₂ photocatalysts absorb with an absorption maximum at localized surface plasmon resonance wavelengths (500–785 nm). It has been observed that pH altered the surface charge (ζ) of TiO₂ (ζ = -4.98, -4.0 and +9.16 at pH = 10, 7 and 3, respectively). The point of zero charge (PZC) at pH 6.3 has been determined from a correlation plot between pH and ζ . Higher rate of degradation was observed at pH = 10 because of electrostatic interaction of cationic MB with anionic TiO₂. Higher photocatalytic activity was shown by Cu-TiO₂ followed by Au-TiO₂ and Ag-TiO₂ photocatalysts in comparison to TiO₂-P25. This enhancement in photocatalytic efficiency is attributed to the plasmonic effect and effective charge separation at the interface between nano size metal deposits and TiO₂ particles. The overall photocatalytic reaction followed pseudo first order kinetics as per Langmuir Hinshelwood kinetic equation. GC and GC-MS studies suggested the formation of thionin after demethylation and derivatives of benzenesulphonic acid which are subsequently degraded to CO₂ after prolonged irradiation time.

Keywords: Au/Ag/Cu-TiO₂ Nanocomposites, Plasmonic Effect, Coinage Metal Cocatalyst, Methylene Blue Degradation, Visible Light Photocatalysis, Photooxidation.

1. INTRODUCTION

Titanium dioxide (TiO₂) photocatalyst¹⁻³ is reported to be widely used for removal of toxic pollutants, solar energy conversion, photovoltaic's, water splitting, water detoxification and self cleaning under UV light irradiation. TiO₂ is photochemically stable, cost effective, abundant and has good oxidizing nature towards organic pollutants. However, its light absorption capacity is in the UV region which comprises 4% of solar irradiation that limits its effective usage under ambient conditions. Hence, many experimental techniques such as dye sensitization,⁴ composite formation,⁵ metal deposition/doping⁶ shape and size modification⁷ have been adopted for optimum photo activity under visible light (44%) of solar irradiation. Several reports reveal the effective role of dye sensitization⁸ and coupled semiconductor⁹ photocatalysis for enhancing TiO₂ activity, but stability of dyes in aqueous conditions

and factors like lattice matching, passivation and structural defects¹⁰ for semiconductor composites have retarded their application. Similarly, surface modification of TiO₂ by photodeposition^{11,12} of metals like Pd, Pt, Rh etc. have improved the photocatalytic activity of TiO₂ in visible region while metals like Cr, Cu have increased the light sensitivity due to formation of schottky barrier and change in electric field properties along interface. Even though transition metal doping on TiO₂ has extended the light response in visible region but there are several reports suggesting the decrease in photocatalytic activity¹³ because of photocorrosion or acting as recombination centers for photogenerated charge carriers.

Recently, plasmonic metals (Au, Ag and Cu) have been preferred over other metals because of their stability in aqueous media, strong sensitizing power, higher thermal and optical response¹⁴⁻¹⁶ upon irradiation with visible light because of the surface plasmon resonance (SPR) phenomenon. The efficiency of these plasmonic metal loaded

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