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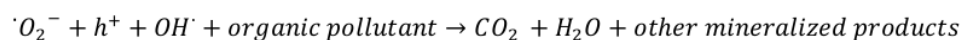
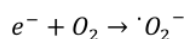
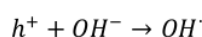
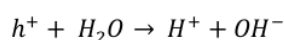
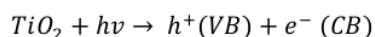
In the present era, the world is facing two significant challenges: the need to protect and restore the environment and the requirement to manage, store, and convert energy in alternative ways. These challenges have arisen due to the substantial growth in global population, industrialization, and the consumption of natural resources. Therefore, it is imperative to discover an effective approach to address the issue of energy scarcity and the harm to the environment. "Semiconductor-based photocatalysis" is considered a promising approach for achieving a clean and sustainable future, considering its purity, inexhaustibility, effectiveness, and low-cost [1]. It mostly involves accelerating the chemical reaction by employing a light-activated SC(semiconductor) catalyst. In this context, the advanced oxidation process (AOP) is one of the most intriguing process that can achieve total oxidation of both organic and inorganic water pollutants. The term "heterogeneous photocatalysis" describes a process wherein a semiconductor material's surface is activated by light to produce reactive species, most notably hydroxyl radicals ($\bullet\text{OH}$), that subsequently mineralize the pollutant of concern.

Among various photocatalysts, Titanium dioxide (TiO_2) is an established photocatalyst known for its robust photocatalytic oxidation, high room temperature activity, and excellent photostability. Titanium dioxide, or titania, is a naturally-found transition metal oxide represented by the scientific notation TiO_2 . Furthermore, it is widely utilised throughout several industrial sectors like paints, varnishes, paper, printer inks, rubber, plastics, cosmetic items, and more[2–4]. As a result of its distinctive structural, optoelectrical, and photocatalytic characteristics, it is recognised as a promising semiconductor nanomaterial[5,6]. The physical-chemical stability, high refractive index, low toxicity, strong reactivity, ease of synthesis, low price, excellent catalytic activity, and excellent energy conversion efficiency of TiO_2 have been widely recognised (**Scheme- 1.1(a)**)[7,8]. For that reason, it is appropriate for a variety of critical technological applications, including the treatment of wastewater, the development of self-cleaning coatings[9], the production of disinfecting materials, the production of fuel cells [5,10], the development of solar cells[11,12], and sensors (**Scheme- 1.1(b)**).

It occurs naturally in the following three forms: anatase, rutile, and brookite. The states are defined by the interaction of TiO_6 octahedra while preserving the overall stoichiometry consistent with TiO_2 [13–15]. This semiconductor photocatalyst demonstrates high efficiency, exhibiting band gaps of ~ 3.2 eV, ~ 3.02 eV, and ~ 2.96 eV across its anatase, rutile, and brookite phases, respectively. It demonstrates absorption in the ultraviolet (UV) region[2,16].

General mechanism of TiO_2 during photodegradation reaction on organic pollutant

Upon exposure to light irradiation, the photocatalyst (TiO₂) facilitates the transition of electrons (e⁻) from the valence band (VB) to the conduction band (CB), allowing them to migrate to the surface of the catalyst, where they subsequently undergo reduction. The holes have the ability to undergo an oxidation process by directly reacting with the organic molecules or generating hydroxyl radicals (OH[·]), which then oxidise organic molecules and break them down into smaller products. Electrons also undergo reactions with organic molecules to produce reduction products. Dissolved O₂ can be reduced to O₂^{-·} radicals by the electrons in the conduction band (**Scheme-1.2**).



Various other shapes and structures of the TiO₂ photocatalysts have been assessed for their effects on wastewater treatment (**Table 1.1**). Degussa P-25 TiO₂ exhibited substantially greater photocatalytic activity than that of other forms of TiO₂ photocatalysts, including UV100 (100% anatase; Hombikat) and PC500 (100% anatase; Millennium inorganic chemicals), among these various forms. References investigated the impact of these three versions of TiO₂ on the degradation of Ethidium Bromide, Triphenylmethane dye and Acridine Orange. It determined that Degussa P-25 TiO₂ exhibited the maximum degradation rate[17]. The reason for this is that the Degussa P-25 is composed of microscopic nano-crystallites of the rutile (18%) which are dispersed inside the anatase matrix (73%). During the photocatalytic activity, these two forms of TiO₂ exhibit a synergistic effect in DegussaP-25 TiO₂.

Although TiO₂ have significant potential for photocatalytic applications, its effectiveness is hindered by its rather small specific surface area, rapid recombination of photogenerated charge carriers, and limited efficiency in utilising solar or visible light due to the wide band gap. The limitations greatly constrain the widespread application of the material. A significant amount of effort has been directed towards the modification of TiO₂ in order to enhance the lifetime of the charge carrier and the light absorption features.

On the contrary, the primary challenge to optimising TiO₂'s photocatalytic efficiency is the broadband gap (approximately 3.0–3.2 eV), which restricts its activity solely to the UV light region, thereby preventing the effective utilisation of the entire solar spectrum, along with a rapid electron-hole recombination rate. Currently, numerous potential approaches are being considered, including stimulating using noble or transition metals and combining them with other semiconductors or carbon-based substances[24]. The enhancement of photocatalytic processes by modifying semiconductor materials with noble metals is ascribed to more efficient e⁻-h⁺ separation, the expansion of photoactivity to the visible range, and the surface plasmon resonance (SPR) exhibited by the metal nanoparticles[25]. Noble metal nanoparticles (Au, Pt, Ag) exhibit a significant absorption of visible light as a result of their surface plasmon resonance (SPR). This phenomenon is characterised by the collective oscillation of their conducting electrons, which is triggered by the electric field of incoming visible light[26]. When the Fermi level of the metal is positioned between its VB and CB, photoinduced electrons transfer from the semiconductor's CB directly to the metal nanoparticles. These metal nanoparticles function as electron sinks owing to the Schottky barriers that are established at the metal-semiconductor contact. Metal nanoparticles' photoinduced electrons are captured by appropriate reactive species. Thus, by depositing metal on the semiconductor surface, the charge transfer distance is reduced, the electron-hole pairs are suppressed from reuniting, and the photocatalyst's response in the visible region is improved.

The absorption and scattering properties of metallic nanoparticles can be optimised by tailoring their morphology and dielectric environment. Noble metals are photoactive to a limited extent when present in bulk. However, when deposited over the semiconductor surface, such as TiO₂, they exhibit electron storage properties, which result in enhanced charge separation. The noble metal nanoparticles exhibit unique optical and catalytic properties that are not typically observed in bulk metal. Deposition of a nano-noble metal over the TiO₂ surface can improve photocatalytic efficiency by facilitating faster electron transfer between semiconductor and metal deposits, as opposed to the surface trapping states caused by bulk modification. The presence of localised surface plasmon resonance (SPR) in gold (Au) and silver (Ag) nanoparticles often results in the appearance of intense and broad absorption bands within the visible light spectrum. Furthermore, this phenomenon is employed to produce photocatalysts that are stimulated by visible light. In this regard, the metal nanoparticle size, synthesis method, and weight loading play a crucial role.

The strong SPR effect and intriguing electrical conductivities of coinage metals (such as Cu, Ag, and Au) have been a subject of considerable attention[27]. In this regard, these materials have been employed in a variety of sizes, forms, and shapes to alter the optical and surface characteristics of TiO₂ photocatalysts[28,29]. Due to their appropriate redox potentials (Cu=0.337eV, Ag=0.799eV, and Au=1eV), these metals have been photo-deposited on the surface of TiO₂ and examined for a variety of environmental photocatalytic applications. For example, mesoporous RuO₂-TiO₂ has been photo-deposited with Au, Pd, and Pt metals for CH₃OH oxidation. RuO₂-TiO₂ composites containing Au exhibited a significant photocatalytic activity in visible light in comparison to Pd, Pt-deposited catalysts[30]. Likewise, TiO₂ nanoparticles modified with Ag and CuO have been identified as effective electron scavengers for the photooxidation of acetic acid and phenol[27]. Moreover, several Ag, Cu, Pt, and Au - modified TiO₂ nanocomposites have been documented in the literature to investigate the efficient oxidation-reduction pathways[31,32].

In an alternative method, the photocatalytic properties of TiO₂ can be improved by immobilising TiO₂ on carbonaceous materials, including carbon nanotubes and graphene[33–35]. The 2D carbon nanostructure graphene exhibits exceptional charge transfer capabilities, chemical stability, and optical characteristics. Graphene is an exceptional material characterized by its atomic sheets consisting of sp²-bonded carbon atoms. It has garnered significant interest due to its remarkable properties, such as an extensive surface area, high chemical and thermal stability, excellent interfacial contact with adsorbents, and outstanding charge carrier mobility. Combining TiO₂ with materials composed of graphene can reduce e⁻-h⁺ recombination, shifting TiO₂'s sensitivity from UV to visible range. The primary drawback of graphene, however, is its extremely limited solubility in ordinary organic solvents[36]. Conversely, graphene oxide (GO) is a perfect substitute for producing solution-processable graphene since it easily produces stable dispersion in a range of solvents[37].

It can be synthesised chemically through a chemical exfoliation process to produce GO. This produces a multilayered-graphene-sheet containing functional groups, including epoxy, hydroxyl, and carboxyl. The functional groups react with metal precursors, which causes metal ions to accumulate and, in the end, immobilises metal nanoparticles onto the GO sheet. The TiO₂/graphene composite exhibits superior photocatalytic performance that possesses improved light absorption as well as high surface activity. Additionally, it creates interfaces between TiO₂ and carbon nanostructures, functioning as p-n heterojunctions[38]. The heterojunctions facilitate the separation of photoinduced electrons and holes, which enhance

the photocatalytic activity of such composites. The TiO₂/graphene composites synthesis has been accomplished using several methods, such as the sol-gel[39,40], solvothermal[41–43], and hydrothermal processes[44–47]. The hybrid composites comprising nanoparticulate metals and graphene oxide (GO) can display superior characteristics, including high adsorption capacity for organic dyes, reduced recombination rate of the photo-generated charge transporters, and excellent π - π stacking with dye chromophores.

Khalid and his colleagues[48] employed the sol-gel method for fabricating Cu-TiO₂ nanoparticles and then used a hydrothermal approach to combine Cu-TiO₂ with graphene. The composites had a broad spectrum of light absorption encompassing both ultraviolet and visible light wavelengths and exhibited superior photoactivity compared to the Cu-TiO₂ and TiO₂/graphene composites. A Pd-TiO₂/graphene composite was synthesised by Song and his team[49] by the incorporation of TiO₂ nanoballs onto the graphene utilising a poly (diallyl dimethyl ammonium chloride) as a linker. The composite was added to a solution of palladium chloride and ammonia and then placed inside a hydrothermal reactor, continuing heating. Katsarakis[37] synthesised an Ag-TiO₂ powder by coupling P25-TiO₂ with an AgNO₃ precursor and dimethylamine borane as a reducing agent. The obtained powder was added to an ethanol-water mixture, followed by the addition of GO and introduced into a hydrothermal reactor. The Ag TiO₂/GO composite exhibited exceptional photoactivity in the photodegradation of methylene blue dye.

In recent years, water contamination has emerged as a significant concern. Numerous hazardous substances, such as pesticides, personal care products, industrial dyes, fertilizers, disinfectants, prescription medications, and inorganic pollutants (specifically heavy metals), are being released into water bodies on a daily basis without undergoing any chemical treatment. The continual presence of these hazardous to-health pollutants in water sources poses dangers to both human and aquatic life. Industrial development is linked to the presence of toxic contaminants, including phenolic compounds, which are harmful to humans, harmful to the environment, and difficult to eliminate through natural means.

Phenolic compounds are aromatic compounds that have one or more hydroxyl groups bonded to the aromatic ring. The subject matter of phenols and their derivatives has garnered an increasing amount of global attention. This category of pollutants is predominantly present in industrial effluents. Phenols, when exposed to the environment in effluent, directly pose a threat to humans due to their rapid absorption by the lungs in a brief period. Because of their

corrosive properties, all forms of phenols and their derivatives can induce irritation in the respiratory tract, eyes, and skin. These chemicals have wide-ranging applications in the textile, pharmaceutical, and agrochemical sectors.

Pharmaceutical pollutants, including antibiotics, analgesics, and disinfectants, have been found in surface water at concentrations ranging from ng/L to g/L. Approximately 70-90% of antibiotics are excreted in either chemically unmodified or active metabolite form by humans and animals. The poor metabolic rate, excessive intake, and insufficient absorption of these compounds make environmental resources vulnerable to contamination. According to reports, these substances are not removed altogether at sewage treatment plants. As a result of the severe repercussions of water pollution caused by pharmaceutical and dye contaminants, researchers have made numerous efforts to remove these potentially harmful substances from the effluent.

Recent studies have investigated and evaluated several environmental strategies for the removal of persistent contaminants from polluted wastewater. These include integrated Fenton oxidation, sonochemical degradation[50], electrochemical treatment[51], adsorption[52,53], ion exchange[54], and biological treatment[55]. Nevertheless, those methods have disadvantages, including high operational costs as a result of their substantial energy consumption. In recent times, photocatalytic degradation has become increasingly attractive as a highly promising approach for eliminating refractory contaminants such as dyes, pharmaceutical drugs, other organic pollutants, etc. This advanced oxidation process provides multiple advantages ranging from minimal operational costs, reusability, ability to utilize solar energy, and contaminant removal from different media.

In recent years, heterogeneous photocatalysis has shown considerable significance as a viable solution for treating wastewater generated by various sectors. The photocatalytic process is predicated on the production of hydroxyl radicals ($\cdot\text{OH}$), which possess a high degree of oxidative power and can efficiently oxidise organic pollutants, as well as disinfect microorganisms. Barakat et al.[56] synthesized $\text{Ni}(\text{OH})_2/\text{graphene oxide}/\text{TiO}_2$ nanocomposite and employed it for wastewater treatment, including toxic organic compounds, microbes, and lipids in dairy effluent. It was examined for both the degradation of 2-chlorophenol (2-CP) and the pre-treatment of dairy effluent to enhance digestibility and remove microbial pollutants through anaerobic digestion. The composite efficiently removed 80% of the 2-CP in 4h under solar light with 25mg/l concentration (pH= 6.0). The organic solubilisation of dairy effluent is enhanced by the pretreatment process, resulting in an increase in soluble chemical oxygen

demand (sCOD) content from 272 to 631 mg/l within six hours of photocatalysis. A study conducted by Moonrasi et al.[57] documented an increased rate of degradation of 4-chlorophenol (4-CP) while employing Pt-deposited (1 mol%) P25 under experimental circumstances, including nitrogen bubbling. Their observation revealed a reduction in the rate of degradation when dissolved oxygen was present. Qi et al.[58] synthesized the Ag-modified GO- TiO₂ (Ag/GO-TMCs) composite using photoreduction deposition method. The study aimed to explore the photocatalytic characteristics of the catalyst for the degradation of Rhodamine B dye (RhB) and dinitro butyl-phenol (DNBP) when exposed to visible light. From the prepared composites, Ag/GO-TMCs-7.5% composite, where 7.5% Ag deposited over GO-TMCs exhibited the highest amount of degrading efficiency for RhB and DNBP when evaluated under visible light illumination for 3h. The enhanced photocatalytic efficiency of Ag/GO-TMCs can be ascribed to the increased affinity of Ag nanoparticles and GO for visible light and the surface plasmon resonance (SPR) effect.

In the forthcoming decades, the primary obstacles will be the energy crisis and environmental contamination issues. Among the diverse alternative energy sources, hydrogen energy is a critical element of the renewable energy strategy of the developed world due to its immediate availability and high fuel efficiency. Researchers have devoted significant focus to the use of hydrogen as an environmentally friendly energy carrier and to the establishment of novel methods for its generation without relying on fossil fuels. Presently, the majority of the energy used by humankind is generated through the combustion of fossil fuels, which are a finite natural resource. According to statistical data, there has been a prevailing tendency in recent years towards economic expansion worldwide, resulting in a rise in energy consumption per unit of gross domestic product[59,60]. Among renewable energy sources include solar and photovoltaic energy, biomass, hydropower, tidal energy, ocean thermal energy[61]. In this instance, solar energy is a strategically significant resource, as it is the major form of renewable energy. Consequently, the direct conversion of light energy into the energy of chemical bonds is one of the most promising areas for the development of solar energy. The ultimate objective may be the photocatalytic production of hydrogen[62,63].

Sodium borohydride, ammonia, borane, methanol, ethanol, formaldehyde, and hydrazine have been assessed as initial substrates in catalytic and photocatalytic reactions for hydrogen generation[64,65]. Benzyl alcohol, glucose, alkanes, and ethanol have recently gained significant interest as potential precursors in photocatalytic hydrogen production systems[66,67]. CdS, TiO₂, Cd_{1-x}Zn_xS, and g-C₃N₄-based heterogeneous catalysts have been

widely preferred in photocatalytic hydrogen production[68,69]. Although there is a wide range of suggested novel photocatalyst materials, titanium dioxide remains one of the most frequently used photocatalysts because of its abundant availability, very low toxicity, and exceptional durability. The photocatalytic efficiency of pure TiO₂ is well-documented to be somewhat poor, given the rapid recombination of electron-hole pairs. Deposition of noble metal co-catalysts onto the surface of TiO₂ is a generally used method to enhance activity. Metal nanoparticles function as electron traps due to the creation of the Schottky barrier at the metal-semiconductor interface, thereby extending the lifespan of electron-hole pairs. A recent study by Zhu et al. revealed that plasmonic Au/TiO₂ displayed exceptional HCHO oxidation activity when exposed to visible light. This high performance is due to the combined effects of plasmonically excited electrons on the Au and active oxygen species on the surface[70]. Bamwenda and colleagues[71] conducted an experiment to examine the catalytic activity of two catalysts, Au/TiO₂ and Pt/TiO₂, for the generation of H₂. The findings indicated that the performance activity of the Pt sample was 30% greater than that of the Au sample. A high production of hydrogen was observed when both Au and Pt samples were calcined in air at 573K.

11 Additionally, carbon-based materials such as graphene oxide, reduced graphene oxide, or graphitic nitride on TiO₂ can be highly beneficial due to their high conductive properties and extensive surface area for electron transfer and delocalisation, which results in a reduced recombination rate of the e⁻/h⁺ pair. Zhang et al.[72] synthesized a ternary graphene-like photocatalyst using Mo and GO over a SiC semiconductor catalyst. The experimental results indicated that the ternary photocatalyst exhibited robust photocatalytic hydrogen production activity in comparison to pure SiC. The maximum quantum yield of 21.69% was observed at the 400–700 nm wavelength when the catalyst was loaded with 2.5 wt% of GO weight. Rayees et al.[73] prepared a Cu-mpTiO₂ photocatalyst for hydrogen production from water under sunlight. Cu-mpTiO₂ generated 1000 μmol of H₂ (AQE = 11.39%) when exposed to sunlight, a significant increase from the amount of H₂ produced by Cu impregnated on commercial P25-TiO₂. In another study[74], they synthesized a GO-coated Au-TiO₂ nanocatalyst that exhibited improved photocatalytic hydrogen production from water due to its core-shell morphology. The structural framework of Au-TiO₂@GO exhibited a thin layer (about 2.5 nm) of graphene oxide shell on top of the Au-TiO₂ core, which had a greater specific surface area (about 100 m²g⁻¹). The Au-TiO₂@GO nanocomposite exhibited the highest rate of H₂ evolution, which increased over a period of 3 hours (110μmol). In comparison to TiO₂ and Au-TiO₂, the lower reduction potential of GO enables a reduction in the recombination rate of charge carriers.

Conversely, the presence of Au loading enhances the sensitivity of TiO₂ to visible light, leading to an improvement in the efficiency of solar to hydrogen-conversion.

These investigations consistently demonstrate a synergistic effect between graphene oxide and metal, resulting in an enhanced photocatalytic activity of the composite material.

1.1 Research Gaps

Through the literature review, we discovered that the photocatalytic activity of bare TiO₂ has been extensively studied for the photocatalytic degradation of organic pollutants and photocatalytic hydrogen generation from water splitting. Various reports have been published on metal-TiO₂ hybrids for enhancing the photocatalytic properties of TiO₂. At the same time, there is still plenty of scope to enhance the photocatalytic capabilities of metal-TiO₂. Several transition metals have been found to suffer oxidation/corrosion processes that effectively decrease the semiconductor's photo-efficiency. By combining it with a carbonaceous material, the stability of metal-TiO₂ can be enhanced. It can be deduced that graphene with unpaired π electrons could be used to change the TiO₂ surface to produce a visible-light-responsive photocatalyst by means of the interaction between unpaired π electrons of graphene and Ti atoms. Thus, the band edge and the significant reduction of the band gap of graphene-TiO₂ can be obtained. The lower reduction potential of GO compared to TiO₂ enables a rapid reduction in the recombination rate of charge carriers. On the other hand, the presence of metal loading enhances the sensitivity of TiO₂ to visible light, leading to a higher efficiency of converting solar energy into hydrogen compared to TiO₂ and metal-TiO₂.

Recent research has demonstrated that the photocatalytic activity of the SC photocatalyst can be significantly enhanced by the combined use of graphene oxide and metals. Exploring the benefits of GO/M-TiO₂ nanocomposites, which include excellent electron conductivity, the specific Schottky barrier of the metal, enhanced light-absorption properties, and a large specific surface area, will greatly enhance the performance of TiO₂ for the various photocatalytic applications.

There are numerous reports on hydrogen production from water splitting, but there are only a handful of studies that have been reported on the generation of hydrogen from alcohols using such GO-modified/metal-TiO₂ catalysts. Moreover, it would be significant to explore both oxidative and reductive photocatalytic properties in the same prepared GO/M-TiO₂ composite. The objective of this research is to optimise the photocatalytic oxidative and reductive activity

of TiO₂ by modulating its band gap and surface-structural properties through the addition of GO and metal. This would result in the development of various ternary (GO/M-TiO₂) heterostructure composites. Furthermore, the several hybrid interfaces formed (M-TiO₂, GO-TiO₂) in the structure would lead to enhancement of the efficiency of separating photo-excited charges, thereby leading to improved photocatalytic efficiency of the ternary composite.

1.2 Objectives

1. Preparation of Graphene oxide (GO) from coal (anthracite, bituminous) /graphite and its coating over TiO₂ for improved surface structural, physical and chemical properties.
2. Preparation of different metal M-TiO₂ (M= Ag, Fe, Cu, Co, Ni, etc) nanocomposites and GO-coated M-TiO₂ composites.
3. Study of surface structural, optical properties and photocatalytic degradation with GO-TiO₂, M-TiO₂, GO@M-TiO₂ nanocomposites.
4. To investigate the H₂ production from photocatalytic dehydrogenation of waste alcoholic solvents by as prepared nanocatalysts under visible light/sunlight irradiation. The photo-deposition method was applied to deposit metal over the TiO₂ surface. In a standard procedure, about 100 mg of the P25-TiO₂ catalyst was dispersed in a 50-vol% aqueous solution of the sacrificial agent in a test tube. For preparing different wt% metal composites, a calculated amount of metal salt solution was added to the above test tube. Afterwards, the test tube was purged with argon gas to remove excess oxygen and prevent oxidation. It was sealed with a rubber septum and placed and stirred under UV light for 2-4h. The obtained solution was centrifuged, washed and dried.

The GO was synthesised using the modified Hummer's method. An initial mixture of 1 g each of graphite and NaNO₃ powder in a 1:1 ratio was combined in a conical flask. This was then followed by the addition of 23 ml of H₂SO₄ and magnetically stirred for 3 h, maintaining the temperature at around 20 °C. The mixture solution was stirred continuously at ~20 °C for 2 h after KMnO₄ (3 g) addition. Distilled water (46 ml) was added slowly to the above-mentioned solution and further stirred for 2 h, maintaining the temperature at ~98 °C. Afterwards, another 100ml of distilled water was added, followed by H₂O₂ (10 ml) after 5 min. The resultant mixture was centrifuged and washed with DI water and HCl 3-4 times, and the sample was dried at 55 °C overnight.

For different wt% GO loadings, the pre-calculated amount of GO (1-5 wt% wrt to TiO₂) was added in (2:1) ethanol: water solution and sonicated for over 2h to exfoliate the solution. To

create a homogeneous suspension, 200 mg of P25 TiO₂ powder (for GO-TiO₂ composite) and 200 mg of M-TiO₂ (for GO/M-TiO₂ composite) were added in the sonicated GO solution and subjected to magnetic stirring at room temperature for 2h followed by transferring it to Teflon autoclave and heated at 180 °C for 5h. The resultant mixture was centrifuged and washed with DI water and ethanol, and dried.

The synthesis of M- TiO₂, GO-TiO₂, and GO/M-TiO₂ nanocomposites involved the use of various modified synthetic methods (specific experimental information can be found in the corresponding chapters). The surface, structural, and physicochemical properties of the as-prepared catalysts were further investigated using a variety of characterisation techniques.

The X-ray diffraction (XRD) technique was employed to quantify the diffraction pattern, crystallinity, and lattice plane of a catalyst that has been synthesised using an X-ray diffractometer (BRUKER) with Cu K α (1.54 Å) and an angle range of 10°–90° at a rate of 5° per minute.

The as-prepared nanocatalysts were analysed for their structural characteristics, including shape and particle size, using electron microscopy techniques such as Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM-7600F) and High-Resolution Transmission electron microscopy (HRTEM, JEOL JEM-2100 model). The elemental composition was determined through an Energy dispersive X-ray spectrometer (EDS) (Bruker, QUANTAX 200) connected to the above-mentioned FE-SEM scanning module.

Raman spectroscopy studies were conducted using a Labram HR 124 Evolution Raman microscope with a 532 nm excitation laser.

The UV-visible diffuse reflectance spectra (DRS) were recorded for the optical absorption properties of catalysts using a diffuse reflectance spectrophotometer (Avantes) with BaSO₄ serving as the reference. The PL emission spectrum was measured at room temperature to investigate the separation of photoinduced e⁻-h⁺ pairs. Samples were dispersed in distilled water, and data was recorded using a spectrofluorometer (SHIMADZU, RF-6000) for the analysis.

The Quanta Chrome Nova 2200 Surface Area & Pore Size Analyser was employed to analyse the surface area and pore size distribution of the samples using the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) methods, respectively (Analysis gas: Nitrogen, Bath Temp: 77.3 K, Outgas Time: 6 h, Outgas temperature: 200 °C).

The XPS analysis was employed to determine the elemental composition and oxidation states present in the composite. Using a monochromatic Al K Alpha X-ray source (1486 eV), the XPS data was recorded on a Thermo Fisher ESCALAB Xi+ spectrometer.

The hydrogen production during the photocatalytic dehydrogenation of alcohol was quantified using a NUCON, a gas chromatograph using argon as a carrier gas, and a molecular sieve (5X A column) with a thermal conductivity detector (TCD). The temperatures of the oven, injector, and detector were set according to the experimental conditions required. The hydrogen produced was quantified against a standard (505 ppm H₂ and 503 ppm CO₂, balanced with Argon).

The intermediates and degradation products were analysed using the HRMS (High-resolution mass spectroscopy) on Waters, QTOF mass spectrometer with UPLC (XEVO G2 XS).

The photocatalytic efficiency of synthesized GO-TiO₂, M-TiO₂, GO/M-TiO₂ nanocomposites was measured by examining the following two photocatalytic reactions:

The photocatalytic degradation efficiency of all composites was investigated for the degradation of various organic pollutants. In the course of photodegradation experiments, a certain quantity of catalyst was introduced into a test tube containing an aqueous solution of a particular pollutant. The test tube was firstly exposed to dark for a certain time period in order to attain adsorption-desorption equilibrium and then light illumination under two sources: UV lamp (125W Hg arc, 104 mW/cm²) and visible light (50W LED lamp, Wipro Garnet B22, with an intensity ~100W/m², $\lambda > 360$ nm) for distinct durations. At regular intervals, the test tube was taken out, the catalyst was separated from the pollutant solution by centrifugation, and the change in the concentration of the solution at different time intervals was measured using a UV-visible spectrophotometer (Shimadzu UV-2600 spectrophotometer). An analysis of the degradation products and intermediates was conducted using HRMS.

The photocatalytic production of hydrogen by the dehydrogenation of different alcohols was investigated using synthesised composites. A test tube containing 10 mL of an aqueous alcoholic solution (50 vol%) was used along with the desired amount of catalyst. The test was sealed with rubber septum to establish an inert atmosphere after being purged with argon gas for 20 minutes. Afterwards, the test tube was placed under light illumination with continuous stirring for a certain time period. A syringe was used to extract 1 ml of the sample gas produced in the test tube, which was then injected into the injector port of the GC and analysed for

hydrogen production. ⁸ The GC chromatogram was subsequently compared to a standard hydrogen chromatogram.

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