

# Hydrogen Production Using TiO<sub>2</sub>-Based Photocatalysts: A Comprehensive Review

Muhammad Rafique,\* Syeda Hajra, Muneeb Irshad, Muhammad Usman, Muhammad Imran, Mohammad A. Assiri, and Waqar Muhammad Ashraf\*

Cite This: <https://doi.org/10.1021/acsomega.3c00963>

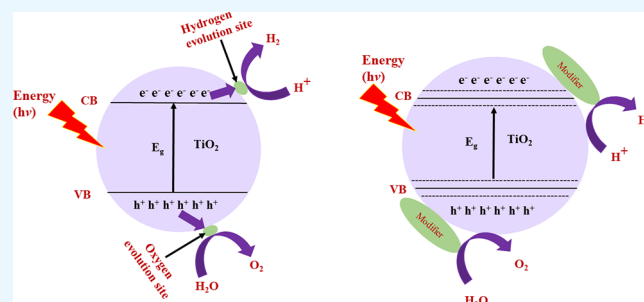
Read Online

ACCESS |

Metrics & More

Article Recommendations

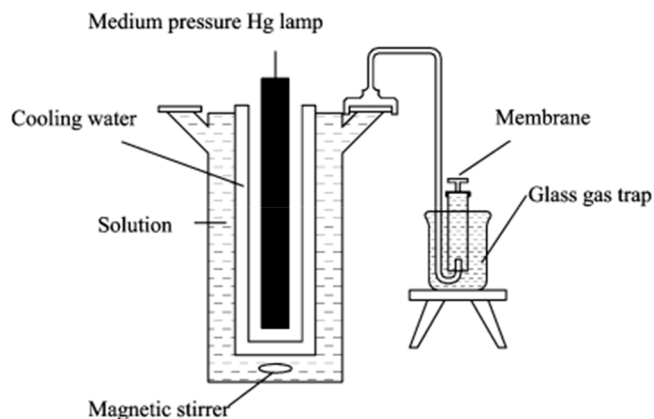
**ABSTRACT:** Titanium dioxide (TiO<sub>2</sub>) is one of the most widely used photocatalysts due to its physical and chemical properties. In this study, hydrogen energy production using TiO<sub>2</sub>- and titanate-based photocatalysts is discussed along with the pros and cons. The mechanism of the photocatalysis has been elaborated to pinpoint the photocatalyst for better performance. The chief characteristics and limitations of the TiO<sub>2</sub> photocatalysts have been assessed. Further, TiO<sub>2</sub>-based photocatalysts modified with a transition metal, transition metal oxide, noble metal, graphitic carbon nitride, graphene, etc. have been reviewed. This study will provide a basic understanding to beginners and detailed knowledge to experts in the field to optimize the TiO<sub>2</sub>-based photocatalysts for hydrogen production.



## 1. INTRODUCTION

Hydrogen is considered an ideal fuel and is highly preferred due to properties such as its life cycle, renewability, environmental friendliness, and cost-effectiveness. Hydrogen can be produced from both renewable and nonrenewable energy resources. There are two main sources of renewable energy: solar energy and wind energy. These two sources are very suitable for the production of clean hydrogen. The main problem associated with these renewable resources is that only 5% of hydrogen is derived from them and they also involve high cost. While about 95% of hydrogen can be produced from nonrenewable resources, scientists are focusing on the methods through which they can produce cost-effective hydrogen. Then, the concept of photovoltaic water electrolysis was developed in which semiconductor materials that have small band gaps are used. This technology produced hydrogen at low costs. Alternatively, for hydrogen production, photocatalytic water splitting using TiO<sub>2</sub> as a photocatalyst through solar energy is very promising. This way of producing hydrogen was very clean, low-cost, and environmentally friendly.<sup>1–5</sup>

Catalytic hydrogen production using semiconductor materials as catalysts has attracted much attention because of the maximum utilization of solar energy. The apparatus for photocatalytic water splitting is shown in Figure 1. Photocatalytic reactions occur when semiconductor materials absorb photons with energy  $h\nu$  equal to or greater than the band gap of the semiconductor. By absorbing this energy, electrons promote from the valence band to the conduction band and create an electron–hole pair. These photogenerated electrons



**Figure 1.** Apparatus for photocatalytic water splitting. Reprinted with permission from ref 6. Copyright 2005 American Chemical Society.

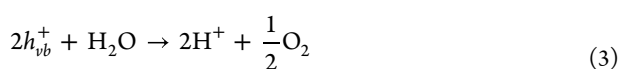
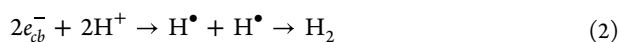
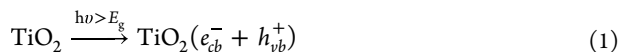
promoted to conduction band and reduce H<sup>+</sup> into H<sub>2</sub>, and holes on the semiconductor surface decompose H<sub>2</sub>O into O<sub>2</sub> and H<sup>+</sup>.<sup>6</sup> The behavior of these photogenerated carriers can have a significant influence on the performance of a

**Received:** February 13, 2023

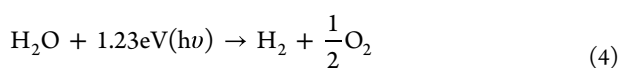
**Accepted:** July 6, 2023

semiconductor photocatalyst. Understanding and controlling the behavior of these carriers can lead to the evolution of efficient photocatalysts having a wide range of applications in environmental and energy-related fields. For example, the photogenerated charge carrier recombination can limit the photocatalyst efficiency. Similarly, controlling the transfer and migration of generated carriers can increase the efficiency of photocatalysts, such as the spatial separation of carriers, elongating their lifetime and thus increasing the photocatalytic performance. This behavior is explained in the following sections.

The overall mechanism of water splitting and hydrogen production is explained in eqs 1–4.<sup>6–8</sup>



The overall reaction can be summarized as



Titanium(IV) oxide naturally exists in two phases, namely, rutile and anatase, with a tetrahedral shape and simple synthesis.<sup>5</sup> Meanwhile, the other third phase is called brookite, which can be synthesized in laboratories and is rhombic in shape. The photocatalytic activity of TiO<sub>2</sub> such as anatase and rutile is influenced by crystal structure, surface area, surface hydroxyl density, porosity, and size<sup>4,5,9</sup> because all these factors affect the production of electrons and holes. These two forms have mostly been used in photocatalytic applications. Anatase is one of the most active phases. The enhancement of photocatalytic activity is related to the Fermi level of about 0.1 eV in the anatase phase, which was higher than that in the rutile phase.<sup>9,10</sup> TiO<sub>2</sub> is available commercially called Degussa P25, which is used in photo catalytic studies. The hydrolysis of TiCl<sub>4</sub> in hot flame produces TiO<sub>2</sub> with a surface area of about 50 m<sup>2</sup>/g, and it contains a 4:1 ratio of anatase and rutile phases.<sup>11</sup>

**1.1. Catalytic Mechanism.** In this process, induced charge carriers cause the oxidation of electrons (such as donor species) in the valence band (VB) and the reduction of electrons (such as acceptor species) in the conduction band (CB). In the photomodernizing reaction, organic substrates behaved as electron donors while H<sup>+</sup> was used as an electron acceptor. In this reaction, radiation energy is converted into chemical energy because in the presence of photocatalyst it absorbs solar energy very efficiently. In recent years, many different metal-oxide-based semiconductors as catalysts have been reported.<sup>12</sup> Some metal oxides such as SrTiO<sub>3</sub>, TiO<sub>2</sub>, BaTi<sub>4</sub>O<sub>9</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub> have a reasonable ability to split water H<sub>2</sub> and O<sub>2</sub> under visible and ultraviolet light radiation.<sup>13,14</sup> From all of these, TiO<sub>2</sub> is favorable due to having a band gap of 3.2 eV in the anatase phase, high stability in the form of an aqueous solution under UV radiation, high reducing and oxidizing power, nontoxicity, and cost effectiveness.<sup>3,5</sup>

**1.2. Limitations.** There are some limitations while using TiO<sub>2</sub>, and the main problem facing TiO<sub>2</sub> is its fast and undesirable electron–hole recombination reaction. In order to avoid this problem, sacrificial reagents can be used along with

TiO<sub>2</sub>, which is also suitable to increase photo-efficiency. The main task of these sacrificial reagents is to keep separate the photoexcited electrons and holes from the recombination process or reversible process. Compounds such as methanol, EDTA (an ethylene diamine tetra acetic derivative), Na<sub>2</sub>SO<sub>4</sub>, ethanol, and Na<sub>2</sub>S and ions such as I<sup>-</sup>, IO<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, and Fe<sup>3+</sup> are used as sacrificial reagents.<sup>6</sup> Simply, we can say that the photocatalytic hydrogen efficiency obtained by simple TiO<sub>2</sub> is low due to the following reasons: rapid recombination of photogenerated charge carriers, fast reverse reaction between H<sub>2</sub> and O<sub>2</sub>, and large production of hydrogen, which becomes over potential.

Furthermore, in a simple aqueous system, pure TiO<sub>2</sub> cannot split into H<sub>2</sub> and O<sub>2</sub>. Therefore, to reduce these problems, many efforts have been made in recent years, such as the addition of sacrificial reagents, metal cation doping, carbon and nitrogen doping, and deposition of noble metals.<sup>15,16</sup>

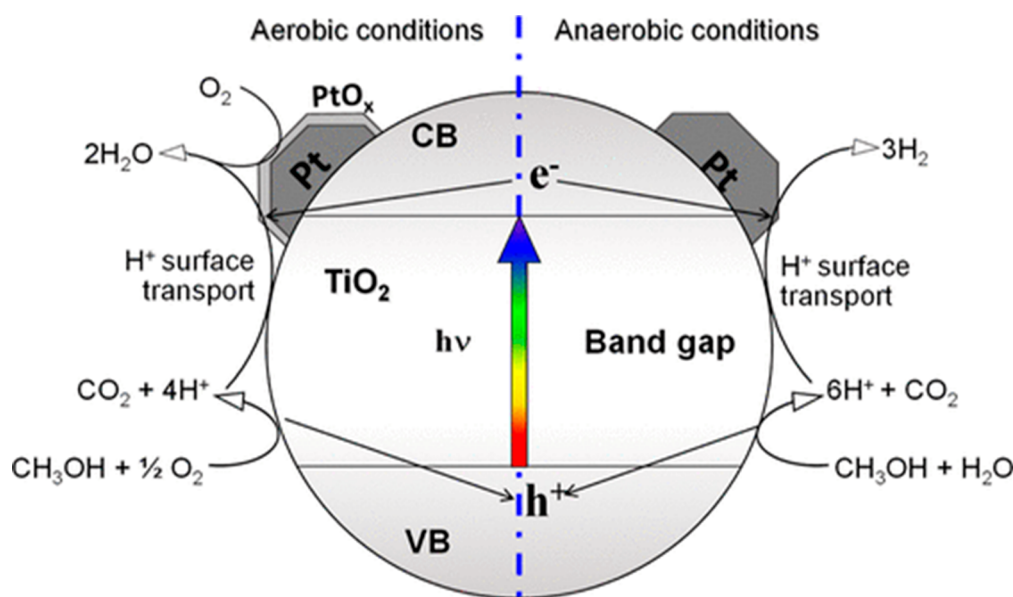
Therefore, diverse techniques have been employed for the modification of TiO<sub>2</sub> nanoparticles in order to attain the maximum possible hydrogen production rate. These methods involve the doping of transition metals, incorporation with other metal oxides, and surface modifications. Doping of transition metals in TiO<sub>2</sub> surpasses the band gap of TiO<sub>2</sub> by creating the quasi-static energy levels of dopants between the conduction and valence bands and also decreases the recombination rate of charge carriers.<sup>17</sup> The reduction in the band gap of the TiO<sub>2</sub> photocatalyst permits the material to harvest more photons during the reaction and thus produces more charge carriers. However, the incorporation of a metal oxide with TiO<sub>2</sub> enhances its activity by transferring the photogenerated electrons to the conduction band in a lower position on the semiconductor while transferring holes to the less anodic valence band under the illumination of both semiconductors. This separation of charge carriers implies the reduction in the recombination rate and hence increases the photocatalytic performance.<sup>18</sup> Therefore, it is claimed that TiO<sub>2</sub>-based photocatalysts enhance the photocatalytic activity due to various factors such as an enhanced charge separation rate, a lower recombination rate, and the presence of oxygen vacancies.

As an example, a study affirmed the efficient hydrogen production rate of 23.5 mmol/g·h having an apparent quantum yield of 19% using the Ag-doped TiO<sub>2</sub> photocatalyst. The observed efficient activity was attributed to the appearance of oxygen vacancies that enhanced the charge separation rate of (TiO<sub>2</sub>) responsible for the higher hydrogen production rate.<sup>19</sup> Furthermore, a Ce<sub>3</sub>O<sub>4</sub>@C/TiO<sub>2</sub> nanocomposite was fabricated by utilizing an incipient wet impregnation method for the photocatalytic production of hydrogen. The fabricated TiO<sub>2</sub>-based photocatalyst exhibited a hydrogen production rate of 11 400 μmol/g·h.<sup>20</sup> These studies claimed the enhancement of the photocatalytic activity of TiO<sub>2</sub> after its modification with different materials.

However, more fabricated modified TiO<sub>2</sub>-based photocatalysts are described in the proceeding sections.

## 2. TRANSITION-METAL-DOPED TiO<sub>2</sub> PHOTOCATALYSTS

**2.1. Platinum (Pt)/TiO<sub>2</sub> Photocatalyst.** For the preparation of TiO<sub>2</sub> nanosheets, a hydrothermal method was used. TiO<sub>2</sub> nanosheets with exposed (001) faces were prepared in a mixed solution of Ti (OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>–HF–H<sub>2</sub>O. Then, the deposition of Pt nanoparticles on the TiO<sub>2</sub> nanosheets was

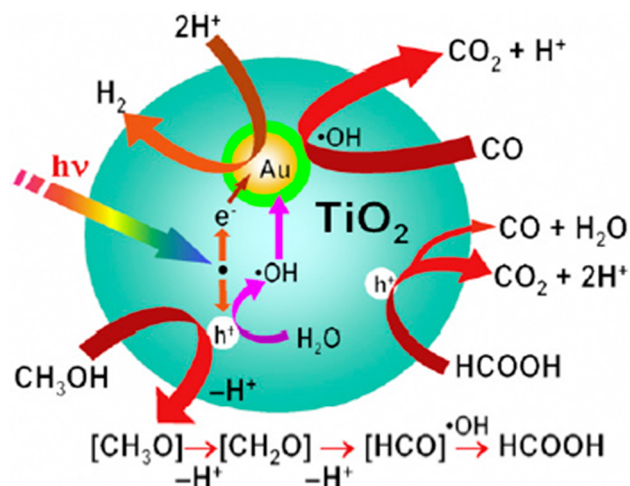


**Figure 2.** Mechanism of photocatalytic oxidation under aerobic and anaerobic conditions. Reprinted with permission from ref 22. Copyright 2022 American Chemical Society.

carried out by a photochemical reduction method under xenon lamp radiation, and a Pt/TiO<sub>2</sub> nanophotocatalyst is shown in Figure 2. The prepared sample was characterized by different characterization techniques such as scanning electron microscopy (SEM), photoluminescence spectroscopy (PS), X-ray diffraction (XRD), etc. Using coumarin as a probe material in photoluminescence (PL) spectroscopy, radicals of hydroxyl (OH•) were detected on the surface of the TiO<sub>2</sub> nanosheets. However, the excited electrons, after migrating toward the conduction band of Pt nanoparticles, react with H<sup>+</sup> ions to form the H<sub>2</sub> molecule. In addition, the rates of photocatalytic H<sub>2</sub> production were studied and discussed when Pt was loaded on the TiO<sub>2</sub> nanosheets in an ethanol aqueous solution. It was shown by results that the loaded Pt on the TiO<sub>2</sub> nanosheets enhanced the photocatalytic hydrogen production rates, and even 2 wt % deposited Pt showed the highest catalytic activity. Consequently, it was shown that, as compared to pure TiO<sub>2</sub>, fluorinated TiO<sub>2</sub> nanosheets exhibited high photocatalytic activity. These Pt/TiO<sub>2</sub> nanosheets have attracted too much interest in different fields such as solar cells, sensors, biomedical engineering, photonic devices, and catalysis.<sup>21,22</sup>

The drawback of using Pt is that it is a rare and very expensive metal, so it has to be replaced, for which numerous efforts have been made.<sup>15</sup> Moreover, when methanol was decomposed during the photocatalytic process on the Pt/TiO<sub>2</sub> catalyst, carbon monoxide (CO), hydrogen, methane, and carbon dioxide were obtained. A concentration of about 2.7 vol % CO in hydrogen was observed. The concentration of CO in H<sub>2</sub> was the main problem because a very small concentration of CO poisons the catalyst. In order to produce high amounts of and ultrapure hydrogen and for the reduction of the concentration of CO in H<sub>2</sub>, scientists are focusing on some other catalysts that could be more suitable and cost-effective as compared to Pt/TiO<sub>2</sub>.<sup>6,23</sup>

**2.2. Gold (Au) /TiO<sub>2</sub> Photocatalyst.** For the production of H<sub>2</sub>, gold as a dopant over a TiO<sub>2</sub> semiconductor can be selected as a catalyst in photocatalysis. The rate of H<sub>2</sub> production is higher using a Au/TiO<sub>2</sub> catalyst, as shown in Figure 3. H<sub>2</sub> was produced during the photocatalytic



**Figure 3.** Schematic diagram of photocatalytic reaction on a Au/TiO<sub>2</sub> catalyst. Reprinted with permission from ref 23. Copyright 2008 Elsevier.

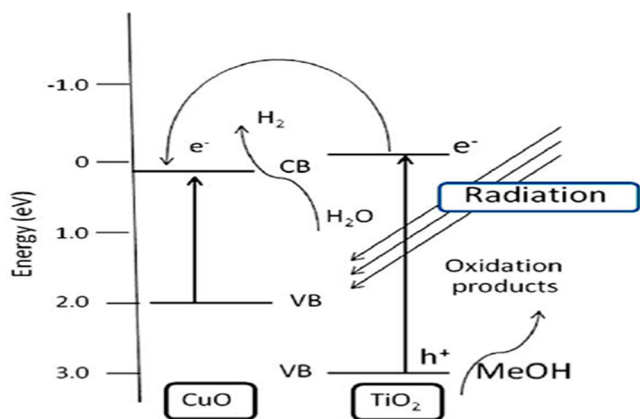
decomposition of methanol on the Au/TiO<sub>2</sub> catalyst using an ultralow concentration of CO. It was observed that when the size of the gold particles was decreased from 10 nm to smaller than 3 nm, the rate of H<sub>2</sub> production was significantly increased. Additionally, it was perceived that the absorption of CO decreased when the size of the Au particles decreased. The suggested reason for reducing the concentration of CO was that when intermediate formic acid species form methanol through decomposition, mainly CO is produced. Because the size of the gold particles was reduced, the decomposition of formic acid (HCOOH) was stopped, which overturned the CO, and only H<sub>2</sub> and CO<sub>2</sub> were produced as byproducts.<sup>6,23</sup>

Bamwenda and co-workers made an experiment in order to compare the catalytic activity of Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts for H<sub>2</sub> production. TiO<sub>2</sub> powder in aqueous suspensions of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O or H<sub>2</sub>AuCl<sub>4</sub>·4H<sub>2</sub>O was used for the deposition of Pt and Au particles through a chemical deposition method. The byproducts obtained during this



reaction were acetaldehyde, carbon dioxide, hydrogen, and formic acid. It was revealed the performance activity of the Pt sample was 30% higher than that of the Au sample. This is because of Au, which is highly dependent on preparation method as compared to Pt. When both Au and Pt samples were calcined at 573 K in air, they showed high production of hydrogen at this temperature. However, it was observed that the production of hydrogen became lower when calcination temperature was increased from 573 K temperature.<sup>24</sup>

**2.3. Copper (Cu)/TiO<sub>2</sub> Photocatalyst.** The photocatalyst of a Cu-doped TiO<sub>2</sub> semiconductor material was used for the production of H<sub>2</sub> under visible light. Complex precipitation and wet impregnation methods were used to prepare the Cu/TiO<sub>2</sub> photocatalyst. The schematic diagram of the Cu/TiO<sub>2</sub> photocatalyst is shown in Figure 4. The copper nitrate



**Figure 4.** Schematic diagram of transfer and separation of charges of the Cu/TiO<sub>2</sub> photocatalyst. Reprinted with permission from ref 25. Copyright 2009 Elsevier.

trihydrate was used as a starting material. The content of the copper dopant on the TiO<sub>2</sub> semiconductor varied from 2% to 15%. The sample of the synthesized Cu/TiO<sub>2</sub> photocatalyst was characterized by different characterization techniques, such as XRD, thermogravimetric analysis (TGA), SEM, and Fourier transform infrared spectroscopy (FTIR). As mentioned above, the Cu/TiO<sub>2</sub> photocatalyst was prepared by two synthesis methods under different concentrations of dopant and different calcination temperatures and showed different trends. The sample with 10% copper loading on TiO<sub>2</sub> and a calcination temperature of 300 °C that was prepared by the complex precipitation method showed better photocatalytic activity than the other, which was prepared by the wet impregnation method. The size of the copper dopant particles varied from 20 to 110 nm. Its rate of H<sub>2</sub> production was much higher than that of TiO<sub>2</sub>.<sup>25</sup>

**2.4. Iron (Fe)- and Chromium (Cr)-Doped TiO<sub>2</sub> Photocatalyst.** Transition metals like Cr, V, Fe, Cu, Ni, and Mn are mainly used as dopants of titania in order to enhance the photoelectrochemical and optical properties of TiO<sub>2</sub>.<sup>26</sup> As compared to other transition metals, Mn, Cu, and Fe can be used for trapping both charge carriers, namely, holes and electrons. While on the other hand, Ni and Cr can trap only one type of charge carrier.<sup>1,27</sup> Two methods were used to synthesize the Fe- and Cr-doped TiO<sub>2</sub> photocatalysts, namely, sol gel and radio frequency magnetron sputtering. It was observed that the Fe-doped TiO<sub>2</sub> catalyst has a high rate of hydrogen production (such as 15.5 μmol/h) as compared to

the Cr-doped TiO<sub>2</sub> catalyst (only 5.3 μmol/h). This is because of the trapping ability of Fe, which can trap both types of charge carriers and also avoid the recombination process. However, Cr only traps one type of carrier and also causes the recombination process, which lowers its ability to produce more hydrogen as compared to Fe.<sup>28</sup>

### 3. TRANSITION-METAL-OXIDE-DOPED TiO<sub>2</sub> PHOTOCATALYSTS

#### 3.1. Indium Tin Oxide/Cr-Doped TiO<sub>2</sub> Photocatalyst.

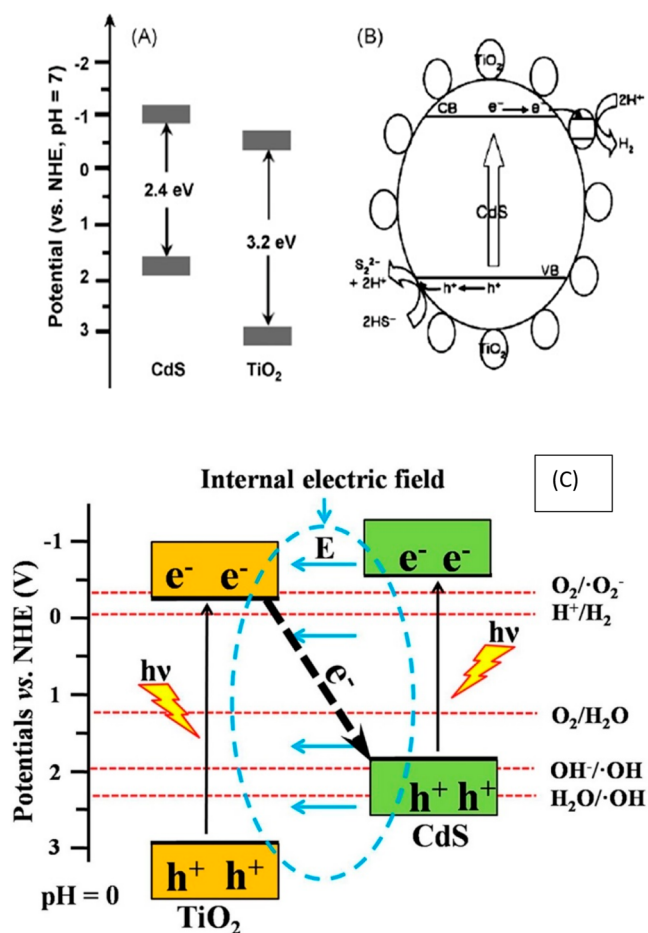
To enhance the hydrogen production rate of a Cr-doped TiO<sub>2</sub> catalyst, a single bilayer of indium tin oxide (ITO) is used with a Cr-doped TiO<sub>2</sub> catalyst. Negligible photocurrent was observed due to increased recombination of charge carriers. To reduce this recombination process, multiple bilayers of indium tin oxide were deposited over TiO<sub>2</sub>. Then, it was observed that the photocurrent increased as the number of bilayers increased. The rate of hydrogen production obtained was about 24.5 μmol/h, which was two times greater than that of the pure titania (12.5 μmol/h).<sup>29</sup>

**3.2. Cadmium Selenide (CdS)/TiO<sub>2</sub> and Cobalt Oxide (CoO)/CdS/TiO<sub>2</sub> Photocatalysts.** CdS/TiO<sub>2</sub> bulk nanocomposite material can be used as a photocatalyst. It was synthesized by using two methods, namely, sol gel and precipitation methods. A high H<sub>2</sub> production rate was observed for the CdS/TiO<sub>2</sub> photocatalyst, as shown in Figure 5. However, CdS has some limitations, such as being unstable against photocorrosion. To overcome this problem, sacrificial agents are used in solutions such as S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup>. In the presence of these sacrificial agents, CdS showed high H<sub>2</sub> production activity under light irradiation.<sup>30</sup>

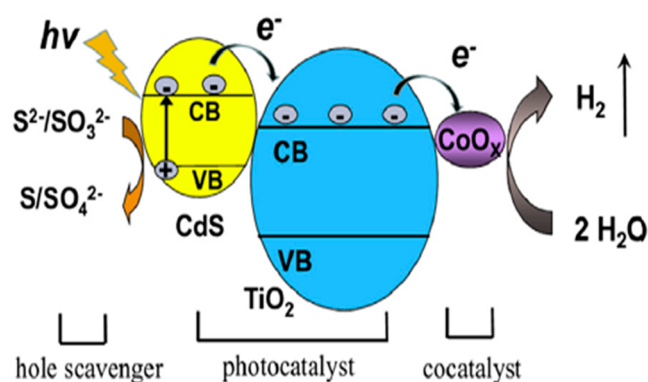
Recently, it was found that noble metal cobalt oxide (CoO) has been used as an electrocatalyst for proton reduction, and also it can be used as a photocatalyst for H<sub>2</sub> production. CoO over TiO<sub>2</sub>/CdS was synthesized using a solvothermal method, as shown in Figure 6. These samples were characterized by TEM, XRD, and XPS in an aqueous solution (having sodium sulfite and sodium sulfide) as hole scavengers under visible light (λ > 400 nm). For a concentration of 2.1 wt % CoO, the hydrogen production rate was 660 μmol/g-h, which was seven times greater than that of the simple TiO<sub>2</sub>/CdS photocatalyst under the same conditions.<sup>32</sup>

**3.3. Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Photocatalyst.** Metal oxide nanomaterials play a vital role in photocatalytic reactions to excite the electron to the CB and create a hole in the VB for the evolution of H<sub>2</sub>. These materials are interesting due to having high stability, low toxicity, and low-cost materials. A metal oxide such as TiO<sub>2</sub> has a large band gap, which is suitable for photocatalytic fuel production but only absorbs UV radiation. For this reason, only 5% of energy is shown in the solar energy spectrum. Metal oxide nanomaterials such as Fe<sub>2</sub>O<sub>3</sub> have suitable band gaps and are ineffective during photocatalytic reactions. A metal-organic framework (MOF) template is used to prepare the titania-based nanocomposite materials, as shown in Figure 7. Iron (Fe)-based MOFs are coated with titanium dioxide. Then, it was calcined to produce nanoparticles of composite Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>. This enables the composite to produce hydrogen when exposed to visible light radiation.<sup>33</sup>

**3.4. Ni(OH)<sub>2</sub>/TiO<sub>2</sub> Photocatalyst.** A Ni(OH)<sub>2</sub> cluster over TiO<sub>2</sub> was used to synthesize a nanocomposite catalyst (Ni(OH)<sub>2</sub>/TiO<sub>2</sub>) via the precipitation method. In this process, Ni(NO<sub>3</sub>)<sub>2</sub> was used as the precursor while the supportive

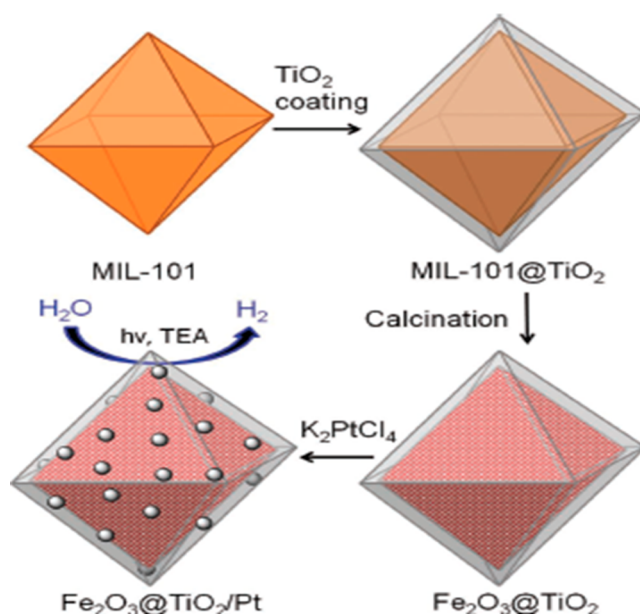


**Figure 5.** (a–c). Schematic diagram of the CdS/TiO<sub>2</sub> photocatalyst. Panels a and b reprinted with permission from ref 30. Copyright 2007 Elsevier. Panel c reprinted with permission from ref 31. Copyright 2017 Elsevier.

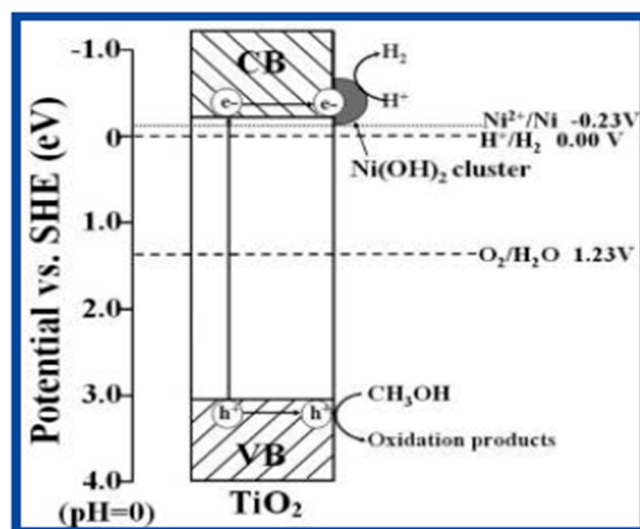


**Figure 6.** Schematic diagram of the CoO-loaded TiO<sub>2</sub>/CdS photocatalyst. Reprinted with permission from ref 32. Copyright 2014 Elsevier.

material was Degussa P25 TiO<sub>2</sub>, as shown in Figure 8. It was observed that the rate of H<sub>2</sub> production increased when a cluster of Ni(OH)<sub>2</sub> was used within an aqueous solution of methanol. It was revealed that applying a Ni(OH)<sub>2</sub> cluster on TiO<sub>2</sub> increased the photocatalytic activity. Moreover, when 0.23 mol % Ni(OH)<sub>2</sub> cluster was used, the rate of H<sub>2</sub> production was increased by 3056 μmol/g·h. It was observed that the prepared sample had a 223× greater quantum



**Figure 7.** MOF template synthesis of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>. Reprinted with permission from ref 33. Copyright 2012 John Wiley and Sons.



**Figure 8.** Schematic diagram of the transfer and separation of charges of the Ni(OH)<sub>2</sub> cluster over modified TiO<sub>2</sub>. Reprinted with permission from ref 34. Copyright 2011 American Chemical Society.

efficiency as compared to that of pure TiO<sub>2</sub>, which was obtained to be 12.4%. The main function of Ni<sup>0</sup> is to separate charges and also for the reduction of water. The potential of Ni<sup>2+</sup>/Ni is more negative as compared to the H<sup>+</sup>/H<sub>2</sub> potential, and it was also smaller than the CB of TiO<sub>2</sub>.<sup>34</sup>

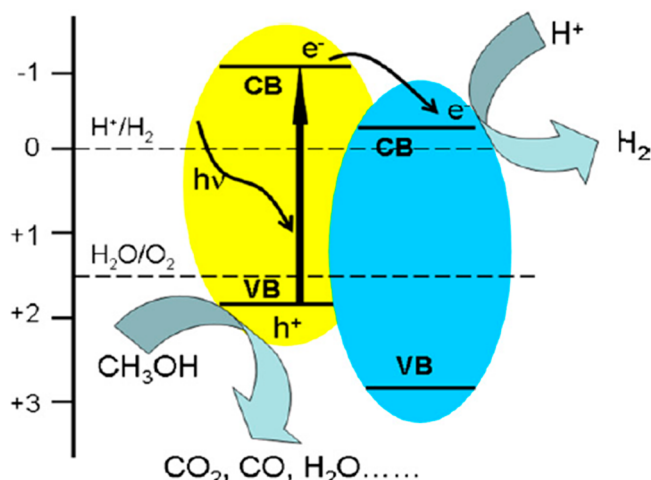
#### 4. NOBLE-METAL-MODIFIED TiO<sub>2</sub> PHOTOCATALYST

TiO<sub>2</sub> photocatalysts based on noble metals, such as Au, a Au alloy, and Pt, and Ag, can be synthesized by different methods, such as spray pyrolysis or deposition. When noble metals were deposited on TiO<sub>2</sub>, a good photocatalytic activity was observed. Moreover, by feeding methanol and water vapor on them, different byproducts were obtained, such as formaldehyde, carbon dioxide, methane, formic acid, dimethyl, methyl formate, ether, and acetaldehyde. These noble-metal-modified photocatalysts showed the best photocatalytic

performance and produced a high  $H_2$  rate and low emission of CO. It was observed that Pt was best for a cocatalyst for the evolution of  $H_2$  as compared to other noble metals.<sup>12</sup>

## 5. GRAPHITIC CARBON NITRIDE (G-C<sub>3</sub>N<sub>4</sub>)/TiO<sub>2</sub> PHOTOCATALYST

Another polymer semiconductor, namely, g-C<sub>3</sub>N<sub>4</sub> over TiO<sub>2</sub>, can be used as a photocatalyst in photocatalytic water splitting under visible light (in the presence of sacrificial reagents), as shown in Figure 9. The benefit of using this polymer



**Figure 9.** Schematic diagram of the transfer and separation of charges of composite TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. Reprinted with permission from ref 35. Copyright 2011 Elsevier.

semiconductor material was its optical band gap, which is 2.7 eV. Moreover, due to strong covalent bonds between nitride and carbon atoms, it shows high stability in water, acid, and base solutions under light irradiation. However, the catalytic activity of this composite TiO<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> is reasonably acceptable, meaning very low.<sup>35,36</sup>

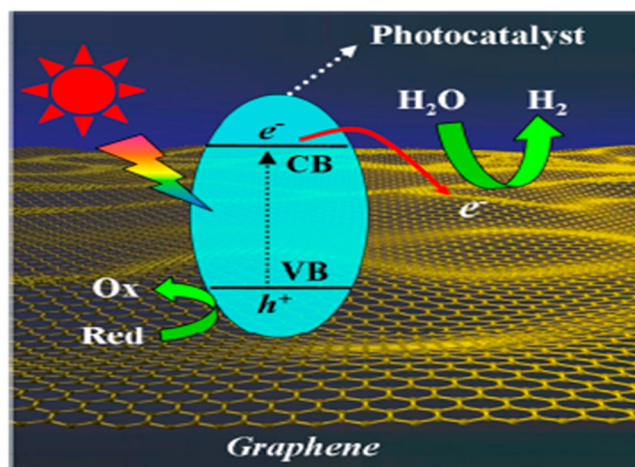
The composite g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> catalyst was prepared and characterized by XRD and FTIR. It was shown that this composite material consisted of peaks of g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>. The FTIR spectrum showed that this composite material has a stronger absorbance band intensity as compared to C<sub>3</sub>N<sub>4</sub> alone. The hydrogen production rate under visible light was remarkably increased by coupling TiO<sub>2</sub> with g-C<sub>3</sub>N<sub>4</sub>.<sup>35</sup>

**5.1. g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub>-Based Photocatalyst.** A g-C<sub>3</sub>N<sub>4</sub>-loaded SrTiO<sub>3</sub> photocatalyst was synthesized by the decomposition of urea at 400 °C. g-C<sub>3</sub>N<sub>4</sub> is a molecular photocatalyst in nature and has many advantages, such as a small band gap, facile absorption of visible light, and a high negative conduction band of about -1.12 eV, which causes facile transfer of photoelectrons to other components and is prepared by a simple and cheap method. In contrast, SrTiO<sub>3</sub> has a conduction band level about -0.5 eV and a forbidden band gap about 3.2 eV; this property provides a close interfacial area to combine the g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub>. The rate of  $H_2$  production was observed to be nearly 440  $\mu\text{mol/g}\cdot\text{h}$ , which was larger than that of the simple anion-doped SrTiO<sub>3</sub> photocatalyst.<sup>37</sup>

## 6. GRAPHENE-BASED GO/TiO<sub>2</sub> PHOTOCATALYST

Many researchers have expressed interest in rational designs of graphene for the performance of photocatalysts. A graphene-

based photocatalyst converts solar energy into chemical energy in order to increase the  $H_2$  production, as shown in Figure 10.



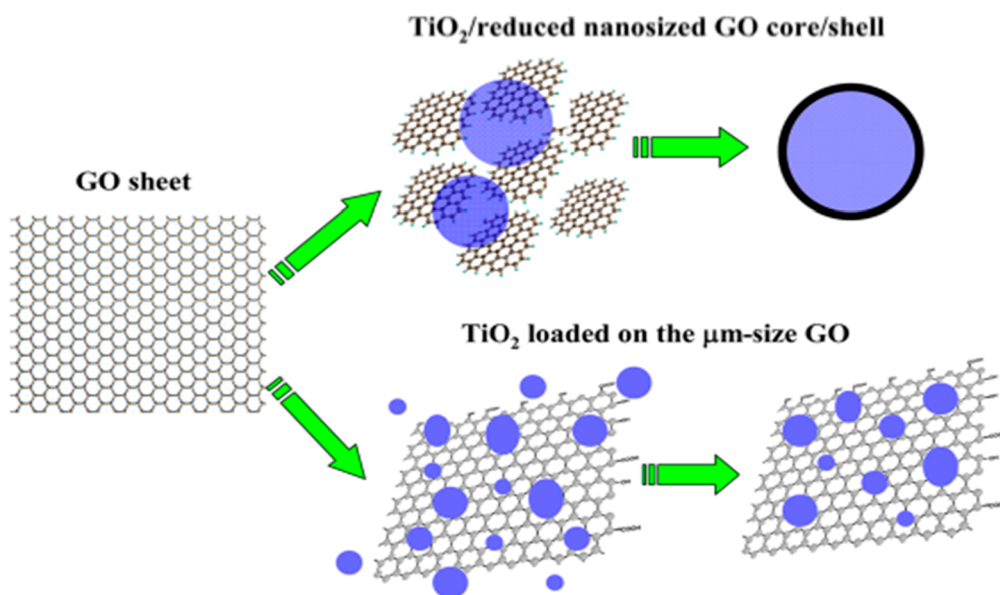
**Figure 10.** Proposed mechanism of graphene photocatalyst to enhance the photocatalytic performance. Reprinted with permission from ref 39. Copyright 2013 American Chemical Society.

Graphene has different properties such as  $sp^2$  hybridization; due to this, it shows high thermal conductivity, which is about 5000 W/m·k. Graphene also offers excellent mobility of about 200,000  $\text{cm}^2/\text{v}\cdot\text{s}$  at room temperature, and its surface area is about 2600  $\text{m}^2/\text{g}$ .<sup>38</sup> For these properties, graphene becomes more interesting as a photocatalyst because it has the ability to increase the transfer and separation of charge carriers. It enhances the efficiency in the following terms: reduces the recombination of electrons and holes, tunes the band gap of a semiconductor material, provides support to adsorption and catalytic sites, and acts as cocatalyst for producing hydrogen.<sup>39,40</sup>

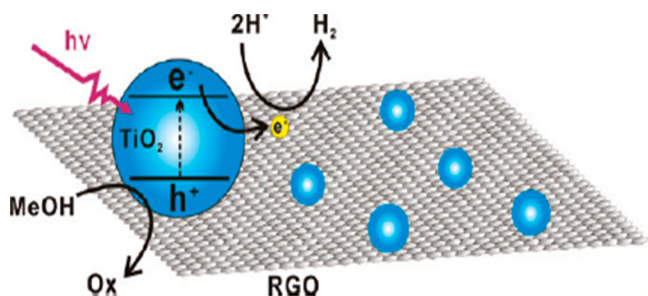
To increase the surface area of the photocatalyst, graphene provides two dimensional (2D) support and enhances its electrical and redox properties.<sup>41</sup> The main problem was observed in using graphene when photocatalyst nanoparticles were applied on graphene sheets, and it was shown that a very small number of particles have direct contact with the graphene sheet, which causes a delay in the transfer of electrons in the photocatalytic reaction and creates weak interaction. To provide the larger specific surface area and strong interaction, the new structure of graphene was found in the form of nanosized graphene oxide with titania (GO/TiO<sub>2</sub>), as shown in Figure 11. This new developed structure of graphene has a self-assembled core and shell structure that shows a high rate of production of  $H_2$ .<sup>39,42</sup>

**6.1. Reduced Graphene Oxide (RGO)/TiO<sub>2</sub> Photocatalyst.** For the production of  $H_2$ , RGO loaded over TiO<sub>2</sub> can also be used as a photocatalyst in an alcohol solution under UV radiation, as shown in Figure 12. It was synthesized through the hydrothermal method, which showed the best photocatalytic activity and best performance. RGO/TiO<sub>2</sub> contents in a ratio of 1:0.2 were used. The titanium dioxide (P25)-RGO was very stable and could be used as a recycle and catalyst for the evolution of  $H_2$ . It was observed that when nanoparticles of P25 about 20–30 nm in size were loaded on RGO sheet, there was strong interaction between RGO and TiO<sub>2</sub>, which suppresses the recombination process and enhances the photocatalytic performance.<sup>43</sup>





**Figure 11.** Schematic diagram of the preparation procedure of GO/TiO<sub>2</sub> and TiO<sub>2</sub>/GO. Reprinted with permission from ref 39. Copyright 2013 American Chemical Society.



**Figure 12.** Schematic diagram of the RGO/TiO<sub>2</sub> photocatalyst. Reprinted with permission from ref 43. Copyright 2011 American Chemical Society.

There are few more recent studies reported that describe the peculiar behavior of modified TiO<sub>2</sub> photocatalysts for the enhancement of hydrogen production rate. A study claimed the production of red phosphorus-modified TiO<sub>2</sub> hollow spheres achieved the highest hydrogen production rate of about 215.5 μmol/g·h. It was revealed that the heterostructure incorporated photoinduced charge separation that enhanced the hydrogen production activity.<sup>44</sup> Moreover, Bi/CdS/TiO<sub>2</sub> nanocomposites were prepared via the successive ionic layer adsorption and reaction method. This nanocomposite manifested 673.81 μmol/h·cm<sup>2</sup>.<sup>45</sup>

Another study reported the preparation of a NiSe<sub>2</sub> nanoparticle as a cocatalyst over TiO<sub>2</sub> using a supercritical fluid process. The fabricated photocatalyst was investigated for hydrogen production and was revealed to possess a 219.2 mmol/g·h hydrogen production rate.<sup>46</sup> Furthermore, a 2584.9 μmol/g·h hydrogen production rate was revealed using the O-ZIS/TiO<sub>2-x</sub> heterojunction.<sup>47</sup>

## 7. CONCLUSION

Hydrogen energy has become an emerging renewable energy resource because it is environmentally friendly, cost-effective, and has a stable life cycle. The most promising technique for hydrogen production is photocatalysis. The TiO<sub>2</sub> photocatalyst is the most widely used in photocatalytic water splitting and

hydrogen production. The noncommercial boundaries of the process are due to the catalyst limitation and are analyzed briefly in this Review. The process can be improved by doping and modifying the catalyst with transition metals, noble metals, graphite, and graphene and has been reviewed deliberately. This Review will provide insight into the TiO<sub>2</sub> and TiO<sub>2</sub>-based photocatalysts to choose the best and optimized photocatalyst for water splitting and hydrogen production. There are various factors that must be focused on and considered to achieve the maximum hydrogen production activity, such as effective preparation methods, sacrificial reagents, photocatalyst stability and most importantly, hydrogen transport and storage as a future perspective.

However, it can be summarized that photocatalytic generation of hydrogen utilizing a TiO<sub>2</sub> based photocatalyst is an economical and effective way to acquire sustainable energy. Doping of various nonmetal and metal materials can increase the performance of the photocatalyst by carefully tuning the band gap of the nanomaterials. Moreover, an optimum amount of the photocatalyst should be employed to achieve maximum activity because a high concentration of photocatalyst can reduce the efficiency of the photocatalyst.

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Muhammad Rafique** – Department of Physics, University of Sahiwal, Sahiwal, Punjab 57000, Pakistan; [orcid.org/0000-0002-2538-2768](https://orcid.org/0000-0002-2538-2768); Email: [mrafique.uet@gmail.com](mailto:mrafique.uet@gmail.com), [mrafique@uosahiwal.edu.pk](mailto:mrafique@uosahiwal.edu.pk)

**Waqar Muhammad Ashraf** – The Sargent Centre for Process Systems Engineering, Department of Chemical Engineering, University College London, London WC1E 6BT, U.K.; [orcid.org/0000-0003-1841-7659](https://orcid.org/0000-0003-1841-7659); Email: [waqar.ashraf.21@ucl.ac.uk](mailto:waqar.ashraf.21@ucl.ac.uk)

### Authors

**Syeda Hajra** – Department of Physics, Faculty of Science, University of Gujrat, Gujrat, Punjab 50700, Pakistan

Muneeb Irshad – Department of Physics, University of Engineering and Technology, Lahore, Punjab 54890, Pakistan

Muhammad Usman – Department of Mechanical Engineering, University of Engineering and Technology, Lahore, Punjab 54890, Pakistan

Muhammad Imran – Research Centre for Advanced Materials Science (RCAMS), King Khalid University, Abha 61514, Saudi Arabia; Department of Chemistry, Faculty of Science, King Khalid University, Abha 61413, Saudi Arabia

Mohammad A. Assiri – Research Centre for Advanced Materials Science (RCAMS), King Khalid University, Abha 61514, Saudi Arabia; Department of Chemistry, Faculty of Science, King Khalid University, Abha 61413, Saudi Arabia

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.3c00963>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors express their appreciation to the Deanship of Scientific Research at King Khalid University, Saudi Arabia, for funding this work through a research group program under Grant RGP-2/370/44.

## REFERENCES

- (1) Ni, M.; et al. A review and recent developments in photocatalytic water-splitting using TiO<sub>2</sub> for hydrogen production. *Renewable and Sustainable Energy Reviews* **2007**, *11* (3), 401–425.
- (2) Moustafa, H. M.; et al. Co–TiO<sub>2</sub> supported on reduced graphene oxide as a highly active and stable photocatalyst for hydrogen generation. *Fuel* **2023**, *338*, 127232.
- (3) Nabi, G.; et al. Green synthesis of TiO<sub>2</sub> nanoparticles using lemon peel extract: their optical and photocatalytic properties. *Int. J. Environ. Anal. Chem.* **2022**, *102*, 434–442.
- (4) Tahir, M. B.; et al. Photocatalytic performance of hybrid WO<sub>3</sub>/TiO<sub>2</sub> nanomaterials for the degradation of methylene blue under visible light irradiation. *Int. J. Environ. Anal. Chem.* **2021**, *101*, 1448–1460.
- (5) Tahir, M. B.; et al. Development of Sol Gel Derived Nanocrystalline TiO<sub>2</sub> Thin Films via Indigenous Spin Coating Method. *Journal of Inorganic and Organometallic Polymers and Materials* **2018**, *28* (1), 1–8.
- (6) Galińska, A.; Walendziewski, J. Photocatalytic water splitting over Pt–TiO<sub>2</sub> in the presence of sacrificial reagents. *Energy Fuels* **2005**, *19* (3), 1143–1147.
- (7) Wafi, A.; et al. Coumarin-based quantification of hydroxyl radicals and other reactive species generated on excited nitrogen-doped TiO<sub>2</sub>. *J. Photochem. Photobiol., A* **2021**, *404*, 112913.
- (8) Eidsvåg, H.; et al. TiO<sub>2</sub> as a photocatalyst for water splitting—An experimental and theoretical review. *Molecules* **2021**, *26* (6), 1687.
- (9) Rafique, M.; et al. Investigation of Photocatalytic and Seed Germination Effects of TiO<sub>2</sub> Nanoparticles Synthesized by Melia azedarach L. Leaf Extract. *Journal of Inorganic and Organometallic Polymers and Materials* **2019**, *29* (6), 2133–2144.
- (10) Tahir, M. B.; et al. Optical, microstructural and electrical studies on sol gel derived TiO<sub>2</sub> thin films. *Indian J. Pure Appl. Phys.* **2017**, *55* (01), 81–85.
- (11) Wold, A. Photocatalytic properties of titanium dioxide (TiO<sub>2</sub>). *Chem. Mater.* **1993**, *5* (3), 280–283.
- (12) Chiarello, G. L.; Aguirre, M. H.; Selli, E. Hydrogen production by photocatalytic steam reforming of methanol on noble metal-modified TiO<sub>2</sub>. *J. Catal.* **2010**, *273* (2), 182–190.
- (13) López-Vásquez, A.; Delgado-Niño, P.; Salas-Siado, D. Photocatalytic hydrogen production by strontium titanate-based perovskite doped europium (Sr 0.97 Eu 0.02 Zr 0.1 Ti 0.9 O 3). *Environmental Science and Pollution Research* **2019**, *26*, 4202–4214.
- (14) Karthik, K.; et al. Barium titanate nanostructures for photocatalytic hydrogen generation and photodegradation of chemical pollutants. *Journal of Materials Science: Materials in Electronics* **2019**, *30*, 20646–20653.
- (15) Jin, Z.; et al. 5.1% Apparent quantum efficiency for stable hydrogen generation over eosin-sensitized CuO/TiO<sub>2</sub> photocatalyst under visible light irradiation. *Catal. Commun.* **2007**, *8* (8), 1267–1273.
- (16) Suhag, M. H.; et al. Application of Rh/TiO<sub>2</sub> Nanotube Array in Photocatalytic Hydrogen Production from Formic Acid Solution. *Journal of Composites Science* **2022**, *6* (11), 327.
- (17) Singh, P.; et al. Review on various strategies for enhancing photocatalytic activity of graphene based nanocomposites for water purification. *Arabian Journal of Chemistry* **2020**, *13* (1), 3498–3520.
- (18) López, U.; et al. Synthesis and Characterization of ZnO-ZrO<sub>2</sub> Nanocomposites for Photocatalytic Degradation and Mineralization of Phenol. *J. Nanomater.* **2019**, 1015876.
- (19) Gogoi, D.; et al. Ag-doped TiO<sub>2</sub> photocatalysts with effective charge transfer for highly efficient hydrogen production through water splitting. *Int. J. Hydrogen Energy* **2020**, *45* (4), 2729–2744.
- (20) El-Bery, H. M.; Abdelhamid, H. N. Photocatalytic hydrogen generation via water splitting using ZIF-67 derived Co<sub>3</sub>O<sub>4</sub>@ C/TiO<sub>2</sub>. *Journal of Environmental Chemical Engineering* **2021**, *9* (4), 105702.
- (21) Yu, J.; Qi, L.; Jaroniec, M. Hydrogen production by photocatalytic water splitting over Pt/TiO<sub>2</sub> nanosheets with exposed (001) facets. *J. Phys. Chem. C* **2010**, *114* (30), 13118–13125.
- (22) Chiarello, G. L.; Bernareggi, M.; Selli, E. Redox Dynamics of Pt and Cu Nanoparticles on TiO<sub>2</sub> during the Photocatalytic Oxidation of Methanol under Aerobic and Anaerobic Conditions Studied by In Situ Modulated Excitation X-ray Absorption Spectroscopy. *ACS Catal.* **2022**, *12* (20), 12879–12889.
- (23) Wu, G.; et al. H<sub>2</sub> production with ultra-low CO selectivity via photocatalytic reforming of methanol on Au/TiO<sub>2</sub> catalyst. *Int. J. Hydrogen Energy* **2008**, *33* (4), 1243–1251.
- (24) Bamwenda, G. R.; et al. Photoassisted hydrogen production from a water-ethanol solution: a comparison of activities of Au–TiO<sub>2</sub> and Pt–TiO<sub>2</sub>. *J. Photochem. Photobiol., A* **1995**, *89* (2), 177–189.
- (25) Yoong, L.; Chong, F. K.; Dutta, B. K. Development of copper-doped TiO<sub>2</sub> photocatalyst for hydrogen production under visible light. *Energy* **2009**, *34* (10), 1652–1661.
- (26) Choi, W.; Termin, A.; Hoffmann, M. R. The role of metal ion dopants in quantum-sized TiO<sub>2</sub>: correlation between photoreactivity and charge carrier recombination dynamics. *J. Phys. Chem.* **1994**, *98* (51), 13669–13679.
- (27) Litter, M.; Navio, J. A. Photocatalytic properties of iron-doped titania semiconductors. *J. Photochem. Photobiol., A* **1996**, *98* (3), 171–181.
- (28) Dholam, R.; et al. Hydrogen production by photocatalytic water-splitting using Cr-or Fe-doped TiO<sub>2</sub> composite thin films photocatalyst. *Int. J. Hydrogen Energy* **2009**, *34* (13), 5337–5346.
- (29) Dholam, R.; et al. Efficient indium tin oxide/Cr-doped-TiO<sub>2</sub> multilayer thin films for H<sub>2</sub> production by photocatalytic water-splitting. *International journal of hydrogen energy* **2010**, *35* (18), 9581–9590.
- (30) Jang, J. S.; et al. Optimization of CdS/TiO<sub>2</sub> nano-bulk composite photocatalysts for hydrogen production from Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> aqueous electrolyte solution under visible light ( $\lambda \geq 420$  nm). *J. Photochem. Photobiol., A* **2007**, *188* (1), 112–119.
- (31) Meng, A.; et al. Direct Z-scheme TiO<sub>2</sub>/CdS hierarchical photocatalyst for enhanced photocatalytic H<sub>2</sub>-production activity. *Appl. Surf. Sci.* **2017**, *422*, 518–527.
- (32) Yan, Z.; et al. Noble metal-free cobalt oxide (CoOx) nanoparticles loaded on titanium dioxide/cadmium sulfide composite for enhanced photocatalytic hydrogen production from water. *Int. J. Hydrogen Energy* **2014**, *39* (25), 13353–13360.



- (33) Dekrafft, K. E.; Wang, C.; Lin, W. Metal-Organic Framework Templated Synthesis of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Nanocomposite for Hydrogen Production. *Advanced materials* **2012**, *24* (15), 2014–2018.
- (34) Yu, J.; Hai, Y.; Cheng, B. Enhanced photocatalytic H<sub>2</sub>-production activity of TiO<sub>2</sub> by Ni(OH)<sub>2</sub> cluster modification. *J. Phys. Chem. C* **2011**, *115* (11), 4953–4958.
- (35) Yan, H.; Yang, H. TiO<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> composite materials for photocatalytic H<sub>2</sub> evolution under visible light irradiation. *Journal of alloys and compounds* **2011**, *509* (4), L26–L29.
- (36) Lin, T.-H.; et al. Nanoscale Multidimensional Pd/TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> Catalyst for Efficient Solar-Driven Photocatalytic Hydrogen Production. *Catalysts* **2021**, *11* (1), 59.
- (37) Xu, X.; et al. g-C<sub>3</sub>N<sub>4</sub> coated SrTiO<sub>3</sub> as an efficient photocatalyst for H<sub>2</sub> production in aqueous solution under visible light irradiation. *international journal of hydrogen energy* **2011**, *36* (21), 13501–13507.
- (38) Xiang, Q.; Yu, J.; Jaroniec, M. Graphene-based semiconductor photocatalysts. *Chem. Soc. Rev.* **2012**, *41* (2), 782–796.
- (39) Xiang, Q.; Yu, J. Graphene-based photocatalysts for hydrogen generation. *J. Phys. Chem. Lett.* **2013**, *4* (5), 753–759.
- (40) Reza, M. S.; et al. Hydrogen Production from Water Splitting through Photocatalytic Activity of Carbon-Based Materials. *Chem. Eng. Technol.* **2023**, *46* (3), 420–434.
- (41) Kamat, P. V. Graphene-based nanoarchitectures. Anchoring semiconductor and metal nanoparticles on a two-dimensional carbon support. *J. Phys. Chem. Lett.* **2010**, *1* (2), 520–527.
- (42) Kim, H.-i.; et al. Solar photoconversion using graphene/TiO<sub>2</sub> composites: nanographene shell on TiO<sub>2</sub> core versus TiO<sub>2</sub> nanoparticles on graphene sheet. *J. Phys. Chem. C* **2012**, *116* (1), 1535–1543.
- (43) Fan, W.; et al. Nanocomposites of TiO<sub>2</sub> and reduced graphene oxide as efficient photocatalysts for hydrogen evolution. *J. Phys. Chem. C* **2011**, *115* (21), 10694–10701.
- (44) Huang, G.; et al. Hierarchical red phosphorus incorporated TiO<sub>2</sub> hollow sphere heterojunctions toward superior photocatalytic hydrogen production. *Journal of Materials Science & Technology* **2022**, *108*, 18–25.
- (45) Wang, Q.; et al. Construction of Bi-assisted modified CdS/TiO<sub>2</sub> nanotube arrays with ternary S-scheme heterojunction for photocatalytic wastewater treatment and hydrogen production. *Fuel* **2022**, *322*, 124163.
- (46) Jayachitra, S.; et al. Highly conductive NiSe<sub>2</sub> nanoparticle as a co-catalyst over TiO<sub>2</sub> for enhanced photocatalytic hydrogen production. *Applied Catalysis B: Environmental* **2022**, *307*, 121159.
- (47) Liu, J.; et al. Synergistic effect of oxygen defect and doping engineering on S-scheme O-ZnIn<sub>2</sub>S<sub>4</sub>/TiO<sub>2-x</sub> heterojunction for effective photocatalytic hydrogen production by water reduction coupled with oxidative dehydrogenation. *Chemical Engineering Journal* **2022**, *430*, 133125.