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Photocatalytic Hydrogen Production From TiO_2

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Abstract

The production of hydrogen by photo-catalysis under solar irradiation is an attractive process for generating green hydrogen to reduce CO2 emissions. Because of their specific physico-chemical properties, TiO2 photo catalysts have generally been used for hydrogen production. However, their wide band gap, which can only be activated under UV light and the rapid recombination of charge carriers, limits their photo-catalytic applications. However, a number of approaches have been put forward to reduce the energy of its band gap for visible light activity. Among them, TiO2 doping can be examined as an effective process not only for shifting light absorption towards the visible region, but also for reducing charge recombination. This study focuses on enhancing the photo catalytic activity of TiO2. In addition, the synthesis processes used for doped TiO2 were meticulously examined. In addition, a metal such as Cu and noble metals such as Au and Pt are the most widely studied dopants for TiO2. In addition, nitrogen was also used as a non- metal because of its ability to decrease the band gap energy of TiO2. The results also revealed that the sol-gel process is widely used in the synthesis of doped TiO2 photo catalysts because of the crystallinity and high surface area of the nanoparticles obtained.

Keywords: Hydrogen production; Photo catalysis; Renewable energy; TiO2

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1. Introduction

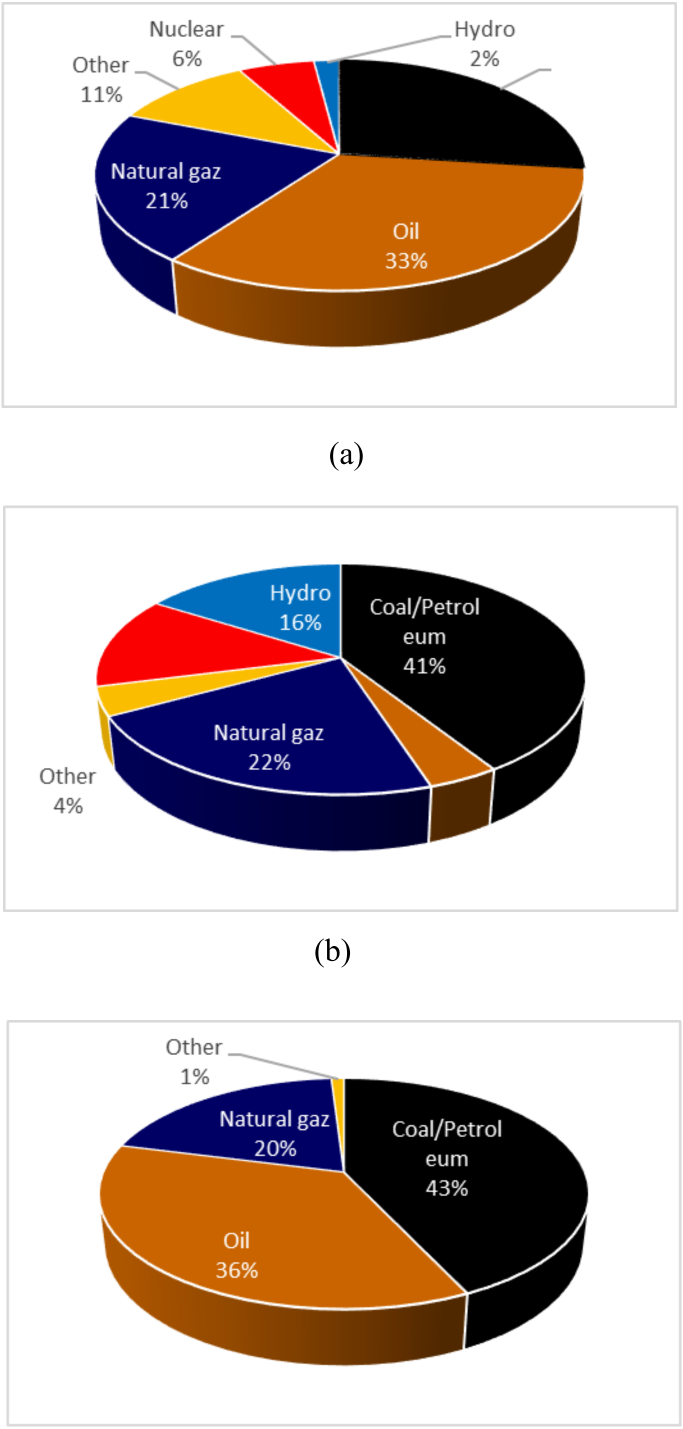
The growing population and improving living standards result in an increase in energy demand. To meet this demand, it is essential to increase energy production. Fossil fuels play an important role in solving energy problems, but they cannot be considered a powerful energy source because of their contribution to global pollution, as they release greenhouse gases. These oxides are toxic to human health and are one of the main causes of global warming. The depletion of fossil fuels also explains their unsatisfactory contribution to the achievement of energy objectives. These energy upheavals and the global pollution resulting from the consumption of fossil fuels are pushing us to seek an alternative path that must use a renewable energy source and provide an environmentally friendly solution to meet global energy needs. Renewable energies that produce fewer greenhouse gas emissions must replace fossil fuels.

Hydrogen is a formidable energy carrier, highly combustible and renewable, which plays a key role in solving the current energy crisis. Hydrogen can be produced from a wide range of sources, stored in different forms and converted into different fuels. Producing hydrogen from water or any other renewable resource will reduce the ecological damage caused by the energy zone, as there are no carbon emissions.

Hydrogen can be produced in several ways, such as steam reforming, coal gasification, thermochemical processes, and biological processes.

Photo catalysis of water using solar radiation is the most efficient method of producing hydrogen, which has the effect of preventing greenhouse gas pollution caused by the use of fossil fuels. This process shows several advantages, including better energy conversion efficiency, separate emission of hydrogen and oxygen and environmental friendliness. Reactors can be built on a small scale, increasing their commercial efficiency and restricting demand for photovoltaic installations.

Water photo catalysis, also called "artificial photosynthesis", is based on the transformation of solar fuel into chemical form by exposure to solar radiation with the help of a suitable catalyst. The photo catalyst is never exhausted during the chemical reaction, but it participates in the dynamics of the photo catalytic reaction. The production of hydrogen on an industrial scale remains a major challenge that requires efficient and suitable methods for converting solar energy into fuel [1].



(a)

(b)

(c)

Figure 1. World's shares of fuel for (a) energy supply, (b) generation of electricity, and (c) emission of CO2 emissions in 2020 [1]

2. Water Splitting

2.1. Basic Principle of Water Splitting

From a thermodynamic point of view, the separation of water is an endothermic process that requires an energy equivalent to □G°=237 kJ/mol or a potential value of 1.23 eV for a single electron. A photon of adequate energy is captured to split water in order to meet this colossal criterion. The evolution of oxygen and hydrogen in the electrochemical splitting of water is based on a four-electron and two-electron process respectively, as shown in the following equations.

Absorption of light:

$SC + hv(>Eg) \longrightarrow e^-_{cb} + h^+_{vb}$ (1)

Water oxidation (OER): $2H_2O + 4h^+_{vb} \longrightarrow O_2 + 4H^+$ (2)

Proton reduction (HER): $2H + 2e^-_{cb} \longrightarrow H_2$ (3)

Overall water splitting: $2H2O \longrightarrow 2H2 + O2$ (4)

□G° = 237.2 kJ mol^{-1}

It is interesting to use a suitable photo catalyst capable of producing e/h pairs by absorbing photons of an appropriate energy. These e/h pairs generated by the photo catalyst are responsible for the oxidation-reduction reactions of the water molecules on the surface of the catalyst with an energy of 1.23 eV to produce a photo excited e/h pair and carry out the oxidation-reduction reactions. [1]

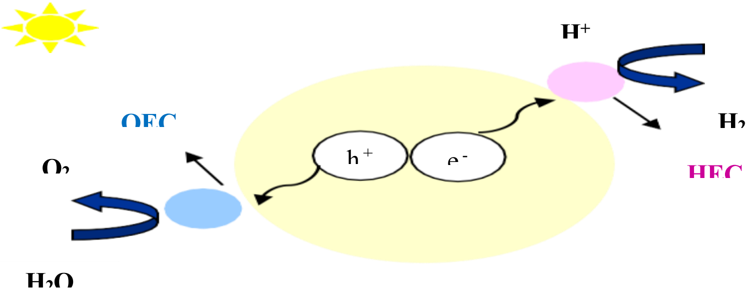


Figure 2. Photocatalytic splitting of H2O [1]

2.2. Types of photo catalytic water splitting reaction

Photochemical water separation can be carried out on two types of photosystems: Particulate photo catalytic systems (PPS) and Photo-electrochemical cells (PEC).

The particulate system is a system in which the photo catalyst is poured into an aqueous solution in powder form. In this system, each particle acts as a microelectrode and is responsible for the oxidation-reduction reactions of the water on the surface of the photo-catalyst. As there is no pelica deposited in the PPS, no additional substrate is required, making it a simple and inexpensive water separation process. The second advantage associated with PPS is the larger surface area of the photo-catalyst, with more active sites. Although PPSs are simple and inexpensive, they are less efficient because of the lower productivity of charge separation and the difficulty of charge recombination, which results in a lower rate of hydrogen production.

The photo-catalytic separation of water in PPS consists of three phases: A photon of desirable energy, i.e. hv, equal to or greater than Eg of the photo-catalytic semiconductor, strikes the photo-catalytic surface and is absorbed by the semiconductor during the first phase. This hv absorption causes charge acquisition on the photo-catalytic semiconductor substrate, with the conduction band (CB) becoming more electronegative while the valence band (VB) becomes more electropositive due to the production of negatively charged entities (electrons) in CB and positively charged entities (holes) photo-generated in VB. The second phase involves charge separation and transport, i.e. the movement of holes and electrons to the reaction sites of the photo catalytic semiconductor. Finally, chemical transformations occur at the surface of the photo catalytic semiconductor, in which the photo generated holes and electrons oxidize and reduce the water molecules adsorbed on the surface of the semiconductor. [1]

3. Types of reactions

There are two types of reaction by which hydrogen can be generated by photo catalysis of water: (i) photochemical cell reactions and (ii) photo electrochemical cell reactions. [2]

Photochemical reactions including the photo catalyst suspension in solution were studied by Liao et al and Jiang et al [3-4] as being accomplished by the dirct use of energy for the occurrence of the chemical reaction. The variation in hydrogen and oxygen is the result of the division of water with the appropriate photo-catalyst after the absorption of sufficient light energy. Certain properties of the photo catalyst, such as its ability to absorb light during suspension, changes in the pH value of the reaction in progress, and the concentration of the substrate, become difficult to control. The hydrogen gas advances to the semiconductor-electrolyte junction, which acts as an interface to produce the potential required for water splitting, but it is difficult to observe the experimental results because the kinetics of the reaction are influenced by these factors, making the operation quite laborious. [2]

4. TIO2 AS PHOTO CATAL.YST

As a photo catalyst, TiO2 is gaining in popularity and is the most studied photo catalyst due to its many advantages, such as its high thermal and chemical stability, low cost, high photo catalytic efficiency, high refractive index and non-toxicity. [5] Chong et al [6] examined the fundamentals of the photo catalyst, photo reactor development, process optimization, kinetic modelling and parameters that affect process efficiency. In another review, Schneider et al [7] have summarized certain aspects of TiO2 photo catalysis, particularly charge carrier transport kinetics, new mechanistic aspects and exceptional doping methods to improve photo catalytic activities and extend the range of accessible wavelengths. Ni et al [8] have highlighted the transformation techniques and chemical additives used to improve the photo- catalytic activity of TiO2 for hydrogen production. However, the efficiency of hydrogen production by photo catalysis is limited because of the energy of the wide band gap and the rapid recombination rate of charge carriers. As a result, a number of experiments have been developed not only to reduce its band gap energy but also to reduce charge carrier recombination, such as doping with a metal or non-metal to reduce the band gap energy and assembly with other semiconductors or loading with cocatalysts to improve charge separation. Titanium dioxide (TiO2) comes in three types of crystals: anatase, rutile, and brookite. Anatase, whose band gap energy is equal to 3.2 eV, is the most active photo catalytic polymorph of titanium because of its greater kinetic stability. Unlike brookite, anatase is readily available in pure form. Rutile, which has the lowest band gap energy (around 2.96 eV), is the most stable form of titanium and is usually used as a white pigment. On the other hand, the brookite phase is not commonly used in photo catalysis because it cannot be obtained in a pure state like anatase or rutile [5].

5. Synthesis of TiO2 Doped Materials

5.1. Sol-Gel Method

The sol-gel process is a fundamental low-temperature process generally used to prepare nanoparticles. It offers a number of advantages, including good homogeneity, a rapid process, low calcination temperature and minimal time. The nanoparticles obtained therefore have good crystallinity and a large specific surface area. In this process, the precursors of the substances obtained were dissolved in a solvent and the pH was checked until the sol was formed. The gel was then obtained by heating the solution containing the precursors; oxide or hydroxide nanoparticles were produced by hydroxylation and poly condensation reactions. Finally, the gel was calcined to form nanoparticles at an ideal calcination temperature. An iron and chromium doped TiO2 thin film using combined RT and soluble gel processes was successfully synthesized by Dholam et al [9]. The activities of doped TiO2 photo-catalysts were tested for the evolution of hydrogen under visible light irradiation. The results showed that the doped substances have higher activities than undoped TiO2, which is attributed to the role of chromium and iron, which act as electron trapping agents. The sol-gel process was used to prepare N-doped TiO2 using ethylene diamine as the nitrogen source for hydrogen evolution and methyl orange degradation by Li et al [10]. The EDTA/TiO2 ratio calcined at 500°C shows superior photo-catalytic performance. The decrease in band gap energy and the enhancement of light absorption are thought to be the cause of the improved activity of nitrogen-doped titanium.

The sol-gel process has been widely used as an encouraging and attractive process for the preparation of TiO2 nanoparticles or thin films. In addition, the sol-gel process does not require a high temperature as in the case of the solid state reaction, nor does it require complex equipment as in the case of the microwave assistant process [5].

5.2. Hydrothermal/Solvothermal Method

The hydrothermal or solvothermal process is commonly used in inorganic chemistry for the synthesis of inorganic nanomaterial of various configurations for a variety of applications. The difference between these two processes lies in the prior use of water as a solvent. This method carries out a chemical reaction at controlled temperature and pressure in solvents enclosed in closed steel autoclaves. This method has two phases: nucleation and crystal growth. What's more, this system accurately controls a number of factors that influence synthesis, such as pH, temperature and additives. Subsequently, nanomaterial with high crystallinity and suitable granulometry and configuration were obtained. Silver and iron were successfully deposited on anatase TiO2 by Sun et al using a solvothermal process. The photo catalytic activity of doubly doped metals was promoted in order to generate hydrogen. Among the various doped substances, the 4.5% Fe-4.5% Ag/TiO2 mixture showed the most potent hydrogen production activity, due to improved light absorption and charge-breaking efficiency. N-doped Nano TiO2 belts with co-exposed faces were successfully produced using the hydrothermal process by Sun et al [11]. The results showed that these co-exposed surface heterojunction faces of the N-doped Nano TiO2 belts showed the highest activity for hydrogen variation. The separate load carrier break provided by this assembly was considered to be the cause of this highest activity. Wu et al. synthesized bismuth-doped titanium dioxide hydrothermally to generate hydrogen [12]. The hydrothermal method is generally used to prepare different metal oxides in distinctive configurations because of its many advantages, such as improved chemical activity in aqueous media, better control of nanoparticle size and shape, and induced crystallization. However, the high cost of the closed autoclave, the inability to observe the reaction process and certain safety issues limit its application to the synthesis of nanomaterial [5].

5.3. Precipitation method

In addition to sol-gel and hydrothermal/solvothermal methods, precipitation is one of the most interesting processes for synthesizing Nano catalysts. This simple method produces a highly active photo catalyst with a large specific surface area and small grain size. In this process, the metal precursors are dissolved in a suitable solvent in a glass beaker. The mixture is then stirred and gently heated. Afterwards, the pH is accurately checked. The oxide photo catalyst can be obtained by centrifugation, filtration and repeated washing with water and alcohol. More recently, Fe(III)-doped TiO_2 has been synthesized by precipitation using $TiCl_4$ and iron nitrate as the titan and iron precursors, respectively by Ismael et al [13]. The photo catalytic activity of photo catalysts has been tested for the production of hydrogen and the degradation of organic pollutants. TiO_2 doped with Fe at 0.1% by mass showed the highest activity. It is important to note that increasing the amount of iron reduces the activity, which is attributed to the fact that iron acts as a recombination element in high concentrations. In their study, Yoong et al [14] used a combination of precipitation and impregnation processes to synthesize various concentrations of Cu-doped TiO_2 to generate hydrogen. They found that 10% by mass of Cu sintered at 300°C showed the highest activity. Enhancing light absorption and reducing band gap energy play a key role in improving photo catalytic activity. Ruiz et al [15] studied the production of hydrogen from gold deposited on the surface of TiO_2. Photo catalysts were assembled by precipitation deposition at various calcination temperatures. The ideal gold loading on the TiO_2 surface was 0.5% by mass. The higher activity of doped TiO_2 compared with undoped TiO_2 was attributed to the function of the gold, which acts as an electron trap and hydrogen evolution site. The presence of gold nanoparticles improved the absorption of visible light. In addition, the photo catalysts were activated at various temperatures, revealing that at 500°C, the absorption spectrum and redshift were at their widest. A novel precipitation process for the synthesis of N-doped meso-macro TiO_2 with a specific structure was developed by Parida et al [16]. The photo catalytic activity of the synthesized photo catalysts was estimated for hydrogen production under visible light irradiation. The catalyst calcined at 400°C showed the highest activity, attributed to its mesoporous assembly and distinctive morphology, which aid charge transport and separation, as well as band gap reduction [5].

5.4. Microwave-Assisted Method

The microwave-assisted process is gaining notoriety in nanoparticle synthesis because of its high reaction speed, simplicity and rapidity, ecological specificity and energy transport efficiency. In this process, the substances were heated by irradiation rather than thermal heating, which is the opposite of the usual process. The interaction of microwave irradiation with the polar molecule is used to obtain the dipole moment of the reaction mixture. Molecule rotation can be influenced by activity. This orientation improves the chance of collision between the molecules and reduces energy activation and heat release, leading to increased reaction and formation of the nanoparticle. Applying this process to the synthesis of nanoparticles therefore offers more advantages than the usual synthesis process. Lin et al [17] synthesized a series of distinct metal ions on N-doped TiO2 using a microwave-assisted process. All the N-TiO2 photo catalysts co-doped with metal ions showed photo catalytic hydrogen production performances incomparable to those of pure N-TiO2 and TiO2. The particularly improved performance of Cu/N-TiO2 was essentially due to the synergistic effects of copper and nitrogen producing an impurity energy level, reducing the band gap energy, as well as their function in improving charge separation, resulting in the highest possible photo catalytic activity.

Microwave-assisted synthesis is considered to be a fundamental branch of green chemistry. It is widely recognized as a simple and ecologically sustainable method, more energy-efficient than conventional methods such as oil or sand baths. However, the high cost of the equipment, the inadequacy of large proportion production and the complication of monitoring the reaction process limit its application to the synthesis of nanoparticles [5].

5.5. Solid-State Reactions Method

Solid-state chemical reaction for the production of nanomaterial is an attractive process that is widely used in photo catalysis. Compared with other processes such as microwave or hydrothermal, it is highly cost-effective and requires no special equipment or solvents. In this method, the nanomaterial powders obtained from the precursor are thoroughly amalgamated, then transferred to a clean alumina crucible and calcined at high temperature. This method also enables the production of high-crystallinity nanoparticles in large quantities and can be used primarily for the photo degradation of organic contaminants. Iron-doped TiO2 using TiO2 powder and FeCl3 was synthesized using a solid-state reaction by Ghorbanpour et al [18]. The photo catalytic activity of the specimen samples was studied for the degradation of methyl orange under visible light irradiation. The Fe-doped proportion of 0.5% by mass shows the highest activity, attributed to the improvement in light absorbance and the decrease in band gap energy.

This method is used for nanoparticle synthesis because of its simplicity, accessibility and low cost. However, this process uses high calcination temperatures, which leads to nanoparticles with a limited surface area and a large particle size, thus reducing their photo catalytic activity [5].

TABLE I. Application of different metal/non-metal doped TiO2 synthesized by different methods for photo catalytic hydrogen production

Dopant	**Synthesis method**	**H2 production**
Platinum	Impregnation/Sol- gel	600 nmol/cm^3
Silver	Sol- gel/solvothermal	180 mmol of H2/gcat
Nitrogen	Oxidation	18 µmol
Nitrogen, Iron, Chromium, Platinum	Hydrolysis	340 µmol
Bismuth, Nitrogen	Sol-gel	1800 µmol/g
Barium, Strontium	Hydrolysis	25 µmol/m^2
Platinum, Nitrogen	Photo deposition	3200 µmol

6. Conclusion

Doping is an attractive process for improving the photo catalytic activity of TiO_2, either by reducing the energy of the band gap or by improving charge separation. Metals such as Cu and noble metals such as Au and Pt are the most frequently studied dopants for TiO_2 because of their superior work function. Nitrogen has been extensively studied as a non- metallic dopant because of its ability to decrease the band gap energy of TiO_2 and enhance the photo catalytic activity of TiO_2. The synthesis processes used to prepare many doped TiO_2 photo catalysts have been explained in detail; many studies have shown that the sol-gel process is still the most commonly used process for synthesizing doped TiO_2 because of certain features, particularly the high surface area and small size of the nanoparticles prepared, recorded at low calcination temperatures. The characterization section illustrated that UV- Vis-DRS spectroscopy, photocurrent and electrochemical impedance spectroscopy are applied to determine the influence of the dopant on the optical properties and charge separation efficiency of TiO_2. Nevertheless, there are a number of key points that should be taken into consideration for further studies on doped TiO_2.

Researchers need to consider the ideal processes for the synthesis of doped TiO_2, as some processes require dangerous and expensive chemicals and very expensive special equipment should be avoided. In addition, it is essential to achieve the ideal amount of dopant on TiO_2 to obtain the highest photo catalytic hydrogen production activity, otherwise the highest dopant concentration may act as a recombination center. In addition, other studies should focus on finding a low-cost dopant to modify dopants based on very expensive noble metals such as Pt or Au. In addition, photo catalytic chemists should finally focus on finding a suitable sacrificial reagent to be used as a hole trap in the hydrogen production reaction. Ultimately, both laboratory-scale and pilot-scale photo reactor designs for H2 production should be debated.

In conclusion, the doping process remains an attractive way of improving the photo catalytic activity of TiO2. However, research should combine theoretical kinetics and computational research with experimental studies to give a more visible picture of the photo catalytic activity of these substances.

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