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Synthesis And Application Of Metal Oxide Nanoparticles In Photocatalytic Water Splitting

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Abstract

Photocatalysis is the scientific field that focuses on using catalysts to accelerate chemical reactions that are dependent on or include light. A photocatalyst is a substance that can absorb light and make electron-hole pairs, which then facilitate chemical reactions and restore its chemical structure after each cycle of interaction. Metal oxide semiconductors are ideal photocatalysts because of their exceptional photosensitivity, stability, affordability, and appropriate band gap. Photoexcited electrons are involved in reduction activities, while photogenerated holes participate in oxidation processes. When exposed to light, these charge carriers that are created by the photons create radical species (•OH-, •O2-) that are accountable for the decomposition of dyes. Photodegradation of dyes is a beneficial method for treating water by eliminating dye pollutants. The results of this study suggest that the electrolysis cell used for generating eco-friendly hydrogen could be enhanced by using nanoparticles, such titanium dioxide, as a coating on one of the metal electrodes. These nanoparticles exhibit photoactive properties, enabling them to produce a higher amount of photocurrent. Consequently, this results in an increased synthesis rate of hydrogen, so enhancing the energy efficiency of the system in the creation of ecologically beneficial green hydrogen.

Keyword: Photocatalysis, water splitting, synthesis, metal oxide, nanoparticles

Introduction

With the growth of people, it is anticipated that global energy demands would rise more in the future, along with their potential environmental consequences. The U.S. Energy Information Administration (EIA) predicts that global energy consumption will increase by approximately 50% from 2018 to 2050 [1]. Fossil fuels accounted for approximately 80% of global primary energy in 2010 [2]. The combustion of fossil fuels causes significant pollution and adds to the greenhouse effect. The climate plays a crucial role in driving the use of hydrogen in the shift to cleaner energy sources. In order to keep global warming below 2 degrees Celsius (°C), it is necessary for carbon dioxide (CO2) emissions to decrease by around 25% by 2030, compared to the levels in 2010, and ultimately reach a state of no net emissions by roughly 2070 (IPCC, 2018) [3]. In order to have a realistic chance of keeping global warming below 1.5 °C, it is necessary for global net anthropogenic CO2 emissions to decrease by around 45% by 2030, compared to the levels in 2010. These emissions should then reach net zero by around 2050 [3]. Hence, it is imperative for the global community to strike a delicate equilibrium between harnessing energy for societal and economic progress and the imperative to decrease carbon emissions, diminish our dependence on fossil fuels, and shift towards energy sources with smaller carbon footprints. Therefore, it is imperative to prioritize the advancement of environmentally friendly and renewable energy sources. Hydrogen is widely regarded as the most optimal alternative clean energy source due to its high calorific value, lack of pollution, and ability to be stored. It is widely acknowledged as the future clean energy carrier in various applications, including environmentally friendly vehicles, domestic heating, and stationary power generation. Currently, the majority of hydrogen production, around 95%, comes from natural gas and coal. This process leads to the emission of 70 to 100 million tonnes of carbon dioxide each year in the European Union (EC, 2020) [4].

In order for hydrogen to effectively contribute to climate neutrality, it is imperative that it is scaled up significantly and its production is completely decarbonized. Approximately 5% of the total output is derived as a secondary product from the process of chlorine generation by electrolysis. Coke oven gas in the iron and steel sector has a significant amount of hydrogen, a portion of which is extracted. At present, there is a lack of substantial hydrogen production derived from renewable sources. Nevertheless, this is likely to be altered in the near future. Presently, hydrogen is mostly utilized in the

process of oil refining and the production of ammonia [5].

Water splitting and alcohol photo-reforming, which include the use of semiconductor photocatalysts and sunlight, are very promising technologies for the manufacture of H2 in the future. Water splitting is a crucial process in the production of environmentally friendly and renewable energy in the form of hydrogen (H2) for future generations. The production of chemical fuels through the combination of water and sunshine is a significant scientific obstacle in the 21st century. Currently, there is a significant production of hydrogen for industrial and commercial applications. However, only a small fraction of commercial hydrogen (5%) is generated using electrolysis of water, whereas the majority relies exclusively on fossil fuel sources [6,7].

Since the initial observation of photocatalytic water splitting on TiO2 electrodes by Fujishima [8], researchers have directed their attention on exploring this phenomenon using several semiconductors, including TiO2 [9], graphitic carbon nitride [10], and CdS [11]. TiO2 has garnered significant interest from numerous research groups and has swiftly emerged as the most extensively investigated and utilized semiconductor for photocatalysis [12-15]. Titanium dioxide (TiO2) is regarded as a highly promising semiconductor because to its several advantages, including its low cost, non-toxic nature, resistance to corrosion caused by light, and simplicity of handling. However, its performance is currently constrained by its wide bandgap, which is roughly 3.2eV for the anatase phase in powders [16-19].

Therefore, in order to overcome these challenges, it is highly advantageous to explore novel materials that have the capability to separate water molecules via visible light absorption. Therefore, making changes to titania to enhance the process of generating hydrogen from water by photocatalysis is a beneficial strategy. Several endeavors have been undertaken to alter TiO2 in order to exhibit a reaction with visible light [20]. Some methods include the introduction of metals [21] and non-metals [22] through doping, as well as various sensitization techniques involving dyes [23], quantum dots [24], and the combination of other semiconductors (as a heterojunction composite) [25,26], among other approaches.

Titanium dioxide (TiO2) has a diverse variety of uses and has been widely examined in earlier research publications for its effectiveness in treating wastewater. This includes its use in photocatalytic degradation of organic chemicals, as well as addressing the issue of micro- and nano-plastics. These topics have been fully covered in studies cited as references [27-31]. Hydrogen is generated during the process of photocatalytic water splitting. Multiple research studies have demonstrated that a greater quantity of hydrogen is generated when an electron donor, such as alcohol (such as methanol, other primary alcohols, or polyols like ethylene glycol), is present in a solution of water and alcohol, along with differentially doped TiO2 photocatalysts [32].

Alcohol, when used as a sacrificial agent, has a lower splitting energy compared to water. Several published publications indicate that the concept of "water splitting" is actually connected to the redox reactions of additives or maybe corrosion, and consequently, these papers do not specifically address the process of water splitting [33,34]. Over the past decade, several types of nanomaterials and their composites have been created and utilized for a diverse array of applications. These applications include, among others, photocatalytic processes, hydrogen production, and fuel cells [35-39].

Methodology

The purpose of this work is to pursue an investigation into the production of metal oxide nanoparticles and their application in the process of photocatalytic water splitting. It is the cathode compartment of the electrodialysis cell that is built by adding a quartz glass onto a newly developed polypropylene frame in order to effectively allow light to travel through the cell. The anode compartment of the cell is directly utilized in the system. The anode and cathode compartments are separated by an anion-exchange membrane (AEM) that measures 110 × 110 mm and is constructed from titanium with a thickness of around 200μm. This membrane is also supplied by the same individual who manufactured the device. The electrodeposition method is used to apply a coating of titanium dioxide to a titanium metal plate that has a thickness of one millimeter and measures 8 centimeters by 8 centimeters (64 square centimeters). In order for it to perform the role of a photocathode, it is then positioned behind quartz glass. The graphic representation of the system's schematic is shown in Figure 2.

Sanding the surface of the metal and washing it with ethanol are two steps that are taken before the coating operation in order to get the metal ready for processing. The coating layer that is applied to the metal is made up of a sol-gel dispersion solution that contains TiO2 nanoparticles that are forty nanometers in size. This substance is used to make the bath. In order to get the bath ready, put two grams of titanium dioxide into a volumetric flask that has a capacity of two hundred milliliters. Next, at a concentration of one hundred percent, add fifty milliliters of acetic acid (CH3COOH), and then fill the flask with deionized water until it reaches the mark of two hundred milliliters. In addition, the solution is processed through ultrasonication for a period of twenty minutes before two milliliters of hydrogen nitrate are added. After that, it is

subjected to magnetic stirring at a speed of 300 revolutions per minute for an entire night, and then the following day, fifty grams of ethanol is added to it as a supplement. The electrodeposition technique is used to apply TiO2 nanoparticles onto the titanium electrode. This is the first step in the process. The cathode in the electrodeposition process is titanium metal, while the anode is steel. Both of these elements are involved in the process. Through the utilization of this particular configuration, the cathode will be coated with nanoparticles.

Following a period of thirty minutes during which the titanium cathode is exposed to a voltage of ten volts, the deposition of titanium dioxide (TiO2) takes place. The metal is then transferred and placed inside the furnace, which is set to undergo annealing for one hour at a temperature of 500 degrees Celsius when it is scheduled to do so. In addition, a scanning electron microscope (SEM) is utilized to investigate the surface in order to ascertain whether or not the coating of titanium oxide nanoparticles (NPs) on the surface of the titanium electrode was successful.

Furthermore, the electrochemical cell is described by utilizing light, bright light, and the absence of light in order to evaluate the photoactive electrode and compare the results using a potentiostat (Gamry Instruments Reference 1000). In the field of applied analysis, the techniques that are utilized include open circuit potential (OCP), linear sweep voltammetry (LSV), power potentiation (PP), and power galvanostatic methods (PG). In order to determine the extent of the potential difference between the photoactive coated metal and the OCP, the OCP is chopped in situations in which the solar light is either on or off. Every single measurement is carried out with the help of the solar simulator, and the irradiation level is set at 1000 W/m2. Additionally, the chopping technique is continued throughout the entirety of the proportional power (PP) and power generation (PG) measurements, specifically while maintaining a steady voltage and ongoing current. In addition, the photoelectrochemical cell is utilized in the process of carrying out the photo-assisted electrolysis operation. An electrolyte solution that is composed of sodium sulfate in a water solvent at a concentration of one gram per liter is utilized for all of the experiments and analyses that take place within the cell. The employment of this electrolyte solution ensures the production of hydrogen on the cathode side of the cell by means of the processes that take place within the cell, which are described in the following manner:

- Anode Reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
- Cathode Reaction: $4H^+ + 4e^- \rightarrow 2H_2$

A diagram illustrating the functioning of the electrochemical cell is shown in both Figure 1 and Figure 2. An illustration of the photoelectrochemical system configuration is also shown in Figure 2. Furthermore, the electrolysis cell is operated for a duration of one hour, during which several analyses are conducted.

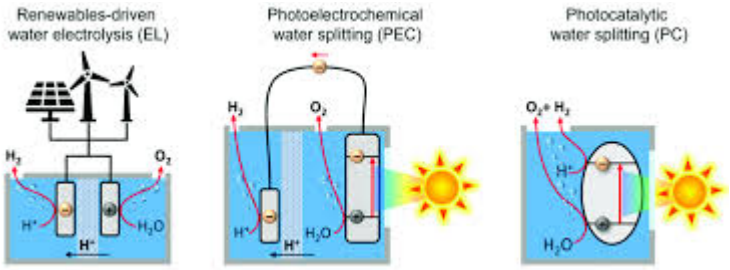

Figure 1(a) Three technological processes include renewable energy-driven water electrolysis (EL), photoelectrochemical water splitting (PEC), and photocatalytic water splitting (PC).

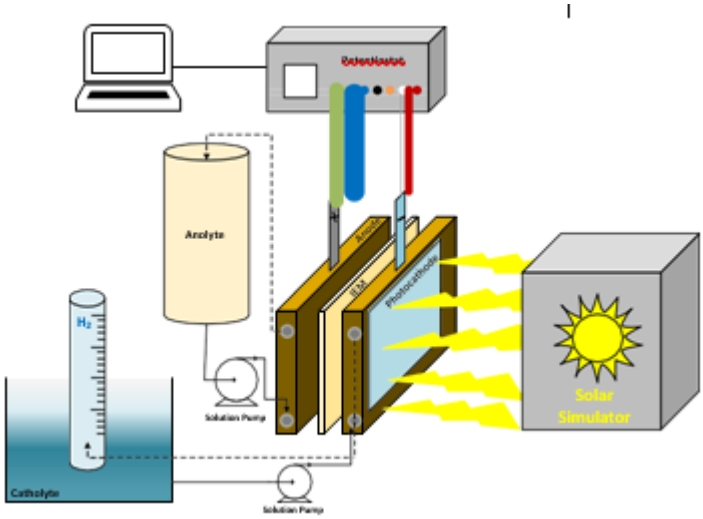

Figure 2 for a diagrammatic representation of the configuration of the photoelectrochemical system, more specifically the ion-exchange membrane (IEM).

In the end, a thermodynamic analysis is carried out by calculating the energy and exergy with the help of an Engineering Equation Solver (EES). In this process, mathematical equations are established as the parameters of the system.

After that, the Faraday law is applied in order to ascertain the amount of hydrogen that is produced, provided that the present parameters have been specified in the previous characterization for each and every circumstance. The difference in hydrogen creation that occurs in experimental conditions with and without the presence of solar light can be linked to the enhanced photo current that occurs when a photoactive coated cathode is utilized.

Interpretation and Analysis of the Data

The image of the scanning electron microscope (SEM) that was displayed in Figure 3(a) revealed that the surface of the metal had some slight scratches. These scratches were most likely caused by the sanding technique that was performed after the coating was applied over the surface. The scanning electron microscopy (SEM) image also demonstrated that the TiO2 nanoparticles have aggregated to expand in size, and the coating can be seen on the surface of the metal. This substantiates the fact that the titanium metal has been effectively coated with TiO2 nanoparticles. As can be seen in Figure 3 (b) and (c), the metal took on a blue color after being coated with the TiO2 nanoparticles. This is a clear indication of the effects of the coating. It is possible that the presence of TiO2 nanoparticles is responsible for the color change that was observed.

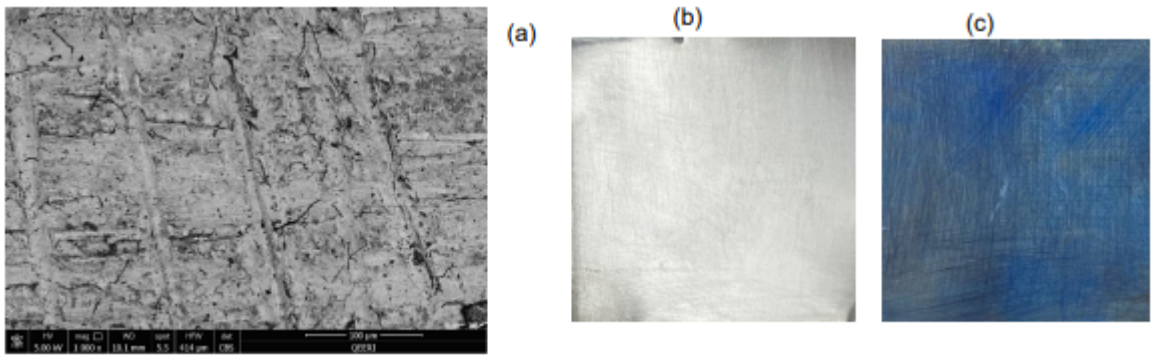

Figure 3 displays the scanning electron microscope (SEM) pictures of the titanium electrode coated with titanium dioxide nanoparticles at a magnification of 1000X. (c) The titanium electrode post-coating with TiO2 nanoparticles and (b) the titanium electrode pre-coating.

A subsequent elemental analysis is conducted on the coated titanium metal using energy-dispersive X-ray spectroscopy (EDS). The accelerating voltages employed are of both high (20KV) and low (5KV) magnitudes. Empirical dispersive spectroscopy (EDS) is a method employed to determine the elemental composition of a material by identifying the distinctive X-rays emitted from the sample upon exposure to an electron beam. At both accelerating voltages, the EDS analysis results, shown in Figure 4, indicate that titanium (Ti) and oxygen (O) particles are more abundant than other elements. This holds true irrespective of the specific element under analysis. Consequently, it can be inferred that titanium

dioxide is found on the surface of the coated metal, as titanium dioxide primarily consists of titanium and oxygen. The observed effectiveness in coating titanium metal with TiO2 nanoparticles can be attributed to the elevated levels of titanium and oxygen present. X-ray diffraction (EDS) analysis is a valuable technique for identifying the elemental makeup of a substance. In this experiment, it successfully helped to verify the existence of titanium dioxide (TiO2) on the surface of the coated metal.

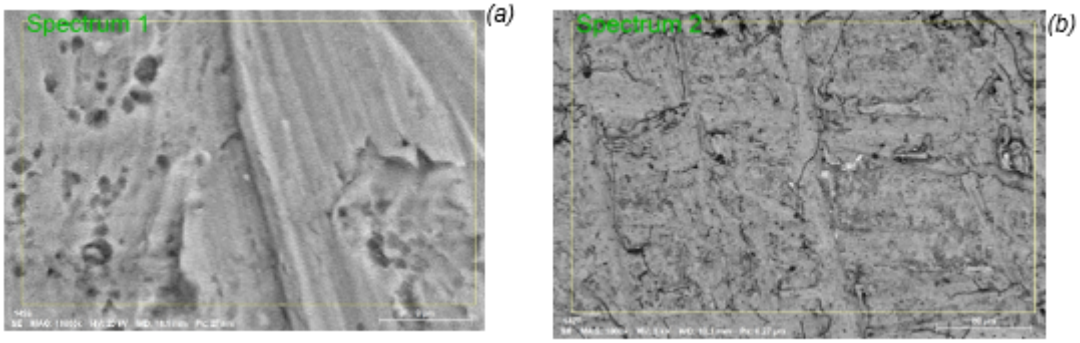

Figure 4: (a)The electron density spectroscopy (EDS) analysis of a titanium electrode that has been coated with titanium dioxide is carried out with two distinct accelerating voltages(b) spectrum 1 is performed at 20 kV, and spectrum 2 is carried out at 5 kV.

TiO2 nanoparticles were successfully coated on the titanium metal electrode, as demonstrated by the SEM and EDS tests, which provided convincing confirmation of this result. Due to the fact that the EDS analysis was carried out at a voltage of 20 kV, it has been determined that the surface of the sample has an equal amount of titanium and oxygen (Figure 5). By using a higher X-ray energy, it is possible to achieve a more comprehensive infiltration into the coating, which in turn provides a more comprehensive view of the sample. The study that was carried out at a voltage of 5 kilovolts, on the other hand, showed that the proportion of oxygen atoms on the surface is approximately twice as high as the proportion of titanium atoms. Titanium dioxide is the compound that is produced on top of the metal substrate as a result of the photo-electrolysis system, which is an important outcome for the system.

After that, several electrochemical characterizations are carried out in order to evaluate the effectiveness of the titanium metal electrode that has been coated in order to function as a photocathode. Methods such as open circuit potential (OCP), linear sweep voltammetry (LSV), power pitch (PP), and power galvanostatic (PG) measurements were included in the characterizations. Quantification of the electrodes' resistance to corrosion and stability can be achieved through the measurement of OCP. This experiment requires the implementation of OCP, which stands for optical current plate, along with the additional step of chopping at regular intervals of one minute. In order to accomplish this, utilize the solar simulator as the source of light and alternate between conditions in which there is no light and those in which there is concentrated light. Through the utilization of the photoactive coating in the absence of any external current, the purpose is to explore the potential difference from the sun. Figure 6 (a) can be used to illustrate this point. According to the findings of the analysis, there is a difference of 20 millivolts (mV) between the scenarios that involve the use of light and those that do not involve the use of light, and there is an additional difference of 80 millivolts (mV) between the use of concentrated sunshine and the absence of concentrated sunlight. This illustrates that the utilization of solar electricity leads to a decrease in the resistance that exists within the system, which in turn makes it possible for a gain in efficiency to ultimately occur.

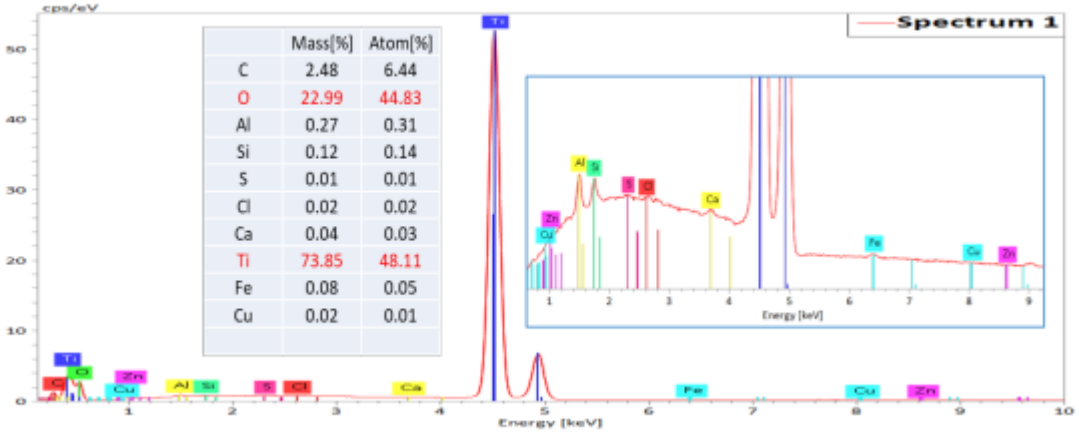

Figure 5 : Electron density spectroscopy (EDS) analysis of a titanium electrode covered with titanium dioxide is conducted using two distinct accelerating voltages. Spectrum 1 is acquired at a voltage of 20 kilovolts, whereas spectrum 2 is acquired at a voltage of 5 kilovolts.

Scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) experiments strongly confirmed that the titanium metal electrode had been effectively covered with TiO2 nanoparticles. Based on the EDS analysis conducted at a voltage of 20 kV, it has been determined that the sample's surface contains an equivalent quantity of titanium and oxygen (Figure 5). This discovery was made as a consequence of the execution of the EDS investigation. By using a higher X-ray energy, it is feasible to achieve a more thorough penetration into the coating, so offering a more comprehensive insight into the sample. This is because the depth of infiltration is more extensive. Conversely, the study carried out at a voltage of 5 kilovolts revealed that the ratio of oxygen atoms on the surface is almost double that of titanium atoms. This is the finding arrived at by the researchers. Titanium dioxide is the chemical produced on the surfaces of a metal substrate during the process of photo-electrolysis. The generation of titanium dioxide is a significant component of the system.

Following this, several electrochemical characterizations are conducted to evaluate the effectiveness of the titanium metal electrode that has been coated for the purpose of functioning as a photocathode. Various methodologies, such as open circuit potential (OCP), linear sweep voltammetry (LSV), power pitch (PP), and power galvanostatic (PG) approaches, were integrated into the characterizations. Measuring the Oxygen Content Potential (OCP) allows for a quantitative assessment of the electrodes' corrosion resistance and stability. Due to the inherent characteristics of this experiment, it is imperative to use OCP, an acronym for optical current plate, together with the supplementary procedure of chopping at systematic intervals of one minute. Leverage the sun simulator as the illumination source and alternate between scenarios of light absence and those of intense illumination. Employing this approach will enable you to attain the intended outcome. The objective of this experiment is to examine the potential electrical potential difference resulting from the sun by utilizing a photoactive coating without any external current source. Diagram 6 (a) is a valuable instrument for elucidating this specific notion. The investigation's findings indicate a disparity of twenty millivolts (mV) between the scenarios that incorporate the use of light and those that do not. Moreover, there exists an extra disparity of eighty millivolts (mV) between the use of focused sunlight and the lack thereof. Indeed, the existence of this phenomenon illustrates that the utilization of solar energy leads to a decrease in the resistance within the system, so enabling a subsequent enhancement in efficiency.

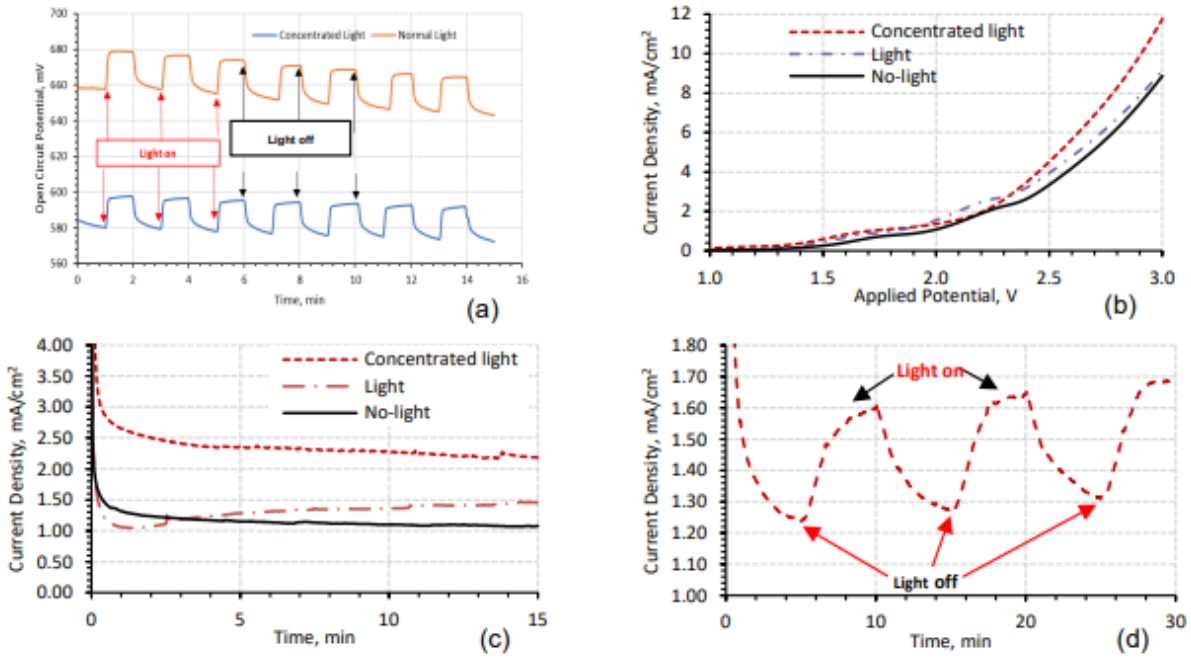

Figure 6: Characterization of electrochemical systems. Potentiometry, linear sweep voltammetry, open circuit potential chopping at one-minute intervals, and potentiometry chopping at five-minute intervals are the methods that are included in the experimental protocols.

In order to carry out galvanostatic measurements, an electrochemical cell is first exposed to a continuous electrical current, and then the voltage or potential that is produced as a result of this process is measured. Solar energy can be used to power the system if titanium dioxide nanoparticles are coated on titanium and used as a photocathode. This allows the system to be powered by the sun. Galavanostatic tests are a method that can be utilized to ascertain the effectiveness of the photoconversion protocol. In this scenario, the nanoparticles of titanium dioxide absorb photons that are emitted by sunlight and use the energy to initiate an electrochemical process. This process ultimately results in the creation of electrons that travel through the external circuit. It is possible to evaluate the relative effectiveness of each method by doing a comparative analysis of the galvanostatic measurements obtained from the two different systems. In the electrolysis cell that is fitted with a titanium cathode, the most important performance metric would be the efficiency with which hydrogen is produced. To the contrary, the efficiency of solar energy conversion would be the most important characteristic to consider when it comes to the photo-cathode system.

For the next step, the Faraday law is utilized in order to do the calculation of the creation of hydrogen. Therefore, by utilizing the data that is available and utilizing the understanding of the Faraday law, it has been discovered that the production of hydrogen is 69.45 µmol/cm2.h when the light is concentrated. Additionally, the production of hydrogen is 38.59 µmol/cm2.h and 33.98 µmol/cm2.h when typically solar light conditions and conditions without light are considered individually. Increasing the rate at which hydrogen is produced can be accomplished by optimizing the usage of bright light within the system. The high-intensity light system has the ability to surpass the H2 generation rate of 41.3 µmol/cm2.h that was published by Tong et al. (2023) for a photoelectrochemical system that utilizes ultra-thin carbon-doped TiO2 nanotube arrays as the photoanode. Furthermore, Ye et al. (2023) demonstrated that a photoelectrochemical system that utilized TiO2 photoanodes that were plentiful in VO was able to achieve a rate of hydrogen generation of 49.2 µmol/cm2 per hour. According to these findings, the incorporation of additional photoactive materials has the potential to bring about significant increases in the rates at which hydrogen is produced.

Application of Theory to Commercial Photocatalysts Based on TiO2 for Hydrogen-Producing Water-Splitting Reactions

As the most promising photocatalyst for hydrogen production via water splitting, TiO2 has already made its commercial debut. Many theoretical estimations for the commercial application of TiO2-based photocatalysts have emerged in recent years to promote their commercialization.

As shown in Figure 7(a), Taghipour et al. [2018] combined the fluidized bed theory, mass transfer effect, optical model,

and catalytic reverse reaction of hydrogen and oxygen dominated by the noble metal Pt loaded on the surface of TiO2 to develop a model to describe the characteristic of photocatalytic water splitting in fluidized bed systems (Figure 8b)). The model estimates several model parameters and provides an accurate prediction of the hydrogen release rate of a given mass of Pt/TiO2 granules and an extended bed height. The model consequently predicts that the mass transfer rate in the separator fast becomes dominant in the apparent quantum efficiency and hydrogen evolution rate of the system. To ensure that the mass transfer rate is much larger than the rate of H2 and O2 reverse reactions catalyzed by Pt, the performance of the system can be enhanced by either increasing the fluidization flow or adjusting the gas–liquid separator (Figure 7(c) and (d)). The author further confirmed this conclusion through experimental validation of the model, since a small improvement to the separation device led to a 350% increase in the system's hydrogen evolution rate. Because it reduces the energy required to produce hydrogen while maintaining the qualities of existing TiO2-based photocatalysts, this model is a useful tool for creating and improving photocatalytic fluidized bed systems.

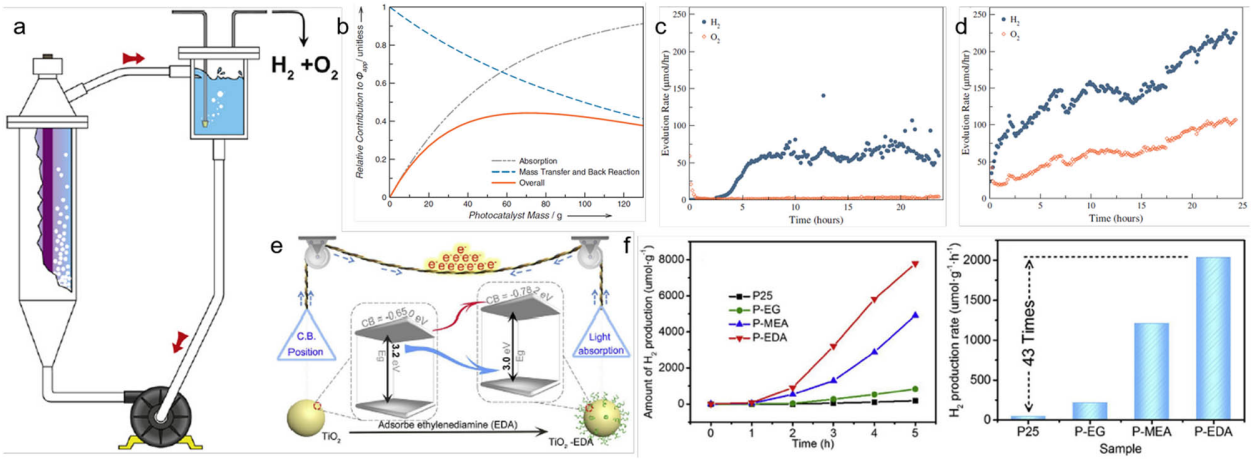

Figure 7(a) schematically depicts the photocatalytic water-splitting reaction in a fluidized bed system. (b) The proportionate contributions to the apparent quantum efficiency related to mass transfer, photon absorption, and the reverse reaction of the photocatalyst. Republished with permission from [Reilly K, 2018], Copyright (2018) Elsevier. The rate of evolution of hydrogen and oxygen over time (c) in a normal environment and (d) with better liquid-gas contact and turbulence. (e) The overall process flow diagram for the preparation of the P-EDA target photocatalyst. (f) Elsevier's 2020 copyright for the rate histogram and photocatalytic hydrogen production curve of the samples, taken from the reference [Hu J, Xie J, 2020]. Hu et al. [2020] used a simple mechanical lapping process to connect organics that could donate electrons to the surface of commercial P25, as seen in Figure 7(e). Theoretical computing results show that more electrons are produced by the organic matter attached to the surface of commercial P25 that donates electrons. These electrons extend the range of light that commercial P25 can absorb by decreasing the attraction of holes to photoinduced electrons and improving the separation efficiency of its photogenerated current carriers. The commercial P25 photocatalytic water-splitting reaction's capacity to produce hydrogen has also been significantly increased, with a consistent increase in the ability of organic functional groups to contribute electrons from small to large: P-MEA < P-EDA < PeEG. Of all these functional groups, P-EDA produces the most H2 (43 times more productive than the commercial P25) (Figure 7(f)). This innovation may provide a new market for the commercialization of TiO2 by adding various organic materials to the surface of TiO2-based photocatalysts. Enhancing the effectiveness of photocatalytic water-splitting reactions to generate hydrogen is the aim of this market.

Conclusions

In essence, the imposition of titanium dioxide over titanium metal would lead to the formation of a layer of photoactive coating. Implementing this layer would enable a traditional electrolysis system to operate with a higher photocurrent, therefore enhancing the amount of hydrogen generated (69.45 µmol/cm2.h) under the influence of intense solar radiation. Further analysis of OCP using electrochemical methods has confirmed a 20 mV difference between light and dark conditions, and an 80 mV difference between the usage of concentrated solar light and non-concentrated solar light, where lower resistance is observed. Furthermore, through the examination of power potentiometry, which operates at a constant voltage, it becomes feasible to attain a higher current density within the system, around 0.40 milliamperes per square centimeter.

Future development directions

A comprehensive examination of the microstructure and related properties of the heterojunction interface formed by TiO2

and other semiconductors is essential to tackle these problems. Through the process of photon absorption, electron and hole excitation, and the following activities of electrons and holes, a photocatalytic system maintains a nonequilibrium state. An accurate and detailed representation of the electronic structure and electronic vibration dynamics is crucial for theoretical calculations that seek to simulate the nonequilibrium state process at the molecular and nanoscale scales. Hence, it is imperative to examine the appropriate crosslinking function and density functionals to offer a more accurate depiction of long-range electron transport, multielectron excited states, bond termination, and other factors that contribute to the nonequilibrium state of the system.

The temporal dimensions of photoexcited electron transport, energy transport, thermal relaxation, and charge recombination phenomena in the photocatalytic interface system are elucidated by the evolution of time-domain density functional theory (DFT) and nonadiabatic molecular dynamics theory [Mehdipour H,2018; Wei Y,2018; Lu T,.2020; Nam Y, 2018]. The essential requirements are obtained via computational simulations [Wei Y, 2017; Muuronen M, 2017; Long R, 2-17]. The present methodology provides unparalleled and extensive theoretical support for the examination of diverse nonequilibrium phenomena occurring in photocatalytic systems. However, the present approach is restricted to providing theoretical calculations for smaller systems, characterized by a simulation time scale of only a few hundred picoseconds. Therefore, future research will give priority to the development of this theory for its application in increasingly complex photocatalytic systems. In contrast, acquiring a thorough understanding of the interface properties and charge dynamics at the heterojunction created by TiO2 and other semiconductors by simulations and calculations would provide a solid theoretical basis for the design of the architecture. Furthermore, the utilization of TiO2 in photocatalytic water splitting presents a new method to improve the effectiveness of hydrogen production.

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New Technologies, Development and Application pp.743-749

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