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Research Article

The effect of TiO_2 and CdS catalysts on hydrogen production under UV radiation

Ebuzer Cengiz[1], Melih Kuncan[2,*], Ömer Şahin[3], Mehmet Said Bayraklılar[4], Sabit Horoz[5]

[1]Siirt University, Technical Sciences Vocational School, Department of Electric and Energy Technologies, Siirt, Turkey
[2]Siirt University, Faculty of Engineering, Department of Electric and Electronic Engineering, Siirt, Turkey
[3]İstanbul Technical University, Faculty of Chemistry and Metallurgy, Department of Chemical Engineering, İstanbul, Turkey
[4]Siirt University, Faculty of Engineering, Department of Civil Engineering, Siirt, Turkey
[5]Sivas Science and Technology University, Faculty of Natural Sciences and Engineering, Department of Engineering Fundamental Sciences, Sivas, Turkey

*Corresponding author: melihkuncan@siirt.edu.tr

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Abstract

Photocatalysis, a phenomenon wherein light energy triggers chemical reactions, has demonstrated its prowess in applications such as water splitting, hydrogen production, and environmental pollutant degradation. A fundamental characteristic of photocatalysis is its reliance on light, particularly in the ultraviolet (UV) region, to initiate and sustain catalytic processes. This reliance on UV radiation offers several advantages, including increased energy input, selectivity, and efficiency. The environmentally benign nature of photocatalysis, in which pollutants are converted into harmless byproducts under sunlight, underscores its significance in sustainable energy solutions. Semiconductor materials, TiO2 and CdS, stand out as key components in the photocatalytic process. These materials exhibit unique electronic structures that enable them to effectively harness UV light and facilitate electron-hole pair generation, which is crucial for driving redox reactions. TiO2, a widely studied material, is valued for its non-toxicity, chemical stability, and exceptional UV-light absorption capabilities. CdS, on the other hand, is notable for its band structure, which permits efficient charge separation and migration. These semiconductors have thus garnered attention for their suitability in various photocatalytic applications. In our study, the effect of TiO2 semiconductor material doped with different concentrations of CdS on Hydrogen production was examined in the UV simulator we designed. The most efficient results were obtained in the reaction enhanced with 5% CdS in an electrolyte containing 50% ethanol.

Keywords: energy, UV, semi-conductor, renewable energy

Introduction

Hydrogen, the first element in the periodic table with an atomic number of 1, is found in the universe at a rate of 77 percent. When hydrogen, which has a high combustion heat, enters the combustion process, it only produces water as the final product. When examining the use of hydrogen, it is a versatile energy source: it can produce heat by reacting with oxygen, drive a generator, or be used to generate electrical energy using PEM fuel cells. Table 1 provides the physical and chemical properties of the hydrogen element. In vehicles, it can be compressed at high pressures and stored in liquid form or as borohydride for use as motor fuel [1].

Table 1. *Chemical and physical properties of hydrogen*

Properties	*Unit*	*Value*
Density	kg/m^3	0,0838
Molecular Weight	Amu	2
High Calorific Value	MJ/kg	141,9
Low Calorific Value	MJ/kg	119,9

Boiling Point	^{0}K	20,3
Liquid Density	kg/m^3	70,8
Critical Temperature Point	^{0}K	32,94
Critical Pressure Point	Bar	12,84
Critical Density Point	kg/m^3	31,4

Although hydrogen is found in nature in high quantities, its production and storage processes are quite costly. When we examine the production methods, it can be said that hydrogen, despite being a green energy source, is not produced using very environmentally friendly methods. In the production of hydrogen worldwide, carbon-based compounds are used in about 96% of the methods, resulting in carbon dioxide gas as the final product. In the remaining 4%, electrolysis is used, and the waste product is oxygen gas [2;3]. While about 96% of the hydrogen demand is met from depletable sources the need for alternative primary sources has emerged, and in recent years, there has been a shift towards hydrogen production methods that do not require fossil fuels, such as the electrolysis method.

Particulate Photocatalytic Systems

One of the particulate photocatalytic systems has two electrodes submerged in an aqueous electrolyte, one of which is a photocatalyst that absorbs light. Photocatalysts in particulate photocatalytic systems are suspended particulates or powders in a solution of water. Each particle in this system functions as a tiny photoelectrode, facilitating the processes of oxidation and reduction of water on its surface. Particulate photocatalytic devices have drawbacks in charge carrier separation as compared with Photoelectrochemical (PEC) systems. These particle systems are less efficient than photoelectrode systems, and there are difficulties in adequately separating to prevent reverse reactions, the stoichiometric combination of hydrogen and oxygen is used. Photocatalytic water splitting, like other photocatalytic processes, proceeds through various steps on semiconductor catalysts, as can be seen when looking at a diagram of the fundamental principle of total water splitting on the system of a particulate photocatalyst [4].

When light photons with energy exceeding the bandgap energy are absorbed by a photo-semiconductor, the process of solar water splitting begins. This absorption, as schematically depicted in Figure, generates excited photoelectrons in the conduction band (CB) and holes in the valence band (VB) of the semiconductor. Following that, the second step in photocatalytic water splitting is charge separation, with photo-generated moving electron-hole pairs through the semiconductor volume to locations of reaction on the photocatalyst surface. Surface chemical reactions are included at the end of the photocatalytic cycle. Without recombination, electrons (e-) and holes (h+) moving to the photocatalyst's surface can reduce and oxidize gas-phase oxygen and hydrogen molecules adsorbed on the semiconductor surface to produce them, as described for water splitting in an acidic environment [4].

Requirements for Photocatalyst Systems

In order to split water on particulate photocatalysts under exposure to visible light, photocatalyst materials must fulfill a number of functional criteria in terms of bandgap energy and electrochemical characteristics: (i) appropriate absorption of light capacity in the visible solar spectrum and sufficient band edge potentials for total water separating; (ii) being able to separate photon-excited electrons from reactive gaps; (iii) minimizing energy losses associated with charge transport and photon-excited charge recombination; (iv) chemical stability in aqueous environments against corrosion and photo-corrosion; and (v) appropriate electron transfer features from the photocatalyst's To carry out the water splitting process under visible light irradiation, certain amounts of photocatalysts, surface characteristics, and energy structures must be present. In order to facilitate the oxidation of water, the valence band edge of the photocatalyst must be larger than the oxidation potential of water. Based on these factors, the entire water splitting reaction requires an approximate semiconductor bandgap energy of 1.23 eV. This energy is comparable to the energy of a photon with a wavelength of roughly 1010 nm, hence 70% of all solar photons are potentially accessible for the water splitting process [4].

***Table 2** Energy distribution in the terrestrial solar spectrum*

Spectral Region	*Wavelength (nm)*	*Energy(eV)*	*Contribution to Total Spectrum (%)*
UV Near	315-400	3,93-3,09	2,9
Blue	400-510	3,09-2,42	14,6
Green/Yellow	510-610	2,42-2,03	16,0
Red	610-700	2,03-1,77	13,8
Near Infrared	700-920	1,77-1,34	23,5
Infrared	920->1400	1,34->0,88	29,4

However, in all solar dissociation processes, due to inevitable energy losses the practical bandgap energy should be higher than the theoretical limit of 1.23 eV.

The fundamental parameter that controls the photocatalyst's light-harvesting ability is its electronic structure, which determines the bandgap energy. Table 2 shows the band positions of various semiconductors concerning potentials for the water oxidation/reduction processes [5]. Semiconductors such as KTaO3, SrTiO3, TiO2, ZnS, CdS and SiC shown in the figure match the thermodynamic conditions required for total water splitting based on their band positions. As previously stated, It is critical to highlight that the semiconductor band structure's potential is just a thermodynamic necessity. The optimal bandgap range for high-performance photocatalysts has been expanded from 1.23 eV to 2.0-2.2 eV due to energy losses associated with solar energy conversion in photocatalysts [6].

Resistance to reactions that can damage the photocatalyst's characteristics at the solid/liquid interface is another critical need. Electrochemical corrosion, photo-corrosion, and dissolution are examples of these reactions [3]. A broad class of photocatalysts with acceptable semiconductor characteristics for solar energy conversion (e.g., CdS, GaP) is unstable in water oxidation reactions because their anions induce more oxidation than water, resulting in degradation [4].

Titanium Oxide and Titanates

The TiO2 nanostructures with different sizes, morphologies, synthesis methods and dopants have been reviewed to study their effect on photocatalysis. The TiO2 photocatalysts are presented to be widely used in energy and eco-friendly applications including water purification, hydrogen production, phenol degradation [6]. Titanium dioxide (TiO2) was the first semiconductor identified for the photocatalytic splitting of water [7]. Although water splitting was originally shown using a TiO2 photoelectrode with specific external modifications [7], powdered TiO2 is unable to effectively split water under visible light. This is owing mostly to TiO2's wide bandgap (3.1 eV), which permits just a tiny amount of the solar spectrum (UV fraction) to be used. A number of experiments have been carried out in order to increase the visible light response of titanium oxide-based catalyst. Chemical doping using metal ions having partially full d-orbitals, such as V5+, Cr3+, Fe3+, Co2+, and Ni2+, is one method for eliciting a visible light response in TiO2. While chemical doping with metal ions induces a visible light response in TiO2, significant reactivity for water splitting under visible light has not been identified for these doped TiO2 photocatalysts.

Through improved ion implantation procedures, the physical integration of transition metal ions into TiO2 has made it possible for modified TiO2 to function in visible light. Utilizing catalytic reduced methanol-containing aqueous solutions, thin TiO2 sheets seeded with metal ions such as Cr3+ or V5+ displayed photoactivity for water splitting in visible light with a quantum efficiency of 1.25%. While the ion implantation procedure allows for the alteration of TiO2 optical properties, the high cost of such modified photocatalysts makes bulk production impracticable. TiO2's visible light sensitivity may also be improved by introducing anions like additives into the oxygen lattice of TiO2. Mixing the p states of the doped anion (S, N, or C) with the O 2p states of TiO2 moves the valence band edge higher and narrows the bandgap energy of TiO2. Only N-doped TiO2 has been studied for the photocatalytic splitting of water among these materials. Under visible light, this Pt-modified photocatalyst catalyzes the formation of O_2 as an electron acceptor from aqueous $AgNO_3$ and an insignificant quantity of H_2 as an electron donor from methanol in solutions of water. A bulk Pt piece is usually used as a counter electrode in such systems because of its high activity and stability in many electrochemical reactions[8].

When TiO_2 is fused with metal oxides (SrO, BaO, Ln_2O_3 (Ln=lanthanide)), metal titanates with intermediate band gaps are obtained. Notable titanates include $SrTiO_3$, $La_2Ti_2O_7$, and $Sm_2Ti_2O_7$. $SrTiO_3$ crystallizes in a perovskite structure and has a bandgap of 3.2 eV, while $La_2Ti_2O_7$ is a layered perovskite with a bandgap of 3.8 eV [4].

Extensive research has been conducted on these titanates and their derivatives in the literature. However, since our semiconductor is TiO_2, we won't go into detail about other titanates.

Metal Sulfides

Metal sulfide systems are appealing photocatalysts for water splitting due to their tiny bandgap, which facilitates visible light absorption. However, metal sulfide photocatalysts are unstable in visible light water oxidation processes because S^{2-} anions are more sensitive to oxidation than water, resulting in photodegradation of the photocatalyst. Using proper sacrificial reductants is a typical strategy for reducing photodegradation of sulfides under irradiation. The photo-corrosion of sulfur-based catalysts can be efficiently reduced by utilizing a sacrificial reductant mixture of Na_2S and Na_2SO_3. Among the existing sulfide semiconductors, wurtzite-structured CdS, with a relatively narrow bandgap of 2.4 eV, can absorb visible light with wavelengths of <510 nm. CdS has a high enough flat band potential (0.87 V) to decrease H_2O, and its valence band edge (1.5 V) is theoretically adequate for water oxidation. Pt-loaded CdS, under visible light, exhibits high light absorption and efficient hydrogen production (25%) [8]. Because the structural characteristics of CdS (crystal stage, crystal dimension, and geometric surface area) govern the structure of the band, studies have been undertaken to assess the influence of preparation procedures on the photophysical characteristics of CdS, in addition to the concentration and activity of photocatalyst. Preparation strategies that result in good crystallinity and fewer crystal flaws have been shown to increase CdS photoactivity."

Please note that this is a lengthy technical text, and some technical terminology may vary depending on the context.

Materials and Methods

Material

The aim of our study is to investigate the hydrogen efficiency of the different metal-doped (Fe, Co, Ni) TiO_2/CdS@Pt catalysts we synthesized under the influence of UV radiation. To achieve this, we first prepared our UV system.

Our system consists of 4 units of 8 Watt UV lamps, a 400 mL quartz reactor where the materials we will synthesize and our solution are placed for UV rays to enter without being refracted, a magnetic stir bar located under the reactor, and a magnetic stirrer placed on top of the system to adjust the stirring speed of the stir bar.

To prevent the solution inside the reactor from being affected by the heat generated by the UV lamps, we use a system that cools the system by directing cold air from the compressor to the system through an air cooling pipe. The schematic representation of the system is shown in Figure 1.

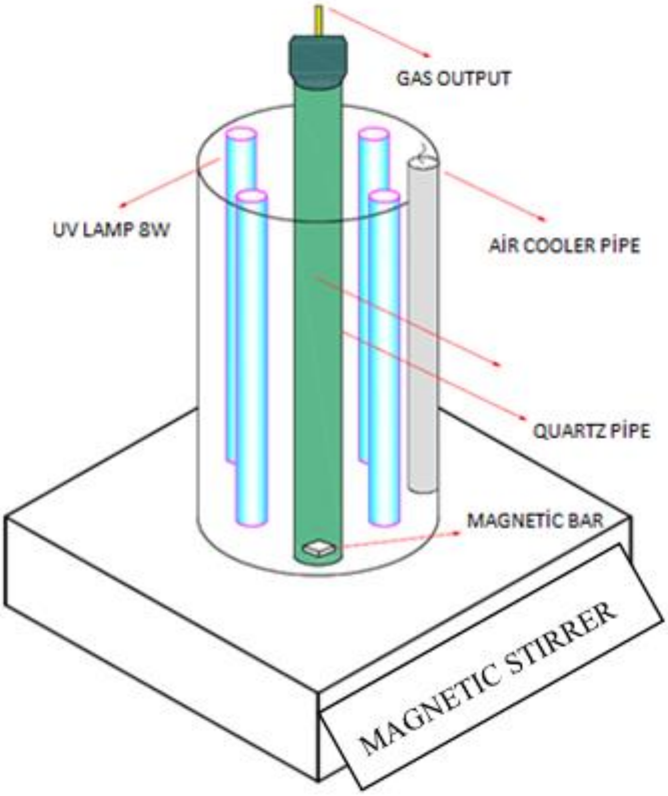

Figure 1. *Photo-Electro Chemical Water Separation Device*

The visual representation of the system is as shown in Figure 1. The system is completely enclosed to the external environment and is only cooled by the air coming from the compressor. To ensure the containment of UV rays within the system, the outer surface of the system is covered with aluminum foil, as seen in the picture, which reflects from the outer surface to the reactor.

Method

Synthesis of TiO2@Pt Catalyst

0.5 g of nanoscale (25 nm) TiO2 was dissolved in 5 mL of ethyl alcohol and stirred at 25°C for 30 minutes. To the TiO2 solution, 0.005 g of Pt and a 1 M NaOH solution were added until the pH reached 10, and the stirring process continued for 60 minutes. For the reduction process at 80°C, 0.8 g (10 mL of pure water) and 5 mL of formic acid were used. After the stirring process was completed, the solution was cooled to room temperature and filtered using filter paper. The TiO2@Pt catalyst precipitate on the filter paper was dried in an oven at 100°C under an argon atmosphere for 4 hours. Finally, 0.1 g of the obtained TiO2@Pt catalyst was used to investigate the alcohol and pH effectiveness in photoelectrochemical water splitting experiments.

Synthesis of TiO2/CdS@Pt Catalyst

For the synthesis of TiO2@Pt catalyst doped with different CdS concentrations (1%, 3%, 5%, 7%), cadmium chloride (CdCl2) as the cadmium source and sodium sulfide (Na2S) as the sulfur source were used in the following mole amounts: 610^-5, 1810^-5, 3010^-5, and 4210^-5 mol, based on the sensor model and the impediment characteristic of the environment, the threshold value may be derived for the system under consideration.

Synthesis of 1% CdS-doped TiO2@Pt (TiO2/CdS (1%)@Pt) Catalyst

0.5 g of nanoscale (25 nm) TiO2 was dissolved in 5 mL of ethyl alcohol and stirred at 25°C for 30 minutes. Then, in the solution, 6*10^-5 mol of cadmium chloride and sodium sulfide were successively added, and the stirring process continued for 30 minutes. For the Pt reduction process, 0.005 g of Pt and a 1 M NaOH solution were added to the TiO2/CdS solution until the pH reached 10, and the stirring process continued for 60 minutes. For the reduction process at 80°C, 0.8 g (10 mL of pure water) and 5 mL of formic acid were used. After the stirring process was completed, the solution was cooled to room temperature and filtered using filter paper. The TiO2/CdS (1%)@Pt catalyst precipitate on the filter paper was dried in an oven at 100°C under an argon atmosphere for 4 hours. Finally, 0.1 g of the obtained TiO2/CdS (1%)@Pt catalyst was used to investigate the CdS effectiveness in photoelectrochemical water splitting experiments.

Results and Discussion

In the thesis study, the photocatalytic decomposition of water using the TiO2-Pt catalyst was the main objective. Additionally, the TiO2-Pt catalyst was doped with CdS, and the photocatalytic effect of water was investigated by measuring the change in gas volumes over time. The impact of the "Sacrificial Agent," as well as the pH parameters, on the photocatalytic decomposition of water was separately examined. To break down the results individually:

Impact of the "Sacrificial Agent": For this purpose, ethyl alcohol was used. The selection of hydrogen producing sacrificial agents as ethanol and preparation of highly charge-efficient catalysts. And it also provides a theoretical basis for hydrogen production from wastewater and environmental remediation[9].

Efficiency of TiO2@Pt Catalyst at Different Alcohol Concentrations

The change in total gas volumes obtained as a result of the decomposition of a 400 ml solution at various ethyl alcohol concentrations over time in the presence of 0.1 g of TiO2@Pt photocatalyst under ultraviolet light is shown in Figure 2. As seen in Figure 2, in the presence of 4% ethyl alcohol, 10 ml of gas was obtained after 100 minutes, while in the presence of 50% ethyl alcohol, 16 ml of gas was obtained in the same time period. Additionally, it can be concluded that, according to Figure 1, equilibrium was reached after 90 minutes in all ethyl alcohol concentrations, and gas production ceased.

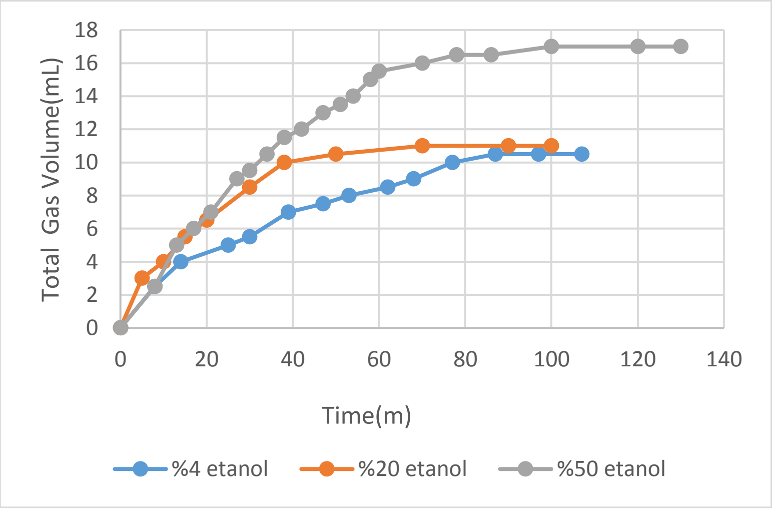

Figure 2. *Change of gas volumes obtained as a result of photocatalysis in 0.1 g TiO2-Pt catalyst, 400 ml solution with pH = 5 and different ethanol percentages over time.*

-According to the results obtained in the presence of different ethyl alcohol concentrations used as a "Sacrificial Agent," it has been determined that the most suitable ethyl alcohol concentration for the TiO2@Pt photocatalyst is 50% ethyl alcohol.

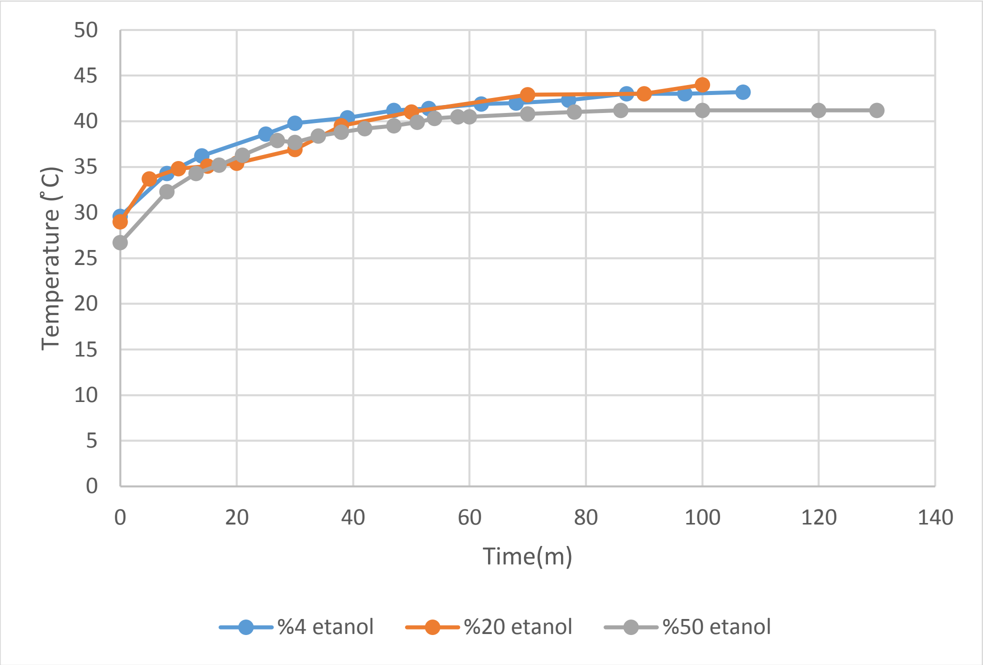

Figure 3. *Temperature change graph over time at different ethyl alcohol percentages*

Photoexcited electron–hole pairs are separated using sacrificial agents such as ethanol, which allow the formation of hydrogen and reduce electron–hole pair recombination [9]. As shown in Figure 3, in the experiment initiated in an air environment, the temperature of the solution gradually increases with the activation of the ultraviolet lamps. When the system temperature is controlled with air cooling, it reaches equilibrium at around 40°C after approximately 30 minutes. It has been observed that the behavior is consistent in almost all experiments conducted in the system.

The Efficiency of TiO2/CdS@Pt Catalyst at Different CdS Values

Figure 4 presents the change in total gas volumes over time obtained using the TiO2@Pt catalyst with different concentrations of CdS added, resulting in the TiO2/CdS@Pt photocatalyst.

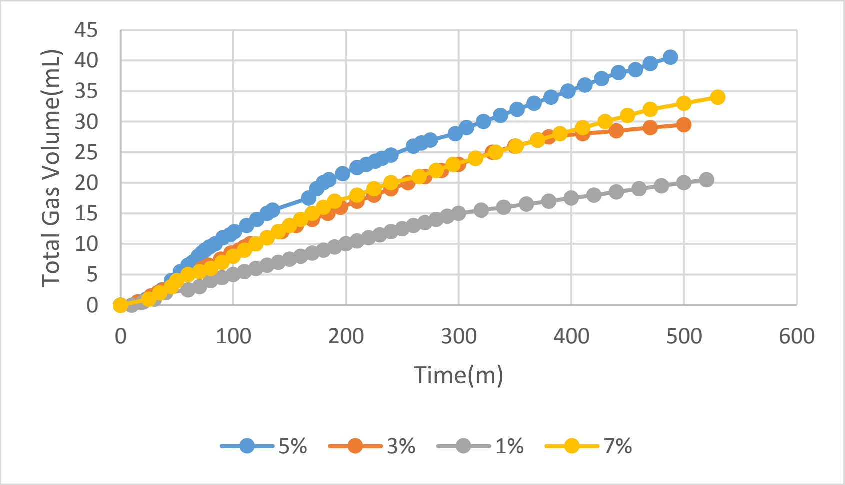

Figure 4. *Time variation of the total gas volumes released in a 400ml solution containing 50% ethyl alcohol at pH=2 in case of different percentages of CdS doped to 0.1 g TiO2-Pt photocatalyst*

As seen in Figure 5, as the CdS concentration added to the TiO2@Pt catalyst increases between 1% and 5%, the total gas yield also increases. However, at higher concentrations, beyond 5% CdS concentration, the photocatalytic effect decreases. The likely reason for this behavior is that low concentrations of CdS enhance the activity of TiO2. However, at higher concentrations of CdS, it completely covers the catalyst's surface, reducing the effectiveness of TiO2. According to Figure 5, the most suitable CdS concentration occurs when it is added at 5% to TiO2-Pt. The change in total gas volumes over time obtained in the presence of the TiO2-CdS-Pt photocatalyst is nearly linear and exhibits continuity, which is highly significant.

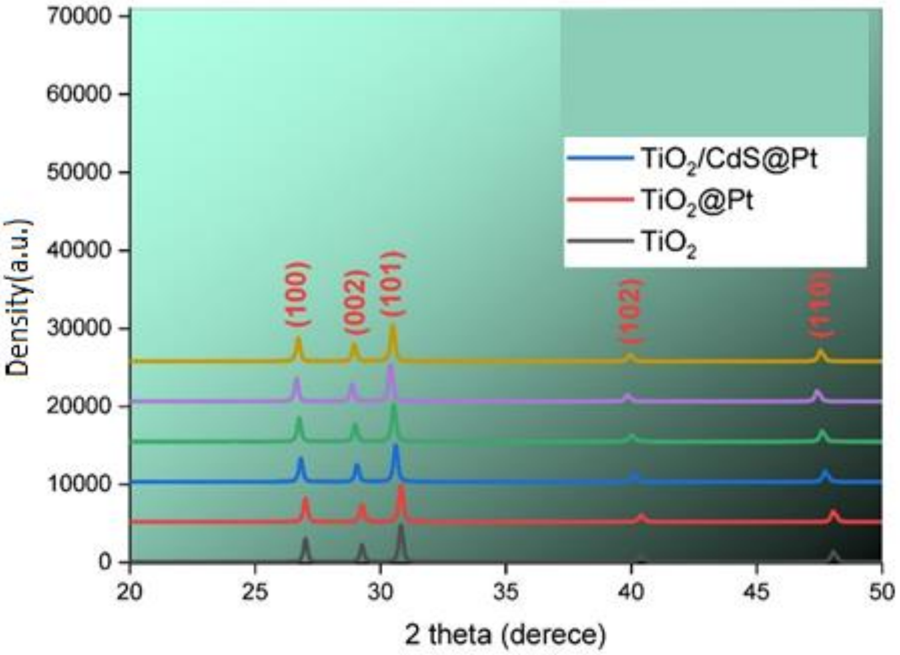

Figure 5. *XRD diffraction patterns of TiO2, TiO2@Pt, TiO2/CdS@Pt, catalysts*

Scanning Electron Microscopy (SEM)

SEM measurements were performed to examine the morphological characteristics of TiO2, TiO2@Pt, TiO2/CdS@Pt catalysts. SEM images obtained for the2 catalysts are shown in Figure 6.

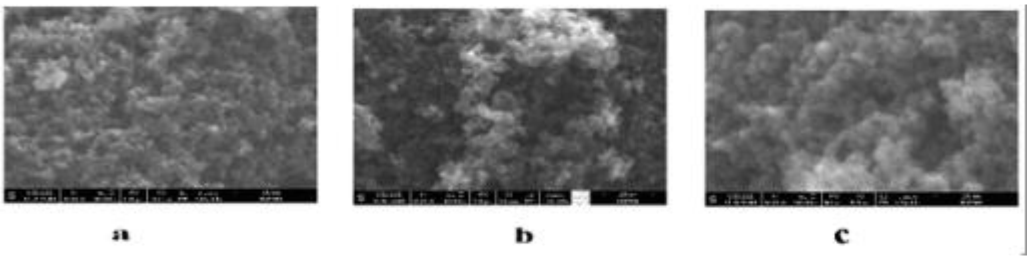

Figure 6 (a) *TiO2,* ***(b)*** *TiO2@Pt,* ***(c)*** *TiO2/CdS@Pt SEM images of catalysts*

"As clearly seen in the figure, all six synthesized catalysts have spherical shapes. Furthermore, upon closer examination of their size, it can be noted that all six catalysts are in the nanometer scale, and their crystallite sizes, as calculated from XRD measurements, closely match."

Energy Dispersive X-ray Spectroscopy (EDX)

The elemental properties of TiO2, TiO2@Pt, and TiO2/CdS@Pt catalysts were examined through SEM-EDX measurements. The SEM-EDX spectra for these three catalysts are shown in Figures 7-9, respectively. It is clearly evident from the spectra that the presence of Ti, O, Pt, and Cd elements can be observed. Based on the SEM-EDX spectra, it can be stated that the synthesis process was successfully carried out.

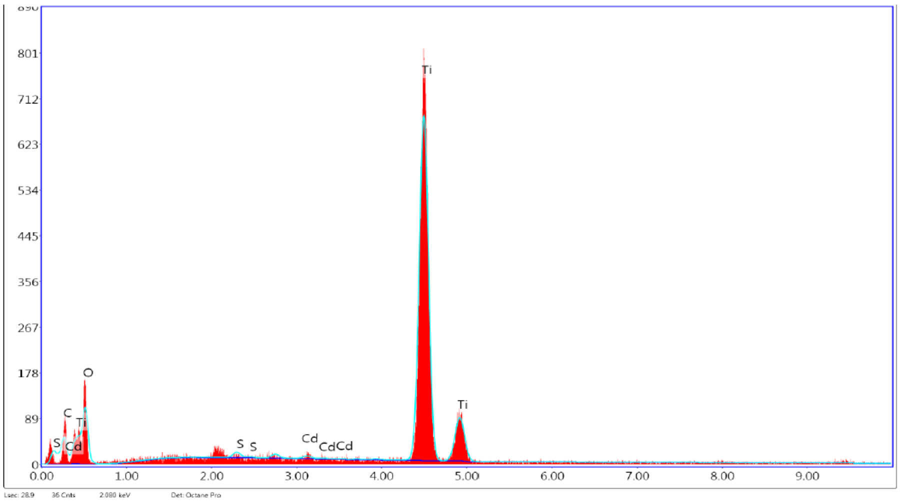

Figure 7. *SEM-EDX spectrum of TiO2 catalyst*

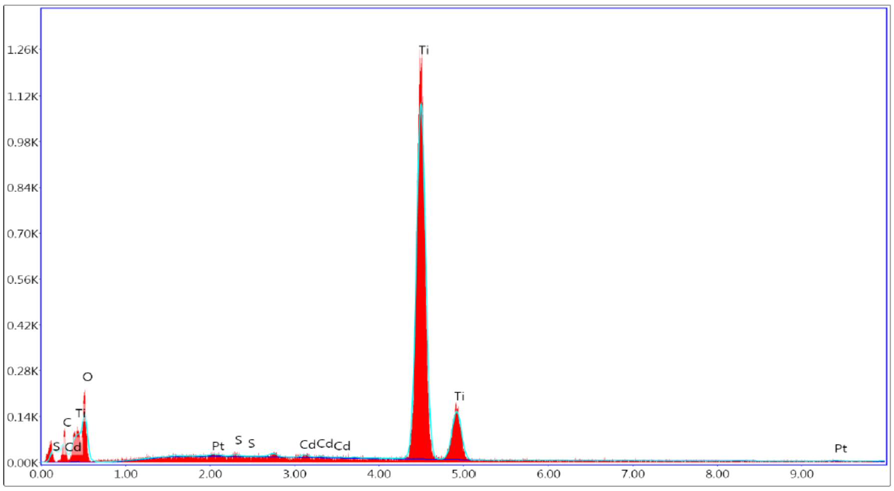

Figure 8. *SEM-EDX spectrum of TiO2@Pt catalyst*

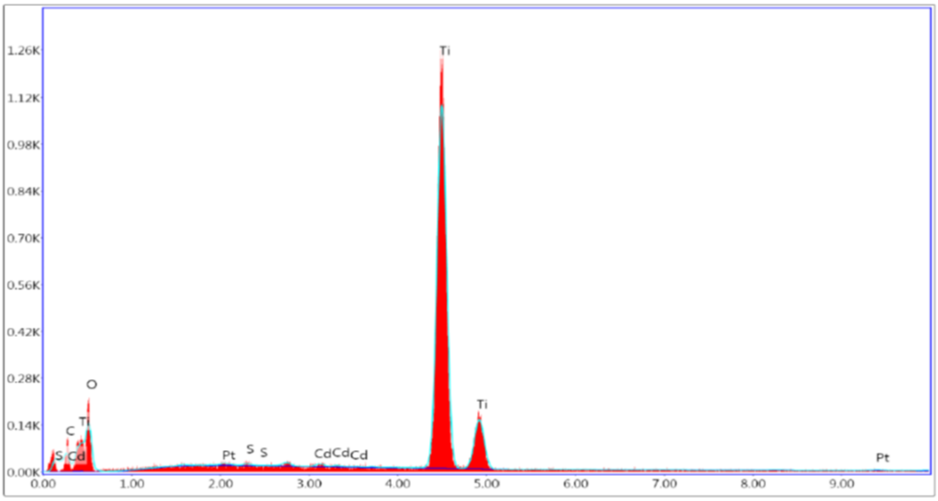

Figure 9. *SEM-EDX spectrum of TiO2/CdS@Pt catalyst*

In this study, we investigated the efficiency of electron-hole pair generation and hydrogen production in a particulate photocatalytic system using nanoscale (25 nm) TiO2 semiconductor loaded with Pt, under different ethanol concentrations. The most effective hydrogen production was found in a 50% ethanol environment. After establishing the appropriate solution conditions, the addition of a semiconductor (CdS) was examined to enhance its activities and hydrogen production efficiency. Subsequently, the efficiency of $TiO2/CdS@Pt$ catalysts with 1%, 3%, 5%, and 7% CdS additions was investigated.

When examining the CdS effectiveness, it was observed that CdS efficiency increased as CdS concentration increased, up to 5%. However, at higher concentrations, above 5% CdS, the photocatalytic effect decreased. The probable reason for this behavior is that lower CdS concentrations enhance the TiO2 activity, while higher concentrations may cover the catalyst's surface, reducing the effectiveness of TiO2.

Based on the results of this study, the catalysts we produced hold promise for hydrogen production. They are expected to yield efficient results, particularly in the production of hydrogen by separating it in Photoelectrochemical (PEC) cells.

Conclusion

Hydrogen could be a universal energy carrier with technically various production, storage, distribution and ultimate trails. Nonetheless, the increases within the price of gas as well as CO2 emissions make growth of sustainable and benign production routes unavoidable[10]. The current carbon-based energy system is undergoing a profound change driven by the increased concerns over the longevity and security of energy supply, as well as energyrelated emissions of carbon dioxide and air pollutions. The evolutionary trend of this transition is toward a smart energy network of the future that is characterized by widespread deployment of clean energy technologies and intelligent energy management technologies. In this transition, hydrogen and fuel/electrolysis cell technologies have crucial roles[11].

In our study, we investigated the efficiency of electron-hole pair generation and hydrogen production in a particulate photocatalytic system using nanoscale (25 nm) TiO2 semiconductor loaded with Pt, under different ethanol concentrations. The most effective hydrogen production was found in a 50% ethanol environment. After establishing the appropriate solution conditions, the addition of a semiconductor (CdS) was examined to enhance its activities and hydrogen production efficiency. Subsequently, the efficiency of TiO2/CdS@Pt catalysts with 1%, 3%, 5%, and 7% CdS additions was investigated.

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