

Research Article

The Characterization and Hydrogen Production from Water Decomposition with Methanol in a Semi-Batch Type Reactor Using In, P-TiO₂s

Joonwoo Kim,¹ Hae-Ri Kim,² and Suk-Jin Choung¹

¹ Department of Chemical Engineering, Kyung Hee University, Yongin-Si, Gyeonggi-Do 446-701, Republic of Korea

² Technical Center, Ordeg Corporation, Mognae-Dong, Ansan 425-100, Republic of Korea

Correspondence should be addressed to Suk-Jin Choung, sjchoung@khu.ac.kr

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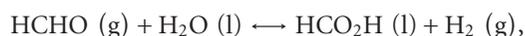
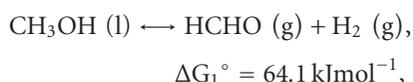
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The photocatalytic production of hydrogen from water using solar energy is potentially a clean and renewable source for hydrogen fuel. This study examines the production of hydrogen over In, P-TiO₂s photocatalysts. 1 mol% In-TiO₂ and P-TiO₂ were produced using the solvothermal method and were treated at 500 and 800°C to obtain anatase and rutile structure, respectively. The photocatalysts were characterized by X-ray diffraction, photoluminescence spectra, X-ray spectroscopy, UV-visible spectroscopy, and scanning electron microscopy. The production of H₂ from methanol photodecomposition was greater over the rutile structure than over the anatase structure of TiO₂. Moreover, the amount of hydrogen was enhanced over In-TiO₂ and P-TiO₂ compared to that over pure TiO₂; the production increased by about 30%. The structural effect and the addition of In, P have significant influence on the H₂ production from methanol/water decomposition.

1. Introduction

The importance of hydrogen as a source of fuel in the near future is due to its application as a compact energy supplier in fuel cells and batteries. Hydrogen fuel can be produced from clean and renewable energy resources, and thus, its life cycle is clean and renewable. Compared to the conventional and expensive methods, the photocatalytic splitting of water using TiO₂ offers a promising way for clean, low-cost, and environmentally friendly production of hydrogen using solar energy. Early work of TiO₂-assisted photo-electrochemical hydrogen production was reported by Fujishima and Honda [1]. Since then, the technology for generating hydrogen by the splitting of water using a photocatalyst has attracted much attention. Recently, hydrogen production has been extended to the photocomposition of methanol which has a lower splitting energy than water. Kawai and Sakata suggested the following overall methanol decomposition reaction [2, 3]:



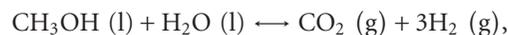
$$\Delta G_2^\circ = 47.8 \text{ kJmol}^{-1},$$



$$\Delta G_3^\circ = -95.8 \text{ kJmol}^{-1}.$$

(1)

Overall,



$$\Delta G^\circ = 16.1 \text{ kJmol}^{-1}.$$

(2)

Consequently, the decomposition energy for methanol is 0.7 eV. Most investigations of hydrogen production via methanol photodecomposition have focused on modifying TiO₂ in many reports, and the photocatalytic method is modified either by anion doping or metal ion doping or by loading with noble metals. Anpo and Takeuchi suggested Pt/TiO₂ [4], Bamwenda et al. compared Au-loaded TiO₂ and Pt-loaded TiO₂ [5], Sakthivel et al. used Pt, Au, and

Pd-loaded TiO₂ [6], Wu et al. studied CuO_x/TiO₂ [7], and Park and Kang used Ag-incorporated TiO₂ [8]. In the case of metal ion doping, transitional metal ion doping and rare earth metal ion doping have been extensively developed for enhancing the TiO₂ photocatalytic activities. Choi et al. studied the photocatalytic activity of 21 metal ions doped into TiO₂, and among of them, Fe, Mo, Ru, Os, Re, and V ions exhibited good activity [9]. Some of the recent reports have studied the photo-electrochemical characteristics of anion (N, F, C, S, etc.) doped TiO₂ powder and colloidal materials under UV-visible and visible illumination [10–13]. However, rapid electron-hole recombination and thermal instability are thought to be the major impediments. However, the number of known photocatalysts is limited, and their activity is still low. There is an urgent need to develop new photocatalysts that have greater hydrogen-producing activity under visible light irradiation.

In this study, we evaluated two new materials, In-TiO₂ and P-TiO₂, to reduce the large band gap of pure TiO₂. To investigate the structural effect of the photocatalysts, we prepared the photocatalysts with anatase and rutile structures using thermal treatment at 500 and 800°C, respectively which were then used to produce hydrogen gas via methanol photodecomposition. To determine the relationship between In, P species and catalytic performance for H₂ production, the In-TiO₂ and P-TiO₂ photocatalysts were examined using X-ray diffraction, photoluminescence, X-ray photon spectroscopy, and UV-Visible spectroscopy.

2. Experimental

2.1. Catalysts Preparation. In this study, a commonly used solvothermal method was employed to synthesize In and P-TiO₂ catalysts. The reagents used for the preparation of sol mixture were titanium tetraisopropoxide (99.95%, Junsei Chemical, Japan), indium trichloride (98%, Aldrich, USA) and phosphoric acid (Wako Pure Chem. Ltd., Japan) as Ti, In, and P precursors, respectively. The metal precursors were mixed with ethyl alcohol (99%, Wako Pure Chem. Ltd., Japan) in an autoclave (model R-211, Reaction Engineering Inc., Korea) heated at 200°C for 10 h at a rate of 10°C min⁻¹. During the thermal treatment, Ti, In, and P were hydrolyzed by the hydroxyl group in solvent leading to the formation of nanosized In and P-TiO₂ crystals. The resulting powder was washed with distilled water until pH-7 was reached and then dried. Finally, the samples were thermally treated at two different temperatures, 500 and 800°C, for 3 h to remove impurities like the residual carbon or chloride ions on the powder surface and also to study the effect of calcination on the phase formation in the prepared catalysts.

2.2. Characterizations. The prepared catalysts were identified through powder X-ray diffraction analysis (XRD, model PW 1830, Philips, The Netherlands) with nickel-filtered Cu K α radiation (40 kV, 100 mA) at 2 θ angles of 5 to 90°. The scan speed was 10° min⁻¹, and the time constants were 1 sec. The scanning electron microscopy (SEM) images were obtained using Leica 440, Beam source is tungsten filament, resolution is 4.5 nm, and probe current was in between 1 pA to 1 μ A.

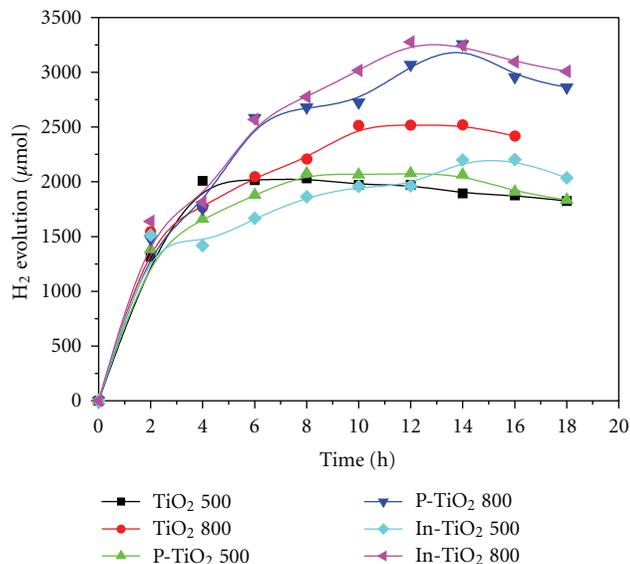


FIGURE 1: Catalytic activity of 1 mol% P, In-TiO₂, and TiO₂ with rutile and anatase phases during the production of H₂ from methanol/water photodecomposition.

For analysis of the binding energy among In3d, P2p, Ti2p, and O 1s, the X-ray photoelectron spectroscopy (XPS, PHI 5700, PHI com) was employed. The 1.0 mol% In and P incorporated TiO₂ powder were pelletized at 2.0×10^4 kPa for 10 min; the 1.0 mm sized pellets were then maintained overnight in a vacuum oven (1.0×10^{-7} Pa) to remove the surface water molecules prior to measurement. The case pressure of the ESCA system was below 1×10^{-9} Pa. The experiments were recorded using a 200 W power source and angular acceptance of $\pm 5^\circ$, with the analyzer axis set at an angle of 90° to the specimen surface. Wide scan spectra were measured over the binding energy range 0 to 1200 eV, with pass energy of 100.0 eV. The Ar⁺ bombardments of the 1.0 mol% In, P incorporated TiO₂s were performed with ion currents between 70 and 100 nA, over a 10.0×10.0 mm area, with a total sputtering time of 2400 s, divided into 60 s intervals. The UV-visible spectrum was obtained using a JASCO V-570 spectrometer equipped with a reflectance sphere. The spectral range varied from 200 to 800 nm. Photoluminescence spectroscopy was measured at room temperature using a Phillips H-9000 using HeCd as the beam source at 325 nm.

2.3. H₂ Production from Methanol/Water Decomposition over In, P-TiO₂. In general, water decomposition systems are based on the evaluation of accumulated H₂ from water, and most of the systems employ semi-batch type reactors like plug flow reactor. In our study, we used a custom-made liquid photoreactor setup for the photodecomposition of methanol/water. For hydrogen generation, 1.0 g of the powdered catalysts was added to 500 ml each of distilled water and methanol in a 1300 mL Pyrex reactor. UV-lamps (3×6 Wcm⁻², 15 cm length \times 2.0 cm diameter) emitting radiation at 365 nm were used. A flask for hydrogen storage

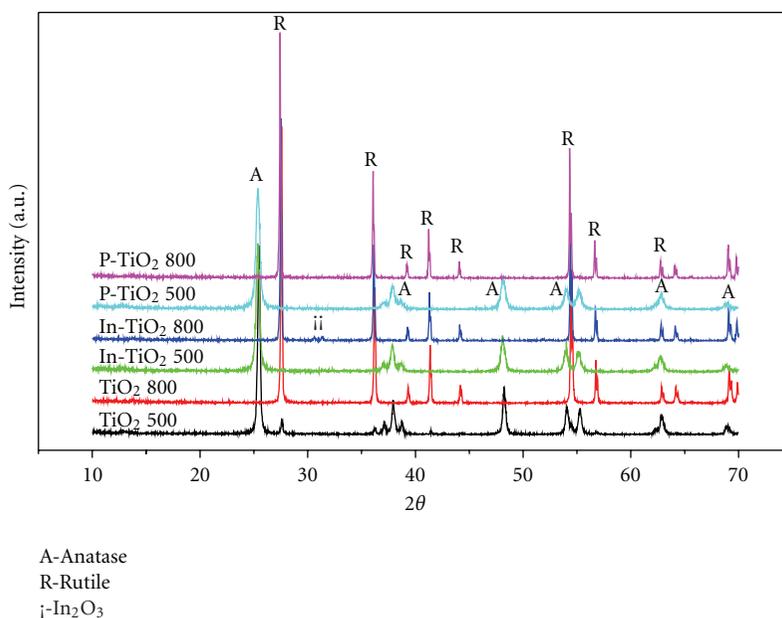


FIGURE 2: XRD patterns of 1.0 mol% P, In-TiO₂, and TiO₂ photocatalysts treated at 500°C (anatase phase) and 800°C (rutile phase).

collects the product from reactor using a vacuum pump. The produced hydrogen was analyzed by GC/TCD (Shimadzu 17A, Japan) using molecular sieve-5A column.

3. Results and Discussion

3.1. H₂ Production from Hydrolysis of Water with Methanol on In, P TiO₂s Photocatalysts. Figure 1 shows the catalytic activity of In and P-TiO₂ with anatase and rutile phase for the production of H₂ from methanol/water photodecomposition. Unfortunately, the GC detector could not sense the H₂ production until 2 h had elapsed because too little product had decomposed. Then rate of H₂ evolution becomes very stable after 2 h, and activities reach to steady-state at 8 h. However In, P incorporated TiO₂ increase rate of H₂ evolution until 12 h. In general, previous researchers plotted continuously increasing graph because H₂ production accumulated by using batch system [4–13]. While, in this study, used system for H₂ evolution is semi-batch system, it can be calculated H₂ production per hour. So, the time to reach steady state can be obtained, and the graph could not increase continuously. The catalysts with rutile phase exhibit relatively higher activity than those with anatase phase in a semi-batch type liquid photosystem. The maximum H₂ production of 3,300 μmol at about 12 h was achieved for In-TiO₂ calcined at 800°C (rutile structure), and with further increase in time, a small decrease in its activity was observed. The increasing activity of the added In and P catalysts may be caused by increased reduction activity, substantial increase in the rate of photo absorption, and change of atomic bonding and composition of catalyst surface.

3.2. Characterization of In, P-TiO₂ Catalysts. Figure 2 shows the XRD patterns of P-TiO₂, In-TiO₂, and TiO₂ powders

treated at 500 and 800°C. Depending on the calcination treatment temperature, well-developed anatase (500°C) and rutile (800°C) phases were formed, and their diffraction pattern are labeled as “A” and “R”, respectively. The peaks of the In, P are very well inserted into the TiO₂ structure and that explains the absence of their peaks in Figure 2. The peaks corresponding to anatase were assigned as $2\theta = 25.2^\circ$ (101), 37.5° (004), 47.5° (220), 53.8° (105), 54.9° (211), 63.0° (204); for rutile as $2\theta = 27.5^\circ$ (110), 36.1° (101), 41.3° (111), 54.4° (211), 56.7° (220). Especially, rutile phase of In incorporated TiO₂ appears peak of In₂O₃ at $2\theta = 30.6^\circ$, 31.4° . It is considered that indium is formed crystalline easily than phosphorus by effect of sintering [14].

Figure 3 shows SEM micrographs of TiO₂, In-TiO₂, and P-TiO₂ particles. The photocatalysts consisted of relatively irregular and spherical particles of varied size between 50 to 500 nm. Among them, the particles with anatase structure prepared at 500°C were smaller than those with the rutile structure prepared at 800°C. This result is related to a sintering effect in which the particle size increases with the calcination temperature due to the increased agglomeration of the particles. Also, TiO₂ without additive material is composed of granules with a smooth surface. However, after incorporating In and P on TiO₂, the granules became irregular and angular with the grain size of about 0.3–50 μm.

XPS analysis of O 1s and Ti 2p orbital of TiO₂, In-TiO₂, and P-TiO₂ are shown in Figure 4. The Ti 2p_{1/2} and Ti 2p_{3/2} spin-orbital splitting photoelectrons for anatase TiO₂ were located at binding energies of 464.34 and 458.57 eV, which were assigned to the presence of general Ti⁴⁺ [15, 16] as shown in Figure 4(a). From Figure 4(b), the binding energy of Ti 2p orbital was observed to decrease due to the added In and P which infers the transformation from higher

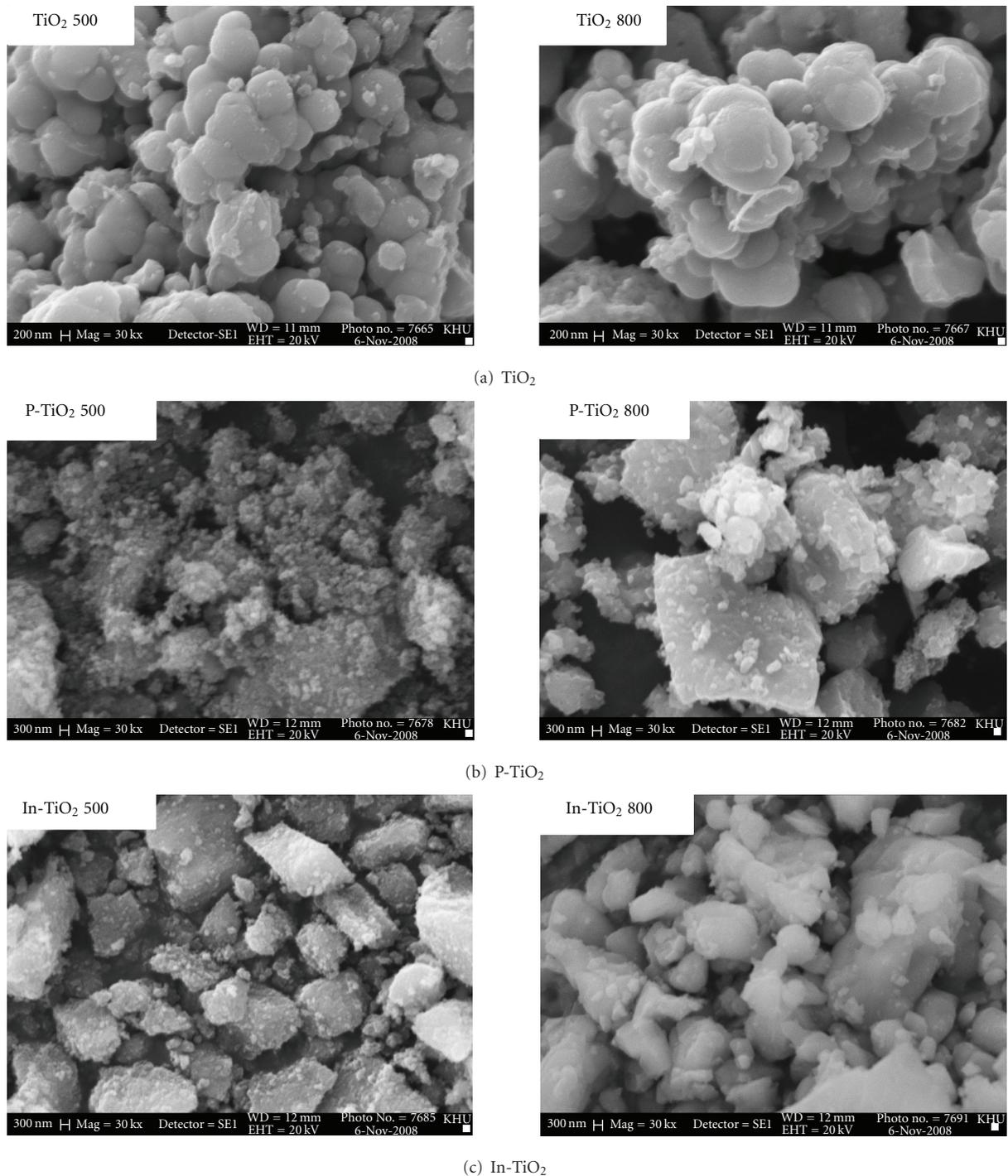


FIGURE 3: SEM micrographs of (a) TiO₂ (b) P-TiO₂, and (c) In-TiO₂ photocatalysts treated at 500°C (anatase phase) and 800°C (rutile phase).

Ti⁴⁺ to lower Ti³⁺ valence state. Generally, a high binding energy means that the metal has a high valence [17]. At this situation, an increase in catalytic activity is expected to change valence as Ti³⁺. In the case of O 1s (Figure 4(c)), the two overlapping peaks were isolated using the Gaussian method. The O 1s peaks at 529.8 and 531.20 eV were assigned to metal oxidation and metal hydroxyl group, respectively.

With increasing area of the hydroxyl group, the hydrophilic and catalytic activities are expected to increase.

From Figure 5, the In 3d_{5/2} and P 2p_{3/2} spin-orbital splitting photoelectrons were located at the binding energies of 444.03 eV and 133.02 eV which is identified with the oxidation state of In³⁺ and P⁵⁺, respectively in TiO₂. Especially, the existence of phosphorous in the pentavalent oxidation

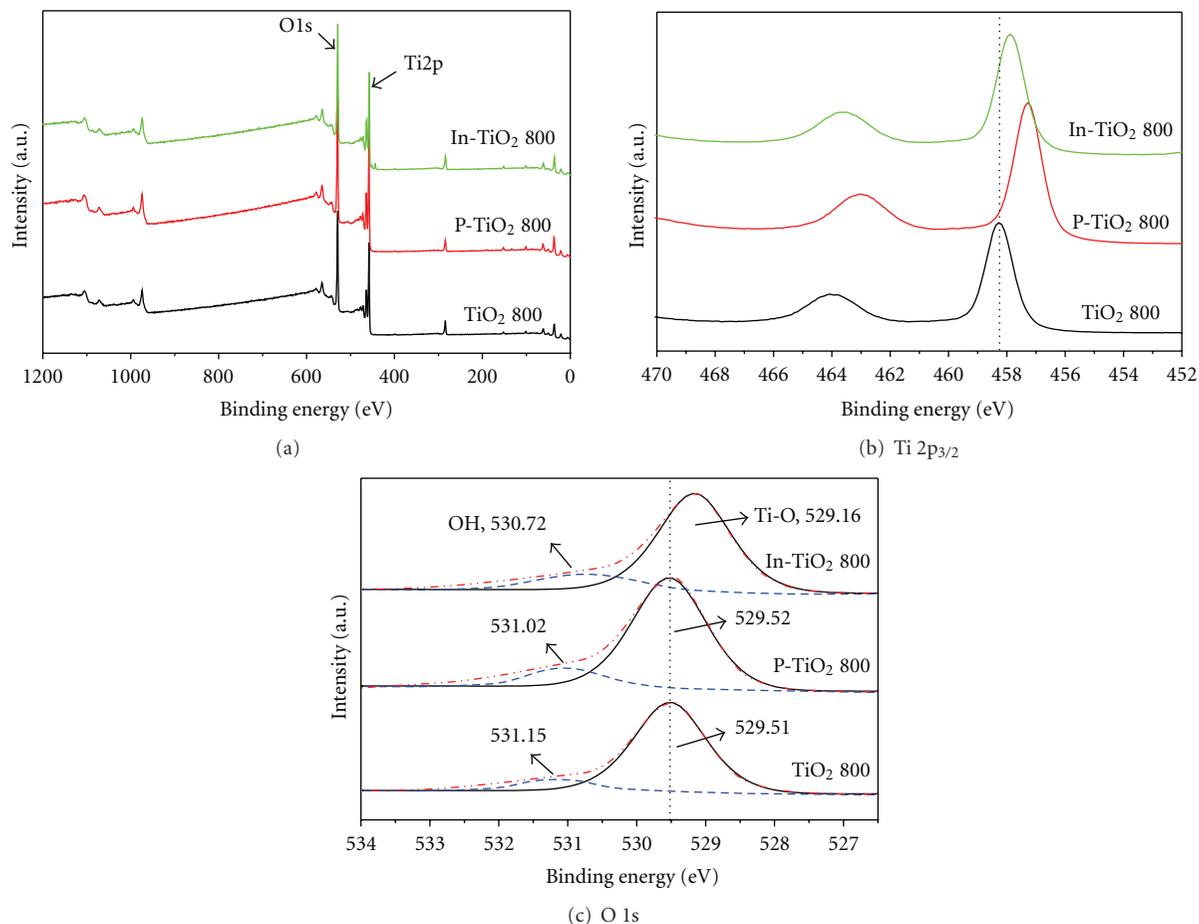


FIGURE 4: XPS analysis of (a) 1.0 mol% In, P incorporated TiO₂ photocatalysts; (b) Ti 2p and (c) O 1s spin orbital.

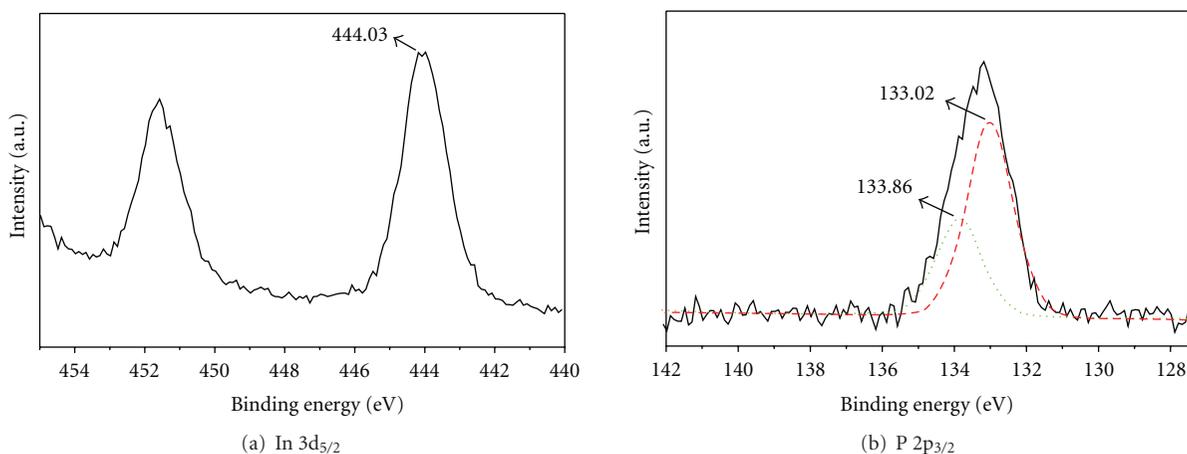


FIGURE 5: XPS analysis of 1.0 mol% In, P incorporated TiO₂ photocatalysts treated at 800°C; (a) In 3d and (b) P 2p spin orbital.

state has a decreasing effect on valence-hole recombination because of the unbalanced electrical charge [18].

UV-Vis spectroscopy was used to examine the light absorption ability of the investigated photocatalysts as shown in Figure 6. The onset absorption wavelength and corresponding band gap energy of the photocatalysts used

in this study as obtained from the UV-Vis spectra are summarized in Table 1. It is clearly seen that the absorption band of the synthesized In and P-TiO₂ is in the UV light range of 200 to 400 nm, and the shift of the onset absorption edges toward longer wavelength with rutile and anatase form [19].

TABLE 1: Summary of the onset absorption wavelengths, band gap energies, and chemical composition of 1.0 mol% In, P incorporated TiO₂ photocatalysts.

Photocatalyst	Calcination temperature (°C)	Onset absorption wavelength, λ_g (nm)	Band gap energy (eV)	Element (wt.%)				
				O K	Ti K	P K	In L	Totals
TiO ₂ -A	500	418	2.97					
TiO ₂ -R	800	430	2.88	39.88	60.12			100.0
In-TiO ₂ -A	500	407	3.05					
In-TiO ₂ -R	800	439	2.82	44.23	55.26		0.51	100.0
P-TiO ₂ -A	500	402	3.08					
P-TiO ₂ -R	800	425	2.92	43.01	56.47	0.52		100.0

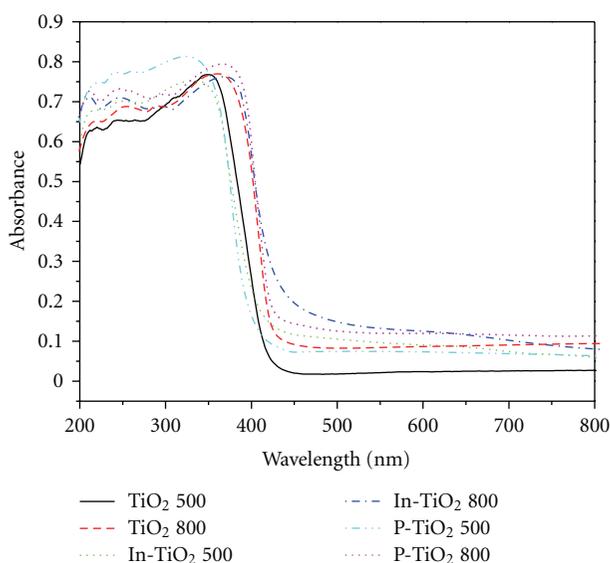


FIGURE 6: UV-Visible spectroscopy of 1.0 mol% In, P incorporated TiO₂ photocatalysts.

Figure 7 shows photoluminescence emission on In-TiO₂, P-TiO₂, and pure TiO₂. The objective of this experiment is to study the addition of In and P on the electro-hole recombination rate. According to the test results, the shape of the peak discloses no change in the spectrum of the used catalysts. However, the peak intensity decreases depending on the doping level of In and P in TiO₂. Generally, when photoluminescence emission value is large, the number of recombination electrons should also large number of electrons are photoexcited. Therefore, the larger the emission value is, the photocatalytic reaction might be. However, in this study the higher the photoluminescence emission values were, the lower the photocatalytic activities that could be indicated. The result could be thought that the metal incorporated TiO₂, the amount of recombination of electron-hole pairs is decreased, which could be due to photoexcited electrons joining in photocatalytic reaction rather than recombining with holes emitting the absorbed energy [20–23].

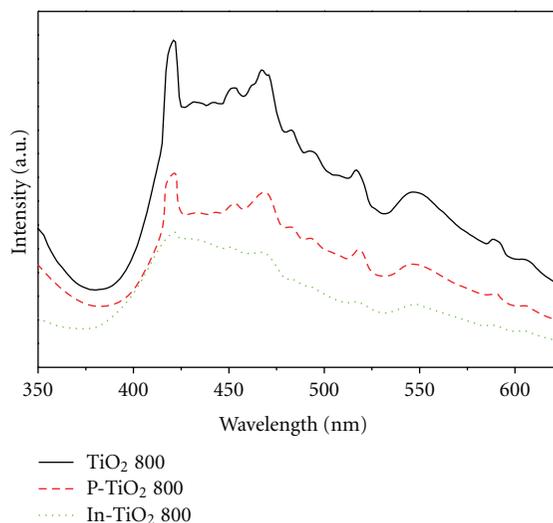


FIGURE 7: Photoluminescence spectra of 1.0 mol% In, P incorporated TiO₂ photocatalysts.

4. Conclusions

This study focused on using In, P incorporated TiO₂ catalysts synthesized by solvothermal method and used for the production of H₂ from methanol/water photodecomposition. Compared to anatase structure, the rutile form exhibited better H₂ production from methanol/water photodecomposition. Compared to P-TiO₂, the production of H₂ was a little better in the case of In-TiO₂ and also showed a 30% increase in the activity than pure TiO₂. The well-defined dispersion of the metal in the TiO₂ was confirmed from XRD result. Increase of the OH group on the catalytic surface, change of Ti structure, increase in the absorption of visible light, and decrease of valence-hole recombination were confirmed using XPS, UV-Vis, and PL data. The prepared catalysts were found to exhibit good activity than pure TiO₂, and our future studies will focus on further improving the catalytic activity.

Acknowledgment

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