

Enhanced Hydrogen Production from Methanol/Water Photo-Splitting in TiO₂ Including Pd Component

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The future use of hydrogen as an energy source is expected to increase on account of its environmentally friendliness. In order to enhance the production of hydrogen, Pd ions (0.01, 0.05, 0.1, and 0.5 mol%) were incorporated TiO₂ (Pd-TiO₂) and used as a photocatalyst. The UV-visible absorbance decreased with increasing level of palladium incorporation without a wavelength shift. Although all the absorption plots showed excitation characteristics, there was an asymmetric tail observed towards a higher wavelength caused by scattering. However, the intensity of the photoluminescence (PL) curves of Pd-TiO₂ was smaller, with the smallest case being observed at 0.1 and 0.5 mol% Pd-TiO₂, which was attributed to recombination between the excited electrons and holes. Based on these optical characteristics, the evolution of H₂ from methanol/water (1:1) photo-splitting over Pd-TiO₂ in the liquid system was enhanced, compared with that over pure TiO₂. In particular, 2.4 mL of H₂ gas was produced after 8 h when 0.5 g of a 1.0 mol% Pd-TiO₂ catalyst was used. H₂ was stably evolved even after 28 h without catalytic deactivation, and the amount of H₂ produced reached 14.5 mL after 28 h. This is in contrast to the case of the Pd 0.1 mol% impregnated TiO₂ of H₂ evolution of 17.5 mL due to the more decreased electron-hole recombination.

Key Words: Pd-TiO₂. Photo catalysis. Water splitting. H₂ production. Pd-impregnated TiO₂

Introduction

The future use of energy from hydrogen should increase on account of its environmentally friendliness. The technology for generating hydrogen by the splitting of water using a photo catalyst has attracted considerable attention. The photo catalytic formation of hydrogen and oxygen on semiconductors, such as MTiO₃¹ and MTaO₂N₂²⁻⁶ has been studied extensively due to the low band gap and high corrosion resistance of these semiconductor materials. However, the photo catalytic decomposition of water on a TiO₂ photo catalyst is ineffective because the amount of hydrogen produced is limited by the rapid recombination of holes and electrons, resulting in the formation of water.

In order to overcome this rapid recombination in water splitting, studies aimed at improving the level of hydrogen production *via* methanol or ethanol photodecomposition, not water, have focused on modified (Ag or Cu) TiO₂,⁷⁻¹⁰ which can be used to activate the photo catalysts, using UV light with longer wavelengths and noble metal (Pt, Rh) doped TiO₂,^{11,13} which has relatively high activity and chemical stability under UV irradiation. In particular, Zou¹¹ and Ikuma¹² reported that the activity for hydrogen generation from water/alcohols is greatly improved on Pt-TiO₂, synthesized using a cold plasma method with the highest rate of H₂ production being obtained from Pt-deposited TiO₂ formed by the formaldehyde method. Idriss¹³ compared the level of hydrogen production from ethanol photo-splitting between Pt- and Rh/TiO₂, where the addition of Pt increased the level of hydrogen production significantly with a quantum yield of approximately 10% at 350 K. On the other hand, Rh-doped TiO₂ is far less active. However, this value is still low to be of economic use. In addition, the photo splitting of light hydrocarbons, such as

methanol and ethanol, is not environmentally desirable due to the emission of CO and CO₂ during the photoreaction. In addition, noble metals are quite expensive. Therefore, there is an urgent need for the development of new inexpensive photo catalysts that are environmentally friendly and possess greater hydrogen-producing activity under visible light irradiation.

In this study, a new photocatalyst, Pd (0.01, 0.05, 0.1, and 0.5 mol%) incorporated TiO₂ (Pd-TiO₂) with an anatase structure, was prepared using a hydrothermal method with the aims of reducing the rate of hole and electron recombination and lowering the material cost. A catalyst over Pd-impregnated TiO₂ was also examined. The relationship between the palladium species and the catalytic performance for the production of H₂ over the Pd-TiO₂ photo catalysts was examined by X-ray diffraction analysis (XRD), X-ray photon spectroscopy (XPS), UV-visible spectroscopy, and Photoluminescence (PL) spectroscopy.

Experimental Section

Pd incorporated TiO₂ (Pd-TiO₂) with various molar fractions of palladium were prepared using a common hydrothermal method.¹⁴ To prepare the sol mixture, titanium tetraisopropoxide (TTIP, 99.95%, Junsei Chemical, Tokyo, Japan) and palladium nitrate (Pd(NO₃)₂, 99.9%, Junsei Chemical, Tokyo, Japan) were used as the titanium and palladium precursors, respectively. Palladium nitrate (0.01, 0.05, 0.1, and 0.5 mol%) were dissolved in distilled water. 0.5 mol TTIP was added slowly to 250 mL distilled water and stirred homogeneously for 2 h. Ammonium hydroxide was then added and the pH was maintained at 9.0 for rapid hydrolysis. The final solution was stirred homogeneously and moved to an autoclave for the thermal treatment. TTIP and palladium nitrate were hydro-

lyzed *via* the OH groups during thermal treatment at 473 K for 8 h under a nitrogen environment at a pressure of approximately 5 atm. The resulting precipitate was washed with distilled water until pH = 7.0 and then dried at 373 K for 24 h. The Pd-impregnated TiO₂ was synthesized by stirring an alcoholic solution of 0.1 mol% Pd ions with anatase structured TiO₂ powder until a homogeneous state was reached. The mixture was then treated thermally at 773 K for 1 h.

The synthesized TiO₂ and Pd-TiO₂ powders were examined by XRD (model PW 1830; Philips, Amsterdam, The Netherlands) with nickel-filtered CuK α radiation (30 kV, 30 mA). The samples were scanned at 2 θ angles ranging from 5 to 70° at a scan speed of 10° min⁻¹ and a time constant of 1 s. The sizes and shapes of the TiO₂ and Pd-TiO₂ particles were examined by high-resolution transmission electron microscopy (TEM) on a JEOL 2000EX transmission electron microscope operated at 200 kV. The UV-visible spectra of the TiO₂ and Pd-TiO₂ powders were obtained using a Shimadzu MPS-2000 spectrometer (Kyoto, Japan) with a reflectance sphere, over the special range, 200 - 800 nm. PL spectroscopy of the TiO₂ and Pd-TiO₂ powders were also carried out to determine the number of photo-excited electron hole pairs in the samples. A 1.0 mm pellet type sample was measured at room temperature using a He-Cd laser source at a wavelength of 325 nm. XPS data of Pd3p, Ti2p, and O1s were recorded using a ESCA 2000 (VZ MicroTech, Oxford, UK) system equipped with a non-monochromatic AlK α (1486.6 eV) X-ray source. The signals were fitted using mixed Lorentzian-Gaussian curves.

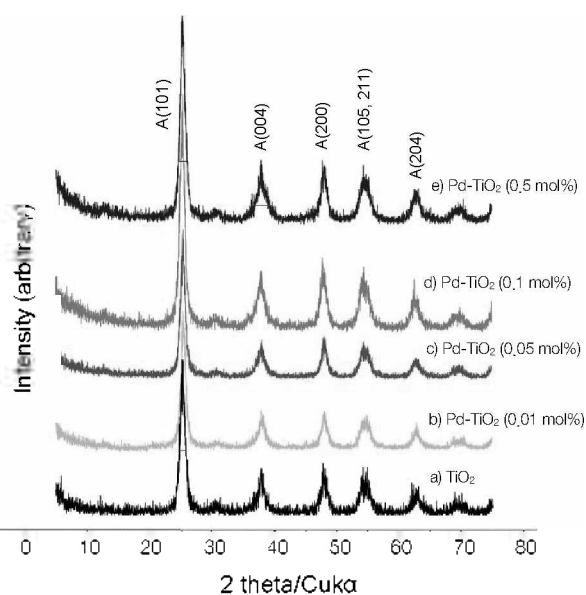
Results and Discussion

Figures 1A and 1B show the crystallinity and expected ion exchanged site obtained from the XRD patterns of the TiO₂ and 0.01, 0.05, 0.1, and 0.5 mol% Pd-TiO₂ powders. The Pd-TiO₂ particles exhibited a pure anatase structure before being thermally treated at 773 K. The XRD patterns showed peaks at 25.3, 38.0, 48.2, 54, 63, and 68°, which were assigned to the (d₁₀₁), (d₀₀₄), (d₂₀₀), (d₁₀₅), (d₂₁₁), and (d₂₀₄) planes, respectively. The peak positions were not changed despite the addition of palladium to the TiO₂ framework. In addition, no peaks assigned to Pd, PdO, and PdO₂ (mainly peaks: 2 theta = 40.00 (111 plane), 33.8 (101 plane), and 54.5° (211 plane)) were observed, indicating that the palladium ions were incorporated into the titanium anatase framework. Compared with the shift of peaks for the anatase structure of pure TiO₂, those of the Pd-TiO₂ were not changed despite the difference in the ionic radii of Ti⁴⁺ (68 pm) and Pd²⁺ (86 pm). Generally, crystalline domain sizes decrease with increasing line-broadening of the peaks. The line broadening of the [101] peak is related to the size of the hexagonal crystalline phase. The full width at half maximum (FWHM) height of the peak at 25.3° 2 θ was 1.593°. Scherrer's equation, $t = 0.9 \lambda / \beta \cos \theta$, where λ is the wavelength of the incident X-rays, β is the full width at half maximum height in radians, and the θ is the diffraction angle, was used to estimate the crystalline domain size. The estimated crystalline domain sizes were 14.3, 16.1, 14.2, 14.7 and 14.7 nm for the TiO₂ and 0.01, 0.05, 0.1, and 0.5 mol%

Pd-TiO₂ powders, respectively. In particular, the [004] plane peak broadening increased with increasing amount of palladium compared to other peaks. This suggests that the larger Pd ions insert into [004] site by substitution with the smaller titanium ions, as shown in Figure 1B.

Figure 2 shows TEM images of the TiO₂ and the 0.01, 0.05, 0.1, and 0.5 mol% Pd-TiO₂ powders. A relatively uniform mixture of rhombic and cubic particles ranging in size from 8 to 15 nm was observed. When palladium was added, their sizes were similar to 0.01 mol% Pd-TiO₂. This corresponds to the XRD patterns shown in Figure 1.

A) XRD spectra of Pd-TiO₂



B) Expected the site exchanged by Pd atom in TiO₂

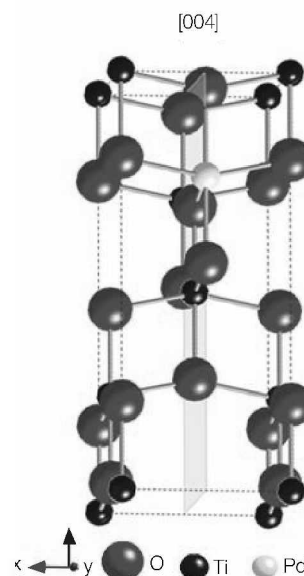


Figure 1. XRD patterns of TiO₂ and Pd-TiO₂ as-synthesized and the expected site exchanged by Pd atoms in TiO₂: a) TiO₂, b) 0.01 mol% Pd-TiO₂, c) 0.05 mol% Pd-TiO₂, d) 0.1 mol% Pd-TiO₂, and e) 0.5 mol% Pd-TiO₂.

Quantitative XPS analyses of the TiO_2 and Pd- TiO_2 particles were performed with the typical survey and high-resolution spectra shown in Figure 3. The $\text{Ti}2\text{p}_{1/2}$ and $\text{Ti}2\text{p}_{3/2}$ spin-orbital splitting photoelectrons for anatase TiO_2 were located at binding energies of 464.20 and 458.56 eV, respectively, and were assigned to the presence of typical Ti^{4+} . In Pd- TiO_2 , the bands were broad, and shifted slightly to a higher binding energy, which was assigned to Ti^{3+} . The differences (Δ) in binding energies between $\text{Ti}2\text{p}_{3/2}$ and $\text{Ti}2\text{p}_{1/2}$ were distributed over the range of 5.65–5.80, and this value was the highest in the 0.1 mol% Pd- TiO_2 sample (5.80). The measured FWHM

of the $\text{Ti}2\text{p}_{3/2}$ peak was larger in the Pd- TiO_2 than in pure TiO_2 . In general, a larger FWHM suggests a larger amount of less-oxidized metals.¹⁵ This suggests that the oxidation state of Ti ions was reduced when palladium ions were added, thereby effecting photocatalysis. The bond between Ti^{3+} and O may be weaker than the bond between Ti^{4+} and O. In this case, electron transfer from oxygen to titanium would occur readily, which would improve photocatalysis. The O1s region was decomposed into two contributions: metal (Ti^{4+} or Ti^{3+})-O (529.7 eV) in the metal oxide and metal-OH (531.2 eV). The ratios of metal-OH/metal-O in the O1s peaks were similar

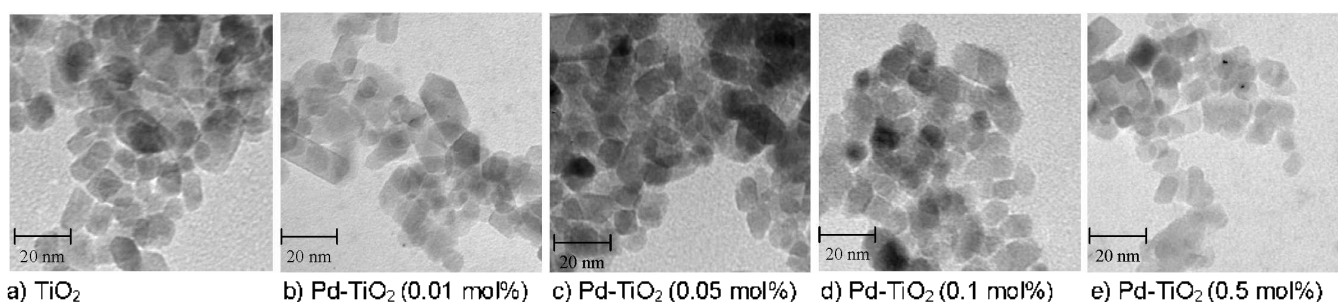


Figure 2. TEM images of TiO_2 and Pd- TiO_2 as-synthesized: a) TiO_2 , b) 0.01 mol% Pd- TiO_2 , c) 0.05 mol% Pd- TiO_2 , d) 0.1 mol% Pd- TiO_2 , and e) 0.5 mol% Pd- TiO_2 .

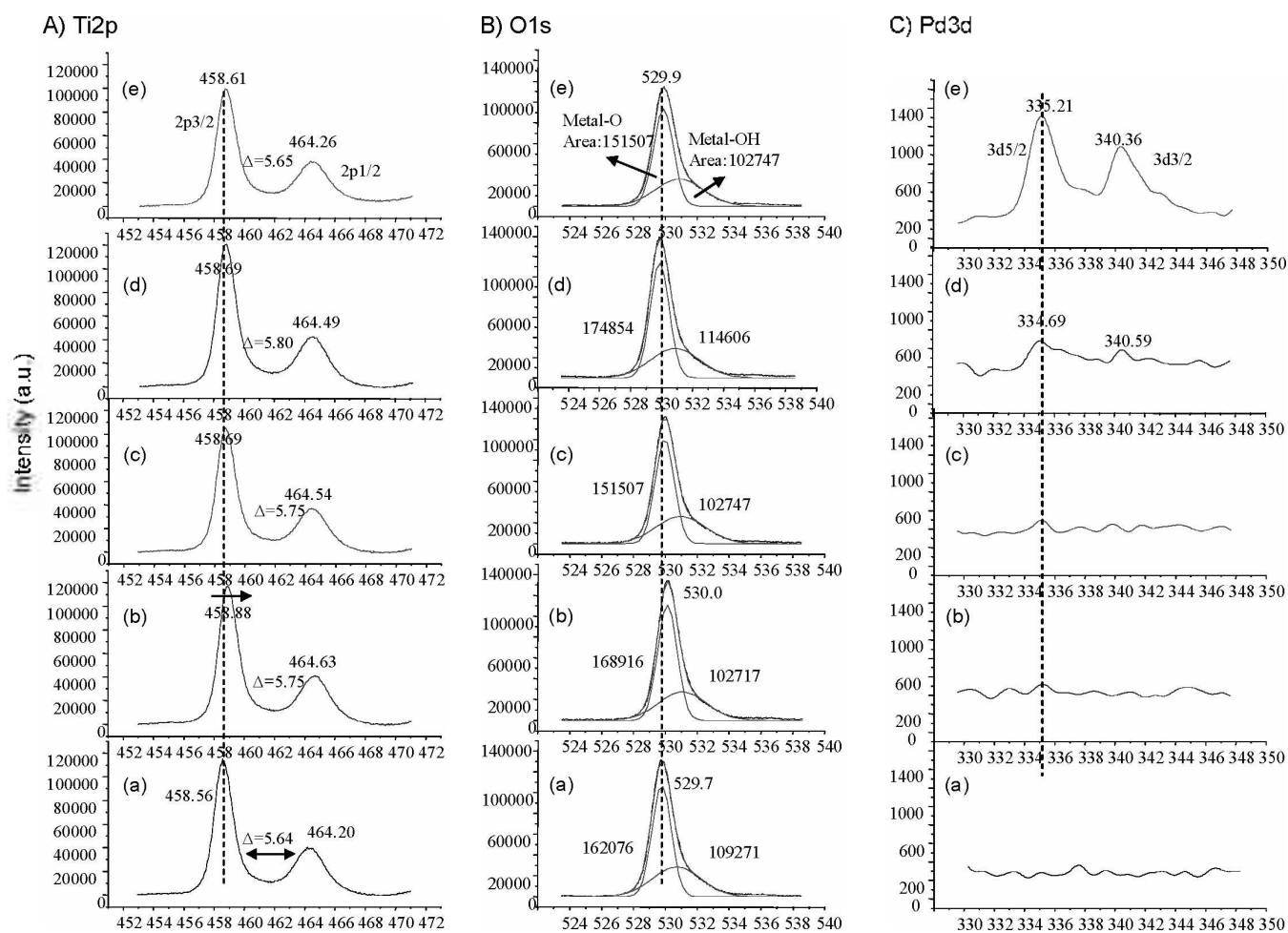


Figure 3. XPS of TiO_2 and Pd- TiO_2 as-synthesized: A) for $\text{Ti}2\text{p}$, B) for O1s, and C) for Pd3d: a) TiO_2 , b) 0.01 mol% Pd- TiO_2 , c) 0.05 mol% Pd- TiO_2 , d) 0.1 mol% Pd- TiO_2 , and e) 0.5 mol% Pd- TiO_2 .

except for the 0.01 mol% Pd-TiO₂ sample. In general, a higher metal-OH peak indicates greater hydrophilicity. The Pd3d_{5/2} and Pd3d_{3/2} spin-orbital splitting photoelectrons for anatase Pd-TiO₂ were located at binding energies of 335.21 and 340.36 eV, respectively in 0.1 and 0.5 mol% Pd-TiO₂. These bands were assigned to Pd.¹⁶ The differences (δ) in binding energies between Pd3d_{5/2} and Pd3d_{3/2} were approximately 5.15.

Figure 4(A) and B) show the UV-visible and photoluminescence (PL) spectra of the TiO₂ and 0.01, 0.05, 0.1, and 0.5 mol% Pd-TiO₂ powders. In A), the absorption for the tetrahedral symmetry of Ti⁴⁺ normally appears at approximately 360 nm. In the spectra for the Pd-TiO₂, the absorption bands were similar to that of pure TiO₂. Generally, the band gap in a semiconductor material is closely related to the wavelength range absorbed where the band gap decreases with increasing absorption wavelength. However, it is believed that the addition of palladium does not alter the band gap energy of TiO₂ significantly. Figure 4B) shows the photoluminescence (PL) spectra of pure TiO₂ and Pd-TiO₂. The PL curve indicates that the electrons in the valence band transferred to the conduction band, and the excited electrons were stabilized by photoemission. In general, the PL intensity increases and the photo activity decreases if there is an increase in the number of emitted electrons resulting from recombination between

excited electrons and holes. Therefore, there is a strong relationship between the PL intensity and photo activity. In particular, the PL intensity decreases significantly when a metal that can capture excited electrons or exhibit conductivity is present. The PL curve of Pd-TiO₂ was shifted to a lower wavelength than that of pure anatase (580 nm) with an emission at 520-540 nm. The PL intensity of the 0.1 and 0.5 mol% Pd-TiO₂ sample was the smallest. This is most likely due to palladium atoms playing the role of electron capturers, which depress the recombination process. Consequently, higher photo catalytic activities are expected.

Figure 5 summarizes the effect of the Pd concentration on the evolution of H₂ from methanol/water photo splitting over TiO₂ and Pd-TiO₂ photo catalysts (B) in a batch-type liquid photo system (A). The photo splitting of methanol/water was carried out using a liquid photo reactor designed at our laboratory.¹⁰ For water photo splitting, 0.5 g of the powdered TiO₂ and Pd-TiO₂ photo catalysts were added to 1.0-L of distilled water in a 2.0-L Pyrex reactor. UV-lamps ($6 \times 3 \text{ W cm}^{-2} = 18 \text{ W cm}^{-2}$, 30 cm length \times 2.0 cm diameter; Shinan, Sunchun, Korea), emitting radiation at 365 nm, were used. Water photo splitting was carried out for 28 h, with constant stirring. Hydrogen evolution was measured after 1 h. The hydrogen gas (H₂) produced during water photo splitting was analyzed

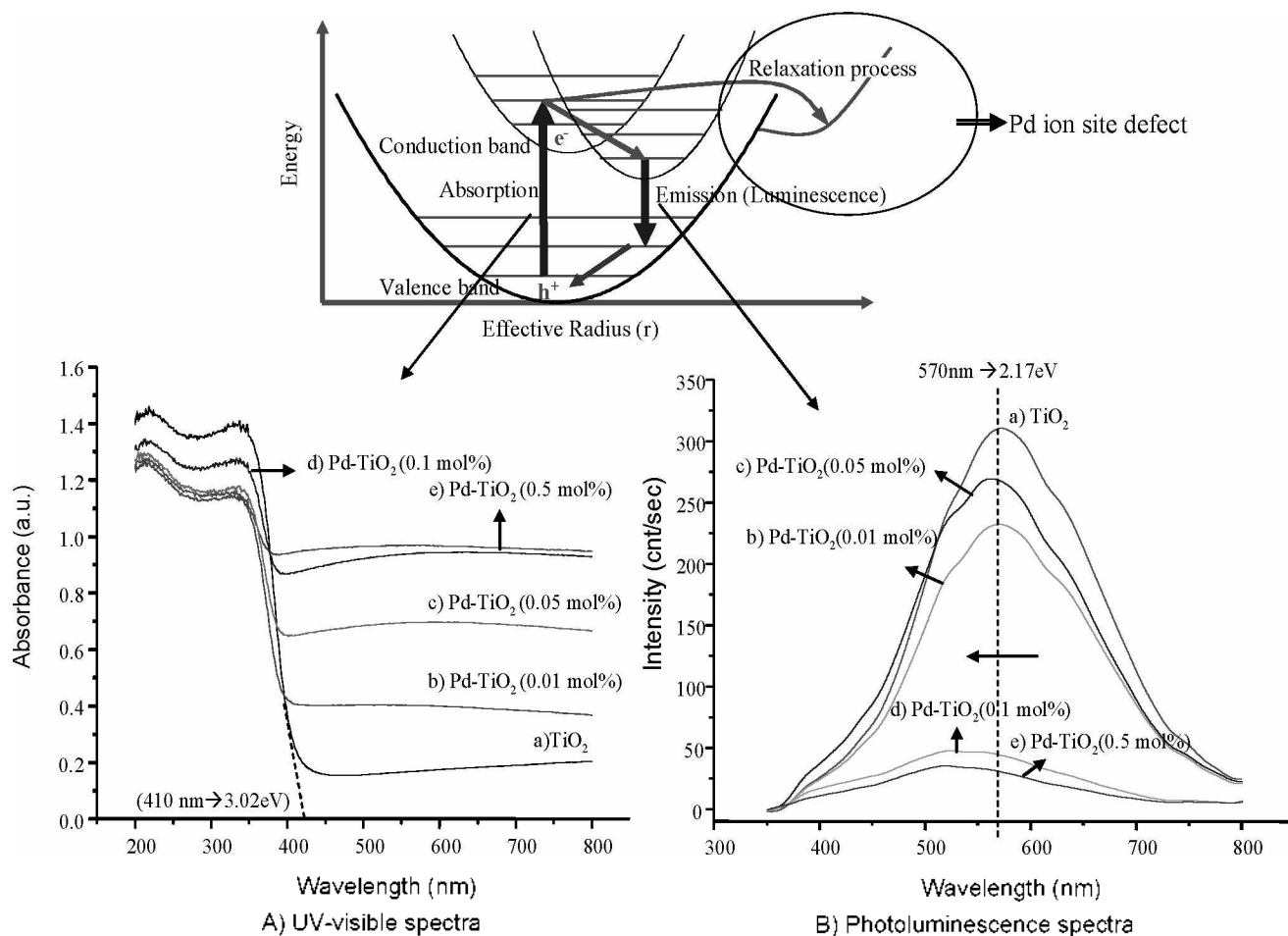
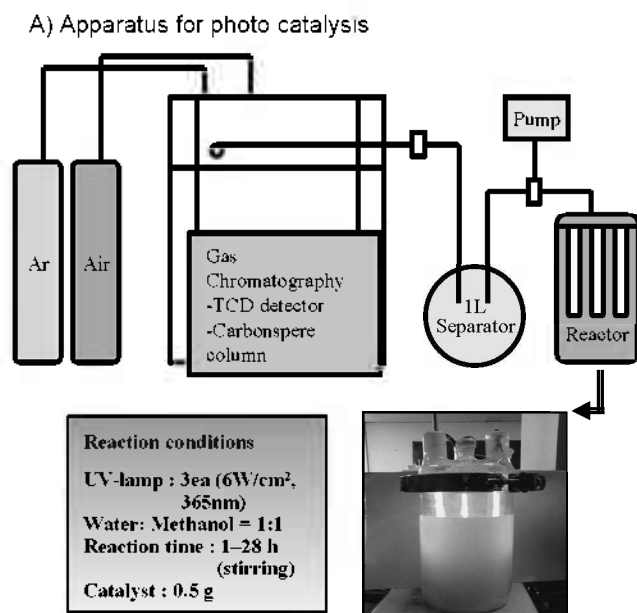


Figure 4. UV-visible and PL spectra of TiO₂ and Pd-TiO₂ as-synthesized: A) UV-visible spectra and B) PL spectra; a) TiO₂, b) 0.01 mol% Pd-TiO₂, c) 0.05 mol% Pd-TiO₂, d) 0.1 mol% Pd-TiO₂, and e) 0.5 mol% Pd-TiO₂.



B) The effect of Pd concentration

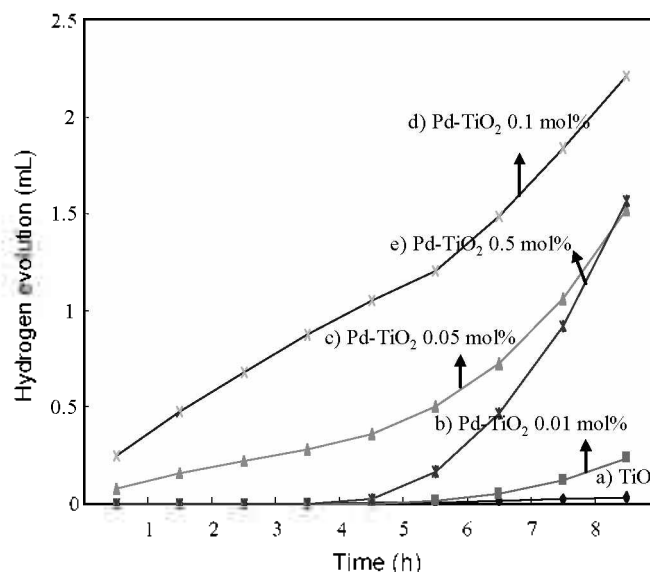


Figure 5. Apparatus for photo catalysis and the H₂ evolution from water photo splitting over TiO₂ and Pd-TiO₂: A) the effect of the Pd concentration and B) the hydrogen production as a function of the reaction time over Pd 0.1 mol% -TiO₂: a) TiO₂, b) 0.01 mol% Pd-TiO₂, c) 0.05 mol% Pd-TiO₂, d) 0.1 mol% Pd-TiO₂, and e) 0.5 mol% Pd-TiO₂.

using a TCD-type gas chromatograph (GC, model DS 6200; Donam Instruments Inc., Gyeonggi-do, Korea). To determine the products and intermediates, the GC was connected directly to the water decomposition reactor. The following GC conditions were used: TCD detector; Carbonspere column (Alltech, Deerfield, IL, USA); 413 K injection temp.; 393 K initial temp.; 393 K final temp.; 423 K detector temp. in Figure B). No H₂ was collected over pure anatase, and 0.1 mol% Pd-TiO₂ after methanol/water photodecomposition for 6 h, while a significant amount of H₂ gas was collected over the other Pd-TiO₂. The amount of H₂ produced reached 2.2 mL over 0.5 g of the 0.1 mol% Pd-TiO₂. However, the amount produced was lower on the 0.5 mol% Pd-TiO₂ catalysts and catalysts with higher palladium loadings. The optimum palladium concentration was found to be 0.1 mol%. This was attributed to the 0.1 mol% Pd-TiO₂ catalyst having less oxidized titanium and a reduced amount of recombination between excited electrons and holes. There are some reasons to express the best performance in 0.1 mol% Pd addition; the defects in semiconductor materials are generally a better effect, and the defect (Pd ion) in the TiO₂ have introduced elements which facilitate the movement of electron and holes, and capturing the transferred electrons from valence band. Especially if the impurity is to easily capture the electron, the recombination between electrons and holes will be reduced. Additionally, the titanium and oxygen combines loosely in TiO₂ because titanium oxidation state, where less than 4 oxidation state (Ti³⁺ as expected) by Pd ion substitution in the skeleton TiO₂ as already described in the XPS results, resulted in the electron movement to the oxygen from the titanium facilitate, therefore electrons and holes makes it easy to create. Furthermore, as noted in the results of PL spectra, the photoluminescence can reduce peak much in a lot added Pd, especially the small peak appears in the Pd addition of 0.1

mol% and 0.5 mol%. On the other hand, the Pd amount is more than 0.5 mol%, the peak broadening phenomenon shows in a UV-visible light absorption owing to the scattering phenomena. The TiO₂ difficult to accept the external light resulted in also less per unit amount suitable TiO₂ actually represents active photocatalyst and the amount of TiO₂ less so the end is that the photocatalytic performance has dropped.

In order to determine the electron capture effect of Pd ion, methanol/water photo splitting were also carried out over 0.1 mol% Pd impregnated TiO₂ and the result were compared with those over the 0.1 mol% Pd-TiO₂ catalyst, as shown in Figure 6. The amount of H₂ evolution reached 14.5 mL after 28 h without catalytic deactivation over the 0.1 mol% Pd-TiO₂. On the other hand, more than 17.5 mL was evolved over 0.1

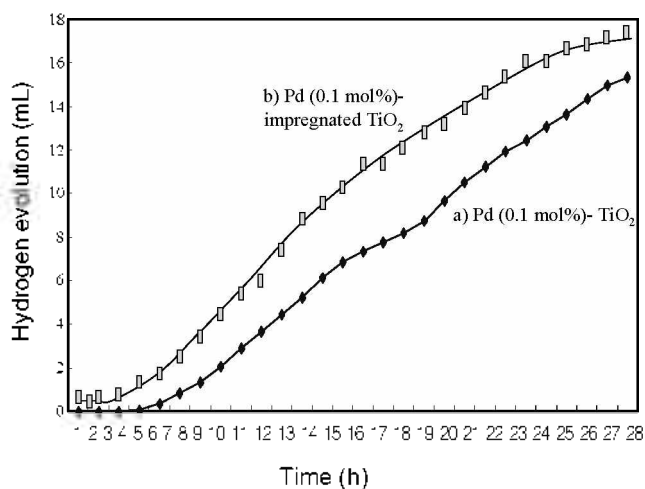
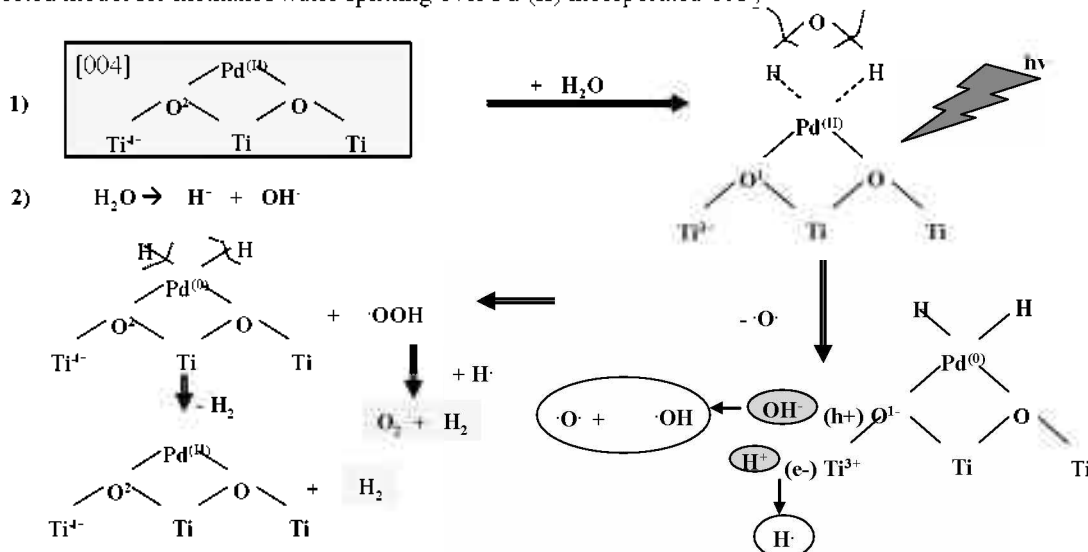


Figure 6. Hydrogen production from methanol/water photo splitting as a function of the reaction time over the Pd 0.1 mol% incorporated TiO₂ and Pd 0.1 mol%-impregnated TiO₂.

A) Expected model for methanol/water splitting over Pd (II) incorporated TiO₂



B) Expected model of band gap when Pd (II) exist on the external surface of TiO₂

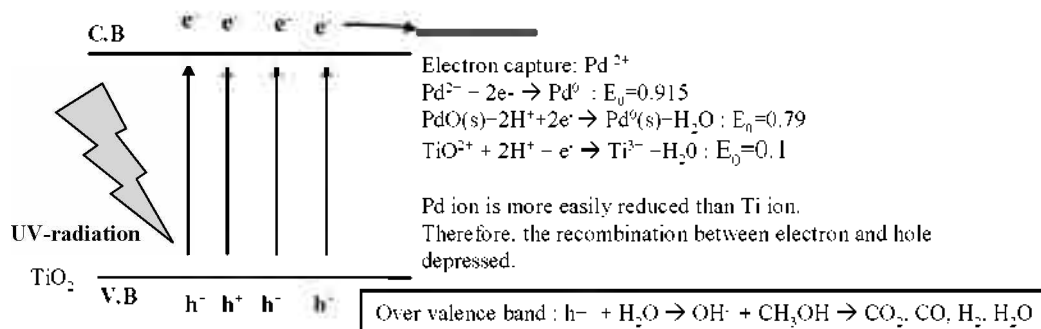


Figure 7. Proposed models for methanol/water splitting over PdO incorporated TiO₂ and the band gap when PdO exists on the external surface of TiO₂.

mol% Pd-impregnated TiO₂ for the same time period. As described in Figure 5, we have confirmed that the catalytic activity in Pd-TiO₂ was enhanced compared to it of the pure TiO₂. Furthermore we here found out a better result in Pd-impregnated TiO₂. This suggests that Pd ions capture the excited electrons from the valence band, which depresses recombination between the excited electrons and holes; the Pd-TiO₂ has the strong ability of the oxidation-reduction than the pure TiO₂, as exposed on the surface of the Pd ion on TiO₂, resulted from the its reduction potential of Pd have a value greater than the Ti. And so the Pd(II) ion is to trap the electrons transferred from valence band of TiO₂. Therefore, the relaxation of excited electrons difficult, resulted in the recombination between holes and electrons reduces, and it goes on in the end the photocatalytic performance will increase. Therefore, when the Pd ion impregnated to TiO₂, the performance this case than in the inserted sample is excellent.

Conclusions

Figure 7 shows a proposed model to explain the effect of Pd in the [004] plane of the anatase structure on H₂ production from the water photo splitting. If a Pd ion with two oxidation

states exists in the framework, it easily attracts water molecules. The water molecules are broken by UV-radiation, which simultaneously reduces the two oxidation states of Pd to a zero, and generates oxygen radicals. On the other hand, the electrons and holes generated on the valence and conduction bands on TiO₂, produce OH and H radicals, respectively. The OH radicals are transferred to OOH radicals by a reaction with oxygen radicals, and the hydrogen and oxygen gases evolve by a reaction between OOH and H radicals. Finally the palladium zero oxidation state is recovered to the +2 oxidation state by the decomposition of hydrogen gas. On the other hand, if PdO exists on the external surface of TiO₂, it will be reduced to Pd⁰ by attracting the electrons excited from the valence band of TiO₂. The reduction of Pd²⁺ to Pd⁰ is possible because the reduction potential of PdO ($E_0 = 0.915$) is greater than that of pure TiO₂. Consequently, the recombination of an electron and a hole is difficult because PdO captures electrons, which increases the number of holes over the valence band, thereby allowing methanol decomposition to continue.

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