Hydrogen production from formic acid solution by modified TiO₂ and titanate nanotubes in a two-step system under visible light irradiation
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ABSTRACT
Hydrogen gas is one of the most promising renewable energy sources, and the final product of hydrogen combustion is nothing but water. However, it is still a big challenge to produce hydrogen and store it. Many studies have been conducted into produce hydrogen from water using photocatalysts. Z-scheme photocatalysis is a two-photocatalyst system that comprises a hydrogen catalyst and an oxygen catalyst to produce hydrogen and oxygen respectively. Compared to the one-step system, the two-step system can promote the efficiency of water splitting. In addition, formic acid (FA) is a convenient hydrogen-storage material and can be safely handled in aqueous solutions. Therefore, this study investigated the photocatalytic conversion of FA solution to hydrogen using visible light with several types of hydrogen catalysts (CdS/titanate nanotubes (TNTs), CdS/TiO₂, Pt/CdS/TNTs) and WO₃ as the oxygen catalyst. The results showed that the yield of hydrogen with CdS/TNTs + WO₃ was much higher than with CdS/TiO₂ + WO₃. Moreover, coating the photocatalysts with metal could further promote the reaction. The optimal platinum loading was 0.01 wt%, and the hydrogen production achieved was 852.5 μmol · h⁻¹ with 20 vol% FA solution.

Key words | cadmium sulfide, formic acid, hydrogen, titanate nanotubes, tungsten trioxide, Z-scheme

INTRODUCTION
Hydrogen gas is a powerful energy transfer medium, which is able to overcome the disadvantages of using conventional fossil fuels as it has high heat conversion efficiency and zero carbon emissions (Navarro et al., 2007). Global hydrogen production is estimated to grow by a compound annual growth rate of 5.6% during 2011–2016 and the hydrogen market is expected to grow in the future (Hay et al., 2013). Since the first report on photocatalytic water splitting using TiO₂ photoelectrodes by Fujishima & Honda (1972) was published, photocatalytic generation of hydrogen from water has received significant research attention. Water and light are abundant in nature and are considered to be a cheap feedstock for hydrogen production. However, the splitting of water into hydrogen and oxygen is a process which requires the input of energy. Researchers have tried to find other energy-saving ways to split water. One such method is light-induced photo-oxidation of water using a semiconductor catalyst, as has been studied recently (Smith et al., 2012). Synthesizing visible-light-driven photocatalysts is a new trend in research because 43% of the solar spectrum is visible light. TiO₂ is relatively nontoxic and cheaper than other semiconductors, and it can absorb UV light energy. TiO₂ combined with other semiconductors, such as CdS, SnO₂, WO₃, Bi₂S₃, Cu₂O and CdSe (Robert, 2007), or active metals, like platinum (Dimitroula et al., 2012), are effective ways to shift its absorbent region to the visible light region and limit the charge recombination phenomena. Compared to TiO₂, titanate nanotubes (TNTs) have a higher surface area, so they can be used as the main carrier to incorporate other semiconductors and metals to increase hydrogen generation efficiency. Thus, microwave-induced TNTs (Ou et al., 2007b) were used in this study.

Recently, tremendous efforts have been focused on the photocatalytic generation of hydrogen gas from solutions containing organic solvents such as methanol (Galinska & Walendziewski, 2005), formic acid (FA) (Enthaler et al., 2010) and alcohol (Johnson et al., 2010). Therefore, hydrogen generation from organic matter using visible-light-responsive
photocatalysts may be one of the most promising and reasonable approaches.

On the other hand, the successful two-step water-splitting systems, called Z-schemes, in which two different photocatalysts are combined using a proper shuttle redox mediator, have been reported (Sayama et al. 2002). In these systems, a wider range of visible light can be utilized because the energy required to drive each photocatalyst is reduced. WO3 is an excellent photocatalyst for water oxidation (oxygen evolution), as was demonstrated by Butler et al. (1976), and no spontaneous hydrogen formation was observed because of its lower conduction band location with respect to the H+/H2 redox level (Alexander et al. 2008). Therefore, WO3 is a suitable candidate as an oxygen evolution photocatalyst for a Z-scheme water-splitting system. In this study, we incorporated CdS particles onto the TNT surface by a hydrothermal process, after which platinum was coated onto CdS/TNTs by the electroless plating method. Modified CdS/TNTs were prepared as a photocatalyst for hydrogen evolution and WO3 as a photocatalyst for oxygen evolution in a Z-scheme water-splitting system. The surface properties of the photocatalysts were investigated by transmission electron microscope (TEM), X-ray diffraction (XRD), UV-Vis. Photocatalytic hydrogen evolution experiments were carried out in FA solution, and the gas products were analyzed by gas chromatograph with thermal conductivity detector (GC-TCD). In this study, we aimed to synthesizing visible-light-driven photocatalysts for the purpose of enhancing hydrogen gas production efficiency.

**MATERIAL AND METHODS**

**Materials**

Commercial TiO2 P25 (>99.5% purity) was purchased from Evonik Industries AG (Germany) and used as the raw material for TNT synthesis and reference support. It is a mixture of 80% anatase and 20% rutile, with a BET surface area of 50 m² g⁻¹ and an average particle size of 30 nm, according to the manufacturer’s specifications. NaOH (>99.5% purity) was purchased from Nihon Shiyaku, Japan. HCOOH (98-100% purity), HCl (35% purity) and H2PtCl6 (98% purity) were purchased from Nacalai Tesque, Inc., Japan. Cd(NO3)2 (99% purity) was purchased from Ferak, Germany. Na2S (98% purity) was purchased from Sigma-Aldrich, Germany. WO3 (99.8% purity) was purchased from Alfa Aesar, England. C2H5OH (95% purity) was purchased from Taiwan Tobacco & Liquor Corporation, Taiwan. NaBH4 (98.5% purity) was purchased from Showa, Japan. All reagents were used without further purification. Deionized water was produced by a Milli-Q system.

**Preparation of microwaved hydrothermal TNTs**

The TNT synthesis method was followed according to Ou et al. (2007b). Briefly, 0.6 g TiO2 P25 was mixed homogeneously in 70 mL, 10 N NaOH for 40 min. Then the mixture was transferred to a microwave digestion system (Ethos touch control, Milestone Corporation) under 400 W microwave irradiation at 405 K for 3 hours. The resulting precipitate was rinsed with 0.5 N HCl three times then deionized water four times. After centrifuging the resulting solution, TNTs were subsequently dried using a vacuum freeze dryer for a minimum of 12 hours (−58.8°C and 100–200 mTorr).

**Preparation of Cds/TNT composite photocatalysts**

Cds-modified TNTs were prepared by the hydrothermal process. The 0.7 g preserved TNTs was mixed with 2 x 10⁻² M Cd(NO3)2(aq) in 40 mL aqueous solution for 24 hours. Then, 40 mL of 2 x 10⁻² M Na2S(aq) was slowly dripped into the solution in order to synthesize fine particles onto the TNTs. Afterwards, the aqueous solution was transferred into a stainless steel autoclave and held at 180°C for another 24 hours. The resulting powders were centrifuged and dried using a vacuum freeze dryer for a minimum of 12 hours (−58.8°C and 100–200 mTorr).

**Preparation of Pt/Cds/TNT composite photocatalysts using electroless plating**

First, 0.25 g CdS/TNTs was suspended in 30 mL alcohol solution along with the selected percentage (0.005, 0.01, 0.05, 0.1, 0.5 wt%) of platinum and stirred for 1 hour. Then, an alcohol solution dissolved with a stoichiometric amount of NaBH4 was added to the suspension. The suspension was centrifuged and dried using a vacuum freeze dryer for a minimum of 2 hours (−58.8°C and 100–200 mTorr).

**Characterization**

The particle size and structural characteristics were examined by TEM (Hitachi, H-7100, Japan). Phase identifications of the catalysts were conducted by XRD equipped with Cu Kα1 radiation (MAC Science MXP 18, Japan) operating under a voltage of 40 kV and a current of 30 mA. The patterns were recorded from 5° to 65° with a scan rate of 2° min⁻¹. The light absorption band edge of the solid catalysts was recorded by
UV-Vis spectrophotometer equipped with an optics integrating sphere and a diffuse reflectance accessory (Cary 100nc, USA).

**Photocatalyst releasing hydrogen from FA solution**

Before the photocatalytic reaction, 200 mL of FA solution (1, 5, 10, 20, 50, 100 vol%) was de-aerated thoroughly for 30 min by nitrogen gas purging. Then, 0.2 g hydrogen catalyst (CdS/TNTs, CdS/TiO2 or Pt/CdS/TNTs) and 0.2 g oxygen catalyst (WO3) were added to the FA solution contained in all-quartz bottles (volume: 225 mL). The suspension was irradiated under a 150 W visible light source (CDM-TD/942, λ > 420 nm, 150 W, Philips, Belgium) outside the bottle. During irradiation, a magnetic stirrer was placed at the bottom of the bottle to ensure the homogeneity of the suspension during reaction. Furthermore, to maintain a constant reactor temperature of 25°C, the bottle and lamp (covered with a quartz tube) were in a water bath which was cooled by recycled water. At the given time (0, 0.5, 1, 2, 3 hours), 1 mL of gas produced via the photocatalytic reaction was extracted with the GC syringe needle and analyzed immediately by GC-TCD (China chromatography GC1000 TCD, Molecular sieve 5A). The GC-TCD was carried out using argon as the carrier gas, at a flow rate of 20 mL/min. The temperature of the injector, oven and detector were set at 60°C.

**RESULTS AND DISCUSSION**

**Characteristics of the photocatalysts**

The TEM micrographs of pure TNTs and CdS/TNT composite are shown in Figure 1. Figure 1(a) shows needle-shaped TNTs. Hydrothermally synthesized CdS particles can have cubic or hexagonal crystal structures (Jang et al. 2006). From Figure 1(b), it can be seen that there were some synthesized CdS particles attached to the surface of TNTs or trapped inside the tube structure.

Figure 2 shows XRD patterns of the photocatalysts. Peaks marked ‘A’ and ‘R’ in Figure 2 correspond to the anatase and rutile phases of titanate respectively. In Figure 2(a), the degrees of CdS diffraction peaks were in agreement with results reported by Jang et al. 2006 and Li et al. 2010. The most distinct diffraction peaks of CdS separately show up in the composite of CdS/TNTs, although not very strongly. There were no diffraction peaks corresponding to anatase or rutile on the XRD pattern of CdS/TNTs. This is consistent with the results demonstrated in previous studies (Seo et al. 2008; Tsai & Teng 2008).

The XRD patterns of different platinum ratios coated onto CdS/TNTs are shown in Figure 2(b). The morphologies of Pt/CdS/TNTs are similar to CdS/TNTs in spite of different platinum ratios. Neither 0.5 wt%Pt/CdS/TNTs nor 0.005 wt%Pt/CdS/TNTs presented obvious changes in XRD spectra. This result can presumably be ascribed to the combinations of low amounts of platinum coating, small particle size, and homogeneous distribution.

The UV-Vis spectra are showed in Figure 3. The main absorbance ranges of TiO2 and TNTs were in the UV light region. However, CdS/TNTs greatly shifted its absorbance to the visible light region, which allowed the photocatalyst to react under visible light. Furthermore, coating platinum onto the CdS/TNT composite also had the ability to shift the absorbance region. The absorption of visible light by metallized samples has been ascribed to low energy transitions between the valence band of TiO2 and localized...
energy levels introduced into the band gap region by noble metal deposits (Zhang et al. 2011). As platinum can delay the charge recombination and can trap electrons in the conduction band, Pt/CdS/TNTs also demonstrates good absorption capacity in the visible spectrum region (Meng et al. 2011). There is no difference between the 0.01 wt%Pt/CdS/TNTs and CdS/TNTs because of low platinum loading. The shift towards the visible region is due to CdS alone.

**Photocatalytic hydrogen production**

The cumulative hydrogen production of TiO$_2$, TNTs, CdS/TiO$_2$, CdS/TiO$_2$ + WO$_3$, CdS/TNTs and CdS/TNTs + WO$_3$ with 10 vol% FA are shown in Figure 4. After visible light illumination for 3 hours, hydrogen production with CdS/TNTs was 179.4 μmol, which is higher than with CdS/TiO$_2$. Under the same conditions, hydrogen production with TNTs was just 0.09 μmol. This could be due to excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor (Linsebigler et al. 1995). The band gap of CdS is 2.4 eV and both the upper edge of the valence band and the lower edge of the conduction band of CdS are higher than those of TNTs. Thus, CdS can be excited by illumination with visible light and the photogenerated electron can be transferred from CdS to TNTs (Li et al. 2010). According to the observed results, it was believed that it is effective to separate electrons and holes to avoid recombination and raise the hydrogen production rate.

The hydrogen production rate with 10 vol% FA solution over CdS/TiO$_2$ + WO$_3$ (the two-step system) was 30.2 μmol·h$^{-1}$, which is about nine times higher than that with CdS/TiO$_2$ (the one-step system). It is obvious that the hydrogen production in the two-step system is higher than the one-step system, because the two-step system could promote the efficiency of water splitting (Sayama et al. 2002). Due to the high specific area of TNTs, more CdS could be attached onto the TNT surfaces, and the hydrogen production rate with CdS/TNTs + WO$_3$ was 115.5 μmol·h$^{-1}$, which is about four times higher than that with CdS/TiO$_2$ + WO$_3$. 

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**Figure 2** | XRD patterns of (a) CdS/TNT and (b) Pt/CdS/TNT composite.

**Figure 3** | UV-Vis spectra of photocatalysts.

**Figure 4** | Hydrogen productions of one step system and two step system in 10 vol% FA.
Effect of FA concentration

The hydrogen production of 0.2 g CdS/TNTs + 0.2 g WO3 in different concentrations of FA are shown in Figure 5. These results suggest that FA was as a good proton capturer and 20 vol% was the best concentration for hydrogen production. The hydrogen production rate with CdS/TNTs + WO3 in 20 vol% was 247.8 $\mu$mol·h$^{-1}$, which is about twice that in 10 vol%. Because no hydrogen gas can be observed in pure water, it suggested that FA is used as an electron donor to trap the holes, and separate electrons and holes to avoid recombination and raise hydrogen production as shown in Equations (1) and (2) (Zhang & Zhang 2009).

\[ \text{HCOOH} + 2h^+ \rightarrow \text{CO}_2 + 2H^+ \]  
\[ 2H^+ + 2e^- \rightarrow \text{H}_2 \]  

However, hydrogen gas was rarely produced in the photocatalytic reaction with 100 vol% FA. Halasi et al. (2002) reported that addition of water to FA markedly diminished the production of CO gas. Therefore, FA decomposed into CO and H$_2$O, not CO$_2$ and H$_2$ in pure FA, so the hydrogen production was extremely low.

Hydrogen production with platinum coating

Platinum was coated onto CdS/TNTs by electroless plating to enhance their activity, and hydrogen production with 20 vol% FA is shown in Figure 6. From experimental results, 0.01 wt%Pt/CdS/TNTs shows the highest hydrogen production, 852.5 $\mu$mol·h$^{-1}$ under visible light, which is about 3.4 times higher than with CdS/TNTs + WO3. Platinum acted as an electron trap which seized photogenerated electrons and subsequently transferred them to H$^+$ ions so that the activity of hydrogen evolution could be enhanced. Li & Li (2002) coated platinum onto TiO$_2$ and successfully enhanced the activity of photocatalysts and increased the separation period of electrons and holes. However, the overload of platinum accumulated on CdS/TNTs and resulted in an inhibitory effect on hydrogen production (Ou et al. 2007a). Equations (3) to (6) are platinum forms which reacted in FA solution (Rice et al. 2005).

\[ \text{HCOOH} + \text{Pt}^0 \rightarrow \text{Pt} - \text{CO} + \text{H}_2\text{O} \]  
\[ \text{Pt}^0 + \text{H}_2\text{O} \rightarrow \text{Pt} - \text{OH} + \text{H}^+ + e^- \]  
\[ \text{Pt}^0 - \text{CO} + \text{Pt} - \text{OH} \rightarrow 2\text{Pt}^0 + \text{CO}_2 + \text{H}^+ + e^- \]  

Overall: \[ \text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \]  

CONCLUSIONS

From the hydrogen gas evolving experiments, CdS/TNT composite was considered a high-potential photocatalyst for producing hydrogen gas from FA solution, and it could be activated under visible light illumination. Coating platinum onto CdS/TNTs could further promote hydrogen production efficiency. In this study, the optimal platinum loading in the case of CdS/TNTs as a hydrogen catalyst was 0.01 wt%. Hydrogen production with 0.2 g CdS/TNTs + 0.2 g WO3 was twice as much as when only 0.2 g CdS/TNTs was used.
Compared to the one-step system, the two-step system could effectively promote hydrogen production, and WO3 is a suitable candidate as an oxygen catalyst for a Z-scheme water-splitting system.

REFERENCES


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First received 5 November 2013; accepted in revised form 28 January 2014. Available online 10 February 2014