Photocatalytic hydrogen production of the CdS/TiO₂-WO₃ ternary hybrid under visible light irradiation
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ABSTRACT
An attractive and effective method for converting solar energy into clean and renewable hydrogen energy is photocatalytic water splitting over semiconductors. The study aimed at utilizing organic sacrificial agents in water, modeled by formic acid, in combination with visible light driven photocatalysts to produce hydrogen with high efficiencies. The photocatalytic hydrogen production of cadmium sulfide (CdS)/titanate nanotubes (TNTs) binary hybrid with specific CdS content was investigated. After visible light irradiation for 3 h, the hydrogen production rate of 25 wt% CdS/TNT achieved 179.35 μmol·h⁻¹. Thanks to the two-step process, CdS/TNTs-WO₃ ternary hybrid can better promote the efficiency of water splitting compared with CdS/TNTs binary hybrid. The hydrogen production of 25 wt% CdS/TNTs-WO₃ achieved 212.68 μmol·h⁻¹, under the same condition. Coating of platinum metal onto the WO₃ could further promote the reaction. Results showed that 0.2 g 0.1 wt % Pt/WO₃ + 0.2 g 25 wt% CdS/TNTs had the best hydrogen production rate of 428.43 μmol·h⁻¹. The resultant materials were well characterized by high-resolution transmission electron microscope, X-ray diffraction, scanning electron microscopy, and UV-Vis spectra.

Key words | hydrogen, photocatalysis, ternary hybrid, titanium nanotubes

INTRODUCTION
Hydrogen is a renewable energy source and has a high-energy content of 122 kJ/g, which is 2.75 fold greater than traditional fossil fuels (Luo et al. 2011). When it is used as an energy source, it generates nothing but water, which can be recycled to make more hydrogen. An attractive and effective method for converting solar energy into this ideal energy transfer medium is photocatalytic water splitting over semiconductors.

Titanium dioxide (TiO₂) has attracted much attention because of their low cost, non-toxicity, stability, and potential applications in industry and technology (Xu et al. 2012). However, the wide band gap of TiO₂ limits its absorption spectrum in the ultraviolet (UV) region. Many efforts have been focused on coupling TiO₂ with narrow band gap semiconductors, typically cadmium sulfide (CdS) (Bessekhouda et al. 2004; Bai et al. 2011; Park et al. 2011), to form visible-light-response composite photocatalysts. In addition, as semiconductors with band gap energies in the region of 2.0–2.5 eV are photochemically unstable (Daskalaki et al. 2010), CdS is susceptible to photocorrosion. The stability and photoactivity of pure CdS are improved when coupling with stable semiconductors such as TiO₂. In this study, microwave-induced titanate nanotubes (TNTs) (based on TiO₂) were used as the main carrier to incorporate CdS for the reason that it holds higher surface area than TiO₂.

The composite of semiconductors with different band gaps and positions has a built-in potential gradient at the interface, which facilitates the separation of electron and hole pairs and reduces the chance of recombination (Kim et al. 2011). In ternary hybrid system such as CdS-TiO₂-WO₃, electron will transfer from CdS (2.4 eV) to TiO₂ (3.2 eV) to WO₃ (2.8 eV) through the potential gradient. Thanks to a two-step process, the lifetime of electron-hole pairs in ternary hybrid is extended further compared with the binary hybrid. The ternary hybrid systems have possesses apparent advantages in solar cell application (Lee & Lo 2009; Kamat et al. 2010) and hydrogen production (Wang et al. 2010; Yeh et al. 2014). More research is urgently needed.

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The study aimed at utilizing organic sacrificial agents in water, modeled by formic acid (FA), in combination with visible light driven photocatalysts to produce hydrogen with high efficiencies. CdS/TiO2-WO3 ternary hybrid was used as photoactive composite. Following, platinum metal was coated onto WO3 to further promote the reaction. Platinum has the ability to trap photogenerated electrons and to catalyze the reduction of water under visible light so that it will have beneficial effect on the rate of hydrogen production.

The resultant materials were well characterized by high-resolution transmission electron microscope, X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray (SEM/EDX), and UV-Vis spectra. The gas products were analyzed by gas chromatography-thermal conductivity detector (GC/TCD).

### MATERIAL AND METHODS

**Synthesis**

**Preparation of TNTs using microwave hydrothermal treatment**

Titanate nanotubes were prepared following a literature procedure (*Ou et al. 2007*). Briefly, a solution of 70 mL of 10 N NaOH (aq) coupled with 0.6 g TiO2 (Degussa P25) was transferred to the Teflon container after stirring homogenously. The prepared samples were treated at 403 K for 3 h under 400 W microwave irradiation using microwave digestion system (Ethos touch control, Milestone Corporation). The resulting powders were then washed by mixing three times with 0.5 N HCl and four times with deionized water. Subsequently, TNTs can be obtained after filtration and drying at about –54 °C overnight.

**Preparation of CdS/TNTs and CdS/TiO2 using conventional hydrothermal treatment**

CdS/TNTs and CdS/TiO2 were prepared by conventional hydrothermal process. 0.7 g preserved TNTs (or TiO2) was mixed with 40 mL Cd(NO3)2 (aq) of desired normal concentration (0.02 M, 0.03 M, 0.04 M, 0.08 M) for 24 h. Then, 40 mL Na2S (aq) of the same normal concentration was slightly dripped into the solution in order to synthesize fine particles onto TNTs. The as synthesized CdS/TNTs were named as CdS/TNTs-2, CdS/TNTs-3, CdS/TNTs-4, CdS/TNTs-8. Afterwards, the aqueous solution was transferred into the stainless steel autoclave and held under 180 °C for 24 h. Subsequently, the compound can be obtained after filtration and drying at about –54 °C overnight.

**Preparation of Pt/WO3 using electroless plating**

0.3 g WO3 was suspended in 20 mL alcohol solution with desired percentage platinum (0.05, 0.1, 0.2, 0.5, 1.0 wt%) followed by stirring for 1 h. Then, 10 mL alcohol solution dissolved with a stoichiometric amount of NaBH4 was added into the suspension. Subsequently, the compound can be obtained after filtration and drying at about –54 °C.

**Characterization**

The surface morphology of the synthesized catalysts was characterized by SEM (JEOL, JSM-6330F, Japan). The particle size and structural properties were examined by transmission electron microscopy (TEM) (Hitachi, H-7100, Japan). Phase identifications of photocatalysts were characterized by XRD (MAC Science MXP 18, Japan) using Cu Kα1 radiation (V = 40 kV and I = 30 mA). The light absorption band was measured by UV-Vis spectrophotometer equipped with an optics integrating sphere and a diffuse reflectance accessory (Cary 100nc, USA).

**Photocatalytic activity**

200 mL 20 vol% FA solution was de-aerated by nitrogen gas purging for 30 minutes. The container was 240 mL quartz made bottle with sealable hole on the top of it. The suspension was irradiated by visible light source (CDM-TD/942, 150 W, 350 < λ < 800 nm, Philips, Belgium). During the irradiation, the solution would be stirred continuously and homogeneously. To maintain a constant reactor of 25 °C, the bottle and lamp (covered by quartz tube) were cooled by recycled water.
At the given duration, 1 mL gas was pulled in the GC syringe needle and analyzed immediately by GC-TCD (China chromatography GC1000TCD, Taiwan). The GC-TCD was carried out under carrier gas, argon in the flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Characterization of the photocatalysts

Figure 2 shows the SEM images of TNTs and CdS/TNTs. Figure 2(a) presents needle-shape titanate tubes. From Figure 2(b), there are some particles attached on the surface of tubes, which indicate that CdS/TNTs were successfully synthesized after hydrothermal treatment.

The TEM images of TNTs and CdS/TNTs composite are shown in Figure 3. A clear tubular structure with the average diameter of 20 nm is observed, supporting the field emission scanning electron microscopy (FESEM) results. The obtained CdS particles are crystals with a diameter of about 50 nm and many of them aggregate together. CdS particles assemble into big particles for decreasing surface energy (Xiang et al. 2011).

Figure 4 shows the UV-Vis absorption spectra of CdS/TNTs. Addition of CdS resulted in the appearance of an additional absorption band in the visible region. The onset of absorption is shifted toward lower wavelengths as the decreasing of CdS content.

The XRD patterns of the precursor TiO₂, synthesized CdS, TNTs, CdS/TiO₂, and CdS/TNTs were shown in Figure 5. Peaks marked ‘A’, ‘R’, ‘C’, and ‘T’ correspond to anatase phase, rutile phase, synthesized CdS, and TNTs. The degrees of CdS, TiO₂, TNTs diffraction peaks were in accordance with earlier reported results (Seo et al. 2008; Li et al. 2010). Figure 5(a) shows that CdS particles coexist with TiO₂ particles and the crystalline structure of TiO₂ was not influenced. Figure 5(b) clearly indicates that TiO₂ was completely transformed into TNTs as there were no diffraction peaks corresponding to anatase or rutile on the XRD patterns of TNTs. The intensity of CdS diffraction peaks is stronger in CdS/TNTs than CdS/TiO₂ with same CdS content. The reason may be that TNTs hold a higher surface area. In addition, the intensity progressively increased with increasing the CdS content of CdS/TNTs.
Hydrogen production of photocatalysts

Binary hybrid system

200 mL 20 vol% FA solution without photocatalysts was irradiated under visible light irradiation and almost no hydrogen gas was produced. After visible light illumination for 3 h, little gas was released from solution with TiO₂ or TNTs because they were hardly activated by visible light. When coupling with CdS, the hydrogen production rate of CdS/TNTs-3 achieved 157.76 μmol·h⁻¹, which is five times higher than that of CdS/TiO₂ with the same CdS content. Due to the high specific area of TNTs, more CdS could be attached onto the TNTs. The results in Figure 6 demonstrate the beneficial effects of combining narrow band gap semiconductor, such as CdS, with wide band gap semiconductor, TiO₂ (or TNTs) in this study.

Using TNTs as the main carrier to incorporate CdS, the cumulative hydrogen productions of CdS/TNTs with variable CdS content are shown in Figure 7. After visible light illumination for 3 h, the hydrogen production of pure TNTs and pure CdS will achieve 0.35 μmol·h⁻¹ and 69.79 μmol·h⁻¹, respectively.

Increasing of the CdS content will result in an increasing of the photocatalytic activity. The production rate of CdS/TNTs-4 (containing 25% CdS) achieved 179.35 μmol·h⁻¹. However, excessive CdS will have passive effect on the improvement of photocatalytic efficiency. The production rate of CdS/TNTs-8 (containing 40% CdS) is only 30.71 μmol·h⁻¹. The overloading of CdS might retard the electron transfer through the internal vacancies within the binary structure or just cannot totally combine with TNTs. Moreover, aggregation of CdS particles could create grain boundaries that would trap charge carriers during the charge-transfer process to decrease the photocatalytic reactions (Fang et al. 2013).
Ternary hybrid system

WO\textsubscript{3} was physically mixed with the optimized CdS/TNTs binary hybrid. First of all, we keep the total dose of catalysis in 0.2 g and change the mixing ratio of CdS/TNTs-4 and WO\textsubscript{3} (1:3, 1:1, 3:1). The ratio of 1:1 and 3:1 show the higher activity and we choose the ratio of 1:1 from the environmental point of view. Semiconductors with different energy band and position will generate a built-in potential gradient, which induce better charge separation in CdS/TNTs-WO\textsubscript{3} ternary hybrid.

Then we change the total dose of catalysis with the ratio of 1:1. The highest hydrogen production rate is 212.68 μmol·h\textsuperscript{-1} with the catalysis of 0.2 g CdS/TNT-4 and 0.2 g WO\textsubscript{3}, which is higher than that of binary hybrid. The results are shown in Figure 8. However, when the total dose is further increased, the photocatalytic performance deteriorates. This may be ascribed to the decline of the transmittance in solution because of excessive catalysis.

Effect of co-catalysts

Platinum was coated onto WO\textsubscript{3} by electroless plating to enhance the photocatalytic activity as co-catalysts. Pt/WO\textsubscript{3} and CdS/TNT-4 were physically mixed. Hydrogen evolution rates of CdS/TNTs-Pt/WO\textsubscript{3} with different amount of Pt are shown in Figure 9. From the results, 0.1 wt% Pt/WO\textsubscript{3}-CdS/TNTs shows the highest hydrogen production rate, which is 428.43 μmol·h\textsuperscript{-1}. Due to the difference in the energy band levels of semiconductors and metal, electrons easily transfer from the conduction bands of CdS and TNTs and WO\textsubscript{3}.

After the co-catalyst is introduced, the formation of a Schottky barrier at the interface of metal and semiconductors improves the separation of electron-hole pairs. Pt may act as an electron trap to capture electrons from the electron pathway or from CdS/TNTs because of physically mixing. However, the coated metals do not always have a positive effect on the improvement of photocatalytic efficiency. The hydrogen production rate of 1 wt% Pt/WO\textsubscript{3}-CdS/TNTs is lower than catalysts without coating. The overload of Pt may act as a recombination center instead of providing an electron pathway. Moreover, the excessive Pt can cause a shelter effect resulting in an inhibitory effect (Ou & Lo 2007), a light harvesting competition may happen between the co-catalyst and the ternary hybrid system.

CONCLUSIONS

The ternary hybrid showed significantly enhanced photocatalytic activity in hydrogen production under visible light irradiation. The enhanced activity could be attributed to the electron transfer from CdS to TiO\textsubscript{2} to WO\textsubscript{3} through the interfacial potential gradient in the ternary hybrid, which effectively reduces the chance of charge recombination compared with the binary hybrid. Coating of platinum metal onto the WO\textsubscript{3} could further promote the reaction thanks to the formation of a Schottky barrier at the interface of metal and semiconductors resulting in longer lifetime of electron-hole pairs.

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