

Concurrent photocatalytic hydrogen production and organic degradation by a composite catalyst film in a two chamber photo-reactor

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Abstract

A novel visible light-driven photocatalyst film, MoS₂/Ag/TiO₂, was synthesized on a glass-fiber membrane. The composite catalyst film had a multi-layer structure with Ag as nanoconjunctions between the MoS₂ and TiO₂ layers. The catalyst film performed well for both photocatalytic hydrogen production and organic degradation in a two-chamber photo-reactor under either solar or visible light. Hydrogen was produced in the cathode side chamber while the model organic was decomposed in the anode side chamber. The specific hydrogen production rate went through a maximum of 85 mmol/m²-h with an energy conversion efficiency of 0.85%, while the maximum specific organic carbon removal for formic acid under solar light reached 1520 mg/m²-h. It is apparent that Ag between the TiO₂ and MoS₂ layers allowed the transfer of photo-excited electrons via TiO₂→Ag→MoS₂ for organic degradation and H⁺ reduction (e.g. hydrogen evolution) in two different chambers.

Keywords

Hydrogen production, MoS₂, organic degradation, photocatalyst, solar energy

INTRODUCTION

Hydrogen is one of the most promising clean and renewable energy carriers in future. Photocatalytic hydrogen generation from water is an attractive and environmentally-friendly method to harvest the solar energy (Lee et al., 2007; Maeda et al., 2006). The photocatalytic process also has attracted significant research attentions as a potential energy-saving technology for effective pollution removal in water and wastewater treatment (Balasubramanian et al., 2004; Carp et al., 2004; Chatterjee and Dasgupta, 2005).

In recent years, MoS₂ has been shown as a promising photocatalyst that responds to visible light. MoS₂ possesses a significant advantage over TiO₂ which is a UV-driven photocatalyst, i.e. the band gap of MoS₂ is small enough to allow absorption of visible light. The MoS₂/TiO₂ catalyst powders have shown their effectiveness in degradation of organic chemical pollutants, such as methylene orange (Hu et al., 2010), 4-chlorophenol (Ho et al., 2004) and phenol (Pourabbas and Jamshidi, 2008). Hence, MoS₂-based materials can be used for development of visible light-driven catalyst for both photocatalytic hydrogen generation and organic degradation. In the present study, a composite MoS₂/Ag/TiO₂ photocatalyst film was synthesized with Ag as the nanojunction between the MoS₂ and TiO₂ layers. The photocatalyst film was placed between two chambers in a photo-reactor to achieve hydrogen production together with organic degradation.

MATERIALS AND METHODS

Preparation of MoS₂ nanoparticles

One hundred mL 1.0 mol/L HCl solution was placed in a flask and then the solution was heated at 90 °C with continuous stirring. Then, 0.88 g (NH₄)₆Mo₇O₂₄·4H₂O and 2.64 g Na₂S·9H₂O were added into the flask. After half an hour, 0.7 g NH₂OH·HCl was added with vigorous stirring. The reaction was kept at 90°C for 6 hrs. During the heating process, the deep red color of the precursor turned to the black color of MoS₂ as expected (Tian et al., 2005). The solid precipitates were separated from the solution by centrifugation. The final product was washed several times with DI water to remove residual reactants. The solids were dried in air to obtain the final MoS₂ powder.

Characterization of MoS₂ photocatalyst

The size distribution of the MoS₂ catalyst particles was measured by a laser diffraction particle size analyzer (DelsaTM Nano, Beckman Coulter). The crystalline phases and structural features of MoS₂ were analyzed by an X-ray diffraction (XRD) system (D8 Advance, Burker AXS) with the Cu K α irradiation from 10 to 90 degrees. The morphology of the MoS₂ particles was examined by SEM and TEM.

MoS₂/Ag/TiO₂ film

Glass fiber (GF) membrane was used as the base material for immobilization of the photocatalysts. The membrane was cut into circles (area = 7 cm²), and Nafion was employed to affix the catalyst film on the membrane surface. The MoS₂ nanoparticles (50 mg) were mixed with Nafion solution and applied to the membrane. Ag was then deposited on the MoS₂ surface by *in-situ* photo-deposition. Finally, a Nafion TiO₂ (Degussa, P-25) paste was applied over the MoS₂ layer on the membrane, and the TiO₂ loading ratio varied from 10 to 200% of the amount of MoS₂ layer on the GF membrane.

The performance of different catalyst films were tested in a photo-reactor with two chambers. The photocatalyst film was placed between the two chambers to separate the chambers. A 300W Xe lamp setup (PLS-SXE Xe light source, Trustech) was used as either a visible light source (light intensity ~ 70 mW/cm²) with a cutoff ($\lambda < 420$ nm) filter or a combined UV and visible light source (light intensity ~ 86 mW/cm²) without the cutoff filter. Light irradiation was applied on the TiO₂ side of the catalyst film from the anode side chamber. The anode chamber was filled with 10% formic acid solution as the model organic at pH = 7. The cathode side chamber was filled with water containing 0.4 M Na₂SO₄ at pH=1.0 for hydrogen production. The gas produced during the photo-tests was collected, and the H₂ and CO₂ contents were analyzed by a gas chromatograph (GC HP5890 Series II, Hewlett Packard). The reactivity of the photocatalyst was evaluated in terms of the specific H₂ production rate (R) and the corresponding energy conversion efficiency (η) using the following equations.

$$R_A = \frac{m_{H_2}}{At}, \text{ and} \quad (1)$$

$$\eta = \frac{R_A \Delta H_c}{I} \quad (2)$$

where m_{H_2} is the moles of H₂ production measured, t is the duration of photo-reaction, W is the weight of catalyst in reactor, ΔH_c is the combustion value of H₂ (286 kJ/mol), and A and I is specify the area (7 cm²) and intensity of the light irradiation, respectively.

RESULTS AND DISCUSSION

Characterization of the MoS₂ catalysts

Figure 1 shows the particle size distribution of the MoS₂ catalyst. The catalyst powder ranged in size from 230 to 340 nm with a number based mean size of about 275 nm. The TEM images in Figure 2 further reveal that the photocatalysts are nano-particles with a size of around 80 nm for the primary particles. The MoS₂ catalyst displayed a good crystallization as shown by its XRD pattern (Figure 3).

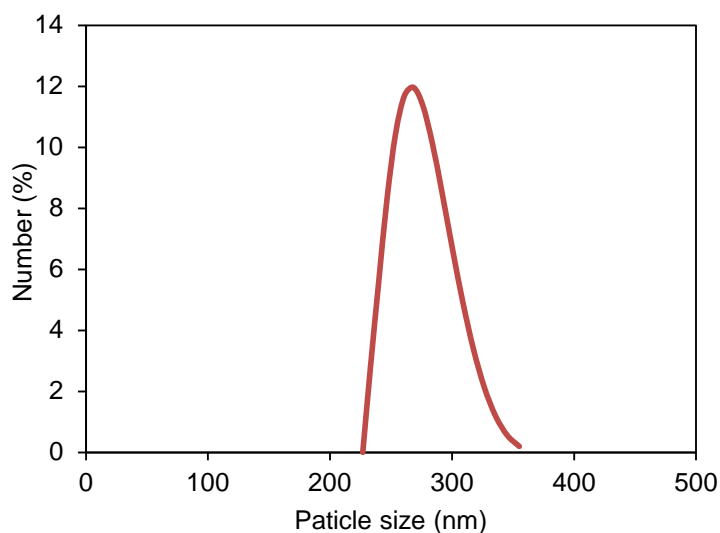


Figure 1. The particle size distribution of MoS₂ catalysts.

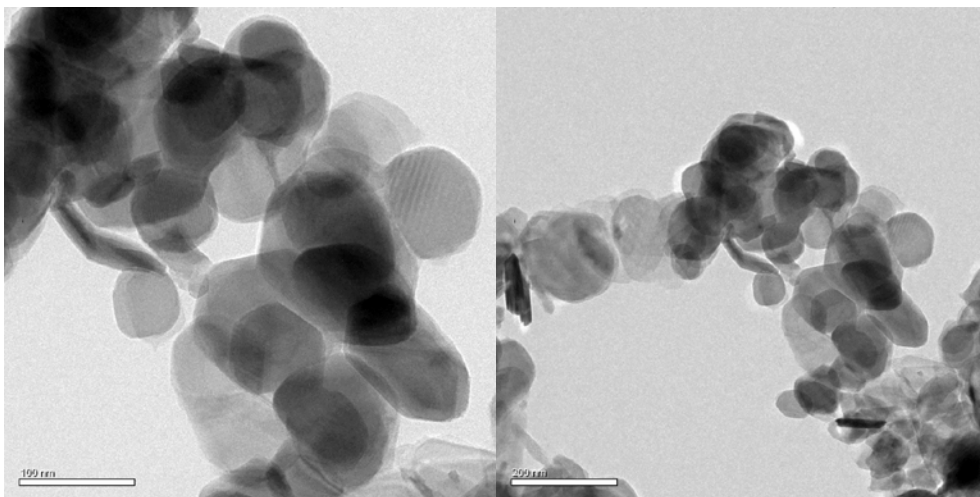


Figure 2. TEM images of MoS₂ nanoparticles.

Figure 4 shows the diffuse reflectance spectrum of the MoS₂ catalyst. Its absorption edge is in the visible light range at about 790 nm, corresponding to a band gap of 1.7 eV. This suggests the visible light-driven feature of MoS₂ for photocatalytic reactions under visible light.

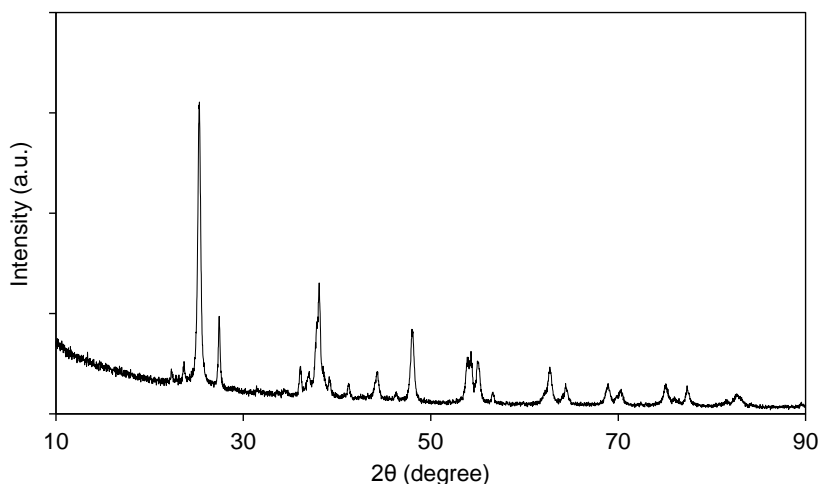


Figure 3. XRD pattern of MoS₂.

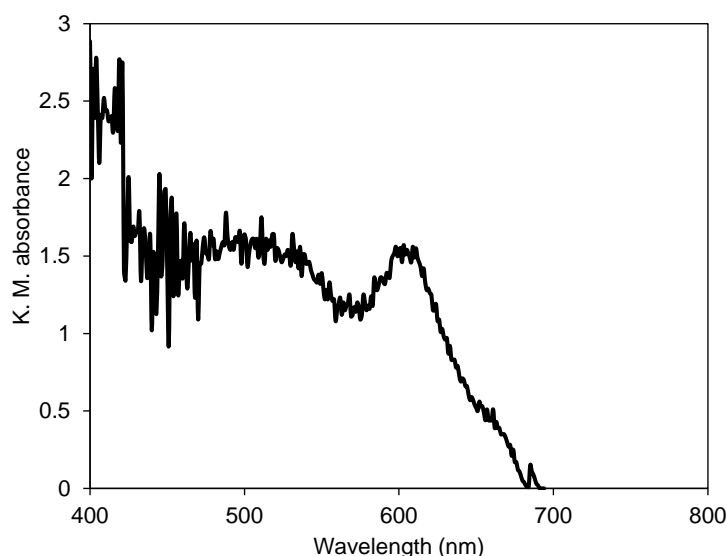


Figure 4. Diffuse reflectance spectrum of the MoS₂ photocatalyst.

MoS₂/Ag/TiO₂ photocatalyst film for hydrogen production

Results of photocatalytic H₂ generation and organic degradation (CO₂ production) obtained with the MoS₂/Ag/TiO₂ film irradiated by the simulated solar light are shown in Figure 5A, where the gas production rates are plotted as a function of the TiO₂ loading ratio.

With 10% formic acid in the anode side chamber, the bare MoS₂ was not capable of photocatalytic hydrogen production. Coating of the outer TiO₂ layer could significantly enhance the photo-reactivity of the MoS₂ catalyst for both H₂ production and organic degradation (Figure 5). As the TiO₂ loading ratio increased to 160% of the MoS₂ layer, the area-based specific H₂ and CO₂ production rates increased to the maximum values of 88 and 85 mmol/m²-h in the respective cathode and anode chambers under solar light (Figure 5A) with an energy conversion efficiency of 0.85% and a quantum yield of 12%. Under only the visible light, similar results for the effect of TiO₂ coating were obtained with somewhat lower specific H₂ and CO₂ production rates (Figure 5B).

Based on the amount of CO₂ production from the anode side chamber, the corresponding specific organic degradation rate in terms of the total organic carbon (TOC) removal was estimated (Figure 6). The maximum specific TOC removal for formic acid under solar light was 1520 mg/m²-h at a TiO₂ load of 160%.

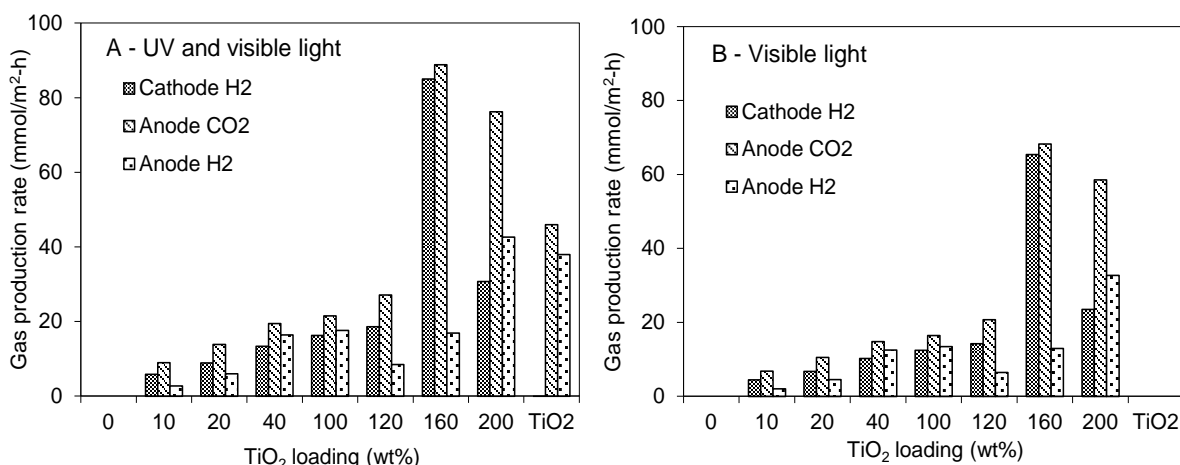


Figure 5. Hydrogen and carbon dioxide production rates for the $\text{MoS}_2/\text{Ag}/\text{TiO}_2$ catalyst films with different TiO_2 loading ratios.

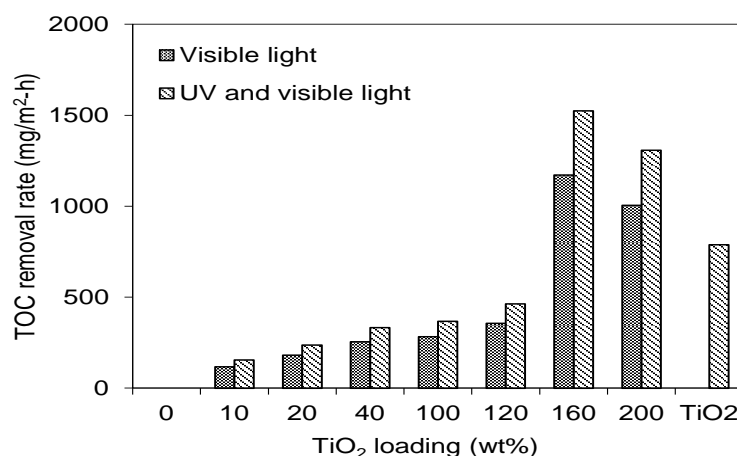


Figure 6. Photocatalytic TOC removal rates by the $\text{MoS}_2/\text{Ag}/\text{TiO}_2$ photocatalyst film with different TiO_2 loading ratios.

It is apparent that the composite $\text{MoS}_2/\text{Ag}/\text{TiO}_2$ multi-layer structure rendered a synergetic effect of the catalyst materials for photocatalytic H_2 generation and organic degradation. The more photosensitive MoS_2 base layer ensured the visible absorbance and induced the reactivity of the photocatalyst. The use of the TiO_2 outer layer would help suppress the recombination of electron/hole pairs formed on the MoS_2 inner layer, making the electrons more available for H^+ reduction and H_2 evolution on the cathode side (Best and Dunstan, 2009; Cao and Banin, 2000). As the electrons transferring from TiO_2 to MoS_2 , the holes left on the VB of TiO_2 would render a considerable oxidation capability for organic degradation on the anode side. Nonetheless, further increase in the TiO_2 loading ratio did not result in any increase in H_2 generation on the cathode side and organic degradation on the anode side (Figure 5).

The photocatalytic mechanism of the $\text{MoS}_2/\text{Ag}/\text{TiO}_2$ multiple-layer system may be expected as follows. During the photocatalytic process, electron transfer via a direction of $\text{TiO}_2 \rightarrow \text{Ag} \rightarrow \text{MoS}_2$ should occur as a result of the excitation of both TiO_2 and MoS_2 . The electron transfer would suppress the recombination of the photo-generated electron-hole pairs. Accordingly, the oxidation and reduction capabilities of the photocatalyst film were greatly improved, resulting in hydrogen production and organic degradation in two chambers on different sides of the catalyst film.

CONCLUSIONS

As an alternative and more environmentally friendly photocatalyst, the MoS₂/Ag/TiO₂ multi-layer catalyst film was synthesized on the glass fiber membrane with Ag as the nanojunctions between the two catalyst layers. The catalyst film was used in a two-chambered photo-reactor to achieve separate photocatalytic hydrogen production and organic degradation. The composite catalyst film performed well for concurrent photocatalytic hydrogen production and organic degradation in the photo-reactors under either solar light or visible light irradiation. The specific hydrogen production rate went through a maximum of 85 mmol/m²-h with an energy conversion efficiency of 0.85%, while the corresponding specific TOC removal for formic acid under solar light reached 1520 mg/m²-h.

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REFERENCES

- Balasubramanian, G., Dionysiou, D.D., Suidan, M.T., Baudin, I. and Lafné, J.M. (2004). Evaluating the activities of immobilized TiO₂ powder films for the photocatalytic degradation of organic contaminants in water. *Applied Catalysis B: Environmental*, 47(2), 73-84.
- Best, J.P. and Dunstan, D.E. (2009). Nanotechnology for photolytic hydrogen production: colloidal anodic oxidation. *International Journal of Hydrogen Energy*, 34(18), 7562-7578.
- Cao, Y.W. and Banin, U. (2000). Growth and properties of semiconductor core/shell nanocrystals with InAs cores. *Journal of the American Chemical Society*, 122(40), 9692-9702.
- Carp, O., Huisman, C.L. and Reller, A. (2004). Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry*, 32(1-2), 33-177.
- Chatterjee, D. and Dasgupta, S. (2005). Visible light induced photocatalytic degradation of organic pollutants. *Journal of Photochemistry and Photobiology C-Photochemistry Reviews*, 6(2-3), 186-205.
- Ho, W.K., Yu, J.C., Lin, J., Yu, J.G. and Li, P.S. (2004). Preparation and photocatalytic behavior of MoS₂ and WS₂ nanocluster sensitized TiO₂. *Langmuir*, 20(14), 5865-5869.
- Hu, K.H., Hu, X.G., Xu, Y.F. and Sun, J.D. (2010). Synthesis of nano-MoS₂/TiO₂ composite and its catalytic degradation effect on methyl orange. *Journal of Materials Science*, 45(10), 2640-2648.
- Lee, Y., Terashima, H., Shimodaira, Y., Teramura, K., Hara, M., Kobayashi, H., Domen, K. and Yashima, M. (2007). Zinc germanium oxynitride as a photocatalyst for overall water splitting under visible light. *Journal of Physical Chemistry C*, 111(2), 1042-1048.
- Maeda, K., Teramura, K., Lu, D.L., Takata, T., Saito, N., Inoue, Y. and Domen, K. (2006). Photocatalyst releasing hydrogen from water - enhancing catalytic performance holds promise for hydrogen production by water splitting in sunlight. *Nature*, 440(7082), 295.
- Pourabbas, B. and Jamshidi, B. (2008). Preparation of MoS₂ nanoparticles by a modified hydrothermal method and the photo-catalytic activity of MoS₂/TiO₂ hybrids in photo-oxidation of phenol. *Chemical Engineering Journal*, 138(1-3), 55-62.
- Tian, Y.M., Zhao, J.Z., Fu, W.Y., Liu, Y.H., Zhu, Y.Z. and Wang, Z.C. (2005). A facile route to synthesis Of MoS₂ nanorods. *Materials Letters*, 59(27), 3452-3455.
- Wang, X., Shih, K. and Li, X.Y. (2010). Photocatalytic hydrogen generation from water under visible light using core/shell nano-catalysts. *Water Science and Technology*, 61(9), 2303-2308.