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# 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, MoS<sub>2</sub>/Ag/TiO<sub>2</sub>, was synthesized on a glass-fiber membrane. The composite catalyst film had a multi-layer structure with Ag as nanojunctions between the MoS<sub>2</sub> and TiO<sub>2</sub> 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/m<sup>2</sup>-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/m<sup>2</sup>-h. It is apparent that Ag between the TiO<sub>2</sub> and MoS<sub>2</sub> layers allowed the transfer of photo-excited electrons via TiO<sub>2</sub>→Ag→MoS<sub>2</sub> for organic degradation and H<sup>+</sup> reduction (e.g. hydrogen evolution) in two different chambers.

## Keywords

Hydrogen production, MoS<sub>2</sub>, 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, MoS<sub>2</sub> has been shown as a promising photocatalyst that responds to visible light. MoS<sub>2</sub> possesses a significant advantage over TiO<sub>2</sub> which is a UV-driven photocatalyst, i.e. the band gap of MoS<sub>2</sub> is small enough to allow absorption of visible light. The MoS<sub>2</sub>/TiO<sub>2</sub> 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, MoS<sub>2</sub>-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 MoS<sub>2</sub>/Ag/TiO<sub>2</sub> photocatalyst film was synthesized with Ag as the nanojunction between the MoS<sub>2</sub> and TiO<sub>2</sub> 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 MoS<sub>2</sub> 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 (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and 2.64 g Na<sub>2</sub>S·9H<sub>2</sub>O were added into the flask. After half an hour, 0.7 g NH<sub>2</sub>OH·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 MoS<sub>2</sub> 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 MoS<sub>2</sub> powder.

### Characterization of MoS<sub>2</sub> photocatalyst

The size distribution of the MoS<sub>2</sub> catalyst particles was measured by a laser diffraction particle size analyzer (Delsa™ Nano, Beckman Coulter). The crystalline phases and structural features of MoS<sub>2</sub> were analyzed by an X-ray diffraction (XRD) system (D8 Advance, Burker AXS) with the Cu K $\alpha$  irradiation from 10 to 90 degrees. The morphology of the MoS<sub>2</sub> particles was examined by SEM and TEM.

### MoS<sub>2</sub>/Ag/TiO<sub>2</sub> film

Glass fiber (GF) membrane was used as the base material for immobilization of the photocatalysts. The membrane was cut into circles (area = 7 cm<sup>2</sup>), and Nafion was employed to affix the catalyst film on the membrane surface. The MoS<sub>2</sub> nanoparticles (50 mg) were mixed with Nafion solution and applied to the membrane. Ag was then deposited on the MoS<sub>2</sub> surface by *in-situ* photo-deposition. Finally, a Nafion TiO<sub>2</sub> (Degussa, P-25) paste was applied over the MoS<sub>2</sub> layer on the membrane, and the TiO<sub>2</sub> loading ratio varied from 10 to 200% of the amount of MoS<sub>2</sub> 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/cm<sup>2</sup>) with a cutoff ( $\lambda < 420$  nm) filter or a combined UV and visible light source (light intensity ~ 86 mW/cm<sup>2</sup>) without the cutoff filter. Light irradiation was applied on the TiO<sub>2</sub> 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 Na<sub>2</sub>SO<sub>4</sub> at pH=1.0 for hydrogen production. The gas produced during the photo-tests was collected, and the H<sub>2</sub> and CO<sub>2</sub> 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 H<sub>2</sub> production rate ( $R$ ) and the corresponding energy conversion efficiency ( $\eta$ ) 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 H<sub>2</sub> production measured,  $t$  is the duration of photo-reaction,  $W$  is the weight of catalyst in reactor,  $\Delta H_c$  is the combustion value of H<sub>2</sub> (286 kJ/mol), and  $A$  and  $I$  is specify the area (7 cm<sup>2</sup>) and intensity of the light irradiation, respectively.

## RESULTS AND DISCUSSION

### Characterization of the MoS<sub>2</sub> catalysts

Figure 1 shows the particle size distribution of the MoS<sub>2</sub> 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 MoS<sub>2</sub> catalyst displayed a good crystallization as shown by its XRD pattern (Figure 3).

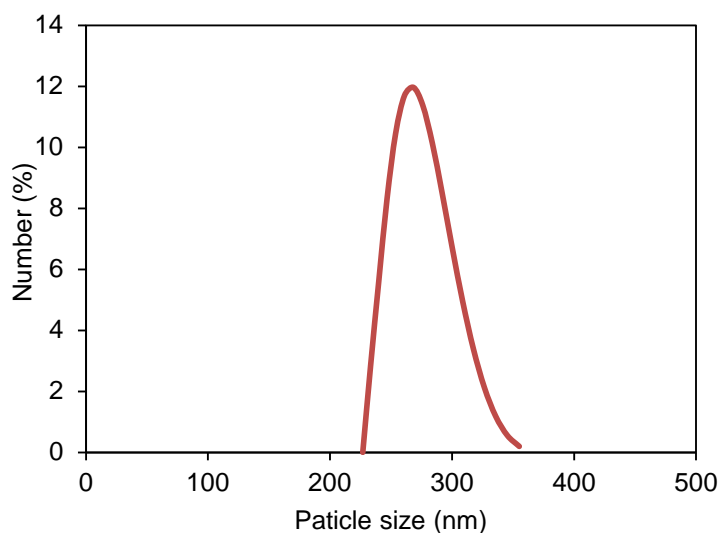


Figure 1. The particle size distribution of MoS<sub>2</sub> catalysts.

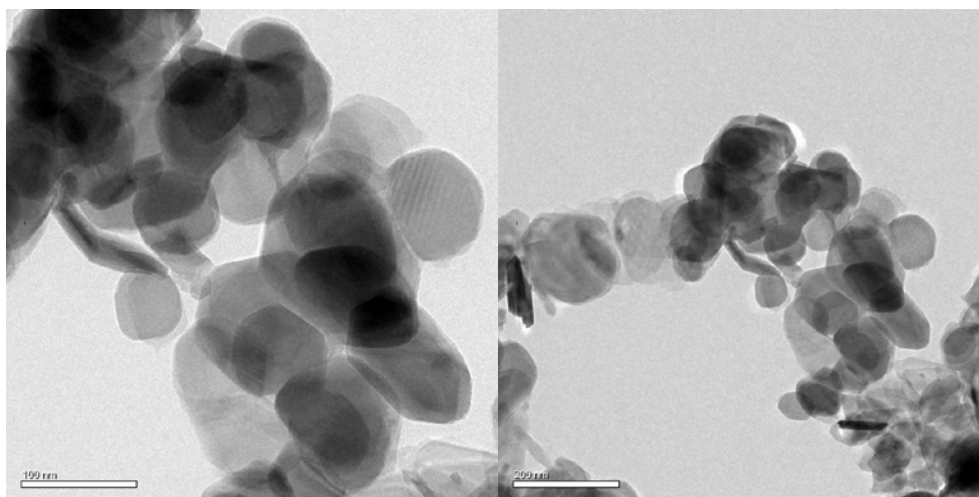


Figure 2. TEM images of MoS<sub>2</sub> nanoparticles.

Figure 4 shows the diffuse reflectance spectrum of the MoS<sub>2</sub> 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 MoS<sub>2</sub> for photocatalytic reactions under visible light.

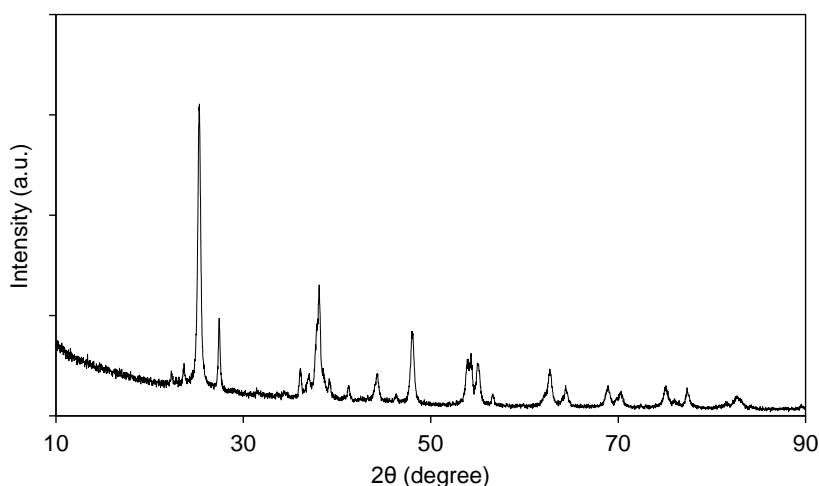


Figure 3. XRD pattern of MoS<sub>2</sub>.

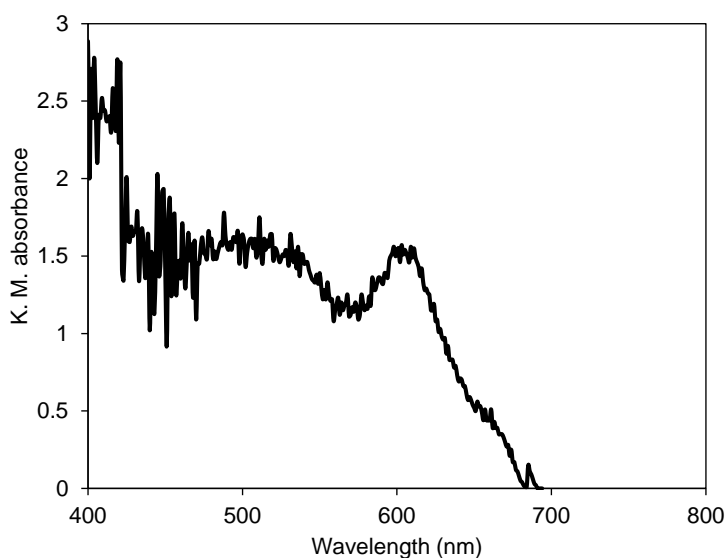


Figure 4. Diffuse reflectance spectrum of the MoS<sub>2</sub> photocatalyst.

### MoS<sub>2</sub>/Ag/TiO<sub>2</sub> photocatalyst film for hydrogen production

Results of photocatalytic H<sub>2</sub> generation and organic degradation (CO<sub>2</sub> production) obtained with the MoS<sub>2</sub>/Ag/TiO<sub>2</sub> film irradiated by the simulated solar light are shown in Figure 5A, where the gas production rates are plotted as a function of the TiO<sub>2</sub> loading ratio.

With 10% formic acid in the anode side chamber, the bare MoS<sub>2</sub> was not capable of photocatalytic hydrogen production. Coating of the outer TiO<sub>2</sub> layer could significantly enhance the photo-reactivity of the MoS<sub>2</sub> catalyst for both H<sub>2</sub> production and organic degradation (Figure 5). As the TiO<sub>2</sub> loading ratio increased to 160% of the MoS<sub>2</sub> layer, the area-based specific H<sub>2</sub> and CO<sub>2</sub> production rates increased to the maximum values of 88 and 85 mmol/m<sup>2</sup>-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 TiO<sub>2</sub> coating were obtained with somewhat lower specific H<sub>2</sub> and CO<sub>2</sub> production rates (Figure 5B).

Based on the amount of CO<sub>2</sub> 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/m<sup>2</sup>-h at a TiO<sub>2</sub> load of 160%.

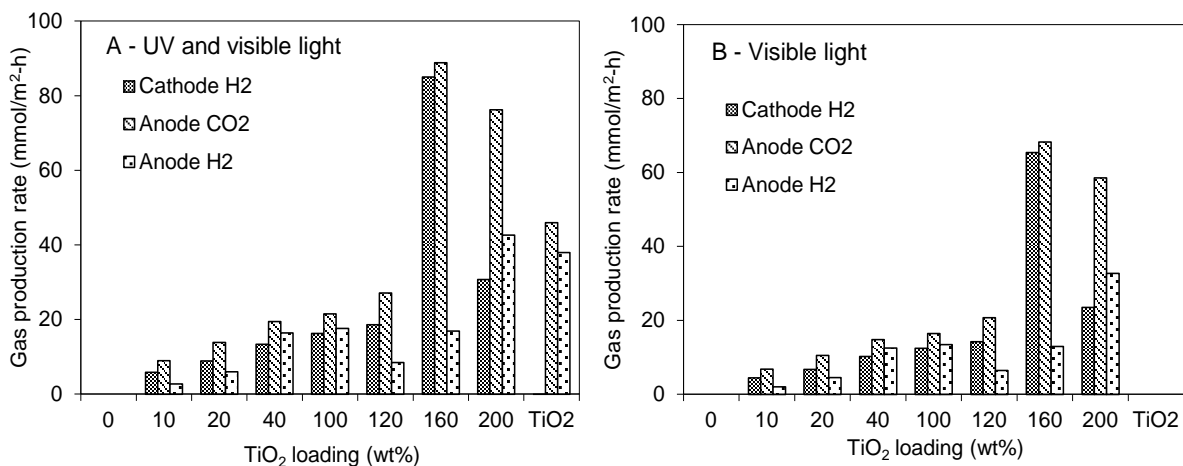


Figure 5. Hydrogen and carbon dioxide production rates for the MoS<sub>2</sub>/Ag/TiO<sub>2</sub> catalyst films with different TiO<sub>2</sub> loading ratios.

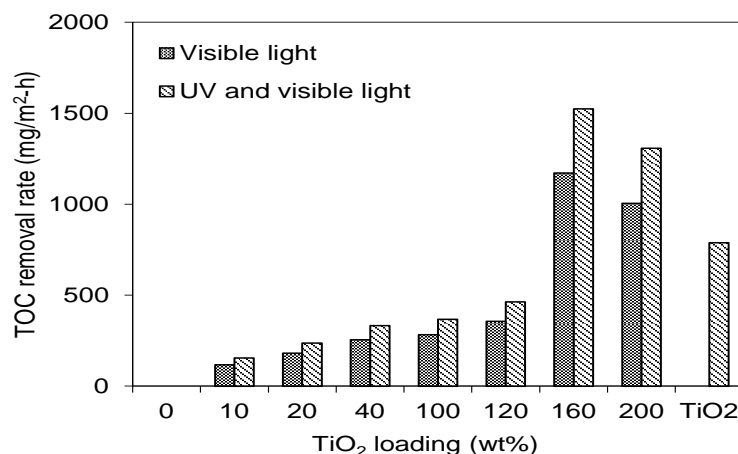


Figure 6. Photocatalytic TOC removal rates by the MoS<sub>2</sub>/Ag/TiO<sub>2</sub> photocatalyst film with different TiO<sub>2</sub> loading ratios.

It is apparent that the composite MoS<sub>2</sub>/Ag/TiO<sub>2</sub> multi-layer structure rendered a synergetic effect of the catalyst materials for photocatalytic H<sub>2</sub> generation and organic degradation. The more photosensitive MoS<sub>2</sub> base layer ensured the visible absorbance and induced the reactivity of the photocatalyst. The use of the TiO<sub>2</sub> outer layer would help suppress the recombination of electron/hole pairs formed on the MoS<sub>2</sub> inner layer, making the electrons more available for H<sup>+</sup> reduction and H<sub>2</sub> evolution on the cathode side (Best and Dunstan, 2009; Cao and Banin, 2000). As the electrons transferring from TiO<sub>2</sub> to MoS<sub>2</sub>, the holes left on the VB of TiO<sub>2</sub> would render a considerable oxidation capability for organic degradation on the anode side. Nonetheless, further increase in the TiO<sub>2</sub> loading ratio did not result in any increase in H<sub>2</sub> generation on the cathode side and organic degradation on the anode side (Figure 5).

The photocatalytic mechanism of the MoS<sub>2</sub>/Ag/TiO<sub>2</sub> multiple-layer system may be expected as follows. During the photocatalytic process, electron transfer via a direction of TiO<sub>2</sub>→Ag→MoS<sub>2</sub> should occur as a result of the excitation of both TiO<sub>2</sub> and MoS<sub>2</sub>. 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 MoS<sub>2</sub>/Ag/TiO<sub>2</sub> 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/m<sup>2</sup>-h with an energy conversion efficiency of 0.85%, while the corresponding specific TOC removal for formic acid under solar light reached 1520 mg/m<sup>2</sup>-h.

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