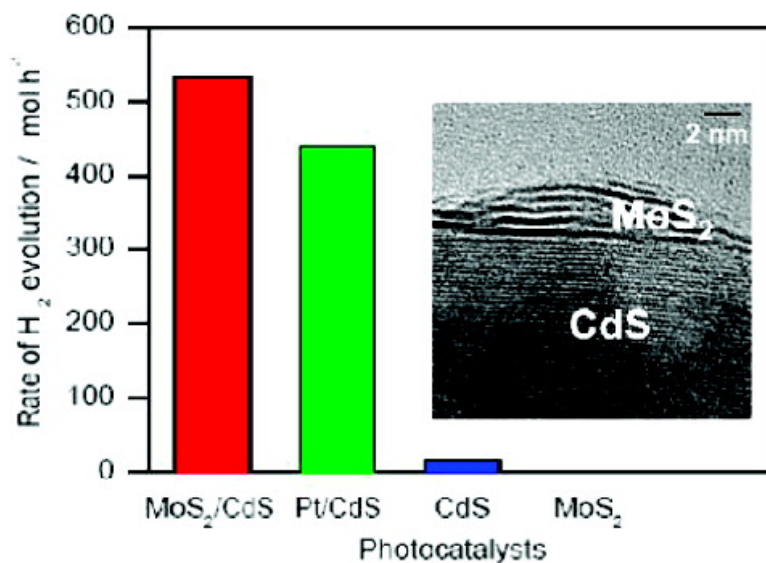


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Enhancement of Photocatalytic H₂ Evolution on CdS by Loading MoS₂ as Cocatalyst under Visible Light Irradiation

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Photocatalytic H₂ production from water splitting using semiconductor photocatalysts is an attractive and challenging issue in the conversion of solar energy into chemical energy.¹ The photocatalysts are usually composed of semiconductor materials and cocatalysts. The cocatalysts loaded on semiconductor photocatalysts play an essential role in the production of H₂ and O₂.² Cocatalysts could promote the separation of photoexcited electrons and holes. Moreover, cocatalysts offer the low activation potentials for H₂ or O₂ evolution and are often served as the active sites for H₂ or O₂ generation.³ Therefore, the loading of proper cocatalysts can greatly enhance the activities of photocatalysts.⁴ In most work reported so far, mainly noble metals or their oxides are used as the cocatalysts, while inexpensive catalysts such as sulfides of transition metals are rarely used as cocatalysts in photocatalytic H₂ production even though metal sulfides have demonstrated high activity in H₂ involved reactions in heterogeneous catalysis.⁵

We report herein that MoS₂ as a cocatalyst loaded on CdS for photocatalytic H₂ production using lactic acid solution as the sacrificial agent under visible light. We found that the activity of CdS can be enormously increased by loading MoS₂ as a cocatalyst, and the activity of MoS₂/CdS could be even higher than that of Pt/CdS under the same reaction conditions.

MoS₂/CdS catalysts with highly dispersed MoS₂ on CdS were prepared by impregnating CdS with an aqueous solution of (NH₄)₂MoS₄, followed by a treatment in H₂S flow at high temperatures for 2 h. X-ray diffraction patterns of CdS and 1 wt % MoS₂/CdS indicated that both cubic and hexagonal phases of CdS are present in CdS and MoS₂/CdS samples after the treatment at 573 K. The MoS₂/CdS sample was characterized by X-ray photoelectron spectroscopy (XPS) to check the valence states of the elements in MoS₂/CdS. The appearance of the S2p peak at 161.7 eV and the Cd3d peaks at 411.9 and 405.1 eV confirm S²⁻ and Cd²⁺ in CdS. In addition, the doublet peaks for Mo3d at 231.9 and 228.8 eV indicate the formation of MoS₂ in the MoS₂/CdS catalyst.⁶ Photocatalytic reactions were carried out in lactic acid solution under visible light ($\lambda > 420$ nm).

Figure 1 shows the rate of H₂ evolution on MoS₂/CdS catalysts with different amounts of MoS₂ loadings, together with those on CdS and MoS₂ for a comparison. No H₂ was detected when MoS₂ alone was used as the catalyst, suggesting that MoS₂ is not active for photocatalytic H₂ evolution.⁷ CdS alone shows activity in photocatalytic H₂ evolution, but the rate of H₂ evolution is very low (ca. 15 $\mu\text{mol h}^{-1}$). After loading only 0.01 wt % of MoS₂ on CdS, the activity in H₂ evolution is increased by up to 22 times. With the increase of the amount of MoS₂ loaded on CdS, the rate of H₂ evolution on MoS₂/CdS is increased further and achieves a maximum when the loading amount of MoS₂ on CdS is about 0.2 wt %. The activity is increased by up to 36 times after loading 0.2 wt % of MoS₂ on CdS. The appearance of a maximum in activity

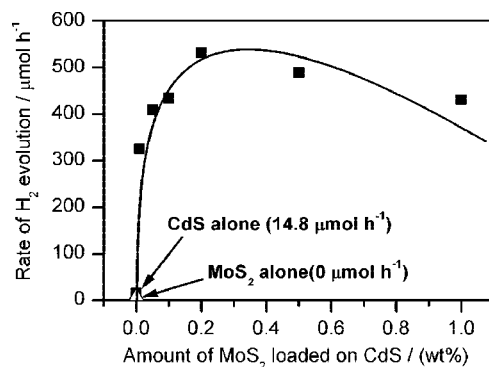


Figure 1. The rate of H₂ evolution on MoS₂/CdS photocatalysts loaded with different amounts of MoS₂ under visible light ($\lambda > 420$ nm). Catalyst (0.1 g); 10 vol % lactic solution (200 mL); light source, Xe lamp (300 W).

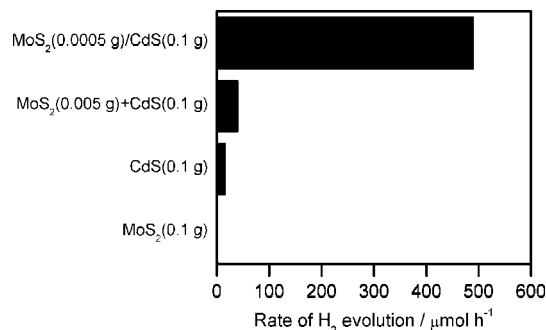


Figure 2. The rate of H₂ evolution on MoS₂, CdS, MoS₂/CdS, and mechanical mixture of MoS₂ and CdS under visible light ($\lambda > 420$ nm); 10 vol % lactic solution (200 mL); light source, Xe lamp (300 W).

with an optimum loading of cocatalyst has also been observed for other photocatalysts loaded with Ru, Pt, RuO₂, or Pd.⁸

Figure 2 shows the rate of H₂ evolution on MoS₂, CdS, MoS₂/CdS, and mechanical mixture of MoS₂ and CdS. The mixture of CdS (0.1 g) and MoS₂ (0.005 g) demonstrates a slightly higher rate of H₂ evolution than CdS (0.1 g) alone. However, MoS₂ (0.0005 g)/CdS (0.1 g) shows much higher activity than the mixture of CdS (0.1 g) and MoS₂ (0.005 g) even though the amount of MoS₂ deposited on CdS is much less. This fact indicates that the intimate contact between CdS and MoS₂ is crucial for the interelectron transfer between the two components.

It is well-known that noble metals such as Pt, Pd, Rh, Ru, and Au function as efficient H₂ evolution promoters for many photocatalysts.^{4,8} For comparison, 0.2 wt % of these cocatalysts was, respectively, loaded on CdS with the photoreduction method from the corresponding complexes of metals. Figure 3 shows the rate of H₂ evolution on CdS loaded with 0.2 wt % of these

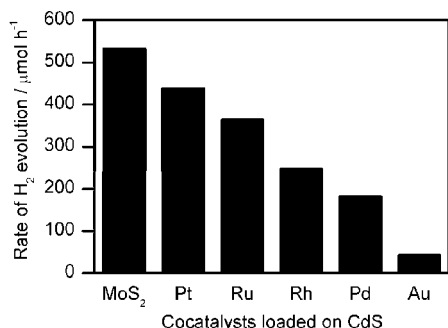


Figure 3. The rate of H₂ evolution on CdS loaded with 0.2 wt % of different cocatalysts. Catalyst (0.1 g); 10 vol % lactic solution (200 mL); light source, Xe lamp (300 W).

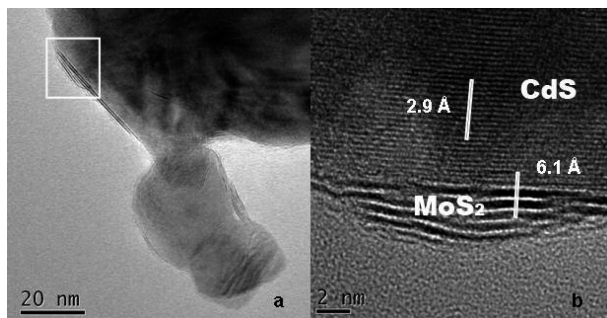


Figure 4. (a) HRTEM image of 1 wt % MoS₂/CdS prepared at 773 K and (b) the magnified HRTEM image of the selected frame from image (a).

cocatalysts. Among the noble metals tested, Pt is demonstrated to be the best promoter for H₂ evolution, while the rate of H₂ evolution on 0.2 wt % Pt/CdS is still lower than that on 0.2 wt % MoS₂/CdS. Our recent work indicates that the surface phase junction formed between the anatase and rutile phase of TiO₂ can greatly enhance the photocatalytic activity for H₂ production.⁹ Heterogeneous junction between MoS₂ and CdS can be derived when the MoS₂/CdS catalyst is treated at high temperatures, and the junction will lead to a more efficient interelectron transfer between the two components. Furthermore, MoS₂ was reported to be able to activate H₂ based on theoretical calculations and experimental results for electrochemical system.¹⁰ Although Pt shows superior performance than MoS₂ for the activation of H₂ in the electrochemical system,¹⁰ the higher rate of H₂ evolution obtained on MoS₂/CdS than on Pt/CdS suggests that the intimate junction formed between MoS₂ and CdS is important for enhancing the photocatalytic activity. In the photocatalytic reactions for H₂ evolution, photoexcited electrons transfer from CdS to MoS₂, where H⁺ is reduced to atomic H and then evolves as H₂, and the holes oxidize the sacrificial agents. We suppose that the better coupling between the structures and electronic configurations of MoS₂ and CdS together with the excellent H₂ activation ability of MoS₂ are mainly responsible for the high activity of MoS₂/CdS catalyst.

In order to visualize the junction structure of MoS₂ and CdS, 1 wt % MoS₂/CdS catalyst was investigated by HRTEM. The HRTEM image in Figure 4a shows that the cocatalyst MoS₂ with typical layered structure is deposited on the CdS surface. The magnified HRTEM image in Figure 4b exhibits fringes with lattice spacing of ca. 2.9 and 6.1 Å, which correspond to the (200) plane of cubic CdS and the (002) plane of hexagonal MoS₂, respectively. The number of the MoS₂ slabs deposited on CdS is about 1–6 (Figure S2), and the MoS₂ slabs are intimately deposited on the surface of CdS. The intimate contact between CdS and MoS₂ favors

the formation of junctions between the two components and, as a result, improves the charge separation and therefore the photocatalytic activity.

In summary, the rate of H₂ evolution on CdS is significantly enhanced by loading MoS₂ as a cocatalyst on CdS for the H₂ production from a lactic acid solution under visible light. The activity of CdS is increased by up to 36 times when loaded with only 0.2 wt % of MoS₂, and the activity of 0.2 wt % MoS₂/CdS is even higher than that of 0.2 wt % Pt/CdS under the same reaction conditions. The junction formed between MoS₂ and CdS and the excellent H₂ activation property of MoS₂ are supposed to be responsible for the enhanced photocatalytic activity of MoS₂/CdS. This work presents not only a possibility for the use of MoS₂ as a substitute for noble metals in the photocatalytic H₂ production but also an important concept that the proper junction structure between cocatalyst and semiconductor is crucial for high photocatalytic activity.

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Supporting Information Available: Details of reaction conditions, XPS spectra, and HRTEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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