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# Mo<sub>2</sub>N: An efficient non-noble metal cocatalyst on CdS for enhanced photocatalytic H<sub>2</sub> evolution under visible light irradiation

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## ABSTRACT

Mo<sub>2</sub>N as an efficient non-noble metal cocatalyst was firstly reported for improving photocatalytic H<sub>2</sub> evolution under visible light irradiation. The activity of 2.0% Mo<sub>2</sub>N/CdS is 6.1 times of CdS alone and 1.4 times of 1.0% Pt/CdS. The longevity test shows the Mo<sub>2</sub>N/CdS is very stable in 42 h. After 42 h, the activity of Mo<sub>2</sub>N/CdS gradually decreases. However, even after 90 h, the activity of Mo<sub>2</sub>N/CdS also keeps the 49% of that fresh catalyst. The molybdenum oxides, CdMoO<sub>4</sub> on the surface of Mo<sub>2</sub>N may combine CdS with Mo<sub>2</sub>N closely, protect Mo<sub>2</sub>N cocatalyst and inhibit the reversible reaction of H<sub>2</sub> production, thus increase the photocatalytic activity and the stability of Mo<sub>2</sub>N/CdS. This study demonstrates Mo<sub>2</sub>N is a new efficient low cost non-noble metal cocatalyst in photocatalytic H<sub>2</sub> evolution.

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## Introduction

In the past several decades, owing to the global problems of energy crisis and environment pollution, photocatalytic H<sub>2</sub> production based on a semiconductor photocatalyst has attracted much more consideration [1–6]. Cocatalyst is a crucial factor to enhance the photocatalytic activity in the system of photocatalytic H<sub>2</sub> production [7–9]. However, the cocatalysts for H<sub>2</sub> production are mainly composed of noble metals which result in the high cost of the photocatalysts [10–12]. The high cost and the low efficiency of the photocatalyst limits the industrialization of the photocatalytic H<sub>2</sub> production technology. Thus, developing new effective cocatalyst with low cost is greatly urgent.

Some alternative cocatalyst based on nonprecious metals have been reported for photocatalytic H<sub>2</sub> production, recently, such as Mo<sub>2</sub>S, WS<sub>2</sub>, NiS, Mo<sub>2</sub>S/graphene, WC, MoP etc. [7,13–19]. The kinds of reported non-noble metal cocatalyst are mainly sulfides and relatively rare, so it is important to develop non-sulphide cocatalysts with low cost. Molybdenum-based compounds including Mo<sub>2</sub>C, Mo<sub>2</sub>N and MoP are typical materials which have similar properties of Pt and extensively been researched in hydrogenation reactions, hydrodesulphurization, hydrodenitrogenation, and electrochemical applications for substitute of noble metals [20–24]. Recently, we have reported Mo<sub>2</sub>C is an efficient cocatalyst for enhanced photocatalytic H<sub>2</sub> evolution [25], and the activity on Mo<sub>2</sub>C/CdS is ten times higher than CdS alone and 2.3 times higher than Pt/CdS. This also demonstrates Molybdenum-

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based compounds with similar properties of Pt has potential prospect as cocatalysts for substitution of noble metals in photocatalytic  $H_2$  evolution. Though, the  $Mo_2N$  has not reported as a cocatalyst in the photocatalytic  $H_2$  evolution to date as far as we know.

Herein, the nitride  $Mo_2N$  was reported for the first time as an effective cocatalyst for photocatalytic  $H_2$  production. When the  $Mo_2N$  combined with CdS, the activity of  $H_2$  production on  $Mo_2N/CdS$  was largely improved and even higher than the Pt/CdS.

## Experimental

### Synthesis of $Mo_2N$ materials

In this paper, all chemicals (Sinopharm Chemical Reagent Co., Ltd) used in the tests were of analytical grade and used directly without further purification. Firstly, amount of molybdic acid ( $H_2MoO_4$ ) was dissolved in excess aqueous ammonia solution, evaporated to dryness then calcined at  $500\text{ }^\circ\text{C}$  for 5 h in the air. Then, the samples were reduced by temperature programmed reduction method for 4 h at the target temperature under flowing gas of  $NH_3$  at a gas flow rate of 100 mL/min. The target temperatures were chosen as 650, 700, 750, 800 and  $850\text{ }^\circ\text{C}$ . The sample was rapidly cooled to room temperature in flowing gas of  $NH_3$  and then passivated in mixed gas of  $N_2$  and  $O_2$  with the ratio of 99 for 12 h to form a stable material.

### Preparation of $Mo_2N/CdS$ and $CdMoO_4/CdS$ photocatalysts

CdS and  $CdMoO_4$  had synthesized by many methods [26–34]. Here, The precipitation and hydrothermal methods were used to prepare CdS and  $CdMoO_4$ , respectively. Then, the coprecipitation method was used to prepare  $Mo_2N/CdS$  and  $CdMoO_4/CdS$ . Typically, amount of  $Mo_2N$  was dispersed in 0.14 mol/L of cadmium acetate solution. Then, 0.14 mol/L of  $Na_2S$  solution was added dropwise under vigorous agitation and then aged for 12 h. Last, the deposit was filtered by distilled water and ethanol several times and then dried at  $60\text{ }^\circ\text{C}$  for 12 h in vacuum drying oven.  $CdMoO_4$  was synthesized according to the previous literature [26]. In a typical synthesis procedure, the mixture of  $Na_2MoO_4 \cdot 2H_2O$  (2 mmol),  $Cd(NO_3)_2 \cdot 4H_2O$  (2 mmol) and 14 mL deionized water was transferred into a Teflon lined steel autoclave of 40 mL after vigorous agitation and the autoclave heated under autogenous pressure at  $200\text{ }^\circ\text{C}$  for 24 h. Then, the autoclave was cooled to room temperature gradually. The white precipitate was washed with distilled water three times and then was dried at  $60\text{ }^\circ\text{C}$  in air. The  $CdMoO_4/CdS$  was prepared using the same method as  $Mo_2N/CdS$ .

### Characterizations of catalysts and cocatalysts

Powder X-ray diffraction (XRD) data of cocatalysts and photocatalysts were acquired on a D/MAX2500 (Rigaku, Japan) diffractometer with Cu K alpha radiation at a voltage of 40 KV. The scanning electron microscopy (SEM) measurements were carried out on a scanning electron microscope (KYKY2800B).

High resolution transmission electronmicroscopy (HRTEM) and TEM measurements were performed on a transmission electron microscope (F20/G20). The UV–Vis diffuse reflection spectroscopies (UV–Vis DRS) were recorded on a spectrometer (U-4100) using the  $BaSO_4$  as the corrected base line. The specific surface areas of the cocatalysts and photocatalysts were measured on a Micromeritics ASAP-2000 Pysisorption analyzer, using the nitrogen adsorption and desorption method of Brunauer–Emmett–Teller (BET) at 77 K. The X-ray photoelectron spectra (XPS) data were obtained on a Thermo ESCALAB 250Xi spectrometer using Al as the exciting source ( $h\nu = 1486.6\text{ eV}$ , 150 W).

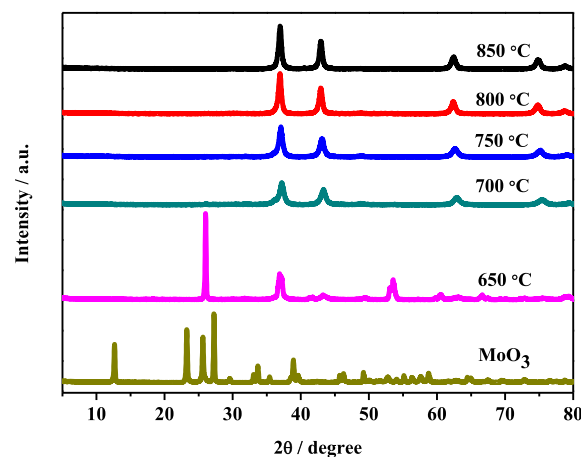
### Photocatalytic experiments

The photocatalytic hydrogen evolution reactions were carried out in a closed gas system using a 300 W Xe lamp (Perfect, China) with 420 nm filter ( $\lambda \geq 420\text{ nm}$ ) as a visible light source. 0.1 g of the  $Mo_2N/CdS$  photocatalyst was dispersed in a 200 mL mixed solution of 1.0 mol/L of  $Na_2S$  and 1.0 mol/L  $Na_2SO_3$  by a magnetic stirrer. The dispersed solutions were firstly degassed by evacuation and then irradiated by the 300 W Xe lamp. The evolved hydrogen gas was measured by an online gas chromatography analysis using 5 Å molecular sieve column, TCD detector and Ar carrier.

For measurements of the activities of photocatalysts with loading of noble metal cocatalyst, the same methods using in situ photo deposition and the same loading amounts of noble metals (1.0%, weight ratio) were adopted as the literature [25].

## Results and discussion

The  $Mo_2N$  cocatalyst is prepared via temperature programmed reduction method under flowing gas of  $NH_3$  using  $MoO_3$  as precursor. Fig. 1 shows the XRD patterns of  $MoO_3$  samples nitrided at different temperatures under  $NH_3$  flow for 4 h. The XRD of the  $MoO_3$  sample was also presented for comparison. It is clearly seen that the sample is reduced to  $MoO_2$  at  $650\text{ }^\circ\text{C}$  (JCPDS#32–0671). At and over  $700\text{ }^\circ\text{C}$ , the  $Mo_2N$



**Fig. 1** – The XRD patterns of  $MoO_3$  samples nitrided at different temperatures under  $NH_3$  flow for 4 h. The XRD of the  $MoO_3$  sample was also presented for comparison.

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