



Short communication

## Synthesis of Mo-doped graphitic carbon nitride catalysts and their photocatalytic activity in the reduction of CO<sub>2</sub> with H<sub>2</sub>O



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## ABSTRACT

Molybdenum doped graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) catalysts were prepared by a simple pyrolysis method using melamine and ammonium molybdate as precursors. The characterization results indicated that the obtained Mo-doped g-C<sub>3</sub>N<sub>4</sub> catalysts had worm-like mesostructures with higher surface area. Introduction of Mo species can effectively extend the spectral response property and reduce the recombination rate of photogenerated electrons and holes. CO<sub>2</sub> photocatalytic reduction tests showed that the Mo-doped g-C<sub>3</sub>N<sub>4</sub> catalysts exhibited considerably higher activity (the highest CO and CH<sub>4</sub> yields of 887 and 123 μmol g<sup>-1</sup>-cat., respectively, after 8 h of UV irradiation.) compared with pure g-C<sub>3</sub>N<sub>4</sub> from melamine.

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### 1. Introduction

The rapidly increasing carbon dioxide (CO<sub>2</sub>) emission in the atmosphere from the combustion of fossil fuels is becoming a global environmental issue, such as the greenhouse effect. While the energy crisis caused by overexploitation of fossil fuels and the environmental burdens is recognized to be the two major problems in the foreseeable future [1]. Among various alternatives, photocatalytic reduction of CO<sub>2</sub> into energy-rich products such as methane (CH<sub>4</sub>) in the presence of H<sub>2</sub>O is a superior way to generate reproducible chemical energy. Since the first report on photocatalytic reduction of CO<sub>2</sub> into organic compounds by Inoue and co-workers in early 1979 [2], tremendous research efforts have been made towards developing efficient photocatalysts to achieve CO<sub>2</sub> conversion more economically [3–6].

Recently, a metal-free photocatalyst polymeric graphitic carbon nitride (C<sub>3</sub>N<sub>4</sub>) with chemically and thermally stable and unique band structure has gained a great deal of scientific interest, and its applications including photodegradation of organic pollutions, hydrogen production by water splitting and photocatalytic reduction of CO<sub>2</sub> were demonstrated [7–9]. However, the photocatalytic reactions over pure g-C<sub>3</sub>N<sub>4</sub> still suffer from low conversion efficiencies due to the rapid electron–hole recombination and the low electrical conductivity.

Therefore, many efforts have been suggested to solve this problem, such as preparing mesoporous structures [10], doping with a metal or nonmetal [11–17], and coupling with other components [18–24]. Among the various strategies, metal doping is one of the most convenient and effective methods to modify the electronic structures of semiconductors as well as their textual properties, thus improving their photocatalytic performances [25]. Wang et al. synthesized Fe-doped g-C<sub>3</sub>N<sub>4</sub> catalysts and suggested that the enhanced photocatalytic performance resulted from the enhanced specific surface area, narrower bandgap and better aligned band structure [17,26]. Our recent results also showed that Ti-doped g-C<sub>3</sub>N<sub>4</sub> catalysts can efficiently increase the photocatalytic activity in dye degradation because of the enhanced optical absorption and accelerated charge carrier transfer rate [27].

Herein, we report a simple pyrolysis method for the synthesis of a series of Mo-doped g-C<sub>3</sub>N<sub>4</sub> catalysts with different doping concentrations. X-ray diffraction (XRD), nitrogen adsorption–desorption, transmission electron microscopy (TEM), UV–vis diffuse reflectance spectra (UV–vis DRS) and photoluminescence (PL) spectroscopy were used to characterize the prepared samples. The photocatalytic activities were evaluated in the photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O to produce CO and CH<sub>4</sub>. Indeed, we found that the Mo-doped g-C<sub>3</sub>N<sub>4</sub> catalysts were capable for photocatalytic CO<sub>2</sub> reduction with much higher activities than that of pure g-C<sub>3</sub>N<sub>4</sub>. Moreover, the correlation between the catalytic performance of the Mo-doped g-C<sub>3</sub>N<sub>4</sub> catalysts and physical properties was investigated.

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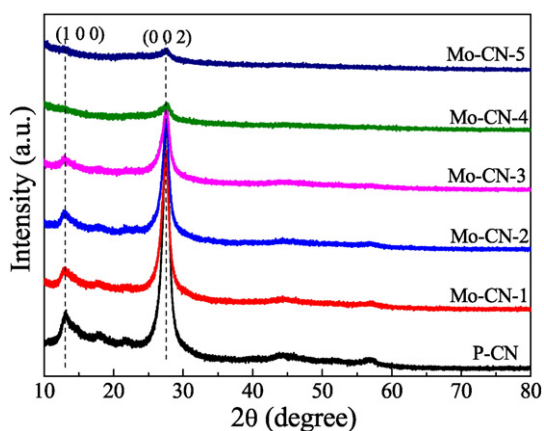


Fig. 1. XRD patterns of P-CN, Mo-CN-1, Mo-CN-2, Mo-CN-3, Mo-CN-4, and Mo-CN-5.

## 2. Experimental

### 2.1. Chemicals

Melamine ( $C_3H_6N_6$ ) was purchased from Aladdin Chemical Reagent Corp. Ammonium molybdate ( $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ) was purchased from Sinopharm Chemical Reagent Corp, PR China. All these reagents were analytical pure grade and used without further purification.

### 2.2. Preparation of Mo-doped $g-C_3N_4$ catalysts

Typical preparation of the Mo-doped  $g-C_3N_4$  catalysts was as follows: a certain amount of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  (0–1 mmol) and 0.1 mol of melamine ( $C_3H_6N_6$ ) was dissolved in 40 mL of deionized water. The solution was stirring for 2 h to obtain a homogeneous solution. The mixture was poured into Petri dishes to evaporate water at 180 °C for 2 h. After being cooled, the resulted product was placed in a semi-closed crucible with a cover to reduce sublimation. The crucible was heated in the muffle furnace at 550 °C for 4 h in air atmosphere with a heating ramp of 10 °C/min. According to this synthesis route, the Mo-doped  $C_3N_4$  catalysts with different initial Mo element/melamine molar percentage (0, 1%, 2%, 3%, 4% and 5%) were synthesized by tuning the dosage of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ . As a result, the samples were labeled as P-CN, Mo-CN-1, Mo-CN-2, Mo-CN-3, Mo-CN-4 and Mo-CN-5, respectively.

### 2.3. Characterization

The crystallographic phase of the prepared products was determined by Bruker D8 Advance diffractometer (Cu  $K\alpha_1$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ), operated at 40 kV and 40 mA (scanning step: 0.02 °/s) in

the  $2\theta$  range of 10–80°. The morphologies and structure of the prepared samples were examined by a transmission electron microscopy (TEM, JEOL JEM-2010). Nitrogen adsorption–desorption isotherms were measured at 77 K on a BeiShiDe 3H-2000PS4 apparatus. Before measurements, the samples were degassed in vacuum at 200 °C for 6 h. The Brumauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The total pore volume ( $V_t$ ) was estimated at a relative pressure of 0.99. The diffuse reflectance spectra of the samples over a range of 200–800 nm were recorded by a Shimadzu UV-2401 spectrophotometer. Photoluminescence (PL) spectroscopy was performed on a Hitachi F-7000 spectrophotometer at room temperature.

### 2.4. Photocatalytic performance tests

The photocatalytic reduction of  $CO_2$  experiments was carried out in a home-made Teflon-lined stainless chamber with a quartz window at the top for light irradiation. The volume of the chamber was 2700 mL. 0.1 g of the test catalyst powder was located on stainless momentum which was placed in the center of a reactor. The bottom of glass wool support was moisturized with 5.0 g of deionized water to gain saturated water vapor in the reactor. A 300 W Hg lamp was used at the light source of the photocatalytic reaction. Light was passed through a quartz window and the circulated cooling water was used to keep the photoreactor at ambient temperature during the reaction. The distance between the substrate and Hg lamp was about 15 cm (the intensity of light measured by a digital Lux meter is around 108,500 lx), the reaction temperature and pressure were maintained at 30 °C and 110 KPa, respectively. Prior to illumination, the reactor was vacuumed and purged with the  $CO_2 + H_2O$  mixture at about 20 mL/min for 2 h to establish an adsorption–desorption balance. After that, the reactor was tightly closed and the Hg lamp was then switched on to start the experiment. The gas phase products were taken at various time during the irradiation and analyzed by gas chromatography.

## 3. Results and discussion

Fig. 1 illustrates the XRD patterns of the synthesized Mo-doped  $g-C_3N_4$  catalysts with different Mo doping concentrations. The typical  $g-C_3N_4$  has two distinct peaks at 27.5° and 13.2° resulting from structure and tri-s-triazine units, which can be indexed for graphitic materials as the (002) and (100) peaks in JCPDS 87-1526 [28–30]. For doped  $g-C_3N_4$  catalysts, the main peaks are still retained, indicating the crystal structure is not changed. No characteristic peaks for molybdenum compounds, such as molybdenum oxides and molybdenum nitrides are observed in all the doped  $g-C_3N_4$  materials, indicating that the Mo species are embedded into in-planes and coordinate to the  $g-C_3N_4$  matrix by Mo–N bonds

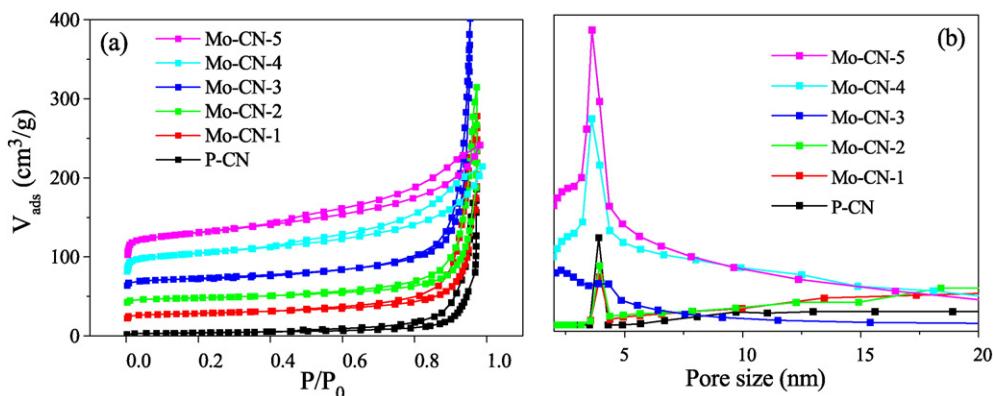


Fig. 2.  $N_2$  adsorption–desorption isotherms (a) and corresponding pore size distribution curves (b) of P-CN, Mo-CN-1, Mo-CN-2, Mo-CN-3, Mo-CN-4, and Mo-CN-5.

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