



## Full Length Article

## Amorphous molybdenum selenide as highly efficient photocatalyst for the photodegradation of organic dyes under visible light



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## ABSTRACT

In this study, a novel nanostructure of amorphous MoSe<sub>x</sub> was produced by a facile low-temperature hydrothermal method. Better adsorption and photodegradation of rhodamine B (RhB) and methylene blue (MB) were achieved with amorphous MoSe<sub>x</sub> than with crystalline MoSe<sub>x</sub> under dark conditions and visible light irradiation. More importantly, the catalytic mechanisms of the amorphous and crystalline samples were compared by free radical-trapping experiments. The results showed that the main active substance that increased the photocatalytic activity in amorphous MoSe<sub>x</sub> was superoxide radicals ( $\cdot\text{O}_2^-$ ), whereas the main active substances for crystalline MoSe<sub>x</sub> were holes ( $h^+$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ). In addition, amorphous MoSe<sub>x</sub> had more unsaturated atoms and a greater specific surface area because of its unique amorphous structure, thus enhancing its photocatalytic performance and adsorption capacity. The study of amorphous molybdenum selenide provides a new idea for improving the photocatalytic activity of two-dimensional materials, which is of great significance.

## 1. Introduction

Using semiconductor photocatalysts for the solar degradation of water pollutants is attractive for alleviating environmental pollution [1,2]. Recently, transition metal dichalcogenides (TMDs) have received much attention owing to their outstanding catalytic activities associated with their two-dimensional (2D) configuration [3–5], i.e., a sandwich structure consisting of X–M–X layers (M = Mo, W and X = S, Se, or Te) [6,7]. In the past few years, researchers have become quite interested in crystalline TMDs nanosheets as photoelectrocatalysts because of their large specific surface area, more active sites, adjustable bandgap, and band position [8,9]. Molybdenum selenide, which has excellent optical absorption and a narrower bandgap (1–2 eV) and is therefore preferred for the photocatalytic degradation of pollutants, has been attracting increased attention recently [10–13]. Nevertheless, the photocatalytic activity of MoSe<sub>2</sub> is limited due to the relatively high reorganization of photogenerated charge carriers and the lack of active sites. Therefore, a great deal of follow-up work was inspired to improve the activity of MoSe<sub>2</sub> nanoparticles by controlling their morphology or design hybrid composites [8,14]. Dai et al. successfully prepared molybdenum diselenide microspheres with a large surface area, thereby improving the photocatalytic performance of the material [15]. Xiong

et al. successfully prepared a heterogeneous structure of perpendicular ultrathin MoSe<sub>2</sub> nanosheets directly grown on grapheme [16]. The heterogeneous structure effectively reduced the recombination of electron holes.

A particularly effective strategy is to prepare a structurally disordered TMD material that can increase the catalytic activity by adjusting the reactive sites [17–19]. Amorphous sulfide (a-MoS<sub>x</sub>; WS<sub>3</sub>), and molybdenum sulfido clusters such as [Mo<sub>3</sub>S<sup>4+</sup>]<sup>4+</sup>, [Mo<sub>3</sub>S<sub>13</sub>]<sup>2-</sup> or [Mo<sub>2</sub>S<sub>12</sub>]<sup>2-</sup> have recently gained attention because of their excellent catalytic activities and robustness [20–24]. Amorphous semiconductor materials have been proven to have higher catalytic performance than crystals [25–27]. Studies have indicated that amorphous MoS<sub>3</sub> particles have higher electrocatalytic activity than other crystalline MoS<sub>2</sub> particles, which may be explained by the greater number of unsaturated sulfur atoms on the surfaces of amorphous sulfide materials composed of S<sub>2</sub><sup>2-</sup> ligands [25]. According to Zhang et al., [26] higher catalytic activity also occurs on amorphous tungsten sulfide, which has a larger surface area and more active sites than crystalline WS<sub>2</sub>. In addition, recent studies have indicated that amorphous MoS<sub>x</sub> could be used as an effective electron-cocatalyst to greatly improve the H<sub>2</sub>-evolution activity of conventional photocatalytic materials [27]. Unfortunately, up to now, the promise of using amorphous molybdenum selenide for the

**Abbreviations:** RhB, rhodamine B; MB, methylene blue; TMDs, transition metal dichalcogenides; 2D, two-dimensional; CTAB, hexadecyltrimethyl ammonium bromide; a-MoSe<sub>x</sub>, amorphous MoSe<sub>x</sub>; a-MoSe<sub>x</sub>, amorphous MoSe<sub>x</sub>; XRD, X-ray diffraction; SEM, Scanning electron microscopy; EDS, Energy dispersive X-ray spectroscopy; XPS, X-ray photoelectron spectroscopy; TEM, transmission electron microscopy; BET, Brunauer–Emmett–Teller; UV–vis, ultraviolet–visible; BZQ, pbenzoquinone; EDTA-2Na, ethylene diamine tetraacetic acid disodium; O<sub>2</sub><sup>-</sup>, superoxide radicals; h<sup>+</sup>, holes; OH, hydroxyl radicals

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photocatalytic degradation of pollutants has not yet been reported, especially the catalytic mechanism as not been studied in detail.

In this study, amorphous molybdenum selenide was prepared by a low-temperature hydrothermal method and applied for visible light degradation of organic dyes. Crystalline  $\text{MoSe}_2$  nanoparticles have been shown to be efficient photocatalysts [28,29]. However, these catalysts are normally prepared at high temperature, in high vacuum or by using expensive instruments. It is notable that the low-temperature hydrothermal method in this paper has the advantages of simple operation, energy saving, time saving and safety, making this amorphous catalyst a promising development prospect. Furthermore, we found that amorphous molybdenum selenide had a higher catalytic activity than crystalline  $\text{MoSe}_x$  and the catalytic mechanisms were studied. Amorphous  $\text{MoSe}_x$  can be considered a promising catalyst as compared to crystalline  $\text{MoSe}_x$  materials.

## 2. Methods

### 2.1. Chemicals

Ammonium molybdatetetrahydrate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$  and sodium selenite ( $\text{Na}_2\text{SeO}_3$ ) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Hydrazine hydrate was obtained from Tianjin Chemical Pharmaceuticals. All chemicals were used without any further purification.

### 2.2. Preparation of amorphous $\text{MoSe}_x$ (a- $\text{MoSe}_x$ )

$\text{Na}_2\text{SeO}_3$  (2.8 mmol) was dispersed in 10 mL hydrazine hydrate and stirred for 30 min to form a brown solution, labeled solution A.  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (0.2 mol) was dissolved in 20 mL distilled water and stirred to form a clear solution, labeled solution B. Then, solution B was slowly added dropwise to solution A. The resulting solution was stirred for 1 h with the color of the mixed solution changed from brown to red and then to dark brown. Thereafter, the above mixed solution was transferred to a 50 mL Teflon-lined autoclave and heated in an oven at low temperatures of 110 °C, 120 °C, 130 °C, and 140 °C for 15 h, respectively. The product was washed with deionized water and alcohol to neutral pH and sonicated for 15 min. The final sample was dried in a drying oven at 60 °C for 6 h.

### 2.3. Preparation of crystalline $\text{MoSe}_x$ (c- $\text{MoSe}_x$ )

For comparison, c- $\text{MoSe}_x$  was also synthesized by using the same proportion of Mo and Se sources and the same cleaning steps. However, calcination condition was performed in a 50 mL Teflon stainless-steel autoclave at 200 °C for 17 h. Then the sample was annealed at 450 °C for 5 h in a nitrogen atmosphere to increase crystallinity.

### 2.4. Characterization

X-ray diffraction (XRD, Bruker D8 Advance) patterns were used to characterize the crystal structures and phase compositions of the samples. The morphology of the samples was characterized by scanning electron microscopy (SEM, LEO1430VP). Energy dispersive X-ray spectroscopy (EDS) was used to identify the constituent components of the sample. The chemical compositions and chemical states of these samples were determined by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). The surface morphology and atomic arrangement of the product were studied using transmission electron microscopy (TEM, Tecnai G2 F20) [30]. The specific surface areas of the products were measured and analyzed by means of a nitrogen adsorption-desorption instrument and a multi-point Brunauer-Emmett-Teller (BET) (Micrometrics TriStar II 3020) method.

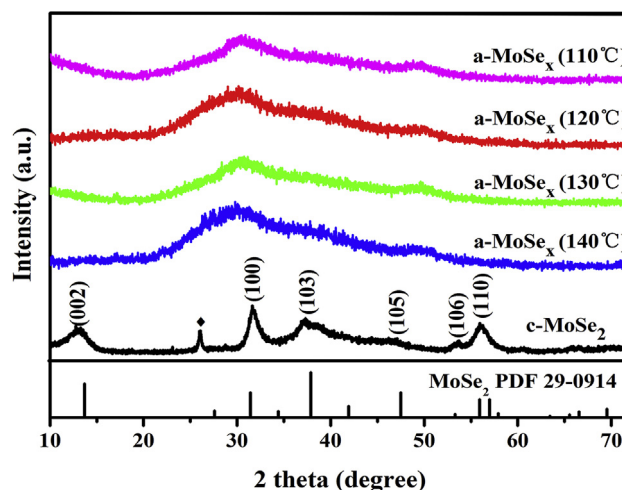


Fig. 1. XRD patterns of a- $\text{MoSe}_x$  samples obtained at reaction temperatures of 110 °C, 120 °C, 130 °C, and 140 °C for 15 h and the c- $\text{MoSe}_2$  sample obtained at 200 °C for 17 h after annealing at 450 °C.

### 2.5. Photocatalytic experiment

The photocatalytic activities of the samples were verified by adsorption and degradation of rhodamine B (RhB) and methylene blue (MB) in dark environments and visible light. The visible light source was a 400 W metal halide lamp equipped with a cut-off filter to completely remove any radiation below 420 nm. The sample powder (10 mg) was added into 30 mL of an aqueous organic dye solution (RhB 30 mg  $\text{L}^{-1}$ , MB 40 mg  $\text{L}^{-1}$ ). Then, the solution was stirred in the dark for 60 min to analyze the adsorption capacity of the sample. After turning on the visible light source, 3 mL of the suspension was collected at the interval of 30 min and analyzed with an ultraviolet-visible (UV-vis) spectrophotometer (Hitachi U-3010).

## 3. Results

### 3.1. Structure investigation

The structures and crystalline phases of the a- $\text{MoSe}_x$  samples were investigated by powder XRD. Fig. 1 shows the XRD patterns of the four a- $\text{MoSe}_x$  samples obtained by calcination at low temperatures of 110 °C, 120 °C, 130 °C and 140 °C for 15 h. C- $\text{MoSe}_x$  as a comparative sample prepared by annealing at 450 °C for 5 h after heating at 200 °C for 17 h. Compared with the diffraction peaks of c- $\text{MoSe}_x$  at approximately  $2\theta = 13.62^\circ, 31.63^\circ, 37.86^\circ,$  and  $55.95^\circ$ , which are indexed to 2H- $\text{MoSe}_2$  (JCPDS Card No. 29-0914) [16], the four a- $\text{MoSe}_x$  samples only show wide diffraction packets near  $2\theta = 30^\circ$ . Significantly, no characteristic diffraction peaks about the molybdenum selenium phases were found in the four a- $\text{MoSe}_x$  samples, indicating that these molybdenum selenium samples had amorphous structures (Fig. 1). The amorphous sample heated at 120 °C for 15 h showed a relatively stable XRD curve. As the reaction temperature increased, the amorphous samples showed crystalline tendencies, whereas when the temperature decreased, the sample yield was small and the curve was very unstable. Combined with the catalytic results, it can be concluded that calcination at 120 °C for 15 h obtain the best amorphous samples.

The low-magnification TEM image of the a- $\text{MoSe}_x$  (120 °C) sample showed that it had an irregular morphology composed of many inhomogeneous nanoparticles (Fig. 2a). The high-magnification TEM image of the same sample clearly revealed that the molybdenum selenide nanoparticles were non-crystalline (no lattice or Moiré fringes

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