Synthesis of CdMoO₄ microspheres by self-assembly and photocatalytic performances

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The role of Cl on the formation of CdMoO₄ microspheres were elucidated in detail. As chloride was taken into the hydrothermal process, CdMoO₄ microspheres were successfully obtained. The Cl absorbed on the surface of the CdMoO₄ microspheres could inhibit the Ostwald ripening process of CdMoO₄ microspheres and it could retard the process of CdMoO₄ microspheres transforming to CdMoO₄ particles. The CdMoO₄ microspheres obtained at 240 °C were the smallest and most porous, which meant a relatively large reaction area. So the photocatalytic activity of CdMoO₄ microspheres obtained at 240 °C was the best of all. Kinetic studies using the radical scavenger technologies suggested that OH was not the dominant photooxidant. Direct hole photooxidation was responsible for the CdMoO₄ microspheres photocatalysis.

1. Introduction

Metal molybdates had a high application potential in various fields such as photoluminescence, microwave applications, optical fibers, scintillator materials, humidity sensors, and catalysis. As an important metal molybate, CdMoO₄ has received increasing attention due to its electronic excitation with VUV synchrotron radiation and pressure-induced phase transformations. Therefore, it is of significance both in fundamental and applied fields to synthesize and characterize CdMoO₄. Recently, a few efforts have been devoted to the exploration of convenient and efficient approaches for the fabrication of CdMoO₄ micro/nanostructures. For example, Ma and co-workers have prepared CdMoO₄ microspheres and nanoparticles through a low temperature hydrothermal method. Single-crystal CdMoO₄ octahedral microparticles also have been produced via a simple microemulsion-mediated route reported by Qian et al. Zhen and co-workers had developed a simple Ostwald ripening process for the preparation of hollow CdMoO₄ microspheres in aqueous solution at room temperature. According to the electronic structures of CdMoO₄ reported by Abraham, CdMoO₄ might possess excellent photocatalytic activity and photoluminescence properties due to its electronic versatility, reactivity, and stability. Therefore, the development of a facile and effective route for synthesizing CdMoO₄ with high photocatalytic activity is of great importance to the potential studies of its physical and chemical properties.

In this work, the chloride ion was taken into the hydrothermal synthesis of CdMoO₄. Because of chemical adsorption of Cl, the Ostwald ripening process of CdMoO₄ was inhibited, and the CdMoO₄ microspheres were successfully obtained.

CdMoO₄ microspheres synthesized by hydrothermal method had not been reported compared with previous work. The effects of temperature and pH value on the formation of CdMoO₄ microspheres were further studied. In addition, the photocatalytic activities and degradation mechanism of CdMoO₄ microspheres in the degradation of methylene blue under ultraviolet light irradiation were investigated in detail.

2. Experimental

2.1 Materials

Methylene blue was of analytical reagent grade quality used without further purification. Other chemicals were commercial products of analytical grade or reagent-grade. All the solutions were prepared with distilled water.
precipitate was washed with distilled water three times. Then, it was dried at 60 °C in air.

2.2.2 Preparation of CdMoO₄ microspheres. In a typical synthesis procedure, Na₂MoO₄·2H₂O (2 mmol) was dissolved in deionized water (14 mL) completely. Under vigorous agitation, an aqueous solution (14 mL) containing CdCl₂·2.5H₂O (2 mmol) was added into the above solution at room temperature. The pH value of the mixture was adjusted with 1 M NaOH and HCl (36%). Then, the mixture was transferred into a Teflon lined steel autoclave of 40 mL and the autoclave heated under autogenous pressure at a series of temperatures for 24 h. Afterwards, the autoclave was cooled to room temperature gradually. The white precipitate was washed with distilled water three times. Then, it was dried at 60 °C in air.

2.3 Characterizations

The degradation rates of methylene blue (MB) solutions were scanned by a Hitachi U-3010 spectrophotometer periodically and the maximum absorption wavelength of MB solution was identified at 664 nm. UV–vis spectra data were recorded in the range from 200 to 800 nm. The pH value was measured by a Model PHSJ-4A pH meter. X-Ray diffraction (XRD) experiments were carried out using a Rigaku DMAX-2400 diffractometer with Cu-Kα radiation. The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5300 ESCA instrument using an Al KR X-ray source at a power of 250 W. The size and morphologies of CdMoO₄ were characterized by the aid of a LEO-1530 field emission scanning electron microscope (SEM). The Brunauer–Emmett–Teller (BET) surface area was measured by ASAP 2010 V5.02H.

2.4 Photocatalytic oxidative degradation

The photocatalytic activities of the CdMoO₄ were evaluated by the MB decomposition under ultraviolet irradiation. Ultraviolet light was obtained by a 12 W Hg lamp (λ = 254 nm, the Institute of Electric Light Sources, Beijing) and the average light intensity was 1 mW cm⁻². The radiant flux was measured with a power meter (the Institute of Electric Light Sources, Beijing).

The photocatalytic degradation of MB in the aqueous solutions was studied by using CdMoO₄ as the photocatalyst under room temperature and normal atmosphere pressure. CdMoO₄ (50mg) and 100ml MB (1 × 10⁻⁵ M) aqueous solution were added into the reactor, and then stirred with a magnetic stirrer prior to irradiation with a Hg lamp at room temperature. After the reaction, the sample solution was put in a centrifuge to remove CdMoO₄ particles from solution. The solution obtained in this way was extracted into a quartz cell. The absorbance of the samples was measured with quartz cells every 5 min.

3. Results and discussion

3.1 Controlling synthesis of CdMoO₄

3.1.1 Synthesis of CdMoO₄ particles. The pH value of the starting precipitate precursors had a crucial effect on the formation of CdMoO₄. The precursor suspensions were adjusted to the desired pH values by adding NaOH solution and HNO₃ solution, and then were hydrothermally treated at 180 °C for 24 h. Fig. 1 showed the XRD patterns of CdMoO₄ samples prepared by a hydrothermal procedure at different pH values. The diffraction peaks of all the samples could be easily indexed as a pure, tetragonal crystalline phase CdMoO₄, which was in good agreement with the standard card (JCPDS Card number: 88-0182). Further increasing the pH value of the starting precipitate precursors to 8 or decreasing the pH value of the starting precipitate precursors to 2 resulted in the product contained in the other phase. The pH value of the starting precipitate precursors had a slight effect on the morphology of CdMoO₄. The microstructures of the as-prepared samples were then investigated by SEM. Fig. 2 shows the SEM micrograph for the
3.1.2 Self-assembly of CdMoO$_4$ microspheres. The precursor suspensions were adjusted to the desired pH values by adding NaOH solution and HCl solution, and then were hydrothermally treated at 180 °C for 24 h. Fig. 3 shows the XRD patterns of CdMoO$_4$ samples prepared by hydrothermal procedure at different pH values. The diffraction peaks of all the samples were also in good agreement with the standard card (JCPDS Card number: 88-0182). Further increasing the pH value of the starting precipitate precursors to 8 or decreasing the pH value of the starting precipitate precursors to 2 also resulted in the product contained in the other phase. The pH value of the starting precipitate precursors had a crucial effect on the morphology of CdMoO$_4$. The microstructures of the as-prepared samples were then investigated by SEM. Fig. 4 showed the SEM micrograph for the sample prepared at different pH values, from which we could find that the morphology of CdMoO$_4$ changed from particles to spheres. Fig. 4a shows the SEM micrograph for the sample prepared at pH 3, from which one could see that the sample were nanoparticles. As the pH value was adjusted to 4, they were a mixture of particles and microspheres, and some microspheres grew on the surface of particles. Some nanoparticles were even embedded inside of the particles. Further increasing the pH value of the starting precipitate precursors to 5 resulted in the obtained products as nearly all microspheres. When the pH value was increased to 6, many of the microspheres were cracked. It became the mixture of microspheres and particles. Upon rising to pH 7, all the uncracked microspheres disappeared. The obtained microspheres were orbicular, but the microspheres were smaller than that prepared at pH 5.

3.2 Formation mechanism of CdMoO$_4$ microspheres

3.2.1 Formation process of CdMoO$_4$. The CdMoO$_4$ particles was a typical hydrothermal ripening process: a highly supersaturated solution was adopted, and irregular microspheres acted as the precursor for the synthesis of crystallized CdMoO$_4$ particles. At the beginning, the direct mixing of the two solutions led to the formation of a lot of irregular microspheres (Fig. 5a).

As hydrothermal treating, irregular microspheres vanished, and larger particles formed, suggesting that the particles grew at the cost of the microspheres (Fig. 5d). The XRD patterns of time series samples treated at 180 °C accorded with SEM, the...
CdMoO₄ crystalline phase appeared after direct mixing of the two solutions (Fig. 6). The diffraction intensities increased along with the reaction time. When the particles formed, the shape of the diffraction peaks became more clean-cut and the intensities increased obviously, indicating a better crystalline phase is formed. For instance, the XRD pattern of the 4 h sample was much more intense than that of the 1 h one.

The CdMoO₄ microspheres grew by a similar hydrothermal ripening process. At the beginning, the direct mixing of the two solutions led to the formation of big microspheres (Fig. 7). It looked like that sphere was assembled by nanoparticles, and the surface of the sphere was very smooth (Fig. 7b). As the reaction continued, the bigger microspheres were broken and smaller microspheres formed (Fig. 7c). The larger particles formed after 8 h hydrothermal treatment. There were cracked microspheres on the surface of the particles, and it looked like the particles were devouring microspheres. That meant the particles formed at the cost of the microspheres, due to the energy difference in solubility between the large particles and the smaller microspheres, according to the well-known Gibbs–Thomson law. But the particles were fewer, the majority were microspheres. The Ostwald ripening process of CdMoO₄ microspheres was restrained, so the microspheres were obtained. On the other hand, the reaction time effects on the crystalline phase were weakened (Fig. 8).

### 3.2.2 Role of Cl on the formation of CdMoO₄ microspheres

The amount of Cl absorbed on the surface of CdMoO₄ microspheres played an important role on the formation of CdMoO₄ microspheres. Because of the strong coordination of the most electronegative Cl⁻ anions to Cd²⁺ cations, which would be accompanied by heterogeneous nucleation, and thus, CdMoO₄ microspheres were preferred. Table 1 showed the XPS results of CdMoO₄ microspheres. The atomic ratio of Cl/Cd increased along with increasing the pH value. The Cl absorbed on the surface of CdMoO₄ could retard the Ostwald ripening process of CdMoO₄ microspheres. The Cl absorbed on the surface of CdMoO₄ also could make nanoparticles which assembled to microspheres excluding each other, so CdMoO₄ microspheres dwindled in size along with atomic ratio of Cl/Cd increasing.

### 3.2.3 Effects of temperature on the formation of CdMoO₄ microspheres

The temperature took a significant effect on the morphology of CdMoO₄. Fig. 9(a–f) showed the morphologies of temperature series samples prepared by self-assembly with addition of chloride ion at pH 7. Based on the SEM images, we found CdMoO₄ microspheres by self-assembly nearly unchanged in size along with temperature increasing from 120 °C to 240 °C. The microspheres obtained at 120 °C were bigger and looked like they were assembled by nanoparticles. The surface of the sphere was smooth and tight. The microspheres became much smaller.
and more porous along with rising temperature. It belonged to Cl absorbed on the surface of CdMoO₄. The Cl atoms could coordinate with Cd atoms of CdMoO₄, and it belonged to chemical adsorption. The increasing temperature could accelerate the speed of Cl atoms absorbed on the surface of CdMoO₄. So CdMoO₄ microspheres dwindled in size along with increasing temperature.

3.3 Optical properties and photocatalytic activity of CdMoO₄ microspheres

Optical absorption of the CdMoO₄ microspheres was measured by using an UV-vis spectrometer. Fig. 10 showed a typical diffuse reflection spectrum of CdMoO₄ obtained at different pH values. The optical absorption of the CdMoO₄ microspheres was nearly the same. The steep shape of the spectra indicated that the absorption was not due to the transition from the impurity level but was due to the band-gap transition.

Fig. 11 showed the degradation of MB using pH series CdMoO₄ microspheres. The first-order linear relationship was revealed by the plots of the ln(C/C₀) vs. irradiation time (t), where C is the concentration of MB at the irradiation time t and C₀ is the concentration in the adsorption equilibrium of the photocatalysts before irradiation. As could be seen from Fig. 10, MB solution could be stably reserved under ultraviolet light irradiation. By the first order linear fit, the determined reaction-rate constants k were 0.0127, 0.01288, 0.03475, 0.05692 and 0.06116 min⁻¹, respectively, for the pH series samples. The catalysts obtained at higher pH value showed higher activity than the ones synthesized at lower pH value. The difference in the photocatalytic activity may partly be attributed to the fact that the microspheres obtained at higher pH value had fewer defects and a larger surface area, which meant a relatively large reaction area. The surface area of CdMoO₄ microspheres obtained at different pH values are shown in Table 2. The photocatalytic activity of CdMoO₄ nanoparticles obtained at pH 3 was the lowest of all. The XRD intensities of samples obtained at pH 3 were the lowest of all, so there were lots of defects in the samples obtained at pH 3. A lot of defects could act as an electron-hole recombination center, so the photocatalytic activity was the lowest. The photocatalytic activity of CdMoO₄ microspheres obtained at pH 4 was similar to CdMoO₄ nanoparticles obtained at pH 3. The reason was that CdMoO₄ obtained at pH 4 had fewer defects than CdMoO₄ nanoparticles obtained at pH 3.

### Table 1 The XPS results of CdMoO₄ microspheres

<table>
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Fig. 9 Morphologies of temperature series CdMoO₄ microspheres: (a) 120 °C, (b) 140 °C, (c) 160 °C, (d) 200 °C, (e) 220 °C, (f) 240 °C.

Fig. 10 UV–vis diffuse reflectance spectra of CdMoO₄ microspheres: pH value series samples treated at 180 °C.

Fig. 11 First-order plots for the photocatalytic degradation of MB using various CdMoO₄ microspheres: pH series samples.
although the surface area of CdMoO$_4$ obtained at pH 4 was the smallest of all. So the photocatalytic activity was similar. The XRD intensity of CdMoO$_4$ obtained at pH 6 was the highest of all, which meant CdMoO$_4$ obtained at pH 6 had the fewest defects among the pH series samples. The CdMoO$_4$ obtained at pH 7 had a relatively larger reaction area. So the photocatalytic activity of CdMoO$_4$ obtained at pH 6 and at pH 7 was similar. The XRD intensity of CdMoO$_4$ obtained at pH 5 was similar to CdMoO$_4$ obtained at pH 4 and 7, and the surface area of CdMoO$_4$ microspheres obtained at pH 5 was between that at pH 4 and 7. So the photocatalytic activity of CdMoO$_4$ obtained at pH 5 was between pH 4 and pH 7.

Temperature took an effect on the photocatalytic activity. Fig. 12 shows the degradation of MB using temperature series CdMoO$_4$ microspheres. By the first order linear fit, the determined reaction-rate constants $k$ were 0.0494, 0.07386, 0.06773, 0.07112, 0.07018 and 0.08857 min$^{-1}$, respectively, for the temperature series samples. Among temperature series samples, the XRD intensities were similar (Fig. 13). The photocatalytic activity may be attributable to the morphology of CdMoO$_4$ microspheres. The CdMoO$_4$ microspheres obtained at 120$^\circ$C were the biggest and the surface of the sphere was tight, which meant a relatively small reaction area. The morphology of CdMoO$_4$ microspheres obtained between 140$^\circ$C and 220$^\circ$C was similar, so the photocatalytic activity of CdMoO$_4$ microspheres obtained between 140$^\circ$C and 220$^\circ$C was similar. The CdMoO$_4$ microspheres obtained at 240$^\circ$C were the smallest and most porous, which meant a relatively large reaction area. So the photocatalytic activity of CdMoO$_4$ microspheres obtained at 240$^\circ$C was the best of all. As the photocatalysis reaction was under a Hg lamp, photo-degradation of MB with CdMoO$_4$ microspheres occurred only via one process: a photocatalytic process. In order to differentiate direct photooxidation of MB with hole and indirect photooxidation with OH radicals, experiments were carried out by adding tert-butyl alcohol to minimize the formation of OH radicals. As shown in Fig. 14, the addition of scavenger of hydroxyl radicals (tert-butanol) caused small changes in the degradation rate of MB, indicating that the free hydroxyl radicals are not the main active oxygen species in the photochemical process. The direct hole photooxidation mainly governs the photocatalytic process, which is consistent with the literature.$^{38,39}$

### 4. Conclusions

The Ostwald ripening process of CdMoO$_4$ was inhibited due to the chemical adsorption of Cl, thus, CdMoO$_4$ microspheres were obtained. It was found that CdMoO$_4$ microspheres obtained at 240$^\circ$C possessed the highest photocatalytic activity towards the degradation of MB. The highly catalytic activity could be attributed to the fact that the CdMoO$_4$ microspheres obtained at 240$^\circ$C were the smallest and most porous, which meant a relatively large reaction area. The direct hole photooxidation could
play an important role. As a result, the photodegradation of MB on CdMoO₄ microspheres was little affected by the presence of the OH radical scavenger.

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Notes and references