

# Synthesis and characterization of decahedral CdMoO<sub>4</sub> microcrystals using ionic liquid surfactant

D. ZHU<sup>a</sup>, K. LI<sup>b</sup>, X. CHEN<sup>b</sup>, T. YING<sup>a,b,\*</sup>

<sup>a</sup>Chuyang Honor College, Zhejiang Normal University, Jinhua, 321004, China

<sup>b</sup>College of Chemistry and Life Science, Zhejiang Normal University, Jinhua, 321004, China

Decahedral CdMoO<sub>4</sub> microcrystals have been synthesized by a reaction for 48 hours at 60 °C from CdCl<sub>2</sub> and Na<sub>2</sub>MoO<sub>4</sub> in the presence of 4 mL ionic liquid 1-n-butyl-3-methylimidazolium chloride ([BMIM]Cl) as a surfactant. Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the structure and morphology of the microcrystals. The photoluminescence (PL) spectrum of the as-synthesized decahedral CdMoO<sub>4</sub> microcrystals exhibits a strong and broad emission at visible zone. A plausible formation mechanism of decahedral CdMoO<sub>4</sub> microcrystals was discussed in detail and evaluates as a typical Ostwald Ripening process. It is expected that this method can be extended to the fabrication of other microcrystals of metallic salts.

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## 1. Introduction

Recent years, metal molybdates as a new kind of photoelectric functional material and semiconducting material have received increasing attention because of their potential applications in photoluminescence, industrial catalysts, sensors, optical fibers, electrode materials, photocatalysts, scintillators [1-7]. Among them, CdMoO<sub>4</sub> is outstanding due to its unique electro-optical properties and high photocatalytic activity [8-11]. Researchers have utilized many methods to synthesis different morphologies of its nano/micro structure. For example, Ma synthesized CdMoO<sub>4</sub> nanoparticles by a hydrothermal process at a low temperature of 90°C [12]. Crystal CdMoO<sub>4</sub> octahedral microparticles were synthesized via microemulsion-mediated route by Qian [13]. Zhen prepared hollow CdMoO<sub>4</sub> microspheres via a template-free aqueous solution method with the assistance of NaCl at room temperature [14].

Nowadays, room-temperature ionic liquids (RTILs) have been studied widely as “green” reaction media due to their unique chemical and physical properties, such as negligible vapor press, good dissolving ability, designable structures, etc [15]. In the field of the inorganic materials, some nano/microdevices with different morphologies have been synthesized successfully via RTILs, such as Bi<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> nanorods [16], CuO nanosheets and nanowhiskers [17], Co<sub>3</sub>O<sub>4</sub> nanoparticles [18], leaf-like CuO [19], TiO<sub>2</sub> Microspheres [20] and so on. All these investigations indicate that RTILs can play a role of a surfactant solvent or template, which made the particles have unique structures and receive some more excellent optical, magnetic and electrical properties.

Recently, we have synthesized CdMoO<sub>4</sub> microtubes

using RTILs as sacrificial template [21]. Furthermore, our results indicate RTILs can also act as surfactant and achieve different morphology of CdMoO<sub>4</sub>. Herein, we report the synthesis of decahedral CdMoO<sub>4</sub> microcrystals by a very simple one-step method using ionic liquid surfactant. This is the first time report for ionic liquid assisted formation of decahedral CdMoO<sub>4</sub> microcrystals. A possible mechanism was discussed to demonstrate the formation of them.

## 2. Experiment section

Cadmium chloride (CdCl<sub>2</sub>·2.5H<sub>2</sub>O), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) and ethanol were all analytical reagents without further purification. [BMIM]Cl was synthesized according to the procedures in the literature [22]. In a typical reaction, CdCl<sub>2</sub> (0.46 g) was dissolved in 10 mL distilled water to form homogeneous solution in a glass flask. Then 4 mL [BMIM]Cl was added to the aqueous solution under stirring ceaselessly. 10 mL Na<sub>2</sub>MoO<sub>4</sub> aqueous solution (0.2mol/L) was added into the above solution and stirring for 1 min. The reaction mixture was then stored at 60°C for 48 h. The white product was separated by centrifugation, washed with distilled water and absolute ethanol, and dried under vacuum at 60 °C for 6 h.

XRD patterns were recorded using an X-ray diffractometer (PW 3040/60, Philips X'Pert, the Netherlands) with high-intensity Cu K $\alpha$  radiation ( $\lambda=0.15405$  nm) operating at 40 kV and 40 mA with 2 $\theta$  ranging from 20° to 80°. Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 apparatus operating at 40 kV. A PL spectrum was recorded

on an Edinburgh FL-920 fluorescence spectrometer using the 310 nm exciton of 50W-Xe laser at room temperature.

### 3. Results and discussion

As the Fig. 1 shows, all these diffraction peaks of the sample can be indexed as the (112), (004), (200), (211), (114), (123), (204), (220), (116), (132), (224), (008), (400), (316). It confirms that the sample is consisted of a single phase of crystalline  $\text{CdMoO}_4$  with a tetragonal structure (JCPDS 88-182) and there're no characteristic peaks related to impurities. The result indicates the sample obtained is pure  $\text{CdMoO}_4$ .

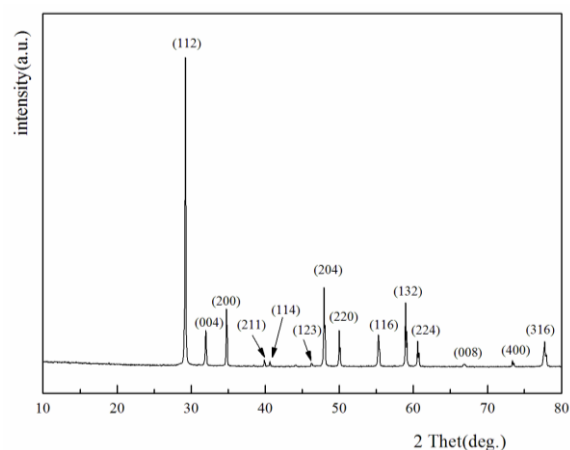


Fig. 1. XRD pattern of the sample obtained in 4 mL [BMIM]Cl at 60 °C for 48 h.

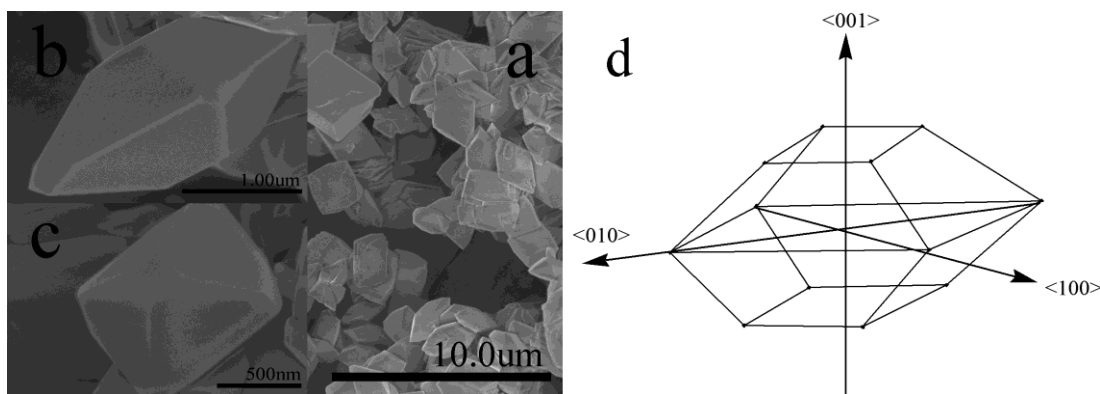


Fig. 2. (a-c) SEM images of sample obtained at optimum condition in different amplification factors; (d) is the structural scheme of the  $\text{CdMoO}_4$  particles.

The general morphology of  $\text{CdMoO}_4$  microstructures prepared is shown in Fig. 2. Decahedral  $\text{CdMoO}_4$  microcrystals with uniform shape and size were obtained on a large scale (Fig. 3(a)). The higher magnification images ((Fig. 2(b-c)) show that those particles are in decahedral morphology, just like an octahedron without two apexes. The structural scheme of the  $\text{CdMoO}_4$  particles is shown as Fig. 2(d). These decahedral undersides were squares and their four hemlines in the range of 0.8-1.0  $\mu\text{m}$ , the thicknesses of microcrystals are about 1.0  $\mu\text{m}$ . And their surfaces are extremely smooth without any small particles attached on them.

In order to investigate the mechanism of this reaction, we applied 2 mL ionic liquid as surfactant to pursue the process. As the Fig 3(a) displays, at the beginning of the reaction, lots of microtube precursors which combined ionic liquid with  $\text{Cd}^{2+}$  cation were formed. When the reaction time was prolonged to 24 hours, many microspheres with diameters about 0.9  $\mu\text{m}$  were emerged and microtube precursors have disappeared (Fig. 3(b)). However, the surfaces of microspheres were rough and they were composed of numerous nanosheets. Further prolonging the reaction time, these nanosheet structures could piece together, assemble, grow, and shed off from

spheres and spherical aggregations with diameter ranging from 1.0  $\mu\text{m}$  to 1.5  $\mu\text{m}$  were obtained. As shown in Fig. 3(c), spherical aggregations like pompons, and the building units of the aggregations were small decahedral microparticles were found in.

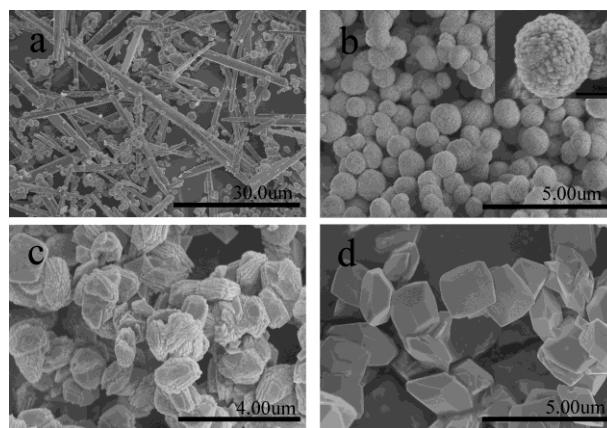


Fig. 3. (a-d) SEM images of samples synthesized by 2 mL [BMIM]Cl for different time at 60 °C: a—0h, b—24h, c—60h, d—96h.

Finally, sphere structures and aggregations disappeared gradually and formed perfect decahedral CdMoO<sub>4</sub> microcrystals which were presented in Fig. 3(d). Based on the above experimental results, we proposed a plausible formation mechanism of decahedral CdMoO<sub>4</sub> microcrystal, which is interpreted in Fig. 4.

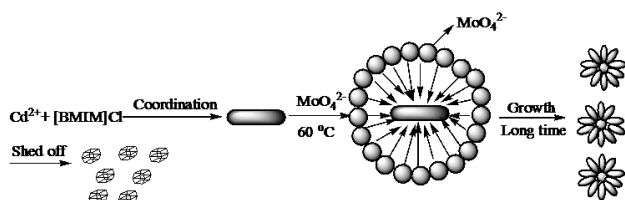


Fig. 4. The formation mechanism of decahedral CdMoO<sub>4</sub> microcrystals.

From the formation mechanism, it is a typical Ostwald Ripening process clearly. During the process, dozens of smaller particles or monomers were consumed in solution and resulted in the occurrence of bigger particles, as prolonging the reaction time. It was confirmed by the transformation from uniform microspheres constructed with nanosheets to the decahedrons with smooth surface (Fig. 3(b-c)). On the other hand, we are sure that the [BMIM]Cl as surfactant molecules played a remarkable ploy. [BMIM]Cl was adsorbed on the faces of the prime crystals selectively and the anisotropic growth habit of CdMoO<sub>4</sub> microcrystals, results in the formation of decahedral CdMoO<sub>4</sub> microcrystals [13,23].

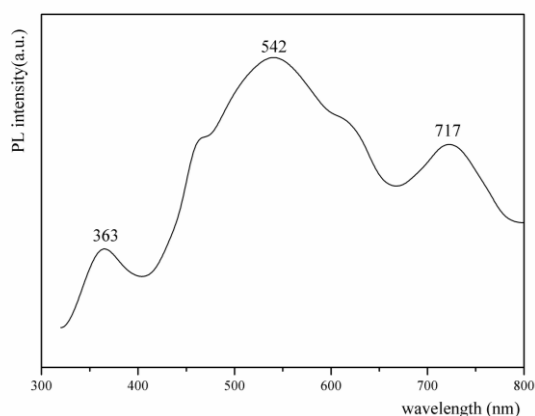


Fig. 5. Photoluminescence spectra of decahedral CdMoO<sub>4</sub> microcrystals.

Fig. 5 presents the PL spectra of this sample with an excitation wavelength of 310 nm at room temperature. It displays an emission peak at 363 nm, and the peak is a blue shift of 16 nm compared with the literature [24] reports at 379 nm. Besides this peak, another two visible emission peaks are also shown distinctly. One of them is a strong and broad emission peak which centered at 542 nm, and the other one is at 717 nm which is weaker than 542

nm. Compared with departed literature [10, 11, 24], the PL spectra of the decahedral CdMoO<sub>4</sub> microcrystals have more emission peaks and their positions shift a lot. It is commonly attributed to the complex morphology of as-synthesized sample. The results show as-synthesized CdMoO<sub>4</sub> microcrystals may have huge potential value on photoelectric material.

## 4. Conclusions

In summary, decahedral CdMoO<sub>4</sub> microcrystals have been fabricated successfully in the presence of ionic liquid. From the possible mechanism, the surfactant molecules [BMIM]Cl and reaction time are key factors for the formation of decahedral CdMoO<sub>4</sub> microcrystals. It is remarkable that the PL spectra display the superior optical property of CdMoO<sub>4</sub> as-synthesized. It indicates that this kind of CdMoO<sub>4</sub> can be used to solar cells, photoelectric materials and photocatalytic materials. It is a simple, convenient and efficient approach to synthesis microcrystals with specific morphology via ionic liquid and this method can be used to synthesize other microcrystals of metallic salts.

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\*Corresponding author: sky50@zjnu.cn