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Morphology-tunable synthesis of $SrWO_4$ crystals via biomimetic supported liquid membrane (SLM) system

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Abstract $SrWO_4$ crystals with various morphologies have been synthesized via a system of supported liquid membrane in the presence of different additive reagents at room temperature. The X-ray diffraction patterns show that the obtained $SrWO_4$ crystals belong to tetragonal structure. Scanning electron microscopy results reveal that additive reagents can highly affect the morphology and size of $SrWO_4$ crystals. In fluorescence spectra there is a blue-shift emission peak at room temperature, which shows that it has potential applications in device designs and photoelectron fields. A possible growth mechanism is discussed.

Introduction

The synthesis of inorganic materials with well-defined morphologies has attracted considerable attention, for the size and morphology of materials can be designed according to the desired requirements of devices [1–4].

Particularly, the hierarchical and complex nano-/microstructures have been assembled by nanoparticles, nanorods, nanoribbons, and nanobelts at different levels in recent years [5–8]. Until now, various kinds of compound materials, such as metal oxide, [9–12] sulfide, [13, 14] hydrate, [15] and other nanostructures [16–18] have been synthesized with controlled hierarchical/complex morphologies.

AWO_4 (A = Ca, Sr, Ba) [19–31] have attracted particular attention because they were found of particular importance as laser host materials in quantum electronics and scintillators in medical applications. The luminescence of AWO_4, which can be excited by short-wavelength ultraviolet radiation, X-rays, and cathode rays, mainly shows a blue emission spectrum. Compared to $CaWO_4$ [19–24] and $BaWO_4$, [25–31] the shape control of $SrWO_4$ nanocrystals were studied limitedly. Meanwhile, there is no report on preparing hierarchical/complex morphologies $SrWO_4$ materials through supported liquid membrane (SLM) system.

The SLM system is composed of membrane solvent, mobile carrier, and porous polymer membrane. It not only plays a role in transporting reversing concentration grades ions like “K-Na pump”, but also in assembling inorganic materials like biomineralization process guided by collagen. Therefore, such system has noticeable biomimetic functions. The SLM system was often used to separate noble metal ions from waster water and enrich sample. In 2004, our research group introduced this system into material synthesis and design for the first time [32]. Further studies indicate that this system is also good at controlling morphologies of materials.

Herein the SLM system is used to synthesize $SrWO_4$ crystals with different morphologies at room temperature. The results reveal that additive reagents and reacting time obviously affect the morphology and size of $SrWO_4$ crystals. Their morphologies, structure, and luminescence properties are investigated. A possible growth mechanism of $SrWO_4$ crystals is proposed. This method may provide a significant reference for preparing more materials with special morphologies and structures.

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Experimental procedure

In a typical procedure, 0.2 g *o*-phenanthroline (Phen), as mobile carrier, was added into 80 mL chloroform under vigorous stirring at 3000 rpm for 15 min to form an oil phase. Then a dried polymer membrane was immersed into the oil phase for 48 h to format SLM. The polymer membrane, a kind of commercial product, is a micro-pore film made by esterified fibrin and the pore diameter is about 200–250 nm. The SLM was treated with filter paper to eliminate remnant oil on the surface. Then the SLM was solidified in a reactor to separate it into two horizontal compartments, which were respectively added into isometric 20 mL of 0.1 M Na_2WO_4 and $SrCl_2$ solutions. Then 3 mL of 0.01 M additive reagent was added into the side of Na_2WO_4. White precipitation was generated in the Na_2WO_4 side and was collected by centrifugation after 48 hours reaction, and then washed the precipitation by distilled water, acetone, and absolute ethanol in turn. The obtained white product was kept in absolute ethanol.

The power X-ray diffraction was performed with a Bruker D8-advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å) (German). Surface microstructures were observed by a Scanning Electron Microscope FEI/Phillips XL30 (SEM, Holland). Fluorescence spectra of the samples were obtained by a Perkin-Elmer luminescence spectrophotometer (LS-55, USA).

Results and discussion

Figure 1 shows the $SrWO_4$ crystal grows in the SLM system in the absence of additive reagent. The crystal is peanut-like and the morphology is uniform. From the high magnification SEM image Fig. 1b, it is clear that the petal is assembled by small bouquets and there are obviously hierarchical nano-architectures. The diameter of bipolar petal is ca. 4 μm.

Figure 2 shows the $SrWO_4$ crystal grows in the SLM system in the presence of citric acid as additive reagent. When the reacting time is 12 h, the obtained $SrWO_4$ crystal shown in Fig. 2a, is uniform flake-like with the length ca. 5 μm, the width ca. 1 μm, and the thickness ca. 100 nm. When reacting time is prolonged, the flakes self-assembled into square tubes and feather-like flakes, which is shown in Fig. 2b. Figure 2c and d are the high magnification SEM images of Fig. 2b. It has potential applications in design materials and devices in the future.

Figure 3 shows the $SrWO_4$ crystal grows in the SLM system in the presence of ethylenediamine as additive reagent. The obtained $SrWO_4$ morphology is uniform bud-like. The stalk is more than 30 μm in length and diameter is ca. 1 μm. It is obvious that every stalk has several shooters, which indicates the crystal growth process. Therefore, we propose that the bud-like $SrWO_4$ is also self-assembled by hierarchical nano-architectures.

From the changes in above SEM images, it is clear that the morphology can be modified by adding different reagents. When citric acid is introduced, the morphology changes from peanut into flake and further assembled into square tubes and feather-like flakes if prolong the reacting time. When ethylenediamine is introduced, the morphology changes into bud-like with several shooters. Therefore, we can design different morphologies according to the applications.

X-ray powder diffraction (XRD) analysis was used to determine the structure of obtained $SrWO_4$. All the XRD patterns are similar. Figure 4 presents the XRD pattern of the typical sample. All peaks in the pattern are well indexed to the tetragonal phases of $SrWO_4$. The cell lattice constants of product are calculated and corrected by MDI Jade (5.0 Edition) software. The calculated lattice constants (a = 5.416 (2) Å, c = 11.95 (4) Å) are accordant with the tetragonal-structure $SrWO_4$ (JCPDS: 08-0490).

Based on above-obtained SEM and XRD results, it is clear that morphologies and sizes of $SrWO_4$ crystals can be controlled by adding different reagents into the SLM system. A mechanism about $SrWO_4$ crystals growth is proposed as follows:

First, Sr^{2+} ions combined with Phen and were carried to other side of SLM system by the selective transportation. Then the ions were captured by WO_4^{2-} ions. In the absence of additive reagents, the nuclear seeds were easily formed under high concentration of free Sr^{2+} ions. Crystals were grown under their own innate habits: anisotropic grain growth along c-axis orientation, which made $SrWO_4$

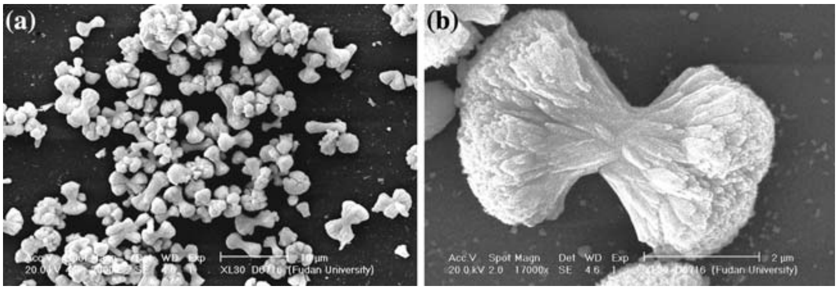

Fig. 1 In the absence of additive reagent: (**a**) Low and (**b**) high magnification SEM images synthesized in the SLM system

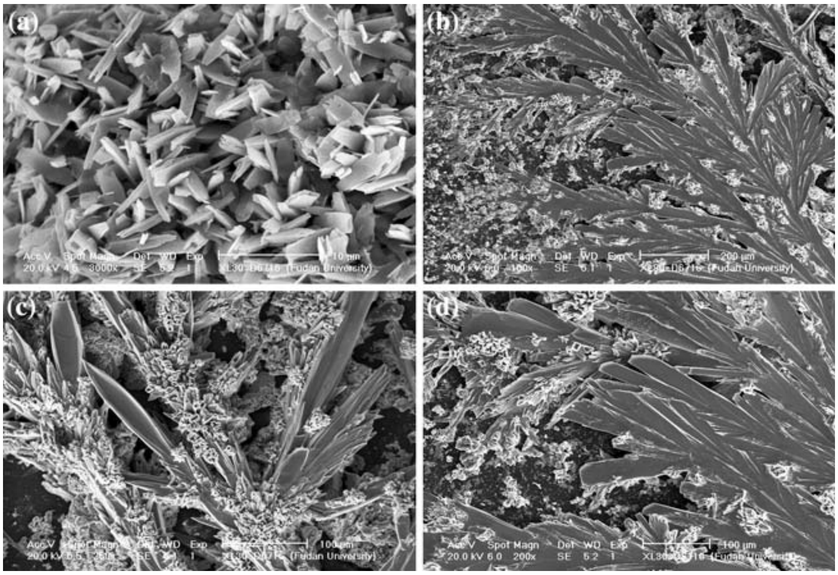

Fig. 2 In the presence of citric acid as additive reagent, (**a**) the reacting time is 12 h, (**b**) the reacting time is 48 h, (**c**) and (**d**) are the parts high- magnification SEM images of (**b**) synthesized in the SLM system

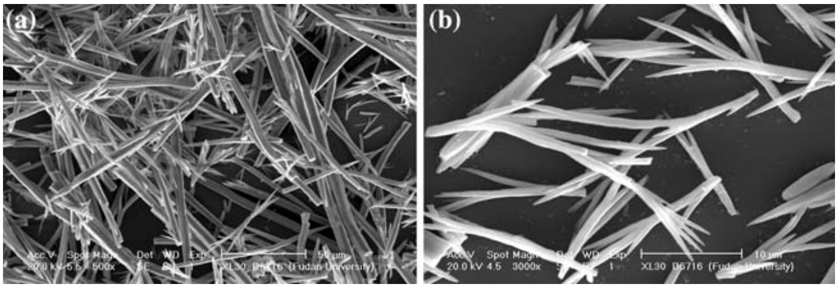

Fig. 3 In the presence of ethylenediamine as additive reagent, (**a**) Low and (**b**) high magnification SEM images synthesized in the SLM system

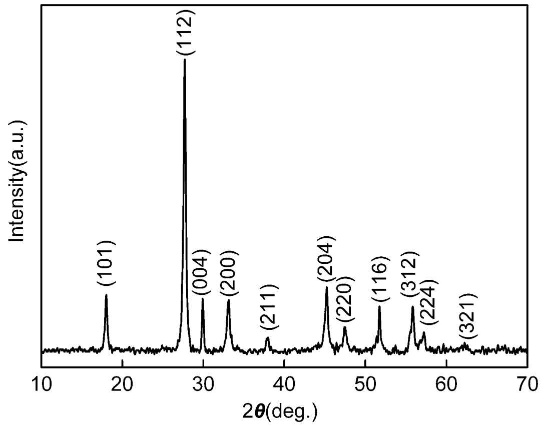

Fig. 4 The typical XRD patterns of obtained SrWO4 crystals

particles grow into pyramidal poles; and then the small pyramidal poles self-assembled into peanut-like morphology. When the additive reagents were applied, the surfactants affected nuclear seeds formation, crystal anisotropic growth, and aggregated orientation. The crystal surface energy can be modulated by different surfactants that absorb onto surfaces of growing crystallites. The line-structure ethylenediamine resulted in the $SrWO_4$ crystal growing in line- or rod-like appearance. Then they self-assembled into bud-like. Citric acid is also line-like structure, but it has three pincers of –COOH functional group. The –COOH group made citric acid strongly absorb on the surface of nuclear seeds and affect the crystal growth tendency. Therefore, the obtained $SrWO_4$ crystal showed flake-like appearance at presence of citric acid. Then the flakes self-assembled into square tubes or feather-like flakes. We purposed the flakes were oriented aggregation into big flakes if they adsorbed by the two bottoms –COOH group, contrarily, if the flakes were absorbed by middle and bottom –COOH groups, the flakes were oriented aggregation into square tubes.

Figure 5 shows the fluorescence spectra of the as-prepared $SrWO_4$ crystals with 3 mL citric acid (0.01 M) for 48 h. It is found that emitting peak is at 375 nm when excited at 300 nm at room temperature. The emitting peak of product is evident blue-shifted compared to other literatures reported at 460 nm [33, 34]. This is probably attributed to the quantum size effect or crystalline imperfection [35], which is in good agreement with the as-prepared $SrWO_4$ crystals composed of nanoparticles. The as-synthesized $SrWO_4$ crystals with excellent blue-shift luminescence have potential applications in photo-electric field and device design.

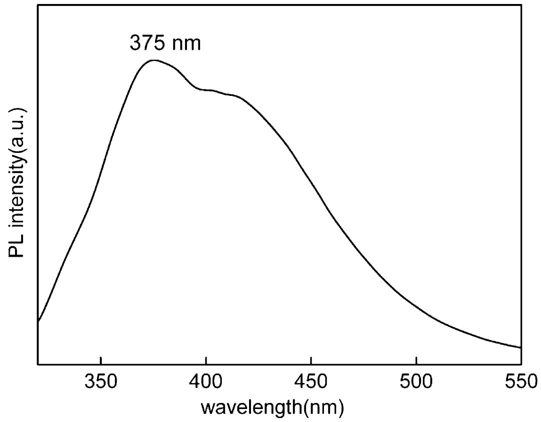

Fig. 5 PL spectra of as-prepared $SrWO_4$ crystals (ex = 300 nm)

Conclusion

At room temperature, tetragonal $SrWO_4$ crystals are synthesized by SLM system. The morphologies and sizes of $SrWO_4$ crystals can be controlled through adding different reagents and adjusting reaction time. The as-synthesized $SrWO_4$ crystals have some potential applications because of their special luminescence. This method is important to widen biomineralization field, and also provide a new route for materials' control synthesis.

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