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Synthesis and Luminescence Property of Hierarchical Europium Oxalate Micropaticles

Wei Zhu, You-jin Zhang*, Hong-mei He, Zhi-yong Fang

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

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Hierarchical europium oxalate $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles were synthesized through a simple precipitation method at room temperature in present of trisodium citrate. The products were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, and photoluminescence. The possible formation mechanism of the hierarchical europium oxalate $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles was discussed.

Key words: Hierarchy, Europium oxalate, Precipitation method, Photoluminescence

I. INTRODUCTION

In current years, the precise design and synthesis of inorganic micro/nanostructure materials with well-defined morphologies and tunable sizes have been still attracting the material scientists' considerable attention because the chemical and physical properties of functional materials consisting of inorganic compounds are fundamentally related to their size, shape, and dimensionality [1–6]. Particularly, the arrangement of micro/nanostructured building blocks into hierarchical structures has been proposed and partially realized [7–10]. To date, a wide variety of inorganic compounds have been successfully prepared with hierarchical structures by various methods [11–15]. Among these methods, precipitation method is a promising method which is cost-effective, efficient, and easy to manipulate. During the preparing process, coordination agents or surfactants usually act an important role in controlling material morphology [16–18].

On the other side, lanthanide compounds such as oxides, sulfides, hydrates, and fluorides, have attractive applications in medicine, biology, chemistry, magnetism and optics [19–23]. As a precursor to prepare lanthanide oxides and functional materials in magnetic sensors, catalysis, ceramics and luminescence, lanthanide oxalates, and mixed lanthanide oxalates such as neodymium praseodymium oxalate, lanthanide metal-organic frameworks, and lanthanide calcium oxalate, have been studied [24–27]. Furthermore, single crystal of $Ln_2(C_2O_4)_3{\cdot}nH_2O$ has been prepared and characterized. Hirai *et al.* prepared spherical $Ln_2(C_2O_4)_3{\cdot}nH_2O$ (Ln=Ce, Pr, Nd, Sm, Eu, Gd, Dy, Y, and Yb) by using an emulsion liquid membrane (ELM) system, consisting of Span 83 as a surfactant and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (EHPNA) ester or bis(1,1,3,3-tetramethylbutyl) phosphinic acid as an extractant [28, 29]. Ollendorff and Weigel obtained single crystals of $Ln_2(C_2O_4)_3{\cdot}10H_2O$ (Ln=La, Ce, Pr, and Nd) by slowly cooling hot and saturated solutions of the oxides in a mixture of sulfuric and oxalic acids [30].

In this work, hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ was successfully synthesized by a precipitation method at room temperature in present of Na_3Cit ($C_6H_5Na_3O_7{\cdot}2H_2O$). The products were characterized. The influence of the experimental parameters such as temperature, time, assistants and the amount of Cit^{3-} on the morphology of the product was investigated. Furthermore, the optical property of hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ was characterized. As far as we know, the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ has not been reported.

II. EXPERIMENTS

All chemical reagents in this work are analytical grade and used as purchased without further purification. In a typical procedure, 0.5 mmol Eu_2O_3 was dissolved in dilute HCl solution under heating with agitation, and a colorless solution of $EuCl_3$ was formed. After removing the solvent, $EuCl_3$ powder was obtained. Then 5 mL distilled water was added to form a clear aqueous solution and an aqueous solution of Na_3Cit (1.2 mmol) was added into the clear aqueous solution. After the solution was stirred at room temperature for 30 min to form europium citrate complexes, 1.5 mmol $H_2C_2O_4$ was added into the solution. After being stirred for 10 min, the as-obtained white colloidal solution was transferred into a beaker and sealed for 24 h. The precipitate was washed several times with distilled water and dried at 80 °C for 6 h. The product was obtained.

X-ray diffraction (XRD) was examined by a Japan

*Author to whom correspondence should be addressed. E-mail: zyj@ustc.edu.cn

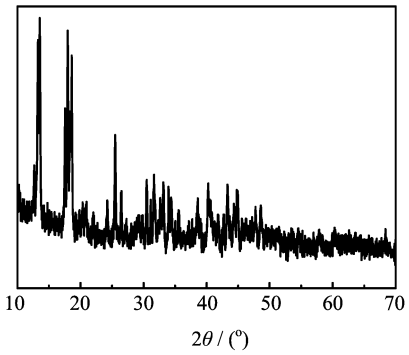

FIG. 1 XRD pattern of the $Eu_2(C_2O_4)_3{\cdot}10H_2O$ sample.

Rigaku D/max rA X-ray diffractometer equipped with graphite-monochromatized high-intensity Cu Kα radiation (λ=0.15478 nm). The scanning rate was 0.05°/s in the 2θ range from 10° to 70°. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB MK II X-ray photoelectron spectrometer, using Mg Kr radiation as the excitation source. Field-emission scanning electron microscopy (FESEM) images were obtained on a JEOL-6300F field-emission scanning electron microscope with an accelerating voltage of 15 kV. Photoluminescence (PL) was carried out using a Jobin Yvon Fluorolog-3-TAU steady-state/lifetime spectrofluorometer.

III. RESULTS AND DISCUSSION

A. XRD

The XRD pattern of the as-synthesized product is shown in Fig.1. The diffraction peaks of the product can be indexed to the monoclinic phase $Eu_2(C_2O_4)_3{\cdot}10H_2O$ (JCPDS card No.00-020-0400; a=1.109 nm, b=0.964 nm, c=1.012 nm).

B. XPS analysis

The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C1s to 284.60 eV. The survey XPS spectrum of the product (Fig.2(a)) indicates that Eu is the only metal element on the surface of the sample. Figure 2(b) shows that the binding energy of 1134.9 and 1164.4 eV are $Eu3d_{5/2}$ and $Eu3d_{3/2}$ respectively [31]. Figure 2 (c) and (d) indicate O1s and C1s respectively.

C. Morphologies of the as-synthesized products

The morphology of the product was investigated by FESEM. The images of the as-synthesized product are shown in Fig.3. The FESEM images of the samples obtained at different reaction conditions were also given in Fig.3.

Figure 3 (a)–(c) show the images of the samples obtained at different temperatures. Figure 4(a) indicates the image of $Eu_2(C_2O_4)_3{\cdot}10H_2O$ with hierarchical structure obtained at room temperature. The product $Eu_2(C_2O_4)_3{\cdot}10H_2O$ obtained at 100 and 120 °C have not clear hierarchical structure (Fig.3 (b) and (c)).

Figure 3 (d)–(f) show the images of the samples obtained at room temperature for 0, 12, and 24 h respectively. As the time was growing, the self-assembling process was observed clearly from Fig.3 (d)–(f). In Fig.3(d), $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-flakes were found, and when prolonging the reaction time, more $Eu_2(C_2O_4)_3{\cdot}10H_2O$ hierarchical structure would be detected (Fig.3 (e) and (f)).

The influence of the amount of Na_3Cit on the morphology of the product was further investigated. Figure 3 (g)–(i) show the FESEM images of the samples obtained at room temperature for 24 h when the different amounts of Na_3Cit (from 0 mmol to 1.5 mmol) were introduced into the reaction system. Without Na_3Cit, $Eu_2(C_2O_4)_3{\cdot}10H_2O$ hierarchical structure could be found (Fig.3(g)). When 1.2 mmol Na_3Cit was added into the reaction system, $Eu_2(C_2O_4)_3{\cdot}10H_2O$ with regular hierarchical morphology could be detected (Fig.3(h)). As the amount of the assistant was increased to 1.5 mmol, there was no regular hierarchical morphology found any more (Fig.3(i)).

Figure 3 (j)–(m) show the images of the samples obtained at room temperature for 24 h with four assistants, ethylenediaminetetraacetic acid (EDTA), Na_3Cit, sodium dodecyl sulfate (SDS) and hexadecyl trimethyl ammonium bromide (CTAB). Hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ could be found in Fig.3 (j)–(l), and a regular hierarchical structure of the sample obtained in the present of Na_3Cit would be observed (Fig.3(k)). The morphology of the product is not hierarchical when CTAB is used as an assistant (Fig.3(m)).

Based on the results of above experiments, the preferable experiment condition to synthesize the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles can be obtained: room temperature, 24 h, and 1.2 mmol Na_3Cit. Europium oxalate ($Eu_2(C_2O_4)_3{\cdot}10H_2O$) was obtained by Na_3Cit-assisted precipitation method at room temperature for 24 h. Hierarchical europium oxalate was observed clearly.

A self-assembly growth mechanism can be proposed for the formation of the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles. The fresh $Eu_2(C_2O_4)_3{\cdot}10H_2O$ crystal nucleus form the micro-flakes due to the anisotropic growth at first, and then the micro-flakes piled up to assemble the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles (Fig.4).

Cit^{3-} as typical complex agent reacted with Eu^{3+} to form Eu^{3+}-Cit^{3-} complexes, which could control the concentration of free Eu^{3+} in solution and the nucleation and growth rate of the crystals in view

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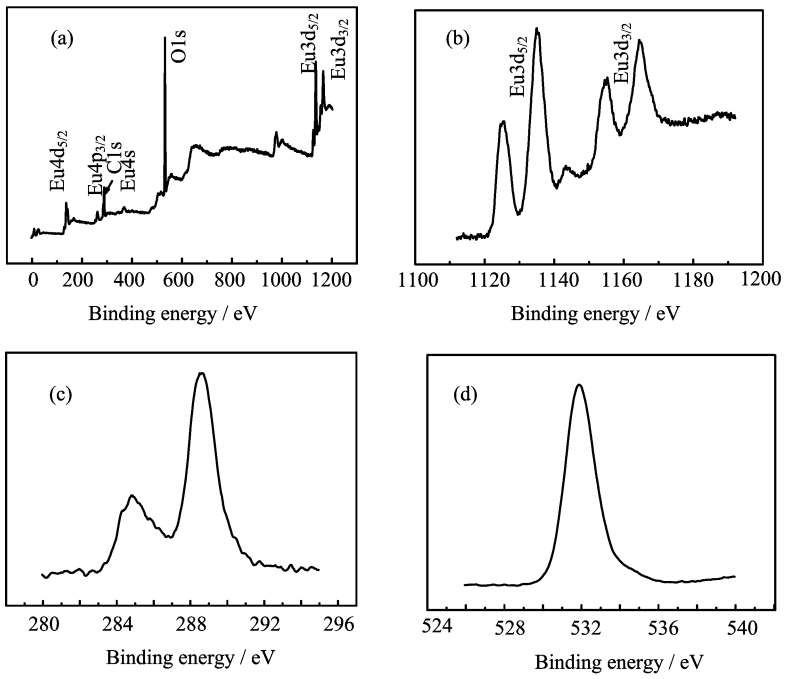

FIG. 2 The XPS of $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles. (a) A survey spectrum, (b) Eu3d region, (c) C1s, and (d) O1s.

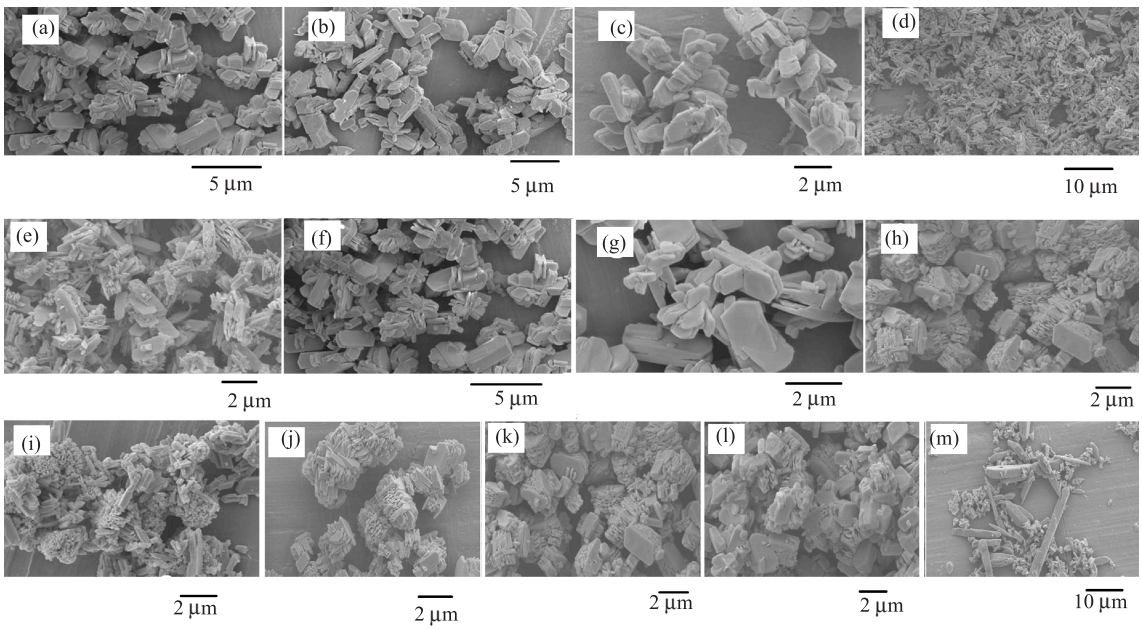

FIG. 3 The FESEM images of the samples obtained at different reaction conditions. Temperature: (a) room temperature, (b) 100 °C, and (c) 120 °C; reaction time: (d) 0 h, (e) 12 h and (f) 24 h at room temperature; amounts of Na_3Cit: (g) 0 mmol, (h) 1.2 mmol, and (i) 1.5 mmol at room temperature for 24 h; assistant: (j) EDTA, (k) Na_3Cit, (l) SDS, and (m) CTAB at room temperature for 24 h with amount of assistant 1.2 mmol.

of the dynamic process. When $H_2C_2O_4$ was added into the solution, the balance of the reaction of Eu^{3+}-Cit^{3-} complexes was changed, and Eu^{3+} was released and formed $Eu_2(C_2O_4)_3{\cdot}10H_2O$ with $C_2O_4{}^{2-}$ and H_2O slowly [16, 33]. The main reactions for the formation of $Eu_2(C_2O_4)_3{\cdot}10H_2O$ can be expressed as follows

$$Eu^{3+} + 2Cit^{3-} \rightarrow Eu(Cit)_2{}^{3-} \quad (1)$$

$$2Eu^{3+} + 3C_2O_4{}^{2-} + 10H_2O \rightarrow Eu_2(C_2O_4)_3{\cdot}10H_2O \quad (2)$$

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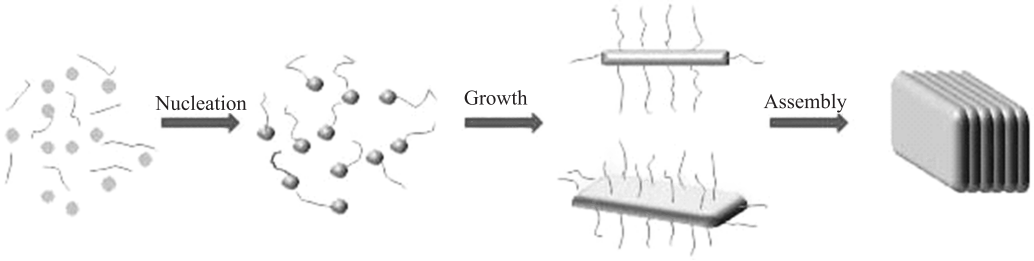

FIG. 4 Possible self-assembly mechanism of the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles.

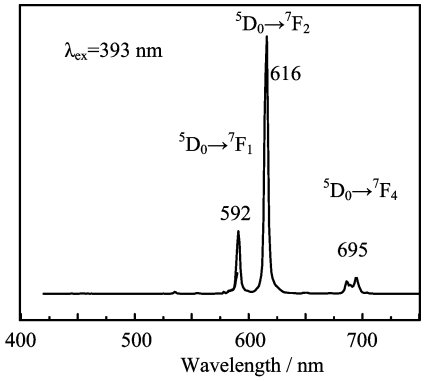

FIG. 5 Photoluminescence spectrum of the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles.

In the reaction, Cit^{3-} as the complex plays two roles. One is to serve as chelating ligand to form a stable complex with Eu^{3+} and further kinetically control the reaction rate, and the other is to act as capping agent to affect the facet growth and their assembly to hierarchical particles [33]. The $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-flakes stack and assemble to the hierarchical particles, which is favorable to the decrease of surface energy and the stability of the product. CTAB, as a cationic surfactant, only reacts with $C_2O_4{}^{2-}$ and can't react with Eu^{3+} and can't control the concentration of Eu^{3+} and the reaction rate. So when CTAB is used as assistant, the product is not hierarchical particles.

D. Photoluminescence property

The room temperature optical property of the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles was investigated by photoluminescence. Figure 5 shows the emission spectrum of hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles under excitation at 393 nm. The two sharp PL emission peaks around 592 and 616 nm attribute to $^5D_0\rightarrow{}^7F_1$ and $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} in the $Eu_2(C_2O_4)_3{\cdot}10H_2O$ lattices, and the emission peak centered at 695 nm is assigned to the $^5D_0\rightarrow{}^7F_4$ transition. The hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles with the emission peak at 616 nm has potential application as a red phosphor for white-light-emitting diodes [34].

IV. CONCLUSION

In summary, hierarchical europium oxalate $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles were successfully synthesized by a simple precipitation method at room-temperature in presence of Na_3Cit. The influence of experiment parameters on the morphology of products has been investigated, and the preferable experiment parameters of room temperature, 24 h, and 1.2 mmol Na_3Cit were obtained to synthesize the regular hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles. A possible formation mechanism of the regular hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ was suggested. Furthermore, the optical property of the hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles was studied, and the two efficient and sharp PL emission peaks at around 592 and 616 nm show a potential application as a red phosphor for light-emitting diodes. The hierarchical $Eu_2(C_2O_4)_3{\cdot}10H_2O$ micro-particles can used as the carrier of catalysis [35, 36]. This simple approach can be extended for the synthesis of other lanthanide oxalates.

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