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Preparation and luminescent properties of self-organized broccoli-like SrMoO₄: Pr³⁺ superparticles



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ABSTRACT

A series of novel self-organized broccoli-like SrMoO₄: Pr_c^{3+} (c = 0.01-0.06) superparticles were synthesized via a polymer-assisted hydrothermal (PAH) method. In this work, the polyetherimide and ethylene diamine tetraacetic acid were employed to bind metal ions for their homogeneous distribution and effectively control the nucleation and growth process of Pr^{3+} doped SrMoO₄. According to scanning electron microscope (SEM) detection, these SrMoO₄: Pr^{3+} superparticles show the broccoli-like three-dimensional architecture composed of highly intensive nanorods. Additionally, the SEM images of different SrMoO₄: Pr^{3+} superparticles with the gradually increasing growth time (0.5–24 h) were used to probe their self-organism grown mechanisms. Moreover, the red emission spectrum peaked at around 646 nm, attributed to the $Pr^{3+} 3P_0 \rightarrow ^{3}F_2$ transition, can be effectively excited by the excitation wavelength of 449, 479 or 487 nm. Moreover, the average lifetimes decreased from 4.064 to 3.834 µs with increasing Pr^{3+} doping concentration. Evidently, this PAH method shows a potential application in synthesis of self-assembling and well-distributed luminescent materials.

1. Introduction

RMoO₄ (R = Ca, Sr and Ba) was proved to be a classical host lattice of luminescent materials due to the stable structure of the central metal ion Mo⁶⁺ surrounded by four O²⁻ with tetrahedral coordination [1–5]. Lots of luminescent center ions, such as Eu³⁺, Dy³⁺, Sm³⁺, Tb³⁺ and Pr³⁺, were doped into the host crystal RMoO₄ for the luminescent materials, especially for *w*-LEDs [6–14]. Among this system, the doping ion is easier to precisely replace the R ion in the [RO₈] clusters than the Mo ion in the stable tetragonal the [MOO₄] clusters. In contrast, it is difficult to make clear which ion in titanates (RTiO₃) with a typical perovskite structure (ABO₃) should be replaced by the doping ion [15,16]. Moreover, its corresponding exciting radiation is usually not absorbed directly by the doping ion. Thus, an additional dopant such as Al³⁺, Fe³⁺, Mg²⁺ or Zn²⁺ has been employed to improve the emission intensity [17–19]. Therefore, RMOO₄ was often selected as a host crystal for luminescent materials.

Besides, the Eu³⁺ ion, a typical red luminescent center, was ascribed to the intrinsic transition of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, and its emission spectrum position was constitutionally centered at about 613 nm, verging the border of red right of 600–700 nm [20–23], reading to

The Pr³⁺-doping SrMoO₄, a typical red luminescent material, can be prepared by conventional solid-state reactions [28] or the Czochralski method [29]. However, these methods have some inherent disadvantages, such as high production cost due to long-period at a high temperature process, poor uniformity of the chemical composition, wide size distribution and irregular morphology. Here, we presented a simple and low-cost polymer assisted hydrothermal (PAH) method to prepare the self-organized broccoli-like SrMoO₄: Pr_c³⁺ (c = 0.01–0.06) superparticles. Compared with the conventional solid-state reactions or the Czochralski method, this PAH method is in possession of low reaction temperature. More importantly, based on a combination effect of hydrogen bonding and electrostatic attraction [30–35], ethylene diamine tetraacetic acid (EDTA) and polyetherimide (PEI) in metal precursors can effectively bind the metal ions for guaranteeing the desired homodisperse of Sr, Mo and Pr ions. Moreover, the synergic

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the lower color rendering index of red luminescent material. However, another rare earth Pr^{3+} ion has the inherent transition of ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$ centered at the red light of about 646 nm upon UV or blue excitation [24–27] and consequently Pr^{3+} -doping luminescent materials will be a promising material to enhance color rendering index of red luminescent material.

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action between EDTA and PEI is in favor of self-assembled and controllable growth. By using PAH method, we successfully obtained the self-assembled three-dimensional (3D) dumbbell-like SrMoO₄ and broccoli-like SrMoO₄: Pr³⁺ superparticles. The size of dumbbell-like SrMoO₄ superparticles mainly focuses on the 2–2.2 μ m, presenting the uniformity of as-grown materials. Additionally, these broccoli-like SrMoO₄: Pr³⁺ superparticles can effectively produce high-performance red light with 646 nm. Furthermore, we get the insight into the energy transfer process and luminescence dynamics of SrMoO₄: Pr³⁺ phosphors based on previous reports [36,37]. These results evidently suggest that this corresponding PAH method will be a potential method to prepare the functional oxidation materials with multiple metal elements.

2. Experimental section

A series of self-organized Pr^{3+} -doped $SrMoO_4$ superparticles were synthesized by a polymer assisted hydrothermal method. EDTA (Aldrich), PEI (99.99%, Aladdin), $Sr(NO_3)_2$ (AR, Keshi), (NH₄)₆Mo₇O₂₄·4H₂O (AR, Keshi), and PrCl₃·6H₂O (99.99%, Aladdin) were used as raw materials. EDTA and PEI were added to 40 mL deionized water with the mass ratio of 1:1. After dissolving, $Sr(NO_3)_2$, (NH₄)₆Mo₇O₂₄·4H₂O, and PrCl₃·6H₂O with certain mass were further dissolved into the above-obtained solution with continuous stirring for 30 min and then transferred into a Teflon-lined autoclave and maintained at 200 °C. After naturally cooling to room temperature, the precipitate was separated and washed with ethanol by centrifuging (10,000 r/min, 10 min) and then dried at 80 °C.

The crystal structure and phase composition of Pr^{3+} -doped SrMoO₄ superparticles were determined by the XPert Pro (Holland) X-ray diffract meter with Cu K_{a1} radiation ($\lambda = 0.154$ nm). Surface morphology and element compositions of the products were examined by scanning electron microscopy (SEM, S4800) and energy-dispersive X-ray spectroscopy (EDX, S4800), respectively. The photoluminescence and photoluminescence excitation were investigated at room temperature using FLS980 (Edinburgh Instruments) spectrometer with a 450 W Xenon lamp. Decay times were obtained with a Xenon flash lamp as a light source at room temperature (FLS 980).

3. Results and discussion

Fig. 1 schematically illustrated the main reaction steps of PAH. PEI (branched) is a thermally stable and hydrophilic polymer with primary, secondary and tertiary amino groups. The molecular structures of PEI (branched) and EDTA unit are presented in the inset of Fig. 1. EDTA has four carboxylate as an efficient chelating agent which can bind almost all metals, but it is slightly soluble in water. Through a combination of hydrogen bonding and electrostatic attraction, the EDTA complexes thereafter bind to PEI to form a stable solution [32]. The rests of the carboxylate and amino bind the metal ions to prevent the formation of metal oxide oligomers and assure that the metal precursors distribute homogeneously, which can control the nucleation and growth of SrMoO₄ [38]. The SEM images of SrMoO₄ synthesized at 200 °C for 24 h with and without polymer were displayed in Fig. 2. The surface microscopy of SrMoO₄ without polymer is composed of many irregular particles, as shown in Fig. 2a. On the contrary, it formed the dumbbelllike SrMoO₄ by means of adding the EDTA and PEI, as illustrated in Fig. 2b. The size distribution of the dumbbell-like SrMoO₄ is illustrated in Fig. 2b as an insert. The diameter of particles ranges from 1.77 to 2.64 µm, a good particle size distribution is obtained and the average diameter is 2.09 µm. Previous studies have found that the shape, size and phase of the samples can be controlled via doping ions [39-41]; we also found the similar phenomenon. Comparing with undoped SrMoO₄, the SrMoO₄: Pr³⁺ superparticles show considerable changes in both morphology and size (Fig. 2c). Hence, the Pr³⁺-doping ion plays a critical role in controlling the shape and size of SrMoO4 and it



Fig. 1. Schematic illustration of the main processing steps used to synthesize $SrMoO_4$: Pr^{3+} phosphors.

originates the surface charge redistribution. Moreover, the XRD patterns of irregular SrMoO₄ particles, dumbbell-like SrMoO₄ and broccolilike SrMoO₄: Pr^{3+} superparticles completely match with the standard pattern of SrMoO₄ (JCPDS 08-0482), as displayed in Fig. 2d. Therefore, the used EDTA and PEI in PAH method as well as Pr^{3+} -doping ion play a key role in effectively controlling the uniformity and unique structure of superparticles.

The XRD patterns of SrMoO₄: Pr^{3+} superparticles with different doped Pr^{3+} concentrations (c=0.01–0.06) are demonstrated in Fig. 3. The high crystallinity of the samples can be indicated by the strong and sharp diffraction peaks. All the diffraction peaks could be perfectly indexed to the standard pattern for a tetragonal phase SrMoO₄ (JCPDS 08-0482) [42] and there was no impurity phases including the rare earth indicating that the Pr^{3+} ions have been diffused into the SrMoO₄ host lattice effectively.

Additionally, the nominal stoichiometry of SrMoO₄: Pr_c^{3+} (c = 0.03) superparticles was verified by EDS-mapping method. As shown in Fig. 4, the element mass ratio of Sr, Mo and O is ca. 1:1:4. Quantitative analysis shows that Pr^{3+} ions prefer to occupy the Sr^{2+} sites due to the similar ionic radii. From the above EDS-mapping results, we made a conclusion that Pr^{3+} -doping ions should be uniformly dispersed in the superparticles, unambiguously and intuitively revealing that this PAH method can effectively control the homogeneity of as-grown superparticles.

The luminescent spectra of SrMoO₄: Pr^{3+} (c=0.01-0.06) are obtained at the room temperature as shown in Fig. 5. All the samples with different doping concentration of Pr³⁺ display similar emission spectra and excitation spectra with various intensity. As shown in Fig. 5a, the excitation spectrum of SrMoO₄: Pr^{3+} ($\lambda_{em} = 646$ nm) consist of a broad band in the range of 240-300 nm, and some sharp peaks at 449 nm, 475 nm and 487 nm corresponding to ${}^{3}P_{2} \rightarrow {}^{3}H_{4}$, ${}^{3}P_{1} \rightarrow {}^{3}H_{4}$ and ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$ transitions, respectively. The broad excitation band can be ascribed to the charge transfer (CT) transition of $O^2 \rightarrow Mo^{6+}$ in the $[MoO_4^{2-}]$ group and $O^{2-} \rightarrow Pr^{3+}$ [43]. It was also discovered that the energy of charge transfer band mildly decreases with increasing of the concentration of Pr³⁺ ions. The relationship between the concentration of Pr^{3+} and the corresponding spectra intensity is illustrated in Fig. 5c. The excitation intensity of SrMoO₄: Pr³⁺ firstly increase gradually to a maximum value (c = 0.03), which has been significantly increased by 1.8 times compared with that of c = 0.01, and then decrease with increasing the concentration of Pr³⁺.



Fig. 2. (a) SEM image of SrMoO4 without PEI and EDTA obtained at 200 °C for 24 h. (b) Morphology and size distribution of SrMoO4 with PEI and EDTA obtained at 200 °C for 24 h. (c) SEM image of SrMoO4: Pr³⁺ with PEI and EDTA obtained at 200 °C for 24 h. (d) XRD patterns of product a, b and c.



Fig. 3. XRD patterns of SrMoO₄: Pr_c^{3+} with different Pr^{3+} concentration (c=0.01–0.06) synthesized at 200 °C for 24 h.

The emission spectra of SrMoO₄: Pr^{3+} under the excitation of 487 nm related on the concentration of Pr^{3+} are illustrated in Fig. 5b. The emission spectra of all the samples with different concentration of Pr^{3+} have similar shapes. The emission lines peaked at 602, 618, 646 and 730 nm correspond to ${}^{1}D_{2}\rightarrow{}^{3}H_{4}$, ${}^{3}P_{0}\rightarrow{}^{3}F_{2}$ and ${}^{3}P_{0}\rightarrow{}^{3}F_{3}$ transitions of Pr^{3+} , respectively. Among them, the luminescent intensity at 646 nm overwhelms that of the other peaks, presenting the fine red color rendering index of luminescent material. Compared with the SrMoO₄: Pr^{3+} phosphors which prepared by the solid-state reactions, our samples show much better monochromaticity [28]. In addition, the intensities of emissions increase with the Pr^{3+} concentrations from 1 to 3 mol%, and then decreases with further higher concentrations as shown in Fig. 5d. The various concentrations of Pr^{3+} with various phosphorescence behaviors are well consistent

with previous report for SrTiO₃: Pr^{3+} [17]. The existence of Pr^{3+} optimum concentration can be attributed to the concentration quenching and it depends on the average distance among Pr³⁺ ions. Nonradiation transition occurs with higher probability when the distance between the Pr^{3+} is shortened [44]. Non-radiation transition might be due to cross-relaxation energy transfer from one Pr^{3+} to a nearby Pr^{3+} . According to the energy level structure, the energy distance between the ${}^{3}P_{0}$ and ${}^{3}H_{6}$ manifolds is about 16,000 cm⁻¹, and the energy distance between the ${}^{3}H_{4}$ and ${}^{1}D_{2}$ is about 16,700 cm⁻¹ [45]. Hence, the concentration quenching occurred mainly via the cross-relaxation process ${}^{3}P_{0} + {}^{3}H_{4} \rightarrow {}^{1}D_{2} + {}^{3}H_{6}$. So the luminescence intensity increases in the low concentration range, then the quench occurs when the concentration is more than 3 mol%. On the other hand, the different ionic radius between Pr³⁺ and Sr³⁺ can result in the crystal dislocation or crystal defects when the Pr³⁺ diffused into the SrMoO₄ host lattice. And this phenomenon could cause non-radiative energy transfer.

To investigate the color performance of the SrMoO₄:Pr³⁺, the 1931 CIE (Commission International de l'Eclairage) system was used to calculate the chromaticity coordinates on the basis of PL spectra. As shown in Fig. 6, the color coordinates of SrMoO₄: Pr³⁺ (c=0.03) superparticles were calculated to be x=0.6676 and y=0.3321, evidently uncovering that the as-grown luminescent materials possess higher red color rendering index.

For further shedding light on the luminescent dynamics of as-grown superparticles, we investigated their luminescence lifetimes. The luminescence decay curves of SrMoO₄: Pr³⁺ superparticles were observed with λ_{ex} = 487 nm and λ_{em} = 646 nm at room temperature as shown in Fig. 7. The decay curves completely fitted with double exponential relation mode by the following equation [46]:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$
(1)

where I(t) is the luminescence intensity, A_1 and A_2 are the constant; t is the time; τ_1 and τ_2 are rapid and slow lifetimes. The value of A_1 , τ_1 , A_2 , τ_2 , τ^* and the errors (x^2) are obtained, as shown in Table 1. The average



Fig. 4. Elemental mapping of SrMoO₄: Pr_c^{3+} (c = 0.03) phosphors.

decay time (τ^*) of the ${}^{3}P_0 \rightarrow {}^{3}F_2$ can be defined by the equation as follows [47]:

$$\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$
⁽²⁾

As shown in Fig. 7a, the curves of different colors represent the various Pr^{3+} doping concentrations. It is clearly demonstrated that all the decay curves were well fitted into a double exponential function. The rapid lifetime, slow lifetime and average lifetime are distinctly

displayed in Fig. 7b–d, respectively. These results demonstrate the doping concentration have an impact on the lifetime. The fast decay time decreases with the increase of the Pr^{3+} doping concentration, while the low decay time follows an uncertain trend. The average lifetime of the SrMoO₄: Pr^{3+} is significantly reduced from 4.064 to 3.834 µs with the increase of Pr^{3+} ions concentrations, ascribing to a concentration quenching effect [48,49]. The double exponential behavior and the quench can be attribute to the cross-relaxation processes



Fig. 5. Excitation (a) and emission (b) spectra of SrMoO₄: Pr_c^{3+} (c=0.01–0.06) synthesized at 200 °C for 24 h with emission wavelength 646 nm and excitation wavelength 487 nm, excitation (c) and emission (d) intensities of SrMoO₄: Pr_c^{3+} (c=0.01–0.06) synthesized at 200 °C for 24 h with the various Pr^{3+} doping concentrations.



Fig. 6. CIE diagram of SrMoO₄: Pr_c^{3+} (c = 0.03) phosphors under 487 nm excitation.

mentioned above.

Furthermore, in order to illustrate the self-organized growth process of broccoli-like superparticles, we investigated the surface morphology of SrMoO₄: Pr_c^{3+} (*c*=0.03) obtained at various growth times of 0.5, 1,

Table 1

Decay lifetimes of SrMoO4: $\mbox{Pr}^{3\,+}$ superparticles excited at 487 nm with the emission monitored at 646 nm.

Samples	τ ₁ (ns)	A ₁	τ_2 (ns)	A_2	τ [*] (ns)	x^2
c = 0.01	1660.61	5604.753	9315.74	457.307	4064.31	2.533
c 0.02	1673.26	5625.845	9341.44	464.095	4091.28	3.336
c = 0.03	1609.70	5934.885	9670.80	423.897	4030.14	3.227
c = 0.04	1554.77	6175.740	9796.06	388.221	3892.87	3.795
c = 0.05	1456.32	5819.416	9393.84	386.652	3837.59	3.205
c = 0.06	1380.20	6133.321	9686.50	366.515	3834.49	3.557

2, 6, 12 and 24 h with the fixed synthesized temperature of 200 °C. The corresponding SEM images were shown in Fig. 8. At the beginning reaction time of 0.5 h, the luminescent materials show dumbbell-like nanorodes with secondary structure (Fig. 8a). The size distribution of SrMoO₄: $Pr_{0.03}^{3+}$ is shown in Fig. 8a (inset). The particle sizes range from 1.24 to 1.6 µm, and the average particle size is 1.43 µm. After the action time of 1 h, the dumbbells rapidly became lager and longer, the secondary structure was also clearly visible in Fig. 8b. When the reaction time reached 2 h, the length of such dumbbells was about 2 µm and some dumbbells fractured from the middle, as demonstrated in Fig. 8c. With prolonged the reaction time to 6 h, the dumbbells with serious aggregation formed the broccoli-like structure. The microstructure of SrMoO₄: $Pr_{0.03}^{3+}$ underwent minor changes when the reacting time prolonged from 6 to 24 h, as shown in Fig. 8d–f. Therefore, 6 h should be an optimal reaction time. Additionally, the asobtained SrMoO₄: $Pr_{c.3^{3+}}$ (*c*=0.03) superparticles exhibit a strong red



Fig. 7. The decay curves (a), fast decay time trace (b), low decay time trace (c) and average decay time trace (d) of SrMoO₄: Pr_c^{3+} (c=0.01-0.06) phosphors excited at 487 nm and monitored at 646 nm.



Fig. 8. SEM images illustrate the formation mechanism of SrMoO₄: Pr_{0.03}³⁺ broccoli-like structure ((a) 30 min, (b) 1 h, (c) 2 h, (d) 6 h, (e) 12 h and (f) 24 h) and the emission (g) spectra and intensities (h) of SrMoO₄: Pr_{0.03}³⁺ phosphors at different time.



Fig. 9. Schematic illustration of the growth mechanism for the formation of 3D hierarchical broccoli-like SrMoO₄: $Pr_{0.03}^{3+}$.

emission at 646 nm under blue light excitation of 487 nm, as illustrated in Fig. 8g. Furthermore, the intensity of luminescence kept almost constant when the reacting time prolonged from 6 to 24 h (Fig. 8h), the rule of which is similar to that of the corresponding microstructures. For better illustrating the growth mechanism, a schematic diagram (Fig. 9) based on the time-dependent morphological evolution indicates a possible growth mechanism for broccoli-like SrMoO₄: Pr_{0.03}³⁺.

4. Conclusion

In conclusion, we successfully employed a PAH method to prepare

self-organized broccoli-like SrMoO₄: Pr³⁺ superparticles with higher uniformity. The EDTA and PEI in PAH method was proved to be a key role during self-organized process of superparticles. Furthermore, the optimal grown time was to be 6 h and the corresponding growth mechanism was also investigated in detail. Additionally, the as-grown luminescent materials presented high-performance of red emission at 646 nm. The Pr³⁺-doping concentration exerted a tremendous influence on the emission intensity of as-grown luminescent materials, the intensity is increased by 1.8 times when the concentration change from 1 to 3 mol%. As the doping concentration of Pr³⁺ is more than 3 mol%, the luminescence concentration process and non-radiation transition. Our work unambiguously indicated that PAH method can be used to prepare the other various high uniformity and low synthetic cost luminescent materials.

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