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Mixed-solvothermal synthesis and applications in sensing for Cu^{2+} and Fe^{3+} ions of flowerlike $LaVO_4$:Eu^{3+} nanostructures

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ABSTRACT

Rare-earth inorganic orthovanadates have been attracting considerable research interest because of their significant luminescent features. In this work, flowerlike $LaVO_4$:Eu^{3+} nanostructures with strong photoluminescence were successfully synthesized via a solvothermal route at 160 °C for 8 h in the co-existences of Na_2EDTA and $CO(NH_2)_2$, employing $La(NO_3)_3$ and NH_4VO_3 as the initial reactants, the water-glycol (water/EG) with the volume ratio of 1/2 as the solvent. XRD analysis showed that the final product belonged to tetragonal $LaVO_4$ phase. It was found that Na_2EDTA and $CO(NH_2)_2$ were indispensable in the formation of flowerlike $LaVO_4$:Eu^{3+} nanostructures. The as-obtained flowerlike $LaVO_4$:Eu^{3+} nanostructures exhibited strong emission peaks in the region of 500–700 nm under the excitation of 335 nm light. Interestingly, the abovementioned strong emission peaks could be quenched by Cu^{2+} or Fe^{3+} ions without the interference of other ions, indicating that the present product could be used as an optical sensor for the detection of the Cu^{2+} and Fe^{3+} ions in water systems.

1. Introduction

As important functional inorganic materials, lanthanide orthovanadates and lanthanide (III)-doped lanthanide orthovanadates ($LnVO_4$:Ln^{3+}) have been attracting extensive research interest over the past decade, owing to their unusual magnetic characteristics, special optical performances and potential applications in catalysis, polarizers, laser hosts and luminescent materials [1–4]. Also, $LnVO_4$ is believed to be an ideal model for systematically investigating the influence of lanthanide contraction, which probably reveals some general rules causing the nucleation, growth process of a crystal and further guides the synthesis of other lanthanide compounds [5]. Generally, $LnVO_4$ nanocrystals crystallize in two kinds of polymorphs: tetragonal (t-) zircon type and monoclinic (m-) monazite type [6]. With the increase of ionic radius, m-$LnVO_4$ can be formed more easily than t-$LnVO_4$ due to its higher oxygen coordination number. La^{3+} ion bears the biggest radius in Ln^{3+} ions, so m-$LaVO_4$ is the thermodynamically stable state [7]. However, m-$LaVO_4$ does not present good fluorescent and catalytic properties because of its special structural features. In contrast, t-$LaVO_4$ exhibits superior properties and is expected to be a promising phosphor host candidate [8]. Hence, the synthesis of t-$LaVO_4$ draws increased interest.

Some methods have been developed for the synthesis of rare earth orthovanadate nanostructures including t-$LaVO_4$, such as the hydrothermal synthesis, the ultrasonic-assisted route, the microwave-assisted method, and the sol-gel technology [6–10]. Rare earth orthovanadate micro/nanostructures with various morphologies have been successfully synthesized, such as hollow sphere [11], nanorods [12], nanoparticles [13], nanosheets [14], dumbbell-like [15], nanowires [16]. In 2006, Fan and coworkers realized the phase-/shape- controlled synthesis of $LaVO_4$ nanocrystals through a simple hydrothermal method without assistance of any additive [17]. Irregular m-$LaVO_4$ nanoparticles and t-$LaVO_4$ nanorods were separately obtained only by tuning the pH value of the system [17]. Under the presence of Na_2EDTA, He et al. successfully prepared t-$LaVO_4$ nanocrystals via the hydrothermal route at 180 °C for 24 h [7]. They found that Na_2EDTA acted as an important role in shape-control of t-$LaVO_4$ [7]. At the same time, the structure-directing role of EDTA was also found in the hydrothermal synthesis of other $LnVO_4$ nanocrystals [18]. However, few reports are found on simultaneously employing EDTA and another additive in the preparation of $LnVO_4$ nanocrystals.

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Usually, Eu^{3+}-doped $LaVO_4$ nanocrystals emit bright red light, which mainly corresponds to the transitions of the Eu 4f multiple states, from the $^5D_0$ level to the ^7F_J states (J = 0–5) [19]. Utilizing the above optical performance, Cui et al. prepared a sensor made from poly(MMA-co-MAA), $LaVO_4$:Eu^{3+} nanoparticles and dithizone for the detection of Hg^{2+} ions in water resource [20]. Due to the dramatic color change, the presence of Hg^{2+} ions in water system can be easily judged. It is well known that Cu and Fe are two important metals in industry and essential elements in maintaining mammals' life action. For instance, abnormal Cu^{2+} levels in human body can cause major health concerns [21]. Furthermore, the lack of Fe element can also lead to the physiological changes, including iron deficiency anemia, mental impairment, and so on. Therefore, the identification and quantification of Cu and Fe elements is of great importance in practical.

In this article, we designed a water–ethyleneglycol (EG) mixed solvothermal route to successfully prepare flowerlike t-$LaVO_4$:Eu^{3+} nanostructures. The reaction to produce $LaVO_4$:Eu^{3+} nanoflowers was carried out at 160 °C for 8 h in the presences of Na_2EDTA and $CO(NH_2)_2$. Experiments showed that Na_2EDTA and $CO(NH_2)_2$ acted important roles in the formation of $LaVO_4$:Eu^{3+} nanoflowers. The as-obtained flowerlike $LaVO_4$:Eu^{3+} nanostructures displayed strong PL emission in the range of 500–700 nm under the excitation of 335 nm light. Interestingly, the above PL emission could be selectively quenched by Cu^{2+} or Fe^{3+} ions, indicating that the present $LaVO_4$:Eu^{3+} nanoflowers have potential application as an optical sensor for the detection of the Cu^{2+} and Fe^{3+} ions in water systems.

2. Experimental

All reagents and chemicals are analytically pure, bought from Sinopharm Chemical Company and used without further purification.

2.1. Preparation of t-$LaVO_4$:Eu^{3+} nanoflowers

In a typical experimental process, 0.95 mmol $La(NO_3)_3 \cdot nH_2O$ and 0.05 mmol $Eu(NO_3)_3 \cdot 6H_2O$ were firstly dissolved into a mixed solvent consisted of 5 mL distilled water and 10 mL ethyleneglycol (EG) under stirring. Then, 1.0 mmol Na_2EDTA, 1.67 mmol (0.1 g) $CO(NH_2)_2$ and 1 mmol NH_4VO_3 were added into the above solution in turn under continuous stirring. Here, a yellow suspension was obtained. After stirring for another 20 min, the pH value of the yellow suspension was adjusted to 9 through adding 1 M NaOH solution. Subsequently, the above suspension was transferred into a 25 mL Teflon-lined autoclave, and heated at 160 °C for 8 h. After the autoclave was cooled to room temperature naturally, the final product was collected by centrifugation, washed with distilled water and absolute alcohol several times, and finally dried at 60 °C for 12 h.

2.2. Characterization

X-ray diffraction (XRD) patterns of the products were carried out on Shimadzu XRD-6000 X-ray diffractometer (Cu Kα radiation, $\lambda = 0.154060$ nm), employing a scanning rate of $0.02^\circ\ s^{-1}$ and 2θ range from 10° to 80°. Morphological and elemental analyses of the as-obtained products were accomplished on a Hitachi S-4800 field emission scanning electron microscope (SEM), employing an accelerating voltage of 5 kV and 15 kV (for energy dispersive spectrum analysis). The holey carbon film was used as the support. Photoluminescence (PL) spectra were recorded on a FLSP 920 with a Xe lamp at room temperature, employing the excitation wavelength of 335 nm from He-Cd laser.

2.3. Sensing for Cu^{2+} and Fe^{3+} ions

To investigate the influences of metal cations on PL property of $LaVO_4$:Eu^{3+} nanoflowers, various metal cation solutions with different concentrations were prepared through dissolving proper amounts of metal nitrate salts into deionized water, respectively. Metal nitrate included $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, KNO_3, $NaNO_3$ and $Zn(NO_3)_2 \cdot 6H_2O$. The concentrations of metal salts were in turn 2×10^{-2}, 2×10^{-3}, 2×10^{-4}, 2×10^{-5}, 2×10^{-6} mol L^{-1}. After metal salt solutions with the equal volume were added into 2×10^{-4} mol L^{-1} $LaVO_4$:Eu^{3+} suspension, the PL spectra were measured. As a control, the PL spectrum of 1×10^{-4} mol L-1 $LaVO_4$:Eu^{3+} suspension was also measured.

3. Results and discussion

3.1. Structure and morphology characterization

The morphology of the product was observed by SEM technology. Fig. 1a depicts a typical SEM image. Abundant flowerlike structures with the sizes of 400–600 nm are clearly visible. Further enlargement shows that flowerlike structures are constructed by nanorod bundles (see the inset in (a)). Moreover, same flowerlike structures could be also formed when no $Eu(NO_3)_3$ was introduced into the system, indicating that the presence of Eu^{3+} ions did not vary the morphology of the final product.

Fig. 1b depicts a typical XRD pattern of the product prepared from the present water-EG system with the pH 9.0 at 160 °C for 8 h. By comparison with the data of JCPDS card files no.32-0504 and previous literatures [22–24], main diffraction peaks can be identified as the t-$LaVO_4$ phase with space group *I*41/*amd*. Some

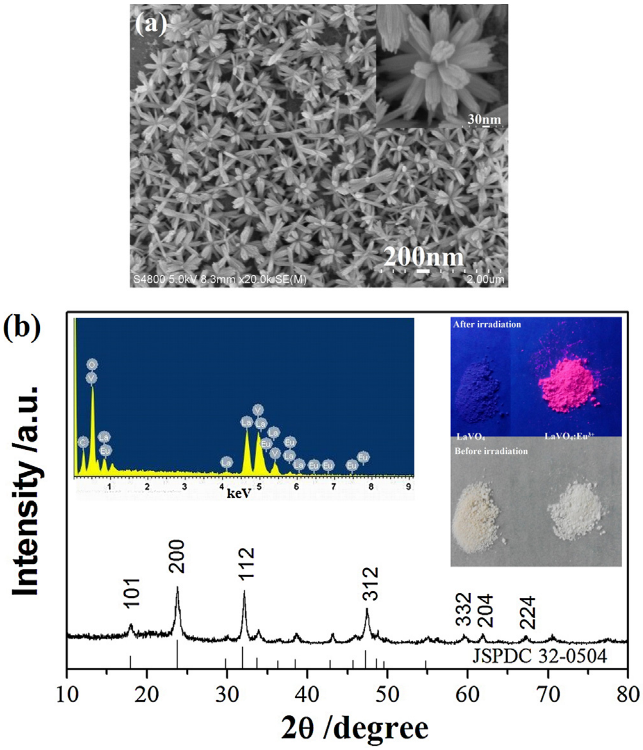

Fig 1. (a) Typical SEM image and (b) XRD pattern of the product prepared from the present water-EG system with the pH 9.0 at 160 °C for 8 h. The inset in (a) is a high-magnification SEM image; and the ones shown in (b) are EDS analysis (right inset) and the color changes of pure $LaVO_4$ and $LaVO_4$:Eu^{3+} before and after irradiation by the UV light.