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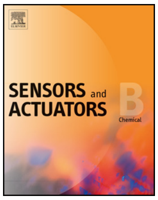

pH modulations of fluorescence $LaVO_4:Eu^{3+}$ materials with different morphologies and structures for rapidly and sensitively detecting Fe^{3+} ions

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ABSTRACT

With the assistance of EDTA, two fluorescence $LaVO_4:Eu^{3+}$ materials have been synthesized via the one-step hydrothermal strategy under different pH conditions, i.e. monoclinic $LaVO_4:Eu^{3+}$ microspheres ($pH = 3$) and tetragonal $LaVO_4:Eu^{3+}$ microbundles ($pH = 9$). Based on series of time-dependent experiments, formation mechanisms of two products have been investigated in detail and proposed in this work. Optical characterizations conform that the luminescence property of $LaVO_4:Eu^{3+}$ materials can be greatly affected by the structure of $LaVO_4$ matrixes. Meanwhile, it is found that the fluorescence property of both $LaVO_4:Eu^{3+}$ products could be rapidly and sensitively quenched by Fe^{3+} ions in water, and the quenching effect strongly depends on the concentration of Fe^{3+} ions, not the crystal structure of $LaVO_4:Eu^{3+}$ phosphors. Consequently, both the $LaVO_4:Eu^{3+}$ products obtained in this work are considered as appropriate functional materials for sensitively and rapidly detecting the Fe^{3+} ions in water.

1. Introduction

Nowadays, water pollution derived from metal ions has become a big environmental and health issue and attracts considerable popular attentions [1,2]. To achieve the sustainable environmental development, a strict sewage discharge standard is highly needed in industrial productions. Therefore, some characterizations acquire the wide study for precisely detecting species and concentration of metal ions in the industrial waste water, such as atomic absorption spectrometry (AAS) [3] and inductively coupled plasma mass spectrometry (ICP-MS) [4,5]. However, existing analysis methods generally involve the huge and expensive instrument and complicated operation, thus failing to exhibit a widespread and conventional application. Consequently, it is eagerly desired to develop a simple, efficient and sensitive analysis method to fast and precisely detect the metal ions in water.

Recently, some materials with fluorescence property, such as quantum dot (QD), [6–8] metal-organic framework (MOF) [9,10] and rare earth phosphors, [11,12] are found to have fluorescence quenching effects in the presence of specific metal ions under the excitation of UV light. This high-selectively photoresponse provides a simple and fast strategy for recognizing specific metal ions in water [13]. Although having good luminescence intensity, QD and MOF generally involve the complex synthesis process, expensive raw materials, and low yield, as well as the low purification efficiency (for QD) and poor chemical stability (for MOF), greatly limiting their practical applications [14–16]. Hence, it is of highly necessary to explore the rare-earth-based fluorescence probes for rapidly and sensitively detecting specific metal ions in aqueous solution.

Among rare-earth materials, Eu^{3+}-doped $REVO_4$ ($RE = Y$, La, Gd, Lu) are considered as promising fluorescence phosphors due to their superior luminescence efficiency, [17–20] particularly Eu^{3+}-

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doped $LaVO_4$ (denoted as $LaVO_4:Eu^{3+}$) with the abundant reserves and low price [21–23]. Therefore, many fluorescence $LaVO_4:Eu^{3+}$ materials have acquired the broad study and development in versatile fields, such as light emitting diode (LED), [24] bioimaging, [25,26] and fluorescent probe [27]. Generally, the $LaVO_4$ matrix includes the monoclinic (m-$LaVO_4$) and tetragonal phases (t-$LaVO_4$), both of which are demonstrated to significantly affect the luminescence property of corresponding $LaVO_4:Eu^{3+}$ materials [28]. It is believed that the hydrothermal method can facilely synthesize and modulate $LaVO_4$ products with various morphologies and crystal structures *via* tuning reaction parameters, such as pH condition, vanadium source, additive species, and reactant concentration [29,30]. Even so, relevant researches are still insufficiency to investigate the potential application of the $LaVO_4:Eu^{3+}$ material for detecting specific metal ions. In 2016, Ni et al. [31] chosen $NaVO_3$ and EDTA of high concentration as the vanadium source and additive to prepare t-$LaVO_4$ samples with multifarious appearance in the pH range of 4–11, while m-$LaVO_4$ microcrystal at pH of 13. They also found that t-$LaVO_4:Eu^{3+}$ nanorod (pH = 11) showed a sensitive fluorescence-quenched effect for Fe^{3+}, thus could be employed to selectively recognize Fe^{3+} in water. An inspirational work has been contributed, however, many problems still need to be figured out: Can m-$LaVO_4:Eu^{3+}$ also rapidly and selectively detect Fe^{3+} ions? If so, will the t- and m-$LaVO_4:Eu^{3+}$ have the discrepant quenched efficiency for the species and concentration of various metal ions?

Herein, NH_4VO_3 and EDTA of low concentration are used as the vanadium source and additive to hydrothermally obtain two $LaVO_4:Eu^{3+}$ materials, e.g. monoclinic $LaVO_4$ microspheres (pH = 3) and tetragonal $LaVO_4$ microbundles (pH = 9). By collecting and analyzing series of intermediates, possible formation mechanisms of two products have been discussed in detail and proposed. Meanwhile, their fluorescence property and quenched effect for various metal ions are also systematically investigated under the UV excitation. In spite of different luminescent properties, both $LaVO_4:Eu^{3+}$ products show the high selectivity for recognizing Fe^{3+} in aqueous solution, and the similar Fe^{3+}-concentration-dependent quenching efficiency.

2. Experimental section

2.1. Preparation of materials

All the reagents were of analytical grade and used as received without further purification. In a typical synthesis process, 1 mmol $La(NO_3)_3$: Eu^{3+} (La: Eu = 0.95: 0.05) aqueous solution was firstly obtained by dissolving $La(NO_3)_3$ (99.99%) and Eu_2O_3 (99.99%) in 10 mL HNO_3 solution (3 mol/L) under heating with agitation, then 0.40 g EDTA was added and vigorously stirred to form the RE^{3+}-EDTA (RE = La, Eu) complex. After dissolving 1 mmol of NH_4VO_3 into 20 mL of distilled water, the resulting NH_4VO_3 solution was mixed with the above $La(NO_3)_3$: Eu^{3+} solution, yielding an orange suspension. pH value of the resulted orange suspension was adjusted to 3 and 9 with NaOH and HNO_3 aqueous solution (3 mol/L), respectively. After that, the resultant mixture was transferred into a 40 mL Teflon-lined autoclave and kept at 180 °C for 24 h. When cooled down to room temperature, hydrothermal products were collected through centrifugation, washed with distilled water and alcohol for several times, and dried at 60 °C for 5 h. Finally, the resultant products obtained at pH = 3 and 9 were denoted as $LaVO_4:Eu^{3+}$ MS and $LaVO_4:Eu^{3+}$ MB, respectively.

2.2. Characterization of materials

Phase purity and crystallinity of products were examined by X-ray diffraction (XRD) on a Brucker-X'Pert X-ray diffractometer equipped with a Cu-Kα radiation source (λ = 1.5418 Å). Morphology and structure of products were characterized by scanning electron microscopy (SEM, JEOL JEM-6300F). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEOL JEM-200CX microscope operating at an accelerating voltage of 200 kV. Photoluminescence (PL) excitation and emission spectra were recorded on a Hitachi F-7000 luminescence spectrometer at room temperature. Zeta potentials of two samples were measured using a Malvern Zetasizer Nano317. Reflectance spectra of $LaVO_4:Eu^{3+}$ phosphors were carried out on a UV–vis spectrophotometer (Thermo Evolution 300) before and after adsorbing various metal ions (20 mM).

2.3. Detection of metal ions

To investigate the influences of metal cations on fluorescence properties of two $LaVO_4:Eu^{3+}$ samples, various metal cation solutions were prepared by dissolving metal salts into deionized water, of which the metal salts included $Fe(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, $Cd(NO_3)_2$, KNO_3 and NaCl, respectively. In the present case, all of metal salt solutions were 2.0×10^{-2} mol L^{-1}. Besides, Fe^{3+} ion solutions with concentrations of 2.0×10^{-2}, 2.0×10^{-3}, 2.0×10^{-4}, 2.0×10^{-5} and 2.0×10^{-6} mol L^{-1} were also separately prepared. After completely grinded, the $LaVO_4:Eu^{3+}$ powders were added into deionized water and ultrasonically dispersed to yield suspensions (2.0×10^{-4} mol L^{-1}). Afterwards, the suspensions were mixed with metal salt solutions in equal volumes, and the PL spectra of mixtures were recorded using a luminescence spectrometer (Hitachi F-7000).

3. Results and discussions

3.1. Structure and morphology of materials

Two hydrothermal products obtained at pH value of 3 and 9 could be measured by SEM to reveal their morphologies, as shown in Fig. 1. From Fig. 1a, it is observed that the sample obtained at pH = 3 is constituted of uniform and well-dispersed microspheres with the average diameter of ∼5 μm. Its magnified SEM image (Fig. 1b) exhibits that those microspheres have a typical hollow nature, which is clearly viewed from several broken monomers. When the pH value of hydrothermal system is increased to 9, the corresponding product exhibits a general bundled rod-like appearance (Fig. 1c), particularly the average length of monomers is about 4 μm (Fig. 1d).

XRD patterns of two products contain discrepant diffraction peaks (Fig. 2), implying different crystal structures. Particularly, all peaks of the sample with pH = 3 can be readily indexed to monoclinic phase of $LaVO_4$ (JCPDS No.50-0367), while the other product has diffraction peaks assigned to tetragonal $LaVO_4$ (JCPDS No.32-0504). It is indicated that the pH condition has a big effect on both the crystal structure and morphology of the hydrothermal products. The absence of diffraction peaks of $EuVO_4$ demonstrates that doped Eu^{3+} fitly occupies the crystal site of La^{3+} in m- and t-LaVO4 matrixes. From EDX spectra (Fig. S1), feature peaks of Eu species could be clearly observed on the surface of both samples, further indicating that Eu^{3+} has successfully doped into the crystal structure of $LaVO_4$ products. In addition, the identical doping contents of Eu^{3+} are generally certified in two products by the equal Eu^{3+}/La^{3+} atomic ratio (1:96 and 1:98 for the $LaVO_4:Eu^{3+}$ MS and $LaVO_4:Eu^{3+}$ MB).

TEM has been utilized to investigate the detailed structure of two hydrothermal products, and their TEM images at different mag-