Effect of the soft-template agents on size, shape and optical properties of YVO$_4$ : Eu$^{3+}$ nanomaterials

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Received 25 April 2012
Accepted for publication 26 June 2012
Published 2 August 2012
Online at stacks.iop.org/ANSN/3/035012

Abstract
Recently YVO$_4$ : Eu$^{3+}$ nanophosphors have attracted more and more attention because of the scientific interest in them and their potential applications in optoelectronics, laser physics, and especially in agrobiology and medicine. In this work we investigated the effect of soft-template agent on size and properties of YVO$_4$ : Eu$^{3+}$ nanoparticles. By using hexadecyltrimethyllammonium bromide (HTAB), sodium dodecyl sulfate (SDS) or dioctyl sodium sulfosuccinate (AOT), the sizes of YVO$_4$ : Eu$^{3+}$ nanoparticles could be controlled in the range from 12 to 16 nm. The fluorescent intensity of YVO$_4$ : Eu$^{3+}$ nanoparticles synthesized in the presence of HTAB, SDS or AOT strongly increased. The structure and morphology of YVO$_4$ : Eu$^{3+}$ nanophosphors have been characterized by x-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy and Fourier transform infrared spectroscopy. The novel fluorescent YVO$_4$ : Eu$^{3+}$ nanocrystals with reduced size to around 15 nm become more effective toward the development of an ultrahigh sensitive fluorescent label in immunoassay for bioactive molecules, cells and tissues.

Keywords: YVO$_4$ : Eu$^{3+}$ nanophosphors, soft-template, nanoparticles

Classification numbers: 4.02, 5.04

1. Introduction

Recently, fluorescent nanoparticles have become a novel biomedical analysis tool due to their potential to develop a labeling immunoassay with high sensitivity, photochemical stability and for increasing the ratio of fluorescent agents to bimolecular–protein (F/P ratio) [1–3]. However, most nanoparticles reported in past immunoassays are larger than 30 nm in diameter. Particles sizes over 30 nm are proven to bring obviously prolonged equilibration time and enhanced nonspecific adsorption [4]. Therefore, nanoparticles with a smaller size could have improved kinetic properties and decreased non-specific adsorption. Moreover, the nanoparticles should be big enough to bind several proteins on the surface, which are expected to increase the immunological affinity [5]. Among the luminescent nanomaterials containing lanthanide, YVO$_4$ : Eu$^{3+}$ nanophosphors increasingly attract much attention because of the scientific interest in them and their potential applications in optoelectronics, laser physics, and especially in agrobiology and medicine [6–8]. We have successfully synthesized YVO$_4$ : Eu$^{3+}$ nanoparticles with size around 20 nm and high fluorescent efficiency. We have developed from these nanophosphors a nanolabel for security and newly for a fluorescent label in biomedicine [9–13].

In this paper we report new results about the effect of soft-template agent on particle size and properties of YVO$_4$ : Eu$^{3+}$ nanoparticles synthesized by wet chemistry. One of the main aims of the research is the synthesis of YVO$_4$ : Eu$^{3+}$ nanophosphors possessing size around 15 nm. We also studied the structure and morphology of the
YVO₄: Eu³⁺ nanoparticles by x-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy and particularly photoluminescent (PL) spectroscopy.

2. Experimental

2.1. Synthesis

The YVO₄: Eu³⁺ nanoparticles were prepared by wet chemistry. In a typical synthesis 0.5516 g of sodium orthovanadate Na₃VO₄ 90% (Sigma-Aldrich) were completely dissolved in 50 ml H₂O. After that, 0.9054 g of yttrium (III) nitrate hexahydrate Y(NO₃)₃.6H₂O 99.8% (Sigma-Aldrich) and 0.1284 g of europium (III) nitrate pentahydrate Eu(NO₃)₃.5H₂O 99.9% (Aldrich) were added to the solution in a 100 ml round-bottomed flask and this was followed by magnetic stirring for 120 min. Then hexadecyltrimethylammonium bromide (HTAB) 99% (Sigma-Aldrich), sodium dodecyl sulfate (SDS) or dioctyl sodium sulfosuccinate (AOT) 96% (Sigma-Aldrich) was added to the solution. The pH of the solution in the range of 12–12.5 was adjusted by 10% sodium hydroxyl solution. The content ratio of Y³⁺ and Eu³⁺ was 9/1. After that, the reaction solution was poured into a Teflon-lined stainless steel autoclave. The autoclave was sealed tightly and heated at 120–120°C for 6 h without AOT (a) and with AOT (b).

2.2. Characterization

The morphology of the as-synthesized samples was observed by using a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800) and transmission electron microscope (TEM, JEM-1010). XRD measurements of the products were performed on an x-ray diffractometer (Siemens D5000 with λ = 1.5406 Å in the range of 15° ≤ 2θ ≤ 75°). The FTIR spectra were measured by IMPACT 410-Nicolet (FTIR). The PL spectra of the nanoparticles were also determined by using a spectrometer HORIBA JOBIN YVON IHR 550 with excitation at 370 nm by an LED at room temperature.

3. Results and discussion

The XRD pattern of the YVO₄: Eu³⁺ nanoparticles prepared without and with HTAB, SDS and AOT have been measured for comparison. The XRD patterns of all samples there are diffraction peaks at 2θ: 18.8°, 25°, 33.5°, 49.8°, 57.9°, 62.8°, 64.8°, 70.3° and 74.2°. These diffraction peaks indicated a Wakefieldite Y-tetragonal phase of YVO₄, when the reference of PDF cards no 17-0341 is used. The XRD analysis stated that the phase of the obtained YVO₄: Eu³⁺ nanoparticles without and with HTAB, SDS, AOT are purely in tetragonal form.

FE-SEM images of the YVO₄: Eu³⁺ nanoparticles without (a) and with (b) AOT are shown in figure 1. From the obtained images it can be estimated that the mean size of the YVO₄: Eu³⁺ nanoparticles prepared without AOT have a size of about 18–20 nm. With the use of AOT the sizes of YVO₄: Eu³⁺ nanoparticles became smaller and decreased down to around 15 nm. In the presence of AOT the average size of YVO₄: Eu³⁺ nanoparticles varied in the range from 12 to 16 nm when the reaction time changed from 4 to 24 h. Therefore, some YVO₄: Eu³⁺ samples have to be imaged by TEM with higher resolution for finer estimation.

Figure 2 shows TEM images of the YVO₄: Eu³⁺ nanoparticles prepared with AOT. The TEM images were obtained in different nanoscales of 20 nm (a) and 100 nm (b). It can be determined that the mean size of the synthesized YVO₄: Eu³⁺ nanoparticles prepared with the use of AOT is about 12–16 nm. With the use of HTAB and SDS the mean size of the synthesized YVO₄: Eu³⁺ nanoparticles is around 15 nm (data were not shown here).

The FTIR spectra of the YVO₄: Eu³⁺ nanoparticles synthesized without or with the use of soft-template AOT have been measured. In figure 3 FTIR spectrum of the YVO₄: Eu³⁺ nanoparticles synthesized with the use of AOT is presented. In the spectrum of YVO₄: Eu³⁺ nanoparticles there are three regions, one from 2926 to 3448 cm⁻¹, the second in the range of 1300–1650 cm⁻¹ and the third in longer wavelength range from 400 to 900 cm⁻¹. In the first region the peak at 2920 cm⁻¹ can be assigned to the C–H stretch vibration. The vibration of O–H group was found in the higher wavenumber region of 3448 cm⁻¹. The stretching vibration of nitrate group can be found in the region of 1300–1650 cm⁻¹. Moreover, the obtained spectrum showed...
the typical spectral characteristic band of VO$_{4}^{3-}$ group in the range of 780–920 cm$^{-1}$. There is a highest pick at 841 cm$^{-1}$. The study of the infrared spectra revealed a small residue of the soft-template agent AOT adsorbed on the surface of YVO$_{4}$: Eu$^{3+}$ nanoparticles.

Excitation spectra of the YVO$_{4}$: Eu$^{3+}$ nanoparticles are presented in figure 4. The obtained spectra showed that YVO$_{4}$: Eu$^{3+}$ nanoparticles can either be optically excited in the charge transfer band at 314 nm of the vanadate group, or in the visible range, at the wavelengths of 365, 370, 380, 395, 467 and 540 nm.

Figure 5 shows the photoluminescence spectra under 370 nm excitation of the YVO$_{4}$ : Eu$^{3+}$ nanoparticles prepared without or in the presence of HTAB, SDS and AOT. Under UV excitation, YVO$_{4}$ : Eu$^{3+}$ nanoparticles exhibit strong red luminescence with narrow bands corresponding to the intra-4f transitions of $^5$D$_{0}$–$^7$F$_{j}$ ($j = 1, 2, 3, 4$) Eu$^{3+}$. The peaks were found at 594 nm ($^5$D$_{0}$–$^7$F$_{1}$), 619 nm ($^5$D$_{0}$–$^7$F$_{2}$), 652 nm ($^5$D$_{0}$–$^7$F$_{3}$) and 702 nm ($^5$D$_{0}$–$^7$F$_{4}$), with the strongest emission at 619 nm. The emission peak at 619 nm of europium ions was split into two sharp peaks at 615 and 619 nm because of the change of ligand field of Eu(III).

From figure 5 it can be pointed out that the luminescence intensities of YVO$_{4}$ : Eu$^{3+}$ prepared with the use of HTAB (line 2), SDS (line 3) and AOT (line 4) are clearly stronger than that of YVO$_{4}$ : Eu$^{3+}$ prepared without soft-template agent (line 1). It can be stated that the soft-template agents HTAB, SDS and AOT play two interesting roles, one for reducing the size of YVO$_{4}$ : Eu$^{3+}$ nanoparticles to around 15 nm
and the other for enhancing the emission of YVO$_4$: Eu$^{3+}$ nanophosphors. These effects seem to be very important for the next stage of development of fluorescent label conjugate for immunoassay method in biomedicine.

4. Conclusion

In summary, the YVO$_4$: Eu$^{3+}$ nanoparticles have been prepared by the wet chemistry method without and with soft-template agent. In using HTAB, SDS and AOT soft-template agents the sizes of YVO$_4$: Eu$^{3+}$ could be controlled in the range from 12 to 16 nm. The XRD pattern states that the phase of the YVO$_4$: Eu$^{3+}$ nanoparticles are Wakefieldite-(Y) single phase. The luminescence intensity of the YVO$_4$: Eu$^{3+}$ prepared with the use of HTAB, SDS and AOT as soft template is much stronger than that of YVO$_4$: Eu$^{3+}$ prepared without soft template. These nanoscale and high-emission characters demonstrate that the YVO$_4$: Eu$^{3+}$ nanoparticles obtained with the use of SDS and AOT have more potential application as a fluorescent label for studying bioactive molecules, cells and tissues.

Acknowledgments

This work is supported by Vietnam Basic Research Programming for application, project 2/2/742/2009/HD-DTDL, in part of Vietnam’s National Foundation for Science and Technology Development (NAFOSTED), project code: 103.06.46.09, and implemented in framework of National Key Lab of Electronic Materials and Devices in Institute of Materials Science, Vietnam Academy of Science and Technology.

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