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One-pot reverse microemulsion synthesis of core–shell structured $YVO_4:Eu^{3+}@SiO_2$ nanocomposites

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ABSTRACT

Core–shell structured $YVO_4:Eu^{3+}@SiO_2$ nanocomposite particles were synthesized using a one-pot reverse microemulsion method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV absorption spectra, and photoluminescent spectra. The nanocomposite particles are well-dispersed and about 20 nm in average size. The synthesis method is of one-pot, simplifying the preparation of this kind of core–shell structured nanocomposites. The formation process of these nanocomposite particles is suggested and the photoluminescence properties of them are studied and compared with those of uncoated $YVO_4:Eu^{3+}$ sample.

1. Introduction

In the past two decades, coating nanoparticles (NPs) with silica to form nanocomposites has been studied widely. For example, noble metal NPs (Au [1–3], Ag [3,4], etc.), magnetic NPs (Fe_3O_4 [5,6], Fe_2O_3 [7], etc.), semiconductor NPs (CdSe [8], CdTe [9], etc.), and lanthanide-doped luminescent NPs [10,11] have been well coated with silica with the well-known Stöber method [12] or the reverse microemulsion method. The reason why silica is used as a coating material is its high chemical stability, optical transparency, easily controllable shell thickness, low cytotoxicity, biocompatibility and inexpensiveness. Semiconductor NPs [13], namely quantum dots (QDs), or lanthanide-doped luminescent NPs [14] can be used as luminescent probes in investigations of biochemical systems. Coating them with silica is favorable for their use as luminescent probes, since the protocol for conjugation of biomolecules to a silica surface has been well established [15].

Bulk $YVO_4:Eu^{3+}$ is a highly photoluminescent material with 70% photoluminescence quantum yield (QY) for an optimum europium content of 5% [16]. Bulk $YVO_4:Eu^{3+}$ also has high luminescence efficiency upon electron-beam excitation [17] and had been widely used as red phosphor in cathode ray tubes before it was replaced by the even more efficient $Y_2O_2S:Eu^{3+}$ in the early 1980s. Due to surface effect, the photoluminescence QY of $YVO_4:Eu^{3+}$ NPs is not as high as bulk $YVO_4:Eu^{3+}$, but $YVO_4:Eu^{3+}$ NPs are still an efficient photoluminescent material and have a potential to be used as luminescent probes. For example, a photoluminescence QY of 38% for $YVO_4:Eu^{3+}$ NPs has been reached under optimized conditions [18].

For the moment the study of coating $YVO_4:Eu^{3+}$ NPs with silica is scarce. Wang et al. prepared $YVO_4:Eu^{3+}$ NPs and then coated them with silica using the Stöber method [19]. Their method is of two-step. In this paper, we prepared well-dispersed $YVO_4:Eu^{3+}@SiO_2$ nanocomposite particles using a one-pot reverse microemulsion method. The synthesis method is simple and propitious to the production of this material.

2. Experimental section

2.1. Materials

Yttrium nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$, 99.99%), europium(III) nitrate hexahydrate ($Eu(NO_3)_3{\cdot}6H_2O$, 99.9%), sodium orthovanadate (Na_3VO_4, 98%), ammonia aqueous solution

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(25–28%), and tetraethyl orthosilicate (TEOS, 99.99% metals basis) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Polyoxyethylene(5)nonylphenyl ether (Igepal CO-520) was purchased from Sigma–Aldrich. Cyclohexane, methanol, and ethanol were all of analytical grade and purchased from Beijing Chemical Factory. All chemicals were used as received without further purification.

2.2. Sample preparation

The core–shell $YVO_4:Eu^{3+}@SiO_2$ nanocomposites were prepared by one-pot reverse microemulsion method. Typically, 56.5 mL cyclohexane, 2.5 mL Igepal CO-520 and a mixture consisting of 45 μmol $Y(NO_3)_3$, 5 μmol $Eu(NO_3)_3$ and 300 μL water were introduced into a 100 mL beaker consecutively under vigorous magnetic stirring. The atomic ratio of Y/Eu was 9:1. To a 500 mL beaker were added 169.5 mL cyclohexane, 7.5 mL Igepal CO-520 and 900 μL water containing 100 μmol Na_3VO_4 consecutively under vigorous magnetic stirring. After 15 min, the mixture in the 100 mL beaker was introduced into the mixture in the 500 mL beaker. 30 min later, 600 μL ammonia aqueous solution was added. Another 30 min later, 2 mL TEOS was added. 5 min later, stirring was stopped, and the 500 mL beaker was seeled, and the reaction was continued without stirring for 48 h. The resulting $YVO_4:Eu^{3+}@SiO_2$ nanocomposite particles were precipitated by adding methanol, and collected by centrifuging at 8000 rpm. The collected $YVO_4:Eu^{3+}@SiO_2$ nanoparticles were redispersed in ethanol, and purified by sonication and centrifugation. The centrifugation and ethanol washes were repeated twice.

In order to prove that the core of the core–shell structured nanocomposite particle was $YVO_4:Eu^{3+}$ nanoparticle and study the influence of silica shell on photoluminescence properties of $YVO_4:Eu^{3+}$, a sample (denoted as sample A) was synthesized under the reaction conditions same as those for the synthesis of $YVO_4:Eu^{3+}@SiO_2$ nanocomposite particles except that TEOS was not added.

2.3. Characterizations

XRD studies were performed using the PANalytical Empyrean diffractometer with Cu Kα radiation (1.5406 Å). TEM was performed using a FEI Tecnai G2 Spirit electron microscope at 120 kV. UV absorption spectra were obtained on a Perkin–Elmer Lambda 900 spectrophotometer. The excitation and emission spectra were recorded using a Hitachi F-4500 spectrophotometer. The QY of the $YVO_4:Eu^{3+}$ sample (sample A) was determined by comparing its integrated emission intensity with the emission from a Rhodamine 6G solution (QY = 95%) in ethanol having the same optical density (OD < 0.3) and excited at the same wavelength (276 nm). The QY of $YVO_4:Eu^{3+}@SiO_2$ nanocomposites was determined by comparing integrated areas of emissions from $YVO_4:Eu^{3+}@SiO_2$ nanocomposites colloid and $YVO_4:Eu^{3+}$ colloid with the same $YVO_4:Eu^{3+}$ concentration. All spectra were collected at room temperature under ambient conditions.

3. Results and discussion

Fig. 1 shows TEM images at three different magnifications of $YVO_4:Eu^{3+}@SiO_2$ nanocomposite particles and the histogram of particle size distribution obtained by measuring 600 particles. It can be seen that these nanocomposite particles are well-dispersed, being beneficial to their applications. The average size of these nanocomposite particles is 19.8 nm with a standard deviation of 6.2 nm. Most of these nanocomposite particles have one $YVO_4:Eu^{3+}$

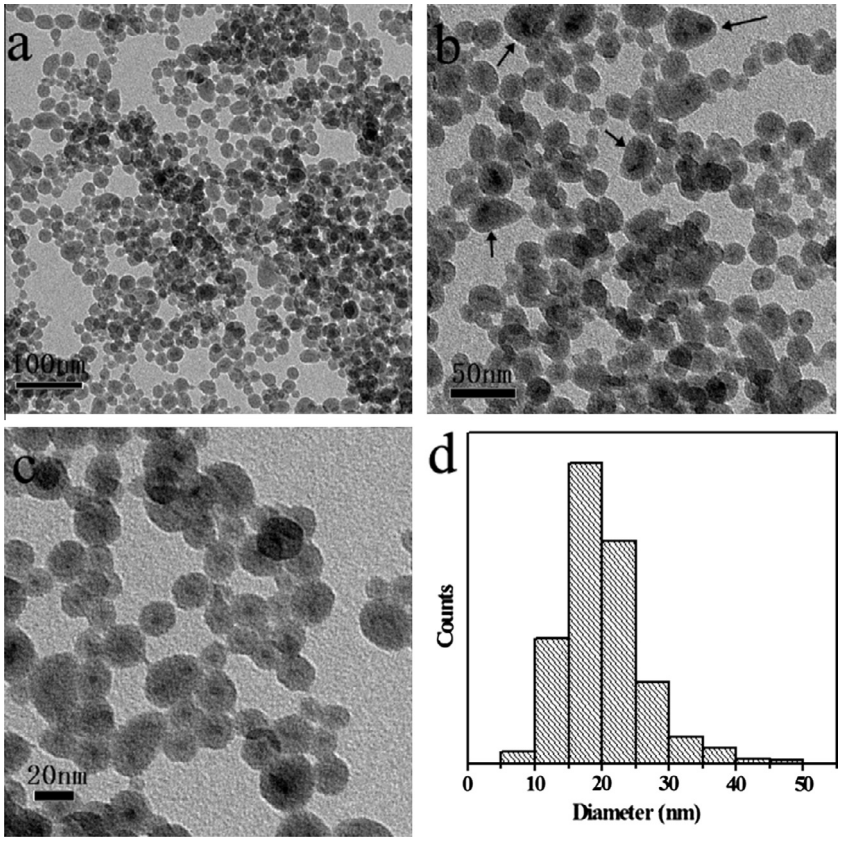

Fig. 1. TEM images at three different magnifications of $YVO_4:Eu^{3+}@SiO_2$ nanocomposite particles (a)–(c), and the histogram of particle size distribution (d). Arrows in (b) denote nanocomposite particles with more than one $YVO_4:Eu^{3+}$ nanoparticle cores.