

A facile method for preparation of lanthanide-doped titania-coated silica nanoparticles

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Received: 28 September 2009 / Accepted: 31 December 2009 / Published online: 13 January 2010
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Abstract Here, we report a facile method for the preparation of monodisperse lanthanide-doped titania-coated silica nanoparticles. By hydrolysis of titanium alkoxide precursors in the presence of lanthanide ions, titania coatings have been deposited on the surface of the silica nanoparticles dispersed in the pure ethanol. Lanthanide ions were directly incorporated into the coating during the coating process. For a given ratio of titanium alkoxide to water, the density of the doped ions is determined by the concentration of the lanthanide ions in the reactant mixture. The final particles were nanosized, discrete, and exhibiting luminescence when excited.

Introduction

In recent years, lanthanide-doped nanoparticles have attracted extensive attention due to their unique properties and prospective applications for photocatalysis [1–3], optical materials [1], plane waveguides [4], solar energy harvesting materials [5], and PBG materials [6]. For these applications, several kinds of materials were used as the host matrix of lanthanide ions [7–15]. Especially, SiO₂ [7, 8] and TiO₂ [10, 14, 15] have been proved to be the ideal host materials of lanthanide ions because of their high

transparency in the visible light region and their excellent thermal, chemical, and mechanical properties.

Lanthanide-doped SiO₂ particles can be made by ion implantation [16], high-temperature vapor phase processing [17], and sonochemical method [18]. However, the amount of the particles obtained by those methods is small and not enough for bulk applications [8]. Large amount of the lanthanide ions-doped particles can be yielded by sol-gel chemistry in acidic catalyzed reaction (because the lanthanide ions will immediately form insoluble lanthanide hydroxide in basic-catalyzed reaction), and the lanthanide ions could be directly incorporated into particles during the process of the hydrolysis and condensation of the tetraethyl orthosilicate (TEOS). Typically, Pr³⁺-doped and Er³⁺-doped silica microspheres have been synthesized using sol-gel method by Moran et al. [7]. In their report, lanthanide-doped SiO₂ were obtained by hydrolysis of TEOS in the presence of the appropriate lanthanide chloride. However, the acid-catalyzed hydrolysis of TEOS generally results in large particles [19–21]. As a result, those lanthanide-doped particles are micrometer-sized and quite polydisperse (0.3–3 μm) [7], which may inhibit their applications as hybrid optical materials. For example, to use lanthanide-doped colloids in organic-inorganic hybrid material waveguide, the size was supposed to be kept below ~80 nm in order to keep the scattering losses below 1 dB/cm [22]. Hence, there is a tremendous demand for monodisperse nanosized lanthanide-doped colloids. And it is a great challenge for us to find a novel wet-chemistry method for the preparation of monodisperse nanosized lanthanide-doped colloids. On the other hand, Titania can be coated on the silica surface by hydrolysis of titanium alkoxide precursors in the presence of lanthanide ions, while the lanthanide ions will not form insoluble hydroxide. And titania was selected as the coating because it has

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lower phonon energies than silica, which may help to increase the probability of radiative transition. In addition, titania was cheap, nontoxic, and transparency in the visible and IR scale. Hence, we design and fabricate the lanthanide-doped titania-coated silica nanoparticles.

In this article, we developed a facile coating process to fabricate Eu^{3+} -doped, Tb^{3+} -doped, or Er^{3+} -doped titania-coated silica nanoparticles. Titania coatings can be deposited on the surface of the silica nanoparticles dispersed in the pure ethanol by hydrolysis of titanium alkoxide precursors in the presence of lanthanide ions. The diameter of the silica particles used to support the titania coating is nanosized. And the lanthanide ions as activator can be directly incorporated into the titania coating during the coating process. The coating growth and luminescence properties of the ions-doped particles were studied using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy. Especially, the density of doping ions in the particles was measured by Inductive Coupled Plasma Spectroscopy (ICP). The final coated particles are nanosized, discrete, mono-dispersive, which are very important for their applications in hybrid optical materials.

Experiment

Materials and characterization

The following materials have been used: tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS), titanium *n*-butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, TBOT), ammonium hydroxide (25–28%, NH_3), ethanol (99.7%), hydrochloric acid (36–38%, HCl), hydrofluoric acid (40% HF), and hydrogen peroxide (Chemical grade, H_2O_2). All the above were purchased from Beijing Chemicals. Europium (III) oxide, Erbium (III) oxide, and Terbium (III) oxide were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without further purification. The lanthanide salts were obtained from the reaction of the lanthanide oxide and HCl . Water was obtained from a Milli-Q water purification system (Millipore). The morphology of the particles were characterized by FESEM (JEOL FESEM-6700F) and TEM (HITACHI-800, operating at 200 kV). TEM samples were prepared by applying a diluted drop of particles on a holey carbon coated copper TEM grid. The ions doping density were analyzed by ICP (Perkin Elmer, Optima 3300DV). Before the measurement, the samples were treated as follows: 0.1 g of the samples were mixed with 20 mL water, 3 mL HF , 3 mL HCl , and 0.5 mL H_2O_2 in the autoclave, and then the mixture were heated at 180 °C for 3 h. The PL spectra of the Tb^{3+} -doped and

Eu^{3+} -doped particles were measured by using a Shimadzu spectrometer (RF-5301 PC). The IR emission spectrum of Er^{3+} -doped particles was measured by using a PTI fluorescence spectrophotometer (QuantaMasterTM 50) with InGaAs detector.

Procedures

Monodisperse silica nanoparticles

Monodisperse silica nanoparticles were synthesized by hydrolysis of TEOS in an ethanol solution containing water and ammonia, which was originally reported by Stöber et al. [23]. In a typical experiment, 5 mL of NH_3 was added to 100 mL pure ethanol, and then 3.5 mL of TEOS was dropped into the mixture. The whole mixture was kept stirring at 25 °C for 24 h. The resulting silica nanoparticles were centrifugally separated from the suspension and ultrasonically washed with ethanol for several times to wash out the ammonia. Then particles were re-dispersed in pure ethanol.

RE-doped titania coating of silica nanoparticles

Titania was coated on silica nanoparticles using a procedure originally reported by Hanprasopwattana et al. [24]. In our work, lanthanide salt was added into the reaction mixture. A stock solution containing 4 mL of TBOT and 100 mL of ethanol was used for the coating precursor. In a typical experiment, 0.10 g silica nanospheres dispersed in 25 mL ethanol were mixed with a certain amount of lanthanide salt, 0.38 g water, and 4.0 mL precursor. More ethanol was added to make the total volume of 50 mL. The mixture was refluxed and kept stirring for 12 h. The final spheres were separated centrifugally and ultrasonically washed with ethanol.

Results and discussion

Titania coatings on silica spheres have been studied by Hanprasopwattana et al. [24]. According to their research, the coating nature was affected by the ratio of titanium alkoxide to water. In our experiment, the mole ratio of titanium alkoxide to water was kept constant at 1:35. Monodisperse silica particles were prepared for coating. Those particles were obtained via the base-catalyzed hydrolysis of TEOS by Stöber method. Figure 1a shows a scanning electron micrograph of an uncoated silica sample. The silica profile of the same sample before coated is shown at a higher magnification in the TEM micrograph in Fig. 1b. From the image we can see that the uncoated silica particles are nanosized, smooth, and unagglomerated.

By hydrolysis of titanium alkoxide precursors in the presence of lanthanide ions, titania coatings were deposited

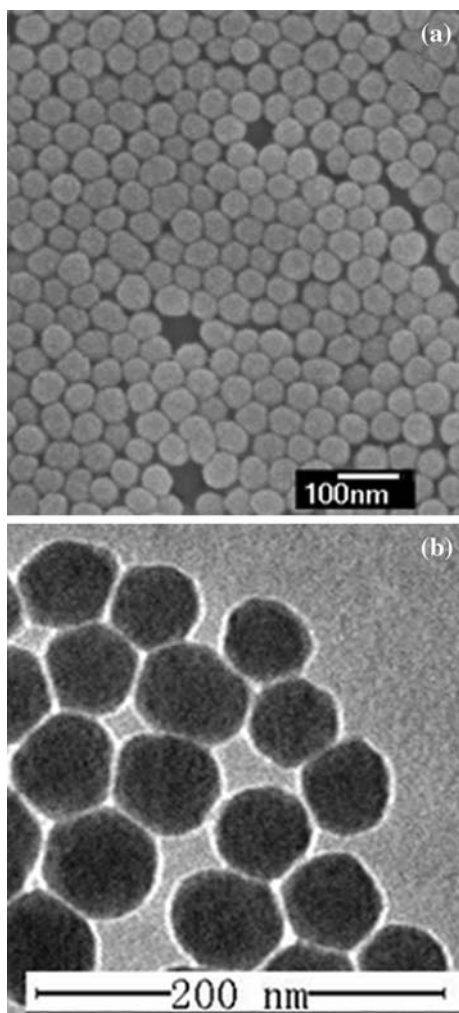


Fig. 1 SEM (a) and TEM (b) images of the uncoated silica particles

on the surface of the silica nanoparticles. Figure 2a shows a TEM micrograph of titania-coated silica particles, and the inset shows the image of a single particles. The noticeable feature is an increase in the surface roughness. It indicates that in the presence of the lanthanide ions, titania have been successfully coated on the surface of the nanosized silica particles. Analyzing ≈ 30 particles reveals the average size of the particles is about 50 nm before coated and 57 nm after coated.¹ The thickness of the titania coating is about 3.5 nm. A multistep procedure was carried out while keeping the amount of water and lanthanide salt constant. After five coating steps, the increase in the surface roughness and the diameter of the particles become more clearly as shown in the TEM image in Fig. 2b. And this

¹ Estimates of the average diameter were obtained by analyzing ≈ 30 particles. Using the Student's distribution and a 95% confidence interval, we estimate that the real average lies between 47.5 and 52.1 nm before coated and between 55.0 and 59.6 nm after coated. See, e.g., [25].

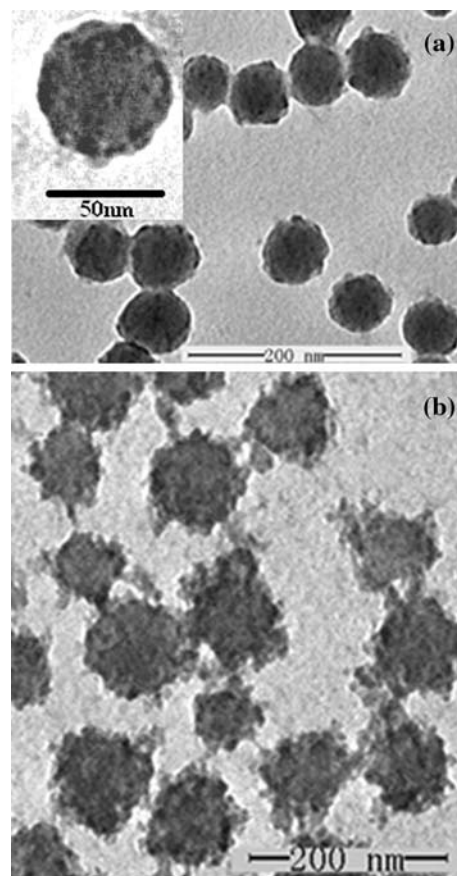


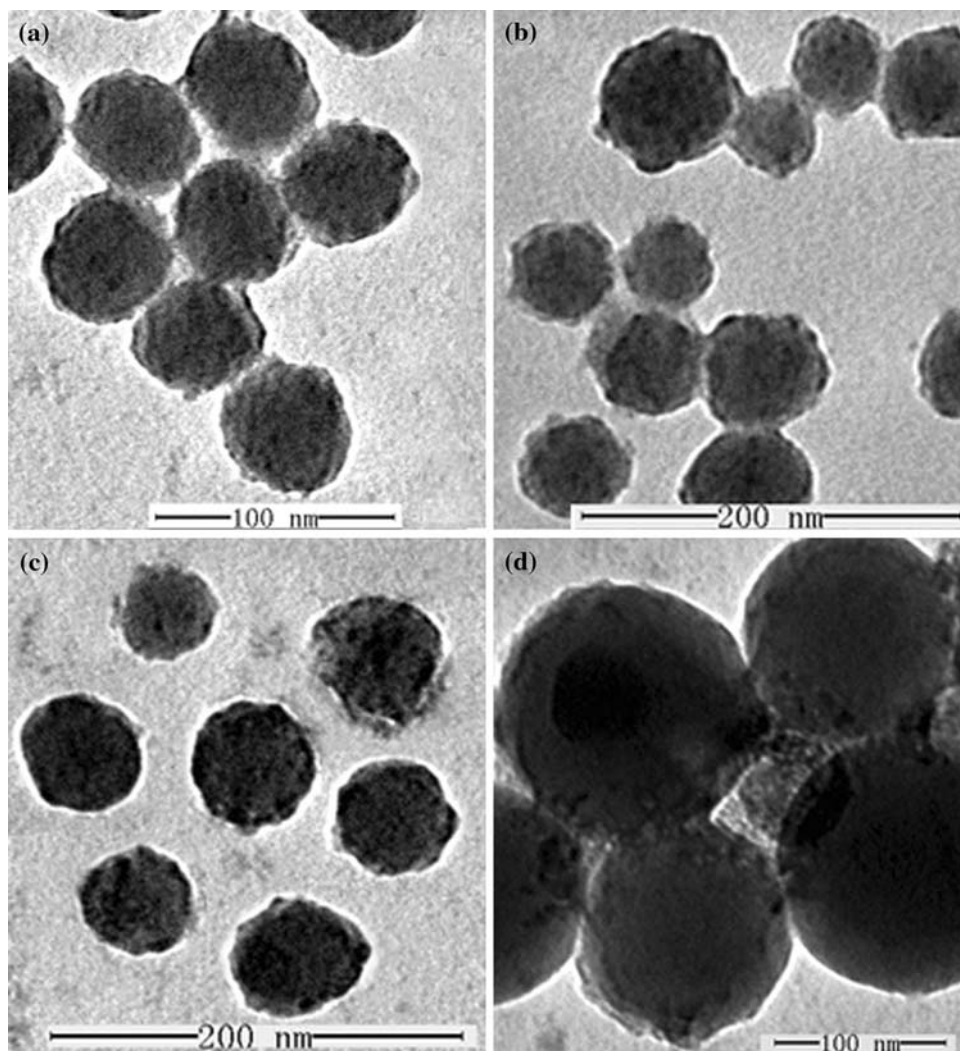
Fig. 2 TEM images of the coated particles (a one coating step, b five coating steps)

further indicates titania have been successfully coated on the surface of the nanosized silica particles.

To confirm the coating can be deposited on the surface of the silica particles at different lanthanide ions concentration, the coating process was carried out at different lanthanide ions concentration. The TEM images of the particles coated with different amount of added salt are shown in Fig. 3 (a: 0.25 g, b: 1.00 g, and c: 2.00 g). From those images we can see that the changing of the concentration of the added lanthanide salt has no great effect on the formation of the titania coating. No matter the concentration is low or high, the titania can be coated on the surface of the silica particles. In addition, we also used the particles with an average diameter of 150 nm as the support for titania coating. The TEM image is shown in Fig. 3d. According our experimental results, the process has been successfully used to deposit titania coatings on the surface of silica particles with a diameter ranging from 50 to 150 nm in the presence of lanthanide ions.

As we all know, silica nanoparticles are dispersive in ethanol because there are large amount of hydroxyl groups on the surface of the silica particles [26]. When a certain amount of lanthanide ethanol solution are added and

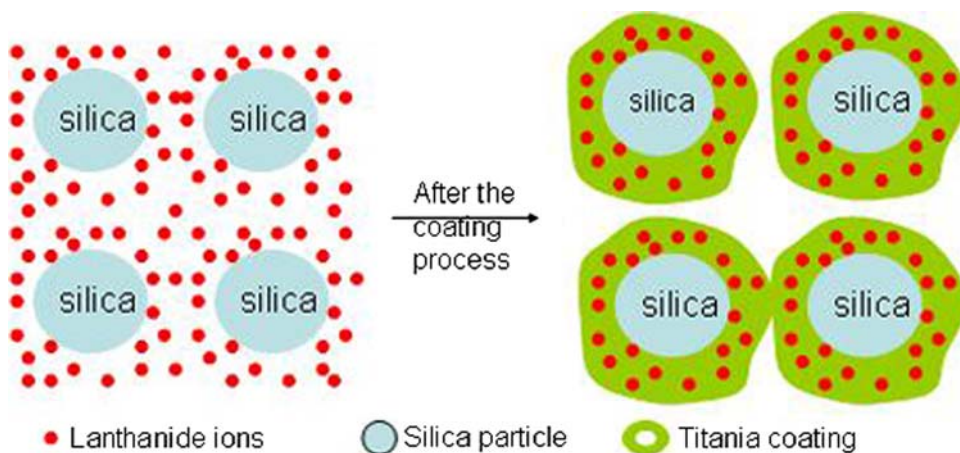
Fig. 3 TEM images of the coated particles with different amount of added lanthanide salts (**a** 0.25 g, **b** 1.00 g, **c** 2.00 g) and TEM image of the coated particles with a large silica core (**d**)



mixed, ions will tend to cluster around isolated silica particle because of the electrostatic force. When the TBOT are dropped into and start to hydrolysis, the TiO_2 network begin to form and cover on the surface of the silica. Simultaneously, the lanthanide ions will become trapped in

favorable sites within the TiO_2 framework. Finally, lanthanide-doped titania-coated silica nanoparticles are obtained. The schematic diagram illustrating the formation of the RE-doped titania-coated silica particles is shown in Scheme 1.

Scheme 1 Schematic diagram illustrating the formation of the RE-doped titania-coated silica particles



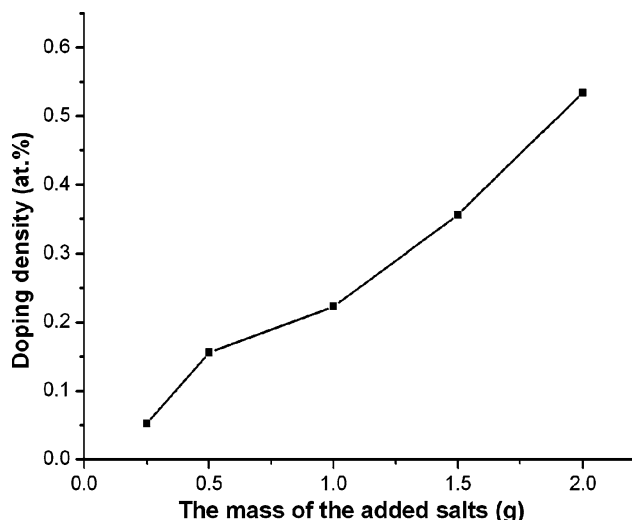


Fig. 4 Relationship between the amount of added lanthanide salt and the ions doping density

The doping density is an important factor for doped materials [20]. By changing the amount of added salt while keeping the ratio of TBOT: H₂O: SiO₂ constant, we are able to control the doping density of the ions in the particles. ICP was used to analyze the doping density of lanthanide ions in the final particles. The quantitative analysis results are shown in the Fig. 4. We can find that the doping density increase with the amount of added LnCl₃·6H₂O. However, the doping density is not linear with the amount of added salt. We believe that it is because not all the TBOT hydrolysis completely and not all the lanthanide ions are incorporated into the particles.

The PL of Eu³⁺-doped titania-coated silica nanoparticles with different doping density is measured at room temperature in air. The powders are heated to 400 °C before PL measurement. After being heat treated, the titania coatings have crystallized into anatase titania [10, 27]. Figure 5a shows the PL spectra of Eu³⁺-doped titania-coated silica nanoparticles. As we can see from the figure, under ultraviolet excitation (393 nm), all samples exhibit the characteristic luminescence of the Eu³⁺ ions at 578, 591, and 613 nm, respectively, of which 613 nm was the most strongest one, indicating that the optical properties of Eu³⁺ were retained in the titania-coated silica nanoparticles. The strongest emission peak at 613 nm is due to the force electric dipole transition (⁵D₀ → ⁷F₂). The peak around 578 nm corresponds to the ⁵D₀ → ⁷F₀ transition and those near 591 nm derive from the magnetic dipole transition (⁵D₀ → ⁷F₁). The luminescence from the ⁵D₀ → ⁷F₃ transition is too weak to be observed. And, the luminescence intensity increases with the increase of the ions doping density.

To demonstrate the feasibility of this strategy, we initially prepared Er³⁺-doped, Tb³⁺-doped particles can be

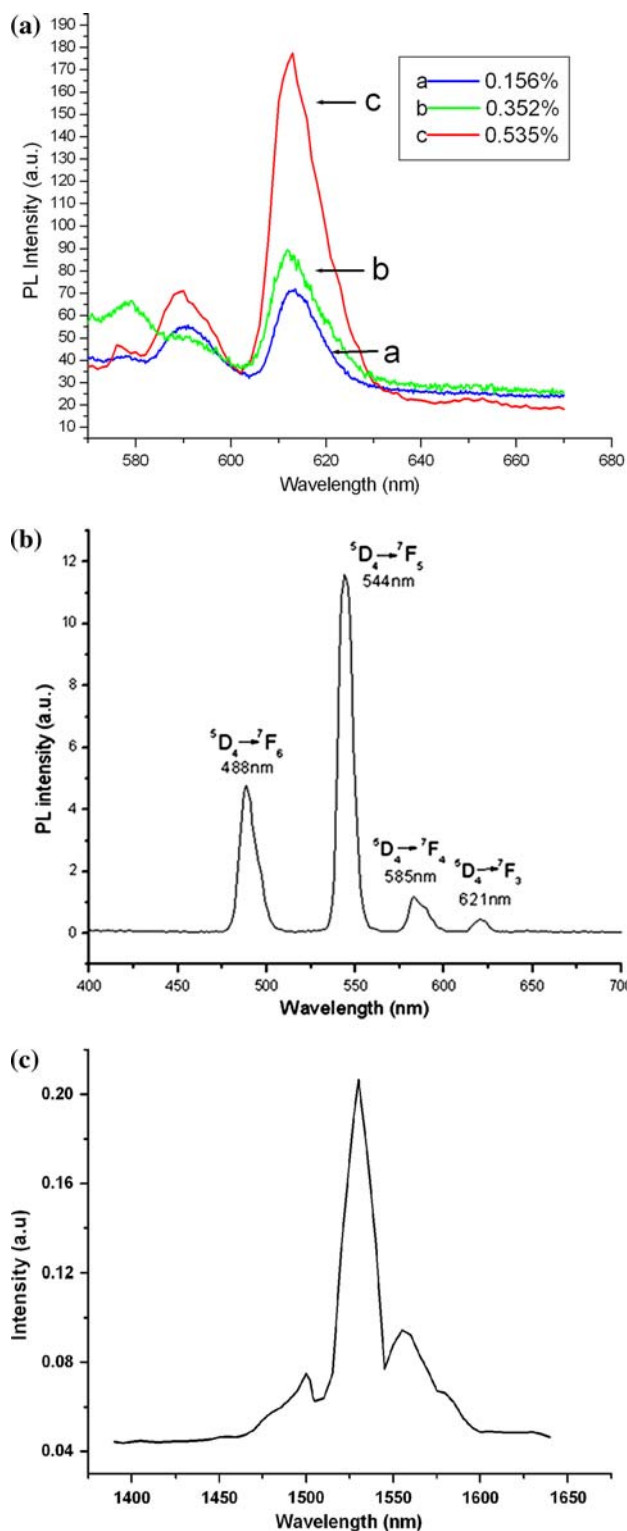


Fig. 5 The photoluminescence spectra of Eu³⁺-doped (a), Tb³⁺-doped (b), and Er³⁺-doped (c) titania-coated silica nanoparticles, for excitation at 393, 354, and 980 nm, respectively

prepared in the same way only using the corresponding lanthanide chloride in place of the Europium chloride. The PL of Tb³⁺-doped titania-coated silica nanoparticles, as

well as Er^{3+} -doped particles, were also measured. Figure 5b shows the PL of Tb^{3+} -doped titania-coated silica nanoparticles. From the figure, we can see that the PL spectrum of Tb^{3+} -doped particles exhibits the characteristic $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ electronic transitions as shown. The IR emission spectrum of Er^{3+} -doped particles was measured after the pretreatment at 700 °C for 2 h. The $^4\text{I}_{13/2} - ^4\text{I}_{15/2}$ transition at 1.5 μm is shown in Fig. 5c. Hence, different lanthanide ions-doped particles can be prepared by this method for different applications in need.

Conclusion

In conclusion, we have successfully applied the titania coating process in the synthesis of nanosized, monodisperse, lanthanide-doped titania-coated silica colloidal particles. Using this process, Eu^{3+} -doped, Tb^{3+} -doped, and Er^{3+} -doped particles were obtained, respectively. The average diameter of the silica core is 50 nm. The average thickness of the titania coating on the silica particles is about 3.5 nm. The ions doping density is controlled by the concentration of the lanthanide ions in the reaction mixture. The typical Ln^{3+} doping density is 0.052–0.535 at.%. The characteristic PL spectra were observed, respectively, from the Eu^{3+} -doped, Tb^{3+} -doped, and Er^{3+} -doped particles. The particles described in this work might find future applications in optical films, PBG materials and so on. Further study is ongoing.

Acknowledgements This work was supported by National Natural Science Foundation of China (No. 50573028), Major State Basic Research Project (G2000036604), Science and Technology Development Project of Jilin province (2006512), and National High Technology Development Project (2001.AA.312160). The authors are grateful to Yao Wang for providing us significant help.

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