Synthesis and luminescent properties of uniform monodisperse LuPO₄:Eu³⁺/Tb³⁺ hollow microspheres

Yu Gao¹,†, He Yu¹,†, Cheng Shi²,†, Guiyan Zhao², Yanfeng Bi¹, Baotong Xu¹, Fu Ding¹, Yaguang Sun¹ and Zhenhe Xu¹

¹The Key Laboratory of Inorganic Molecule-Based Chemistry of Liaoning Province, College of Applied Chemistry, Shenyang University of Chemical Technology, Shenyang 110142, People’s Republic of China
²College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun 113001, People’s Republic of China

Uniform monodisperse LuPO₄:Eu³⁺/Tb³⁺ hollow microspheres with diameters of about 2.4 µm have been successfully synthesized by the combination of a facile homogeneous precipitation approach, an ion-exchange process and a calcination process. The possible formation mechanism for the hollow microspheres was presented. Furthermore, the luminescence properties revealed that the LuPO₄:Eu³⁺ and LuPO₄:Tb³⁺ phosphors show strong orange-red and green emissions under ultraviolet excitation, respectively, which endows this material with potential application in many fields, such as light display systems and optoelectronic devices. Since the synthetic process can be carried out at mild conditions, it should be straightforward to scale up the entire process for large-scale production of the LuPO₄ hollow microspheres. Furthermore, this general and simple method may be of much significance in the synthesis of many other inorganic materials.

1. Introduction

Nowadays, rare earth luminescent micro/nanomaterials which have lots of excellent physical and chemical properties arising...
from their intra-4f transitions have attracted great attention from scientists and also been widely applied to lasers, displays, sensors, solar cells, electroluminescent devices and biomedical research [1–7]. Furthermore, to the best of our knowledge, the properties of rare earth luminescent micro/nanomaterials have a strong dependence on their chemical composition, size, morphology and crystallinity [8–13]. Therefore, regulating and controlling the size, shape and morphology of rare earth luminescent micro/nanomaterials are the focuses of chemistry and materials science [14,15]. Significant interest has recently been directed towards the formation of hollow spheres, which have porous shell, low density, high surface-to-volume ratio, low coefficients of thermal expansion and low refractive index, and have widespread applications in drug-delivery carriers, efficient catalysis, waste removal, sensors, active-material encapsulation, photonic crystals, batteries and so on [14–19]. Among the methods employed for the preparation of hollow spheres, template method has been widely used. Generally, the desired materials firstly are coated onto the core templates (e.g. SiO$_2$ [20], carbon spheres [21], polymers [22], metal particles [23]). Then, the core templates are removed by chemical etching or thermal treatment. Among the various core templates, considerable research efforts have been devoted to using colloidal polystyrene (PS) as template to synthesize hollow spheres, because they can be conveniently removed by selective dissolution in an appropriate solvent or by calcination at elevated temperature in air. To date, many inorganic hollow nano/microspheres, such as TiO$_2$ [18], BaTiO$_3$ and SrTiO$_3$ [24], have been successfully prepared via the template-directed synthesis route using PS as template. Hence, a facile, economic and green method to synthesize rare earth hollow micro/nanomaterials for large-scale industrial preparation with defined shape and multiple properties should be highly promising.

Among all of rare earth luminescent materials, lanthanide orthophosphates (LnPO$_4$) have excellent characteristics due to their low solubility in water, high chemical/thermal stability and high refractive index [2,8,14], which make them promising candidates for a variety of applications in down/up-conversion luminescence, magnets, lasers and bio-labeling [25,26]. Recently, many researches have reported on the synthesis of YPO$_4$ [27], LaPO$_4$ [28], CePO$_4$ [29] and GdPO$_4$ [14] micro/nanomaterials. Compared with a great deal of work on other orthophosphate materials, the study on the synthesis of LuPO$_4$ material has rarely been reported [30–34]. LuPO$_4$ is an excellent candidate for lanthanide ion substitution because of its favourable physical properties, such as high chemical stability, high melting point, high quantum yield and low toxicity. Up to now, some typical morphologies of LuPO$_4$, such as zero-dimensional nanoparticles [31], microspheres [32], one-dimensional nanorods [30] and three-dimensional microtetrahedron [30], have been successfully synthesized.

In our prior study, we reported the synthesis of the monodisperse LuPO$_4$ hollow spheres by using the Lu(OH)$_3$CO$_3$ precursor spheres as templates through the hydrothermal process [34]. However, to the best of our knowledge, there have been few reports on the synthesis of uniform, well-dispersed micrometre-scaled rare earth-doped LuPO$_4$ hollow spheres and their corresponding luminescence properties. Therein, the novel LuPO$_4$ hollow microspheres with diameters of about 2.4 µm were prepared by the combination of a facile homogeneous precipitation approach, an ion-exchange process and a calcination process. The structure, morphology, formation process and luminescence properties of the as-obtained hollow microspheres were investigated in detail. Moreover, the special structural geometry and excellent photoluminescent properties of the as-obtained LuPO$_4$ hollow microspheres will have promising potential to serve as solid-state lasers and display devices. Furthermore, this synthetic methodology may be promising for the synthesis of other hollow spherical materials because of its simplicity and the low cost of the starting reagents.

2. Experimental section

2.1. Materials

The rare earth oxides Ln$_2$O$_3$ (99.99%) (Ln = Lu and Eu) and Tb$_4$O$_7$ (99.99%) were purchased from GZSUNKO new material Co., Ltd. Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical-grade reagents and used as purchased without further purification. Rare earth chloride stock solutions were prepared by dissolving the corresponding metal oxide in hydrochloric acid at an elevated temperature.

2.2. Preparation of monodispersed polystyrene microspheres

Monodisperse PS colloidal microspheres were prepared by dispersion polymerization [35]. In a typical synthesis, the poly(N-vinylpyrrolidone) stabilizer (1.0 g) was dissolved in ethanol (38.2 ml) in
a three-necked round bottom flask fitted with a condenser and a magnetic stirrer. The reaction vessel was then heated to 70°C under a nitrogen blanket and purged with nitrogen for 2 h. Then, a solution of azoisobutyronitrile (0.15 g) pre-dissolved in styrene monomer (15 g) was added to the reaction vessel with vigorous stirring. The styrene polymerization was allowed to proceed for 12 h before cooling to room temperature. The product was purified by repeated centrifugation and washed with ethanol. A white fine powder (PS) was finally obtained after being dried in a vacuum oven at 50°C.

2.3. Preparation of monodisperse PS@Lu(OH)CO₃ microspheres

In the preparation procedure, 1 mmol of LuCl₃ aqueous solution and the as-prepared PS microspheres (100 mg) were added to 50 ml deionized water and well dispersed with the assistance of ultrasonication for 30 min. Then, 2.0 g of urea was dissolved in the solution under vigorous stirring. Finally, the mixture was transferred into a 100 ml flask and heated at 90°C for 2 h with vigorous stirring before the product was collected by centrifugation. The precursors were washed by deionized water and ethanol three times.

2.4. Preparation of monodisperse hollow LuPO₄ microspheres

In a typical synthesis, the as-obtained PS@Lu(OH)CO₃ sample was dispersed in deionized water by ultrasonication for 30 min. Then, 0.2 g of NH₄H₂PO₄ dissolved in 10 ml deionized water was dripped into the dispersion followed by further stirring. After additional agitation for 60 min, the as-obtained mixing solution was transferred into a Teflon bottle held in a stainless steel autoclave, sealed and maintained at 180°C for 12 h. As the autoclave was cooled to room temperature naturally, the precipitates were separated by centrifugation, washed with deionized water and ethanol in sequence, and then dried in air at 80°C for 12 h. The final hollow LuPO₄ microspheres were obtained through a heat treatment at 800°C in air for 4 h with a heating rate of 1°C min⁻¹. Hollow LuPO₄:Ln³⁺ (Ln³⁺ = Eu³⁺, Tb³⁺) spheres were prepared in a similar procedure except by adding corresponding Eu₂O₃, and Tb₄O₇ together with Lu₂O₃ as the starting materials as described above.

2.5. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a D8 Focus diffractometer (Bruker) with Cu-Kα₁ radiation (λ = 0.15405 nm). Fourier transform infrared spectroscopy (FT-IR) spectra were measured with a Perkin–Elmer 580B infrared spectrophotometer with the KBr pellet technique. Thermogravimetric data were recorded with Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) with the heating rate of 10°C min⁻¹ in an air flow of 100 ml min⁻¹. The morphologies and composition of the as-prepared samples were inspected on a field emission scanning electron microscope (FESEM, SU8010, Hitachi). Low- to high-resolution transmission electron microscopy (TEM) was performed using FEI Tecnai G² S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multiple CCD camera. The PL excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All measurements were performed at room temperature.

3. Results and discussion

The synthesis protocol of the hollow LuPO₄ microspheres is shown in scheme 1. In accordance with the previous reported method, the well-monodispersed PS colloidal microspheres were prepared by dispersion polymerization, and coated with a Lu(OH)CO₃ layer using urea-based chemical precipitation to form a monodisperse core-shell PS@Lu(OH)CO₃ microspheres (equations (3.1) and (3.2)). Subsequently, the core-shell PS@Lu(OH)CO₃ microspheres were reacted with NH₄H₂PO₄ under hydrothermal process, involving the replacement of the anions between CO₃²⁻ and PO₄³⁻ based on the Kirkendall effect [2,14]. The LuPO₄ bumpy skin layer was constructed and assembled on the surface of the PS microspheres as the reaction progress (equation (3.3)). Finally, the PS microspheres were removed through calcination of the PS@LuPO₄ sample and LuPO₄ hollow microspheres were formed.

\[
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2\text{NH}_3, \quad (3.1)
\]

\[
\text{PS} + \text{Lu}^{3+} + 3\text{NH}_3 + \text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{PS@Lu(OH)CO}_3 + 3\text{NH}_4^+ \quad (3.2)
\]

and

\[
\text{PS@Lu(OH)CO}_3 + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{PS@LuPO}_4. \quad (3.3)
\]
PS sphere \[\rightarrow\] \text{PS@Lu(OH)CO}_3\text{ core-shell sphere} \[\rightarrow\] \text{PS@LuPO}_4\text{ hollow sphere}

**Scheme 1.** Schematic illustration of the possible growth mechanism of the LuPO\(_4\) hollow microspheres.

**Figure 1.** SEM and TEM images of (a,b) the PS spheres, (c,d) the core-shell PS@Lu(OH)CO\(_3\) microspheres and (e,f) the core-shell PS@LuPO\(_4\) microspheres.

**Figure 1** shows SEM (left) and TEM (right) images of the PS microspheres (a and b), the core-shell PS@Lu(OH)CO\(_3\) microspheres (c and d), and the core-shell PS@LuPO\(_4\) microspheres (e and f). The as-obtained PS microspheres template consists of uniform microspheres with diameters of about 2.30 µm (figure 1a). It can be observed in the TEM image that the surfaces of monodisperse PS microspheres are very smooth (figure 1b). After deposition of Lu(OH)CO\(_3\) layer, the surface of PS@Lu(OH)CO\(_3\) core-shell microsphere is bumpier than PS microsphere. The size of the PS@Lu(OH)CO\(_3\) core-shell-structured microsphere (ca 2.50 µm) is larger than that of the bare PS microspheres (ca 2.4 µm) due to the amorphous Lu(OH)CO\(_3\) shell (figure 1c). From the TEM image (figure 1d), the core-shell structure can be easily found via the dark cores and the grey shell. Then, the core-shell-structured PS@LuPO\(_4\) microspheres with spiky LuPO\(_4\) shell were synthesized through an ion-exchange process under hydrothermal reaction conditions. The SEM image (figure 1e) shows that the core-shell PS@LuPO\(_4\) sample has an average size of about 2.55 µm and very rough surfaces with spikes. The TEM image (figure 1f) reveals that the sample with a diameter of 2.55 µm has a spiky surface and a solid structure, which agrees well with the SEM image.

**Figure 2** shows the SEM, TEM, HRTEM and HAADF-STEM images of the LuPO\(_4\) sample. The low- and high-magnification SEM images in figure 2a,b show that monodisperse and uniform LuPO\(_4\) hollow microspheres can be prepared by this approach. The size of the hollow microspheres is about 2.45 µm, which implies that the PS templates essentially determine the shape and structure of the final...
products. A small quantity of broken hollow microspheres further imply that the LuPO₄ microspheres have hollow structures because of the release of gaseous carbon/nitrogen oxides and water when the oxidation process of PS microspheres occurred during the calcination process. We also can see that the wall thickness of the hollow microspheres is about 75 nm. To provide further insight into the LuPO₄ hollow microspheres, a TEM investigation was performed. The TEM image (figure 2c) of the LuPO₄ hollow microspheres, and the corresponding elemental maps for (f) Lu, (g) P and (h) O.
hollow microspheres exhibits spherical morphology and a spiky surface. The strong contrast between the dark edge and the pale centre is direct evidence of the hollow nature of the microspheres. The average size of the hollow spheres and the thickness of the shells are estimated to be about 2.45 µm and 75 nm, respectively, which is in good agreement with the SEM observations. The obvious lattice fringes in the HRTEM image (figure 2d) confirm the high crystallinity. The interplanar distance between the adjacent lattice fringes is 0.253 nm, which can be indexed as the d spacing of the (112) plane of LuPO$_4$ crystal. Elemental mapping of the LuPO$_4$ hollow microspheres indicates that Lu, P and O elements are evenly distributed on the LuPO$_4$ hollow microspheres (figure 2e–h).

Figure 3 shows the XRD results of the PS spheres, the core-shell PS@Lu(OH)CO$_3$ microspheres, the core-shell PS@LuPO$_4$ microspheres and the final LuPO$_4$ hollow microspheres. In figure 3a for the PS spheres, an obviously broadened diffraction peak at 19° is observed, which can be assigned to the typical XRD pattern of PS spheres [10,36]. For the core-shell PS@Lu(OH)CO$_3$ microspheres (figure 3b), two broad bands at 30° and 47° can be observed, which imply that the as-formed core-shell PS@Lu(OH)CO$_3$ microspheres are amorphous. Figure 3c shows the XRD pattern of the sample that the core-shell PS@Lu(OH)CO$_3$ microspheres were treated with NH$_4$H$_2$PO$_4$ in the hydrothermal process. All of the diffraction peaks can be indexed as pure tetragonal phase, and coincide well with the standard data of LuPO$_4$ (JCPDS No. 84-0337). It means the product is the core-shell PS@LuPO$_4$. After annealing of the core-shell PS@LuPO$_4$ microspheres at 800°C for 4 h, the position of all peaks does not change (figure 3d). However, the diffraction peaks become stronger and sharper due to the increase of crystallinity. This is important for phosphors, because high crystallinity generally means less traps and stronger luminescence. Thus, it can be concluded that the calcination process has a dual function: elimination of the PS spheres cores to form hollow microspheres and increase of crystallinity.

To further examine the chemical compositions of the samples, FT-IR spectroscopy was conducted for all the products (figure 4). For the PS microspheres (figure 4a), the characteristic adsorption peaks at about 3150–2800, 1650–1350 and 600–820 cm$^{-1}$ can be attributed to the stretching vibrations of aromatic C–H in-plane, stretching vibrations of aromatic C–C and bending vibrations of aromatic C–C out-of-plane, respectively [37]. Compared with the PS microspheres, the core-shell PS@Lu(OH)CO$_3$ microspheres not only exhibit characteristic absorption bands of the PS microspheres, but also
Figure 4. FT-IR spectra of (a) the PS spheres, (b) the core-shell PS@Lu(OH)CO₃ microspheres, (c) the core-shell PS@LuPO₄ microspheres and (d) the LuPO₄ hollow microspheres.

Figure 5. TGA curves of (a) the PS spheres and (b) the core-shell PS@LuPO₄ microspheres.

show the bands at 1543, 1408, 838, 760, 698 and 664 cm⁻¹, corresponding to CO(νₐs), CO (νₛ), CO (δ), OH− (δ) and CO (δ) (νₐs = asymmetric stretch; νₛ = symmetric stretch; δ = deformation) (figure 4b) [10,36]. This result further indicates that the compositions of the core-shell PS@Lu(OH)CO₃ are the PS microspheres and Lu(OH)CO₃. For the core-shell PS@LuPO₄ microspheres (figure 4c), the vibration bands at 648 and 1023 cm⁻¹ represent the characteristic adsorption of the phosphate groups [14,38]. It means that the core-shell PS@Lu(OH)CO₃ microspheres can convert to the core-shell PS@LuPO₄ microspheres during the hydrothermal process. In the FT-IR spectrum of the LuPO₄ hollow microspheres, all of the functional groups of the PS microspheres nearly disappear, and the characteristic adsorptions of the phosphate groups do not change, which demonstrates that the PS template can thoroughly be removed by calcination. We also studied the thermal behaviour of the PS spheres and the core-shell PS@LuPO₄ microspheres by thermogravimetric analysis (TGA) technique (figure 5). There is one stage of weight loss for the PS spheres (line a), which can be attributed to the splitting burning of the PS spheres. For the core-shell PS@LuPO₄ microspheres, there are two stages of weight loss (line b): One is a slow weight loss because of the dehydration and densification of the PS microspheres. The other one is the burning of the PS microspheres. Finally, the residual weight percentage is about 70.53%, which accounts for the final LuPO₄ hollow microspheres, suggesting the considerably high yield of the hollow phosphors prepared by this method.

Figure 6a shows the excitation and emission spectra of the LuPO₄:Eu³⁺ hollow microspheres. The excitation spectrum is composed of a broadband from 200 to 280 nm and some sharp peaks from 280 to 450 nm. The broad excitation band can be ascribed to the charge transfer band between the O²⁻ anions and the Eu³⁺ ions. The other peaks are attributed to the f → f transitions within the Eu³⁺ 4f⁶ electron configuration. Upon excitation at 232 nm, the emission spectrum consists of the ⁵D₀ → ⁷F_J (j = 1, 2, 3, 4) transition lines of the Eu³⁺ ions. The strongest orange-red emission arises from the forced magnetic-dipole ⁵D₀ → ⁷F₁ (592 nm) transition of the Eu³⁺ ions. All the other emission peaks can be
Figure 6. Excitation (left) and emission (right) spectra of (a) LuPO₄: 5 mol% Eu³⁺ and (b) LuPO₄: 5 mol% Tb³⁺ hollow microspheres.

assigned to the $^{5}D_{0} \rightarrow ^{7}F_{2}$ (618 nm), $^{5}D_{0} \rightarrow ^{7}F_{3}$ (649 nm) and $^{5}D_{0} \rightarrow ^{7}F_{4}$ (694 nm) transitions of Eu³⁺ ions, respectively.

Figure 6b depicts the excitation and emission spectra of the LuPO₄:Tb³⁺ hollow microspheres. The excitation spectrum is composed of two bands with a maximum at 225 and 270 nm due to the $f \rightarrow d$ transitions of Tb³⁺ in the LuPO₄ lattice, and some weak lines in the longer wavelength. The peaks with weaker intensity are assigned to the transitions from the $^7F_6$ ground state to the different excited states of the Tb³⁺ ions, that is, $^{5}G_{2}$ (350 nm), $^{5}D_{2}$ (354 nm), $^{5}G_{6}$ (370 nm) and $^{5}D_{3}$ (381 nm), respectively. Upon the excitation at 225 nm, the obtained emission spectrum exhibits four obvious lines centred at 490, 545, 588 and 623 nm, that can be attributed to the transitions from the $^{5}D_{4}$ excited state to the $^7F_J$ ($J = 6, 5, 4, 3$) ground states of the Tb³⁺ ions, respectively. The $^{5}D_{4} \rightarrow ^{7}F_{5}$ transition at 545 nm is the most prominent group.

4. Conclusion

In summary, well-dispersed and homogeneous LuPO₄ hollow microspheres have been successfully achieved by the combination of a facile homogeneous precipitation approach, an ion-exchange process and a calcination process. The possible mechanism for the overall formation process of the hollow microspheres has been discussed in detail. Under UV excitation, the LuPO₄:Ln³⁺ (Ln³⁺ = Eu, Tb) hollow microspheres exhibit orange-red and green emissions, respectively. Furthermore, it is expected that our synthetic approach may open a new way for monodisperse hollow microspheres that exhibit promising physicochemical properties.

Data accessibility. This paper does not have any additional data.

Authors’ contributions. Y.B., F.D. and Z.X. conceived and designed the study; Y.G., C.S. and H.Y. performed the experiments and collected data; G.Z. and Y.S. analysed the data. Y.G. and Z.X. wrote the paper. All authors gave final approval for publication.

Competing interests. The authors have no competing interests.

Funding. This work is financially supported by the National Natural Science Foundation of China (NSFC 51402198, 21671139), the Natural Science Foundation of Liaoning Province (201602592, 20170540715), Educational Bureau of Liaoning Province for the Fundamental Research of Key Lab (grant no. LZZ2014028, LZZ2016003), the talent scientific research/scientific research cultivation fund of LSHU (no. 2015XJJ-009/2016PY-003).
