Controllable Fabrication and Optical Properties of Uniform Gadolinium Oxysulfate Hollow Spheres

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Uniform gadolinium oxysulfate (Gd2O2SO4) hollow spheres were successfully fabricated by calcination of corresponding Gd-organic precursor obtained via a facile hydrothermal process. The Gd2O2SO4 hollow spheres have a mean diameter of approximately 550 nm and shell thickness in the range of 30–70 nm. The sizes and morphologies of as-prepared Gd2O2SO4 hollow spheres could be deliberately controlled by adjusting the experimental parameters. Eu-doped Gd2O2SO4 hollow spheres have also been prepared for the property modification and practical applications. The structure, morphology, and properties of as-prepared products were characterized by XRD, TEM, HRTEM, SEM and fluorescence spectrophotometer. Excited with ultraviolet (UV) pump laser, successful downconversion (DC) could be achieved for Eu-doped Gd2O2SO4 hollow spheres.

Hollow spheres have been attracting great attention due to their superior properties such as high specific surface area, low density, high permeability and therefore show promising potential applications in various fields such as lithium batteries, catalysis and sensing, drug controlled release and delivery, and photonic building blocks, etc.1–6. Plenty of chemical and physicochemical strategies such as Ostwald ripening7, Kirkendall diffusion8, chemically induced self-transformation9, template-assisted synthesis10, and spray drying followed by annealing11,12 have been applied for the design and controlled fabrication of various micro/nanospheres with hollow interiors. In particular, template-assisted synthesis has been demonstrated to be the most effective and versatile synthesis method. The templates can be generally divided into hard templates13–15 and soft templates16–18, which have been widely used to fabricate hollow spheres. Among them, biomolecules, as attractive templates for the synthesis of metal and inorganic compound nanostructures, have been exploited for the precise control of the size and shape of various micro/nanomaterials, owing to the well-defined chemical and structural heterogeneity19–22. In spite of these pioneering work, it is still challenging and imperative to exploit an efficient but simple way for the synthesis of hollow spheres.

Rare earth oxysulfate (RE2O2SO4) have aroused great interest in recent years due to the unique magnetic23 and luminescent properties24,25 as well as significant applications in large volume oxygen storage26,27. RE2O2SO4 is also an important matrix compound for luminescent rare-earth ions to fabricate downconversion (DC) or upconversion (UC) phosphors due to the incompletely filled 4f electron shell of rare-earth ions28–30. RE2O2SO4 could be synthesized by the thermal decomposition of the corresponding hydrous sulfates (RE2(SO4)3∙nH2O), layered rare-earth hydroxides intercalated with dodecyl sulfate (DS) ions, and layered rare-earth hydroxysulfate (RE2(OH)4SO4∙nH2O)31–34. Nevertheless, the size and morphology of RE2O2SO4 products prepared by the above methods are not well controlled and no particular shape or uniform size can be achieved. Recently, we reported a unique synthetic process to prepare Y2O2SO4 hollow structure, which was mainly intended for the use of photoluminescence host materials35.

For Gd2O2SO4, due to its unique half-filled outer electron shell in rare-earth elements, it is promising in combining magnetic and luminescent properties. A peculiar hollow structure further endows Gd2O2SO4 to be

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Figure 1. (A) XRD patterns of as-prepared Gd-organic precursor and corresponding Gd$_2$O$_2$SO$_4$. The inset depicts the corresponding crystal structure of Gd$_2$O$_2$SO$_4$. The Gd, O, and S species are represented by violet, red, and yellow balls, respectively. (B) TG and DSC curves of as-prepared Gd-organic precursor annealing from 25 to 650°C at a heating rate of 10°C min$^{-1}$ in air.

a multifunctional nanomaterial for biomedical applications, such as magnetic resonance imaging, drug delivery host carriers and diagnostic analysis. This brings far-reaching impact than the availability of Y$_2$O$_2$SO$_4$ hollow structure. Herein, we present a facile biomolecule-assisted route to prepare uniform Gd$_2$O$_2$SO$_4$ hollow spheres via the calcination of corresponding spherical Gd-organic precursor obtained by using L-cysteine (Cys) as a biomolecule template. The size and morphology of as-prepared Gd$_2$O$_2$SO$_4$ hollow spheres can be deliberately controlled by adding different surfactants with varied amount. The formation process of the hollow spheres is elucidated by monitoring the species change and crystal structure evolution with elevated annealing temperature. Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres have also been successfully synthesized and the luminescence properties of as-prepared products were studied in detail.

**Results**

X-ray diffraction (XRD) was carried out to illuminate the change and evolution of chemical composition and crystal structures. Figure 1A shows the XRD patterns of the Gd-organic precursor and corresponding Gd$_2$O$_2$SO$_4$ obtained by calcination at 600°C for 2 h. No diffraction peaks were verified, indicating the initial precursor with broad featureless peaks was amorphous or non-crystalline. After annealing at 600°C for 2 h, the precursor was converted into a single phase of Gd$_2$O$_2$SO$_4$, and no other impurity phases can be observed. All the reflections can be indexed to the literature values (JCPDS 29–0613). The crystal structure of Gd$_2$O$_2$SO$_4$ can commonly be depicted as an alternative stacking of Gd$_2$O$_2$SO$_4$ tetrahedra unit is coordinated with two Gd atoms, and anion groups of sulfate (SO$_4$$^{2-}$) layers along the a-axis, as shown in the inset of Figure 1A. The Gd$_2$O$_2$SO$_4$ layer consists of [GdO$_4$] tetrahedra linked together by shared of edges. Every [SO$_4$]$^{2-}$ tetrahedral unit is coordinated with two Gd atoms. The thermal decomposition behaviors of Gd-organic precursor was investigated in the temperature range of 25–650°C at a heating rate of 10°C min$^{-1}$ in air. As shown in Figure 1B, the weight loss in the temperature range from 25 to 200°C was about 5.9% by mass, which can be associated with the removal of loosely bound water and organic residues on the Gd-organic precursor surfaces. The subsequent weight loss took place rapidly at a much higher temperature range. The continuous stages of weight loss in the range of 200 to 600°C were 18.2% and 14.1% by mass. The tremendous decrease of weight can be attributed to the oxidation or combustion of the initial precursor and crystallization into Gd$_2$O$_2$SO$_4$. Corresponding to the two remarkable mass loss, the DSC curve of the sample displayed three major exothermal peaks in the gravimetric gain region centered at 274°C, 516°C and 535°C respectively. As shown in the TG curve, little weight change can be observed at temperatures higher than 600°C, suggesting that the relatively stable compound was obtained. Therefore, the hydrothermal products were annealed at 600°C for the crystallization of Gd$_2$O$_2$SO$_4$ hollow spheres.

Fourier transform infrared (FT-IR) spectroscopy was employed to investigate the structural and functional group information of the Gd-organic precursors and powders calcined at different temperatures. As shown in the Figure 2A, the FT-IR spectra reveal the existence of absorbed water, crystal water, hydroxyl groups (~3410 cm$^{-1}$ and 1640 cm$^{-1}$), carbonates anions (~1580 cm$^{-1}$ and 1415 cm$^{-1}$) and sulfates anions (~680 cm$^{-1}$) in the Gd-organic precursors. The weak peaks at 2965 cm$^{-1}$ and 2927 cm$^{-1}$ are assigned to the C-H vibration mode of -CH$_2$-$\bar{\nu}$. As the temperature of calcination increasing to 200°C and 400°C, the broad band at 3410 cm$^{-1}$ becomes weaker and weaker while the small peak at 1640 cm$^{-1}$ disappears at 400°C, which can be attributed to the removal of absorbed water and crystal water from the Gd-organic precursors. A similar behavior of carbonates absorption bands at 1580 cm$^{-1}$ and 1415 cm$^{-1}$ can be observed, suggesting that the carbonate anions in the precursors decomposed or vaporized with increasing the temperature. These results are in good agreement with the results of TG-DSC analysis. Both the broad band at 3410 cm$^{-1}$ and carbonates absorption bands are significantly reduced at a higher calcination temperature of 600°C; while a broad sulfates absorption band at 1130 cm$^{-1}$ appears at 400°C and splits into three narrow and sharp peaks at 1198 cm$^{-1}$, 1121 cm$^{-1}$ and 1063 cm$^{-1}$ at 600°C. The broadened sulfates absorption band at 680 cm$^{-1}$ in the precursors becomes weaker and splits into three narrow and sharp peaks at 663 cm$^{-1}$, 621 cm$^{-1}$ and 603 cm$^{-1}$ in the final products. These two group of narrow and sharp sulfates absorption bands are assigned to the deformation vibrations and the asymmetric stretching of SO$_4$$^{2-}$ anions, respectively.
These results are in accordance with those obtained from TG-DSC, XRD patterns in Figure S1 and ICP analysis in Table S1, illustrating the composition and structural evolution of the Gd$_2$O$_2$SO$_4$ products.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to characterize the sizes and morphologies of as-prepared products. Figure 3A,B show the spherical Gd-organic precursors with a smooth surface and an average size of approximately 650 nm. After calcinating the Gd-organic precursors at 600 °C for 2 h, as shown in Figure 3C,D, Gd$_2$O$_2$SO$_4$ hollow spheres with relatively rough surfaces were obtained. The average diameter of the hollow spheres was estimated to be approximately 550 nm, as shown in Figure S2, with a slightly decreasing in comparison with that of the precursor, implying the tendency to shrink after calcination. The strongly contrast between the dark periphery and greyish center of Gd$_2$O$_2$SO$_4$ spheres reveals that these spheres were of hollow structures, and the shell thickness was about 60 nm. The inset in Figure 3D represents a

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**Figure 2.** FT-IR spectra of the Gd-organic precursors (A) and the powders after calcinating at 200 °C (B), 400 °C (C) and 600 °C (D) for 2 h.

**Figure 3.** (A) SEM and (B) TEM images of spherical Gd-organic precursors. (C) SEM and (D) TEM images of Gd$_2$O$_2$SO$_4$ hollow spheres. The inset in (D) is corresponding SAED pattern; (E) HRTEM image of Gd$_2$O$_2$SO$_4$ hollow sphere.
typical selected area electron diffraction (SAED) pattern, which can be indexed to the monoclinic structure of Gd$_2$O$_2$SO$_4$, consistent with the XRD result presented above. Figure 3E displays the corresponding high-resolution TEM (HRTEM) image, in which the lattice fringes were measured to be about 0.27 and 0.30 nm, corresponding to the interplanar spacings between (112) and (013) crystallographic planes, respectively. The current synthetic route could be adopted as a general strategy for the preparation of a series of rare-earth oxysulfate hollow spheres.

L-Cys, as a biomolecule template, possesses abundant functional groups, such as -SH, -NH$_2$, and -COOH, which can coordinate to Gd$^{3+}$ and form homogeneous Gd-organic coordination compound on the basis of metal-ligand interaction in the solution$^{3,4,35}$, leading to the formation of spherical precursors through aggregation and coagulation. Calcination temperature-depended formation mechanism of hollow spheres was investigated in detail as shown in Figure S3. After calcinating the solid spherical Gd-organic precursors at 200 °C for 2 h shown in Figure S3A, dark periphery and slightly greyish center of the spheres could be observed in the product. As the temperature of calcination increasing to 400 °C, the area of the greyish center of the spheres increased. Finally, the spheres with apparent hollow structure were obtained at the calcination temperature of 600 °C. We consider that the formation mechanism of the hollow spheres may involve two steps: First, a dense rigid shell formed in the surface of the solid spheres as the existence of the a large temperature gradient (∆T) along the radial direction at initial stage$^{40}$. Then in the subsequent calcination, as the adhesion force ($F_a$) surpasses the contraction force ($F_c$), the inner part shrinks outward, a hollow cavity in the center of the spheres were obtained$^{41}$. The organic substances were all burnt out at 600 °C and the Gd-organic precursors were gradually crystallized into Gd$_2$O$_2$SO$_4$ at the peripheries, meanwhile, the hollow structure was formed.

It was generally believed that surfactants played an important role in the control of morphologies and sizes of nanomaterials. Xia et al. studied the metal crystal growth kinetic process by using the different surfactants, such as cetyltrimethyl ammonium bromide (CTAB), polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and so on, to maneuver the surface energies and growth rates for different facets$^{42,43}$. The ratio between growth rates of different facets determined the growth habit of a nanocrystal, leading to the formation of different sizes and morphologies of nanomaterial. PVP had been widely introduced into the shape controlled synthesis of nanomaterials, such as and nanowires, nanosheets, nanospheres and so forth$^{44,45}$. In this paper, we have studied the effect of surfactants on the synthesis of Gd$_2$O$_2$SO$_4$ hollow spheres. Figure 4A shows the SEM image of as-prepared Gd$_2$O$_2$SO$_4$ without using any surfactants. Although Gd$_2$O$_2$SO$_4$ hollow spheres with broken shell could be observed in the absence of surfactant, the products had a tendency to agglomerate into block, and the size also reached the micrometer range. As shown in Figure 4B, when 0.15 g PVP was introduced into the synthesis of Gd$_2$O$_2$SO$_4$ hollow spheres. The resulting product was mainly uniform spherical particles with smooth surfaces. However, with increasing the amount of PVP to 0.6 g (Figure 4C), the surface of hollow spheres became relatively rough. Thus, 0.3 g PVP was chosen as an optimal amount in the typical synthetic procedure of Gd$_2$O$_2$SO$_4$ hollow spheres. The exact mechanism of the function of PVP on the morphology and size of Gd$_2$O$_2$SO$_4$ hollow spheres is yet to be fully understood, it is believed that the strong interaction between the surfaces of Gd-organic precursors and PVP through coordination bonding with the O and N atoms of the pyrrolidone ring played a major role in determining the product morphology and size$^{45}$. We also found that the CTAB as surfactant has similar functions in the synthesis of Gd$_2$O$_2$SO$_4$.
hollow spheres, as shown in Figure 4D. CTAB was used instead of PVP while other synthetic parameters were kept unchanged. The resulting product was mainly uniform Gd$_2$O$_2$SO$_4$ spheres with rough surface and the average size decreased to approximately 350 nm. These results further proved the indispensable role of surfactants in the formation of Gd$_2$O$_2$SO$_4$ hollow spheres.

The introduction of other rare-earth ions such as Eu$^{3+}$ ions into Gd$_2$O$_2$SO$_4$ host lattice caused little change both on morphology and crystal phase. As shown in Figure 5, when 5% Eu$^{3+}$ was added into the Gd$_2$O$_2$SO$_4$ host lattice, the morphology of final products, as well as the organic precursor shown in Figure S4, remained unchanged compared with the pure Gd$_2$O$_2$SO$_4$. The crystalline nature of Gd$_2$O$_2$SO$_4$:Eu hollow spheres was confirmed by HRTEM. Figure 5C clearly shows the lattice fringes were measured to be about 0.18 nm, corresponding to the interplanar spacing of (024) crystallographic plane, which fairly well agree with the standard interplanar spacing. The result of X-ray diffraction analyses further proved that the introduction of 5% Eu$^{3+}$ ions into the Gd$_2$O$_2$SO$_4$ host lattice has no significant change on the crystal structure, as show in Figure S5, owing to the same trivalent state and similar ionic radius of Gd$^{3+}$ ions ($r$(Gd$^{3+}$) = 0.0938nm) and Eu$^{3+}$ ions ($r$(Eu$^{3+}$) = 0.095 nm). The elemental maps of the 5% Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres obtained on TEM were displayed in Figure 5D, which clearly demonstrates a homogeneous distribution of Gd, Eu, S and O elements. The energy dispersive spectrometer (EDS) spectrum in Figure S6 reveals that the as-obtained product mainly contains Gd, Eu, S and O elements (Au signals were come from the spray-gold treatment to enhance the electrical conductivity of the material). The molar ratio of Eu:Gd was about 3.23:96.77, which was consistent with the ratio of used reagents in synthetic process. The above results confirm that successful doping could be achieved through current synthetic strategy.

**Discussion**

The excitation spectra of the 5% Eu-doped Gd$_2$O$_2$SO$_4$ phosphors was recorded in the wavelength range of 200–500 nm at room temperature, as shown in Figure 6A, one can see that a broad absorption band with a maximum at around 270 nm exists, which is resulted from the typical $^{5}S_{7/2} ightarrow ^{5}I_{7/2}$ transition of the Gd$^{3+}$ ions$^{46}$. Furthermore, other two comparatively weak peaks centered at 394 nm and 465 nm can be respectively assigned to the typical f-f transition of Eu$^{3+}$ ions, corresponding to the $^{7}F_{0} ightarrow ^{5}L_{6}$ and $^{7}F_{0} ightarrow ^{5}D_{2}$ transitions$^{37}$. Excitation spectra of the 5% Eu-doped Gd$_2$O$_2$SO$_4$ phosphors was taken by monitoring the wavelength of 617 nm.

The emission spectrums of 5% Eu-doped Gd$_2$O$_2$SO$_4$ under 270 nm light excitation (Figure 6B) demonstrate the characteristic $^{3}D_{0} ightarrow ^{7}F_{J}$ (J = 1, 2, 3, 4) and $^{3}D_{1} ightarrow ^{7}F_{J}$ (J = 3, 4) transitions of Eu$^{3+}$ ions, indicating the effective cooperative luminescence between Gd$^{3+}$ and Eu$^{3+}$. The strongest emission which splits into two peaks centered at 613 nm and 617 nm can be attributed to the forced electric dipole $^{3}D_{0} ightarrow ^{7}F_{2}$ transition of Eu$^{3+}$ ions. All the other emission peaks are easily assigned to the $^{3}D_{1} ightarrow ^{7}F_{2}$ (579, 586 nm), $^{3}D_{0} ightarrow ^{7}F_{1}$ (594, 596 nm), $^{3}D_{1} ightarrow ^{7}F_{1}$ (627 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (639 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (651 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (663 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (675 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (687 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (699 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (711 nm), $^{3}D_{1} ightarrow ^{7}F_{0}$ (723 nm), and $^{3}D_{1} ightarrow ^{7}F_{0}$ (735 nm) transitions of Eu$^{3+}$ ions.

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**Figure 5.** (A) SEM and (B) TEM images of as-prepared 5% Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres. Inset is the corresponding SAED pattern. (C) HRTEM image of 5% Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres; (D) STEM HAADF and elemental maps of Gd, Eu, O and S of 5% Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres.
$^{5}D_{0} \rightarrow {^{7}F}_{3}$ (649 nm), $^{5}D_{0} \rightarrow {^{7}F}_{4}$ (693, 701 nm) transition of Eu$^{3+}$ ions, respectively$^{47-50}$. In this process, trivalent Gd$^{3+}$ ions, as sensitizer, absorb ultraviolet excitation light and subsequently transfer energy to the neighboring Eu$^{3+}$ ions act as activator, resulting in the overall red emission of Eu$^{3+}$. The detailed energy level and transfer scheme was shown in inset of Figure 6B. Upon excitation by 270 nm, Gd$^{3+}$ ions will be excited into $^{6}I_{7/2}$ state from ground state in the first step and then fast relax from this high excitation state to the $^{6}P_{J}$ state. Secondly, the Gd$^{3+}$ ions in the $^{6}P_{J}$ state can easily transfer the excitation energy to the Eu$^{3+}$ ions (5HJ) because of the energy level match between $^{6}P_{J}$ state and $^{5}H_{J}$ state$^{50}$. Fast non-radiative relaxation from 5HJ state to the 5D1 or 5D0 state occurs. The electron on high excitation 5D1 and 5D0 states further relaxes radiatively to the ground-state to generate different wavelength visible emissions. Furthermore, as shown in Figure S7, the emission intensity of the Gd-organic precursors with poor crystallinity can be negligible comparing to the final products with high crystallinity.

Conclusions
In summary, uniform gadolinium oxysulfate hollow spheres have been successfully achieved by a facile hydrothermal process combining with a calcination of Gd-organic precursors. Based on the experimental results, we found both the amount and the type of surfactants play an important role for the formation of Gd$_2$O$_2$SO$_4$ hollow spheres. Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres have also been successfully synthesized with little change both on size and crystal phase. Optical properties reveal that the Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres can be used to down-convert UV light to visible light under the UV excitation. It is expected that the uniform Gd$_2$O$_2$SO$_4$ hollow spheres have potential applications in various research field, such as large volume oxygen storage, drug delivery host carriers, optical/display devices and luminescence probes.

Methods
All the reagents are of analytical grade and used as starting materials without further purification.

Preparation of gadolinium oxysulfate hollow spheres. In a typical synthetic procedure of Gd$_2$O$_2$SO$_4$ hollow spheres, 1 mmol of hydrated gadolinium nitrate (Gd(NO$_3$)$_3$·6H$_2$O), 2.0 mmol of L-Cys (L-cysteine) and 0.3 g of PVP (polyvinylpyrrolidone) were dissolved in 20 ml deionized water under vigorous magnetic stirring. Then the resulting solution was transferred into Teflon-lined stainless steel autoclave of 50 ml capacity and maintained at 140 °C for 24 h. After cooling to room temperature naturally, the resulting precipitates were washed with distilled water and anhydrous alcohol for several times, and dried at 50 °C for 4 h. Finally, the precursors can be transformed into Gd$_2$O$_2$SO$_4$ hollow spheres by calcination the Gd-organic precursor at 600 °C for 2 h. Furthermore, the 5% Eu-doped Gd$_2$O$_2$SO$_4$ hollow spheres were also obtained by similar process.

Characterization. X-ray diffraction patterns were recorded by a D/max2550 VB+ diffractometer with Cu Kα radiation (λ = 0.15405 nm) in the 2θ range of 10°–70°. The morphology of the as-prepared products was examined by a field emission scanning electron microscopy (FE-SEM, Sirion 200) with an accelerating voltage of 15 kV. The energy dispersive spectrometer (EDS) was taken on the SEM. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED), high-resolution TEM (HRTEM) and the elemental mapping were recorded on a Tecnai G2 F20 transmission electron microscope with an accelerating voltage of 200 kV. Thermogravimetric and differential scanning calorimetry (TG-DSC) were carried out using a simultaneous thermal analysis (STA, NETZSCH STA 449C) in a temperature range of 25–650 °C at a heating rate of 10 °C min$^{-1}$ under an air flow. Fourier transform infrared (FT-IR) spectroscopy were obtained on a Nicolet Nexus 6700 instrument. Baird PS-6 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) were used to evaluate the element content. The photoluminescence (PL) excitation and emission spectra were obtained on a fluorescence spectrophotometer (Hitachi F-4500) at room temperature.
References
1. Lou, X. W., Archer, L. A. & Yang, Z. Hollow micro-/nanostructures: synthesis and applications. Adv. Mater. 20, 3987–4019 (2008).
2. Tian, G. et al. Facile fabrication of rare-earth-doped Gd2O3 hollow spheres with upconversion luminescence, magnetic resonance, and drug delivery properties. J. Phys. Chem. C 115, 23790–23796 (2011).
3. Liu, X. et al. General synthetic strategy for high-yield and uniform rare-earth oxysulfate (RE2O2SO4, RE=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, and Yb) hollow spheres. RSC Adv. 2, 9362 (2012).
4. Chen, G. et al. Controlled fabrication and optical properties of uniform CeO2 hollow spheres. RSC Adv. 3, 3544 (2013).
5. Wang, B. et al. Uniform magnesia silicate hollow spheres as high drug-loading nanocarriers for cancer therapy with low systemic toxicity. Dalton Trans. 42, 8918–8925 (2013).
6. Zhang, H. et al. Tailoring the void size of iron oxide@carbon yolk-shell structure for optimized lithium storage. Adv. Funct. Mater. 24, 4337–4342 (2014).
7. Zeng, H. C. Synthetic architecture of interior space for inorganic nanostructures. J. Mater. Chem. 16, 649–662 (2006).
8. Zhang, F., Shi, Y., Sun, X., Zhao, D. & Stucky, G. D. Formation of hollow upconversion rare-earth fluoride nanospheres: nanoscale kirkendall effect during ion exchange. Chem. Mater. 21, 5237–5243 (2009).
9. Yu, J. G., Guo, H., Davis, S. A. & Stephen, M. Fabrication of hollow inorganic microspheres by chemically induced self-transformation. Adv. Funct. Mater. 16, 2035–2041 (2006).
10. Zhang, J. et al. Preparation and size control of sub-100 nm pure nanodrugs. Nano lett. 15, 313–318 (2015).
11. Zhou, L. et al. Cheap and scalable synthesis of α-Fe2O3 multi-shelled hollow spheres as high-performance anode materials for lithium ion batteries. Chem. Commun. 49, 8695–8697 (2013).
12. Padashbarmchi, Z. et al. A systematic study on the synthesis of α-Fe2O3 multi-shelled hollow spheres. RSC Adv. 5, 10304–10309 (2015).
13. Tritirici, M. M., Antonietti, M. & Thomas, A. A. Generalized synthesis of metal oxide hollow spheres using a hydrothermal approach. Chem. Mater. 18, 3808–3812 (2006).
14. Salgueiriño-Maceira, V., Spasova, M. & Farle, M. Water-stable, magnetic silica-cobalt/cobalt oxide-multishell submicrometer spheres. Adv. Funct. Mater. 15, 1036–1040 (2005).
15. Xia, Y. & Mokaya, R. Hollow spheres of crystalline porous metal oxides: A generalized synthesized route via nanocasting with mesoporous carbon hollow shells. J. Mater. Chem. 15, 3126–3131 (2005).
16. Fowler, C. E., Khusabali, D. & Mann, S. Interfaceal synthesis of hollow microspheres of mesostructured silica. Chem. Commun. 2008–2029 (2001).
17. Schmidt, H. T. & Ostañín, A. E. Liposome directed growth of calcium phosphate nanoshells. Adv. Mater. 14, 532–533 (2002).
18. Hentze, H. P., Raghavan, S. R., McKelvey, C. A. & Kaler, E. W. Silica hollow spheres by templating of cationic vesicles. Langmuir 19, 1069–1074 (2003).
19. Knez, M. et al. Biotemplate synthesis of 3-nm nickel and cobalt nanowires. Nano lett. 3, 1079–1082 (2003).
20. Lu, Q., Gao, F. & Komarneni, S. Biomolecule-assisted synthesis of highly ordered snowflake-like structures of bismuth sulfide nanorods. J. Am. Chem. Soc. 126, 54–55 (2004).
21. Zhao, P., Huang, T. & Huang, K. Fabrication of indium sulfide hollow spheres and their conversion to indium oxide hollow spheres consisting of multipore nanoflakes. J. Phys. Chem. C 111, 12890–12897 (2007).
22. Li, B., Xie, Y. & Xue, Y. Controllable synthesis of Cu3 nanoparticles from self-assembled precursors with biomolecule assistance. J. Phys. Chem. C 111, 12181–12187 (2007).
23. Paul, W. Magnetism and magnetic phase diagram of Gd2O3S. I. Experiments. J. Magn. Magn. Mater. 87, 23–28 (1990).
24. Song, L., Du, P., Jiang, Q., Cao, H. & Xiong, J. Synthesis and luminescence of high-brightness Gd2O2SO4:Tb3+ nanopieces and the enhanced luminescence by alkali metal ions co-doping. J. Lumin. 156, 50–54 (2014).
25. Wei, X., Wang, W. & Chen, K. Preparation and characterization of ZnS:Te, Gd and ZnS:Er, Yb, Gd nanoparticles for bimodal magnetic-fluorescent imaging. Dalton Trans. 42, 1752–1759 (2013).
26. Machida, M., Kawamura, K. & Ito, K. Novel oxygen storage mechanism based on redox of sulfur in lanthanum oxysulfate/oxysulfide. Chem. Commun. 662–663 (2004).
27. Machida, M., Kawano, T., Eto, M., Zhang, D. & Ikuse, K. Ln dependence of the large-capacity oxygen storage/release property of Ln oxysulfate/oxysulfide systems. Chem. Mater. 19, 954–960 (2007).
28. Auzel, F. Upconversion and anti-stokes processes with f and d ions in solids. Chem. Rev. 103, 139–174 (2004).
29. Wang, F. & Liu, X. Recent advances in the chemistry of lanthanide-doped upconversion nanocrystals. Chem. Soc. Rev. 38, 976–989 (2009).
30. Lian, J., Sun, X., Li, J., Xiao, B. & Duan, K. Characterization and optical properties of (Gd5+ Pr3+O3)NPs synthesized using a novel co-precipitation method. J. Phys. Chem. Phys. 122, 354–361 (2010).
31. Kijima, T., Shinbore, T., Sekita, M., Uota, M. & Sakai, G. Abnormally enhanced Eu3+ emission in Y2O2SO4·Eu3+ from their precursory dodecysulfate-templated concentric-layered nanocrystals. J. Lumin. 128, 311–316 (2008).
32. Kijima, T., Isayama, T., Sekita, M., Uota, M. & Sakai, G. Emission properties of Tb3+ in Y2O2SO4 derived from their precursory dodecysulfate-templated concentric-and straight-layered nanocrystals. J. Alloys Compd. 485, 730–733 (2009).
33. Machida, M., Kawamura, K., Ito, K. & Ikuse, K. Large-capacity oxygen storage by lanthanide oxysulfate/oxysulfide systems. Chem. Mater. 17, 1487–1492 (2005).
34. Liang, J., Ma, R., Geng, F., Ebina, Y. & Sasaki, T. Ln(OH)3·nH2O·Ln (Ln = Pr to Tb; n ~2): A new family of layered rare-earth hydroxides rigidly pillared by sulfate ions. Chem. Mater. 22, 6001–6007 (2010).
35. Chen, G. et al. Hollow spherical rare-earth-doped yttrium oxysulfate: A novel structure for upconversion. Nano Res. 7, 1093–1102 (2014).
36. Zhukov, S. et al. Structural study of lanthanum oxysulfate (La2O2SO4). Mater. Res. Bull. 32, 43 (1997).
37. Lian, J., Sun, X., Liu, Z., Yu, J. & Li, X. Synthesis and optical properties of (Gd5+ Eu3+)O3·nH2O nano-phosphors by a novel co-precipitation method. Mater. Res. Bull. 44, 1822–1827 (2009).
38. Ru, T., Je, Q., Min, L. & Liu, G. Synthesis of yttrium aluminum garnet (YAG) powder by homogeneous precipitation combined with supercritical carbon dioxide or ethanol fluid drying. J. Eur. Ceram. Soc. 28, 2903–2914 (2008).
39. Jayaveer, R. S., Mahadevan Pillai, P. V., Nayyar, V. U., Odnevall, I. & Kerszberg, G. Raman and infrared spectral analysis of corrosion products on zinc NaZn4Cl(OH)6SO4·6H2O and ZnCl2(OH)4SO4·5H2O. Mater. Chem. Phys. 99, 474–478 (2006).
40. Guan, J., Mou, F., Sun, Z. & Shi, W. Preparation of hollow spheres with controllable interior structures by heterogeneous contraction. Chem. Mater. 46, 6605–6607 (2010).
41. Zhao, Z. L. & Lou, X. W. Double-shelled CoMo2O4 hollow microcubes as high-capacity anodes for lithium-ion batteries. Adv. Mater. 24, 745–748 (2012).
42. Xia, Y., Xiong, Y., Lim, B. & Skrabalak, S. E. Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics. Angew. Chem., Int. Ed. 48, 60–103 (2009).
43. Jin, M. et al. Shape-controlled synthesis of copper nanocrystals in an aqueous solution with glucose as a reducing agent and hexadecylamine as a capping agent. Angew. Chem., Int. Ed. 50, 10560–10564 (2011).
44. Wang, J., Wang, X., Peng, Q. & Li, Y. Synthesis and characterization of bismuth single-crystalline nanowires and nanospheres. Inorg. Chem. 43, 7552–7556 (2004).
45. Zhou, F., Zhao, X., Xu, H. & Yuan, C. CeO2 spherical crystallites: synthesis, formation mechanism, size control, and electrochemical property study. J. Phys. Chem. C 111, 1651–1657 (2007).
46. Liu, Y. et al. A strategy to achieve efficient dual-mode luminescence of Eu3+ in lanthanides doped multifunctional NaGdF4 nanocrystals. Adv. Mater. 22, 3266–3271 (2010).
47. Lian, J. B., Sun, X. D. & Li, X. D. Synthesis, characterization and photoluminescence properties of (Gd1-x,Eu)x2O3 sub-microphosphors by homogeneous precipitation method. Mater. Chem. Phys. 125, 479–484 (2011).
48. Song, Y. et al. Highly uniform and monodisperse Gd2O2S:Ln3+(Ln=Eu, Tb) submicrospheres: solvothermal synthesis and luminescence properties. Inorg. Chem. 49, 11499–11504 (2010).
49. Chen, Q. et al. A novel co-precipitation synthesis of a new phosphor Lu2O3:Eu3+. J. Eur. Ceram. Soc. 27, 191–197 (2007).
50. Wegh, R. T., Donker, H., Oskam, K. D. & Meijerink, A. Visible quantum cutting in LiGdF4:Eu3+ through downconversion. Science 283, 663–666 (1999).

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Author Contributions
F.C., X.L., J.L. and R.M. conceived and designed the experiments, and X.L., R.M. and G.Q. supervised the research; G.C., T.L., N.Z., J.L. and L.C. helped to synthesize the hollow spheres; H.L. assisted in the optical properties studies; F.C. performed the synthesis and characterization, interpreted the data and wrote the paper with help from X.L. and R.M.

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