Supporting information for

General synthetic strategy for high-yield and uniform rare-earth oxysulfates ($RE_2O_2SO_4$, RE= La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, and Yb) hollow spheres

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Experimental Details

All rare-earth nitrates used were of 99.99% purity. L-cysteine and polyvinylpyrrolidone are analytical grade from the Beijing Chemical Factory, China. These chemicals were used as received without further purification. Milli-Q water was used throughout the experiments.

Synthesis of rare-earth oxysulfates and oxides hollow spheres. In a typical procedure, hydrated lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$, 1.0 mmol), L-cysteine (2.0 mmol) and polyvinylpyrrolidone (PVP, 0.3 g) were dissolved in 40 ml deionized water under vigorous magnetic stirring. The pH of the initial mixture was about 7. The solution was then transferred into a Teflon-lined autoclave of 50 ml capacity and was sealed and maintained at 140 ºC for 24 h. Subsequently, the system was allowed to cool to room temperature. The resulting La-coordination compound was collected by filtration and washed with ethanol and distilled water for several times and dried at 50 °C for 4 h, which can be transformed into $La_2O_2SO_4$ by calcination at 600 °C for 2 h. The yield of $La_2O_2SO_4$ is about 85% based on the calculation of lanthanum nitrate.

Synthesis of Eu-doped $La_2O_2SO_4$ and CeO_2 oxides hollow spheres. In a typical procedure, hydrated lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$, 0.95 mmol), hydrated 1 europium nitrate ($Eu(NO_3)_3 \cdot 6H_2O$, 0.05 mmol) and L-cysteine (2.0 mmol) were dissolved in 40 ml deionized water under vigorous magnetic stirring. The solution was then transferred into a Teflon-lined autoclave of 50 ml capacity and was sealed and maintained at 140 ºC for 24 h. The resulting Eu-doped La-coordination compound was collected by filtration and washed with ethanol and distilled water for several times and dried at 50 °C for 4 h, which can be transformed into 5% mol Eu-doped $La_2O_2SO_4$ by calcination at 600 °C for 2 h.

Synthesis of ZnS-coated $La_2O_2SO_4$ and CeO_2 hollow spheres. The preparation process of ZnS-coated $La_2O_2SO_4$ and CeO_2 hollow spheres was similar to our previous work.[1] In a typical procedure, the obtained La-coordination compounds (1 mmol) were redispersed into 100 ml thioacetamide (0.5 mmol) solution under vigorous magnetic stirring for 2 h. Subsequently, hydrated zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, 0.5 mmol) was added to the above solution, which were then ultrasonicly treated for 30 min and calcinated at 600 °C for 2h to fabricate ZnS-coated $La_2O_2SO_4$ hollow spheres.

Characterizations. XRD data were collected by a D/max2550 VB+ diffractometer with Cu K_α radiation (λ = 0.15405 nm). Morphology of the synthesized products was examined using a JEOL JSM–6700F field emission scanning SEM. TEM was performed on a JEOL JEM–3100F energy-filtering (Omega type) transmission microscope. Thermogravimetric differential thermal measurements (TG-DTA) were carried out using a Rigaku TGA-8120 instrument in a temperature range of 25-1000 ºC at a heating rate of 1 ºC min^{-1} under an air flow. The photoluminescence excitation and emission spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer under the same conditions at room temperature. Magnetic measurements were conducted using a Quantum Design MPMS XP-5 superconducting quantum interference device (SQUID).

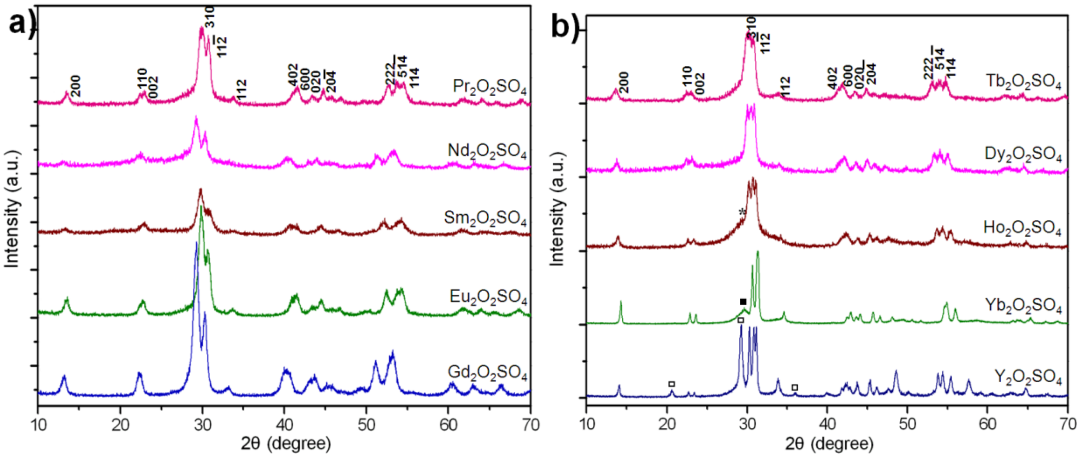

Fig. S1-1 XRD patterns of a) light and b) heavy rare-earth oxysulfates hollow spheres obtained by calcination of corresponding rare-earth coordination compounds in air at 600 ºC for 2 h. The peaks marked with asterisk, filled and empty squares are from Ho_2O_3, Yb_2O_3 and Y_2O_3, respectively.

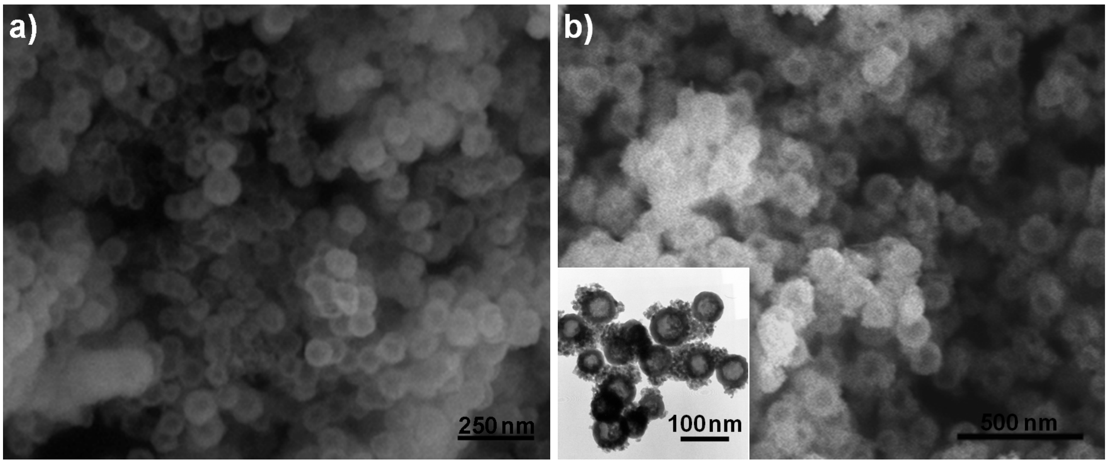

Fig. S1-2 Typical SEM images of the light rare-earth oxysulfates hollow spheres: a) $Nd_2O_2SO_4$; b) $Gd_2O_2SO_4$. The inset in b) is a typical TEM image of $Gd_2O_2SO_4$ hollow spheres.

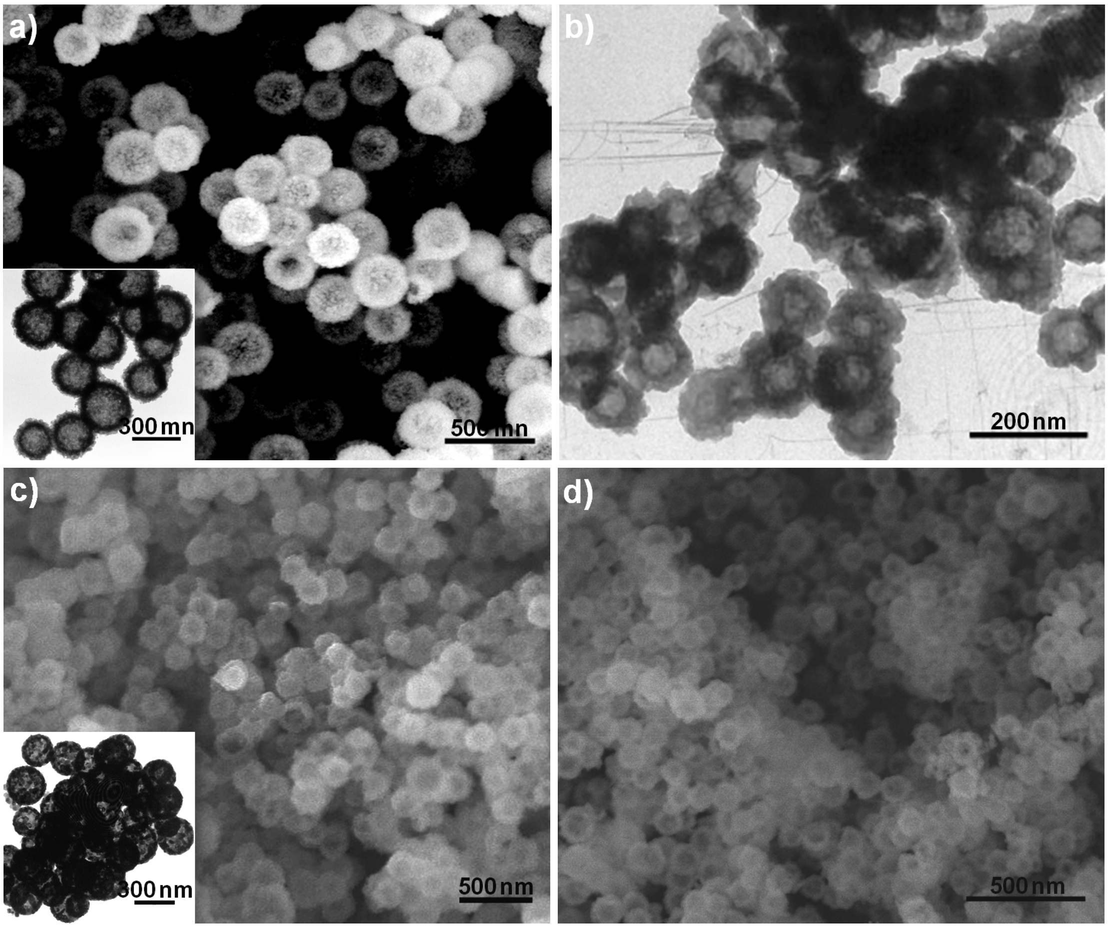

Fig. S1-3 Typical SEM and TEM images of the heavy rare-earth oxysulfates hollow spheres: a) $Dy_2O_2SO_4$; b) $Y_2O_2SO_4$; c) $Ho_2O_2SO_4$; d) $Yb_2O_2SO_4$. The insets in a) and c) depict the corresponding TEM images.

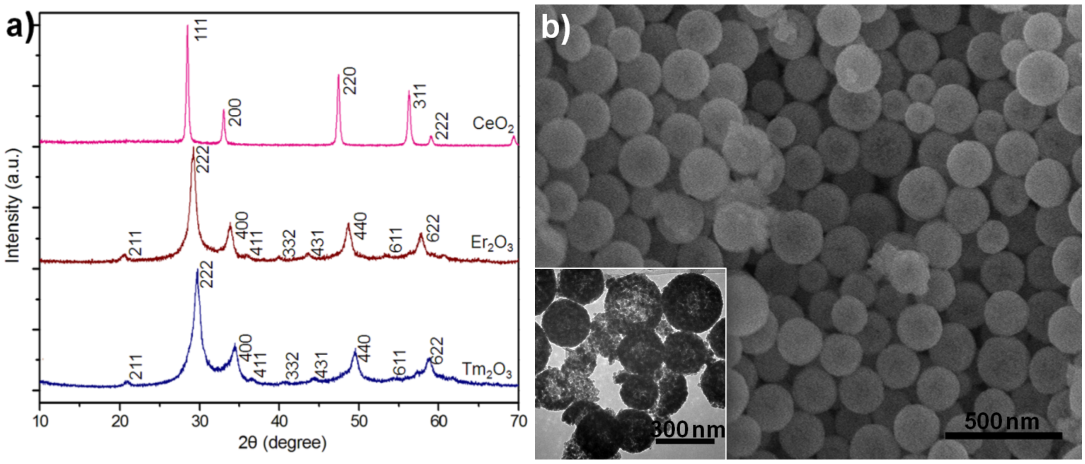

Fig. S2 a) XRD patterns of rare-earth oxides hollow spheres: face-centred cubic CeO_2 (JCPDS 04-0593), body-centred cubic Er_2O_3 (JCPDS 01-0827) and Tm_2O_3 (JCPDS 10-0350). b) Typical SEM image of Eu-doped CeO_2 hollow spheres. The inset in b) depicts the corresponding TEM image.

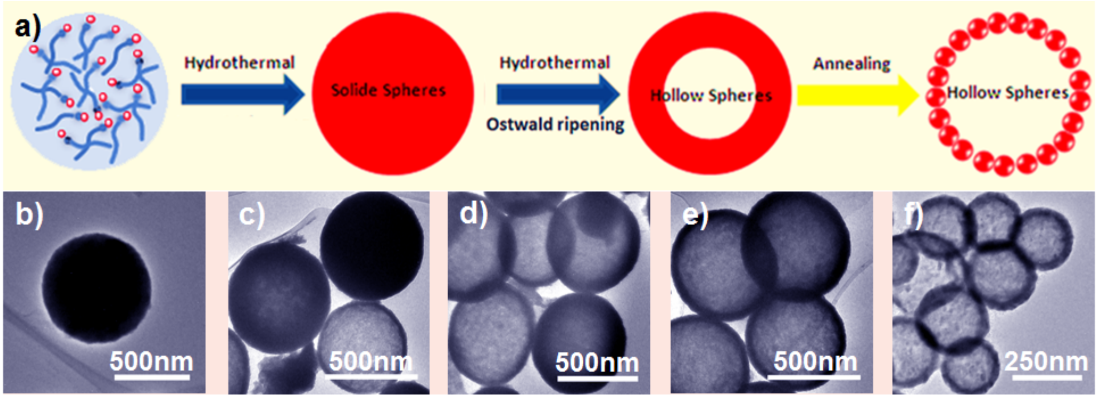

Fig. S3 a) Schematic illustration of the formation of rare-earth oxysulfates and oxides hollow spheres. b)–e) TEM images exhibit the formation stages of La-coordination compounds. f) TEM image of $La_2O_2SO_4$ hollow spheres.

Fig. S3a illustrates the possible scenario for the formation of rare-earth oxysulfates and oxides hollow spheres. L-cysteine plays an important role in the present synthesis procedure, which serves as both biomolecular template and sulfide source. Firstly, L-cysteine is dispersed in deionized water and simultaneously capped by rare-earth ions due to the coordination of functional groups in the L-cysteine molecules, such as $-NH_2$, -COOH, and -SH, which has a strong tendency to coordinate with inorganic cations. Subsequently the freshly rare-earth coordination compound is unstable due to the high surface energy and tend to aggregate into spherical product driven by the minimization of interfacial energy, which can then convert into hollow spheres due to the Ostwald ripening process.[2] Finally, rare-earth oxysulfates or oxides hollow spheres can be achieved via the calcination of corresponding rare-earth coordination compounds. Fig. S3b–e indicate the typical TEM images of La-coordination compounds, in which solid spheres can gradually convert into hollow spheres due to the Ostwald ripening process. Fig. S3f depicts a typical TEM image of $La_2O_2SO_4$ hollow spheres obtained by the calcination of corresponding La-coordination compound.

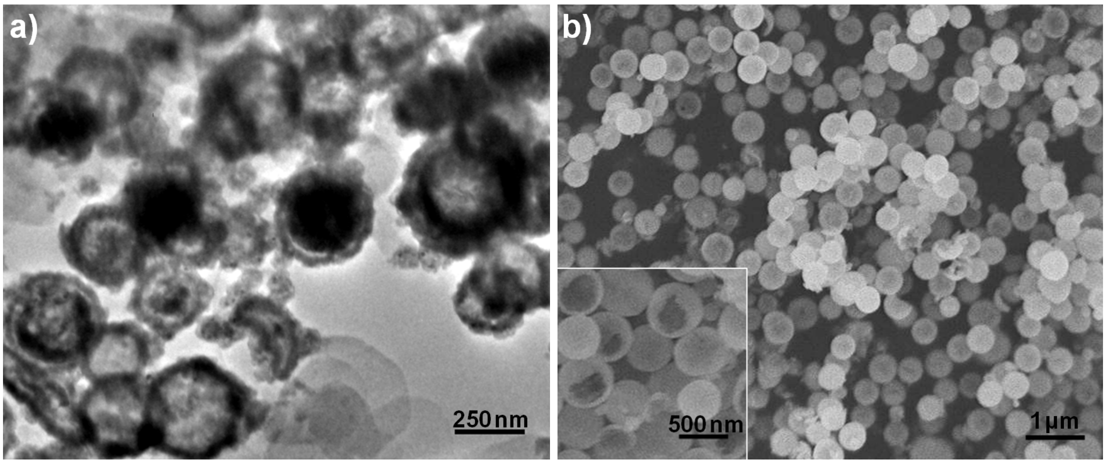

Fig. S4 a) TEM image of as-prepared double-shelled $La_2O_2SO_4$/ZnS. b) SEM image of Eu-doped $La_2O_2SO_4$ hollow spheres. The inset in b) indicates a few Eu-doped $La_2O_2SO_4$ hollow sphere with broken shell.

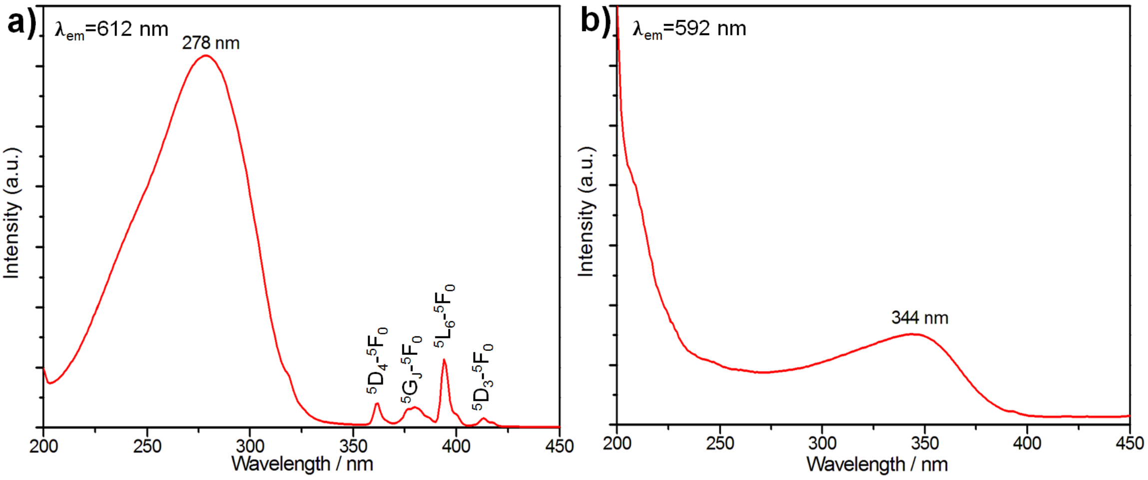

Fig. S5 Room-temperature excitation spectra of Eu-doped a) $La_2O_2SO_4$ and b) CeO_2 hollow spheres monitored at 612 and 592 nm, respectively.

The excitation spectrum of $La_2O_2SO_4$:0.05Eu exhibits a broad excitation band ranged from 205 to 350 nm with the main peak centered at about 278 nm, which can be attributed to the

Eu–O charge-transfer (CT) transition (Fig. S4a). The relatively weak peaks in range from 350 to 430 nm were caused by the f–f transitions excitation lines of Eu(III) ions, which are assigned to transitions between the ground $^7F_0$ level and the excited $^5D_4$, ^5G_J, $^5L_6$, and $^5D_3$ levels, respectively. Fig. S4b indicates the excitation spectrum of CeO_2:0.05Eu.[3] It can be seen that the spectrum only exhibits one CT transition band centered at around 344 nm, while the f–f transitions excitation lines of Eu(III) ions are not observed.

References:

[1] Y. B. Li, R. Yi, X. H. Liu, *J. Alloys Compd.* **2009**, *486*, L1.

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[3] G. Mao, H. Zhang, H. Li, J. Jin, S. Niu, *J. Electrochem. Soc.* **2012**, *159*, J48.