

Supporting information

Fabrication of lanthanide oxides microsphere and hollow spheres by thermolysis of pre-molding lanthanide coordination compounds

*Zhu-Rui Shen, Jin-Gui Wang, Ping-Chuan Sun, Da-Tong Ding, and Tie-Hong Chen**

Institute of New Catalytic Materials Science, Key Laboratory of Energy-Material Chemistry (Tianjin) and Engineering Research Center of Energy Storage & Conversion (MOE), College of Chemistry, and College of Physics, Nankai University, Tianjin 300071, PR China

Experimental section:

For synthesis of lanthanide organic microspheres and their oxides, 6 mmol L-asparagine was dissolved in 24 mL deionized water at 45 °C. Then 12 mmol lanthanide salt ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, etc.) was added under stirring and the solution was transferred to a 30 mL Teflon-lined autoclave, sealed and hydrothermal treated at 160 °C for 24 h. The products were washed with deionized water and ethanol thoroughly. Diluted HCl and NaOH were used to tune the pH value when necessary.

For synthesis of lanthanide organic hollow spheres and their oxides, the procedure is similar to that of the microspheres, except that 0.125 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was added. The quantity of lanthanide salts could be tuned from 0.125 mmol to 0.15 mmol if necessary.

For synthesis of doped lanthanide oxides, 6 mmol L-asparagine was dissolved in 24 mL deionized water at 45 °C, then 4 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 4 mmol $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (or 7.6 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.4 mmol $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, or 7.2 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.8 mmol $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were added under stirring. After stirring for about 10 minutes, the solution was transferred to a 30 mL Teflon-lined autoclave, sealed and hydrothermal treated at 160 °C for 12 h. The as-prepared products washed with deionized water and ethanol thoroughly. All products were calcined at 720 °C in air for 2 h to obtain the oxides.

For synthesis of Co-, Ni- doped CeO_2 , 6 mmol L-asparagine was dissolved in 24 mL deionized water at 45 °C, then 6.4 mmol $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 1.6 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were added under stirring. After stirring for about 10 minutes, the solution was transferred to a 30 mL Teflon-lined autoclave, sealed and hydrothermal treated at 160 °C for 24 h. The as-prepared products washed with deionized water and ethanol thoroughly. All products were calcined at 360 °C in air for 1 h to obtain the oxides.

XRD patterns were recorded with a Rigaku D/max-2500 diffractometer. SEM and TEM images were measured on Shimadzu SS-550 and Philips Tecnai F20 instruments, respectively. N₂ adsorption isotherms were measured on a BELSORP mini II analyser. XPS spectra were obtained with a Kratos Axis Ultra DLD spectrometer. The UV/Vis spectra were measured on a JASCO V-570 Spectrophotometer, and the fluorescence spectrum was measured on a Varian Cary Eclipse Fluorescence spectrophotometer.

Table S1. The Elementary Analysis (EA) results of the time-dependent synthesized samples of

La-organic coordination compound solid microspheres and hollow spheres.

Samples	Reaction time	EA analysis results	
		C wt%	N wt%
Solid spheres	4 h	20.89	5.79
Solid spheres	12 h	19.74	4.47
Solid spheres	48 h	19.70	4.15
Hollow spheres	1.5 h	27.81	8.79
Hollow spheres	4 h	26.48	8.35
Hollow spheres	12 h	25.63	7.01

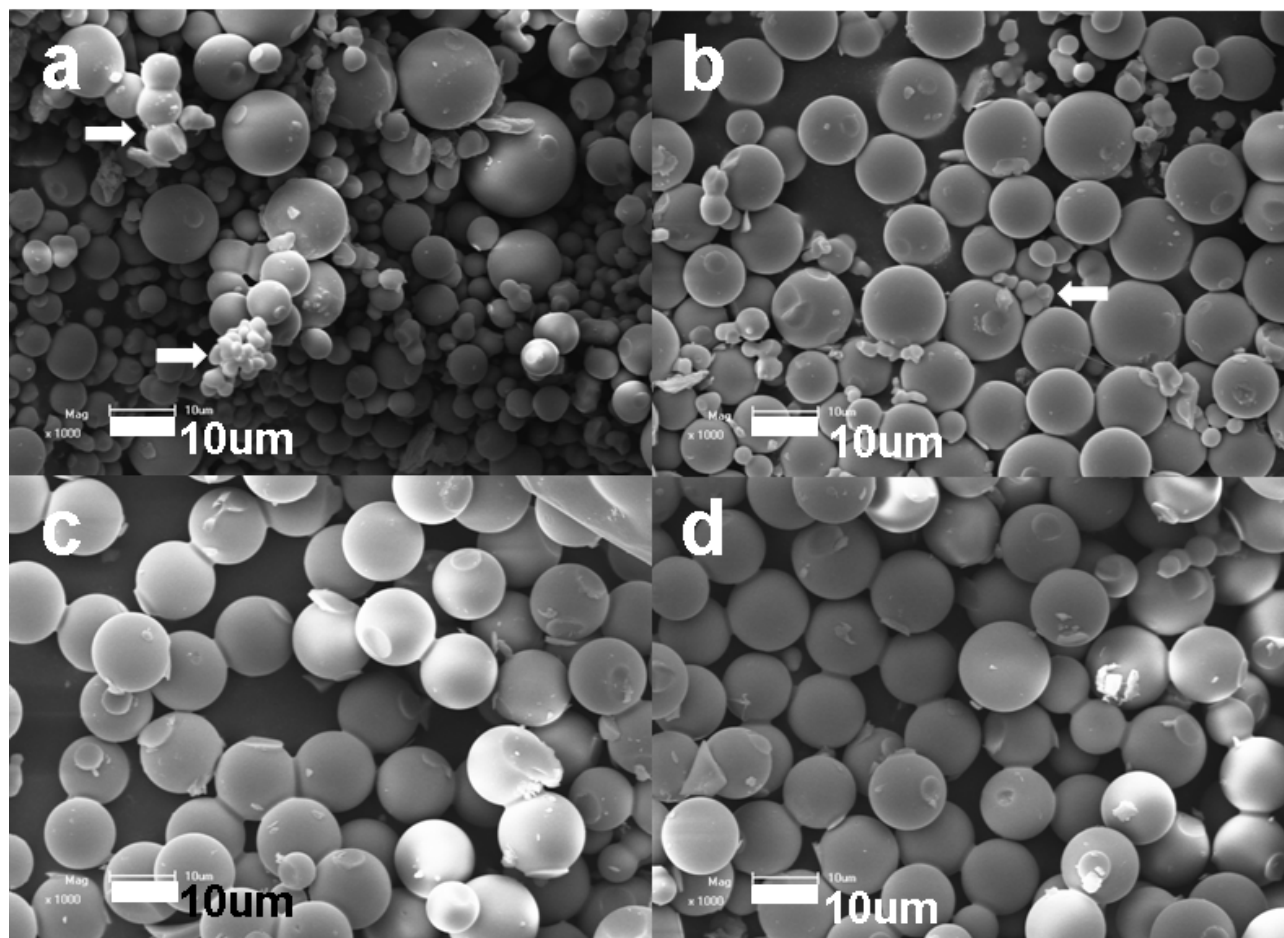


Figure S1. SEM images of Ce-organic coordination polymer spheres obtained after reaction at 160 °C for (a) 6 h, (b) 8 h, (c) 24 h, (d) 48 h at reactant molar ratio (asparagine / Ce^{3+}) =6:12, the asparagine is 6 mmol. The arrows in (a, b) indicate some aggregated spheres.

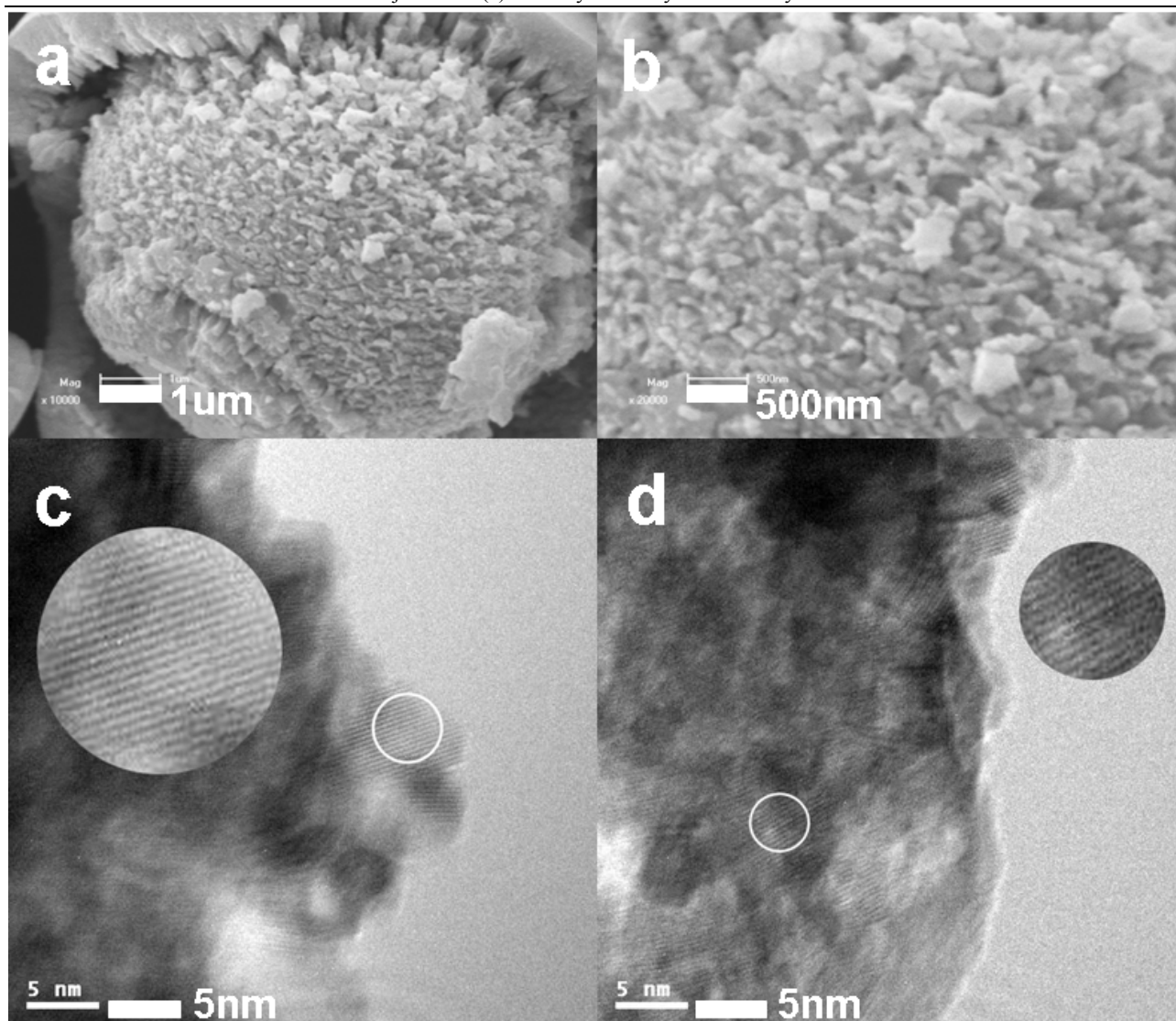


Figure S2. (a, b) HRSEM images of core particles of Ceria core-shell spheres (c, d) HRTEM images of nanocrystals of ceria core-shell spheres, the inset in (c, d) displays interplanar spacing of the (111) facet.

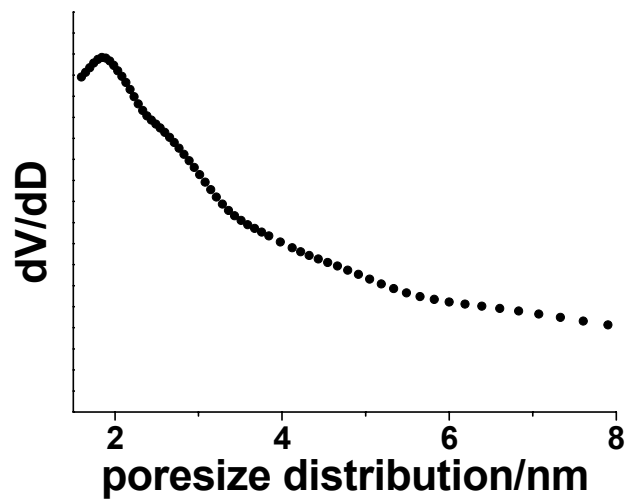


Figure S3. The pore size distribution curve of CeO₂ core-shell microspheres in Figure 1 (e, f).

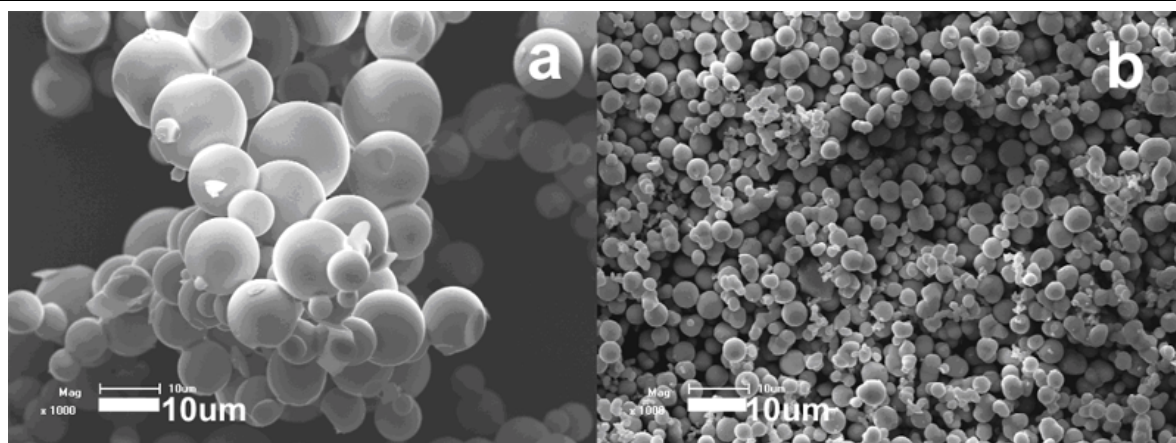


Figure S4. SEM images of Ce-organic coordination polymer spheres obtained when the pH value is (a) 2.0, and (b) 4.7 after reaction at 160°C for 24 h at reactant molar ratio (asparagine / Ce^{3+}) = 4:8, and the asparagine is 4 mmol.

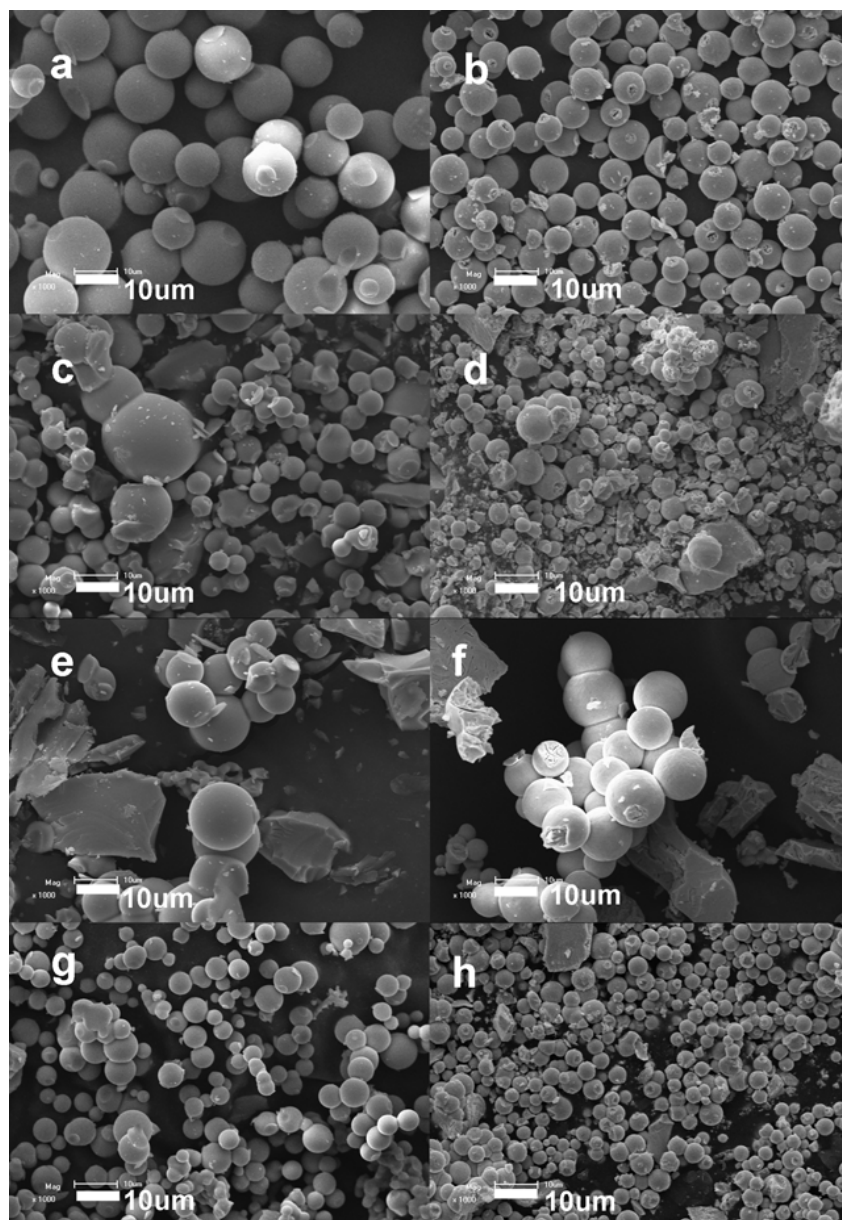


Figure S5. SEM images of (a) Pr organic microspheres and (b) its corresponding P_6O_{11} microspheres, (c) Nd organic microspheres and (d) its corresponding Nd_2O_3 microspheres, (e) Sm organic microspheres and (f) its corresponding Sm_2O_3 microspheres, (g) Eu organic microspheres and (h) its corresponding Eu_2O_3 microspheres. All the organic microspheres were obtained after reaction at $160^\circ C$ for 24 h at reactant molar ratio (asparagine / Ln^{3+}) = 6: 12, and the asparagine is 6 mmol.

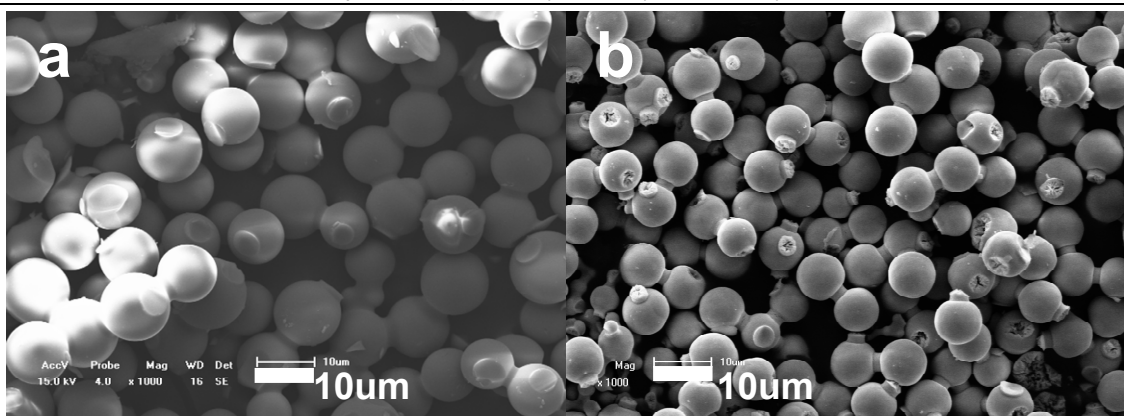


Figure S6. SEM images of (a) La-Ce organic microspheres (1: 1, molar ratio) obtained after reaction at 160 °C for 24 h, the asparagine is 6 mmol, (b) its corresponding La-Ce oxide microspheres.

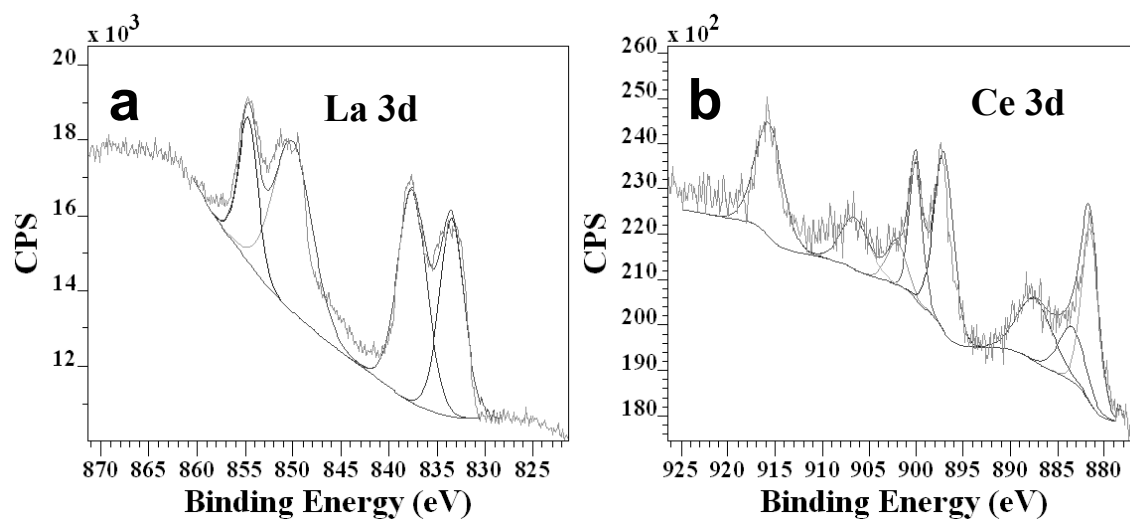


Figure S7. XPS spectra of La-Ce oxides microspheres (1: 1, molar ratio).

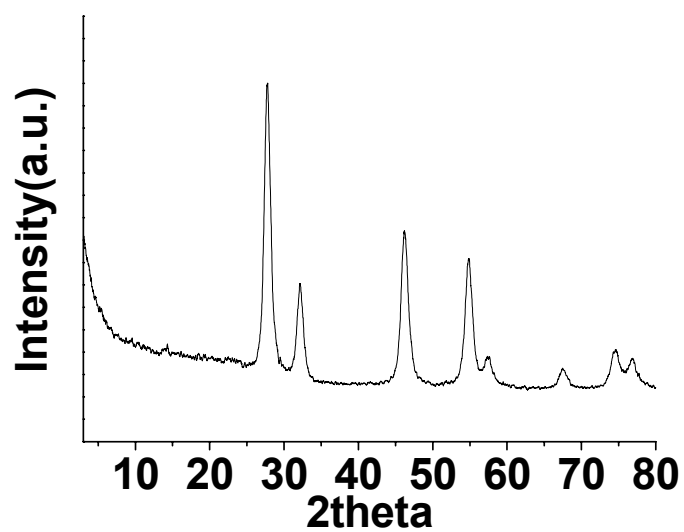


Figure S8. XRD pattern of La-Ce oxide microspheres (1: 1, molar ratio)

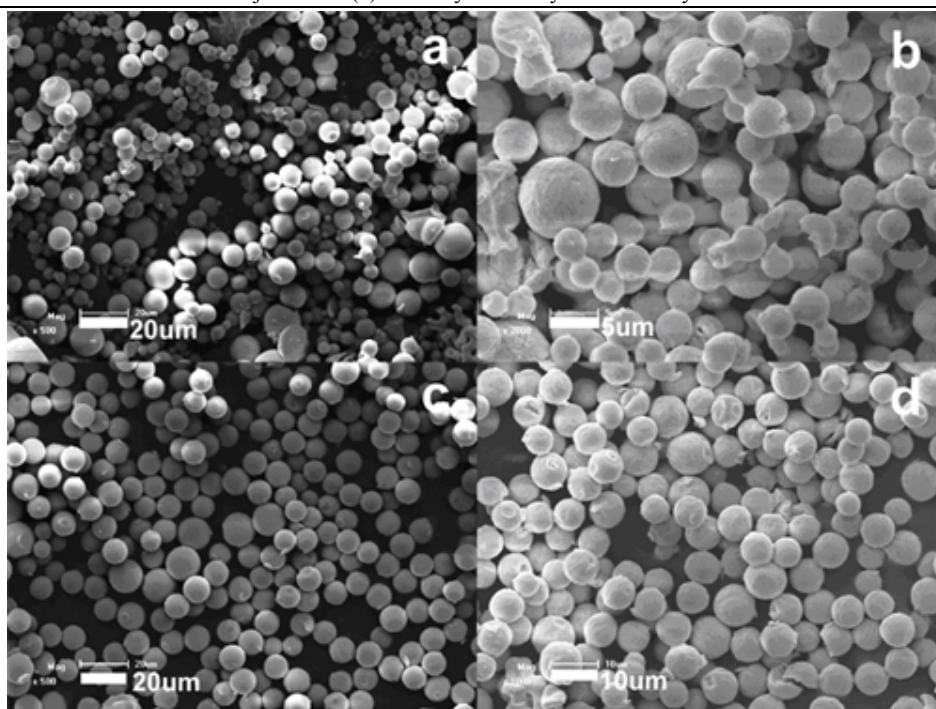


Figure S9. SEM images of (a) La-Eu organic coordination polymer spheres obtained at the reactant molar ratio (asparagine /La³⁺ /Eu³⁺) = 6: 7.6: 0.4 after reaction at 160 °C for 24 h, the asparagine is 6 mmol, (b) its corresponding La-Eu oxide spheres obtained by calcination, (c) La-Eu organic coordination polymer spheres obtained at the reactant molar ratio (asparagine /La³⁺ /Eu³⁺) = 6: 7.2: 0.8 after reaction at 160 °C for 24 h, the asparagine is 6 mmol, (d) its corresponding La-Tb oxide spheres obtained by calcination.

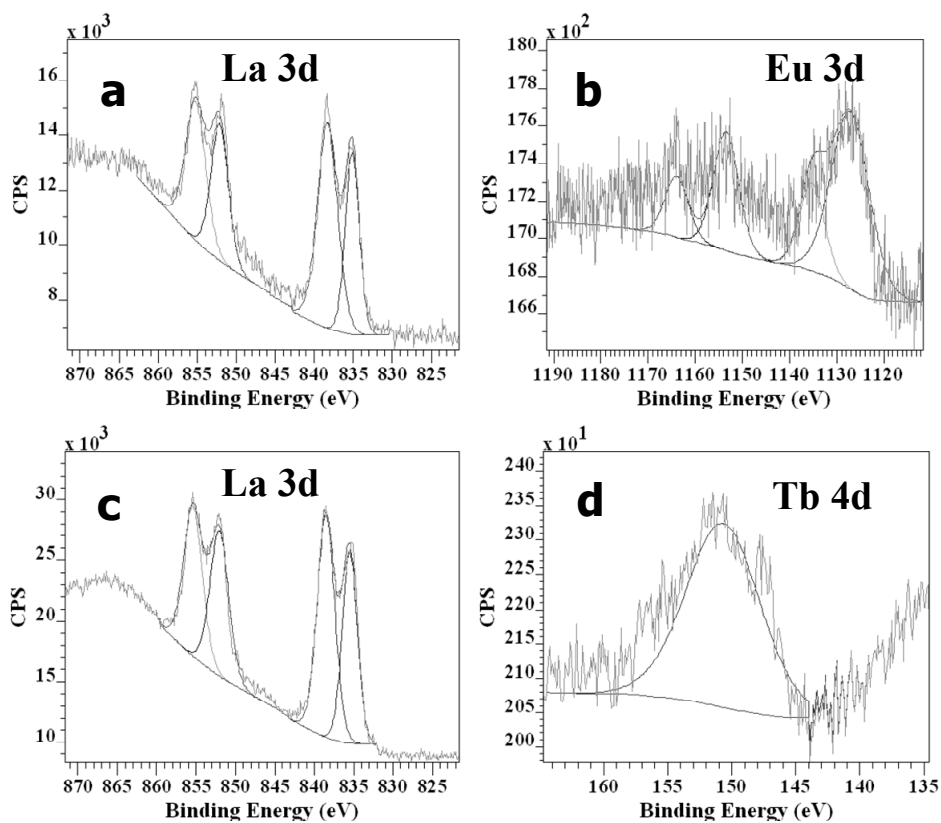


Figure S10. XPS spectra of (a, b) La-Eu (0.95: 0.05, molar ratio) organic coordination polymer microspheres, (c, d) La-Tb (9:1, molar ratio) organic coordination polymer microspheres.

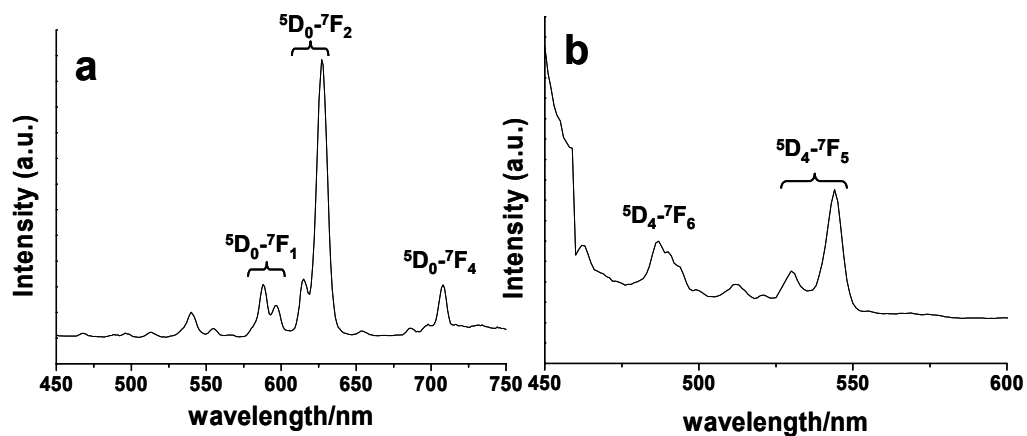


Figure S11. Photoluminescence spectra of (a) La-Eu oxide spheres (La: Eu=0.95: 0.05, molar ratio), $\lambda_{\text{ex}} = 280$ nm, (b) La-Tb oxide spheres (La: Tb=9: 1, molar ratio), $\lambda_{\text{ex}} = 396$ nm

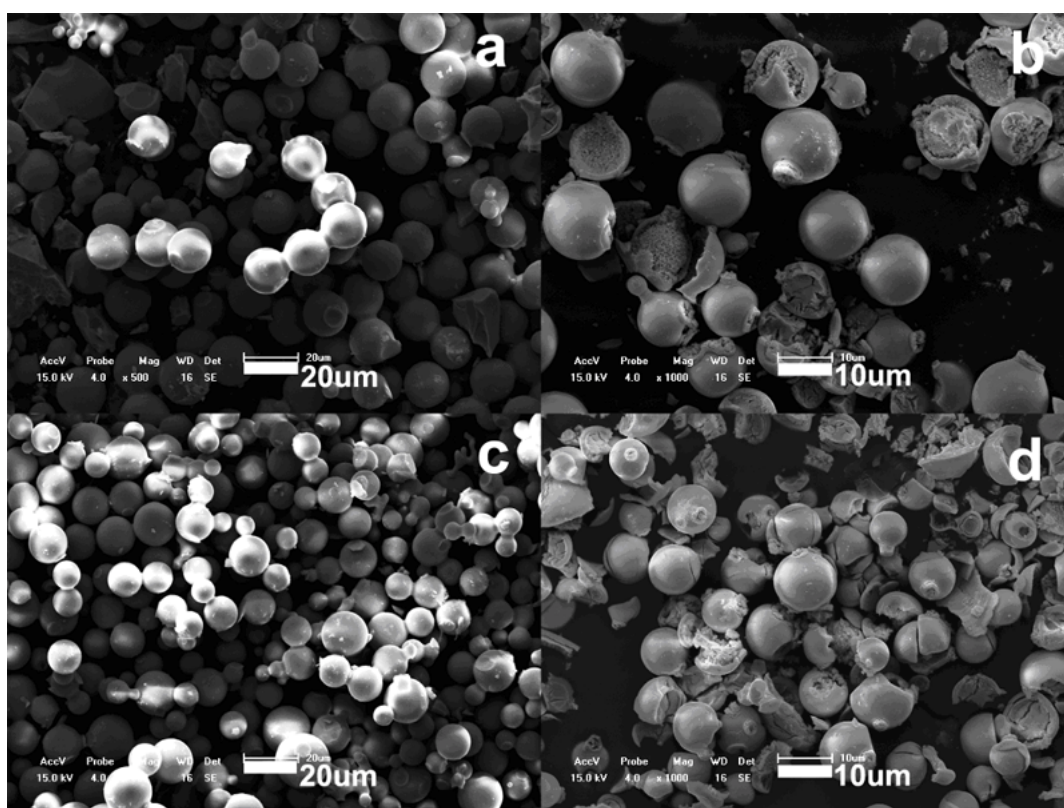


Figure S12. SEM images of (a) Ce-Ni organic coordination polymer spheres obtained at the reactant molar ratio (asparagine /Ce³⁺ /Ni³⁺) = 6: 7.2: 0.8 after reaction at 160 °C for 24 h, the asparagine is 6 mmol, (b) its corresponding Ce-Ni oxide spheres obtained by calcination, (c) Ce-Co organic coordination polymer spheres obtained at the reactant molar ratio (asparagine /Ce³⁺ /Co³⁺) = 6: 7.2: 0.8 after reaction at 160 °C for 24 h, the asparagine is 6 mmol, (d) its corresponding Ce-Co oxide spheres obtained by calcination.

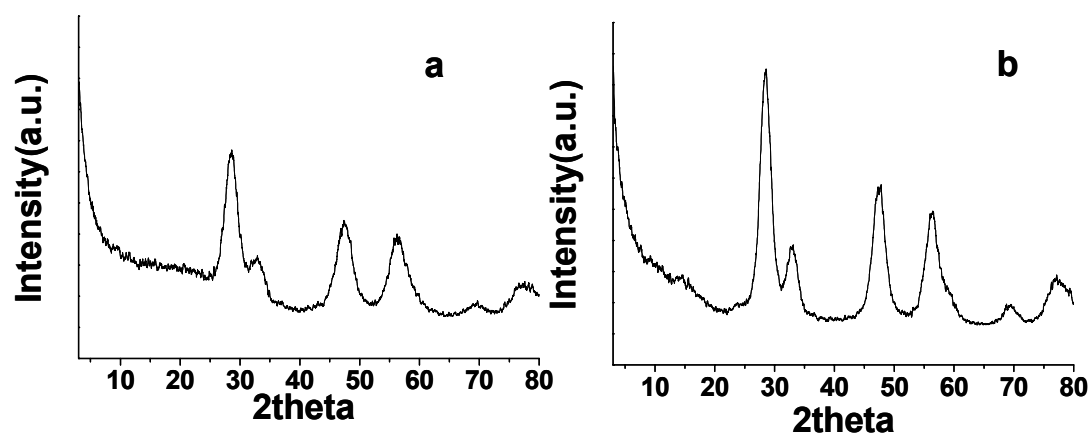


Figure S13. XRD patterns of (a) Ce-Co oxide microspheres, (b) Ce-Ni oxide microspheres.

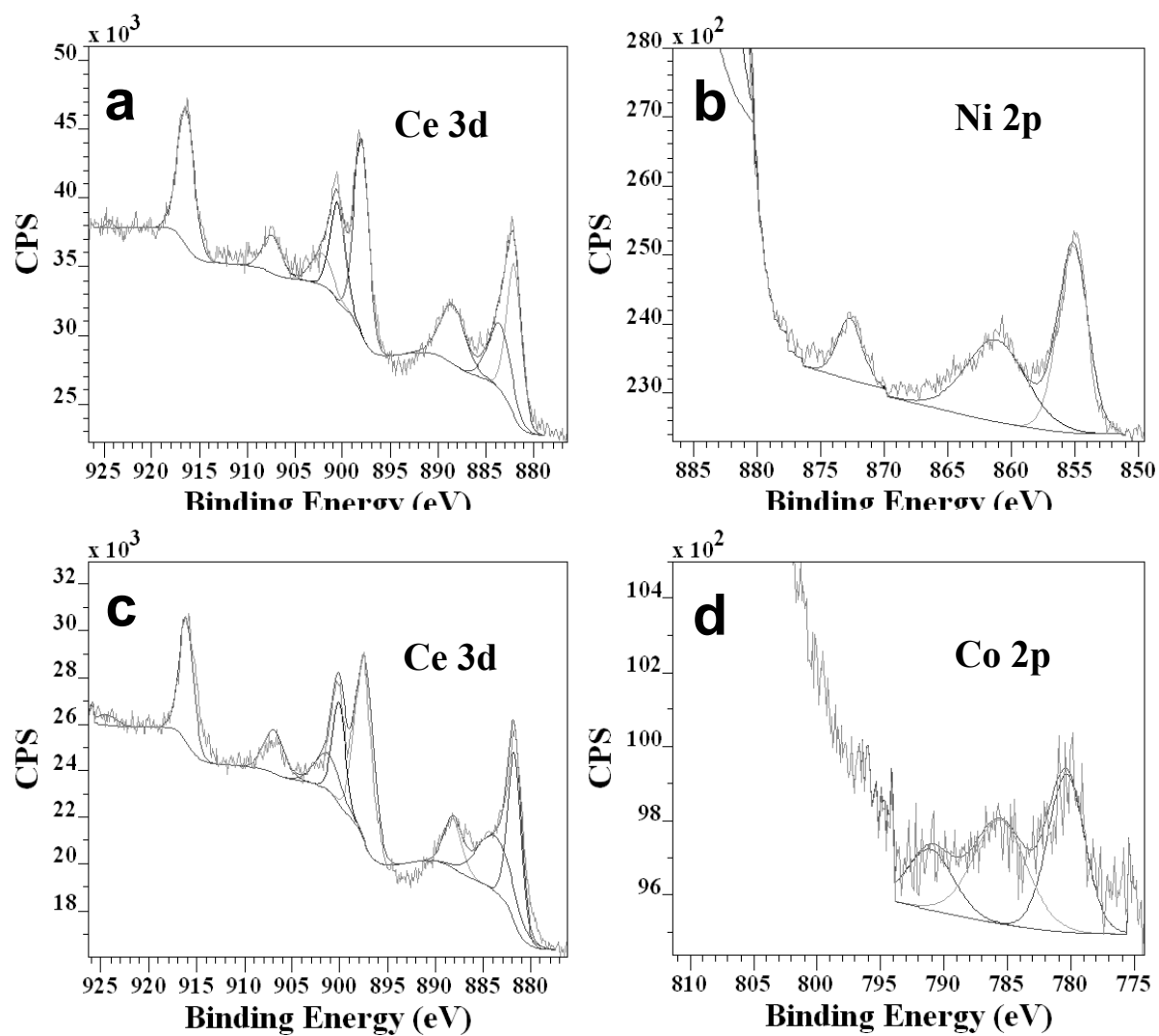


Figure S14. XPS spectra of (a, b) Ce-Ni oxide microspheres,, (c, d) Ce-Co oxide microspheres,

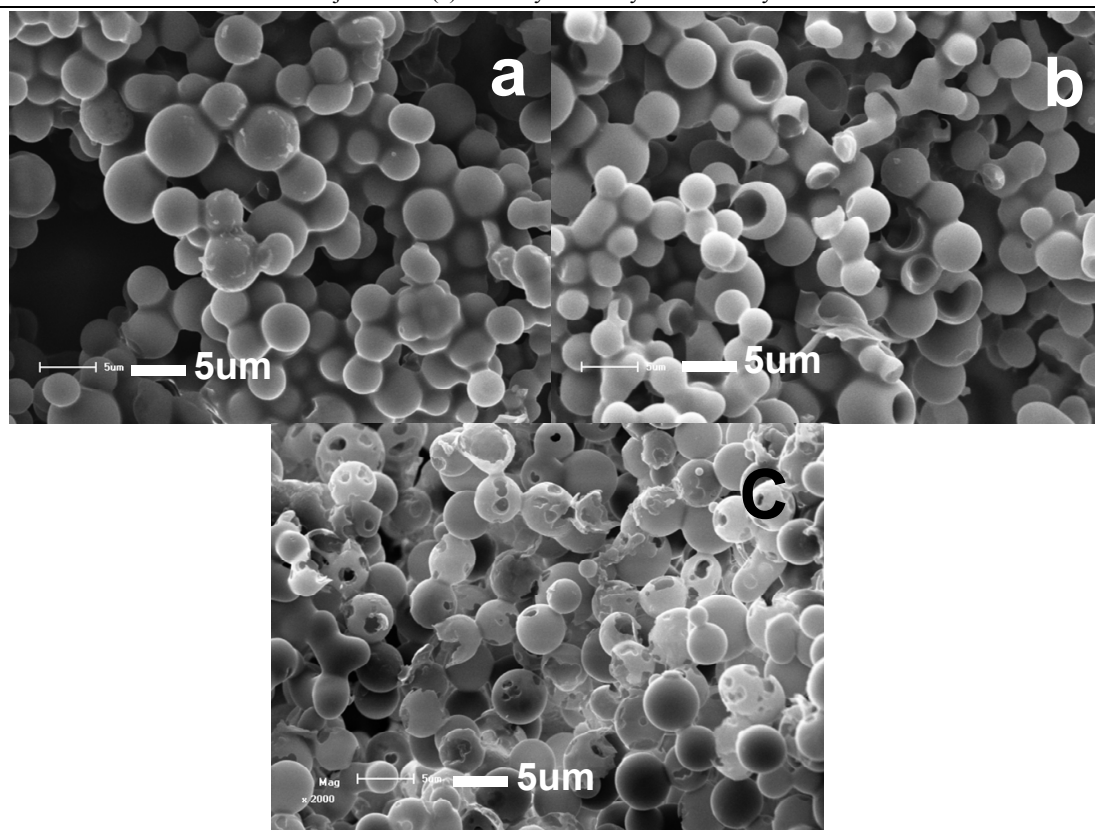


Figure S15. SEM images of La-organic coordination polymer obtained after reaction at 160 °C for (a) 1.5 h, (b) 4 h, (c) 12 h at reactant molar ratio (asparagine / La^{3+}) = 6: 0.125, the asparagine is 6 mmol.

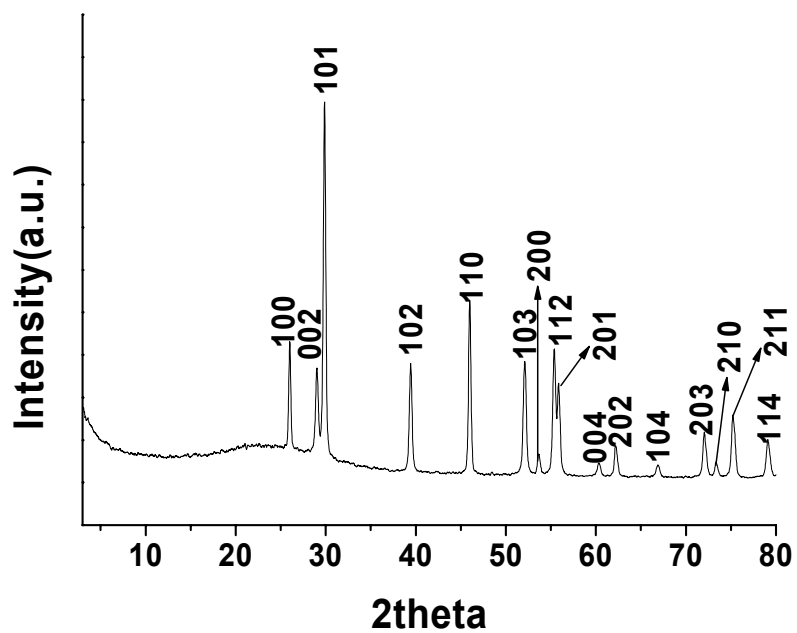


Figure S16. XRD pattern of La_2O_3 hollow spheres, the peaks were indexed according to the card of JCPDS No. 05-0602.