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Supporting Information

Facile Access to Ultrasmall Eu_2O_3 Nanoparticles Functionalized Hollow Silica Nanosphere Based on the Spontaneous Formation and Decomposition of a Cross-Linked Organic/Inorganic Hybrid Core

Xiaolei Wang,[a] Tieyu Cui,*[ab] Fang Cui,[b] Yajing Zhang,[a] Da Li,[a] Zhidong Zhang[a]

[a]*Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, PR China;* [b]*The Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin 150001, PR China.*

*Correspondence to: Tieyu Cui. cuit@hit.edu.cn

Experimental Section

Materials. (3-Aminopropyl)triethoxysilane (APTES, 99%) was purchased from Fluka. Eu_2O_3, bromoacetic acid (BA), tetraethylorthosilicate (TEOS, >99%), ammonia and absolute ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PR China). All these chemicals were of analytical reagent grade and used as received. The water used in the experiments was deionized with a resistivity of 18.2 $M\Omega\cdot cm^{-1}$.

Synthesis of EUBA. In a 250 mL three-necked flask, Eu_2O_3 (8.8 g, 0.025 mol) was added to absolute ethanol solution (100 mL) containing BA (22.0 g, 0.158 mol). The mixture was continuously stirred for at least 4 hours at 60 ºC to ensure the complete reaction of Eu_2O_3. The produced EUBA is insoluble in absolute ethanol and thus were separated out gradually. The white deposits were collected by centrifugation and washed with absolute ethanol to remove the unreacted BA. In order to remove the trace quantities of unreacted Eu_2O_3, which may be mixed with EUBA, a small quantity of water was added to the white powder to dissolve EUBA. After filtration, the filter liquor was vacuum distilled at 60 ℃ to remove some of the water, and then the remainder was cooled to separate out the white powder of EUBA. The resulting white powder was collected by filtration and dried in a vacuum oven at room temperature for 24 h.

Preparation of Eu_2O_3@H-SiO_2 nanospheres. Typically, APTES (0.566 g, 2.56 mmol) and EUBA (0.485 g, 0.853 mmol) were added to a three-necked flask containing 20 mL of water, and the solution was continuously stirred at room temperature for at least 2h to yield the cross-linked organic/inorganic hybrid cores through spontaneous nucleophilic substitution and subsequent hydrolyzation and polycondensation. Then, ethanol (35 mL), TEOS (1.04 g, 5 mmol) and ammonia (6.0 mL) were introduced into the core suspension under stirring. After a coating time of 12h for silica, four repeated centrifugation and washing (in alcohol/water mixture) cycles were performed. Eu_2O_3@H-SiO_2 nanospheres were produced by drying the above composite nanospheres in a vacuum oven at room temperature for 24 h, and then calcining at 800 ºC under air for 4 h.

Characterization. X-ray powder diffraction data were colleted on a D/max-2400 diffractometer using a Cu target radiation source. ^{1}H NMR spectrum was recorded in D_2O using a Bruker AVANCE500 500MHz NMR spectrometer. TEM image and SEAD pattern were obtained by employing a FEI Tecnai G2 F30 transmission electron microscope, using an accelerating voltage of 300 kV (this instrument was equipped with energy dispersive X-Ray spectroscopy capabilities). FTIR spectra were taken on an AVATAR 360 FT-IR infrared spectrophotometer. Fluorescence measurements were performed with the assistance of a Shimadzu RF-5301 spectrofluorimeter. The luminescence lifetime data were collected on a Lecroy WaveRunner 6100 digital oscilloscope (1 GHz) using a 390 nm laser (pulse width = 4 ns) from a Sunlite OPO (Continuum) pumped by a Nd: YAG pp-8000(355nm) as the excitation source. The Field-Magnetization dependence of the Eu_2O_3@H-SiO_2 nanospheres was measured using a MPMS-7 superconducting quantum interference device (SQUID) magnetometer at magnetic fields up to 30 koe.

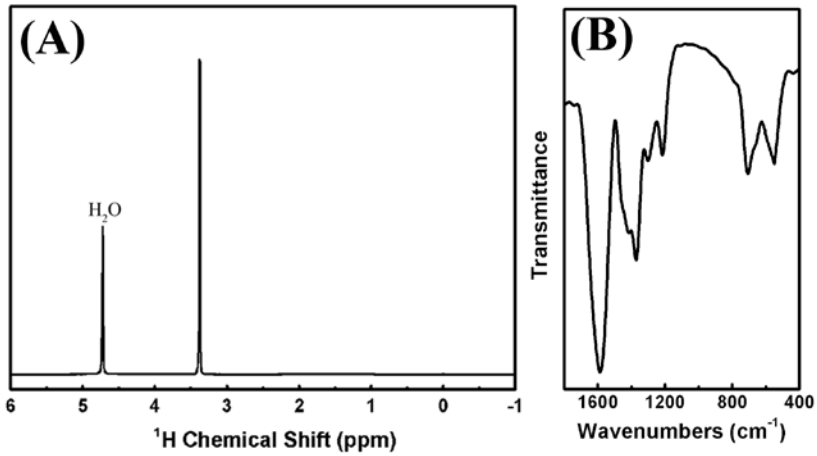

Figure S1. (A) ^{1}H NMR spectrum of EUBA in D_2O. (B) FTIR spectrum of EUBA powder.

^{1}H NMR and FTIR spectra confirm the successful synthesis of EUBA. The ^{1}H NMR spectrum (Figure S1(A)) shows a chemical shift at 3.38 ppm, which can be assignable to the methylene protons of EUBA. FTIR spectrum (Figure S1(B)) reveals three strong bands of the carboxylate groups at 1573 cm^{-1}, 1373 cm^{-1} and 707 cm^{-1} for the antisymmetric stretching vibration, symmetric stretching vibration and deformation vibration respectively. The two bands at 1417 cm^{-1} and 550 cm^{-1} are attributed to the variable-angle vibration of the -CH_2- groups and the C-Br vibration.

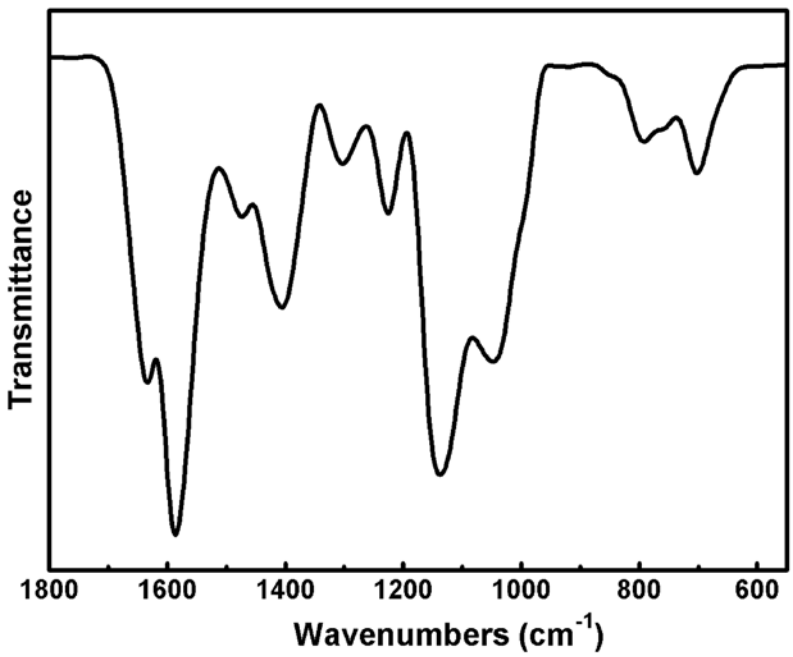

Figure S2. FTIR spectrum of the cross-linked organic/inorganic hybrid cores.

Five features are observed that provide evidence for the formation of the expected cross-linked organic/inorganic hybrid cores through spontaneous nucleophilic substitution reaction and subsequent self-catalytic hydrolyzation and polycondensation. (1) The C-N stretch of the primary amine (1167 cm^{-1}) of APTES and the C-Br vibration (550 cm^{-1}) of EUBA virtually disappear, whereas the expected C-N stretch of secondary amine (1137 cm^{-1}) is obviously present, suggesting the occurrence of nucleophilic substitution reaction between the terminal bromine groups of EUBA and the amine groups of APTES. (2) The intensity peak appearing at 1635 cm^{-1} is assignable to the variable-angle vibration of the protonated amine groups, which act as catalyst sites for the hydrolysis of ethoxysilyl groups. (3) The Si-O-Si stretching band appearing at 1045 cm^{-1} confirms the inorganic polymerization within the cores. (4) The presence of the Si-C stretching band (792 cm^{-1} and 759 cm^{-1}) demonstrates the organic alkyl chains are covalently bonded to the Si-O-Si networks. (5) Three strong bands at 1593 cm^{-1}, 1403 cm^{-1} and 701 cm^{-1} are attributed to the antisymmetric stretching, symmetric stretching and deformation vibration of the carboxylate, which demonstrate that the europium carboxylate groups are well-preserved in the process of core formation.

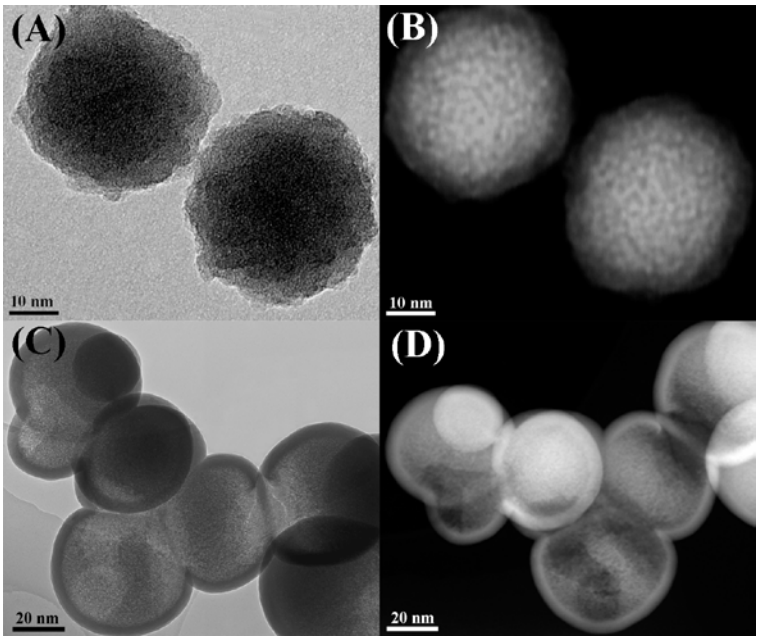

Figure S3. (A and B) TEM and STEM images of the hybrid cores@silica shell structures. (C and D) TEM and STEM images of Eu_2O_3@H-SiO_2 nanospheres.

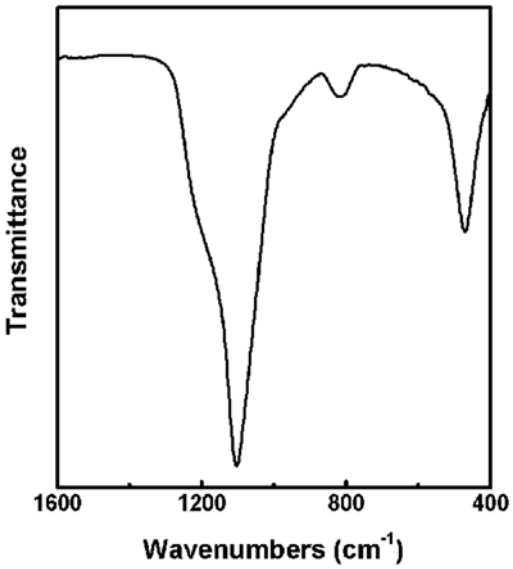

Figure S4. FTIR spectrum of Eu_2O_3@H-SiO_2 nanospheres.

In the FTIR spectrum, both the Si-O-Si stretch (1103 cm^{-1} for antisymmetric stretch and 802 cm^{-1} for symmetric stretch) and Eu_2O_3 vibration (470 cm^{-1}) are obviously revealed.

Table 1. Selected area electron diffraction data for Eu_2O_3 nanoparticles.

n_d	Calc. (d/ Å)	Card (d/ Å)	h k l	Difference
1	3.1415	3.1400	1 1 1	0.0015
2	2.7233	2.7200	2 0 0	0.0033
3	1.9171	1.9200	2 2 0	-0.0029
4	1.6395	1.6400	3 1 1	-0.0005

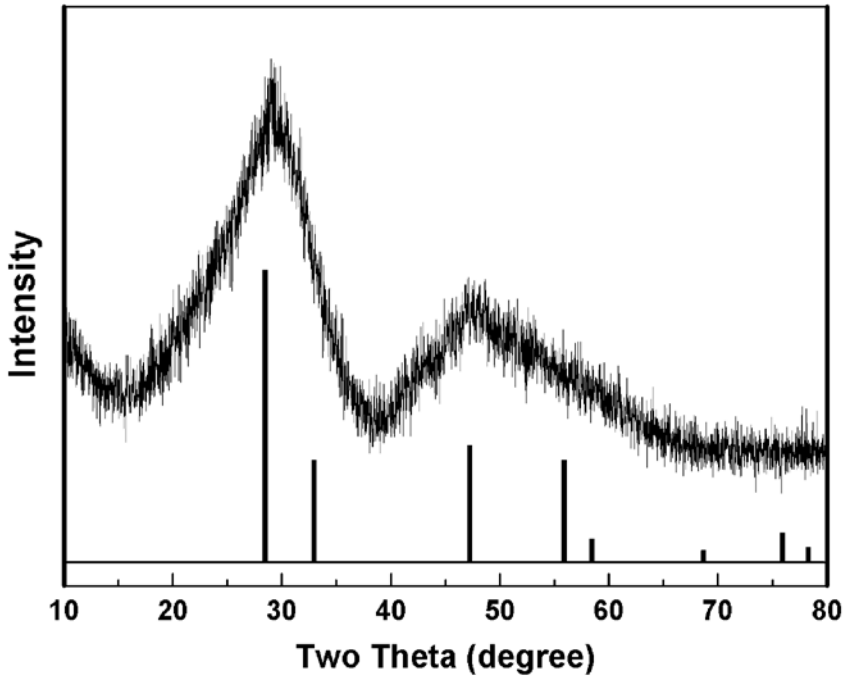

Figure S5. XRD pattern of Eu_2O_3@H-SiO_2 nanospheres.

The diffraction peaks in the XRD pattern can be indexed to the fcc structure of the Eu_2O_3 phase with the cell parameter a = 5.44 Å for Eu_2O_3 nanoparticles (JCPDS 32-0380), which is in good agreement with the result of the SAED pattern shown in Figure 2(A) in the text.

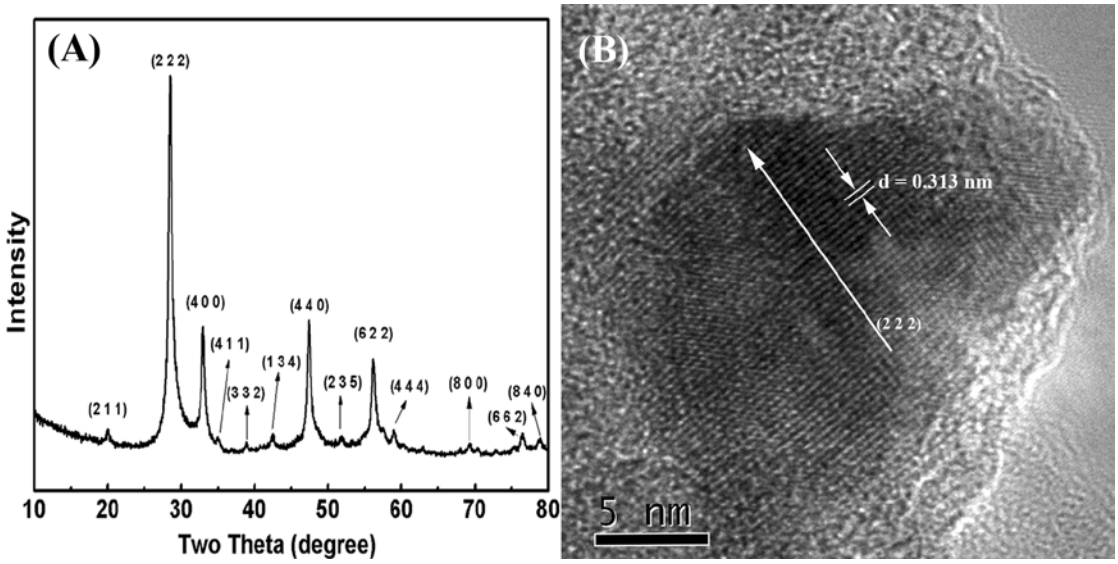

Figure S6. (A) XRD pattern of the Eu_2O_3 nanoparticles synthesized by calcining the naked hybrid cores without silica shell. (B) HRTEM image of a single Eu_2O_3 nanoparticle with clearly resolved lattice fringe of (222) planes (*d*=0.313)

To demonstrate the significant impact of the high pressure, which is resulted from the thermal decomposition of the organic components of the cores, on the crystal structure of Eu_2O_3 nanoparticles, a control experiment was performed. We calcined the naked hybrid cores without silica shell encapsulation under the same heating conditions. In contrast to the face-centered cube (fcc) structured Eu_2O_3 nanoparticles synthesized in the presence of the silica shell, XRD analysis reveals that the Eu_2O_3 nanoparticles from the control experiment have a cubic body-centered (bcc) structure (cell parameter a = 10.84 Å and V = 1274 Å^3, JCPDS 74-1988). The crystal structure of Eu_2O_3 nanoparticles synthesized without the out silica shell was further confirmed by high-resolution TEM (HRTEM) shown in Figure S6(B). The interplanar spacing is about 0.313 nm, which corresponds to the [222] plane of bcc Eu_2O_3 structure.

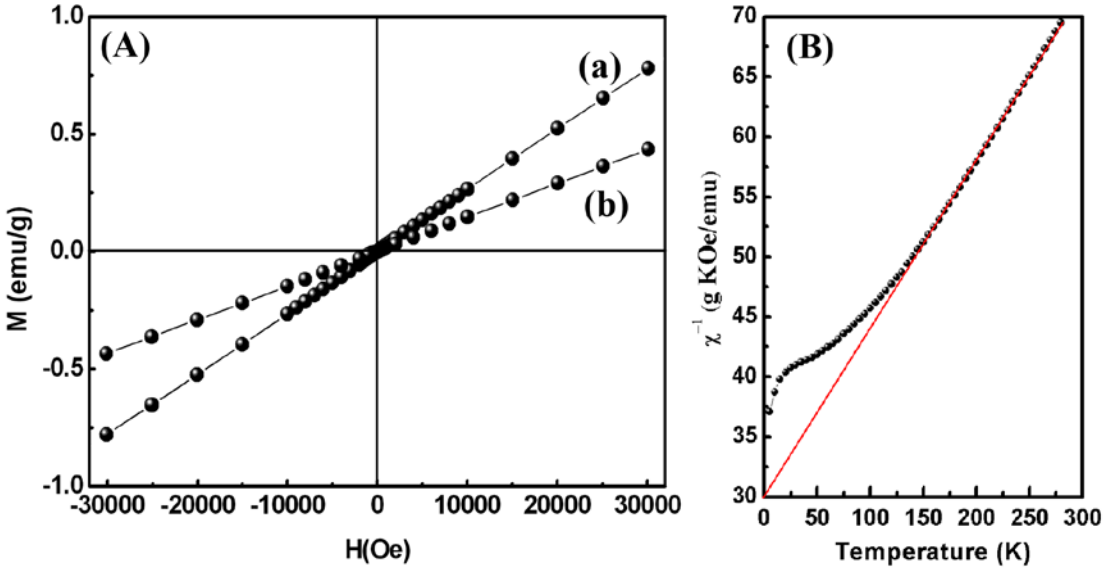

Figure S7. (A) Magnetic field dependence of magnetization for Eu_2O_3@H-SiO_2 nanospheres at 5 K (a) and 295 K (b). (B) Temperature dependence of inverse magnetic susceptibility for Eu_2O_3@H-SiO_2 nanospheres.

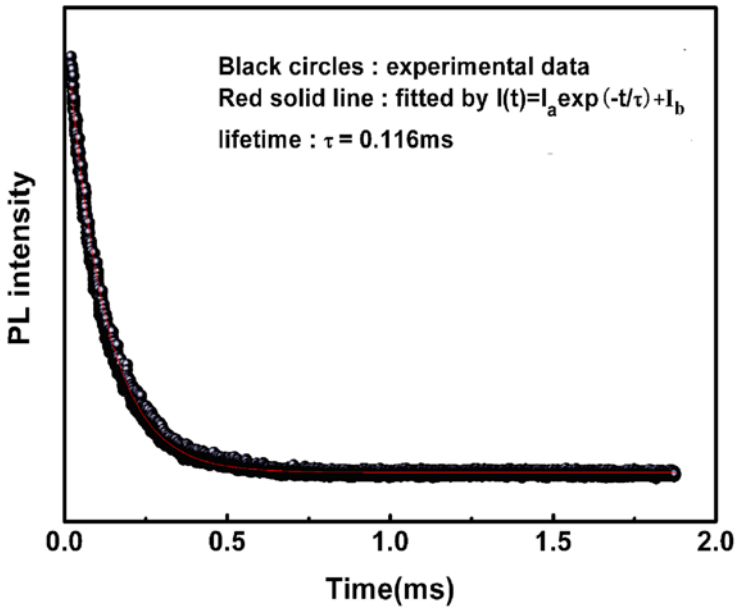

Figure S8. Decay curve of Eu^{3+} luminescence (615nm) in Eu_2O_3@H-SiO_2 nanospheres in solid state (λ_{ex}=390nm).