

Cite this: *Chem. Commun.*, 2011, **47**, 6329–6331

www.rsc.org/chemcomm

COMMUNICATION

Facile access to ultrasmall Eu₂O₃ nanoparticle-functionalized hollow silica nanospheres 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 and Zhidong Zhang^a

Received 11th December 2010, Accepted 20th April 2011

DOI: 10.1039/c0cc05510g

We report a promising strategy for the facile synthesis of ultrasmall nanoparticle-functionalized hollow silica nanospheres by using a functional cross-linked organic/inorganic hybrid core, which can be obtained simply through successive spontaneous reactions in water.

Hollow inorganic nanospheres have emerged as intriguing materials for applications in drug delivery, catalysis, imaging and photonic crystals, *etc.*¹ To fully exploit these versatile tiny containers in these applications, it is essential to invent facile ways to install diverse functionality in the sphere interior.² As a family of advanced materials, inorganic nanoparticles (NPs), especially with diameters sub-10 nm, have attracted much attention for their unique properties arising from quantum confinement or surface effects.³ By incorporating electrical, optic and magnetic NPs into hollow spheres, multifunctional nanocomposites can be obtained.

To date, there are mainly two strategies to prepare hollow silica (H-SiO₂) nanospheres encapsulating multiple NPs. One strategy is *via* multistep assembly pathway,⁴ in which the template core is coated sequentially with pre-synthesized NPs and silica shell first, and then the core is removed using a solvent or calcination. While quite flexible, the tedious assembly procedures are time consuming. Besides, for functionalization of small H-SiO₂ spheres this method is rather limited due to the poor surface interactions and tendency to aggregation of both the cores and NPs. An alternative strategy is the so-called “top-down” approach.⁵ The shells are constructed first, followed by formation of the NPs by infiltrating particle precursors into the cavity. However, it is notable that this approach has inherent difficulty in ensuring the reaction takes place exclusively inside the shells, so resulting in a procedure with low efficiency. Despite the progress made in the preparation of nanocomposites of H-SiO₂ and multiple

NPs, the present methods are complex and of low efficiency. Furthermore, these methods are often challenging in terms of preventing ultrasmall NPs from aggregation, which is very important for maintaining the unique properties of inorganic NPs. Therefore, synthesis of H-SiO₂ nanospheres with well dispersed ultrasmall NPs inside *via* a simple, effective and general way is still a great challenge.

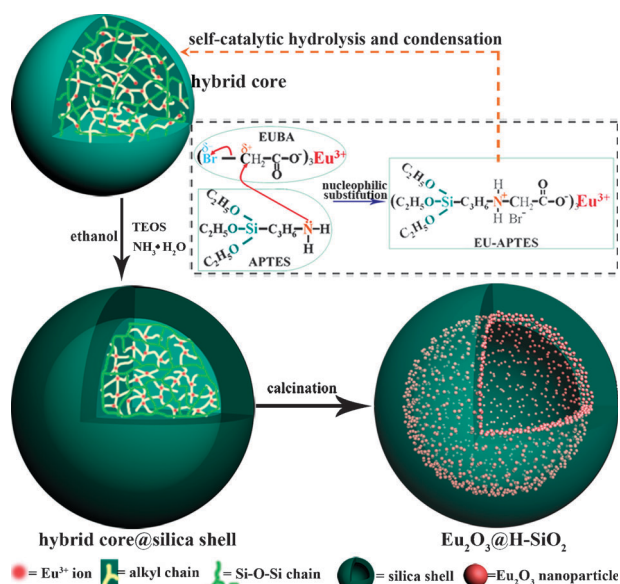
Preparation of NPs *in situ* in a cross-linked matrix provides an efficient way to obtain well dispersed NPs with uniform size and good stability.⁶ Herein, we designed and synthesized a functional cross-linked organic/inorganic hybrid core in an effort to establish a facile strategy for the synthesis of uniform and well dispersed NPs inside H-SiO₂ nanospheres. The multifunctional cores include three parts and each part plays an important role. First, the metal ions bonded to carboxyl groups provide an opportunity to generate uniform NPs *in situ* in hollow spheres. Second, the alkyl chains on one hand act as bridging units to link the metal ions to cross-linked Si–O–Si networks covalently, while on the other hand are utilized to create void space inside the spheres by thermal decomposition. Finally, the cross-linked Si–O–Si networks can favor formation of uniform NPs in the entire inner shell of H-SiO₂ spheres. More significantly, by rational selection of reactant molecules, these functional hybrid cores can be obtained simply through successive spontaneous reactions in water.

Here, we successfully synthesized Eu₂O₃ NP decorated H-SiO₂ (Eu₂O₃@H-SiO₂) by the spontaneous formation and decomposition of a functionalized cross-linked organic/inorganic hybrid core. The entire synthetic pathway is illustrated in Scheme 1. The first step is the formation of hybrid cores through two successive spontaneous reactions in water. (3-Aminopropyl)triethoxysilane (APTES) and europium bromoacetate (EUBA) were selected as the reactants. It has been proven that APTES is stable in water without catalyst,⁷ but when it was mixed with EUBA, nucleophilic substitution reaction between the terminal bromine group of EUBA and the amine group of APTES took place⁸ to afford the complex Eu-APTES (Scheme 1). The FTIR spectrum of the complex (Fig. S2, ESI†) provides support for the covalently bound europium acetate group to APTES. The C–N stretch of the primary amine (1167 cm⁻¹) of APTES disappears after addition of EUBA, whereas the C–N stretch of secondary

^a Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, PR China. E-mail: cui@hit.edu.cn; Fax: (+86) 24-23971215; Tel: (+86) 24-23971859

^b The Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin 150001, PR China

† Electronic supplementary information (ESI) available: Experimental procedures, ¹H NMR and FTIR spectra, TEM image, SAED data, XRD patterns, magnetization and luminescence decay curve. See DOI: 10.1039/c0cc05510g



Scheme 1 Synthetic pathway for the preparation of $\text{Eu}_2\text{O}_3@H\text{-SiO}_2$ nanospheres.

amine (1137 cm^{-1}) is obviously observed. More importantly, a protonated amine group (1635 cm^{-1}) is produced, which acts as acid catalyst for the hydrolysis of ethoxysilyl groups.⁹ Therefore, self-catalytic hydrolyzation proceeded spontaneously without introducing any other catalyst. The $-\text{Si}(\text{OC}_2\text{H}_5)_3$ groups were hydrolyzed into $-\text{Si}(\text{OH})_3$ and further polycondensed into cross-linked polysilsesquioxane. The Si–O–Si stretching band at 1045 cm^{-1} in the FTIR spectrum (Fig. S2, ESI[†]) clearly confirms the inorganic polymerization within the cores.

The inorganic polysilsesquioxane component endows the functional cores with significant chemical affinity towards silica. Thus, silica encapsulation was accomplished by directly adding tetraethylorthosilicate (TEOS), ethanol and ammonia to the core suspension. Neither surface treatment nor solvent exchange is needed. In addition, collection the cores by centrifugation is also not required, which effectively avoids the conglomeration of the cores and the final hollow nanospheres. The selective deposition of silica on the hybrid cores is attributed to the reactive silanol groups on the core surface.¹⁰ Furthermore, the cross-linked Si–O–Si network can effectively protect the metal carboxylate groups in the encapsulation process.

Calcination the nanocomposites at $800\text{ }^\circ\text{C}$ in air is used to remove the organic components of the cores and prepare Eu_2O_3 NPs *in situ*. A hollow interior was generated in each silica nanosphere. Fig. 1A illustrates a transmission electron microscope (TEM) image of the nanospheres obtained after calcination of the composites prepared at a molar ratio of EUBA:APTES:TEOS of 1:3:5.8. Almost all the $\text{Eu}_2\text{O}_3@H\text{-SiO}_2$ nanospheres have a spherical shape with a smooth shell. The outer diameter of the particles is 30–50 nm, and the thickness of the wall is 4–6 nm. Energy-dispersive spectroscopy (EDS) spectrum (inset of Fig. 2A) of the spheres clearly shows the presence of Si, O and Eu.

Fig. 1B shows a TEM image of a single $\text{Eu}_2\text{O}_3@H\text{-SiO}_2$ nanosphere. We can see that the Eu_2O_3 NPs with diameters of

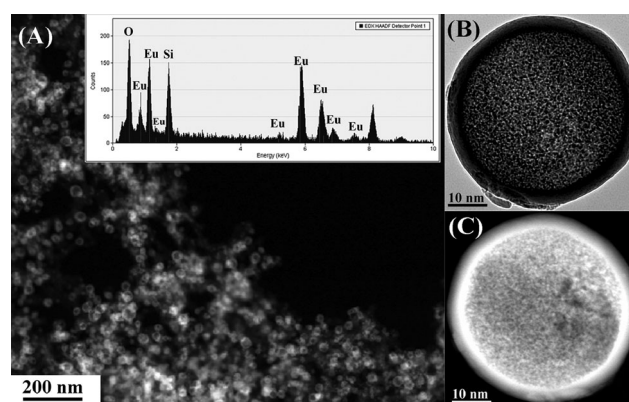


Fig. 1 (A) TEM image and EDS spectrum (inset) of $\text{Eu}_2\text{O}_3@H\text{-SiO}_2$ nanospheres. TEM (B) and STEM (C) image of a single $\text{Eu}_2\text{O}_3@H\text{-SiO}_2$ nanosphere.

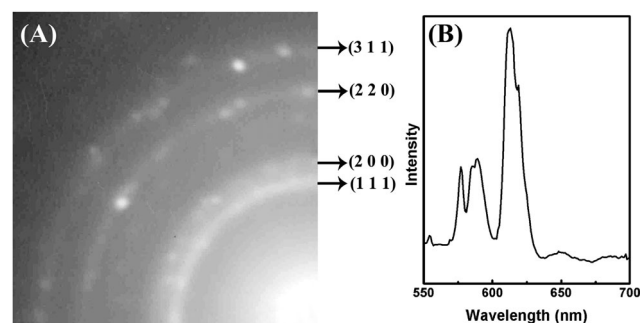


Fig. 2 SAED pattern (A) and emission spectrum ($\lambda_{\text{ex}} = 394\text{ nm}$) (B) of $\text{Eu}_2\text{O}_3@H\text{-SiO}_2$ nanospheres.

approximately 1 nm are separated from each other and are well dispersed in the inner shell of the H-SiO₂ nanosphere. This is mainly because, throughout the heating process, the Eu^{3+} ions are always surrounded by the cross-linked Si–O–Si networks, which effectively limit the growth rate of the Eu_2O_3 particles. On the other hand, the deposition rate of inorganic components on the internal wall of silica shells was remarkably accelerated pushed by the expanding gases (generated by thermal decomposition of the organic components); the formed compact silica matrix prevents the Eu_2O_3 particles from growing further after nucleation, resulting in their small size and uniform dispersion. To further characterize the structure of $\text{Eu}_2\text{O}_3@H\text{-SiO}_2$, scanning transmission electron microscopy (STEM) measurement was carried out. As shown in Fig. 1C, the brightness of the inner shell is obviously higher than that of the outer shell, suggesting the distribution of Eu_2O_3 NPs is uniform throughout the entire inner shell of H-SiO₂ nanosphere (the “bright” spots correspond to Eu in the STEM image). Although small H-SiO₂ nanospheres (< 50 nm in diameter) are ideal candidates in intracellular applications,¹¹ their interior functionalization with multiple inorganic NPs is here reported for the first time.

The selected-area electron diffraction (SAED) (Fig. 2A) of the Eu_2O_3 NPs displays diffraction rings which can be perfectly indexed to a face-centered cube (fcc) structure of the Eu_2O_3 phase with the cell parameter $a = 5.44\text{ \AA}$ (JCPDS 32-0380). It should be noted that fcc is an uncommon crystal

structure for Eu_2O_3 and has rarely been reported. We speculate that high pressure within hollow spheres, which results from thermal decomposition of the hybrid cores, is essential for the formation of fcc structured Eu_2O_3 . Upon heating, organic components of the hybrid core decomposed and quickly oxidized into a mass of gaseous small molecules restricted in the limited space. As a result, high pressure was undoubtedly generated in the interior of every hollow sphere.¹² It is well known that pressure and temperature have significant impact on the crystal structure of materials. Moore and Ferguson reported fcc structured Eu_2O_3 with the assistance of high temperature ($>1350\text{ }^\circ\text{C}$) and blending with zirconia.¹³ In our case, it is assumed that the high pressure decreases the formation temperature of fcc structured Eu_2O_3 .

To further demonstrate our speculation, naked hybrid cores without silica encapsulation were calcined under the same heating conditions. XRD data (Fig. S6A, ESI[†]) reveals that only Eu_2O_3 with cubic body-centered (bcc) structure (cell parameter $a = 10.84\text{ \AA}$ and $V = 1274\text{ \AA}^3$, JCPDS 74-1988) was obtained from the control experiment, confirming the significant effect of pressure on the crystal structure of Eu_2O_3 NPs. That means in our strategy, the H-SiO₂ spheres serve as high temperature and pressure nanoreactors for preparation of ultrasmall Eu_2O_3 NPs with fcc structure. This convenient synthesis of ultrasmall NPs opens up a new avenue to synthesis of a broad range of functional nanocomposites.

Fig. 2B shows the room-temperature emission spectrum of $\text{Eu}_2\text{O}_3@/\text{H-SiO}_2$ powder with an excitation wavelength of 394 nm. The prominent lines are assigned to Eu^{3+} transitions from $^5\text{D}_0$ to $^7\text{F}_j$ ($j = 0-4$) with the red $j = 2$ line as the dominant feature. An interesting phenomenon is that the peak of $^5\text{D}_0$ to $^7\text{F}_2$ split into two peaks of 614 and 618 nm. We consider this unusual behavior is possibly related to the surface effect resulting from size reduction. It is known that surface atoms, which have a low coordination number, usually have lower symmetry than bulk ones. In the present Eu_2O_3 NPs, the size is very small and thus the surface fraction of Eu^{3+} ions is very high. Since the electric dipole transition of Eu^{3+} ions is extremely sensitive to the crystal field, the lower crystal field symmetry at the surface is considered to be the main origin of this unusual behavior.¹⁴ Magnetic measurement of $\text{Eu}_2\text{O}_3@/\text{H-SiO}_2$ nanospheres was performed using a superconducting quantum interference device (SQUID) magnetometer. The nanospheres exhibit paramagnetic behavior attributed to Eu_2O_3 ,¹⁵ which further confirms the existence of Eu_2O_3 nanoparticles in the silica spheres.

In summary, we have shown for the first time that small (30–50 nm) multifunctional silica spheres, which possess hollow structure and fluorescent and paramagnetic properties in a single unit, can be simply synthesized by using a spontaneously formed cross-linked organic/inorganic hybrid core. The covalent incorporation of Eu^{3+} ions as well as the cross-linked structure of the hybrid cores favor formation of uniform and well-dispersed Eu_2O_3 NPs in the entire inner shell of H-SiO₂ nanospheres. Since the carboxyl group of bromoacetic acid can bond not only with europium but also with a wide range of other metal ions, it is anticipated that this procedure can be easily broadened to hollow nanocomposites with

diverse functionality. Extension to other morphological and structured silicon-based nanomaterials will open up a wider route to various functional materials for promoting the fabrication of new types of optical, electric and magnetic devices.

This work has been supported by the National Natural Science Foundation of China (No. 50703046), the Fundamental Research Funds for the Central Universities (Grant No. HIT.NSRIF.2009082), the China Postdoctoral Science Foundation (Nos. 20090450978, 201003417) and the Heilongjiang Postdoctoral Science Foundation (No. LBH-Z09123).

Notes and references

- (a) F. Caruso, R. A. Caruso and H. Möhwald, *Science*, 1998, **282**, 1111; (b) X. W. Lou, L. A. Archer and Z. Yang, *Adv. Mater.*, 2008, **20**, 3987; (c) J. Liu, Q. Yang, L. Zhang, H. Yang, J. Gao and C. Li, *Chem. Mater.*, 2008, **20**, 4268; (d) Z. Zhong, Y. Yin, B. Gates and Y. Xia, *Adv. Mater.*, 2000, **12**, 206; (e) J. Du, Y. Chen, Y. Zhang, C. C. Han, K. Fischer and M. Schmidt, *J. Am. Chem. Soc.*, 2003, **125**, 14710; (f) P. Jiang, J. F. Bertone and V. L. Colvin, *Science*, 2001, **291**, 453; (g) L. Du, S. Liao, H. A. Khatib, J. F. Stoddard and J. I. Zink, *J. Am. Chem. Soc.*, 2009, **131**, 15136; (h) Y. Zhu, J. Shi, W. Shen, X. Dong, J. Feng, M. Ruan and Y. Li, *Angew. Chem., Int. Ed.*, 2005, **44**, 5083.
- (a) K. Kamata, Y. Lu and Y. Xia, *J. Am. Chem. Soc.*, 2003, **125**, 2384; (b) L. Tan, D. Chen, H. Liu and F. Tang, *Adv. Mater.*, 2010, **22**, 4885; (c) K. M. Yeo, J. Shin and I. S. Lee, *Chem. Commun.*, 2010, **46**, 64; (d) Q. Zhang, J. Ge, J. Goebel, Y. Hu, Z. Lu and Y. Yin, *Nano Res.*, 2010, **2**, 583.
- (a) A. Henglein, *Chem. Rev.*, 1989, **89**, 1861; (b) R. Si, Y. W. Zhang, L. P. You and C. H. Yan, *Angew. Chem., Int. Ed.*, 2005, **44**, 3256.
- (a) Z. Chen, Z. M. Cui, F. Niu, L. Jiang and W. G. Song, *Chem. Commun.*, 2010, **46**, 6524; (b) X. W. Lou, C. Yuan, E. Rhoades, Q. Zhang and L. A. Archer, *Adv. Funct. Mater.*, 2006, **16**, 1679.
- (a) Y. Yamada, M. Mizutani, T. Nakamura and K. Yano, *Chem. Mater.*, 2010, **22**, 1695; (b) W. S. Choi, H. Y. Koo and D. Y. Kim, *Langmuir*, 2008, **24**, 4633.
- (a) L. Li, J. L. Shi, L. X. Zhang, L. M. Xiong and J. N. Yan, *Adv. Mater.*, 2004, **16**, 1079; (b) Y. Guari, C. Thieuleux, A. Mehdi, C. Reyé, R. J. P. Corriu, S. G. Gallardo, K. Philippot, B. Chaudret and R. Dutartre, *Chem. Commun.*, 2001, 1374; (c) T. Cui, F. Cui, J. Zhang, J. Wang, J. Huang, C. Lü, Z. Chen and B. Yang, *J. Am. Chem. Soc.*, 2006, **128**, 6298; (d) T. Cui, J. Zhang, J. Wang, F. Cui, W. Chen, F. Xu, Z. Wang, K. Zhang and B. Yang, *Adv. Funct. Mater.*, 2005, **15**, 481.
- N. Hüsing, U. Schubert, R. Mezei, P. Fratzl, B. Riegel, W. Kiefer, D. Kohler and W. Mader, *Chem. Mater.*, 1999, **11**, 451.
- S. S. Bae, D. K. Lim, J. I. Park, W. R. Lee, J. Cheon and S. Kim, *J. Phys. Chem. B*, 2004, **108**, 2575.
- A. Khanal, Y. Inoue, M. Yada and K. Nakashima, *J. Am. Chem. Soc.*, 2007, **129**, 1534.
- (a) R. K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979; (b) G. H. Bogush, M. A. Tracy and C. F. Zukoski IV, *J. Non-Cryst. Solids*, 1988, **104**, 95.
- J. Zhu, J. Tang, L. Zhao, X. Zhou, Y. Wang and C. Yu, *Small*, 2010, **6**, 276.
- N. Kawahashi and E. Matijevic, *J. Colloid Interface Sci.*, 1991, **143**, 103.
- D. A. Moore and I. F. Ferguson, *J. Am. Ceram. Soc.*, 1982, **65**, 414.
- (a) C. H. Yan, L. D. Sun, C. S. Liao, Y. X. Zhang, Y. Q. Lu, S. H. Huang and S. Z. Lü, *Appl. Phys. Lett.*, 2003, **82**, 3511; (b) F. Zhao, M. Yuan, W. Zhang and S. Gao, *J. Am. Chem. Soc.*, 2006, **128**, 11758.
- (a) J. Hite, G. T. Thaler, R. Khanna, C. R. Abernathy and S. J. Pearton, *Appl. Phys. Lett.*, 2006, **89**, 132119; (b) *The Oxide Handbook*, ed. G. V. Samsonov, IFI/Plenum, New York, 1973, p. 402 (translated from Russian by C. Nigel Turton and Tatiana I. Turton).