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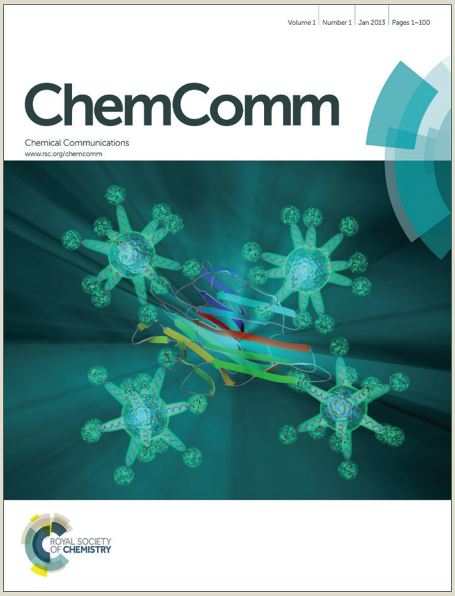

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Self-catalytic synthesis of metal oxide nanoclusters@mesoporous silica composites based on successive spontaneous reactions at near neutral condition

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A facile self-catalytic approach for the synthesis of metal oxide nanoclusters@mesoporous silica was proposed by subtly making use of successive spontaneous reactions in solution at near neutral condition.

Silica with micro- or mesoporous structures has received tremendous research interest over the last decade expanding their functionality by the incorporation of functional organic compounds or addition of other inorganic materials.[1-3] For instance, incorporation of metal or metal oxide nanoparticles (NPs)/nanoclusters (NCs) into the mesoporous silica structures has been persistently pursued in order to develop novel composites for wide applications, such as catalysis, separation, drug delivery, and imaging.[4-6] NPs/NCs@silica composites can usually be prepared by encapsulating presynthesized NPs/NCs in silica.[7-9] This method is often challenging, however, in terms of the high density of NPs/NCs and the aggregation of NPs/NCs in the matrix, which are required for most of the applications. Alternatively, preparation of NPs/NCs in situ in cross-linked silica matrix offers an effective approach to control the size, the homogeneity and the stability of the NPs/NCs in silica.[10,11] The key issue is how to protect the precursors of metal oxide, such as metal organic coordination groups or metal salts, from being destroyed in the sol-gel process.

Although there are many reports on metal oxide@silica composites, this area still faces significant challenges, some of which we address here. First, sol-gel method is the current workhorse for preparing silica-based materials, however, the conventional sol-gel method inevitably used base catalyst (e.g. ammonia aqueous solution), or sometimes acid catalyst (e.g. hydrochloric acid aqueous solution) to catalyze the hydrolysis and condensation of silicon alkoxides, which poses significant limitations on the introducing pH sensitive groups or molecules, such as most of metal organic coordination groups and biomolecules, into silica without any damage. Further, the commonest NH_4OH catalyst in conventional so-gel method would also break many metal organic coordination groups by the strong coordination effect caused by the lone pair electrons on the nitrogen atoms. So far, the incorporation of pH sensitive groups or molecules into silica without any damage has proved challenging to satisfy.[12] Second, to preserve the properties of NPs/NCs (especially optical and catalytic properties), it is often important that they remain small size and separated in the matrix. Although the in situ method provides the possibility to control the particle size and

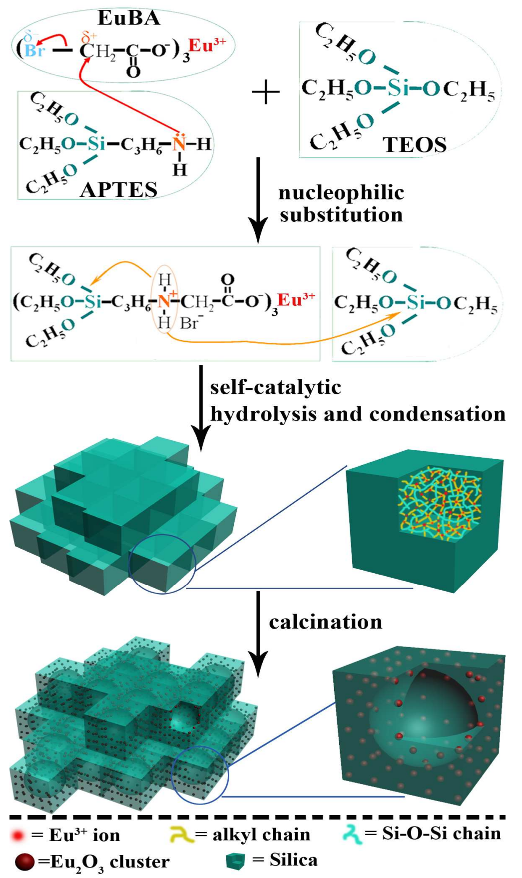

Fig. 1 Synthetic pathway for the preparation of Eu_2O_3 NCs@*m*SiO_2 composites.

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avoid the aggregation of NPs/NCs, it is still a great challenge to ensure the molecular-level dispersion of the metal organic precursor in matrix. Third, previous reports on metal oxide@ silica composites were often sufficiently complex that widespread adoption of these methods has been limited.

Here, we present a facile self-catalytic strategy for the synthesis of Eu_2O_3 NCs@mesoporous silica (Eu_2O_3 NCs@$m$$SiO_2$) composites based on successive spontaneous reactions in water/ethanol solution at near neutral condition. In this strategy, we design a novel multifunctional precursor, which combines not only a silicon alkoxide and a metal carboxylate group, but also a protonated amine group in a single molecule. The covalent bound of europium carboxylate group to silicon alkoxide ensures a molecular-level dispersion of Eu^{3+} ion, which favors the formation of small Eu_2O_3 NCs without aggregation in the entire matrix. Although the modification of silicon alkoxide with organic groups, such as amine and diketonate group, has been widely studied,[13,14] it is seldom to achieve sol-gel molecule based carboxylate groups, which can be ligated to nearly every metal in the periodic table. More significantly, a protonated amine group is generated directly on the alkyl chains of the multifunctional molecule, thus self-catalytic hydrolyzation and condensation will proceed spontaneously. To our knowledge, this is the first time that catalytic sites are introduced in sol-gel molecule. Since no additional base or acid catalyst, as well as toxic organic solvent is needed in the whole process, this strategy is an enviromentally improved route to silica-based materials.

The synthetic pathway for the preparation of Eu_2O_3 NCs@ $m$$SiO_2$ composites is illustrated in Fig. 1. For this self-catalytic method, the formation of the designed multifunctional precursor molecule is critical. To achieve the target molecule, we selected (3-Aminopropyl)triethoxysilane (APTES) and europium bromoacetate (EuBA) as the reactants. It has been proven that APTES is stable in ethanol and water without catalyst,[15] but when mixed with EuBA, a nucleophilic substitution reaction between the terminal bromine group of EuBA and the amine group of APTES would take place.[16] As a result, the europium acetate group was covalently bounded to APTES, which was confirmed by the FTIR spectrum (Fig. S2). As expected, the C-N stretch of the primary amine (1167 cm^{-1}) of APTES and C-Br vibration (550 cm^{-1}) of EuBA are not observed, while the C-N stretch of secondary amine (1128 cm^{-1}) is present. More significantly, a protonated amine group (1634 cm^{-1}) was generated directly on the multifunctional molecule, which can act as mild catalytic site for the hydrolysis and condensation of ethoxysilyl groups.[17] Therefore, self-catalytic hydrolyzation and condensation would proceed spontaneously at near neutral pH without any additional catalyst. Different amount of tetraethylorthosilicate (TEOS) could also be added for adjusting the structure and metal loading of the composites. The crosslinking of the silicon groups was confirmed by FTIR spectrum (Fig. S2), in which the Si-O-Si stretching band are apparent at 1047 cm^{-1}.

The successive spontaneous reactions afforded crosslinked organic/inorganic hybrid silica material, which includes three parts and each part plays an important role. First, the europium carboxylate groups provide an opportunity to generate uniform Eu_2O_3 NCs in situ in silica matrix. Second, the alkyl chains on one hand act as bridging units to link the europium carboxylate groups to Si – O – Si networks covalently, on the other hand are utilized to create mesopores inside the matrix by thermal decomposition. Finally, the cross-linked Si – O – Si networks can prevent the growth and aggregation of the Eu_2O_3 NCs, thus favoring the formation of small sized and well-dispersed NCs in the entire SiO_2 matrix.

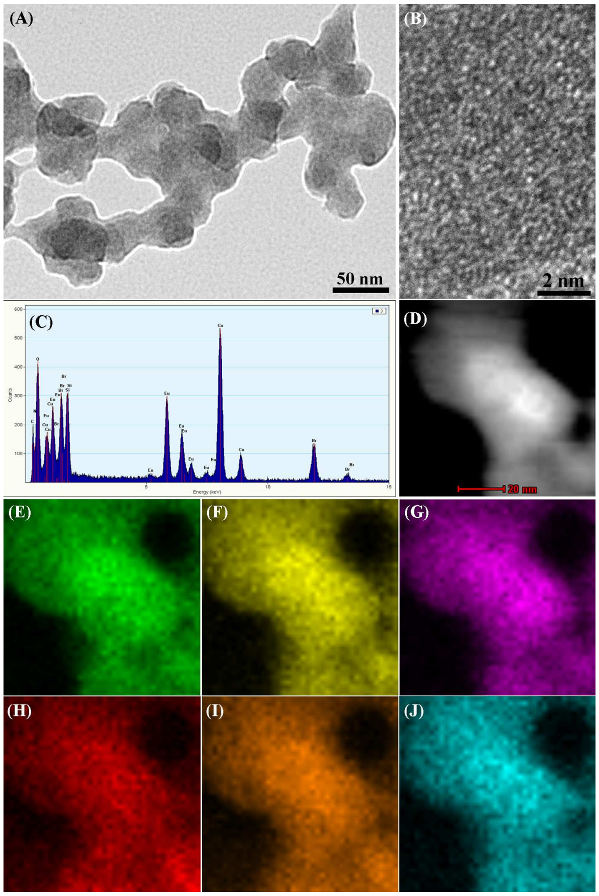

Fig. 2 TEM bright-field images (A and B), EDS spectrum (C) and STEM image (D) of the organic/inorganic hybrid silica material. (E-J) EDX element mappings showing the Si (green), O (yellow), Eu (pink), C (red), N (orange) and Br (blue) signals.

Fig. 2A shows a transmission electron microscope (TEM) image of the organic/inorganic hybrid silica material prepared at a molar ratio of EuBA : APTES : TEOS of 1 : 3 : 0.5, which shows the material consists of a large quantity of particles with irregular morphologies. Higher magnification TEM image (Fig. 2B) demonstrates the compact and homogeneous structure of the material. In the energy dispersed spectrum (EDS) (Fig. 2C) , the peaks of Si, O, Eu, C, N and Br are presented as expected. Since the hydrolyzation and condensation reactions were catalyzed by the intramolecular protonated amine groups at near neutral pH, the europium carboxylate groups could be well protected. The scanning TEM (STEM) analysis (Fig. 2D) of the hybrid sample yields a clear contrast between the metal domains and the nonmetal matrix, suggesting the well dispersion of Eu ions. The element distribution of the hybrid material was further examined by energy-dispersive X-ray (EDX) spectroscopy

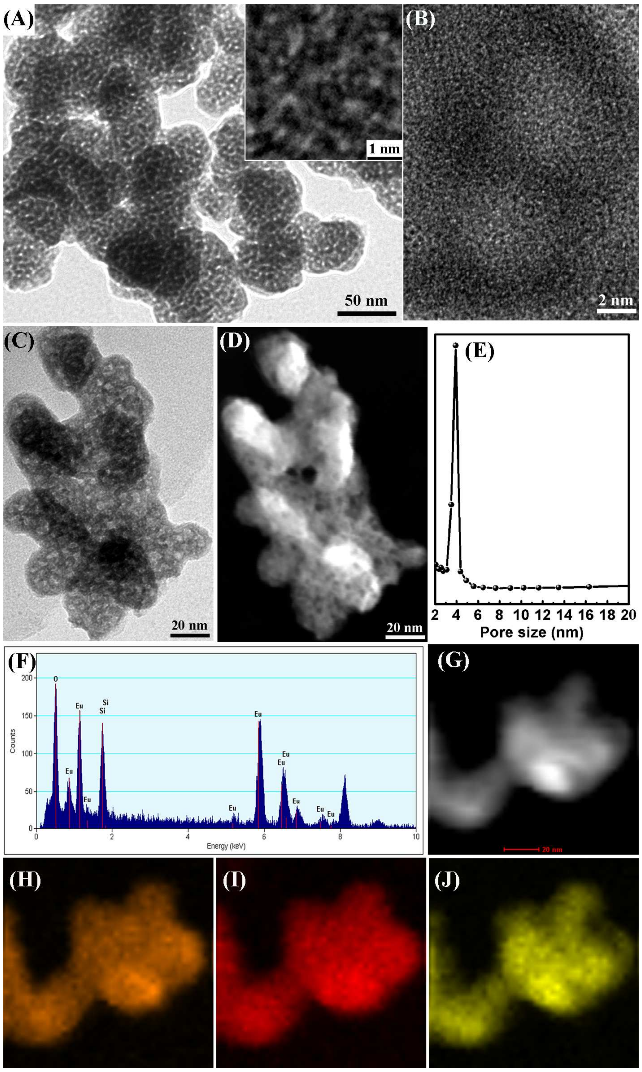

Fig. 3 TEM bright-field images (A-C), STEM image (D, G), pore size distribution (E) and EDS spectrum (F) of the Eu_2O_3 NCs@*m*SiO_2 composites. (H-J) EDX element mappings showing the Si (orange), O (red) and Eu (yellow) signals.

element mappings of Si, O, Eu, C, N and Br (Fig. 2(E-J)). It is worth mentioning that, the hybrid material is prepared from the multifunctional molecules, thus all the elements distribute uniformly in the hybrid material, which is the crucial premise for prepare the uniform Eu_2O_3 NCs@*m*SiO_2 composites.

Calcination of the organic/inorganic hybrid material at 550 ^{o}C in air is used to remove the organic components and generate Eu_2O_3 NCs. Fig. 3(A, B) illustrate the TEM images of the as-prepared Eu_2O_3 NCs@*m*SiO_2 composites. Uniform mesopores with diameters about 3-4 nm are generated throughout the composites. The pore size distribution (Fig. 3E) exhibits a sharp peak centered at the mean value of ~3.9 nm, which is in good agreement with the result of the TEM image. During the thermolysis of the hybrid material, the alkyl chains were transformed into organic (or carbonaceous) moieties via chemical decomposition and were confined as vesicles in the solids. These organic vesicles acted as self-generated porogens, which later were converted into mesopores.

The covalent bound europium carboxylate groups to silica matrix offers an opportunity to generate small and densely dispersed Eu_2O_3 NCs in the entire matrix. From the higher magnification TEM image of the silica wall shown in the inset of Fig. 3A, we can see that the Eu_2O_3 NCs with diameters smaller than 1 nm are separated from each other and are well dispersed. That is because, throughout the heating process, the Eu^{3+} ions are always surrounded by the crosslinked Si-O-Si networks, which effectively prevents the Eu_2O_3 NCs from growing further after nucleation. By comparing the TEM image of the composites shown in Fig. 3C and its corresponding STEM image shown in Fig. 3D, the homogeneous dispersion of the Eu_2O_3 NCs can be reliably determined. Further evidence for the uniform dispersion of the Eu_2O_3 NC in silica matrix is provided by the element mappings shown in Fig. 3(H-J). The Eu^{3+} ionic states can be confirmed by the X-ray photoelectron spectroscopy (XPS) spectrum (Fig. S4). By the way, we noticed that, the mesopores would collapse under continuous electron beam irradiation, which may due to the relatively thin thickness of the silica walls (about 3-5 nm).

The emission spectrum of the Eu_2O_3 NCs@*m*SiO_2 is shown in Fig. 4A. For comparison, the photoluminescent property of the commercial Eu_2O_3 powder was also tested (Fig. 4B). The peaks ascribed to Eu^{3+} transition from $^5D_0$ to ^7F_J (J = 0-4) are presented in the emission spectra of both the two samples, for instance, $^5D_0 \rightarrow {}^7F_0$, 581 nm; $^5D_0 \rightarrow {}^7F_1$, 590 nm; $^5D_0 \rightarrow {}^7F_2$, 612 nm; $^5D_0 \rightarrow {}^7F_3$, 649 nm; $^5D_0 \rightarrow {}^7F_4$, 697 nm. Although the major peak positions in the emission spectra are identical to each other, the peak width and the intensity patterns are quite different. Compared to the Eu_2O_3 powder, the intensity ration of $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ of the Eu_2O_3 NCs@*m*SiO_2 decreases dramatically, which indicates the silica matrix has a strong influence on the symmetry of Eu^{3+}.[18] Moreover, the emission spectrum is obviously broadened for the Eu_2O_3 NCs@*m*SiO_2 compared with that of the Eu_2O_3 powder sample, which can be recognized as a characteristic of ultrasmall NCs.[19] Different from Eu_2O_3 powder, the transitions from higher energy excited states of $^5D_1$ ($^5D_1 \rightarrow {}^7F_0$, 521 nm; $^5D_1 \rightarrow {}^7F_1$, 529 nm) are emerge in the emission spectrum of Eu_2O_3 NCs@*m*SiO_2. We speculate this unusual phenomenon should be correlated to the ultrasmall size and high dispersion of the Eu_2O_3 NCs, which largely slow down the rate of the cross-relaxation, which occurs only between neighboring Eu^{3+} ions. The photographs of the Eu_2O_3 NCs@*m*SiO_2 composites under visible- and UV-light irradiation are shown in Fig. 4(C,D).

In conclusion, we demonstrated a self-catalytic route to metal oxide@*m*SiO_2 composites without any additional catalyst. In contrast to previous reports on silica composites need several preparation steps, our strategy simply relies on the successive spontaneous reactions in water/ethanol solution. The key of this method is the design and synthesis of the multifunctional precursor molecules, which combine metal carboxylate groups with silicon alkoxides through protonated amino groups. The covalent introduction of metal carboxylate groups and the crosslinked structure of the Si-O-Si networks favor the formation of small and well-dispersed Eu_2O_3 NCs in the mesoporous silica matrix. Since the carboxylate group can bond with not only europium but also nearly every metal in the periodic table, we anticipate that this strategy can be

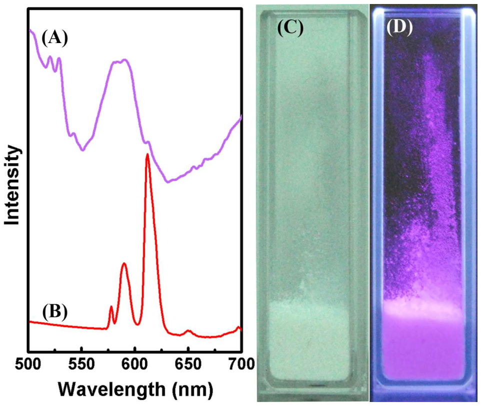

Fig. 4 Emission spectra of the Eu_2O_3 NCs@*m*SiO_2 composites (A) and commercial Eu_2O_3 powder (B) (λ_{ex} = 394 nm). Photographs of the Eu_2O_3 NCs@*m*SiO_2 composites under visible- (C) and UV-light (D) irradiation.

exploited as a general method for the fabrication of various functional silica-based composites.

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Notes and references

1 Y. Wan and D. Y. Zhao, *Chem. Rev.*, 2007, **107**, 2821.
2 H. Frank, C. Maximilian, M. Jurgen and F. Michael, *Angew. Chem. Int. Ed.*, 2006, **45**, 3216.
3 B. G. Trewyn, I. I. Slowing, S. Giri, H. T. Chem and V. S. Y. Lin, *Acc. Chem. Res.*, 2007, **40**, 846.
4 S. H. Joo, J. Y. Park, C. K. Tsung, Y. Yamada, P. Yang and G. A. Somorjai, *Nat. Mater.*, 2009, **8**, 126.
5 J. E. Lee, N. Lee, T. Kim, J. Kim and T. Hyeon, *Acc. Chem. Res.*, 2011, **44**, 893.
6 T. Xie, L. Shi, J. Zhang and D. Zhang, *Chem. Commun.*, 2014, **50**, 7250.
7 Y. Xu, J. Ma, Y. Xu, L. Xu, L. Xu, H. Li and H. Li, *RSC Adv.*, 2013, **3**, 851.
8 F. Lu, A. Popa, S. Zhou, J. J. Zhu and A. C. S. Samia, *Chem. Commun.*, 2013, **49**, 11436.
9 T. D. Nguyen, W. Y. Hamad and M. J. Maclachlan, *Adv. Func. Mater.*, 2014, **24**, 777-783.
10 C. Garcia, Y. Zhang, F. DiSalvo and U. Wiesner, *Angew. Chem. Int. Ed.*, 2003, **42**, 1526.
11 M. Malenovska, M. A. Neouze, U. Schubert, A. Peled and J. P. Lellouche, *Dalton Trans.*, 2008, 4647.
12 A. Bernecker, R. Wieneke, R. Riedel, M. Seibt, A. Geyer and C. Steinem, *J. Am. Chem. Soc.*, 2010, **132**, 1023.
13 U. Schubert, S. A. Schwab and B. Breitscheidel, *Chem. Mater.*, 1989, **1**, 576.
14 U. Schubert, *Polym. Int.*, 2009, **58**, 317.
15 N.Hüsing, U. Schubert, R. Mezei, P. Fratzl, B. Riegel, W. Kiefer, D. Kohler and W. Mader, *Chem. Mater.*, 1999, **11**, 451.
16 S. S. Bae, D. K. Lim, J. I. Park, W. R. Lee, J. Cheon and S. Kim, *J. Phys. Chem. B*, 2004, **108**, 2575.
17 A. Khanal, Y. Inoue, M. Yada and K. Nakashima, *J. Am. Chem. Soc.,* 2007, **129**, 1534.
18 J. A. Capobianco, P. P. Proulx, M. Bettinelli and F. Negrisolo, *Phys. Rev. B*, 1990, **42**, 5936.
19 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.