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Synthesis and luminescence properties of mesostructured thin films activated by *in-situ* formed trivalent rare earth ion complexes†

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Incorporation of trivalent rare earth ions and 1,10-phenanthroline into mesostructured block-copolymer/silica thin films produces spectrally pure emission from *in-situ* formed rare earth ion complexes.

The sharpness of the intra-f-shell emission lines of trivalent rare earth (RE) ions makes them particularly interesting for a variety of photonic applications.[1] However, because almost all absorption lines of RE ions arise from parity forbidden f–f electronic transitions, their absorption cross sections are small and direct optical excitation is inefficient. On the other hand, it is known that the emission of RE ions can be enhanced through indirect excitation mechanisms using organic[2] and inorganic[1,3] sensitizers. Among the organic, complexes with β-diketones and heterocyclic ligands efficiently sensitize trivalent europium (Eu^{3+}) and terbium (Tb^{3+}) ions *via* non-radiative energy transfer from the ligand's triplet state to the crystal field states of the central RE ion.[2] For technological applications, these complexes have to be incorporated into a stable solid matrix.[4–6] Usually, this is done in a two-step process, where first the RE complexes are synthesized separately and then—in a second step—incorporated into sol–gel-derived composite materials.[5,6]

Here, we report a simple one-step synthesis procedure for preparing block-copolymer/silica mesostructured thin films activated by *in-situ* synthesized highly luminescent 1,10-phenanthroline (phen) RE complexes. Local separation of organic/inorganic regions in mesostructured silica composites provides substantial versatility for adjusting host/guest optical properties. The hydrophobic regions are compatible environments for organic dopants, enhancing their overall solubilities and preventing their aggregation. In addition, the rigid inorganic framework protects and stabilizes the included species.[7] Furthermore, block-copolymer/silica precursor solutions can be processed into films,[8,9] fibers,[10] and micron-scaled structures[11] with excellent mechanical and optical properties.

A typical sample was prepared by dissolving 1.37 g Pluronic P123 surfactant [poly(ethylene oxide)$_{20}$–poly(propylene oxide)$_{70}$–poly(ethylene oxide)$_{20}$, BASF] and the appropriate amounts of RE–chlorides–hexahydrates and 1,10-phenanthroline (molar ratio RE : phen of 1 : 3) in 15 g EtOH. Separately, 5.2 g tetraethylorthosilicate (TEOS, Aldrich) was hydrolyzed with 1.8 g H_2O/HCl (pH ~ 2). The two solutions were mixed together and further stirred for 15 min. From this mixture with a final molar composition of TEOS : P123 : H_2O : HCl : EtOH : RE–phen = $1 : 9.4 \times 10^{-3} : 4 : 9.0 \times 10^{-4} : 13 : 3.4 \times 10^{-3}$–$1.0 \times 10^{-2}$, thin films were prepared by dip-coating onto cleaned glass slides at 10 cm min^{-1}. The films were stored at room temperature for at least four days to allow for drying and evaporation of HCl prior to all measurements. The final concentrations of the RE–phen complex in the films was between 2 and 6 wt%.[12]

Mesostructural characterization of the films was performed on calcined samples[13] by both X-ray diffraction (Scintag X2 powder diffractometer with Cu-Kα radiation) and TEM measurements. The XRD pattern shows two peaks at 2θ 1.59 and 3.22° , which can be indexed as the 100 and 200 reflections of a 2D hexagonal structure, more precisely, of hexagonally arranged channels parallel to the substrate plane.[9] This structure is also in agreement with TEM investigations using a JOEL 2000FX electron microscope operating at 200 kV. A typical TEM result is presented in Fig. 1 and confirms the suggested *p6mm* symmetry.

Photoluminescence (PL) emission spectra were recorded using the 351 nm output of a cw-Argon ion laser as the excitation source. The emission was dispersed by a monochromator (150 grooves mm^{-1}) and detected by a liquid-nitrogen-cooled CCD camera. Fig. 2A and B present the PL emission spectra of mesostructured P123/silica thin films doped with 2 wt% Tb^{3+}–phen and Eu^{3+}–phen complexes, respectively. Both spectra show the characteristic narrow bandwidth intra-f-shell rare-earth crystal field transitions. The Tb^{3+}–phen emission spectrum (Fig. 2A) exhibits four main transitions between the Russell–Saunders multiplets $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3). The most intense peak centered at 542 nm is assigned to the $^5D_4 \rightarrow {}^7F_5$ transition and is responsible for the pure green emission color. The five emission peaks in the Eu^{3+}–phen spectrum (Fig. 2B) arise from transitions between $^5D_0 \rightarrow {}^7F_J$ crystal field components (J = 0, 1, 2, 3, 4). The typical red color of the europium emission is mostly attributed to the strongest transition ($^5D_0 \rightarrow {}^7F_2$), with its maximum intensity at 614 nm in our samples. The fine splitting of the $^5D_4 \rightarrow {}^7F_5$ terbium peak and especially of the $^5D_0 \rightarrow {}^7F_2$ europium peak into distinct crystal field components points to an ordered 'crystalline' rare-earth ion environment, rather than an amorphous one and indicates that in fact a RE–phen complex is formed *in-situ* during synthesis of the composite films.

Excitation spectra of the emission at 542 nm (Tb^{3+}) and 614 nm (Eu^{3+}) were recorded on a Cary Eclipse spectrophotometer and are presented as insets in Fig. 2A and B, respectively. Both

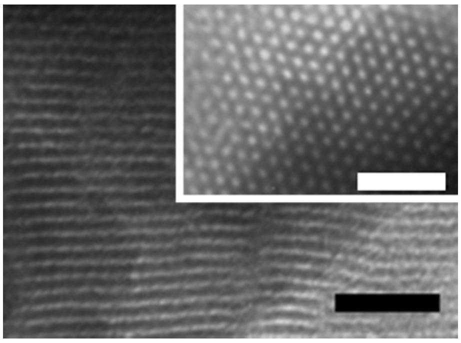

Fig. 1 TEM images of calcined mesostructured silica thin films recorded along the [110] and [100] (inset) zone axes. Both scale bars are 50 nm.

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† Electronic supplementary information (ESI) available: Experimental section; Fig. S1: PL emission spectrum of a Eu^{3+}–phen doped (2 wt%) Pluronic P123 film after excitation at 351 nm. See http://www.rsc.org/suppdata/cc/b2/b206433b/

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spectra look almost identical and exhibit a broad excitation band between 330 and 250 nm, which can be assigned to absorption of the phen ligands and indicates that the green and red emission arise from non-radiative energy transfer of the triplet state of the phen ligands to the central Tb^{3+} and Eu^{3+} ions, respectively.[2]

To determine the efficiency of the energy transfer, the PL quantum yield was measured using an integrating-sphere technique similar to that described elsewhere.[14] The results obtained for RE–phen complex concentrations ranging from 2 to 6 wt% are between 17 and 25% for terbium and between 22 and 24% in the case of europium. It is worth mentioning that the PL quantum yields of our *in-situ* formed complexes are as high as that reported for europium–phen complexes synthesized beforehand and doped in a second step into various sol–gel SiO_2 composite materials.[6]

To investigate the influence(s) of the organic components in mesostructured P123/silica films on the formation of the RE–phen complexes, pure silica sol–gel glass films were prepared, and the emission properties of the rare earth complexes incorporated into the two different host matrices were compared. The *in-situ* doped silica glass films were synthesized in exactly the same manner as described for the mesostructured films with the exception that no P123 surfactant was added. Illumination of mesostructured and glass films—both doped with the same concentration of RE–phen complex[12]—with a UV-lamp results in much more intense luminescence in the case of the mesostructured host material. Furthermore, a striking difference can be observed in the luminescence color purity. While the RE–phen complexes doped into mesostructured films emit deep green (Tb^{3+}) and red (Eu^{3+}) light, the color of the emitted light from the glass films becomes impure and changes to turquoise (Tb^{3+}) and violet (Eu^{3+}). This observation is also in agreement with the PL emission spectra (excitation at 351 nm) of a Eu^{3+}–phen complex (6 wt%) incorporated in the two host matrices, as shown in Fig. 3. In mesostructured P123/silica only the Eu^{3+} emission lines at around 615 nm are observable, whereas in the pure sol–gel silica glass, in addition to these narrow transitions, a broad emission band in the blue—between 400 and 500 nm—is present. This emission band is assigned to free phen molecules and clusters, which are not able to transfer the absorbed energy to the central RE ion, but relax radiatively from their triplet state to their ground state.[15] The phen molecule clustering in the pure silica glass films can be attributed to a poor solubility of the organic phen molecules in the pure inorganic silica matrix. This results in insufficient RE–phen complex formation during dip-coating of the films accompanied by evaporation of the organic solvent—in contrast to the mesostructured composite films, where the P123 surfactant nano-domains provide a more hydrophobic environment for the phen molecules, thus enhancing their solubility and facilitating formation of the RE–phen complexes (see also Electronic Supplementary Information—ESI†).

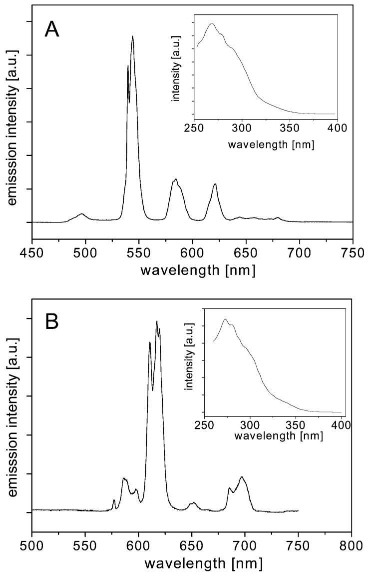

Fig. 2 PL emission and excitation (insets) spectra of Tb^{3+}–phen (A) and Eu^{3+}–phen (B) doped mesostructured films (both 2 wt%).

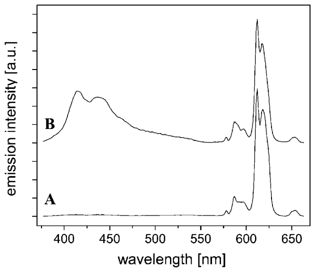

Fig. 3 PL emission spectra of 6 wt% Eu^{3+}–phen complex doped into (A) mesostructured P123/silica and (B) pure silica glass thin films. The emission intensities of the two spectra are normalized with respect to the Eu^{3+} crystal field transition $^5D_0\rightarrow{}^7F_2$ at 615 nm.

Concluding, we have shown that mesostructured composite thin films are excellent host matrices for the incorporation of *in-situ* synthesized organic/rare-earth-ion complexes. The high solubility of the ligands within the hydrophobic triblock-copolymer regions of the P123/silica composite facilitates the formation of the RE–phen complexes, even at high concentrations and prevents aggregation of free phen molecules. This results in a simple one-step synthesis approach to processible materials that exhibit efficient narrow bandwidth emission of green and red light with high spectral purity.

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Notes and references

1 R. G. Denning, *J. Mater. Chem.*, 2001, **11**, 19; J. Ballato and J. S. Lewis and P. Holloway, *MRS Bull.*, 1999, **24**, 51.

2 G. A. Crosby, R. E. Whan and R. M. Alire, *J. Chem. Phys.*, 1961, **34**, 743; W. R. Dawson, J. L. Kropp and M. W. Windsor, *J. Chem. Phys.*, 1966, **45**, 2410; S. Sato and M. Wada, *Bull. Chem. Soc, Jpn.*, 1970, **43**, 1955.

3 K. L. Frindell, M. H. Bartl, A. Popitsch and G. D. Stucky, *Angew. Chem., Int. Ed.*, 2002, **41**, 959.

4 R. Hernandez, A. C. Franville, P. Minoofar, B. Dunn and J. I. Zink, *J. Am. Chem. Soc.*, 2001, **123**, 1248; H. J. Zhang, L. S. Fu, S. B. Wang, Q. G. Meng, K. Y. Yang and J. Z. Ni, *Mater. Lett.*, 1999, **38**, 260.

5 B. Yan, H. Zhang, S. Wang and J. Ni, *Mater. Res. Bull.*, 1998, **33**, 1517; T. Jin, S. Inoue, S. Tsutsumi, K. Machida and G. Y. Adachi, *J. Non-Cryst. Solids*, 1998, **223**, 123.

6 H. H. Li, D. Ueda, S. Inoue, K. Machida and G. Adachi, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 161.

7 B. J. Scott, G. Wirnsberger and G. D. Stucky, *Chem. Mater.*, 2001, **13**, 3140.

8 Y. F. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. L. Gong, Y. X. Guo, H. Soyez, B. Dunn, M. H. Huang and J. I. Zink, *Nature*, 1997, **389**, 364.

9 D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka and G. D. Stucky, *Adv. Mater.*, 1998, **10**, 1380.

10 F. Marlow, M. D. McGehee, D. Y. Zhao, B. F. Chmelka and G. D. Stucky, *Adv. Mater.*, 1999, **11**, 632.

11 P. D. Yang, G. Wirnsberger, H. C. Huang, S. R. Cordero, M. D. McGehee, B. Scott, T. Deng, G. M. Whitesides, B. F. Chmelka, S. K. Buratto and G. D. Stucky, *Science*, 2000, **287**, 465; H. Y. Fan, Y. F. Lu, A. Stump, S. T. Reed, T. Baer, R. Schunk, V. Perez-Luna, G. P. Lopez and C. J. Brinker, *Nature*, 2000, **405**, 56.

12 The RE–phen concentration in wt% was calculated with respect to the amount of P123 and SiO_2 (mesostructured films) and SiO_2 only (glass films) and assuming full transformation of TEOS to SiO_2.

13 The films were calcined to avoid degradation of the organic components during TEM investigations.

14 N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. Kessiner, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1995, **241**, 89.

15 Excitation at 351 nm of an ethanol solution (1 M) of uncomplexed 1,10-phenanthroline molecules results in blue luminescence.