Study on high-efficiency fluorescent microcapsules doped with europium β-diketone complex by LbL self-assembly†

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Rare-earth β-diketone complex doped microcapsules with high efficiency fluorescence fabricated by the LbL technique based on electrostatic and charge–dipole interactions are reported.

Rare-earth compounds have unusual spectroscopic characteristics, including sharp emission peaks with small peak width at half-height, and long millisecond lifetimes.[1] Among them, the luminescent rare-earth β-diketone complexes with intense light emission have been used as laser materials, in display screens and as probes in fluorescence immunoassays.[1a,2] Their high fluorescence quantum yield is due to the high absorbance coefficient of the ligand and efficient intramolecular energy transfer to the Eu^{III} ions.[3] It is essential to fabricate this type of fluorescent compounds in highly ordered 2D and 3D materials by techniques at the molecular scale. Layer-by-layer (LbL) self-assembly is a technique meeting such requirements.[4] Both planar films containing lanthanum phosphate nanoparticles[5] or [DNA/Eu]$_n$[1b] and microcapsules containing inorganic rare-earth compounds have been fabricated by LbL assembly.[6–8] As a result, scientifically and practically, it is fundamental to incorporate rare-earth β-diketone complexes into microcapsules by LbL and study their fluorescence properties, as well as the morphology of microcapsules for potential applications.

In this work, we propose a method for the LbL self-assembly of microcapsules containing a europium β-diketone complex (EuC) by stepwise deposition of poly(sodium 4-styrenesulfonate) (PSS), poly(allylamine hydrochloride) (PAH) and the Eu^{III} complex (EuC) on a colloidal template. The obtained microcapsules emit intense fluorescence, even though there is only one layer of Eu(DBM)$_3$(Phen) (EuC) doped in the microcapsules (Phen and HDBM are 1,10-phenanthroline and the β-diketone, dibenzoylmethane, respectively). The luminescence can be directly observed visually under ultraviolet irradiation. In addition, the EuC layer was assembled homogeneously in microcapsules by the LbL technique owing to charge–dipole and van der Waals interaction.

The preparation of the fluorescent microcapsules is illustrated in Fig. 1 with melamine formaldehyde (MF) particles as the core, and EuC as the fluorescence molecules.

The EuC doped microcapsules we fabricated have good emission efficiency. A typical fluorescence micrograph is illustrated in Fig. 2(a), confirming the successful deposition of EuC in the microcapsules. Careful investigation of the micrograph demonstrates that the fluorescent spheres appear as rings. The microcapsule shell is brighter than the core interior. A cross section profile of fluorescence intensity along the microcapsule diameter is shown in Fig. 2(b), where two side peaks confirm that EuC is self-assembled on the microcapsule shell. The hollow EuC doped microcapsules after dissolution of the MF core also appear as bright fluorescent rings under fluorescence microscopy. No obvious difference exists between the luminescence of the hollow and the intact-core microcapsules, which provides potential applications in display materials and fluorescence reagents for the hollow microcapsules.

To get surface information of EuC doped microcapsules, the morphology of dried hollow microcapsules was studied by atomic force microscopy (AFM) in tapping mode. In Fig. 3(a), a typical AFM height image of a microcapsule consisting of [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] is shown. All AFM images indicate that the three-dimensional [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] shells are continuous films. The EuC doped films exhibit many folds, which are due to the evaporation of the solvent molecules.[9] The EuC-containing hollow microcapsules are not rigid and they do not appear as air-filled round spheres. The average height of the dried

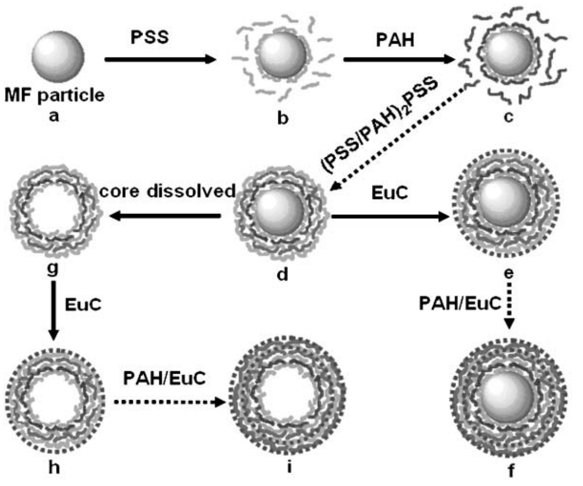

Fig. 1 Illustration of the LbL assembly of PSS, PAH and EuC on MF particles and hollow microcapsules. The first stage (a–d) involves stepwise deposition of polyelectrolytes on MF colloidal particles. (e) EuC layer assembly. (f) On further assembling PAH/EuC layers, fluorescent [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] microcapsules on MF are obtained. (g) Template dissolution. (h) The pH of the (PSS/PAH)$_3$PSS microcapsule suspension is adjusted to neutral and EuC layer is assembled in the shell. (i) Finally, hollow microcapsules of [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] are obtained.

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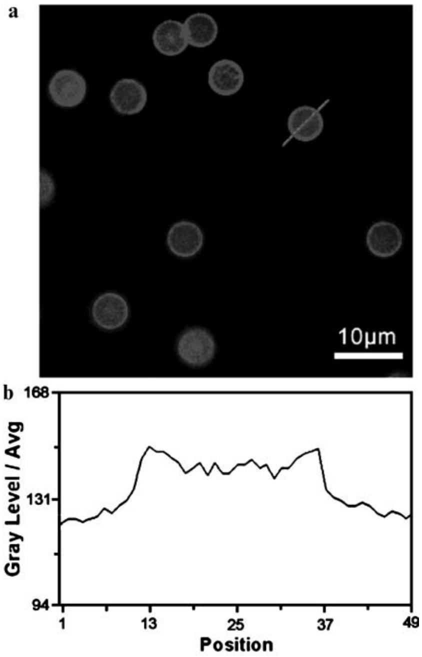

Fig. 2 (a) Fluorescence micrograph of [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] microcapsules self-assembled on MF dispersed in water. (b) The fluorescence intensity profile along the line drawn in the fluorescence micrograph.

hollow microcapsule at the thinnest parts is about 32 nm, corresponding to two superimposed microcapsule shells, because the microcapsules are continuous spherical films. So the average thickness of either every polyelectrolyte layer or every EuC layer is about 1.6 nm. This is in good agreement with the single layer thickness of 1.5 nm obtained by others with single particle light scattering measurements performed in solution.[10] This essential observation shows that EuC has little influence on the thickness of the microcapsule shell and EuC is very homogeneously assembled in the microcapsules. Analysis of a fold-free area further reveals that [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] microcapsules have a small roughness of 2.9 nm, also similar to the value obtained for PSS/PAH microcapsules.[11]

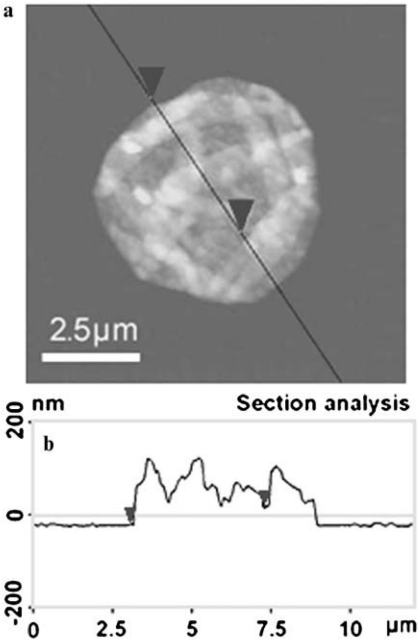

Fig. 3 (a) AFM height image of hollow [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] microcapsules. (b) The height profile along the line drawn on the microcapsule in (a).

It is essential to note why the height and the roughness of fluorescence microcapsule are nearly the same as those of the pure PSS/PAH microcapsules without EuC, although the rare-earth complexes are so easy to crystallize.[1d] A reasonable explanation is the existence of EuC clusters as ultrafine nanoparticles in microcapsules. Otherwise, if EuC formed microcrystals, the morphology and roughness would be on the scale of micrometers. In other words, the LbL technique aids the homogeneous distribution of EuC in the shell of the microcapsules, even after the removal of the core template. As a result, very homogeneous intense fluorescence is visibly observed although only one layer of EuC is assembled in the microcapsules. Consequently, the LbL technique not only can assemble luminescent β-diketone rare-earth complexes in three-dimensional microcapsules, but also can improve the distribution of these rare-earth complexes.

The morphology of the bare MF core and the [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] microcapsules on MF was also examined for comparison by scanning electron microscopy (SEM). The microcapsule has a rougher surface than the MF core, due to the coverage of polyelectrolyte and the EuC. There are a few protruding and concave parts on the formed microcapsules (Fig. S1, ESI†).

TEM measurement for the microcapsules was carried out, which confirms that the luminescent hollow microcapsules without MF core is intact (Fig. S2, ESI†)

Since the EuC has been doped in microcapsules homogeneously and the microcapsules can emit intense red light, it is essential to investigate their detailed fluorescence spectra. Fig. 4 shows the emission spectrum of EuC doped microcapsules and that of Eu(DBM)$_3$(Phen) in ethanol. The emission spectra of the microcapsules show intense fluorescence peaks, further indicating that EuC is successfully assembled in the microcapsules. The

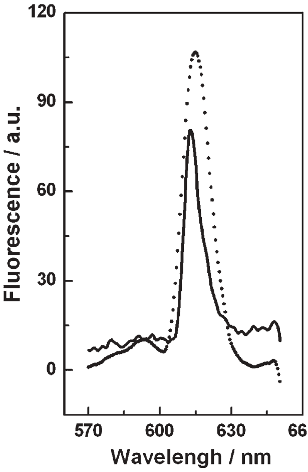

Fig. 4 Fluorescence emission spectra of [(PSS/PAH)$_3$/PSS/EuC/PAH/EuC] microcapsules self-assembled on MF (solid line) and EuC ethanol solution (dotted line): $\lambda_{\text{excitation}}$ = 350 nm.

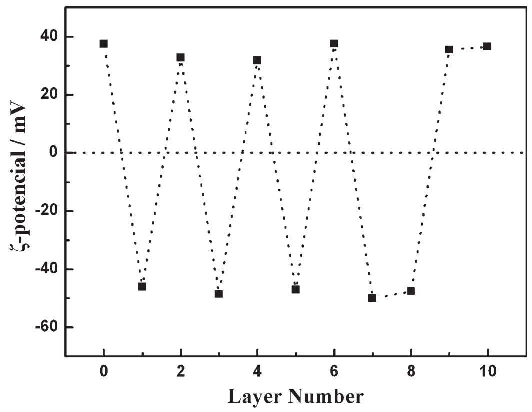

Fig. 5 ζ-Potential *vs.* layer number for the LbL self-assembly of PSS, PAH and EuC on MF. The layer numbers 1, 3, 5 and 7 correspond to PSS assembly and layer numbers 2, 4 and 6 correspond to PAH adsorption. Layer numbers 8 and 10 correspond to EuC assembly. Layer number 9 corresponds to PAH assembly. Layer number of zero corresponds to the MF particles.

microcapsules have the same luminescence wavelengths as the corresponding EuC in solution. Although the peak at 595 nm is not very sharp, this could be due to the scattering effect from the MF core. The main peak at 612 nm corresponds to the energy transition of Eu^{III} from the excited state $^5D_0$ to the ground state $^7F_2$, which is demonstrated in the energy level diagram of EuC (Fig. S3, ESI†). Firstly, the β-diketone ligand, DBM, is excited by ultraviolet light. Energy transition occurs from the singlet ground state (S_0) to the excited state (S_1). After intersystem crossing, energy transfers to the triplet state (T_1). Intramolecular energy transfer from the DBM to Eu^{III} ions then takes place. Radiative transition from the excited state, $^5D_0$, to the low level states, $^7F_2$, induces the intense fluorescence emission.

As an effective means to characterize elemental composition, energy dispersive X-ray spectroscopy (EDS) is employed for the EuC doped microcapsules. The results show that about 15 wt% of Eu is in the microcapsules, although the possibility of EuC being adsorbed on the surface instead of being incorporated into the shell can not be ruled out in this work. This value was obtained by analyzing a selected area in a square region of each microcapsule (Fig. S4, ESI†).

The removal process of the MF core was also monitored by optical microscopy. The optical micrographs show that the EuC doped microcapsules are monodisperse and that the hollow microcapsules are stable after the core dissolved (Fig. S5, ESI†).

For the LbL self-assembly technique, electrostatic force is generally the main interaction in the shell, where the polyelectrolyte molecules carry the negative (PSS) and positive (PAH) charges. Since EuC carrying no charges is assembled homogeneously in the shell, it is necessary to confirm that it has nearly no influence on the surface electrostatic properties of different polyelectrolyte layers. The ζ-potential of the microcapsules during the self-assembly was monitored as shown in Fig. 5. The statistical average data with the ζ-potential absolute value in the range of 35–50 mV against layers strongly suggest the sequential adsorption of PSS, PAH and EuC on the template MF particles. In the previous eight steps, the ζ-potential of the microcapsules is reversed due to the alternative adsorption of polyelectrolyte layers carrying positive or negative charges. However, the ζ-potential value of microcapsules changes little after the EuC assembly. This demonstrates that EuC has negligible influence on the surface charges of the previously deposited polyelectrolyte layers. As a result, EuC can be incorporated by successive assembly after polyelectrolyte layers.

Different to the polyelectrolytes in the microcapsules, EuC does not carry any charge. Since EuC has been excellently assembled in microcapsules, the intermolecular interaction[12] between the previously assembled PAH or PSS layer and the EuC layer should be noted. Calculation by the MM2 program shows that EuC has a dipole moment about 4 D. Thus the charge–dipole interaction plays a role during alternatively assembling polyelectrolytes carrying charges and EuC having a dipole moment, besides van der Waals interaction, responsible for the LbL assembly.

In conclusion, high quality $[(PSS/PAH)_3/PSS/EuC/PAH/EuC]$ microcapsules with MF core and hollow microcapsules without MF are assembled using the LbL technique utilising charge–dipole and van der Waals interactions.

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