Improved Thermal Stability of Europium Complex Nanoclusters Embedded in Silica Colloidal Spheres

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(Received December 16, 2004; CL-041543)

Europium complex nanoclusters are introduced into monodisperse colloidal silica spheres by a modified Stöber method. Transmission electron microscopy measurements confirm that the hybrid spheres possess smooth surface and core-shell structure. The hybrid spheres display strong characteristic luminescence of the Eu^{3+} ions. Furthermore they exhibit an improved thermal stability compared with the pure rare earth (RE) complex.

In recent years, the synthesis of inorganic–organic hybrid materials has attracted considerable attention for their chemical and optical properties that can be specifically tailored by mixing inhomogeneous compositions at the nanometer scale.[1,2] The hybrid materials possess advanced properties that depend on both the organic and inorganic components, such as modified thermal and mechanical stability,[3,4] high optical nonlinearity,[5] enhanced luminescent intensity[6,7] and so on. The RE complexes with desired luminescent properties have been intensively studied for the potential applications in new technologies, such as luminescence device[8,9] and luminescence sensors.[10] However, the pure RE complexes show low thermodynamic stability, which is a critical shortcoming to their applications. Therefore, it is necessary to search for a suitable coating material to enhance their thermodynamic stability. Silica is an ideal, low-cost inorganic matrix for its high stability, optical transparency, chemical inertness, and processability.[11] In addition, the deposition process of the silica colloids can be controlled and the colloids can form different shapes under well-adjusted conditions. Especially, they can be easily made as spherical morphology with truly monodisperse sizes and in copious quantities by the typical base-catalyzed reaction. In this letter, we attempt to use modified Stöber method to introduce RE complexes into colloidal silica spheres in order to enhance the thermal stability of RE complexes. The obtained optically active hybrid spheres provide bright red emission with colorimetric purity and improved stability. They are promising materials for stable luminescence display devices. Furthermore, these hybrid spheres with monodispersion can be used as building blocks for photonic crystals and the RE complex inside the colloids can be used as optical probes to study the effect of photonic band structure on the spontaneous emission.

The preparation route for fabricating the silica spheres embedded with Eu complex nanoclusters is as follows. Europium tris(dibenzoylmethanato)phenanthoroline [$Eu(DBM)_3phen$] complex was prepared by the method reported in the literature.[12] The purified RE complex was completely dissolved into acetone (Aldrich) to form 1 M solution. Then the solution was poured into ethanol bath under well stirring. According to the Stöber method,[13] the $NH_3{\cdot}H_2O$ (Aldrich, 28% NH_3), the tetraethoxysilane (TEOS, Aldrich) and distilled water were added under continuous stirring for an hour. The products were rinsed thoroughly with ethanol and acetone, dried in air at 80 °C. The final concentration of RE complex is about 0.05 M in the colloidal silica spheres. The general morphology of the samples was characterized by a scanning electron microscope (SEM, KYKY 1000B) and the detailed structure analysis of spherical particles was carried out by a transmission electron microscope (TEM, JEOL 2010). The specimens for TEM investigations were placed on holey copper grids with carbon film. Infrared absorption spectra were measured by a Bio-Rad Fourier transform infrared (FTIR) spectrometer. To obtain luminescence spectra, the samples were excited with a third harmonic of a Nd:YAG pulsed laser at 355 nm. All the experiments were performed at room temperature.

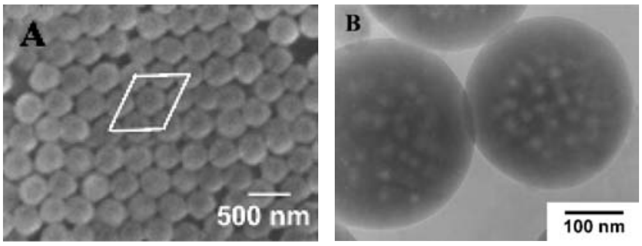

Figure 1. (A) SEM image of $Eu(DBM)_3phen$/silica hybrid spheres. (B) Magnified TEM image of an individual hybrid sphere.

A typical SEM image is shown in Figure 1A. The diameters of the hybrid spheres in the sample are considerably uniform. The size polydispersity was estimated to be 3% by analyzing 100 particles. The monodispersed spherical colloids have a tendency to organize themselves into a packed structure, as indicated in the SEM image, which suggests that the hybrid spheres can be used as building blocks to achieve photonic crystal under well-controlled conditions. Figure 1B presents TEM image of an individual sphere. Obvious diffraction contrast can be identified between the central part and the outer shell. The central part consists of many light spots which may originate from the RE complex nanoclusters, while the shell was composed of silica. It should be noted that the introduction of rare earth complex do not change the spherical morphology and the smooth surfaces, although the sphere size deviates a little from the original data described in Ref. 13.

Figure 2 shows IR absorption spectra of pure $Eu(DBM)_3$-phen complex, and the hybrid colloidal particles with the diameter about 300 nm. The IR spectrum of $Eu(DBM)_3phen$ complex presents a large complexity of peaks. The peak around $3050\,cm^{-1}$ is attributed to CH=CH stretching vibrational mode ($\nu_{=CH}$) corresponding to phenyl units of the complex. The typical absorption bands in the region from 1600 to $1400\,cm^{-1}$ are

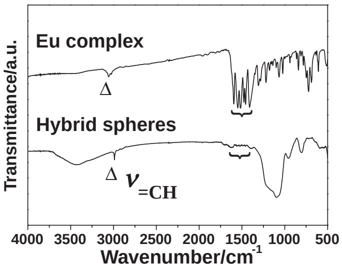

Figure 2. Infrared absorption spectra of the europium complex and the hybrid spheres.

based on C=O, C=C, and C=N stretching modes corresponding to the β-diketonate and phenanthroline ligands. In regard to the set of spherical hybrids, the intensities of the characteristic bands of the organic ligands were much weaker than that of the strong absorption peak at 1098 cm^{-1}, which is attributed to Si–O asymmetrical stretching vibration (ν_{Si-O}). Compared with the pure europium complex, the CH=CH stretching vibrational mode in the hybrids shifts to around 2990 cm^{-1}. It indicates that there exist some interaction between the Eu complex and the silica shell. In addition, the weak absorption peaks in the region from 1600 to 1400 cm^{-1} are compatible with the C=O, C=C, and C=N stretching modes. The presence of characteristic bands of the Eu(DBM)$_3$phen complex suggests that the Eu complex is incorporated into the silica spheres.

Figure 3 shows the emission spectra of the pure Eu complex and the hybrid spheres under the 355-nm excitation that corresponds to the absorption of the β-diketonnato ligands. They both present strong characteristic emissions of Eu^{3+} ions. The peak at 610 nm is due to the forced electric dipole transition ($^5D_0 \rightarrow {}^7F_2$), which is allowed on condition that the europium ion occupies a site without inverse center. Its intensity is hypersensitive to crystal environments. The peak around 580 nm corresponds to the $^5D_0 \rightarrow {}^7F_0$ transition, and those near 590 nm derive from the allowed magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$). Compared with the emission spectrum of the europium complex, the peak near 618 nm, corresponding to $^5D_0 \rightarrow {}^7F_2$ transition, becomes weak, which means that the silica host may modify the local environment of some Eu^{3+} ions.[14] The concentration of the Eu complex in the hybrid spheres is about 0.05 M. However, the luminescent intensity of the hybrid spheres can reach 80% of that of the pure Eu complex powder under the same measurement conditions. It indicates that the coating of silica has no marked decrease of the luminescent intensity.

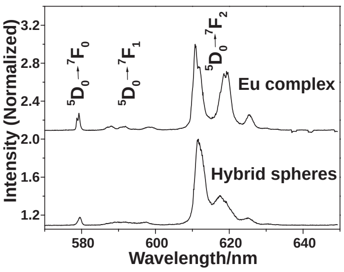

Figure 3. Emission spectra of the europium complex and the hybrid spheres.

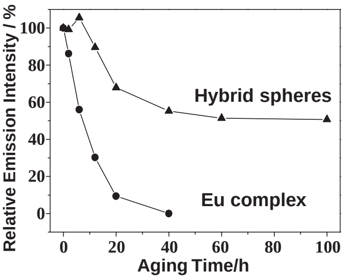

Figure 4. Relative emission intensities as a function of the aging time for the europium complex and the hybrid spheres.

Figure 4 presents the dependence of luminescence intensity on thermal treatment for both pure Eu complexes and hybrid spheres. The samples were heated continuously in an oven at 180 °C. The data for the as-aged samples were normalized to those without thermal treatment. As can be seen, the relative luminescence intensity of the europium complex decreases rapidly with increasing the aging time and the luminescence is completely quenched after 40 h because of the thermal decomposition of the RE complex. In contrast, the hybrid spheres exhibit an improved thermal stability. The increase at the early stage may be due to the removal of OH group, which was introduced during the material preparation and could induce the luminescence quenching by multiphonon relaxations. Subsequently, the luminescent intensity shows a slow decrease with time until it is unchanged after 60 h. The luminescence intensity of hybrid spheres can be enhanced via a proper thermal annealing.

In conclusion, the Eu complexes were successfully embedded in silicate spheres by a modified Stöber method, thereby exhibiting an improved thermal stability.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 10274082 and 10474096).

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Published on the web (Advance View) February 12, 2005; DOI 10.1246/cl.2005.366