Self-assembly of 3D Ordered $Eu(DBM)_3Phen/SiO_2$ Colloidal Spheres via Sedimentation

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Abstract 300 nm $Eu(DBM)_3Phen/SiO_2$ colloidal hybrid spheres were synthesized by modified Stöber method. The silica spheres were self-assembled into 3D ordered crystal structure with 5 mm thick and over relative large areas (12 cm^2) via sedimentation. The scanning electron microscopy (SEM) images indicate that the cubic-close-packed structure extends almost all of the layers along the direction perpendicular to the surface of the bottom of the beaker and the close-packed order extends throughout the colloidal crystal. Furthermore, elemental analysis of silica spheres by EDAX establishes that the fluorescent molecules contained in the SiO_2 colloidal spheres. Under 355 nm continuous excitation, the ordered structure exhibits characteristic emission of trivalent europium ions.

Key words: $Eu(DBM)_3Phen/SiO_2$; self-assembly; sedimentation; 3D ordered structure

CLC number: O482.31 **PACC**: 3250F; 7855 **Document code**: A

1 Introduction

In recent years, much attention has been paid to silica-coated colloidal particles due to their capability of forming regular three-dimensional (3D) ordered structure which is useful in many areas. For example, as diffractive elements in the fabrication of photonic crystals[1~4]. Photonic crystals are highly ordered materials that have a spatially periodic dielectric constant with a lattice parameter comparable to the wavelength of the electromagnetic wave. Periodicity affects the propagation of electromagnetic waves in the material due to Bragg reflections on lattice planes. The resulting photonic band gap (PBG or stop band) may exhibit a frequency band in which the propagation of electromagnetic wave is forbidden, irrespective of their directions of propagation in reciprocal space.

Luminescence of lanthanide ions has several special properties, such as very long decay time, large Stokes shift and sharp emission profile, which make them widely used in the fields of luminescence device, luminescence sensor, and luminescence biological labeling[5~9]. However, the problem of color purity sometimes affects their further expansion in practical applications. An alternative route is coating lanthanide materials with silica and then forming regular three-dimensional (3D) photonic crystals. Such a photonic crystal can be used to localize luminescence from rare-earth (RE) ions to specific areas, to inhibit some spontaneous emission of RE ions, and to guide propagation of emission wavelengths of RE ions along certain directions at restricted frequencies. On the other hand, the spontaneous emis-

Received date: 2007-02-09; **Revised date**: 2007-11-15

Foundation item: The project supported by National Science Foundation of China (10474096, 50672030, 10774142)

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sion of lanthanide ions can be modified by the photonic crystals with a bandgap. Therefore, in this report, we used sedimentation, a simple, inexpensive and effective method, to self-assembly $Eu(DBM)_3Phen/SiO_2$ into 3D ordered crystal structure. This crystal presents a close-packed lattice assembled from 300 nm silica-coated europium complex. This crystalline assembly exhibits a relative large area ordered structure through SEM observation and presents characteristic emission of Eu^{3+} ions.

2 Experiments

The 3D ordered $Eu(DBM)_3Phen/SiO_2$ colloidal spheres were prepared through three steps. Firstly, the Eu tris (dibenzoylmethanato) phenanthroline [$Eu(DBM)_3Phen$] complex was prepared as follows: 3 mmol DBM, 1 mmol 1, 10-phenanthroline and 1 mmol $EuCl_3$ were dissolved in 40 mL ethanol under stirring. The sodium ethylate was added dropwise until the pH of the reaction mixuture reached 6~ 7. The solution was stirred for 3~ 4 h at constant temperature to get the stable and water free octacoordinated form. The precipitate was washed with acetone and absolute ethanol, recrystallized with acetone. Secondly, the silica colloid is formed by the Stöber method[10]. The 100 mg purified complex was dissolved into 5 mL acetone. After completely dissolving, the mixture was poured into 100 mL ethanol bath containing $NH_3 \cdot H_2O$ (25%) and distilled water under well stirring for more then 1 h. Then 0. 03 mol tetraethoxysilane (TEOS) solution was added dropwise to the solution. After continuously stirring for 3 h, the samples were rinsed thoroughly with ethanol and acetone, dried in air. The white particles were acquired. At last, the as-prepared product was dispersed into 20 mL water and then transfered into a 25 mL clean beaker. The beaker was covered by a 1 000 mL beaker to keep out external airflow and contamination. The entire apparatus is placed on a vibration-free table until water in the colloidal suspensions evaporated to leave well-ordered $Eu(DBM)_3Phen/SiO_2$ colloidal spheres at room temperature.

The colloidal spheres were characterized by using scanning electron microscopy (XL 30 ESEM FEG, FEI Company). The sample used for SEM was prepared by moving it out of the beaker and placing on the silica slides. Room-temperature emission spectra under 355 nm excitation were performed with a Hitachi F-4500 fluorescence spectrometer.

3 Results and Discussion

Lanthanide chelates with π-conjugated ligands such as β-diketonnato are a kind of materials with excellent luminescent properties. The RE ions surrounded by the ligands are excited via intramolecular energy transfer from the triplet excited stated of the ligands, which leads to a high inner quantum efficiency. DBM and Phen and their derivatives are generally used for lanthanide complexes that are commercially available. Fig. 1(a) and Fig. 1(b) give the molecular structure and energy transfer process of $Eu(DBM)_3Phen$ prepared in the experiment. The Fig. 1(c) presents the absorption spectrum of $Eu(DBM)_3Phen$ chelate in acetone solution. The 355 nm absorption band is attributed to the absorption of dibenzoylmethane.

The $Eu(DBM)_3Phen/SiO_2$ colloidal crystals directly deposited on bottom of the beaker. Fig. 2 shows SEM micrographs of $Eu(DBM)_3Phen/SiO_2$ colloidal spheres with 5 mm thick and 12 cm^2 areas. Although there are some silica spheres do not present 3D ordered structure, which mainly result from artificial vibration when we taken the sample out from the beaker, the close-packed arrays of $Eu(DBM)_3Phen/SiO_2$ spheres are clearly observed. Fig. 2(a) and 2(b) show a portion of the assembly at high magnification, which indicate the silica spheres size is 300 nm. Fig. 2(a) and 2(c) show the top views of a portion of the crystalline assembly. The silica spheres in the top layer form a closely packed and hexagonal array from the SEM images. As can be seen, the 300 nm silica spheres spontaneously organized into a highly ordered face-centered cubic (fcc) close-packed structure with the (111) plane paralleling to the bottom of the beaker. Fig. 2(b) and 2(d) show cross-sectional SEM images of the assembled structure. These SEM images indicate

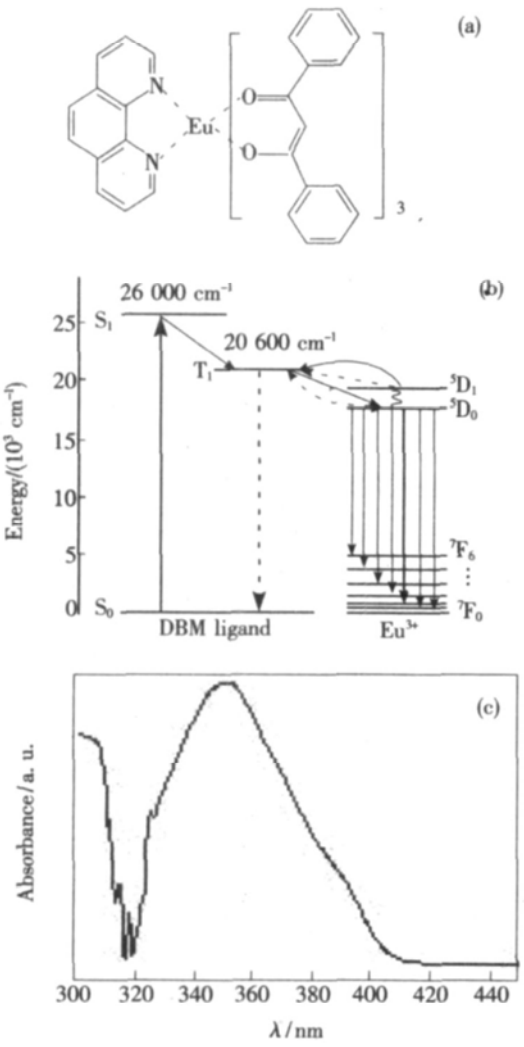

Fig. 1 The molecular structure (a), energy transfer process (b) and absorption spectrum (c) of $Eu(DBM)_3Phen$ chelate in acetone solution.

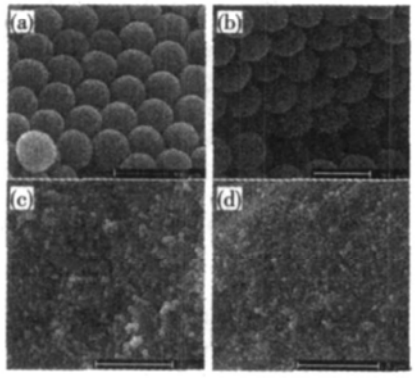

Fig. 2 SEM micrographs of ordered $Eu(DBM)_3Phen/SiO_2$ colloidal crystals. (a) and (c) are the top view of a portion of the crystalline assembly. (b) and (d) are the cross-sectional SEM images of the assembly structure.

that the cubic-close-packed structure extends almost all of the layers along the direction which is perpendicular to the surface of the bottom of the beaker Note that the close-packed order extends throughout the colloidal crystal All these points reflect the high degree of crystalline order achieved in $Eu(DBM)_3Phen/SiO_2$ colloidal crystals Furthermore, elemental analysis of silica spheres by EDAX (Fig 3) establishes that the fluorescent molecules are contained in the SiO_2 colloidal spheres

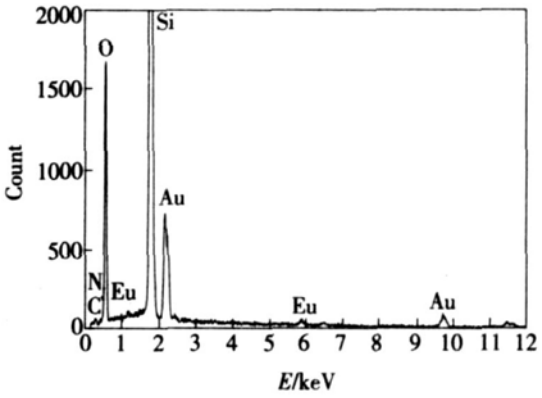

Fig 3 EDAX spectrum of ordered $Eu(DBM)_3Phen/SiO_2$ colloidal crystals

Fig 4 presents the room temperature emission spectra under the 355 nm excitation which corresponds to the absorption of the DBM ligands In the emission spectrum of the ordered structure, the dominating emission at 611 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 and its intensity is hypersensitive to crystal environments The peak near 590 nm corresponds to $^5D_0 \rightarrow {}^7F_1$ transition, which derives from allowed magnetic dipole transition, and the emission around 580 nm origins from the $^5D_0 \rightarrow {}^7F_0$ transition In addition, emission peaks near 616 nm and 623 nm are corresponding to the Stark splitting of $^5D_0 \rightarrow {}^7F_2$ transition

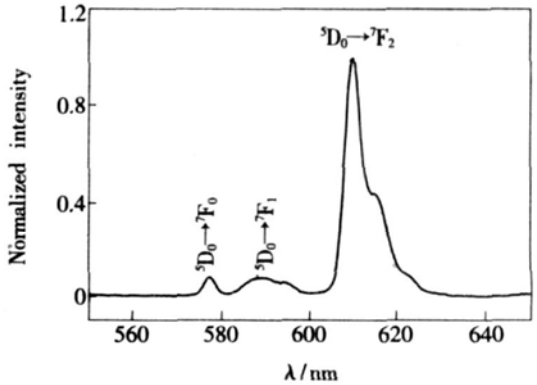

Fig 4 Emission spectra of 3D ordered $Eu(DBM)_3Phen/SiO_2$ colloidal crystals (λ_{ex} = 355 nm).

4 Conclusion

In conclusion, we have prepared 300 nm $Eu(DBM)_3Phen/SiO_2$ colloidal spheres using Stöber method. And then self-assemble the silica spheres into 3D ordered crystal structure with 5 mm thick and 12 cm^2 areas via sedimentation. The sample presents ordered structure, as indicated by scanning electron microscopy images. In addition, EDAX established that the fluorescent molecules were contained in the SiO_2 colloidal spheres. The ordered structure shows characteristic emission of europium ions under 355 nm excitation. In the future work, the attention should be paid to self-assemble different size SiO_2-coated lanthanide materials and TiO_2-coated lanthanide materials into three-dimensionally ordered structure, and subsequently form photonic crystals with a complete bandgap.

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沉积法自组装三维有序的 $Eu(DBM)_3Phen/SiO_2$ 胶体球

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摘要: 采用修饰的 Stöber法合成了 300 nm 的 $Eu(DBM)_3Phen/SiO_2$ 胶体杂化球, 并通过沉积法将这种胶体杂化球组装成厚度为 5 mm, 面积为 12 cm^2 的三维有序结构。通过扫描电子显微镜观察发现这些胶体球在垂直

于烧杯底面的所有层面中都显示了立方密堆积的结构。元素分析进一步证实了荧光分子被包埋在 SiO_2 胶体球中。在 355 nm 的激发下,这种三维有序结构具有铕离子的特征发射。

关 键 词: $Eu(DBM)_3Phen/SiO_2$; 自组装; 沉积法; 三维有序结构
中图分类号: O482.31 **PACC**: 3250F; 7855 文献标识码: A
文章编号: 1000-7032(2008)05-0784-05

收稿日期: 2007-02-09; 修订日期: 2007-11-15
基金项目: 国家自然科学基金资助项目(10474096, 50672030, 10774142)
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