

Synthesis of Well Dispersed Uniform Sub-4 nm $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ Colloidal Nanocrystals

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Well dispersed uniform sub-4 nm $\text{Y}_2\text{O}_3:\text{Eu}$ colloidal nanocrystals have been synthesized through the non-hydrolytic high-temperature thermal decomposition technique. The as-synthesized nanocrystals can be stably dispersed in nonpolar solvents due to the capping organic ligands on their surface. Compared with bulk materials, the nanocrystals exhibited different luminescence features, including the intensity enhancement of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition observed in the emission spectrum.

Keywords: Sub-4 nm Nanocrystals, Rare Earth, High-Temperature Thermal Decomposition, Photoluminescence.

1. INTRODUCTION

At nanoscale, the size of materials strongly influences the fundamental properties, such as electrical, optical, magnetic, chemical, catalytic and melting properties.¹⁻³ Size-dependent properties are the reason that nanoscale materials have the potential to significantly impact both science and industry. Precise control of the size can manipulate the properties of the nanocrystals as desired.⁴ Recently, synthesis of uniform colloidal inorganic nanocrystals with small size, especially sub-5 nm, has gained great fundamental and industrial interest due to their alterable surface properties and their applications as building blocks for organized complex nanostructures.^{5,6} When the size of the colloidal nanocrystal is controlled to be smaller than 5 nm, the colloidal stability is much improved due to the enhancement of ligand density, and the chemical and physical properties are modified because of the increased surface atoms.

$\text{Y}_2\text{O}_3:\text{Eu}$ is widely used as a red phosphor in the display field and in biological imaging for its efficient emission.^{7,8} In these applications, such as high-resolution displays and luminescence probes, the small size and colloidal stability of nanocrystals are important. The smaller size and better dispersion in solvents of the nanocrystals, the higher resolution and quality in the resulting images. At present, there is still a challenge to produce well dispersed uniform sub-5 nm $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals. During the synthesis of $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals, the metal precursors have a large

influence on the size and morphology of the products.^{8,9} The metal-oleate complex is an effective precursor for the synthesis of uniform small size metal oxide nanocrystals via the high-temperature thermal decomposition method. In this work, we prepared the rare earth-oleate (RE-oleate) first and then, using the metal-oleate as precursor, synthesized the uniform, colloidally stable sub-4 nm $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals via nonhydrolytic high-temperature thermal decomposition method. The as-synthesized nanocrystals can be well dispersed in non-polar solvents, and the luminescence properties of the nanocrystals are studied.

2. EXPERIMENTAL DETAILS

The well dispersed sub-4 nm $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals were synthesized from the thermal decomposition of RE-oleate in tri-*n*-octylamine solution under nitrogen. Firstly, the yttrium-oleate doped with europium ions (5 at%) was produced using a similar method according to Ref. [10]. The metal-oleate complex was prepared by reacting yttrium chloride (Aldrich, 99%), europium chloride (Aldrich, 99%), and sodium oleate (TCI, 95%). 3.8 mmol YCl_3 and 0.2 mmol EuCl_3 were dissolved in 6 ml distilled water, and 12 mmol sodium oleate was added. Then, another 8 ml ethanol and 14 ml hexane were added to the solution. The resulting mixture was heated under strong stirring in an oil heater. The temperature of the oil was kept at 70 °C for 4 h. When the reaction was completed, the upper organic layer containing the RE-oleate complex was washed three times with 30 ml distilled water in a separatory funnel. After washing, hexane was evaporated off,

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resulting in a waxy RE-oleate complex. In the second step, the as-synthesized RE-oleate complex was used as a thermal decomposition precursor. In a typical synthesis of sub-4 nm $Y_2O_3:Eu$ nanocrystals, 0.5 mmol RE-oleate was added to 5 ml TOA (TCI, 95%) to form a slightly yellowish solution at 70 °C for 1 h. Under a constant N_2 flow, the solution was heated to 110 °C for 15 min to purge, and then the temperature was increased to 365 °C at an average rate of 15 °C/min⁻¹. The reaction was kept at 365 °C for 30 min. The resulting brown solution was cooled to room temperature. The nanocrystals were precipitated by adding 30 ml ethanol. To clean the nanocrystals efficiently, the precipitate was centrifuged and redissolved in non-polar solvent, such as toluene or hexane, then precipitated again by adding ethanol. This cleaning process was repeated several times, and the precipitate of nanocrystals was obtained.

To determine the thermal decomposition property of the RE-oleate, thermogravimetric analysis (TGA) was performed under N_2 atmosphere at a heating rate of 5 °C/min using a TGA Q50 analyzer (TA instruments). Fourier transform infrared (FT-IR) spectra were examined using a JASCO FT-IR 680 plus at 4 cm⁻¹ resolution. Transmission electron microscopy (TEM) images of the nanocrystals were recorded using a JEOL JEM-2000 EX electron microscope operating at 200 kV. The photographs of the nanocrystal solution were taken by a standard camera. Room-temperature photoluminescence spectra were examined under continuous Xe lamp excitation with a Hitachi F-4500 fluorescence spectrometer.

3. RESULTS AND DISCUSSION

The generated RE complex emits a slight red light under the common ultraviolet (UV) lamp. To confirm the molecular bondings of the metal complex, the FT-IR spectrum was investigated (Fig. 1). The characteristic peaks of the RE-oleate are present in the spectra. The peaks at

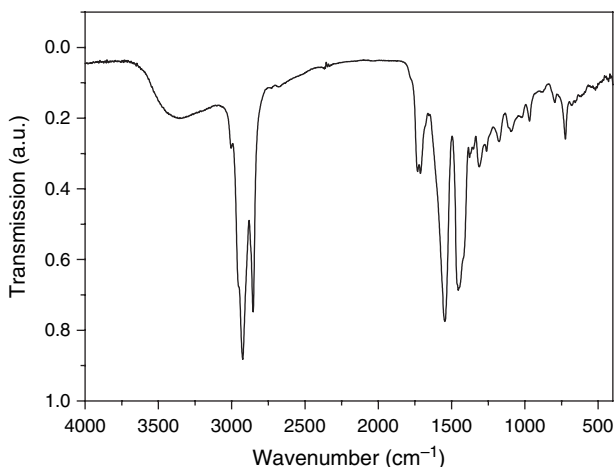


Fig. 1. FT-IR spectrum of the synthesized metal-oleate.

2911 cm⁻¹ and 2866 cm⁻¹ are attributed to the C–H vibration of the alkyl chains.^{11,12} The peak at 1715 cm⁻¹ is assigned to the C=O stretching mode, while the characteristic peaks at 1552 and 1448 cm⁻¹ are due to the symmetric $\nu_s(\text{COO}^-)$ and asymmetric $\nu_{as}(\text{COO}^-)$ vibrational stretching modes, respectively.^{10,11} The FT-IR spectrum confirms the formation of metal-oleate. To study the thermal decomposition behavior of the synthesized Y:Eu-oleate precursor, TGA measurement was carried out. The TGA pattern is shown in Figure 2. A sharp drop in weight was observed in the temperature range of 345–370 °C. It indicates that a burst of decomposition occurs during this temperature range. Because we used the thermal decomposition of the Y:Eu-oleate complex method to get $Y_2O_3:Eu$ nanocrystals, the selected solvent must have a high boiling point. TOA, which has a boiling point of 365 °C, was selected as the solvent. This temperature is high enough to afford the decomposition reaction of Y:Eu-oleate complex.

According to the experiment, after heating the precursor solution at 365 °C for 30 min, the slight brown precipitation was formed. The precipitation was redissolved in toluene to carry the TEM observation. TEM images (Fig. 3(a)) and electron diffraction patterns (Fig. 3(b)) of the precipitation revealed that the sub-4 nm nanocrystals were formed, and their sizes were relatively uniform. The high resolution TEM image (Fig. 3(c)) shows that the crystal lattice of nanocrystals and the interplanar distance are about 0.19 nm.

The as-synthesized nanocrystals can stably disperse in nonpolar solvents (such as toluene or hexane) due to the capping ligands on their surfaces (Fig. 4(a)). This kind of colloidal stability of nanocrystals is very important for the formation of smooth thin films and their utilization as luminescence biological probes. The properties of the ligands covered on the surface of nanocrystals, including their types and the adsorption/desorption equilibrium, decide the colloidal stability of the nanocrystals.¹²

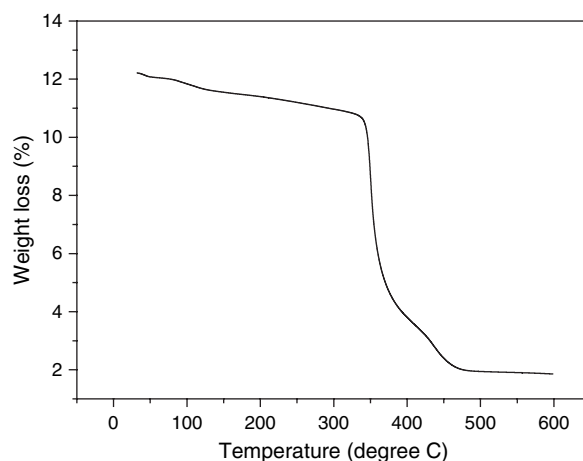


Fig. 2. TGA curve of the synthesized metal-oleate.

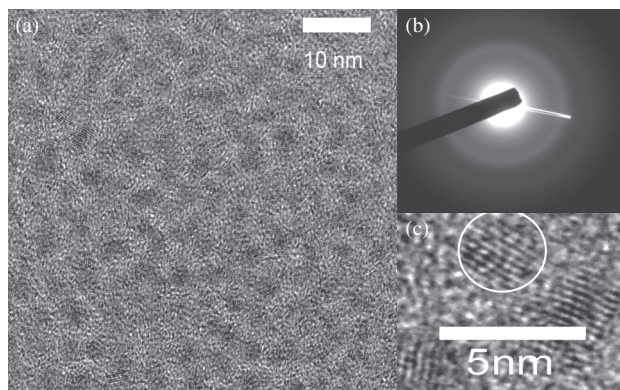


Fig. 3. (a) TEM image, (b) electron diffraction pattern, and (c) high resolution TEM image of nanocrystals.

Using a nonhydrolytic high-temperature thermal decomposition method to synthesize inorganic nanocrystals, the long-chain alkanes with polar groups of oleate can be chemically banded on the nanocrystals' surfaces, which results in the dissolution of inorganic nanocrystals in non-polar solvents. The surface binding can be probed by FT-IR spectrum of the produced nanocrystals, as shown in Figure 4(c). The peaks located at 2927 cm^{-1} and 2851 cm^{-1} confirm that the alkyl chains remained after heating at $365\text{ }^\circ\text{C}$. The peaks at 1450 cm^{-1} and 1549 cm^{-1} were assigned to the symmetric $\nu_s(\text{COO}^-)$ and asymmetric $\nu_{as}(\text{COO}^-)$ vibrational stretching modes.¹² Compared with the original metal-oleate complex, the peak near 1715 cm^{-1} , which is a characteristic peak of the C=O stretch mode, is absent. This fact indicates the absence of free carboxylic acid. The carboxylate group is binding as chelating bidentate to the surface of nanocrystals (see the possible schematic diagram in Fig. 4(b)).

The characteristic optical properties of the synthesized sample also confirm the formation of $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals. The as-synthesized nanocrystals were deposited

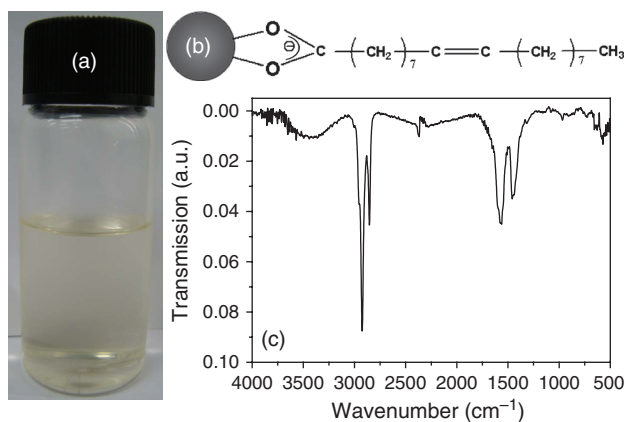


Fig. 4. (a) Transparent solution of as-synthesized nanocrystals in toluene, (b) schematic diagram of nanocrystals binding with organic ligand, and (c) FT-IR spectrum of nanocrystals.

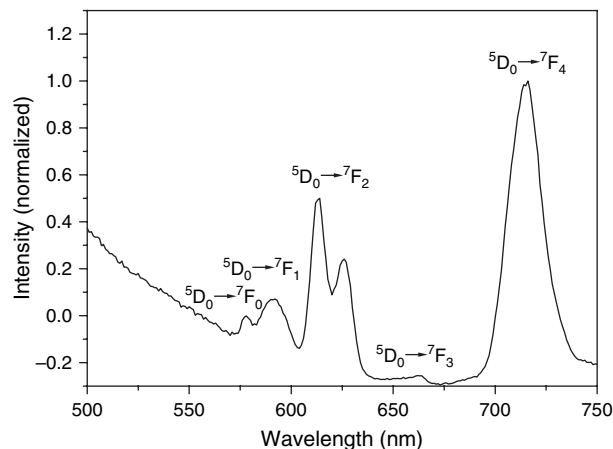


Fig. 5. Emission spectrum of nanocrystals.

on a silicon wafer and dried at $120\text{ }^\circ\text{C}$ for 2 h. The photoluminescence (PL) spectrum (excited at 254 nm by a Xe lamp) from the sample is shown in Figure 5. The characteristic emission peaks of Eu^{3+} were present in the spectrum. The peaks at 578, 592, 613, 663, and 713 nm are attributed to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0, 1, 2, 3,$ and 4) transitions of Eu^{3+} ions, respectively. The peak near 592 nm derives from the allowed magnetic dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$), which has no electric dipole contribution.¹⁴ This transition is practically independent of the ion's surroundings. The peaks around 613 nm and 715 nm are due to the induced electric dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_{2,4}$), which is allowed on the condition that the europium ion occupies a site without an inverse center. Their intensities are hypersensitive to crystal environments. Peaks corresponding to the transitions of ${}^5\text{D}_0$ to ${}^7\text{F}_{0,3}$ appear at approximately 578 nm and 663 nm. Their intensities depend upon both odd parity-even parity state mixing and $J-J'$ mixing within the 4f-electron state manifold.^{13,14} It should be noted that in the emission spectrum of sub-4 nm nanocrystals, the induced electric dipole ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition makes a dominant contribution to the emissions. The spectrum feature is quite different with the bulk $\text{Y}_2\text{O}_3:\text{Eu}$. Considering the hypersensitive character of the induced electric dipole transitions of Eu^{3+} ions, the intensity enhancement of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition may come from the small size. The crystal environment of the Eu^{3+} ions located at the surface is quite different from those at the inner crystal. There are more defects, and the crystal symmetry is lower on the surface, which may cause the intensity enhancement of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition. Compared with bulk material, the ratio of surface atoms to inner atoms is greatly increased in the sub-4 nm nanocrystals. The large numbers of luminescence atoms are located at the surface of the nanocrystals. This may be the reason, but more experiments are needed to confirm. We will continue to study the luminescence mechanism of the sub-4 nm nanocrystals.

4. CONCLUSION

In summary, well dispersed uniform sub-4 nm Y₂O₃:Eu colloidal nanocrystals were synthesized through the non-hydrolytic high-temperature thermal decomposition of RE-oleate. The nanocrystals can be well dispersed in non-polar solvents to form a stable colloidal solution because of the organic ligands attached to their surfaces. Due to the small size of sub-4 nm, the nanocrystals exhibited novel luminescence features in the emission spectrum. The intensity enhancement of ⁵D₀ → ⁷F₄ transition was observed in the emission spectrum. This kind of sub-4 nm Y₂O₃:Eu colloidal nanocrystals has potential applications in high-resolution displays and luminescence probes.

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