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Fabrication of Luminescent Eu$_2$O$_3$ Superstructures

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ABSTRACT This Letter demonstrates a solvent-free efficient synthesis process to prepare self-assembled two-dimensional Eu$_2$O$_3$ luminescent nanoplates to yield a superstructure. In the first step, Eu$_2$O$_2$CO$_3$ superstructures are fabricated by the thermolysis [700 °C] of a single precursor, europium acetate, in a closed reactor under autogenic pressure. The as-prepared Eu$_2$O$_2$CO$_3$ superstructures are further heated in air to 750 °C to facilitate the fabrication of Eu$_2$O$_3$ superstructures. A systematic morphological, structural, and compositional characterization of Eu$_2$O$_3$ superstructures is carried out. The photoluminescent properties and mechanism for the strong red emission of the photoexcited Eu$_2$O$_3$ superstructures is proposed.

SECTION Nanoparticles and Nanostructures

Rare earth compounds have been extensively utilized as high-performance magnets, luminescent devices, and catalysts based on the electronic, optical, and chemical characteristics arising from their 4f electrons.[1] Because of the long luminescence lifetimes ($\sim$1 ms), nano-sized rare earth materials have become candidates for luminescent probes in immunoassay applications to nanophosphors in electroluminescent[2] displays. Most of these useful functions depend strongly on their composition and structures, which are sensitive to the bonding states and local environment of rare earth atoms or ions. Europium oxide (Eu$_2$O$_3$) is one of the most important oxide phosphors and has been widely applied in low-voltage cathodoluminescent devices, high-density optical storage devices, and lasers because the central emission band of Eu^{3+} is at about 612 nm, which is one of the three[3] primary colors.

Considering the various applications of Eu$_2$O$_3$, several nanostructures such as nanoparticles, nanorods, nanowires, hollow spheres, and nanotubes have been prepared previously by diverse methods. Wakefield et al. reported room-temperature colloidal precipitation[4] to synthesize zero-dimensional (0D) Eu$_2$O$_3$ nanocrystals. Pol et al. synthesized Eu$_2$O$_3$ nanorods by thermal conversion (700 °C) of amorphous Eu(OH)$_3$ nanorods[5] prepared by ultrasonication. Cui et al. reported the synthesis of luminescent europium methacrylate nanowires[6] and their thermal conversion into Eu$_2$O$_3$ nanotubes. Wu et al. reported the synthesis of Eu$_2$O$_3$ nanotube arrays[7] through an improved sol–gel approach using porous anodic alumina as templates. Submicrometer-sized hollow[8] Eu$_2$O$_3$ spheres with a shell thickness of about 75 nm and inner diameter of about 690 nm have been synthesized by Zhang et al. through a sol–gel method using PS/PE microspheres as templates. Mesoporous Eu$_2$O$_3$ microspindles have been prepared by a facile solution process followed by subsequent heat treatment.[9] The self-assembly of europium oxide (Eu$_2$O$_3$) nanocrystals into anisotropic one-dimensional europium hydroxychloride (Eu(OH)$_2$Cl)[10] nanostructures is also reported.

However, the above-mentioned processes need solvents and a process control. Furthermore, synthesis of 2D nanoplates of Eu$_2$O$_3$ and their luminescence properties are not yet reported.

In this Letter, a solvent-, catalyst-, and template-free efficient synthesis process to prepare self-assembled 2D Eu$_2$O$_3$ plates to fabricate a luminescent superstructure is demonstrated. The thermolysis of a europium acetate precursor in a closed reactor at 700 °C under autogenic pressure [$\sim$3 MPa] yielded self-assembled europium oxycarbonate (Eu$_2$O$_2$CO$_3$) nanoplates[11] to fabricate superstructures. Those Eu$_2$O$_2$CO$_3$ superstructures were further heated in air to 750 °C to yield Eu$_2$O$_3$ superstructures. We have systematically characterized Eu$_2$O$_3$ superstructures to determine their morphology (scanning electron microscopy, SEM), structure (X-ray diffraction, XRD, high-resolution transmission electron microscopy, HR-TEM), and composition (energy dispersive X-ray, EDX). The photoluminescence (PL) studies are also presented for the obtained Eu$_2$O$_3$ superstructures.

The reaction time of 1 or 2 h initiated the growth process of Eu$_2$O$_2$CO$_3$ (Figure 1a and b). However, it was insufficient for complete growth to fabricate a flower-like morphology. At 700 °C, the thermal decomposition of EA for 3 h in a closed reactor converted the micrometer-size EA particles into Eu$_2$O$_2$CO$_3$ superstructures composed of nanoplates. The SEM image in Figure 1c evidently demonstrates the fascinating organization of hundreds of nanoplates. The precursor, micrometer-size EA particles were consumed to grow upward to fabricate superstructures of Eu$_2$O$_2$CO$_3$ under critical experimental conditions (Figure 1d). More than 3 h of reaction time did not show any morphological difference in the appearance of the formed superstructures. These superstructures were
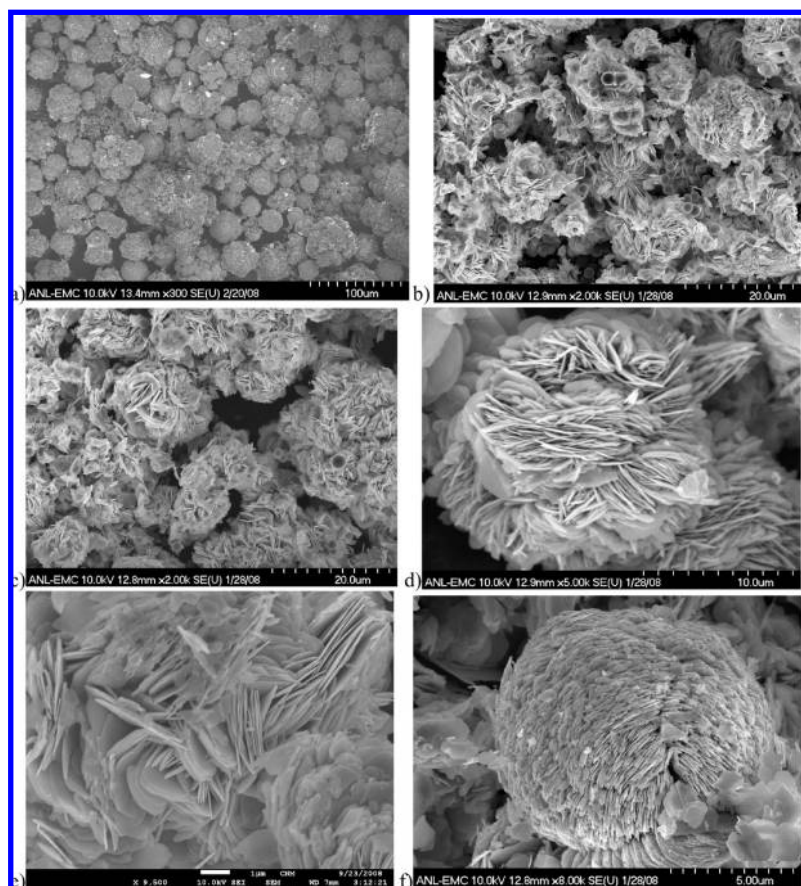
Figure 1. The SEM of (a) $Eu_2O_2CO_3$ fabricated in 1 h, (b) $Eu_2O_2CO_3$ fabricated in 2 h, (c) $Eu_2O_2CO_3$ fabricated in 3 h, (d) high-resolution SEM of $Eu_2O_2CO_3$ fabricated in 3 h, (e) Eu_2O_3 superstructures, and (f) self-assembly of Eu_2O_3 nanoplates.

further heated in an air atmosphere to 750 °C to yield Eu_2O_3 superstructures. During the combustion of $Eu_2O_2CO_3$ to fabricate Eu_2O_3, the shape, size, and overall morphology were retained (Figure 1e and f). The 2D plates of Eu_2O_3 were stacked together, keeping the superstructure unchanged. The diameters of the plates were ∼30 nm, while the widths were of several micrometers.

The XRD pattern of the as-synthesized $Eu_2O_2CO_3$ super-structure is reported elsewhere.[11] The $Eu_2O_2CO_3$ superstructures are converted to Eu_2O_3 superstructures via further heating in an air atmosphere to 750 °C. Figure 2a shows the XRD pattern of the Eu_2O_3 superstructures. The diffraction lines are indexed (blue lines) and in agreement with the standard value (JCPDS No. 34-0392) of Eu_2O_3 with a body-centered cubic structure (S.G. $Ia3$, 206), indicating the complete conversion of the $Eu_2O_2CO_3$ to Eu_2O_3. The EDX spectrum (inset of Figure 2a) of Eu_2O_3 superstructures detected Eu and O as the major elements without any impurities. The Eu_2O_3 superstructures were ground and dispersed in ethanol, and the formed plates were mounted on the carbon-coated Cu grid for TEM measurements. Figure 2b depicts a single plate possessing sharp edges. The selected area electron diffraction is shown in the inset of Figure 2b. The highly crystalline nature of the plates is depicted by the assigned complex electron diffraction dot pattern. The interplanar

distance of the lattice planes was measured to be ∼3.1 Å (HR-TEM, Figure 2c), which matched the {222} lattice plane spacing of body-centered cubic Eu_2O_3. It further provides evidence for the highly crystalline nature of the Eu_2O_3 plates. The nanoplates of Eu_2O_3 were grown in the ⟨400⟩ direction.

Rare earth ions are particularly suitable for applications as light emitters due to their well-defined transitions within the 4f shell. The room-temperature PL spectrum obtained from the Eu_2O_3 superstructures is displayed in Figure 3b. Upon excitation to Eu_2O_3 superstructures at 300 nm, the dominant narrow red emission at 612 nm is measured. The $^5D_0 \rightarrow {}^7F_1$ transition at 590 nm is the parity-allowed magnetic dipole transition ($\Delta J = 1$). The $^5D_0 \rightarrow {}^7F_2$ electric dipole transition at 612 nm ($\Delta J = 2$) was very sensitive to the local environment around the europium ion, and the intensity was dependent on the symmetry of the crystal field around the europium ion. A low symmetry around the europium ion increases the intensity of the electric dipole transition. It indicates that the body-centered cubic[12] Eu_2O_3 crystalline structure possesses $Ia3$ symmetry (Th^7). The emission bands at 654 nm, which originated from $^5D_0 \rightarrow {}^7F_3$ transitions is also detected. All of the emission bands correspond to the $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions of Eu^{3+} ions, which mainly contributed by the localized rare earth 4f energy levels. Our Eu_2O_3 superstructures provided a pure red light emission, indicating that Eu
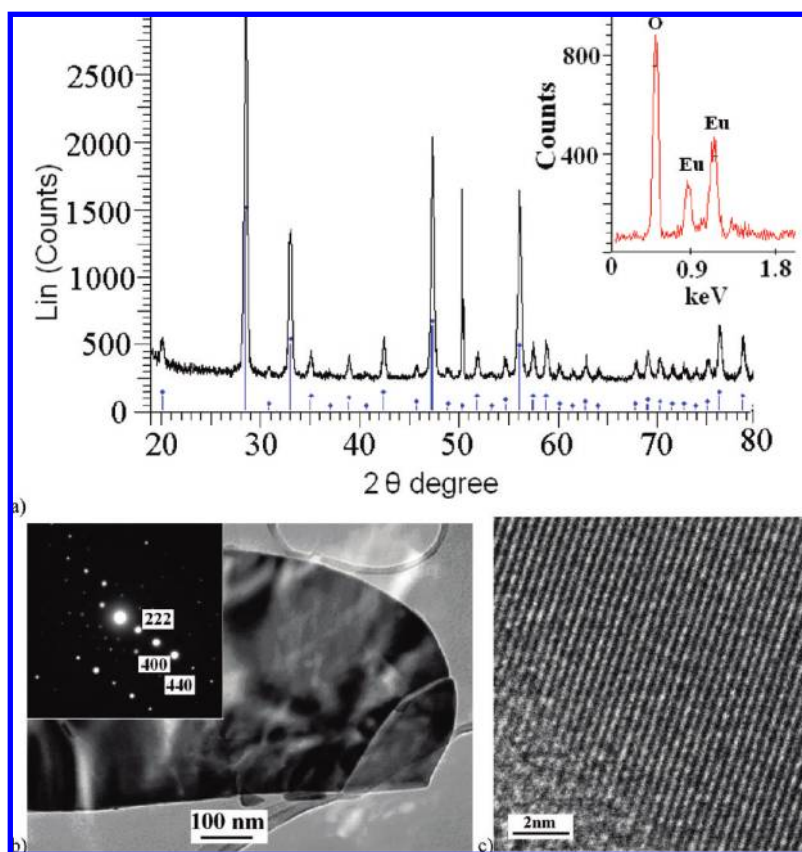
Figure 2. (a) X-ray diffraction pattern of Eu_2O_3 superstructures (inset: EDS of the same sample), (b) TEM of a single Eu_2O_3 plate (inset: electron diffraction pattern), and (c) HR-TEM of a Eu_2O_3 nanoplate.
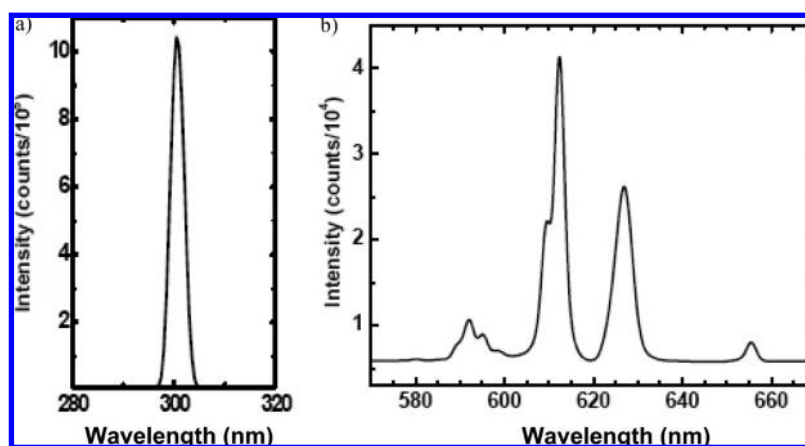

Figure 3. Room-temperature (a) excitation and (b) luminescence spectra of Eu_2O_3 superstructures.

atoms are stabilized in the 3^+ state in Eu_2O_3. The luminescence spectrum is very close to that obtained by Wakefield[4] for the cubic nanocrystalline pure Eu_2O_3 and Wang et al. for mesoporous Eu_2O_3 microspindles.[9] The obtained Eu_2O_3 superstructures exhibit a good thermal stability, undergoing thermal treatment for 3 h at 750 °C without morphological changes, confirmed by SEM, XRD, TEM, and PL measurements. In comparison with $Eu_2O_2CO_3$, most of the $^5D_0 \rightarrow {}^7F_J$ transitions were also retained during additional heat treatment. Recently, similar luminescent polar ZnO flowers[13] consisting of ZnO nanopencils were reported, where the zinc acetate was decomposed by employing analogous reaction conditions.

A possible mechanism for the strong red emission of the photoexcited Eu_2O_3 superstructures is proposed as follows. Previously, Yang et al. presented a systematic schematic

illustration of the probable mechanism of the photolumine-scence[14] of europium oxide nanotubes and nanowires. The excitation of the Eu_2O_3 nanoplates starts with the creation of an electron—hole pair. The electron is promoted from the valence band to the conduction band, producing a hole in the valence band. The active hole can be trapped either at the $v^{\bullet}o$ center directly to form the $v^{\bullet\bullet}o$ center or on the surface of the nanoplate. Then, the surface-trapped hole may tunnel back into the nanoplate to recombine with an electron in a deep trap ($v^{\bullet}o$ center) to form the $v^{\bullet\bullet}o$ center. Thereafter, recombi-nation of a $v^{\bullet\bullet}o$ center with a conduction band electron yields the red emission. We believe that red emission mechanism for the 2D Eu_2O_3 plates is analogous to one-dimentional entities.

In conclusion, a solvent-free, efficient synthesis process to prepare Eu_2O_3 a luminescent 2D plate assembly in a super-structure is demonstrated. In the first step, $Eu_2O_2CO_3$ super-structures are fabricated by the thermolysis of a single europium acetate precursor in a closed reactor at 700 °C under autogenic pressure. The $Eu_2O_2CO_3$ superstructures are further heated in air to 750 °C to yield Eu_2O_3 superstructures, which are systematically characterized to determine mor-phology, structure, and composition. The PL properties and mechanism for the strong red emission of the photoexcited Eu_2O_3 superstructures are also proposed.

Experimental Methods

$Eu(O_2C_2H_3)_3$ (europium acetate, EA) was purchased from Sigma—Aldrich and used as received. In a typical synthesis of Eu_2O_3 superstructures, 2 g of EA was introduced in a 10 mL reactor (made up of Haynes 230 alloy) at room temperature in an inert nitrogen atmosphere. The partially filled reactor with EA was closed tightly in an inert nitrogen environment and heated uniformly. The temperature of the furnace was ramped up to 700 °C at a rate of 30 °C/min and maintained at that temperature for 3 h. The maximum pressure of ~3 MPa was measured at 700 °C during EA dissociation in a closed reactor. Upon natural cooling of the reactor to room tempera-ture, we obtained ~1 g of gray powder of $Eu_2O_2CO_3$, which was further heated in the same reactor in an air atmosphere to 750 °C to yield Eu_2O_3 superstructures. These Eu_2O_3 were superstructures directly characterized and did not need any further solvent processing. The phase purity and crystal structure of the Eu_2O_3 were determined using XRD, recorded by using a Bruker AXSD* Advance powder X-ray diffract-ometer (Cu Kα radiation, wavelength 1.5406 Å). The morpho-logy and composition of the thin Eu_2O_3 films was observed by SEM and an EDX-equipped SEM instrument.

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