Functional Nanocrystals

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A Simple Reducing Approach Using Amine To Give Dual Functional EuSe Nanocrystals and Morphological Tuning**

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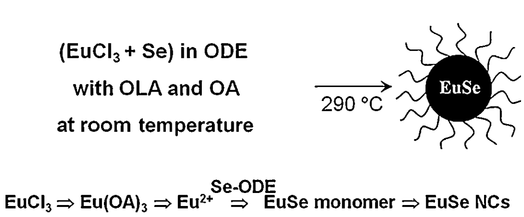
Rare-earth nano-materials with controlled structures are of great interest owing to possible luminescent and magnetic properties resulted from lanthanide cations,[1–3] and thus promise many applications, such as in solar cells and biological labeling and imaging.[4–6] Host matrices used in these materials usually were Ln^{3+} ions,[7–10] but it was problematic to prepare low-valent lanthanide materials on nano-meter scales.[11] Low-valent lanthanide mono-chalcogenide nanocrystals (NCs), and especially stable europium mono-chalcogenide EuX ($X = O$, S, Se, and Te) NCs started to become available with appealing optical and magnetic properties.[12] The EuX NCs have degenerate 4f orbitals which locate between the conduction band (5d orbitals of Eu^{2+}) and the valence band (p orbitals of O^{2-}, S^{2-}, Se^{2-}, and Te^{2-}).[13] Their 4f–5d electronic transitions and spin configuration lead to unique magneto-optical properties.[14] During the past a few years, several research groups reported various routes to prepare the EuX NCs, such as with high temperature reduction, thermal or optical decomposition of single-source precursors, and a liquid-phase synthesis.[15–18] However these methods usually required special instruments and extra ligands for Eu^{3+}, which were time-consuming with the product; meanwhile, the resulting EuX NCs exhibited poor optical and magnetic properties, with little potential in applications.

Moreover, these previous studies focused on, mostly, the magnetic property of the EuX NCs, especially EuS NCs.[19,20] The optical properties of the EuX NCs were rarely reported. Though it has been acknowledged that bulk EuX does not exhibit luminescence at room temperature,[21,22] while surface-modified EuO and EuS exhibited characteristic luminescence under UV excitation.[23,24] No luminescent EuSe NCs have been documented. It has been an enduring challenge to prepare high-quality EuSe NCs with good luminescent and magnetic properties as well as with controlled morphologies.

Herein, we report a one-step synthesis of blue luminescent, magnetic EuSe NCs. Also, we present our data on the experimental parameters affecting the change of the morphologies. We propose that the formation of the EuSe NCs requires the amine to act as a reducing agent.[25–32] Our approach is simple and effective, using $EuCl_3\ (H_2O)_6$ and elemental selenium as Eu and Se sources, respectively. The overall synthetic procedure for EuSe NCs is depicted in Scheme 1. This method demonstrates several advantages, 1) the resulting NCs are highly monodisperse and shape controlled; 2) no extra ligands are needed for the starting Eu^{3+}, leading to the presence of few impurities in the resulting NCs, these NCs have strong luminescent and magnetic properties; 3) it is suitable for gram-scale production with high synthetic reproducibility and easy handling.



Scheme 1. Synthesis of dual-functional EuSe NCs using 1-octadecene (ODE), oleic acid (OA), and oleyl amine (OLA). The amine behaves as a reducing agent.[25–32]

The dual functional EuSe NCs which are spherical were prepared with a reaction of $EuCl_3\ (H_2O)_6$ (0.1 mmol) and Se (0.4 mmol) at 290 °C for 3 h in a reaction medium consisting of 1-octadecene (ODE, 47.5 mmol), oleic acid (OA, 0.38 mmol), and oleyl amine (OLA, 3.2 mmol). OA and OLA act as be stabilizing reagents. Figure 1 a shows a typical transmission electron microscopy (TEM) image of the resulting EuSe NCs. The NCs are spherical and highly monodisperse with an average size of approximately 20 nm (Supporting Information Figure S1). The X-ray diffraction (XRD) pattern (Figure 1 b) confirms their cubic crystal structure. The diffraction peaks of 23.7°, 29.8°, 35.9°, 40.1°, 46.9°, and 52.6° in 2θ are assigned to the (111), (200), (420), (220), (311), and (222) planes of typical cubic EuSe NCs, respectively. Energy dispersive spectrometry (EDS; Support-

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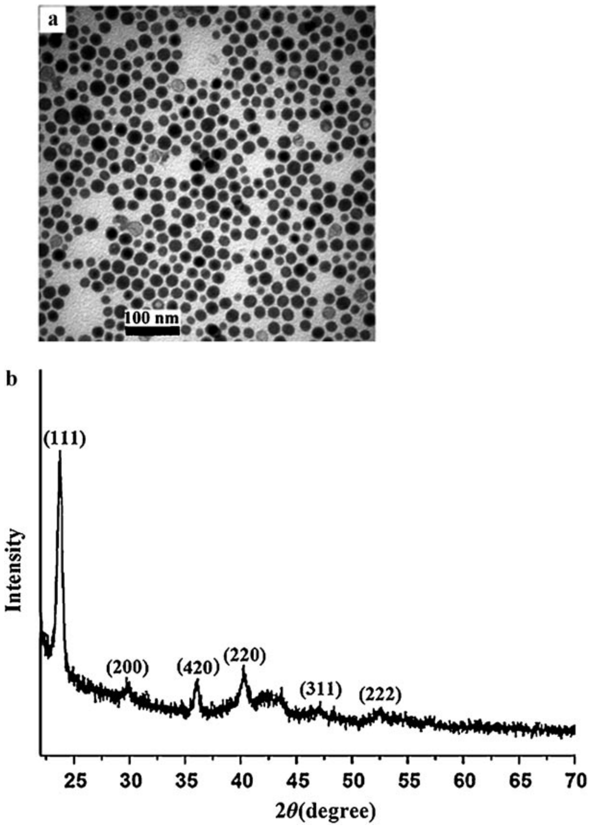

Figure 1. A typical TEM image (a) and XRD pattern (b) of the spherical EuSe NCs prepared from a synthetic batch with a molar ratio of Eu:Se of 1:4 and using 0.38 mmol OA and 3.2 mmol OLA at 290 °C.

ing Information Figure S2) illustrates the presence of Eu and Se with a composition stoichiometry (expressed with the number percentage of atoms) of Eu (55 %) : Se (45 %), which agrees with the stoichiometry of bulk EuSe. The FT-IR spectrum (Supporting Information Figure S3) suggests that the resulting EuSe NCs are mainly capped by OLA (based on the vibration bands at 1080.4 cm^{-1} of C-N and 3423.1 cm^{-1} of N-H).

The optical properties of these spherical EuSe NCs were investigated by photoluminescence (PL) spectroscopy at room temperature. The excitation (EX) and emission (EM) spectra are shown in Figure 2. When the EuSe NCs were irradiated at 353 nm, a strong blue emission peak was observed at 403 nm with a full width at half maximum (FWHM) of approximately 40 nm. Clearly, the absence of the characteristic luminescence of Eu^{3+} in the range of 580 nm to 650 nm, proposes that the Eu ions of the as-prepared EuSe NCs are in their divalent state instead of trivalent state. We argue that it is the 4f–5d electronic transition of the Eu^{2+} of our EuSe NCs with their surface passivation of OLA and OA that leads to such photoemission peaking at 403 nm.

The inset in Figure 2 is an image of a cuvette under 365 nm radiation, containing the EuSe NCs dispersed in toluene. The strong blue fluorescence is indicative of the absence of Eu^{3+} emission. The quantum yield of the as-prepared EuSe NCs was estimated to be approximately 2.8 % (based on quinine sulfate as a reference at room temperature).

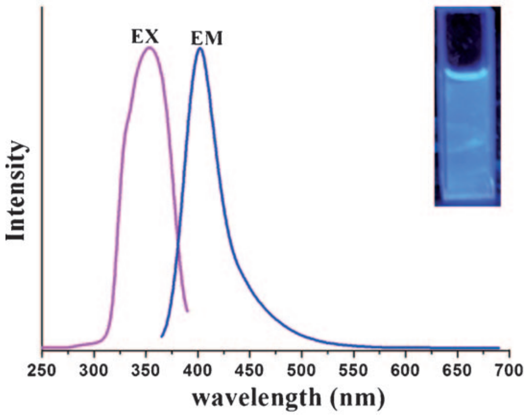

Figure 2. The excitation (EX) and emission (EM) spectra of spherical EuSe NCs. Inset: photograph of the corresponding curvet under 365 UV radiation.

Electron spin resonance (ESR) measurements (Supporting Information Figure S4) also support the presence of only Eu^{2+} in our EuSe NCs. In addition to the divalent state, the ESR spectrum of the resulting EuSe NCs also specifies that the paramagnetic property of the Eu ions are associated with the local 4f moments of the Eu^{2+} ions ($J = 7/2$). Europium (0) has a $4f^7 5s^2 p^6 6s^2$ electronic configuration. In the EuSe NCs, europium may lose its two 6 s electrons to form Eu^{2+}. Therefore, the seven single electrons in 4f orbitals may result in the paramagnetic property observed from the EuSe NCs.

Figure 3 shows the room-temperature magnetization measurement of the spherical EuSe NCs. The hysteresis loop suggests that these spherical NCs have a coercivity (Hc) of 80.2 Oe at 298 K.

To understand the formation mechanism of the EuSe NCs, the first question is what is the reducing agent in the reaction (described in Scheme 1)? There is a limited body of literature on the preparation of colloidal nanocrystals (NCs) by a reduction route,[25–29] even when amines were used.[30–32] It was reported that OLA could reduce Ag^+ and Au^{3+} ions to form

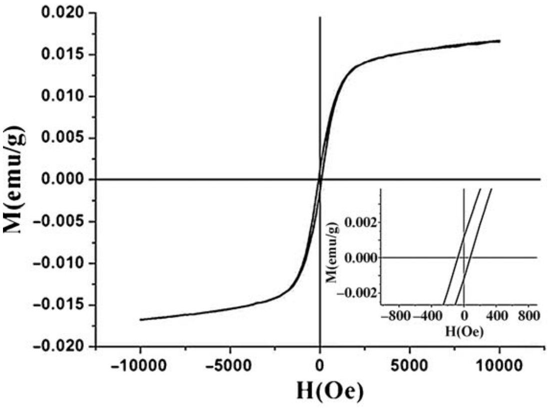

Figure 3. Magnetic characterization of the spherical EuSe NCs prepared under conditions identical to those NCs used for obtaining the data in Figure 1 and Figure 2.

Ag and Au nanoparticles, respectively.[33–35] Note that for our EuSe NCs prepared in the absence of OLA, we observed the characteristic luminescence of Eu^{3+} peaking at 592 nm and 615 nm (Supporting Information Figure S5a). We have proposed a general amine reduction mechanism in the synthesis of colloidal NCs.[25–27] Accordingly, we conclude that OLA acts as a reducing agent in the formation of our nanocrystals.

Furthermore, it is important to point out that in the absence of OLA, no nanocrystals were formed but bulk materials (Supporting Information Figure S5b). Consequently, it is easy to understand that OLA also played a significant role in the control of the NC morphologies.[36,37] In this case, OLA played an important role not only as a reducing agent but also as a capping ligand. OLA and OA had different binding strengths to the surface of our EuSe NCs. With an increase of the OLA amount, long rod-shaped NCs were produced. Therefore, we carried out systematic experiments, using different amounts of amines, to investigate the morphological control. Spherical and monodispersed EuSe NCs (Figure 1a) were prepared with 3.2 mmol OLA. Non-spherical NCs were appeared with 6.4 mmol OLA (Figure 4a). When the OLA amount was increased to 9.6 mmol, the aspect ratio of the resulting nanorods increased (Figure 4b).

In addition to the amine amount, the precursor molar ratios and reaction temperatures were investigated to tune the morphologies of the EuSe NCs. For example, hollow NCs (Figure 4c) were obtained when the precursor molar ratio was 1 Eu:1 Se. To our knowledge, these hollow EuSe NCs are the first reported. When the precursor molar ratio was 4 Eu:1 Se, the hollow NCs obtained were less monodisperse (Supporting Information Figure S6). A very high precursor molar ratio (such as 1 Eu:10 Se) led to the disappearance of the hollow morphology but the presence of solid NCs again (Figure 4d).

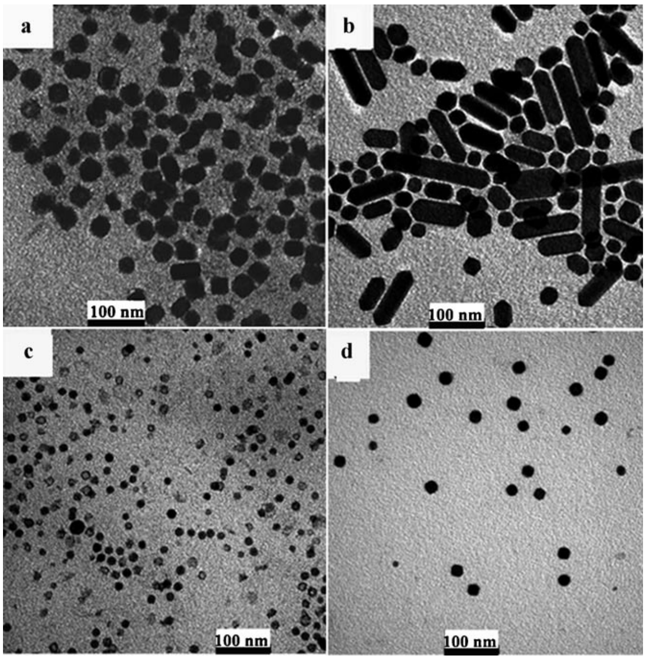

Figure 4. The TEM images showing the various morphologies observed from the EuSe NCs obtained at 290 °C. a) short nanorods (6.4 mmol OLA and 1 Eu:4 Se), b) nanorods (9.6 mmol OLA and 1 Eu:4 Se), c) hollow spheres (1 Eu:1 Se and 3.2 mmol OLA), d) solid spheres (1 Eu:10 Se and 3.2 mmol OLA).

Reaction temperatures were acknowledged to have a significant influence on tuning the morphology of various NCs.[37,38] To investigate the temperature effect, we fixed the molar ratios of 1 Eu:4 Se and 4 OLA:1 OA. Figure 5 demonstrates that relatively thin (small in diameter) and long nanorods were formed at 220 °C (Figure 5a), while relatively thick (large in diameter) and short nanorods were obtained at 250 °C (Figure 5b). The formation of the hollow NCs (Figure 5c; for a larger view, See Supporting Information Figure S7) with the size of around 20.6 nm and the wall thickness of approximately 4.0 nm was observed at 290 °C. See Supporting Information Figure S8 for another example but obtained at 280 °C.

Moreover, the morphological transition could be induced by the OLA:OA molar ratio. When the feed molar ratio was decreased to 1 OLA:1 OA, no EuSe NCs were formed in the temperature range of 220–290 °C (Supporting Information Figure S9). In contrast, when the feed molar ratio was increased to 9 OLA:1 OA, uniform solid EnSe NCs were formed at 290 °C, while no nanorods were obtained at lower temperatures (220 °C and 250 °C; Supporting Information Figure S10).

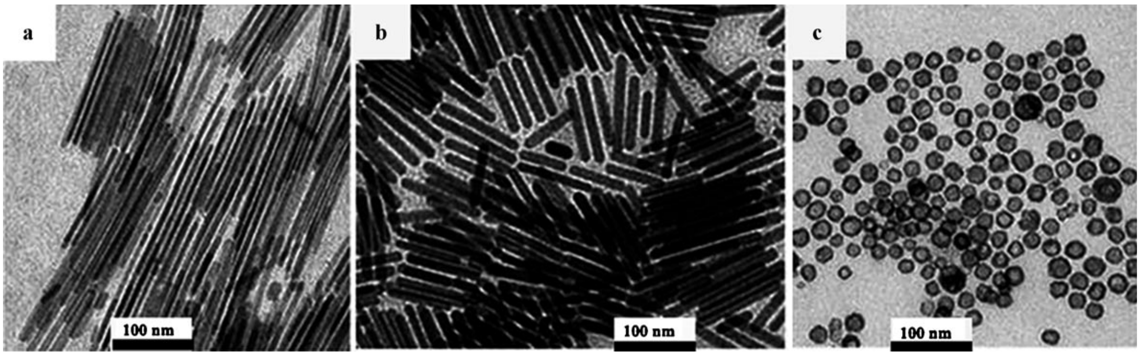

Figure 5. The TEM images of the EuSe NCs prepared with the feed molar ratios of 1 Eu:4 Se and 4 OLA:1 OA at: a) 220 °C, b) 250 °C, and c) 290 °C.

The origin of our EuSe PL is due to the 4f–5d electronic transition of Eu^{2+}. Also, the magnetic properties are due to the presence of seven single electrons in 4f orbitals of Eu^{2+}. Therefore, the EuSe NCs with the various morphologies should also exhibit similar photoluminescent and magnetic properties (Supporting Information Figure S11–S15).

In conclusion, we have developed a ready synthetic approach to prepare highly monodispersed divalent EuSe NCs, using EuCl$_3$ (H$_2$O)$_6$ and elemental selenium as the Eu and Se sources, respectively. The resulting NCs with narrow size distribution exhibited a strong blue luminescence (quantum yield of 2.8 %) and magnetic properties. The various synthetic parameters and the interplay between them, affected the morphologies of the resulting EuSe NCs. The experimental parameters investigated include the OLA amount, Eu:Se molar ratio, and reaction temperature. Note that the amine OLA acts as a reducing agent. Also, our approach is simple, highly reproducible, and suitable for gram-scale production, facilitating the potential in various applications including opto-magnetic devices, optical isolators, optical catalysis, and photo magnetic memories.

Experimental Section

1-octadecene (ODE, 90 %), oleic acid (OA, 90 %), selenium powder (Se, 99.5 %, 100 mesh), and oleyl amine (OLA, 70 %) were purchased from Sigma–Aldrich. Toluene, methanol, and acetone were obtained from Beijing Chemical Company in China. All the chemicals were used as received without purification. Europium trichloride hexahydrate [EuCl$_3$·(H$_2$O)$_6$] was prepared from europium oxide [Eu$_2$O$_3$] treated with hydrochloric acid (36.5 wt %).

Spherical EuSe NCs: a mixture of EuCl$_3$·(H$_2$O)$_6$ (0.1 mmol), Se (0.4 mmol), OA (0.13 mL, 0.38 mmol), OLA (1.54 mL, 3.2 mmol), and ODE (16.7 mL, 47.5 mmol) was degassed at room temperature and heated up to 120 °C under vacuum for 2.5 h while stirring. The resulting homogeneous solution was switched to a dry argon atmosphere, heated to 290 °C slowly and maintained at this temperature for 3 h. The temperature of the solution was allowed to cool to under 100 °C. The resulting EuSe NCs were precipitated by addition of acetone, rinsed with methanol, and then redispersed in toluene. Using a similar method, other samples with different morphologies were prepared under different experimental conditions.

Photoluminescence (PL) experiments were performed with a Shimadzu RF-5301 PC spectrofluorimeter. Structural and compositional characterizations were performed by transmission electron micrographs (TEM, Hitachi H-800 electron microscope operating at 200 kV), energy dispersive spectrometer (EDS, OXFORD-ISIS-300 EDS with a Si detector on the JEOL JXA-840 scanning electron microscope), electron spin resonance (ESR, JEOL JES-FA-200), and powder X-ray diffraction (XRD, Siemens D5005 diffractometer using Cu$_{K\alpha}$ (1.5418 Å) radiation) at room temperature. For TEM characterization, the purified sample dispersed in toluene was deposited on a carbon-coated copper grid. For EDS measurements, all the samples were sputtered with a layer of platinum (ca. 2 nm in thickness) prior to test. The hysteresis loop was measured on a LakeShore 7410 at room temperature.

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