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COMMUNICATION

A facile reduction of Eu^{3+} to Eu^{2+} in gadolinium monosulfide nanoparticles using a mixed solvent of oleic acid/hexadecylamine†

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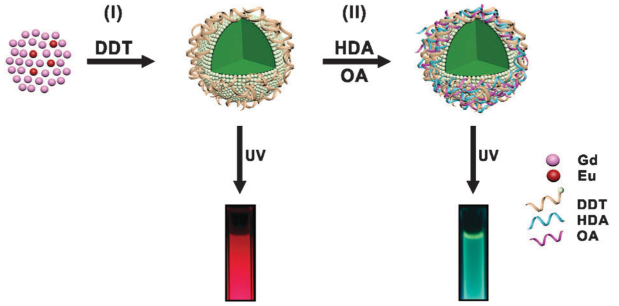
We prepared GdS:Eu^{3+} by simple thermal decomposition under 1-dodecanethiol. A reduction process was observed from Eu^{3+} to Eu^{2+} when oleic acid and hexadecylamine were injected into GdS:Eu^{3+}. Under UV excitation, GdS:Eu^{3+} showed an intense orange-red emission and GdS:Eu^{2+} showed a broad green band.

Rare-earth monochalcogenides have been investigated extensively because of their unique luminescent, magnetic, and photomagnetic properties.[1–3] In particular, gadolinium monosulfide (GdS) belongs to the family of rare-earth monochalcogenides and this compound has been investigated owing to its interesting electrical and magnetic properties.[4] Because the Gd^{3+} ion possesses a very stable half-filled 4f shell with seven unpaired spins, GdS prefers the trivalent ionization state and it is regarded as a suitable host for obtaining efficient luminescence by doping with a trivalent ion, such as Eu^{3+}.[5] Eu^{3+} has been used in many luminescent compositions, because it can emit intense red fluorescence *via* transitions from the $^5D_0$ energy level.[6,7] On the other hand, the luminescent properties of Eu^{2+}-doped solid-state materials have been widely investigated in order to obtain efficient green emission, which usually consists of a broad green band due to transitions between the $4f^7$ ($^8S_{7/2}$) ground state and the $4f^65d$ excited state.[8] In general, it is necessary to reduce Eu^{3+} to Eu^{2+} in order to prepare green-emissive Eu^{2+}-doped solid-state materials. Numerous methods have been studied and developed for reducing Eu^{3+} to Eu^{2+}, such as heat treatment of Eu^{3+}-containing materials under a reducing atmosphere (N_2/H_2, H_2, carbon or CO gas) and irradiation of Eu^{3+}-containing materials with UV light, γ-rays or X-rays.[9,10] Moreover, some groups have systemically studied the anomalous reduction of Eu^{3+} to Eu^{2+} in oxide complexes, with the materials prepared under an oxidizing condition (air or O_2 atmosphere) at high temperatures.[11]

Typically, the Eu^{3+}-doped GdS nanoparticles exhibit a strong red emission *via* the $^5D_0 \rightarrow {}^7F_2$ transition. However, we observed green emission bands *via* the spin-allowed transition $4f^65d^1 \rightarrow 4f^7$ ($^8S_{7/2}$) for the Eu^{2+} ion in GdS nanoparticles because the reduction of Eu^{3+} to Eu^{2+} was realized when oleic acid (OA) and hexadecylamine (HDA) were added to the initially formed Eu^{3+}-doped GdS nanoparticles solution. Although the method of synthesis for GdS nanoparticles has been reported,[12] there have been no reports on the luminescent properties of Eu^{3+}- and Eu^{2+}-doped GdS nanoparticles or the successive reduction of Eu^{3+} to Eu^{2+} by the injection of OA and HDA (Scheme 1).



Scheme 1 Synthetic routes for (I) preparing Eu^{3+}-doped GdS nanoparticles and (II) reducing Eu^{3+} to Eu^{2+} in GdS nanoparticles.

In this communication, we propose a convenient method to synthesize red-emitting Eu^{3+}-doped GdS and green-emitting Eu^{2+}-doped GdS nanoparticles. The Eu^{3+}-doped GdS nanoparticles were prepared in solution by using $Gd(acac)_3 \cdot xH_2O$ and $Eu(acac)_3 \cdot xH_2O$ in the presence of dodecanethiol (DDT). The DDT was used as a sulfur source as well as a surface capping agent.[13] Moreover, it facilitates the thermal decomposition of $Gd(acac)_3 \cdot xH_2O$ and $Eu(acac)_3 \cdot xH_2O$ because it has a high boiling point (266–285 °C).[14] After being thoroughly stirred for 20 min, the mixed solution was heated to 200 °C for 2 h under vigorous stirring in DDT.

The solution was then cooled to room temperature, and excess ethanol was added to yield a greenish-yellow precipitate that was separated by centrifugation after being washed several times to remove unreacted precursors and DDT. In general, the Eu^{2+}-doped GdS nanoparticles were prepared by the same procedure as that for the Eu^{3+}-doped GdS nanoparticles, except for the successive injection of the OA and HDA solutions into the reaction system containing Eu^{3+}-doped GdS nanoparticles under a continuous heat supply. When OA and HDA were injected, the solution turned orange, indicating that the reduction of Eu^{3+} to Eu^{2+} had proceeded; then, we observed a green emission under a UV lamp.

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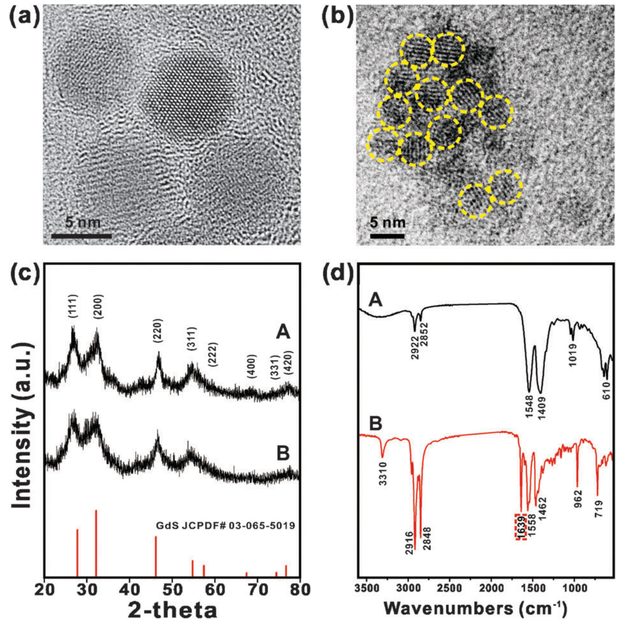

Fig. 1 (a) TEM image of Eu^{3+}-doped GdS nanoparticles. (b) TEM image of Eu^{2+}-doped GdS nanoparticles. (c) X-Ray diffraction patterns of (A) Eu^{3+}- and (B) Eu^{2+}-doped GdS nanoparticles. (d) FT-IR spectra of GdS nanoparticles: (A) after preparation under DDT and (B) after injection of OA and HDA.

The transmission electron microscopy (TEM) image of the synthetic Eu^{3+}-doped GdS nanoparticles revealed a spherical shape with an average core size of 5 nm (Fig. 1a). When the OA and HDA solutions were injected into the reaction system containing Eu^{3+}-doped GdS nanoparticles, Eu^{3+} was reduced to Eu^{2+}, and Eu^{2+}-doped GdS nanoparticles were found to be aggregated (Fig. 1b) with a spherical shape and a particle size about 5 nm, which are consistent with the observations for the Eu^{3+}-doped GdS nanoparticles. The aggregation of this sample can be explained by complex surface capping, first by DDT, and then by OA and HDA; this facilitates the formation of a network on the particles,[15] which is consistent with the energy dispersion X-ray analysis (EDS) result. EDS analysis revealed that around 10% of sample is composed of Gd, Eu, and S, and around 90% of it is composed of organic molecules that surround the nanoparticles (Fig. S1, ESI†). The X-ray diffraction (XRD) peak positions of these Eu^{3+}- and Eu^{2+}-doped GdS nanoparticles are in good agreement with those of crystalline face-centered-cubic GdS, with no evidence of secondary phases, particularly Gd_2O_3 (Fig. 1c), which indicates well-formed single crystals.

In order to propose the reduction mechanism under the injection of OA and HDA, FT-IR measurements were performed on nanoparticles obtained from reactions carried out under DDT and under successively injected OA and HDA solutions. In the case of nanoparticles prepared under DDT, the presence of a DDT layer can be confirmed. The bands at 2922 cm^{-1} and 2852 cm^{-1} can be ascribed to the antisymmetric- and symmetric stretching modes of $–CH_2–$ in DDT, respectively, whereas the bands at 1548 cm^{-1} and 1409 cm^{-1} can be attributed to the bending vibration of C–H in DDT. The specific stretching vibration of the C–S linkage can be ascribed to the region observed around 610 cm^{-1}. Therefore, this indicates that the DDT was successfully capped on the surface of Eu^{3+}-doped GdS nanoparticles (Table S1, ESI†).

Note that the reduction of Eu^{3+} to Eu^{2+} occurred without any additional reducing agents such as H_2. Recently, a long-chain acid or an amine has been used as a reducing agent or surfactant for the synthesis of iron nanoparticles, and a reduction mechanism has been proposed.[16] On the basis of this mechanism, we suppose the reduction mechanism in the present synthesis of Eu^{3+}- and Eu^{2+}-doped GdS nanoparticles. When we add the OA and HDA to Eu^{3+}-containing solutions, OA may act as a subsidiary reducing agent and HDA facilitates the formation of an imine. Because of the oxidative transformation of the primary amine into an imine, some of the electrons released after the injection of HDA are captured by the Eu^{3+}, which is then reduced to Eu^{2+} as observed *via* characterization, such as emission spectroscopy and X-ray photoelectron spectroscopy (XPS). We confirmed the stretching mode of an imine group at 1639 cm^{-1} (indicated by the dotted line in Fig. 1d) (Fig. S2, ESI†).

In order to confirm the Eu^{3+} and Eu^{2+} ionic states, XPS was applied to the as-prepared GdS nanoparticles. The XPS spectra of the Eu^{3+}- and Eu^{2+}-doped GdS nanoparticles, recorded in the energy region of the Eu (3d) transition, are shown in Fig. 2a. Even in a Eu^{3+}-doped sample the existence of a divalent peak is observed, and indeed this always accompanies the XPS of Eu^{3+} ions.[18b] This kind of mixed-valence state has been observed before in many rare-earth metallic compounds containing Eu.[17] As compared with the prominent spin–orbit components $Eu^{3+}3d_{3/2}$ and $Eu^{3+}3d_{5/2}$ ($3d^4f^6$) at around 1165 eV and 1134 eV, the $Eu^{2+}3d_{3/2}$ and $Eu^{2+}3d_{5/2}$ ($3d^4f^7$) configurations

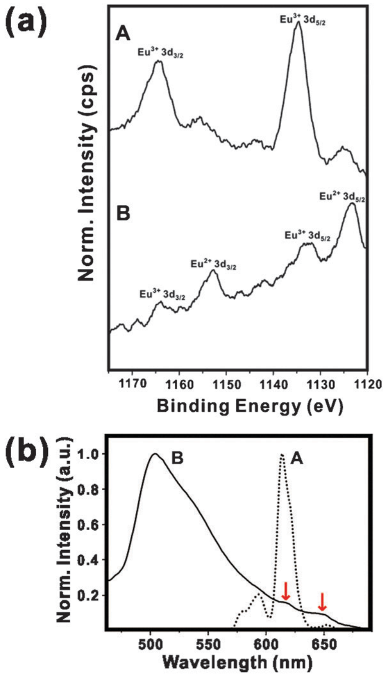

Fig. 2 (a) XPS 3d spectra of Eu in the GdS nanoparticles showing (A) the $Eu^{3+}3d_{3/2}$ and $Eu^{3+}3d_{5/2}$ ($3d^4f^6$) doublet binding energies of 1165 eV and 1134 eV, respectively, and (B) the $Eu^{2+}3d_{3/2}$ and $Eu^{2+}3d_{5/2}$ ($3d^4f^7$) doublet binding energies of 1156 eV and 1125 eV, respectively. (b) Emission spectra of (A) Eu^{3+}- and (B) Eu^{2+}-doped GdS nanoparticles.

were clearly observed at around 1156 eV and 1125 eV. This is consistent with the XPS results for Eu^{3+} and Eu^{2+}.[18] It can be said that the process of reduction from Eu^{3+} to Eu^{2+} effectively took place in GdS:Eu, when OA and HDA were successively injected into the Eu^{3+}-containing GdS nanoparticle solution.

Under UV light excitation, the Eu^{3+}-doped GdS nanoparticles dispersed in chloroform exhibited a bright red color (Fig. S3, ESI†). The emission spectra are shown in Fig. 2b. Under 365 nm excitation, Eu^{3+}-doped GdS nanoparticles yield an intense orange-red emission corresponding to the intra-configurational f–f transition $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1 and 2). As seen in the figure, the emission spectrum of Eu^{3+} in Eu^{3+}-doped GdS nanoparticles consists of a strong peak at 614 nm and several weak peaks. The $^5D_0 \rightarrow {}^7F_1$ transition (at around 584 nm) and $^5D_0 \rightarrow {}^7F_2$ transition (at around 614 nm) are the expected magnetic and electric dipole–dipole transitions, respectively. It is known that the $^5D_0 \rightarrow {}^7F_2$ transitions are highly dependent on the local symmetry of the Eu^{3+} ions. When OA and HDA were added to the Eu^{3+}-containing solution, we obtained the green emission spectrum due to transitions between the $4f^7$ ($^8S_{7/2}$) ground state and the $4f^65d$ excited state of Eu^{2+}, which exhibited the broad band feature of Eu^{2+} with the maximum at 505 nm and several weak emission lines around 614 nm and 650 nm (see the downward arrows in Fig. 2b). In order to determine the optimum experimental conditions with respect to green emission intensity, several factors were taken into account, such as OA amount, HDA amount, Eu concentration, temperature, and reaction time (Fig. S4, ESI†). For Eu^{3+}- and Eu^{2+}-doped GdS nanoparticles, different excitation bands are observed at 365 nm and in the range of 450 nm–475 nm, respectively (Fig. S5, ESI†).

In conclusion, we have described a method for the synthesis of red-emitting Eu^{3+}-doped GdS nanoparticles under DDT solution, which plays the role of a sulfur source as well as a surface capping agent. Moreover, we demonstrated the reduction of Eu^{3+} to Eu^{2+} in the GdS compound by using OA and HDA. The reduction process was realized immediately when the OA and HDA solutions were injected into the reaction system containing Eu^{3+}-doped GdS nanoparticles. We confirmed the Eu^{3+} and Eu^{2+} ionic states by XPS, which were recorded in the energy region of the Eu (3d) transition.

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