Supporting Information

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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Methods

Synthesis of Eu^{3+}-doped GdS nanoparticles

In a typical reaction, the 5 nm Eu^{3+}-doped GdS nanoparticles were prepared as follows. Gadolinium (III) acetylacetonate hydrate (99.9%), Europium (III) acetylacetonate hydrate (99.9%), 1-Dodecanethiol ($CH_3(CH_2)_{11}SH$, 98%), and Hexadecylamine ($CH_3(CH_2)_{15}NH_2$) were purchased from Aldrich. The Oleic acid ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$) was purchased from Junsei. Chloroform and ethanol were used in the isolation of nanoparticles. All chemicals were used without further purification. The appropriate compositions of $Gd_{1-x}S$ with various concentration of Eu_x were added to a flask containing 20 mL of 1-Dodecanethiol. After being stirred for about 20 min at room temperature, the mixture was heated to 200 °C and held there for 2 h. The solution was then cooled to room temperature and excess ethanol was added to yield a greenish yellow precipitate following washed several times to remove unreacted precursors and DDT, and then separated by centrifugation.

Reduction of Eu^{3+} to Eu^{2+} in GdS nanoparticles

While holding the Eu^{3+}-containing GdS solution at 200 °C, OA/HDA mixed solvents, which was prepared by mixing for various OA/HDA ratio with rapid stirring for 20 min at RT, were rapidly injected into the flask. The reaction solution changed color from green to orange immediately after the injection of the OA/HDA mixed solvent, which indicated that the reduction of Eu^{3+} to Eu^{2+} proceeded and then we observe a green emission under the UV lamp. After the reaction went to completion, the solution was washed with several times and then separated by centrifugation.

Characterization. The resulting nanoparticles were identified using a Bruker D8 X-ray diffractometer with CuK α radiation (Ni filter). TEM and HRTEM images were obtained using a Tecnai G2 transmission electron microscope and with a JEOL JEM-2010F high-resolution transmission electron microscope at an accelerating voltage of 200 KV. The X-ray photoelectron spectroscopy signals were recorded on a VG scientific ESCA 3MK Ⅱ spectrometer operated at a base pressure better than 10^{-9} Torr. FT-IR spectra were collected by FT-IR spectrometer (Nicolet Nexus 470) with the KBr method. Photoluminescence measurements were performed on nanoparticles using a Perkin-Elmer LS-50B spectrometer equipped with a Xenon flash lamp. The compositions of the nanoparticles were analyzed by an energy-dispersive X-ray spectrometer (EDS).

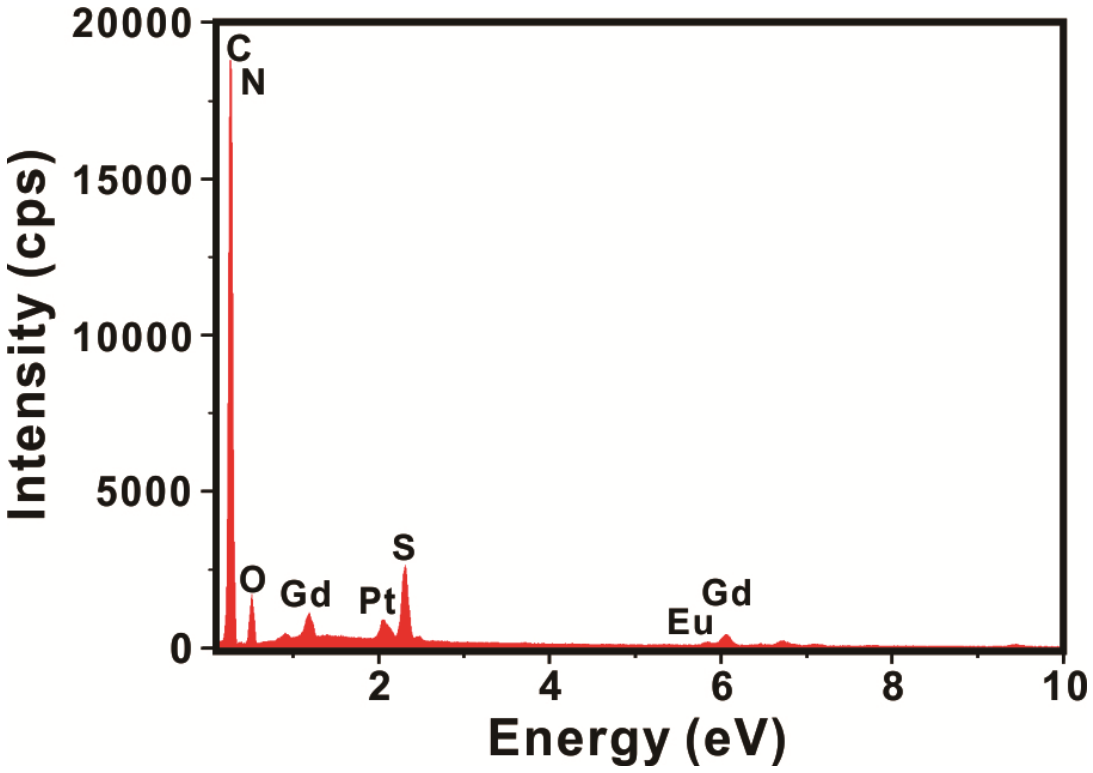

Fig. S1. A representative EDS analysis of Eu^{2+}-doped GdS nanoparticles.

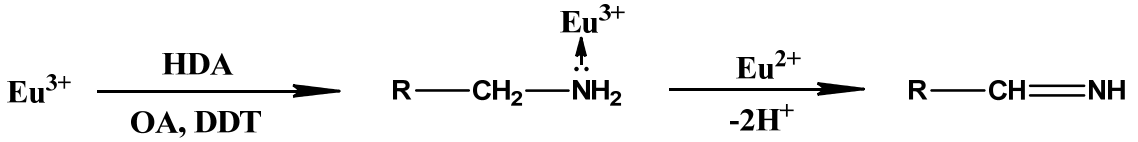

Fig. S2. The scheme of reduction process from Eu^{3+} to Eu^{2+} when OA/HDA added into the Eu^{3+}-containing GdS nanoparticles solution.

Table 1. FT-IR bands for Eu^{3+}- and Eu^{2+}-doped GdS nanoparticles.

(bands position in cm^{-1})

Assignment	GdS : Eu^{3+}	GdS : Eu^{2+}
N-H	-	3310
CH_3 stretching	2930	2955
CH_2 stretching (asymmetric, symmetric)	2922, 2852	2916, 2848
C=N (imine)	-	1639
COO^-	-	1558, 1462
C-H bending vibration	1548, 1409	1377
C-C stretching	1019	962
Long chain band	-	719
C-S linkage	610	618

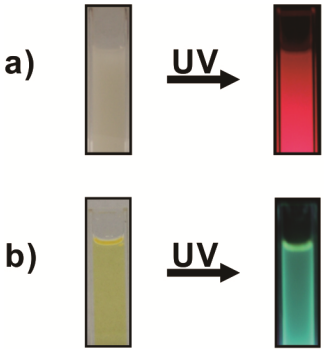

Fig. S3. Photographs of a) Eu^{3+}- and b) Eu^{2+}-doped GdS nanoparticles under UV irradiation. The GdS nanoparticles were completely dissolved into the chloroform.

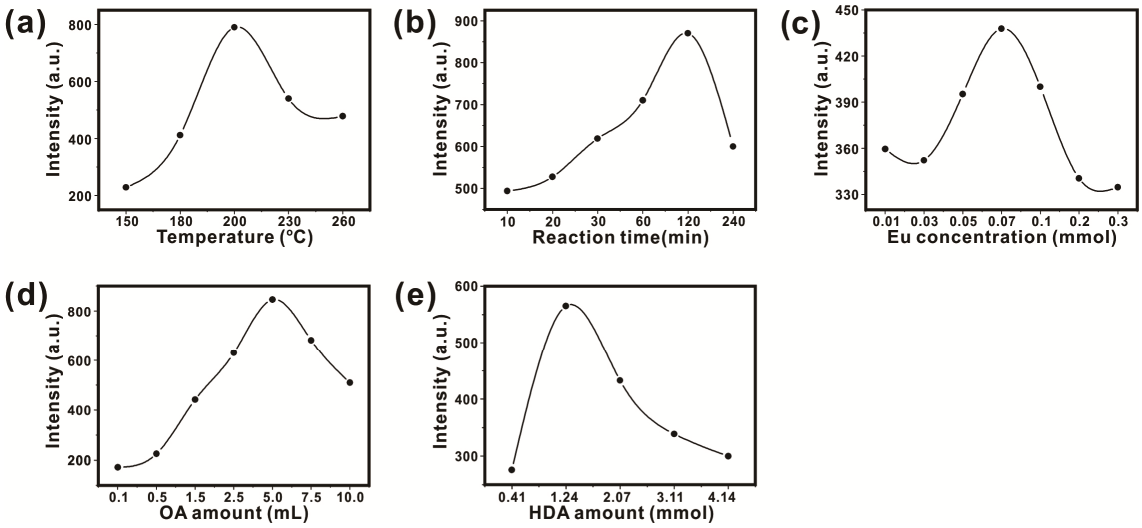

Fig. S4. Photoluminescence intensities as a function of (a) prepared temperature, (b) prepared time, (c) Eu concentration, (d) OA amount, and (e) HDA amount.

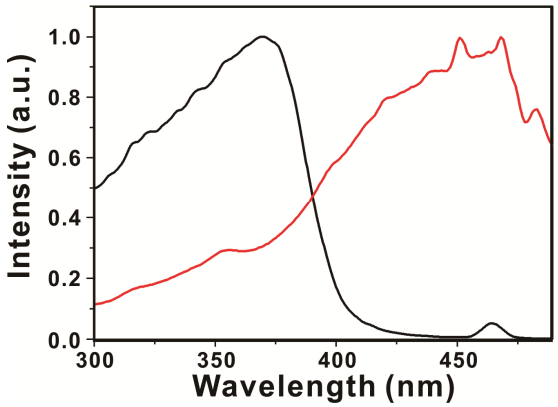

Fig. S5. Excitation spectra of Eu^{3+}(black line) and Eu^{2+}(red line) –doped GdS nanoparticles .