Near-IR Photo-stimulated Luminescence of CaS:Eu\textsuperscript{2+}/Dy\textsuperscript{3+} Nanophosphor

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Supporting Information

1. Synthesis

CaS:Eu\textsuperscript{2+} and CaS:Eu\textsuperscript{2+}/Dy\textsuperscript{3+} nanophosphors were synthesized by co-precipitation method following the procedure of Sun et al. [6]. All starting reagents were obtained from Sigma Aldrich with purities of 99.99%. CaCl\textsubscript{2}⋅2H\textsubscript{2}O (0.62 mmol) was dissolved in 50 mL of ethanol. Stock solutions of Eu(NO\textsubscript{3})\textsubscript{3}⋅5H\textsubscript{2}O (0.01 M) and Dy(NO\textsubscript{3})\textsubscript{3}⋅H\textsubscript{2}O (0.01 M) were prepared in ethanol. Na\textsubscript{2}S⋅9H\textsubscript{2}O (0.62 mmol) was dissolved in ethanol and sonicated for 30 min. An ethanolic solution of 50 mL of Na\textsubscript{2}S⋅9H\textsubscript{2}O was injected to a mixture of CaCl\textsubscript{2}⋅2H\textsubscript{2}O, Eu(NO\textsubscript{3})\textsubscript{3}⋅5H\textsubscript{2}O and Dy(NO\textsubscript{3})\textsubscript{3}⋅H\textsubscript{2}O at a rate of 20 mL/min at room temperature and under a flow of argon. The mixture was stirred vigorously for 16 h. The nanophosphor CaS:Eu\textsuperscript{3+}/Dy\textsuperscript{3+} was precipitated under reduced pressure followed by a dropwise addition of 20 mL of tetrahydrofuran, and stirred vigorously for 2 hours under a flow of argon. CaS:Eu\textsuperscript{3+}/Dy\textsuperscript{3+} nanophosphor was recovered by centrifugation and dried under vacuum. To reduce Eu\textsuperscript{3+} to Eu\textsuperscript{2+}, the nanophosphor was annealed with sulfur powder for 4 h at 700°C under N\textsubscript{2} flux in a Mini Mite\textsuperscript{TM} Tube Furnace (from Lindeberg/Blue).

2. Powder X-ray Diffraction Analysis

The powder diffraction patterns of CaS:Eu\textsuperscript{3+}, CaS:Eu\textsuperscript{2+} and CaS:Eu\textsuperscript{2+}/Dy\textsuperscript{3+} were collected at room temperature with the K\textalpha (45 kV and 40 mA) radiation of Cu using a Scintag XDS-2000 diffractometer equipped with a Si(Li) Peltier-cooled solid state detector. The scanning step size was 0.02 2θ with a counting time of 0.5 s per step. A quartz zero background insert disk was used as a sample holder.
3. ICP-MS analysis

ICP-MS (Agilent 7500) measurements were performed to determine the concentrations of Eu and Dy in the sample of CaS:Eu$^{2+}$/Dy$^{3+}$. Helium was used as the carrier gas. The nanophosphor was digested in concentrated HNO$_3$. The digested sample was diluted in a 5% HNO$_3$ solution. A calibration curve of 5 points was established using a SPEX lanthanide multi element standard solution (10 mg/L). The concentration of Eu and Dy were found to be 0.017 %mol and 0.0016 %mol respectively. These results are in agreement with the initial concentrations used in the mixture.

4. Luminescence experiments

The visible emission spectra of the nanophosphor samples of CaS:Eu$^{2+}$ and CaS:Eu$^{2+}$/Dy$^{3+}$ were measured by exciting the samples with the 3rd harmonic, 355 nm wavelength, of a Nd:YAG Q-switched laser (Quanta Ray from Spectra Physics) with a
pulse frequency of 10 Hz and a pulse width of 6 ns. The measurements were performed on powder samples placed in quartz capillary tubes. The visible emissions were collected from the samples at $\pi/2$ with respect to the incident beam and then dispersed by a 1 m Jarrell-Ash Czerny-Turner double monochromator with an optical resolution of approximate 0.15 nm. A thermoelectrically cooled Hamamatsu R943-02 photomultiplier tube was used to detect the visible emissions. The photomultiplier signals were processed by a preamplifier and transferred to a gated photon-counter model SR400 Standard Research System data acquisition system. The visible emission spectra were recorded using the Standard Research Systems SR465 software.

The lifetime measurements were performed by exciting the samples with a Nitrogen Pulsed Laser (337 nm wavelength). The visible emission signal was detected by a photomultiplier tube with GaAs photocathode (model R636, Hamamatsu) Peltier cooled processed by a by a digital oscilloscope (mode Waverunner LT372, Lecroy, bandwidth 500MHz). The trigger level was adjusted by using as reference the entrance signal of the laser. The excitation beam was focused using a lens of 15 cm focal distance. The luminescence from the simple was collected at 90 degrees by a lens of focal length of 5 cm to be focused into the detection system with another lens of focal distance 15 cm.

The charging time of the nanophosphor was carried out using a UV lamp EB-280C (from Spectroline). The excitation wavelength used was 312 nm. Excitation spectra and detrapping measurements were performed using a 980 nm laser diode, with a maximum power 1000 mW, and a Ti-Sapphire laser (model 3900S from Spectra Physics, 850-1000 nm wavelength); the excitation power was varied by using neutral density filters of different optical densities. The emission and excitation spectra were recorded using the same experimental set up described above.
Figure S2. (Red line) Emission spectra of undoped CaS using Na$_2$S as precursor and (Black line) using K$_2$S as precursor.

Figure S3. Stimulated Emission Time (PST) as a function of the power of excitation.
Figure S4. Excitation spectrum of CaS:Eu$^{2+}$/Dy$^{3+}$ using UV light and photo stimulation of CaS:Eu$^{2+}$(0.02 % mol)/Dy$^{3+}$ (X % mol).

Table S1. Photo-stimulated time of CaS:Eu$^{2+}$ (0.02 % mol)/Dy$^{3+}$ (X % mol) using 980 nm, 950 and 900 nm excitation wavelength and power of 29 mW.

<table>
<thead>
<tr>
<th>( \lambda_{\text{EXC}} ) (nm)</th>
<th>0.001 ( \text{Dy}^{3+} ) (% mol)</th>
<th>0.002 ( \text{Dy}^{3+} ) (% mol)</th>
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<tbody>
<tr>
<td>980</td>
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