

# A novel method for synthesizing EuS nanocrystals from a single-source precursor under white LED irradiation†

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EuS nanocrystals, with an average diameter of 9 nm, have been synthesized by the photolysis of  $\text{Na}[\text{Eu}(\text{S}_2\text{CET}_2)_4] \cdot 3.5\text{H}_2\text{O}$ ; the first quantum confined particles of EuS to be reported.

Chalcogenide semiconductors such as EuO, EuS, EuSe and EuTe are promising materials for optical isolators and opto-magnetic devices because of their unique photo- and magneto-properties.<sup>1</sup> The quantum-confined model predicts that EuS nanocrystals will show enhanced opto-magnetic properties including large Faraday and Kerr effects.<sup>2</sup> Previously, we have reported EuS nanocrystals prepared by a liquid ammonia method from Eu-ingots. However, the crystals had dimensions  $>20$  nm.<sup>3</sup>

Single-source precursors (SSP) have been utilised for the synthesis of nanoparticles decomposed in a suitable capping agent.<sup>4</sup> Scholes *et al.* have reported the synthesis of EuS nanocrystals using a single-source precursor.<sup>5</sup> However, these nanostructures do not exhibit quantum confinement in their optical properties.<sup>5</sup> Previously, nanodimensional EuO has been synthesised by a photochemical reduction method.<sup>6,7</sup> The melding of these two techniques has now led to a novel route for lanthanide semiconductor nanoparticles containing Eu(II) ions. In this communication, we report the synthesis of EuS nanocrystals by the white LED irradiation of the air-stable, single-source precursor,  $\text{Na}[\text{Eu}(\text{S}_2\text{CNET}_2)_4] \cdot 3.5\text{H}_2\text{O}$  and the structural and optical properties of the resultant material.

The precursor  $\text{Na}[\text{Eu}(\text{S}_2\text{CNET}_2)_4] \cdot 3.5\text{H}_2\text{O}$  was synthesised by the literature method and the purity was confirmed by micro-analysis results.<sup>8</sup>  $\text{Na}[\text{Eu}(\text{S}_2\text{CET}_2)_4] \cdot 3.5\text{H}_2\text{O}$  (0.1 g) was dissolved and stirred in acetonitrile (100 ml) and irradiated with a white LED light at 25 °C in air. After 3 days, a white-yellow powder of EuS was obtained and analysed.

The HR-TEM image shown in Fig. 1a indicates well-defined oblate particles, with an average diameter of 9 nm. The crystallinity is clear and well-resolved (111) lattice planes of the NaCl-type EuS phase are observed. The selected area electron diffraction pattern (Fig. 1c) of the nanocrystals indicates *d*-spacing values of 3.44, 2.98, 2.11, 1.80, and 1.34 Å, corresponding to (111), (200), (220), (311) and (420) planes of NaCl-type EuS nanocrystals which are in agreement with the literature values (JCPDS 75-0868) (see ESI for *d* values†). Quantitative EDAX analyses in TEM measurements confirmed the stoichiometry of EuS nanoparticles; Eu (52%) : S (48%). IR analysis was carried out to confirm the

purity of product and did not indicate the presence of sulfate (see ESI for spectra†).

The most important feature of this method is the photo-reaction induced by a white LED. Previously Yamase *et al.* have reported the absorption and excitation spectra of  $\text{Na}[\text{Eu}(\text{S}_2\text{CNET}_2)_4] \cdot 3.5\text{H}_2\text{O}$  showing a  $\text{S} \rightarrow \text{Eu}$  LMCT band at 450 nm.<sup>8</sup> The LMCT bands correspond well with the emission band of our white LED (see ESI for spectra†). We observe a decrease in the LMCT band of the Eu(III) complex in the solution under white LED irradiation over 3 days. A possible photochemical reaction mechanism for the formation of EuS nanocrystals is shown in Fig. 2. Irradiation into the  $\text{S} \rightarrow \text{Eu}$  LMCT bands can induce photoreduction to give an Eu(II) ion and  $\text{S}_2\text{CNET}_2$ . The radical intermediate  $\text{S}_2\text{CNET}_2$  gives  $\text{S}^{2-}$  as a by-product. Thus, EuS nanoparticles are gradually formed by the crystal growth of Eu(II) and  $\text{S}^{2-}$  in the solution. Such a growth process could also lead to the formation of organic species such as  $(\text{Et})_2\text{NC}(\text{S})\text{--}(\text{S})\text{CN}(\text{Et})_2$  in solution, which were not identified. This reaction mechanism could only arise from the molecular architecture.

The first emission and excitation spectra of EuS nanocrystals are shown in Fig. 2. Generally, the f-d transition of Eu(II) is observed in the visible region.<sup>7</sup> We propose that the emission process in a

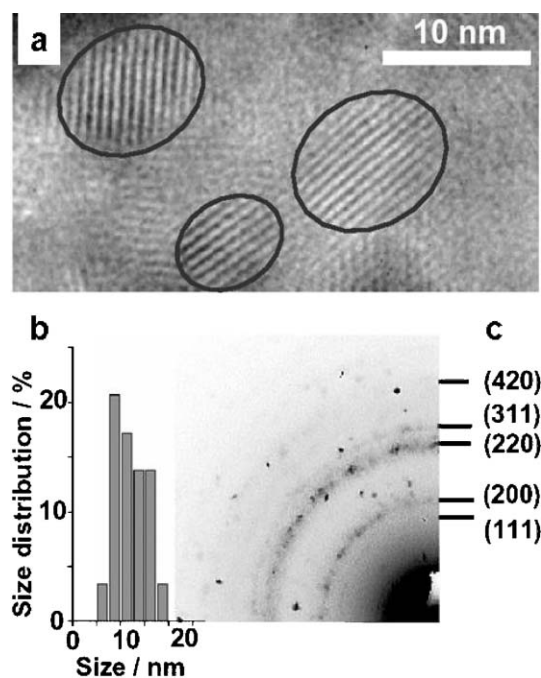
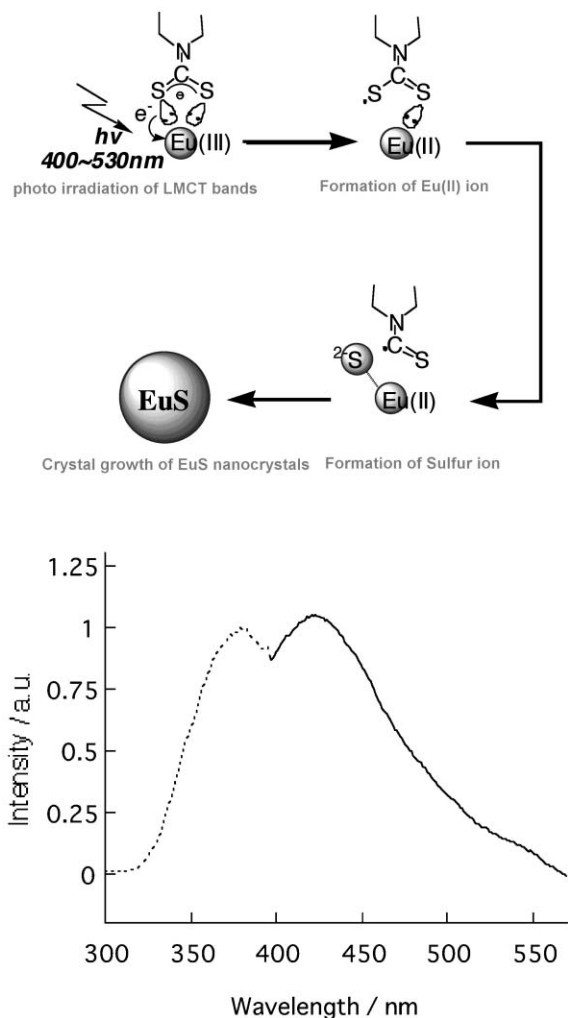


Fig. 1 (a) HR-TEM image of nanocrystals. (b) Particle size histogram. (c) A Bright-field SAED image.

† Electronic supplementary information (ESI) available: *d*-spacings of EuS, IR spectra of the precursor and EuS nanoparticles, and LED emission spectrum of the precursor. See <http://www.rsc.org/suppdata/cc/b4/b413252a/>

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**Fig. 2** The photochemical reaction mechanism, excitation (dotted line: monitor at 470 nm) and emission spectra (bold line: excited at 370 nm) of the EuS nanocrystals in acetonitrile, respectively.

solution including EuS nanoparticles is also due to an  $f-d$  transition. The energy band gap in nanocrystals (of *ca.* 10 nm) was estimated to be about 3.1 eV, a blue shift in comparison to bulk EuS (1.7 eV)<sup>9</sup> and is significantly larger than that observed for the 20 nm EuS particles (1.9 eV).<sup>3</sup> The level of the conduction band constructed from 5d orbitals should be affected by the crystal size of EuS (a quantum size effect). The 10 nm semiconductor particles confine the excited electron in the conduction band, resulting in an emission.<sup>9</sup> The quantum yield for EuS particles was found to be only 0.05%. This observation represents the first example of the luminescence of EuS at room temperature. Since the emission depends on the surface condition of the EuS nanoparticles, work is being carried out to modify the EuS surface in order to enhance the emission. §

The above results demonstrate that reasonably monodispersed EuS nanoparticles can be prepared by a simple and convenient

route from  $\text{Na}[\text{Eu}(\text{S}_2\text{CNET}_2)_4] \cdot 3.5\text{H}_2\text{O}$  with white LED irradiation. To the best of our knowledge, this is the first example of EuS particles from SSP which have luminescent properties. The white LED system also differs from UV irradiation systems and has significant advantages including low cost and improved safety. This new route may open the way to the creation of nanostructures and avoid the use of high temperatures and toxic substances. Studies are being carried out to fabricate EuS thin films by decomposing the SSP in a suitable CVD process.

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## Notes and references

‡  $\text{Na}[\text{Eu}(\text{S}_2\text{CNET}_2)_4] \cdot 3.5\text{H}_2\text{O}$  was prepared according to the reported method<sup>6</sup> and characterized. All manipulations and reactions were carried out in air. Analysis of  $\text{C}_{12}\text{H}_{31}\text{N}_4\text{O}_{3.5}\text{NaS}_8\text{Eu}$ : calcd. (found) %: C 28.00 (27.64), H 5.87 (5.45), N 6.53 (6.42), Eu 17.71 (17.95).

§ White LED irradiation (3 V AC, 9000  $\text{cd m}^{-2}$ , Marks & Spencer) was employed during the experiment. TEM and EDAX analyses of prepared EuS nanocrystals were carried on Philips CM200, 200 kV DX4EDS. The sample was briefly sonicated in acetonitrile, and then a drop of suspension was placed on a TEM grid and allowed to dry. Absorption spectra were measured by Thermo Spectronic Heλios β. Solutions in quartz cells (optical path length 5 mm) were excited at 345 nm using a spectrometer (JOBIN YVON SPEX FL3-22). The spectra presented here have been corrected for detector sensitivity and lamp intensity. The quantum yields were determined by standard procedures using an integrating sphere and quartz cells (optical path length 5 mm).<sup>10</sup>

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