



Dye-coated europium monosulfide

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ABSTRACT

Nanoparticles of EuS were synthesized using europium dithiocarbamate complexes. The resulting nanoparticles were coated with the dye, 1-pyrene carboxylic acid and the resulting material was characterized using X-ray powder diffraction, TEM, and UV-visible spectroscopy. Fluorescence spectroscopy was used to determine the relative energy of the conduction band edge to the excited state energy of the dye.

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1. Introduction

Advancement of new technology is likely to come from the development of multifunctional materials that have highly coupled properties (optical, electronic or magnetic) [1]. Coupling means that a change in one property can induce a change in another. Examples include magneto-resistive materials in magnetic reader heads [2] or opto-electronic materials in LED displays [3]. We would like to develop a novel system which would use light to trigger a change in the magnetic properties of magnetic semiconducting materials, through dye-sensitized magnetic semiconductors.

Photomagnetism has been observed in spin crossover (SCO) systems based on iron (II) coordination complexes [4,5]. The absorption of light causes a LS–HS transition, increasing the net magnetic moment. Light induced magnetism was discovered in Prussian Blue analogs caused by a Charge Transfer Induced Spin Transition (CTIST) mechanism [6,7]. For example, the Fe^{II}–CN–Co^{III} compound, having no unpaired electrons is converted to Fe^{III}–CN–Co^{II} with 3 unpaired electrons or 2.2 Bohr magnetons per formula unit. The systems which exhibit this type of photo-induced magnetization effect, CoFe and MnFe Prussian Blues, as well as the recent Os analog, are quite limited [8]. In addition, studies have indicated that the response is weak and inefficient and heat is required in order to reverse the effect [9].

The photomagnetic system we are targeting depends on the magnetic coupling in europium monochalcogenides, EuO and EuS,

Abbreviations: Ln, lanthanide; phen, phenanthroline; OA, oleylamine; PCA, 1-pyrene carboxylic acid

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which possess both intrinsic magnetic and semiconducting properties [10]. The Eu²⁺ ion has a half-filled 4f shell which leads to a large localized magnetic moment of 7.94 Bohr magnetons. The ferromagnetic interactions have been explained by the Ruderman–Kittel–Kosuya–Yosida (RKKY) type indirect exchange which arises from the polarization of conduction electrons [11,12]. Evidence for the role of conduction electrons has been established through electron doping, Eu_{1-x}M_xE (where M is a non-redox active lanthanide such as, Gd, Tb, Dy, Lu, La and Y; E=S and Se). This results in an increase in the paramagnetic Curie temperature [13–15].

The magnetic coupling through conduction electrons provides a handle for using light to manipulate the magnetism in this special class of compounds. Molecular photovoltaics provides a template for the photo-injection of electrons from surface attached dyes to semiconductor materials [16], such as the sensitization of TiO₂ using ruthenium polypyridyl complexes [17,18]. The dye molecule absorbs light and injects an electron to an acceptor semiconductor conduction band [19]. The requirements for photo-injection have been well defined for TiO₂, and the minimum requirement is that the excited state of the dye should be moderately (~0.2 V) higher in energy than the flat band potential or lowest energy state in the conduction band.

Photo-injection could be an alternative method to increase the concentration of conduction electrons which has been shown to result in enhanced magnetic coupling in magnetic semiconductors [20–22]. Preliminary evidence from ultra high vacuum PES (Photo-emission spectroscopy) studies suggest that the conduction band energy for EuS is ~ -1.9V ± 0.1 V (versus NHE), which is quite high in energy [23]. Using this as a guide, we have selected a well characterized dye, 1-pyrene carboxylic acid, which has an excited state energy of -1.75 V (versus NHE) [24]. Although it is close in

energy, if these values are correct there should be no photo-injection. However, using a magnetic field to split the energy of the conduction band it should be possible to lower the energy of the conduction band to below -1.29 V, lower than that of the dye excited state. Here we report the first step in our study, and simply demonstrate the surface attachment of the dye, and full photophysical characterization of the dye-sensitized EuS semiconductors.

2. Experimental section

2.1. Materials

1-pyrene carboxylic acid was purchased from Tokyo Chemical Industry Co. Ltd. All other chemicals were purchased from Aldrich Chemical Co. and used as received, unless otherwise noted.

2.2. Synthesis of EuS nanoparticles

The EuS nanoparticles were prepared by solution-phase thermolysis of the tetrakis dithiocarbamate precursor, $\text{NH}_2\text{Et}_2[\text{Eu}(\text{S}_2\text{CNET}_2)_4]$, following previously published procedures [25,26]. Briefly $\text{NH}_2\text{Et}_2[\text{Eu}(\text{S}_2\text{CNET}_2)_4]$ (0.2 g, 0.244 mmol) was dissolved in 4.8 ml (14.6 mmol) oleylamine (OA) resulting in a red–orange solution. In a three-neck flask, 4.8 ml (14.6 mmol) OA was heated to 265°C under nitrogen. The total volume of OA used was 9.6 ml (29.3 mmol), giving an [OA]/[precursor] ratio of 120:1. The precursor was quickly injected into the hot OA and temperature was maintained at 265°C for 1 h. The nanoparticles were collected by repeated precipitation by EtOH and dissolution in heptanes, followed by centrifugation and drying in vacuum.

2.3. Surface coating

The 1-pyrene carboxylic acid (PCA)-coated EuS nanoparticles were prepared by mixing a solution of an excess amount of PCA with a solution of EuS nanoparticles in degassed tetrahydrofuran (THF) at room temperature and stirring overnight. As a typical example, a PCA solution, 0.022 (M) in THF was added to EuS nanoparticles, 16.4×10^{-5} (M) in THF. The total volume of the solution in THF was 10 ml. The solution was stirred in the glovebox at room temperature overnight. The PCA-coated EuS nanoparticles were

precipitated with EtOH, washed thrice with EtOH and dried under vacuum. The coated nanoparticles were redissolved in degassed heptanes for recording UV–vis and fluorescence spectra.

2.4. Characterization

UV-visible spectra were recorded from 200 to 800 nm on a Perkin Elmer Lambda 35 UV/VIS spectrometer in quartz cuvettes. Infrared spectra were measured in the range of $450\text{--}4000\text{ cm}^{-1}$ as pressed pellets in KBr on Nicolet 380 FT-IR. Fluorescence spectra were recorded on Photon Technology International (PTI) fluorimeter (model QM-2001-4) in quartz cuvettes. Wavelength of excitation was 353 nm. Slit width was set to provide a band-pass of 2 nm for excitation and emission. X-ray powder diffraction patterns were obtained using a Rigaku RAPID Curved X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation and an image plate detector. Samples were prepared for TEM measurements by dipping carbon coated copper TEM grids five to six times into solutions of the nanoparticles, allowing the grids to dry briefly before re-immersion. Images were taken on a Hitachi H-7600 with an EDAX eds analysis system and an AMT digital camera.

3. Results and discussion

We have developed the use of single source precursors based on lanthanide dithiocarbamates, and have chosen the tetrakis

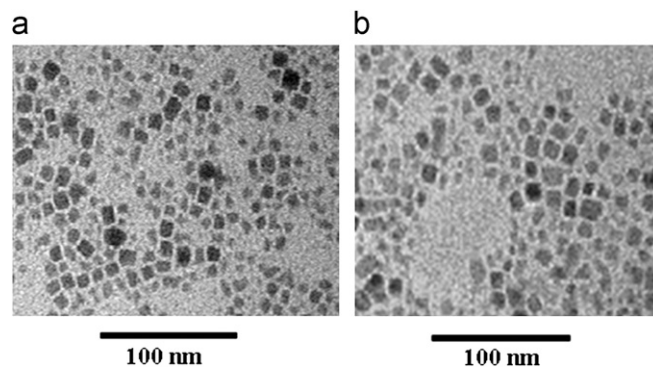


Fig. 2. (a) TEM of EuS and (b) TEM of dye-EuS.

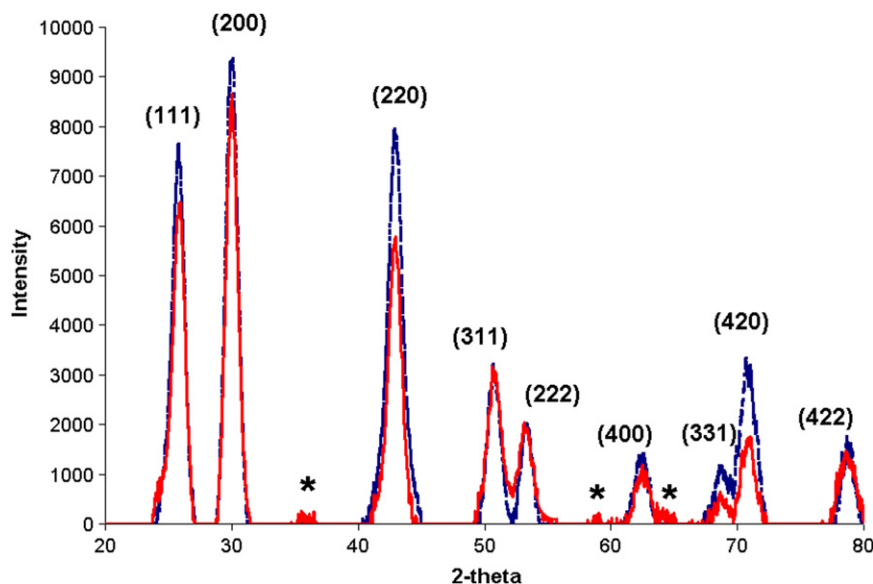


Fig. 1. X-ray powder diffraction pattern of dye-EuS nanoparticles (blue dotted is uncoated EuS, red is dye-EuS). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

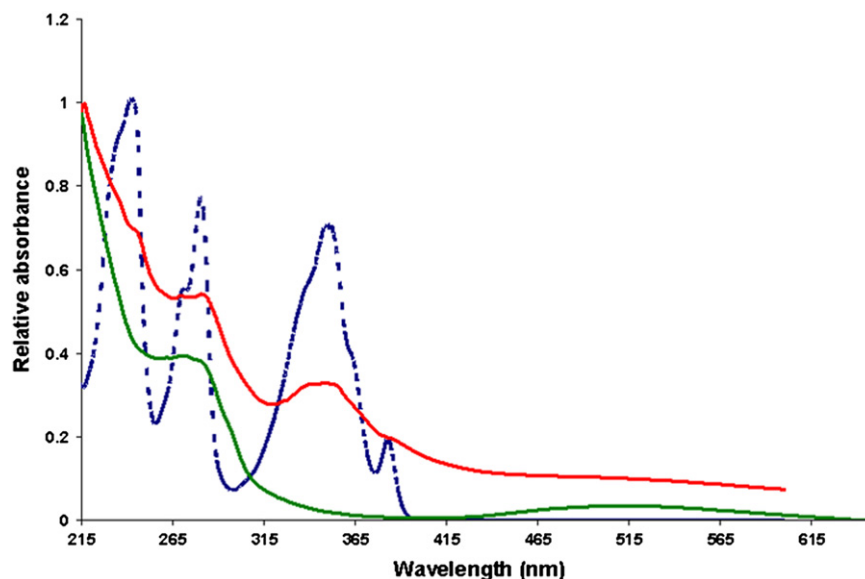


Fig. 3. UV-visible spectrum of EuS nanoparticles (green), coated nanoparticles (red), dye (blue dashed). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

precursor, $\text{NH}_2\text{Et}_2[\text{Eu}(\text{S}_2\text{CNET}_2)_4]$, to remove ambiguities in the optical properties, with the advantage that this complex is readily soluble in the capping ligand and solvent oleylamine (OA) at room temperature.

The solvent, oleylamine (OA) passivates the surface of the nanoparticles, and is readily exchangeable with the 1-pyrene carboxylic acid (PCA). The EuS nanoparticles prepared were characterized by powder XRD and TEM. The XRD confirms the material to be crystalline, single phase EuS, and the TEM images show the particles to be monodisperse in nature (average particle size 11.1 ± 2.4 nm from measurement of ~ 100 individual particles).

The dye-coated nanoparticles were characterized by X-ray powder diffraction which demonstrated that the crystallinity and phase were mostly unaffected by the dye surface attachment. The X-ray powder diffraction pattern of the uncoated and dye-coated material were in close agreement, as seen in Fig. 1, however, the presence of small amount of $\text{Eu}_2\text{O}_2\text{SO}_4$ could be assigned to 3 peaks (36° , 59° and 66°) [27]. This was unexpected, as our experience has been that EuS decomposes to form $\text{Eu}_2\text{O}_2\text{S}$. The TEM, Fig. 2, shows there is no significant change in nanoparticle size after attachment of the dye (diameters were 11.4 ± 2.8 nm from 100 particles).

We confirmed the surface attachment of the dye through the carboxylate linker using FTIR (see Appendix A). The decrease in the characteristic bands of OA appearing at 2920 , 2850 cm^{-1} ($-\text{CH}_3$ stretching) and 1300 – 1600 cm^{-1} ($-\text{NH}_2$ bending) suggest a loss of OA [28]. The appearance of bands at 1510 , 1400 and 843 cm^{-1} is evidence of surface attached PCA [29]. In Fig. 3, the UV-vis spectroscopy of the dye-coated nanoparticles resuspended in degassed heptanes show the clear presence of the peaks ($\lambda = 242$, 280 , and 348 nm) characteristic of the dye [30]. The absorption spectrum of EuS nanoparticles has had differing interpretations, but generally the absorption at 273 nm appears to be an anion band to cation band transition, while the weak absorption at 510 nm across the band gap, corresponds to the $4f^7 \rightarrow 4f^6 5d^1$ transition [31].

The peaks in the fluorescence spectra are consistent with the pyrene carboxylate, with emission at 386 , 406 , and 428 nm (see Appendix A) [30]. The shape of the fluorescence spectra provides further evidence of the attachment of the dye onto the surface of the nanoparticles via carboxylate-type linkages [32,33]. In addition,

depending on the relative energy of the excited state of the dye either emission or quenching should be observed. Thus the fluorescence can be used to determine the relative energy of the dye excited state (e.s.) to the conduction band (CB) of the EuS. Here, the presence of the characteristic peaks of the dye in the emission spectra of the dye-coated nanoparticles demonstrates that the energy of the CB is higher than the energy of the dye excited state. The pyrene carboxylate is a potent excited state reductant, which suggests that the CB energy in europium monochalcogenides is extremely high.

4. Conclusion

We have synthesized monodisperse EuS nanoparticles and have successfully attached PCA molecules onto their surface. Based on our experiments we believe that, the energy of the CB is greater than -1.75 V, suggesting a high energy conduction band. At room temperature in the absence of a magnetic field PCA cannot photo-inject to the EuS due to this energy mismatch. Because the energy of the CB is known to depend on temperature and magnetic field, we plan to use a magnetic field to tune the energy of the CB to allow photo-injection to occur.

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Appendix A. Supporting materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.03.028.

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