Quantum Confined High-Entropy Lanthanide Oxysulfide Colloidal Nanocrystals

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ABSTRACT: We have synthesized the first reported example of quantum confined high-entropy (HE) nanocrystals, using the lanthanide oxysulfide, Ln₂SO₄, system as the host phase for an equimolar mixture of Pr, Nd, Gd, Dy, and Er. A uniform HE phase was achieved via the simultaneous thermalization of a mixture of lanthanide dithiocarbamate precursors in solution. This was confirmed by powder X-ray diffraction and high-resolution scanning transmission electron microscopy, with energy dispersive X-ray spectroscopic mapping confirming the uniform distribution of the lanthanides throughout the particles. The nanoparticle dispersion displayed a significant blue shift in the absorption and photoluminescence spectra relative to our previously reported bulk sample with the same composition, with an absorption edge at 330 nm and a λ₂ at 410 nm compared to the absorption edge at 500 nm and a λ₂ at 450 nm in the bulk, which is indicative of quantum confinement. We support this postulate with experimental and theoretical analysis of the bandgap energy as a function of strain and surface effects (ligand binding) as well as calculation of the exciton Bohr radii of the end member compounds.

KEYWORDS: high entropy, nanocrystal, quantum dot, lanthanide oxysulfides

High-entropy (HE) compounds are a family of crystalline materials with high configurational entropy arising from at least five different elements in approximately equal atomic ratios randomly dispersed throughout a single crystalline phase.¹⁻³ HE phases that have received much interest in recent years include oxides⁴⁻⁶ and alloys⁷ as well as chalcogenides,⁸⁻¹¹ though this list continues to grow.⁹⁻¹¹ The synthesis of HE materials with controllable composition at a variety of length scales to explore emergent properties associated with particle size is a particularly interesting challenge that is currently unmet.

Semiconducting inorganic materials that display emergent widening of the bandgap when the particle size falls below a critical size are known as quantum dots (QDs).¹²,¹³ The widening of the bandgap is a consequence of the physical confinement of excitons below their exciton Bohr radii in the bulk semiconductor. QDs have been applied to theranostics,¹⁴ LEDs,¹⁵ light harvesting,¹⁶ sensing,¹⁷ and catalysis.¹⁸,¹⁹ Quantum confined HE nanocrystals, i.e., HE quantum dots, present a potentially vast range of accessible bandgaps through control of both nanocrystal composition and size, with potential applications as thermoelectrics and catalysts based on current studies on HE materials. HE materials have attracted significant attention as thermoelectric materials due to high levels of lattice distortion and consequent poor thermal conductivity.²⁰ They have also been investigated for their promising catalytic properties due to the so-called “cocktail effect” caused by the simultaneous presence of multiple elements in close proximity to one another.²¹

The lanthanides, particularly the lanthanide oxysulfide system, Ln₂SO₄, represent a promising area of exploration for HE materials owing to the particular stability of the +3 oxidation state, as well as the relatively small variation in their crystallographic radii.²² They have found applications in a number of areas, such as multimodal medical imaging agents in the form of Gd₂SO₄ nanoparticles²³ and as tunable bandgap materials in the form of bimetallic (Ce/Gd)₂SO₄ nanoparticles for solar cell applications.²⁴ The 4f→4f transitions in the lanthanides means they also exhibit unique optical properties and so have found use as high-quantum-yield X-ray scintillators for exposure reduction.²⁵

Bulk lanthanide oxysulfides have been produced by three routes, viz., by the partial sulfurization of the desired lanthanide oxide using a sulfur containing agent such as...
ammonium thiocyanate, via the thermolysis of a molecular precursor such as a lanthanide dithiocarbamate derivative, and by calcination of urea-based precursors in the presence of elemental sulfur. Nanoparticles have also been produced, most commonly via solution-based synthetic procedures. During this process, inorganic lanthanide complexes are heated in a solvent or mixture of solvents that can act as capping agents for the resultant nanoparticles. As with bulk materials, this can be achieved with lanthanide salts and a sulfur source or with molecular precursors.

The use of molecular precursors for the synthesis of nanomaterials has distinct advantages over other synthetic routes. The most significant are the prearranged atomic proximity of the elements present in the desired material and the ability to purify, characterize, or mix together in the desired ratios at the level of the molecule. Metal dithiocarbamate precursors, as used in this work, have been shown to allow the synthesis of a wide range of bulk materials, including main group, transition metal, and lanthanide sulfides, with compositions ranging from binary systems to high-entropy materials. However, there are limited examples of the production of nanoparticles using lanthanide dithiocarbamate precursors—to the best of our knowledge, the only prior published work explores the synthesis of Eu₂SO₄ and EuS nanoparticles.

HE nanomaterials, specifically HE oxides, have been produced using techniques ranging from spray pyrolysis to mechanochemistry and sonochemistry. These methods require high processing temperatures due to the high stability of oxide materials and also require strategies to reduce residence times so as to avoid agglomeration. HE chalcogenide nanomaterials have been produced via a number of “top-down” synthetic techniques including ion exchange, extended elemental annealing, and high-temperature pulsed annealing. Unfortunately, both of these elemental annealing procedures require high temperatures, while the ion exchange route is highly specific to particular materials and has so far only been demonstrated using copper sulfide as a parent structure. A “bottom-up” synthesis approach for HE nanomaterials has not yet been reported and would be highly attractive in allowing new high-entropy materials to be built atom by atom. Such a bottom-up design would represent a true tailored synthetic approach, which is something that does not exist currently for HE nanomaterials and is limiting progress in the field.

Focused on this goal, we report herein the first example of the synthesis of HE lanthanide oxysulfide nanoparticles with tunable composition and the potential for controlled morphology via a novel bottom-up strategy. The ability to control the composition of the nanoparticle via our precursor route allows for the direct comparison of a semiconducting HE material in bulk and nanoparticle form with near identical composition, thus allowing the first unambiguous observation of emergent properties produced purely by altering the size of the material.

In this study, we used the same selection of lanthanides as previously used in the synthesis of bulk HE Ln₂SO₄ materials. The chosen lanthanide elements are relatively closely grouped within the lanthanide series and have ionic radii within 0.1 Å. The theoretical maximum molar configurational entropy of mixing for an ideal HE Ln₂SO₄ sample, i.e., with equimolar proportions of each constituent metal element and a perfectly random distribution of the lanthanide elements, is calculated to be $S_m = 5.35 \text{ J K}^{-1} \text{ mol}^{-1}$ (see SI for details).

In previous work by Stoll et al., the thermogravimetric analysis profiles of the Ln precursors used in this work were discussed (see SI for detail on the synthesis and characterization of the molecular precursors). The Pr, Nd, and Gd...
precursors were shown to have similar decomposition profiles, decomposing fully between 250 and 400 °C. The Dy and Er precursors were found to follow a slightly different profile, decomposing at a lower temperature and doing so more gradually as the temperature increases, although the decomposition completes around 380 °C. We postulate that these different breakdown profiles may be responsible for the need to use a reduced amount of the Er precursor in order to produce nanoparticles with near equimolar elemental composition. As observed previously, even when using dried precursors, thoroughly degassed solvents and protective atmospheres, the oxophilicity of the lanthanides consistently leads to the production of the oxysulfide over the sulfide.

Studying the decomposition of the solid precursors is informative but can only be used to guide the synthesis, as decomposition of the europium precursor is possible in solution at the significantly lower temperature of 290 °C as shown by Gao et al. Relative to experiments done to produce bulk crystalline material, this is a substantial reduction in both the reaction time and reaction temperature. It was established that oleylamine, present both here and in the work of Gao et al., plays a complex role in the nanoparticle synthesis and likely plays a part in the decomposition of the precursor.

The X-ray diffraction pattern for the nanomaterial shows broad diffraction peaks, as expected for a nanocrystalline material, in positions that match our predicted pattern for the HE material (Figure 1). The peaks seen at 2θ ≈ 26, 29 and 47° are noticeably sharper than others, suggesting a significant proportion of plate-like nanoparticles extending outward in the (0001) plane. This is also expected, as oleic acid has been found to bind strongly to this plane and encourage lateral growth by stabilizing the (0001) surface. In order to deconvolute the effect of strain and crystallite size on the

Figure 2. HAADF-STEM images of HE Ln₂SO₄ nanoparticles at lower (a,e) and higher magnifications (b−d,f). The inset to (c) shows the FFT image of the highlighted area, demonstrating that the particle is being viewed along the [0001] direction, and the inset to (d) shows the crystal structure viewed along the same direction as the STEM image. The plot in (g) shows the HAADF STEM intensity profiles along the [10T0] and [01T0] directions marked out in (d). The plots in (h) and (i) show respectively the particle size distribution of nanocrystals along the longest lateral dimension (N = 190) and the distribution of thicknesses (N = 90).
diffraction peak broadening, we carried out Williamson-Hall analysis on the XRD data. This suggests that the broadening is dominated by the small crystallite size rather than strain; the crystallite size is predicted to be 7.86 ± 0.89 nm, with strain of 0.55 ± 0.13%. Further discussion is provided in the SI.

The high-resolution scanning transmission electron microscopy (HR-STEM) images confirm the formation of plate-like nanocrystals with the largest dimensions in the (0001) plane (Figure 2a−d). Analysis of the atomic resolution imaging data suggests good agreement with the predicted crystal structure as viewed along the [0001] direction (Figure 2d,g). The mean high-angle annular dark field (HAADF) STEM intensity of individual nanocrystals shows step changes, indicating that the nanoplates contain terraces of different thickness. Some orientations other than along the (0001) plane were also observed, but these appear to be partial rotations and so could not be indexed. The inset to Figure 2c shows the fast Fourier transform (FFT) image of the highlighted area, which matches predicted single crystal patterns along the [0001] zone-axis. Intensity profiles along the [10T0] and [01T0] directions are shown in the plot in Figure 2c, giving a direct measurement of the unit cell length averaged over the two directions as \(a = 3.72 ± 0.08 \text{ Å}\), which is contracted compared to our predicted \(a = 3.87 \text{ Å}\).

Figure 2f displays a size distribution of the mean lateral dimension of the (0001) basal plane determined from 190 particles in the image in Figure 2a, and Figure 2i also shows a distribution of nanoparticle thicknesses. From the latter analysis, we see a bimodal distribution of particle thicknesses, peaking between 1.0 and 1.2 and 1.6−1.8 nm, which corresponds to particles of two and three unit cells thick, respectively.

STEM energy dispersive X-ray (EDX) spectroscopic imaging confirmed a random distribution of all five lanthanide elements throughout the material with no signs of colocalization (Figure 3). Elemental quantifications from the summed
The chemical formula was determined to be $\text{Pr}_3\text{Gd}_{0.43}\text{Nd}_{0.43}\text{Er}_{0.43}\text{SO}_4$, which equates to a $S_m = 5.34 \text{ J K}^{-1} \text{ mol}^{-1}$, which is close to the theoretical maximum for this class of compound. S and O are not included in the compositional quantification due to the large error associated with EDX analysis of light elements, especially in the presence of the carbon support grid.

The optical absorption spectra of the nanoparticles display an absorption edge at approximately 330 nm (3.76 eV), with a significant increase in absorption intensity at approximately 250 nm (4.9 eV) as seen in Figure 4. A Tauc analysis was attempted, but a linear fit to obtain a bandgap was not possible, which we attribute to the bandgap being shifted into the UV-C region due to quantum confinement (vide infra). The absorption profile is significantly blue-shifted relative to that of the bulk samples produced in our previous work (Figure 4; $E_g = 3.7$ eV). This behavior is characteristic of the quantum confinement observed in quantum dots, where the increase in the bandgap is caused by the nanoparticle size being below the Bohr radius of the excitons in the bulk semiconductor.

The photoluminescence (PL) spectrum recorded using $\lambda_{ex} = 300$ nm gives a broad signal with a peak in intensity at approximately 410 nm. In comparison to reported work on bimetallic $\text{Gd}_{0.4}\text{Ce}_{0.6}\text{SO}_2$ nanoparticles, the PL spectra of the HE nanoparticles are shifted to shorter wavelengths, and the features are significantly broader. The emission spectrum does, however, have the same general shape, with the intensity tailing off more gradually toward longer wavelengths with a shoulder-like feature at 450 nm. We tentatively attribute this broadening to the increased complexity of the band structure due to the large number of elements in the sample. We also analyzed the time-resolved photoluminescence of the nanocrystals and were able to fit the curve to three photoluminescence lifetimes, the longest of which was $4.1 \pm 0.2$ ns (see SI for fitted time-resolved PL decay curve), which suggests a number of pathways are available for the decay of the luminescent state.

Comparing the optical properties of the HE nanomaterials to those of the bulk $\text{Ln}_3\text{SO}_4$ material we reported previously reveals that both the absorption and PL spectra are significantly blue-shifted in the former (Figure 4). The absorption onset is substantially shifted to higher energy (ca. 1.3 eV) compared to the bulk data we previously published. To investigate whether this is a surface or strain effect, we performed theoretical modeling using density functional theory (DFT; see SI for further details). To quantify the impact of strain, we predicted the change of bandgap of the five single-component lanthanide oxysulfide endpoints over a range of morphologies/particulate size, to tune the physical properties of these new systems. The most significant and deeper aspect resulting from this work therefore is the exciting prospect of unlocking new materials for a wide range of applications such as photonics and optoelectronics, photocatalysis and thermoelectric energy generation.
measurement and characterization, and details of the computational modeling and extended results (PDF).

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

B.W.-O’B. is funded by an EPSRC DTA studentship. D.J.L. and P.D.M. thank the EPSRC for funding (grant no. EP/R022518/1). TEM access was supported by the UK Catalysis Hub for resources and support provided via the membership of the UK Catalysis Hub Consortium and funded by EPSRC grant: P/R027129/1. J.M.S. and J.M.F. are supported by a UKRI Future Leaders Fellowship (MR/T043121/1). The calculations were performed using the UK ARCHER2 HPC facility, via J.M.S.’s membership of the UK Materials Chemistry Consortium, which is funded by the EPSRC (EP/R029431).

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