

# Synthesis and optical properties of naturally occurring fluorescent mineral, ferroan sphalerite, inspired (Fe,Zn)S nanoparticles

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**Abstract** Inspired by the naturally occurring fluorescent mineral, ferroan sphalerite, [(Fe,Zn)S] nanoparticles were synthesized by a three component reaction of  $[\text{Fe}(\text{Mes})_2]_2$  (Mes = mesityl or  $\text{C}_6\text{H}_2\text{Me}_{3-2,4,6}$ ),  $[\text{Zn}(\text{Et})(\text{ONep})(\text{py})]_2$ , and elemental S via both solution and solvothermal routes. The resultant nanoparticles are  $\leq 3$  nm and absorb at  $\lambda_{\text{max}} = 281$  nm emitting a bright blue color ( $\lambda_{\text{em}} \sim 400$  nm).

Nanocrystals of the semi-conducting materials cadmium and lead chalcogenides (CdE and PbE where E = S, Se, Te) have proven to be excellent optoelectronic materials and are being integrated into a wide variety of devices including: infrared sensors, photonic devices, and in various biological applications. Because of the quantum confinement effect, these materials can be used as “tags” for concurrent analysis of multiple event systems based on the particle size or color, since the size of these particles dictates the emission wavelength [1]. Unfortunately, the toxic properties of Cd and Pb could ultimately limit the widespread use of these materials for both electronic and biological research [2]. In an effort to synthesize luminescent materials that are lower in toxicity but still

possess the characteristics of the chalcogenide-based materials, we have been investigating the synthesis of various (non-lead and non-cadmium) based nanoceramic materials. Recently, our interests have focused on exploiting the naturally occurring fluorescent (NOF) minerals, a number of which are composed of what is classically thought to be inert cations. One NOF that possesses a simple composition with species that are considered benign is ferroan sphalerite or iron zinc sulfide [(Fe,Zn)S]. Naturally, occurring sphalerite is reported to have an absorbance that is highly dependent on the composition and size of the material [3–5].

Little work has been reported on the synthesis and properties of FeS nanoparticles, wherein the majority of research indicates that bulk FeS is a high-energy metastable structure with important magnetic, electronic and tribological properties [6, 7]. In contrast, studies involving the luminescent ZnS nanoparticles are widely reported [8–10]. For example, in a manganese doped zinc sulfide (ZnS:Mn) system, the PL spectra revealed an optical absorption that could be varied from 589 to 691 nm depending on the doping level and surface passivation agent [11]. Thin films of (Fe,Zn)S and single crystals of (Fe,Zn)S composite molecular species are being investigated for their magnetic susceptibility in diluted magnetic semiconductors, absorption coefficients, and band gap energy, which are attractive for solar energy conversion [12–15]. One study has reported on the synthesis of (Fe,Zn)S particles through reverse micelle processing using  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Na}_2\text{S}$  (the Fe precursor was not identified) [16]. Based on the measured band gap, the mean size of the (Fe,Zn)S particles were proposed to be nano, although no direct size evidence was reported.

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The synthesis of fluorescent ferroan sphalerite nanoparticles that emit at  $\sim 400$  nm was realized through solution and solvothermal routes.

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Since we were interested in investigating the nanoscale properties of NOF materials wherein the band gap could be manipulated for electronic (photonic) and biological (imaging) applications, ferroan sphalerite was our first attempt at synthesizing NOF materials.

The component nanomaterials species of the ferroan sphalerite (i.e., FeS and ZnS) are typically synthesized using commercially available precursors (i.e., nitrates, halides, sulfates, and carboxylates). A number of these are bidentate in nature that lends stability but limits reactivity. Therefore, the inclusion of others cations is restricted since the decomposition will depend upon the metal–ligand bond strength of each individual component. In contrast, metal alkoxides and alkyls have not been as widely used for ferroan sphalerite synthesis, possibly due to their high reactivity, lack of availability, and sensitivity to water that these precursors inherently possess. However, metal alkoxides are excellent precursors to both simple and complex ceramic materials due to the low temperature of decomposition, high solubility, the ease with which the hydrolysis and condensation rates can be manipulated. Further, metal alkoxides tend to oligomerize due to the low charge to radius ratio that often leads to facile incorporation of alternative cations. We have synthesized a variety of metal alkoxide precursors and established novel routes using these precursors to generate complex ceramic nanoparticles [17–19]. In addition, metal alkyls are often thought to be too reactive for materials production; however, we have recently proven this family of reagents to be valuable for nanoparticles synthesis using the mesityl (Mes = C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>) derivatives to generate coinage metal nanoparticles [20].

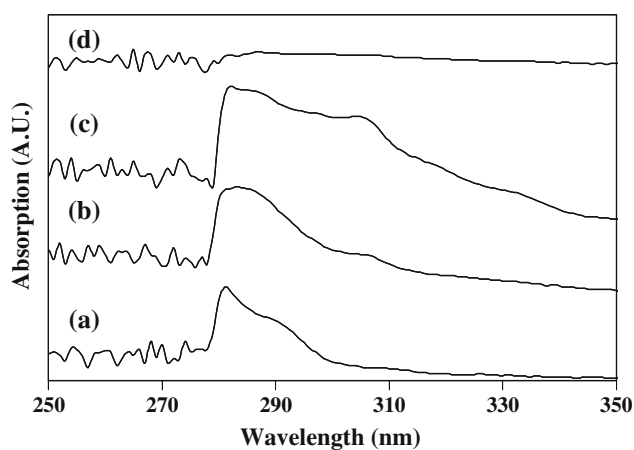
Combining these synthetic precursor families, we were successful in generating nanoparticles of the ferroan sphalerite NOF materials [21] by mixing iron (II) mesityl ([Fe(Mes)<sub>2</sub>]<sub>2</sub>) [20] and the pyridine (py) adduct of zinc ethyl neo-pentoxide ([Zn(Et)(ONep)(py)]<sub>2</sub> [19] where ONep = OCH<sub>2</sub>CMe<sub>3</sub>). This mixture was heated in toluene to reflux temperatures (~200 °C). To this mixture elemental sulfur, dissolved in octadecene (ODE), was injected and a brown precipitate formed immediately. After cooling to room temperature, the mother liquor was separated from the precipitate. The mother liquor shown in Fig. 1 is pale yellow in natural light but appears pale blue (~400 nm) under a hand held multi-wavelength UV light. Powder XRD of the precipitate and dried mother liquor revealed an amorphous nature of the material that is indicative of the presence of nanoparticles.

A UV–vis spectrum of this solution (diluted) revealed an absorption maximum at 281 nm along with a shoulder near ~290 nm (Fig. 2a). By altering the

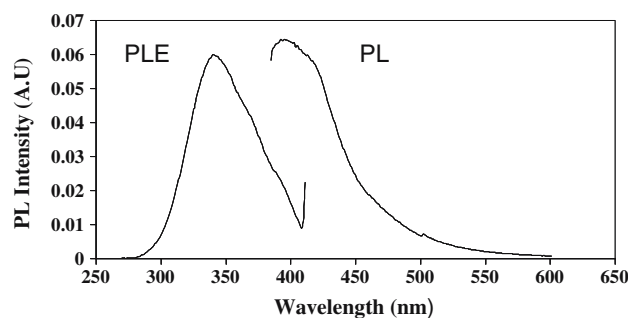


**Fig. 1** Solution of synthesized ferroan sphalerite nanoparticles under (a) white light and (b) UV light from handheld emitter

ratio of [Fe(Mes)<sub>2</sub>]<sub>2</sub> to [Zn(Et)(ONep)(py)]<sub>2</sub> [4], the UV–vis absorption was shifted as noted in Fig. 2b and 2c. No absorption was observed when the largest ratio of Fe stoichiometry was used (Fig. 2d) which is consistent with the literature reports on FeS. This decrease may be a result of having excess (Fe<sup>2+</sup> and Fe<sup>3+</sup>) paramagnetic species, which are known to decrease fluorescence [22]. The widths of the UV–vis absorption peaks indicated a variation in size distribution of these sphalerite nanoparticles. The photoluminescence excitation (PE = 320 nm) and emission (PLE = 397 nm) spectra of Fe/Zn ratio = 0.33 is shown in Fig. 3 and are similar to results observed with ZnS nanoparticles found in the literature [23, 24]. While the peaks were broad, the PL spectral emission was sharp enough to deduce that the sphalerite nanoparticles were excited simultaneously, implying a relatively pure



**Fig. 2** UV–vis absorption spectra of (Zn,Fe)S where the Fe/Zn ratio = (a) 0.5:95 [from Fe(Mes)<sub>2</sub> precursor], (b) 5:95 [from Fe(ONep)<sub>2</sub> precursor], (c) 25:75 [from Fe(Mes)<sub>2</sub> precursor], (d) 75:25 [from Fe(Mes)<sub>2</sub> precursor]



**Fig. 3** Photoluminescence excitation (PLE) and emission (PL) spectra for (Zn,Fe)S from  $\text{Fe}(\text{Mes})_2$  precursor where the Fe/Zn ratio = 0.33

sample was used. The transmission electron microscopy (TEM) image shown in Fig. 4 reveal polydispersed particles on the order of  $\leq 3$  nm; however, attempts to obtain high resolution TEM images of these particles were not successful. Energy dispersive spectroscopy (EDS) analysis quantitatively confirmed the presence and ratios of the Fe, Zn, and S atoms. Alternative precursors for the synthesis of the sphalerite NOF nanoparticles were investigated such as alkyl derivatives (i.e.,  $\text{Zn}(\text{Et})_2$ ) for the Zn precursors and alkoxides (i.e., “ $\text{Fe}(\text{ONep})_2$ ”) for the iron precursor coupled with alternative processing routes (i.e., a Parr acid digestion bomb) in a variety of organic solvents (i.e., toluene, hexanes). Every route using the alkoxide and/or alkyl precursors led to ferroan sphalerite materials with identical analytical characteristics. Adsorption data for (Fe,Zn)S synthesized from the “ $\text{Fe}(\text{ONep})_2$ ” is shown in Fig. 2b. Combined, these alternative routes eliminated any possibility of an organic moiety causing the emission characteristics observed and thus the fluorescence can only be

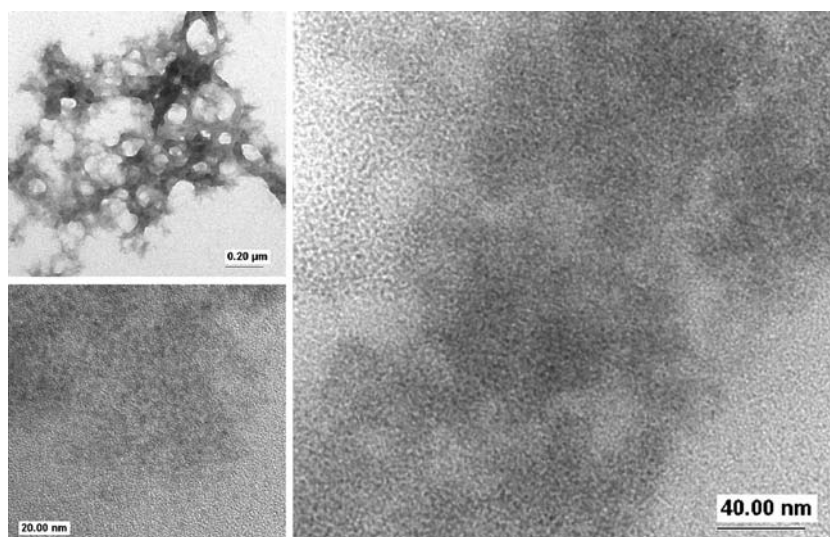
attributed to the inorganic sphalerite NOF nanoparticles.

Several experiments are underway to grow larger sphalerite nanoparticles using solvothermal routes. In addition, we are currently examining a number of routes to generate water-soluble derivatives of these particles for materials [25, 26] and biological [27] applications. While preliminary encapsulation results with CTAB interdigitation are encouraging, our inability to separate the particles from excess surfactant has been problematic in utilizing the more biologically relevant PEG-phospholipid method [27]. Further work to optimize this process is underway.

### Conclusion

Inspired by the naturally occurring fluorescent (NOF) mineral ferroan sphalerite, luminescent [(Fe,Zn)S] nanoparticles were synthesized using various solvothermal and solution routes. These nanoparticles were shown to be  $\leq 3$  nm and found to emit a blue luminescent color ( $\sim 400$  nm) when excited in the UV. While altering the Fe/Zn cation stoichiometry gave only subtle changes in the absorption/emission spectra, these studies indicate that NOF-inspired nanoparticles could possibly provide an alternative to the potentially toxic cadmium and lead chalcogenide based nanomaterials and warrant further investigation. The band-gap of these sphalerite nanoparticles is being optimized through various (non-toxic) cation doping and particle size effects to tune the absorption and emission wavelengths. These results, as well as the biological applications of NOF-nanoparticles will be reported shortly.

**Fig. 4** TEM micrographs of the sphalerite nanoparticles



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21. *General Synthesis of (FeZn)S Nanoparticles*. Two routes were explored to synthesize the ferroan sphalerite nanoparticles. All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glove box techniques. Octadecene and toluene were stored under argon and used as received (Aldrich) in SureSeal™ bottles. (A) The first route used a mixture of [Fe(Mes)<sub>2</sub>]<sub>2</sub> (0.022 g, 0.037 mmol) and [Zn(Et)(ONep)(py)]<sub>2</sub> (0.25 g, 0.69 mmol) dissolved in 25 mL of toluene. This solution is placed in three-neck round bottom equipped with a reflux condenser and a septum. Under flowing argon, the solution is brought to reflux conditions (~200 °C) and 1 mL of a solution of S (0.023 g, 0.73 mmol) dissolved in octadecene was injected via syringe. A turbid dark brown solution formed immediately and the mixture stirred for 30 min at reflux conditions then was cooled to room temperature. After centrifugation, a yellow mother liquor and brown precipitate was collected. (B) The second route used a 48 mL Parr acid digestion bomb. In the glove box, 15 mL of toluene was added to [Fe(Mes)<sub>2</sub>]<sub>2</sub>, [Zn(Et)(ONep)(py)]<sub>2</sub>, and elemental sulfur in the Teflon vessel. The reaction was heated at 10 °C/min to 200 °C and held at this temperature for 48 h. After cooling, a turbid dark brown solution was collected and centrifuged. Again, a yellow mother liquor and brown precipitate was isolated. An aliquot of the particles dispersed in the mother liquor was placed directly onto a Carbon Type-B copper Transmission Electron Microscopy (TEM). TEM grid (300 mesh) purchased from Ted Pella, Inc. The aliquot was then allowed to dry overnight. The resultant particles were studied using a Philips CM 30 TEM operating at 300 kV accelerating voltage
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