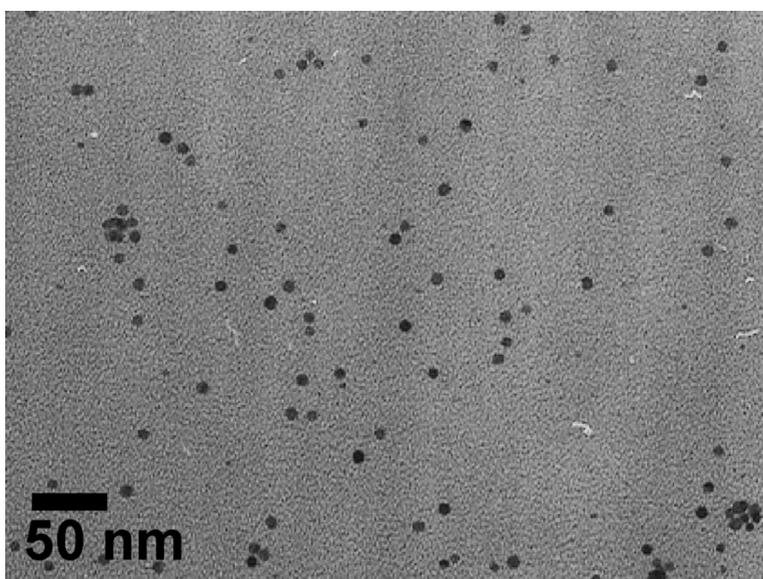


Phase Control in the Synthesis of Magnetic Iron Sulfide Nanocrystals From a Cubane-Type Fe₄S Cluster

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Phase Control in the Synthesis of Magnetic Iron Sulfide Nanocrystals From a Cubane-Type Fe–S Cluster

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The sulfides of iron exhibit a wide range of properties ranging, for example, from semiconducting, nonmagnetic pyrite (FeS_2) to the ferromagnetic, metallic Fe_3S_4 .¹ The synthesis of iron sulfide solids is challenging as small variations in stoichiometry often leads to large changes in the structural, chemical, and physical properties. Unsurprisingly, the synthesis of the more reactive and less stable nanoscopic forms² of the above solids is a significant challenge.

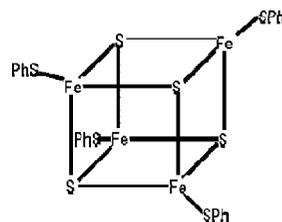
Presently, there is widespread interest in nanoscopic forms of materials, due to their unique properties and potential for applications. Uses in medicine³ and cell separation⁴ have been foreseen for nontoxic, magnetic iron sulfide nanocrystals. Recent advances have resulted in fairly mature synthetic schemes for metal sulfides such as CdS.^{5,6} However, methods suited for complex solids such as iron sulfides are rather rare.

Magnetotactic bacteria are known to synthesize intracellular pyrrhotite and greigite nanocrystals.⁷ Artificially, precipitates of pyrrhotite nanowires⁸ and polydispersed greigite nanocrystals⁹ have been obtained by solvothermal means. Nanosheets of pyrrhotite and greigite have been obtained by decomposition of iron thiocarbamate based complexes.¹⁰ A network of pyrrhotite nanorods and nanosheets have been obtained by a high temperature process.¹¹ While it is possible to obtain low-dimensional nanostructures, it has been impossible to obtain high-quality dispersions of magnetic iron sulfide nanocrystals. Our interest is to devise a reliable synthetic scheme for dispersible magnetic iron sulfide nanocrystals, drawing on our previous experiences in this area.^{5,12} Herein, we have prepared and characterized nanocrystalline iron sulfide particulates employing a single source precursor (SSP), $[\text{N}^n\text{Bu}_4]_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$, bis(tetra-*n*-butylammonium) tetrakis[benzenethiolato- μ_3 -sulfido-iron],¹³ a cubane-type cluster (**1**, Scheme 1).

We find that **1** cleanly decomposes under extended reflux in alkylamines to yield nanocrystals whose composition, structure, and dimensions are dependent on the temperature employed. X-ray diffraction patterns of the iron sulfide nanocrystals obtained at 180 °C (octylamine) and at 200 °C (dodecylamine) are in Figure 1. At 180 °C, pyrrhotite type Fe_7S_8 nanocrystals were obtained. The reflections are characteristic of the pyrrhotite 4M (JCPDS 00-029-0723) structure. This specific pyrrhotite substructure is a lower symmetry (monoclinic) modification of the normally hexagonal solid and is observed in iron sulfide crystals grown at low temperatures.^{1,10} Nanocrystals obtained at the higher temperature are of the composition Fe_3S_4 with greigite structure (JCPDS 00-016-0713). Cubic greigite is a thiospinel, the sulfide analogue of magnetite. Bulk forms of both pyrrhotite 4M and cubic greigite are noted metallic ferromagnets. The former is a two-dimensional magnet.

Energy dispersive X-ray analysis of the pyrrhotite nanocrystals revealed Fe/S ratios of 1:1.15, close to the expected ratio 1:1.14. In the case of Fe_3S_4 nanocrystals the experimentally obtained ratios ranged from 1:1.33 to 1:1.35.

Scheme 1. Structure of the Anionic Part of 1: Bis(tetra-*n*-butylammonium) Tetrakis[benzenethiolato- μ_3 -sulfido-iron]



Transmission electron microscopic (TEM) images reveal that the octylamine capped Fe_7S_8 nanocrystals are uniform and spherical with an average diameter of 5.6 nm (Figure 2). A large fraction of nanocrystals are present as individuals. TEM images of Fe_3S_4 nanocrystals obtained at higher temperatures (200–230 °C) using longer chain amines are shown in Figure 3. In all cases, spherical nanocrystals, similar to ones above, are obtained. In addition to causing changes to the structure and composition of nanocrystals,

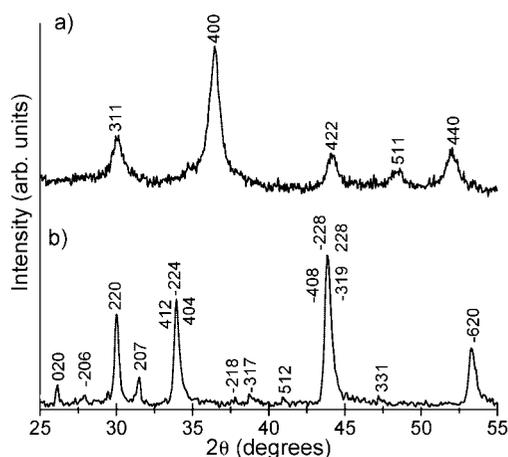


Figure 1. X-ray diffraction patterns of nanocrystals obtained by decomposing **1** at (a) 200 °C, dodecylamine; (b) 180 °C, octylamine.

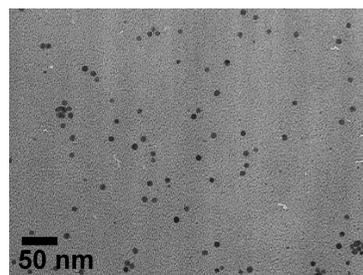


Figure 2. TEM image of octylamine capped Fe_7S_8 nanocrystals.

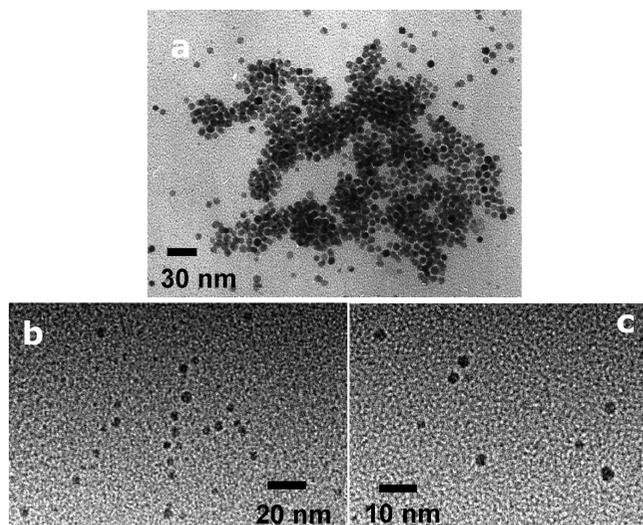


Figure 3. TEM image of Fe_3S_4 nanocrystals obtained using (a) dodecylamine, at 200 °C; (b) hexadecylamine, at 215 °C; (c) oleylamine, at 230 °C.

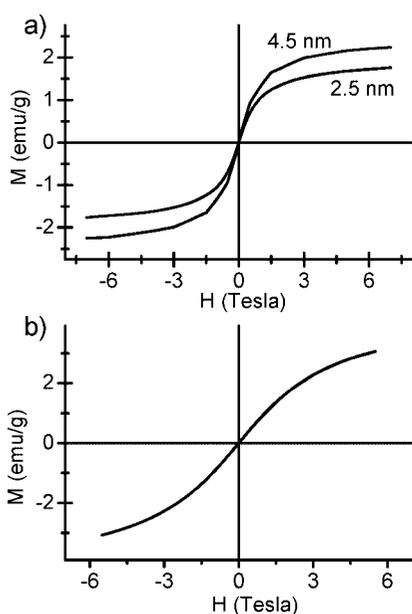


Figure 4. Hysteresis loops obtained from (a) Fe_3S_4 nanocrystals; (b) Fe_7S_8 nanocrystals. The loops in (a) correspond to nanocrystals of different diameters. The diameters of the nanocrystals are indicated.

the growth temperature also affects the dimensions of the crystallites. The increase in temperature from 200 to 230 °C results in the average diameter of the nanocrystals falling from ~ 4.5 to ~ 2.5 nm. This can be attributed to higher temperatures promoting a burst of rapid nucleation following the injection of the precursor, resulting, ultimately, in smaller particles as more effective nucleation depletes the monomer availability. XRD patterns indicate that all particulates obtained at higher temperatures are cubic with greigite structure.

Magnetic hysteresis measurements on dry dispersions of nanocrystals reveal that the particulates are superparamagnetic at room temperature (Figure 4). The Curie temperature of bulk Fe_3S_4 is reported to be 527 °C¹⁴, while it is 310 °C¹⁵ for Fe_7S_8 . Therefore, the observed behavior is in line with expectations from fine

particulate systems. The intensity of magnetization (in emu/g) is clearly greater for the larger greigite nanocrystals and is possibly due to a higher Fe content. Despite the similarity in overall behavior, the phases are distinguishable from each other by the distinctive gradients around the point (0,0) in the hysteresis loops. The gradient is lower for the greigite nanocrystals. The physical origins of this change are not clear. It is not a size related phenomena as samples of pyrrhotite with differing sizes exhibit similar gradients.

The phase purity and morphological control obtained using **1** are indeed remarkable. Such tight control over these two critical parameters has hitherto not been possible in iron sulfides presumably due to their complex nature.

The cluster **1** is virtually unexplored as an SSP. However, **1** and related complexes have been extensively studied as synthetic analogues to the metal sites in iron–sulfur proteins such as rubredoxin and bacterial ferredoxin.¹³ As a result, it is possible to obtain such clusters in high yields from inexpensive and readily available reagents. We envisage that these complexes could be valuable SSPs to iron sulfide materials.

In conclusion, **1** is a very effective precursor for the synthesis of iron sulfide nanocrystals. Morphology, phase, and particle size can be controlled by carrying out thermolysis at different temperatures in alkylamines. Temperatures below 200 °C result in spherical pyrrhotite nanocrystals with the composition Fe_7S_8 . Higher temperatures yield greigite- Fe_3S_4 nanocrystals. The diameters of the Fe_3S_4 nanocrystals can be varied in the range 2.5 to 4.5 nm. Both Fe_3S_4 and Fe_7S_8 nanocrystals are superparamagnetic.

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Supporting Information Available: Experimental procedures for the synthesis of **1** and additional TEM images of iron sulfide nanocrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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