equipped with a 150 lines mm⁻¹ grating and registered by an optical multichannel analyzer (OMA, Hamamatsu Photonics, PMA50).

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[15] Note that data represented by Fig. 4 are relevant for a practitioner who needs to select appropriate dopant for the given laser wavelength, e.g., custom available and low-cost second harmonic of the Nd:YAG laser.

Synthesis and Characterization of Magnetic Iron Sulfide Nanowires

By Manashi Nath, Amitava Choudhury, Asish Kundu, and C. N. R. Rao*  

A variety of inorganic nanowires have been synthesized in the last three to four years.[1] Among these, magnetic nanowires are of interest because of their potential applications in magnetic recording and other areas. Nanowires and nanorods of magnetic metals, such as Fe, Co, and Ni,[2] and their alloys[3] have been prepared by employing template-directed synthesis. Although there are reports of nanotubes, nanorods, and nanowires of several metal chalcogenides,[4,5] oxides,[6] and nitrides,[6,7] there is no report to date on iron sulfide nanowires, possibly because of the inherent difficulty in the synthesis and control of stoichiometry of these materials. The Fe–S system has a complex phase diagram, with broad range of compositions of Fe₁₋ₓS (pyrrhotite) phases[7] occurring between FeS and FeS₂, showing interesting magnetic[8–10] and electrical properties.[11] FeₙSₘ is a well-defined phase in this region, showing ferrimagnetism with Tₘ = 600 K.[9] We deemed it important to synthesize iron sulfide nanowires by virtue of their interesting chemistry and magnetic properties. In this communication, we report the first successful synthesis of semiconductor nanowires of Fe₁₋ₓS (x = 0.12, 0.09), of which the Fe₉₅S₅ (Fe₇S₈) nanowires are ferrimagnetic, showing magnetic hysteresis at room temperature.

In order to synthesize Fe₁₋ₓS nanowires, a hybrid composite (I) with ethylenediamine was first prepared by solvothermal procedure (see Experimental). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the composite I showed the presence of a high yield of lengthy nanowires with diameters in the range of 80–150 nm and lengths of several micrometers as shown in Figure 1. The infrared (IR) spectrum showed characteristic peaks of the amine, although the bands due to C–N and N–H stretching frequencies were considerably shifted towards lower values due to the bound nature of the amine. Energy dispersive X-ray (EDX) analysis of several samples of I carried out over different regions of each sample gave an average Fe/S ratio of

![Image](image_url)

Fig. 1. a) SEM image of the organic–inorganic composite, Fe₁₋ₓS(eth)_x. I. b) Low-magnification TEM image of composite I. Apart from nanowires, some layer-rolled kind of structures are also observed (as seen in the center of the image).
~0.7–0.81. The C, H, N analysis of I gave the percentages to be 11.2462, 3.8355, and 11.9318 %, respectively, corresponding to the nominal formula, Fe\(_{1-x}\)S(en)\(_{0.5}\) (x = 0.2–0.3, en = ethylenediamine). Thermogravimetric analysis of I showed a sharp weight loss around 200 °C due to the loss of the amine bound to the metal center.[12] The powder X-ray diffraction (XRD) pattern of I showed the presence of a low-angle line at ~8 Å, in addition to broad, weak reflections. The low-angle line is similar to that found in many of the organic–inorganic composites of CdE and ZnE (E = S, Se) containing metal-chalcogen layers pillared by an amine.[12,13] The nanowires of Fe\(_{1-x}\)S(en)\(_{0.5}\) were paramagnetic, showing insulating behavior at room temperature.

The amine in I could be removed partially under vacuum. It could, however, be removed completely by heating I to 200–300 °C under Ar flow (200 sccm, standard cubic centimeters per minute), yielding pure inorganic Fe\(_{1-x}\)S nanowires (see Experimental). IR spectra of I heated to 200 °C and 300 °C (designated as II, III, respectively) showed the absence of the peaks corresponding to the amine. The XRD patterns of II and III were characteristic of pyrrhotite phases (prominent lines at d = 2.98, 2.63, 2.05, 1.72 Å).[14]

The SEM image of II in Figure 2a shows an abundant presence of nanowires with lengths of the order of micrometers. EDX analysis of individual nanowires revealed a Fe/S ratio of 0.88:1, indicating the composition to be Fe\(_{1-x}\)S. Low-magnification TEM images of II (Fig. 2b) show the diameters to be in the range 40–180 nm. High-resolution TEM (HRTEM) images show the presence of different domains with interesting lattice fringes (Fig. 2c), but they all belong to the same crystallographic phase. The inset in A shows the simulated fast Fourier-transform (FFT) pattern obtained from the boxed region of the HRTEM image corresponding to a hexagonal close-packed (hcp) lattice with a hexagonal arrangement of the spots that can be indexed to the (204) plane of the 4C phase of Fe\(_{1-x}\)S\(_{8}\) (a = 12.811, b = 6.870, and c = 11.885 Å, \(\beta = 117.17^\circ\), JCPDS file, card number: 29-0723). The layer spacing obtained from the lattice fringes from a different part of the image is ~2.6 Å, corresponding to d(004) of 4C-Fe\(_{1-x}\)S\(_{8}\). The electron diffraction (ED) pattern in the inset in B shows spacings of 3.2, 2.6, and 1.7 Å due to the (202), (004), and (040) planes, respectively. The d(004) spots in the ED pattern show splitting due to superstructures of Fe\(_{1-x}\)S\(_{8}\). 4C-Fe\(_{1-x}\)S\(_{8}\) is known to be a stable, ordered phase at room temperature.[74]

The SEM image of III in Figure 3a reveals the presence of a large proportion of nanowires. EDX analysis on these nanowires showed the composition to be Fe\(_{1-x}\)S with x = 0.08–0.1, showing that the amine composite heated at a higher temperature (300 °C) to be less Fe deficient. Low-magnification TEM images show the presence of short nanowires of 80–100 nm diameter in addition to rolled structures as can be seen from Figure 3b. The rolled structures are not nanotubes or scrolls, but are incompletely folded structures. The HRTEM image of the nanowires shows the lattice fringes marked by the presence of alternate dark and light strips, indicating the presence of a two-layer periodicity. The distance between two dark strips is ~5.6 Å, while that between the
light strips is ~2.9 Å, which correspond to the (102) and (200) planes of 5T-Fe_{1-x}S phase [JCPDS file, card number: 29-0724]. The ED pattern from the nanowires shows spots due to (200), (205), and (220) reflections of the 5T-pyrrhotite phase (a = 6.888 and c = 28.670 Å).

Most pyrrhotites exhibit some superstructures as a result of the Fe vacancy ordering, giving rise to varied magnetic and electrical properties and complex phase relations.\(^{[5-31]}\) The ordered structure of Fe_{x}S that can be achieved by the maximum separation of iron vacancy sites is formed by the alternation of partially filled Kagome net layers with fully filled iron layers, i.e., there is an Fe vacancy in every alternate layer. The structure of Fe_{1-x}S (x = 0.1) is based on the Fe_{7}S_{8} structure, where partially filled kagome net layers and iron filled layers are stacked in such a way that long-range order is established along the c-direction.

The temperature variation of the magnetic susceptibility of II (Fig. 4a) shows a ferrimagnetic behavior with a transition temperature of ~600 K, characteristic of Fe_{7}S_{8}.\(^{[9]}\) The Weiss-type behavior can be reversed upon cooling with a thermal hysteresis of 20–25 K. More importantly, nanowires, II, show a hysteresis loop at room temperature (297 K) (see

![Fig. 3](image3.png)

**Fig. 3.** a) SEM image of the 300 °C heat-treated product. III, showing a good yield of the nanowires. b) TEM image of III showing some incompletely rolled structures along with nanowires. c) HRTEM image of the nanowires showing periodic stacking of the layers in some region. The inset shows the ED pattern obtained from the nanowires.

![Fig. 4](image4.png)

**Fig. 4.** a) The temperature variation of the magnetic susceptibility between 300-650 K of II. The inset shows the hysteresis loop obtained at 297 K. b) The temperature variation of the susceptibility between 300-650 K of III showing peak-type transition in the heating cycle.
The synthesis procedure of Fe$_\text{II}$S$_2$ nanowires comprises two steps. In the first step, solvothermal methods have been employed to obtain an organic–inorganic composite (I). Fe$_\text{II}$S$_2$(en)$_2$. The amine removal from this composite by heating under a flow of Ar at 200–300 °C yielded nanowires of Fe$_\text{II}$S$_2$. Preparation of the Organic–Inorganic Composite: I. A typical synthesis procedure, FeCl$_2$·4H$_2$O (0.298 g, 1.5 mmol) was mixed with CH$_3$CN:H$_2$O (thio-acetamide, 0.2254 g, 3 mmol) in a Teflon-lined steel autoclave (23 ml capacity) and 10 mL ethylenediamine was added to it. The container was sealed and heated to 180 °C for 4 days under solvothermal conditions. A purple-blackish wool-like flocculate was obtained, which was immediately sonicated in methanol, filtered, washed with methanol, and dried in vacuum. It should be noted that the as-synthesized product is always stored under vacuum as longer exposure to air under ambient conditions leads to conversion of the iron-sulfide phases to the oxide/hydroxide phases. For this reason, after opening the autoclave, sonication and filtration were carried out in minimum time.

Synthesis of Fe$_\text{II}$S$_2$ (II) and Fe$_\text{II}$S$_3$ (III) Nanowires by Amin Removal from the Composite: I. The composite I was taken in a quartz boat and placed inside a quartz tube, which was put in a horizontal tubular furnace. The sample was heated under a flow of Ar (200 scm) to 200–300 °C and kept at that temperature for 20–30 min. The furnace temperature was allowed to come down to room temperature naturally before taking out the product. The color of the reactant powder changed to black after the thermal treatment. Fe$_\text{II}$S$_2$ nanowires (II) were obtained at 200 °C, while at 300 °C, Fe$_\text{II}$S$_3$ (x = 0.08–0.11) nanowires (III) were produced.

Characterization: The samples were characterized by powder XRD (Seifert 3000T), SEM (Leica S440 fitted withLeo software for EDX analysis), TEM (JEOL JEM 3010, operating at 300 kV), IR spectroscopy (Bruker IFS-66V/S). Magnetic measurements were carried out using a VSM (LakeShore) and by the Faraday technique (Lewis Coil force magnetometer, George Associates).

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Experimental

Molecular-Scale Interface Engineering of TiO$_2$ Nanocrystals: Improving the Efficiency and Stability of Dye-Sensitized Solar Cells**

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During the last decade, dye-sensitized solar cells (DSCs) have attracted considerable interest as low-cost alternatives to conventional inorganic photovoltaic devices.[1–3] Although an impressive 10 % solar-to-electricity conversion efficiency could be attained with a panchromatic dye, the achievement of long-term stability at temperatures of ~80–85 °C has remained a major challenge for a long time. Very recently, an amphiphilic heteroleptic ruthenium sensitizer referred to as Z-907 (cis-Ru(H$_2$dpb)(dnpy)(NCS)$_2$), where the ligand


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