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# Effect of temperature on structural and optical properties of iron sulfide nanocrystals prepared from tris(*N*-methylbenzyldithiocarbamato) iron(III) complex

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#### ABSTRACT

Tris(*N*-methylbenzyldithiocarbamato)iron(III) complex was used to prepare iron sulfide (FeS) nanocrystals, Fe**S1** at 120, FeS**2** at 180 and FeS**3** at 240 °C. P-XRD revealed that the nanocrystals FeS**1** and FeS**2** are in hexagonal pyrrhotite, Fe<sub>3</sub>S<sub>10</sub>, crystalline phase whereas FeS**3** nanocrystal is in pyrrhotite-6C, Fe<sub>11</sub>S<sub>12</sub>, crystalline phase. TEM images showed nanocrystals with an average diameter of 5.42 and 25.07 nm for FeS**1** and FeS**2**, respectively, while cluster of iron sulfide with an average particle size of 6.40 nm was obtained for FeS**3**. The optical band gaps obtained from the Tauc plots are 3.90, 3.90 and 3.96 eV for FeS**1**, FeS**2** and FeS**3** nanocrystals, respectively, which indicate blue shifts ascribed to quantum confinement. ARTICLE HISTORY Received 29 May 2019

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KEYWORDS Dithiocarbamate; iron(III); iron sulfide; nanocrystals; XRD

#### Introduction

Interest in the preparation and study of nanomaterials are due to their fascinating properties that offer potential applications in many fields such as medicine,<sup>[1]</sup> energy storage,<sup>[2]</sup> catalysts for industrial transformations and communications.<sup>[3,4]</sup> Nanocrystals are relatively small particles with diameter in the range 1–100 nm.<sup>[5,6]</sup> They exhibit unique optical and structural properties with respect to corresponding bulk materials. Their physical properties such as the small size distributions, surface morphologies and crystalline nature result in noticeable quantum confinement effect.<sup>[7,8]</sup> Optical properties of nanocrystals depend on the crystal size of their internal structure.<sup>[9]</sup> Thus, as the size of the crystal becomes smaller, more atoms are accommodated on the crystal surface that enhances the optical properties resulting in exceptionally reactive nanocrystals.<sup>[10]</sup>

As particle is reduced toward nanoscale level, it approaches the de Broglie wavelength of the valence electrons of atoms composing the nanocrystal and behaves as if it were "free."<sup>[11,12]</sup> When this happens, quantum confinement results whereby the electronic energy levels in the nanocrystal become discrete.<sup>[13]</sup> Thus the electrical and optical properties of nanocrystals differ remarkably from those of the bulk materials.<sup>[14]</sup> It is of paramount importance to control the morphology of small particles especially nanocrystals. Small ligands lead to small single source precursors that decomposes cleanly during thermolysis and influences the particle sizes of as-prepared nanocrystals by balancing the growth ratio of different crystallographic surfaces.<sup>[15]</sup> Several methods have been reported for the preparation of metal sulfide nanocrystals among which the single source precursor method is preferred because it is convenient, efficient and yields facile and reproducible monodispersed nanocrystals.<sup>[16-18]</sup> Although metal dithio-carbamates have been used to prepare metal sulfide nanocrystals, the resultant structural attributes of the nanocrystals depend on the reaction conditions such as the temperature, concentration of the precursor and capping agents.<sup>[19–22]</sup> In continuation of our effort to prepare iron sulfide nanocrystal from iron(II/III) dithiocarbamate complexes,<sup>[23–26]</sup> we present the use of tris(*N*-methylbenzyldithiocarbamato)iron(III) complex as precursor to prepare iron sulfide nanocrystals at 120, 180 and 240 °C to study the effect of thermolysis temperature on the crystallite sizes of the as-prepared nanocrystals

#### Experimental

#### Materials and characterization techniques

All chemicals and reagents were procured from Merck and used as supplied. Potassium *N*-methylbenzyldithiocarbamate was synthesized using a revised literature procedure.<sup>[23,27]</sup> Fourier-transform infrared (FTIR) spectra were recorded in the range  $4000 - 650 \text{ cm}^{-1}$  using a Perkin Elmer 100 FTIR spectrometer. Thermogravimetric analysis (TGA) was achieved by a Perkin-Elmer TGA 4000. The analysis was performed under nitrogen atmosphere with a heating rate of 20 °C/min and recorded from 50 °C to 950 °C. Powder X-ray diffraction patterns of the nanocrystals were obtained from a Bruker D8 advance diffractometer using Cu K $\alpha$ 

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Figure 1. TGA curves for the decomposition of tris(*N*-methylbenzyldithiocabamato)iron(III).

radiation. The samples were flattened on flat steel sample holder and scanned at a  $2\theta$  range of 5° – 85°. Transmission electron micrographs were acquired from JEOL JEM-2100 electron microscope while the SAED patterns and lattice fringes were obtained from a high resolution transmission electron microscopy (HRTEM) JEOL JEM-2100 electron microscope. Field emission scanning electron micrographs were acquired by a ZEISS FEGSEM Ultra plus and EDS spectra from an EDS attached to the ZEISS FEGSEM Ultra plus apparatus with an accelerating voltage of 20 kV. Absorption measurements of the nanocrystals were obtained by a Perkin Elmer Lambda 25 spectrophotometer while the photoluminescence measurements were obtained by a Perkin Elmer LS-45 luminescence spectrometer.

#### Synthesis of tris(Nmethylbenzyldithiocarbamato)iron(III) complexes

An aqueous solution of iron(III) chloride hexahydrate (10 mmol, 2.70 g) was added dropwise to an aqueous solution of potassium *N*-methylbenzyldithiocarbamate (30 mmol, 6.22 g) and stirred for 4 h until complete precipitation. Dark-grey precipitate obtained was filtered, washed several times with ethanol then with diethyl ether and desiccated. Yield (%): 79, m.p (°C): 182, selected IR,  $\nu$ (cm<sup>-1</sup>): 2925 (C-H), 1489 (N-C), 1193 (C-S).

#### Synthesis of iron sulfide nanocrystals

Tris(*N*-methylbenzyldithiocarabamato)iron(III) dissolved in 3 mL of oleic acid (OA) was injected into hot 5 g of octadecylamine (ODA) and rapidly stirred. The reaction was maintained at 120 °C, 180 °C or 240 °C under nitrogen. After 1 h, the reaction mixture was allowed to cool to about 70 °C after which an excessive quantity of ethanol was added, and the nanocrystals were isolated by centrifugation. The obtained iron sulfide nanocrystals were labeled FeS1, FeS2, and FeS3 prepared at 120 °C, 180 °C and 240 °C, respectively.

## Synthesis of iron sulfide hydroxyethyl cellulose nanocomposites

Solution casting method was used to prepare the iron sulfide/HEC nanocomposites. An aqueous viscous hydroxyethyl cellulose (HEC) (0.5 g) was stirred for 1 h at 60 °C, followed by addition of iron sulfide nanocrystals (0.015 g) in THF and continued stirring rapidly at 60 °C for 1 h to allow the HEC to interact with the nanocrystals. The contents were then transferred into a petri-plate and dried in open atmosphere.

#### **Results and discussion**

#### Analysis of the tris(Nmethylbenzyldithiocarbamato)iron(III) complex

The complex was obtained as a dark-grey powder in substantial yield (78%) with a melting point of 182 °C. The FTIR showed bands at  $2925 \text{ cm}^{-1}$ , ascribed to the alkyl (C-H) stretch. The band at  $1491 \text{ cm}^{-1}$  was due to the v(N-C). A single band in the region 950–1050 cm<sup>-1</sup> was observed due to the v(C-S) signifying the bidentate coordination of the dithiocarbamate ligand to the metal ion. To evaluate whether the complex is a suitable single-source precursor for the preparation of the nanocrystals, thermogravimetric analysis (TGA) was utilized. The thermal decomposition profile of the complex is shown in Figure 1. The decomposition occurred in two steps, first step at around 402 °C ascribed to the loss of the phenyl group. The second step occurred at about 512 °C, indicating the loss of the DTC moiety.

### *Powder X-ray diffraction (P-XRD) studies of iron sulfide nanocrystals*

Powder X-ray diffraction is a nondestructive procedure used to study crystalline phases of materials.<sup>[28]</sup> It allows the determination of the structural parameters of crystalline materials such as the phase, average crystal size and crystallinity. The crystalline phases of the iron sulfide nanocrystals were identified by means of P-XRD. The P-XRD patterns of the FeS1, FeS2 and FeS3 nanocrystals obtained at 120, 180



Figure 2. P-XRD patterns of the nanocrystals. Where \* = oleic acid and \*\* = octadecylamine.

and 240 °C, are shown in Figure 2. Miller indices were determined using the Bragg's law ( $\lambda = 2d\text{Sin}\theta$ ) combined with the plane spacing equation.<sup>[23,29]</sup> The diffraction patterns of FeS1 and FeS2 iron sulfide nanocrystals at  $2\theta = 19.07$ , 27.66°, 29.63°, 43.13°, 46.95° and 51.64°

correspond to (001), (111), (220), (400), (320) and (422) miller indices of hexagonal pyrrhotite,  $Fe_9S_{10}$  crystalline phase [ICDD Ref Code: 040-020-0793]. The diffraction patterns of FeS3 nanocrystals obtained at 240 °C appear at  $2\theta = 19.73$ , 27.28, 39.62, 43.69°, 47.35° and 51.46° indexed



Figure 3. TEM micrograph (a), lattice fringes (b) and SAED patterns (c) of FeS1 nanocrystals prepared at 120 °C.

to (001), (111), (200), (201), (320) and (220) crystallographic planes of pyrrhotite-6C,  $Fe_{11}S_{12}$  [ICDD Ref Code: 04-017-9146] crystalline phase. The P-XRD patterns of the iron sulfide nanocrystals showed capping agents as indicated by asterisks in the diffraction patterns.

#### Morphological studies of iron sulfide nanocrystals

The thermolysis temperature of precursor play significant role in the structural features such as the particle size, shape and crystalline phase of the as-prepared nanocrystals.<sup>[30]</sup> TEM images, lattice fringe and SAED patterns of the iron sulfide nanocrystals are shown in Figures 3–5. The TEM

micrograph of FeS1 nanocrystals obtained at  $120 \,^{\circ}\text{C}$  show spherically shaped nanocrystals with average diameter of about 5.42 nm (Figure 3). The SAED patterns are not uniformly distributed and the lattice fringes are not equidistant which suggest that the particles have a mixture of both crystalline and amorphous iron sulfide nanocrystals.

The FeS2 obtained at  $180 \,^{\circ}$ C show mixture of cubic and spherically shaped nanocrystals having an average particle size of 25.07 nm with sharp ring and organized SAED patterns (Figure 3) which indicates that the particles are crystalline. The lattice fringes are equidistant without any lattice divergence. This suggests that the particles are crystalline as confirmed from the SAED patterns.



Figure 4. TEM micrograph (a), lattice fringes (b) and SAED patterns (c) of FeS2 nanocrystals prepared at 180 °C.

When the temperature was raised to  $240 \,^{\circ}$ C, a mixture of clustered iron sulfide nanocrystals and some smaller particles with diameter of 6.00 nm as shown in Figure 5. The lattice fringes are not well defined and the SAED patterns show some sharp spots with diffused rings which imply that the nanocrystals obtained at that temperature consist of both amorphous and crystalline materials.

FESEM was used to study the surface morphology of the iron sulfide nanocrystals and the EDS was used to verify the existence of the Fe and S atoms. FESEM images and EDS spectra of the iron sulfide nanocrystals obtained at 120, 180 and 240 °C are shown in Figure 6. FESEM image of FeS1

iron sulfide nanocrystals, shows leaf-like and irregular surface morphology while the EDS spectrum displays the elemental composition of the iron sulfide nanocrystals. The EDS spectra also show the presence of some carbon and oxygen atoms which are from the carbon tape used to mount the sample and excess capping agent. FESEM image of FeS2 iron sulfide nanocrystals, shows thick grass-like morphology with white patches attributed to octadecylamine capping agent. FESEM image of FeS3 iron sulfide nanocrystals shows thin grass-like morphology that appeared white on the surface ascribed to the presence of excess capping agent on the nanocrystals. The change observed in the surface



Figure 5. TEM micrograph (a), lattice fringes (b) and SAED patterns (c) of FeS3 nanocrystals prepared at 240 °C.

morphologies of the iron sulfide nanocrystals suggest that temperature influences the observed surface morphologies of the as-prepared nanocrystals.

#### **Optical studies of iron sulfide nanocrystals**

The absorption and emission spectra of the iron sulfide nanocrystals are presented in Figure 7. Absorption spectra (Figure 7a) display sharp peaks at 281, 283 and 283 nm for FeS1, FeS2 and FeS3 obtained at 120 °C, 180 °C and 240 °C, respectively, which suggest the as-prepared iron sulfide have small particle sizes that are blue shifted due to quantum confinement of the nanocrystals with respect to their bulk materials. Consequently, the emission maxima are observed at 394, 393 and 394 nm. Absorption band edges and emission maxima for nanocrystals obtained at different temperatures are very similar and are red shifted. This implies that the thermolysis temperature has little effect on the absorption and emission properties of the as-prepared iron sulfide nanocrystals.

The optical band gaps (Eg) of the iron sulfide nanocrystals were obtained from their absorption measurements using the Tauc plot method.<sup>[31]</sup> In this paper, we make use of the electron transition  $n = \frac{3}{2}$  which denotes that we are examining the forbidden transition for a  $d^5$  transition metal ion.<sup>[23]</sup> The Tauc's linear region was extrapolated to  $(\alpha hv)2 = 0$ , to establish



Figure 6. FESEM micrographs and EDS spectra of the nanocrystals.

the optical band gaps of the iron sulfide nanocrystals as shown in Figure 7c.<sup>[32,33]</sup> FeS1, FeS2 and FeS3 iron sulfide nanocrystal were found to be 3.90, 3.90 and 3.96 eV, respectively. The optical band gap of the nanocrystals thermolyzed at different temperatures are very similar, which indicates that temperature, has little effect on the optical band gap of the as-prepared iron sulfide nanocrystals.

#### FTIR spectra studies of iron sulfide/HEC nanocomposites

HEC is an organic compound consisting of hydroxyl and aldehyde groups on its chains.<sup>[34]</sup> It is distinguished by its

good water solubility and biocompatibility which makes it very suitable for pharmacological applications.<sup>[35,36]</sup> The iron sulfide nanocrystals were synthesized for potential cytotoxicity application but they lack solubility and could be toxic to the normal cells. So, in this study, the nanocrystals were coated with the HEC to improve their solubility and toxicity. The interaction of the iron sulfide nanocrystals and the HEC was investigated by FTIR spectroscopy and the results presented in Figure 8. The FTIR spectrum of the pure HEC shows the v(O-H), v(C-H), v(C=O) and v(C-O) stretching frequencies<sup>[37,38]</sup> and similar bands are observed for all the iron sulfide/HEC nanocomposites with



Figure 7. Absorption spectra (a), emission (b) spectra and Tauc plots of nanocrystals from tris(*N*-methylbenzyldithiocarbamato)iron(III) thermolyzed at 120, 180 and 240 °C.



Figure 8. FTIR spectra nanocomposites.

diminished intensities in FeS1/HEC and FeS2/HEC while FeS3/HEC is much pronounced than the HEC and the other two nanocomposites. This suggests the combination of HEC and the FeS1 or FeS2 nanocrystals leads to lower vibrational bands in the composites suggesting that nanocrystals are notably small. These changes confirm the interaction between the nanocrystals and HEC.

The FESEM surface morphology and EDS of the iron sulfide/HEC nanocomposites presented in Figure 9. FESEM micrograph of FeS1/HEC morphology appeared leaf-like or flake-like and some with hollow surfaces. FESEM image of FeS2/HEC shows the surface of the nanocomposites to be rough with small spherically shaped particles. The overall surface contained about four sheets or layer structures and some white particles. EDS shows peaks from Fe and S confirming the presence of iron sulfide nanocrystals within hydroxyethyl cellulose. The FeS3/HEC image shows almost smooth sheet-like morphology with some rough/contour on the surface which might be ascribed to the nanocomposites molded-like nature.

#### Conclusions

Iron sulfide nanocrystals were prepared from thermolysis of tris(N-methylbenzyldithiocarbamato)iron(III) complex in octadecylamine and oleic acid at 120, 180 and 240 °C to investigate the effect of thermolysis temperature on the structural and optical properties of the as-prepared iron sulfide nanocrystals. Powder XRD confirmed that FeS1 and FeS2 iron sulfide nanocrystals obtained at 120 °C and 180 °C, are in pyrrhotite (Fe<sub>9</sub>S<sub>10</sub>) crystalline phase whereas FeS3 iron sulfide nanocrystals obtained from the same complex at 240 °C is in the pyrrhotite-6C (Fe<sub>11</sub>S<sub>12</sub>) crystalline phase. The TEM images showed various iron sulfide shapes and sizes of 5.42, 25.07 and 6.40 nm for FeS1, FeS2 and FeS3 nanocrystals, respectively. The nanocrystals obtained at 180°C are monodispersed with high degree of crystallinity. The absorption band edges and emission maxima for the iron sulfide nanocrystals were similar with optical band gap of 3.90, 3.90 and 3.96 eV for FeS1, FeS2 and FeS3 nanocrystals, respectively. The interaction of the HEC polymer with iron sulfide nanocrystals was studied by FTIR and showed



Figure 9. FESEM micrographs and EDS spectra of iron sulfide/HEC nanocomposites.

that the iron sulfide nanocrystals are well dispersed into HEC matrix. FESEM showed leaf-like with triangular hollow spheres for FeS1/HEC nanocomposites whilst rough small spherically shaped particles and smooth sheet-like with rough surface were obtained for FeS2/HEC and FeS3/HEC nanocomposites, respectively.

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