

SYNTHESIS AND CHARACTERIZATION OF COPPER SULFIDE AND COPPER-IRON SULFIDE NANOPARTICLES

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Abstract

Copper sulfide and copper-iron sulfide nanoparticles were prepared from bis(N-(pyrrol-2-ylmethyl)-N-butylthiocarbamate-S,S')copper(II) (1) and bis(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamate-S,S')-copper(II) (2), respectively and they were characterized by PXRD, TEM, EDS, UV-Vis, photoluminescence and FT-IR spectroscopy. The TEM images of copper-iron sulfide reveals that the particles are spherical and oval shaped, respectively.

Key words: Copper(II) Dithiocarbamates; Copper Sulfide; Copper-Iron Sulfide; Photodegradation.

Introduction

Dithiocarbamate ligands, have found ample use in coordination chemistry [1,2]. Their wide range of applications e.g. industry, agriculture and medicine has generated a large collection of crystallographic data for their metal complexes [3]. Dithiocarbamates are versatile ligands capable of stabilizing transition metals in both high and low oxidation states [4] and complexes of Cu(I), Cu(II) and Cu(III) are all known, being interconvertible via reversible one-electron redox process [5]. Metal sulfides can also serve as an important semiconductor photocatalysts which offer the potential for complete elimination of toxic chemicals [27]. Here in we report synthesis, characterization and anion sensing properties of copper(II) dithiocarbamate complexes containing pyrrole and ferrocene moieties. In addition, synthesis, characterization and photocatalytic activities of copper sulfide and copper-iron sulfide nanoparticles, which are synthesized from as-prepared from **2-4**, are also presented.

Experimental

2.1. Materials and techniques

Reagent grade chemicals were purchased from commercial sources and used as such. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer (range: 4000–400 cm^{-1}) as KBr pellets. A Shimadzu UV-1650 PC double-beam UV-vis spectrophotometer was used for recording the electronic spectra. The spectra of complexes were recorded in CHCl_3 and the pure solvent was used as the reference. PXRD was performed using EQUINOX 1000, respectively. TEM images were recorded using TECNAI T2 G2 make-FEI, respectively. EDS were performed by SUPRA 55VP CARL. Photoluminescence spectra were recorded using Perkin Elmer 1555 fluorescence spectrophotometer at room temperature.

2.3. Preparation of Copper sulfide and Copper-iron sulfide

0.5 g of **1** was mixed in 15 ml triethylenetetraamine in a round bottom flask and then the content of the flask was refluxed for 15 minutes. The black precipitate obtained was filtered off and washed with methanol. Similar procedure was adopted for the preparation of copper-iron sulfide from **2**.

Characterization of copper sulfide and copper-iron sulfide nanoparticles

Copper sulfide and copper-iron sulfide nanoparticles obtained from complexes **1** and **2** are represented as copper sulfide and copper-iron sulfide, respectively. The XRD patterns of copper sulfide and copper-iron sulfides are shown in **Figure 1** (a) and (c). The diffraction pattern of the dominant phase in copper sulfide is Cu_9S_5 in cubic with major diffraction peaks of (0015), (1010), (0114), (110), (0027), (1112) and (2017) planes (JCPDS card No: 47-1748). The diffraction patterns of the copper-iron sulfide are indexed to the cubic phase of Cu_5FeS_4 with characteristic (111), (200), (220), (331) and (222) planes (JCPDS card No: 73-1667). In the case of copper-iron sulfide, the diffraction peaks at $2\theta = 29.45^\circ$, 48.67° and 58.0° are assigned to the (111), (220) and (311) planes of cubic structure (JCPDS Card No: 81-1378). The XRD patterns of copper sulfide and copper-iron sulfide are good quality being indicative of good crystallinity and presence other phases.

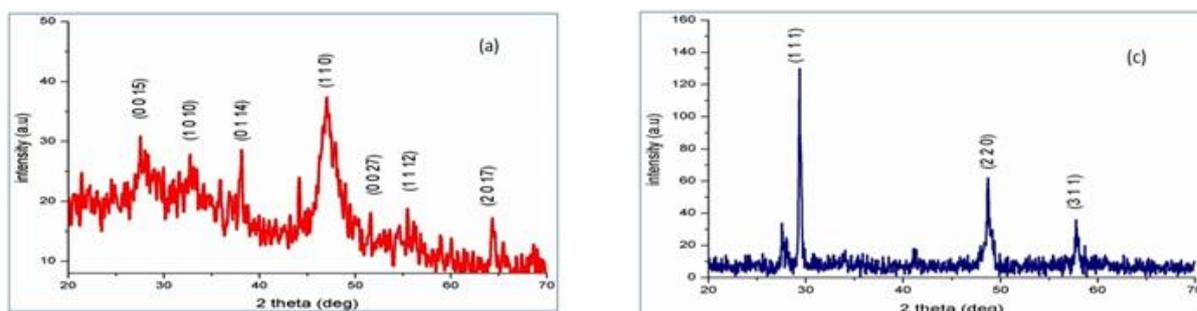


Figure 1. Powder X-ray diffraction pattern of (a) Copper sulfide and (c) Cobalt-iron sulfide

The morphology of the as-prepared metal sulfide nanoparticles were investigated by TEM analysis. TEM images of copper sulfide and copper-iron sulfides are shown in **Figure 2**. The TEM image of copper sulfide particles obtained from complex **1** are close to spherical with diameter in the range 10-18 nm (Fig. (a) and (b)). TEM image of copper-iron sulfide reveals that the shapes of the particles are spherical (diameter = 11-20 nm) Fig. 2 (d) and (e).

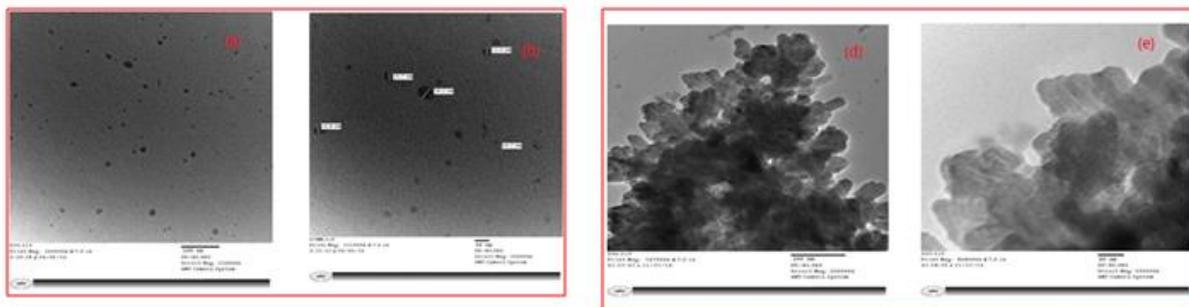


Figure 2. TEM image of (a & b) Copper sulfide and (d & e) Cobalt-iron sulfide

The elemental composition of copper sulfide and copper-iron sulfide nanoparticles was investigated. Energy dispersive X-ray spectra of products obtained from complexes **1** and **2** are shown in **Figure 3**. The energy-dispersive x-ray spectrum of the product obtained from solvothermal decomposition of complex **1** reveals the formation of copper sulfide. The atomic ratio of Cu:S (9:5.6) shows that there is some vacancy of Cu^{2+} ions or some sulfur dangling bands are present in the sample. EDS analysis of copper-iron sulfide and **2** indicate the presence of two metals (Cu and Fe) and sulfur. The Cu:Fe:S ratio of copper-iron sulfide are 3.5:1.0:3.7, respectively.

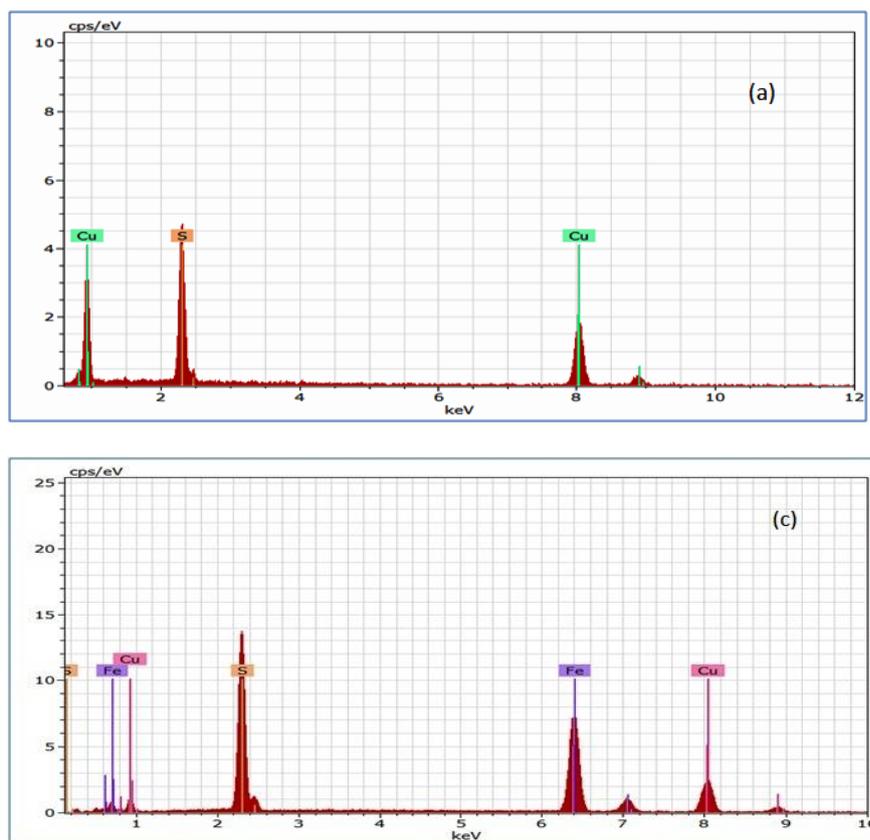


Figure 3. Energy dispersive spectroscopy of (a) Cobalt sulfide of (c) Cobalt-iron sulfide

The expected Cu:S and Cu:Fe:S ratio for copper sulfide (Cu_9S_5) and copper-iron sulfide (Cu_5FeS_4) from powder X-ray diffraction studies are 9:5 and 5:1:4, respectively. But the ratios observed from EDS are different. This supports the presence of various phases. In the case of copper-iron sulfide-2 (CuFe_2S_3) the ratio of Cu:Fe:S determined from PXRD (1:2:3) and EDS (1:2:2.8) are almost same.

Figure 4 illustrate the UV-vis absorption spectra of copper sulfide and copper-iron sulfide nanoparticles dispersed in distilled ethanol at room temperature. A broad band appeared at 272 nm for copper sulfide whereas as band at 270 nm and a weak band 260 nm are observed for copper-iron sulfide-1, respectively. Compared with the bulk copper sulfide [54], the absorption maxima of copper sulfide and copper-iron sulfide nanoparticles exhibit a large blue shift, which is attributed to the quantum confinement of charge carriers in the nanoparticles.

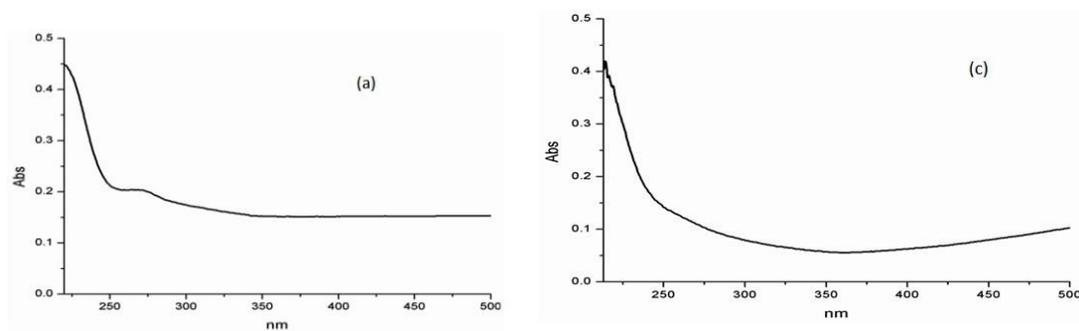


Figure 4. UV-Vis spectra of (a) Copper sulfide of (c) Cobalt-iron sulfide

Figures 5 show the photoluminescence spectra recorded at room temperature for copper sulfide and copper-iron sulfide nanoparticles. The emission spectra of both the nanoparticles exhibit a peak around 400 nm

corresponding to the band-edge emission. Along with this emission another red shifted intense peak observed at 432 nm in the spectrum of copper-iron sulfide. The red-shifted emission results from the trap related electron-hole recombination.

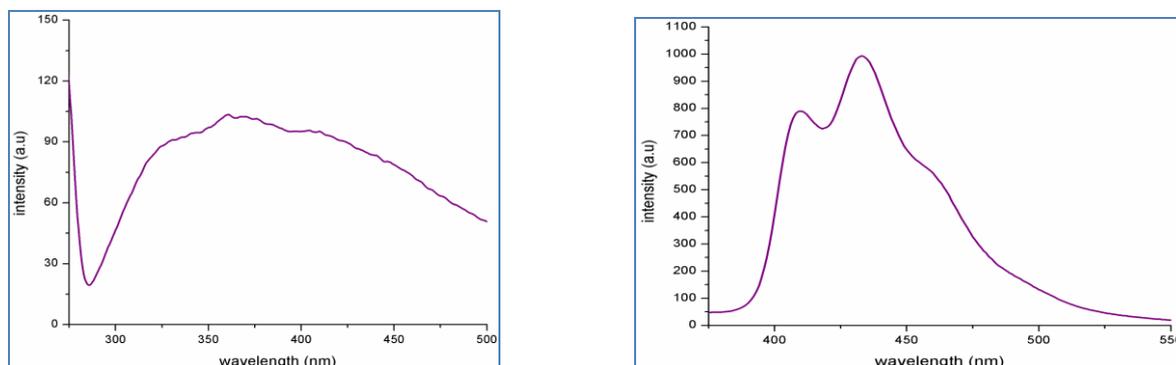


Figure 5. Photoluminescence spectrum of copper sulfide & copper-iron sulfide

IR spectra of copper sulfide and copper-iron sulfide nanoparticles (**Figures 6 & 7**) exhibit three bands in the region $2850 - 2964 \text{ cm}^{-1}$ due to aliphatic $\nu_{\text{C-H}}$. The bands in the region $3415 - 3485 \text{ cm}^{-1}$ are assigned to N-H stretching vibrations. These data indicate the presence of capping agent triethylenetetraamine in the copper sulfide and copper-iron sulfide. The lack of aromatic C-H and N- CS_2 stretching vibration indicate the absence of dithiocarbamate ligands in the as-synthesized copper-iron sulfide nanoparticles.

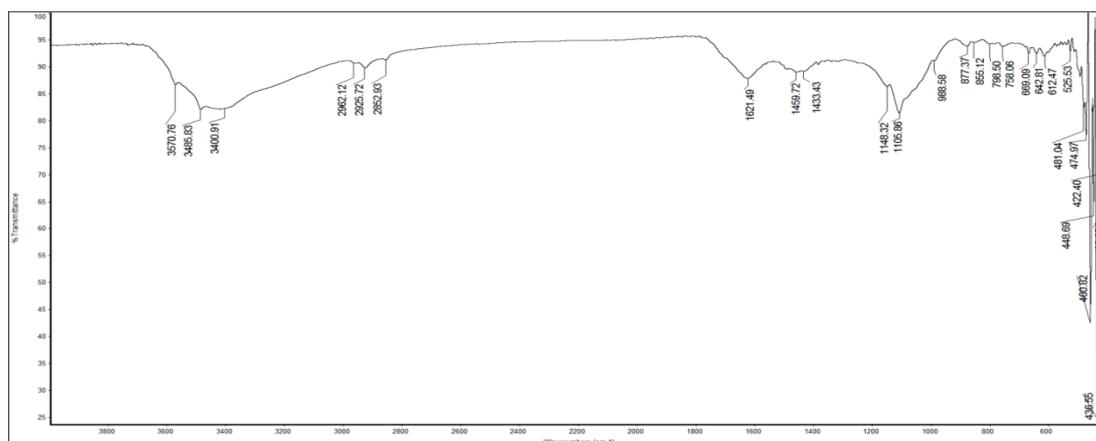


Figure 6. FT-IR spectrum of copper sulfide

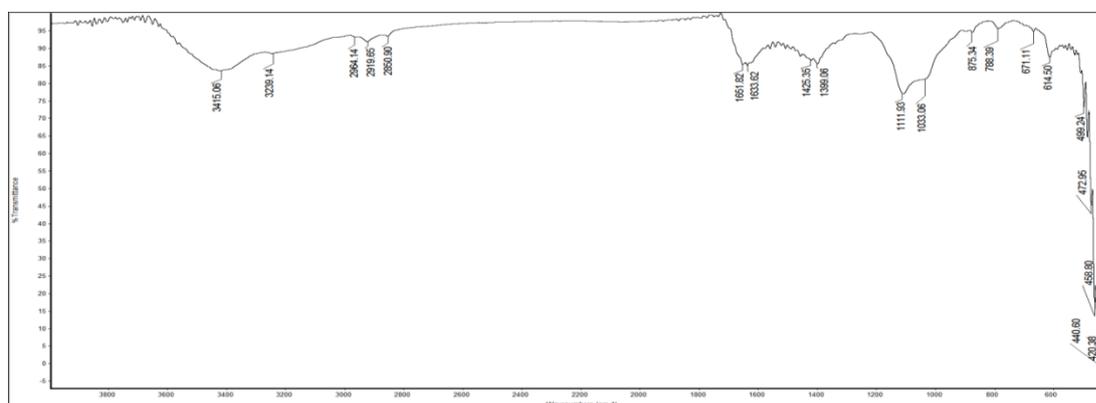


Figure 7. FT-IR spectrum of copper-iron sulfide

Conclusions

Copper(II) dithiocarbamate complexes (**1** and **2**) containing pyrrole and ferrocene moieties were prepared and characterized. This study demonstrates spherical shape copper sulfide and copper-iron sulfide and oval shape copper-iron sulfide can be prepared from copper dithiocarbamate complexes. Copper-iron sulfide (bimetallic) nanoparticles revealed better photocatalytic activity for the photo degradation of methylene blue and rhodamine-B under UV light compared to copper sulfide (monometallic). This study indicates that preparation of new copper(II) dithiocarbamate complexes containing various N-bound organic moiety is useful for sensing anions and preparing effective photocatalysts (copper sulfide and copper-iron sulfide nanoparticles with various shape).

References

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