

Synthesis and Characterization of Cobalt Sulfide and Cobalt-Iron Sulfide Nanoparticles from Cobalt(III) Dithiocarbamate Complexes

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Abstract: Tris(N-(pyrrol-2-ylmethyl)-N-butyldithiocarbamato-S,S')cobalt(III) (1), bis(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamato-S,S')nickel(II) (2) complexes were used as single source precursors for the preparation of cobalt sulfide and cobalt-iron sulfide nanoparticles. Morphological characterization of nanoparticles was carried out using TEM and the optical properties by UV-Vis and photoluminescence spectroscopic techniques. The elemental compositions of the nanoparticles were confirmed by energy dispersive X-ray spectroscopy. IR spectral studies on nanoparticles confirm the presence of capping agent (triethylenetetramine).

Keywords: Cobalt(III) dithiocarbamate; cobalt sulfide; cobalt-iron sulfide; nanoparticles; single source precursors

INTRODUCTION

A wide range of metal-dithiocarbamate complexes is known with examples finding use in applications as diverse as industry, agriculture, medicine and material science [1-7]. Metal sulfide nanoparticles have shown vital applications in many fields as an advanced material such as IR detectors [6], photocapacitors for energy conversion and storage [7], sensors [8], photonic materials [9] and advanced optoelectronic devices [10]. In recent years, transition metal dithiocarbamate complexes have received a great deal of attention because of their importance as single source precursors for the preparation of metal sulfide nanoparticles [11,12].

EXPERIMENTAL

Materials and Instrumentation

Reagent grade chemicals were procured from commercial sources and used as such. The synthesis of the compounds was carried out under an inert-gas atmosphere of nitrogen. Solvents were purified according to standard procedures and dried before use whenever required. IR spectra were recorded on a thermo NICOLET AVATAR 330 FT-IR spectrophotometer. The ¹H/¹³C NMR spectra were recorded on BRUKER 400/100 MHz NMR spectrometer at room temperature in CDCl₃ solvent. SHIMADZU UV-1650 PC double beam UV-visible spectrophotometer was used for recording the electronic spectra of the complexes.

Photocatalytic experiments

The photocatalytic activity of cobalt sulfide and cobalt-iron sulfide was evaluated by degradation of aqueous solution of methylene blue and rhodamine-B. All the solutions were prepared using double distilled water. A typical photocatalytic experiments, 0.1 g of catalyst was added to 50 ml of an aqueous solution of rhodamine-B in the concentration of 1.0 X 10⁻⁴ M. The solution was maintained under

darkness for 30 min to reach dye solution adsorption–desorption equilibrium. The solution with the suspended nano-photocatalyst was irradiated by UV light from mercury vapour lamp. At given time intervals, 3ml of aliquots was withdrawn and centrifuged to remove catalyst, concentration of both dye solution was determined with the help of UV-Vis spectrophotometer.

Preparation of Cobalt sulfide and Cobalt-iron sulfide

0.5 g of **2** 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 cobalt-iron sulfide from **2**.

RESULTS AND DISCUSSION

Characterization of metal sulfide nanoparticles

The morphological characterization of both nanoparticles were carried out using TEM and is shown in **fig.1**. Spherical and ring shapes of cobalt sulfide nanoparticles are clearly seen from the TEM images (**fig. 1 (a)**). Spherical nanoparticles have average diameter of 20 nm. The diameter of the nanorings and cavity are 15 nm and 4 nm, respectively. TEM image (**fig.1(b)**)

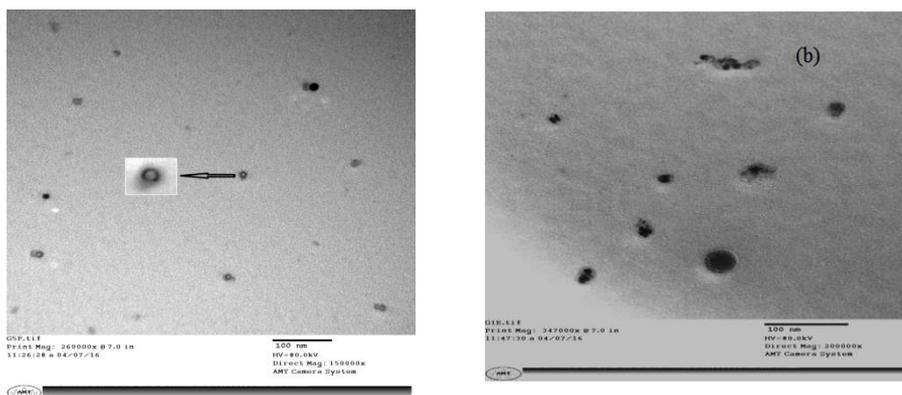


Fig. 1. TEM images of cobalt sulfide and cobalt-iron sulfide nanoparticles demonstrated that cobalt-iron sulfide are perfect spherical and quasispherical in shape and the particles diameter are in the range 11-35 nm. .

To confirm the chemical composition of the products, cobalt sulfide and cobalt-iron sulfide are analyzed using Energy dispersive X-ray spectroscopy (EDS). Energy dispersive X-ray spectra of cobalt sulfide and cobalt-iron sulfide nanoparticles are displayed in **fig. 2**. This confirms the formation of cobalt sulfide and cobalt-iron sulfide nanoparticles.

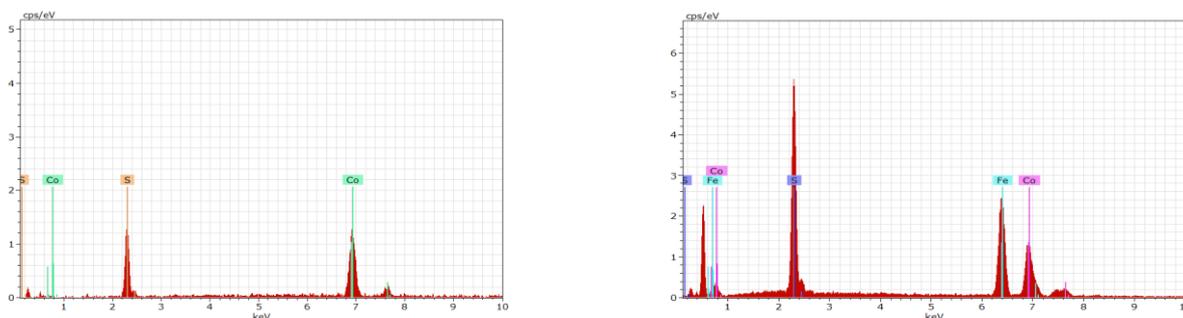


Fig. 2. EDS of cobalt sulfide and cobalt-iron sulfide nanoparticles

Optical properties of cobalt sulfide and cobalt-iron sulfide were studied by the UV-vis absorption and photoluminescence (PL) spectroscopic techniques and are shown in **Fig.3 and 4**. The room temperature absorption and emission spectra were recorded by displaying the samples in ethanol. Optical absorption spectra of cobalt sulfide exhibit a band at 276 nm, which is blue shifted from the absorption edge of the bulk cobalt sulfide [13], indicating great influence of small size of cobalt sulfide nanoparticles. The absorption band further shifted towards the shorter wavelength in cobalt-iron sulfide (264 nm). The PL spectra of cobalt sulfide and cobalt-iron sulfide show a sharp peak at 552 nm and a broad peak at 422 nm, respectively. These are due to the radiative transition of electrons from shallow trap states near the conduction band to sulfur vacancies residing near the valance band [14, 15].

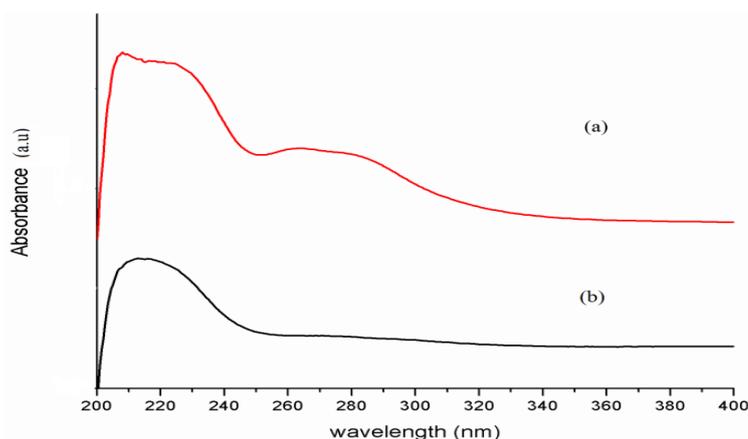


Fig. 3. UV-Vis spectra of cobalt sulfide and cobalt-iron sulfide nanoparticles

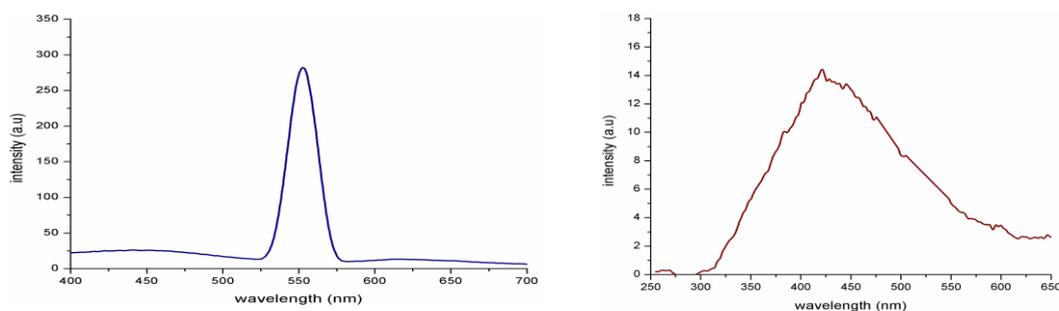


Fig. 4. Photoluminescence spectra of cobalt sulfide and cobalt-iron sulfide nanoparticles

In IR spectra of both metal sulfides, the bands in the region $2850\text{-}2960\text{ cm}^{-1}$ are assigned to C-H vibrations of the samples. A broad peak observed around 3400 cm^{-1} can be assigned to the N-H stretching mode. These observations suggest the presence of capping agent triethylenetetramine. The absence of bands around 1480 cm^{-1} and $3060\text{-}3150\text{ cm}^{-1}$ due to C-N (thioureide) and C-H (aromatic) stretching modes confirms that dithiocarbamate ligands are not present with the cobalt sulfide and cobalt-iron sulfide.

CONCLUSION

These complexes have been exploited as single source precursors for the preparation of cobalt sulfide and cobalt-iron sulfide nanoparticles. Cobalt sulfide and cobalt-iron sulfide nanoparticles were characterized using TEM, EDS, UV-vis, Photoluminescence and IR spectroscopy. TEM image of cobalt-iron sulfide nanoparticles demonstrated that the particles are spherical and ring shapes. We expect this simple approach can be used for the synthesis of monometallic and bimetallic sulfide semiconductor nanoparticles with different morphologies, compositions and properties from single source precursors.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGMENTS

The encouragement and support from Bharath University, Chennai is gratefully acknowledged. For provided the laboratory facilities to carry out the research work.

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