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Single molecular precursor route to nanocrystalline Jaipurite: Synthesis, characterization and magnetic property

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Abstract

Nanocrystalline cobalt monosulfide (Jaipurite) has been synthesized from corresponding cobalt xanthate complexes using solvothermal method. Thermolysis of cobalt tris ethylxanthate in ethylene glycol at 196 °C for 4 h yielded black particles of Jaipurite. The nanoparticles obtained were characterized using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). EDX analysis showed 63.90 wt.% of Co and 36.10 wt.% of S, which is in good agreement with the calculated wt.% of 63.98 for Co and 36.02 for S. The nanoparticles were found to be spherical with a diameter in the range of 7–9 nm. The magnetic property of the nanoparticles was measured by plotting M *vs* H hysteresis curves, at different temperature.

Keywords: Nanomaterials; Magnetic materials; X-ray techniques

1. Introduction

Transition metal sulfides are of interest for their application as catalysts, heavy metal sponge absorbents, chemical sensors, luminescent devices, superconductors and also in dry lubrication and ionic intercalation in secondary batteries [1–5]. Among the variety of transition metal sulfides, cobalt monosulfide (Jaipurite) is an important catalyst for hydrodesulferization and hydrodearomatization [6] and also shows interesting paramagnetic properties [7]. Conventionally, cobalt sulfide powders have been synthesized by mixing stoichiometric amounts of the constituent elements in an evacuated silica tube in the temperature range of 500–1200 °C [8,9]. However, the higher temperature required in this type of synthesis, leads to a larger particle size and inhomogeneity. Consequently, various low temperature synthetic routes like hydrothermal [10–13], solvothermal [14,15] and also microwave assisted techniques [16] have been developed to fabricate monodispersed cobalt sulfide nanocrystals. However, most of the work reported is on Co_9S_8 and CoS_2 phases of cobalt sulfide with only a couple of papers on synthesis of Jaipurite, *i.e.*, cobalt monosulfide [17,18]. In this paper, we report for the first time, a single molecular source precursor route to nanocrystalline cobalt monosulfide using corresponding cobalt xanthate complexes which act as single molecule precursors. Single source precursors are discrete molecules that contain all the elements required in the final material. These precursors can be designed with many properties in mind, including stoichiometry and reduce the chances of impurities in the final product. Recently, we have reported a facile cleavage of carbon sulfur bond in metal xanthates, which can be used as single source precursors for indium sulfide [19,20]. We have also synthesized $CuInS_2$ nanoparticles by solvothermal treatment of stoichiometric mixtures of copper and indium xanthates [21]. In the above perspective, it was considered worthwhile to explore the chemistry of cobalt xanthates with the hope that these complexes would serve as single source precursors for cobalt sulfides.

2. Experimental

In a typical reaction procedure, aqueous solution of $CoCl_2 \cdot 6H_2O$ and NaS_2COEt (prepared by the reaction between ethanol

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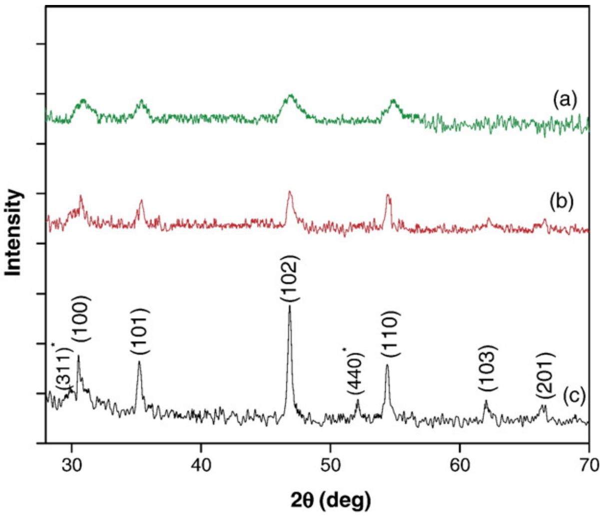

Fig. 1. XRD patterns of β-CoS nanoparticles obtained by solvent thermolysis of $Co(S_2COEt)_3$ for (a) 4 h and (b) 8 h. (c) Bulk β-CoS obtained by furnace heating. Note: Peaks marked with * are from Co_9S_8 (JCPDS file no. 190364) present in small amount in the furnace heated sample.

and CS_2 in the presence of NaOH) was mixed in 1:3 stoichiometric ratio and stirred in air for 4 h. The black precipitate obtained was filtered and dried thoroughly. It was then taken in a round bottom flask fitted with a Liebig condenser under nitrogen. Ethylene glycol was added to it and the mixture was stirred and heated at temperature of 196 °C for different time periods (4 h, 8 h) using an oil bath. Solution was cooled to room temperature and then centrifuged after addition of methanol (5 ml). The supernatant was decanted and the residue dried thoroughly *in vacuo*. The precursor complex was also pyrolysed in a furnace at 400°C for 6 h and the residue obtained was characterized by powder XRD (X-ray diffraction), SEM (scanning electron microscopy), EDX (energy dispersive X-ray analysis) and TEM (transmission electron microscopy).

XRD measurements were carried out on a Philips Instrument, operating with monochromatized Cu-Kα radiation (λ= 1.5417 Å). The scan rate was 0.02°/s in the 2θ range of 20 to 70°. SEM micrographs of the samples were obtained using a Vega MV2300t/40 scanning electron microscope. EDX analyses

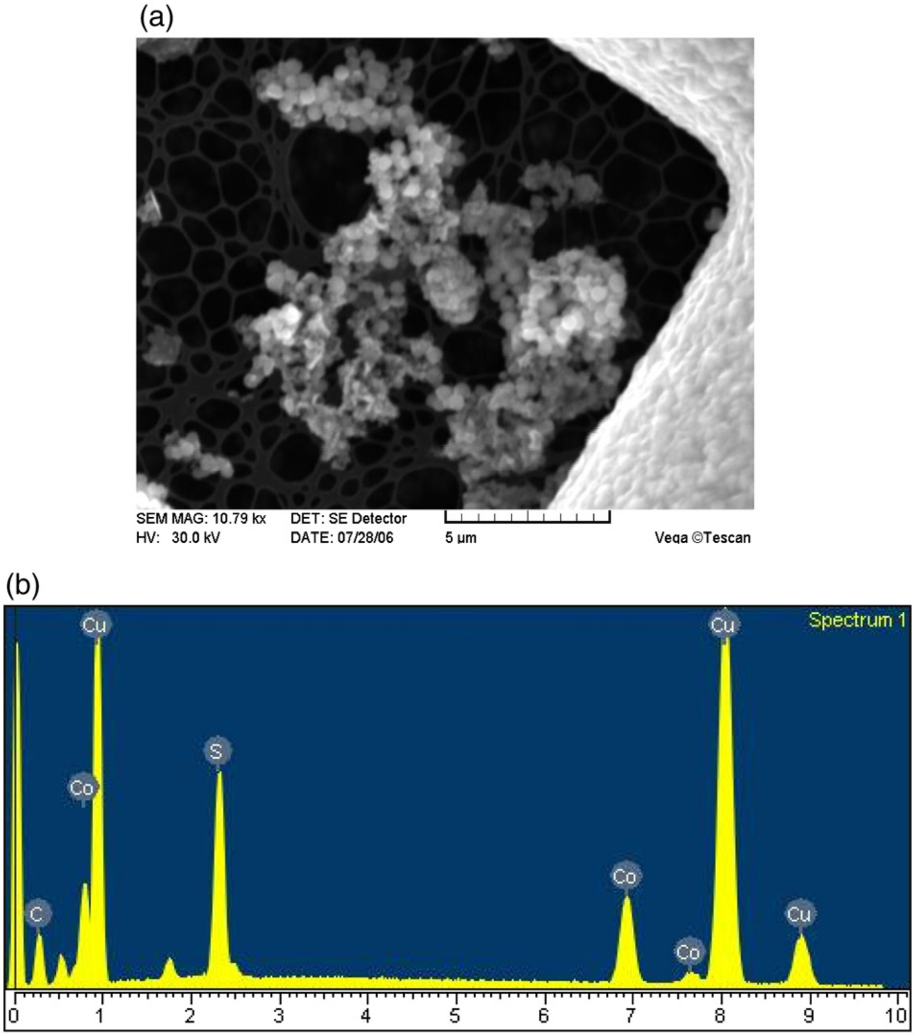

Fig. 2. SEM image of β-CoS nanopowders obtained from 4 h thermolysis, showing ball-like spherical morphologies in micrometer range. (b) EDX spectrum showing Co and S peaks. Note: The Cu and C peaks are due to the carbon coated copper grids used for dispersing the powder sample.