

## Simple Hydrothermal Method for Preparation of CoS<sub>2</sub> Nanostructures with Different Morphologies

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CoS<sub>2</sub> nanostructures were synthesized successfully via hydrothermal approach with new precursor. The products were characterized with X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effect of different sulfur sources were investigated on product size and morphology.

**Keywords:** CoS<sub>2</sub>, Hydrothermal, Nanostructures.

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### 1. INTRODUCTION

Metal sulfides nanomaterials have been the focus of considerable interest due to their unique optical and electrical properties and their wide variety of potential applications in nanoscale devices such as electroluminescence and nonlinear optical devices [1, 2]. As one of the most complicated metal chalcogenides, cobalt sulfides are of particular interest for their unique catalytic, electrical, optical and magnetic properties [3]. Cobalt sulfides have also been used in solar cells for its high solar absorption, which is due to the strong intrinsic absorption coupled with surface morphology effects [4]. Among these cobalt sulfides, CoS<sub>2</sub> with a pyrite structure has received considerable attention due to their electric and magnetic properties [5]. Nanocrystalline cobalt disulfides have been prepared using the solvent-thermal process by Qian's group [6]. Cobalt sulfides of different stoichiometric composition such as CoS, CoS<sub>2</sub>, and Co<sub>9</sub>S<sub>8</sub> have attracted great attention due to their potential application in catalysis [7] semiconductor [8] magnetic materials [9] lithium-ion batteries [10] and other fields [11]. Many approaches have been explored to synthesize metal sulfides, including the high temperature solid phase process [12] the hydrothermal and solvothermal method [13] arc-discharge method [14] low-temperature procedures [15] chemical vapor decomposition [16] and so on [17]. In this work CoS<sub>2</sub> nanoparticles were synthesized via simple hydrothermal method from Cobalt complex. Different sulfur sources were used in this work. The products were characterized via SEM and XRD analysis.

### 2. SYNTHESIS AND CHARACTERIZATION

#### 2.1 Method of Sample Manufacturing and Analysis

All the chemical's reagents used in experiments such as Co(NO<sub>3</sub>)<sub>2</sub>, ethylenediamine (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>) and hydrazine (N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O) were of analytical grade and used as received without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation.

Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy.

For synthesis of the precursor, ligand-contain and metal-contain solutions were prepared separately. Ligand contain solution was obtained from addition of 2 mmol Phthalic acid (C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>) to 30 ml ethanol as solvent. Also metal contain solution was created from addition of 2 mmol of cobalt nitrate ([Co(NO<sub>3</sub>)<sub>2</sub>]. H<sub>2</sub>O) to 30 ml distilled water as solvent. Then Co<sup>2+</sup> contain solution was slowly added to other solution and stirred 30 minutes at 40 °C temperature. After evaporation of solvent, obtained powder washed with ethanol and distilled water several times and dried at oven. In a typical experimental process, different mole ratio of ([Co(Pht)(H<sub>2</sub>O)]<sub>n</sub> and different sulfur sources were added to 100 ml distilled water. After 40 min stirring the reagent was transferred to the autoclave. The reaction was done at 160 °C for 12 h. Then the autoclave was cooled to room temperature. Obtained precipitate was centrifuged and washed with ethanol and distilled water several times for removing the probably by pass products and dried at 60 °C for 8 h. Experimental condition for preparation of CoS<sub>2</sub> nanostructures are shown in Table 1.

**Table 1** – Experimental conditions for preparation of CoS<sub>2</sub> nanostructures

Sample No	Sulfur source	Temperature (°C)	Time (h)
1	(NH <sub>4</sub> ) <sub>2</sub> S	160	12
2	TAA	160	12
3	TGA	160	12
4	Tu	160	12
5	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	160	12
6	CS <sub>2</sub>	160	12
7	TSC	160	12
8	Cystein	160	12

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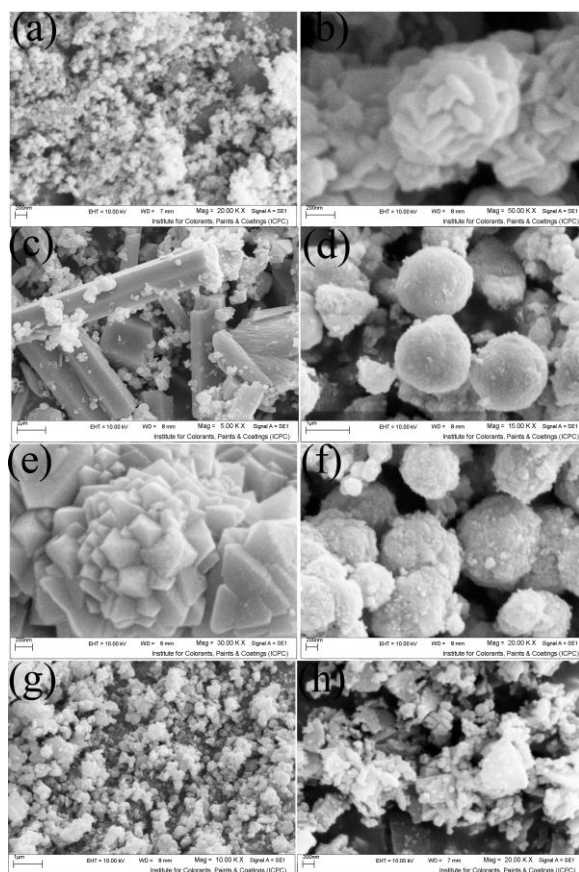


Fig. 1 (a-h) – SEM images of sample No 1-8 respectively

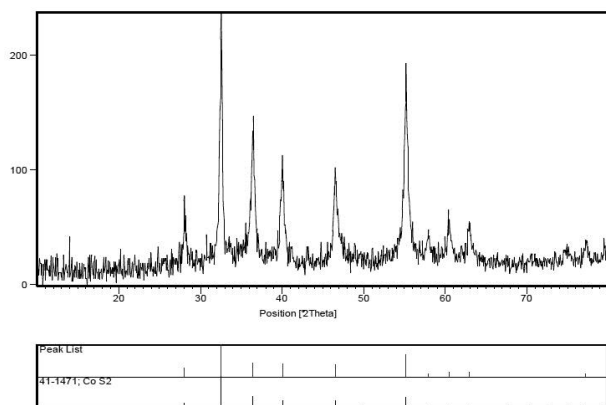


Fig. 2 – XRD pattern of  $\text{CoS}_2$  prepared with thiourea as sulfur source

### 3. RESULT AND DISCUSSION

Fig. 1a shows SEM image of as-synthesized product from  $[\text{Co}(\text{Pht})(\text{H}_2\text{O})]_n$  and  $(\text{NH}_4)_2\text{S}$ . The release of  $\text{S}^{2-}$  from this sulfur source is very fast and hence the product was made from very small particles. SEM image of the product that composed from cobalt source and TAA

is shown in Fig. 1b. Thioacetamid has an electron donor group ( $\text{NH}_2$ ) and an electron acceptor group ( $\text{CH}_3$ ). So in releasing sulfure,  $\text{NH}_2$  is a useful group and  $\text{CH}_3$  is inappropriate group. Therefore the release of  $\text{S}^{2-}$  from thioacetamide is mediocre and hence the product is composed from aggregated large particles. Fig. 1c shows SEM image of as-synthesized product from cobalt complex and thioglycolic acid as sulfur source. Thioglycolic acid is a sulfur source with a strong electron acceptor that is caused sulfur release fastly. So interaction between two sources become fast and finally small sphere and large lump-like structures are created. SEM image of the product that is composed from the reaction between cobalt complex and thiourea in hydrothermal medium is shown in Fig. 1d. Thiourea has two electron resonance groups but their electron donor ability is less than TSC. So larger spheres in comparison to the product of TSC have been created. SEM image of the product that is synthesized with cobalt complex and  $\text{Na}_2\text{S}_2\text{O}_3$  is shown in Fig. 1e. The use of this sulfur source was led to formation of flower-like structure that is composed from 100-150 nm fragments. Fig. 1f shows SEM image of as-synthesized product from cobalt source and  $\text{CS}_2$  as sulfur source.  $\text{CS}_2$  release sulfur slowly and therefore there is more time for reaction of sulfur source with cobalt source. So the product will be composed from too many small particles that aggregated together. TSC has two resonance groups that are caused that  $\text{S}^{2-}$  release as soon as possible. So interaction between these two sources leads to formation of very small sphere-like structures that aggregated together (Fig. 1g). The effect of cysteine on product morphology is nearly to TAA. Because both of them have an electron acceptor and an electron donor that were affected on release of  $\text{S}^{2-}$  from sulfur source. So the product is composed from very small particles beside the irregular and bulk structure (Fig. 1h).

Fig. 2 shows XRD pattern of the sample that was prepared with thiourea as sulfur source. In fact this sulfur source release its sulfur easily and reacts with Co source to form pure  $\text{CoS}_2$  structure. The phase of synthesized  $\text{CoS}_2$  was cubic with JCPDS = 41-1471. There aren't any other peaks in this pattern that indicate the product has high purity.

### 4. CONCLUSION

$\text{CoS}_2$  nanostructures were synthesized via hydrothermal method. The complex precursor  $[\text{Co}(\text{Pht})(\text{H}_2\text{O})]_n$ , was served for synthesis of this nanostructures. The effects of different sulfur sources were studied on product size and morphology and it was found that different sulfur sources were led to synthesis of different structure of cobalt and just some sulfur sources were led to synthesis of pure  $\text{CoS}_2$  nanostructures.

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