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# Synthesis and characterization of CoS<sub>2</sub> nanostructures via hydrothermal method

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#### Synthesis and characterization of CoS<sub>2</sub> nanostructures via

hydrothermal method

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#### Abstract

 $CoS_2$  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.

KEY WORDS: 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 their high solar absorption, which is due to the strong intrinsic absorption coupled with surface morphology effects [4]. Among these cobalt sulfides,  $CoS_2$  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, 7] and hydrothermal method [8]. Cobalt sulfides of different stoichiometric composition such as  $CoS_2$ ,  $CoS_2$ , and  $Co_9S_8$  have attracted great attention due to their potential application in catalysis [9] semiconductor [10] magnetic materials [11] lithium-ion batteries [12] and other fields [13]. Many approaches have been explored to synthesize metal sulfides, including the high temperature solid phase process [14] the hydrothermal and solvothermal method [15] arc-discharge method [16] low-temperature procedures [17] chemical vapor decomposition [18] and so on [19]. In this work  $CoS_2$  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. Experimental

#### 2.1. Materials and physical measurements

All the chemical's reagents used in experiments such as  $Co(NO_3)_2$ , ethylenediamine ( $C_2H_8N_2$ ), phthalic acid and hydrazine ( $N_2H_4.H_2O$ ) 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.

2.1. Synthesis of precursor  $([Co(Pht)(H_2O)]_n)$ :

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  $(C_8H_6O_4)$  to 30 ml ethanol as solvent. Also metal contain solution was prepared from addition of 2 mmol of cobalt nitrate ( $[Co(NO_3)_2]$ . 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 was washed with ethanol and distilled water several times and dried at oven.

#### 2.2. Synthesis of CoS<sub>2</sub> nanostructures:

In a typical experimental process, different mole ratio of  $([Co(Pht)(H_2O)]_n$  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 carried out at 160 °C for 12 h. Then the autoclave was cooled to room temperature. Obtained precipitate was centrifuged and washed with ethanol and distilled

### <sup>3</sup> ACCEPTED MANUSCRIPT

water several times for removing the probable by pass products and dried at 60  $^{\circ}$ C for 8 h. Experimental condition for preparation of CoS<sub>2</sub> nanostructures are shown in table. 1.

#### 3. Result and Discussion

#### X-Ray Diffraction pattern (XRD)

Fig. 1 shows XRD pattern of sample no 1. as shown in this figure beside the  $CoS_2$ ,  $CoSO_4$  was created when  $(NH_4)_2S$  was selected as sulfur source. So by using this sulfure source we coudn't form pure CoS<sub>2</sub>. The use of thioacetamid (TAA) as a sulfure source can not lead to preparation of  $CoS_2$  and the product is composed from CoS and  $Co_3S_4$  (Fig. 2). So this sulfur source is not proper for creating CoS<sub>2</sub> structure, too. By using Co complex and thioglycolic acid as sulfur source, the product is mainly composed from  $C_2CoO_4H_2O$  and  $Co(OH)_2$  (Fig. 3). It can be said that thioglycolic acid couldn't release its S<sup>2-</sup> in hydrothermal medium and final product show any sulfur in its structure. Thiourea releases its sulfur easily and reacts with Co source to form  $CoS_2$  structure (Fig. 4). This product has cubic structure with JCPDS= 41-1471. Estimated particle size from Deby-Sherrer formula was 28.9 nm that is in agreement with obtained SEM result. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is other sulfur source that can release  $S^{2-}$  and react with Co source to form CoS<sub>2</sub> structure with JCPDS=19-0362 (Fig. 5). The particle size of this product was obtained to 38.5 nm from deby-sherrer formula. Table 2. list information about XRD pattern of samples No. 1-5. Fig. 6 shows SEM image of as-synthesized Cobalt complex. As shown in this figure, this complex has composed from large, irregular and inconsistent particles. Fig. 7 shows SEM image of as-synthesized product from  $[Co(Pht)(H_2O)]_n$  and  $(NH_4)_2S$ . The release of  $S^{2-}$  from this sulfur

### <sup>4</sup> ACCEPTED MANUSCRIPT

source is very fast and hence the product contains very small particles. SEM image of the product that composed from cobalt source and TAA is shown in Fig. 8. Thioacetamid has two electron donor groups (NH<sub>2</sub>, CH<sub>3</sub>) with different strength. So each group has different role in releasing  $S^{2-}$  from TAA. Therefore the release of  $S^{2-}$  from thioacetamide is mediocre and hence the product is composed from aggregated large particles. Fig. 9 shows SEM image of assynthesized product from cobalt complex and thioglycolic acid as sulfur source. Thioglycolic acid is a sulfur source with a strong electron acceptor that causes the release of sulfur 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. 10. Thiourea has two electron resonance groups but theirs 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 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is shown in Fig. 11. The use of this sulfur source led to formation of flower-like structure that is composed of 100-150 nm fragments. Fig. 12 shows SEM image of as-synthesized product from cobalt sourse and CS<sub>2</sub> as sulfure source. CS<sub>2</sub> release sulfure slowly and therefore there is more time for reaction of sulfure source with cobalt source. So the product will be composed from too many small particles that are aggregated together. TSC has two resonance groups that cause  $S^{2-}$  release as soon as possible. So interaction between these two sources leads to formation of very small sphere-like structures that are aggregated together (Fig. 13). The effect of cystein on product morphology is nearly to TAA. Because both of them have an electron acceptor and an electron donor that affected on release of  $S^{2-}$  from sulfur source. So the product is composed from very small particles beside the irregular

and bulk structure (Fig. 14). Table 3 and 4 give morphology of the products and sulfur structures, respectively.

#### 4. Conclusion

CoS<sub>2</sub> nanostructures were synthesized via hydrothermal method. The complex precursor [Co(Pht)(H<sub>2</sub>O)]<sub>n</sub>, 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 source were led to synthesis of pure CoS<sub>2</sub> nanostructures.

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#### **Figure caption**

- Fig. 1. XRD pattern of sample no. 1.
- Fig. 2. XRD pattern of sample no. 2.
- Fig. 3. XRD pattern of sample no. 3.
- Fig. 4. XRD pattern of sample no. 4.
- Fig. 5. XRD pattern of sample no. 5.
- Fig. 6. SEM image of cobalt complex.
- Fig. 7. SEM image of sample no. 1.
- Fig. 8. SEM image of sample no. 2.
- Fig. 9. SEM image of sample no. 3.
- Fig. 10. SEM image of sample no. 4.
- Fig. 11. SEM image of sample no. 5.
- Fig. 12. SEM image of sample no. 6.
- Fig. 13. SEM image of sample no. 7.
- Fig. 14. SEM image of sample no. 8.

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

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Table 2. XRD pattern information of samples No. 1-5.

Table 3. Morphology of the samples No. 1-8.

**Table 4.** The sulfur sources stucture.

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Table	1.	Experimental	conditions	for	preparation	of	$CoS_2$	nanostructures.
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Sample No	Sulfur source	Temperature (°C)	Time ((h)
1	$(NH_4)_2S$	160	12
2	TAA	160	12
3	TGA	160	12
4	Tu	160	12
5	$Na_2S_2O_3$	160	12
6	$CS_2$	160	12
7	TSC	160	12
8	Cystein	160	12

# <sup>11</sup> ACCEPTED MANUSCRIPT

Sample No	Sulfur source	Component	JCPDS No	Crystal system	XRD pattern
1	(NH <sub>4</sub> ) <sub>2</sub> S	$CoS_2$	41-1471	Cubic	- which with the the the the manual and
	(=	CoSO <sub>4</sub> .H <sub>2</sub> O	15-0701	Monoclinic	4 1
2	ТАА	CoS	75-0605	Hexagonal	- Mar had a see we
_		$Co_3S_4$	75-1561	Cubic	
3	TGA	$C_2CoSO_4.2H_2O$	14-0741		
5	1011	Co(OH) <sub>2</sub>	74-1057	Hexagonal	
4	Tu	CoS	<i>A</i> 1_1 <i>A</i> 71	Cubic	
т	Tu			Cubic	
5	$Na_2S_2O_3$	$CoS_2$	19-0362	Cubic	
		-			Nord Head Plane

Table 2. XRD pat	tern information	of samples No.	1-5.
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# <sup>12</sup> ACCEPTED MANUSCRIPT

Sample No	Morphology	Figure	SEM image
1	particles	7	
2	Aggregated particles	8	
3	Large rod-particles	9	
4	Sphere	10	
5	Flower-like	11	
6	Sphere	12	
7	Sphere-particles	13	

#### **Table 3.** Morphology of the samples No. 1-8.

0
0

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Aggregated particles 14



#### Table 4. The sulfur sources stucture

Sulfur source	abbreviation	structure
Thioacetamide	TAA	
Thioglycolic acid	TGA	
Thiourea	Tu	
Carbon disulfide	$CS_2$	S=C=S
Thiosemicarbazide	TSC	H <sub>2</sub> N <sup>Å</sup> NH <sub>2</sub>
Cysteine	Cysteine	
Ammonium sulfide	$(NH_4)_2S$	$(NH_4)_2S$
Sodium thiosulfate	$Na_2S_2O_3$	$Na_2S_2O_3$

# <sup>14</sup> ACCEPTED MANUSCRIPT



Fig. 1. XRD pattern of sample no. 1.

# <sup>15</sup> ACCEPTED MANUSCRIPT



Fig. 2. XRD pattern of sample no. 2.

# <sup>16</sup> ACCEPTED MANUSCRIPT



Fig. 3. XRD pattern of sample no. 3.

# <sup>17</sup> ACCEPTED MANUSCRIPT



Fig. 4. XRD pattern of sample no. 4.

# <sup>18</sup> ACCEPTED MANUSCRIPT



Fig. 5. XRD pattern of sample no. 5.

<sup>19</sup> ACCEPTED MANUSCRIPT



Fig. 6. SEM image of cobalt complex.



Fig. 7. SEM image of sample no. 1.

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Fig. 8. SEM image of sample no. 2.



Fig. 9. SEM image of sample no. 3.



Fig. 10. SEM image of sample no. 4.



Fig. 11. SEM image of sample no. 5.



Fig. 12. SEM image of sample no. 6.



Fig. 13. SEM image of sample no. 7.



Fig. 14. SEM image of sample no. 8.

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