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Multi-objective optimization of reaction parameters and kinetic studies of cobalt disulfide nanoparticles

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ABSTRACT

In this study, cobalt disulfide (CoS_2) nanoparticles have been successfully synthesized through a simple and facile solvothermal method. The experiments were carried out based on the thermodynamic calculations using FactSage software. The black nano-sized CoS_2 powder has been produced in an autoclave reactor. The reaction parameters, such as the ratio of primary salts, effect of solvents, temperature and surfactant were optimized to obtain fine and uniform nanoparticles. The band gap energy of the samples was measured with butler relations. The results proved the production of highly pure CoS_2 nanoparticles with a semi-spherical morphology.

1. Introduction

The design and synthesis of materials with nanometer dimensions are currently the focus of intense attention because of their interesting and considerably different properties than those found in their corresponding bulk materials [1]. Transition metal dichalcogenides have drawn considerable attention because of their technological importance as catalysts for the oxygen reduction reaction [2], photoactive materials, dehydrosulfurization catalysts, solid-state lubricants, cathode materials for high-energy density battery, and so forth. Schleich and Martin [25,26] proposed metathesis reactions between transition metal halides and alkali-metal sulfides or covalence sulfiding agents to obtain amorphous transition metal disulfides in non-aqueous solvents [3]. Cobalt disulfide (CoS_2) is an important half-metallic material and has fundamental physics in spintronics and potential applications in spin-electronic devices due to their open bands containing electrons with a single spin state [4].

In recent years, considerable efforts have been made to the preparation of CoS_2 for its specific properties. It is known that CoS_2 possesses higher electronic conductivity and thermal stability compared to other metal sulfides [5,6]. Uniform hollow spheres of CoS_2 have been successfully synthesized via a solvothermal method and electrochemically investigated as anode material for lithium-ion batteries [5]. Cobalt sulfides have attracted great attention due to their potential application in catalysis [7,8], semiconductor [9], magnetic materials [10], lithium-ion batteries [5,6], and other fields. Many different approaches and methods have been explored to synthesize metal sulfides, including the high temperature solid phase process [11,12], chemical vapor decomposition [13–15], low temperature procedures [16,17], hydrothermal and solvothermal method [10,18], and arc-discharge method [19]. Among these methods, hydrothermal and solvothermal methods are facile according to rein the reaction terms.

In this study, CoS_2 nanoparticles were first synthesized through a simple and facile solvothermal method in an autoclave reactor and then characterized. The experiments were carried out based on the thermodynamic calculations using FactSage software. The reaction parameters, such as the ratio of primary salts, effect of solvents, temperature and surfactant were optimized to obtain fine and uniform nanoparticles.

2. Experimental

In this research, 0.1 mol cobalt chloride hexahydrate and 0.2 mol sodium thiosulfate dissolved in different purity percentages of ethanol which are specified mixtures of ethanol and distilled water. Solvents include pure, 80, 70 and 50% aqueous ethanol solutions. Then solutions were added into 2 l stirred autoclave reactor and maintained for 4 h under strong stirring. After cooling the reactor to room temperature, the solution was filtered and black precipitates were washed with distilled water several times and then dried at 60 °C for 4 h. Then the

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washing process continued with carbon disulfide to remove sulfur content of the final product. All chemical reagents were of analytical grade and used as received without further purification. To find the effect of sodium thiosulfate to cobalt chloride hexahydrate ratio on final product, this item was fixed in four levels as 1, 2, 4 and 8. Then the effect of temperature was compared at three levels which are 75, 110, and 140 °C. Perusal of surfactant impress was carried out using sodium dodecyl sulfate and cetyltrimethyl ammonium bromide (CTAB) at low temperature. Based on the obtained results, one of these surfactants was implemented at high temperature.

The samples were analyzed by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), energy dispersive analysis of X-ray (EDAX), ultraviolet–visible spectroscopy (UV–Vis) and field emission scanning electron microscopy (FESEM). XRD were carried out using a Philips PW170 based diffractometer (CuKα radiation, 35 kV, 40 mA). XRD patterns, in the range of 20–60° 2θ, were collected under air using the following settings: 0.1 mm receiving slit, 0.4 s/0.02° 2θ counting time. The FTIR, EDAX patterns and FESEM micrographs have been taken by (IRsolution) 8400S, ISI-SR50 and Hitachi S-4160, respectively.

3. Results and discussion

3.1. Effect of solvent

In the investigation of the effective reaction parameters on the synthesis of CoS_2, nanoparticles including the molar ratio of the precursors, temperature and surfactant were essential objects on this attempt. In all the experiments, the obtained products in different solvents were black powders, and by increasing the amount of distilled water in the system, the final amount of the product decreased. In order to find the correct structural composition, the synthesized samples in pure and 50% aqueous ethanol solutions, were characterized using XRD patterns. The XRD analysis results are shown in Fig. 1, demonstrating that the patterns of both as-synthesized samples are almost the same. The dominant diffraction peaks of both samples correspond to CoS_2, which can be indexed to the standard cubic phase CoS_2 (JCPDS No. 65-3322). It is worth mentioning that no obvious peaks relevant to Co and S impurities could be found in the patterns. In addition, FTIR spectra have been used to determine the chemical bonds in the final products, shown in Fig. 2.

Fig. 2 shows the FTIR spectra of the final products obtained in pure ethanol and 50% aqueous ethanol solution. The FTIR spectra indicate that there are no Co–O bond vibrations [20], and the appearance of one strong band (due to the S–O modes) around 970 cm^{-1} is a clear evidence for the formation of CoS_2 nanoparticles. Fig. 3 shows the EDAX result of the as-synthesized sample prepared in pure ethanol. Moreover, the EDAX result of the as-synthesized sample prepared in the aqueous ethanol solution showed similar double bond of cobalt and sulfide (the data is not shown). The EDAX patterns revealed that the molar ratio of sulfur was two times higher than that of cobalt, indicating successful production of CoS_2 nanoparticles.

Fig. 4 depicts the FESEM micrographs of the synthesized samples, demonstrating the quasi spherical-like morphology of the CoS_2 particles with the average particle size of about 32 nm. In addition, by utilizing the aqueous ethanol solution, nearly similar but smother morphology was obtained for the CoS_2 particles with the average particle size of about 33.8 nm. The difference between the samples that synthesized in the presence of different solvents, is mainly in terms of the particle aggregation. In this regard, by using pure ethanol as the solvent, less aggregations happened while the presence of water molecules which have higher polarity, has resulted in more aggregation of the particles. From the observed sequels mentioned above, it was found that the different solvent sources could have different influences on the size, morphology and final amount of the products. Due to the amount of products (4.5 g and 1.5 g for pure ethanol and aqueous ethanol solution, respectively) considering FTIR spectra that illustrates less unwanted peaks, pure ethanol was chosen as the main solvent.

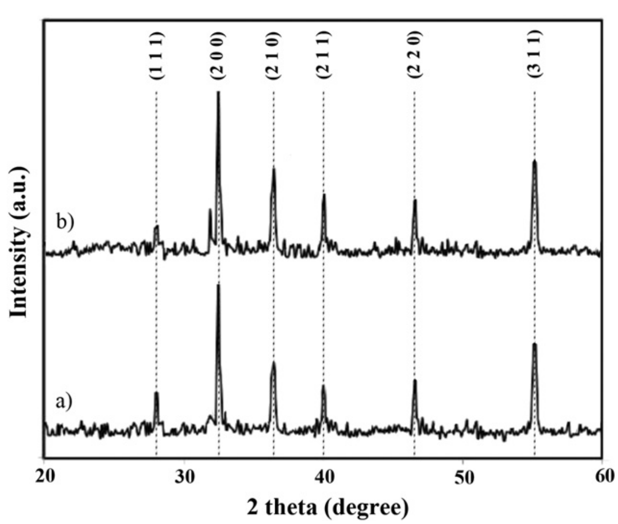

Fig. 1. XRD patterns of the synthesized samples: (a) in pure ethanol and (b) in 50% aqueous ethanol solution.

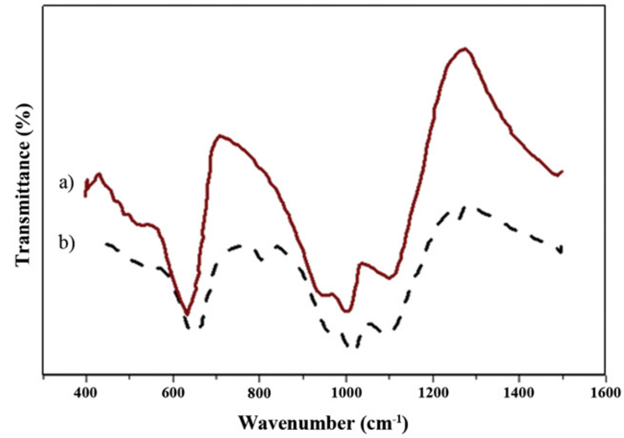

Fig. 2. FTIR spectra of the synthesized samples: (a) in pure ethanol and (b) in 50% aqueous ethanol solution.

3.2. Effect of precursor ratio

3.2.1. Experiment

Fig. 5a shows the FESEM micrograph of the CoS_2 sample prepared with the ratio of sodium thiosulfate to cobalt chloride equal to 0.5,

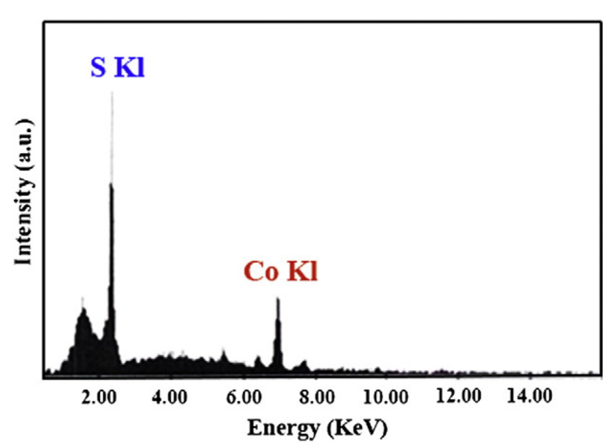

Fig. 3. EDAX consequence of the as-synthesized sample prepared in pure ethanol.