

SYNTHESIS AND CHARACTERIZATION OF COBALT SULFIDE/FNBR NANOCOMPOSITES BY SILAR METHOD

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We have prepared cobalt sulfide (Co_xS_y) nanoparticles through a successive ionic layer adsorption and reaction (SILAR) method at room temperature. $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ aqueous solution was used as a cobalt precursor, $\text{Na}_2\text{S} \times 9\text{H}_2\text{O}$ and thiourea $[(\text{NH}_2)_2\text{CS}]$ aqueous solutions were used as sulfur precursors. Functionalized nitrile butadiene rubber (FNBR) was used as a stabilizing agent for the formation of nanoparticles and contains $-\text{PO}(\text{OH})_2$ and $-(\text{O})\text{PO}(\text{OH})_2$ acid groups. Obtained $\text{Co}_x\text{S}_y/\text{FNBR}$ nanocomposites were annealed at 100°C in a vacuum for 6 h. The prepared nanocomposites were characterized by XRD, SEM, EDX, UV-Vis and FT-IR spectrometer. In case thiourea is used as a sulfur source, mixed phases of Co_3S_4 , $\text{CoS}_{1.097}$ and CoS_2 were obtained with the dominance of Co_3S_4 phase. A possible formation mechanism, physical and chemical stabilization into the functional polymer matrix (FNBR) for the growth processes have been discussed.

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1. Introduction

Cobalt sulfide has potential applications in solar selective coatings, IR detectors and as a storage electrode in photoelectrochemical storage device [1]. Due to its band gap and good adsorption properties, CoS can be used as a photocatalyst. It is also one of the more complicated metal sulfide systems, with a number of phases and differing chemical compositions, including Co_4S_3 , Co_9S_8 , CoS , Co_{1-x}S , Co_3S_4 , Co_2S_3 and CoS_2 [2].

Considering the recent research work done in cobalt sulfide based supercapacitors, Tao et al. reported a specific capacitance of 369 (F/g) for amorphous Co_xS_y nanoparticles [3]. Cobalt sulfide (CoS) in-situ hybridized with carbon nanotube (CNT) is achieved through a hydrothermal process with the presence of polyvinylpyrrolidone (PVP) [4]. The results show that the product consists of CoS nanoparticles with the diameter of 30–50 nm that well dispersed on the outer surface of CNTs. Furthermore, CoS/CNT hybrid has shown excellent electrochemical capacitance and exhibited favorable electrochemical cycling stability with 93.4% capacitance retention over 1000 cycles. Therefore, the CoS/CNT hybrids can be considered as promising electrode materials for supercapacitor [4].

The aim of this work was the synthesis and study of Co_xS_y nanoparticles using cost effective and convenient stabilizing agent (FNBR) for gaining interesting properties. In this paper, we successfully prepared $\text{Co}_x\text{S}_y/\text{FNBR}$ nanocomposites by successive ionic layer adsorption and the reaction (SILAR) method into functionalized nitrile butadiene rubber (FNBR). The reaction was carried out at room temperature. The results obtained from X-ray, SEM, EDX, UV-Vis and FTIR spectroscopy experiments are reported.

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2. Experimental

2.1. Materials and sample preparation

Polymers containing PO(OH)₂ and -(O)PO(OH)₂ functional active groups were synthesized from the oxidative chlorophosphorylation reaction of NBR with PCl₃ and oxygen. 10% solutions were prepared from NBR-26 with CHCl₃. To carry out oxidative chlorophosphorylation reaction was used an apparatus consisting of a four-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser and a bubbler for oxygen [5, 6]. The oxygen rate was 7 l/h and 1:6 PCl₃ was added by intervals to a stirred solution. The reaction was exothermal and the temperature was raised up to 45° C in 18 hours by stirring. The functionalized polymer sorbents are dark brown powder. This powder sample was used for loading the nanoparticles.

The preparation of cobalt sulfide nanoparticles was carried out by a successive ionic layer adsorption and reaction (SILAR) method. Two solutions of 25 ml 0.5 M Co(NO₃)₂ × 6H₂O were prepared as a cobalt precursor. 0.2 g of FNBR powders were added to every solution. After 24 h, polymers containing Co²⁺ ions were washed to remove unexchanged ions. The sulfurizing processes were carried out with 25 ml 0.1 M of Na₂S × 9H₂O and 25ml 1M of SC(NH₂)₂ and stirred 24 h. Samples were rinsed up with distilled water and this process was repeated in 6 and 8 cycles and air-dried. Obtained Co_xS_y/FNBR nanocomposites were heated at 100 °C in a vacuum for 6 h.

In case thiourea used as a sulfur source the below mechanism is postulated (1), (2). The nucleation process occurs in the first cycle and then the process goes with the formation of copper sulfide nanoparticles (3).



2.2. Characterization

X-ray diffraction (XRD) patterns were recorded by a Bruker D2 Phaser X-ray diffractometer ($\lambda = 1.54060 \text{ \AA}$) using Ni-filtered Cu K α radiation.

Fourier transform infrared (FT-IR) spectra were recorded within 400–4000 cm⁻¹ region on a Varian 3600 FTIR spectrometer using the KBr pellet.

Optical absorption studies were carried out using a UV–Vis spectrophotometer (Specord 250) in the wavelength range 300–1100 nm.

Scanning electron microscopy (SEM) images were obtained on JEOL JSM- 7600F with X-max 50 energy-dispersive X-ray spectrometer (EDX).

3. Results and discussions

All the measurements were done for the samples obtained before and after annealing at 100°C for 6 h in vacuum.

3.1. Structural properties by XRD

Fig.1a shows a typical XRD pattern of cubic linnaeite (Co₃S₄) was prepared using Na₂S as a sulfur source (JCPDS No.42-1448). No other impurity peaks can be detected, demonstrating that the as-prepared sample is highly pure.

The XRD pattern in Fig.1B corresponds to the formation of cobalt sulfide in thiourea. In this case mixed phases of Co₃S₄, CoS_{1.097} and CoS₂ were obtained with the dominance of Co₃S₄ phase. The diffraction peak at 2 θ value of 26.7°, 38° and 55° correspond to the planes of (220), (400) and (330), respectively and indicate the formation of cubic Co₃S₄ [JCPDS no.42-1448] (Fig.1B).

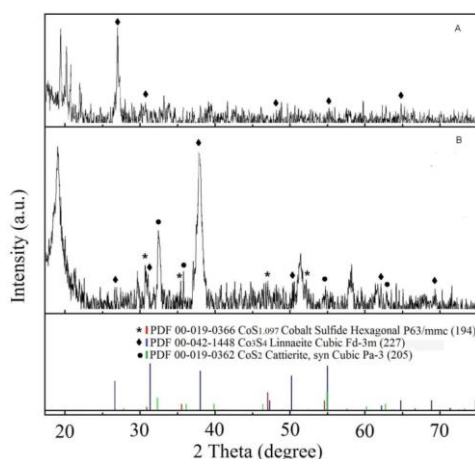


Fig. 1. XRD patterns of (a) $\text{Co}_3\text{S}_4/\text{FPS}$ prepared using $0.1\text{M Na}_2\text{S}$ and $0.5\text{M Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursors and (b) $\text{Co}_x\text{S}_y/\text{FPS}$ prepared using 1M thiourea and $0.5\text{M Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursors.

The average particle diameter of cobalt sulphide obtained in different reaction medium was calculated by the Debye-Scherrer's equation (4)

$$D = \frac{\alpha\lambda}{\beta \cos \theta} \quad (4)$$

where, D - is the particle diameter of nanocrystallite, α - is constant (0.9), λ - the X-ray wavelength (1.5418 \AA), and β - is the half-width of the diffraction peak. The average size of Co_3S_4 nanoparticles obtained using Na_2S in 8 cycles of the reaction was estimated 15.8 nm . The average size of Co_xS_y nanoparticles in mixed phases obtained using thiourea at 8 cycles of the reaction was estimated 9.8 nm .

3.2. Optical properties

The optical transmission and absorption spectra of cobalt sulfide/FNBR nanocomposites in different reaction medium were taken within the wavelength range of $300\text{-}1100 \text{ nm}$. The variation of obtained transmittance $T\%$ of cobalt sulfide is shown in Fig.2A. In all samples, the transmittance increases slowly from the lowest wavelength region to higher wavelength region. It can be seen that every sample has one step transmission. Band gap energy and transition type were derived from mathematical treatment (5) of the data obtained from the optical absorbance versus wavelength data with the following relationship for near-edge absorption:

$$A = [k(h\nu - E_g)^{n/2}] / h\nu \quad (5)$$

Where ν - is the frequency, h - is the Planck's constant; k -equals a constant while n carries the value of either 1 or 4.

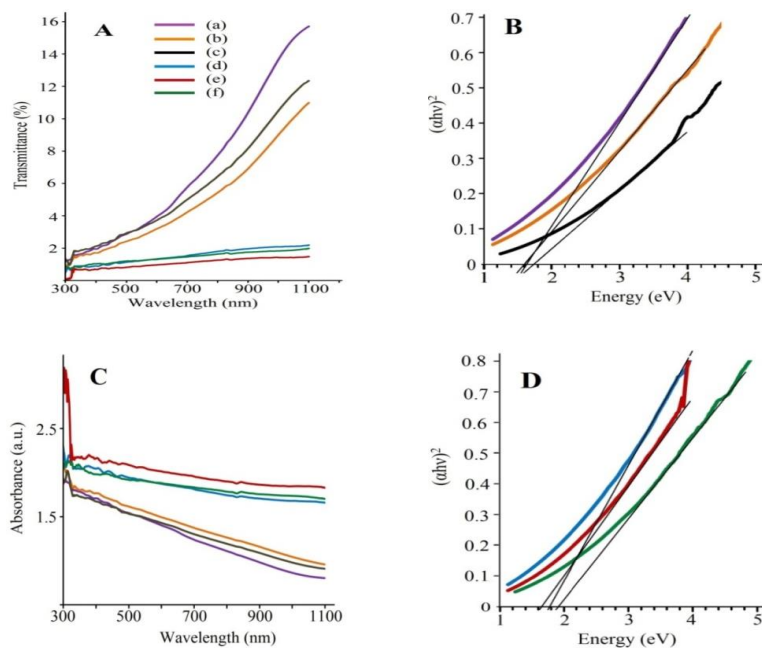


Fig.2. Optical transmission (C), absorption (A) and band gap (B, D) of cobalt sulfide/FNBR nanocomposites obtained (a)- in 6 cycles using thiourea; (b)- in 8 cycles using thiourea; (c)- in 8 cycles using thiourea, annealing at 100°C for 6 hours in a vacuum; (d)- in 6 cycles using Na₂S; (e)- in 8 cycles using Na₂S; (f)- in 8 cycles using Na₂S, annealing at 100°C for 6 hours in a vacuum.

The band gap E_g could be obtained from a straight line plot of $(\alpha h\nu)^{2/n}$ as a function of $h\nu$. Extrapolation of the line to the base line, where the value of $(\alpha h\nu)^{2/n}$ is zero, will give E_g . If a straight-line graph is obtained for $n = 1$, it indicates a direct electron transition between the states of the semiconductors, whereas the transition is indirect if a straight-line graph is obtained for $n = 4$ [7, 8]. For the determination of band gap, we have considered the direct transition. A plot of $(\alpha h\nu)^2$ vs. $h\nu$ (direct transition) of cobalt sulfide/FNBR nanocomposites having different reaction medium and annealing temperature are shown in Fig.3. The band gap energy for every sample was obtained from the intercept of the energy axis after extrapolation of the straight lines section of $(\alpha h\nu)^2$ vs. $h\nu$ curve. Optical band gaps obtained for direct transition are given in Table 1 and Table 2.

Table 1 Band gaps of Co₃S₄ obtained using Na₂S as a sulfur source (eV).

6 cyc.	8 cyc.	8 cyc. (100°C)
1.77	1.65	1.9

Table 2 Band gaps of Co_xS_y obtained using thiourea as a sulfur source (eV).

6 cyc.	8 cyc.	8 cyc. (100°C)
1.62	1.59	1.72

From the Table 1 and Table 2, it is seen that the energy band gap decreases, with increasing reaction cycles for obtained cobalt sulfide nanoparticles. But optical band gaps increased with increasing particle sizes using different sulfur sources. This result happened due to the formation of mixed nanocrystals by using thiourea.

And also after annealing the samples at 100°C for 6 hours in vacuum optical band gaps have decreased. This result may happen due to the first-grade destruction of the polymer under the temperature.

3.3. Morphology

Fig.3 and Fig.4 exhibit SEM and EDX images of as-prepared $\text{Co}_x\text{S}_y/\text{FNBR}$ nanocomposites obtained using thiourea as a sulfur precursor in 8 cycles. As shown in Fig.3, the obtained cobalt sulfide nanocrystals display a rice-like morphology with a length of ~500nm and with a width of 140nm. In sharp contrast on nanoparticles size with the XRD pattern. The coalescence of crystallites highly occurred to form larger particles to lower Gibb's free energy. During the nucleation and growth of cobalt sulfide nanoparticles, FNBR acts as a support material and suppress the aggregation of Co_xS_y nanoparticles.

The sample of cobalt sulfide/FNBR nanocomposite was studied the elemental composition of the phases (Fig 3B). Energy dispersive X-ray analysis of cobalt sulfide was performed using energy dispersive spectrometer. The quantitative elemental composition of spectra revealed that the light phase is mainly composed of carbon, oxygen, cobalt and sulfur elements and the ratio of Co:S was found 2:1. To confirm the elemental composition of the phase was carried out mapping of the distribution of elements on the surface (Fig. 4).

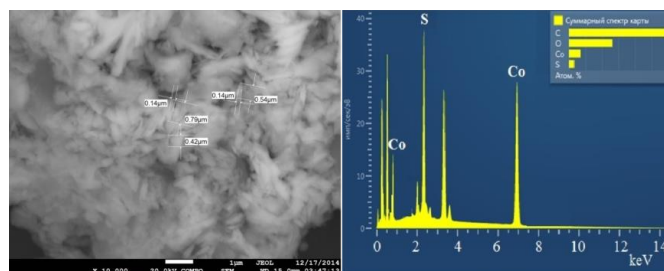


Fig. 3. SEM and EDX result of cobalt sulfide obtained using thiourea as a sulfur precursor.

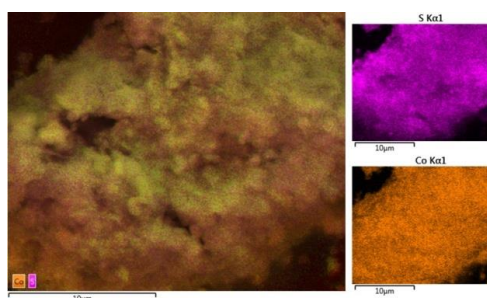


Fig. 4. Mapping of images of $\text{Co}_x\text{S}_y/\text{FNBR}$ nanocomposite obtained using thiourea.

3.4 FTIR spectroscopy study

The FTIR spectra of $\text{Co}_x\text{S}_y/\text{FNBR}$ nanocomposites obtained using different sulfur sources and annealed samples at 100 °C for 6 hours in a vacuum are shown in Fig.5. The broadband at 2100 cm^{-1} and 2191 cm^{-1} can be assigned as the O–H stretching peak of the $-\text{OPO}(\text{OH})_2$ group formed by the chlorophosphonation reaction of the polymer. Upon the formation of Co_3S_4 and Co_xS_y nanoparticles, these peaks have been disappeared by formation of Co_3S_4 using Na_2S and/ or shift to 2183 cm^{-1} using thiourea. By our knowledge practically all these functional groups participated in the formation of cobalt sulfide nanoparticles using Na_2S than using thiourea. Concentration and masses of attached atoms also influence the intensity and frequency of the peak. As masses of attached atoms increase, wavenumber decreases and as concentration decreases, the intensity is also decreased. The 480 cm^{-1} peak corresponded to the S–S stretching [9] of the

disulfide group indicating in Fig.5a and Fig.5b. The peak of PO_3^{2-} at 977 cm^{-1} (Fig.5e) shift to 970 cm^{-1} (Fig.5a) upon the formation of Co_xS_y nanoparticles by thiourea. After heating, the peak of 989 cm^{-1} is shown with high intensity. The FTIR spectra also confirmed the stability of the prepared cobalt sulfide by the absence of any CoO peak at 580 cm^{-1} [10] in FTIR spectrum.

The weak peak at 2920 cm^{-1} shown in all samples are due to C–H stretching modes of the FNBR carbon chain, indicating that the nanoparticles are covered by polymer macromolecules. The peak at 3429 cm^{-1} can be ascribed to the absorption of H_2O in all samples [11,12] (Fig. 5). Other corresponding bands as O–H (in P–O–H): 2854 cm^{-1} , C–O (in P–C–O): 1109 cm^{-1} are shown on the polymer spectra also changed after formation of nanoparticles.

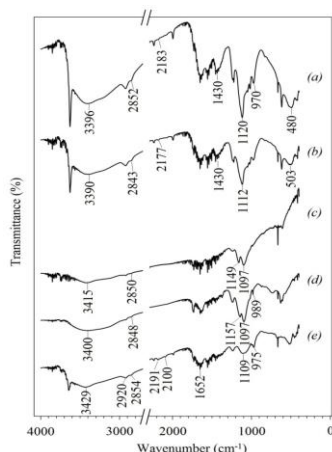


Fig. 5. FTIR spectroscopy results of a- $\text{Co}_x\text{S}_y/\text{FNBR}$ obtained in 8 cycles using thiourea, b- $\text{Co}_x\text{S}_y/\text{FNBR}$ obtained in 8 cycles using thiourea (100°C), c- $\text{Co}_3\text{S}_4/\text{FNBR}$ obtained in 8 cycles using Na_2S , d- $\text{Co}_3\text{S}_4/\text{FNBR}$ obtained in 8 cycles using Na_2S (100°C), e- FNBR.

4. Conclusions

Rice-like cobalt sulfide (Co_xS_y) nanoparticles were synthesized using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and thiourea $[(\text{NH}_2)_2\text{CS}]$ as precursors by successive ionic layer adsorption and reaction (SILAR) method at room temperature. By changing the reaction parameters and sulfur sources, different composition and crystal structure were obtained.

Using Na_2S as sulfur source cubic linnaeite (Co_3S_4) was formed and using thiourea as a sulfur precursor, mixed phases of Co_3S_4 , $\text{CoS}_{1.097}$ and CoS_2 were obtained with the dominance of Co_3S_4 phase. The optical band gap of the Co_xS_y and Co_3S_4 nanoparticles were found as 1.59 eV and 1.65 eV for different sulfur sources like thiourea ($\text{S}=\text{C}(\text{NH}_2)_2$) and sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), respectively. The influence of different sulfur sources on the formation of cobalt sulfides was discussed in detail.

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