

Formation of NiS and CoS semiconductor nanoparticles inside mordenite-type zeolite

M.S. Sadjadi^{a,*}, A. Pourahmad^{a,b}, Sh. Sohrabnezhad^c, K. Zare^a

^a Department of Chemistry, Science and Research Campus, Islamic Azad University, Poonak, Tehran, Iran

^b Department of Chemistry, Faculty of Science, Islamic Azad University, Rasht Branch, Rasht, Iran

^c Department of Chemistry, Faculty of Science, University of Mohaghegh Ardebili, Ardebil, Iran

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Abstract

The crystallization of semiconductor nanoparticles, NiS and CoS embedded in mordenite zeolite (NaMOR) was carried out by ion exchange method. Structural, morphological and compositional studies of the materials were realized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX). The obtained XRD results showed the presence of the well-crystallized mordenite before and after manipulation. SEM showed that the NiS and CoS nanoparticles are inside the zeolite channels and EDS gave us the chemical composition of the host matrix as well as the relative weight percent of Ni, Co and S. Measurements of the absorption spectra by UV–Vis spectroscopy indicate that the optical band gap varies in the range 3.53–3.90 eV. BET results reveal that the NiS and CoS nanoparticles are encapsulated in the channels and cavity of mordenite. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Among the different types of hosts where semiconductor nanoparticles have been synthesized, zeolites have been the focus of intense research work in the last few years [1–6]. Due to their structures, zeolites are similar to three-dimensional superlattices in which semiconductor nanoparticles can be embedded. The nanocomposite properties can be varied either by modifying the superlattice structure using different kind of zeolites, or, by changing the type of semiconductor nanoparticles. These properties make semiconductor embedded in zeolites very attractive for many technological applications such as photocatalysis, nonlinear optics, flat panel displays, sensors, etc [7].

The physical properties of some semiconductor nanocrystals encapsulated in mordenite zeolites have been reported elsewhere [2,8–12]. In this work, we studied the formation of NiS and CoS nanoparticles embedded inside mordenite-type zeolite.

2. Experimental

NaMOR-type zeolite was synthesized hydrothermally following the standard procedure reported in literature [13]. The unit cell composition of zeolite, calculated from our obtained EDS data, was $\text{Na}_{7.4}[(\text{AlO}_2)_{7.4}(\text{SiO}_2)_{40.6}]\cdot 23.7 \text{ H}_2\text{O}$. As precursors of NiS and CoS semiconductors, two solutions of NiSO_4 and CoSO_4 (0.1 mol l^{-1}) were prepared. To 50 ml of NiSO_4 and CoSO_4 solutions, 1 g of NaMOR powder was separately added and stirred for 12 h at 250°C . The samples were then washed to remove nonexchanged Co^{2+} and Ni^{2+} ions and air-dried. Sulfidizing of the Ni^{2+} and Co^{2+} ions exchanged zeolites were carried out with 0.1 mol l^{-1} Na_2S solution. To make the reaction with the S^{2-} ions, 1 g of Ni^{2+} or Co^{2+} -exchanged zeolite was added to 50 ml of Na_2S solution (0.1 mol l^{-1}) at 25°C and stirred magnetically for 2 h. The samples were then washed with deionized water and collected by filtration. The obtained samples were fine powders in dark grey color, stable at ambient conditions.

In this competence, the bulk NiS and CoS were prepared in the conventional precipitation method by adding 0.1 mol l^{-1} of Na_2S solution to the stirred equimolar amount of NiSO_4 or CoSO_4 solutions (0.1 mol l^{-1}). The resulting bulk precipitated products were then repeatedly washed with distilled water until free from S^{2-}

* Corresponding author.

E-mail address: msadjadi@yahoo.com (M.S. Sadjadi).

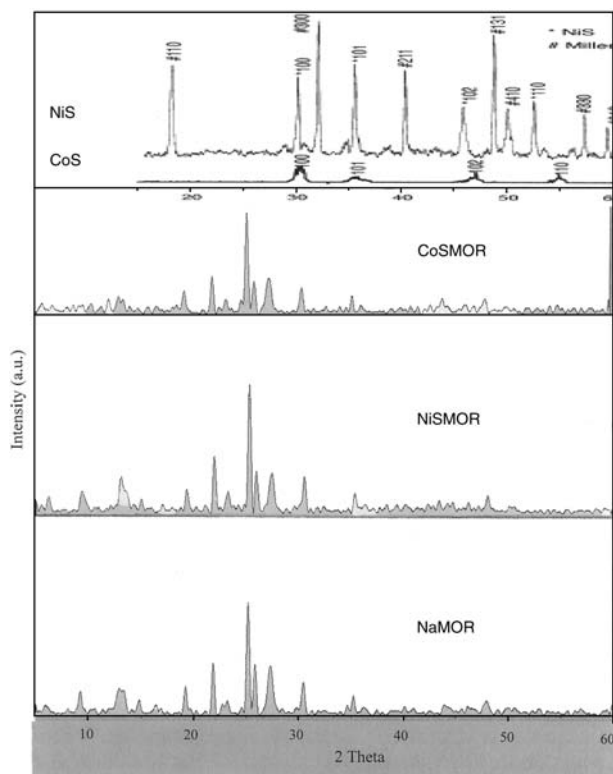


Fig. 1. X-ray diffraction patterns of NaMOR and NiSMOR and CoSMOR. The insert shows XRD patterns of the transition metal sulfides of CoS and NiS [16].

ions, dried in an air-oven and calcined at 500 °C for 4 h. The samples were dark color fine powders.

Powder X-ray diffraction patterns were recorded on a Philips X-ray diffractometer using Cu K_{α} radiation ($\lambda=1.54$ Å). UV–Vis absorption spectra were recorded using a Shimadzu spectrophotometer (model 1600 PC) instrument in the range of 190–900 nm. The specific surface area and pore volume were measured using a Sibata Surface Area Apparatus 1100. Chemical analysis was done by EDX joined to a Philips XL 30 SEM. The surface morphology of the samples was obtained using a Jeol-JSM-5610 LV SEM and the water content of the samples was determined by thermogravimetry method.

3. Results and discussion

The powder XRD results of the NaMOR and the host–guest composite materials, MOR–NiS, CoS (Fig. 1) show similar diffraction

Table 1

Band gap, specific surface area (BET), pore volume and absorption edge of CoSMOR and NiSMOR samples prepared from zeolite and bulk CoS and NiS samples

Sample	Band gap (eV)	Specific surface area (m ² /g)	Particle size (nm)	Pore volume (cm ³ /g)	Absorption edge (nm)
NaMOR		315		0.14	
CoSMOR	3.86	24	10	0.052	322
NiSMOR	3.90	46	6	0.073	318
CoS bulk	3.58	14	25	0.036	347
NiS bulk	3.53	20	18	0.046	350

peaks indicative of mordenite zeolite. But, some differences, such as the broadening of the diffraction peaks, increasing or decreasing of some peaks intensity as well as the shift of the peak position to the slightly lower angles can be observed in the spectra. In fact, the intensities of the (200), (330), (350), (511) and (080) peaks in the host–guest nanocomposite materials are decreased with respect to those of NaMOR. This decrease of the peak intensities, in agreement with the reported results for other zeolites [14,15] can be related to the presence

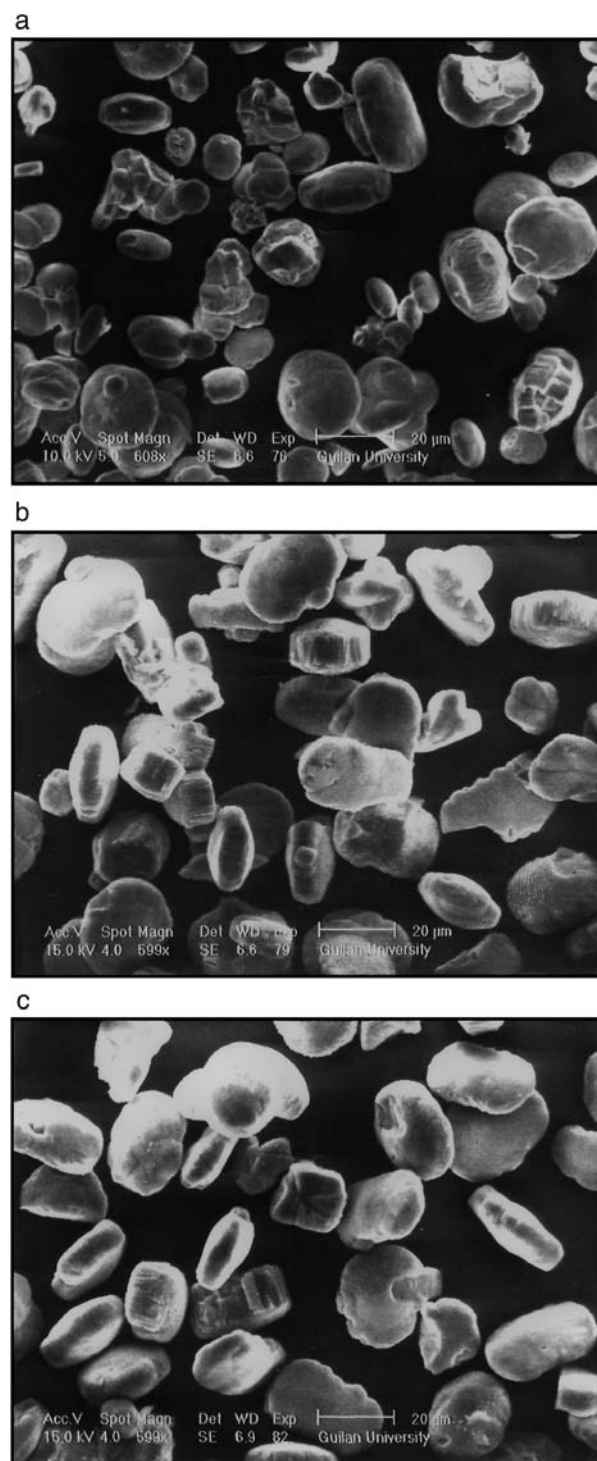


Fig. 2. Scanning electron micrograph of (a) NaMOR, (b) CoSMOR and (c) NiSMOR.

or incorporation of semiconductors inside the matrix structure. In the present patterns there is an increase in some peak intensity when the CoS particles are present in the mordenite zeolite. These peaks are located approximately at 2θ equal to 47.5° and 55° which are due to the reflection of the (102) and (110) planes, in the CoS phase, respectively [16]. Proceeding in the same way, we found an increase in intensity of some peaks in the case of NiS, at 32.5° , 39° and 46° which are related to the (300), (211) and (102) planes of NiS phase [16].

Analysis of the β , excess of width line of the diffraction peak in radians and θ , the Bragg angle in degrees and using the Debye–Scherrer formula, $d = 0.9 \lambda / \beta \cos \theta$, where d is the average diameter of the crystal and λ the wavelength of X-ray, we determined the average size of NiS and CoS nanoparticles to be 6 and 10 nm, respectively.

To investigate the locations of the guest materials in the composite materials, we measured the specific surface area and pore volumes of the MOR zeolite and our prepared NiSMOR and CoSMOR composite materials.

The results of the specific surface area and pore volume measurements for NaMOR, NiSMOR and CoSMOR (Table 1), show that the pore volumes of the host zeolite, which was 0.14 ml g^{-1} for MOR zeolite, decreased to 0.073 and 0.052 ml g^{-1} for the NiSMOR and CoSMOR composite materials respectively. Similarly, the specific surface areas of the composite materials were decreased from $315 \text{ m}^2 \text{ g}^{-1}$ for NaMOR to $46 \text{ m}^2 \text{ g}^{-1}$ and $24 \text{ m}^2 \text{ g}^{-1}$ for NiSMOR and CoSMOR respectively. Decreasing of the volumes of the pores and the specific surface area of the MOR zeolite demonstrates that the guests are located in the cages of MOR zeolite. The guests may mainly be located in the supercages of MOR zeolite.

The surface morphology of NiSMOR and CoSMOR nanocomposite was studied by scanning electron microscopy. The SEM pictures of unloaded MOR zeolite and the prepared composite materials are presented in Fig. 2. The crystallites of the unloaded MOR zeolite, with sizes between 10 and $20 \mu\text{m}$, have a very well defined rice-grain and were needle shape and rectangular parallelepiped crystals. The image of the CoSMOR and NiSMOR composites shows that the rice-grain and needle shape of the MOR zeolite crystallites is not affected by the NiS and CoS loading. These micrographs show also no significant CoS and NiS outside the zeolite pores.

In Table 2, we summarized the weight percent of each element for all samples, obtained by EDS. These reported values were a qualitative pointer of the semiconductor incorporation inside the matrix.

UV–Visible absorption spectra for bulk CoS and NiS and nanocomposite materials are given in Fig. 3. Comparison of the absorption edge of bulk CoS and NiS with CoSMOR and NiSMOR samples shows a blue shift in the onset of absorption observed in mordenite samples. This phenomenon has been ascribed to a decrease in particle size. It is also well known that in the case of semiconductors, the band gap between the valence and conduction band increases as the size of the particle decreases in the nanosize range.

The magnitude of the band gap depends on the particle size of the semiconductor. In the present work, we calculated the band gap of the nanoparticles in NiSMOR and CoSMOR samples (Table 1) from the onset of the absorption edge, using the method of Tandon and Gupta

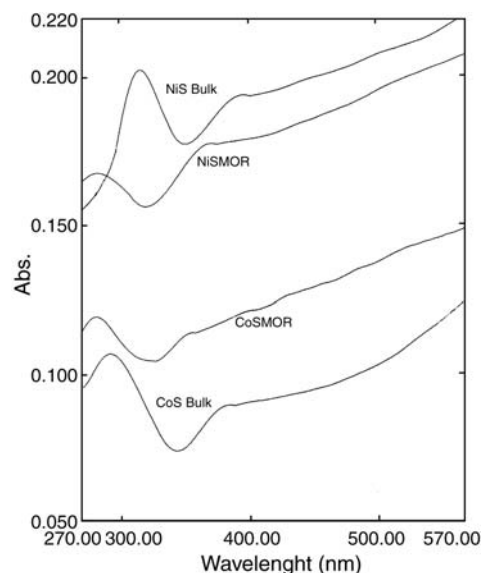


Fig. 3. Absorption spectra of CoS and NiS particles in mordenite zeolite.

[17]. The band gap is found to increase in the order NiSMOR > NiS bulk and CoSMOR > CoS bulk (Table 1). These results confirm the presence of NiS and CoS particles in the zeolite channels and cavities that could show quantum confinement effects. The magnitude of the band gaps was approximately similar to those observed in the composite material CoSY and NiSY [16,18].

4. Conclusions

In this work, we have studied a simple method for the synthesis of NiS and CoS nanoparticles inside mordenite zeolite. The growth of nanoparticles was started by ion exchange of NaMOR in a solution of Co^{2+} or Ni^{2+} ions, followed by treatment of the exchanged samples with Na_2S solution. The results obtained show the formation of nanoparticles only inside the zeolite pores. The samples exhibit blue shifts in the absorption edges with respect to the bulk samples. In spite of some changes which were appreciated in the zeolite framework, powder XRD results reflect that the zeolite structure is essentially maintained and the average size of the nanoparticles was 6–10 nm in the channels and cavities of zeolites.

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Table 2

Semi-quantitative chemical compositions obtained by EDS

Sample	Weight percent (%)						
	Na	Si	Al	O	Co	Ni	S
NaMOR	7.4	40.6	7.2	44.8	–	–	–
CoSMOR	7.1	37.2	7.5	43.5	4.0	–	0.7
NiSMOR	7.2	38.3	7.3	43.9	–	3.0	0.3

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