

Preparation and characterization of host (mesoporous aluminosilicate material)–guest (semiconductor nanoparticles) nanocomposite materials

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Abstract

We report the optical and structural properties of NiS and CoS nanoparticles in AIMCM-41 zeolite. The samples were obtained by sulfidation of the Ni²⁺ and Co²⁺ ion exchange zeolite in a Na₂S solution at room temperature. The optical properties of the samples were studied by UV–Vis spectroscopy. Their crystalline structure and morphology were studied by XRD and scanning electron microscopy (SEM). The results show that the nanoparticles grow outside the mesopore AIMCM-41 matrix. Exciton absorption peaks at higher energy than the fundamental absorption edge of bulk NiS and CoS indicate quantum confinement effects in nanoparticles as a consequence of their small size. The absorption spectra show that the optical band gap varies in the range 3.53–4.47 eV.

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1. Introduction

Since the discovery of buckminsterfullerene [1], nanostructured materials have attracted great interest due to their potential impact in many areas such as electronics, photonics, catalysis, and sensing [2,3]. Many applications are possible including one-dimensional superconductors, high-density semiconductor nanowire sensor arrays, gigahertz nanomechanical resonators, and high-density molecular electronics circuits [4,5]. In 1992, the synthesis of a new family of nanoporous molecular sieves designated as M41S was reported [6]. MCM-41, one member of this family, has uniform cylindrical pores in hexagonal arrangement and is produced using rod-like micelles of cationic surfactant molecules as a template. The main characteristics of MCM-41 are its high pore volume ($\sim 1 \text{ cm}^3 \text{ g}^{-1}$), large surface area ($\sim 1000 \text{ m}^2 \text{ g}^{-1}$) and very narrow pore-size distribution (2–10 nm). Due to the regularly hexagonal arrays of nanoporous channels and changeable pore diameters, MCM-

41 has become the particular focus of extensive investigations, and these properties make MCM-41 material among the best candidates as the hosts for many guest materials [7–10], especially semiconductor nanoparticles, which may prove useful in optoelectronic device applications.

In this work we reported the synthesis and characterization of AIMCM-41 loaded with NiS and CoS nanoparticles. MCM-41 is a mesoporous molecular sieve and their nanoparticle-loaded forms can be prepared by addition of the nanoparticles into the sol–gel mixture arranged for the synthesis of mesoporous material [11,12]. However, incorporation of aluminum into the structure of MCM-41 materials via isomorphous substitution of aluminum for silicon, generated ion exchange sites in this mesoporous molecular sieves [13]. Therefore, cationic metals such as nickel and cobalt can be reacting with AIMCM-41 by ion exchange method. AIMCM-41 zeolite, which has been used in the present work has Si/Al ratio equal to 5.6 with diameter size 24.4 Å. Here the growth of NiS and CoS nanoparticles in AIMCM-41 zeolite host obtained by Co and/or Ni ion exchange followed by treatments in Na₂S solution in studied. The results obtained from X-ray, UV–Vis, SEM experiments are reported.

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2. Experimental

The MCM-41 and AlMCM-41 materials were synthesized by a room temperature method with some modification in the described procedure in the literature [14]. We used tetraethylorthosilicate (Teos, Merck, 800658) as a source of silicon and hexadecyltrimethylammonium bromide (HDTMABr, BDH, 103912) as a surfactant template for preparation of the mesoporous materials. The molar composition of the reacting mixture was as follows:



EA stands for ethylamine. The MCM-41 prepared was calcined at 550 °C for 5 h to decompose the surfactant and obtain the white powder. This powder was used as the parent material to prepared AlMCM-41 free surfactant materials by post-synthesis alumination method. The AlMCM-41 surfactant-free material is white. This powder sample was used for loading the nanoparticles.

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 AlMCM-41 powder was separately added and stirred for 12 h at 25 °C. The samples were then washed to remove nonexchanged Co^{2+} and Ni^{2+} and air-dried. Finally, sulphurizing of the Ni^{2+} and Co^{2+} ions was carried out with 0.1 M Na_2S solution. To make the reaction with the S^{2-} ion, one g of Ni^{2+} or Co^{2+} -exchanged zeolite was added to 50 mL of 0.1 M solution of Na_2S at a fixed temperature and magnetically stirred for 2 h. The samples were washed with deionized water and collected by filtration. The obtained samples were fine powders with color grey. The samples were stable at ambient conditions that are their color did not change when exposed to the contact of atmospheric moisture.

For the sake of comparison, bulk NiS and CoS particles were prepared by a conventional precipitation method. In this

Table 1

Band gap, specific surface area (BET), pore volume and absorption edge of nanoparticle 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 (cc/g)	Absorption edge (nm)
AlMCM-41		949		0.89	
CoSAIMCM-41	4.47	1005	5	1.2	278
NiSAIMCM-41	4.44	1002	6	1.1	280
CoS bulk	3.58	20	18	0.046	347
NiS bulk	3.53	14	25	0.038	350

method, an equimolar amount of Na_2S solution was added dropwise to a stirred solution of 0.1 M NiSO_4 or CoSO_4 resulting in the formation of bulks precipitates. The NiS and CoS precipitates were washed repeatedly with distilled water until free from S^{2-} ions, dried in an air-oven and then calcined at 500 °C for 4 h in air. The obtained samples were fine powders with color dark.

Powder X-ray diffraction patterns of the samples were recorded using a Philips X-Pert diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). UV–Vis absorption spectra were recorded using a shimadzu 1600 PC in the spectral range of 190–900 nm. The specific surface area and pore volume of the samples were measured using a Sibata Surface Area Apparatus 1100. All of the samples were first degassed at 250 °C for 2 h. Chemical analysis of the samples was done by energy dispersive X-ray analysis (EDX) joined to a Philips XL 30 scanning electron microscopes. The water content of the samples was determined gravimetry. The surface morphology of the samples was obtained using a Jeol-JSM-5610 LV scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of NiS, CoS doped samples and the AlMCM-41, synthesized zeolite with no guest, to be used as a reference. In this figure, we observed that all X-ray patterns are very similar. But, some differences, such as the broadening of the diffraction peaks as well as the decrease of their intensity can be observed in the spectra. This should be attributed to the porefilling effects that can reduce the scattering contrast between the pores and the framework AlMCM-41 materials. This decreases of the peak intensities, in agreement with the reported results for other zeolites [15–17].

The specific surface area and pore volume of the AlMCM-41, nanoparticles samples and bulks are presented in the Table 1. As can be seen from Table 1, the pore volume of AlMCM-41, which was 0.89 mL/g, increased to 1.1–1.2 mL/g in NiS or CoS AlMCM-41 nanoparticles. The increase in the surface area and volumes of the pores of the AlMCM-41 in nanoparticle samples has demonstrated that the guest could grow outside the mesopore AlMCM-41 matrix. [16,17].

The surface morphology of AlMCM-41 and nanoparticle samples has been studied by scanning electron microscopy. The SEM pictures of the unloaded AlMCM-41 and samples are presented in Fig. 2. It can be seen that the crystallites of the unloaded mesopore zeolite, with size between 1–2 μm , have a very well-defined shape. The image of the nanoparticle samples shows that nanoparticles aggregates attached to

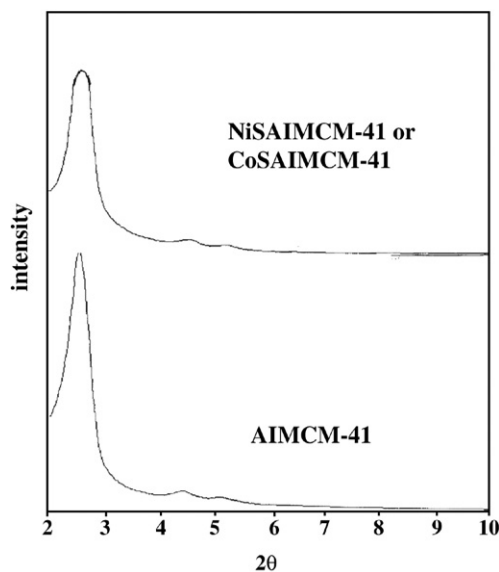


Fig. 1. X-ray diffraction patterns of AlMCM-41 and NiSAIMCM-41 or CoSAIMCM-41.

the face of the mesopore zeolite but shape of the mesopore zeolite crystallites is not affected by the NiS or CoS loading. It is clear that nanoparticles with size about 5–6 nm can not located into pores of zeolite with size 2.44 nm.

From EDX results for this samples the presence of sulphur, nickel and cobalt atoms and a Si/Al ratio of 5.6 were estimated.

UV–Visible absorption spectra for bulk CoS and NiS nanoparticle materials are given in Fig. 3. Comparison of the absorption edge of bulk CoS and NiS with CoSAIMCM-41 and NiSAIMCM-41 samples shows a blue shift in the onset of absorption observed in AIMCM-41 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.

This behavior is agreement with that reported in other studies where similar behavior in nanoparticles of the same semiconductors is observed [17–19]. The phenomenon of blue shift of absorption edge has been ascribed to a decrease in particle size. From the onset of the absorption edge, the band gap of the nanoparticles was calculated using the method Tandon and Gupta [20]. In Table 1, the calculated values for the band gap of bulk CoS and NiS are 3.58 and 3.53 eV respectively, while the measured values are modified by quantum confinement size

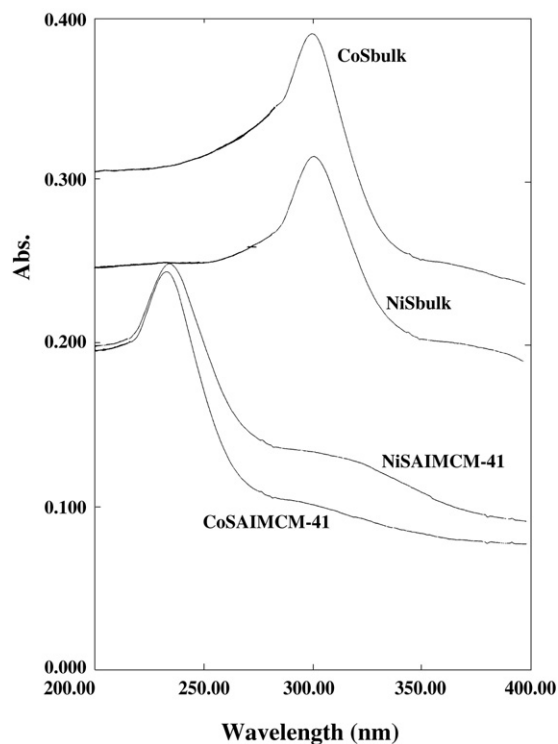


Fig. 3. Absorption spectra of CoS and NiS particles in AIMCM-41 zeolite.

effects due to the formation of nanoparticles. The band gap is found to increase in the order CoSAIMCM-41 > NiSAIMCM-41 > bulks (Table 1). The magnitude of the band gaps was approximately similar to those observed in the composite material CoSY and NiSY [18,21].

4. Conclusions

In this paper, AIMCM-41 mesopore zeolite was synthesized and characterized. The growth of nanoparticles of NiS and CoS were performed by ion-exchange of AIMCM-41 zeolite in a solution of Co^{+2} or Ni^{+2} ions, followed by treatment of the exchanged samples with Na_2S solution. The results obtained here show the formation of nanoparticles on the surface AIMCM-41 zeolite with size about 5–6 nm. The samples exhibit blue shifts in the absorption edges with respect to the bulk samples. The powder XRD results reflect that the zeolite structure is essentially maintained.

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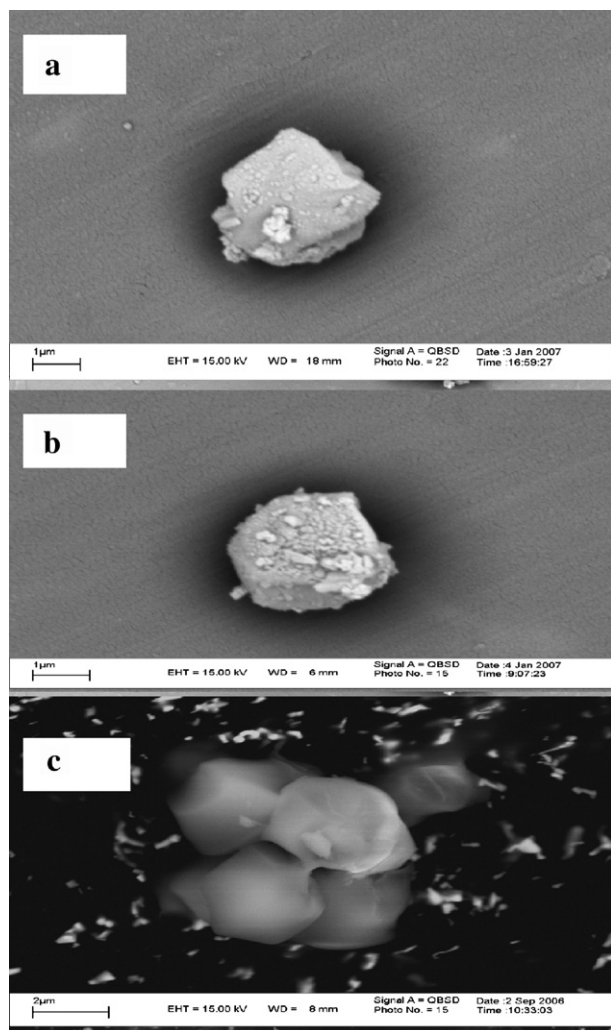


Fig. 2. Scanning electron micrograph of (a) NiSAIMCM-41, (b) CoSAIMCM-41 and (c) AIMCM-41.

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