THE INFLUENCE OF ION EXCHANGE OF CdS NANOPARTICLES WITH Ag+ IONS TO PHYSICAL PROPERTIES OF CdS NANOPARTICLES

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CdS nanoparticles have been synthesized by sonochemical method. In this work, we investigated the influence of ion exchange with Ag+ ions on the structural and optical properties of cadmium sulfide nanoparticles. The structure and morphology of both of sample were characterized by X –ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscopy (SEM), Absorbsion spectra of ion exchange of CdS nanoparticles with Ag+ ions has been studied in different time intervals by Uv-vis spectroscopy.

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1. Introduction

In recent years II-VI groups' chalcogenids have attached much attention due to unique optical properties. These groups semiconductor has been applied materials of sensor and lasers, solar cells, optical filters and etc [1]. Cadmium sulfide is one of the most important semiconductors of II-VI element with direct band gap of 2.42 eV at room temperature [2]. CdS nanoparticles with n-type and p-type semiconductors,on the photovoltaic performance of heterojunction solar cells [3]. As a result of numerous studies that have been determined theproperties of nanoscale particles differ sharply from the properties of bulk crystals. CdS nanoparticles are one of the interesting materials with properties of quantum-confinement and surface effect. These fascinating systems exhibit optical and electronic properties quite different from their corresponding bulk semiconductor materials, due primarily to phenomena arising from quantum confinement effects, and may eventually form the basis of new and unusual molecular electronic devices [4]. The ion exchange in semiconductors leads to changes in the properties of acquired nanoparticles [5].Cadmium sulfide is one of the most investigated samples in this process. The new properties appears in the Se doped CdS nanocrystals [4,6].In other element such as Mn and Zn doped CdS appears ferromagnetic behavior [7]. Ag is active metal of IB groups and at the same time easily diffuse at room temperature [8]. Because of that was used in dopping and ion exchange process.

Sonochemical method is a profitable and inexpensive process for formation of nanoparticles. Sonochemical process provides smaller-sized particles than other synthesis method. For this reason this synthesis method has been widely used to synthesis of nanomaterials [9,10].

Doping is important for semiconductors, which plays a critical role in tunning their optical and electrical properties [11], for the potential applications in wavelength-controlled lasers [12] biotechnology [13] and solar cells [14]. Also, some experiments have confirmed that by means of small amounts of metal doping, the crystallization progress of semiconductors can be affected [15].At the same time, ion exchange process of metal chalcogenide is important process.

In recent years, doping of CdS nanostructures has attracted intensive attentions due to ion exchange by different elements. However, Ag is an active metal which can be easily diffuse even

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at room temperature [8].

In this study, we have discussed structural and optical properties of the synthesized CdS nanoparticles by sonochemical method and the changes structure and other properties of ion exchange process (Cd2+↔Ag+) dependence from ion exchange time and concentration. These studiessuggest that the ion exchange process of CdS nanoparticles with Ag+ ions and pure CdS nanoparticles are promising candidate for charge-collecting devices including photovoltaics and photodetectors.

2. Experimental

2.1. Synthesis of Cadmium Sulfide nanoparticles

0.01M solution of $Cd(CH_3COO)_2•2H_2O$ and 0.07 M solution of Na_2S were separately dissolved in 50 ml distilled water. 3-Mercaptopropionic acid was used as capping agent. Percent of capping agent were selected 5%. For to prevent oxidation, reaction medium was constantly exposed with nitrogen gas. Reaction was carried out for 2 hours. As a result of the reaction, a yellow solution was formed. Solution were centrifuged, washed 3 times with distilled water and then alcohol and dried at roomtemperature.

2.2. Ion exchange process of CdS nanoparticles with Ag+ ions

For ion exchange of CdS nanoparticles with Ag^+, 0.005M and 0.1M of $Ag(NO_3)_2$ solutions were added in CdS dried powder, separately. In small concentration - 0.005M solution of ion exchange of CdS nanoparticles with Ag^+ ions (*A sample*) gradually turns into black color. In 0.1M solution (*B sample*) suddenly turns into a black color. Changing of optical properties has been studied at different times in order to observe with UV- visible.

3. Result and discussion

3.1. Structural properties

XRD is one of the important analysis method for determination unknown materials and its lattice parameter, structural properties and crystal planes. In Fig.1 is shown XRD pattern (20° ≤ 2ϴ≤ 60°) of pure CdS powder and A and B samples. In fig1.a shown the prominent peaks of pure CdS with 2ϴ values of 25.87°, 43.10°, 53.07° conform well cubic structureofCdSwithinagreementwithliteraturevalues(JCPDS Card No. 10-0454) and can be indexed as (110), (220), (311) Miller indices. At the same time the XRD pattern of A sample is shown in Fig. 1.b, 2ϴ values of 23°, 26°, 34°, 43°, 48°, 55° corresponds to CdS nanoparticles formed in cubic phase.However, the peaks shifted to a smaller wavelength. In Fig.1.c describe the XRD result of B sample containing silver sulfide nanoparticles and may be assigned to the (-121),(-122) (110), (013), (-104),(031), (-202) Miller indices. The formed particles are compatible to the monoclinic silver sulfide Ag_2S from literature review [16]. The crystal structure of the samples has changed from the cubic phase of cadmium sulfid to monoclinic silver sulphide with increasing Ag^+ ions concentrations.

The crystallite size (D) of nanomaterials was estimated from Debye-Scherer equation [9]:

$$D=0.9\lambda/\beta\cos\Theta$$

where, λ is the wavelength of Cu Kα radiation (λ = 1.5406 Å), β is the full-width at half maximum, θ is the diffraction angle. The average size of particles has been appointed approximately 28 nm, 33 nm and 24 nm according to CdS, A and Bsamples.

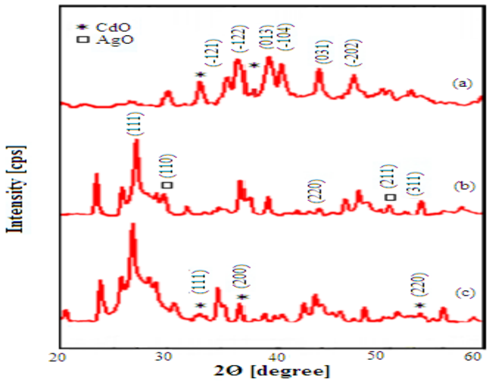
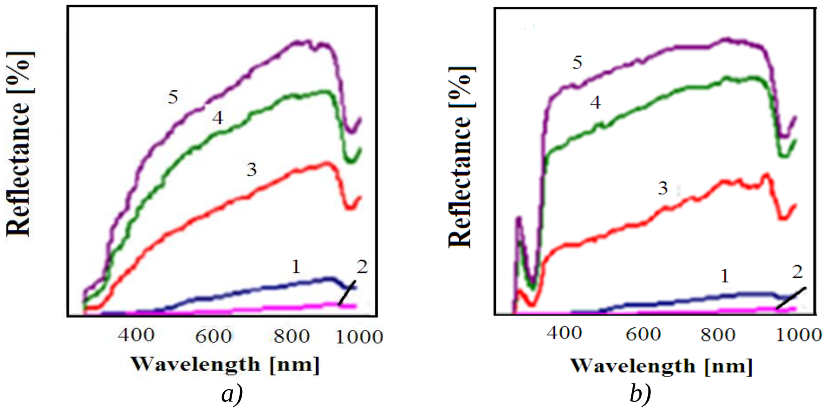


Fig.1. XRD patterns of (a) pure CdS nanoparticles; (b) A sampleand (c)Bsample.

3.2. Optical properties

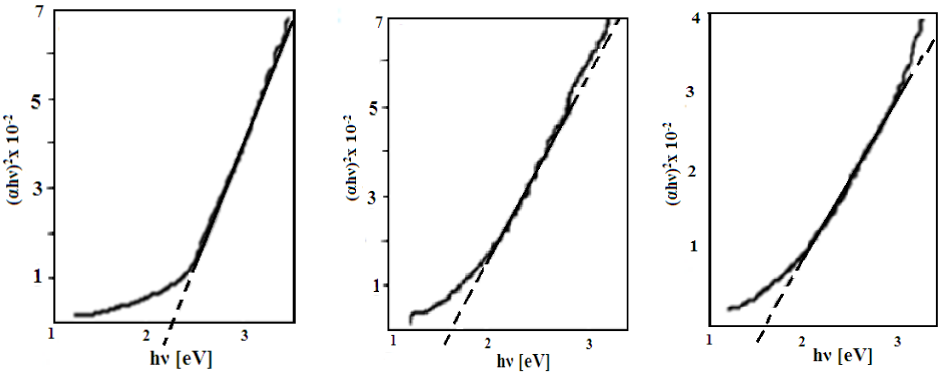
The optical transmission spectra of CdS nanoparticles and ion exchanged samples were recorded as a function of wavelength in the wavelength range 190-1100 nm in Specord 250 spectrophotometer at different time: 0 min, after 15 min, after 45 min, after 75 min. In Fig.2 is shown the UV-visible transmittance spectra of pure CdS nanoparticles and ion exchanged samples in differenttime.



a) *b)*

Fig.2. UV spectra in different time: a) A sample; b) B sample
(1-CdS;2-0 min; 3-15 min; 4-45 min; 5-75 min).

The plot showing the variation of $(\alpha h\nu)^2$ against hν is shown in Fig. 3. The value of band gap $E_g$has been determined in a direction touching the curve in y axis. Band gap were determined 2.25 eV, 1.62 eV and 1.60 eV according to CdS, B and A sample. The band gap of bulk Ag_2S crystals is 0.9 eV [17]. The value of the band gap zone decreases with increasing of concentration of Ag^+ ions. B sample partially retains the physical properties of pure CdS. The results show that by increasing of concentration of ion exchange solution, Ag_2S nanoparticles are formed more rapidly. Consequently, the band gap decreases and it results increasing conductivity of the semiconductor. The ion exchanger- Ag^+ will act as an acceptor [18]. The value of the band gap depends on the inverse proportionality with particle size. But this result does not coincide with the size of particles from XRDresults.



a) *b)* *c)*

Fig.3. Band gap value of nanoparticles.
a) CdS b) A sample; c) B sample

In Table1 is given the value of the band gap zone of nanoparticles measured indifferent times. However, band gap zone is divided into two parts. This is show that, in the sample are formed two structures: CdS and Ag_2S. The results show that the value of the band gap is increasing bytime.

Table1.Band gap value of ion exchange of CdS nanoparticles in different time intervals.

Samples	15 min	45 min	75 min
0.1M solution of $Ag(NO_3)_2$	1.2eV; 1.65eV	1.4 eV; 1.9 eV	1.4 eV; 2.0eV.
0.005M solution of $Ag(NO_3)_2$	1.7eV; 2.45eV	1.7eV; 2.52eV	2.0eV; 2.8eV.

As can be seen in Table 1, in small concentrations the band gap value corresponds to the band gap value of theCdS. In a high concentration, this value is compatible to band gap value of Ag_2S. It is possible to observe the transformation process depending on time by optical measurements at different times. During the next measurement, with increasing of the value of the band gap zone, the size of the particle is decreases.

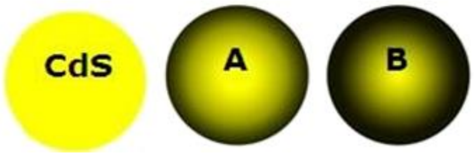
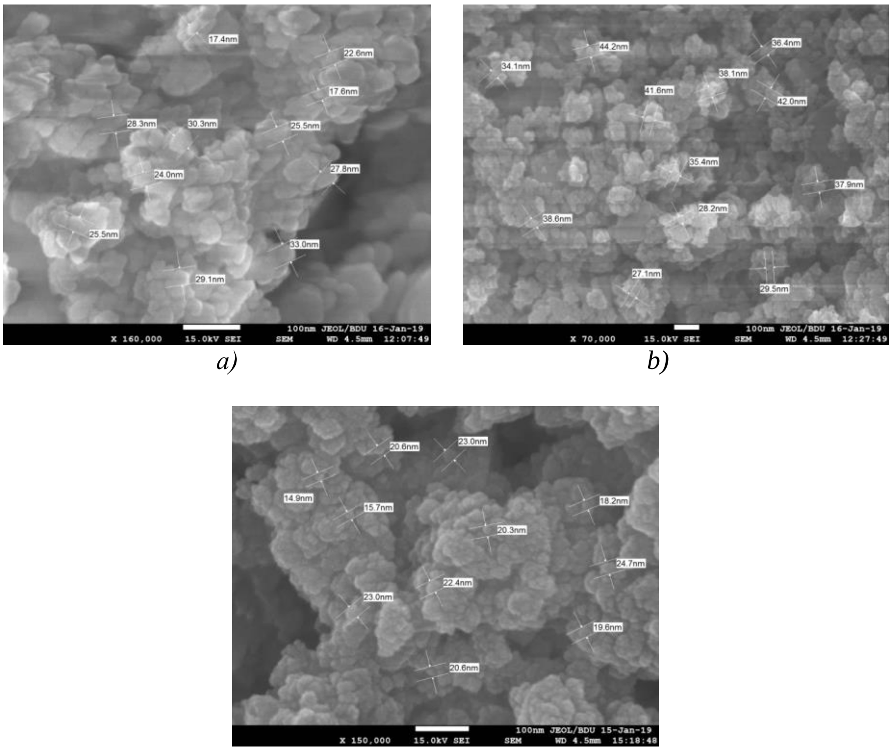


Fig.4.The transformation process of samples.

Transformation process of CdS nanoparticles to Ag_2S nanoparticles is shown in Fig. 4. In the ion exchange with the Ag^+ions form a diffuse bound with CdS nanoparticles. Squeezing out of Cd^{2+}ions by Ag^+ions carry out diffuse character.

3.3. Surface morphology

SEM analysis is an indispensable method of studying the morphology of the surface particles. It also allows the determination of the size and shape of the particles and determining of the sequence of their position on the surface. The size of the particles depends on concentration of ion exchange ions. The SEM images of pure CdS nanoparticles is shown in Fig. 5.



a)

b)

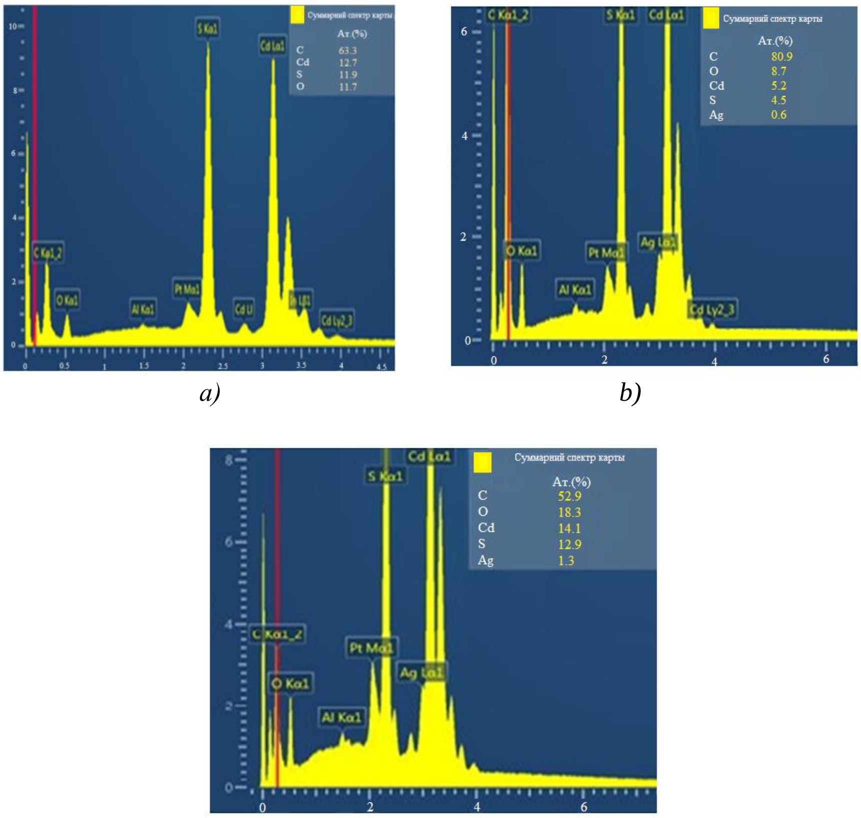
c)

Fig.5. SEM images of nanoparticles.
a) pure CdS; b) A sample; c) B sample

As seen from the SEM images, particles were distributed non-uniformly. The dimensions of nanoparticles are in range of 17-33 nm. After ion exchange process of small concentrations, the particles size is larger than the pure CdS nanoparticles size, where the particles sizes are 27-42 nm in Fig.8. Which is explained that in the small concentration of ion exchange process simultaneous formation of CdS and Ag_2S nanoparticles. The SEM image of 0.1M solution of ion exchange process of CdS nanoparticles are show that the particles sizes are in the range of 14-24 nm. The particles are intensively located one-another. All of SEM results are compatible with XRDresults.

3.3. Element analysis

EDAX analysis allows precise determination of the atomic percentage of the elements contained in the elemental analysis of the substance to be investigated. The purity of CdS nanoparticles and ion exchange process of CdS nanoparticles with Ag^+ ions determined by EDAX study reveal the presence of Cd, S and Ag as elementary constituents. Quantitative atomic percentages of the compositional elements (Cd, S and Ag) present in nanoparticles are given in Fig.6.



a) *b)*

c)

Fig.6. EDAX spectrum of nanoparticles.
a) pure CdS; b) A sample; c) B sample

In CdS nanoparticles the ratio of elements are Cd:S 51,4:13,8. After an ion exchange process of CdS nanoparticles, the Cd elements have been partially replaced by Ag atoms. In A sample the ratio of atomic percentage of Cd:Ag:S is 5,2:0,6:4,5. But in B sample the ratio of atomic percentage of Cd:Ag:S is 14,1:1,3:12,9. At higher concentrations, the Cd atoms are more replaced by silver atoms. It should be noted that speed of the process of transformation can be affected by the concentration, temperature and other environmental factors [5]. The presence of the carbon element depends on the presence of a carbon substrate and İn, Se and Al elements are related to the uncleanglass of the microscope. The oxygen is considered to be a residue element.

4. Conclusions

In summary, CdS nanoparticles have been synthesized by the ultrasound-assisted microwave synthesis method. The obtained samples were ion exchange process with Ag$^+$ ions at two different concentrations. The structural transformation occurred from cubic to monoclinic silver sulfide with increasing molar ratios of Ag$^+$ ions. The band gap was diminished with increasing of concentration. From SEM images is shown that some particles have agglomerated and form larger sized clusters. The particle size of A sample is 14-24 nm from SEM images, from XRD results had been calculated at 24nm.

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