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FORMATION OF THE COPPER SULFIDE NANOPARTICLES BY ION EXCHANGE FROM ELECTROLYTE SOLUTIONS

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Abstract:

CuS nanoparticles were formed within polymer matrix using combination of the successive ionic layer adsorption and reaction (SILAR) and ion exchange methods from aqueous solution. The process of transformation of cadmium sulfide nanoparticles into copper sulfide nanoparticles has been studied. The morphology, stoichiometric composition and optical properties of these structures have been investigated depending on ion exchange time of CdS/polymer samples in $CuS0_4$ solution.

1. Introduction

One of the interesting materials for optoelectronics, solar cell, photo detectors and photovoltaic devices is copper sulfide semiconductor. This is due to the fact that this material can be formed in various stoichiometric forms [1]. These materials possess very different physical properties and physico-chemical properties of these compounds strongly depend on stoichiometric composition. It should be noted that various forms of copper sulfide can be transformed to each other depending on temperature and other conditions. Copper sulfide films have a very wide range of specific resistance ($8.10^{-3}\div5,2\cdot10^{3}$ ohm·sm). As it is noted in the work [1] with increasing sulfur content specific resistance of samples decreases and there is observed transition from high-resistance Cu_2S semiconductor to CuS with metal properties. According to the literature the band gap of these materials varies between 0,6eV-2,35eV [1,2] and depends on crystal structure and chemical composition. There are various methods of formation nanomaterials on the basis of copper sulfide: chemical bath deposition from electrolyte solutions [3], pyrolysis [4], vacuum evaporation [5], sonochemical synthesis [6] and others. Among them there is an attractive one-successive ion layered adsorption and reaction (SILAR) [7-12]. Use of this method allows to controlling the thickness of grown thin films and sizes nanostructures on level monolayer.

One of perspective directions of the modern nano materials science is formation of nanoparticles with complex composition and desired chemical compound and structure. It needs developing technologies which can purposefully change chemical composition of nanomaterials. The combination of various methods of formation with an ion exchange from electrolyte solutions [15] can become one of such methods. This method will allow obtaining a core/shell type structures with diffuse boundary, and also transforming chemical composition of nanomaterials. By changing chemical composition of nanomaterials it is possible to operate their physical properties.

In this work there was studied the possibility of transformation of cadmium sulfde nanoparticles into copper sulfide nanoparticles by an ion exchange from electrolyte solutions.

2. Experimental

2.1. Materials and methods

All the chemicals were of analytical reagent grades. UV-vis spectra were measured on a UV-visible SPECORD 250 PLUS. Atomic Force Microscopy (AFM) images have been taken with Veeco AFM instrument using nanocomposite film as the sample. Transmission Electron Microscopy (TEM) images have been taken with FEI TECNAİ G2 20 X–TWIN device using 200 kV voltage. Energy Dispersive X–ray analysis (EDX) have been carried out with EDX RÖNTEC Quantax analytical device. Powder XRD patterns have been taken with Rigaku MiniFlex Desktop X–ray Diffractometer. Atomic Absorption Spectrometer ZEEnit 650P was used for optical measurements. Fourier Transform Infrared (FTIR) results were taken by Varian 3600 spectrometer.

2.2. Technology of sample preparation

Two steps were used for obtaining copper sulfide nanoparticles in a polymer matrix. In the first step cadmium sulfide nanoparticles were formed in a polymer matrix (gelatin, poly(vinyl alcohol) or polybutadien) using successive ionic layer adsorption and reaction (SILAR) method [8]. Electrolyte solutions of $Cd(NO_3)_2{\cdot}5H_2O$ and $Na_2S{\cdot}9H_2O$ salts were used as sources of cations and anions. The concentrations of electrolyte solutions were 0,2M. Distilled water was used as the solvent in the case when the gelatin and polybutadiene were used as a polymer matrix. But in the other case when poly(vinyl alcohol) was used as the matrix for cadmium sulfide nanoparticle formation, ethylene glycol was the solvent.

The growth process was initiated by immersing the sample (glass substrate covered with thin films of polymer) into the electrolyte solution which contains cadmium ions. Sorption time was 30 s. Then the sample was washed three times in a solvent to remove the residues of electrolyte solution containing cadmium ions. After the washing process, the sample was immersed into the electrolyte solution which contains sulfur ions. The sorption time of sulfur ions on aqueous solution was 30 s. The sorption time was 15 minutes for the case when ethylene glycol was used as solvent (in case when PVA was used as the matrix). After sorption of sulfur anions, the remaining electrolyte was eliminated with the help of triple washing in solvents. The washing time was 90 s. Thus, one cycle of CdS nanoparticle growth was completed. For increasing of the sizes of particles the above-stated process was cyclically continued. By means of the given process the samples with various growth cycles were prepared. The method of the formation of the nanoparticles with help of SILAR technique, their, growth and structural investigations have been described in [14,15].

The second step of this method is the transformation of the cadmium sulfide nanoparticles into copper sulfide by an ion exchange from aqueous solution. An aqueous solution of $CuSO_4{\bullet}4H_2O$ containing copper ions was prepared for carrying out an ion exchange process. An ion exchange process is taken place when samples are immersed into the solution. The copper ions displace cadmium ions from the sample to solution.

$$CdS+Cu^{2+} \Rightarrow CuS+Cd^{2+}$$

As a result of ion-exchange, cadmium ions move into the electrolyte solution. In the polymer matrix, cadmium sulfide nanoparticles are transformed to copper sulfide nanoparticles.

3. Results and discussion

3.1. Kinetics of the process

The dependence of the concentration of cadmium ions in the solutions and powders of CdS from ion exchange time was investigated for studying the kinetics of ion exchange process. Powders of cadmium sulfide (Merck, chemically pure grade) were used as a model object. Cadmium sulfide powders were milled in a ball mill to reduce the size. The particles with sizes less than 1 micron were used for the experiments. Sedimentation method was used for separation of the particles. Figure 1 shows the changes in the ratio of concentrations of copper and cadmium ions in a powder and solution, depending on the time of ion exchange. It can be seen from the figure that the amount of copper in the powder increases with increasing ion exchange time. When the ion exchange time reaches 5 hours the saturation is reached. This is apparently due to the following factors: a) cadmium ions are replaced with copper ions on the surface region with increasing the exchange time. b) As a result, the amount of cadmium ions decreases in the surface region of the particle. c) At the same time, penetration of the copper ion into the inner region of the particles of cadmium sulfide is hindered. Due to these factors, the ion exchange speed is slowed down.

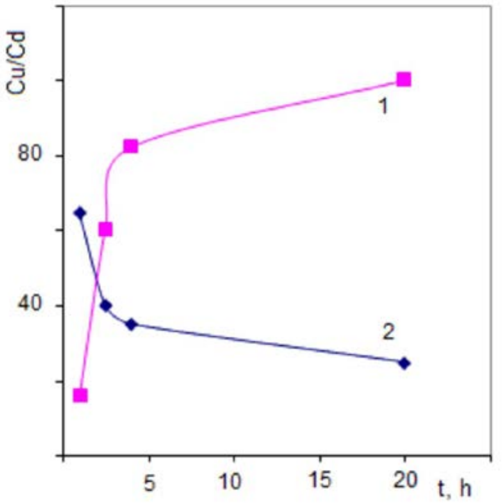

Fig. 1 The dependence of the ratio of concentrations of copper and cadmium ions in the powders (1) and solutions (2) from ion exchange time

3.2. Microscopic characterization

3.2.1. AFM

The morphologies of the obtained samples was investigated by the AFM. The AFM images of the surfaces of CdS/gelatin samples with 3 and 5 cycles of growth were shown in the figure 2. It can be seen from figure 2 (a) the average size of particles for 3 cycles of growth (initial stage of growth) is about 3 nm. On the initial stage nanoparticles basically are formed in the field of defective structure of polymer. It is evidently connected with prevalence of the broken bonds in this area. The probability of formation of nucleation centers and nanostructures in this area is high. The sizes of growing nanoparticles depend on the quantity of formation cycles. The particles are growing with increasing of quantity of cycles. At 5 growth cycles the average size of particles is 14 nm. Figure 1 (b) shows that the particles are heterogeneous in the sizes. Heterogeneity of particles in the sizes is basically related to the following factors: a) formation of new particles during the growth process; b) coalescence of the particles. It should be noted that the heterogeneity in the size and distribution of particles on film thickness can be formed with increasing the quantity of cycles.

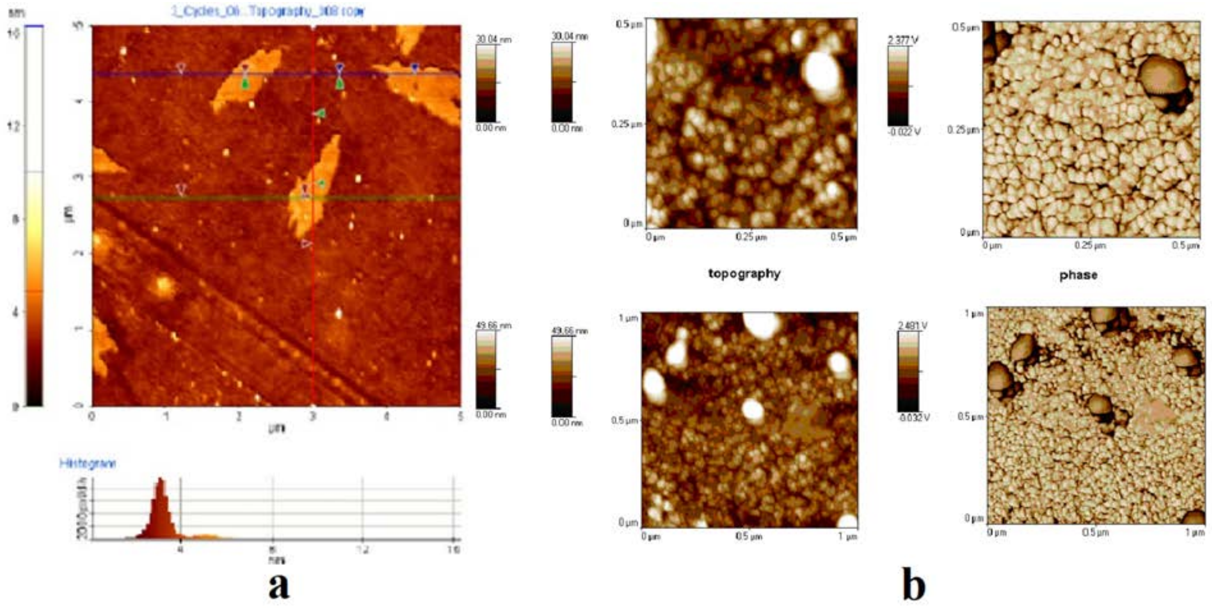

Fig. 2 AFM image for CdS/gelatin with 3 (a) and 5 (b) growth cycle

3.2.2. TEM

Figure 3 shows the TEM images of the obtained nanoparticles formed in 3 and 5 growth cycle. It can be seen from the images that obtained nanoparticles are in the 7-17 nm range. Besides the surfaces of these nanopartricles are seen distinctice. Surface areas are light colored than the internal dark part. It shows that copper ions are located on the surface which is characteristic for the process used in this work.

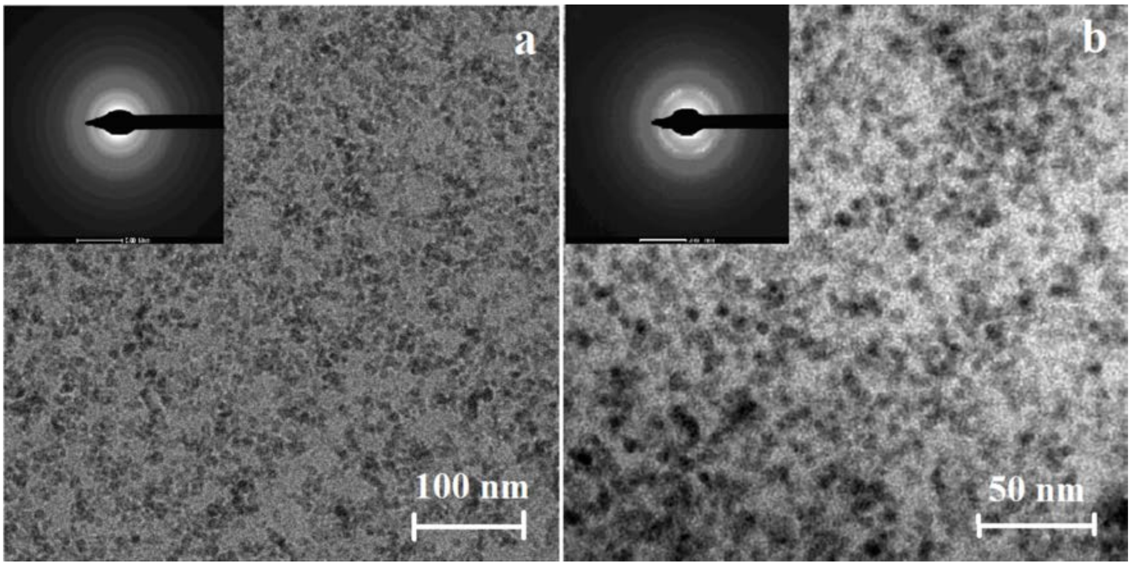

Fig. 3 TEM images for CdS/gelatin with 3 (a) and 5 (b) growth cycle

3.3. EDX

The stoichiometric composition of the obtained samples was investigated by the EDX. The results of the EDX are shown in figure 4. In CdS/polymer samples with 5 growth cycles the ratio of elements Cd : S is 44,58 : 55,42. After an ion exchange in a water solution cadmium atoms in nanoparticles are replaced by copper atoms. When exchange time is 0,4 hours the ratio of Cd : Cu : S is 29,14 : 26,58 : 47,27. But when the exchange time reaches ~29 hours cadmium sulfide nanoparticles are completely transformed into copper sulfide nanoparticles. The reflexes from cadmium atoms are not visible for such kind of samples. It should be noted that speed of the process of transformation can be affected by the concentration, temperature and other environmental factors.

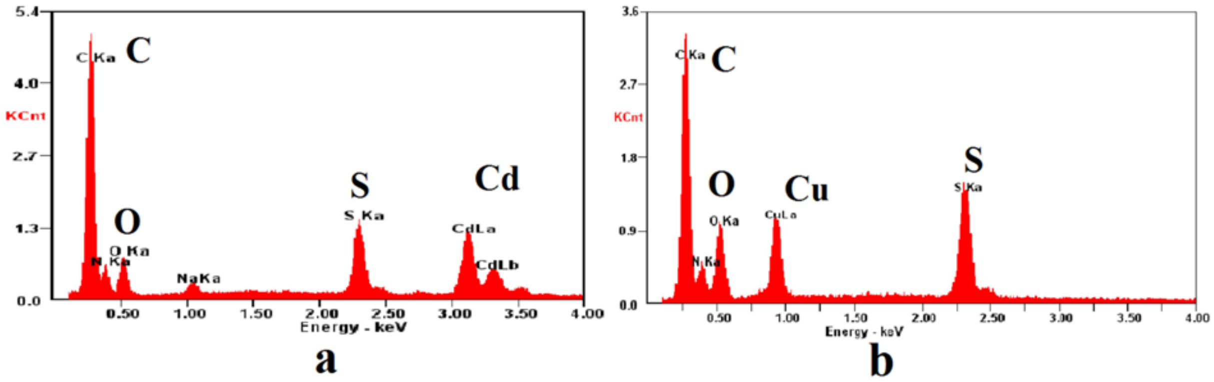

Fig. 4 The results of EDX for CdS/gelatin samples (a) and CdS/gelatin probes kept in $CuS0_4$ solution for 29 hours (b).

3.4. XRD

Figure 5a shows XRD pattern for 15 cycles CdS/polybutadiene before and after ion exchange process. The time of ion exchange process was 29 hours. But figure 5b represents the XRD patterns for CdS/gelatin samples with 15 cycles of growth before and after ion exchange. In this case the ion exchange time was 22 hour. It can seen from this figure that, after an ion exchange process the cadmium sulfide nanaparticles was transformed to copper sulfide nanoparticles.

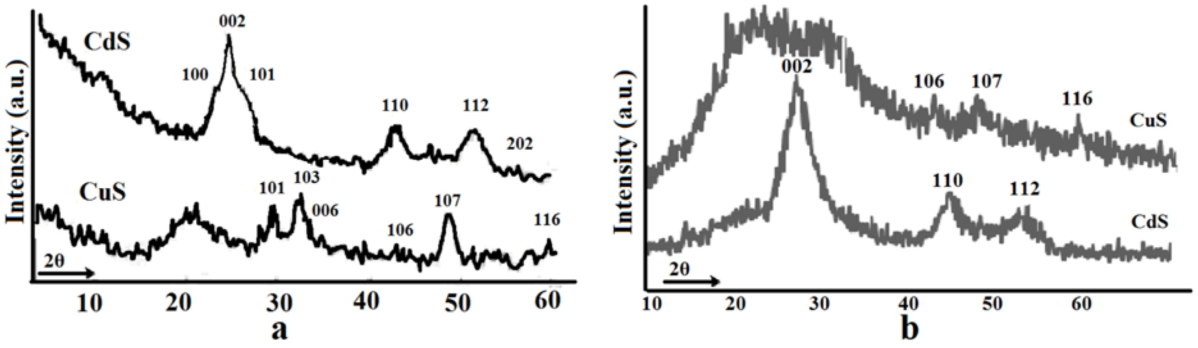

Fig. 5 a) XRD patterns for CdS/polymer (polybutadiene) samples with 15 cycles of growth before (CdS) and after (CuS) ion exchange process. The concentration of aqueous solutions of $CuSO_4 \cdot 5H_2O$ was 0,001M; the time of ion exchange process was 29 hour. b) XRD patterns for

CdS/gelatin samples with 15 cycles of growth before and after ion exchange. The ion exchange time was 22 hour.

3.5. UV-Vis

Figure 6 shows the transmission spectra for initial samples of CdS/gelatin and for samples after 2 and 3 hour ion exchange time. As we can see from this figure dependence of time of ion exchange the spectra of sample were changing and they look like the copper sulfide nanoparticles spectra.

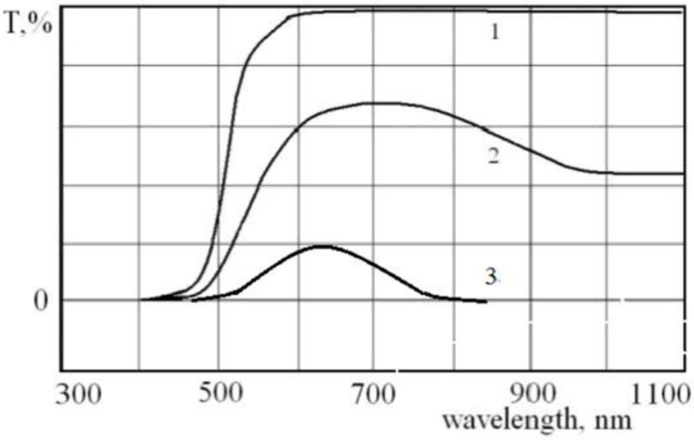

Fig. 6 (a) UV-Vis spectra of initial samples of CdS/gelatine with 5 growth cycles (curve 1), after 2 hours stay in the aqueous solution of CuSO4 with concentration 0,001M (curve 2) and after 3 hours stay in the solution (curve 3)

On the basis of the obtained optical spectra there were plotted the dependence of $(\alpha h\nu)^2$ on hν**.** The band gaps of the nanocomposites before and after an ion exchange were calculated using these data. Figure 7 shows the dependence of $(\alpha h\nu)^2$ on hν for CdS/gelatin samples with 5 growth cycles before and after ion exchange process. The band gap of samples decreases with increasing of ion exchange time. For initial CdS/gelatin samples band gap is 2,5eV, after 1 hour ion exchange 2,3eV, after 2 hour 2eV. Figure 8 shows the dependence of $(\alpha h\nu)^2$ on energy of photons (hν) for CdS/polymer samples with 15 growth cycles before and after ion exchange process. The band gaps of CdS/gelatin samples and samples kept in $CuS0_4$ solution for 1 and 2 hours are 2,5 eV, 2,3 eV and 1,95 eV, respectively.

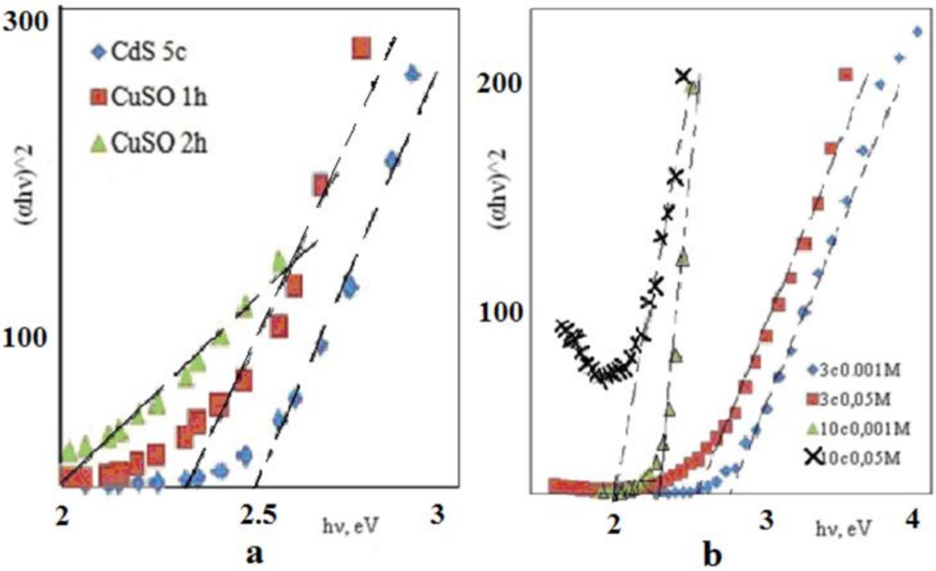

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Fig.7 (a) Dependence of $(\alpha h\nu)^2$ on hν for initial CdS/gelatin samples and for samples after 1 and 2 hour ion exchange time in $CuS0_4$ solution. (b) Dependence of $(\alpha h\nu)^2$ on hν for CdS/gelatin samples with 3 and 10 growth cycles dependence on concentration of aqueous solution $CuSO_4$. The ion exchange time is 2 hour.

In the dependence of $(\alpha h\nu)^2$ on hν for samples CdS/gelatine with 3 and 5 cycles of growth, the band gaps of initial samples are 2,7eV and 2,42eV. After ion-exchange in aqueous solution of $CuS0_4$ with concentration 0,001M (the time of ion exchange process was 2 hour) the band gap of structures is displayed to low energy region. The band gaps for 3 and 5 cycles growth are 2,62 and 2,33 eV. An increases in difference between band gaps of initial samples and samples after ion exchange process proceed with increasing of the concentration of solutions up to 0,05M. In this case the band gaps of samples are 2,56 eV (for 3 cycles of growth) and 2,05eV (for 5 cycles of growth). These results prove that the rate of an ion exchange process in solutions increases with increasing of the concentration of solution. Therefore, the process of transformation of cadmium sulphide nanoparticles to copper sulphide nanoparticles increases.

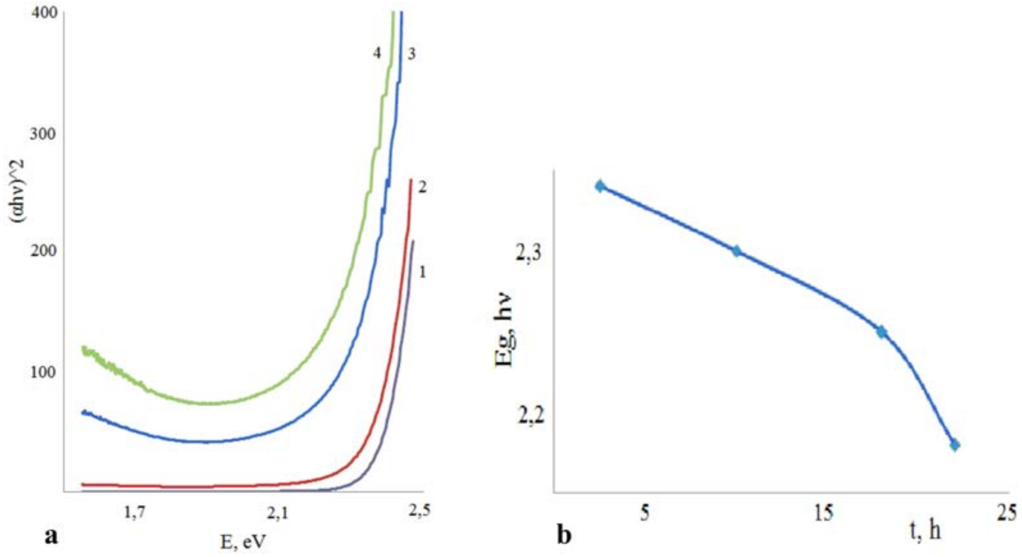

Fig. 8 (a) Dependence of $(\alpha h\nu)^2$ on hν for CdS/gelatin samples with 15 growth cycles; before (1) and after an ion exchange 2,5 h (2), 18 h (3), 22 h (4)
(b) Dependence of the band gap on an ion exchange time

3.6. FTIR

FTIR spectra of nanocomposite samples on the basis of cadmium sulfide and poly(vinyl alcohol) were taken in far infrared region. A range of wave lengths was 70sm^{-1}-500 sm^{-1} and the resolution on wave lengths was 0,1 sm^{-1}. The spectral analysis of samples was carried out by using diffuse reflection method. Figure 9 shows reflection spectra of CdS/polymer nanocomposites - initial and subjected to an ion exchange. It can be seen from the figure that, in initial samples maximum absorption peak of vibration spectrum (316 cm^{-1}) is characteristic for cadmium sulfide. After an ion exchange an absorption maximum is displaced to the high energy area. The dependence of absorption frequencies on an ion exchange time in 0, 1, 2.5, 4, and 20 hours were 316 cm^{-1}, 317 cm^{-1}, 318 cm^{-1}, 328 cm^{-1}, and 332 cm^{-1} respectively. This image is characteristic for the replacement of heavy atoms by light ones. If the lattice consists of two types of atoms, the frequency-mass dependence is:

$$\omega=(2C(1/m+1/M))^{1/2} \qquad (M > m).$$

Where ω is a frequency; C is a force constant, which characterizes forces between atoms in lattice; m and M are the masses of atoms. It is easy to understand that, if we change heavy atoms to light-weight atoms in the lattice, the frequency of vibration increases.

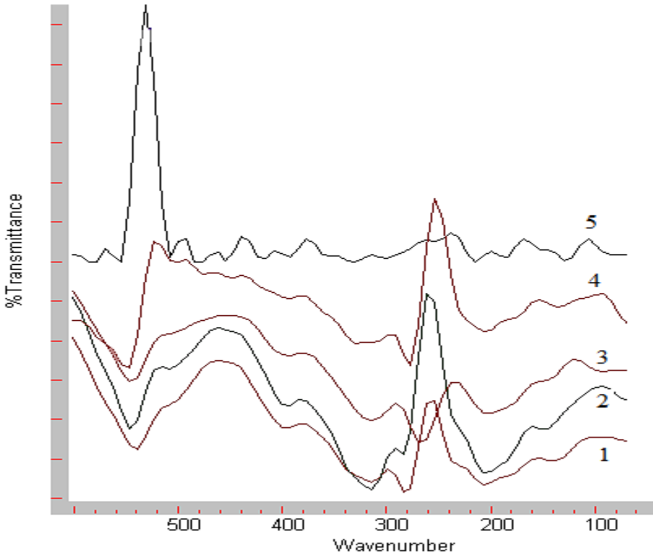

Fig. 9 FTIR spectra of CdS/polymer nanocomposites before (1) and after an ion exchange-1 h (2), 2,5 h (3), 4 h (4), 20 h (5)

Conclusions

In the present work the formation technique of copper sulfide nanoparticles by an ion exchange of CdS/polymer samples from electrolyte solutions is offered. It is shown that it is possible to transform particles of CdS into CuS by an ion exchange. With increasing of quantity of cycles fundamental absorption edge of samples are displaced into long-wave region. The rate of ion exchange depends on concentration of solutions and ion exchange time. The maximum of absorption of vibration spectra of samples depends on the time of ion exchange process and it was displaced to high energy region. This was explained with changing cadmium atoms to light copper atoms on nanoparticles.

Acknowledgements

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