Study of optical properties of metallic sulphide dispersions

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Abstract

The work is devoted to optical properties study of water dispersion and cadmium and zinc sulphide films, obtained by chemical deposition in the concentration range below the threshold. On the basis of the spectra absorption the forbidden-band width has been determined, and the calculations of the particle sizes of the synthesized samples have been made. The desposition of optical absorption band edge to a shorter short-wave region with decreasing particle sizes has been defined. The possibility of particle sizes control by varying the concentration of initial salt solutions has been demonstrated.

Keywords: semiconductor nanoparticles; waterdispersions; film; optical properties; forbidden-band width

1. Introduction

Due to the unique physical and chemical properties of nanoparticles and nanostructures there is a great interest in the functional nanomaterials creation based on the properties [1-2]. Recently, great attention is given to magnetic and semiconductor nanomaterials, and the interest is increasing. Identifying the influence features of particle sizes on their physical and chemical properties is one of the fundamental issues of modern chemistry [3].

Semiconductor nanoparticles are intensively studied because of their electronic properties [4-5]. The presence of discrete levels in the electrons energy spectrum allows to change forbidden-band width, the wavelength of the luminescence and absorption by varying the nanocrystals sizes. These nanocrystals features make it possible to create biological tags, light-emitting diodes, solar cells, lasers, adsorbents, catalysts and others. In this regard, the development of simple and accessible methods of nanoparticles synthesis of the type with given sizes, and the study of their optical properties are urgent.

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For the semiconductor nanocrystals synthesis the methods are used based on self-organization and particle growth limitation, namely controlled immersion plating in water solutions in the stabilizers presence or absence [7-8], the synthesis in reversed micelles [9], colloidal nanoreactors [1-3], in polymeric matrices [10-11], and others.

Method of immersion plating from unreal solution are widely used for the synthesis of high-dispersive powder, as well as continuous and discrete films of metal chalcogenides [8,11-12].

The objective of the paper is the synthesis of cadmium sulfide and zinc nanoparticles in water solutions and in polymer films by immersion plating and the study of their optical properties.

2. Experimental

Subject of research is water dispersion and cadmium sulfide and zinc films obtained by reacting the corresponding salts with sodium sulfide.

Salt solutions CdCl2 (CM = 1.25 - 10.00 mmol/L), ZnSO4·6H2O (CM = 10.00 - 37.50 mmol/L) and Na2S (CM = 0.1 mmol/L) were prepared in the double distilled water. Selecting a solutions concentration range was carried out on the basis of the coagulation threshold determination by optical method.

Metal sulphide films were obtained by layer-by-layer ions chemosorption from water solutions of the corresponding salts in the polymer matrix. The bats on object glass were used as carrying base.

The optical properties of cadmium sulfide and zinc water dispersion were examined by transmission in the wavelength range \( \lambda \) between 190 and 1100 nm Specol1500 spectrometer at 293 K.

The dependence of the forbidden-band width \( E_g \) on the particle sizes was determined from optical transmission spectra. For \( E_g \) calculation the spectral windows of the with a noticeable change in transmittance depending on the wavelength \( \lambda \) were used i.e, spectral windows from 270 to 600 nm, corresponding to photon energies of 2.07 to 4.59 eV.

Since the forbidden-band width is a function of the absorption coefficient \( \alpha \), which depends on the sample optical density, then after plotting the graph in \((\alpha \cdot E)^2 = f(E)\) coordinates (E is photon energy eV), we can calculate \( E_g \). The spectral dependence of the absorption coefficient \( \alpha \) for direct allowed transition has the form [12]:

\[
(\alpha \cdot E)^2 = A \cdot (E - E_g), \quad (1)
\]

where \( A \) is a factor independent from the incident radiation frequency.

The forbidden-band width is defined as the intercept on the axis E of the tangent to the linear part of the experimental absorption curve.

The radius of the synthesized particles (R) is determined by the formula [13]:

\[
E = E_g + \frac{\hbar^2 \pi^2}{2m^* R^2}, \quad (2)
\]

where \( E \) is the forbidden-band width of the nanocrystal semiconductor with a particle sizes \( R \); \( E_g \) is the forbidden-band width of the bulk semiconductor, \( m^* \) is the reduced mass of the exciton, \( \hbar \) is the Planck's constant. For cadmium sulfide \( E_g = 2.5 \) eV and \( m^* = 0.16 \) me (me is electron mass).

3. Results and discussion

Fig. 1, Fig. 2 show the transmission spectra of water dispersion of cadmium and zinc sulfides, depending on embedded reactants concentration in Na2S solution. The spectra analysis shows that the samples with a minimal salts concentration have maximum transmittance. Reducing the concentration of the initial reactants leads to the absorption edge shift to a shorter wavelengths area, indicating a reduction in particle sizes with decreasing of initial solutions concentrations. It should also be noted that the optical density of the systems rises in increasing the initial solutions concentrations, indicating the increase in the particles concentration of zinc sulphide and cadmium in the dispersion.
The inflection points in the spectra indicate the polydisperse composition of synthesized particles and the corresponding value of the forbidden-band width [12]. Accordingly, defined by the formula (1) the forbidden-band width will be an additive function of the values \( E_{gi} \), corresponding to particles of different sizes. Thus, the forbidden-band width for particles CdS (Fig. 4), obtained at concentrations of CdCl\(_2\) solution equals to 1.25 and 5.0 mmol/l, is to 3.65–3.54 eV, respectively. \( E_g \) values decrease with increasing of the initial reactants concentration, and, therefore, as the particles sizes grow. A similar relationship is typical for samples ZnS.

The transmission spectra comparative analysis of the cadmium sulfide synthesized films and dispersion, obtained from solutions with CdCl\(_2\) = 5.0 mmol/L concentration (Fig. 3) and the absorption spectra built on the energy scale, and also the calculations conducted on the basis showed that the films are polydisperse. It should be noted that under similar synthesis conditions, the average particle size in the polymer film is smaller than the particles size of waters dispersions and equals 19 nm, which is explained by the particles limited growth in a gelatin matrix [11].

![Fig. 1. The transmission spectra \( T(\lambda) \) of water dispersions of cadmium sulfide at various concentrations of CdCl\(_2\): 1 is 1.25 mmol/l; 2 is 3.75 mmol/l; 3 is 5.0 mmol/l.](image1.png)

![Fig. 2. Transmission spectra \( T(\lambda) \) of water dispersions of zinc sulfide at various concentrations of ZnSO\(_4\)-6H\(_2\)O: 1 is 10.0 mmol/l; 2 is 12.5 mmol/l; 3 is 25.0 mmol/l.](image2.png)
Fig. 3. The transmission spectra $T(\lambda)$ of the film (1) and of water dispersions (2) of cadmium sulfide obtained at a concentration CdCl$_2$ = 5.0 mmol/L.

Fig. 4. The absorption spectrum of cadmium sulfide nanoparticles at a concentration CdCl$_2$ = 1.25 mmol/L, built on the energy scale.

Estimation of the dispersion mean particle size according to the equation (2) showed that at the concentration of the cadmium chloride and zinc sulphate solutions below the threshold, the average particle sizes of the CdS and ZnS water dispersions are in the range from 12 to 24nm. Thus, the correspondence between the particles sizes of the cadmium sulfide and zinc water dispersions and the forbidden-band width is conditional, but it reveals the influence of particles sizes on the $E_g$ value. When reducing the particles sizes the forbidden-band width increases and the absorption band shifts to a shorter wavelengths spectrum area.

4. Conclusions

Zinc sulfide and cadmium nanoparticles in the form of water dispersion and films are synthesized by the method of immersion plating. The particles sizes in the samples are determined with the concentration of the cadmium
chloride and zinc sulphate solution below the threshold. The average particles size of water dispersions was 12 and 24nm at concentrations CdCl2 1.25 mmol/l and 5.0 mmol/l, respectively. The forbidden-band width of the nanoparticles water dispersions increases with the decrease in the average particles size. The average size of the synthesized particles in the films is less than the average particles size of the water dispersions obtained under the same conditions.

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