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Formation of nano- and microparticles CdS from thiourea solutions

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Effect of synthesis conditions (precipitation temperature, thiourea concentration) on CdS particles morphology has been studied under precipitation from 0.01, 0.1 and 1 M cadmium nitrate solutions using thiourea. Decrease of temperature to 20–25°C or increase of thiourea concentration above the stoichiometrical value leads to formation of the spherical particles. Use of microwave promotes formation of the spherical particles with the form of "flowers" consisting of small plates with wall thickness of 50–80 nanometers.

Изучено влияние условий синтеза на морфологию частиц CdS при осаждении 0.01, 0.1 и 1 М растворов нитрата кадмия тиомочевиной. Установлено, что основными факторами, влияющими на формирование частиц CdS, являются концентрация тиомочевины в растворе и температура осаждения. Снижение температуры до 20–25°C или увеличение содержания тиомочевины выше стехиометрического приводит к формированию сферических частиц. Использование микроволновой активации способствует образованию сферических частиц в виде "цветов", состоящих из небольших пластинок с толщинами стенки 50–80 нм.

1. Introduction

Semiconductor nanoparticulars are investigated intensively because their optical, electronic and catalytic properties essentially differ from those for macro-crystals materials and depend on morphological characteristics of the particles. Changing geometrical sizes and form of the particles it is possible to control their optical, electric and structural properties. One of the perspective semiconductor materials is CdS (E_g = 2.4 eV). CdS nanoparticulars attract a great attention because of potential possibility of their use in elements of solar batteries [1–3], optoelectronics [4, 5], biomarkers [6–8] and photochemistry [9]. Such nanoparticulars can be also considered as perspective sorbents of radio nuclides and ions of heavy metals from water solutions [10–12].

There are many methods of CdS nanoparticulars production: electrochemical [13], micelle [14], solvothermal [15–17], hydrothermal [18, 19] and other methods. The most simple and efficient method of CdS particles obtaining is precipitation from water solutions using thiourea or sodium sulfide. Despite of apparent simplicity of the method, the particles formation process will depend on many factors (temperature and duration of synthesis, concentration of components, etc.) that allows to obtain particulars with various morphology and, consequently, with different optically, catalytic

and electronic properties. In spite of the fact that the mechanism of metal sulfides formation from thiourea solutions is well studied [20, 21], the attention to influence of synthesis parameters on morphological properties of cadmium sulfide particles wasn't sufficiently investigated.

The aim of this work was study of the effect of precipitation conditions (temperature and concentration thiourea) on the morphological characteristics of the CdS particles obtained from thiourea solutions.

2. Experimental

For preparation of solutions $Cd(NO_3)_2 \cdot 4H_2O$ (99.9 %), $(NH_3)_2CS$ (TM) and water solution of ammonium hydroxide from "Reachim" were used. All solutions were prepared on the distilled water.

Precipitation CdS carried out as follows: 100 ml of solution $Cd(NO_3)_2$ with pH = 12 were placed in 250 ml flasks. Concentrations of $Cd(NO_3)_2$ solutions were 0.01, 0.1 or 1 M. pH was corrected by addition of water solution of ammonium hydroxide. Then thiourea was added in these flasks in mole ratios Cd^{2+}/TM 1:1, 1:2 or 1:4 at continuous mixing. The received mixtures were heated (t = 20, 70, 90°C) and maintained set time. The CdS precipitates were centrifuged and washed several times with distilled water, and dried at 60°C for about 6 h. Depending on synthesis conditions the precipitates are obtained lemon yellow or red colors.

Microwave synthesis was carry out in microwave equipment MARS (GEM Corporation Matthews, USA). 50 ml of 0.1 M $Cd(NO_3)_2$ solution with pH = 12 (pH was corrected by adding of water solution of ammonium hydroxide) were placed to 100 ml teflon flasks. Then thiourea was added in mole ratios Cd^{2+}/TM 1:1, 1:2 or 1:4 at continuous mixing. The reaction was performed under microwave irradiation (2450 MHz) for 30 min at 90 and 150°C. After cooling to ambient temperature, the precipitates were centrifuged and washed several times with distilled water, and dried at 60°C for about 6 h. In result yellow colors precipitates were obtained.

To obtain the FT-IR spectra, a SPECTRUM ONE (PerkinElmer) infrared spectrometer operating with a spectral resolution of 1 cm^{-1} was used. The X-ray diffraction (XRD) patterns of the samples were measured on a Siemens D500 diffractometer using monochromatized Cu–K_α radiation (λ = 1.5418 Å) at 40 kV and 100 mA. The scanning range was $10 < 2\theta < 90°$ and exposition was 10 s per point. The morphologies and microstructures of as-prepared samples were analyzed by a JSM-6390LV scanning electron microscope (SEM) and EM-125 transmission electron microscope (TEM). During both microwave and thermal heating processes, the composition of gas mixture and partial pressures of components were measured by an IPDO-2 mass-spectrometer [22].

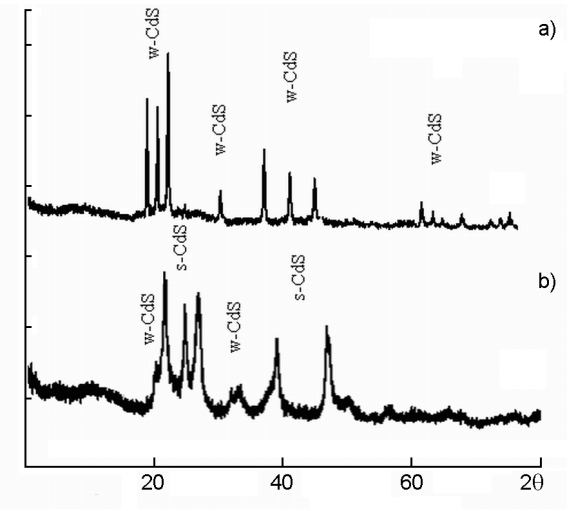

Fig. 1. Typical XRD pattern of ZnS lemon yellow (a) and red (b) by synthesized from 0.1 M cadmium nitrate solutions.

3. Results and discussion

At the initial stage of precipitation process from 0.01–1 M $Cd(NO_3)_2$ solutions formation of lemon yellow precipitates is observed. In the following course of synthesis the precipitates gradually acquire red colour. Duration of the first stage formation of lemon yellow precipitates is about 15 min at 90–95°C and it increases when the precipitation temperature decreases. So, at temperature of 70°C lemon yellow coloring of a powder remains within 25 min of precipitation. It was revealed that concentrations of an initial solution of cadmium nitrate and thiourea don't effect essentially on lemon yellow cadmium sulfide formation.

Fig. 1 shows the XRD patterns of lemon yellow and red precipitates obtained from 0.1 M cadmium nitrate solution. All synthesized samples are CdS powders: lemon yellow precipitates is wurtzite modification with lattice constant of a = 4.136 Å and c = 6.713 Å is consistent with standard literature data, and red precipitates is a mixture consist of wurtzite and blende modifi-

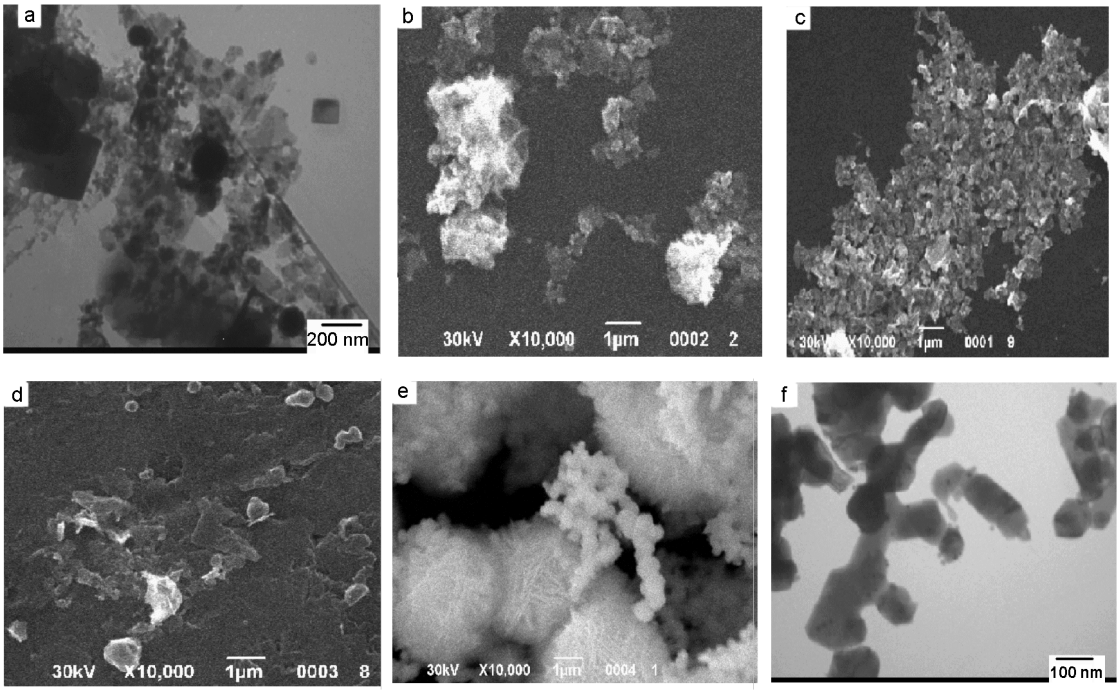

Fig. 2. SEM abd TEM images of the as-prepared CdS samples: a — 1 M $Cd(NO_3)_2$ solution, 90°C, 10 min, mole ratio Cd^{2+}:TM=1:1 (lemon yellow colors); b — 1 M $Cd(NO_3)_2$ solution, 90°C, 40 min, Cd^{2+}:TM=1:1 (red colors); c — 0.1 M $Cd(NO_3)_2$ solution, 90°C, 20 min, Cd^{2+}:TM=1:1 (red colors); d — 0.1 M $Cd(NO_3)_2$ solution, 90°C, 40 min, Cd^{2+}:TM=1:1 (red colors); e — 1 M $Cd(NO_3)_2$ solution, 90°C, 40 min, Cd^{2+}:TM=1:4 (red colors); f — after anneal at temperature of 700°C and 1 h.

cations. The calculated blende modifications lattice constant of a = 5.818 Å is consistent with standard literature value. The concentration wurtzite modification in red precipitates doesn't exceed of 10 mass.%.

Fig. 2 shows the microphotos of synthesized powders. Irrespective of concentration of an initial solution of cadmium nitrate and temperature at the initial stage precipitation (lemon yellow CdS) it is observed the particles formation as in the form of small plates with various shapes (Fig. 2a) and with sizes from 50 to 100 nm as more larger particles in the form of rectangular plates with sizes from 100 to 300 nm. An increase of precipitation time leads to formation of larger particulars (Fig. 2b–d) with sizes from 500 to 1500 nm (red powder).

The most essential factor influencing on morphological characteristics of CdS particles is thiourea concentration at the synthesis of CdS particulars. So, introduction of 2 or 4 multiple excess of thiourea promotes the formation of spherical particles of two forms (Fig. 2e): spherical particles with a size of 0.8–1 μm and spherical particles with a size about 5 μm that consisting of plates with thickness of a wall of 30–50 nm.

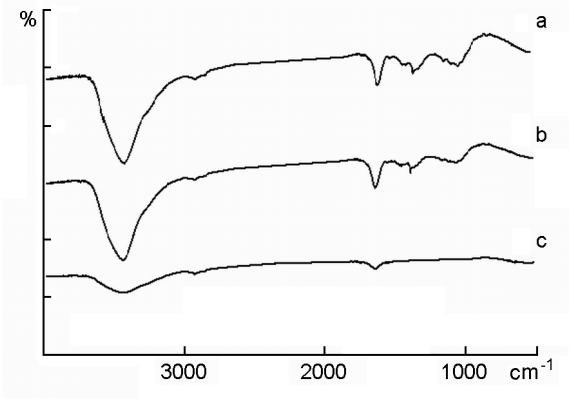

Fig. 3. FT-IR spectra of ZnS lemon yellow (a), red (b) and after anneal at temperature of 700°C and 1 h (c).

On Fig. 3 the FT-IR spectra of CdS powders synthesized from thiourea solution are presented. For the all samples we can see the bands at 3000–3600 cm^{-1} with a maximum at 3430 cm^{-1} and 1632 cm^{-1} related to the presence of adsorbed water on surface of cadmium sulfide particles. Besides, we can see the band at 1384 cm^{-1} and band at 900–1200 cm^{-1} with maximum at

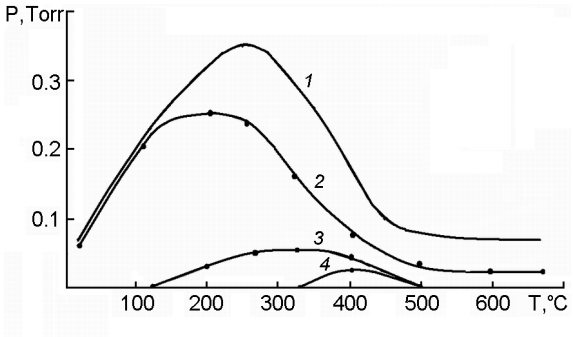

Fig. 4. Variations of the total (*1*) and partial pressure of water (*2*), NH_3 (*3*) and NO_2 (*4*) at the heating of CdS powders synthesized from 1 M cadmium nitrate solutions at temperature of 90°C.

1060 cm^{-1}. We connect their existence in the spectra with the presence of NO^{3-}-ion impurity owing to use of cadmium nitrate at synthesis.

During the process of vacuum annealing of CdS powders the removal of H_2O in the temperature range of 25–450°C, NH_3 (120–500°C) and NO_2 (350–500°C) from the particles surface occurs that confirms by the data of mass spectrometer analysis (Fig. 4). Also we can see small increase of N_2 and H_2 concentrations (it is not shown in the Figure) in gas atmosphere at temperature 300–500°C that is related to decomposition of NH_3 at these temperatures. Irrespective of synthesis conditions for the all powders we can see emission of NO_2 at the temperature of 350–500°C that is testified to presence at initial samples of nitrates impurity. For example in the FT-IR spectrum of the annealed samples we did not observe the bands at 1384 cm^{-1} and in the range of 900–1200 cm^{-1} (Fig. 3c) that confirms that the given bands have been connected with the presence of nitrates impurity. It should be noticed that in thermal annealing process of CdS samples it was not fixed the presence of products of thermal decomposition of the organic impurities in gas atmosphere. According to TEM data the thermal processing of CdS particles at the temperature of 700°C results to baking nanoparticulars in larger particles (Fig. 2f).

It is known that decreasing of temperature precipitation can promote production of particles with the smaller size because of slowdown of velocity of particles growth. As modeling solutions 0.1 and 1 M nitrate cadmium solutions were used. Precipitation was carried out at temperature of 20°C for 3, 6 and 12 h. As a result of synthesis the lemon yellow CdS powders were obtained

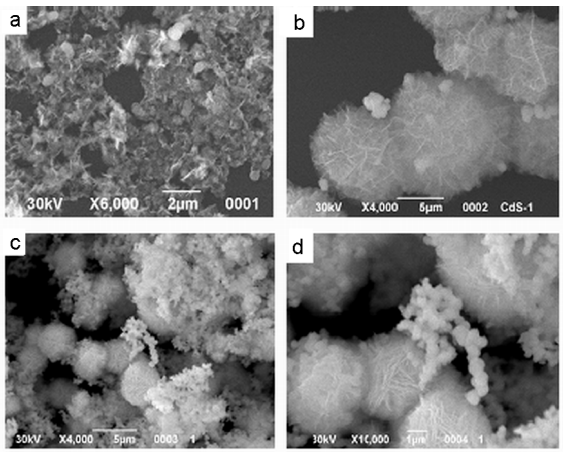

Fig. 5. SEM images of the as-prepared CdS samples synthesized from 0.1 M cadmium nitrate solutions at 20°C: a — Cd^{2+}:TM=1:1; b — Cd^{2+}:TM=1:2; c, d — Cd^{2+}:TM=1:4.

(wurtzite modification with lattice constant of a = 4.136 Å and c = 6.713 Å). It was revealed that initial concentration of solution $Cd(NO_3)_2$ and precipitation time don't effect essentially on the morphology of CdS particles. As results for 0.1 and 1 M solutions $Cd(NO_3)_2$ are almost identical that further we will consider only results that obtained for 0.1 M solutions.

Fig. 5 shows the microphotos of CdS particles obtained from 0.1 M of cadmium nitrate solution with various thiourea concentrations. At room temperature and mole ratio Cd^{2+}/TM 1:1 the primary formation of spherical particles with the sizes 300–500 nm (Fig. 5a) is observed in the solution. TM excess in solution leads to formation two kinds of particles: massive spherical particles with the 4–6 μm that consisting of plates with thickness of 50–80 nm and smaller spherical particles with the sizes to 1 μm. Thus concentration of massive spherical particles increases at increase of thiourea concentration.

Recently the attention to the new methods of chemical processes activation is paid. In particular, the microwave synthesis of zinc sulfide is actively researched [23]. In comparison with thermal heating the microwave synthesis has a number of advantages: increasing speed of many chemical processes and control simplicity. Therefore we have been done precipitation of cadmium sulfide particles by microwave heating.

As a result of synthesis the lemon yellow CdS powders are obtained. The samples can be characterized by wurtzite modification with lattice constant of a = 4.136 Å and

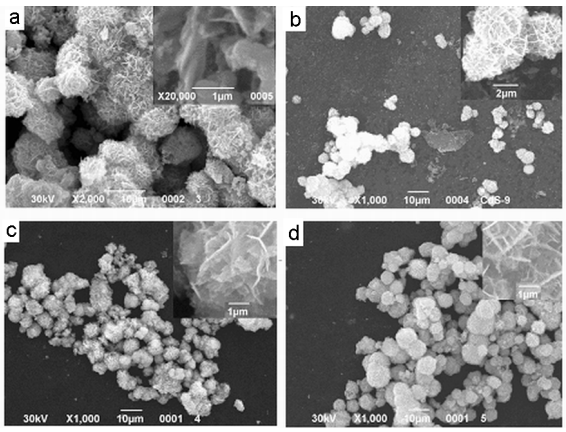

Fig. 6. SEM images of the as-prepared CdS samples synthesized by microwave from 0.1 M cadmium nitrate solutions: a — Cd^{2+}:TM=1:1, 90°C; b — Cd^{2+}:TM=1:4, 90°C; c — Cd^{2+}:TM=1:1, 150°C; Cd^{2+}:TM=1:4, 150°C.

c = 6.713 Å that is similar to the samples obtained in the precipitation under heating (Fig. 2a). Fig. 6 shows the microphotos of synthesized by microwave powders. Independent of precipitation temperature and thiourea concentration the massive spherical particles formed with the sizes of 4–6 μm consisting of plates with thickness of a wall of 50–80 nm.

4.Conclusions

The influence of synthesis conditions on CdS micro- and nanoparticulars formation at precipitation from 0.01, 0.1 and 1 M cadmium nitrate solutions by thiourea has been studied. It was revealed that at initial stage of precipitation process under the temperature 90–100°C it is observed the formation of CdS particles primarily in the form of plates with the sizes from 50 to 100 nanometers. As a rule, synthesized powders are colorized in lemon yellow tints. Along with the synthesis duration more than 20 min splicing of small plates in large agglomerates (0.5–1 μm) occurs and the powder acquires the red color.

Variation of initial cadmium nitrate concentration in the range of 0.01–1 M doesn't effect on morphology and size of CdS particles under precipitation by thiurea. The major factors influencing on CdS particles formation are thiourea concentration and temperature. Decrease of temperature to 20–25°C or increase of thiourea concentration above stoichiometric value results in the formation of spherical particles of two types: with the sizes of 300–500 nm and the sizes of 4–6 μm consisting of plates with thickness of a wall of 50–80 nm.

Application of microwave method allows to obtain homogeneous spherical particles with the sizes of several micrometers, which consists of plates with thickness of a wall of 50–80 nm, and the process does not depend on temperature and thiourea concentration. Such CdS powders can find potential application as effective sorbents.

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Формування нано- та мікрочасток CdS з тіосечових розчинів

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Досліджено вплив умов синтезу на морфологію часток CdS при осадженні 0.01, 0.1 та 1 М розчинів нітрату кадмію тіосечовиною. Встановлено, що основними чинниками, що впливають на формування часток CdS, є концентрація тіосечовини у розчині та температура осадження. Зниження температури осадження до 20–25°С або збільшення вмісту тіосечовини вище стехіометричного приводить до формування сферичних часток. Використання мікрохвильової активації сприяє формуванню сферичних часток у вигляді "квітки", які складаються з невеликих пластинок з товщиною стінки 50–80 нм.