Chemistry: Bulgarian Journal of Science Education | *Volume 27 Number 6, 2018* | *Природните науки в образованието*

From the Research Laboratories
В изследователските лаборатории

ELECTROSYNTHESIS OF CADMIUM SELENIDE NANOPARTICLES WITH SIMULTANEOUS EXTRACTION INTO P-XYLENE

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Abstract. Colloidal solutions of ~2 nm CdSe nanoparticles have been obtained by electrosynthesis with simultaneous extraction into p-xylene. The effect of electrolyte composition on the structure of electrodeposited CdSe nanoparticles has been established, their absorption and photoluminescence spectra have been analyzed. Exciton absorption of light by synthesized CdSe nanoparticles splits into three bands, which is characteristically for the small CdSe nanoparticles. Photoluminescence excited at wavelengths corresponding to curve bending decreases in intensity within the 350 -550 nm region with a maximum of 430 nm. This fact indicates on the formation of small (~ 2 nm) of CdSe nanoparticles in the process of electrosynthesis as well. Studies have shown that by the proposed method of electrochemical synthesis it is possible to obtain nanoparticles that are promising for the creation of optical liquid–crystalline composites.
Keywords: electrosynthesis**;** CdSe nanoparticles; colloidal solution

Introduction

CdSe nanoparticles are promising in optical and optoelectronic devices, solar cells and as fluorescent marks (Trindade et al., 2001). In most cases CdSe nanoparticles are grown by synthesis using molecular precursors (Hambrock et al., 2001), synthesis in structured environments (Bacherikov et al., 2010) and controlled deposition from solutions with surfactants as anticoagulants (Bacherikov et al., 2006). The last synthesis method is the most popular and simplest (Mi et al., 2012). Using this method, one can fabricate nanoparticles of necessary size and shape (Mi et al., 2012). However, their synthesis involves an excessive amount of reactants, which remain afterwards in the dissolved form. The isolation of nanoparticles from micellar or colloidal solutions, which contain reactants and anticoagulants as undesirable impurities, is very difficult. To solve this problem, we proposed a method for the fabrication of CdSe nanoparticles by electrosynthesis from aqueous solutions of cadmium chloride and selenious acid with their simultaneous extraction into xylene (Fomanyuk et al., 2016). The amount of extracted small nanoparticles was content of up to 0.05 g in 1cm^3 xylene

(~0.3 mol/L) (Fomanyuk et al., 2016). During electrosynthesis without using of anti-coagulating agents, CdSe nanoparticles in the form of powder or dendrite-like deposit are formed on the cathode. The presence of water-immiscible xylene and vigorous hydrogen evolution leads to formation of a cathode water-xylene emulsion layer. In this emulsion layer, synthesis and simultaneous extraction of CdSe nanoparticles take place. The proposed method of electrochemical synthesis it is possible to obtain nanoparticles, which by optical properties are quantum dots promising to obtain an optical liquid–crystalline composites. Thermotropic liquid crystal compounds and CdSe or CdS nanoparticles are frequently used in photonic applications, and a hybrid of these two materials is expected to demonstrate further enhancements in the photonic properties. (Lee et al., 2010), (Barmatov et al., 2007).

Methodology

To carry out the electrosynthesis of CdSe nanoparticles, ammonia complexes of cadmium hydroxide and selenious acid were chosen. Electrolytic solutions were prepared by dissolving cadmium hydroxide in ammonia with subsequent dilution with water and addition of selenious acid. Three solutions on the basis of cadmium and selenic acid concentrations were prepared: (1) H_2SeO_3, 0.01 mol/L; $Cd(OH)_2$, 0.05 mol/L; NH_4OH, 3 mol/L; (2) H_2SeO_3, 0.02 mol/L; $Cd(OH)_2$, 0.05 mol/L; NH_4OH, 3 mol/L; (3) H_2SeO_3, 0.03 mol/L; $Cd(OH)_2$, 0.05 mol/L; NH_4OH, 3 mol/L.

The structure of CdSe nanoparticles was investigated by X-ray phase analysis on a diffractometer (DRON-2). The electrowinning processes of CdSe nanoparticles from an ammonia electrolyte were studied by cyclic voltammetry in a YaSE-2 three-electrode cell by means of an EP-21 potentiostat. The working electrode was a titanium foil, the counter electrode was graphite, and the reference electrode was a silver-chloride electrode. The electrosynthesis was carried out in the two-electrode mode in a thermostatted cell using a BVP-30 direct current source. The electrosynthesis current was 250 mA/cm^2. The temperature was 75-80 ^0C. For the simultaneous extraction of CdSe nanoparticles during electrosynthesis, the one-quarter cell was filled with p-xylene. The optical absorption and photoluminescence spectra of CdSe nanoparticles in p-xylene were analyzed on Perkin Elmer UV/VIS Lambda 35 and Perkin Elmer LS 55 spectrophotometers.

Results and discussion

Selenic acid is known to change its ionic form depending on solution pH. Fig. 1 shows plots of the distribution of the ionic species of selenious acid against pH, calculated by the procedure presented in (Benedicto et al., 2013) for the first and second dissociation constants of selenious acid. Increase in pH value and in the concentration of H_2SeO_3 increases its ability to dissociate into ions. In ammonia electrolyte at a NH_4OH concentration of 3 mol/L, pH is within the limits of 10, which leads to the formation of SeO_3^{2-} ions.

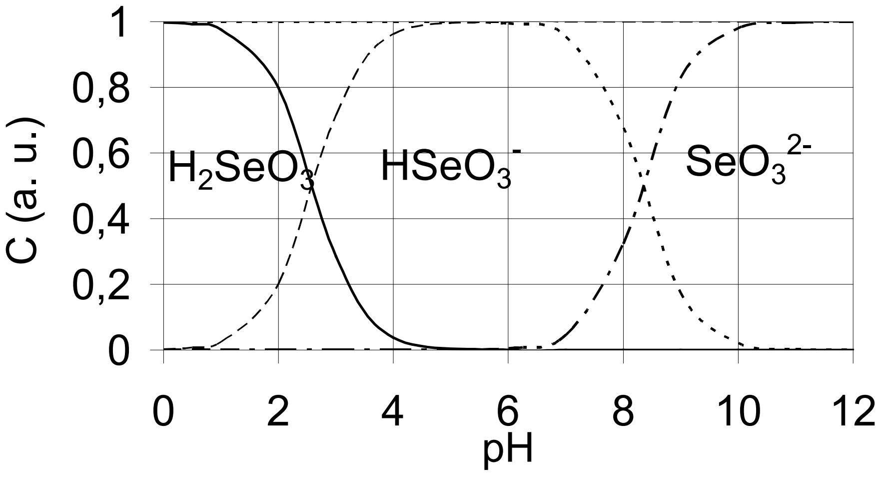

Figure 1. Influence of pH on the distribution of the ionic species of selenic acid

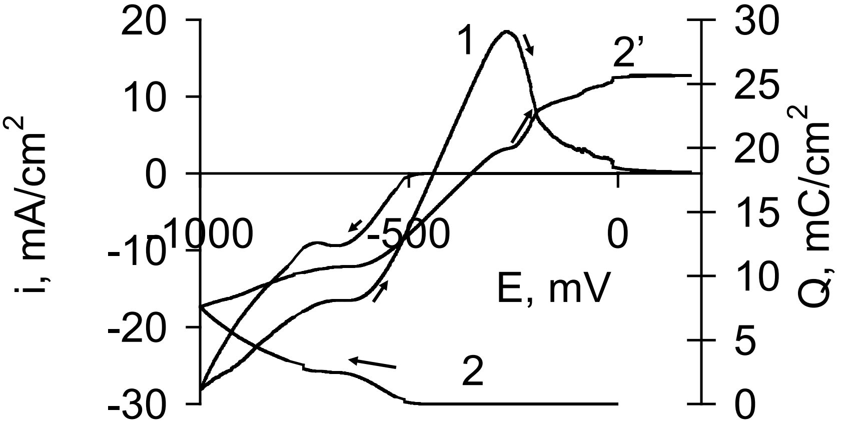

Figure 2. Cyclic voltammogram 1 and the quantity of injected and removed charge, 2 and 2’, for the process of CdSe electrosynthesis from an ammonia electrolyte based on cadmium hydroxide and selenic acid

In Fig. 2, CdSe formation reaction wave in the forward and reverse sweep of the cyclic voltammogram in the cathodic polarization region at E=-610 mV is clearly visible:

$$SeO_3^{2-} + 3H_2O + 6e = Se^{2-} + 6OH^- \quad (1)$$

$$[Cd(NH_3)_4]^{2+} + Se^{2-} = CdSe + 4NH_3 \quad (2)$$

Unlike acid or neutral CdSe deposition solutions, where there are two Se and CdSe formation current waves (Murray et al., 1993; Pawar et al., 2007), there is one wave in ammonia electrolyte

Besides the main CdSe formation reactions, a part of energy is expended on the formation of metallic cadmium. An anodic wave of cadmium dissolution can be seen in Fig. 2. The difference between forms of curves for the quantity of injected and removed charge (2 and 2') shows that a part of energy is expended on the reversible reaction of metallic cadmium formation and dissolution:

$$[Cd(NH_3)_4]^{2+} + 2e^- = Cd + 4NH_3 \quad (3)$$

The structure of electrosynthesized CdSe nanoparticles in the form of powder was determined from diffractograms. The diffractograms in Fig. 3 showed the presence of peaks typical of CdSe. It has also been found that at the ion concentration ratio $Cd^{2+} : SeO_3^{2-} = 5:2$ (the composition of the solution 2), electrosynthesis at equal current parameters and electrolysis temperature leads to the appearance of nanocrystals with cubic structure (Fig. 3). The peaks of the wurtzite structure (Sapra et al., 2006) of cadmium selenide (Fig. 3 (1) and (3)) appears when the initial concentrations (the compositions of the solutions 1 and 3) deviates from the ratio ($Cd^{2+} : SeO_3^{2-} = 5:2$) to larger or smaller value.

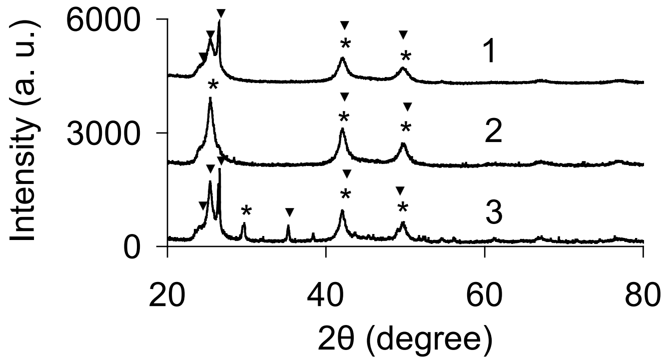

Figure 3. Diffractograms of CdSe powders synthesized at different cadmium and selenious acid concentration ratios in 3M NH_4OH: (1) (H_2SeO_3, 0.01 mol/L; $Cd(OH)_2$, 0.05 mol/L), (2) (H_2SeO_3, 0.02 mol/L; $Cd(OH)_2$, 0.05 mol/L), (3) (H_2SeO_3, 0.03 mol/L; $Cd(OH)_2$, 0.05 mol/L) where ▼- CdSe wurtzite structure *- CdSe cubic structure

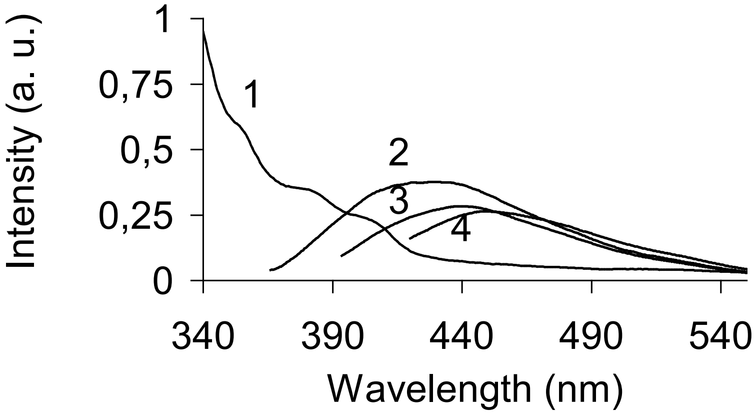

Figure 4. Optical absorption spectrum (1) and photoluminescence spectra CdSe nanoparticles extracted into xylene in the case of excitation by light with a wavelength of 360 nm (2), 380 nm (3), 400 nm (4)

The research of the optical properties of colloidal solutions of CdSe in p-xylene showed them to have strong ultraviolet light absorption with characteristic curve bends at three areas Fig. 4 (1) The excitation of photoluminescence at the wavelengths corresponding to these bends showed that each of the light absorption bands makes a contribution to the photoluminescence of such colloidal solutions Fig. 4 (2, 3, 4). Depending on the wavelength of photoexcitation, the maximum of photoluminescence spectra shifts and decreases. As is known exciton energy in CdSe nanoparticles is split into three levels depend strongly on crystal size, shape, and energy band parameters. In our case, three bent inflections in absorption spectra with an average distance of 25 - 30 nm are also observed. Such a distance, according to the authors (Sapra et al., 2006; Efros et al., 1996; Norris et al., 1996) statement is characteristic of CdSe nanoparticles of spherical shape of the cubic structure. Analysis of literature of similar absorption (Holmes et al., 2012) and photoluminescence (Mi et al., 2012) spectra shows the dominance in the solution of small CdSe nanoparticles ~ 2 nm.

At the incorporation of electrochemically synthesized CdSe nanoparticles into a liquid-crystalline matrix from a colloidal solution allows one to obtain an optical composite. Thermo-optical nonlinearity a liquid-crystalline matrix containing CdSe nanocrystals are characterized by extremely large value of the nonlinear refractive index under relatively low-powered CW laser irradiation (Lyashchova et al., 2013). Large optical nonlinearity parameters and fast response times, together with the excellent photo and thermo–stability of nanocomposites make them extremely promising for optical processing applications signals. It is new perspective materials for many applications including lasers, sensors of near-ultraviolet and blue visible spectral range and solar cells.

Conclusions

Colloidal solutions of CdSe nanoparticles have been obtained by electrosynthesis using the method of extraction into p-xylene. An X-ray phase analysis of powders of CdSe nanoparticles, obtained by electrosynthesis from electrolytes with different molar ratio of selenium to cadmium, showed that deviation from the ratio Cd^{2+} : SeO_3^{2-} = 5:2 to larger or smaller value results in the appearance of a cubic modification of CdSe. An analysis of absorption and photoluminescence spectra showed that the colloidal solutions obtained consist of ~2 nm CdSe nanoparticles. Researches have shown that by the proposed method of electrochemical synthesis it is possible to obtain nanoparticles, which by optical properties are quantum dots promising to obtain an optical liquid–crystalline composites.

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