ELECTROSYNTHESIS AND OPTICAL PROPERTIES OF CADMIUM SELENIDE NANOPARTICLES

FOMANYUK S.S., SMILYK V.O., ASAULA V.N., KOLBASOV G.Ya, RUSETSKYI I.A., MIRNAYA T.A.
V.I. Vernadskii Institute of General and Inorganic Chemistry of the Ukrainian NAS, prospect Palladina 32-34, 03142, Kyiv, Ukraine
fomanyuk@gmail.com

Colloidal solutions of ~2 nm CdSe nanoparticles in p-xylene have been obtained by electrosynthesis with simultaneous extraction. It is a promising way of preparing concentrated colloidal solutions of such nanoparticles. The influence of electrolyte composition on the structure of electrodeposited CdSe nanoparticles has been established, and their absorption and photoluminescence spectra have been analyzed. It has been found that at the ion concentration ratio Cd^{2+} : SeO_3^{2-} = 5:2, the electrosynthesis at equal current parameters and electrolysis temperature results in the appearance of nanocrystals with cubic structure. The research of the optical properties of colloidal solutions of CdSe in p-xylene showed a strong ultraviolet light absorption. Exciton absorption of light by synthesized CdSe nanoparticles splits into three bands, which is characteristically for the small CdSe nanoparticles. In our case, the exciton absorption peaks give ~2 nm 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 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.

CdSe nanoparticles are promising in optical and optoelectronic devices, solar cells and as fluorescent marks [1]. In most cases, CdSe nanoparticles are grown by synthesis using molecular precursors [2], synthesis in structured environments [3] and controlled deposition from solutions with surfactants as anticoagulants [4]. The latter is the most popular and simplest [5]. Using this method, one can fabricate nanoparticles of necessary size and shape [5]. 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 [6]. The amount of extracted small nanoparticles was content of up to 0.05 g in 1cm^3 xylene (~0.3 mol/L) [6]. During electrosynthesis without using of anticoagulating 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.

Research 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 based on cadmium and selenious 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 with 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 ^{0}C. 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

Selenious acid is known to change its ionic form depending on solution pH. Figure 1 shows plots of the distribution of the ionic species

of selenious acid against pH, calculated by the procedure presented in [7] for the first and second dissociation constants of selenious acid. Increase in pH value and in the concentration of H_2SeO_3 enhances its ability to dissociate into ions. In ammonia electrolyte at an NH_4OH concentration of 3 mol/L, the pH is within the limits of 10, which leads to the formation of SeO_3^{2-} ions.

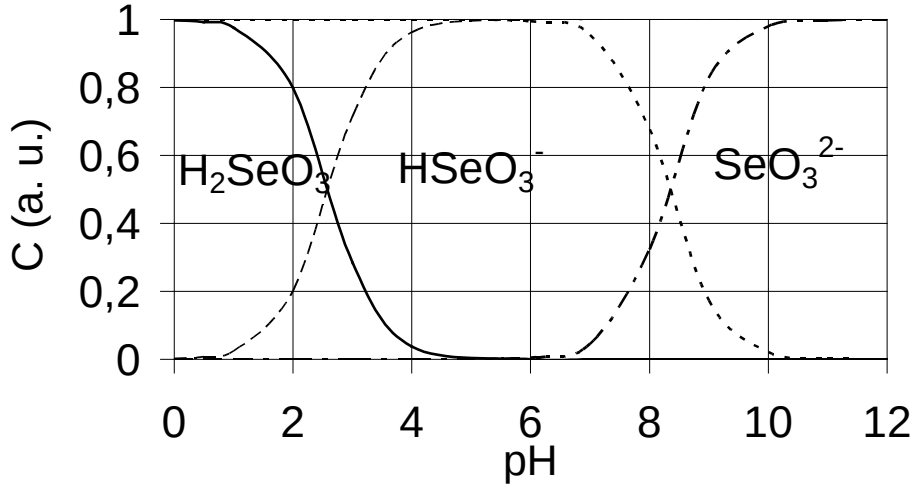

Fig. 1. Influence of pH on the distribution of the ionic species of selenious acid

In Fig. 2, a 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 [8, 9], 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:

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

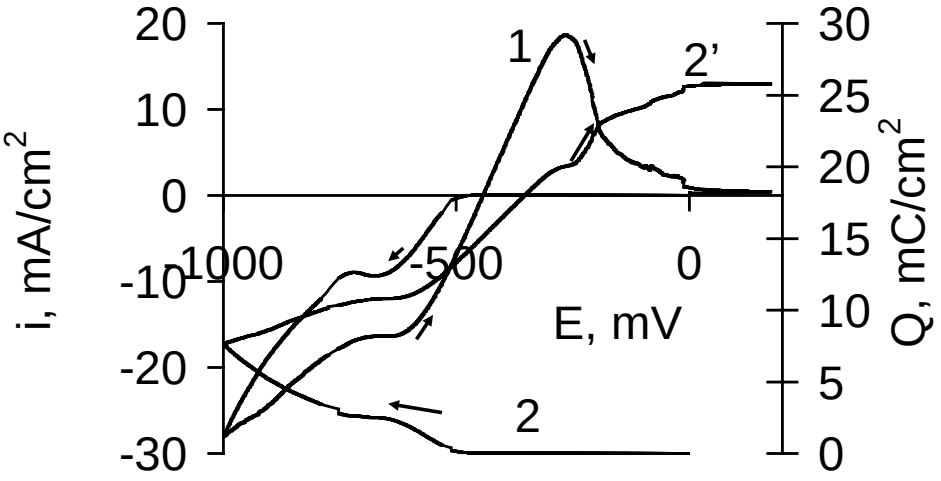

Fig. 2. Cyclic voltammogram (1) and the quantity of injected and removed charge (2 and 2') for the process of CdSe electrosynthesis from an ammonia electrolyte based on cadmium hydroxide and selenious acid.

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), the electrosynthesis at equal current parameters and electrolysis temperature leads to the appearance of nanocrystals with cubic structure (Fig. 3 (2)) [10]. The peaks of the wurtzite structure [10] of cadmium selenide (Fig. 3 (1) and (3)) appear when the initial concentrations (the compositions of the solutions 1 and 3) deviates from the ratio (Cd^{2+} : SeO_3^{2-} = 5:2) to a larger or smaller value.

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 in 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 depending 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 [10-12] is characteristic of CdSe nanoparticles of spherical shape of the cubic structure. Analysis of literature of similar absorption [13] and

photoluminescence [5] spectra shows the dominance in the solution of small CdSe nanoparticles ~ 2 nm.

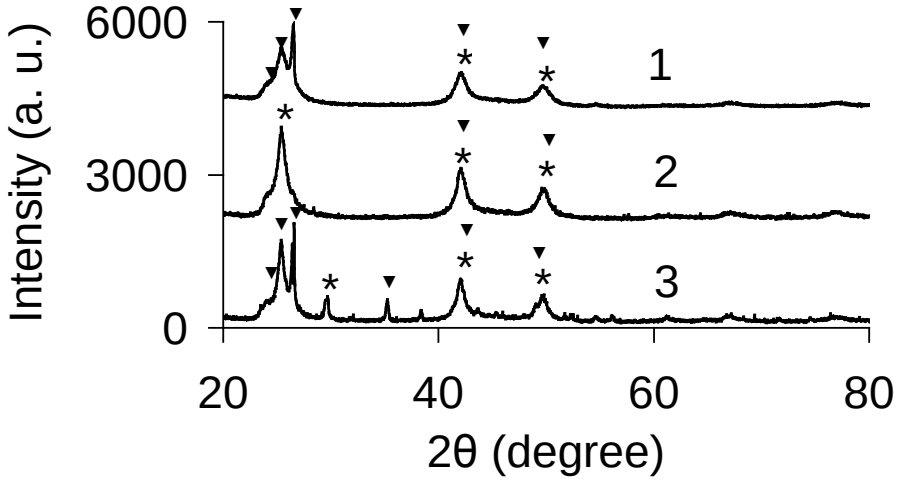

Fig 3. Diffractograms of CdSe powders synthesized at different cadmium and selenious acid concentration ratios in 3M NH_4OH : (1) (H_2SeO_3, 0.01 mol/L; $Cd(OH)_2$, 0.05 mol/L), (2) (H_2SeO_3, 0.02 mol/L; $Cd(OH)_2$, 0.05 mol/L), (3) (H_2SeO_3, 0.03 mol/L; $Cd(OH)_2$, 0.05 mol/L) where ▼- CdSe wurtzite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

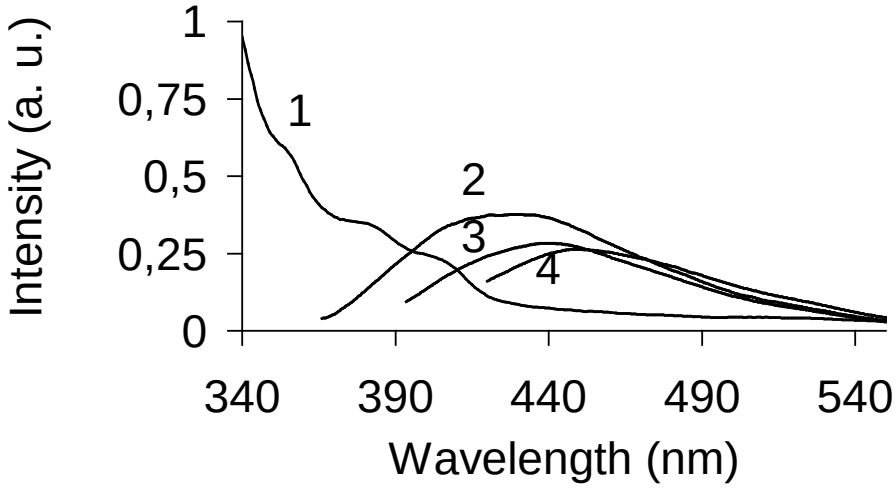

Fig 4. Optical absorption spectrum (1) and photoluminescence spectra CdSe nanoparticles extracted into xylene in the case of excitation by light with a wavelength of 360 nm (2), 380 nm (3), 400 nm (4)

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 of a liquid-crystalline matrix containing CdSe nanocrystals is characterized

by an extremely large value of the nonlinear refractive index under relatively low-powered CW laser irradiation [14]. 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. They are new promising 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 analysis of absorption and photoluminescence spectra showed that the colloidal solutions obtained consist of ~2 nm CdSe nanoparticles. 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 a larger or smaller value results in the appearance CdSe of wurtzite structure. 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 optical liquid–crystalline composites.

References

[1] T. Trindade, P. O'Brien, N.L. Pickett, Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives // Chemistry of Materials – V.13, N.11 – P.3843-3858 (2001).

[2] J. Hambrock, A. Birkner, R.A. Fischer Synthesis of CdSe nanoparticles using various organometallic cadmium precursors // Journal of Materials Chemistry – N11 – P. 3197–3201 (2001).

[3] Yu.Yu. Bacherikov, I.Z. Indutnyi, I.Yu. Maidanchuk,O.B. Okhrimenko, S.V. Optasyuk, P.Ye. Shepeliavyi Formation of nano-structured CdSe compositesIn porous SiO_x layers // Ukrainian Journal of Physics – Vol. 55, N 7 – P.817-821 (2010).

[4] Yu.Yu. Bacherikov, M.O. Davydenko, A.M. Dmytruk et al. CdSe nanoparticles grown with different chelates Semiconductor Physics, Quantum Electronics & Optoelectronics. – V. 9, N. 2 – P.75-79 (2006).

[5] W. Mi, J. Tian, W. Tian, J. Dai, X. Wang, X. Liu Temperature dependent synthesis and optical properties of CdSe quantum

dots Ceramics International – V. 38, N7 – P.5575–5583 (2012).
[6] S. S. Fomanyuk V. N. Asaula G. Ya Kolbasov T. A. Mirnaya Electrochemical synthesis and optical properties of ultra-fine CdSe nanoparticles // Journal of Nanostructure in Chemistry – V. 6, N 4 – P. 289–297 (2016).
[7] A. Benedicto, T. Missana, C. Degueldre, Predictions of TiO_2-driven migration of Se(IV) based on an integrated study of TiO_2 colloid stability and Se(IV) surface adsorption // Science of the Total Environment – V. 449 – P.214–222 (2013).
[8] C.B. Murray, D.J. Norris and M.G. Bawendi, Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites // Journal of the American Chemical Society – V.115 N.19 – P.8706–8715 (1993).
[9] S.M. Pawar, A.V. Moholkar, C.H. Bhosale, Influence of pH on electrochemically deposited CdSe thin films // Materials Letters – V. 61, N. 4–5 – P.1034–1038 (2007).
[10] S. Sapra, A. L. Rogach, J. Feldmann Phosphine-free synthesis of monodisperse CdSe nanocrystals in olive oil // Journal of Materials Chemistry – N.16 – P.3391–3395 (2006).
[11] Al. L. Efros and M. Rosen M. Kuno, M. Nirmal, D. J. Norris, and M. Bawendi Band-edge exciton in quantum dots of semiconductors with a degenerate valence band: Dark and bright exciton states Physical review B – V. 54, N. 7 – P. 4843–4856 (1996).
[12] D. J. Norris Al. L. Efros, M. Rosen M. G. Bawendi Size dependence of exciton fine structure in CdSe quantum dots Physical review B – V. 53, N. 24 – P.16347–16354 (1996).
[13] Michael A. Holmes, Troy K. Townsend and Frank E. Osterloh Quantum confinement controlled photocatalytic water splitting by suspended CdSe nanocrystals Chemical Communications – V. 48, N. 3 – P. 371–373 (2012).
[14] A. Lyashchova, D. Fedorenko, Yu. Garbovskiy, G. Klimusheva, T. Mirnaya, V. Asaula Strongthermal optical nonlinearity caused by CdSe nanoparticles synthesised in smectic ionic liquid crystal // Liquid Crystals– V. 40, N. 10 – P.1377–1382 (2013).