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Synthesis and Optical Properties of Liquid Crystalline Nanocomposites of Cadmium Octanoate with CdS Quantum Dots

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Nanosized CdS semiconductor crystals have been synthesized in liquid crystalline and isotropic melts based on cadmium octanoate. Glassy mesomorphic nanocomposites have been obtained by cooling melts. It has been shown that CdS nanocrystals in vitrified matrices are quantum dots (QDs) which are characterized by a high degree of monodispersity and have a size of 2-4 nm depending on synthesis conditions. The fluorescence properties of CdS QDs in two-dimensionally ordered cadmium octanoate glass have been investigated for the first time and can serve as a model for studying radiative processes in such new matrices.

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I. Introduction

In recent years, composite materials with nanoscale cadmium chalcogenides have been actively investigated [1]. These materials attract attention primarily owing to the unique properties of 1-10 nm nanocrystals being part of them. Such nanoparticles differ in properties (absorption band width, spectral characteristics, electron transfer) both from bulk material and from individual atom or molecule. The creation of stable heterogeneous nanostructured composites, which are both semiconducting and optical media at the same time, is of high priority for the development of components for nonlinear optics and information technologies. The synthesized nanocrystals must satisfy the shape uniformity and narrow size distribution requirements. The most popular method for the fabrication of such nanocrystals is controlled synthesis based on structured media-matrices such as zeolites, micelles/microemulsions, gels, polymers, glasses and liquid crystals [2]. One of the promising template synthesis methods is synthesis using liquid crystalline matrices [3], which permits one to obtain nanoparticles of required geometrical shape and size, which are stable in time. Liquid crystals can be used not only as nanoreactors for the synthesis of nanoparticles of predetermined shape and size, but also as matrices for their stabilization with resultant creation of novel optical materials, which combine the properties of an anisotropic liquid crystalline medium and semiconductor nanoparticles. Such liquid crystals are ionic liquid

crystals of metal alkanooates, which possess the ability to form mesomorphic glasses [4].

Mesogenic metal alkanooates have a bilayer structure, which is due to a combination of electrostatic interionic interaction between metal cations and carboxyl group and Van der Waals interaction between the alkyl chains of alkanooate anions. They exhibit thermotropic mesomorphism, i.e. form liquid crystals on heating. An example of such an ionic mesogen is cadmium octanoate $\text{Cd}(\text{C}_7\text{H}_{15}\text{COO})_2$, hereinafter referred to as CdC8, which forms a mesophase (smectic A) at 98 °C and is able to supercool to form at room temperature a glass having a smectic bilayer structure [5].

The aim of the present work was to create a new optical mesomorphic nanocomposite medium with CdS QDs and to study its structural and spectral characteristics.

II. Synthesis

CdS nanoparticles were synthesized in a CdC8 matrix by two methods, which made it possible to obtain two glassy nanocomposites (I and II), in which CdS nanoparticles of different size were stabilized. Nanocomposite I was prepared thus: a CdC8 powder impregnated with a saturated aqueous-alcoholic solution of thiourea was held in a furnace at $t=150$ °C (temperature of mesophase existence of CdC8) in argon atmosphere for one hour. On the rapid cooling of the melt, a mesomorphic glass was obtained, in which ≈ 2 nm CdS nanoparticles were stabilized, as further

investigations showed. Nanocomposite II was prepared by melting a mechanical CdC8-thiourea solid-phase mixture in argon atmosphere at $t \approx 300$ °C (temperature of existence of isotropic CdC8 melt) during several minutes; as has been found in this investigation, >3 nm nanoparticles were formed in this case. The starting amount of thiourea for the preparation of both composites was 6 mol %. The cadmium octanoate used for synthesis was prepared by a method described by us earlier [5].

III. Methods of investigation

The absorption spectra were recorded in a range of 250-800 nm on a Perkin Elmer UV/vis Lambda 35 spectrophotometer. Quartz cells of 40 μ m thickness were used. The fluorescence spectra were recorded on a Perkin Elmer LS 35 fluorescence spectrophotometer.

Small-angle X-ray (SAXS) measurements were performed using a small angle diffractometer AMUR with a slit collimation system. $\text{CuK}\alpha$ radiation from a 1.2 kw X-ray tube with focus size of 0.4×8 mm², and Ni-foil monochromator were used. The distances between source and sample, and between sample and detector were 500 and 350 mm, respectively. Scattered radiation reached the detector via a vacuum chamber. The intensity of scattered radiation was measured in the 2θ angle range from 0.10 to 7° with steps of 0.02°. The samples of pure matrix and nanocomposite were placed into a thin wall Lindemann capillary 1 mm in diameter, this was mounted in a temperature-controlled camera. The temperature was measured with a copper-constantan thermocouple with an accuracy of 0.2 C. The ATSAS 2.3 comprehensive program complex was applied for the treatment of experimental results and calculation of sizes and shapes of CdS particles [6].

The morphology of the sample and the particle size were investigated by high-resolution transmission electron microscopy HRTEM JEOL JEM 3010. The texture of molten and vitrified nanocomposites was studied by polythermal polarization microscopy by means of an Amplival hot-stage polarizing microscope.

IV. Results

Nanocomposites I and II, which are a vitrified CdC8 mesophase, in which CdS nanoparticles (6 mol %) were stabilized, have been studied by polarization microscopy. Their texture in polarized light had the same appearance as the texture of the pure CdC8 mesophase, i.e. an appearance typical of smectic A: it is a fan-shaped or focal conic texture [7]. Because of a strong tendency to homeotropic orientation of liquid crystal domains and their small size, however, the observed texture was fine-grained both for pure CdC8 mesophase and for its mixture with CdS nanocrystals.

Figure 1 shows Small-angle X-ray data in mesophase for the pure matrix, nanocomposites I and II, respectively. The obtained data gives evidence of the existence of ultra small sized particles, so-called

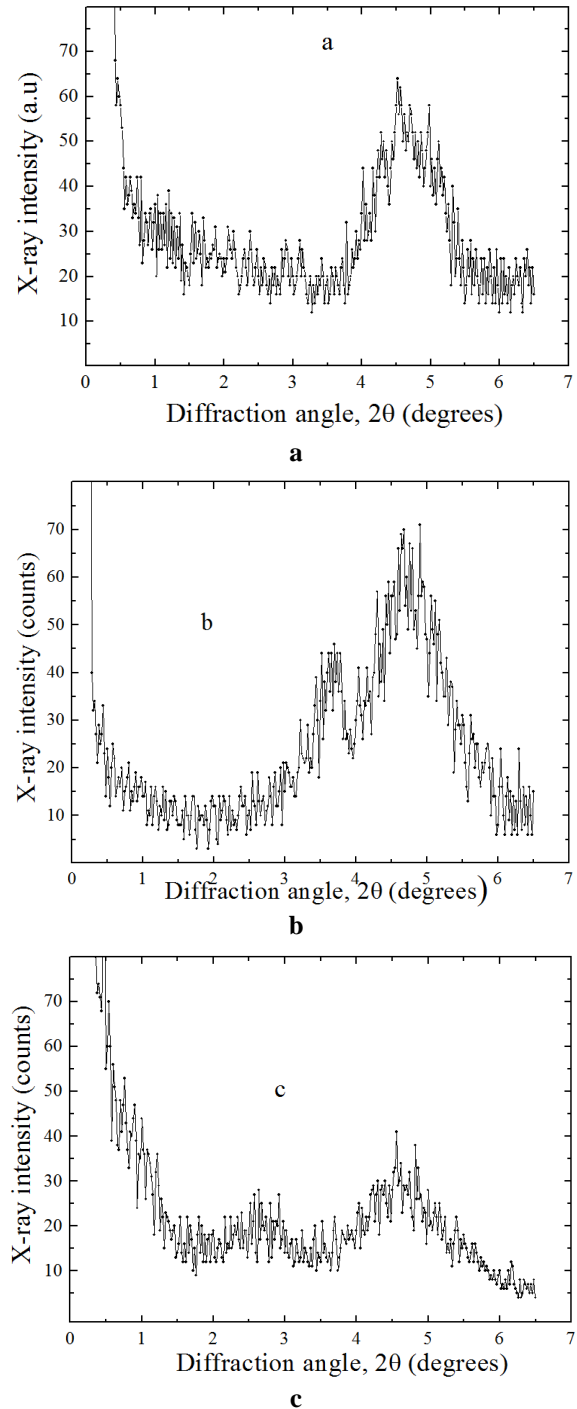


Fig. 1. Small angle X-ray scattering intensity for pure matrix (a), nanocomposite I (b) and nanocomposite II (c) in mesophase, $t = 120$ °C.

quantum dots (QDs).

The small angle X-ray diffraction pattern of nanocomposite I shows two peaks. Higher peak ($2\theta_1 \approx 4.7^\circ$) corresponds to the bilayer smectic spacing ($d_{sm} = 1.85$ nm) in the CdC8 mesophase [5], lower peak ($2\theta_2 \approx 3.7^\circ$) is caused by diffraction from the CdS particles. The size of particles was calculated using the distance distribution function for a monodisperse system of solid spheres and make upon the average $D_1 \approx 2.4$ nm.

The small angle X-ray diffractogram of nanocomposite II also demonstrates two diffraction

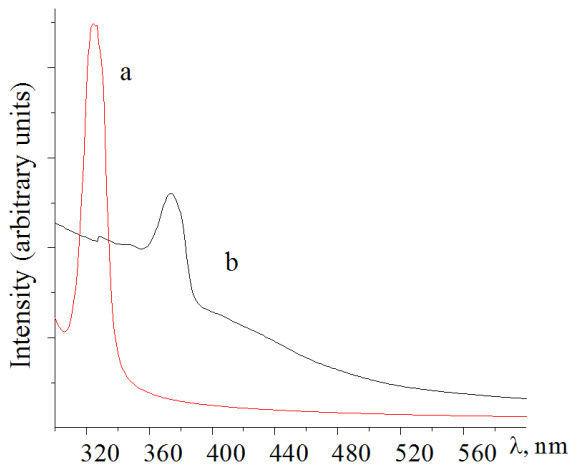


Fig. 2. Absorption spectra of nanocomposites I (a) and II (b).

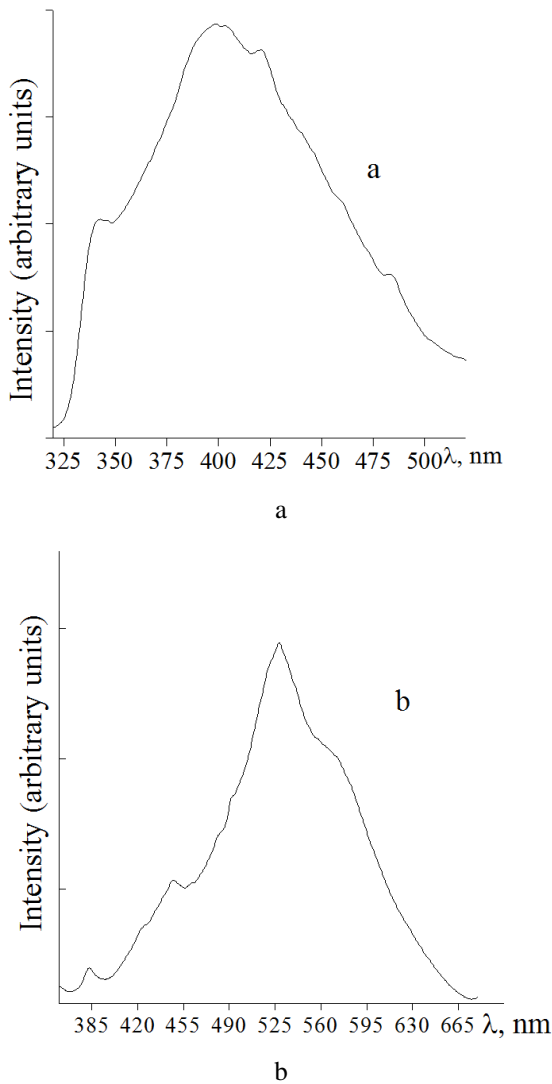


Fig. 3. Fluorescence spectra of nanocomposites I (a) and II (b), excitation wavelength 275 nm (a) and 330 nm (b).

peaks $2\theta_1 \approx 4.7^\circ$ and $2\theta_2 \approx 2.6^\circ$, one of which corresponds to the bilayer period of the CdC8 matrix ($d_{sm}=1.85$ nm), and the other is due to presence of CdS nanoparticles with the size $D_{II} \approx 3.4$ nm in the nanocomposite.

Figure 2 shows absorption spectra of nanocomposites I and II with CdS quantum dots. The spectrum of nanocomposite I has a narrow intense band with maximum at 325 nm. In the spectrum of nanocomposite II, a narrow absorption band with maximum at 375 is discernible. The position of the absorption bands for the nanocomposites is shifted to shorter wavelengths in comparison with the absorption spectrum of CdS bulk crystal [1] and indicates the presence of CdS QDs in the nanocomposites. Semiconductor nanocrystals are known to be characterized by an absorption band which is shifted relative to that of bulk crystal to the short-wavelength spectral region. This “blue” shift is caused by a quantum size effect, which arises when the semiconductor nanocrystal radius (r) is smaller than the exciton Bohr radius (r_B).

The gap energy for CdS bulk crystals is 2.58 eV [8]. The blue shift of the absorption band of nanocomposites indicates the presence of nanoparticles in the system. The dependence of nanoparticle size on first exciton transition energy (E_n) can be calculated in an effective mass approximation.

The dependence $E_n(r)$ has been verified by experiment many times; using it one can estimate the size of nanocrystals from absorption spectra of nanocomposites [9, 10]. As seen from the spectra shown in Fig 4 the absorption bands in both nanocomposites are shifted to higher energy values relative to the gap energy of CdS bulk crystal, E_g . To estimate the nanoparticle size, we employed known relations and an empirical formula [11], which relates particle size to absorption edge:

$$2R_{CdS} = 0.1 / (0.1338 - 0.0002345 \lambda),$$

where λ is absorption edge wavelength. An analysis of maxima and absorption edges showed that in nanocomposite I CdS nanoparticles with an absorption band at 325 nm predominate, which corresponds to QDs size of ≈ 2 nm. The fact that the absorption band is narrow indicates a low size dispersity of the nanocrystals synthesized. In the case of nanocomposite II, for which an absorption band with maximum at 375 nm is observed, CdS QDs have a size of ≈ 3.4 nm.

Figure 3 shows fluorescence spectra of nanocomposites I (a) and II (b). To excite fluorescence of CdS QDs in nanocomposites, xenon lamp radiation with wavelengths of 275 nm and 330 nm was used. In the fluorescence spectrum of nanocomposite I, the short-wavelength band edge at 340 nm may be attributed to exciton luminescence. It is caused by the recombination of free excitons in the CdS QDs. The long-wavelength edge of the same band may be attributed to exciton capture to local surface levels of QDs. PL spectrum of nanocomposite II shows a weak intense peak centered around 385 nm, which is assigned to band-edge emission. The long-wavelength bands are due to exciton capture to local states both on the surface of QDs and

inside them. Peak located around 450 nm is termed as acceptor level and another peak at 530 nm is termed as green band luminescence. This peak arises due to interstitial sulphur sites [12].

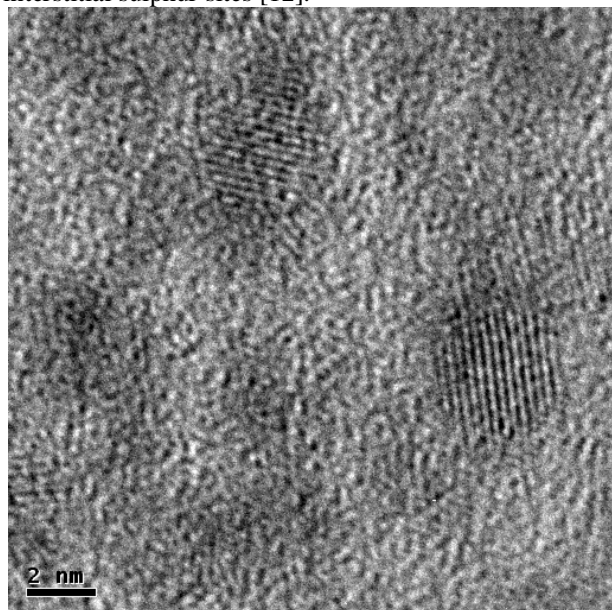


Fig. 4. High-resolution transmission electron microscopy photograph of nanocomposite I, with CdS nanoparticle size ≈ 2 nm

The morphology of the template synthesised CdS nanoparticles is shown in Figure 4. Transmission electron microscopy photograph of CdS nanocrystals

show that they are polyhedron-spherical quantum dots (QDs). The spacing between nanocrystals indicates that an organic matrix is likely to be capping the QDs. The average nanoparticle diameter is in the range of 2 - 3 nm, which is very close to the values obtained from the optical spectra and the small-angle X-ray measurements.

Conclusions

Thus, in this work the nanocomposites containing CdS nanocrystals have been obtained by template synthesis in molten phases (isotropic and liquid crystalline) of cadmium octanoate. It has been found that depending on synthesis conditions, nanoparticles of 2 - 4 nm size can be obtained. CdS QDs are characterized both by exciton photoluminescence and by luminescence from the QDs surface. Thus, ionic molten cadmium alkanoate phases are nanostructured matrices, which enable one to synthesize and stabilize semiconductor nanoparticles and to create new hybrid optical nanocomposites.

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- [1] T.Trindade, P.O'Brien, N. L. Pickett. *Chem. Mater.* 13, 3843 (2001).
- [2] Soumitra Kar, Subhadra Chaudhuri. *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry* 36, 289 (2006).
- [3] T. Hegmann, H. Qi, V.M. Marx. *J.Inorg. Organometallic Polym. Mater.* 17, 483 (2007).
- [4] T.A. Mirnaya. S.V. Volkov. *Ionic liquid crystals as universal matrices (solvents). Main criteria for ionic mesogenicity in Green industrial applications of ionic liquids.* Eds. R.D. Rogers. K.R. Seddon, S.V. Volkov, (Kluwer Academic Publishers, London, 2002).
- [5] V.M. Asaula, T.A. Mirnaya, G.G. Yaremchuk, A.S.Tolochko. *Ukrainian Chemistry Journal* 77, 24 (2011).
- [6] P. Konarev, M. Petoukhov, V. Volkov, D. Svergun. *J. Appl. Cryst.* 39, 277 (2006).
- [7] D. Demus, L. Richter. *Textures of liquid crystals* (Dt. Verl. für Grundstoff-industrie. Leipzig, 1980).
- [8] L.E. Brus. *J. Chem. Phys.* 80, 4403 (1984).
- [9] T. Vossmeier, L. Katsikas, I.G. Popovic. *J. Phys. Chem.* 98, 7665 (1994).
- [10] Y. Wang, N. Herron. *J. Phys. Chem.* 95, 525 (1991).
- [11] K. Suresh Babu, C. Vijayan, P. Haridoss. *Mater. Res. Bull.* 42, 1251 (2007).
- [12] V. Singh, P. Chauhan. *J.Phys.Chem.Solids* 70, 1074 (2009).

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Синтез та оптичні властивості рідкокристалічних нанокompatитів на основі октаноату кадмію з квантовими точками CdS

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Синтезовано напівпровідникові нанокристали CdS в рідкокристалічному та ізотропному розплавах кадмію октаноату. Одержано скловидні мезоморфні нанокompatити шляхом охолодження розплавів. Показано, що CdS нанокристали в скловидних матрицях представляють собою квантові точки (КТ), які характеризуються високим ступенем монодисперсності та мають розмір 2-4 нм в залежності від умов синтезу. Вперше досліджено фотолюмінесцентні властивості CdS квантових точок у двовимірній впорядкованій склоподібній матриці кадмію октаноату, що може служити в якості модельного дослідження випромінювальних процесів в таких нових матрицях.