Morphology and luminescence properties of nanocomposites films on the base of poly(*n*-vinylcarbzole) and semiconductor nanocrystals CdSe/ZnS

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In this paper the concentration dependence of morphology and luminescence characteristics of polymer-inorganic nanocomposites based on core-shell nanocrystals CdSe/ZnS and polyvinylcarbazole prepared by spin-coating method was investigated. It has been established that nanocrystals form closely packed clusters with sizes from 20 nm to several micrometers depending on the nanocrystals concentration. The photoluminescence intensity of the nanocomposite has a maximum at the nanocrystals concentration of 75 wt.%. The photoluminescense quenching was observed at the higher concentration due to nanocrystals aggregation.

В работе исследуется концентрационная зависимость морфологии и люминесцентных характеристик полимер-неорганических нанокомпозитов на основе полупроводниковых нанокристаллов типа ядро-оболочка CdSe/ZnS и поливинилкарбазола, полученных методом spin-coating. Наблюдается ассоциация нанокристаллов в кластеры размерами от 20 нм до нескольких микрометров, в зависимости от концентрации их в матрице, с сохранением индивидуальности нанокристаллов. Максимальная интенсивность люминесценции нанокомпозита отмечается при концентрации нанокристаллов 75 масс.%, после которой происходит уменьшение интенсивности излучения, обусловленное образованием нелюминесцирующих плотноупакованных агрегатов нанокристаллов.

1. Introduction

In the last decade, many efforts have been devoted to the development of nanostructured organic-inorganic materials useful for the fabrication of multilayer light emitting devices (LED). Composite and hybrid materials have long been drawing attention because various properties of polymer such as mechanical and thermal stabilities can be modified by adding inorganic semiconductor nanocrystals (NC). The polymer is employed as a carrier transporting layer and NC act as luminescence centers. In particular, using the NC in the emitter material may provide increase stability, color saturation, the quantum efficiency of electroluminescence, extended spectral range of existing organic structures [1–3].

Efficient Forster resonance energy transfer from polymer (donor) to NC (acceptor) is required for the optimization of LED structure [4–6]. Therefore, the investigation of spatial arrangement of the NCs in the polymer matrix is important for the development of new nanocomposite materials. However, despite the large number of publications on nanocomposite organic-inorganic materials [1–13], analysis of the published data shows that the structure of nanocom-
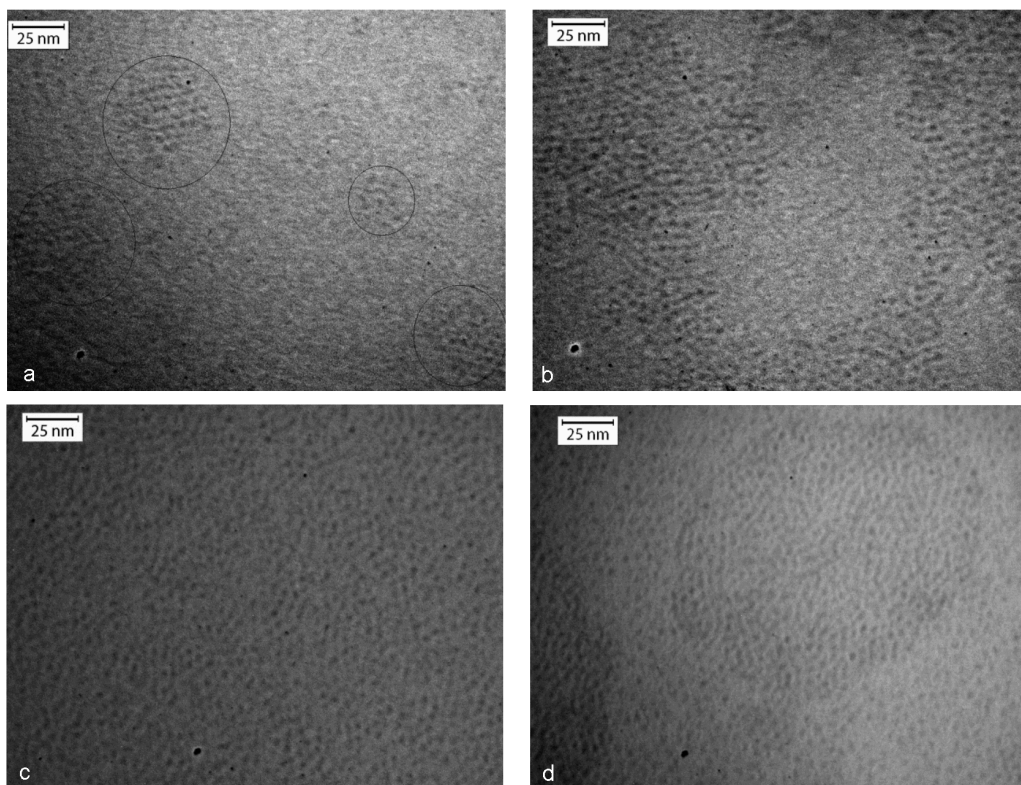
Fig. 1. TEM image of the nanocomposite films of CdSe/ZnS-PVK with a thickness about 80–100 nm for different mass ratios of NC/PVK: a — 0.2:1, b — 1:1, c — 3:1, d — 4:1.

posite films based on organic semiconductor and semiconductor NC has not been sufficiently studied to date, especially for the films prepared by spin-coating method.

Thus, in [7] photoluminescence (PL) quenching resulting from the aggregation of the NC in a system based on semiconductor CdSe NC and poly(*n*-vinylcarbazole) (PVK) with the mass ratio of CdSe/PVK 9:1 was observed. S.Coe-Sullivan et al. demonstrated a phase separation process, which takes place in a system based on N, N′-diphenyl-N, N′-bis (3-methylphenyl)-(1, 1′-biphenyl)-4, 4′-diamine (TPD) and semiconductor NC [8, 9].

The goal of the present reserach is to determine patterns of influence of the NC concentration on the morphology of polymer-inorganic nanocomposite films based on core-shell NC CdSe/ZnS and PVK obtained by spin-coating and to study the behavior of the NC, incorporated in the polymer film, as well as to establish the correlation of the luminescence, the distribution and concentration of the NC in the PVK matrix.

2. Experiment

Poly(*n*-vinylcarbazole) (M_w = 72000) was purchased from Aldrich and was used as a hole transporting matrix without prelimi-

nary cleaning. Monodisperse (~10 %) colloidal CdSe/ZnS core-shell nanocrystals with diameter of 4 nm (λ_{lum} = 530 nm) with a surface passivated with trioctylphosphine oxide (TOPO) were synthesized by chemical colloidal organometallic method [10, 11].

Thin composite emitting films (PVK-CdSe/ZnS) with a thickness about 80–100 nm were obtained by spin-coating method (2500 rpm) from the mixed toluene solution of PVK and NC in different mass ratios of NC to PVK on glass substrates coated with transparent ITO anode (Merck) and then heated to 85°C for 60 min. The mass ratio NC:PVK in a solution was changed in the range from 0.1:1 to 6:1.

Morphology of the nanocomposite films was determined by transmission electron microscopy (TEM) with EM-125 microscope (Selmi, Ukraine) operated at 125 kV accelerating voltage. Evaluation of the degree of filling the NC clusters of visible field microscopic images was performed using Adobe Photoshop program. Photoluminescence spectra were performed by SDL-2 spectrophotometer. The surface elemental composition of the film was characterized by X-ray photoelectron spectroscopy (XPS-800 Kratos spectrometer using MgK_α radia-

Table. Atomic concentration of elements in the surface layer of the samples

The NC concentration in the nanocomposite, (wt.%)	C_{at}, %								
	N	Zn	Cd	S	Se	In	Sn	O	C
50	2.1	4.2	1.6	7.3	1.8	0	0	4.0	79.1
75	1.8	5.6	2.0	8.8	2.6	0	0	4.4	74.7

tion ($h\gamma = 1253.6$ eV). The thickness of the analyzed layer was ~5 nm.

3. Results and discusssion

Investigation of morphology of PVK-CdSe/ZnS nanocomposite films with various concentrations of NC by TEM (Fig. 1) shows that the NC embedded inside the PVK matrix have narrow size distribution and form closely packed clusters even at the low NC concentration. By "clusters", we mean a kind of "congestion" of CdSe/ZnS/TOPO nanoparticles in which the particles are separated by layers of the matrix (PVK in this case).

So, in the mass ratio NC/PVK — 0.2:1 — 17 wt.% NC (Fig. 1a) the formation of clusters with sizes ranging from 10 to 20 nm was observed, and the configuration corresponding to dense packing of spherical nanoparticles in the film plane. At this concentration the packing density of the nanocrystals in the cluster (ρ_{NC}) is 0.03 NC/nm^2, and the NC coverage degree of visible surface of the film is about 10 %. At higher concentration (Fig. 1b) the extended regions of close packed NC of 100–200 nm are formed, while the distance between the NCs maintans about 8 nm and the packing density of ~ 0.03–0.04 NC/nm^2. The coverage degree was approximately 60 %.

At concentration NC 75 wt.% solid monolayer domains with sizes larger than 1 μm (surface coverage is ~100 % in area; $\rho_{NC} = 0.04$ NC/nm^2) are formed. When the concentration of the NC in composite thin films is increased to 80 wt.% (NC/PVK 4:1) (Fig. 1d) the NC tend to formation of more closely packed aggregate, consisting of the clusters ($\rho_{NC} = 0.05$–0.06 NC/nm^2), and the distance between the centers of NC decreases to 6 nm. This clusterization behavior indicates the phase separation in the nanocomposite films obtained by spin-coating.

Conclusion about formation of planar layers of the NC near the surface of PVK films was confirmed by XPS method (see Table). The surface area of the polymer-inorganic film (thickness of the analyzed layer ~5 nm) composed of chemical elements Cd, Se, Zn and S in the state of CdSe

(E_b.Cd3$d_{5/2}$ = 405.2 eV, E_b.Se3d = 54.2 eV) and ZnS (E_b.S2p = 162.1 eV), belonged to the NC. Position of the nitrogen peak (E_b.N1s = 400.2 eV) corresponds to N–C bond in the PVK. Changing the concentration ratio Zn/N (3.1 for 75 wt.% NC; 2.0 for 50 wt.% NC) correlates with changing in surface coverage of the film by the NC determined from TEM images (100 % and 60 %, respectively).

The high content of oxygen and carbon is typical for all types of films formed in atmosphere. The absence of peaks of substrate elements (In and Sn) indicates that the films deposited from solution by the spin-coating are continuous and porousless.

Optical spectra of NC/PVK films are largely dependent on an efficient Forster resonance energy transfer from PVK (donor) to CdSe/ZnS NC (acceptor).

In accordance with [7, 12–14], the efficiency of radiationless energy transfer photoexcitation of the inductive-resonance mechanism (Forster energy transfer) depends on the overlap integral of the donor luminescence spectra and acceptor absorption spectra, and on the distance between them. In these donor-acceptor systems the luminescence spectrum is a superposition of the spectra of individual components of the system. An intensity of the luminescence of the donor in the presence of the acceptor decreases with increasing concentration of the acceptor.

The intensity of the donor luminescence can be determined by the expression [14]:

$$\frac{I_{DA}}{I_D} = 1 - 3.71\sqrt{\pi}\,C_A R_0^3, \qquad (1)$$

where I_{DA} is the fluorescence intensity of the donor (polymer) in donor-acceptor mixture; I_D is the donor emission intensity in the absence of an acceptor, C_A — the concentration of the acceptors (NC) and R_0 — Forster radius.

The most obvious manifestation of the energy transfer in nanocomposite systems PVK/NC is quenching of PVK (donor) photoluminescence (PL) intensity in peak at $\lambda_{max} = 410$ nm and the simultaneous in-

creasing the NC PL intensity (λ_{max} = 530 nm) upon photoexcitation in the absorption band of the donor.

The relative quenching of the PVK fluorescence (I_{PVK}) as function of C_A is plotted in Fig. 2 (curve *1*). It is seen, that PL intensity of PVK in the films linearly decreases with increasing NC concentration. The R_0 can be expressed by approximation of experimental points by expression (1). And R_0 for PVK — CdSe/ZnS nanocomposites was determined to be 5.3 nm.

The emission intensity of CdSe/ZnS (I_{NC}) in the nanocomposite films (Fig. 2, curve *2*) linearly increases with increasing concentration to 50 wt. %. Therefore, as can be seen from Fig. 1, that clusterization behavior of NC in polymer films ("congestion" in quasi-two NC clusters) at low NC concentrations has no influence on the spectral characteristics of PL of the NC.

The I_{NC} has a maximum at the NC concentration in 75 wt. %. When the concentration of NC in the composites is more than 80 wt. %, a reduction of I_{NC} observed. Also it can be seen (Fig. 1d) the changing of the configuration of NC clusters. Nanocrystals form three-dimensional structures (aggregates) with more dense packing than for two-dimensional clusters of nanoparticles. Possibly, in these close-packed structures, the electronic excitations are delocalized over the set of the NC with non-radiative degradation of the excitation energy.

Consequently, the relative decrease of concentration of independent acceptors (NC) with increasing concentration of aggregates of closely packed NC is a major cause of I_{NC} quenching.

In accordance with [15], the organization of the NC in polymer matrix can be described by three model scheme (Fig. 2, I–III). In general, each states of NC organization occur depending on the parameters of exponential polymer-NC attractive pair potential of Eq. 2.

$$U_{PC}(r) = -\varepsilon_{PC}\exp(-\frac{r - \sigma_{PC}}{\alpha d}), \qquad (2)$$

where σ_{PC} = $(D+d)/2$, α — the spatial range parameter (material depend); D — diameter of polymer macromolecule; d — NC diameter; r — the distance between the centers of NC; ε_{PC} — the attractive minimum energy of monomer-NC interaction, which is:

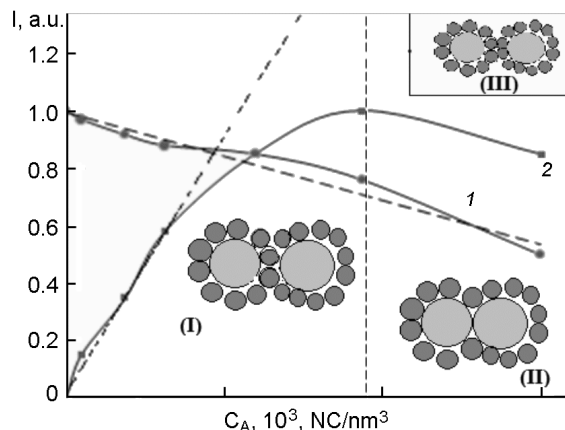$$\varepsilon_{PC} \approx \frac{E_{PC}d}{2b}, \qquad (3)$$

Fig. 2. Relative PL intensity of PVK (1) and NC of CdSe/ZnS (2) as function of the NC concentration in the nanocomposite films. The inset shows the schematic illustration of three states of the particles organization in the polymer matrix: (I) — thin layer of polymer between NC; (II) — direct contact of NC-NC; (III) — steric stabilization of NC by polymer layers.

where E_{PC} — the Lennard-Jones potential parameter for the elementary units with size b ($b < d << D$).

For model I (Fig. 2), in which bridging of polymer monomers presents between the NC, can be characterized by the following parameters: α = 0.25, ε_{PC} = 2.25. For α = 0.25, ε_{PC} = 2.2 the contact of NC aggregation exhibits (model II). Finally, for α = 1.0, ε_{PC} = 2.0 (model III), it is dominant the tendency for NC to be sterically stabilized by the longer-range d strong attractions between polymer and NC.

We calculated the distance between the centers of NC CdSe/ZnS in the linear concentration dependence of I_{NC}.

In particular, at the concentration of NC in the nanocomposite of 15–50 wt.% the distance between centers of the NC is 8 nm (Fig. 1a, b). Since the diameter of the NC is 4 nm and the thickness of TOPO ligand shell is about 1 nm, a thin polymer layer between the NC (about 2 nm) is present that corresponds to the model (I). Interestingly, the same distance between the NC is observed at lower concentrations of NC.

At the mass ratio NC/PVK 4:1 (Fig. 1d) the distance between the centers of NC is 6 nm. Taking into account the thickness of the TOPO layer, one can conclude that there is direct contact of the ligand shell nanocrystals and their interaction via dispersion forces. This morphology of the com-

posite film corresponds to the model (II) with parameters $\alpha = 0.25$, $\varepsilon_{PC} = 2.25$.

It is obvious, that model (I) and (II) describe the state of the composite system for different stages of phase separation of the components of the system.

In order to minimize or eliminate the formation of aggregates, causing PL quenching of the nanocomposite, and to maximize the concentration of isolated NC, it is necessary to provide conditions for steric stabilization of NC (model III in Fig. 2). Such conditions can be ensured, in particular, by choosing the material for ligand shell on the surface of NC, which is the subject of our further research.

4. Conclusions

In the present work the structure and optical characteristics of thin polymer-inorganic nanocomposite films obtained by spin-coating method on the basis of poly(n-vinyl-carbazole) and semiconductor nanocrystals of CdSe/ZnS are studied. The energy transfer efficiency from PVK to CdSe/ZnS is estimated by the Forster radius as 5.3 nm. It was shown, that PL intensity of the composite had a maximum at the NC concentration of 75 wt.%.

The PL quenching observed at the higher concentrations (>75 wt.%) is explained by the NC aggregation that is confirmed by TEM. Using X-ray photoelectron spectroscopy and transmission electron microscopy it has been established, that in full concentration scale CdSe/ZnS nanocrystals form plane closely packed structures from 20 nm to several micrometers on the PVK film surface, that is attended by the NC center-to-center distance decrease with the NC concentration increasing. Phase separation process is considered in the framework of Schweitzer's models.

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Морфологія та люмінесцентні властивості нанокомпозитних плівок на основі полівінілкарбазолу та напівпровідникових нанокристалів CdSe/ZnS

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У роботі досліджується концентраційна залежність морфології та люмінесцентних характеристик полімер-неорганічних нанокомпозитів на основі нанокристалів типу ядро-оболонка CdSe/ZnS та полівінілкарбазолу, одержаних за допомогою методу покриття центрифугуванням. Спостерігається асоціація нанокристалів у кластери розмірами від 20 нм до декількох мікрометрів, в залежності від концентрації нанокристалів у матриці, зі збереженням індивідуальності нанокристалів. Максимум інтенсивності люмінесценції нанокомпозиту відзначається при концентрації нанокристалів 75 мас.%, після якої спостерігається спад інтенсивності люмінесценції, обумовлений утворенням нелюмінесцентних щільнопакованих агрегатів нанокристалів.