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Dispersion and aggregation of quantum dots in polymer–inorganic hybrid films

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The mechanisms of dispersion of spherical CdSe/ZnS quantum dots (QD) in the polymer–inorganic nanocomposite thin films based on two types of polymers poly(9-vinylcarbazole) (PVK) and poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) have been studied. The radial distribution function (RDF) and the potential of mean force (PMF) in these composite films with QD concentration from 17 to 80 wt.% were determined. Analysis of RDF and PMF of the obtained composites PVK/QD and PFO/QD has revealed the three different states of QD spatial organization as a function of the polymer–QD interaction. Using transmission electron microscopy and X-ray photoelectron spectroscopy, it was shown that the PVK/QD composites tend to phase segregate with the formation of bilayer structures, whereas in the PFO/QD composites uniform distribution of QDs occurs. The results showed that the morphology has a significant impact on the optical properties of nanocomposites. In the PVK/QD nanocomposites a photoluminescence quenching is observed with the increase of QD concentration unlike in the PFO/QD nanocomposites.

1. Introduction

Organic–inorganic nanocomposite films containing quantum dots (QDs) have recently attracted considerable attention due to their wide application for organic/polymeric light-emitting diodes [1–6] and solar cells [7–10]. This interest is based on the possibility to combine the strong quantum size confinement effects of QDs [11] and attractive technological properties of polymer hosts [12,13]. Thus, a wide variety of nanocomposites containing different QDs assembled into multilayers have been developed for high-efficient devices [1–3,6,10,12,14]. Despite the large number of reports on electro- and photoluminescence properties of polymer–inorganic nanocomposites [1–9,15–25], the morphological characteristics of such materials continue to be under considerable attention [1,2,15–25]. In earlier works, *e.g.* by S. Coe-Sullivan et al., the phase-segregation was shown to occur during a spinning process when the core–shell-type CdSe/ZnS QDs coated with trioctylphosphine oxide (TOPO) and hole-transporting N,N′-diphenyl-N,N′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4-diamine (TPD) were used [2]. B. Torriss et al. and F. Teng et al. suggested that an observed concentration quench of photoluminescence (PL) and a reduction of the energy transfer from poly(9-vinylcarbazole) to CdSe/ZnS QD are caused by aggregation of QDs [15,16]. More recent work [17] reported a phase segregation of the mixture of the electroluminescent (EL) polymer poly[2-methoxy-5-2(2′-ethylhexyloxy-p-phenylenevinylene)] (MEH-PPV) and CdSe QD coated with octadecylamine as a ligand. C. Lee et al. demonstrated the uniform dispersion of CdSe/ZnS/TOPO QD in MEH-PPV films [18]. However, such kind of composite materials is insufficiently studied and many aspects of these films are unclear to the moment. In particular, the interaction forces between QD and polymer molecule are often not taken into account, although the aggregation in the nanocomposite polymer–inorganic blends is considered as a key factor for well balanced emission in the PL and EL devices [1,2,16]. Recently it has considered some thermodynamic aspects of formation of one-dimensional dipolar equilibrium nanostructures in model QD/decalin system [23,24].

The main objective of this work is to study the effect of conducting polymer chemical nature on the dispersion of QD in the nanocomposite polymer–inorganic films and to apply selected theoretical methods [26–29] of qualitative and quantitative characterizations of the dispersion of nanoparticles in polymer.

2. Experimental details

The conjugated aromatic polymers poly(9-vinylcarbazole) (PVK, $M_w = 72.000$) and poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO, $M_w = 58.200$) were purchased from Sigma-Aldrich and used as is. Monodispersed colloidal CdSe/ZnS core–shell nanocrystals, where CdSe is core, ZnS is shell, total diameter of 4 nm (size deviation ~ 10 %, λ_{Lum} = 530 нм) grafted mainly with TOPO were synthesized by organometallic method [11].

The polymer–inorganic nanocomposites with varied QD content (17–80 wt.%) were fabricated by solution-blending method using toluene as a solvent. The polymer–QD stock solution was deposited through a single spin-coating step on quartz or glass substrate coated with indium tin oxide film.

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The thickness of spin-cast polymer thin films (50–100 nm) was adjusted through varying the stock solution concentration from 1 to 15 mg/ml at the fixed rotation speed 2500 rpm.

The morphology of nanocomposite films was determined by transmission electron microscopy (TEM) on an EM-125 microscope (Selmi, Ukraine) operated at 125 kV accelerating voltage. Evaluation of the surface QD fraction on visible field microscopic images was performed using ImageJ program. The photoluminescence spectra were recorded on SDL-2 spectrophotometer. The element analysis of the film surface was carried out with X-ray photoelectron spectroscopy (XPS-800 Kratos spectrometer using MgK_α radiation ($h\gamma = 1253.6$ eV). The depth of the analyzed layer was ~5 nm.

3. Results and discussion

Two types of polymer–inorganic films based on PVK and PFO conductive polymers and containing varied concentration of CdSe/ZnS QDs were prepared. Both PVK and PFO matrices possess similar molecular weights and polydispersion degrees and have been chosen as polymer hosts owing to their differences in chemical nature (see Fig. 1) that might be affected on the morphology of the resulted composites, *e.g.* on the QD distribution in polymer films. The principle differences in the chosen polymers consist in alteration between the main chain and lateral substituent nature, namely, PVK contains an aliphatic backbone with aromatic side substituents, whereas PFO consists of the aromatic main chain and aliphatic side arms. Taking into account that QDs have an alkyl-aliphatic type of outer organic shell originated from TOPO (three *n*-octyl substituent), one can assume that the dispersion of such type of QD in PFO might be more homogeneous than the same QDs in PVK host due to be interaction between the aliphatic chains of TOPO and the aliphatic side arms of PFO.

The particle distribution in the prepared composite films was studied experimentally by TEM. The TEM images taken from polymer/QD thin films with various contents of QDs reveal essential differences in morphology between PVK/QD and PFO/QD nanocomposites (see Fig. 2). Thus, upon increase of the particle concentration in PVK/QD systems the morphology of the films is changed from small (10–20 nm) isolated domain structures of QDs (Fig. 2a) through percolating domains (100–200 nm, Fig. 2b), and comes eventually to compact domains with closely packed aggregates (Fig. 2c). These TEM patterns are unambiguous evidence that phase separation occurs upon the spin-coating process with formation of a nanocomposite film bilayer structure, *i.e.* polymer film with a monolayer of nanoparticles on the surface. This conclusion is also indirectly supported by the XPS analysis and by the surface fraction of QDs calculated from TEM images [see Table 1]. The analyzed layer (in ~5 nm depth) of PVK/QD films was found to contain 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), ZnS (E_b.S2p = 162.1 eV), referred to QD inorganic core and P (E_b.P2s = 190.1 eV) originated from QD organic shell, TOPO. Position of the N peak (E_b.N1s = 400.2 eV) corresponds to the N – C bond in the PVK.

As it can be seen at the Table 1, the increased Zn/(Zn + N) atomic ratio (55% on surface *vs* 11% calculated from feed ratio indicates that the majority of QDs are collected at the film surface. The surface QD fraction reaches 100% at 75 wt.% of total concentration of QDs, *i.e.* at such critical loading of QDs the film surface is actually saturated with QDs and further increase of QD concentration in a stock solution can lead to their compaction with formation of close-packed aggregates. The absence of element peaks from the substrate (In and Sn) in the XPS indicated that the prepared films are continuous and porousless.

In contrast to PVK/QD system, in the PFO/QD films a uniform distribution of QDs is revealed in the whole concentration range (from 17 to 80 wt.%, see Fig. 2d, e). However, the application of the XPS technique to analyze the PFO/QD composites is hampered because of absence of nitrogen or another appropriate reference element in chemical composition of PFO.

A more precise way to study the distribution of QDs in the composite films is calculation of the corresponding radial distribution function (RDF, g(r)) and potential of mean force (PMF, βW(r)) based on the distances between the centers of the QDs. RDF for two-dimension images are defined by [26–29]:

$$g(r) = n(r)/(\rho \times S_{shell}), \tag{1}$$

where g(r) is the radial distribution function, n(r) – the mean number of particles in a shell of area S_{shell} at distance r, and ρ is the mean particle density (QD/nm^2).

And PMF is given by:

$$\beta\ W(r) = -\ln(g(r)), \tag{2}$$

where $\beta = 1 / k_BT$, and k_B is the Boltzmann constant.

The RDF curves for PVK/QD films with QDs concentration in a range 17–75 wt.% (Fig. 3a) possess a clear first maximum at $r_1 = 8$ nm, which corresponds to a primary cluster – “repetitive link”. These observations are evidence that two QDs, each of 4 nm diameter surrounded with 1 nm thickness TOPO shell, are separated by a polymer layer about 2 nm in thickness (see Fig. 3a (II)). The relations of intensities of the first and the following peaks at $r_2 = 12$ nm, $r_{3,4} = 18$ and 22 nm are constant in QD concentration range 17–75 wt.%, showing that the increase of QD concentration do not affect on the QD–QD attraction strength.

The peak at $r_5 = 36$ nm and next following are broad and gradually decrease, approaching 1. The location of these maxima differs in the whole QD concentration interval that indicates chaotic distribution of primary clusters of QDs on the long distances and thickening of the polymer layer up to 14 nm and more (Fig. 3a (III)). This behavior of

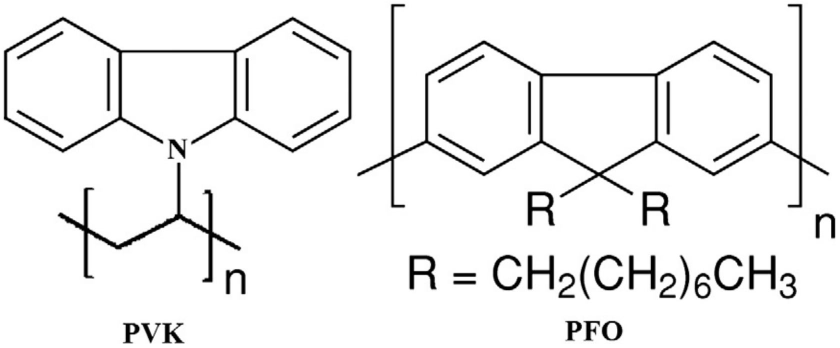

Fig. 1. Chemical structures of poly(9-vinylcarbazole) (PVK); and poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO).