Conference Paper

Technology for Creation and Detailed Analysis of Polymer Composites with Uniform Distribution of Quantum Dots and Liquid Crystals

Mochalov K.E. 1,2, Bobrovsky A. 3, Solovyeva D.O. 1, Mokrova D.V. 1, and Oleinikov V.A. 1,2

1Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, RAS, Moscow, Russia
2National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow, 115409, Russia
3School of Chemistry, Moscow State University, Leninskie Gory, Moscow, Russia

Abstract

One of the most actual tasks in biotechnology is the creation of a new generation of nanobiosensors with improved brightness, photo stability, and sensitivity. Compositions of polymers and colloidal quantum dots (QDs) are the most promising base to develop such sensors. This work presents the technology for creation and detailed analysis of nanostructured composite films based on polypropylene matrices with uniformly distributed CdSe/ZnS quantum dots and liquid crystals. Methods of optical microscopy, scanning probe microscopy and confocal fluorescent microspectroscopy were used. The presence of liquid crystals in the composite allows additional control of QDs fluorescence. The methodology proposed is applicable not only to polypropylene, but also to other porous polymers. The results of this work indicate the possibility of creating high-quality polymer/QDs composite materials and open the way to the development of nanomaterials (nanosensors) with optical properties sensitive to various environmental parameters (electric field, photo irradiation, mechanical action, etc.).

Keywords: quantum dot-polymer composites, nanoporous polypropylene, fluorescence

1. Introduction

Nowadays one of the most relevant area in research and development is the design of new types of fluorescent hybrid materials. The most popular modern hybrids are composites based on polymer matrices with inorganic additives with specific optical, electrical and other characteristics [1]. The most promising fluorescent inorganic additives
are semiconductor quantum dots (QDs) due to their unique optical properties. They are characterized with a wide absorption band and a high intense narrow emission band, whose spectral position varies from IR to UV region. Furthermore, the wavelengths of the absorption and emission maxima due to the presence of quantum-size effect can be easily changed by variation of the QDs’ size [2, 3].

Over the last decade, many articles devoted to this subject have been published and, accordingly, a vast number of different design techniques and fields of application of QDs-polymer hybrid structures have been proposed. [4-13, 26].

The main trend in this area is to develop different organic matrices with high homogenous distribution of QDs [4-7]. E.g., in [4], a method for creation of polystyrene-based composites is described by means of radical copolymerization in the presence of QDs coated with octadecyl-p-vinyl-benzyl dimethyl ammonium chloride (OVDAC). The researchers demonstrated that in this way it is possible to obtain transparent composites with QDs characterized by intense emission of different colors incorporated into them. Another interesting method for producing such hybrid materials is based on assembling the layers of the composite by means of inkjet printing. CdSe QDs and five different kinds of organic polymers were used to produce such hybrids. The method allows to produce composites with a quite uniform QDs distribution and a good signal-to-noise ratio [6].

There is also significant progress in the field of nanosensorics [8-11]. For example, in [8], by adding trace amounts of QDs to the outer surface of an organo-modified composite, a QDs-bihydroxide type structure was developed capable to react to nitrite by increasing the intensity of chemiluminescence.

Nowadays, hybrids are quite popular which include not only QDs, but also liquid crystals attached to the polymer matrix. Our research team was actively involved in the development [13-15, 17-22] of methods for characterization [16] of devices with similar structure. In the course of the study, some possibilities of photo- and electro-manipulation by circularly polarized fluorescence were demonstrated and a new approach to the introduction of high concentrations of QDs in a cholesteric liquid crystal (LC) matrix was developed.

The main advantage of such structures is the ability to easily control orientation of LC by affecting them with external electric and magnetic fields. For example, in [12], zinc oxide-containing polymer elements of a solar battery were modified by layers of a LC copolymer with integrated CdSe QDs. Under the effect of the electric field applied, the QDs “recessed” in the liquid crystal layer acquired a more ordered structure, thereby
increasing the device’s performance. The main problem in to create this type of composite materials is extremely low concentrations of uniformly distributed QDs, which hinders their use in high-luminescent devices.

To solve this problem, our research team developed a new strategy to introduce QDs into the structure of polymer matrices. Earlier we published some papers [17-22], that described production of hybrid polymer structures with thin polyethylene (PE) porous films prepared according to [23]. One of the papers [24] described a simple but extremely reliable method to create composite films based on porous polypropylene (PP) and CdSe/ZnS QDs.

To summarize, the above studies showed the expediency of using porous polymer materials, such as PE or PP films, due to their excellent mechanical properties, flexibility, high porosity (more than 60%), low price and good thermal stability. It also became clear that the structure of the composite material should include not only the polymer matrix and QDs, but also the LC component. In this paper, we consider in detail some specific features when creating QDs-PP-LC hybrid structures. The effect of washing of the resulting hybrids, as well as their subsequent burning out on the final properties of the resulting composite, is considered. The paper presents a complete technique to characterize hybrid structures of this kind by combining methods of optical, atomic force, scanning probe microscopy, and confocal fluorescence microspectroscopy. The approach proposed makes it possible to control morphological, physical, mechanical, and optical properties of the sample. This methodology is applicable not only to polypropylene, but to other porous polymers as well. The results of this work indicate the fundamental possibility of creating high-quality polymer/QDs composite materials and demonstrate the possibility of qualitative integration of additional fluorescence regulating factor-liquid crystals.

2. Materials and Methods

As the polymer matrix, we used nanoporous (55% porosity) PP films purchased from Celgard (Celgard 2500 microporous monolayer membrane) with an average pore size of 0.064 μm and a film thickness of 25 μm.

The CdSe/ZnS QDs were synthesized by technique described in [25]. CdSe cores with diameter of ~2.9 nm were obtained by high-temperature organometallic synthesis using n-hexadecylphosphonic acid as blocking agent. After isolation and purification of CdSe, the cores were covered with three monolayers of ZnS solution in the octadecene–oleylamine mixture. Thus, the initial blocking ligands were replaced by
three(n-octyl)phosphine oxide (TOPO). The quantum yield of the obtained QDs was 68%. Immediately before the introduction of QDs into the PP matrix, the nanoparticles were dissolved in 1-octadecene (20 mg/ml).

Two types of PP-QDs-LC composites were prepared. To produce the first-type composite, stretched matrices of nanoporous PP (Fig. 1.1) were coated with a concentrated solution of QDs in octadecene (20 mg/ml) (Fig. 1.2). Then, excess solution was removed by filling the films with a filter paper. After that, we introduced a mixture of nematic LCs MLC6816 into the PP-QDs composite (Fig. 1.3). To produce the second-type composite, we repeated all the above steps but after that, these samples were washed with acetone (Fig. 1.4) and then annealed at the temperature 170°C (Fig. 1.5).

The fluorescence spectra were recorded using an M266 automated monochromator/spectrograph (SOLAR Laser Systems) with an U2C-16H7317 CCD (Omins) and a homemade light-collecting inverted system using a 100X/0.80 MPLAPON lens (Olympus) and a homemade confocal unit with two 100-mm objective lenses, a 100-µm pinhole, and two Semrock 488-nm RazorEdge® ultrastep long-pass edge filters (Semrock). An LGN-519M Ar+ laser (Plazma) operating at 488 nm was used for fluorescence excitation at a light intensity of 0.1 mW, as measured with a LaserMate-Q (Coherent) intensity meter. An integration time for recording confocal images is 0.03 sec. The scan area was 10×10 µm (100×100 points). Fluorescence confocal images were in the spectral range of 583–592 nm for all samples.
AFM and upright microscopy images were acquired using an SPM equipped with an Optem Zoom 125C upright microscope (Qioptiq). This SPM base was combined with the aforementioned inverted microscopic system, allowing us to obtain AFM, inverted microscopic, and upright microscopic images from the same area of the sample. For AFM images, a scan area of 8×8 µm (512×512 points) and AFM cantilevers of the ETALON HAFM series (NT-MDT) were used.

The equipment listed is a part of a unique scientific setup “System for Probe-Optical 3D Correlative Microscopy” of the IBCh RAS (http://ckp-rf.ru/usu/486825/). Equipment was provided by the IBCH core facility (CKP IBCH, supported by the Russian Ministry of Education and Science, Grant RFMEFI62117X0018).

3. Results and Discussion

Figures 2 and 3 show images of the first- and second-type composites obtained by direct and inverted microscopy methods.

Figure 2: Direct (a) and inverted (b) images of the first-type composite. Dark spot 2 on image (a) the same place as shown on the image (b). The bright spot 1 on image (a) – the spot from laser that stimulated emission of QDs into the composite.

Figure 3: Direct (a) and inverted (b) image of the second-type composite.
The main distinguishing feature of the first-type composite is its homogeneous opaque surface, which strongly diffuses light when the image is obtained in the direct mode (Fig. 2a).

On the opposite, the second-type composite’s surface is clearly visible in the direct mode (Fig. 3a). It is characterized by domain-like structure formed by densely packed optically transparent “domains”, separated by opaque boundaries.

The first-type composite’s image obtained by inverted microscopy is a continuous dark field to the great extent (Fig. 2b). These areas are the only transparent areas in this optical image. This composite demonstrates a very high level of light scattering without localized regions of transparency.

The second-type composite with the same light intensity is completely transparent (Fig. 3b). It should be emphasized that the image clearly shows the internal radial structure of domains converging to the center, as well as their opaque boundaries.

It is also seen that both types of composites are intensely colored in color, characteristic for the embedded quantum dots. The color appears uniform, but the samples differ in their degree of transparency.

The original PP films have low transparency and, in addition, strong scatter light due to their own porous structure. However, as mentioned above, the first step in the preparation of composite structures of this kind is to fill the pores of the polymer matrix with concentrated QDs solution in octadecene, which leads to a rapid (on the order of a few seconds) and a noticeable increase in their optical transparency. This is due to the proximity of transparency coefficients in the PP and octadecene. This phenomenon is typical not only of PP films, but also of other porous polymers, for example of PE.

The next step of our work was to study the properties of the resulting composites by AFM methods. Figure 4 shows the images of the CelgardR 2500 matrix (Fig. 4a); in Figures 5 and 6 there are the first-type and second-type composites, respectively. The scanning direction of each of the samples coincides with the direction of stretching of the PP matrix.

First of all, let us consider the structure of a PP film in detail. Figure 4 (a, b) shows relatively long (up to tens of microns) filamentary structures of about 100 nm in height and of several hundred nanometers in width. These structures are interconnected with an almost uniform discontinuity along the direction of extension of the PP matrix and have a wave-like period of about 1 μm. Perpendicular to the “large” structures described above, filamentary structures with a period of 100 nm are located. These “small” structures are most likely formed by fragments of the PP matrix remaining after the spatial separation of “large” filamentary structures (Fig. 4a, c). Unfortunately, the
ratio of the cantilever tip sides does not allow it to penetrate between the “small” fibers, which excludes the possibility of accurate measurement of their transverse parameters by means of AFM methods. Nevertheless, we made the assumption that the film has the same network-like structure throughout its continuation, consisting of the bulk of “large” and “small” threads. Further, assuming that the average ratio of the width of “large” filaments to the distance between them is \( 1/3 \), and the same ratio for “small” filaments is \( 1/2 \), we found that the average porosity of our composite is about 60%. An estimate of the same porosity by conventional methods [26] yielded results of about 55%. A good coincidence of these values means that the surface structure of the sample, revealed by means of AFM methods, corresponds to its real morphology. It is also worth noting that such a percentage of porosity indicates the possibility of introducing very significant volumes of QDs and LCs into the polymer matrix.

Having thoroughly studied the structure of the original film, one can proceed to study the characteristics of the composites obtained. First, let us consider the first-type composite that was not annealed and washed.

As regards the morphology of QDs’ distribution into the composite, the AFM image shows (Fig. 5a) that the QDs are not evenly distributed on the composite’s surface—instead they form islands (they are marked by dotted circles in Figure 5a). Moreover, by comparing the AFM with optical microscope images, we noticed that all regions in the cluster of QDs in the AFM image coincide with dark spots in the optical image obtained in direct mode. The AFM image of the first-type composite’s surface in the region marked with number 2 (Fig. 2a) is shown in the Figure 5b. Clusters of micrometer sizes are clearly visible in it. Probably, the formation of such large clusters of QDs contributes
Figure 5: (a) AFM image of the first-type composite. The QDs’ cluster area is pointed out by dotted circle. (b) enlarged image of the QDs’ cluster area.

to a significant change in the scattering properties of the composite structure, without changing the overall morphology of the PP matrix.

As the next step, we analyzed the surface of the first-type composite by confocal fluorescence microspectroscopy, thus obtaining even more detailed information about the homogeneity of QDs distribution (Fig. 6).

Figure 6 shows that the total difference in fluorescence intensity in the first-type composite is over 60%, and it is mainly due to the share of local inhomogeneity. It should also be noted that the location of these inhomogeneity is in line with the location of dark spots in optical images (Fig. 2a). Once again, it confirms the correctness of the methodology selected to study such hybrid structures. However, it is worth to
note that a very heterogeneous distribution of fluorescence intensity of QDs is also observed in regions that appear completely homogeneous in the images obtained by means of optical microscopy.

Figures 3 and 7 show the second-type composite whose preparation includes washing and annealing.

![Figure 7](image)

**Figure 7**: (a) AFM image of the second type composite; the dotted line shows the cross section. (b) profile of the cross-section that pointed out on (a).

Figure 7 demonstrates that “large” filamentary structures that were observed in the PP film are here strongly contracted. They were compressing until there are not gaps between them, while the dimensions of the filaments themselves remained unchanged. Unfortunately, the second-type composite’s surface structure does not allow us to use AFM to determine the exact location of QDs on its surface, however, the AFM analysis did not reveal the presence of any QDs’ clusters, which agrees with the optical microscopy results (Fig. 3).

Now let us look at the images obtained by means of fluorescent confocal microspectroscopy (Fig. 8).

Figure 8 shows that the second-type composite is characterized by a much more uniform QDs distribution in the matrix as compared with the first-type composite. The total difference in fluorescence intensity in each of the “domains” does not exceed 10%. It is also worth to note that there are almost no QDs at the domain borders (Fig. 8a, top right).

Such metamorphoses in the PP matrix’s structure, as well as uniform QDs distribution are due to the fact that the second-type composite was subjected to annealing at a temperature close to the melting point of the PP matrix, as well as preliminary washing with acetone. Acetone promotes a more “strong” and deep deposition of QDs inside the pores of the PP matrix, and burning, in turn, leads to an almost complete shrinking
of polymer fibers thereby “locking” the QDs inside themselves. This prevents their loss in future and provides a high flexible material with uniform fluorescence intensity.

The same process is responsible for the follow-up increase in the transparency coefficient of our composite. The point is that, as mentioned above, the introduction of octadecene into the pores of the PP matrix helps to increase its transparency; however, the technique is such that octadecene must be removed from the samples. It can be washed out in the way as it is the case with the second-type composite, or it can simply be dried as in the case with the first-type composite. Washing and drying of composites naturally leads to deeper deposition of QDs due to removing of octadecene. Nevertheless, after it the transparency level of the composite drops. However, since annealing of composite films leads to compression of pores in the polymer matrix, light scattering decreases and, accordingly, the transparency of the sample also increases.

The last step of our research is investigation of fluorescence (Fig. 9a) and absorption (Fig. 9b) spectra of the resulting composites.

It should be noted that the fluorescent maximum of the second-type composite (589 nm) is shifted to the red region of the spectrum relative to the maximum of the first-type composite (585 nm), which, most likely, was due to energy transfer. Another important aspect is a decrease in the fluorescence intensity of the second-type samples in about two times, that is shown in Figure 9a. Therefore, we can conclude that the decrease in light scattering on the surface of the annealed composite (i.e., an increase in its transparency) led to fluorescence quenching. Nevertheless, both
types of composite films are characterized by a very high intensity level. Analyzing the absorption spectra, it is evident that both composites are characterized by the presence of an intense and wide absorption peak in the blue and UV regions of the spectrum, which grows with decreasing wavelength, and shows a small peak with a maximum at 566 nm. Such spectral characteristics are specific characteristics of QDs and it is direct evidence of their high concentration in the composite sample [27, 28].

4. Summary

We developed a new simple method to synthesize hybrid structures based on porous polymers doped with QDs and LCs. The composites obtained contain high concentrations of QDs (at least 15% of the weight of the composite), characterized by high fluorescence intensity and exhibit impressive thermal stability, flexibility and good mechanical properties that are preserved even after annealing composite films. The composites obtained are stable at time (a decrease in fluorescence intensity as well as degradation of mechanical properties of the material was not observed when it was stored for a year). We also developed the method of sequential structural and morphological analysis of such hybrid materials. Our method consists in step-by-step investigation by means of AFM, SPM, optical microscopy, and confocal fluorescence microspectroscopy.

While using the methods described, we established that stretching of the initial porous matrices leads to the formation of mutually perpendicular “small” and “large” filamentary structures. The washing of porous polymer–QDs–LCs hybrids with acetone and its subsequent burning at temperatures close to the melting temperature of the
polymer matrix leads to a uniform distribution and tight shrinkage of QDs in the sample. Annealing of composite films increases the homogeneity of QDs distribution within each of the sample “domains” by a factor of 6.

Despite a slight drop in the fluorescence intensity, the second-type composites turned out to be more successful. They are characterized by uniformly distributed intensity with a degree sufficient to use this kind of composite structures in the constructions of high luminescent devices.

Hybrid structures synthesized by our method can easily be used as a base material for nanosensors. The procedure is applicable not only to PP and PE, but also to other porous polymers. The sequential method of analysis of such composite structures developed by us makes it possible to control the conformity of the manufactured sample with the requirements declared for it at each stage of the work.

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References


