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Toward Linear Arrays of Quantum Dots via Polymer Nanofibers and Nanorods

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Linear arrays of quantum dots are predicted to show localization effects for light traveling along the linear dimension quite similar to the case of the Anderson localization phenomenon known for electron transport. A basic requirement is to have stable arrays of such quantum dots at hand that might be incorporated into potential devices. To prepare such linear arrays, we dispersed ZnSe quantum dots in a polymer solution and used this solution in a first approach to electrospin polymer nanofibers from this solution using polystyrene and polylactide as polymer matrix. Nanofibers with quantum dots with dimensions ranging from several 100 nm to about 10 nm were achieved in this way. Using frame type and cylindrical rotating electrodes, an enhanced mutual orientation of these fibers was achieved. In a second approach, we used the wetting assisted template approach based on porous alumina templates to obtain parallel sets of polystyrene nanorods containing quantum dots.

Introduction

Quantum dots are highly interesting objects for a broad range of applications in optoelectronics, telecommunication, lasers, as optical sensors, as well as for biomarkers.[1−4] A major advantage of quantum dots is that one and the same set of materials can be used to tune the optical response, absorption and emission, within the IR to UV range significantly, the key parameter being the size of the quantum dot.[5,6] Zinc selenide is an example.[7] The bulk material is characterized by a band gap of 2.7 eV, which corresponds to an absorption band edge of 460 nm. The absorption band gap is blue-shifted for quantum dots, and the same holds for the photoluminescence spectra. Shifts of up to 1 eV can be achieved via variation of the size of the quantum dot.

Depending on the application, different kinds of assemblies of quantum dots will be required. The incorporation of quantum dots into nanotubes is an example.[8] Such nanotubes may act as single photon or directional emitters, as nanostructured light source in integrated optics, or as a photonic crystal with internal light source. In this contribution, we will consider linear arrays of quantum dot assemblies. One prediction is that one-dimensional chains of quantum structures such as quantum films and quantum dots, characterized by a certain degree of spatial and energetic disorder, may give rise to interesting optical phenomena such as localization effects for electromagnetic fields, etc.[9] The Anderson localization phenomenon is known from electron transport.[10,11] It involves a disorder-induced transition from a classical diffusion behavior (Ohms law) to a localized state (insulator). This effect originates from the interference of electrons subjected to multiple scattering by defects. A similar effect is expected to take place for electromagnetic waves;[12] that is, localized wave functions are predicted to exist. Systems which should display such effects, according to theory, are linear arrays of quantum dots or quantum films.[9,13] These effects are furthermore predicted to depend on the distance between the quantum structures along the chain, on their energetic disorder, related to the size distribution, as well as to the spatial disorder.

A major step toward studying such phenomena and toward possible applications consists of devising preparation methods allowing one to come up with stable arrays of quantum dots that might in addition be integrated into specific devices. Our basic concept is to incorporate quantum dots into appropriate polymer matrices and to prepare nanofibers (infinitely long) and nanorods (well-defined length) from such compound systems. In the ideal case, the diameter of the nanofibers will approach that of the quantum dots. The polymer matrix may be replaced in a second step by other materials such as for instance ceramics if required. Precursor materials are added in this case to the polymer/quantum dot

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fibers and chemically modified after the fiber formation. This approach will not be discussed in the present paper.

To prepare infinitely long nanofibers from the compound materials, we have made use of the electrospinning technique.[14−22] Electrospinning of polymer nanofibers involves the application of a strong electric field to a droplet of a fluid such as a melt or solution emerging from the tip of a die. The electrical charging of a droplet is known to lead to a conical deformation and finally at still higher fields to the formation of a jet emanating from the droplet. Important processes that control fiber formation are the occurrence of the axisymmetric instability causing bead formation and of the so-called whipping instability, a bending instability which sets in at a sufficiently high field strength and the corresponding surface charge density. This instability causes a strong elongation of the fluid jet and a strong decrease of the diameter of the jet.[20,21] The final result is the deposition of solid nanofibers at the counter electrode, the solidifications resulting either from the evaporation of the solvent in the case of solution spinning and from cooling in the case of melt spinning. To obtain linear arrays of the quantum dots considered here, fibers with diameters of the order of 10 nm have to be approached. Using specific counter electrodes, we are able to obtain a set of parallel fibers.

In addition, parallel sets of rods of a well-defined length and arrangement in space would be beneficial for the optical evaluation of localization effects and the corresponding optical susceptibilities. In a second approach, we used porous aluminum oxide templates where the pores were completely filled by polystyrene containing various amounts of quantum dots. The filling is controlled by a wetting process in this case as described in detail previously.[23−26] It gives rise to an array of such nanorods. The removal of the template, for instance by selective solvents, yields individual nanorods, the sizes of which are controlled by the diameter and length of the pores.

Experimental Section

Preparation of the Quantum Dots. The ZnSe quantum dots were synthesized by a slight variation of the experimental protocol reported by Cheon et al.[7]

Preparation of $Zn(SePh)_2$. A sample of 0.419 g (1 mmol) of diphenyldiselenide was dissolved in 30 mL of THF, and the solution was cooled to −78 °C. An amount of 2.5 mL of a 1 M solution of $Li[Et_3BH]$ was added, and the reaction mixture was stirred for 2 h. A colorless solution was obtained. A solution of 0.135 g (1 mmol) of $ZnCl_2$ in THF was added at −78 °C. The reaction was allowed to warm to room temperature within 12 h, and the solvent was removed under reduced pressure. A colorless solid was obtained (3.2 g, 73%).

Preparation of $Zn(SePh)_2$·TMEDA. A suspension of 2.5 g (8.43 mmol) of $Zn(SePh)_2$ in 30 mL of toluene was stirred at room temperature, 2 mL (13.0 mmol) of TMEDA was added, and the mixture was stirred for an additional 24 h. Next, 15 mL of pyridine/octane (1:2 vol/vol) was added to the light yellow solution, and the solution was filtered. The filtrate was evaporated to dryness, and the residue was dissolved in 20 mL of toluene. The solution was filtered again, the toluene was removed under vacuum, and a light yellowish solid was obtained (2.7 g, 60%).

Pyrolysis of $Zn(SePh)_2$·TMEDA to Nanocrystalline ZnSe. A sample of 75 mg (0.15 mmol) of $Zn(SePh)_2$·TMEDA was dissolved in 5 mL of trioctylphosphin (TOP), and the solution was degassed for 1 h. This solution was added to a melt of 2.6 g (6.72 mmol) of degassed trioctylphosphinoxide (TOPO) held at 340 °C. The mixture was held at this temperature for an additional 40 min before it was allowed to cool to 80 °C, and an excess of methanol was added. The yellow precipitate was centrifuged, washed with methanol repeatedly, and dried under vacuum.

Preparation of Nanofibers with Quantum Dots. Nanofibers were prepared both from polystyrene and from polylactide. Polystyrene (PS, Mw = 350 000 g/mol, Aldrich) was dissolved in chloroform or a mixed solvent composed of chloroform and tetrahydrofuran (THF) (1:1 w/w). Lithium chloride (LiCl, Aldrich) was used as an additive to increase the conductivity of the solution. ZnSe quantum dots were added to the solution with a concentration of 10% (relative to PS, w/w), the solution was agitated by ultrasonic excitation for 10 min, and then stirred 1 h at room temperature. Electrospinning was performed as follows. The mixture was placed into a syringe, and the polymer solution was pumped continuously through the die via a syringe pump. A potential of 20 kV was applied to the die, the distance between the die and counter electrodes amounting to 15−20 cm. The fibers were finally deposited on an aluminum foil located on top of the counter electrode.

To prepare electrospun ultrafine fibers from poly(L-lactide) (PLLA, Mw = 670 000 g/mol, Boehringer, Ingelheim), the polymer was dissolved in dichloromethane with concentrations in the range between 0.8−1.5 wt %. Pyridinium formiate (PF) was used as additive to control the electric conductivity of the polymer solution. PF was formed by mixing equal molar parts of pyridine and formic acid. ZnSe quantum dots were added to the solution with weight ratios amounting to 10% and 50% (relative to PLLA), respectively. All electrospinning parameters were the same as reported above for PS except that the voltage was increased to 40 kV.

A parallel orientation of the nanofibers was achieved by two techniques. We have already reported one previously.[19] The fibers were deposited on an aluminum frame, the frame dimensions amounting to about 5 cm × 1 cm × 1 cm. The other method consisted of using a cylindrical collector rotating at a speed of up to 3500 rpm (see Figure 1). The cylindrical collector was enwrapped tightly by an aluminum foil in this case. The distance between the die of the syringe and counter electrode was 5−10 cm, and a voltage of 15−20 kV voltage was applied to the die. The aspect ratio of the nanofibers approaches, in principle, infinity because the fiber length as obtained from electrospinning amounts to several 100 m.

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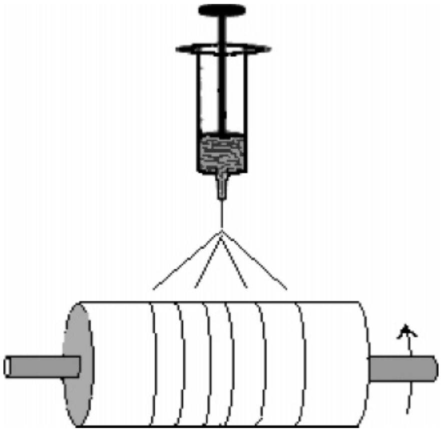

Figure 1. A schematic diagram of the rotating collector for oriented electrospun fibers.

Preparation of Nanorods with Quantum Dots. To prepare nanorods composed of quantum dots dispersed within a polymer matrix, we used a simple and very versatile method. It consisted of wetting the pore walls of porous templates and a subsequent removal of the template. We used ordered porous alumina with pore diameters of about 100 nm and a pore depth of 100 μm for this purpose. To obtain the nanorods, we brought a polymer solution composed of the solvent chloroform, polystyrene as polymer matrix, and ZnSe quantum dots dispersed in the polymer solution into contact with the porous alumina. Nanotubes are known to result in the case of pore diameters significantly larger than the ones used here because wetting leads only to a thin film covering the pore walls. For such small diameters as used here, wetting leads to a complete filling of the pores and thus to nanorods. After the evaporation of the solvent, we removed the residual polymer from the surface of template by mechanical methods and placed the template into a 3 M KOH solution to dissolve the alumina template. It was independently checked that the chemical structure of the nanoparticles was not affected by this treatment. The lye was removed with a syringe, and the nanorods were washed by adding deionized water. The aspect ratio of the nanorods was controlled by the thickness of the porous template, which was 100 μm. The aspect ratio thus typically amounts to 1000 for the rods.

Characterization. The electrical conductivity of the polymer solutions was determined at 23 °C using a conductometer inoLab Cond Level 3 equipped with a LR325/01 detector. The morphology of electrospun fibers and the nanorods was characterized by scanning electron microscopy (SEM) using a Camscan 4 at 15 kV accelerating voltage and a Hitachi S-4100 at 10 kV accelerating voltage as well as by transmission electron microscopy (TEM) using a JEM 3010 operated at 300 kV. Higher resolution images could not be achieved because all polymers, in particular also polylactide, tend to decompose strongly if subjected to the electron beam. Fluorescence spectra of the samples were recorded with a Shimadzu RF1502 fluorescence spectrophotometer. The fibers were electrospun directly onto pieces of quartz glass for this purpose. The fluorescent optical microscopic image was observed with a Leica DMRX microscope equipped with a Leica DC 200 digital camera and a UV lamp emitting in the 340−380 nm wavelength range.

Results and Discussion

Nanofibers. Bulk composites composed of semiconductor nanocrystals and a transparent polymer have been considered previously, for instance, for biological labeling.[27] The target application considered here requires a linear distribution of such nanocrystals in a polymer matrix, that is, fiberlike or tubelike arrangements. To obtain nanofibers with ZnSe quantum dots, we dispersed these quantum dots in solutions with polystyrene and polylactide as polymer matrix. Polystyrene is a transparent amorphous polymer and should thus be a suitable material for the preparation of linear arrays of quantum dots displaying particular optical properties. Unfortunately, polystyrene is not very easy to handle in electrospinning for reasons that are not apparent currently. Fibers with diameters down to a few nanometers can be achieved with polylactide, on the other hand, rather easily. Polylactide is, however, partially crystalline and therefore turbid in thicker layers. We decided to evaluate both types of fiber materials in the investigations reported here. To check the state of dispersion of the quantum dots within the solution and the solid state, we prepared thin films from a solution composed of 0.08 wt % ZnSe and 0.8 wt % PLLA in CH_2Cl_2 solution. The solution was dropped on a grid coated with a carbon film, and a TEM image (Figure 2) was obtained after the solvent had evaporated. It is obvious that ZnSe quantum dots (dark spots) with diameters in the range from 3 to 7 nm are dispersed uniformly within the PLLA matrix; only a weak tendency toward aggregation was observed.

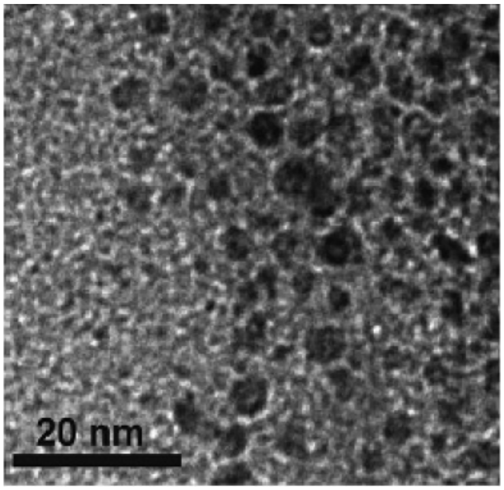

Figure 2. TEM of a film from 0.8 wt % PLLA solution in CH_2Cl_2 with 0.8 wt % PF and 0.08 wt % ZnSe (dark spots, quantum dots; scale bar, 20 nm).

Polystyrene Nanofibers. An effective way toward fine fibers consists of electrospinning polymer solutions with the concentration chosen as low as possible. Yet we observed the formation of beads located along the fibers for polystyrene even at high concentration of PS solution in $CHCl_3$. H. F. Jia added 0.5 wt % LiCl into 8 wt % PS/MEK (methyl ethyl ketone) solution and gained electrospun fibers with diameters ranging from 120 nm to ~1 μm with significantly less beads.[22] The reason obviously is, as predicted by theory,[20,21] that the increase of the conductivity causes a corresponding increase of the surface charge density resulting in the enhancement of the whipping instability and suppression of the axisymmetric instability.

We prepared a series of polymer solution by dissolving 6 wt % PS in a mixture of $CHCl_3$ and THF (1:1 w/w), LiCl does not dissolve in pure chloroform, containing different concentrations of LiCl. The effect of the addition of LiCl

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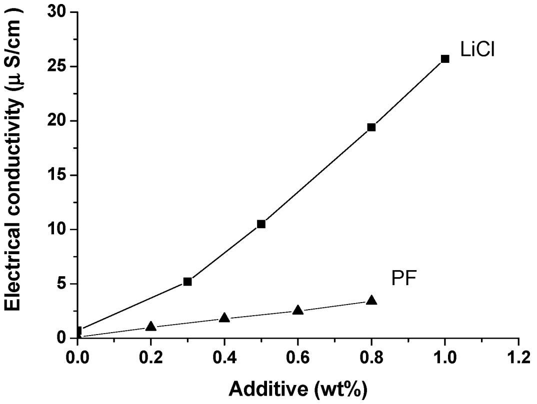

Figure 3. Upper curve: variation of the electrical conductivity in a 6 wt % PS solution in a mixture of $CHCl_3$ and THF (1:1 w/w) as a function of the concentration of LiCl. Lower curve: 1.5 wt % poly(L-lactide) solution in dichloromethane with pyridinium formiate (PF) as additive.

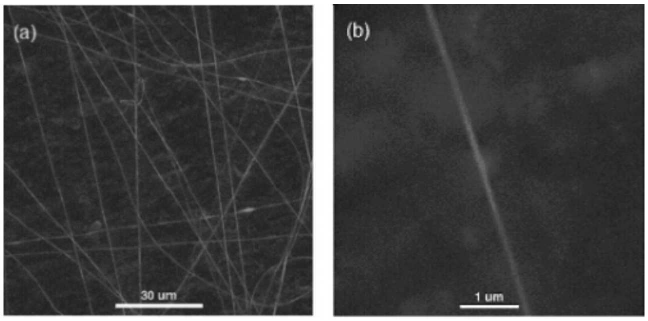

Figure 4. SEM images of electrospun fibers from (a) 6 wt % PS solution in a mixture of $CHCl_3$ and THF (1:1) with 1 wt % LiCl, and (b) 6 wt % PS solution in a mixture of $CHCl_3$ and THF (1:1) with 1 wt % LiCl and 0.6 wt % ZnSe quantum dots.

on the electric conductivity of the polymer solution is shown in Figure 3. The electrical conductivity of the solution increased linearly with increasing contents of LiCl. The addition of 1 wt % LiCl, for instance, gave rise to an increase of the electric conductivity from 0.7 to 25.6 μS/cm.

Fibers with diameters ranging from 100 to 200 nm with only a few beads were obtained by electrospinning in this case (Figure 4a). Polystyrene fibers down to 100 nm in diameter were achieved via electrospinning for mixtures containing 0.6 wt % ZnSe quantum dots in a 6 wt % PS solution containing 1 wt % LiCl (Figure 4b). To our knowledge, these are the smallest diameters reported in the literature for polystyrene fibers free of beads.

Polylactide Nanofibers. To obtain ultrafine electrospun fibers from poly(L-lactide), we prepared solutions in dichloromethane with concentrations of 0.8−1.5 wt %. Pyridinium formiate (PF) was used as additive to enhance the conductivity and suppress the generation of beads. The dependence of the electrical conductivity of the solution on the concentration of PF is shown in Figure 3. The electrical conductivity of the solution increased also linearly with increasing contents of PF, but the increase was not as strong as in the case of the LiCl additive.

Figure 5 shows electrospun fibers from PLLA solution in CH_2Cl_2 with 0.8 wt % PF. They scarcely show any beads, and the fiber diameters obtained for 1.5 wt % PLLA solutions ranged from 50 to 150 nm (Figure 5a). If the concentration of PLLA is decreased to 0.8 wt %, ultrafine fibers in the diameter range of 10−70 nm were obtained (Figure 5b).

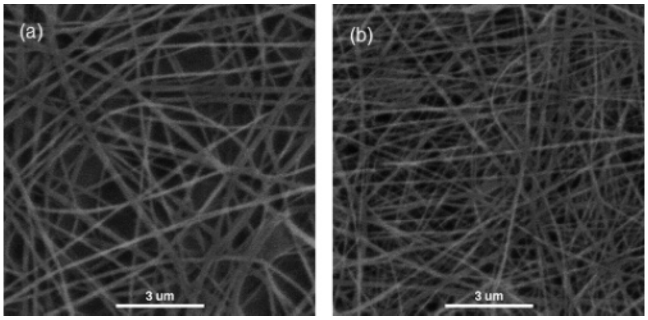

Figure 5. SEM image of electrospun PLLA fibers from (a) 1.5 wt % PLLA solution and (b) 0.8 wt % PLLA solution in CH_2Cl_2 with 0.8 wt % PF.

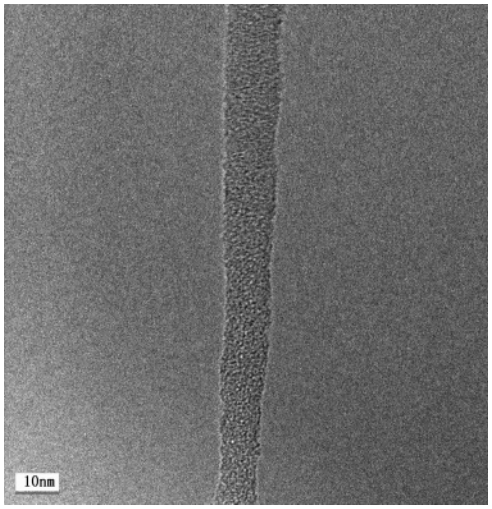

Figure 6. TEM micrograph of the electrospun PLLA fiber obtained via the frame collector approach.

Although the diameters achieved for the electrospun PLLA fibers are reasonably thin for the purpose considered here, the fibers have the disadvantage that they are bended to a certain extent and that they are randomly oriented. To obtain extended fibers characterized by a certain degree of mutual orientation, we applied the two approaches introduced above: the use of a frame-shaped counter electrode and of a rotating counter electrode.

The jet tends to jump back and force on the frame electrode, giving rise to a preferred alignment of the nanofibers as reported previously. Extended fibers are obtained by this simple method with diameters approaching 10 nm starting, for instance, from a 0.8 wt % PLLA solution (Figure 6). SEM of gold-coated electrospun fibers shows only fibers with diameters above 10 nm due to the gold coating, while TEM of uncoated electrospun fibers revealed fiber average diameters as low as 10 nm (Figure 6). It is obvious from Figure 7a and b that the fibers tend to orient parallel to a direction given by the frame collector. One disadvantage of this method is that some fibers tend to deviate quite significantly from a parallel orientation.

The other orientation technique involved the use of a rotating cylindrical collector as counter electrode characterized by a high rotation speed (see Figure 1). The fibers were deposited tightly onto the surface of the cylinder in a circumferential manner if the linear speed of the rotating cylinder matched that of the jet depositions. Figure 7c and d shows a set of fibers obtained in this way. The orientational

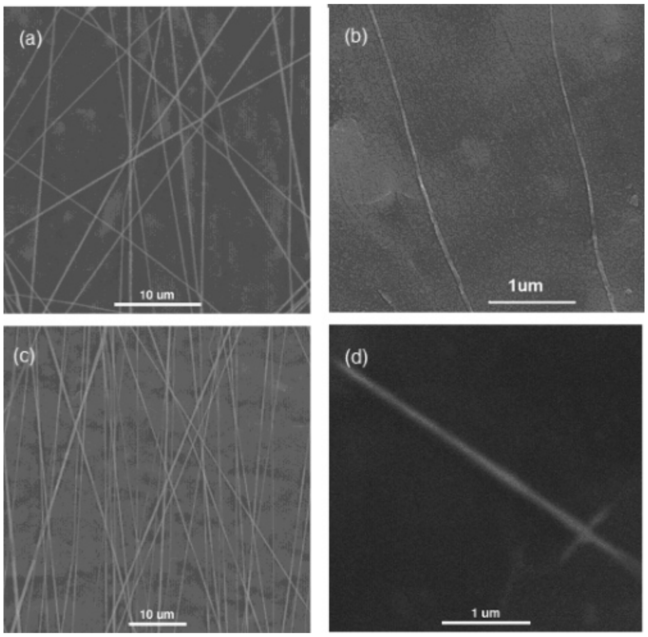

Figure 7. SEM images of oriented fibers from (a) 1.5 wt % PLLA solution containing 0.15 wt % ZnSe and (b) 0.8 wt % PLLA solution contains 0.08 wt % ZnSe by the frame collector method, (c) 1.5 wt % PLLA solution containing 0.15 wt % ZnSe, and (d) 0.8 wt % PLLA solution contains 0.08 wt % ZnSe obtained by the rotating collector method.

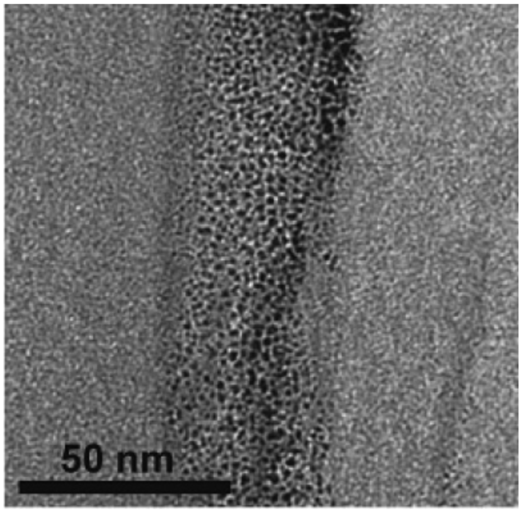

Figure 8. TEM micrograph of a PLLA fiber (50−60 nm) with embedded ZnSe quantum dots.

order is to a certain extent increased, and fibers with average diameters of 50 nm were obtained by electrospinning a 0.8 wt % PLLA solution containing 0.08 wt % ZnSe quantum dots. The increase of the fiber diameter as compared to the frame electrode results from the reduced voltage applied.

The SEM analysis performed on the electrospun fibers revealed that the ZnSe quantum dots were completely embedded within the polymer fibers. A TEM micrograph of a PLLA fiber with $d \approx 50$ nm with the embedded quantum dots is shown in Figure 8. The fluorescent optical microscopic image of electrospun PLLA fibers containing 50 wt % ZnSe quantum dots which are shown in Figure 9 confirms the presence of the quantum dots within the electrospun polylactide fibers.

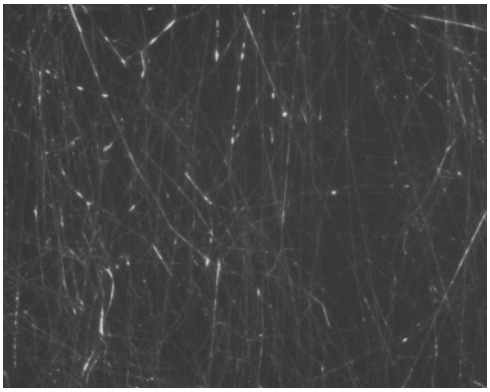

Figure 9. Fluorescent optical microscopic image of electrospun PLLA fibers containing 50 wt % ZnSe quantum dots (200× magnification).

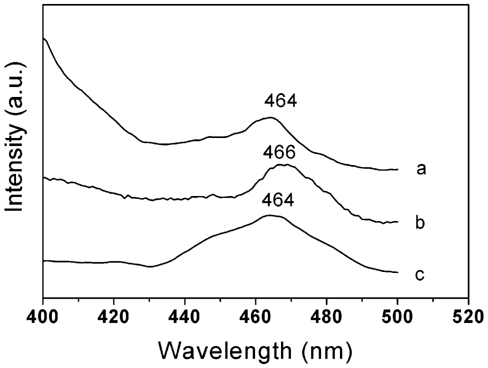

Figure 10. Fluorescence emission spectra of (a) ZnSe quantum dots from CH_2Cl_2 solution, (b) electrospun PLLA fibers containing 10 wt % ZnSe, and (c) electrospun PS fibers containing 10 wt % ZnSe.

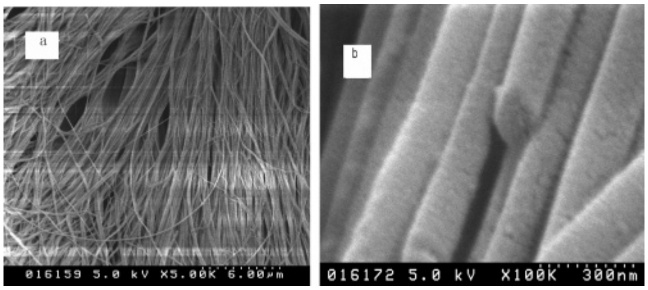

Figure 11. SEM images of (a) the PS nanorods with ZnSe quantum dots obtained after dissolution of the alumina template and (b) high magnification image showing ordering rods.

Fluorescence Spectra. The fibers prepared by electrospinning were subjected to UV-irradiation, and the emitted fluorescence was determined. Figure 10 shows the fluorescence emission spectra (EM) of ZnSe quantum dots dispersed in a CH_2Cl_2 solution and in the electrospun fibers using an excitation wavelength of 311 nm. The ZnSe quantum dots in the CH_2Cl_2 solution showed a broad emission peak with the maximal emission wavelength located at 464 nm. Similarly, the electrospun fibers containing 10 wt % ZnSe quantum dots (related to PLLA) also showed a maximum emission wavelength at 466 nm for PLLA fibers and at 464 nm for PS fibers. The results imply that the polymer matrix does not have a significant influence on the photoluminescence properties of ZnSe quantum dots, which is a requirement for the applications aimed at.

Nanorods. Figure 11 shows the scanning electron micrographs of the PS nanorods with ZnSe quantum dots obtained after dissolution of the alumina template. The array consists of parallel nanorods having a diameter of 100 nm and a length of 10−100 μm; the weight % of the quantum dots with respect to the polymer matrix amounts to 1%. It is

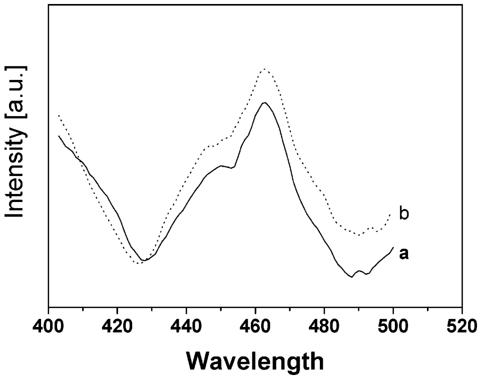

Figure 12. Fluorescence emission spectra of (a) PS film containing 10 wt % ZnSe and (b) PS nanorods containing 10 wt % ZnSe quantum dots.

obvious that highly uniform rods both with respect to the diameter as well as the length can be achieved in this way. In fact, one might even leave the rods within the aluminua template, which would allow one to study the optical properties of highly regular arrays of such rods.

Using such an array, we determined the fluorescence by irradiation along the nanorods long axis direction. The template itself does not absorb light to an appreciable extent in the wavelength range considered here. The fluorescence spectrum is displayed in Figure 12b, and it is compared to the one obtained from a random dispersion of the quantum dots in a polystyrene film. The spectra agree obviously very well. Actually, we might have expected deviations due to localization effects discussed above. It seems that the narrow parallel packing of the rods considered here obviously disturbs the one-dimensionality of the propagation of the light. We have to consider templates with a more dilute arrangement of parallel pores in the next step.

Summary

We have shown that stable arrangements of quantum dots approaching a linear arrangement can be achieved via polymer nanofibers and nanorods. Such nanofibers and nanorods can be prepared using the electrospinning and the wetting assisted template methods. We were able to prepare nanofibers as small as 10 nm in diameter containing quantum dots with diameters in the range of 3−7 nm; that is, the diameters match very well. Using specific counter electrodes and templates, respectively, we are able to align the fibers and rods in parallel fashion. A further decrease of the diameter of the nanocomposite fibers down to below 10 nm (as shown for pure PLLA fibers) and a more dilute arrangement of parallel nanorods will have to be the next step toward devices showing the localization effects predicted by theory. One important aspect as far as future applications are concerned is that the mechanical properties of the nanofibers considered here are superior to those of the corresponding macroscopic fibers. Using the wetting assisted approach, we were able to let the exciting light propagate along the one-dimensional rods containing the quantum dots. No localization effects were observed probably due to a packing of the rods, which was too dense.

A further step will have to consist of constructing an experimental setup which will allow one to excite a set of less dense parallel nanofibers or nanorods along the fiber direction and to measure localization effects via the determination of the optical susceptibility along the fibers and rods.

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