Alignment of Colloidal CdS Nanowires Embedded in Polymer Nanofibers by Electrospinning


Semiconductor nanocrystals (NCs) exhibit size-controlled spectral tunability and chemical flexibility, making them attractive materials for use in new and emerging applications, such as fluorescent tagging,[1] lasing,[2] light-emitting diodes[3] and nanoelectronics.[4] One-dimensional quantum wires (QWs) and quantum rods (QRs) have become a class of attractive materials as their dimensional anisotropic behaviour gives rise to unique physical properties; for example, recent observations of CdSe QRs showed a non-monotonic change of the fluorescence Stokes shift with an increase in the aspect ratio (length/width), exhibiting a linearly polarized photoluminescence.[5] Semi-empirical pseudo-potential calculations of CdSe rods predicted a crossover of the electronic states at a certain aspect ratio, leading to a transition from plane-polarized to linearly polarized light emission.[3] Recent work[6] on QRs shows a reduced lasing threshold, compared with spherical NCs, an increase in the absorption cross-sections, a reduced Auger recombination rate and an increase in the optical gain lifetime (all of which are properties that improve the lasing performance).

The manipulation of the shape of nanoscale materials has been achieved in the past mainly by growth on a static template; for example, pyramidal InAs dots and wires are obtained by strain growth on an epitaxial GaAs substrate.[7] GaN QWs were recently prepared inside carbon nanotubes.[8] Hollowed polystyrene and silica nanotubes were prepared by the deposition of these materials on Au nanorods, followed by dissolution of the Au core.[9] Liang et al.[10] produced arrays of CdS rods in the nanopores of anodized aluminum oxide (AAO) followed by the removal of the AAO matrix. Nanocables of SiC nanowires sheathed with an amorphous SiOx coating were prepared by a carbothermal reduction of SiO2 xerogel containing carbon nanoparticles.[10] Other coaxial nanocables, containing silicon carbide and silicon oxide sheathed with boron nitride and carbon, were prepared by laser ablation.[11] Semiconductor/polymer cables were produced by the formation of hollowed polyvinylacetate polymer tubes, with hydrophilic inner surfaces that permit the formation of inorganic CdSe wires.[10]

There have been several attempts to prepare free-standing QWs. Duan and Lieber[12] developed laser-assisted catalytic growth of GaAs QWs. Chang et al.[13] used an electrochemical method which yielded anisotropic gold particles. Alivisatos and co-workers[14] developed a controlled colloidal synthetic method for the formation of rods and multipod-shaped CdSe nanoscale structures. Lifshitz et al.[15] produced PbSe rods, wires and multipods using template-coordinating surfactants during a colloidal growth at 10–60°C. Lee et al.[16] produced QWs and QRs of MnS and CdMn1−xS, using template ligands, controlled by a delicate balance between kinetic and thermodynamic growth.

Thus, the chemical synthesis of free-standing or template semiconductor QWs and QRs has shown substantial progress in recent years. In contrast, a well-controlled one-dimensional arrangement of QWs and QRs remains a problem. These anisotropic structures could be very important for polarized light sources, for high-resolution detection of polarized light, and for nano-electronic circuity. A few attempts to assemble nanowires (NWs) and nanotubes into one- or two-dimensional ordered arrays have recently been successful. Electric[17] and magnetic[18] fields have been used to manipulate dielectric NWs that are suspended in liquid media. These methods require extensive lithography to fabricate the microelectrodes. Fluid-based methods for aligning NWs have proved successful in generating parallel and cross-bar NW assemblies. Whang et al.[19] aligned NWs with nanometer-to-micrometer-scale control using the Langmuir–Blodgett technique and then transferred the NWs to planar substrates using the layer-by-layer process. Alignment through Marangoni convection of NWs within microchannels was demonstrated by Salalha and Zussman.[20] The alignment of nanowires within microchannels was demonstrated by Salalha and Zussman.[20]

This Communication describes a promising route for unidirectional alignment of free-standing CdSe QWs and nanowires, formation of a semiconductor–polymer core–shell fiber by electrospinning, QW colloids with a polymer solution. Electrosprinning is a generic method attained when an appropriate electrostatic field is applied to a pendant droplet of a polymer solution.[21] When the electric Maxwell stresses overcome the polymer solution surface tension, a jet is injected from the droplet, which is stretched by bending instabilities and eventually solidified into an ultrathin fiber. Polymer nanofibers prepared by electrospinning can be used for various applications, such as in drug-release systems, in protective clothing, as a load substrate for...
catalysts, as fibers for optical applications or as conductors for microelectronics. Herein, electrospinning was used for the encapsulation of semiconductor QWs inside polymer nanofibers. QWs suspended in a polymer solution are randomly orientated; however, due to the sinklike flow at the start of the electrospinning process, they gradually align themselves and enter the electrospun jet, orientating in the manner predicted by the mathematical model presented by Dror et al.\[23\] The QW alignment is then improved during the fiber stretching and thinning process.\[24\] By manipulating the electrostatic field within the electrospinning process,\[25\] the QWs embedded in the oriented polymeric nanofibers are arranged into a one-dimensional nanorope.

The Experimentation Section describes the preparation procedures of the colloidal CdS QWs and the combined QW–polymer electrospinning process. The subsequent sections represent the structural and functional properties of the semiconductor QWs and the QW–polymer nanofibers, as characterized by X-ray diffraction (XRD), selected-area electron diffraction (SAED), high-resolution scanning and transmission electron microscopy (HR-SEM, TEM), cross-section SEM and photoluminescence (PL) spectroscopy.

**Experimental Section**

Preparation of CdS QWs: CdS QWs were prepared by the thermolysis process of single molecules of cadmium bis(diethylthiocarbamate) [(Cd(DTDC)₂)₂], which act as single-source precursors for both the cadmium and sulfur ions. The preparation of the molecules is outlined in ref.\[33\] while the thermolysis process follows the description given in ref.\[31\]. One gram of the indicated precursor was dissolved in 30 mL of ethylene-diamine solution. This solution was heated to 117°C under an Argon flow. The color of the solution changed to yellow within 2–3 min, after which the reaction was quenched by a rapid cooling to room temperature. The CdS QWs were separated from the solution by addition of 2 mL ethanol and centrifugation. Dry ethylene-diamine-capped QWs were dissolved in a solution consisting of oleic acid (OA) either in dimethyl formamide (DMF) or in ethanol. After sonication for about 10 min, the QWs were separated from the solution by centrifugation. This process was repeated several times, causing either the exchange of the ethylene-diamine with OA molecules or the formation of a second molecular layer at the surface.

Electrospinning: The electrospinning of a suspension of QWs and polymer solution is used to form an aligned nanocomposite. The QWs were dispersed in ethanol (10% w/w) and sonicated for 10 min (Delta Ultrasonic Cleaner D200, 200 Watt, 43 kHz mid sonication), resulting in a stable suspension. The addition of the ethanol to a poly-ethylene oxide (PEO, Aldrich, 6% in water, MW 600000) solution with a 1:1 ratio, resulted in a spinable suspension.

The suspension was electrospun from a 5 mL syringe with a hypodermic needle with an inner diameter of 0.5 mm. Back pressure of 180 mbar of air was applied to the solution to control its flow rate. A copper electrode was placed in the polymer solution and the suspension was spun onto the sharp edge of a grounded collector disc.\[28\] The strength of the electrostatic field was 0.92 kV cm⁻¹. The linear speed on the edge of the disc collector was \(V = 8.8 \text{ m s}^{-1}\). All the experiments were performed at room temperature. Nanoropes formed by well-aligned nanofibers embedded with QWs were collected on the disc edge. The nanoropes were then detached from the disc and analyzed. In order to observe the cross-section, the nanoropes were immersed in a liquid nitrogen bath and cut with a sharp knife.

Structural and Optical Characterization: The high-resolution scanning electron microscopy (HR-SEM) observations were carried out on a Zeiss Leo 982 instrument operated at 4 kV. The QW–polymer nanocomposite samples were prepared by direct deposition of the electrospun nanofibers onto a lacy carbon transmission electron microscopy (TEM) grid. The samples were investigated using low electron dose imaging and an acceleration voltage of 120 kV in a Philips CM120 TEM. Images were recorded with a Gatan MultiScan 791 CCD camera (Gatan Digital Micrograph 3.1 software package). Electron diffraction data were recorded using the selected-area diffraction mode (SAED) (aperture diameter: 280 nm, camera length: 970 nm).

Continuous-wave photoluminescence (PL) spectra were collected by immersing the sample in a cryogenic Dewar (1.4 K). The sample was irradiated with an Argon ion laser and the emitted light was passed through a grating monochromator with the appropriate grading for the IR spectral regime. The emission intensity was detected by Si or Ge detectors.

**Results and Discussion**

CdS QWs

Previous efforts reported the deposition of cadmium and sulfur precursors into an anodic aluminum oxide filter or nuclear track-etched polycarbonate membranes, permitting the formation of QWs with a diameter of 9 nm.\[29\] The work presented here utilizes the thermolysis process of a single-molecule precursor in ethylene-diamine solution for the preparation of free-standing CdS QWs with a diameter range of 2–6 nm. The thermolysis process was discussed by Yan et al.,\[31\] who suggest that the precursor [Cd(DTDC)₂]₂ can be regarded as a [Cd₂S₂] core with four thione capping groups. Nucleophilic attack, by ethylene-diamine, of the thione carbon can lead to the removal of the capping groups. The Cd₂S₂ cores can then combine with each other and under appropriate chemical conditions, they exhibit preferential growth along the unique axis. Lifshitz et al.\[33\] and Li et al.\[34\] showed that the ethylene-diamine acts also as a coordinating molecular template, creating an intermediate Cd–(ethylene-diamine), complex, slowing down the growth of the wire in the short axis, while permitting the growth along the perpendicular direction. Eventually, the ethylene-diamine molecules form a monolayer coating on the external periphery of the QWs.

Figure 1A shows an HR-SEM image of randomly distributed free-standing CdS QWs with a diameter of \(\approx 6 \text{ nm}\) and a length of 100–150 nm. The X-ray diffraction (XRD) spectra of these CdS QWs exhibit characteristic peaks associated with a hexagonal structure, as shown in Figure 1B. The narrow and strong diffraction peak (002) reflects a preferential growth along the c axis of a hexagonal CdS structure. The average diameter of the QWs, determined by the Scherrer formula, was found to be 6 nm. The HR-SEM image in Figure 1A reveals the formation of a bundle of CdS QWs that cannot be separated.
upon dilution or sonication, presumably due to the existence of hydrogen-bonded bridges among the diamine surfactants. These diamine ligands, when exchanged with oleic acid surfactants, enable the isolation of the synthesized QWs, as shown in the TEM image in Figure 1C.

Semiconductor QW–Polymer Composite Nanofibers

Electrospinning of a mixture of oleic acid-capped CdS QWs with a PEO polymer results in the encapsulation of separated QWs along the nanofiber axis, as shown in Figures 2A and 2B. In general, the QW alignment is independent of their width and length (not shown).

Figure 3 shows a continuous collection of the QW–polymer nanofibers on a rotating disc generating a one-dimensional nanorope, comprised of a bunch of nearly parallel nanofibers.

The PL spectra of CdS QWs, embedded in the electrospun nanorope, are shown in Figure 4. These spectra were excited at $E_{\text{ex}} = 2.7$ eV with linearly polarized light parallel to the long axis (l.a.) of the QWs and detected either parallel (l.a. || $E_{\text{em}}$) or perpendicular (l.a. \perp $E_{\text{em}}$) to this axis. These spectra comprise of a single emission band with a relatively large shift with respect to the excitation energy. The degree of linear polarization, defined as $\text{DLP} = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel = E_{\text{ex}} || \text{l.a.} || E_{\text{em}}$ and $I_\perp = E_{\text{ex}} || \text{l.a.} \perp E_{\text{em}}$, is evaluated to be 87% (see Figure 4). This DLP value designates a high degree of alignment, with a small divergence from complete polarization. This deviation can be due to a small percentage of misaligned QWs within the fibers or due to a minor misalignment of the nanofibers within a nanorope.

Linear polarization observed in Figure 4 is related to the anisotropy of the QW structure, induced either by a uniaxial crystalline symmetry or shape distortion. CdS QWs have a hexagonal wurtzite structure, where the top of the valance band is composed of the Se 4p atomic orbitals and the bottom of the conduction band of the Cd 5s atomic orbitals. Due to the interaction of the 4p orbitals with the crystal field, the spin–orbit coupling, and the quantum-size effect, these 4p orbitals give rise to a heavy-hole (polarized in the x–y plane) and a light-hole (polarized along the z direction) state. It was recently shown that in II–VI spherical NCs, the heavy-hole state is the upper level, while a crossover occurs for rods with an aspect ratio larger than two, bringing the light-hole state to a higher energy. Then, a polarized emission is anticipated in hexagonal NCs with a one-dimensional structure. The high degree of polarization shown in our case reveals the involvement of the light-hole state in the recombination process. However, the large shift of the emission energy with respect to...
the excitation energy, with emission energy below the bulk bandgap, suggests that the emission process is concerned with a trap-to-band recombination, such as donor-to-hole annihilation. The large shift is also associated with the larger binding energy of photogenerated carriers, due to a special confinement created by the width of the wire.

The linear polarization is further influenced by the dielectric screening of the surrounding area. Let us consider a QW with a unique axis along the z direction: Because of a difference in the dielectric constant of the QW and its surroundings, an induced charge is formed on the QW surface, which induces a polarization field inside it. This induced field has the smallest amplitude in the z direction and therefore, the smallest effect on the absorbed light. Hence, the maximum absorption is obtained when the long axis of the QW is oriented parallel to the direction of the electric field of the excitation light. The QWs also emit polarized light in the z direction, and the emitted light becomes polarized in the same direction as the excitation light. Hence, linear polarization of the CdS QWs depend both on the ratio of the dielectric constants in- and outside the wires and on the uniaxial crystalline symmetry of the hexagonal structure. The polarization measurements further support the existence of anisotropic physical properties of the QWs and the feasibility of aligning them unidirectionally.

Summary

Colloidal synthesis of CdS QWs at relatively low temperatures (117 °C) using the thermolysis process led to the formation of wires with a typical width of ≈6 nm and a length of ≈100 nm. Electrospinning of the QWs with a PEO polymer solution produced nanofibers embedded with concentric QWs, with unidirectional alignment of their long axis with respect to the stretching direction of the fibers. Furthermore, the static electric field induced a collection of these nanofibers on a rotating wheel to form one-dimensional nanoropes. The emission spectra of the aligned QWs showed a linear polarization, which is significantly important for polarized-light sources in high-resolution detection of polarized light or in other optical elements in the visible and near-IR spectral regime.

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