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# Switchable Assembly of Ultra Narrow CdS Nanowires and Nanorods

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Anisotropic semiconductor nanomaterials are of significant interest due to their potential applications in optoelectronics, nanoelectronics, and nanobiotechnology.[1] The micrometer scale ordered assembly of anisotropic nanoparticles (NPs) achieved in a controllable manner might also possess unique properties which could serve as a bridge between the nano- and micrometer size regimes. CdS is an important direct band gap (2.5 eV) material with a broad range of potential applications. However, the narrowest reported one-dimensional CdS is larger than the Bohr radius (2.8 nm), thus limiting quantum confinement effects.[2] Moreover, limited efforts have been made to make these nanocrystals compatible simultaneously in aqueous and organic phase, which is important for biological and optoelectronic applications.

In this communication, we report a simple, one-step benchtop synthesis of uniform luminescent 80−150 nm long CdS wires with ultra narrow width (1.7 nm) that are controllably breached into ∼15−40 nm long rods which can exist in aqueous or organic medium upon ligand exchange. Switchable centimeter long 3D assemblies of wires/rods are formed by an electric field (EF) of 300−800 V/cm applied directly via two graphite electrodes in a 2 mg/mL toluene suspension. The assemblies exhibit strong anisotropic optical properties that are attractive for optoelectronic applications.

The synthesis makes use of hexadecylamine (HDA), a liganding solvent which enables a low temperature, one-step, benchtop decomposition of relatively innocuous single precursor cadmium hexadecylxanthate, producing CdS nanowires.[3] Reaction conditions favor the wurtzite modification of CdS, and the wires assemble into ordered arrays whose structure is imposed by the HDA.[4,5] Ligand exchange of the HDA by ethanethiol or 1-hexadecanethiol in toluene, or mercaptoethylamine in water, breaks them into rods.[3] The water-soluble rods readily form a nanoscale bioinorganic assembly with DNA in a pH range of 5−6 (see Supporting Information).

Figure 1a,b shows transmission electron microscopy (TEM) images of HDA-coated wires and rods of 1.7 and 1.7−2.9 nm diameter, respectively. The wire-to-wire lateral distance can be controlled by varying the chain length of the alkylamine capping agent.[5] HRTEM of individual wires and rods (Figure 1c,d) shows well-resolved lattice planes with an inter-planar distance of 0.33 nm, consistent with the (00.2) *d* spacing of the CdS wurtzite structure. EDS analysis carried out in the TEM (see Supporting Information) gives, in most cases, a Cd to S molar ratio of ∼1:1 as expected for a stoichiometric crystal. The wurtzite structure of the wires and rods is further evident by XRD (see Supporting Information).

The UV−vis absorption spectrum shows a sharp discrete absorbance peak at 3.3 eV (Supporting Information). The photoluminescence (PL) spectrum shows a strong band edge emission at 2.87 eV. Our spectral features are sharper from those reported earlier,[2] suggesting higher degree of uniformity and stronger quantum confinement along the short axis of the wires/rods.

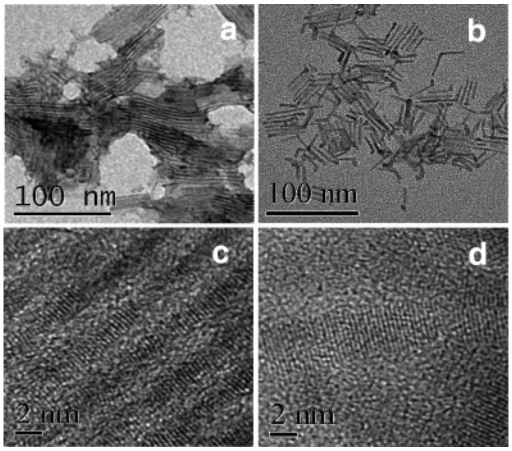

***Figure 1.*** TEM images of CdS (a) wires and (b) rods. HRTEM images of (c) wires and (d) rods.

The use of thiol as stabilizer in the synthesis of type II−VI semiconductor nanocrystals has been previously established.[6] However, dissociation of stable HDA-coated wires into well-defined rods by stabilizing thiol is more unusual and has not been reported to the best of our knowledge. This preparative approach most probably relies on the different adsorption and desorption rates of the two ligands with Cd,[1c] along with the higher liganding strength of thiols compared to that of primary amines, such as HDA. The thiols are covalently bound and may have a stronger influence on the structure of the rods, in line with the size-selective preparation of the rods upon varying thiol concentration (Patla et. al, unpublished data). It should be noted that the morphology, size, and size distribution of the water-soluble rods are very similar to those of the HDA-coated (insoluble) rods shown in Figure 1b,d.

As a demonstration of medium friendly flexibility of our rods for potential applications, a bioinorganic assembly of water-soluble CdS rods and plasmid DNA can be formed (see Supporting Information). Furthermore, water-insoluble rods form 2D Langmuir monolayers (not presented here) which exhibit well-defined pressure-driven liquid crystalline phase transitions.[7]

A centimeter long switchable assembly of the HDA-capped wires or thiol-capped rods into elongated microstrings can be induced by applying an EF via two graphite/gold electrodes in a toluene suspension (Figure 2). In absence of EF, the NPs remain in submicron-sized random aggregates (Figure 2a). When an EF is applied, the NPs align from cathode toward the anode along the field lines into macroscopic strings (Figure 2b). The microstrings exhibit strong birefringence under cross-polarizers and are 4−6 $\mu$m in width, while the length can be controlled by the separation distance between the electrodes. The morphology of the microstrings depends on the suspension concentration and EF gradient. The

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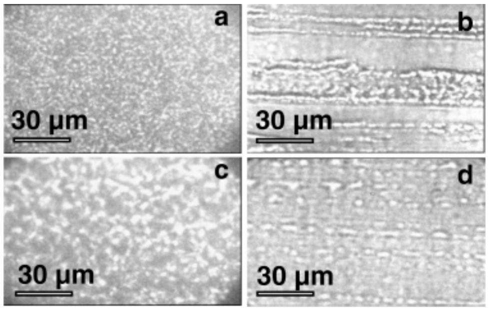

***Figure 2.*** Optical micrograph of CdS wires/rods suspension and microstrings observed under cross-polarizers (a) without field, (b) 500 V for 10 min, (c) reversing of field to −300 V for 5 min, and (d) intermediate stage of microstring formation obtained applying −300 V for 10 min.

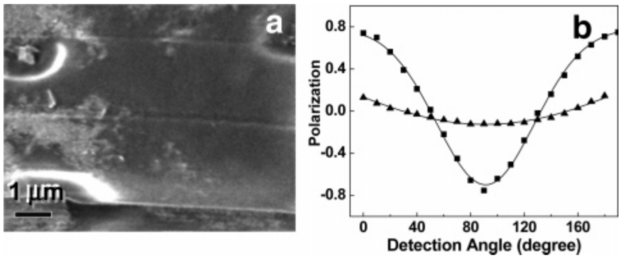

***Figure 3.*** (a) SEM image of aligned microstrings collected on silicon wafer. (b) Plot of emission intensity ratio, *r*, versus detection angle for the microstrings (squares) and stirred suspension (triangles) fitted with sine function (solid curves).

ferroelectric assembly along the field lines shows reversible behavior. If the field is turned off, the oriented string-like aggregation is retained. A mild shaking of the cell destroys the long-range ordering and converts the microstrings into randomly aligned configuration.

Alternatively, when one switches the direction of the EF, the strings first lose their original preferred orientation, the aggregates break down and relax to randomly oriented micron-sized clusters (Figure 2c). Then the EF reorders the clusters opposite to the original direction (Figure 2d), forming microstrings once again. Direction reversal switching times are on the order of tens of minutes.

The string-like ordering appears to be associated with the *c*-axis of the wurtzite structure being oriented along the major axis of the wires/rods (and eventually of the microstrings). Along this direction, wurtzite CdS is intrinsically anisotropic with alternating packing of anions and cations. Hence, while one end is terminated with a $Cd^{2+}$ plane, the other will always be terminated with a $S^{2-}$ plane, thus inducing a chemical bipolarity. When subjected to an EF, the polar NPs align along the field lines and order in a head-to-tail fashion into macroscopic strings. A part of such aligned microstrings collected onto a flat silicon wafer shows (Figure 3a) a thickness of 4−6 $\mu$m, in line with those observed in optical microscopy. This also demonstrates that the microstrings can exist *both* in “wet” and “dry” environments, enabling flexibility in possible future applications. The EDS and XRD of the microstrings deposited on silicon wafer show similar composition and structure as observed for the wires/rods (Supporting Information).

Interestingly, the photoluminescence (PL) spectra of the field-induced oriented microstrings show strong polarization dependence (Figure 3b). The most intense spectrum appears with the parallel polarizer (both excitation, detection) setting. The ∼430 nm emission is strongly polarized in a direction parallel to the microstrings. The broad surface emission is also polarized in the same direction, but to a much lesser degree. The polarization ratio is determined by rotating the excitation polarizer along a pair of angles with respect to the microstrings with simultaneous detection of the emission angle (see Supporting Information). The polarization ratio, *r*, for the microstrings was found to be 0.78 ± 0.02 by fitting the intensity ratio $r = (I_{||} - I_{\perp})/(I_{||} + I_{\perp})$ versus detection angle with a sine function. Here $I_{||}$ and $I_{\perp}$ are the intensities parallel and perpendicular to the *c*-axis of the wires/rods (or microstrings). In a control experiment with the stirred solution of wires/rods, the polarization factor is found to be <0.13 (Figure 3b) and is likely to further decrease with lower concentrations of the NPs. Notably, the polarization direction is the same as that of the microstrings. The high polarization ratio confirms the presence of oriented wires/rods within the microstrings along the direction of the EF. The PL polarization along the long axis is in line with previous reports for InP wires,[8] CdSe nanorods,[1c,9] and CdSe/ZnS core/shell quantum rods.[10]

In summary, we have reported a simple route for the production of uniform and ultra narrow wurtzite CdS nanowires and medium friendly nanorods. The centimeter range ordering of the NPs into switchable 3D microstrings by application of low magnitude DC electric field is demonstrated. More sophisticated electrodes can be used for the same system to achieve more complex and fine patterns that can find potential use in nanoelectronics. The polarized emission with respect to the unique *c*-axis makes the system suitable for orientation sensitive devices.

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**Supporting Information Available:** EDS, XRD, UV−vis, PL, assembly with DNA, image of long-range ordering, and scheme of polarization measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) Cadmium hexadecylxanthate (0.13 g) was added to molten hexadecylamine (HDA, 2 g, purchased from Aldrich, >98% purity) at 60 °C with continuous stirring under $N_2$. When clear yellow color appears, the temperature was increased to 90 °C, and after 30 min, the temperature was increased further to 130 °C and annealed for 1 h to complete the reaction. Subsequently, the temperature was slowly decreased to 70 °C, and methanol was added for flocculation. For ligand exchange, $2.2 \times 10^{-3}$ mol of ethanethiol or 1-hexadecanethiol for water-insoluble rods or mercaptoethylamine in water for water-soluble rods was added to a solution of CdS wires in toluene (130 mg/15 mL). In the case of mercaptoethylamine (water-insoluble rods), the suspension was left for 12 h after vigorous shaking to obtain complete phase separation between water and toluene. The water-insoluble phase was removed by pipette and separated from the CdS particles.

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