

# Highly emissive nanowires grown from CdTe nanocrystals in a phosphate buffer solution

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## ABSTRACT

We present details on the CdTe nanowires formation, which were found to grow in a standard physiological phosphate-buffered solution, including *in-situ* observation of growth with a confocal microscope. The choice of proper nanocrystals concentration allowed reasonably slow growth rates and thus a controllable formation of nanowires. Once formed in solution, nanowires showed a significant degree of structural rigidity and resistance to externally applied mechanical stress. Luminescence and Raman spectroscopy data evidence on re-crystallization processes during the nanowire formation.

**Keywords:** In-situ growth, luminescence, nanowires, Raman spectroscopy, self-assembly

## 1. INTRODUCTION

The steady scaling down the size of electronic devices in modern integrated circuits demands new approaches in fabrication of interconnectors capable of efficient guiding electromagnetic energy on nanometer scale. It is now becoming widely appreciated that the chemical synthesis of nanoscale circuits could offer real advantages in terms of both device density and processing cost<sup>1</sup>. Over the past several years, considerable advances have been made toward the synthesis of colloidal semiconductor nanorods and nanowires with diameters sufficiently small to produce a quantum confinement of charge carriers<sup>2-4</sup>. Such confinement permits free-electron behaviour in only one direction, along the length of the wire and therefore improved electronic transport can be achieved compared to that of semiconductor quantum dots. Unique structure and optical and electrical properties of these one-dimensional (1D) nanostructures make them the key building blocks for a new generation of nanoelectronics, sensors, and nanophotonic devices.

A number of direct synthetic methods towards nanowires of controlled composition, uniform thickness and variable aspect ratios have been developed, including the use of hard (alumina membrane)<sup>5</sup> and soft (rod-like micelle)<sup>6</sup> templates, seed-mediated growth in solution<sup>7-8</sup> and catalyst-mediated phase separation approach based on point-initiated uniaxial growth of the crystal<sup>7,9</sup>.

An alternative approach to obtain wires makes use of assembly of pre-formed nanoparticles from colloidal suspensions<sup>4, 10-11</sup>. Recently, Kotov and co-authors<sup>4</sup> have shown the possibility of spontaneous organization of CdTe nanocrystals (NCs) into crystalline nanowires during a several day aging process, promoted by removal of stabilizer ligands through an intermediate methanol washing step.

In this paper we present further details on the CdTe nanowires formation and properties, which were found to grow much faster in a standard physiological phosphate-buffered solution, including *in-situ* observation of growth with a confocal microscope. Confirmatory evidence for re-crystallization processes during the nanowire formation is obtained by correlating luminescence and Raman spectroscopy data.

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## 2. EXPERIMENT

CdTe NCs which are building blocks for the nanowires, were synthesized in aqueous solution using thioglycolic acid as stabilizer following the previously reported approach<sup>12</sup>. Post-preparative size-selective precipitation<sup>12</sup> was applied to the crude solution of NCs to remove the non-reacted species and separate the strongly emitting fractions of NCs with narrow size distribution (photoluminescence quantum yield of 20-25%). The selected fractions were dissolved in water providing stock solutions of CdTe NCs of two different sizes (2.0 nm and 3.5 nm in diameter) with concentration of 0.05 M referred to Te. CdTe nanowires were obtained by addition of the stock solution of CdTe NCs in to the standard physiological phosphate-buffered solution at pH 7.2, followed by incubation at 4°C in 8-well chambered borosilicate coverslips (Nunc, USA) at the ambient atmosphere conditions for a time period of up to 24 h. (Composition of the buffer: KCl (5.4 mM), Na<sub>2</sub>HPO<sub>4</sub>×7H<sub>2</sub>O (0.3 mM), KH<sub>2</sub>PO<sub>4</sub> (0.4 mM), NaHCO<sub>3</sub> (4.2 mM), CaCl<sub>2</sub> (1.3 mM), MgCl<sub>2</sub>×6H<sub>2</sub>O (0.5 mM), MgSO<sub>4</sub>×7H<sub>2</sub>O (0.6 mM), 8.0 g NaCl (137 mM).) Incubation at low temperature was motivated by minimization of chances of potential bacterial contamination which might be important for potential biomedical applications. However, it was also found that increase of the incubation temperature to 37°C did not significantly alter either the dynamics or the pattern of nanowires formation. As the self-assembled CdTe nanowires retain the luminescence of the NC building blocks<sup>4</sup>, their formation in the chambered coverslips could be followed in-situ with a confocal microscope.

Fluorescent images were acquired with a Nikon Eclipse TE2000-U inverted microscope with a 100× oil immersion lens and epifluorescence attachment. 3D image acquisition and analysis of fluorescent nanowire images were performed with a 100× oil objective lens using a Perkin-Elmer UltraView LCI laser confocal workstation powered by a Kr/Ar laser. Fluorescence excitation and emission filter combinations were: Ex488/10nm, Em525/50nm and Ex568/10nm, Em600/45nm for the green- and red-emitting nanowires, respectively. 3D image processing was performed using Velocity-2 software (Improvision, USA).

Luminescence spectra of nanowires were measured using RENISHAW micro-Raman system (1800 mm<sup>-1</sup> grating, ~ 1 cm<sup>-1</sup> resolution) equipped with a microscope objective (× 50) and a CCD camera. As an excitation source, an Ar<sup>+</sup> laser ( $\lambda_{\text{ex}} = 514.5$  nm, 1.5 mW power) was used. Raman spectra were excited by an 488 nm line of Ar<sup>+</sup> laser with power of 3 mW and measured using the same micro-Raman system.

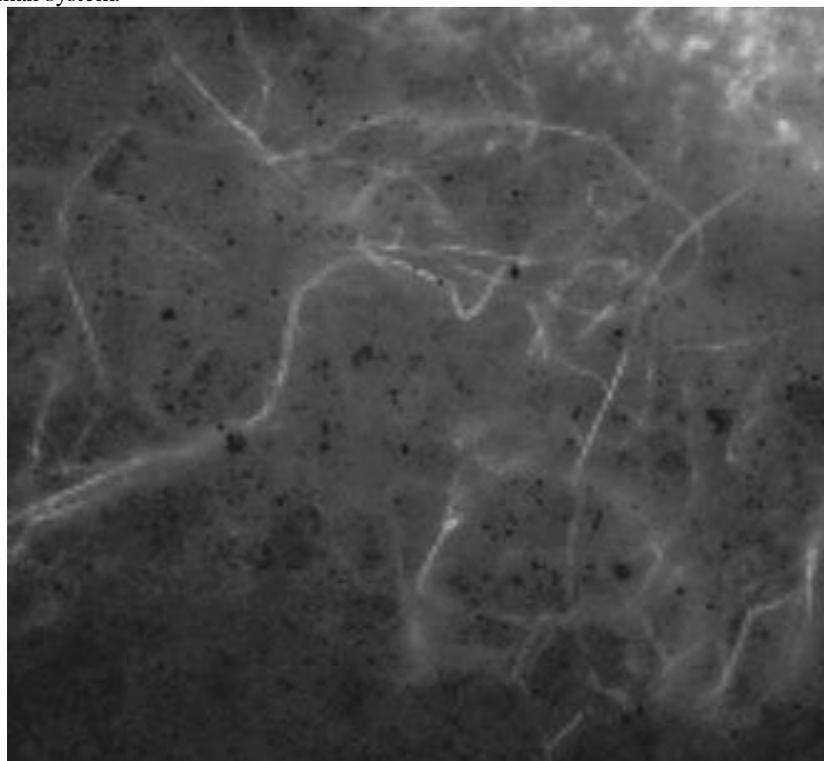


Figure 1: Confocal microscopy images of nanowires self-assembled from CdTe NCs.

### 3. RESULTS AND DISCUSSION

Different volume ratios of the CdTe NC stock solution and the phosphate buffer were tested, namely 1:1, 1:5, 1:10, 1:50, 1:100 and 1:1000. Extremely dilute solutions precluded the formation of nanowires whereas highly concentrated solutions did not permit to observe the wires due to the very strong background luminescence signal. The optimum volume ratio was found to be 1:50, which was used in all further experiments.

Figure 1 shows typical confocal 3D image of several nanowires assembled from the red-emitting (3.5 nm size) CdTe NCs. Growth of nanowires started after 45-60 minutes of incubation emerging from the high luminescence intensity “nucleation patches” and continued progressively with the maximum number and lengths (up to 70-80  $\mu\text{m}$ ) of observed nanowires reached after 6-8 h. Nanowires assembled from red-emitting NCs often formed branching structures, bundles and 3-D resolved networks (Figure 1). Prolonged incubations (18 h and more) resulted in formation of dark precipitates, confirming the presumed mechanism of the nanowire assembly as a result of partial destabilization of the CdTe NC ligand shells<sup>4</sup>. At the conditions of our experiments, the destabilization is apparently promoted by the reducing of electrostatic repulsion of CdTe NCs due to the electrolytic properties of phosphate buffer solution. The choice of proper NCs concentration allowed reasonably slow growth rates and thus a controllable formation of nanowires. Noteworthy, the formation of nanowires was significantly inhibited by addition of 0.1-3% v/w bovine serum albumin protein playing a role of additional capping ligand for CdTe NCs in solution because of the residual sulfur groups. Ones formed in the buffer solution, nanowires retained their luminescence for at least 10-12 hours. This result is in a good agreement with our recently reported data on the compatibility of luminescent CdTe NCs with phosphate buffered saline<sup>13</sup>.

Once formed in solution, nanowires showed a significant degree of structural rigidity and resistance to externally applied mechanical stress. A bundle of nanowires formed from the red-emitting NCs loosely attached to the bottom of glass chamber was exposed to a pulling (suction) force applied from the tip of micromanipulation needle with marginal negative pressure sufficient to hold the nanowires inside the tip opening. The nanowires proved to be rigid enough to withstand dislocation for over 6  $\mu\text{m}$ , which is a remarkable distance compared to the thickness of an isolated and even bundled nanowires.

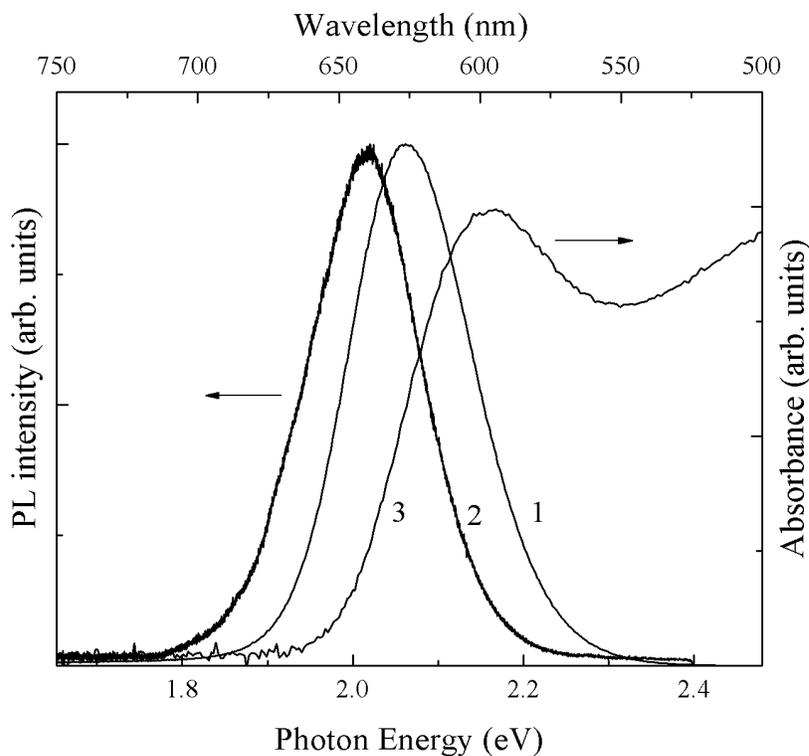


Figure 2: Photoluminescence (PL) spectra of 3.5 nm CdTe NCs (1) and nanowires grown thereof (2). Curve 3 shows absorption spectra of aqueous solution of CdTe NCs.

Figure 2 provides a comparison of luminescence spectra of red-emitting CdTe NCs and nanowires formed thereof. The absorption spectra of original aqueous solution of CdTe NCs shows a well-resolved absorption maximum of the first electronic transition indicating a sufficiently narrow size distribution of the NCs. For CdTe NCs PL band was observed at 72 meV below the absorption maximum with full width at half-maximum about 140 meV.

The luminescence maximum of CdTe nanowires is red-shifted by 54 meV (~10 nm) from PL band of the NCs, pointing on the decrease of electronic confinement in these 1D objects. This is an indirect confirmation of re-crystallization processes taking place during the nanowire formation, leading to the fusion of single NCs together<sup>4,11</sup>.

Further confirmation of the crystallographic re-organization comes from the Raman spectra (Figure 3). Each spectrum was averaged over 20 measurements with accumulation time of 20 s. The luminescence backgrounds due to the lowest energy optical transitions were subtracted. The Raman spectrum of CdTe NCs shows pronounced mode at 160 cm<sup>-1</sup> (Fig. 3,a) which arises from the longitudinal optic phonon mode red-shifted with respect to the bulk mode (170 cm<sup>-1</sup>)<sup>14</sup>. The shift originates from two sources: a redshift due to confinement of the optical phonons, and a blueshift caused by lattice contraction<sup>15</sup>.

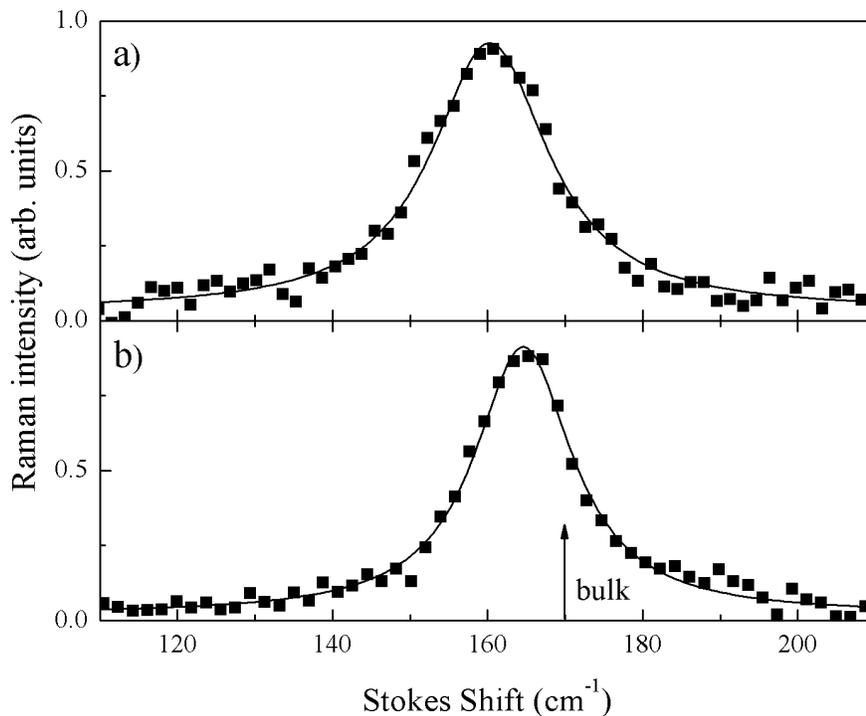


Figure 3: Raman spectra of 3.5 nm CdTe NCs (a) and nanowires grown thereof (b). The solid curves are the result of the fitting procedure by the Lorentzian peak.

The Raman spectrum of CdTe nanowires shows mode centred at 165.3 cm<sup>-1</sup>, still red-shifted with respect to the bulk CdTe modes, however blue-shifted in comparison to the Raman peak of parent CdTe NCs (Fig. 3b). Gaining a better insight into these experimental findings we have to take into account complex structure of the surface of NC assuming the very large surface-to-volume ratio. It is well known that depending on the size the NC have 10%–50% of their total atoms exposed on the surfaces<sup>12,16</sup>. Therefore, various passivation ligands have to be used during synthesizing the colloidal NCs to neutralize the surface dangling bonds and to sterically prevent the nanocrystals from touching each other and permanently fusing together<sup>17</sup>. The surface of the resulting NCs might then be considered as an ensemble of dangling and terminated bonds and various point defects<sup>16</sup>. As a result, the complex surfaces of the obtained colloidal semiconductor NCs play an important role in the photoluminescence (PL) quantum yield and stability<sup>17</sup>, and in Raman scattering<sup>15</sup>. Any surface (interface) modification during the crystallographic re-organization due to the partial removal of stabilizer from the surface must be accompanied by the changes in the phonon frequencies and lineshape of Raman bands. Observed shift of the Raman peak of nanowires towards the bulk CdTe in comparison to the Raman peak of CdTe NCs together with shift in the position of PL band are

indicative of the weakening of quantum confinement of optical phonons, which can be possible in the single-crystal structures only.

#### 4. CONCLUSIONS

In conclusion, we have shown a simple and fast approach of growing luminescent CdTe nanowires in phosphate buffer solution, and have followed the growth *in-situ* with a confocal microscope. In agreement with Ref. 4, the formation of nanowires is induced by the partial removal of stabilizer from the surface of parent CdTe nanocrystals, followed by the re-crystallization process. Structural integrity of nanowires in standard buffer solutions and the stability of their luminescence properties make them attractive objects for future biological and/or biomedical experiments, most of which require the use of liquid phase conditions and rely on intactness of the utilized structures (here – nanowires) at physiological concentrations of salts and inorganic ions. Bright fluorescent signal emitted by nanowires enables them to be readily traceable in biological systems (e.g. cell and tissue culture) with currently available imaging equipment. Relative resistance to mechanical manipulations and substantial achievable length opens up a challenging perspective of using the nanowires as extended scaffolds for multimeric bio-molecular assembly. Last but not the least, the possibility of inducing nanowire formation at ambient temperatures could represent a factor of significant benefit in the systems employing larger molecular weight organic biologically active molecules and peptides subject to heat-induced denaturation or degradation.

#### ACKNOWLEDGEMENTS

The partial financial support for this work was provided by the Science Foundation Ireland under grant number 02/IN.1/47, the Enterprise Ireland, Higher Education Authority of Ireland (HEA), and the Foundation of the Chemical Industry.

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