Highly emissive CdTe nanowires grown in a phosphate buffer solution: FLIM imaging and spectroscopic studies

Y.P. Rakovich ^{*a}, Y. Gun'ko ^b, N. Gaponik ^c, A.L. Rogach ^d, Y. Volkov ^{e,f}, J.F. Donegan ^{a,f}
^a Semiconductor Photonics Group, School of Physics, Trinity College Dublin, Dublin 2, Ireland;
^b School of Chemistry, Trinity College Dublin, Dublin 2, Ireland;
^c Physical Chemistry/Electrochemistry TU Dresden, Bergstr. 66b 01062 Dresden, Germany;
^d Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians
Universität München, 80799 Munich, Germany;
^e Dublin Molecular Medicine Centre and Department of Clinical Medicine and CRANN
Nanoscience Institute; Trinity College Dublin 8, Ireland
^f Principal Investigator CRANN Research Centre, Trinity College Dublin, Dublin 2, Ireland

ABSTRACT

We present details on the formation and optical properties of CdTe nanowires, which were found to grow in a standard phosphate-buffered solution, including micro-photoluminescence and fluorescence lifetime imaging.

Keywords: CdTe, quantum wires, self-assembly, FLIM imaging

1. INTRODUCTION

The steady scaling down of the size of electronic devices in modern integrated circuits demands new approaches in fabrication of interconnects capable of efficiently guiding electromagnetic energy on the 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 ¹. 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 ²⁻⁴. 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)⁵ and soft (rod-like micelle)⁶ templates, seed-mediated growth in solution ⁷⁻⁸ and the catalyst-mediated phase separation approach based on point-initiated uniaxial growth of the crystal ^{7,9}.

An alternative approach to obtain nanowires makes use of assembly of pre-formed nanoparticles from colloidal suspensions ^{4, 10-11}. Recently, Kotov and co-authors ⁴ have shown the possibility of spontaneous organization of semiconductor nanocrystals (NCs) into crystalline nanowires during a several day aging process, promoted by removal of stabilizer ligands through an intermediate methanol washing step. Among others, water-soluble thiol-capped CdTe nanocrystals were demonstrated to be ideal building blocks self-assembling into micrometer-long nanowires through dipole-dipole interactions promoted by partial removal of stabilizer ligands ^{4,12}. In this paper we summarize our data on fast self-assembly of CdTe nanocrystals into nanowires in phosphate buffer solutions, and report on the optical properties of CdTe nanowire networks.

*Yury.Rakovich@tcd.ie; phone (+)353 1 896 1821; fax (+) 353 1 1-671-1759

2. EXPERIMENTAL

CdTe NCs – building blocks for the nanowires – were synthesized in aqueous solution using thioglycolic acid as stabilizer following the previously reported approach¹².

Post-preparative size-selective precipitation¹² 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 with concentration of 0.01 mM.

CdTe nanowires were obtained by addition of the stock solution of CdTe NCs in to the standard physiological phosphate-buffered solution (PBS) at pH 7.2. Typically, 1 μ l of aqueous CdTe NC solution was put on a glass slide. Depending upon the density of NWs required, 1-20 μ l of PBS buffer solution was put onto the NC drop.

Fluorescent images were acquired with a Nikon Eclipse TE2000-U inverted microscope with a 100 $\times$ oil immersion lens and epifluorescence attachment. Image acquisition and analysis were performed with a 100 $\times$ 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.

PL spectra of nanowires were measured using a RENISHAW micro-PL/Raman system equipped with a microscope objective ($\times 100$), a notch and plasma filters and a CCD camera. An Ar⁺ laser (wavelength $\lambda = 488$ nm) was used in the micro-PL measurements. PL decays were measured using time-correlated single-photon counting (Time-Harp, PicoQuant). The samples were excited by using 480 nm picosecond pulses generated by using a PicoQuant, LDH-480 laser head controlled by a PDL-800B driver. The setup was operated at a 20 MHz repetition rate with an overall time resolution of ca. 350 ps. Fluorescence lifetime images were collected with the FLIM system (Microtime200 time-resolved confocal microscope system, PicoQuant) equipped with an Olympus IX71 inverted microscope. Lifetime maps were calculated on a pixel-by-pixel basis by fitting the lifetime of each pixel to the logarithm of the intensity. The FLIM system response was negligible compared with typical lifetimes of the quantum wires (ca. 2-5 ns).

3. RESULTS AND DISCUSSION

Figure 1 shows a typical confocal image of several nanowires assembled from the red-emitting (3.5 nm size) CdTe NCs. Formation of nanowires starts in solution close to the edge of the droplet upon evaporation of water which takes ~ 20 minutes; further growth proceeds quickly, on the time scale of minutes, leading to formation of nanowire network, which covers the support.

Fig.1 (a) Confocal microscopy images of nanowires self-assembled from CdTe nanocrystals.

The PL spectrum of a nanowire network on glass substrate is presented in Figure 2 in comparison with spectrum taken from original solution of nanocrystals. The luminescence maximum of the CdTe nanowires is red-shifted by 8 nm. PL decay curve for network of nanowires show strong (more than 7 times) decrease in luminescence lifetime ($\tau_{1/e}$) as compared with solution of nanocrystals. Both these experimental findings point towards a decrease of the electronic confinement in these 1D objects.

Fig.2 Photoluminescence spectra (a) and PL decays (b) of CdTe NCs (thin line) and nanowires grown thereof (thick line). ($\tau_{1/e}$ (ns): 14.4 (NCs); 1.9 (NWs)).

The recorded decay curve for nanowires show multi-exponential recombination kinetics: both two- and three-exponential decay models failed to provide a satisfactory fit to the decay data. The observed multiexponential decay kinetics are consistent with a PL model that includes multiple emission pathways and is indicative of a broad lifetime distribution caused by the corresponding distribution of defect or trap states due to thinning or partial removal of the stabilizer coating on the nanocrystals. Considering nanowires as a nano-heterogeneous system, the PL decays can be best understood by a model of continuous distributions of decay times.¹³ In this case fitting procedures cannot distinguish sufficiently between, for example, a single Gaussian distribution of lifetimes and the sum of two exponentials, or a bimodal Gaussian distribution and the sum of at least three exponentials.¹⁴ Therefore, to gain a better insight into the spatial distribution of lifetimes, the PL dynamics were evaluated using fluorescence lifetime imaging microscopy (FLIM), that is, maps of two-dimensional in-plane variations of the PL decay times.

Fig.3 FLIM image of CdTe nanowire network on glass substrate (a) and the corresponding lifetime histogram. The image was collected at 390×350 pixel resolution with 4096 time channels; 2 ms acquisition time per pixel and a total recording time of 12.78 min.

Each pixel in the FLIM image gives the lifetime at a particular position in space (x,y), while monitoring the entire PL spectrum. The lifetime image of a nanowire network clearly demonstrates the distribution of emitting species over a wide area. (Figure 3a) The corresponding PL lifetime histogram (Figure 3b) show lifetime distribution that consist of a first maximum centered at 2.4 ns with value of full-width-at-half-maximum (FWHM) equal to 1.3 ns followed by wide (FWHM = 4.8 ns) band of lifetimes ranging from 5 to 14 ns.

The two-band structure shown in Figure 3b implies that at least two different mechanisms are involved in the decay processes. A distribution of decay times causing non-exponential decays in II-VI NCs has been generally discussed in terms of a variation in the non-radiative decay rates caused by trap states.^{13,15-17} In the case of nanowires, the PL decay kinetics may also be affected by resonance energy transfer between different parts of a single nanowire or between different nanowires forming the network. Indeed, observed structure of lifetime distribution is slightly altered in going from one nanowire to another.

Figure 4a shows a FLIM image of a single isolated CdTe nanowire. Both components observed in the lifetime histogram (Figure 4c) are shifted as compared to data presented in Figure 3b, displaying a first peak centered at 1.2 ns and the second one with center at 4.7 ns. It is noteworthy that both peaks are much more narrow now with estimated values of FWHM equal to 0.6 ns (first peak) and 3.7 ns (second peak). Corresponding PL decay measured from the whole nanowire shows pronounced non-exponential kinetics (Figure 4b) with a time constant $\tau_{1/e} = 1.5$ ns, implying nano-heterogeneous recombination dynamics. To monitor the quality of fabricated nanowires, we have studied the micro-PL spectra obtained for different positions of the exciting laser spot along the selected nanowire (Figure 4d). It turned out that position of PL maximum shifts less then 3 nm over a scanning distance of 14 μm , although the corresponding PL intensity depends on excitation position. (Figure 4a,d)

Fig. 4 FLIM image (a), corresponding PL decay (b) and lifetime histogram (c) of a single CdTe nanowire. Panel (d) shows PL spectra recorded from the nanowire positions as indicated by arrows in panel (a).

Closer look on wire network revealed different lifetime kinetics in crossed and branched quantum wires. (Figure 5) Although short-lifetime component dominates in both histograms, the contribution of long-lifetime band is clearly different. The most remarkable result is strong suppression of long-lifetime component in the branching region (Figure 5b,d) which is accompanied by a reduction in emission intensity. Considering the closeness of the nanoparticles forming

the quantum wire, this process is likely to involve energy transfer between nearest neighbors when the resonant conditions are satisfied.

Fig. 5 Magnified FLIM image of crossed (a) and branched (b) quantum wires and the corresponding lifetime histograms (c) and (d) measured from the indicated regions.

4. CONCLUSIONS

In conclusion, we have shown a simple and fast approach for growing luminescent CdTe nanowires in phosphate buffer solution, and have followed the growth with confocal microscopy, micro-PL spectroscopy and FLIM imaging. The 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. The 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. The relative resistance to mechanical manipulations and substantial achievable length (what is it?) 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.

5. ACKNOWLEDGEMENTS

This work was supported by Science Foundation Ireland under its CRANN Research Centre, Project PR23.

REFERENCES

1. G.Y. Tseng G.Y., J.C. Ellenbogen, "Enhanced: Toward Nanocomputers", *Science* 294, 1293-1294 (2001).
2. J. Hu, L.-S. Li, W. Yang, L. Manna, L.W. Wang, A.P. Alivisatos, "Linearly Polarized Emission from Colloidal Semiconductor Quantum Rods", *Science* 292, 2060-2063 (2001).
3. D.J. Milliron, S.M. Hughes, Y. Cui, L. Manna, J. Li, L.-W. Wang, P. Alivisatos, "Colloidal nanocrystal heterostructures with linear and branched topology", *Nature* 430, 190-195 (2004).
4. Z. Tang, N.A. Kotov, M. Giersig, "Spontaneous Organization of Single CdTe Nanoparticles into Luminescent Nanowires". *Science* 297, 237-240 (2002).
5. C.A. Foss, G.L. Hornyak, J.A. Stockert, C.R. Martin, "Template-Synthesized Nanoscopic Gold Particles: Optical Spectra and the Effects of Particle Size and Shape", *J. Phys. Chem.* 98, 2963-2971 (1994).
6. Y.-Y. Yu, S.-S. Chang, C.-L. Lee, C.R. Wang,, "Gold Nanorods: Electrochemical Synthesis and Optical Properties", *J. Phys. Chem. B* 101, 6661-6664 (1997).
7. J.T. Hu, T.W. Odom, C.M. Lieber, "Chemistry and physics in one dimension: Synthesis and properties of nanowires and nanotubes", *Acc. Chem. Res.* 32, 435-445 (1999).
8. N.R. Jana N.R., L. Gearheart, C.J. Murphy, "Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio", *Chem. Commun.* 7, 617-618 (2001).
9. M.C. McAlpine, R.S. Friedman, S. Jin, K.H. Lin, W.U. Wang, C.M. Lieber, "High-performance nanowire electronics and photonics on glass and plastic substrates", *Nano Lett.* 3, 1531-1535 (2003).
10. K.D. Hermanson, S.O. Lumsdon, J.P. Williams, E.W. Kaler, O.D. Velev, "Dielectrophoretic Assembly of Electrically Functional Microwires from Nanoparticle Suspensions", *Science* 294, 1082-1086 (2001).
11. C. Pacholski, A. Kornowski, H. Weller H., "Self-Assembly of ZnO: From Nanodots to Nanorods", *Angew. Chem. Int. Ed.* 41, 1188-1191 (2002).
12. Y. Volkov, S. Mitchell, N. Gaponik, Y.P. Rakovich, J.F. Donegan, D. Kelleher, A.L. Rogach, "Observation of Nanowires Growth from Luminescent CdTe Nanocrystals in a Phosphate Buffer Solution", *Chem. Phys. Chem.* 5(10), 1600-1602 (2004).
13. A.M. Kapitonov, A.P. Stupak, S.V. Gaponenko, E.P. Petrov, A.L. Rogach, A. Eychmuller, "Luminescence Properties of Thiol-Stabilized CdTe Nanocrystals", *J. Phys. Chem. B* 103, 10109-10113 (1999).
14. D.R. James, Y.-S. Liu, P. De Mayo, W.R. Ware, "Distributions of fluorescence lifetimes: consequences for the photophysics of molecules adsorbed on surfaces", *Chem. Phys. Lett.* 124, 460 (1985).
15. X. Wang, L. Qu, J. Zhang, X. Peng, M. Xiao, "Surface-Related Emission in Highly Luminescent CdSe Quantum Dots", *Nano Lett.* 3(8), 1103-1106 (2003).
16. S.F. Wuister, C. de Mello Donegá, A. Meijerink, "Influence of Thiol Capping on the Exciton Luminescence and Decay Kinetics of CdTe and CdSe Quantum Dots", *J. Phys. Chem. B* 108(45), 17393-17397 (2003).
17. Y.P. Rakovich, S.A. Filonovich, M.J.M. Gomes, J.F. Donegan, D.V. Talapin, A.L. Rogach, A. Eychmüller, "Anti-Stokes photoluminescence in II-VI colloidal nanocrystals", *Phys. Stat. Sol. (b)* 229(1), 449-452 (2002).