

Polymer-Controlled Growth of CdSe Nanoparticles into Micro- and Nanowires

A. Fahmi*, U. Oertel**, V. Steinert**, P. Moriarty* and M. Stamm**
*Department of Physics, University of Nottingham, Nottingham NG7 2RD,
United Kingdom. Amir.Fahmi@nottingham.ac.uk

**Leibniz-Institut für Polymerforschung Dresden e.V. (IPF), Hohe Straße 6, 01069 Dresden, Germany
Stamm@ipfdd.de

ABSTRACT

This work reports an easy and effective method to prepare CdSe semiconductor nanoparticles stabilized by an amphiphilic diblock copolymer polystyrene-block-polyvinylpyridine [PS-b-P4VP] in a nonaqueous medium [1]. The CdSe nanoparticles are held in the polymeric matrix via the lone pairs of electrons in the pyridine rings of the block copolymer. We find that the structure of the polymeric CdSe nanoparticles depends strongly on solvent polarity. For instance, spin coating of the stock CdSe(PS-b-P4VP) in DMF onto native oxide terminated Si-wafers lead to a core-shell structure (CdSe nanoparticles in the core, encased in a shell of the block copolymer). However, a non-polar solvent can be used to switch the structure from core-shell to flat ring structure decorated with CdSe nanoclusters on the edge. After a specific thermal treatment of CdSe/PS-b-P4VP thin film CdSe nano- and micro wires were formed. The aggregation of CdSe nanoparticles during the thermal elimination of the polymer phase causes the growth of wires [2,3]. The wires have a diameter between 0.4- 2 μm (depending on the film thickness) and a length of 250 μm . SEM was used to observe the mechanism of the wire formation on the Si-wafer substrate. It is believed that the thermal treatment of the polymer CdSe complex leads to dewetting of the polymer phase, which causes the CdSe nanoparticles to aggregate into wires.

Keywords: block copolymer, CdSe nanoparticles, Nanoring, core-shell structure, CdSe wires

Introduction

Fabrication of semiconductor nanostructures has attracted considerable attention owing to their potential applications in electronics, optics, catalysis, ceramics and magnetic storage [4,5]. Nanostructured materials often display optical, electronic, and structural properties different from those of the bulk [6,7,8,9]. For example, nanoparticles may adopt various shapes, and the form adopted plays a critical role in determining these properties. The unusual properties of nanoparticles can be attributed to two main factors: high surface area to volume ratio and the quantum confinement of electronic states.

During the past decade, many synthetic methods based on polymer materials have been developed, among which the synthesis of nanoparticles in a polymer matrix is prominent

[10,11,12,13]. The use of a polymeric matrix as a medium for metal nanoparticle formation does not only provide improved stabilisation and fine control of the growth of the nanoparticles, it also imparts new properties to the polymeric material [14,15]. Block copolymer micelles, especially those formed by well-defined block copolymers, with well-chosen block length and chemical composition in selective solvents turned out to be an excellent model system. In particular, it is easy to delineate their advantages in colloid synthesis, compared to classical stabilisation systems by surfactants or in microemulsion. In principle, microphase-separation of the block copolymer could be harnessed to promote the ordering of the particles and thereby selectively create high degree of organisation in one block of the diblock copolymer (Fig.1). In such a system, the unpolar blocks form the corona, which provides solubility and stabilisation, while the polar block forms the core, which is able to dissolve metal compounds due to coordination.

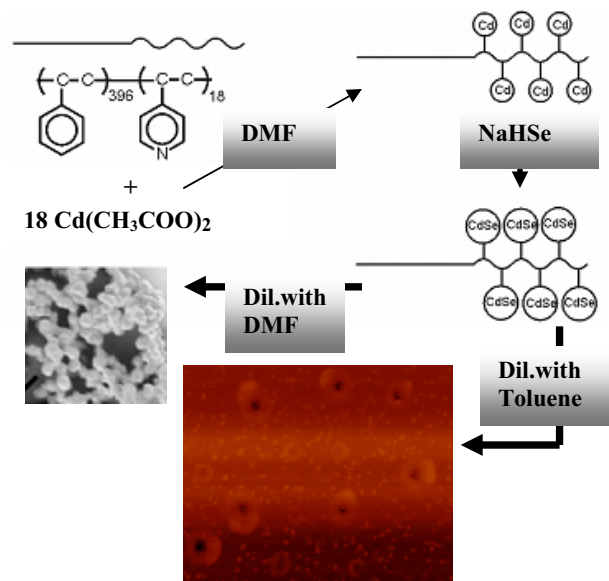


Fig. 1: demonstrating the switching process by dilution with different solvents. Such a micelle core can be considered as a quasi nanoreactor, where nucleation and growth of metal particles upon reduction are restricted to the mesoscale level.

This study describes a method to prepare CdSe nanoparticles with controllable size and stability as shown in (Fig 1). We used Poly(styrene-block-4-vinylpyridine) (PS-b-P4VP) block copolymer to form compound micelles upon a complex of 4VP with a stoichiometric molar amount of cadmium ions (Cd^{2+}) in dimethylformamide (DMF).

The formation of nanoparticles in PS-b-P4VP was studied very thoroughly and enabled the identification of the principles underlying the control of the particles size. Dissolution of metal salts for example in the solution of PS-b-P4VP micelles (that are otherwise insoluble in the solvents) means that these are salts incorporated only in the micelle core, due to the coordination with corresponding groups of polymer^[11,13]. For instance, CdSe nanoparticles grow in the core of the micelles after inserting sodium hydrogen selenide (NaHSe) into the solution of PS-b-P4VP(Cd) to produce a yellow colour as evidence for CdSe formation.

DETERMINATION OF THE CORE-SHELL STRUCTURE OF CdSe

Fig. 2 shows a SEM image of CdSe/P4VP-b-PS film spin cast onto native oxide terminated Si-wafers. The image demonstrated a spherical structure with a reasonable diameter around 100 nm.

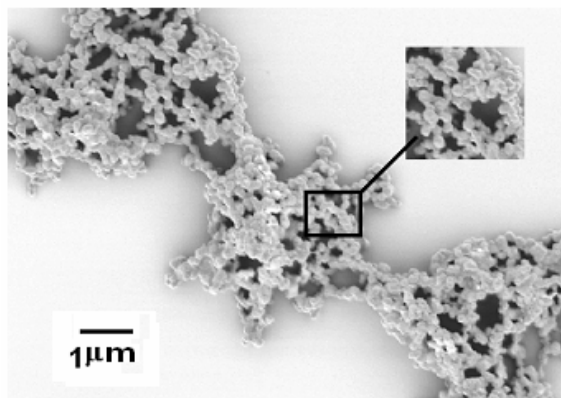


Fig. 2: SEM micrograph of core-shell structure CdSe in core and the shell occupied from block copolymer

FLAT RING CdSe STRUCTURE

Additional insight into the change in structure can be gained after dilution with a non-polar solvent (toluene). Fig. 3 shows an AFM image obtained from cast film on Si-wafer. The film shows that ionomer diblock copolymer micelles in toluene can exhibit extraordinary kinetic stability. The film allows the forming of flat uniform ring structures of the block copolymer decorated with CdSe nanoparticles on the edge. A cross-section demonstrates

that the flat ring structures have a diameter of 250 nm and ≈ 2 nm height. However, the CdSe-nanoparticles occupied a sector onto the ring structures with ≈ 4 nm height. Moreover, XPS results have confirmed the structure switching on the substrate (It does not appear in this manuscript).

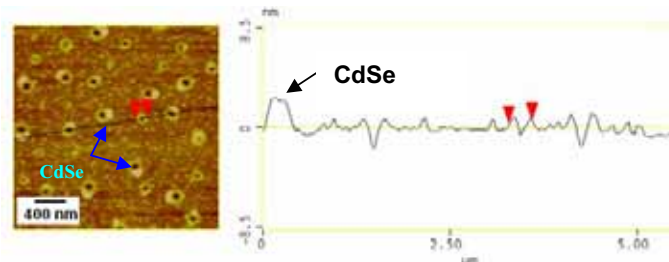


Fig. 3: AFM image of CdSe/P4VP-b-PS ring structure in ultrathin film was spin-casting onto native oxide Si-wafer

THERMAL DEGRADATION AND PARTICLES AGGREGATION

Thermal degradation of CdSe/PS-b-P4VP thin film (spin-cast) on native oxide Si-wafers has produced CdSe wires in micro- and nanometer scales. The aggregation of CdSe nanoparticles during the thermal elimination of the polymer phase caused the growth of wires [3]. The wires have a diameter between 0.4- 2 μm (depending on the film thickness) and length of 250 μm . SEM was used to observe the CdSe wires on Si-wafer substrates (Fig 4).

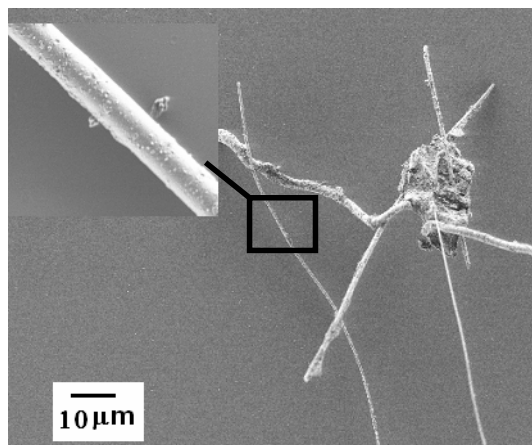


Fig. 4: SEM micrograph of CdSe microwires on Si-wafer developed after thermal treatment of thin film of CdSe/P4VP-b-PS.

CdSe complex leads to a dewetting of the polymer phase, which causes the CdSe nanoparticles to aggregate into

wires. This strategy could open a new avenue to produce nanoparticle assemblies derived from core-shell and hollow colloids into semiconductor wires, which may provide new application in areas such as photonics, photoelectronics and microelectronics.

We have performed a preliminary electrical transport measurement to confirm the conductivity of the CdSe wires. The insert in Fig. 5 shows an optical image detailing the microwire alignment between two parallel AuTi electrodes supported on a silicon oxide substrate (the thickness of the oxide was more than 200 nm). The current changes were measured with applied potential up to 10 V across the CdSe-wire at 4.2 K. Fig. 5 shows a measurement of the current flow through the wire as a function of the voltage applied between the AuTi electrodes. Although the asymmetry in the I(V) characteristic arises from variations in the quality of the contacts, it is clear that the wire conducts. A probe measurement are planned (so as to alleviate the contact problem).

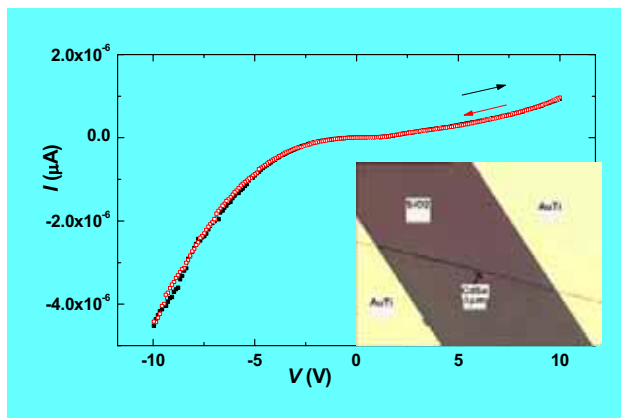


Fig.5: Electrical conductivity measurement on an individual CdSe wires that 1 μ m in diameter. An optical micrograph (insert) detailing the alignment of the CdSe wire with respect to the two parallel AuTi electrodes.

CONCLUSION

An amphiphilic block copolymer (PS-b-P4VP) has been used to form “nanoreactors” for the synthesis of CdSe nanoparticles in a non-aqueous medium. Switching the structures from core-shell into flat ring structures of the polymeric CdSe nanoparticles strongly depends on solvent polarity. A specific thermal treatment of PS-b-P4VP/CdSe thin film produces nano- and micro CdSe wires. We found that the wires diameter depended on the film thickness. It is believed that the thermal treatment of the polymeric CdSe complex leads to dewetting of the polymer phase, which causes the CdSe nanoparticles to aggregate into wires.

An initial experiment to measure the conductivity of the CdSe wire has shown current flow (across 1 μ m diameter CdSe wire) through the two AuTi electrodes. We believe this simple approach for producing CdSe wires, which is a functional material, is needed in future for many applications such as photonics, photoelectronics and microelectronics.

ACKNOWLEDGMENT

The authors thank the European Commission for funding the SUSANA Research and Training Network (Supramolecular Self-Assembly of Interfacial Nanostructures) Project No. HPRN-CT-2002-00185. we would like to thank Dr. F.Pulizzi and D. Taylor for the conductivity measurement.

REFERENCES

- [1] A. Fahmi, U. Oertel, V. Steinert, C. Froeck, M. Stamm *Macromol. Rapid Commun.* 24, 625–629, 2003.
- [2] Amir Fahmi “Nanotemplates via self-assembly of diblock copolymers and their metallization” Dissertation Technische Universitaet Dresden Germany 2003
- [3] A. Fahmi, U. Oertel, V. Steinert, Philip moriarty, M. Stamm under preparation
- [4] A. Henglein; *Chem. Rev.* 89, 1861, 1989.
- [5] Y. Sun, J. E. Riggs; *Int. Rev. Phys. Chem.* 18, 43,1999.
- [6] L. N. Lewis; *Chem. Rev.* 93, 2693, 1993.
- [7] A. P. Alivisators; *Science* 271, 933,1996.
- [8] L. E. Brus; *J. Chem, Phys.* 80, 4403, 1984.
- [9] Y. Wang, N. Herron; *J. Phys. Chem.* 95, 525, 1991.
- [10] W. Casert; *Macromol; Rapid Commun.* 21, 705, 2000.
- [11] R. S. Kane, R. E. Cohn, R. Silbey; *Chem. Mater.* 8, 1919, 1996.
- [12] J. Yue, V. Sankaran, R. E. Cohn, R. R. Schrock; *J. Am.Chem. Soc.* 115, 4409, 1993.
- [13] M. Moffitt, A. Eisenberg; *Chem. Mater.* 7, 1178, 1995.
- [14] M. Breulmann, H. Cölfen, H. -P. Hentze, M. Antonietti; *Adv. Mater.* 10, 237, 1998.
- [15] M. Michaelis, A. Henglein; *J. Phys. Chem.* 96, 4719 1992.