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Synthesis of monodisperse CdS nanowires and their photovoltaic applications

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ABSTRACT

Cadmium sulphide (CdS) nanowires with a monodisperse diameter of 3.6 nm and an aspect ratio of 10–170 were successfully synthesized using a simple and reproducible hot coordinating solvents method. The morphology and optical properties of the CdS nanocrystals were investigated using transmission electron microscopy (TEM), high-resolution TEM (HRTEM) ultraviolet–visible (UV–Vis) absorption spectroscopy and photoluminescence (PL) spectroscopy. It was found that using a long alkyl chain phosphonic acid-octadecylphosphonic acid (ODPA) causes a low diffusion rate and low reactivity which help to control the morphology of the nanocrystals. The timing of the injection process was also found to have critical effect on the morphology of the nanocrystals. Sharp peaks in both the UV–Vis absorption and PL spectra indicate that the size distribution of the diameter is nearly monodisperse. The photovoltaic properties of photovoltaic devices made with a blend of our nanowires and poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) were also investigated. Devices made with the nanowires were found to have double the I_{sc} observed in devices made with lower aspect ratio CdS nanorods. The possible reason of low photocurrent and high V_{oc} is maybe due to the presence of ligand in the nanocrystals.

1. Introduction

In recent years, semiconductor nanowires have been increasingly studied as a potential material for future electronic applications due to their attractive size-dependent physical and electronic properties [1–8]. Nanowires with small diameters (less than 5 nm) are attractive both as interconnect and critical device elements because the bandgap and other physical properties strongly depend on their diameter [9]. It has recently been proposed that nanowires with such small diameters are ideal for the fabrication of nanowire MOSFETs for studying true one dimensional transport at room temperature. Furthermore, nanowires have the potential to improve charge transfer and charge collection efficiency in photovoltaic devices [7,10,11]. This is because nanowires can easily form an interconnected network in a conducting polymer thin film when prepared using spin-coating. The network structure may enhance exciton separation, diffusion of free charges and charge collection efficiency [12].

A variety of methods such as the vapour–liquid–solid (VLS) method, solution–liquid–solid (SLS), the hydrothermal method and the hot coordinating solvents method using tri-n-octylphosphine oxide (TOPO) and trioctylphosphine (TOP) have been employed to synthesize semiconductor nanowires recently. Growth of nanowires via VLS often suffers from the requirements of high temperature, special conditions and complex procedures. In general, the size and aspect ratio distributions of these nanowires are difficult to control [13]. Bottom-up approaches such as those using surfactants as the regulating agents are very effective for the synthesis of one-dimensional nanostructures because of their high efficiency, controllability and simplicity. Alivisatos et al. and Peng et al. have successfully developed a high temperature (around 300 °C), non-aqueous based method to synthesize cadmium chalcogenide nanocrystals with different shapes, such as dots, rods and tetrapods [14–18]. This method can generate well-defined nanodots and rods due to the separation of the nucleation and growth stages [19,20]. However, it is still a challenge to synthesize nanowires and solution based synthesis of nanowires is rarely reported [21].

Pradhan et al. reported the synthesis of cadmium selenide (CdSe) nanowires, in which attachment occurred in specific orientations via a loose and weak interaction between the nanoclusters [21]. Very recently, Kang et al. reported their research on preparing cadmium sulphide (CdS) nanowires using tetradecylphosphonic acid as a ligand. They only studied the effect of temperature on the morphology of the nanowires [22] and the nanowires they produced are mixed with many dots and branches. On top of that, their synthesis is rather complicated because it requires a two step heating process to prepare the Cd-complexes.

In this study, we report a simple route to synthesize high quality CdS nanowires. The ligand we used has a long alkyl chain — phosphonic acid-octadecylphosphonic acid (ODPA). Increasing the length of the alkyl chain reduces the diffusion rate and decreases the reactivity which we believed would improved control over the morphology of the nanocrystals. Our preliminary results showed that ODPA is better at controlling the morphology than dodecylphosphonic acid or hexylphosphonic acid [23].

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We also studied the effect of the timing of the precursor injection on the morphology of nanocrystals. Finally, the potential applications of these highly dispersible and high aspect ratio nanowires in hybrid nanowire/polymer solar cells using a blend of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and our CdS nanowires will be investigated.

2. Experimental details

2.1. Synthesis of nanocrystals

Trioctylphosphine oxide (TOPO) and poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene](MEH-PPV) were purchased from Sigma-Aldrich. Trioctylphosphine (TOP) and cadmium oxide were purchased from Fluka. Octadecylphosphonic acid (ODPA) and sulphur were purchased from Polycarbon Inc. and Chemicon respectively. PEDOT:PSS (Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) was purchased from Bayer AG. The CdS nanowires were prepared using a modified Peng's procedure for cadmium chalcogenide nanocrystals [20]. 128 mg of CdO, 0.668 g of ODPA and 3.00 g of TOPO were added to a 25 ml three-neck flask equipped with a condenser and a thermocouple adapter. The flask was then filled with N_2 and the temperature was gradually raised to 330 °C to dissolve the CdO. The temperature was then lowered to 310 °C and stablised, and a solution of 32 mg sulphur in 2.0 g TOP was injected using multiple injections (4 times at 2 min intervals). After the final injection, the temperature of the reaction mixture was maintained at 310 °C for further growth. The reaction was terminated by stopping the heating.

2.2. Device fabrication

Hybrid solar cells were fabricated using a structure consisting of ITO/PEDOT:PSS/MEH-PPV:CdS nanowires blend/Al layers. A layer of PEDOT:PSS was spin-coated onto the etched ITO glass and dried at 120 °C for 20 min. After the synthesis, CdS nanocrystals were dispersed in 20 ml pyridine and stirred under reflux for 4 days, allowing for ligand exchange. Nanocrystals were then precipitated with n-hexane and then redissolved in pyridine. The above process is repeated one more time. After ligand exchange, the nanocrystals and MEH-PPV were dissolved in pyridine separately. A mixture of the nanocrystals and MEH-PPV with 70% nanocrystal loading was prepared. The mixture was spin-coated on top of the dried PEDOT:PSS and dried at 130 °C for 30 min. Finally, aluminum was evaporated on top of the film.

2.3. Characterization

Transmission electron microscopy (TEM) was carried out using a JEOL 2010 microscope fitted with a LaB_6 filament and an acceleration voltage of 200 kV. Ultraviolet–visible (UV–Vis) absorption and photoluminescence (PL) spectra of the nanocrystals were obtained using a Shimadzu UV2501PC spectrophotometer and a Shimadzu RF-5301 PC fluorometer respectively. The excitation wavelength for the PL test was 350 nm. The ligand content of nanocrystals studied using a TA instruments Q500 thermogravimetric analyzer (TGA) from ambient to 650 °C at the rate of 10 °C min^{-1} under nitrogen atmosphere, with a gas flow of 60 ml min^{-1}. Photocurrent measurements were carried out using a 150 W xenon lamp with an air-mass (AM) 1.5 filter. The optical power on the sample was 100 mW cm^{-2}. Current–voltage measurements (*I*–*V* curve) were conducted in ambient atmosphere.

3. Results and discussion

3.1. Synthesis and characterization of the nanocrystals

The monomer concentration in the solution is an important factor that influences the morphology of the resulting nanocrystals. In this study, we investigated the effect of precursor injection processes on the morphology of nanocrystals. Fig. 1a shows a TEM image of self-aligned nearly monodisperse CdS nanorods prepared with an interval between precursor injections of more than 5 min. The aspect ratio of the nanowires is around 10 and their diameter is 3.5 nm. However, decreasing the interval between the precursor injections to around 2 min can lead to a great increase in the aspect ratio of nanocrystals.

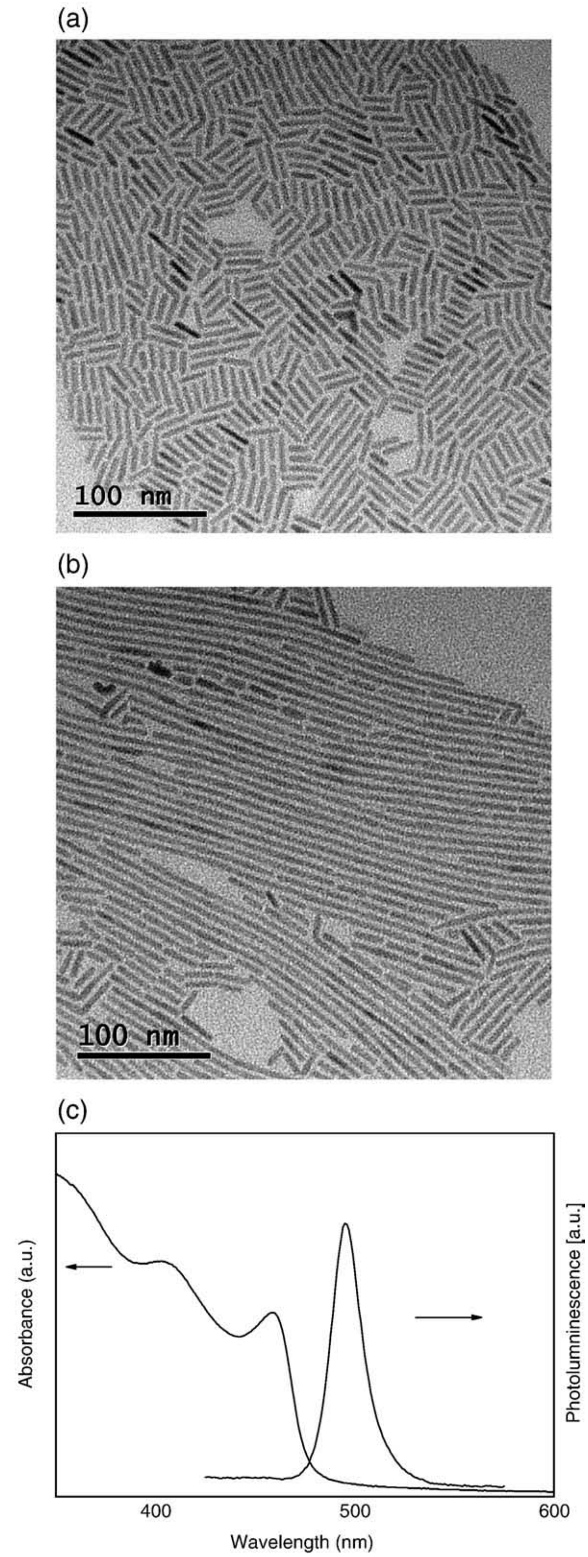

Fig. 1. Bright-field TEM images of CdS nanocrystals: (a) nanorods, (b) nanowires and (c) UV–Vis absorption and PL spectra of the CdS nanowires shown in b.