Effect of Tributylphosphine for the Solution-Liquid-Solid Synthesis of CdSe Nanowires

Hee Su Jang and Jin Seok Lee*

Department of Chemistry, Sookmyung Women’s University, Seoul 140-742, Korea. *E-mail: jinslee@sookmyung.ac.kr
Received November 26, 2012, Accepted December 4, 2012

Semiconductor CdSe nanowires (NWs) can serve as model systems for investigating the physical properties of one-dimensional (1D) nanostructures and have great potential for applications in electronics and photonic nanodevices. With numerous attractions arisen from their physical properties, CdSe NWs have been synthesized by vapor-liquid-solid (VLS) methods, but they have some limitations of high reaction temperature and low production. Here, we synthesized CdSe NWs via the solution-liquid-solid (SLS) mechanisms using bismuth (Bi) covered substrates as a low-melting point catalyst and compared the products after injecting identical amount of Se and different amount of tributylphosphine (TBP). CdSe NWs have similar diameters but longer lengths with decreasing TBP, so we proposed the role of TBP as a solvent and capping agent of Se.

Key Words: CdSe Nanowires, Solution-Liquid-Solid, Tributylphosphine, Morphology

Introduction

One-dimensional (1D) semiconductor nanostructures have been regarded as promising materials for fundamental studies and exhibit valuable properties for electronic, optical, and life sciences applications. To achieve 1D nanostructured materials, various techniques were attempted over the past few years by wet chemical and non-wet chemical approaches such as vapor-liquid-solid (VLS) mechanism. However, the VLS method has trouble in control the size and aspect ratio of nanowires because it requires high temperature, special conditions, and complex procedures. Solution-liquid-solid (SLS) method has attracted interest because this approach uses low-melting-point catalysts in solution, so it has advantages like a comparably lower reaction temperature, easily control of the mean diameter, and narrow diameter distributions.

Cadmium Selenide (CdSe) is a direct bandgap semiconductor with a bandgap of 1.73 eV at 300 K. It has two crystal forms, the cubic zinc blende structure and the hexagonal wurtzite structure. In these crystal structures, the cadmium and selenium atoms are four coordinate and are organized into isotropic or anisotropic connection for zinc blende or wurtzite structure, respectively. Based on their atomic connectivity, all CdSe nanorods and nanowires have represented wurtzite structure while zinc blend structure has organized into isotropic or anisotropic connection for zinc blende or wurtzite structure, respectively. We believe that this method has a great potential to be applied to controllably synthesize cadmium chalcogenide axial heterostructures with individually predesigned aspect ratio.

Experimental Section

Chemicals. Cadmium oxide (CdO, 99.99%), tributylphosphine (TBP, 97%), tri-n-octylphosphine oxide (TOPO, 99%), selenium (Se, 99.999%) were purchased from Aldrich. Bismuth spheres (Bi, 99.999%) and n-tetradecylphosphonic acid (TDPA, 98%) were purchased from Alfa Aesar. SiO2/Si wafers were purchased from University Wafer.

Preparation of Bi-Covered Substrates. Si/SiO2 wafers were cleaned with acetone and 2-propanol before being loaded into a high vacuum thermal evaporator. 4 nm of Bi were thermally evaporated on top of a thin (2.5 nm) primer layer of Cr. The Bi-covered substrates were kept in a nitrogen glove box. The Bi-covered substrates were cut into ~0.6 cm × 0.6 cm chips and treated with N2 flow to remove wafer flakes.

Synthesis of Cadmium Precursors. CdO (0.0048 g, 0.037 mmol), TDPA (0.0214 g, 0.074 mmol), 5 g of TOPO, and magnetic stirring bar were loaded into a 50-mL three neck round bottom flask equipped with a thermocouple, condenser, and home-made glass apparatuses. The ~0.6 cm
Effect of Tributylphosphine for the Synthesis of CdSe Nanowires


Synthesis of CdSe Nanowires on Substrates. The reaction setup and scheme are shown in Figure 1. For the growth of CdSe nanowires on substrates, the Bi-covered Si/SiO$_2$ wafer was slowly moved down using external magnet and soaked in the Cd/TDPA precursor in TOPO solution at around 150 °C under nitrogen flow (Figure 1(a)). The flask was heated to 270 °C with gentle stirring, and then pre-prepared Se/TBP clear solution was injected into the Cd/TDPA precursor. After 10 min, the substrate was retrieved from the solution by moving up external magnet and the heating mantle was removed. The flask was allowed to cool to room temperature and the remaining solution was dispersed by 5 mL toluene. The substrate was washed with copious amounts of hexane to remove residual TOPO and unreacted trace chemicals. The CdSe nanowires with Bi catalyst particles attached to one end were found on the substrate.

Characterization of Samples. The scanning electron microscope (SEM) images were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 20 kV. To get the high resolution images, a platinum/palladium alloy (in the ratio of 8 to 2) was deposited on top of the as-synthesized product. And, low-magnification transmission electron microscope (TEM) image was analyzed with a JEOL 2010. Samples for TEM imaging were made by depositing a hexane solution of nanowires (prepared by sonication of as-synthesized substrate in hexane) onto holey carbon 300 mesh copper grids (Ted Pella). The energy-dispersive X-ray spectrum (EDS) data was obtained from FE-SEM (JSM-7600F, at 15 kV). The X-ray diffraction (XRD) patterns for the identification of produced nanowires were measured on a Rigaku diffractometer (D/MAX-1C) with Cu K$_\alpha$ radiation by $2\theta$ scanning with the speed of 1° min$^{-1}$.

Result and Discussion

Previous studies of solution-phase synthesis have demonstrated successful 1D growth of CdSe NWs with the assistance of catalytic nanocrystals.$^{8,16-18}$ Bi nanocrystals have recently been demonstrated as an ideal catalyst to assist 1D growth of CdSe NWs in solution at relatively low temperatures based on the SLS mechanism.$^{19,20}$ By the same analogy, it was also reported that a thin layer of Bi deposited on a substrate could be used to form catalyst nanoparticles at the reaction temperature due to its low melting point.$^{16}$ The main advantage of using substrate-bound catalyst particles is that massive purification and reconcentration step for reaction products are not necessary during the following procedures. And, based on the fact that most of the reaction products were found on substrates, with very few Bi-bound CdSe NWs found in the TOPO solution, it should be noted that the Cr underlayer is critical for the adhesion of the nanocrystals to the substrates. This approach using thin layer of Bi as a catalyst quite be useful for the sequential surface treatment of products and the synthesis of other axial NWs with built-in heterojunctions.

Considering that all reactants as well as Bi thin layer should be isolated from oxygen and moisture during the whole synthetic procedure, in situ loading system of Bi-covered substrate in a flask is necessary for the successful growth of CdSe NW with single crystalline. With this reason, we designed the glass apparatuses for loading and unloading the substrate in our reactions which are composed of two glass components such as a glass rod and a glass tube (Figure 1(a)). The former is made up of a square spoon, small pierced at the bottom to take in and off a Bi-covered substrate, with a long handle like as a ladle. A magnet is attached at the end of handle and then sealed with teflon tape. The latter is made up of a one-side-blocked long glass tube with a glass adaptor to be connected to multi-neck flask. By controlling several magnets located out of glass tube, the ladle-like glass rod could be moved up and down.

As increasing temperature, the TOPO solution containing...
CdO and TDPA looked reddish color due to brown CdO powders, but the solution turned colorless around 300 °C; it indicates a formation of Cd/TDPA complex in TOPO solution.\textsuperscript{21,22} Therefore, although not very accurate, the reddish color change of solution served as a good visible probe for monitoring the formation of Cd/TDPA complex. After the Bi-covered substrate was soaked into the Cd precursor, with raising the solution temperature, the thin layer of Bi forms Bi nanodroplets with a narrow size distribution due to its low melting point (271 °C). They nucleate and take a role as catalyst for the crystal growth of CdSe NWs (Figure 1(b)). Compared to Bi nanocrystal synthesized by chemical methods,\textsuperscript{8,23} the Bi thin film makes reaction system simple due to removing the number of cases originated from Bi precursor.

In this study, we tried to investigate the effect of TBP usually used as solvent of selenium in solution-phase synthesis. The Se/TBP solutions were prepared by dissolving Se into TBP in sealed vial with nitrogen flow. Different volume was taken from each different concentrated Se/TBP solution to equalize the mole of Se (0.051 mmol). During synthesis, various morphologies of CdSe NWs are realized by changing the amount of TBP. We characterized the morphology and crystallinity of produced CdSe NWs by SEM and TEM study. Figure 2 shows representative SEM images of CdSe NWs grown on the Bi-covered substrate which were synthesized at 270 °C with 0.14, 0.10, and 0.06 mmol of TBP for 10 min, illustrating that the reaction produces straight CdSe NWs with Bi catalysts attached to one end. At the largest amount of TBP (0.14 mmol, Figure 2(a)), the density of produced CdSe NWs looks low and their length is shorter than ~1 µm. At the middle amount of TBP (0.10 mmol, Figure 2(b)), the products have high density and longer length than the CdSe NWs grown at the largest amount of TBP. And, CdSe NWs were synthesized with highest density and longest length at the lowest amount of TBP (0.06 mmol, Figure 2(c)). By decreasing TBP amount, longer CdSe NWs were mainly obtained with high density.

Figure 3(a) shows representative low-magnification TEM image of CdSe NW detached from Bi-covered substrate; there is Bi alloy on the tip of the NW. Interestingly, the average diameters of most CdSe NWs from different amount of TBP were similar in the range of 30–40 nm. The above result therefore suggests that the diameter of CdSe NWs depends on the thickness of Bi layer and has nothing to do with the amount of TBP in flask.

To characterize the crystal structure of produced CdSe NWs, X-ray diffraction (XRD) was measured. Figure 3(b) shows that XRD patterns of produced CdSe NWs exhibit the hexagonal structure [space group: P6\textsubscript{3}mc (No.186)] with lattice constants a, b = 4.299 Å and c = 7.01 Å (PDF#00-008-0459). CdSe has two crystal lattices, wurtzite (hexagonal) and zincblend (cubic). Based on the fact that wurtzite structure is anisotropic while zinc blend structure is isotopic, the crystal lattices of CdSe NWs with 1D structures was expected to hexagonal wurtzite structure.\textsuperscript{11,12} Figure 3(d) represents energy dispersive X-ray (EDX) spectroscopy data taken from the area designated on high-magnification SEM image of CdSe NW as shown Figure 3(c). The quantitative atomic ratio of Cd and Se prove that composition of CdSe crystals matches 1:1 ratio.

The above results clearly support that the TBP concentration in flask affects the growth and morphology of CdSe NWs. Mixed phosphine/phosphine oxide solutions have previously been found to be a Lewis base organic solvent bonding to metal ions and passivating crystallite surface.\textsuperscript{24} Bawendi et al. reported on synthesis and characterization of CdE semiconductor nanocrystallites where they studied the capping groups such as alkylphosphine and alkylphosphine oxide solvents bring about a significant steric barrier to the addition of material to the surface of a growing crystallite, and slow the growth kinetics.\textsuperscript{18} Recently, Alexander et al. studied the differences of the alkyl chain length between
trioctylphosphine (TOP) and TBP which are used as Se stabilizers affects the growth and morphology of CdSe nanorods. Both TOP and TBP have three alkyl chain connected to phosphorus atom. When using TOP which has 8-carbon in a chain, the products were spherical particles while the nanowires were synthesized with TBP. They discussed this situation that 8-carbon three chains should considerably slow down the diffusion process and 4-carbon three chains allow increasing the diffusion coefficient. Interestingly, in our results, the diffusion of Se is prevented with increasing the amounts of TBP.

In our results to length differences, the length of CdSe NWs was increased with a decrease of the TBP concentration while the average diameters of products are similar. During synthesis of CdSe NW as shown Figure 4, Bi nanodroplets were formed on substrate at reaction temperature and Cd precursors were previously prepared in the form of complex with TDPA; it functions as ligands of Cd in TOPO solution. And, Se precursors in the form of TBP-capped Se ions were injected. Then, TDPA-capped Cd ions and TBP-capped Se ions dissolve into Bi droplets. In this process, excess TBP cause a steric barrier to the addition of Se precursors to the Bi droplets, and then the growth kinetics from Bi catalysts was slower. As a result, though provided reactants were identical, only length was different under same reaction condition such as reaction time and reaction temperature.

**Conclusion**

We report the effect of TBP in synthesis of CdSe NWs on Bi-covered substrate via Solution-liquid-Solid (SLS) mechanism. From length differences of CdSe NWs produced with
different amount of TBP, longer CdSe NWs were mainly obtained with high density as decreasing TBP amount, while the average diameters were similar. These results support that TBP acts as not only solvent but also capping agents of Se, so it would prevent dissolving of Se into bismuth catalysts and control solubility of Se. It would be helpful to understand catalyst-based solution phase reaction.

Acknowledgments. This Research was supported by the Sookmyung Women’s University Research Grants 2010.

References