One-pot synthesis of ultranarrow single crystal ZnSe nanowires

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Abstract
High-quality wurtzite-type ultranarrow single crystal ZnSe nanowires were synthesized via a one-pot, solution-based approach for the first time. The as-prepared nanowires have diameters ranging from 1.0 nm to 3.5 nm and lengths up to 300 nm. The optical characterizations indicate that the as-synthesized ZnSe nanowires have a band gap of 3.31 eV, whose absorbance spectra are different from recent literatures. Both the quantum confinement and the vacancies of Zn in ZnSe or impurities were accounted for the phenomenon. The solvent employed in the synthesis is also playing a dominant role in the size and morphology control of the ZnSe nanowires. A reasonable mechanism was proposed to describe the function of solvent. The excellent properties of the ZnSe nanowires would render it a promising alternative functional material which might be widely used in short-wavelength lasers and other photoelectronic devices.

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1. Introduction
Wide-bandgap II–VI semiconductor is one of the most important functional materials widely used for optoelectronic applications [1–4]. As an important II–VI compound, ZnSe is a direct band gap semiconductor with a band gap energy (Eg) of 2.8 eV, which has drawn intensive research attention owing to its unique photophysical phenomena and potential applications in short-wavelength lasers and other photoelectronic devices [5–8].

The physicochemical properties of functional materials strongly depend upon the size and shape at the nanoscale [3, 9], which render the controllable synthesis of nanostructures a large challenge. ZnSe nanowires have been synthesized by different methods, such as metal–organic chemical vapor deposition (MOCVD) [10–14] and so on. But the diameters of ZnSe nanowires and nanorods were larger than the bulk exciton Bohr radius (3.8 nm) of ZnSe. Currently, there have been only a few reports about ultrathin ZnSe nanowires with diameters in the quantum confinement regime. [15, 16] Unfortunately, the existing synthetic schemes are very complicated, and always involve organo-phosphines as the ligands for introducing Se precursor and other expensive chemical reagents. Therefore, it is necessary to explore a simple, non-toxic and low-cost synthetic technique for ultranarrow ZnSe nanowires and nanorods.

In this letter, we demonstrate a simple solution-based approach to synthesize high-quality wurtzite-type ultranarrow ZnSe nanowires with average diameters of 2 nm. To our knowledge, this is the first example of solution-based synthesis of ultranarrow ZnSe nanowires with uniform diameters.

2. Experimental

2.1. Typical synthesis of ZnSe nanowires

All of the chemical reagents and solvents utilized in the experiment were purchased without further purification. 2 mmol Se, 2 mmol Zn(acac)2, and 30 mL oleylamine (OM) were added into a three-necked flask (100 mL) at room temperature. Then, the mixture was heated to 110 °C and kept for 30 min after vacuum pumping and N2 bubbling. The Zn–Se solution was heated to 250 °C and kept for 4 h with vigorous stirring under N2 atmosphere. Finally, the resultant mixture was washed by adding excess ethanol and chloroform, and sonicated for 20 min and centrifuged (3000 rpm and 10 min) to remove unreacted raw materials. The upper supernatant were continued to centrifuge for another 10 min at 10,000 rpm. The products were collected after ultrasonic dispersion–centrifugation cycles.

2.2. Structural and optical characterization of ZnSe nanowires

An Oxford INCA energy-dispersive X-ray spectroscopy (EDS) detector was employed to analyze the element composition and proportion. The crystal structure was characterized by powder X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.54 Å). Transmission electron microscopy (TEM) images were taken by using a JEM 2100 microscope at 200 kV accelerating voltage. A Lambda 20 UV–vis spectrometer and A Hitachi F-4600 spectrometer were used to carry out
UV–vis absorption spectra and photoluminescence (PL) spectra to evaluate the optical properties.

3. Results and discussion

Fig. 1a illustrates the XRD pattern of as-synthesized ZnSe nanowires with standard card (JCPDS 15-0105, space group: p63mc). The nanowires exhibit nearly pure hexagonal wurtzite structure. The EDS pattern (Fig. 1b) also indicates that the atomic ratio of Zn to Se was nearly 1:1. As shown in TEM images (Fig. 1c), the product consists of uniform ultranarrow ZnSe nanowires with the length up to 300 nm in a high yield close to 90%. The diameters of ZnSe nanowires (inset in Fig. 1c) are in the range of 1.0 nm to 3.5 nm. High-resolution TEM (HRTEM) image (Fig. 1d) reveals that ZnSe nanowires are single crystalline with an interplanar distance of ~0.33 nm, which corresponds to the (002) facet of wurtzite ZnSe. Also, we could conclude that the anisotropic growth of ZnSe nanowires was along the (001) direction [9, 16]. In addition, the diameter of ZnSe nanowires are not always uniform, a series of “steps” on the surface of some ZnSe nanowires can be observed, indicating that the nanowires contain extremely high defect density sites during the crystallization process.

A sharp exciton absorption peak at high energy (350 nm/3.54 eV) in UV–vis absorbance spectra (Fig. 2a) was detected, which is different obviously from reported spectra of ZnSe nanowires. And the Eg calculated by band edge (375 nm) is 3.31 eV. Compared with that of bulk ZnSe (2.6–2.8 eV = 450–480 nm), the absorption peak displayed a blue shift of about 100 nm, which originate from the quantum confinement [15, 17, 18]. The absorption spectra of ultranarrow ZnSe nanowires and nanorods reported by A.B. Panda [15, 17] indicate that the narrow width is the major controlling factor for the confinement effect. Fig. 2b shows the room-temperature PL spectrum of the ZnSe nanowires when excited at 380 nm, the wide emission band at 496 nm was attributed to the vacancies of Zn in ZnSe [19], or impurities [20]. Since the diameter of ZnSe nanowires is smaller than Bohr radius of ZnSe, strong quantum-confinement will influence the excitonic emission to some extent [15]. In addition, the electronic structure in ZnSe nanowires may be also affected by length increase-ment [4], resulting in a blue shift of PL spectrum.

Interestingly, ZnSe nanostructures can be also successfully synthesized when using oleic acid as solvent (Fig. 3a), only the morphologies...
of the ZnSe differ from the aforesaid ZnSe nanowires because of different solvents. Further experiments show the morphologies of the ZnSe are inclined to nanoparticles, rather than nanowires when the mixed solvents consist of oleic acid and oleylamine. The diameters of ZnSe nanoparticles (inset in Fig. 3a) are in the range of 4 nm to 10 nm. HRTEM image (Fig. 3b) illustrates that the ZnSe nanoparticles are single crystalline, with an interplanar distance of ~0.33 nm, which is consistent with the (002) plane of wurtzite ZnSe (viz. 0.325 nm). The EDS data display the same to those shown in Fig. 1b with the atomic ratio of Zn to Se about 1:1. Fig. 3c and d show the optical properties of ZnSe nanoparticles, which are clearly different from those of ZnSe nanowires. There are two absorbance peaks at 370 nm (3.35 eV) and 427 nm (2.90 eV), which can be attributed to the increase in diameter. [18] PL result shows a main emission band at around 468 nm when excited at 380 nm (Fig. 3c), which is attributed to the donor–acceptor pair emission in ZnSe[11].

Since different ZnSe nanostructures were successfully prepared using different solvents, the solvents play dominant roles in controlling the morphologies of ZnSe nanostructures. We proposed a mechanism for the ZnSe nanowires formation as follow: First, ZnSe nuclei were formed from the reactions between Zn(acac)$_2$ and Se$^{2-}$, in which oleylamine or oleic acid as both reducing agent of Se and stabilizer, and then several structurally heterogeneous nanocrystals may be generated simultaneously during the growth process of ZnSe nuclei. [4] However, only elongated ZnSe nanodots with mixed phase are favorable to form high aspect ratio nanostructures. [4] Due to the differences in the reactivity of solvents, the ZnSe nanostructures turn to nanowires (oleylamine) or nanoparticles (oleic acid). For wurtzite ZnSe nanowires, the high energy crystal face was (001) plane (Fig. 1c), the formed nanodots attach favorably to (001) plane because of the elimination of high energy faces [9], resulting in the formation of nanowires or nanorods. In addition, the oleylamine was assembled onto the ZnSe nanodots, and served as a highly confined and high-aspect ratio template for further growth of ZnSe nanowires along the <001> direction [18].

4. Conclusion

In summary, ultranarrow ZnSe nanowires with average diameter of 2.0 nm were successfully synthesized via a low-cost one-pot strategy. The as-synthesized ultranarrow ZnSe nanowires exhibit excellent optical properties, which are attributed to the quantum confinement, the vacancies of Zn in ZnSe or impurities. The oleylamine play a dominant role in forming ZnSe nanowires. It is reasonable to expect the convenient and simple synthetic strategy will be applicable for the synthesis of other selenides nanowires or complex nanostructures.

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References