

Video Article

Synthesis of Hierarchical ZnO/CdSSe Heterostructure Nanotrees

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Abstract

A two-step chemical vapor deposition procedure is here employed to prepare tree-like hierarchical ZnO/CdSSe hetero-nanostructures. The structures are composed of CdSSe branches grown on ZnO nanowires that are vertically aligned on a transparent sapphire substrate. The morphology was measured via scanning electron microscopy. The crystal structure was determined by X-ray powder diffraction analysis. Both the ZnO stem and CdSSe branches have a predominantly wurtzite crystal structure. The mole ratio of S and Se in the CdSSe branches was measured by energy dispersive X-ray spectroscopy. The CdSSe branches result in strong visible light absorption. Photoluminescence (PL) spectroscopy showed that the stem and branches form a type-II heterojunction. PL lifetime measurements showed a decrease in the lifetime of emission from the trees when compared to emission from individual ZnO stems or CdSSe branches and indicate fast charge transfer between CdSSe and ZnO. The vertically aligned ZnO stems provide a direct electron transport pathway to the substrate and allow for efficient charge separation after photoexcitation by visible light. The combination of the abovementioned properties makes ZnO/CdSSe nanotrees promising candidates for applications in solar cells, photocatalysis, and opto-electronic devices.

Video Link

The video component of this article can be found at <https://www.jove.com/video/54675/>

Introduction

ZnO is a II-VI semiconductor featuring a band gap (BG) of 3.3 eV, a high electron mobility, and a large exciton binding energy^{1,2}. It is an abundant semiconducting material with a plethora of present and future applications in optical devices, solar cells, and photocatalysis. However, ZnO is transparent, which limits its application in the visible spectral range. Therefore, materials absorbing visible light, such as narrow-gap semiconductors³, dye molecules⁴, and photosensitive polymers⁵, have frequently been employed for sensitizing ZnO to visible light absorption.

CdS (BG 2.43 eV) and CdSe (BG 1.76 eV) are common II-VI narrow-gap semiconductors and have been intensively investigated. The BG and lattice parameters of the ternary alloy CdSSe can be adjusted by varying the mole ratios of the VI components^{6,7}. ZnO/CdSSe nanocomposites have been reported to result in efficient photovoltaic energy conversion^{8,9}.

Combining the efficient electron transport pathway of vertically aligned ZnO nanowires towards a substrate with the improved visible light absorption of the CdSSe branches led to efficient electron transfer between the stem and branches^{9,10}. Thus, we synthesized a new tree-like ZnO/CdSSe nanostructure, where vertically aligned ZnO nanowires are decorated with CdSSe branches. This composite material can act as a building block for novel solar energy conversion devices.

This protocol describes how ZnO nanowire arrays are grown on a sapphire substrate by one-step chemical vapor deposition (CVD) from ZnO and C powders, following a procedure that has previously been published¹¹. Following the growth of ZnO nanowires, a second step of CVD is employed to grow CdSSe branches on the ZnO nanowires. We employ X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) to measure the crystal structures, morphology, and composition of the ZnO/CdSSe nanotrees (NTs). The optical properties and charge carrier transfer mechanism between the branches and stem have been investigated by photoluminescence (PL) spectroscopy and time-resolved PL lifetime measurements.

Protocol

1. Synthesis of Tree-like ZnO/CdSSe Nanostructures

1. Pretreatment and gold coating of sapphire substrates

NOTE: The gold film acts as a catalyst in the growth of the ZnO nanowires.

1. Clean sapphire slides (a-plane, 10 × 10 × 1 mm) in 99.5% ethanol with 5 min of sonication to prepare the substrate for Au sputtering.

2. Deposit a 10-nm (± 2 nm)-thick film of gold onto the sapphire slides with a sputter coater and gold target.

2. Synthesis of ZnO nanowires

NOTE: The sonication step 1.2.2 results in a homogeneous ZnO and carbon (ZnO/C) mixture. After mixing, the mixture changes to a gray color. The compaction step 1.2.3 ensures that no air is present in the mixture and that the ZnO and carbon are in close contact. After CVD, a white film of ZnO nanowires should be deposited on the substrate, side facing down towards the boat.

1. Mix 1 g of ZnO nanopowder and activated carbon (mass fraction of 50:50) in 10 ml of 99.5% ethanol and stir well with a spatula.
2. Sonicate the mixture in a water bath at 20 °C for 30 min, and then dry it in an oven for ~5 hr at 80 °C.
3. Place the ZnO/C mixture in an alumina boat and compact it well with a spatula.
4. Place the gold-coated sapphire slides on top of the alumina boat, with the gold-coated side facing down. Place the alumina boat in the center of the quartz tube in a horizontal tube furnace.
5. Purge the quartz tube for 1 hr with Ar at a flow rate of 40 sccm at room temperature (RT). Increase the temperature from RT to 900 °C at a rate of 80 °C/min and keep the argon flow rate constant.
6. Hold the temperature at 900 °C for 2 hr. Open the quartz tube on both ends by removing the rubber stopper gas inlets and let air enter the tube to provide oxygen for the reaction.
7. Keep the reaction temperature at 900 °C for 3 hr with the rubber stoppers removed. Cool down to RT at a rate of 10 °C/min.
8. Take the boat and the slide out of the furnace.

3. Deposition of CdSSe branches on ZnO nanowires

NOTE: The alumina boat of CdS/Se was displayed in the center the quartz tube. The prepared ZnO nanowires were facing upward and were 10 cm downstream from the boat. After this second CVD, an orange/yellow film, which is the ZnO/CdSSe nanostructure, should be deposited on the slide.

1. Mix 0.5 g of CdS and CdSe (CdS/Se) powder well (mass fraction of 50:50) and place the mixture in an alumina boat. Compact the mixture well.
2. Place the alumina boat of CdS/Se and the previously prepared ZnO nanowire sample in the quartz tube.
3. Purge the tube with Ar at a flow rate of 40 sccm at RT for 1 hr. Increase the reaction temperature to 820 °C at a rate of 80 °C/min. Hold the temperature at 820 °C for 30 min.
4. Cool down to RT at a rate of 10 °C/min. Take the boat and the slide out of the furnace.

4. Synthesis of control samples: ZnO and CdSSe nanowires

1. Synthesize ZnO nanowires as in section 1.2 under the same experimental conditions.
2. Synthesize CdSSe nanowires as in section 1.3, under the same experimental conditions, with the same amount of CdS and CdSe composition, but with a clean, gold-coated sapphire slide as the substrate instead of the ZnO-deposited slide.

2. Morphological and Crystallographic Characterization

1. Mount the sample on the SEM stage with a clamp and place the sample in the vacuum chamber of the SEM instrument. Take SEM images on high-resolution mode with a working distance of 12.0 mm at a voltage of 3 kV and a magnification between 3,000X and 10,000X^{11,12}.
2. Take EDS data with the same sample using the X-ray detector at the same working distance of 12.0 mm. Set the instrument to analysis mode and adjust the voltage to 20 kV, resulting in a current of 20 to 40 μA ¹³.
3. Collect XRD spectra on an X-ray powder diffractometer using filtered Cu K α radiation ($\lambda=1.5418$ Å)^{11,12}.

3. PL Emission Spectroscopy and Time-resolved PL Lifetime Measurements

NOTE: PL spectra and time-correlated single photon counting (TCSPC) measurements at RT were carried out using an amplified Ti:sapphire oscillator after second harmonic generation (SHG), producing a train of 50 fsec pulses centered at a 400-nm wavelength and with an output power of 1.76 mW¹⁴.

1. Fix the sample into a sample holder that positions the sample face up to the laser and to the detector. Align the laser to focus on the sample. Measure the PL emission spectra of the samples from 500-nm to 900-nm wavelengths using a fiber spectrometer.
2. Use a single-photon detector (avalanche photo diode or phototube) to measure time-resolved PL lifetimes with a color glass filter and a 500- or 650-nm interference bandpass filter.
3. Insert ZnO, CdSSe, or ZnO/CdSSe slides into the sample holder. Measure the pure ZnO nanowires with the 500-nm bandpass filter and the CdSSe or ZnO/CdSSe samples with a 650-nm bandpass filter.
4. Use a time-correlated single photon counter or a fast oscilloscope to measure the time-resolved fluorescence decay lifetimes.

Representative Results

Figure 1 shows the growth mechanism of ZnO/CdSSe NTs. The procedure involved a catalytic vapor-liquid-solid (VLS) process followed by a non-catalytic vapor-solid (VS) growth. In the first VLS step, ZnO and C react in the Ar atmosphere, resulting in metallic Zn and carbon oxide. Zn is subsequently dissolved in the gold precursor on the sapphire substrate. ZnO nanowires grow from the dissolved Zn and residual oxygen. In the second step, exposure to air results in the growth of long ZnO nanowires by VLS-VS on top of the short ZnO seeds. The VLS-VS mechanism has been discussed in detail previously^{11,12}. In the last step, the CdSSe branches grow directly, without a catalyst, on the ZnO nanowire.

SEM images of the ZnO nanowires obtained after the first step (Protocol 1.2) are shown in **Figure 2(a)**. SEM images of tree-like nanostructures obtained after the second step (Protocol 1.3) are shown in **Figure 2(b)** and **(c)**. We employed EDS to determine the composition of the NTs. The branches contained S and Se, with a mole percentage ratio of around 0.53:0.47. EDS element scans were performed at three different positions on the NT, indicated in **Figure 2(c)**. **Figures 2(d)**, **(e)**, and **(f)** show the composition of the stem, the branch, and the cap, respectively. An element line scan mapping along the line in **Figure 2(g)** is shown in **Figure 2(h)**. The element scan shows that the cap and stem can be clearly distinguished in the scan that shows only contributions from Zn and O in the area of the stem. The crystal structures of the NTs were measured via XRD. They are compared to the crystal structures of pure ZnO and CdSSe nanowires, shown in **Figure 3**. Pure ZnO and CdSSe nanowires show the expected hexagonal wurtzite structure, with characteristic peaks at (100), (002), (101), and (102)^{13,15}. A very strong and narrow peak at (002) for ZnO can be explained by the one-directional growth of the vertically aligned ZnO nanowires. The XRD measurement of the NTs shows a combination of ZnO and CdSSe wurtzite structures. According to Vegard's law, the mole ratio of S:Se was determined from the XRD data to be 0.54:0.46, which corresponds to the EDS result. The CdSSe in the NTs showed an additional peak that is assigned with the (111) plane of the zincblende phase and is discussed later.

PL spectra and time-resolved PL measurements employing TCSPC are shown in **Figure 4(a)** and **(b)**, respectively. In **Figure 4(a)**, the fluorescence emissions of ZnO, CdSSe, and ZnO/CdSSe have maxima at 514 nm, 646 nm, and 627 nm, respectively. A 500-nm bandpass filter was chosen for the ZnO PL lifetime measurement, while a 650-nm filter was used for measuring the emission from CdSSe and ZnO/CdSSe NTs. Time-resolved PL measurements were fitted using single- or bi-exponential functions. In **Figure 2(b)**, the PL lifetime of ZnO/CdSSe NTs (0.11 nsec) is shorter than the lifetimes of either ZnO (3.67 nsec) or CdSSe (1.06 nsec) at a 400-nm excitation. This can be explained by fast electron transfer from the conduction band (CB) of CdSSe to the CB of ZnO. In the isolated nanowires, excited electrons recombine radiatively on a nanosecond time scale. If the CdSSe branches are in contact with the ZnO stem, excited electrons can transfer non-radiatively from CdSSe to ZnO, with a time scale that depends on the interface and that can be much faster than the radiative lifetime. Therefore, the PL lifetime of ZnO/CdSSe NTs is reduced by electron transfer across the interface.

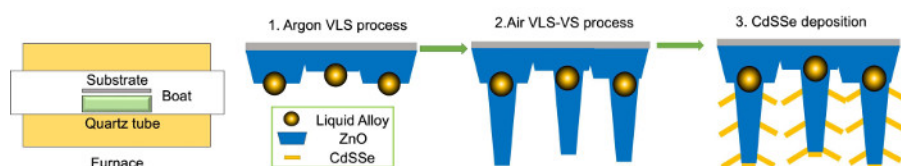


Figure 1. Schematic synthesis of ZnO/CdSSe NTs. The set-up inside the furnace is shown on the left. The following images show the three steps of NT preparation involving: the VLS process in Ar, the VLS-VS process in air, and the deposition of CdSSe branches. Reproduced from Ref. 17. [Please click here to view a larger version of this figure.](#)

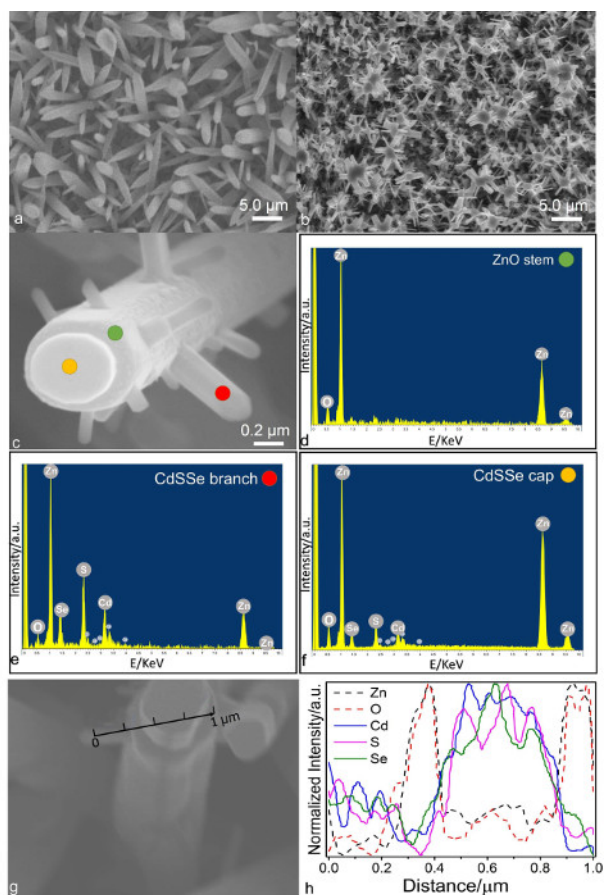


Figure 2. SEM images and EDS spectra. a) SEM image of ZnO nanowires prepared via CVD; b) and c) SEM images of ZnO/CdSSe NTs prepared via CVD; EDS spectra of the ZnO stem, CdSSe cap, and CdSSe branch of ZnO/CdSSe NTs are shown in d), e), and f), respectively; h) The element line scan along the line shown in g), reproduced from Ref. 17. [Please click here to view a larger version of this figure.](#)

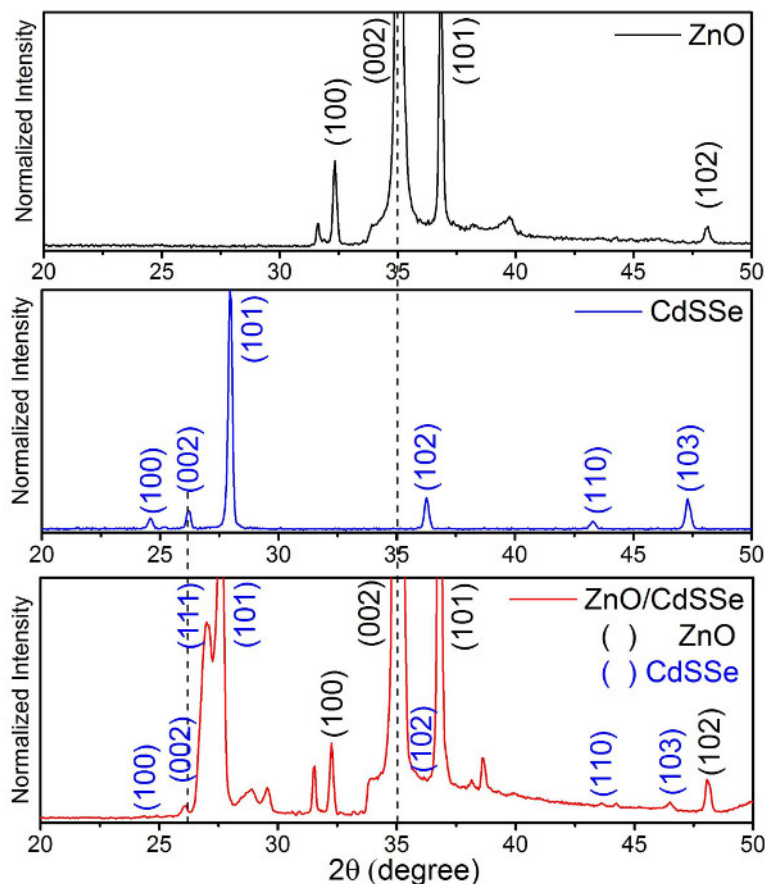


Figure 3. XRD Spectra of ZnO, CdSSe, ZnO/CdSSe NTs. (100), (002), (101), and (102) peaks, characteristic of the ZnO and CdSSe wurtzite structure for the bare nanowires, are shown. The additional peaks from the NTs can be identified with the (111) plane of CdSSe in the zincblende structure, as discussed in the text. Reproduced from Ref. 17. [Please click here to view a larger version of this figure.](#)

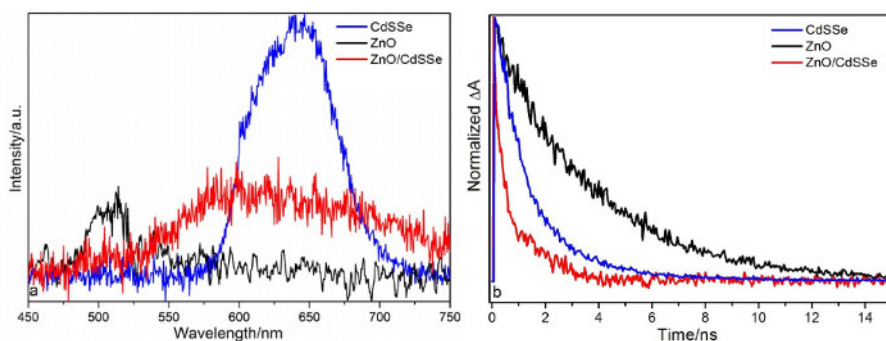


Figure 4. PL spectra and TSCPC measurements. PL spectra (a) and TSCPC measurements fitted with single-exponential decay (b) of ZnO, CdSSe, and ZnO/CdSSe NTs excited with a 400-nm-wavelength laser. The PL spectra show fluorescence of ZnO, CdSSe, and ZnO/CdSSe at 514 nm, 646 nm, and 627 nm, respectively. Lifetimes of ZnO, CdSSe, and ZnO/CdSSe are 3.67 nsec, 1.32 nsec, and 0.72 nsec, respectively. Reproduced from Ref. 17. [Please click here to view a larger version of this figure.](#)

Discussion

The vertical alignment of ZnO nanowires (stems) is based on epitaxial growth on the substrate. ZnO nanowires grow preferentially along the $\langle 0001 \rangle$ direction that matches with the periodicity of the a -plane of sapphire¹². Therefore, the type and the quality of the substrate are very important. Different thicknesses of the gold coating on the substrate, from 5 nm to 20 nm, have been tested and showed no significant difference in the growth of ZnO nanowires. The length of the ZnO nanowires can be adjusted by changing the amount of the ZnO/C mixture that is used, the Ar flow rate, and the air exposure time. For synthesizing ZnO nanowires with a consistent length, an oxygen/argon mixture with a well-defined ratio or artificial air (oxygen/nitrogen mixture) is recommended as the carrier gas. So far, the longest ZnO nanowires that have been grown in our lab using this method were 30 μm , and the shortest were 5 μm .

During CdSSe deposition, the temperature at the substrate position is the key parameter that controls the composition of the ternary alloy. Inside the quartz tube, the temperature gradient from the center of the furnace towards the ends is controlled by the furnace settings, the tube length and diameter, and the flow rate of the carrier gas. The position of the substrate determines the growth temperature and consequently, the composition. Since we have strong indications that the growth of the CdSSe branches on the ZnO stem is epitaxial, as discussed below, it is important to find the position in the quartz tube with the correct temperature for the growth of a 50:50 S:Se mole ratio (around 720 °C)¹⁴. For tuning the mole ratio of S and Se, several trials may be necessary to find the correct settings and position in the tube. The color of the resulting ZnO/CdSSe NTs is a first indicator of whether the proper ratio was achieved; it should be orange. A bright yellow color indicates a high sulfur content, while a dark red color indicates too much selenium in the CdSSe. The actual ratio can be measured by EDS or XRD.

The reason for the formation of CdSSe branches instead of a CdSSe/ZnO core-shell structure can be explained by the measurements of the crystal structure. The XRD shows a shoulder at 26.5° that is identified as the (111) plane of the zincblende phase of CdSSe (Figure 3)¹⁶. The growth of the CdSSe branches is likely initiated by point defects on the (1010) surface of the hexagonal ZnO stem. The occurrence of the zincblende phase can be explained by the growth of cubic CdSSe on the (1010) surface of ZnO that differ in their lattice parameters by integer numbers and can give rise to epitaxial growth. As the branches grow longer, the crystal structure merges into the more stable hexagonal phase that accounts for the strong (101) signal in the XRD. Since the lattice parameters are determined by the mole ratio, and the mole ratio depends on the growth temperature, careful adjustment of all parameters that influence the temperature is critical.

This is one demonstration of tree-like nanostructures composed of different materials in the branches and stem. The method should in principle work for other material combinations. However, some relationship between the lattice parameters of the stem and the branches is required in order to grow branches instead of a core-shell structure. In addition, the deposition temperature of the branch material must be below that of the stem material to prevent the destruction of the stem in the last preparation step. An alternative method for nanoparticle synthesis involves solvothermal growth. There have been a handful of reports about tree-like composite NTs synthesized by solvothermal methods. Compared with solvothermal methods, solvent-free CVD is more environmentally friendly and enables the preparation of materials with higher purity. However, CVD also has some limitations. CVD is usually operated at high temperatures to vaporize precursors, and prepared samples may have different compositions at elevated temperatures.

In summary, we prepared a novel ZnO/CdSSe vertically aligned tree-like nanostructure. Both the ZnO stems and the CdSSe branches were predominantly in wurtzite structure. TCSPC measurements show fast charge transfer from the CdSSe branches to the ZnO stems. The tunable BG of the CdSSe branches, the transparent ZnO stems, and the efficient charge transfer between both makes ZnO/CdSSe NTs a promising material for optical, photovoltaic, and photoelectrochemical applications.

Disclosures

Data and figures in this article are cited from the literature in nanotechnology by Li *et al.*¹⁷.

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