

Novel CdS Nanostructures: Synthesis and Field Emission

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Here, we reported the success in the synthesis of novel CdS nanostructures, nanotubes, core-sheath nanowires, and tube–wire nanojunctions, by thermal evaporation of CdS powder and proposed a model for the growth mechanism. The core–sheath nanowires consist of a crystalline core and amorphous sheath. The photoluminescence characterization indicated that the CdS nanostructures were crystalline and showed a narrow peak at 516.5 nm. In addition, the CdS nanostructures exhibited better field emission properties with a field enhancement factor of 1.5×10^4 and turn-on field of 1.4 V/ μm .

Introduction

Nanostructured materials are of both fundamental and technological interest for their intriguing and potentially useful structural, physical, and chemical properties. Semiconductor nanostructures play an important role in many areas of modern science and technology, especially in nanoscale photonic and electronic devices, such as direct-current nanogenerator, light-emitting diodes, polarization sensitive photodetectors, and optically and electrically driven lasers.^{1–5} Various morphologies of semiconductor nanostructures have been reported, including nanowires, nanobelts, nanocombs, nanosprings, nanorings, nanotubes, and nanodots.⁶ As a II–VI semiconductor compound, CdS has attracted considerable interest in optoelectronic applications because of its band gap energy (2.52 eV) in the visible region and due to its nonlinear properties.⁷ CdS has been widely used as an *n*-type window material in thin-film solar cell devices. Naturally, a lot of research has been done on bulk as well as nanostructured CdS. CdS nanostructures, including nanowires, nanotubes, and nanobelts, have been synthesized using various methods.^{8–11} The lasing and electronic transport properties of the CdS nanostructures had been reported.^{10–13} To the best of our knowledge, CdS core–sheath nanowires and tube–wire nanojunctions have not been reported. In this letter, 1-D CdS nanostructures, nanotubes, core–sheath nanowires, and tube–wire nanojunctions were synthesized by the thermal evaporation of CdS powder. These CdS nanostructures showed higher emission efficiency with lower threshold voltage.

To synthesize the 1-D CdS nanostructures, the CdS powder was placed at the center of a quartz tube. The silicon (100) wafer with one face polished and sputtered with a layer of gold (7 nm) was placed 10 cm away from the CdS powder at the downstream. The powder was heated to 900 °C as quickly as possible in a protective helium (99.999% in purity) flow at a rate of 100 sccm. The temperature was maintained at 900 °C for several minutes without changing the conditions. The tube was cooled down to room temperature with the protective He flow. The CdS nanostructures were characterized by scanning electron microscope (SEM, JEOL JSM-6700F) and transmission

electron microscope (TEM, JEOL 2010). The photoluminescence (PL) was characterized by the laser pulses generated by a Ti:sapphire amplifier (Quantronix, Titan) at room temperature, which was seeded by an erbium-doped fiber laser (Quantronix, IMRA). The laser was operated at a repetition rate of 1 kHz with a pulse duration of 1.6 ps and a wavelength of 780 nm. The measurements of field emission (FE) of the samples were carried out in a two-parallel-plate setup with a high vacuum of about 5×10^{-7} Torr.¹⁴ The Si wafer with the 1-D CdS nanostructures was attached to a Cu substrate, which serves as cathode, by using double-sided copper tape. Indium tin oxide (ITO) glass covered with a layer of phosphor was employed as the anode. A polymer film was used as a spacer and the distance between the electrodes was kept at 200 μm . A high voltage source measurement unit (SMU, Keithley 237) was used to apply a voltage from 0 to 1100 V and to measure the emission current. All the measurements were performed at room temperature.

SEM image shows that the 1-D CdS nanostructures as-grown on silicon substrate have diameters in a range from 400 to 150 nm and lengths up to a few hundreds of micrometers (see Supporting Information). The surface of the CdS nanostructure was not smooth, but decorated with smaller particles. Figure 1 provides the TEM images of the 1-D CdS nanostructures. Figure 1a shows that the center part of one CdS nanowire consists of a core and a sheath. The crystalline structure of the core is clearly illustrated by the selected area electron diffraction (SAED). As shown in the inset of Figure 1a, the diffraction pattern was taken from a selected area covering a 1.0 μm segment of the wire, indicating the single crystallinity and wurtzite structure of the core. However, the sheath is amorphous (SAED not shown here). The elements, S and Cd, were confirmed by the energy dispersive X-ray spectroscopy (EDX) spectra (insets in Figure 1a). Cu was from the copper grid. Si should be from the substrate. For the core, the intensities of S and Cd are almost equal to each other, while the intensity of S is larger than that of Cd for the sheath. The intensity ratio of Si/S (or Si/Cd) in the sheath is larger than that in the core, indicating that Si mainly entered the sheath. The presence of oxygen in the EDX indicated that silicon in the sheath was partially oxidized. The core–sheath structure was also observed on the top part of one nanowire (Figure 1b). A particle can be

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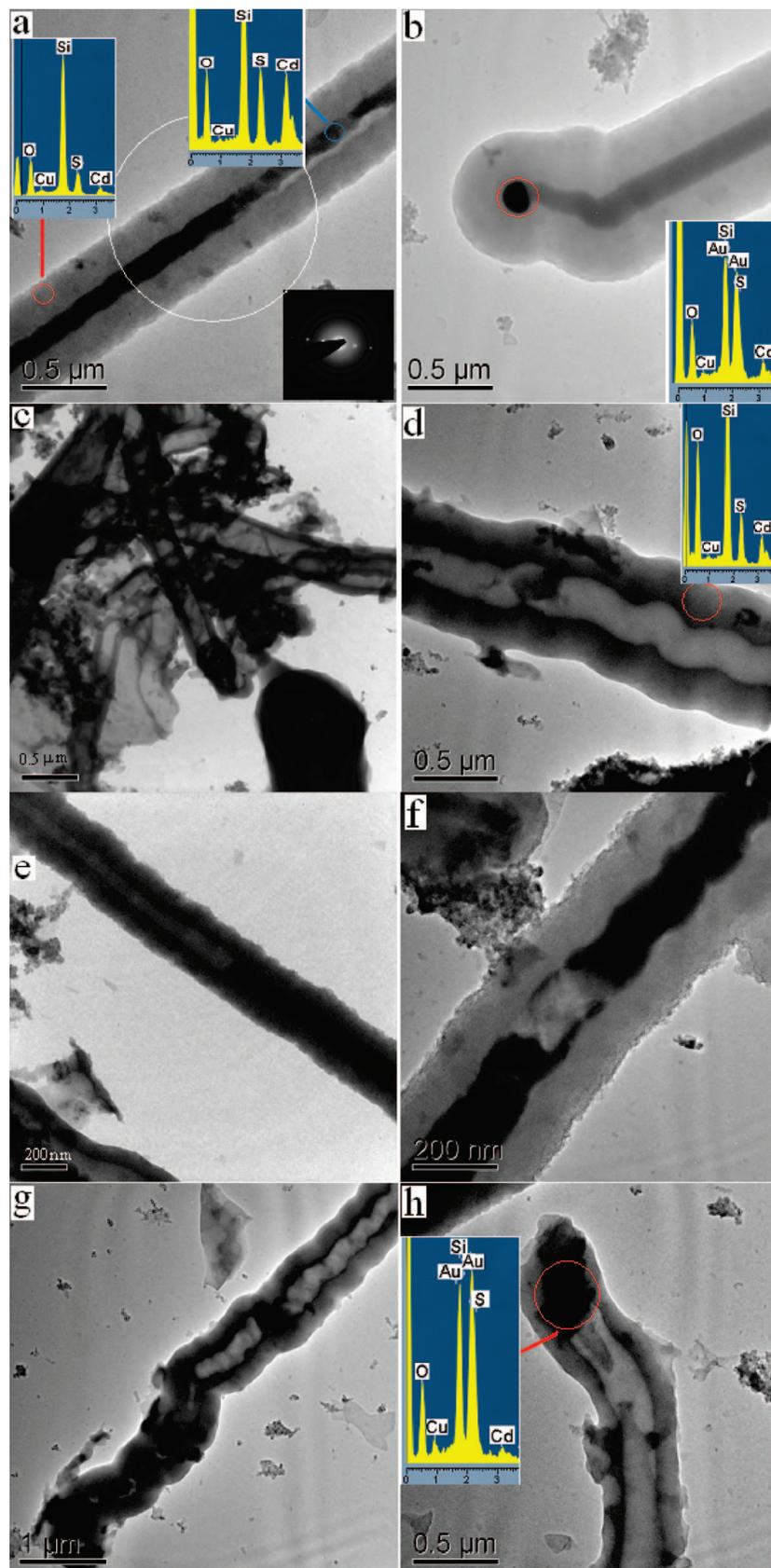


Figure 1. TEM images of the 1-D CdS nanostructures: (a) a core–sheath nanowire with the insets (EDX of the core and the sheath and SAED of the core); (b) the top of a core–sheath nanowire with the inset (EDX of the catalyst); (c) and (d) CdS nanotubes; (e) tube–wire nanojunction; (f) wire–tube–wire nanojunction; (g) the top part of a nanotube with nanoparticles with the channel; and (h) the top part of one nanotube with the catalyst (inset shows the EDX of the particle).

seen located at the top of the core nanowire within the sheath. The EDX analysis indicated that it is the gold catalyst (inset in

Figure 1b). Besides the core–sheath nanowires, CdS nanotubes can also be observed from the TEM images, as shown in Figure

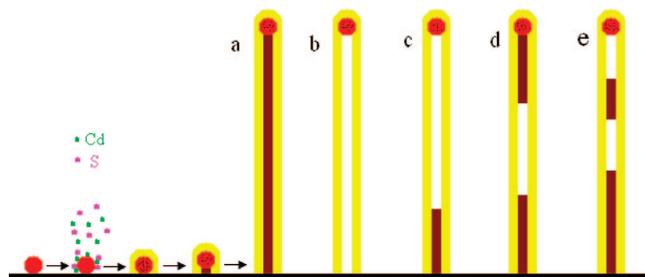


Figure 2. Schematic presentation of the growth mechanism for the variety of 1-D CdS nanostructures.

1c. We can see that the channel in the nanotube was not smooth, but like the path of an “earthworm”, from a fine view to one nanotube (Figure 1d). The SAED indicated that the wall of the nanotube is amorphous. Also, the EDX analysis shows that intensity of S is larger than that of Cd on the wall of the nanotube (inset in Figure 1d). Figure 1e illustrates another structure of the 1-D CdS nanostructures, the heterojunction of nanotube and core–sheath nanowire. The core in the core–sheath structure suddenly stopped growing, which leaves the channel empty, leading to the formation of the nanotube, and results in the tube–wire junction structure. Figure 1f shows the CdS nanowire–nanotube–nanowire structure, where the nanowire is a core–sheath structure. It looks like the core stopped growing and retained late, and an empty channel was formed in the interval. Figure 1g shows that some CdS nanoparticles were embossed in a CdS nanotube with the catalyst (Au) at the top and within the narrow channel. A CdS nanotube with the catalyst and an empty large channel was also shown in Figure 1h. The EDX pattern (inset in Figure 1h) clearly shows that the particle within the top of the tube is gold.

For the catalyst-assisted synthesis of the 1-D CdS nanostructures, the catalyst (Au) plays a role as seed and enhances the growth of the nanostructure. To understand the mechanism for the formation of a variety of the 1-D CdS nanostructures, a growth model was proposed as follows. When the furnace reached the designated temperature, the CdS powder decomposed and the Au film became separate liquid nanoballs. S and Cd atoms reached the Si substrate with the protective gas, then entered and covered the Au catalysts. When the concentrations of the S and Cd were saturated, a layer of CdS was formed between the nanoball and the substrate, which leads to the formation of the core nanowire. This vapor–liquid–solid process (VLS) results in the crystalline structure of the core (inset in Figure 1a). At the same time, the S and Cd atoms that covered the surface of the Au nanoball also formed an interface with the substrate and a sheath around the core. The formation of the sheath is a vapor–solid process (VL). If the growth rate of the core is equal to that of the sheath, the core–sheath nanowire can be produced (Figure 2a), as illustrated in the TEM images (Figure 1a,b). If the growth rate of the sheath is much quicker than that of the core, the catalyst would be pushed up before the formation of the core and only a nanotube can be formed (Figure 2b), as seen in Figure 1c,d,h. In some cases, the core–sheath nanowire was initially formed, but the core stopped growing due to interaction between the core and the sheath, the insufficient source supply from the catalyst, or/and the quicker growth rate of the sheath, and the sheath continues to grow, which leads to the nanotube–nanowire junction (Figure 2c) (see Figure 1e). The inside core may survive to grow in the late stage due to the interaction between the sheath and the catalyst (because the nanotube channel is not smooth as indicated in Figure 1d) and the sufficient supply of the source, which

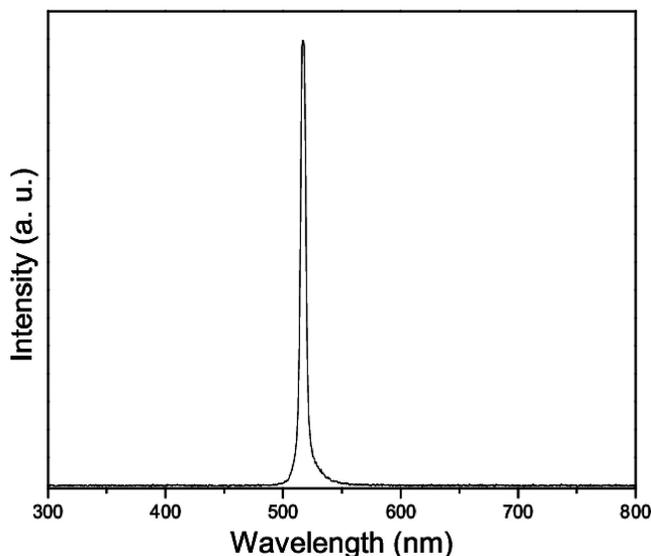


Figure 3. PL characterization of the CdS nanostructures.

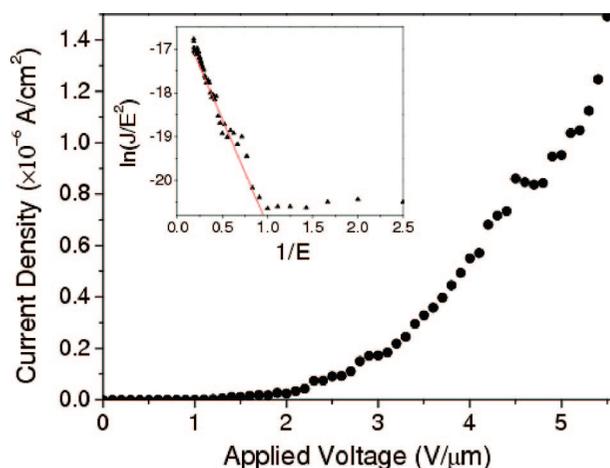


Figure 4. Field emission property of the nanostructures.

leads to the formation of the nanowire–nanotube–nanowire structure (Figure 2d,e) (see Figure 1f). In other cases, the survived core cannot keep growing for a long time and CdS nanoparticles were produced within the sheath (Figure 1g). The variety of 1-D nanostructures grown by thermal evaporation should be attributed to the complex interactions among the catalyst, the core, and the sheath, the source supply, and the size of the catalyst.

Figure 3 shows the PL of the CdS nanostructures. The PL peak is at 516.5 nm (2.4 eV) and has a full width at half-maximum (fwhm) of about 4 nm. The corresponding energy is less than its bulk band gap (2.52 eV) due to the room-temperature band-edge emission from CdS. The smooth curve with a sharp peak indicates that the cores of the CdS nanowires are highly crystalline and can serve as single-mode optical waveguide. And the PL characterization also illustrates that the core of the CdS nanowires is pure, although Si and O existed in the sheath of the nanostructures as indicated in EDX patterns (Figure 1).

The field emission current density as a function of the macroscopic electric field is shown in Figure 4. It is clear that the 1-D CdS nanostructure exhibits a low turn-on field (1.4 V/μm), whereas comparable films of pure multiwalled carbon nanotubes require higher applied fields in order to observe the onset of electron emission. The Fowler–Nordheim (FN) plot for

the measured sample is shown in the inset (Figure 3). It is clear that the measured data fit well with the FN equation:¹⁵

$$\ln\left(\frac{J}{E^2}\right) = \ln\left(\frac{A\beta^2}{\phi}\right) - \frac{B\phi^{3/2}}{\beta E} \quad (1)$$

where J is the emission current density (A/cm^{-2}), E is the applied field ($\text{V } \mu\text{m}^{-1}$), $A = 1.543 \times 10^{-6} \text{ A eV V}^{-2}$, $B = 6.833 \times 10^3 \text{ eV}^{-3/2} \text{ V } \mu\text{m}^{-1}$, β is the field enhancement factor, and ϕ is the work function of emitter material (4.7 eV for CdS¹⁶). The calculated field enhancement factor β from the slope of the inset (as indicated by the line) is 1.5×10^4 . The turn-on field is much lower than that of CdS nanowires, and the β value is much higher than that of nanowires.¹⁷ The lower turn-on field and higher field enhancement factor contributed to the low density, long length, and high crystalline structure of the core. Also, the sheath prevents the cores from interacting with each other, contributing to the lower turn-on field.

In summary, a variety of 1-D CdS nanostructures, including nanotubes, core-sheath nanowires, and tube-wire nanojunctions, were synthesized by a simple method, the thermal evaporation of CdS powder with gold as the catalyst. The complex interaction among the catalyst, the core, and the sheath contributed to the variety of the 1-D nanostructures. The cores of the core-sheath CdS nanowires are highly crystalline and exhibit good optical properties. These materials are potentially applicable to nanodevices.

Supporting Information Available: Figure of SEM image. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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