

Preparation and Periodic Emission of Superlattice CdS/CdS:SnS₂ Microwires

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Abstract: Semiconductor superlattice micro-/nanowires could greatly increase the versatility and power of modulating electronic (or excitonic, photonic) transport, optical properties. In this communication, we report growth of a semiconductor CdS/CdS:SnS₂ superlattice microwire through a coevaporation technique with microenvironmental control. Such a novel superlattice microwire can modulate the exciton and photons to show multipeak emissions with periods in a wide spectral range, which arise in the 1-d photon crystal and confined exciton emission. This system can be widely used in producing multicolor emissions, low-threshold lasing, study light-matter interaction, slow light engineering, and weak nonlinear optical devices.

One-dimensional (1D) nanostructures with modulated compositions and microstructures have gained a tremendous amount of attention in the past few years due to their fascinating chemistry and size-, shape-, and material-dependent properties. Among 1D segmented structures, semiconductor superlattice nanowires with a periodic composition modulation along the axial direction have recently become of particular interest. This is due in part to the exciting electronic and optical applications of new 1D nanophotonic building blocks.^{1–4} For example, the “excitonic lattice” can provide coherent interaction of local excitons and modulate light propagation which opens up possibilities for studying new states formed when excitons interact with their emitted photons.⁵ To date, several well-developed chemical vapor deposition techniques have successfully been used to synthesize the superlattice structures.^{6–8} In these studies, the vapor–liquid–solid (VLS) growth mechanism^{9,10} takes effect in superlattice nanowire growth via altering the reaction atmosphere periodically. Other synthetic methods such as the template-based electrochemical method,^{11–13} partial cation exchange techniques,¹⁴ and atomic layer deposition¹⁵ have also been reported. All these techniques can tune the electronic band location of the products, but not to modulate light propagation. Therefore, developing methods to obtain building blocks of superlattice nanowires with tunable interfaces, size, and composition in a predictable manner and modulate both electrons and photons *in situ* is very important for the realization of multifunctional nano- and micrometer scale photonic devices.

In this communication, we report the fabrication of CdS/CdS:SnS₂ superlattice wires through a coevaporation technique with local environmental control. Such a novel superlattice wire with a thickness of 400 nm to 5 μm can modulate exciton emission and photon propagation with spectral periodical multi-peaks, which may be used in producing multicolor emissions and low-threshold lasing, studying light-matter interaction, slow light engineering, and weak optical nonlinearities.

1D superlattice wires were produced by a precisely controlled thermal evaporation. A mixture of CdS (0.1 g, Alfa Aesar, 99.995% purity) and SnO₂ (0.01 g, 99.5% purity) was placed in the center of a single zone tube furnace which was evacuated for 2 h to purge oxygen in the tube. A treated Si (100) substrate was placed 8 cm away from the source powders and along the downstream side of flowing Ar (90%) and H₂ (10%). Typically, the source site was heated to about 980 °C at a rate of about 120 °C/min. During the growth process, the 40 sccm mixture of carrier gas was injected into the tube. Then, the superlattice microwires with varied segment lengths can be achieved by changing the deposition time, location, and some other factors.

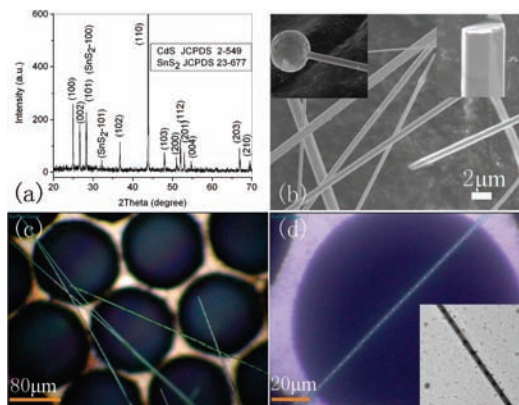


Figure 1. (a) Normalized X-ray diffraction patterns and (b) SEM image of the as-grown sample prepared by evaporating CdS and SnO₂ mixed powders. Insets in (b) are the magnification morphology images of a typical sample, ending with a microsphere and a hexagonal solid wire at two sides, respectively. (c and d) Optical images at different magnifications of periodic alternating microwire dispersion on a copper grid, showing a superlattice structure. Inserted image in (d) shows transmission confocal mode.

The product covering an approximately 10 mm region on the end of the Si substrate (where the temperature was about 650 °C during reaction) was collected, and then its X-ray powder diffraction (XRD) pattern (Figure 1a) was obtained. The results show that the as-grown product is composed of two crystalline phases, a hexagonal (wurtzite) form of CdS (JCPDS: 2-549) and hexagonal SnS₂ (JCPDS: 23-677). No characteristic peaks from other impurities, such as CdO, SnO, and SnO₂, were detected in the XRD spectrum. Figure 1b presents an SEM image of the sample which shows their diameter ranging from 400 nm to 2 μm. Most of the wires were capped with a microsphere on their tops (left inset in Figure 1b), indicating a likely VLS process for the formation of these wires. The inserted top right image shows the typical hexagonal facet end of a wire. Far-field optical images of the products at different magnifications are shown in Figure 1c and 1d, respectively. It can be clearly seen that the products are long microwires with regions of periodic and alternating indices of refraction, that is, microwire superlattices. The inserted image in Figure 1d obtained in transmission mode further confirms a superlattice structure. In Figure

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S1, the position dependent TEM image and related EDS profiles indicate the long section in the periodic wire is mainly composed of Cd and S, while the short section is mainly made up of Cd, Sn, and S. Combined with the analysis of the micro-Raman spectrum in Figure S2, it can be concluded that the long section is CdS and the short section is the composite CdS:SnS₂. Possible growth processes for this superlattice wire are schematically shown in Figures S3.

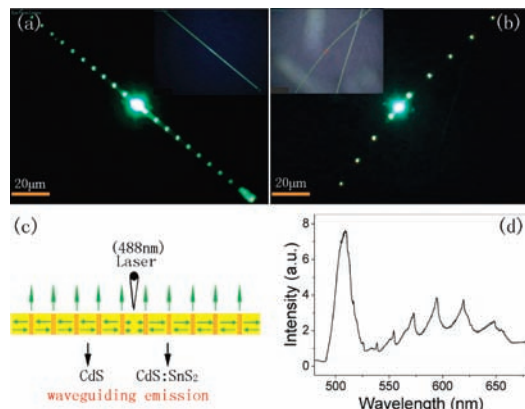


Figure 2. Far-field PL images of an excited sample with different reaction times: (a) 20 min; (b) 30 min. Insets in (a) and (b) are corresponding optical images. (c) Schematic representation of emission process of the 1D superlattice wire, $\lambda_{\text{exc}} = 488$ nm. (d) Micro-PL spectrum of the periodic CdS/CdS:SnS₂ superlattice wire in (a).

As a wide band gap semiconductor, CdS with near-cylindrical geometry and large dielectric constants exhibits good waveguiding.^{16,17} However, what happens if CdS was separated by an inactive SnS₂ layer in a 1D superlattice wire? Figure 2 exhibits the emission behavior of an individual wire from the CdS/CdS:SnS₂ superlattice wires which was characterized by a confocal optical system using an Ar-ion laser with an excitation wavelength of 488 nm at room temperature. Figure 2a shows the microphotoluminescence (PL) image with well-defined emission periodicity for a wire obtained under constant temperature growth for 20 min. The inset is the corresponding far-field optical image. In addition to a bright facula on the excitation center, several periodic green spots separated by dark regions can be seen; each spacing between two bright spots is about 7.3 μm , which is equal to the length of the CdS segment. That is, the positions of the points of luminescence are the precise locations of CdS:SnS₂ junctions. In contrast to the previous reports, which shows a single emission peak from the low band gap component locations in a Si/Ge⁶ and GaAs/GaP⁸ superlattice nanowire, a multiple-peak PL spectrum is obtained from a superlattice wire here.

In our wires, CdS has a direct band gap of 2.4 eV and refractive index of 2.4. The SnS₂ has a smaller indirect band gap of about 2.0 eV and refractive index of 3–3.3. The CdS segments in the superlattices may form many optical microcavities in queue which confine and transport photons, while SnS₂ with a larger refraction index in the short CdS:SnS₂ section might work as both reflection end faces and emission center. The periodic bright emissions arise exactly from the interference of coherently scattered light waves on the end faces of the microcavities (Figure S6) and SnS₂ emission. Figure 2c and 2d illustrate the emission profile of a superlattice wire and corresponding micro-PL spectrum, which exhibits a strong CdS band edge emission at ~ 509 nm and multi-peak range of 525–650 nm. The multi-peaks are not Fabry–Perot modes, since the calculated mode spacing suggests a 2.9–3.4 μm cavity and the true dimension is 7.3 μm . The modes likely originate from the longitudinal photon propagation selection in the coupled optical microcavities.¹⁸ Images of the selected waveguiding are shown in Figure S6.

A single-microwire PL study was used to assess the degree of control in our superlattice wire growth. It was found that systematic variations in the growth time lead to microwire superlattices with well-defined changes in periodicity. Figure 2b shows the PL image of the product with a growth time of about 30 min. Its separation distance between bright emission spots is about 15 μm , which is larger than double the size of the wire shown in Figure 2a. Moreover, partially hollow cavity structures, as reported in ref 19, can be found if the constant-temperature growth time is longer than 60 min with high Sn concentration. The constant temperature heating time is crucial for formation or controlling the length of a CdS microcavity in this superlattice structure growth as shown in Figure S7. In addition to the growth time and source temperature, other microenvironmental parameters including heating rates, carrier gas flow rates, and the weight ratio of the two source precursors also influence this 1D superlattice wire growth. A relatively high heating rate and strong carrier gas flow produce more source vapor, generally leading to more wires with thicker bases and tapered ends, but not superlattices. The uniform Sn-core/CdS-shell microwires can form when the weight ratio of SnO₂/CdS is increased to 1/5–3/5.

In summary, we reported the fabrication of a CdS/CdS:SnS₂ superlattice microwire through a coevaporation technique with microenvironmental control. Tuning the growth time and source temperature can modify the domain periodicity of the superlattice microwires. The novel multi-peak emission with controllable periods was observed for the first time. The emission profiles were produced by the combined contributions of 1-d photonic crystal and periodical exciton confinement which could provide a new materials platform for a wide range of applications from optical microbarcodes, low-threshold lasers, one-dimensional waveguides to 1D photonic crystals, and exciton–light interaction, all of which are currently being pursued.

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Supporting Information Available: The position dependent TEM image and related EDS, micro-Raman spectrum, schematic of growth process, typical optical images and mapping images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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