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Supplementary Information

Growth of CdS Nanotubes and their Strong Optical Microcavity Effects

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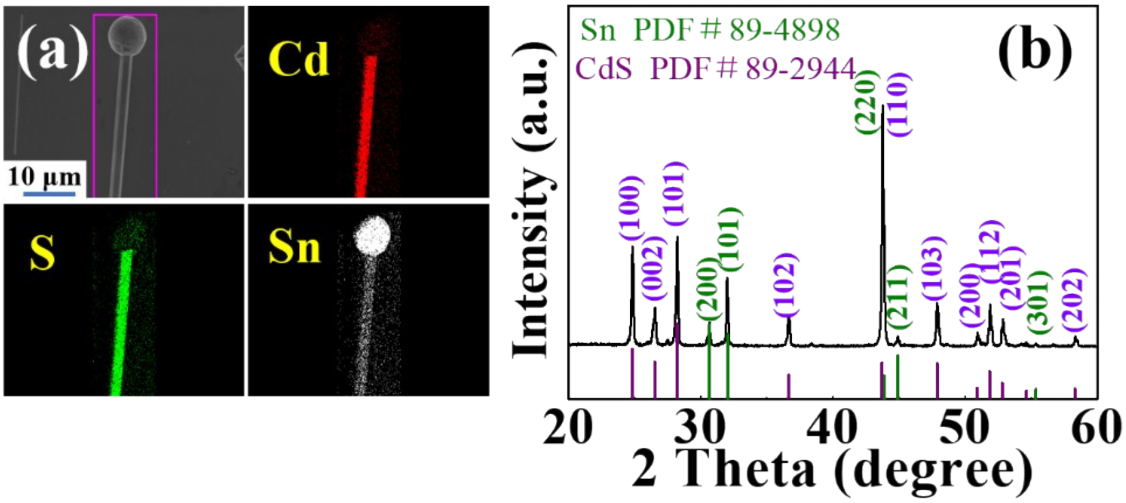

Figure S1. (a) EDS mapping and (b) XRD pattern for a Sn/CdS core-shell nanowire.

Figure S1 shows the EDS mapping and XRD pattern of a Sn/CdS core-shell nanowire. Figure S1(a) confirms that Sn core is uniformly distributed within the nanowire and the wire terminates at a Sn nanocluster. The as-grown product is composed of two crystalline phases shown in figure S1(b), i.e., the hexagonal (wurtzite) structure of CdS with lattice constants of a = 4.14 Å and c = 6.715 Å and the tetragonal Sn metal with lattice constants of a = 5.831 Å and c = 3.182 Å, which are consistent with the JPCDS cards of #89-4898 and # 89-2944, respectively. There is no other peak to show the existence of other impurities or secondary phase (such as CdO, SnO, SnO_2, SnS, and SnS_2) in the XRD pattern.

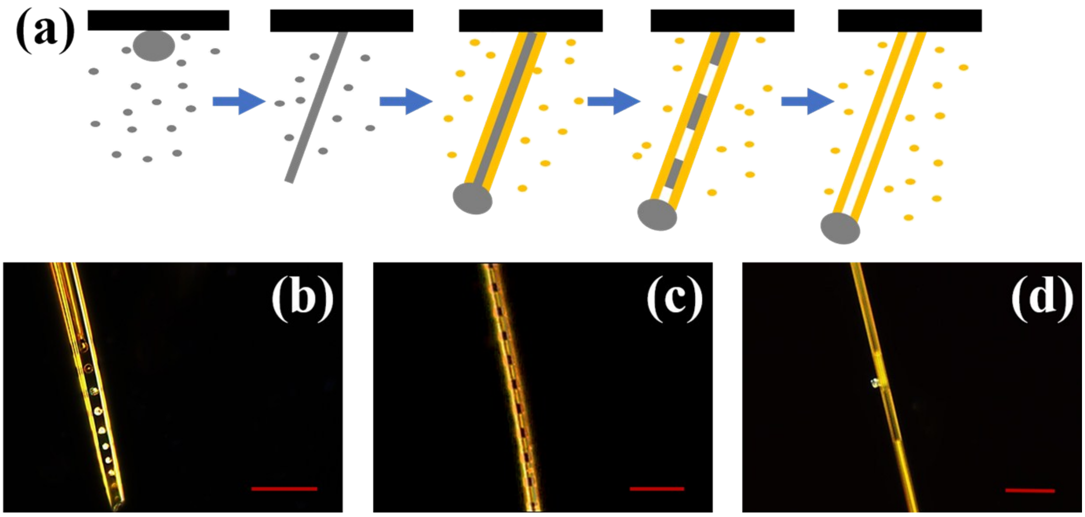

Figure S2. (a) Schematic illustration of the growth process of the Sn/CdS core-shell nanowires. (b-d) Real-color images of the Sn/CdS core-shell nanowires in the dark field of microscope ($\boldsymbol{r}$ = 15:1, $\boldsymbol{T}$ = 900 ℃, $\boldsymbol{t}$ = 20 min). The scale bars in the pictures are 10 μm.

According to Ref. [1], the growth process of the Sn/CdS core-shell nanowires was shown in Figure S2(a), which is also similar with that for the CdS/CdS:SnS_2 superlattice microwires. [1] For convenience, we denote the experimental parameters of the mass ratio of CdS to SnO_2 powders, reaction temperature, and growth time as $\boldsymbol{r}$, $\boldsymbol{T}$, and $\boldsymbol{t}$, respectively. Firstly, the mixed powders of SnO_2 and CdS (as precursors) react with H_2 in the carrier gas of Ar at a certain temperature. Some of them were reduced to metal Sn, Cd, H_2S, H_2O gases. The Sn gas was firstly formed (melting point of Sn is 232 ℃) and transported to a low-temperature region (deposition zone) in the tube by the carrier gas to form small Sn liquid clusters or droplets. The Sn droplets provide a preferential surface site for the adsorption of Sn gas or other droplets, resulting in the one-dimensional growth of the Sn metal. As the temperature increases quickly (～100 ℃/min), the Sn and Cd vapor mixed with the CdS sublimation were transported to the deposition zone and deposited on the surface of the Sn nanowire to form the CdS shell. Addition of H_2 could reduce SnO_2 to O_2 and Sn gas and improve the yield of CdS vapors via the reaction: $CdS + H_2 \leftrightarrow Cd + H_2S$. The oxygen can combine with H_2 to form H_2O gas, taken out by the carrier gas from the tube. The Cd vapor forms alloy with Sn on the Sn nanowire surface and then react with S or H_2S to form the CdS shell. After some heating time, Sn nanowire could be liquefied and ejected out of the CdS wire due to the instability liquid at high temperature. Finally, the CdS nanotubes were formed. In this process, the Sn nanowire as template helps the Sn/CdS core-shell nanowire and CdS nanotubes to form. The Sn doped CdS nanotubes need more growth time than the Sn doped Sn/CdS core-shell nanowires under the same experimental conditions.

The growth time is an important parameter to modulate the Sn ejecting and CdS growth. Long growth time can cause the dopant to eject out of the host matrix during the growth process. It has been reported that SnS_2 segment can be modulated to periodical pieces by controlling reaction temperature and growth time. [1-4] Here, the growth time is chosen to be the only factor to regulate and synthesize different Sn doped nanostructures. When $\boldsymbol{t}$ is about in the range of 10-15 min, 15-25 min, 25-35 min, the Sn/CdS core-shell nanowires, the mixtures of the Sn/CdS core-shell nanowires and CdS nanotubes, and the CdS nanotubes could be obtained, respectively. For them $\boldsymbol{T}$ = 900 ℃ and $\boldsymbol{r}$ = 15:1. The Sn ejecting process from as-formed nanowires is clearly shown in Figures S2(b-d). Figure S2(b) shows the beginning of the Sn core ejecting when $\boldsymbol{t}$ is up to 15 min, where the Sn core nanowire and Sn droplets are demonstrated explicitly. The Sn core segment can uniformly and nonuniformly distribute in the CdS shell, see Figures S2(c-d). These results suggest vivid growth process and clear microstructure information of Sn doped CdS nanowires.

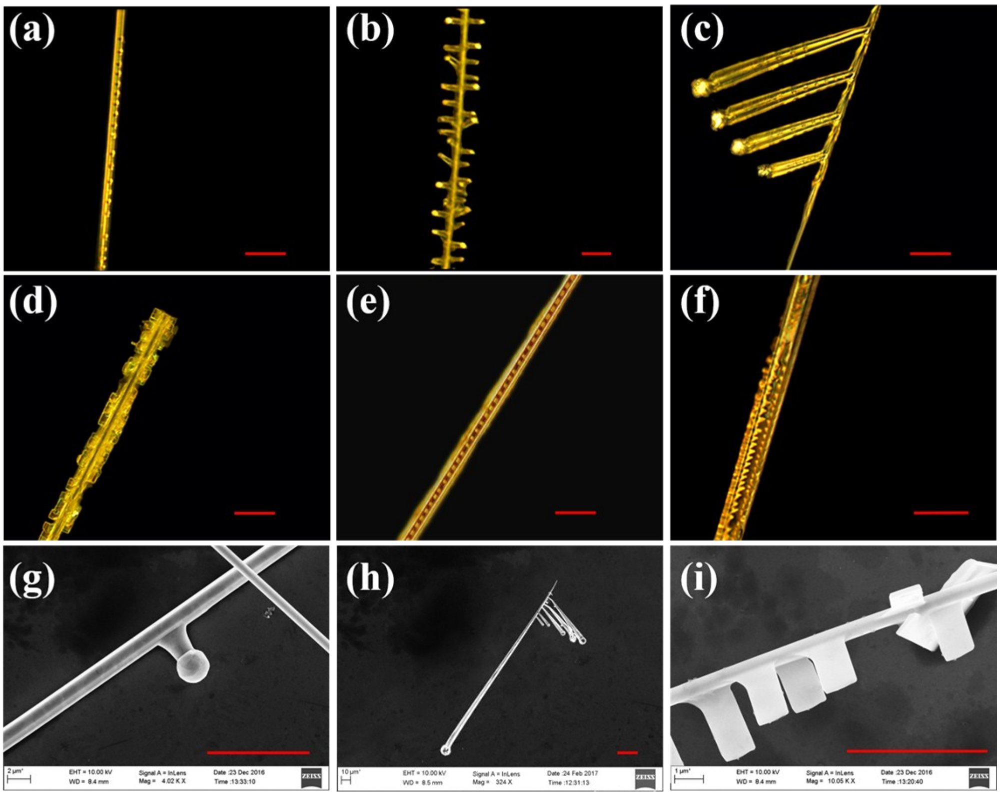

Figure S3. (a-f) The real-color images of Sn doped CdS nanostructures in the dark field of microscope under other growth conditions different from those for the Sn/CdS nanowires and CdS nanotubes. (g-i) SEM images of branching structures dispersed on Si substrates. The scale bars in the pictures are 10 μm.

Many other types of nanostructures can also be synthesized by modulating the experimental conditions. Higher growth temperature with larger mass ratio of SnO_2 to CdS powder speed up the Sn droplet depositing and ejecting and CdS shell growth, see Figure S3(a) ($\boldsymbol{r}$ = 10:1, $\boldsymbol{T}$ = 950 °C, and $\boldsymbol{t}$ = 20 min). The Sn droplets can also provide preferential surface sites on the nanowires, which is responsible for the branch structures, see Figure S3(b) ($\boldsymbol{r}$ = 10:1, $\boldsymbol{T}$ = 950 °C, and $\boldsymbol{t}$ = 30 min). When $\boldsymbol{t}$ is up to 50 min, the comb structures [5] can be found, see Figure S3(c) ($\boldsymbol{r}$ = 10:1, $\boldsymbol{T}$ = 950 °C, and $\boldsymbol{t}$ = 50 min). Figure S3(d) shows a flaky branch structure, which need higher growth temperature ($\boldsymbol{T}$ = 990 °C). When $\boldsymbol{r}$ = 10:1, $\boldsymbol{T}$ = 850 °C, and $\boldsymbol{t}$ = 25 min, one could obtain the one-dimensional superlattices of the CdS/CdS: SnS_2 nanowires, see Figure S3(e), for which the experimental conditions must be controlled precisely. [1] When the temperature rises faster, the Sn core can bust out of the CdS shell, see Figure S3(f).

Figures S3(g-i) show the SEM images for some nanostructures similar with those discussed above. Their experimental conditions are the same with those in Figures S3(b-d), respectively.

Figure S4. show the SEM images for the thicker hole and thinner wall with more SnO2 powder used, for the hard controlling of temperature rising rate and carrier gas rate in more accurate way, we often obtain a broken nanotube or the tube with several holes on their side wall, which influence their optical properties seriously.

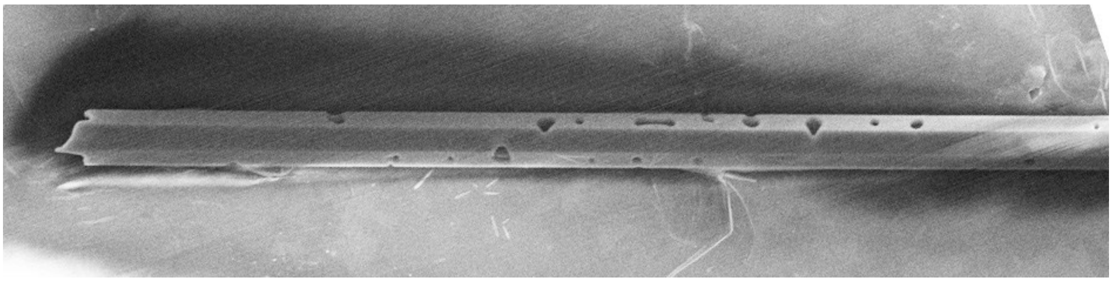

Figure S4. The SEM image of the nanotube of thinner wall.

To summarize, high reaction temperature with more Sn amount can speed up or enhance the ejecting of Sn from the CdS shell or tube in axial directions. On the other hand, faster rising of the temperature also influences the formation of the CdS nanostructures. Different experimental conditions induce different Sn phases which are responsible for the abundant types of the CdS nanostructures.

References

1. G. Dai, B. Zou and Z. Wang, *Journal of the American Chemical Society*, 2010, **132**, 12174-

12175.

2. G. Dai, S. Yang, M. Yan, Q. Wan, Q. Zhang, A. Pan and B. Zou, *Journal of Nanomaterials*, 2010, **2010**, 6.
3. G. Dai, G. Gou, Z. Wu, Y. Chen, H. Li, Q. Wan and B. Zou, *Applied Physics A*, 2015, **119**, 343-349.
4. G. Dai, Y. Chen, Q. Wan, Q. Zhang, A. Pan and B. Zou, *Solid State Communications*, 2013, **167**, 31-35.
5. R. Liu, Z. A. Li, C. Zhang, X. Wang, M. A. Kamran, M. Farle and B. Zou, *Nano Lett*, 2013, **13**, 2997-3001.