Silica-coated and annealed CdS nanowires with enhanced photoluminescence

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Abstract: The CdS/SiO_2 core/shell nanowires (NWs) with controlled shell thickness were successfully synthesized and subsequently heat-treated at 500 °C. The influences of silica shell coating and annealing processes on their optical properties have been investigated. Compared with original CdS NWs, the annealed CdS/SiO_2 NWs exhibited an enhanced band-edge emission with slowed photoluminescence lifetime, while the intensity of defect emission decreased. The results were ascribed to the surface passivation and recrystallization by shell coating and annealing. We believe our finding would help improving the optical properties of semiconductor NWs, and facilitate its applications in various realms, such as nanoscale emitter, sensor, and photoelectric device.

OCIS codes: (160.6000) Semiconductor materials; (250.5230) Photoluminescence; (300.6500) Spectroscopy, time-resolved.

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1. Introduction

As a one-dimensional wide band gap (2.42 eV) semiconductor, CdS nanowires (NWs) have received considerable attention owing to their attractive optical properties [1–20]. Especially, the stimulated emission and lasing of CdS NWs have blossomed increasingly in recent years, attributed to the efforts from a large number of research groups [10–16]. For example, optically pumped lasing of CdS NWs at 75 K was reported by Lieber and associates in 2005 [11]. Stimulated emission was observed by Pan et al. for the silica coated CdS NWs under high-intensity excitation at room temperature [12]. Low threshold lasing of CdS NWs at room temperature was further revealed by Geburt's group [13]. In addition, electrically pumped CdS NWs laser was also reported by Duan and associates [15], which demonstrated their feasibility for producing integrated electrically driven photonic devices. Based on these interesting optical properties, CdS NWs have been regarded as wonderful optical material for various applications, such as telecommunications, solar cells, highly integrated devices [1–4,16–18].

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Based on above considerations, great recent efforts have been devoted to synthesize CdS NWs with high crystallinity and efficient photoluminescence (PL) [19–26]. Hydrothermal method is the most employed route for the preparation of CdS NWs due to some significant advantages such as cost-effective, controllable particle size, low-temperature, and easy-operation techniques [24–27]. However, such as-prepared CdS NWs synthesized by hydrothermal method have defects inevitably owing to the surface absorption of surfactant, ligands, or other groups, which reduce the PL efficiency of the CdS NWs [25–27]. In order to further improve the PL efficiency of the as-prepared CdS NWs, the researchers have suggested several processing methods [28–32]. The typical strategy included growing silica shells to passivate the surface of CdS NWs [28–31]. Annealing is an efficient strategy for surface recrystallization [32,33], however the CdS NWs were often damaged under long-term heating in air due to the surface degradation.

In this paper, we investigated the influences of silica shell coating and annealing processes on the PL of CdS NWs. The CdS/SiO_2 core/shell NWs were synthesized, and annealed at 500 °C for 5 h. Compared with the original CdS NWs, such annealed CdS/SiO_2 core/shell NWs exhibited highly efficient band-edge emission of CdS.

2. Experimental section

The original CdS NWs were synthesized by the solvothermal method using ethylenediamine as a solvent [12,24]. In brief, 33.5 mL of ethylenediamine was added to a Teflon-lined stainless-steel autoclave of 45 mL capacity, then 0.0025 mol of cadmium nitrate hexahydrate and 0.002 mol of thiacetamide were dissolved in the above solvent. After stirring for about 10 mins, a viscous gel-like solution was obtained. Then, the Teflon-lined stainless-steel autoclave was sealed and heated without stirring at 180 °C for 24 h. The obtained yellow product was centrifuged (5 mins, 4500 rps) and washed with distilled water and ethanol.

Subsequently, the CdS/SiO_2 core/shell NWs were prepared by a modified Stöber method. 10 mg of the as-prepared CdS NWs was dispersed in the mixed solution containing 10 mL ethanol, 450 μL distilled water, and 325 μL of 28% ammonia. Then, 35 μL of TEOS was added to the above mixture and sonicated for about 2 h at room temperature. A white-yellow precipitate was obtained by centrifugation at 4000 rpm, and then re-dispersed in ethanol. As thus, the high-yielded and uniform silica coated CdS NWs were successfully synthesized. In this method, the thickness of silica shell could be controlled by the amount of TEOS. In order to study the joint action of silica shell and annealing processes on the optical properties of the CdS NWs, part of the as-prepared sample was annealed at 500 °C in air atmosphere for 5 h.

The transmission electron microscope (TEM) images were obtained with a JEOL 2010 HT transmission electron microscope (operated at 200 kV). The absorption spectra were measured with a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Powder X-ray diffraction (XRD) analyses were performed on a Bruker D8-advance X-ray diffractometer with Cu Kα irradiation (λ = 1.5406 Å). The PL spectra of the samples were recorded using a spectrometer (Spectrapro 2500i, Acton) equipped with a liquid nitrogen cooled CCD (SPEC-10, Princeton). The excitation laser of 400 nm with a pulse width of around 3 ps and a repetition rate of 76 MHz was generated by a mode-locked Ti:sapphire laser (Mira 900, Coherent) equipped with an optical frequency doubling system.

3. Results and discussion

3.1 Controllable synthesis of CdS/SiO_2 core/shell NWs

The CdS/SiO_2 core/shell NWs with controlled shell thickness were produced in a modified Stöber method which is facile, high-yielded and reproducible. Compared with the typical procedure [12], methanol is replaced by ethanol in our method. Sonic oscillation was used as a stirring method during the synthesizing procedure, which greatly shortens the synthesis period of silica shell. Figure 1 displays the TEM images of the original CdS NWs and CdS/SiO_2 core/shell NWs with different shell thickness. Figure 1(a) shows the low and high magnitude TEM images of original CdS NWs. It can be seen that the diameter of CdS NWs is

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about 70 nm. In addition, the CdS/SiO_2 core/shell NWs with different shell thickness could be obtained by changing the amount of TEOS in the synthesis. Typically, when 2.5 μL, 10 μL, and 35 μL of TEOS were used, the shell thickness was 11 nm, 25 nm, and 70 nm, respectively. Their TEM images of the corresponding CdS/SiO_2 core/shell NWs are shown in Figs. 1(b)-1(d). From the images, it also can be seen that the silica shells are uniform and precisely controllable.

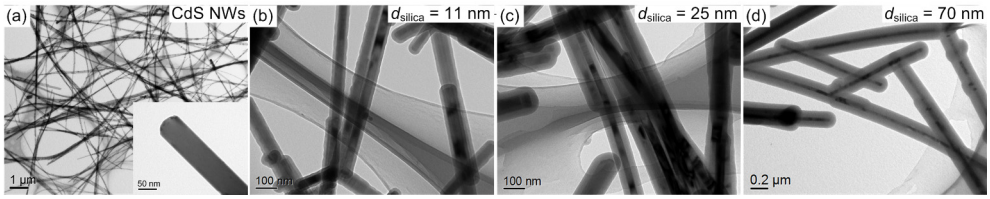

Fig. 1. (a) Low and high magnitude TEM images of CdS NWs. (b-d) CdS/SiO_2 core/shell NWs with shell thickness of around (b) 11 nm, (c) 25 nm and (d) 70 nm.

3.2 Thermal stability of CdS/SiO_2 core/shell NWs

The XRD patterns of the as-prepared CdS NWs, annealed CdS NWs, CdS/SiO_2 core/shell NWs, and annealed CdS/SiO_2 core/shell NWs are shown in Fig. 2. The annealed CdS NWs have a distinct XRD pattern from the others, which can be indexed as the orthorhombic $Cd_3O_2SO_4$ phase (JCPDS card No.32-0140). It indicated that the structure of CdS NWs is damaged due to the surface degradation (such as oxidation) under long-term heating in air. All the other diffraction peaks in Fig. 2 can be clearly seen and indexed as the hexagonal CdS phase (JCPDS card No.41-1049). Meanwhile, due to the amorphous structure of silica shell, no peaks for silica were detected in the coated sample. The results imply that the silica shell can prevent CdS NWs from being oxidized by oxygen at high temperature, and it offers the feasibility for next optical properties research of CdS NWs under stronger laser excitation.

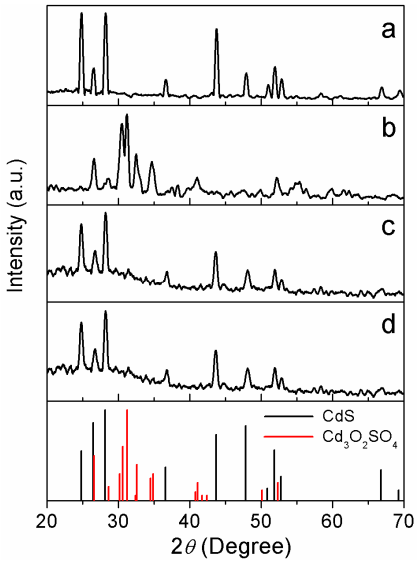

Fig. 2. XRD patterns of (a) CdS NWs, (b) uncoated CdS NWs annealed at 500 °C, (c) CdS/SiO_2 core/shell NWs, and (d) CdS/SiO_2 core/shell NWs annealed at 500 °C.

3.3 Optical properties of the annealed CdS/SiO_2 core/shell NWs

The absorption spectra of the as-prepared CdS NWs, CdS/SiO_2 NWs and annealed CdS/SiO_2 core/shell NWs are shown in Fig. 3. All the samples have a pronounced absorption bump at

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about 486 nm, which is similar with the results obtained by the other groups [26,27]. By comparing the absorption line shape of the CdS NWs, CdS/SiO_2 NWs, and annealed CdS/SiO_2 NWs, we found that the absorption bump position of CdS NWs is insensitive to the shell coating and annealing processes.

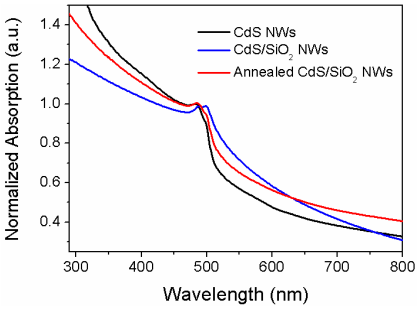

Fig. 3. Normalized absorption spectra of CdS NWs, CdS/SiO_2 NWs, and annealed CdS/SiO_2 core/shell NWs.

The PL spectra of the CdS NWs, CdS/SiO_2 NWs and annealed CdS/SiO_2 NWs are presented in Fig. 4(a). The samples show a sharp emission band at around 505 nm with the excitation of a 400 nm laser, which is attributed to the typical band–band transitions of CdS crystal since the spectral position is very near the band gap of CdS at room temperature [31]. Meanwhile, a broad emission band at around 700 nm can also be observed in these samples, which may be ascribed to structural defects such as crystalline surface structure defects, ionized vacancies and/or impurities [26,27].

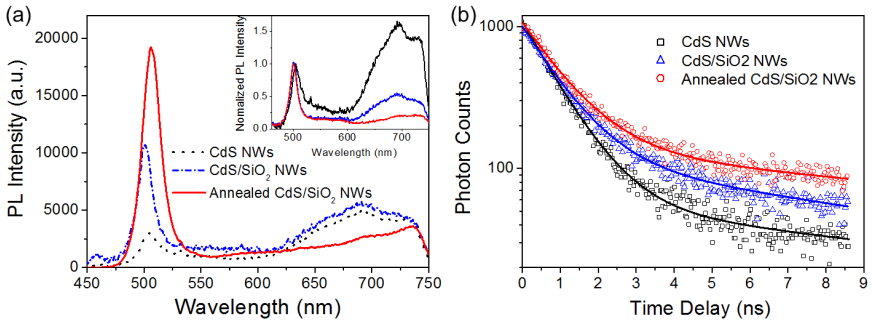

Fig. 4. (a) PL spectra of CdS NWs, CdS/SiO_2 NWs and CdS/SiO_2 NWs annealed at 500 °C. (b) Time-resolved PL of CdS NWs, CdS/SiO_2 NWs and annealed CdS/SiO_2 NWs at ~505 nm.

Most interesting, compared with the original CdS NWs, the band-edge emission of the silica coated CdS NWs enhances nearly 4 times, and that of the annealed CdS/SiO_2 NWs enhances about 8 times. Here, silica coating could passivate the surface of CdS NWs, which prevent the surface adsorption of surfactant, ligands, or other chemical groups. Therefore, it could reduce the number of nonradiative energy channels so as to improve the band-edge emission efficiency. Furthermore, annealing process could improve the crystal quality of CdS NWs under the protection of silica shell. Then the defect (trap) emission was depressed and the band-edge emission efficiency was further enhanced. It can be seen that the defect emission at about 700 nm was decreased by nearly 50% when the CdS/SiO_2 NWs were annealed at 500 °C, which also reveals the improvement of CdS crystal quality. In addition, the full width at half maximum (FWHM) of the band-edge emission peaks for the CdS NWs, CdS/SiO_2 NWs, and annealed CdS/SiO_2 NWs are 20 nm, 17 nm, and 16 nm, respectively. It demonstrates that both the shell coating and annealing processes induce the decreased FWHM of the band-edge emission, which indicate that the trap density near band edge decreases and the quality factor of band-edge emission increases.

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To further investigate the dynamics of the band-edge emission, time-resolved PL experiments were performed. As shown in Fig. 4(b), two decay processes with fast lifetime (τ_f) and slow lifetime (τ_s) were observed for the CdS NWs, CdS/SiO_2 NWs and annealed CdS/SiO_2 NWs. We have fitted the PL decay rate of the samples by double exponential, and the fitted values of τ_f are 0.86 ns (94%), 0.95 ns (89%) and 0.99 ns (85%) for the CdS NWs, CdS/SiO_2 NWs, and annealed CdS/SiO_2 NWs, respectively. The decrease of density of trap states was expected to reduce the exciton-trap interaction and thus increase the observed lifetime [34,35]. The increased lifetime of band-edge emission for annealed CdS/SiO_2 NWs coincided with their enhanced emission efficiency induced by surface passivation and crystal improvement.

Figure 5(a) displays the excitation power (P_{exc}) dependence of the PL intensity (I_{PL}) at around 505 nm of the samples. From these data, the slopes ($\nu = \partial \log I_{PL}/\partial \log P_{exc}$) are fitted as 1.56, 1.76 and 1.82 for the original CdS, CdS/SiO_2 and annealed CdS/SiO_2 NWs, respectively. It can be seen that, with the increasing of excitation power, the PL intensity of CdS/SiO_2 NWs and annealed CdS/SiO_2 NWs increase nonlinearly. In contrast, as shown in Fig. 5(b), the defect emission at about 700 nm is nearly linear with slopes of 1.10, 1.19 and 1.11 for the original CdS NWs, CdS/SiO_2 NWs and annealed CdS/SiO_2 NWs, respectively.

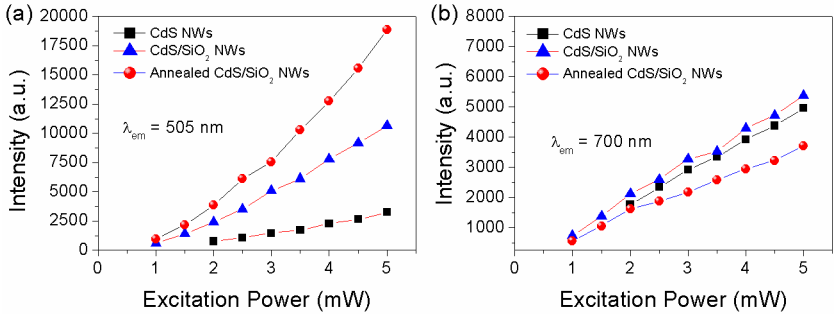

Fig. 5. Excitation power dependence of PL intensity for CdS NWs, CdS/SiO_2 core/shell NWs and annealed CdS/SiO_2 core/shell NWs at (a) 505 nm and (b) 700 nm with excitation wavelength of 400 nm.

4. Conclusion

In summary, the thickness-controlled CdS/SiO_2 core/shell NWs have been successfully prepared in an improved Stöber method, and the influences of silica shell coating and annealing processes on their optical properties have been investigated. The band-edge emission of the annealed CdS/SiO_2 NWs was enhanced with slowed lifetime, and the defect emission was depressed. The results indicated that the joint action of silica coating and annealing processes was beneficial for the band-edge emission efficiency, owing to that silica coating could reduce the nonradiative energy channels by the surface state, and annealing process could improve the crystal quality. We believe our finding would help improving the optical properties of semiconductor NWs, and facilitate its applications in various realms, such as nanoscale emitter, sensor, and photoelectric device.

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