Fabrication and Red-Color Lasing of Individual Highly Uniform Single-Crystal CdSe Nanobelts

Anlian Pan,*,†,‡ Ruibin Liu,† Qinglin Zhang,† Qiang Wan,† Pengbin He,† Margit Zacharias,‡,§ and Bingsuo Zou*,†

Micro-Nano Technologies Research Center, Hunan University, Changsha 410082, P. R. China, MPI of Microstructure Physics, Weinberg 2, Halle 06120, Germany, and Department of Physics, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany

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Highly uniform single-crystal CdSe nanobelts were prepared via a simple thermal evaporation route. Photoluminescence (PL) from a single belt indicates that the obtained nanostructures can produce stable and ultrafine red-color lasing under pulsed light excitation. The corresponding PL decay profiles show that the PL lifetime under high excitation is sharply shortened compared to that at low excitation power, which further supports that the PL in the nanobelt cavities can realize resonance and give stimulated emission. Comparative experiments with tapered belts show that the high PL emissions are mainly attributed to the uniform configuration of these nanostructures which can serve as a very effective waveguide cavity to realize high optical gain under high excitation. This kind of CdSe nanostructures may find potential applications in red-light nanolasers.

1. Introduction

In recent years, considerable effort has been made to study one-dimensional (1D) semiconductor nanostructures (nanowires and nanoribbons) for their promising properties and potential wide applications in nano/microscaled devices.[1−5] More importantly, 1D wide-band semiconductor nanostructures have been observed to work as waveguide cavities and can give stimulated emission or lasing under high-intensity excitation[6−13] and thus be used as nanolasers. Where ZnO, GaN, and ZnS nanowires or nanobelts are candidates for near-ultraviolet (UV) nanolasers,[10−12] a blue or green light emitting nanolaser might be possible if using 1D CdS nanostructures.[13] Red light emitting nanolasers would be very interesting for their potential applications in biology imaging, fluorescence labeling, telecommunication, surgery, and small lighting devices. However, a 1D red emitting nanowire laser has not been realized yet. CdSe, with a band-gap value of ∼1.74 eV at room temperature, can emit red band edge photoluminescence (PL) under light excitation. The PL efficiency of bare CdSe nanocrystals is commonly very low because the band edge luminescence arises from an optically inactive fine structure state or "dark" exciton.[14] It is expected that the PL efficiency of 1D CdSe nanostructures could be enhanced if the light emission is guided by well-confined structures such as wires or belts which might result in optical gain. In this work, we present high-quality and highly uniform CdSe nanobelts prepared via a simple thermal evaporation route and demonstrate for the first time that such uniform 1D CdSe nanostructures can also produce optical gain under high power excitation suitable to realize ultrafine red-color lasing.

* To whom correspondence should be addressed. E-mail: pananlian@hotmail.com and bszou@hnu.cn.
† Hunan University.
‡ MPI of Microstructure Physics.
§ University of Paderborn.

2. Experimental Section

The CdSe nanobelts were grown on Si(111) substrates through a metal-catalyzed physical evaporation route. Before growth, commercial-grade CdSe powders were placed onto a ceramic plate at the center of a quartz tube, which was then inserted into a horizontal tube furnace. Next to the ceramic plate several pieces of silicon wafers sputter coated with a thin Au film of 10 nm thickness were placed downstream of the gas flow working as deposition samples. Prior to heating, high-purity He was introduced into the quartz tube with a constant flow rate (5 sccm) to remove the O_2 inside. After a period of time (≥1 h) the furnace was rapidly heated to 900 °C and maintained at this temperature for ∼2 h without changing the conditions. Due to the natural temperature profile of the furnace uniform CdSe nanobelts were deposited on the surface of silicon wafer pieces which were at a place having a temperature of ∼700 °C.

The structure and morphology of the obtained nanobelts were characterized with a scanning electron microscope (SEM, S-4200), an energy dispersive spectroscope (EDS), and a high-resolution transmission electron microscope (HRTEM, Philips Tecnai 20). PL measurements were done with a micro-PL detection system using the third harmonic of a Nd:YAG laser (355 nm; spot size ≈ 0.5 mm^2) with a pulse width of 6 ns as the excitation source. The PL was dispersed by a monochromator with a 150 grooves/mm grating and detected with a liquid-nitrogen-cooled charge-coupled device (CCD) camera (Roper Scientific). The spectral resolution of the system is 0.26 nm. The PL lifetime decay profiles of the samples were investigated in a PL ultrafast detection system with femtosecond pulses (266 nm) as the excitation source. The output of emission light was focused into a monochromator and detected using a photon counting streak camera (Hamamatsu C2909). The time resolution is 30 ps, and the spectral resolution of the monochromator with 150 grooves/mm grating is 0.2 nm.

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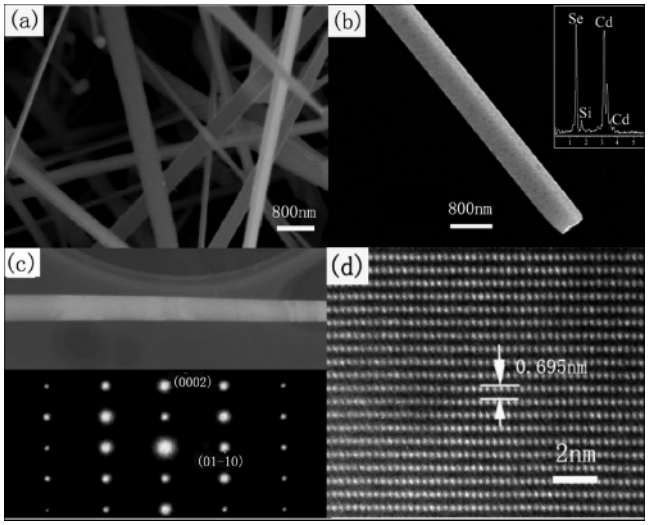

Figure 1. (a) SEM images of the as-prepared nanobelts and (b) a representative individual belt in high magnification and its in-situ energy-dispersive X-ray spectrum (inset); (c) TEM image of a selected CdSe nanobelt (upper) and the selected-area electron diffraction (SAED) pattern (down); and (d) the corresponding HRTEM lattice image.

3. Results and Discussion

Figure 1a and b shows SEM images of the as-prepared nanobelts and a representative single belt in high magnification, respectively, which indicate that the nanobelts have smooth side surfaces along their length and most of them possess uniform rectangular cross sections with depths of several tens of nanometers, widths of 100−800 nm, and lengths up to tens of micrometers. Figure 1b also indicates that the belts have very sharp cleaved end facets. The in-situ energy-dispersive X-ray spectrum (inset of Figure 1b) shows that the nanobelts contain only Cd and Se and that the atomic ratio is very close to 1, indicating stoichiometric formation of CdSe. The upper image of Figure 1c represents the TEM image of a single CdSe nanobelt, which further proves the uniform dimensions of the belts. The selected-area electron diffraction (SAED) pattern (down of Figure 1c) confirms the single-crystal quality of the belts which can be indexed to have a hexagonal structure with lattice parameters of $a = 0.428$ nm and $c = 0.698$ nm and a growth direction along [01−10]. The corresponding HRTEM lattice image (Figure 1d) further demonstrates that the CdSe nanobelt is single crystalline and free from dislocations and stacking faults. The lattice spacing of 0.695 nm corresponds to the (0001) interplanar distance of hexagonal CdSe.

The uniform dimensions and the high crystallinity of the obtained CdSe nanobelts indicate that these structures may serve as effective optical waveguides and cavities to realize stimulated emission or lasing under high excitation. To examine the optical properties of single nanostructures, the as-prepared CdSe nanobelts were removed from the Si substrate through sonication processing and dispersed onto the surface of a SiO_2 glass. Then the PL spectra of single belts were investigated with the micro-PL system. Figure 2a shows the power-dependent excitation PL spectra from a single CdSe nanobelt at room temperature. At low excitation power density only a broad band centered at ~705 nm appears, which originates from the near band edge emission of wurtzite CdSe.[15] The intensities of the band edge emission band strongly increase with the pump power, and a sharp peak with the full width at half-maximum (fwhm) of about 1.2 nm emerges superimposed on the broad band when the excitation density was increased to about 100 kW cm^{-2}. With further increasing the power density we observed additional sharp emission lines near the band edge emission band. Figure 2b shows the excitation power dependence of the peak PL intensity for the band edge emission, which demonstrates that the PL intensity has a superlinear increase with the excitation power with a threshold of ~100 kW cm^{-2}. At the same time, the dependence of the fwhm of the emission band on the excitation power (inset of Figure 2b) shows that the fwhm value drastically decreases around the excitation threshold. Such spectral signatures are normally discussed as evidence for amplified stimulated emission or lasing of semiconductor structures.[15]

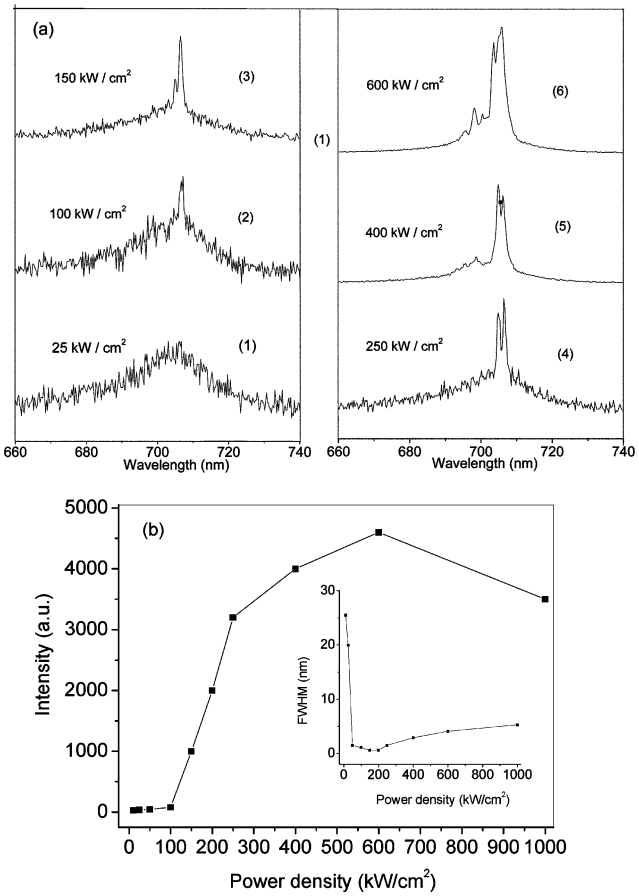

Figure 2. (a) Excitation power-dependent PL spectra from an individual uniform CdSe nanobelt at room temperature, and (b) excitation power dependence of the emission intensity and the fwhm (inset) for the PL band.

Usually bare CdSe nanocrystals have a very poor band edge emission because the bottom of the conduction band represents "dark" exciton states and transitions from these states to the valence band are formally spin forbidden.[14] Our results show that the belt-like CdSe nanostructures have very high emission intensity and can realize stimulated emission under pulsed light excitation. The strong emission may be attributed to the following two factors. On one side, high excitation will result in a very high population of the lowest conduction band level. The interactions between the occupied states can lead to some modification of the forbidden transitions and induce a possible high PL emission. On the other side, the regular dimensions of the belts make them very good waveguides. The emitted light can be accumulated and amplified through reflecting from both ends of the belts and finally produce stimulated emission under enough high excitation.

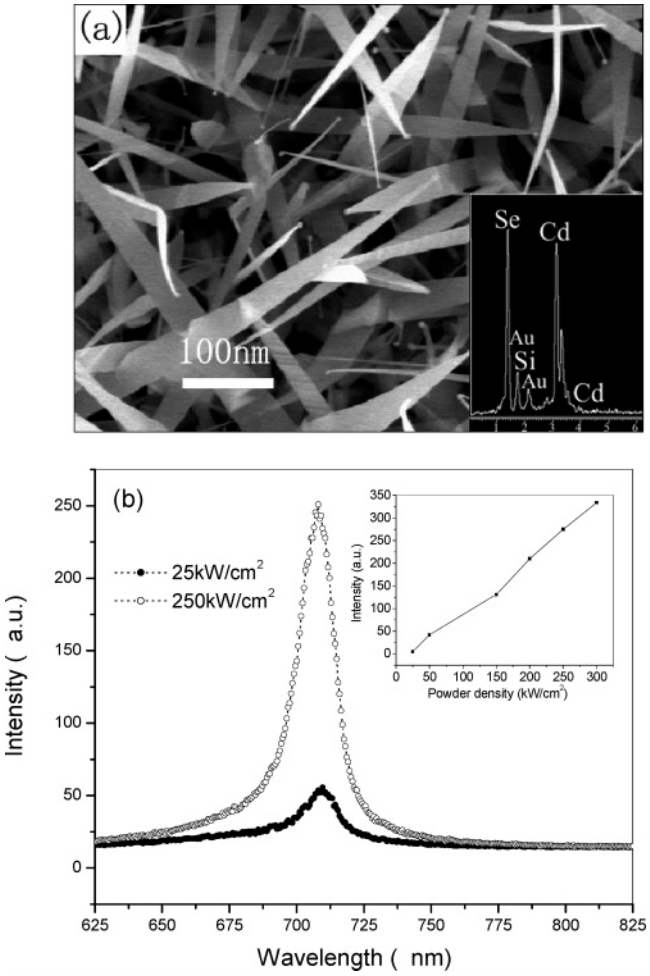

Figure 3. (a) SEM image of the tapered CdSe belts obtained at a growth time of 40 min and the in-situ energy-dispersive X-ray spectrum of a representative particle at the tip of the belt (inset); (b) PL spectra of a tapered belt under low excitation (25 kW cm^{-2}) and high excitation (250 kW cm^{-2}).

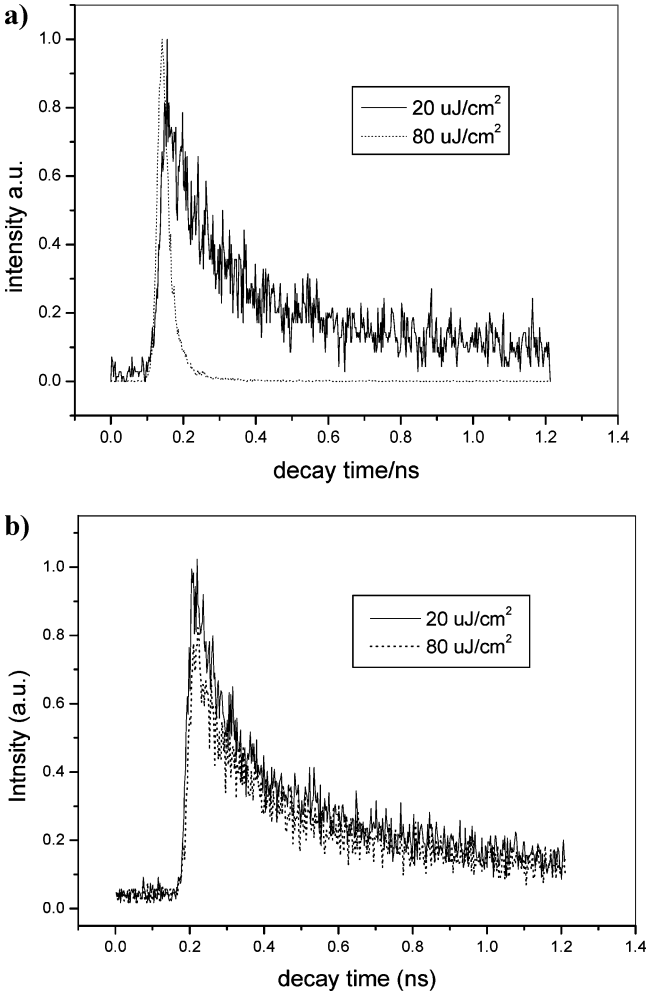

Figure 4. PL decay profiles of the uniform belts (a) and tapered belts (b) under high- and low-excitation intensity, respectively.

To investigate the formation process of the uniform belts and confirm if the uniformity in dimension of these structures has a decisive effect on their PL properties we comparatively investigated CdSe sample with a growth time of 40 min. Figure 3a shows that the so-grown sample is composed of tapered belts with spherical particles at the tip of them. The in-situ energy-dispersive X-ray spectrum of a representative spherical particle (inset of Figure 3a) at the tip of the tapered belts shows that the particles are composed of element Cd, Se, and Au, indicating that the CdSe nanobelts follow the VLS+VS growth mechanism.[16] TEM examinations show that these sharp belts are also single-crystalline hexagonal CdSe. During growth, the Au catalyzers induce the VLS growth of the CdSe nanostructures in length, whereas the direct VS deposition process simultaneously contributes to their growth at the transverse directions, which finally leads to formation of the long and uniform CdSe nanobelts.

Figure 3b shows the PL spectra of a tapered belt under low excitation (25 kW cm^{-2}) and high excitation (250 kW cm^{-2}), respectively, both displaying a broad emission band near the band edge with a fwhm of 25 and 23 nm. Obviously, the emission is similar to broad spectra observed under low excitation (below the stimulated emission threshold) for the uniform CdSe belts. The inset of Figure 3b gives the corresponding excitation power dependence of the emission intensity for the observed broad band, which indicates that the optical intensity has a near-linear rising with excitation power. That means that even though the PL intensity of the tapered belt has a pronounced increase with excitation power, it can only be produced by spontaneous emission. The mode selection realized by the waveguide cavity is missing, and hence, no sharp peak corresponding to stimulated emission can be found. This result indicates that the uniform configuration is truly a crucial point for the lasing process of the 1D CdSe nanostructures. It is understandable since the tapered belts are not uniform in width but have very sharp tips, which prevents the emitted PL from being effectively guided and reflected at their ends, then the contained PL cannot have enough gain to reach the threshold of lasing. The highly uniform CdSe nanobelts, however, can work well as optical resonators to realize stimulated emission and mode selection under high excitation.

Figure 4 shows the respective PL lifetime decay profiles of both the highly uniform and the tapered belts under different excitation intensities. The PL decay profiles of the uniform belts show clear pump intensity dependence (Figure 4a). The PL lifetime at high excitation power (80 $\mu J/cm^2$) is sharply shortened compared to that at low excitation power (20 $\mu J/cm^2$). This shortened PL lifetime indicates that the confined PL in the cavity realizes resonance under high excitation, which further confirms that the stimulated emissions take place in these uniform structures. However, the tapered belts show similar decay profiles (PL lifetime) under both high and low excitation

powers (Figure 4b), which demonstrates that these nonuniform structures can only give spontaneous emission under different excitation. These results show good agreement with the observed excitation power dependent photoluminescence (see Figure 3).

In our experiment, we found that the emission from the uniform CdSe nanobelts is very stable in air and can bear an excitation intensity up to ~300 kW cm^{-2}. However, too high excitation power will bring instability of the lasing emission. Curves 5 and 6 in Figure 2a are the emission spectra with the excitation density increased to 400 and 600 kW cm^{-2}, respectively. It clearly shows that the emission lines apparently become much broader with further increasing the power density (see inset of Figure 2b). When the excitation intensity is increased to 1 MW cm^{-2}, the PL emission intensity decreases and even breaks down after a long time pump. The broadening of the emission lines should come from the immense heating of the belt by too high excitation. The decrease and breakdown of the PL emission under too high excitation should be a result from ionization and oxidation, even destruction of the belts. Low-temperature and -vacuum conditions are expected to improve the lasing stability of these belts at least partly.

4. Conclusion

In summary, highly uniform and single-crystalline CdSe nanobelts were prepared through an Au-catalyzed physical evaporation route. Investigations of PL and the corresponding lifetime decay profiles show that the prepared nanostructures can serve as effective waveguide cavities to realize mode-selected red-color lasing under pulsed light excitation. The lasing emission is very stable in air and can bear an excitation intensity up to ~300 kW cm^{-2}. This finding indicates that highly uniform 1D CdSe nanostructures can be good candidates as red-light nanolasers.

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References and Notes

(1) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
(2) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature* **1996**, *380*, 325.
(3) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.
(4) López, C. *Small* **2005**, *1*, 378.
(5) Pan, A.; Yang, H.; Liu, R.; Yu, R.; Zou, B.; Wang, Z. L. *J. Am. Chem. Soc*. **2005**, *127*, 15692.
(6) Law, M.; Sirbuly, D. J.; Johnson, J. C.; Goldberger, J.; Saykally, R. J.; Yang, P. *Science* **2004**, *305*, 1269.
(7) Barrelet, C. J.; Greytak, A. B.; Lieber, C. M. *Nano Lett.* **2004**, *4*, 1981.
(8) Pan, A.; Liu, D.; Liu, R.; Wang, F.; Zhu, X.; Zou, B. *Small* **2005**, *1*, 980.
(9) Johnson, J. C.; Yan, H. Q.; Yang, P. D.; Saykally, R. J. *J. Phys. Chem. B* **2003**, *107*, 8816.
(10) (a) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897. (b) Yan, H.; Johnson, J.; Law, M.; He, R.; Knutsen, K.; McKinney, J. R.; Pham, J.; Saykally, R.; Yang, P. *Adv. Mater*. **2003**, *15*, 1907.
(11) (a) Ding, J. X.; Zapien, J. A.; Chen, W. W.; Lifshitz, Y.; Lee, S. T.; Meng, X. M. *Appl. Phys. Lett.* **2004**, *85*, 2361. (b) Zapien, J. A.; Jiang, Y.; Meng, X. M.; Chen, W.; Au, F. C. K.; Lifshitz, Y.; Lee, S. T. *Appl. Phys. Lett*. **2004**, *84*, 1189.
(12) Johnson, J. C.; Choi, H. J.; Knutsen, K. P.; Schaller, R. D.; Yang, P.; Saykally, R. J. *Nat. Mater*. **2002**, *1*, 106.
(13) (a) Duan, X.; Huang, Y.; Argarawal, R.; Lieber, C. M. *Nature* **2002**, *421*, 241. (b) Agarwal, R.; Barrelet, C. J.; Lieber, C. M. *Nano Lett.* **2005**, *5*, 917. (c) Pan, A.; Liu, R.; Yang, Q.; Zhu, Y.; Yang, G.; Zou, B.; Chen, K. *J. Phys. Chem. B* **2005**, *109*, 24268.
(14) Kuno, M.; Lee, J. K.; Dabbousi, B. O.; Mikulec, F. V.; Bawendi, M. G. *J. Chem. Phys.* **1997**, *106*, 9869.
(15) Iga, K. *Handbook of Semiconductor Lasers and Photonic Integrated Circuits*; Chapman & Hall: London, 1994.
(16) (a) Pan, A. L.; Liu, R. B.; Zou, B. S. *Appl. Phys. Lett*. **2006**, *88*, 173102. (b) Liang, C.; Shimizu, Y.; Sasaki, T.; Umehara, H.; Koshizaki, N. *J. Phys. Chem. B* **2004**, *108*, 9728.