

Low-Temperature Solution-Phase Synthesis of Quantum Well Structured CdSe Nanoribbons

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Semiconductor nanocrystals have been intensively studied due to their quantum confinement effect and size-dependent photoemission characteristics.¹ In particular, three-dimensionally (3-D) confined CdSe-based quantum dots have been extensively studied for biological labeling, light emitting diodes, and lasers.² Several 2-D confined nanorods and nanowires were synthesized.³ Although ribbon- or belt-shaped semiconductor nanostructures have been synthesized recently,⁴ 1-D confinement is rarely observed for these nanoribbons and nanobelts because of their large thickness. On the other hand, 1-D confined quantum well thin films were fabricated using molecular beam epitaxy or metallo-organic chemical vapor deposition at high temperature.⁵ Herein we report on the low-temperature solution-phase synthesis of free-standing CdSe nanoribbons with a uniform thickness of 1.4 nm in a multigram scale. Very interestingly, these ultrathin CdSe nanoribbons exhibited an extremely narrow photoluminescence band.

The significant surface energy differences between the various facets and the selective adhesion of surfactant molecules on specific facets have made it possible to synthesize many one-dimensional semiconductor nanostructures. For example, the significantly higher surface energy of the (000 $\bar{1}$) facet of the hexagonal wurtzite crystal structure compared to the other facets led to the formation of many nanorods and nanowires of CdS, CdSe, and CdTe from the colloidal chemical reactions.⁶ To synthesize ribbon-shaped wurtzite nanostructures, there should be a significant surface energy difference between the crystal facets perpendicular to the (000 $\bar{1}$) facets. Although the surface energy of $\pm(1\bar{1}00)$ facets is higher than that of $\pm(11\bar{2}0)$ facets,⁶ CdSe nanoribbons could not be synthesized using the conventional colloidal synthetic routes employing thermal decomposition of precursors at a high temperature of ~ 300 °C because the difference in the surface energies is quite small and becomes insignificant at the high reaction temperature. Consequently, we performed the reaction at a low temperature of < 100 °C in order to make the best use of the relatively small surface energy difference between these two crystal planes perpendicular to the (000 $\bar{1}$) facet, which is the key idea that made it possible to synthesize nanoribbons rather than nanowires (Supporting Information). However, this low-temperature synthetic strategy is confronted with two critical problems. First, the nucleation and subsequent growth of the nanocrystals are generally achieved by performing the reaction at high temperature. Consequently, a new chemical reaction pathway is needed that is sufficiently reactive to induce nucleation and subsequent growth at low temperature. In the current synthesis, we used a Lewis acid–base reaction between a cadmium cation and selenocarbamate anion. Second, the selection of appropriate stabilizing surfactant molecules having optimum binding strength and steric bulkiness is critical for the synthesis of nanocrystals at low temperature. After conducting the synthesis using several different surfactants (Supporting Information), we

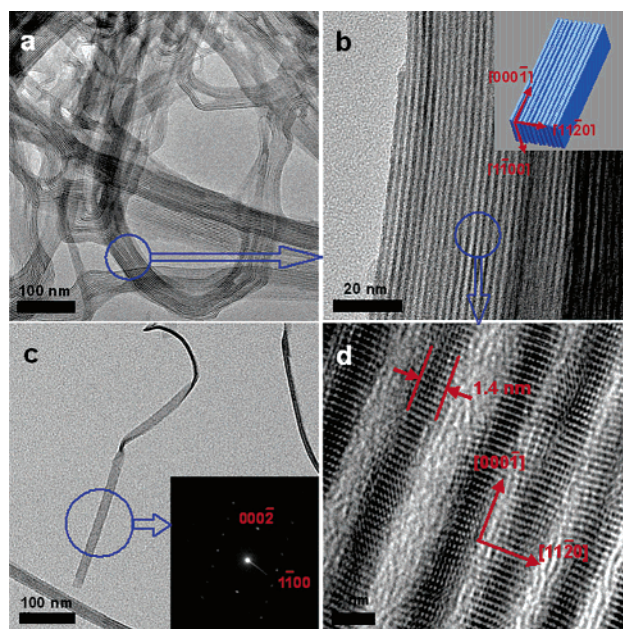


Figure 1. TEM images of CdSe nanoribbons. (a) Low-magnification TEM image. (b) TEM image showing parallel array of nanoribbons with uniform thickness. (c) Twisted image showing ribbon-shaped structure. Inset showing SAED pattern of circled area. (d) HRTEM image.

chose octylamine as the stabilizing surfactant because of its optimum binding strength and relatively small steric bulkiness.

The reaction between Lewis acidic cadmium cation and Lewis basic selenocarbamate was so effective that the nucleation and subsequent growth of CdSe nanoribbons could be performed at a temperature as low as 70 °C (detailed procedures in Supporting Information).⁷ The low magnification transmission electron microscopy (TEM) image (Figure 1a) revealed that the length of the CdSe nanoribbons is in the micrometer range. These nanoribbons self-assembled face to face to generate parallel arrays due to their high surface energy, as shown in Figure 1a and b. The nanoribbons had an extremely uniform thickness of 1.4 nm. The TEM images of several separated nanoribbons showed twisted and bent structures with widths of 10–20 nm, demonstrating the ribbon-shaped structure (Figure 1c and Supporting Information). A further tilting experiment and microtomed TEM images confirmed the nanoribbon structure rather than nanowire structure (Supporting Information). The high-resolution TEM (HRTEM) image (Figure 1d) and selected area electron diffraction (SAED) pattern (inset of Figure 1c) revealed that the CdSe nanoribbons grew along the [000 $\bar{1}$] direction and were encased by the $\pm(1\bar{1}00)$ (width direction) and $\pm(11\bar{2}0)$ (thickness direction) facets. The X-ray diffraction (XRD) pattern showed that the CdSe nanoribbons had a hexagonal wurtzite structure with diffraction peaks shifted to higher angles, reflecting

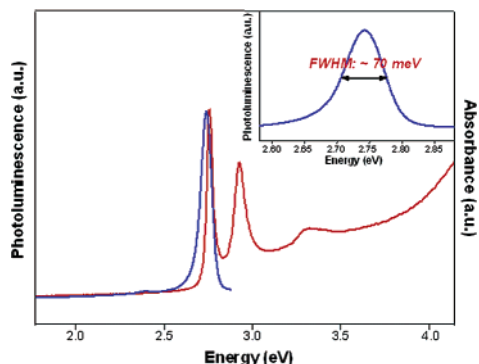


Figure 2. UV-vis absorption (red curve) and room temperature PL (blue curve) spectra of CdSe nanoribbons. Inset is an enlarged PL spectrum, showing a fwhm of 70 meV.

the lattice contraction induced by the high surface tension produced during the growth of nanoribbons (Supporting Information).⁸ The lattice parameters calculated from (100) and (101) peaks were $a = 4.19 \text{ \AA}$ and $c = 6.95 \text{ \AA}$. Compared to those of bulk CdSe ($a = 4.299 \text{ \AA}$ and $c = 7.010 \text{ \AA}$), lattice contractions of $\Delta a = 2.53\%$ and $\Delta c = 0.85\%$ occurred, which were reasonable considering the gigapascal order of the compressive stress exerted on the 1.4 nm thick nanoribbons.⁸ Two extremely weak peaks of (002) and (101) planes, which were resulted from the parallel orientation of nanoribbons to substrate, demonstrated their elongated structure.³ⁱ

The optical properties of the CdSe nanoribbons were characterized by UV-vis absorption and photoluminescence spectroscopy. The UV-vis absorption spectrum (Figure 2) showed unusually sharp and intense first and second excitonic transitions at 2.75 eV (449 nm) and 2.92 eV (423 nm), respectively. These two distinct blue-shifted peaks (the band gap energy of bulk CdSe is 1.7 eV) demonstrated that the oscillator strength was concentrated in these two electronic transitions due to the strong quantum confinement effect derived from the uniform and ultrathin (1.4 nm) characteristics of the CdSe nanoribbons. The room temperature photoluminescence spectrum (Figure 2) showed a sharp peak at 2.74 eV (451 nm) with an unprecedented narrow band of a full width at half-maximum (fwhm) of as small as $\sim 70 \text{ meV}$ (11 nm), which approaches the limit of homogeneous line broadening of a single quantum dot at room temperature.⁹ Because the CdSe nanoribbons have broad width and length distributions, these sharp UV-vis and PL spectra clearly demonstrated that the quantum confinement effect resulted from the uniform and ultrathin thickness of 1.4 nm. Photoluminescence excitation (PLE) spectrum measured at the emission energy of 2.74 eV at room temperature was similar to the absorption spectrum, demonstrating the uniform thickness of the nanoribbons (Supporting Information). The current well designed low-temperature reaction made it possible to synthesize CdSe nanoribbons with an extremely uniform thickness by the cluster-like growth characteristics and suppressing the Ostwald ripening process. The thickness of the CdSe nanoribbons (1.4 nm) is well within the range of the size of molecular clusters, and it is well-known that these clusters grow discontinuously to form discrete sized products.¹⁰ The UV-vis absorption and PL spectra of the CdSe nanoribbon samples synthesized at 70 °C for various reaction times showed neither red-shifts nor line broadening of the peaks, which clearly demonstrates the suppression of the Ostwald ripening process in the current low-

temperature synthetic procedure (Supporting Information). The quantum yield (QY) of the nanoribbons was in the range of 1–2%, which is high considering that the length of the nanoribbons is in the micrometer regime.¹¹

In summary, we synthesized free-standing quantum well structured nanoribbons with uniform thickness of 1.4 nm from the designed low-temperature reaction of Lewis acidic cadmium cation and Lewis basic selenocarbamate. The synthetic procedure is simple, highly reproducible, and consequently readily applicable for large-scale production (Supporting Information). Using a similar synthetic procedure, we synthesized CdS nanoribbons and Mn²⁺-doped CdSe nanoribbons with uniform and ultrathin thickness, and the detailed characterization is currently underway.

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Supporting Information Available: Experimental details, TEM images, XRD pattern, photoluminescence, and UV-vis absorption spectra of CdSe nanoribbons. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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