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Gold-Catalyzed Low-Temperature Growth of Cadmium Oxide Nanowires by Vapor Transport

Tz-Jun Kuo and Michael H. Huang*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

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Ultralong cadmium oxide nanowires were synthesized in high yield on gold-coated silicon substrates by using a vapor transport process. Cadmium vapor generated by the carbothermal reduction of CdO powder in a tube furnace heated to 500 °C was carried to the substrate zone by an argon flow with a trace amount of oxygen. The CdO nanowires grew via a vapor−liquid−solid growth mechanism. The diameters of the nanowires are ∼40−80 nm, and can reach lengths of 30−50 μm. Because the nanowire formation was gold particle catalyzed, patterned nanowire growth on substrates can be achieved. These nanowires grew along the [111] direction and have slightly rough surfaces due to the presence of crystalline CdO shells formed via a physical vapor deposition process. Interesting CdO nanowires with a necklace-like morphology were also observed in a small region of the substrate, where the oxygen supply may be ample to facilitate the lateral growth of rhombohedron-shaped crystals over the straight wires. Electron diffraction and high-resolution TEM results suggest that these side crystals should grow epitaxially on the wire surfaces. The band gap of the CdO nanowires with smoother surfaces was determined to be ∼2.53 eV. These nanowires exhibit a relatively weak emission band centered at ∼550 nm.

Introduction

Bulk CdO with NaCl cubic structure is an n-type semiconductor with a direct band gap of 2.5 eV and an indirect band gap of 1.98 eV.[1−4] Interestingly, reports of bulk CdO with a direct band gap of approximately 2.32 eV and an indirect band gap of 1.36 eV are also available.[4−6] CdO thin films have been shown to exhibit large third-order nonlinear optical properties.[7] Wurtzite Cd-doped ZnO thin films have been prepared and shown to display a substantial photoluminescence shift from 375 to ∼410 nm depending on the level of cadmium substitution.[8] The successful growth of Zn-doped CdO nanowires may offer an opportunity to study their photoluminescence properties. Given the potential scientific interests that may arise with the growth of high-quality CdO nanowires, it is a wonder that there are relatively few studies on the synthesis of one-dimensional CdO nanostructures.[2,3,9−11] Wang et al. synthesized CdO nanobelts and micron-sized sheets by directly evaporating CdO powder at 1000 °C without the presence of catalyst.[9] Zhou et al. grew CdO nanoneedles with square cross section via vapor phase transport of cadmium vapor generated at 350 °C from cadmium metal and a trace amount of oxygen in an argon flow to the substrate zone heated to 850−900 °C.[10] The substrates were precoated with a 2−3 nm gold film. The preparation of CdO nanowires by the electrodeposition of cadmium within 60-nm channels of anodic alumina membranes followed by thermal oxidation in air at 400 °C for 20 h has been reported.[11] The nanowires are uniform and continuous but are polycrystalline and without any referred growth orientation. In all these studies, the optical properties of the synthesized CdO nanowires were not characterized, and their detailed crystal structures were in general not extensively examined. Furthermore, the reaction temperatures used were relatively high, making the processes less desirable. A procedure that can produce a large quantity of high-quality CdO nanowires at a lower temperature should allow further examinations of the unique physical properties of these nanowires.

Here we report the high-yield synthesis of uniform CdO nanowires by a simple vapor transport method. Carbothermal reduction of CdO powder was employed to provide a steady supply of cadmium vapor and lower the nanowire growth temperature to just 400 °C. The crystal structure of the nanowires was analyzed by X-ray diffraction (XRD) patterns and electron microscopy characterization. CdO nanowires with unique side-growth morphology were produced in a confined region of a substrate and were also carefully examined. Absorption and fluorescence spectra of the nanowires were taken to study their optical properties.

Experimental Section

Cadmium oxide powder (Aldrich, ∼1 μm, 99.5%) was well mixed with fine graphite powder (Riedel-de Haën) by grinding (CdO:C = 4:1 by weight for a more controlled release of Cd vapor). The powder mixture was transferred to a ceramic boat, which was placed into a 1-in. quartz tube. Silicon (111) wafers cut to 1 cm × 1 cm were first boiled with piranha acid (H_2SO_4:H_2O_2 in 4:1 volume ratio) for 45 min and sonicated in acetone and 2-propanol for 5 min, respectively. After being dried

* To whom correspondence should be addressed. E-mail: hyhuang@mx.nthu.edu.tw.

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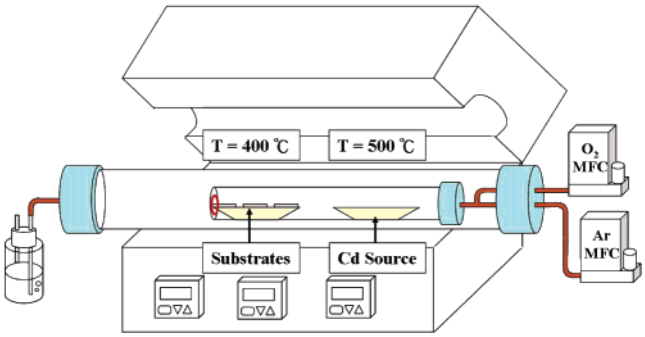

Figure 1. A schematic illustration of the experimental setup for the growth of CdO nanowires. Temperatures for the three zones were set at 300, 400, and 500 °C with the cadmium source placed in the center of the 500 °C zone. Actual zone temperatures measured by the thermocouples were 375 and 425 °C for the 300 and 400 °C zones, respectively. Since the substrates were placed between these two zones, the temperature over the substrates should be ~400 ± 5 °C.

with a nitrogen stream, these substrates were sputtered with a 1-nm gold thin film as the catalyst for nanowire growth. For the patterned growth of nanowires, a 200-mesh copper grid was placed on a substrate as a mask for the gold film deposition. The substrates were mounted on a ceramic boat and placed at the downstream end of the 1-in. quartz tube approximately 25 cm away from the center of the cadmium source boat. The 1-in. quartz tube was fitted to an end cap and carefully loaded into a 2-in. quartz tube placed in a 3-zone tube furnace (Lindberg/Blue). The schematic diagram for the experimental setup is shown in Figure 1. The quartz tubes were first purged with 250 sccm of argon and 0.32 sccm of oxygen for 20 min. Then the furnace temperature was raised to 500 °C for the reagent zone and 400 °C for the substrate zone in 30 min under the same carrier gas flow. A trace amount of oxygen presence was found to be necessary for good nanowire growth. After reaction for 2 h, the furnace was allowed to cool to collect the nanowire product.

The morphology of the as-synthesized CdO nanowire samples was examined with use of field emission scanning electron microscopes (FE-SEM, Hitachi S4700 and JEOL JSM-6330F). A JEOL JEM-4000EX transmission electron microscope (TEM) operated at 400 kV was used for the detailed structural characterization of the nanowires. Powder XRD patterns of the nanowire samples were taken with a MAC Science MPX-18 diffractometer with Cu Kα radiation. Reflective UV−vis absorption spectra of the samples were recorded on a Hitachi U-3310 spectrophotometer equipped with an integrating sphere. Photoluminescence spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer with a solid sample holder.

Results and Discussion

In this study, gold was used as the catalyst because gold is a common catalyst for the growth of binary oxide nanowires. Other catalyst metals have also been shown to be suitable for nanowire growth as in the case of tin oxide nanowires.[12] Since very few reports on CdO nanowires are available and the synthesis of ultralong CdO nanowires with gold as the catalyst metal has not been demonstrated before, we began our study using the gold catalyst. The silicon substrates looked dark yellow after the nanowire growth. The CdO powder used for the nanowire growth, however, is dark brown in color. Figure 2a shows a FE-SEM image of the CdO nanowires grown on a silicon substrate. There was a dense growth of uniform and long nanowires. Figure 2b gives a SEM image of the CdO nanowires

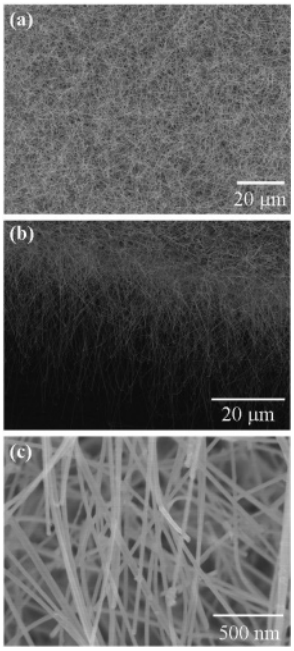

Figure 2. SEM images of the dense CdO nanowire growth (a) over an entire silicon substrate and (b) near the edge of a substrate for a better observation of the lengths of the nanowires. (c) A high-magnification SEM image of individual CdO nanowires for a better observation of their morphology.

grown near the edge portion of the substrate. Most of the nanowires are very long and can easily reach lengths of 30−50 μm or more. The nanowires can grow to such long lengths because a growth time of 2 h was used; nanowires with lengths of a few microns can be synthesized by reducing the growth time to less than 1 h. Figure 2c shows a high-magnification view of the CdO nanowires. The nanowires appear straight and flexible with smooth surfaces. The diameters of these nanowires range mostly between 40 and 80 nm, with many nanowires having diameters of 50−70 nm. These nanowires have small diameters because a very thin 1-nm gold film was deposited on the substrates for the nanowire growth.

The identity of these nanowires was verified with powder XRD patterns and is shown in Figure 3. The diffraction pattern matches well with that of face-centered cubic CdO with a unit cell constant *a* of 4.695 Å (JCPDF No. 05-0640), confirming that the nanowires are indeed CdO nanowires. No impurity such as cadmium metal was found on the substrate. The sharp peaks indicate that the CdO nanowires possess good crystallinity. The intensities of the (111) and (222) peaks are particularly strong relative to the other peaks, suggesting that the CdO nanowires grow along the [111] direction.

To further analyze the crystal structure of single CdO nanowires, TEM characterization of the nanowires was conducted. Figure 4a is a TEM image of a single CdO nanowire. The nanowire has a uniform diameter, but its surface is not very smooth. A dark particle can be found at the tip of this nanowire, which presumably is the gold catalyst particle (see the Supporting Information). The particle size is smaller than the wire diameter, which is unusual as most catalyst particles have similar or larger sizes than the diameters of the nanowires.[10,13−16] The presence of this catalyst particle suggests that the nanowires were formed by the vapor−liquid−solid (VLS) growth mechanism.[17] In this study, cadmium vapor was generated by the carbothermal reduction of CdO powder with graphite powder at 500 °C, which was transported to the substrate zone by the argon carrier gas. The substrate temperature was ~400 °C,

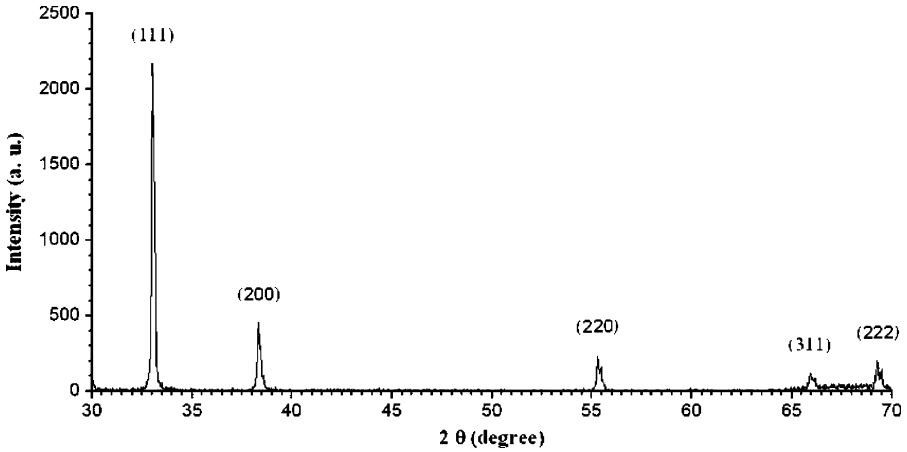

Figure 3. Powder XRD pattern of the CdO nanowires grown on a silicon substrate. The positions of the (111), (200), (220), (311), and (222) peaks are at 33.00, 38.27, 55.26, 65.92, and 69.28° 2θ, respectively, using the Cu Kα_1 radiation at $\lambda = 1.5405$ Å. The presence of Cu Kα_2 radiation at $\lambda = 1.5443$ Å possibly resulted in the appearance of the (220), (311), and (222) peaks at 55.45, 66.12, and 69.50° 2θ.

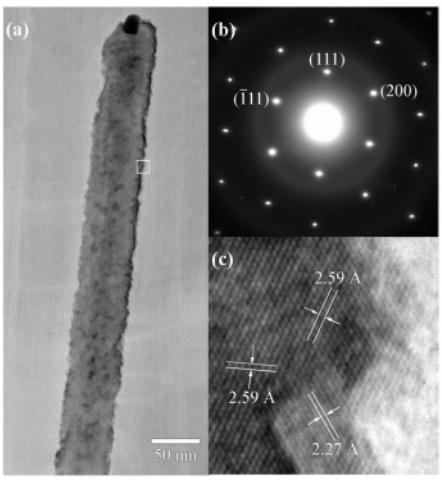

Figure 4. (a) TEM image of a single CdO nanowire. A gold catalyst particle is observed at the tip of the nanowire. (b) SAED pattern over this single CdO nanowire. (c) High-resolution TEM image of the square region of the nanowire in panel a showing the lattice fringes.

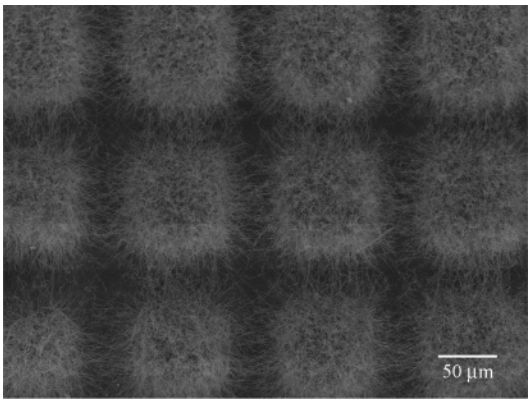

Figure 5. SEM image of the patterned growth of CdO nanowires. Nanowires only grew from the square-patterned areas coated with a thin gold catalyst film.

which should be high enough that the cadmium vapor was incorporated into the gold particles forming liquid alloy particles. Au−Cd forms alloy liquid at temperatures above 309 °C with a high cadmium atomic percentage.[18] When the alloy particles became supersaturated with the cadmium atoms and in the presence of a trace amount of oxygen, 1-dimensional CdO nanostructures were formed and extruded from the catalyst particles. Continuous elongation of the 1-dimensional nanostructure led to the eventual formation of ultralong CdO nanowires. The presence of a catalyst particle smaller than the diameter of the CdO nanowire can be explained. The nanowire grew via a typical VLS growth mechanism and formed the nanowire, which has a diameter similar to the size of the catalyst particle. Due possibly to a rich presence of cadmium vapor and a sufficient supply of oxygen, there was a concurrent lateral growth of the CdO shell over the nanowire by a physical vapor deposition process. The dangling bonds on the nanowire surface may also promote this side growth of CdO shell (see discussion later). This growth mechanism is partially supported by the somewhat different texture of the central portion from the outer regions of the nanowire. In fact, some CdO nanowires with completely enclosed catalyst particles have been observed (see the Supporting Information). Despite the growth of a CdO shell, no crystal defects such as twin boundaries can be recognized. A selected-area electron diffraction (SAED) pattern taken over the nanowire is given in Figure 4b. The single crystal fcc diffraction pattern indicates that the CdO nanowire is not polycrystalline. By indexing the diffraction spots, it was determined that the nanowire grew along the [111] direction. Figure 4c is a high-resolution TEM image of an edge portion of the CdO nanowire. The image reveals that the outer surface of the nanowire is also highly crystalline. The surface is not atomically smooth but is somewhat saw-toothed. The *d*-spacings of the three discernible sets of lattice planes are 2.59, 2.59, and 2.27 Å, which should correspond to the (111), ($\bar{1}$11), and (200) lattice planes of CdO. The determined *d*-spacings are slightly shorter than those calculated from the XRD pattern of the CdO nanowires as a result of a slight measurement uncertainty with the TEM image. This image provides another evidence of the entire nanowire growth along the [111] direction.

The catalyst-assisted synthesis of CdO nanowires allows patterned growth of the nanowires on substrates. Figure 5 presents an SEM image of the square-patterned growth of CdO nanowires on a silicon substrate. The nanowire growth was so dense that the entire square regions were covered with ultralong CdO nanowires. In the masked regions without the gold catalyst thin film, no wire growth was observed. This image is reminiscent of the reported hexagonally patterned growth of ZnO nanowires, but here the CdO nanowires are much longer and very straight.[19]

It is interesting to note that some necklace-like CdO nanowires were found in a region of the silicon substrate near the open end of the 1-in. quartz tube, as indicated by a red circle in

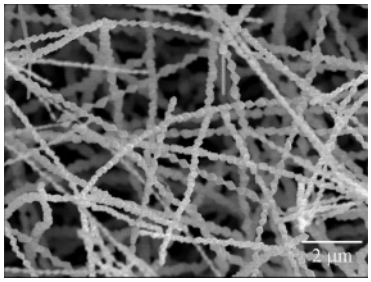

Figure 6. SEM image of the CdO nanowires with necklace-like morphology.

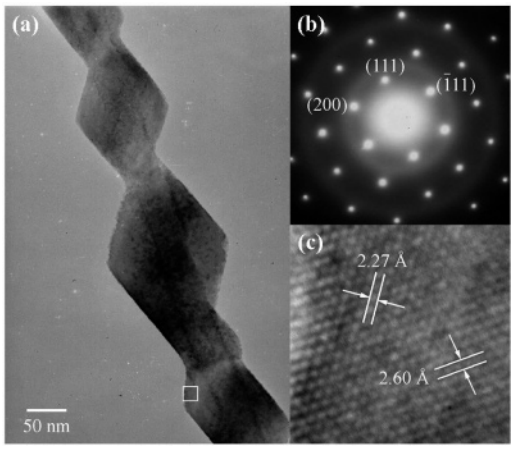

Figure 7. (a) TEM image of a single necklace-like CdO nanowire. Lateral growth of CdO crystals over the central nanowire stem can be clearly observed. (b) SAED pattern of the necklace-like CdO nanowire. (c) High-resolution TEM image of the square region in panel a showing the lattice fringes.

Figure 1. Figure 6 gives a SEM image of the CdO nanowires with this special morphology. Some nanowires with smooth surfaces were still present, suggesting that the necklace-like nanowires were formed by a lateral growth of the rhombohedron-shaped CdO nanocrystals over the smooth nanowires. Such side growth of 1- and 2-dimensional nanostructures resulting in the formation of double-side comblike ZnO structure and stacked-cone GaN nanowires has been reported.[20,21] ZnO and GaN both have hexagonal wurtzite crystal structure. The explanations for the formation of side growth features in these materials were focused on the surface polarity[20] and the diffusibility of adatoms on polar planes,[21] which are minor factors in crystal growth with a fcc structure. A TEM image of a single CdO nanowire with necklace-like morphology is presented in Figure 7a. The image shows clearly that this nanowire contains a straight stem and many rhombohedron-shaped crystals grown over the central wire. The SAED pattern of the nanowire, shown in Figure 7b, reveals that the nanowire is single crystalline and the side crystals should grow epitaxially over the surface of the wire core. The growth direction of this CdO nanowire is also [111]. A high-resolution TEM image of an edge portion of a rhomboid crystal is displayed in Figure 7c. Again three sets of lattice fringes can be observed, which should correspond to the (111), ($\bar{1}$11), and (200) lattice planes of CdO. The angle between the two edges of a single rhombus is ~125°, which agrees with the results obtained from the electron diffraction pattern and the high-resolution TEM image as the angle formed by the ($\bar{1}$11) and (200) lattice planes. The lattice image shown also indicates that the (111) lattice planes of the side crystals are parallel to the [111] growth direction of the central wire, hence verifying the formation of the side crystals via an epitaxial growth over the stem surface. This is

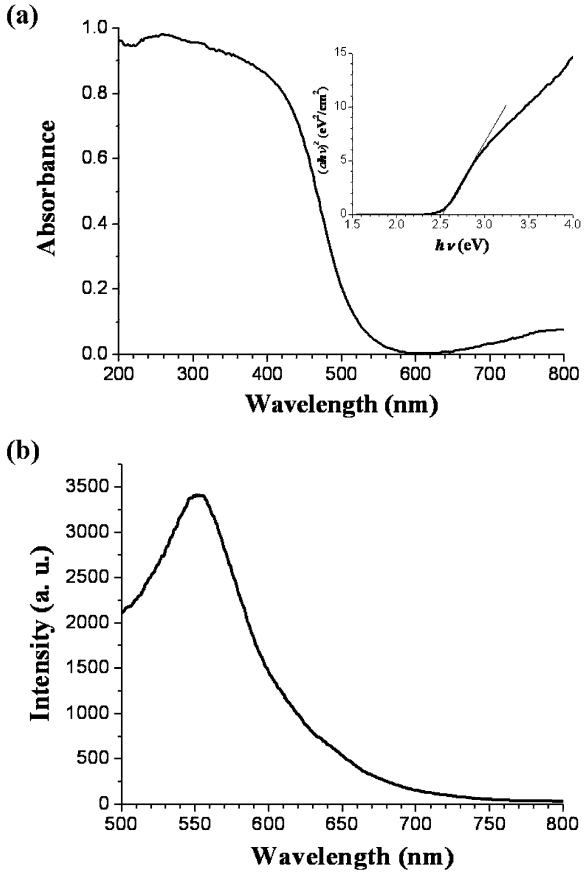

Figure 8. (a) Reflective UV−vis absorption spectrum of the smooth-surfaced CdO nanowires on a substrate. The inset shows a plot of $(\alpha h\nu)^2$ vs $h\nu$ for the determination of the direct band gap of the nanowires. The numerical values of $(\alpha h\nu)^2$ may not be right due to a lack of information on the sample thickness or path length. (b) Photoluminescence spectrum of the CdO nanowires excited at 220 nm.

why only one set of electron diffraction spots was recorded for the necklace-like CdO nanowire. The explanation for the growth of CdO nanowires with this unique morphology is probably similar to that proposed for the formation of In_2O_3 nanowires with wedge-like triangular ridges.[22] According to the SAED pattern analysis, the side faces of the straight CdO nanowires may be bounded by the {211} surfaces. The dangling bonds on the family of (211) planes may likely be minimized by adatom deposition, which leads to sidewall epitaxial deposition and the formation of rhombohedron-shaped structures. There is probably a sufficient amount of oxygen in the 2-in. quartz tube. When the cadmium vapor in the carrier gas stream meets with an ample supply of oxygen near the open end of the 1-in. quartz tube, they react and deposit CdO layers through an epitaxial growth mechanism on the surfaces of the straight CdO nanowires. Instead of growing into thicker nanowires, the CdO films deposited on the side surfaces quickly reconstructed to lower index {111} and {100} faces. Since the surface free energy of the {111} and {100} faces is lower than that of other high-index faces, surface reconstruction can enhance the stability of the whole system and CdO nanowires with this unique necklace-like morphology were produced.[23]

The optical properties of the CdO nanowires were characterized. Figure 8a gives a reflective UV−vis absorption spectrum of the smooth-surfaced CdO nanowires on a silicon substrate. To further determine the band gap of these nanowires, a plot of $(\alpha h\nu)^2$ vs $h\nu$ was made and is shown in the inset of Figure 8a. The band gap of the CdO nanowires obtained was ~2.53 eV, which is in good agreement with the reported value for the direct

band gap of bulk CdO at 2.5 eV.[1−4] CdO nanoparticles with diameters of 4−18 nm have been shown to exhibit pronounced quantum confinement effects, yet our CdO nanowires are too thick and long to observe such effects.[24] Figure 8b is a photoluminescence spectrum of these CdO nanowires excited at 220 nm. An emission peak at ∼550 nm was recorded, which should correspond to the near band-edge emission of CdO. We found that these CdO nanowires do not show strong luminescence. By contrast, ZnO nanowires exhibit much stronger luminescence.

Conclusion

In summary, we have successfully grown ultralong CdO nanowires on silicon substrates via a vapor transport approach. The nanowires were synthesized by a VLS growth mechanism with gold as the catalyst at a relatively low growth temperature of 400 °C. These nanowires were found to grow along the [111] direction. They typically have diameters of a few tens of nanometers, and can reach lengths of 30−50 μm. CdO nanowires with necklace-like morphology were also formed through an epitaxial vapor deposition process under an ample supply of oxygen. The band gap of the smooth-surfaced CdO nanowires is ∼2.53 eV, and an emission peak centered at ∼550 nm was observed. The ability to prepare ultralong CdO nanowires at such a low growth temperature should allow further investigations of their physical properties. It is also envisioned that Zn-doped CdO nanowires may be prepared by using a mixed source reagent to examine the doping level-dependent optical properties of the resulting nanowires.

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Supporting Information Available: SAED pattern of a single CdO nanowire taken over the tip region of the nanowire and TEM image of a single CdO nanowire showing the gold alloy catalyst particle at the tip of the nanowire. This material is available free of charge via the Internet at http://pubs.acs.org.

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