# Ultralong Cadmium Chalcogenide Nanotubes from One-Dimensional Cadmium Hydroxide Nanowire Bundles by Soft Solution Chemistry

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Herein, we report a soft solution method for CdX (X = S, Se, Te) nanotubes (NTs) with a high aspect ratio directly onto the substrate of a large area using one-dimensional (1D) $Cd(OH)_2$ nanowire bundles (NBs) which were grown by a low-temperature soft chemical approach. A simple anion exchange route was designed to synthesize CdX NTs using the $Cd(OH)_2$ NBs as a Cd source as well as a template. By the reaction of $Cd(OH)_2$ NBs on the substrates with an aqueous solution of $X^{2-}$, the anion exchange reaction takes place, and due to the difference in the solubility products, as well as the diffusion rates, the nanocrystalline CdX NTs are formed. The CdX NTs were characterized by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) analysis, and X-ray diffraction (XRD). On the basis of a series of experiments and characterizations, the formation mechanism of the CdX NTs from $Cd(OH)_2$ NBs is proposed. This work demonstrates a cost effective method for the synthesis of ultralong CdX NTs via reaction with an $X^{2-}$ ion source employing $Cd(OH)_2$ NBs.

## Introduction

During the past decade, with a pioneering discovery of $WS_2$ nanotubes (NTs),[1] the NTs of various kinds of inorganic materials have been prepared due to their unique physical and chemical properties and potential applications in nanoscale devices.[2–4] The NTs of inorganic semiconductors can be considered a new class of materials which exhibit properties quite different from those of their 1D nanowire form, as the physical properties and electronic structure combine characteristics of both two-dimensional (2D) and 1D materials.[5] There are several approaches to forming NTs such as rolling up existing thin film to form nanoscrolls of layered materials,[6,7] use of a hard template like anodized aluminum oxide (AAO),[8,9] use of a core template (nanowires) to deposit the shell material and subsequent removal of the core material by selective etching,[10,11] transformation of a solid nanowire through interface reactions through the so-called Kirkendall effect, etc.[12] The sacrificial template approach is analogous to transformation involving the Kirkendall effect in which the nanowires of the template are converted to desired material having the hollow 1D morphology by reaction with an appropriate material under controlled conditions. The sacrificial template approach offers advantages such as the following:[13–15] (1) The template is consumed during replacement reactions, which results in hollow products with the original shape of the templates; thus, the size of the product can be tuned with respect to the template. (2) The transformation reactions take place under soft conditions in solution, which avoids requirement of sophisticated instruments. (3) As sacrificial templates act as reactive precursors as well as templates, the strategy is not only free from additional

post-processing procedures to remove the templates but also free from the limited morphologies of hard templates. Thus, relatively pure products can be expected as compared to the hard-template route. Moreover, the precursors can be fabricated through many techniques developed for morphosynthesis of nanomaterials. (4) Massive products can be produced, which is important with respect to technical applications. However, only very few 1D nanomaterials have been found to be suitable as sacrificial templates for NTs in comparison with their spherical counterparts.[15]

CdX (X = S, Se, Te) are the potential materials from II–VI group semiconductors, which have shown interesting optical, electrical, and optoelectronic properties via quantum confinement in nanocrystals.[16–19] These have been promising candidates for the construction of solar cells, phototransistors, light-emitting diodes, lasers, optoelectronics, etc.[20] As the important semiconductors for optoelectronics, the majority of the research on CdX has been concentrated on quantum dots,[21–23] and most recently, nanorods,[24–26] tetrapods,[27–29] nanoneedles,[30] and nanowires[31–33] have been extensively explored. However, reports on the synthesis of CdX NTs are limited with success by a few groups who were able to generate CdTe NTs by templating against cadmium thiolate polymer nanowires,[15] CdSe NTs by templating against cylindrical micelles assembled from organic compounds,[34] t-Se nanowires,[35] Sn nanowires,[36] or AAO,[37] and CdS NTs by in situ micelle–template interface reaction,[38] Cd(OH)Cl sacrificial template,[39] $Cd(OH)_2$ nanowire template[40] self-assembly of nanoparticles, and hard templates.[41] However, to our knowledge, little work has been reported on the ultralong polycrystalline NTs of CdX.

Herein, we report a cost effective fabrication method of NTs directly onto the substrate over a large area using a sacrificial template of 1D structure grown by a simple soft chemical process at a low temperature. As an example, a sacrificial template approach for synthesis of ultralong CdX NTs with high

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**SCHEME 1: Schematic Illustration of the Proposed Mechanism for CdX NT Formation on Substrate from Cd(OH)$_2$ NBs via Interdiffusion and Anion Exchange Reaction**
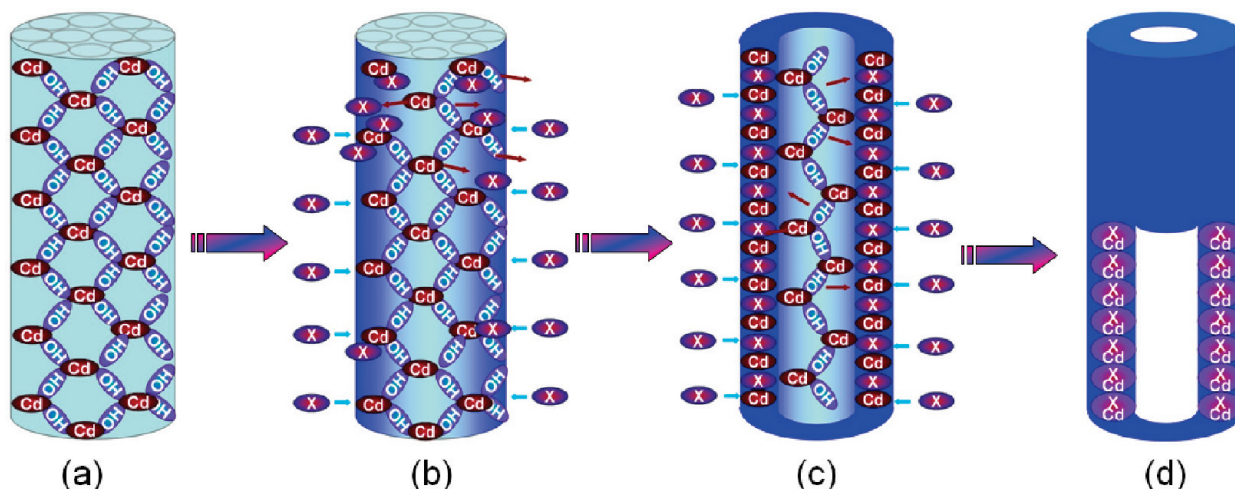


aspect ratio, from a template of Cd(OH)$_2$ nanowire bundles (NBs), is described here.

## Experimental Methods

In a typical synthesis of CdX NTs, the first step was to obtain Cd(OH)$_2$ NBs on the substrates. For Cd(OH)$_2$ NBs, an aqueous solution of 0.1 M Cd(NO$_3$)$_2$ (Aldrich Chemicals) was prepared, and to this solution, aqueous NH$_3$ solution (28%) was added under constant stirring. A white precipitate was initially observed, which subsequently dissolved back into solution upon the further addition of the NH$_3$ solution. The solution was maintained at a pH of ca. 12. The precleaned substrate (glass/ITO/Si) was placed vertically in the solution, and the reaction bath was heated to a temperature of 333 K for 12 h, resulting in the direct growth of NBs onto the substrate.[42] The substrate coated with the Cd(OH)$_2$ nanostructures was then removed from the reaction bath, washed with deionized water, and dried under air. The grown Cd(OH)$_2$ NBs were used as the sacrificial template for the transformation to CdX NTs by reaction with an aqueous solution of NaHX for CdTe and CdSe NTs and thioacetamide (TAA) for CdS NTs. The aqueous solutions of NaHSe or NaHTe were prepared by adding 20 mM NaBH$_4$ to 10 mM Se or Te and then dissolving in water followed by heat treatment at 60 °C for 1 h. After a reaction, the color of the Cd(OH)$_2$ NBs was changed from white to gray-black, dark red, and dark yellow for CdTe, CdSe, and CdS NTs, respectively. The as-converted films were removed from the reaction bath. In the case of CdSe NTs, the uniform NTs were obtained when the unreacted Cd(OH)$_2$ core was removed by thermal treatment at 300 °C for 1 h in an Ar/H$_2$ atmosphere.

The morphology and size of Cd(OH)$_2$ NBs and the CdX NTs obtained by ionic transformation were characterized by field-emission scanning electron microscopy (FE-SEM) (XL30 ESEM FEG), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) (Philips CM-30 TEM unit with an acceleration voltage of 300 kV coupled with an EDAX-DX-4 analyzer). The semiquantitative elemental composition of the film was determined using energy-dispersive X-ray (EDX) analysis using a Horiba-EX-200 instrument with a spatial resolution of 134 eV. The phase identification of the sample deposited on the glass substrate was further investigated using a Rigaku X-ray diffractometer for thin films using Cu K$_{\alpha1}$ radiation ($\lambda = 1.5406$ Å).

## Results and Discussion

To synthesize CdX NTs using the Cd(OH)$_2$ NBs, a simple anion exchange route was designed. Scheme 1 illustrates the proposed mechanism of the sacrificial template process for synthesis of CdX NTs. The first step involved synthesis of ultralong Cd(OH)$_2$ NBs (Scheme 1a) onto substrates via a soft solution chemical process, as described in ref 42. When the Cd(OH)$_2$ NBs coated onto the substrates were reacted with an aqueous solution of NaHX for CdTe and CdSe and TAA for CdS NTs, the reaction between Cd$^{2+}$ ions at the surface and X$^{2-}$ supplied from the solution source takes place. Due to the lower solubility of CdX in the solution, nanocrystals are formed onto the surface of the precursor NBs and decomposed OH$^-$ ions would be dissolved into aqueous solution (Scheme 1b) by the possible chemical reaction

$$Cd(OH)_2 + NaHX \rightarrow CdX + NaOH + H_2O \quad (1)$$

Further, due the interdiffusion between X$^{2-}$ and Cd$^{2+}$ species analogous to the Kirkendall effect and owing to different rates of outward and inward diffusion, the NTs are formed (Scheme 1c and d) at the expense of precursor NBs. It is worth noting that the NB structure of Cd(OH)$_2$ can provide more pathways for diffusion of X$^{2-}$ ions inside than the singular wire structure. Considering the ultralong NBs of Cd(OH)$_2$ in NaHX solution, the outward diffusion of Cd$^{2+}$ ions from the inner part of 1D Cd(OH)$_2$ appears to be dominant due to their chemical potential difference. Such a diffusion process will be stopped when the core source of Cd(OH)$_2$ is consumed completely, giving rise to hollow NTs.

Many of the solution synthesis methods such as an aqueous precipitation for CdX from inorganic reactants of Cd$^{2+}$ and X$^{2-}$ [43−46] result in the formation of fine CdX nanocrystals due to a very small solubility product ($K_{sp}$) for CdX. Due to the small solubility product, fast nucleation of CdX occurs with respect to the growth rate of CdX and tiny clusters are generated.[47] Moreover, CdX compounds do not possess a layered structure, so the hollow structures of CdX are mostly formed by a template route. In comparison to the synthesis process of other templates, Cd(OH)$_2$ NB templates can be prepared by simple aqueous precipitation of Cd$^{2+}$ in basic solution. Additionally, due to the high solubility of Cd(OH)$_2$,

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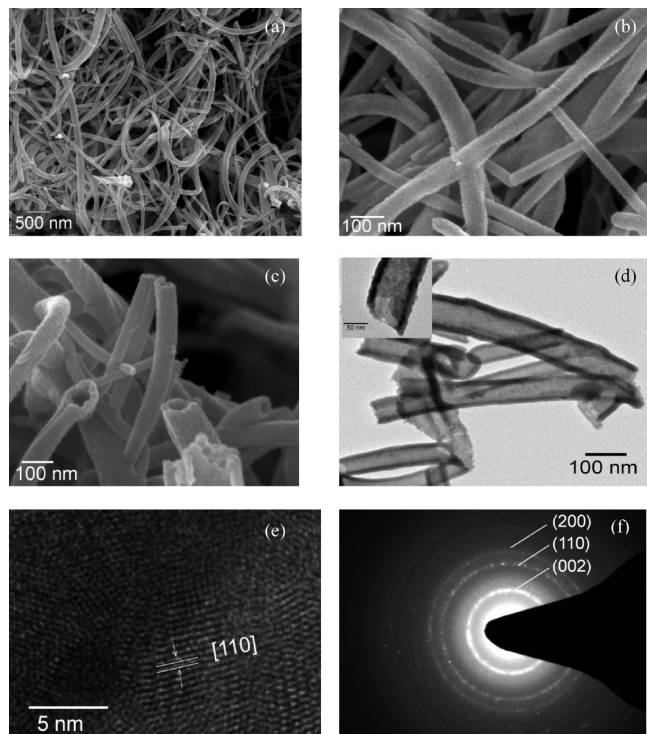*J. Phys. Chem. C, Vol. 113, No. 32, 2009* **14181**



**Figure 1.** Characterization of CdTe NTs: SEM [(a) low magnification, (b) high magnification, (c) cut cross-sectional view], (d) TEM (inset, single NT), (e) HRTEM, and (f) SAED pattern of a single NT.
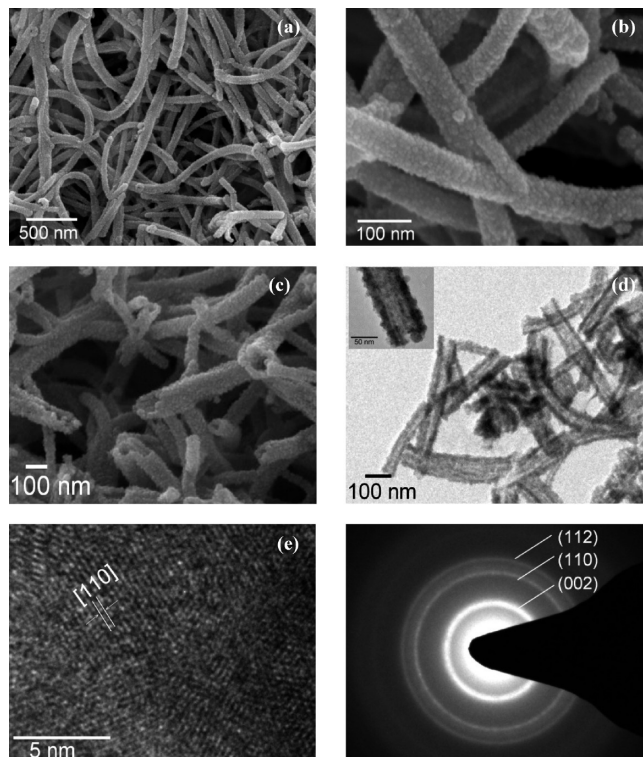


**Figure 2.** Characterization of CdS NTs: SEM [(a) low magnification, (b) high magnification, (c) cut cross-sectional view], (d) TEM (inset, single NT), (e) HRTEM, and (f) SAED pattern of a single NT.

the nucleation/growth rate of $Cd(OH)_2$ can be controlled at a relatively slow rate by maintaining the pH of the solution, which results in the formation of size-controlled $Cd(OH)_2$ NBs. Furthermore, the size of $Cd(OH)_2$ NBs can be controlled via deposition period, concentration of precursor solution, etc. Thus, the size tunable CdX NTs can be synthesized from $Cd(OH)_2$ NBs by an $X^{2-}/OH^-$ ion exchange reaction which proceeds from the outer surface to the inside of the $Cd(OH)_2$ NBs. These CdX NTs with a high aspect ratio can be grown on virtually any (conducting/nonconducting) substrate material regardless of the shape of the substrate, since $Cd(OH)_2$ NBs can be grown on any substrates.[42]

The structural and morphological details and size controllability of the $Cd(OH)_2$ NBs grown onto the substrates can be found in ref 42. Characterizations by FE-SEM showed that a large quantity of nanowires were produced with lengths ranging up to several tens of micrometers and diameters of 70−90 nm. A high-magnification FE-SEM image revealed that the individual nanowires are actually constituted of several smaller nanowires (i.e., bundled) of 7−10 nm in diameter.[42] This observation was well supported by TEM images. The X-ray diffraction (XRD) pattern showed that the NBs are well crystallized with the monoclinic crystal structure of $Cd(OH)_2$.[42]

Figure 1a shows a FE-SEM image of as-synthesized CdTe NTs obtained by reaction of the $Cd(OH)_2$ NBs with aqueous NaHTe solution at room temperature. The product consists exclusively of 1D wire-like nanostructures with lengths ranging from several micrometers exhibiting a high aspect ratio. The NTs have circular cross sections, mostly with closed ends and uniform diameters along their lengths. The high-magnification FE-SEM image (Figure 1b) shows that the walls of NTs are actually composed of a continuous nanoparticle array in a geometrical shape of 1D structure. Generally, the walls of NTs produced by the Kirkendall effect are composed of multigrains.[13] A cross-sectional FE-SEM image (Figure 1c) reveals a hollow

1D nanostructure. Typically, these CdTe NTs have outer diameters of 80 ± 10 nm and thin walls of 12−15 nm size. The morphology and composition of the products were further investigated by using TEM and EDS. The low-magnification TEM image of the CdTe NTs (Figure 1d) shows the formation of smooth NTs with outer diameters in accordance with the SEM results. In the TEM image, the several shorter NTs than the precursor nanowires or as observed in SEM images are seen which are possibly because of breaking of the NT during TEM sample preparation. The EDS spectra of the CdTe NT were analyzed to check their compositions for Cd and Te, which indicated that the NT is composed of Cd and Te atoms with an approximate atomic ratio of 49:51, which is close to the stoichiometry of CdTe. Further detailed structural analysis of the products was carried out by using HRTEM and selected-area electron diffraction (SAED). Figure 1e is the lattice-resolved HRTEM image of the CdTe NT which indicates that the CdTe NT is polycrystalline with an individual crystal size of 7−8 nm. The corresponding SAED pattern in Figure 1f indicates the diffusive rings, confirming the formation of polycrystalline walls with the composition indexed to pure CdTe.

Similarly, CdS NTs were obtained by reaction of $Cd(OH)_2$ NBs with an aqueous TAA solution at room temperature. The FE-SEM images of CdS NTs (Figure 2a and b) show that, similar to CdTe NTs, the bundled structure has vanished and a single wire-like structure assembled with nanoparticles is formed. These walls of individual NTs consist of CdS nanoparticles by the interdiffusion of $Cd^{2+}$ and $S^{2-}$ ions. The cross-sectional SEM image (Figure 2c) revealed the formation of CdS NTs with an average inner diameter and wall thickness of 50 ± 5 and 15 ± 2 nm, respectively. Further, the characterization of CdS NTs by TEM revealed that the $Cd(OH)_2$ NBs were completely converted to CdS NTs by retaining the 1D structure.
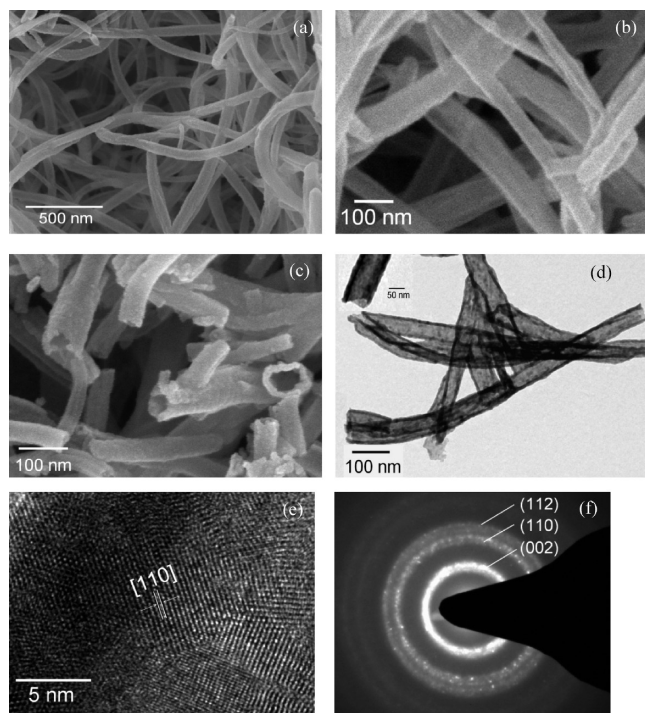
**Figure 3.** Characterization of CdSe NTs: SEM [(a) low magnification, (b) high magnification, (c) cut cross-sectional view], (d) TEM (inset, single NT), (e) HRTEM, and (f) SAED pattern of a single NT.

The HRTEM image displays a clear lattice of CdS nanocrystals, demonstrating the product was polycrystalline NTs, which is consistent with the apparent morphology of NTs consisting of primary nanograins. The SAED of a single NT showed similar diffused rings to those CdTe NTs, confirming that each NT is polycrystalline. The EDS spectra of the CdS NT material were analyzed to check their compositions for Cd and S, which indicated that the NT is composed of Cd and S atoms with an approximate atomic ratio of 51:49, which is close to the stoichiometry of CdS.

In the case of the formation of CdSe NTs, the direct formation of CdSe NTs was not observed and one additional intermediate step was necessary.[48] When the $Cd(OH)_2$ NBs were reacted with NaHSe solution, initially an intermediate phase of $Cd(OH)_2$/CdSe core/shell was formed and subsequent removal of core material by thermal treatment in an $Ar/H_2$ atmosphere resulted in smooth NTs, as shown in Figure 3. Figure 3a and b shows a typical SEM image of the CdSe NTs, which was observed after removal of the unreacted $Cd(OH)_2$ core part through thermal evaporation, clearly depicting the change in the surface. After the thermal treatment, the nanowires with lengths ranging up to several micrometers and diameters ranging from 70 to 90 nm are seen. A cross-section FE-SEM image (inset of Figure 3c) reveals that the individual nanowires have hollow structured NTs with a wall thickness of ca. 12−15 nm and an inner pore diameter of ca. 40−45 nm. The TEM image as shown in Figure 3d clearly demonstrates the tubular structure of CdSe. The HRTEM image at the walls of CdSe shown in Figure 3e indicates that the CdSe NTs are polycrystalline with the individual crystal size below 10 nm. Figure 3f shows the SAED taken from a random assembly of such crystals, which confirms the polycrystalline walls. The elemental analysis was carried out only for Cd and Se; the average atomic percentage ratio of Cd:Se was 51:49, showing that the film was in a good stoichiometric ratio.

## Conclusions

In summary, the synthesis of ultralong CdX NTs with crystallinity has been demonstrated by using $Cd(OH)_2$ ultralong NBs as sacrificial templates. Ultralong $Cd(OH)_2$ NBs have been successfully synthesized directly onto the substrates using a simple, low-temperature, and economical soft solution chemical process. The present work demonstrated an effective method for the synthesis of ultralong CdX NTs via reaction with an $X^{2-}$ ion source employing $Cd(OH)_2$ NBs as the sacrificial template. The soft solution approach for direct formation of nanostructures on substrates extended to the sacrificial template route to give hollow nanostructures overcomes the major challenge of large scale fabrication at low cost. The method is useful in the fabrication of massively large numbers of nanodevices for future circuits leading to commercial reality of devices with a major improvement in cost/performance ratio. This approach will find wide acceptance and use in the field of sacrificial template-directed NT synthesis. The efforts to tune the particle size of the tube wall and extension to the quantum confinement effect of CdX NTs are under investigation.

**Supporting Information Available:** The XRD and EDX results of the ultralong CdTe, CdS, and CdTe samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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