

# Controllable size reduction of CdSe nanowires through the intermediate formation of Se-coated CdSe nanowires using acid and thermal treatment

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## Abstract

Thinning of CdSe nanowires (NWs) with controllable size was achieved by a simple acid treatment and subsequent annealing on thick CdSe NWs synthesized from vapour phase growth. During acid treatment, not only the undesired impurities such as native oxides of Cd and Se could be etched, but surface reactions of CdSe NWs were also observed, resulting in the formation of a layer of elemental Se around a thinner CdSe core. As a result, a heterostructure of Se@CdSe nanostructure formed after acid treatment of CdSe NWs. Upon thermal annealing, the Se shell was effectively removed and thinned stoichiometric single-crystalline CdSe NWs could be obtained. It was observed that NWs could be thinned by up to ~60% in diameter by acid treatment and subsequent Se thermal desorption. The degree of thinning was controllable by adjusting the duration of acid treatment. The success of the thinning of CdSe NWs by simple acid treatment and the annealing process reported here opens a new processing route for obtaining stoichiometric CdSe NWs with controllable size reduction and improved aspect ratio. This can undoubtedly broadly improve the range of applications of 1D CdSe nanostructures and allow more exploration of their uni-directional properties.

 Supplementary data are available from [stacks.iop.org/Nano/18/415607](http://stacks.iop.org/Nano/18/415607)

## 1. Introduction

Since the successful synthesis of nanostructured CdSe [1], it has been a promising candidate in the application of optoelectronics, biosensors and microelectromechanical systems [1–4] owing to its extraordinary optoelectronic and semiconducting properties with quantum-sized effects. In particular, one-dimensional (1D) nanostructures such as nanowires (NWs), nanorods, nanobelts and nanotubes are expected to play an important role as both interconnects and functional units in fabricating nanoscale devices [5]. It has been demonstrated that a CdSe 1D nanostructure with

high aspect ratio can improve the conversion efficiency of solar cells because of its uni-directional channels for charge transport. For example, Huynh *et al* have reported an enhanced conversion efficiency by employing a hybrid system of CdSe nanostructures and organic materials [6]. So as to fully exploit the use of 1D CdSe NWs in nanodevices for optoelectronics and biosensing, it is essential to prepare stoichiometric CdSe NWs with controllable diameter and aspect ratio. In general, solution growth, templated growth and vapour phase growth are general techniques to prepare CdSe 1D nanostructures [7]. With these successes in synthesis, a convenient and practical post-growth method to reduce the size controllably with the preservation of the desirable stoichiometry and crystallinity

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is very much needed in order to manipulate these 1D nanostructures and to tailor-prepare them for different types of applications in which the size, stoichiometry and crystallinity are all important and influential factors.

In this paper, we report a simple acid treatment of relatively thick CdSe NWs with high aspect ratio synthesized by vapour phase growth. Such chemical treatment leads to thinner CdSe NWs covered by an ultra-thin Se coating ( $<40$  Å). After annealing, the Se coating could be desorbed, leaving thinner CdSe single-crystalline NWs with the same or even higher aspect ratio. The diameter of the thinned CdSe NWs can actually be controlled by adjusting the duration of acid treatment.

## 2. Experimental details

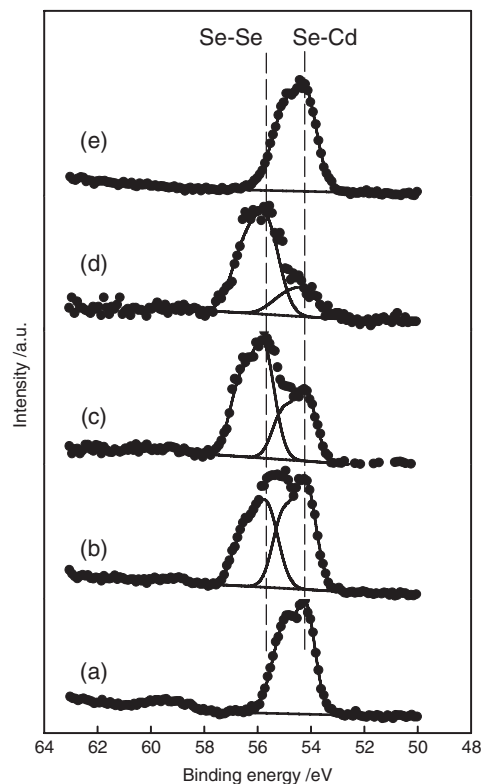
CdSe NWs were obtained using the vapour phase growth method. Commercial CdSe powder as purchased (IL USA 99.9999% with a particle size of  $<2$   $\mu\text{m}$ , CAS 1306-24-7) was placed in the centre of an alumina tube mounted horizontally inside a high-temperature furnace. The tube was then pumped down to a base pressure of  $2 \times 10^{-2}$  Torr. The furnace was heated to  $1200$  °C and kept at this temperature for 2 h before it was cooled to room temperature. A constant flow of argon was introduced at a flow rate of 50 sccm, and the total pressure in the tube was maintained at 300 Torr during the growth process. Synthesized CdSe NWs were collected from the inner wall of the alumina tube. In general, the NWs prepared have an average diameter of  $\sim 100$  nm with an average length of  $\sim 1.5$   $\mu\text{m}$ . As revealed by high-resolution transmission electron microscopy (HRTEM), the NWs synthesized are of hexagonal wurtzite structure with a universal growth direction along the CdSe [002] direction (see supplementary data available from [stacks.iop.org/Nano/18/415607](http://stacks.iop.org/Nano/18/415607)). X-ray diffraction analysis (XRD) characterization also confirmed the hexagonal structure of the CdSe NWs (space group  $P6_3mc$ , JCPDS Card No. 08-0459, see supplementary data available from [stacks.iop.org/Nano/18/415607](http://stacks.iop.org/Nano/18/415607)).

In acid treatment, 5 mg of as-prepared NWs were firstly dispersed in 2 ml of 0.3 M HCl with sonication at room temperature. The dispersed NWs were allowed in the HCl solution for 2 to 12 days with occasional shaking, stirring and replenishing. Acid-treated NWs were then centrifuged and rinsed with deionized (DI) water for three times so as to completely wash away the acid. The acid-treated CdSe NWs were finally re-suspended in toluene for further analyses.

As-prepared and treated CdSe NWs were characterized using TEM (Philips CM 120, 120 kV in general and Tecnai F20, 200 kV for high resolution images), XRD (Rigaku RU-300 x-ray diffractometer with Cu  $K\alpha$  radiation), X-ray photoelectron spectroscopy (XPS, Kratos AXIS-HS XPS system) and scanning electron microscopy (SEM, FEI Quanta 400, 20 kV).

## 3. Results and discussions

XPS measurement was made on the as-prepared and treated CdSe NWs (with acid treatment from 2, 4 and 12 days) which were dispersed onto Si substrates. XPS analysis shows the presence of Si substrate, Cd and Se from the NWs,



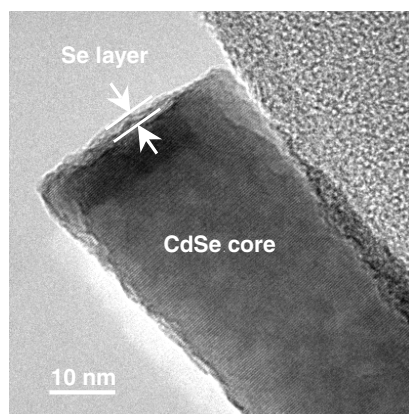
**Figure 1.** (a)–(d) Se 3d spectra of CdSe NWs after 0, 2, 4 and 12 days of acid treatment; (e) Se 3d spectra of CdSe NWs after acid treatment and annealing.

C and O from the adsorbed surface hydrocarbons or native oxides in the case of as-prepared CdSe NWs. No other contaminants were observed. Fine scan XPS signals for Cd 3d and Se 3d were acquired. The Cd 3d signals of both as-prepared and treated CdSe NWs show a single component (not shown here) at  $405.1 \pm 0.2$  eV; while Se 3d XPS spectra show more interesting and obvious differences among them, implying subtle and significant changes on Se species after acid treatment. Figures 1(a)–(d) show the Se 3d XPS spectra of as-prepared and acid-treated CdSe NWs. An additional component at  $\sim 55.7$  eV can be observed after acid treatment. This extra peak becomes more significant for prolonged acid treatment. Based on a parallel XPS study on CdSe(0001) single crystals, the Se  $3d_{5/2}$  at  $54.1 \pm 0.2$  eV is confirmed to originate from Se in CdSe [8]. The emerging component at  $55.7 \pm 0.2$  eV along the acid treatment corresponds to elemental Se [8], implying the formation of an elemental Se layer on the CdSe NWs after acid treatment. It is consistent with the observation by Kirovskaya *et al* [9] of a layer of elemental Se ( $\sim 100$  Å) on a CdSe single crystal surface after etching with HCl. In addition, the Se overlayer was further confirmed by TEM analysis. Figure 2 shows the TEM images of typical CdSe NWs after 12 days of acid treatment. An obvious amorphous Se overlayer can be observed in sharp contrast to the inner crystalline CdSe core whose lattice planes can still be clearly located after treatment.

Table 1 lists the Cd:Se ratios and the thickness of elemental Se coating formed after acid treatment estimated by XPS depth profiling [10]. As reported for as-prepared CdSe

**Table 1.** The compositional ratio of Cd, Se<sub>tot</sub> (total Se), Se<sub>CdSe</sub> (Se from CdSe compound), Se<sub>Se</sub> (Se from elemental Se) and elemental Se thickness after acid treatment for different times (a) before annealing and (b) after annealing.

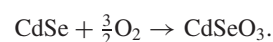
Days of acid treatment	(a)				(b)
	Cd:Se <sub>tot</sub>	Cd:Se <sub>CdSe</sub>	Se <sub>CdSe</sub> :Se <sub>Se</sub>	Se thickness (Å)	Cd:Se <sub>CdSe</sub>
0	1.39	1.39	—	—	—
2	0.64	1.12	1.32	11.0	1.00
4	0.46	1.18	0.63	19.8	1.01
12	0.20	1.04	0.24	37.5	0.93

**Figure 2.** TEM image of typical CdSe NWs after 12 days of acid treatment.

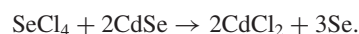
nanostructures (nanoparticles, nanorods and NWs) [11], our as-prepared CdSe NWs are also Cd rich on the surface. This has been explained, as in the case of the CdSe surface, by the air-oxidized Cd in the form of CdO<sub>x</sub> and Cd<sub>x</sub>Se<sub>y</sub>O<sub>z</sub>, which are typical products of surface oxidation on CdSe [12, 13], although our XPS data could not show clearly whether the excess Cd was in metallic or oxide form since the binding energies of Cd with different oxidation states are very close to each other (difference <0.5 eV) [8].

It is evident from table 1 that the ratio of Cd:Se<sub>tot</sub> decreased drastically after acid treatment, indicating excess Se on the NW surfaces in comparison to the XPS and TEM analyses (figures 1 and 2). As mentioned before, Se 3d can be resolved into two components after acid treatment: Se in CdSe and elemental Se. While the elemental Se is on the surface, the CdSe core in NWs is stoichiometric within the error range, as revealed by the ratio of Cd:Se<sub>CdSe</sub>. Meanwhile, the Se<sub>CdSe</sub>:Se<sub>Se</sub> ratio decreased with extended acid treatment. With the estimation of elemental Se thickness in table 1, it was deduced that a thicker Se coating was formed on the NWs with CdSe as the core after prolonged acid treatment. Although, it should be noted that the thickness calculation here is based on a thin layer structure, which is not identical to the current situation for NWs, the calculation results did provide the general trend of Se formation after acid treatment. We propose that acid treatment can firstly remove the surface contaminants (e.g. native oxides of Cd and Se). Then, as CdSe nanomaterials such as nanocrystals are susceptible to oxidation [14], the surfaces of the cleaned CdSe NWs are expected to undergo gradual oxidation with the dissolved oxygen in the acid solution in accordance with the following

equation, giving mainly CdSeO<sub>3</sub>, which is the most probable product from thermodynamic considerations [14]:



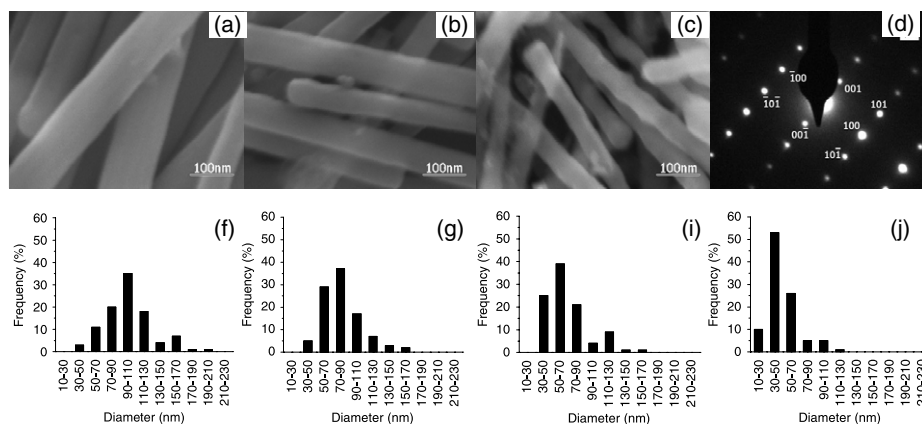
Strong oxidants were avoided here in order to reduce the reaction rate so that the chemical process could be finely controlled more easily. The CdSeO<sub>3</sub> formed on the surfaces of NWs would then react with HCl to give Se as the following equations, in analogy to the reaction between CdTeO<sub>3</sub> and HCl [15]:



As a result, a heterostructure of the Se@CdSe nanostructure formed after the acid treatment of CdSe NWs as CdCl<sub>2</sub>, which is soluble in HCl solution, leaving an elemental Se layer on the treated CdSe NWs.

The Se@CdSe NWs formed were then annealed in vacuum and characterized by XPS and SEM. It was found that the Se coating effectively desorbed under annealing at 350 °C for 1 h at a base pressure ~10<sup>-9</sup> Torr in the XPS analysis chamber. Although current annealing experiments were carried out in vacuum so as to facilitate *in situ* XPS analysis, it should be emphasized that ambient annealing under inert atmosphere could induce the same effect of Se desorption although the desorption temperature should be higher. The annealed sample was analysed by XPS immediately after annealing under UHV. The peak positions of Cd 3d<sub>5/2</sub> and Se 3d<sub>5/2</sub> were 405.2 ± 0.1 eV and 54.2 ± 0.1 eV respectively, which are consistent with the Cd and Se signals measured on CdSe(0001) single crystals. It is important to note that no elemental Se signal was detected after annealing (figure 1(e)). In addition, the ratios of Cd:Se<sub>CdSe</sub> were ~1 (table 1) from all samples after acid treatment and annealing. It shows that stoichiometric CdSe NWs were left after complete desorption of the elemental Se layer during annealing. This is important as it reveals an effective way of producing stoichiometric CdSe NWs.

Furthermore, it was found that NWs could be thinned up to ~60% in diameter by acid treatment and subsequent Se thermal desorption. The degree of thinning was controllable by adjusting the duration of the acid treatment. Figure 3 shows the SEM images and the size distribution of untreated and acid-treated NWs for 2–12 days after annealing. The histograms of size distribution were obtained by measuring the diameters of at least 100 randomly chosen NWs from each batch of samples. NWs became narrower after extended acid treatment, with the median diameter decreasing from ~100 nm (as-prepared



**Figure 3.** SEM images of CdSe NWs ((a)–(c)) after 0, 2 and 4 days of acid treatment with annealing; (d) TEM image of a typical acid-treated CdSe NW; size distribution ((f)–(j)) of CdSe NWs after 0, 2, 4 and 12 days of acid treatment with annealing respectively.

NWs) to  $\sim 40$  nm (NWs after acid treatment for 12 days). In addition, the selected area electron diffraction (SAED) analysis (figure 3(d)) shows that the single-crystallinity of CdSe NWs remains intact even after acid and thermal treatment. The SAED pattern was indexed by a hexagonal system with zone axis [010]. The calculated lattice parameters from the SAED pattern are  $a = 4.19$  Å and  $c = 6.94$  Å, which matches the theoretical hexagonal system with a wurtzite structure ( $a = 4.30$  Å and  $c = 7.01$  Å) of CdSe within the experimental error.

Table 2 shows the median diameter, standard deviation of diameter and the aspect ratio of as-prepared and acid-treated NWs after annealing. The diameter of NWs decreases monotonously with the time of acid treatment. Also, the size distribution became narrower after treatment as reflected by a maximum decrease of 35% in the standard deviation of diameter,  $\sigma_{\text{diameter}}$ . Also, the average aspect ratio has increased by 25% from  $\sim 16$  to  $\sim 20$ . If the maximum aspect ratio is considered, it increased from 26.5 for untreated NWs to 46.2 for NWs after 12 days of acid treatment and subsequent thermal desorption of Se. Further, in accordance with table 2, the thickness etched after the 12-day acid treatment and subsequent thermal desorption is  $\sim 56$  nm (from the median diameter of 99.7 to 43.2 nm). Assuming the same etching depth along both axial and radial directions, the original NWs, which have a diameter of  $\sim 100$  nm and a length of  $\sim 1600$  nm, should be thinned to NWs of  $\sim 44$  nm in diameter and  $\sim 1544$  nm in length after treatment. Under this assumption of isotropic etching, the aspect ratio should increase from 16 to 35, which falls within the range of the observed average and maximum aspect ratios achieved after treatment in the present study. As such, despite an obvious increase of aspect ratio, there is no strong evidence of an anisotropic etching process. Upon consideration of the proposed mechanism and chemical equations described above, preferential etching in either the axial or radial direction is not probable. Therefore, isotropic etching is expected here. Nevertheless, all these demonstrate a controllable size reduction of CdSe NWs from the originally thick NWs while improving the size distribution and aspect ratio.

**Table 2.** Median diameter, standard deviation and aspect ratio of the NWs with different acid treatment conditions.

Days of acid treatment	Median diameter (nm)	$\sigma_{\text{diameter}}$ (nm)	Aspect ratio <sub>average</sub>
0	99.7	30.0	16.7
2	78.8	23.3	16.5
4	61.9	24.7	20.3
12	43.2	19.4	20.9

#### 4. Summary and conclusion

Previously, application of CdSe-based nanomaterials in device fabrication was mostly restricted to nanocrystals and quantum dots. Despite their unique uni-directional carrier transport characteristics, the formation of 1D CdSe nanostructures like NWs has been hampered. This is because preparation of CdSe NWs with exact dimensions by chemical synthesis needs relatively complicated chemical recipes and delicate control of reaction conditions. Although physical methods like vapour phase growth can achieve easier synthesis of CdSe NRs or NWs, the corresponding size is usually thick and is difficult to control. Their surfaces are always contaminated with surface oxide and non-stoichiometric species. The success of the thinning of CdSe NWs by simple acid treatment and an annealing process, as reported here, opens up a new processing route for obtaining stoichiometric CdSe NWs with controllable size reduction and improved aspect ratio. This can undoubtedly broadly improve the application scope of 1D CdSe nanostructures, and allow more exploration of the utilization of their uni-directional properties. Besides, the capability of generating Se@CdSe NWs reported here should allow more viable surface engineering by using appropriate coupling reactions with the Se-terminated surface.

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