Supporting information

Low temperature solution-phase growth of ZnSe and ZnSe/CdSe core/shell nanowires

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1. ZnSe NWs

1.1 Materials characterization

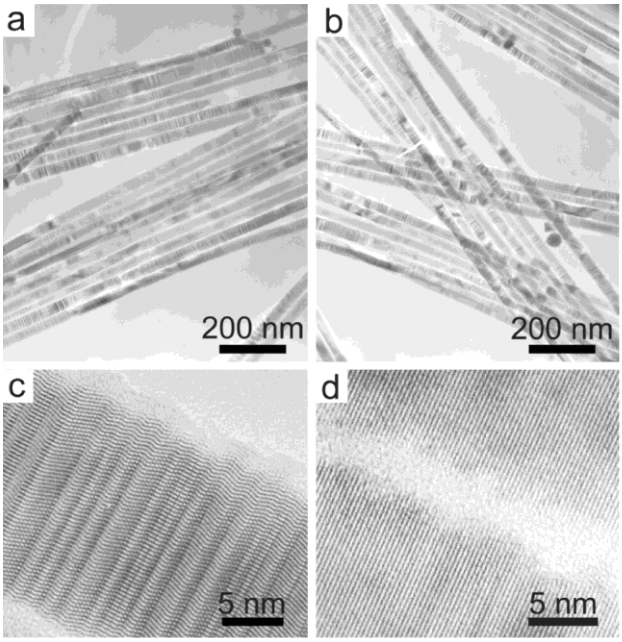

Figure S1. (a,b) Low and (c,d) high resolution TEM images of ZnSe NWs synthesized at 300˚C where the average diameter is *d*=28 nm (σ=5 nm). Apart from temperature, all other synthetic conditions were as described in the main text.

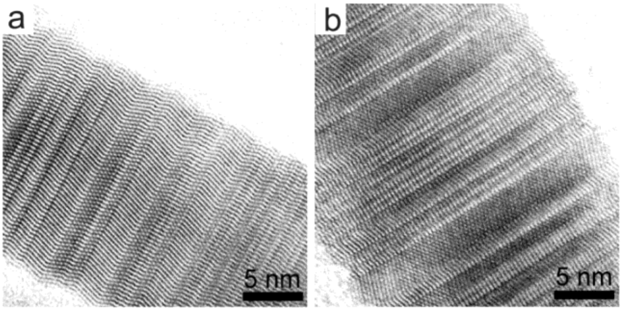

Figure S2. Additional HRTEM images of <110>-oriented ZnSe NWs, illustrating the presence of both ZB and W phases.

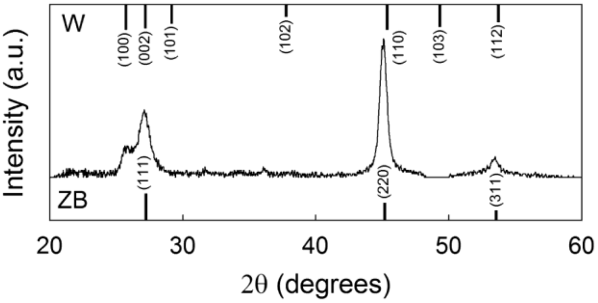

Figure S3. Representative ensemble powder XRD pattern of ZnSe NWs, showing the existence of a ZB/W phase admixture. The top and bottom stick patterns correspond to the W and ZB phases, respectively.

1.2. Synthesis

For the synthesis of ZnSe NWs, various reaction parameters were altered to optimize their growth. These parameters include the metal/chalcogen precursor stoichiometry, the growth solvent coordinating ability, the amount of Bi catalyst introduced, and the overall injection/growth temperature. We briefly discuss each of these reaction parameters to highlight trends in the solution phase growth of ZnSe NWs using Bi salts.[1]

Introduced metal/chalcogen stoichiometry

The metal/chalcogen precursor stoichiometry is an important parameter in solution-based NW reactions. By varying this parameter we not only alter NW diameters and lengths but also their overall morphology. Specifically, in the case of CdSe, a 7:1 Cd:Se ratio yields predominantly straight NWs whereas ~2:1 ratios result in branched wires with characteristic tripod, v-shape and y-shape morphologies that are dictated by the underlying NW crystal lattice.[2] Similar behavior has been seen in both CdTe[3] and PbSe[4] NWs.

In the case of ZnSe, we varied the metal/chalcogen ratio between 16:1 and 1:32. Highly metal rich preparations (i.e. 16:1) yield no wires while 8:1 ratios result in low quality wires with rough surfaces and broad diameter distributions. More stoichiometric ratios of 4:1 and 2:1, yield high quality wires with diameters of ~20 nm, narrow size distributions, and lengths on the order of 10 μm. Stoichiometric as well as chalcogen rich preparations (ratios between 1:1 and 1:32) result in slightly narrower diameters where the wires are of comparable quality. No significant changes in NW diameters or size distributions were seen going from near-stoichiometric to highly chalcogen-rich preparations. From the range of stoichiometries studied, the 2:1 ratio was therefore chosen for further optimization since it reproducibly yielded high-quality wires.

Growth solvent

The coordinating or non-coordinating nature of the growth solvent is also an important parameter in these reactions. Empirically, TOPO appears to be a good

NW growth solvent since it has been used to prepare various solution-based NW materials such as CdSe, CdTe and ZnTe.[2] However, other solvents such as octadecene can be used in these syntheses and can simultaneously alter reaction kinetics through their different metal ion coordinating strength.[5] A number of coordinating or non-coordinating solvents were therefore tried in the current study: TOPO, TOP, oleylamine, phenyl ether, n-octyl ether, octadecene and squalane (in order from coordinating to non-coordinating).

In general, we find that wires cannot be obtained using TOP, phenyl ether or n-octyl ether. However, TOPO and oleylamine as well as octadecene and squalane produce wires. Empirically, TOPO yields the best wires in terms of their length, width and apparent surface smoothness. As observed in the earlier synthesis of CdSe QDs and NWs[6], the TOPO purity in these reactions is important. Reactions carried out under optimized conditions using lower purity TOPO 90% results in very low quality NWs compared to identical reactions performed using 99% TOPO. All reactions were consequently optimized using 99% TOPO.

Amount of Bi catalyst added

Prior NW syntheses using pre-made Bi particles have shown that the amount and diameter of the catalyst particles alters the resulting NW diameter, length and morphology. Namely, introducing larger concentrations of catalyst NPs generally decreases NW diameters. This presumably occurs because of the many NW nucleation sites available, leading to the formation of numerous wires that quickly deplete the local concentration of metal and chalcogen precursors. Radial NW growth is therefore suppressed under these conditions. However, beyond a critical NP concentration the particles tend to aggregate, leading to short and thick NWs of poor quality.[7] At the other extreme, adding only small amounts of NPs results in thicker wires. Using the same logic as above, the lack of a sizable NP concentration means that large amounts of metal and chalcogen precursors are available in the immediate vicinity of a given nucleated wire and can, in turn, promote its radial growth. NP diameters also influence resulting NW diameters. Namely, a relation between the seed and product NW diameters exists.[5]

Analogous studies using $BiCl_3$ to promote the growth of CdSe nanowires show that varying the amount of $BiCl_3$ introduced into a reaction alters the diameter of resulting NWs.[1] Specifically, small amounts of $BiCl_3$ added result in thin wires. Conversely, large $BiCl_3$ concentrations yields thicker wires. This behavior has been explained by different $BiCl_3$ concentrations yielding different sized Bi NPs which, in turn, yield NWs having commensurate diameters.[1]

Because of these observations, the amount of $BiCl_3$ added to ZnSe NW reactions was investigated. To keep the volume of the reaction mixture constant, we varied the concentration of the $BiCl_3$ solution introduced from 1.68 mM to 13.44 mM. Using 60 µL aliquots of these solutions, the amount of $BiCl_3$ added was therefore varied from 0.1 µmol to 0.8 µmol. These experiments show that increasing the amount of added $BiCl_3$ from 0.1 µmol to 0.2 µmol generally results in *thinner* wires. In particular, NW diameters shrink from 28 nm (σ = 5 nm) [sample size = 99] to 18 nm (σ = 3 nm) [sample size = 75] when the reaction is carried out at 300 °C using a 2:1 Zn:Se mole ratio. The trend observed is opposite to what was found in the synthesis of CdSe nanowires using bismuth salts. Our experiments also show that introducing 0.4 and 0.8 µmol of $BiCl_3$ results in short NWs (lengths less than 4 µm).

Injection and growth temperatures

Finally, the injection and growth temperatures were varied to test their effect on NW growth. In this regard, past studies have shown that temperature plays an important role in determining both the quality and morphology of resulting NWs. For example, in the case of CdSe NWs low growth temperatures on the order of 280 °C aid the formation of branched wires.[7] Raising the temperature to 330 °C, however, leads to NW ensembles that are predominantly straight.

To explore the influence of temperature on ZnSe NW growth, syntheses were conducted at 250 °C, 270 °C, 300 °C, 310 °C, 325 °C and 350 °C. The general trend which emerges is that higher temperatures lead to narrower diameter NWs. Specifically, at 300 ºC, resulting ZnSe NW diameters are approximately d=30 nm. At 310 °C, average diameters fall to d~20 nm and decrease even further at 325 °C to d=15-20 nm. At 350 °C no NW growth is observed. In all cases, no branching is observed.

There is one last temperature related observation important to mention. Namely, we find that the stability of the injection/growth temperature is critical to the resulting NW ensemble diameter distribution. In order to obtain narrow size distributions, reaction temperatures must be stabilized quickly after injection.

Growth time

Finally, to conclude our optimization studies, the reaction time was investigated to see its effect on NW growth. Prior studies have shown that Bi seeded reactions are quite fast and NWs can be produced on timescales ranging from 1 to 5 minutes.[6,8] However, in the case of ZnSe we find that reactions take place over much longer periods. Specifically, 2 minute reactions yield short NWs with lengths of ~2 µm and low overall yields. Increasing the growth time significantly increases the overall length as well as yield of resulting NW ensembles. Subsequent experiments with growth times of 10 and 30 minutes were therefore carried out. Reaction times beyond this yielded no apparent differences. We therefore determined that an optimal growth time was 30 minutes.

2. Core-Shell NWs

2.1 Materials characterization

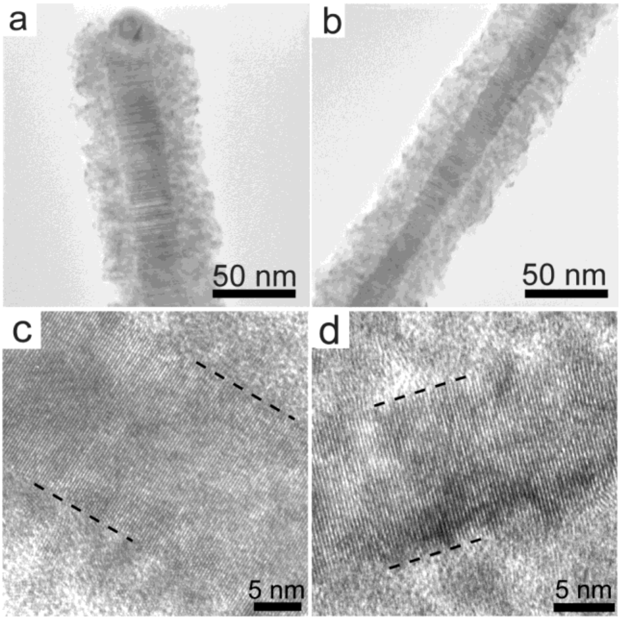

Figure S4. Representative HRTEM images of ZnSe/CdSe core/shell NWs. Dashed lines outline the NW core.

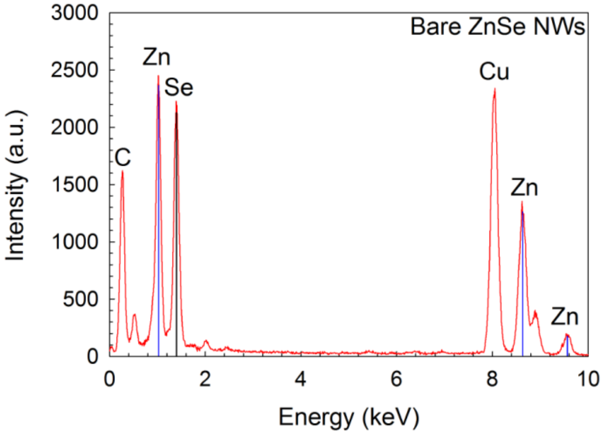

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Figure S5. EDXS spectrum taken from an ensemble of ZnSe NWs, showing a near stoichiometric metal/chalcogen element ratio (Zn:Se 49:51%).

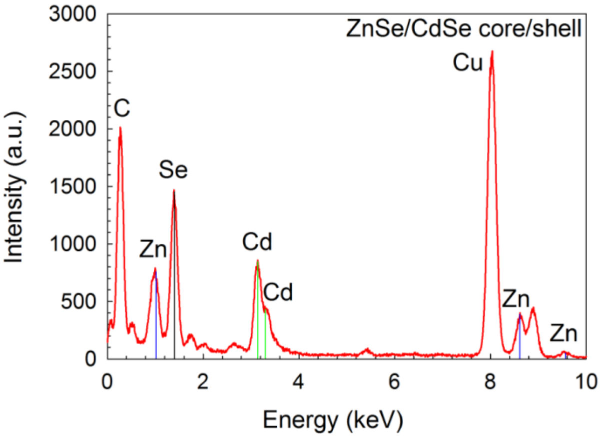

Figure S6. EDXS spectra for an ensemble of ZnSe/CdSe core/shell NWs showing a metal/Se ratio of ~1:1 (i.e. Cd:Zn:Se 46:10:44%).

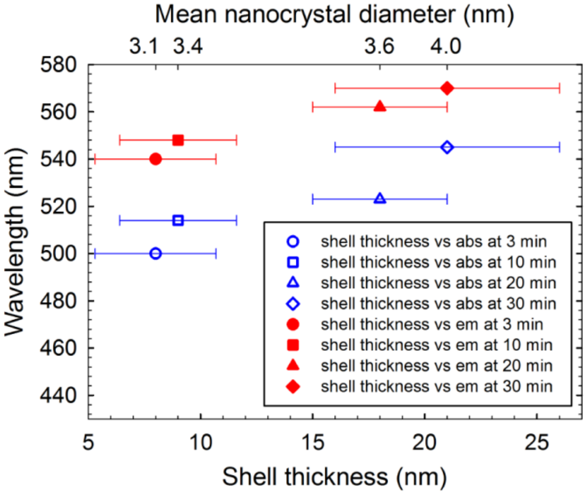

Figure S7. Band edge absorption (open symbols) and emission (solid symbols) of CdSe in ZnSe/CdSe core/shell NWs as a function of shell thickness with corresponding mean nanocrystal diameters on the top axis. Error bars represent shell thickness variations.

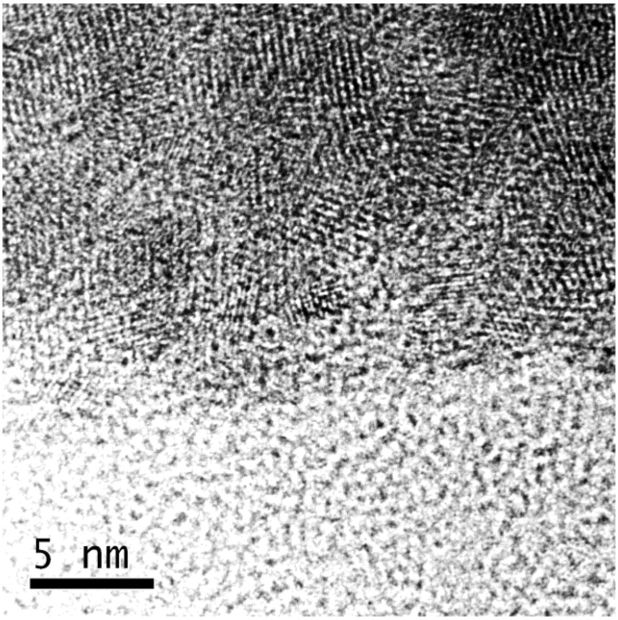

Figure S8. A representative HRTEM image of the CdSe shell

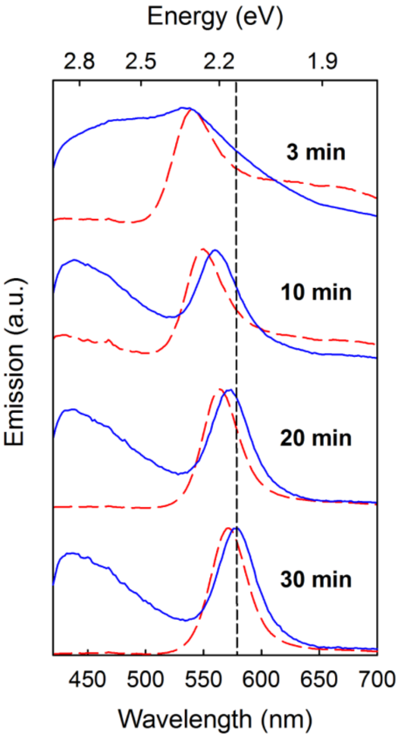

Figure S9. Emission spectra of "free" nanocrystals in solution taken during the overcoating synthesis (solid blue lines) and of purified ZnSe/CdSe core/shell NWs (dashed red lines).

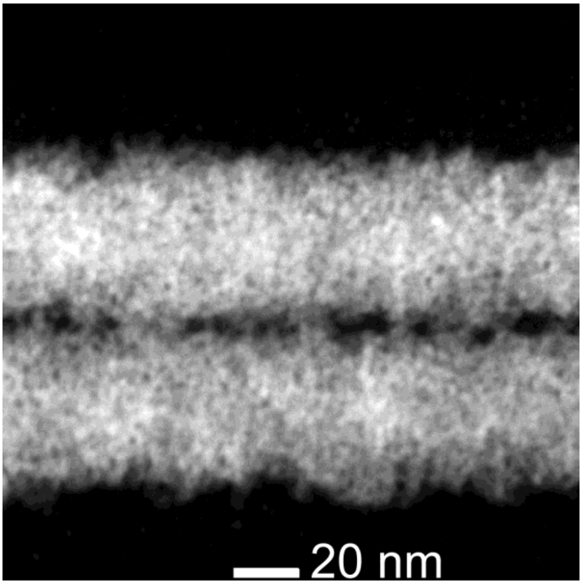

Figure S10. A Z-contrast HAADF STEM image of two core/shell NWs.

2.2 Synthesis

Growth temperature and reaction time

Both the growth temperature and reaction time are important factors that affect the size of CdSe nanocrystals which form the shell. In the present study, the temperature is varied from 90 ºC to 130 ºC. Even though syntheses conducted at higher temperatures result in core/shell structures, a large number of (unwanted) CdSe QDs can be found in solution. Lower temperatures appear to suppress the formation of unwanted nanocrystal byproducts. As a consequence, temperatures below 140 ºC were explored. Furthermore, increasing the overcoating reaction time increases the resulting shell thickness.

Precursor amount

In the first set of reactions, the amount of cadmium precursor added, $Cd(Ac)_2$, was varied from 0.01 g to 0.2 g (37.5 µmol to 750 µmol), keeping all other reaction parameters the same. Small amounts of $Cd(Ac)_2$ (0.01 and 0.05 g) resulted in poor overcoatings. Survey TEMs of these samples show that considerable parts of the NW core were not coated. The minimum amount of cadmium precursor resulting in a uniform coating was therefore found to be 0.1 g. Increasing this value up to 0.2 g produced a thick CdSe shell. All subsequent overcoating reactions were carried out using 0.1 g (375 µmol) of $Cd(Ac)_2$.

In a similar fashion, we changed the amount of selenium precursor to ascertain its role in producing the shell. In this second set of experiments, 10, 20 100, 200, 1000 and 2000 µL of 1M TOPSe were used. However, no correlation was observed between the amount of TOPSe added and the resulting shell quality. As a consequence, all subsequent coating reactions use 100 µL of 1M TOPSe. Control experiments conducted without adding TOPSe or Cd(Ac) do not result in core/shell

NWs.

2.3 Calculations

ZnSe NW concentration

NW absorption cross sections were calculated using the expression[9]

$$\sigma(cm^2) = \left(\frac{\omega}{n_I c}\right)(\pi r^2 l)\left|\frac{4\varepsilon_I}{\varepsilon_I+\varepsilon_s}\right|^2 2n_s k_s \qquad (1)$$

where σ is the NW absorption cross section, ω is the incident light angular frequency (rad/s), n_I is the refractive index of the surrounding medium, c is the speed of light, r is the NW radius, l is the average NW length, ε_I is the complex dielectric constant of the surrounding medium, ε_s is the NW complex dielectric constant, and n_s (k_s) is the real (imaginary) part of the NW's refractive index.

Using the above absorption cross section (σ), the corresponding molar extinction coefficient (ε) is:

$$\sigma(cm^2) = \frac{2.303(1000)}{N_A}\,\varepsilon. \qquad (2)$$

In practice, the ZnSe NW stock solution absorbance at 310 nm was adjusted to 0.97 using a 2 mm cuvette. Beer's Law was then used to calculate the NW concentration through ε derived from σ. In our calculations, the average NW radius and length are assumed to be 7.5 nm and 6 µm, respectively.

Example:
$\omega = 6.1\times10^{15}$ rad/sec (310 nm);
$n_I = 1.5$ (toluene);
$c = 2.98\times10^{10}$ cm/sec;
$r = 7.5\times10^{-7}$ cm;
$l = 6\times10^{-4}$ cm;
$\varepsilon_I = 2.2$ (toluene);
$\varepsilon_s = 10.0076 + i4.536$ (at 4 eV);
$n_s = 3.24$ (at 4 eV);
$k_s = 0.7$ (at 4 eV).

From the above equations and parameters we obtain $\sigma = 2.99\times10^{-10}$ cm^2 and $\varepsilon = 7.80\times10^{10}$ M^{-1}cm^{-1} at 310 nm. For an absorbance of 0.97 this yields a stock solution concentration of C=6.21×10^{-11} M (4.6×10^{-14} mol in 0.75 mL).

References

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