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Controlling Growth of CdSe Nanowires through Ligand Optimization

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We have successfully synthesized nearly monodisperse CdSe nanowires with a length of 220 nm and a diameter of 8 nm. We achieved this through a systematic investigation of the reaction parameters, including the type of ligand for both Cd complexes and Se complexes, the reaction temperature, the precursor concentration, and the precursor injection process. It is proposed that the formation of high aspect ratio nanocrystals is the result of achieving a good balance between nucleation and growth. The optimum conditions to achieve a high aspect ratio require the use of dodecylphosphonic acid (DDPA) and trioctylphosphine (TOP) as the complexing ligands for Cd and Se respectively and a high precursor concentration. Contrary to the previous findings, we found that a high reaction temperature (310 °C) favors a higher aspect ratio nanocrystal growth than a low reaction temperature (250 or 280 °C). The effective monomer model can still be used to explain the shape evolution of CdSe nanowires. Although the aspect ratio (28) of the CdSe nanowires produced using this method is smaller than that obtainable using the solution−liquid−solid method (> 100), this study demonstrates a promising way of producing nanowires via a catalyst-free and solution-based method.

Introduction

In recent years, significant progress has been made in controlling the morphology and chemical and physical properties of nanocrystals using the hot coordinating solvents method.[1−6] This method was pioneered by Murray et al. in 1993 for the synthesis of nearly monodisperse cadmium chalcogenide semiconductor nanodots.[1] Their synthesis is based on the pyrolysis of organometallic precursors ($CdMe_2$) by injection into a hot coordinating solvent. In the past 15 years, their recipe has been modified by several groups. For example, a less toxic and more convenient precursor, cadmium oxide (CdO), was introduced to replace $CdMe_2$,[7,8] and noncoordinating solvents, such as octadecene (ODE),[9] were used to replace trioctylphosphine oxide (TOPO). Over the years, cadmium selenide (CdSe) nanocrystals have become one of the most well studied materials with control of its properties and morphology being the key focus.[9] Despite the success in producing high-quality CdSe nanodots,[1] nanorods,[2−4] tetrapods,[10] and quantum dot−quantum well structures,[11] nanowires with a high aspect ratio synthesized in a controllable manner using this method are still rarely reported.[12]

There are several other methods that can be used to synthesize nanowires in solution, including the solution−liquid−solid (SLS) method, the solvothermal/hydrothermal method and the oriented attachment process. The SLS method has been proven to be a useful approach for producing nanowires in recent years.[13−15] This method has several advantages, such as narrow diameter distributions and comparatively low reaction temperature (< 350 °C).[13,16] However, the growth of nanowires via SLS suffers from the requirement for a metal catalyst at the beginning of the growth which may contaminate the nanowires and thus potentially change their properties.[17] Another method to synthesize nanowires is through the use of dot-shaped nanocrystal self-assembly via an oriented attachment process. The driving force for this process is either the presence of a dipole moment in the nanocrystal or the reduction of surface tension through the elimination of surfaces via attachments.[12,18−20] The advantages of this method are that

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it is catalyst-free and low temperature unlike the SLS method. Several materials, including ZnO[21] and ZnSe[22] nanorods and CdSe,[12,20] CdTe,[20] and PbSe[23] nanowires, have been obtained through this process. In the case of CdSe nanowires, a long reaction time (> 8 h) is required for prewire aggregation of the nanoclusters and the subsequent fusion of fragments into wires.[12] Furthermore, using this method to synthesize nanowires requires further studies to better explore its general applicability.[17]

As a result of the degree of control that is offered by the hot coordinating solvents method together with a catalyst free growth condition, we are keen to extend this method to the synthesis of higher aspect ratio CdSe. Previously, it was reported that when the length of the nanorods reached 50 nm, the uniformity of the nanorods along the growth direction becomes poor and branching was often observed.[3,12,24] Very recently, Kang et al.[25] and our group[26,27] reported the successful synthesis of CdS nanowires using this method. The nanowires synthesized by our group were around 600 nm in length and 3.5 nm in diameter. In that study, we optimized the parameters that affect the formation of high aspect ratio nanocrystals via systematic investigation. Using the same conditions as that for CdS nanowires, only short CdSe nanorods were produced. We proposed that the reason for this is due to the faster cleavage rate of P=Se compared to P=S which leads to more nuclei and hence more rapid depletion of the monomers. As a consequence, the concentration of precursors available for the rods to grow into nanowires is reduced substantially. Thus, we think that it is possible to produce CdSe nanowires if we can manipulate the cleavage rate of P=Se and P=Cd complexes via a change in the type of ligands used to form the complexes to achieve a good balance between nucleation and growth.

Experimental Section

Materials. TOPO (trioctylphosphine oxide, 99%) was purchased from Sigma-Aldrich. TOP (trioctylphosphine, 90%), TBP (tributylphosphine, 90%), and cadmium oxide (CdO, 99.95%) were purchased from Fluka. TPP (triphenylphosphine, 95%) was purchased from Tokyo Kasei Kogyo Co. Ltd. HPA (hexylphosphonic acid, 100%), DDPA (dodecylphosphonic acid, 100%), ODPA (octadecylphosphonic acid, 100%), and selenium (99.99%) were purchased from Polycarbon Inc. and Kanto Chemicals Inc., respectively.

Methods. In a typical synthesis, 0.128 g of CdO, 0.500 g of DDPA (0.668 g of ODPA or 0.232 g of HPA), and 3.0 g of TOPO were added to a 25 mL three-neck flask equipped with a condenser and a thermocouple adapter. The mixture was degassed at room temperature for 15 min. The flask was then filled with N_2, and the temperature was gradually raised to 330 °C to dissolve the CdO. After the CdO was dissolved and Cd complexes formed, the solution turns colorless. When the temperature was lowered to 310 °C, a solution of 0.078 g of selenium in 2.0 g of TOP (2.0 g of TBP or TPP which is heated up to 200 °C due to its high boiling point) was injected in multiple injections (four times at 2 min intervals). After the last injection of selenium, the temperature of the reaction mixture was maintained at 310 °C for further growth. The reaction was stopped by removing the flask from the heating mantle. The nanowires were then washed twice with toluene/ethanol and redissolved in toluene for further characterization.

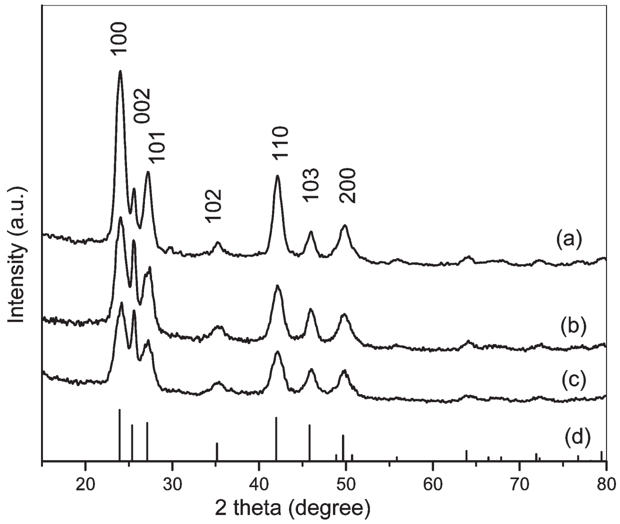

Figure 1. Typical X-ray diffraction (XRD) patterns of CdSe nanocrystals with different dimensions: (a) nanowires (220 × 8 nm), (b) long nanorods (83 × 9 nm), (c) short nanorods (20 × 7 nm), and (d) JCPDS hexagonal CdSe pattern.

TEM was carried out using a JEOL 2010 microscope fitted with a LaB_6 filament and the acceleration voltage used was 200 kV. Ultraviolet−visible (UV−vis) absorption spectra of the nanocrystals were obtained using a Shimadzu UV2501PC spectrophotometer. Thin film X-ray diffraction (XRD) studies were carried out on a Rigaku DMAX 2200 using Cu Kα radiation.

Results and Discussion

Phase Analysis. Typical X-ray diffraction (XRD) patterns from the as-prepared CdSe nanocrystals are shown in Figure 1. It can be seen that all the nanocrystal peaks can be indexed as wurtzite CdSe (JCPDS card No. 08-0459). In addition, it was found that, for these three samples, some peaks are enhanced while others are suppressed compared to the bulk wurtzite CdSe pattern (see Figure 1d). These changes likely arise from the substrate-induced nanocrystal orientation.[28] This phenomenon has been observed with CdSe[24] and CdTe[29] nanowires. Grebinski et al. and Kuno et al. proposed that that in an X-ray diffractometer (powder or thin film) only planes parallel to the substrate surface produce strong diffraction lines.[24,28] They assumed that one-dimensional (1D) nanocrystals lie nearly flat on the substrate during

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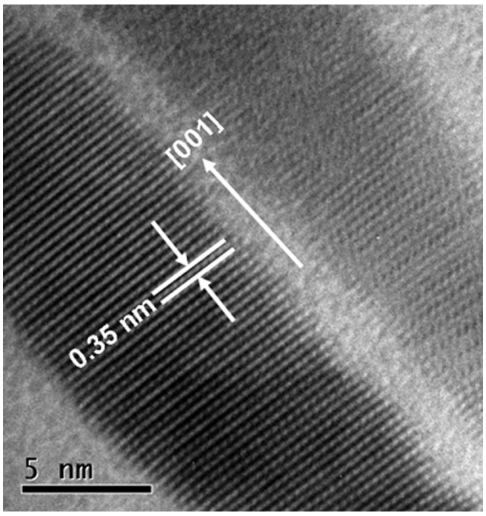

Figure 2. High-resolution TEM (HRTEM) image of CdSe nanowires.

sample preparation. The samples are prepared by drop casting the nanocrystal solution onto the substrate. As the solvent dries, the nanocrystals are packed and aligned. In the case of 1D wurtzite CdSe nanocrystals with a [001] growth axis all the nanocrystals lie nearly flat on the surface so only planes with normals perpendicular to [001] diffract strongly.[24,28] Therefore the planes which contribute significantly to the XRD patterns are (100), (110), and (200) planes as shown in Figure 1. As the aspect ratio increases, the intensity of the (100) and (110) reflections becomes stronger. This is because the probability of the higher aspect ratio nanocrystals lying flat on the substrate is higher. In the case of the short rods, not all the rods lie flat on the substrate, and hence the (001) reflections are seen to be stronger compared to the other reflections.

A high-resolution TEM (HRTEM) image of the CdSe nanowires is shown in Figure 2. The lattice fringes show that the nanowires are single crystals, and the 0.35 nm spacing is consistent with the (002) lattice plane spacing of wurtzite CdSe. These results also indicate that the nanowires grow along the [001] direction, which is in agreement with results from both our group[30] and other research groups.[1,4,5,8,25] Additional HRTEM images of nanowires and a diffraction pattern of a single nanowire are shown in the Supporting Information (see Figure S1). In this study, even though these HRTEM images do not show any defects, some stacking faults and branches can still be observed in some of the TEM samples.

Nanowire Morphology. *1. Influence of the Different Ligands on Cd Complexes.* In the past, the major role of surfactants such as phosphonic acids, phosphines, amines, and carboxylic acids has long been believed to be their selective adhesion to certain nanocrystal surfaces, as well as controlling monomer solubility.[31] Recent studies show that these surfactants are also ultimately responsible for cleavage of the phosphorus chalcogenide double bond.[32] This process is supposed to lead to the formation of semiconductor monomers, while the rate of this cleavage affects crystal nucleation and growth.

In this study, three different phosphonic acids and phosphines are used as ligands for Cd complexes and Se complexes in the reaction. Their chemical structures are shown in Figure 3. We first investigated the effect of the different ligands for Cd complexes on the morphology of nanocrystals. It was found that the phosphonic acids with longer alkyl chains, such as ODPA and DDPA, are better at controlling the morphology of the nanocrystals than those with shorter alkyl chains, such as HPA. HPA produces nanocrystals with morphologies ranging from dots and rods to branches. The diameter was not uniform along the growth direction; hence, this ligand has very poor control over the morphology of the nanocrystals formed (see Figure 4a). Using DDPA and ODPA, nearly monodisperse nanorods with diameter of 9 nm are formed as shown in Figure 4b,c, respectively. The length of the nanorods synthesized using DDPA is 83 nm, and using ODPA we obtained nanorods with lengths of about 41 nm. The morphology of the nanocrystals synthesized using DDPA is well controlled compared to those synthesized using ODPA. This result is not as we expected and is different from that of CdS nanowires which we reported previously.[26,27] Previous studies showed that the reactivity of Cd complexes affects the P=S cleavage kinetics and the nucleation and growth rate of anisotropic nanocrystals.[32] Complexes with lower reactivity allow the monomers to adjust their position on the surface of the nanocrystals before the binding occurs.[8] If this is the only reason affecting the length of nanorods, Cd−ODPA complexes which can provide both a low diffusion rate and low reactivity should be a good candidate for generating higher aspect ratio CdSe nanorods. As we see from Figure 4, DDPA generates the highest aspect ratio nanorods. Hence, there is at least one other factor that also affects the growth. We think that it is highly probable that the rate at which the P=Se bond is broken affects the morphology of the nanocrystals strongly. It is reported that the cleavage rate of the P=Se bond is faster than that of the P=S bond[26,32] which results in more nuclei and hence more rapid depletion of the monomers. As a result, the rods had no more precursors to grow longer. The different cleavage rate of the P=S and P=Se bonds also affects balance between nucleation and growth. A good balance will favor formation of high aspect ratio nanocrystals. In the following discussion, we will present the studies of the effect of the different Se ligands on the nanocrystal morphology when DDPA is used as the Cd ligand.

2. Influence of the Different Ligands on Se Complexes. Compared with Cd complexes, the different ligands for Se complexes were found to have a strong effect on the morphology of the nanocrystals. In this study, it was observed that the time taken for the color of the solution

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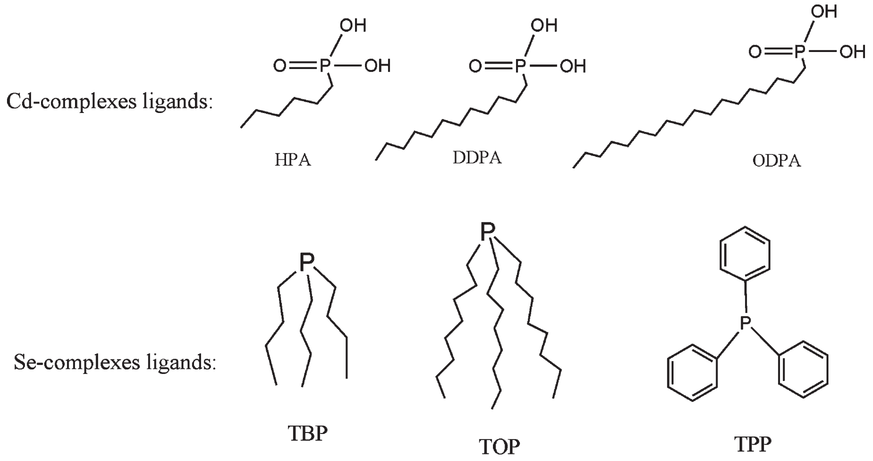

Figure 3. Chemical structures of ligands for Cd complexes and Se complexes.

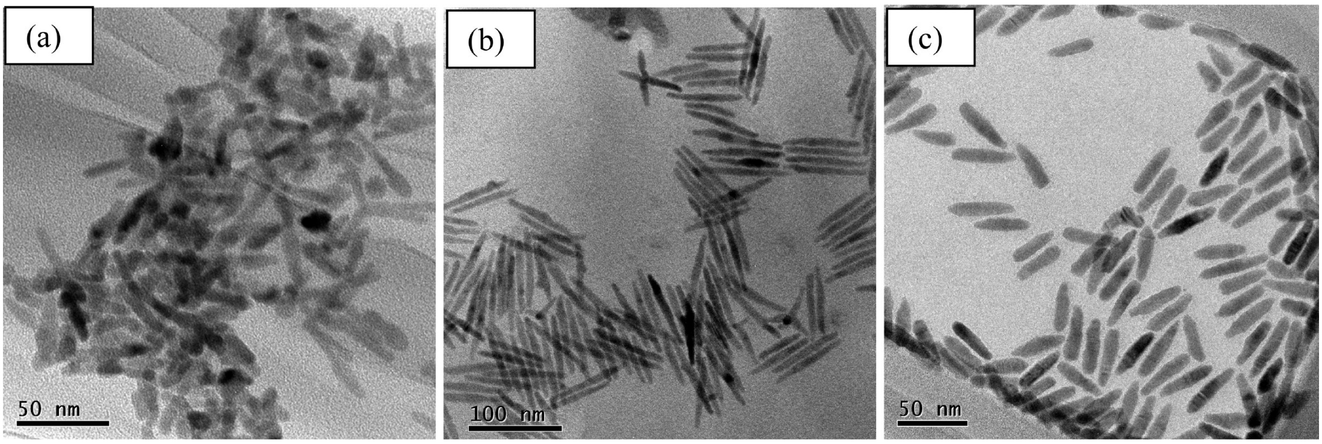

Figure 4. TEM images of CdSe nanocrystals synthesized with different ligands for Cd complexes at 310 °C: (a) HPA, (b) DDPA, and (c) ODPA. The ligand used for Se complexes is TOP.

with TBP=Se to change is slower by several minutes compared to that taken by the solution containing TOP=Se. The color of the solution containing TBP=Se went from red after the second injection, to brown after the third injection, then to dark brown after the fourth injection. For the solution containing TOP=Se, the changes take place between the first and the second injection. This difference in color change between the TBP complexed solution and the TOP complexed solution was also found during CdS nanowire synthesis, which will be discussed in a separate paper. This observation is different from that of other groups.[9,33] They found that the reactivity of TOP is lower than that of TBP and attributed this to the steric effect. This difference in observation may be due to the difference in the reaction conditions. Yu et al. synthesized CdTe nanocrystal dots, rods, and tetrapods in noncoordinating solvents (ODE and oleic acid).[9] Wahington et al. prepared CdSe nanocrystals using alkane solvents (pentane, heptane, octane, or decane), cadmium stearate, and microwave based dielectric heating.[33]All these differences in reaction conditions may affect the cleavage rate. Figure 5 is a diagram showing how the proposed attack may take place in the presence of the three different ligands. The scheme was first proposed by Liu et al. very recently in the study of precursor evolution in colloidal group II−VI nanocrystal synthesis.[32] Figure 6a,b shows TEM images of nanocrystals grown with TBP and TPP. Using TBP, the nanorods formed are mainly 43 nm in length and 5 nm in diameter. Compared with the nanocrystals produced by TOP (refer to Figure 4b), both the length and diameter are reduced by nearly half for those nanocrystals synthesized using TBP. However, the aspect ratio of the nanocrystals is similar. This is due to the binding effect of TBP on both the facets on the short axis and on the long axis of the nanocrystals. TBP binds more strongly to the facets than TOP; hence, there is a reduction in the reaction rate in the presence of TBP. Furthermore, the steric effect difference

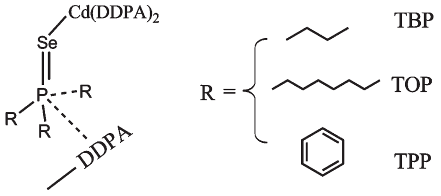

Figure 5. Steric effect comparing of different ligands on Se complexes.

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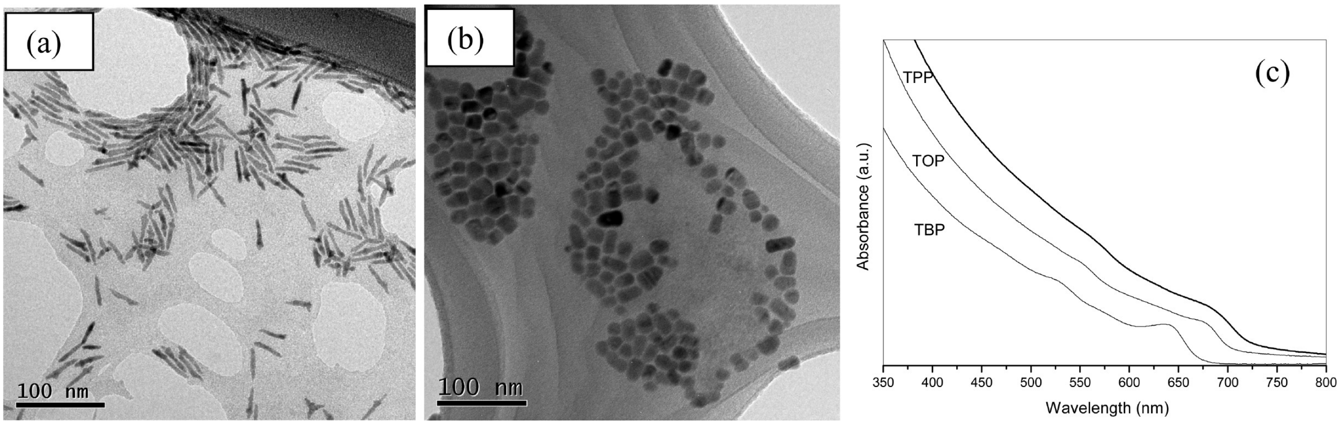

Figure 6. TEM images of CdSe nanorods synthesized with DDPA and (a) TBP and (b) TPP. (c) UV−vis absorption spectra of nanocrystals synthesized with TBP, TOP, and TPP ligands.

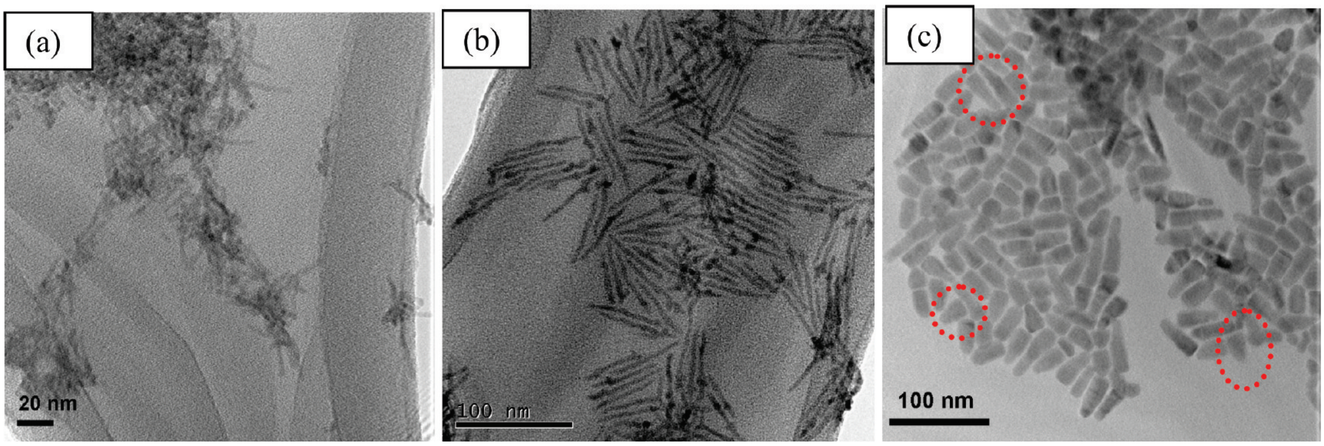

Figure 7. TEM images of CdSe nanocrystals synthesized with DDPA at (a) 250 °C, (b) 280 °C, and (c) 340 °C.

between TBP and TOP is not so big compared to TPP (refer to Figure 5). Thus, the steric effect cannot be used to explain the reaction rate difference between TOP and TBP observed in our experiment.

On the other hand, the difference in reaction rate is readily observed when using TPP. During the synthesis, the time taken for the color change for the TPP complexed solution is significantly shorter (around 30 min) compared to that for TOP and TBP complexed solutions. During the cleavage of the P═Se bond, its three benzene rings will prevent alkylphophonate attack on the (TPP═Se)-Cd complex. We proposed that this difference is indeed due to the steric effect (refer to Figure 5). Using TPP, we can get a mixture of dots, short rods, triangle rods, and hexagonal disks as shown in Figure 6b (also refer to Figure S2a,b for less well-grown hexagonal disk and an irregular disk synthesized using TPP). It can be seen that there is less control over the morphology when using TPP. The reason for the different morphologies when using TBP, TOP, and TPP is the difference in cleavage rate of the P═Se bond. A lower cleavage rate such as TPP and TBP results in lower CdSe monomer concentrations at the initial stage. The lower CdSe monomer concentration did not favor anisotropic growth.[2,4,8] Thus, it was proposed for the synthesis of high aspect ratio CdSe that the ideal combination will be the use of TOP as ligand for Se complexes and DDPA as ligand for Cd complexes. Figure 6c shows the UV−vis absorption spectra of nanocrystals grown using TBP, TOP, and TPP. The red shift in the absorption peak from 636 nm for TBP, to 677 nm for TOP, and then around 685 nm for TPP grown nanocrystals indicates that the diameter of the nanocrystals has increased. The relative broad peak for TPP is due to the size distribution and the differences in morphology of the nanocrystals (see Figure 6b).

3. Influence of the Reaction Temperature. The reaction temperature was found to be another factor that affects the cleavage rate. It is because regardless of the growth mechanism, cleavage is a thermodynamic process. In previous studies, it was found that the required reaction temperature for 1D CdSe nanocrystals (260−290 °C) is lower than that of CdS nanocrystals (300−315 °C).[5,25−27,30,32] Contrary to these findings, we observed that decreasing the reaction temperature can lead to a decrease in the highest aspect ratio of the nanorods (see Figure 4b and Figure 7a,b). The diameters of nanorods synthesized at 250 and 280 °C are 3.3 and 6 nm, respectively, while the lengths are 10−30 and 64, nm respectively. As shown in Figure 4b, 1D CdSe nanocrystals synthesized at 310 °C are 9 nm in diameter and 83 nm in length. It can be seen that when the synthesis is carried out at 310 °C the morphology of these nanocrystals is well controlled compared to those synthesized at lower

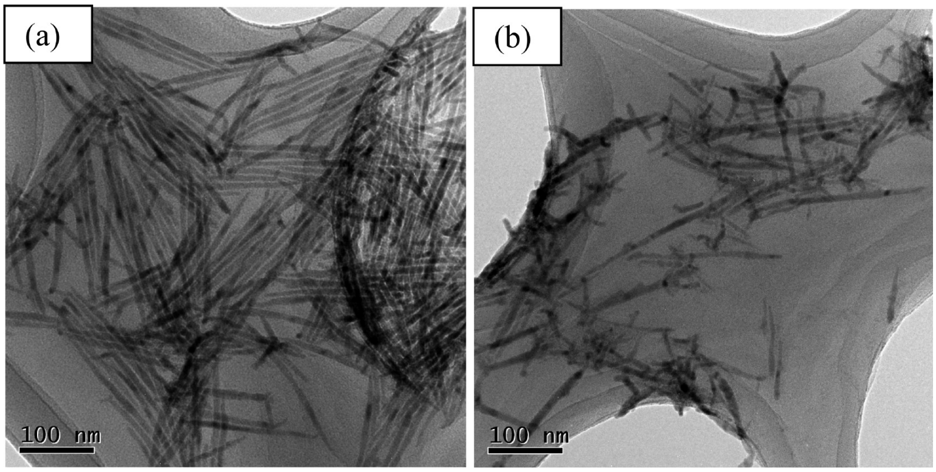

Figure 8. TEM images of CdSe nanowires synthesized using DDPA and with varying precursor concentration (in comparison with the concentration used to synthesize CdSe nanorods shown in Figure 4b): (a) double the concentration and (b) triple the concentration. Note: The concentration here refers to both precursor concentrations (Cd and Se) in all reagents. If the baseline concentration is 0.18 mol/kg, double the concentration is 0.35 mol/kg, and triple the concentration is 0.53 mol/kg.

temperature. In addition, the surface of CdSe nanorods synthesized at lower temperature (250 and 280 °C) is less uniform than that synthesized at 310 °C. The temperature dependence of the aspect ratio can be seen as another form of concentration dependence.[8] As mentioned above, cleavage is a thermodynamic process and hence affected by temperature. A lower reaction temperature results in a lower cleavage rate and therefore a lower monomer concentration in the solution. As a result of the low monomer concentration, anisotropic growth is not favored since such growth requires a high monomer concentration after the nucleation stage.[2,4,8] When the reaction temperature is increased to 340 °C, nanorods with a diameter of 16 nm and a length of 42 nm are obtained and the aspect ratio decreases. This is because although a high reaction temperature leads to a higher cleavage rate and higher monomer concentrations, the reaction produces a higher number of nuclei at the initial stage of the reaction. The speed of nucleation and growth is greatly accelerated. The monomers have less time to adjust their position on the surface of the nanocrystals before the binding occurs. Thus, the morphology of the nanocrystals is less controlled (see Figure 7c). In addition, there exist some sphenoid structures, which are indicated by the dotted circles shown in Figure 7c (also refer to Figure S3 for a HRTEM image). This structure is observed after the second injection. As the reaction continues, the diameter increases and the tip becomes blunt because of intraparticle ripening. From this study it was found that 310 °C is the optimum temperature for high aspect ratio growth where a good balance between nucleation and growth can be achieved.

4. Influence of the Precursor Concentration. In this study, with the total amount of reactants fixed at 5.706 g, changing the precursor concentration was found to change the aspect ratio of the nanocrystals substantially. When the precursor concentration doubles, the reaction yields nanowires with a nearly monodisperse diameter of 8 nm and a length of 220 nm (see Figure 8a). These results show that in order for nanowires to grow longer, a higher precursor concentration is required (see Figure 4b).[2] However, a further increase in the precursor concentration will result in an adverse effect on the distribution of the length, diameter, and aspect ratio of the nanocrystals. The length of the nanocrystals ranged from 20 to 300 nm and the diameter ranged from 5 to 12 nm (see Figure 8b). In the previous studies, as the precursor concentration was increased, the morphology of the nanocrystals was found to change from spherical, to short rods, to long rods, and then to branched rods.[8,34] A higher precursor concentration may result in either longer or branched anisotropic nanocrystals. In our case, this is true when the precursor concentration is increased by a factor of 2 (compared to the baseline concentration of 0.18 mol/kg). But this effect is not seen when the concentration is increased by a factor of 3. The overall precursor concentration that we are working with when the concentration was trebled (0.53 mol/kg) is higher than that used by other groups (0.43 mol/kg).[8] It is possible that the reason why this trend is different from that observed by other groups is the difference in the reactants (for example, they used ODPA or TDPA as the Cd complexing agent and TBP mixed with TOP as the Se complexing agent) and the injection conditions (for example, the injection and growth temperature in their studies are at 350 and 300 °C, respectively). It was found by several groups that the injection process can also affect the nanocrystal morphology.[8,26,27,31] We will discuss this effect in the next section. However, we think that the reason for the formation of a mixture of nanowires and nanorods at even higher concentration may be due to the higher number of nuclei present at the initial stage of the reaction.[26] The speed of nucleation and growth can be accelerated by increasing the precursor concentration.[8] A fast nucleation and growth speed may leave less time for monomers to arrange themselves before binding on the surface as we discussed above. Thus the morphology of

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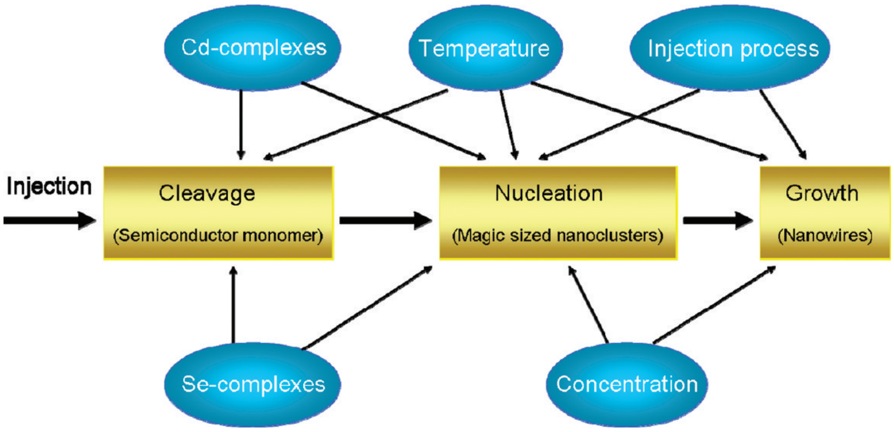

Figure 9. Scheme showing how various reaction parameters affect the growth of nanocrystals.

nanocrystals when the concentration is trebled is less well controlled.

5. *Influence of the Precursor Injection Process.* We studied the effect of the injection process on the morphology of nanocrystals when the precursor concentration is doubled. It was found that there is no obvious difference in morphology between a continuous injection for 16 min and multiple injections (four injections each lasting 2 min with a 2 min interval between them). The length of the nanorods was about 220 nm and their diameter around 8 nm. However, when the injection interval was increased to 4 min or even longer, the length of the nanocrystals decreased while their diameter remained constant. These nanorods had length of about 170 nm and a poor size distribution. The long interval between the monomer injections meant that a high monomer concentration in the solution was not maintained which is thought to be prerequisite for anisotropic growth.[2,34] Thus the optimum conditions for the growth of CdSe nanowires are to use DDPA and TOP as ligands for the precursors, the concentration should be twice the baseline concentration, and there should be multiple injections at short intervals or continuous injections.

A summary of the effect of the various reaction parameters on the growth of nanocrystals is shown in Figure 9. (1) The Cd complexes and Se complexes affect both the cleavage and the nucleation processes. It was found that both Cd complexes and Se complexes mainly affect the cleavage of the phosphorus chalcogenide double bond.[32] Cleavage of the double bond leads to the formation of semiconductor monomers, and the rate of this cleavage mainly affects the nucleation process. (2) The precursor concentration in the solution can influence the nanocrystal growth mode by affecting both the nucleation and the growth.[4,8,34] (3) The reaction temperature affects all three stages: cleavage, nucleation, and growth of the nanocrystals. The cleavage process is essentially a thermodynamic process, and hence it is temperature sensitive. (4) The injection process affects the monomer concentration in the solution.

6. *Time-Dependent Studies.* A time-dependent study of the growth of CdSe nanocrystals is shown in Figure 10. It can be seen that after the third injection of TOP=Se, nanoneedles with a length of 75 nm and a diameter of 6.5 nm (see Figure 10a) are formed. After more precursor was injected and as the reaction progressed these nanoneedles grew longer and the diameter increased slightly. Seven minutes after the fourth injection the length of the nanowires had grown to 220 nm and their diameter increased to 8 nm (see Figure 10b). This observation is consistent with previous work.[4,8,35] Thirty minutes after the fourth injection the length of the nanorods had grown from 85 to 230 nm and the diameter had increased to 9 nm as shown in Figure 10c. An increase in the diameter and a decrease in the aspect ratio of the nanorods is due to intraparticle ripening, which means that the monomer migrated from the long sharp end to the side of the nanorods.[10,36,37] Similar behavior was often observed during the synthesis of other II−VI nanorods using this method.[2,4,8,10,36,37] It is proposed that a balance between the kinetic and the thermodynamic growth regimes strongly affects the final morphology of the nanocrystals.[38] Anisotropic growth of nanocrystals along their *c*-axis is favored under a kinetic growth regime if a high precursor concentration is present. On the basis of the above time-dependent TEM images, we can deduce that the most widely accepted model, the effective monomer model, proposed by Peng et al., can still explain the shape evolution of CdSe nanocrystals.[4,8,34] This model suggests that the growth of anisotropic nanocrystals mainly depends on the effective monomer concentration. Thus, these nanocrystals go through three stages, the 1D growth stage, the 3D growth stage, and the 1D to 2D ripening stage, as the effective monomer concentration decreases. However, in some cases, we observed that the nanocrystals may follow an oriented attachment mechanism (see Figure 11). Looking at Figure 11a, it is observed that there are lots of tiny nanodots accompanying the nanorods. With the injection of a new precursor, these tiny nanodots grow and attach to the neighboring nanorods

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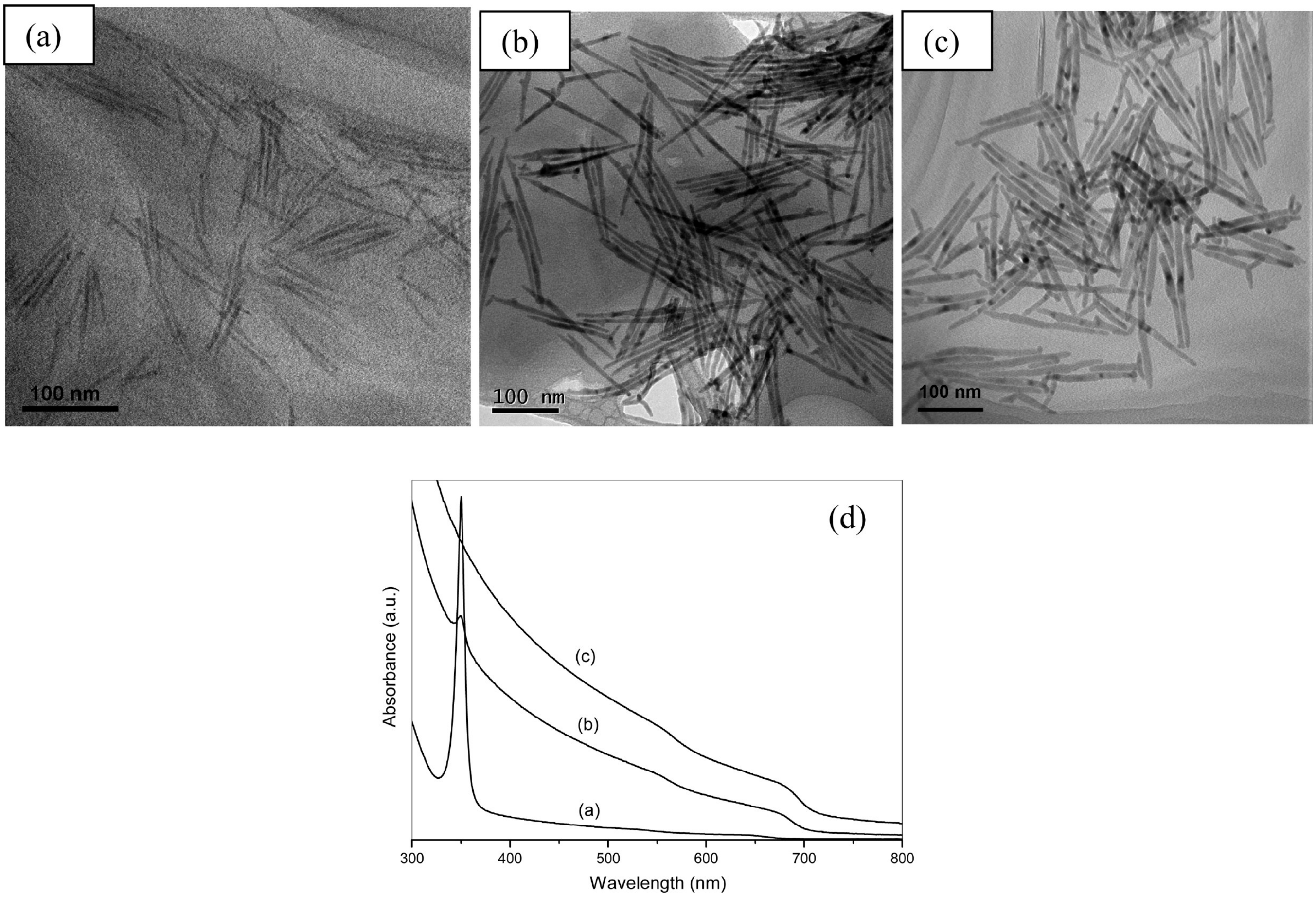

Figure 10. Time-dependent TEM images of CdSe nanowires (a) 2 min after the third injection, (b) 7 min after the fourth injection, and (c) 30 min after the fourth injection. (d) Time-dependent UV−vis absorption spectra of CdSe nanowires.

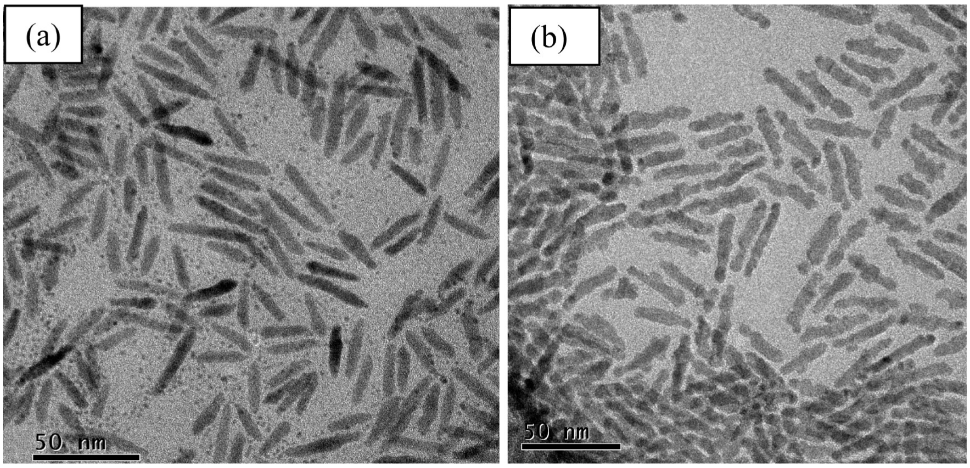

Figure 11. TEM images of CdSe nanocrystals most probably grown via oriented attachment.

(see Figure 11b). As the reaction goes on, these dots fused and became part of the nanocrystals.[39] The most possible reason for the oriented attachment is the presence of a dipole moment in these CdSe nanodots.[12,20]

Figure 10d shows UV−vis absorption spectra of the CdSe nanorods at different stages of growth. It can be seen that there are two obvious peaks observed in the absorption spectra. The first peak is centered at 349 nm. It is proposed that the existence of a sharp peak at 349 nm is an indicator of CdSe clusters containing 17 Cd atoms (Cd_{17}) which has a size of about 1−2 nm.[8,20] They are commonly known as the magic sized nanoclusters, and they have a tetrahedron close-shell configuration with a zinc blend core.[3,34,40] As the reaction progressed, the peak

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intensity at 349 nm is gradually decreased. It almost completely vanished 7 min after the fourth injection. This change tells us that the previously formed CdSe clusters (Cd_{17}) have been converted to larger or more complicated nanoclusters. The second peak, namely, the first exciton absorption, is located at around 650−690 nm. Its intensity gradually increases, and the peak center becomes red-shifted as the reaction proceeds. This shift is consistent with the increase in diameter of the nanorods.

Conclusions

In summary, nearly monodisperse CdSe nanowires with a diameter of 8 nm and length of 220 nm were successfully synthesized using a catalyst-free solution-based method. Varying the precursor concentration as well as other reaction conditions such as the ligands for Cd complexes or the reaction temperature allows for a variety of morphologies from short rods to wires. It was found that the morphology of the nanocrystals synthesized using DDPA is well-controlled compared to those synthesized using ODPA and HPA. This is due to the moderate reactivity of Cd−DDPA complexes. It is also found that the cleavage rate at which the P═Se is broken is another key factor affecting the morphology of nanocrystals. TOP as the ligand for Se complexes is well matched with DDPA as the ligand for Cd complexes. A good balance in the reaction condition is achieved when these ligands are used, and thus anisotropic growth is favored. It is also found that decreasing the reaction temperature can lead to a decrease in the highest aspect ratio of the nanorods which is contrary to previous results obtained by other groups. Doubling the precursor concentration can greatly increase the aspect ratio of nanocrystals from 9 using the baseline concentration to 28 for twice the concentration. Further increases in the precursor concentration result in an increase in both branching and the size distribution of the nanocrystals. The effect of these reaction parameters on the growth of CdSe nanowires is also summarized. Time-dependent morphological and optical studies imply that the most widely accepted model, the effective monomer model, can still be used to explain the shape evolution of CdSe nanowires. Nearly monodisperse CdSe nanowires with high dispersibility can be potentially used in devices such as photovoltaic cells and transistors.

Supporting Information Available: Figure S1 shows HRTEM images of CdSe nanowires and a diffraction pattern of a single CdSe nanowire. Figure S2 shows HRTEM images of CdSe nanocrystals synthesized with TPP ligands: (a) hexagonal disk and (b) irregular disk. Figure S3 shows the HRTEM image of the CdSe sphenoid structure synthesized with DDPA at 340 °C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.