A SOLUTION-BASED APPROACH TO SEMICONDUCTOR NANOWIRES

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Abstract

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The solution phase synthesis of narrow diameter (< 10 nm) straight and branched CdSe and PbSe nanowires (NWs) is described. Crystalline NWs with lengths up to 10 microns are grown in solution, where NW growth is initiated by Au/Bi core/shell nanoparticles (NPs). These NPs have diameters less than 5 nm and are catalytically active towards the growth of similar diameter NWs. Such wires may exhibit quantum confinement effects since the exciton Bohr radius of CdSe (PbSe) is 5.6 (46) nm. Branched NWs are also obtained by varying the reaction conditions, yielding tripod, v-shaped, and y-shaped NWs in the case of CdSe and right angle and t-shape NWs in the case of PbSe. The morphologies obtained in each case emphasize the influence of crystal phase on NW growth. A geminate nucleation mechanism is described to explain NW branching.
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SYMBOLS

NW………………………….nanowire
NP…………………………nanoparticle
QD…………………………quantum dot
NR…………………………nanorod
0D…………………………zero dimensional
1D…………………………one dimensional
2D…………………………two dimensional
3D…………………………three dimensional
ZB…………………………zincblende
W…………………………wurtzite
TOP………………………trioctylphosphine
TOPO……………………trioctylphosphine oxide
HDA……………………hexadecylamine
TOPSe……………………trioctylphoshpine selenide
TEM……………………transmission electron microscopy
HRTEM……………………high resolution transmission electron microscopy
SAD……………………selected area diffraction
EDXS……………………energy dispersive X-ray spectroscopy
XRD……………………X-ray diffraction
SEM……………………scanning electron microscopy
INTRODUCTION

Recent shape control experiments, emphasizing the effects aspect ratio and morphology have on the optical and electrical properties of nanoscale materials, complement well-developed studies of quantum confinement in colloidal semiconductor nanocrystals (NCs). [1,2] In this regard, a key focus of these studies has been to adopt existing preparations for colloidal semiconductor NCs, extending them towards promoting one-dimensional (1D) and quasi zero-dimensional (0D) growth. [3] Underlying this solution-based approach to nanostructure shape control is the understanding that surfactants play an important role in controlling the morphology, the growth mechanism, and even the phase of low dimensional materials. [4,5] This is underscored by the work of Peng and Alivisatos who have actively sought a working hypothesis for the growth mechanism of CdSe in both nanoparticle (NP) and nanorod (NR) forms. [6,7] Additional quasi 0D structures such as tetrapods, recently developed for a number of II-VI materials, directly advance these shape control studies, providing different systems where the interplay between thermodynamic, kinetic, and surfactant effects can be investigated. [8-11] In each case, the all-encompassing goal has been to understand and ultimately control nanoscale crystallization.

Beyond studies associated with 0D and quasi 0D materials, there exists a need for high quality 1D and quasi 1D structures. These systems may be used to further understand the evolution of nanoscale optical, electrical, and physical properties with size, shape and
dimensionality. The recent realization that colloidal (or laser ablated) metal NPs can be used to catalyze nanowire (NW) growth has been key to developing this class of materials using a variety of techniques such as vapor-liquid-solid (VLS), [12-15] solution-liquid-solid (SLS), [16,17] and supercritical-fluid-liquid-solid (SFLS) growth [18]. In all cases, high quality straight NWs have been the end result of these syntheses. However, unlike the situation with colloidal NCs, the analogous transition from straight to branched NW morphologies has been relatively slow, evidenced by the scarcity of reports on branching. [17, 19-21] Notable progress, however, has been made very recently in terms of “higher order” structures with multiple branching points. Specific examples include branched “nanotrees” and “hyperbranched” NW structures, created by depositing catalyst NPs onto previously grown straight NWs and applying additional VLS growth steps. [20,21] More recent studies in our group complement these synthetic advances by providing a solution-phase approach that enables self-induced NW branching. This has been demonstrated for the case of CdSe, a well-developed semiconductor system in quantum dot (QD) form. [17]

Whereas most NW syntheses follow VLS schemes, the NWs described here are made using a solution-based approach first introduced in the mid 90’s. [16] Common to both synthetic schemes is the use of metal NPs to absorb precursor atoms and, in turn, to promote the asymmetric crystallization of NWs. A distinguishing feature of the solution-based approach, however, is the need for low melting metal NP catalysts allowing reactions to be conducted at temperatures sustainable by solution chemistry (<400 °C). [16,17] By contrast, VLS is typically carried out at much higher temperatures (> 800 °C) using gas phase precursors. [12-15] Potential advantages of a solution-based approach
include the possibility of higher yields and an increased flexibility by which the resulting NWs can be processed since they are soluble in common organic solvents. [16,17] At the same time, their solubility also opens the door to future NW surface derivatization chemistries which may aid the creation of functional 1D nanostructures.

Described in this work are the methodologies for producing high quality semiconductor NWs. Au/Bi core/shell NPs have been developed and are used to catalyze the growth of both CdSe and PbSe wires through the solution-based approach. The wires produced are within the strong confinement regime for their respective materials, and therefore, are interesting from both fundamental science and applied perspectives.
CHAPTER 1

AU/Bi CORE/ SHELL NANOPARTICLES: A PRECURSOR TO SEMICONDUCTOR
NANOWIRES

1.1 Introduction

The advent of VLS growth has opened up distinct possibilities for controlled 1D crystal growth. [12] In the classic VLS example, Wagner and Ellis used molten Au droplets on a substrate to catalyze the asymmetric growth of macroscopic Si whiskers. [12] More recently, size tunable metal nanoparticles (NPs), such as laser ablated [22] or chemically synthesized and size-selected species [23,24], have been used to catalyze confined 1D materials. The resulting NWs have narrow diameters similar to their corresponding catalyst NPs. Alternative solution-based approaches such as SFLS [18] and SLS [16,17] growth also incorporate a metal catalyst particle into their reaction schemes, though, in the case of SLS, particles with melting points accessible through solution chemistry must be utilized. [16] Choices for suitable catalyst materials are therefore restricted to such low-melting substances as In, Sn, Bi, and Ga. Unfortunately, few preparations exist for high quality NPs of these elements, particularly those with narrow size distributions. Existing procedures for synthesizing NPs of In [25,26], Sn [27,28], and Bi [29-31] typically yield particles with diameters on the order of tens of

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nanometers making them unsuitable for catalyzing quantum confined wires. This necessitates the development of a template mediated approach where a shell of a low melting metallic species is deposited on the surface of Au particles, taking advantage of facile procedures that already exist for synthesizing narrow diameter, high quality particles. Such bimetallic core/shell particles are effectively NPs of the low melting element because of their large surface to volume ratio. When employed in the SLS growth mechanism, the core/shell NPs are shown to be catalytically active towards the growth of semiconductor NWs.

1.2 Experimental

1.2.1 Preparation of Au NPs

A modified preparation of Au NPs follows Hutchison’s procedure for synthesizing triphenylphosphine stabilized Au particles. [32] Hydrogen tetrachloroaurate (III) trihydrate (H\textsubscript{Au}Cl\textsubscript{4}
\cdot3H\textsubscript{2}O, 0.125 g, 0.317 mmol) is dissolved in 6.25 mL of water then mixed with a phase transfer solution consisting of tetra-n-octylammonium bromide (TOAB, 0.200 g, 0.366 mmol) in 8.125 mL of toluene. Once the gold ions completely transfer into the organic phase, a solution of trioctylphosphine (TOP, 0.10 mL, 0.22 mmol) in 2.00 mL of toluene is injected into the gold solution. The solution immediately turns dark red whereupon additional TOP is added dropwise until the solution turns milky white. The mixture is stirred for 5-10 more minutes, then an injection solution containing sodium borohydride (NaBH\textsubscript{4}, 44 mg, 1.16 mmol) in water (5.00 mL) is added at a rate of 7 mL/hr via syringe pump.
After the gold is completely reduced, the organic layer is extracted from the aqueous layer. The resulting gold NPs are then precipitated from the toluene layer with an excess of methanol (~10 mL) and centrifuged at 4400 rpm for 10 minutes. The supernatant is then discarded, and the recovered NCs are redispersed in toluene (4.00 mL). The product is subsequently divided into four portions and used for separate Bi overcoatings.

1.2.2 Bi Overcoating Procedure

Surface passivation of Au with elemental Bi is achieved by thermolysis of triethylbismuth [Bi(Et)$_3$] in the presence of previously prepared Au NPs. A mixture containing phenyl ether (Ph$_2$O, 4.00 mL, 25.2 mmol), trioctylphosphine (TOP, 0.600 mL, 1.34 mmol), and a fourth of the aforementioned gold NP synthesis is purged with N$_2$ and heated to 100 °C. An injection solution containing Ph$_2$O (4.29 g, 4.00 mL, 25.2 mmol), TOP (0.499g, 0.600 mL, 1.34 mmol) and Bi(Et)$_3$ (54.6-182 mg, 30-100 µL, 0.184-0.615 mmol) is prepared in a nitrogen glovebox and then added to the gold NP solution via syringe pump. Geometric considerations allow one to estimate the volume of Bi precursor necessary to sufficiently coat the Au NPs. Once the Bi has been added, the reaction mixture is cooled to room temperature, and the resulting Au/Bi NPs are precipitated with acetonitrile. The suspension is then centrifuged at 4400 rpm for 10 min; the recovered NPs are redispersed in a solution of toluene and a few drops of oleic acid. They are then stored in a glovebox freezer where they remain stable for several months. The Au/Bi NPs are normalized to an absorbance of 0.126 at a wavelength of 500 nm; the NP concentration for each of the resulting Au/Bi stock solutions is approximately equivalent (~0.38 mM), ensuring the reproducibility of successive NW syntheses. The
resulting core/shell particles range in size from 1.4-3.0 nm in diameter, with direct correlation between the size of the particles and the amount of Bi precursor introduced.

1.3 Results and discussion

The lack of existing preparations for high quality, low melting NPs capable of catalyzing NW growth necessitates the transition to a template mediated approach. Bi, the low melting species of interest, is deposited on the surface of Au to give, effectively, NPs of the low melting metal. These core/shell particles are characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV/Visible spectroscopy.

1.3.1 Synthesis

The synthesis of Au NPs proceeds by way of a biphasic gold reduction step. HAuCl₄·3H₂O is dissolved in water then added to a solution consisting of toluene and a phase transfer reagent, TOAB. Once the gold ions have transferred to the organic phase, a solution of TOP diluted in toluene is rapidly injected. The resulting dark red mixture is a metastable intermediate Au (I) species that has been reported previously. [33] The UV-Visible spectrum of these Au clusters is shown in Figure 1.1(a). TOP is then added dropwise to the vessel until the color changes to a milky white color, attributed to light scattering. At this point, a solution consisting of NaBH₄ in water is added dropwise via syringe pump over the course of ~45 minutes. The UV/Visible spectrum shown in Figure 1.1(b) was obtained from the resulting Au NPs after they were dropped out of solution with methanol and resdispersed in toluene. The absence of the characteristic plasmon band around ~530 nm is indicative of the small size of the NPs. TEM further confirms
the size of these particles, and a low resolution TEM image is given in Figure 1.1(c). Direct TEM measurements of over 300 NPs reveals an average diameter of 1.5 nm with a diameter distribution of 18%. Size selective precipitation can reduce this distribution to ~10%, but this step has been omitted due to uncertainties introduced to the NP concentrations.
Figure 1.1 (a) Absorption spectrum of Au(I) clusters before addition of NaBH₄. (b) Absorption spectrum of Au NPs after reduction with NaBH₄. (c) TEM micrograph showing an ensemble of 1.5 ± 0.3 nm diameter Au NPs.
A series of control experiments to produce CdSe NWs were conducted using Au NPs alone (no Bi) to determine whether Au is catalytically active towards the growth of CdSe NWs. In all NW preparations, which were conducted above the melting point of 1.5 nm Au NPs, only rod-like or elongated CdSe NCs were formed. Other experiments in the absence of Au produce similar nanorods, indicating that the Au NPs contribute very little to nanorod formation. Therefore, an additional lower melting metal appears to be necessary for catalyzing higher aspect ratio materials.

1.3.2 Optical characterization

Absorption spectra of the Au NPs before and after overcoating are shown in Figure 1.2 for the case of 2:1 (a) and 7:1 (b) BiEt₃:Au NP. No observable changes in the spectrum occur when small amounts of Bi are added, though small increases in the absorbance around 500 nm are seen when larger amounts of Bi precursor are used. These changes may be due to a broadening of the NP size distribution. There may also be some reactivity with the Au core since the changes occur in the same spectral regions as the plasmon resonance of larger Au NPs in solution. Additional experiments were conducted to investigate Bi’s plasmon resonance but were inconclusive, perhaps due to the small quantities of Bi present. Therefore, the plasmon bands of neither Au nor Bi were studied in detail, preventing specific core/shell assignment based on expected spectral changes.
Figure 1.2  Absorption spectrum of (a) Au NPs before (solid line) and after (dashed line) addition of Bi(Et)$_3$ in a 2:1 (Bi(Et)$_3$:Au NP) molar ratio and (b) Au NPs before (solid line) and after (dashed line) addition of Bi(Et)$_3$ in a 7:1 (Bi(Et)$_3$:Au NP) molar ratio.

1.3.3 XRD characterization

The NPs were characterized by XRD for both structural and sizing purposes. Figure 1.3 shows powder patterns of Au NPs and Au/Bi NPs with increasing molar ratios of Bi:Au NP. The diffraction data obtained correspond to icosahedral Au [34] and rhombohedral Bi (JCPDS: 44-1246). The major two peaks observed, namely the Bi (012) and the Au (111) reflections, exhibit broadening that is primarily due to the small particle size. The broadening could also be due to the amorphous nature of the material, but high resolution TEM (HRTEM) confirms the small particle size. Separate Au and Bi reflections as well as a lack of peak shifting suggest that the two metals do not alloy to any significant degree. The peaks slightly overlap, though, which make it difficult to accurately determine the size of the particles via Scherer analysis. Applying the Scherer equation to the Bi (012) reflection shows that the core/shell particles range in size from ~1.00 to 1.53 nm as the amount of Bi(Et)$_3$ is increased in the reaction mixture.
1.3.4 TEM characterization

Direct analysis of Au/Bi core/shell particles through TEM measurements further confirms their size. Figure 1.4 shows corresponding low and high resolution TEM micrographs of Au/Bi NPs ranging in size from ~1.43 to 2.53 nm (top to bottom) in diameter, with each pair representing different molar ratios of Bi:Au. The size distribution in each case is 20%, in keeping with initial Au NP diameter distributions of 18%. Furthermore, the particles are clearly crystalline, as revealed by the appearance of lattice fringes in the high resolution TEM photos. Definitive core/shell assignment could not be made on the basis of TEM alone largely because Au and Bi have similar atomic numbers.
Figure 1.4  (a) Low resolution TEM micrograph of Au/Bi NPs made using a 2:1 (Bi(Et)₃:Au NP) molar ratio, (b) Corresponding high resolution images.  (c) TEM micrograph of Au/Bi NPs made using a 3:1 (Bi(Et)₃:Au NP) molar ratio.  (d) Corresponding high resolution images.  (e) TEM micrograph of Au/Bi NPs made using a 7:1 (Bi(Et)₃:Au NP) molar ratio.  (f) Corresponding high resolution images.
1.4 Conclusions

High quality Au/Bi core/shell NPs have been successfully synthesized and are seen through powder XRD and HRTEM to be highly crystalline. In the proceeding chapters, these particles will be shown to be catalytically active towards the growth of both CdSe and PbSe NWs through a solution phase growth method. Such NPs may also be used to catalyze NW growth in a variety of other semiconductor systems--a future area of exploration.
CHAPTER 2

CONFINED STRAIGHT AND BRANCHED CdSe NANOWIRES

2.1 Introduction

Over the past decade, CdSe has been one of the most extensively developed and best understood mesoscopic systems (in QD form). This is true not only from a synthetic standpoint, but also from physical, optical, electrical and theoretical perspectives. [35-42] Similar studies have also been conducted on nanorods [1,6,7], but little has been done to understand confinement in 1D CdSe systems. [16,17] The work here described adds to this body of knowledge by expanding the opportunities for studying confined straight and quasi 1D branched CdSe NWs. A solution based approach is used to grow NWs with narrow diameters and lengths up to 10 µm. The appearance of branched structures provides an opportunity for studying not only their size- but also their shape-dependent properties.

2.2 Experimental

2.2.1 Synthesis of straight NWs

A mixture consisting of trioctylphosphine oxide (TOPO, 2.50 g, 6.47 mmol), CdO (25.0 mg, 0.194 mmol) and octanoic acid (0.23 mL, 1.43 mmol) is heated to 100 °C under vacuum to dry and degas the reagents. The reaction vessel is subsequently

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backfilled with N₂. The orange/red slurry is then heated to 330 °C whereupon the solution becomes clear as the octanoic acid coordinates with the Cd. The minimum 2.5:1 mole ratio of octanoic acid to CdO ensures complete transformation of the initial oxide. In a glovebox, an injection solution consisting of normalized Au/Bi NP stock solution (230 µL, ~0.38 mM) and 1.0 M trioctylphosphine selenide (TOPSe, 25 µL, 25 µmol) is prepared. TOPSe is synthesized as described in previous literature. [38] This solution is injected into the Cd mixture, initiating a reaction that results in a rapid color change. The dark red/brown mixture is briefly maintained at high temperatures. It is then cooled, and toluene is added to the pot prior to the TOPO solidifying. Once the reaction mixture reaches room temperature, it is centrifuged at 4400 rpm for 10 min to remove any precipitated material. The supernatant containing the product is retained, with the synthesized NWs indefinitely stable in this form. However, a short chain alcohol such as methanol, ethanol, isopropanol, or butanol can be added to precipitate the material. The recovered NWs are redispersed in a common organic solvent such as toluene, with varying degrees of stability depending upon the amount of excess surfactant present.

2.2.2 Synthesis of branched NWs

The synthetic scheme for branched CdSe NWs is similar to that for straight NWs. Differences include the quantities of CdO (17.5 mg, 0.136 mmol) and octanoic acid (0.16 mL, 0.997 mmol) as well as the injection temperature (300 °C rather than 330 °C). In addition, the concentration and quantity of TOPSe (2M, 40 µL, 80 µmol) varies from the straight NW preparation. Whereas methanol and ethanol can be used to precipitate straight wires from solution, longer chain alcohols are preferred for branched wires since
they mitigate NW bundling. All other aspects of the experimental procedure are identical to straight NW preparations.

2.2.3 Instrumentation

Samples for low and high resolution TEM analysis were prepared by dropping a dilute toluene solution of NWs onto ultra-thin carbon-coated copper grids (Ladd) and wicking off the excess. Survey TEMs during the synthesis of straight and branched CdSe NWs were conducted on a JEOL JEM-100SX electron microscope. Low resolution TEM micrographs were obtained with both a Hitachi H-600 and a JEOL-2010 electron microscope. HRTEM micrographs were obtained with a JEOL-2010 TEM. UV/Visible absorption experiments were conducted on a Cary 50-Bio UV/Visible spectrophotometer.

2.3 Results and discussion

The current work demonstrates the seeded solution growth mechanism as a viable synthetic scheme for producing high quality NWs. Previously described Au/Bi core/shell NPs provide small, catalytically active precursors for the growth of both straight and branched NWs. NWs obtained through this method have correspondingly narrow diameters and size distributions similar to the initial NPs. Structural characterization shows NW growth along either the <111> or <0001> directions of zincblende (ZB) and wurtzite (W) phases respectively for both straight and branched NWs. HRTEM imaging reveals that the NWs alternate between ZB and W sections along their length, and that ZB segments have a very high incidence of twinning. Characterization through UV/Visible spectroscopy suggests the presence of additional quantized transitions as well as corresponding subbands that invite future exploration. By manipulating the reaction
conditions, particularly the Cd:Se ratio, a transition from straight to branched NWs occurs, with a number of different branched morphologies observed. A scheme for NW branching has also been developed and is described.

2.3.1 Synthesis

The synthesis of both straight and branched NWs has been optimized in terms of reaction mixture concentration, temperature, apparent Cd:Se ratio, Au/Bi NP size, and Au/Bi NP volume. The optimized conditions are described above in the experimental section, and detailed explanations of these experiments are given in reference [17]. Figure 2.1 shows representative low resolution TEM micrographs of straight CdSe NW ensembles obtained from the previously outlined synthesis. The NWs have an average diameter of 7 nm and lengths ranging from 1 to 10 microns.
2.3.2 TEM analysis of straight NWs

The NWs exhibit a high degree of crystallinity, seen by the appearance of lattice fringes in high resolution TEM micrographs. The wires are found to grow along $<111>$ ZB and $<0001>$ W crystal directions respectively. The random admixture of ZB and W sections likely results from the low energy difference between the two crystal phases. A model has been constructed and is pictured below in Figure 2.2(a,b) to facilitate a better understanding of the crystal structure. A lateral view of the CdSe NWs down the $<110>$ ZB direction results in the appearance of zig-zag lattice fringes, as shown in Figure 2.2(a,c). A twin boundary between two ZB sections (equivalent to a single layer of W)
gives rise to the off-axis zig-zag pattern. Conversely, when viewed down a non <110> direction, such as in Figure 2.2 (b,d), only parallel lattice fringes are seen. Twinning is observed only when viewing down <110> directions and is obscured when the wires lie in any other orientation. We expect that all CdSe NWs exhibit twinning, though different orientations of the wires often prevent one from observing this phenomenon.

Figure 2.2 Color photograph of a twinned NW model grown along the <111>/<0001> direction. Zincblende and wurtzite regions are denoted by ZB and W. T denotes a twin boundary between two ZB segments of different orientation, and B is a phase boundary between a ZB and a W segment. (a) Viewed down <110>. (b) Viewed down <112>. (c) HRTEM micrograph of a CdSe NW viewed down <110> directions. Selected twin boundaries (T) as well as ZB and W sections are highlighted. (d) HRTEM micrograph of a CdSe NW viewed down an intermediate direction between <110> and <112>.
2.3.3 TEM analysis of branched NWs

In addition to straight wires, branched CdSe NWs can also be obtained simply by varying the reaction conditions. Empirically, straight NWs are formed from a high Cd:Se ratio (~7:1) where a Se deficiency induces single wire growth from any given catalyst particle. Conversely, a smaller Cd:Se ratio (~1:1) produces branched NWs. In this case, multiple arms nucleate on the surface of each Au/Bi NP. The diameters and lengths of branched NW arms are comparable to those of the straight NWs.

Four different morphologies commonly arise from branched NW preparations: v-shapes, tripods, y-shapes and merged-y NWs. A low resolution TEM ensemble of branched NWs is shown in Figure 2.3(a). V-shapes, y-shapes, and tripods all result from equivalent arms growing out of the \{111\} faces of a ZB core along <111> and <0001> ZB and W directions respectively. In the case of v-shapes, two arms grow along unique \(<111>/<0001>\) ZB/W directions from a ZB core with an average separation of 109° (\(\sigma = 2°\)), consistent with a tetrahedral zincblende core. In addition, a twin occurs at each of the core/arm interfaces. High and low resolution TEM micrographs are shown in Figure 2.3(e,f). Similarly, y-shapes have two arms that are identical to those of the v-shape, although an additional third arm grows along the same \(<111>\) ZB direction as one of the other two arms. This particular arm is unique in that no twin exists at its core/arm interface. High and low resolution photos of characteristic y-shapes are given in Figure 2.3(g,h). Tripods are a third morphology and are comprised of three identical arms growing along \(<111>/<0001>\) ZB/W crystal directions from unique \{111\} faces of the ZB core. Micrographs of these structures are given in Figure 2.3(b,c,d). Twinning is exhibited in two, or possibly three, core/arm interfaces.
Figure 2.3 (a) Low resolution TEM micrograph of branched CdSe NWs. (b) HRTEM micrograph of a tripod NW center. (c) Low resolution TEM micrograph of a tripod NW. (d) HRTEM micrograph of a tripod NW center. (e) Low resolution TEM micrograph of a v-shaped NW. (f) HRTEM micrograph of a v-shape NW center. (g) Low resolution TEM micrograph of a y-shaped NW. (h) HRTEM micrograph of a y-shape NW center.
A fourth morphology observed is the merged-y NW, whose structural characteristics are considerably different than those of the first three branched NWs. The merged-y has no ZB core, so the arms are not confined to spacings of 109°. The angle between the α and β arms varies from one merged-y to the next, with an average spacing of 74° (σ=10°). The γ arm consists of two fused wires held together by a high-angle grain boundary along its length. This morphology is the least common, likely due to the high energy associated with grain boundary formation.
Figure 2.4  (a) Low resolution TEM micrograph of a merged-y NW.  (b) HRTEM micrograph of a merged-y NW junction.  (c) Cartoon depicting the growth directions of the $\alpha$ and $\beta$ arms in merged-y NWs.

Higher order structures with multiple branching points are also obtained in the branched NW preparations. These NWs are best understood as linear combinations of the primary morphologies (v-shapes, tripods, y-shapes, and merged-y NWs) previously described. There appears to be a higher incidence of these structures when the reaction mixture is doped with TOP prior to injection of the Se and Au/Bi precursors.
2.3.4 Branching growth mechanism

Branched structures are believed to form through a geminate nucleation mechanism, which is outlined in Figure 2.6. If sufficient Cd and Se are present, two NWs nucleate on the surface of a molten catalyst NP. Provided the two NWs have a mutual angle below a critical value, they eventually merge and touch forming a grain boundary. This may result in a merged-y NW. However, easy motion on a liquid NP surface, on-axis rotation, and motion along the grain boundary can act to eliminate the initial junction. A ZB core can eventually form resulting in v-shapes, tripods, or y-shapes. If growth terminates at this point, v-shapes result. However, if growth continues along a unique <111> ZB direction, tripods are obtained. Y-shapes result from the case where a third arm grows along the same <111> direction as one of the initial two arms. Finally, higher order structures are formed if any of these primary morphologies grow additional arms.

Figure 2.5  (a-d) Low resolution TEM micrographs of higher order NWs.
Figure 2.6 CdSe NW branching mechanism.
2.3.5 Optical characterization

Characteristic UV/Visible absorption spectra for both straight and branched NW preparations reveal a strong absorption edge between 600 and 700 nm as shown in Figure 2.7. A blue shift from the bulk band gap energy of CdSe (1.74 eV or 712 nm) occurs indicating that the wires are quantum confined. Small shoulders at higher energies suggest that other quantized transitions are present as well. Notably, this is consistent with the fact that the NW radii are below the exciton Bohr radius of CdSe and that the wires exhibit a high degree of crystallinity. Straight and branched NW preparations have similar UV/Visible spectra. This may be due to the dominating influence of the branched arms on the optical transitions. Finally, the modest size distributions (~25 %) of NW ensembles reduce the inhomogeneous broadening of spectral peaks.
2.4 Conclusions

In summary, the seeded solution growth mechanism is a viable means by which to synthesize narrow diameter NWs. Interest in CdSe has led to the development of a procedure for the synthesis of CdSe NWs with diameters below 10 nm and with lengths ranging from 1-10 µm. The growth of the wires is catalyzed by previously synthesized Au/Bi core/shell NPs. Structural characterization of the NWs through TEM allows one to conclude that CdSe NWs grow along <111>/<0001> ZB/W directions with a high incidence of twinning occurring in ZB sections. Branched NWs, exhibiting v-shape,
tripod, y-shape, and merged-y morphologies, are observed. Higher order NWs can also be obtained from branched preparations. The seeded solution growth mechanism is suggested as a general means to obtain semiconductor NWs, as demonstrated in the following chapter.
3.1 Introduction

Pb chalcogenides are an attractive class of materials, which have, only recently, been intensively investigated in colloidal NC form. In particular, PbSe nanostructures are potentially useful for telecommunication and sensing applications in the 1.3 to 1.55 µm range since the room temperature bulk bandgap of PbSe (0.26 eV (~4.7 µm)) enables confinement-induced tunability over a wide range of wavelengths in this region. Impact ionization has also been demonstrated in PbSe QDs making this material potentially useful in photovoltaic devices. From a basic science standpoint, PbSe is an attractive material characterized by a large bulk exciton Bohr radius (46 nm), nearly identical electron and hole effective masses, and sparse electronic spectra near the band edge. All facilitate the study of quantum confinement in this system.

Towards realizing both fundamental and applied interests of this material, nearly monodisperse colloidal PbSe NCs have recently been prepared through solution chemistry. These NCs are generally grown in noncoordinating or mildly

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coordinating solvents such as TOP and are passivated with oleic or other fatty acids. While the overall growth temperatures are relatively low (< 200 °C), the solution-based particles exhibit a high degree of crystallinity and have exceptionally high room temperature quantum yields that approach unity (~0.8). [45-50] This suggests that colloidal Pb chalcogenide NCs, despite their low growth temperature, are generally free of internal and/or surface defects which could adversely affect their optical and electrical properties. [53] Growing interest in other nanoscale morphologies has recently led to the development of quasi 0D PbSe structures through analogous solution chemistry routes. [54] However, significant success remains to be seen in the 1D realm. Thus, the current work on straight and branched PbSe NWs begins to address this need.

3.2 Experimental

3.2.1 Materials

The solvents: chloroform, toluene, hexanes, and acetone were all used as received from Fisher Scientific. To prepare straight and branched PbSe NWs, trioctylphosphine (TOP, 90% Aldrich), Ph$_2$O (99% Acros), Brij 30 (Acros), selenium powder (99% Aldrich), octanoic acid (98% Lancaster), and lead acetate trihydrate (Pb(Ac)$_2$·3H$_2$O, 99.999% Acros) were all purchased and used as received. Solutions of trioctylphosphine selenide (TOPSe), with molarities ranging from 1.0-2.0 M, were prepared by mixing elemental Se with TOP. [38]

3.2.2 Synthesis of straight and branched NWs

A mixture consisting of TOP, Ph$_2$O or Brij 30, Pb(Ac)$_2$·3H$_2$O, and octanoic acid is heated to 120 °C under vacuum to dry and degas the reagents. When complete, the
reaction vessel is backfilled with N\textsubscript{2}, and the solution is heated to 175 °C. This temperature is maintained until injection of the Se precursor. In a glovebox, an injection solution consisting of “standardized” Au/Bi NPs and 1.0 M TOPSe is prepared. This solution is then injected into the reaction mixture at 175 °C to initiate the reaction. A dark brown/black solution is formed and is briefly kept at high temperatures before cooling to room temperature. Chloroform is added, and the reaction mixture is centrifuged at 4400 rpm for 10 minutes. It is then washed with acetone and/or chloroform as necessary to remove any excess surfactant.

3.2.3 Controls

To test whether straight or branched NWs can be grown without a catalyst particle, control experiments were conducted under the same conditions described above without Au/Bi NPs. In such experiments, apparent uncatalyzed PbSe NW growth was obtained in certain cases. Such wires however, have qualitative structural differences distinguishing them from catalyzed NWs. This will be described in more detail in the results and discussion section. Additional experiments were carried out to test whether NWs could be grown using either Pb or Se alone in the presence of Au/Bi NPs. However, no NWs were obtained and typical energy dispersive X-ray spectroscopy (EDXS) Pb:Se ratios found in the product of abovementioned (catalyzed) straight and branched NW syntheses [1:1.3(2)], are in good agreement with the stoichiometry of PbSe.

3.2.4 Instrumentation

TEM samples were prepared by dropping dilute toluene or chloroform solutions of PbSe NWs onto ultra-thin carbon-coated copper grids (Ladd). Survey TEMs were
conducted during the synthesis of straight and branched PbSe NWs using a JEOL JEM-100SX electron microscope. All TEM micrographs were obtained from a JEOL-2010 TEM operating at 200 kV. A Bruker D8 Advance X-ray diffractometer (Cu Kα, λ=1.54 Å) was used to collect wide angle XRD powder patterns. For either experiment, NWs were washed repeatedly with acetone and/or chloroform to remove excess surfactant. In the XRD studies, the NWs were resuspended in acetone and deposited onto a quartz single crystal (0001) off-axis substrate. Single and ensemble NW EDXS spectra were taken with a JEOL-2010 electron microscope using specimens supported on ultra-light carbon substrates (Ladd).

3.3 Results and discussion

The PbSe NWs described here have diameters on the order of 5-10 nm, placing them well within the strong confinement regime of the material, given that the bulk exciton Bohr radius is 46 nm. [43] Corresponding NW lengths range from 1-5 µm, and all NWs grow along equivalent <100> directions of the rock salt lattice. By varying the Pb/Se ratio used for straight NW preparations, branching can be induced in the wires. Resulting morphologies include right angles, t-shapes, and merged-y structures. The branching in these wires appears to follow a “geminate” nucleation mechanism, first described for CdSe NWs. In this scheme, multiple arms nucleate within the same catalyst NP and eventually coalesce to form a single branched wire. [17] A critical angle between the two (initially) independent arms appears to dictate whether right angles/t-shapes or merged-y’s structures are formed. This critical angle can be determined experimentally or estimated using simple geometric considerations. The overall branching scheme
developed for PbSe is consistent with that for CdSe and should also be applicable to other semiconductor systems. As a consequence, this generalized route to branched semiconductor nanostructures is of fundamental interest.

3.3.1 Synthesis

The present method for making high quality, quantum confined, straight and branched PbSe NWs draws from the above PbSe NC syntheses leveraging advances in the choice of precursors and coordinating/noncoordinating surfactants [45-52] with recent developments in the solution phase growth of NWs. [16,17] In particular, the choice of Pb precursor is a salt or metal oxide, which is readily coordinated with a fatty acid such as oleic acid. The actual choice of Pb precursor does not appear to affect the preparation significantly, and Pb(Ac)$_2$·3H$_2$O, PbO as well as Pb(acac)$_2$ have all been used successfully. Octanoic acid, previously employed to synthesize CdSe NWs, is employed as a Pb binding species. An apparent advantage of the metal salt/fatty acid approach is that it obviates the need for pyrophoric organometallic precursors. It also provides improved control over the NW synthesis since precursor decomposition rates and subsequent growth kinetics rely, not on impurities in the surfactants, but rather upon a deliberate choice of metal/chalcogen coordinating ligands. [55] The selection of a Se precursor is rooted in a family of stable phosphine chalcogenide compounds first utilized by Steigerwald to demonstrate the synthesis of solid state materials from molecular precursors. [55] These chalcogenide precursors have been used to successfully synthesize high quality low dimensional II-VI materials [3, 5-10, 16, 17, 38] and are convenient compounds since they are relatively easy to prepare and are air stable in many cases.
Characterizing the growth of both PbSe QDs and NWs is a strong preference for weakly coordinating surfactants such as TOP, phenyl ether, Brij 30 or Triton X-45. While other more strongly coordinating ligands such as TOPO or amine-based species have been successfully employed in the growth of other QD/NW systems such as CdSe, they appear to retard or even prevent the growth of PbSe nanostructures. Temperatures in the NW synthesis are typically lower than 200 °C, which parallels the conditions in the synthesis of PbSe QDs. This contrasts to CdSe and other systems where growth temperatures are typically much higher (> 300 °C). In either case (PbSe QDs or NWs), however, a crystalline product is obtained as demonstrated for the case of NWs in HRTEM micrographs below. The requirement of a low growth temperature appears to be predominantly rooted in the temperature instability of the fatty acid-coordinated Pb complex which leads to a precipitation of the starting material at higher temperatures. However, even when growth temperatures above 200 °C have been achieved in the current case, resulting PbSe NWs generally have large diameters (>10 nm) and rough surfaces, suggesting an optimal growth temperature between 150-200 °C.

Optimization of the synthesis has been conducted by exploring a parameter space analogous to that described in the synthesis of straight and branched CdSe NWs. [17] In particular, the reaction mixture concentration, overall reaction temperature, Pb:Se ratio, catalyst NP size, and catalyst NP concentration, were all varied to test whether qualitative trends developed for CdSe could be applied to PbSe. In all cases, with the exception of the branching dependence on the metal:chalcogen ratio, the trends established for CdSe appear to hold for PbSe as well. To illustrate, an increase of the reaction mixture concentration enables the competitive growth of PbSe QDs over NWs. Conversely, a
decrease of the reaction mixture concentration appears to promote the uncatalyzed transverse growth of PbSe NWs increasing their overall diameters. NW growth therefore occurs at intermediate concentrations that are empirically determined. This highlights the competition between catalyzed and uncatalyzed growth in solution-based NW reactions. [17] The effects of catalyst concentration are also identical to that for CdSe. [17] In this respect, too little catalyst enables the independent nucleation of PbSe NPs to become competitive with NW growth. Conversely, too much catalyst leads to the formation of irregular Au/Bi aggregates. This problem appears to be more severe in PbSe than in CdSe and appears to ultimately limit resulting PbSe NW size distributions. An intermediate catalyst concentration, between these two extremes, is therefore used to grow the PbSe NWs.

The effects of temperature are difficult to determine given the relatively narrow range of temperatures suitable for PbSe NW growth. No strong preference for straight versus branched wires is seen with temperature. By contrast, in CdSe, higher temperatures (> 330 °C) favor the growth of straight NWs whereas lower temperatures (~270 °C) favor the growth of branched NWs. This behavior was suggested as resulting from a competition between kinetic and thermodynamic effects, with a preference for the CdSe zincblende phase over the wurtzite phase at lower temperatures. [17] However, in PbSe no such phase admixtures exist, potentially explaining why no apparent temperature dependence delineates straight from branched NW growth.

Effects of the Au/Bi NP size, which range from ~1.5 nm to 3 nm in diameter, are generally more straightforward to interpret. Here a direct correlation is found between the diameter of the initial metal NP and the diameter of the resulting NW. In particular,
smaller particles yield narrow NWs whereas larger particles yield thicker wires. This agrees with previous observations of a catalyst NP/NW diameter correlation in both VLS and SLS based systems. [13-17] Straight NWs are commonly made using ~1.4 nm diameter NPs. In the case of branched NWs, slightly larger catalyst particles (2.2 nm diameter) are often used, consistent with previous observations in CdSe of a NP size below which branching becomes inefficient. [17] However, a more thorough mapping of the NW diameter dependence with catalyst size in straight and branched preparations is complicated by the tendency of the catalyst NPs to aggregate during growth of the NWs. The amount of Au/Bi NPs added to the preparation also appears to follow the trend seen in CdSe, namely, too little catalyst enables the growth of QDs or nanorods at the expense of NWs.

By far, however, the greatest impact on straight or branched NW growth is the metal to chalcogen ratio. In this respect, straight PbSe NW syntheses are conducted with initial Pb:Se ratios of 2:1. This differs from CdSe where an asymmetric ~7:1 Cd:Se ratio is used to promote straight NW growth. [17] Branched PbSe NW growth is conducted under less stoichiometric conditions, with Pb:Se ratios of ~4:1. This again differs from CdSe where a more stoichiometric Cd:Se ratio of ~1.7:1 promotes branched NW growth. [17] In either case, CdSe or PbSe, the actual origin for this sensitivity of branching to initial metal/chalcogen precursor ratios is not understood. It may, however, ultimately be tied to differences in the solubility or even reactivity of metal and chalcogen species in the Au/Bi catalyst. In particular, the differing solubilities of Pb or Cd in Bi or Bi$_2$Se$_3$ must be considered if a deeper understanding of this behavior is to be developed.
Optimization of both straight and branched NW syntheses is conducted by empirically varying all of the above parameters. The resulting straight (branched) PbSe NWs are synthesized with 1.4 (2.2) nm diameter Au/Bi NPs at 175 °C. They have narrow diameters between 5-10 nm and grow exclusively along the <100> direction of the underlying rock salt lattice. This has been determined by examining high resolution transmission electron microscopy (HRTEM) images of both straight and branched NWs. Images such as those in Figure 1 further show that the NWs produced from such preparations are crystalline and have relatively smooth surfaces.

An interesting point is that the initial diameter of the catalyst NPs ranges from 1.4 to 3.0 nm. Since the resulting PbSe NWs have significantly larger diameters (5-10 nm), this suggests that the catalyst must itself increase in diameter during growth of the NWs. This is supported by low and high resolution TEM micrographs of straight NWs with catalyst particles still attached to one of their ends. The growth of the Au/Bi NP therefore suggests an induction period before which supersaturation can be achieved, leading to the seeded growth of PbSe NWs. Aggregation of catalyst particles also provides a mechanism by which the size of the NP can increase. Such aggregation has been observed in our preparations and appears to be the primary effect limiting the overall narrowness of the resulting NW diameter distributions. In more optimal cases, sections of an ensemble have diameter distributions as low as 12 (5)%. However, larger diameter wires, presumably originating from catalyst aggregation, routinely cause the overall ensemble distribution to swell to values at or above 30%. Nevertheless, the noticeable appearance of many regions having narrow size distributions within a given ensemble suggests that further improvements in the preparation are possible provided that issues
with catalyst aggregation are resolved. At the same time, within a given NW, the
diameter appears to be fairly uniform. In this respect, NW widths are measured at 7 or
more positions along their length using HRTEM images. Results from this study indicate
a 7 (3)% fluctuation of the NW diameter along the length of a given wire with occasional
wires that are tapered at one end.

Figures 1(a,b) provide visual examples of both the narrow diameter distributions that
are possible and the uniform NW thicknesses. In particular, we see regions where NW
bundles exist having uniform diameters and narrow diameter distributions. All wires are
crystalline and exhibit lattice fringes apparent in Figures 3.1(c,d) as well as Figure 3.2.
While these results would suggest that the diameter distributions of either PbSe or CdSe
NWs are ultimately influenced by the initial size distribution of the Au/Bi catalyst NPs
(~20 %), the apparent growth of catalyst NPs during the reaction as well as catalyst
aggregation complicates any simple statement as to the primary cause of resulting
ensemble NW diameter distributions. Corresponding NW lengths vary from 1-5 μm,
with no strong length dependence on the reaction conditions. Low resolution TEM
micrographs, such as Figures 3.1(a,b), show that wire preparations optimized for straight
wires result in a low incidence of branching.
Figure 3.1 (a-b) High resolution TEM micrographs of straight PbSe NW sections. (c) Low resolution TEM micrograph of a characteristic straight PbSe NW ensemble.

Powder XRD patterns (described below) obtained from various straight NW samples support the HRTEM analysis and indicate that all NWs exhibit the rock salt structure of PbSe. In addition, the XRD pattern exhibits peak broadening due to the narrow diameters of the wires. A preliminary Scherrer analysis of X-ray diffraction patterns results in sizes in good agreement with direct TEM measurements of the ensemble NW diameters. FESEM measurements show that all NWs possess cylindrical morphologies as opposed to rectangular shapes. Cylindrical wire geometries are rationalized by the spherical shape of the catalyst NP used to grow the NWs. By contrast, in cases where PbSe nanostructures such as QDs are grown in an uncatalyzed fashion, a cubic or rectangular shape reflecting the underlying rock salt crystal structure is observed in large particles where facets are allowed to develop. [45,52,54]
3.3.2 TEM characterization

PbSe NWs are generally lattice imaged under two primary orientations (Figure 2), specifically <100> and <110>, which are both normal to the <100> growth direction. The top of Figure 3.2(a,b) shows a <100> oriented wire. Under this condition, the lattice image appears as a square pattern and is depicted in more detail in the accompanying cartoon. Alternatively, the PbSe NWs may be <110> oriented [bottom, Figure 3.2(a,b)]. Under this condition, the wires will exhibit either criss-crossed or parallel lattice fringes depending upon the exact orientation of the wire and the actual imaging conditions of the microscope. The criss-cross fringes originate from \{111\} planes both 70.5° and 109.5° apart while the (vertical) parallel lattice fringes originate from neighboring \{200\} planes. This is illustrated in the accompanying cartoon and in the actual HRTEM micrograph in Figure 3.2 (bottom) where the left side of the <110> oriented wire exhibits criss-cross fringes whereas the right shows more or less perpendicular lattice fringes. A measurement of the fringe spacings in experimental HRTEM images supports the assignment, showing good agreement with predicted \{111\} and \{200\} d-spacings (3.65 Å experiment versus 3.53 Å theoretical and 3.02 Å experiment versus 3.06 Å theoretical, respectively).
3.3.3 NW branching

Variations of the straight NW preparation, in particular the Pb:Se precursor ratio, leads to branched PbSe NWs. In general, increasing the Pb:Se ratio towards an asymmetric 4:1 limit increases the degree of catalyzed branching in these preparations. Beyond this, NWs are observed to develop rough surfaces potentially due to a competition between NP catalyzed longitudinal growth and uncatalyzed transverse growth onto the surfaces of the wires. This sensitivity of branching to precursor stoichiometry has also been observed with CdSe and we speculate that it arises from the creation of conditions amenable to nucleating multiple NWs within a given catalyst particle (described below). The limited solubility of Pb (or Cd) relative to Se in Bi as well
as the ability of Se to form a solid solution with Bi is suggested as a reason for why more (less) Pb (Cd) enables NW branching.

Two general branched morphologies are commonly observed in PbSe NWs. They are t-shapes/right angles and “merged-y’s.” Figures 3.3(a,b) provide two examples of t-shaped NWs. Occasionally right angles are observed but this shape probably originates from an incomplete reaction to form a t-shaped wire. These morphologies should be contrasted to that seen in branched CdSe NWs where tripods, v-shapes, and y-shapes are seen. [17] Differences in shape originate from the crystal phase of the material. Whereas rock salt is the dominant phase of PbSe, both tetrahedrally-bonded zincblende (ZB) and wurtzite (W) phases are the predominant phases in CdSe. As such, the growth direction of straight and branched PbSe NWs are normal to the {100} faces of the rock salt lattice whereas in the case of CdSe, the preferred faces are the low energy {111}/{0001} facets of the ZB and W lattice. This leads to structures with characteristic angles of 109.5°.

![Figure 3.3](image)

Figure 3.3 (a-c) High resolution TEM micrographs of t-shape PbSe NWs.
HRTEM micrographs of t-shapes shown in Figure 3.3 indicate that the wires are crystalline and have smooth surfaces. T-shaped arms grow orthogonal to one another, along equivalent <100> directions. An average angle of 90.1° ($\sigma = 1.01°$) is measured between the NW arms of over 40 different t-shaped and right angle wires. Because of the <100> growth directions of the different arms, branched NWs naturally align themselves in a <110> orientation, unlike the case of straight NWs. This is analogous to the case of branched CdSe NWs which are all <110> oriented due to the presence of a ZB center with arms extending out of equivalent <111> faces. [17]

A third class of branched PbSe NWs are “merged-y” structures which consist of two <110> oriented arms ($\alpha, \beta$) fused together along a twin or grain boundary along the <112> direction of an additional “arm” denoted $\gamma$. An example of this morphology is given in Figure 3.4(a) The interesting feature of this class of branched NWs is that it does not appear to be unique to a given material. This was suggested earlier in a qualitative branching mechanism developed for CdSe NWs [17] and appears to be borne out by the appearance of similar merged-y structures here. We hypothesize that such wires occur when multiple (two) arms are nucleated on a given catalyst particle with a mutual angle below a critical value. Under these conditions, rapid growth of both arms prevents the wires from reorienting on a liquid NP surface. Therefore, upon meeting, both arms accommodate each other through either a low energy twin or high angle grain boundary.
The predominant occurrence of a twin boundary in the present merged-y PbSe NWs is explained by the fact that the twin boundary is the lowest energy configuration possible between two single crystal FCC grains. This should be contrasted to CdSe merged-y’s where a high angle grain boundary is formed exclusively. [17] Other examples of twinning in FCC materials include Au of Ag nanorods which show five-fold twinning along the length of the rod. [57, 58] Less common are merged-y PbSe NWs which exhibit a high angle grain boundary. Out of 35 recorded TEM images, only 6 are shown to exhibit apparent high angle grain boundaries. This is likely due to the high energy
associated with this grain boundary relative to the twin. Figure 3.4(b) shows an end of a merged-y NW with a catalyst particle still attached. This micrograph shows that the end of the merged-y NW exhibits a characteristic angle of 109.5° which corresponds to the angle between equivalent \{111\} faces on either side of the twin boundary. We therefore suggest that the $\gamma$ branch of the merged-y structure grows by adding atoms to low energy \{111\} faces.

More structural information about the merged-y NWs can be extracted from HRTEM micrographs. In particular, a close examination reveals that merged-y NWs are generally viewed down $\langle110\rangle$ induced by a twin boundary between $\alpha$ and $\beta$ (Figure 3.4), which grow away from it along equivalent $\langle100\rangle$ directions. A HRTEM micrograph of the merged-y junction is shown in Figure 3.5(a), with an idealized cartoon of the atomic arrangement provided in Figure 3.5 (b). In all cases, a \{111\} twin boundary runs down the center of the structure, with parallel \{200\} planes observed on either side. The angle between these planes is 70.5° and rationalizes the $\alpha\beta$ angle in Figure 4. Likewise, a complementary angle of 109.5° faces downward, opposing the upper 70.5° angle. This is again due to the same \{100\} planes on either side of the twin boundary. Both angles are in excellent agreement with measured $\alpha\beta$ angles of the merged-y wires as well as the d-spacings between \{200\} planes. Furthermore, the 109.5° angle matches the apparent angle seen in Figure 3.4(b) and suggests that catalyzed growth of $\gamma$ occurs by addition to low energy \{100\} faces. Occasionally an upward facing 140° angle will be observed in HRTEM images such as Figure 3.5. This is due to the angle between \{111\} planes on either side of the twin boundary. Both a dashed and a solid line have been provided in Figure 3.5(b) to aid in visualizing this.
Figure 3.5 (a) HRTEM and (b) cartoon of twinned merged-y junction in a PbSe NW.

3.3.4 XRD characterization

Apart from TEM images, the crystallinity of all PbSe NWs is further established by powder X-ray diffraction patterns such as that shown in Figure 3.6. Theoretical peaks for the underlying FCC based PbSe lattice are shown at the bottom of the figure and correspond well with those obtained from the NWs. Peak broadening is also observed and can be attributed to finite size effects. A rough Scherrer analysis of the sample used in Figure 6 produces a domain size of ~15 nm, using either the {200} or {220} reflections, in good agreement with direct sizing of the same ensemble through TEM.
In Figure 3.6, several peaks are slightly enhanced or suppressed in the powder pattern. This can be attributed to preferred orientation of the NWs lying parallel to the plane of the substrate. For example, both the (111) and (220) peaks are suppressed compared to their nominal intensities in isotropically distributed samples. This can be seen by comparing the intensity ratios of the JCPDS pattern to the experimental data. Corroborating this, a simple analysis of texture in the sample suggests that the (111), (311), (222), (331), and (422) reflections will be absent in <001> oriented wires. Suppression of the (220) as well as the (420) peak, both relative to the (200) reflection, is also expected. While the latter prediction is seen in Figure 3.6, the (111), (311), (222), (331), and (422) reflections are all present in the experimental data and can be accounted for by incomplete orientation of the sample on the substrate. It should also be noted that
in the case of branched samples a high incidence of right angles/t-shapes or merged-y NWs will enhance the relative intensities of the (200) and (220) lines respectively, due to their specific shape and preferred <110> orientations on a substrate.

3.3.5 Branching mechanism

Previous investigations of straight and branched CdSe NWs suggest that they follow a geminate nucleation mechanism. [17] The current study of branching in PbSe NWs indicates that the growth mechanism is likely the same and, hence, represents a general scheme for NW branching irrespective of material. As noted previously, straight wires are formed when Pb is in excess of Se, whereas branched wires result when the Pb:Se ratio approximates 1:1. Therefore, if sufficient quantities of both Pb and Se are present, two arms nucleate on the surface of the catalyst particle. If the angle \( \theta \) between the two arms is below a critical angle (\( \theta < \theta_{\text{crit}} \)), each arm is able to rotate or reorient within (or on) the molten catalyst to an appropriate orientation that allows them to touch, forming a low energy twin boundary. The result is a merged-y NW that has an average \( \alpha \beta \) angle of \( 70.4^\circ \) (\( \sigma = 1.4^\circ \)) and a complementary angle of \( 109.5^\circ \) between \{100\} planes facing the opposite direction along \( \gamma \). This is shown on the left side of Figure 3.7 along with actual TEM micrographs capturing such structures mid growth. If instead the initial angle \( \theta \) between the two arms is greater than this critical angle (\( \theta > \theta_{\text{crit}} \)), the arms have sufficient time during growth to rotate until their mutual angle is approximately \( 90^\circ \). A common rock salt section can then form, locking the two arms into place. Such a scenario is shown on the right side of Figure 3.7.
While the value of $\theta_{\text{crit}}$ can be inferred experimentally by noting both the average and the largest $\alpha\beta$ angles observed in both PbSe and CdSe merged-y NWs, the critical angle can also be calculated through geometric arguments. For example, assuming the radius of each arm is initially smaller than the catalyst particle (say ~80% of the catalyst NP radius), the calculated value for $\theta_{\text{crit}}$ is 77.25°. This corresponds well with observed
angles of 67.3° (σ = 9.6°) as well as a maximum angle of 87.0° for all merged-y PbSe NWs, both twinned or with a grain boundary along γ.

3.3.6 Higher order NWs

Higher order PbSe NWs are observed in branched NW preparations. These structures form when the catalyst particle is retained on the wire after an initial round of branching. The geminate NW nucleation mechanism assumes that under certain circumstances, possibly initiated by changes in the precursor metal to chalcogen ratio, multiple NWs can develop on a given catalyst particle during growth. We have suggested that the number of nucleated wires is typically two but do not exclude the possibility of more. However, the statistical likelihood of generating three, four or more arms on a single catalyst particle is thought to be small given the finite size of the NP which, in turn, increases the likelihood of multiple nucleated arms coalescing during early stages of the growth.

Figures 3.8 shows four additional examples of higher order structures. True to the underlying rock salt crystal structure of PbSe, the structures exhibit 90° angles on each arm. Although relatively large, the current PbSe structures are typically smaller than their analogous higher order CdSe counterparts. [17] Structures such as Figure 3.8(b,c,d) appear to be readily explained by a geminate branching mechanism where each branching point can be thought of as a location where NW growth was partitioned between two arms, the primary trunk and an emerging side arm. This step is then followed by continued growth along the primary arm. At the same time, we note that some branching in higher order structures may not strictly follow a geminate nucleation mechanism. For example, more complex higher order structures such as that in Figure 3.8(a) are difficult
to rationalize based solely on a model where only two arms emerge from a given catalyst particle. It appears to be better explained by a scenario where catalyst fission can occur. In this scenario, the catalyst particle breaks up into multiple fragments, each of which is capable of promoting branched NW growth. Indeed, examples of higher order NWs with multiple catalyst particles attached to different branches have been observed. By contrast, catalyst fission has not been observed with solution grown CdSe NWs. A more thorough description of this and other potential branching mechanisms can be found in Reference 17.

Figure 3.8  (a-d) Low resolution TEM micrographs of higher order PbSe NWs.

A final mechanism by which higher order branching may occur includes uncatalyzed growth. In this respect, examples exist in the literature showing uncatalyzed wires that appear to exhibit branching. [54] This is further supported by control experiments we have conducted showing similar behavior. As a consequence, this phenomenon cannot be completely excluded as a potential growth mechanism. However, based on control
experiments for uncatalyzed growth (described below), the primary route to branching appears to be catalyzed. In this respect, control experiments indicate a very low incidence of uncatalyzed growth with the major species in such experiments being irregular spherical PbSe aggregates. Examples of both are shown in TEM micrographs in Figure 3.9. Furthermore, TEM observations reveal distinct signatures of catalyzed versus uncatalyzed growth, allowing one to distinguish the two mechanisms (described below). As a consequence, the primary branching scheme for PbSe NWs is thought to be a catalyzed, primarily geminate, growth mechanism. [17]

Figure 3.9 (a-d) Low resolution TEM micrographs of straight and branched uncatalyzed PbSe wires.
3.3.7 Uncatalyzed growth

Control experiments conducted under the same conditions as (catalyzed) straight and branched NW preparations show a small incidence of uncatalyzed NW growth. These wires have noticeably different morphologies than the catalyzed NWs described above. Namely, the uncatalyzed wires have a polycrystalline structure composed of smaller spherical aggregates of PbSe. Examples can be seen in Figure 8 where both straight and “branched” uncatalyzed wires are seen. Most of the observed polycrystalline wires appear straight and tapered (Figure 8a) but branched wires are also seen. Figures 8(b,c,d) are examples of “right angles” and “t-shapes”. In all cases, the bulk of the sample consists of spherical PbSe aggregates which can also be seen in Figures 8(a,c). Such NWs have previously been observed and are thought to form by partial alignment of the individual spherical particles through dipole-dipole interactions in solution, however, the actual origin of this dipole is still speculative and remains open to investigation. [54]

Distinguishing catalyzed from uncatalyzed NWs are the following features which enable us to conclude that the primary branching mechanism in the current synthesis is catalyzed. First, catalyzed NWs often have a Au/Bi NP attached to one end of the wire, providing indirect evidence for a seeded growth mechanism. Second, the surfaces of the catalyzed NWs are also smooth. This has been confirmed by measurements of NW diameter fluctuations, yielding intrawire variations of 7(3)%. In addition, the catalyzed NWs are single crystals as can be seen in Figures 1-4. By contrast, HRTEM images of uncatalyzed wires reveal them to be universally polycrystalline, identical to what has been observed previously. [54] The diameters of the catalyzed NWs are more closely
associated with the initial diameters of the catalyst NPs despite their apparent growth in solution. This should be contrasted to the size of uncatalyzed NWs which have average diameters of 38 (12) nm. Along these lines, the uncatalyzed wires are almost always dramatically tapered whereas the catalyzed wires are not. Finally, a major distinction between catalyzed and uncatalyzed growth is the absence of any merged-y structures in preparations based on the latter growth scheme. In this respect, just as merged-y structures were characteristic of a geminate NW nucleation mechanism, they also appear to be a unique signature of catalyzed NW growth.

3.4 Conclusions

The successful solution-based synthesis of quantum confined PbSe NWs has been demonstrated for both straight and branched NWs. The current work provides one of the first examples of self-induced branching in NWs and addresses an emerging need for shape control in 1D materials. A qualitative scheme developed to explain this behavior suggests that branching observed in both CdSe and PbSe NWs follows a general mechanism and is potentially applicable to other systems as well. This, in turn, provides a method for creating nanostructures of varying morphology. As such, the work is relevant to improving our understanding about the evolution of mesoscopic optical, electrical and physical properties with size, shape and dimensionality. Furthermore, in addition to being of interest for basic science reasons, such straight and branched NWs may also have potential technological applications.
REFERENCES


