Shape-controlled synthesis and application of one-dimensional cadmium chalcogenide nanocrystals

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SHAPE-CONTROLLED SYNTHESIS AND APPLICATION
OF ONE-DIMENSIONAL CADMIUM CHALCOGENIDE
NANOCRYSTALS**

XI LIFEI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2009

SHAPED-CONTROLLED SYNTH. AND APPL. OF
1D CD-CHALCOGENIDE NANOCRYSTALS

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School of Materials Science and Engineering

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Abbreviations

1D	one-dimensional
PV	photovoltaic
HNS	heteronanostructure
AOT	sodium bis(2-ethylhexyl) sulfosuccinate
CdS	cadmium sulfide
CdSe	cadmium selenide
CdTe	cadmium telluride
CdO	cadmium oxide
N ₂ H ₄ · H ₂ O	hydrazine hydrate
Na ₂ SeO ₃	sodium selenite
HPA	hexylphosphonic acid
DDPA	dodecylphosphonic acid
TDPA	tetra-decylphosphonic acid
ODPA	octadecylphosphonic acid
TBP	tributylphosphine
TOP	trioctylphosphine
TOPO	trioctylphosphine oxide
P3HT	poly(3-hexythiophene)
MEH-PPV	poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]
PEDOT: PSS	poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
SEM	scanning electron microscope
TEM	transmission electron microscope
UV-Vis	ultraviolet-visible
PL	photoluminescence
XRD	X-ray diffraction
EDAX	energy dispersive analysis of X-ray
SAED	selected area electron diffraction
EELS	electron energy-loss spectroscopy
FT-IR	Fourier transform infrared spectroscopy
TGA	thermogravimetric analyzer
PCE	power conversion efficiency
EQE	external quantum efficiency

Contents

Acknowledgements.....	I
Abbreviations	II
Contents.....	III
List of Figures.....	VI
List of Tables	X
List of Schemes.....	X
Abstract.....	XI
Chapter 1 Introduction.....	1
1.1 Motivation.....	1
1.2 Objectives.....	5
1.3 Organization of Thesis.....	6
Chapter 2 Literature Review.....	8
2.1 Synthesis Methods of 1D Nanocrystals.....	9
2.1.1 Vapor-liquid-solid (VLS) method.....	10
2.1.2 Solution-liquid-solid (SLS) method.....	11
2.1.3 Microemulsion method.....	13
2.1.4 Hydrothermal method.....	15
2.1.5 Hot coordinating/ noncoordinating solvents method.....	17
2.2 Third Generation Photovoltaic (PV) Devices.....	20
2.2.1 Organic solar cells	21
2.2.2 Dye-sensitized solar cells	23
2.2.3 Organic/inorganic hybrid solar cells.....	25
2.2.4 All-inorganic nanocrystals solar cells.....	27
Chapter 3 Synthesis and Characterization of CdSe Nanorods Using a Novel Microemulsion Method at Moderate Temperature.....	29
3.1 Introduction.....	29
3.2 Experimental Section.....	32
3.2.1 Materials	32
3.2.2 Synthesis of CdSe nanocrystals	32
3.2.3 Characterization	33
3.3 Results and Discussion.....	35
3.3.1 Phase analysis.	35
3.3.2 Morphologies studies.	36
3.3.2.1 Influence of the water to AOT molar ratio (<i>R</i>)	36

3.3.2.2 Influence of the hydrazine hydrate to AOT molar ratio (S)	38
3.3.2.3 Influence of the precursor concentration	40
3.3.3 Crystallography of nanocrystals	42
3.3.4 Spectra analysis of nanocrystals	43
3.3.5 Optical characterization.....	44
3.3.6 Growth mechanism.	45
3.4 Conclusions.....	50
Chapter 4 Synthesis and Characterization of CdSe Nanorods by a Novel Reverse Micelle Assisted Hydrothermal Method	52
4.1 Introduction.....	52
4.2 Experimental Section.....	54
4.2.1. Materials.	54
4.2.2 Synthesis of CdSe Nanocrystals.	54
4.2.3 Characterization.	55
4.3 Results and Discussion.....	56
4.3.1 Phase analysis.....	56
4.3.2 Morphological studies.....	57
4.3.2.1 Influence of the AOT amount.....	57
4.3.2.2 Influence of the hydrazine hydrate amount	60
4.3.2.3 Influence of the reaction temperature.....	62
4.3.3 Crystallography of nanocrystals	62
4.3.4 Optical characterization.....	64
4.3.5 Raman spectroscopy	65
4.3.6 Growth mechanism	66
4.4 Conclusions.....	70
Chapter 5 Growth of Monodisperse CdS Nanowires in Solution.....	72
5.1 Introduction.....	72
5.2 Experimental Section.....	74
5.2.1 Materials	74
5.2.2 Synthesis of CdS nanowires	74
5.2.3 Characterization	75
5.3 Results and Discussion.....	75
5.3.1 Phase analysis.....	75
5.3.2 Morphological studies.....	75
5.3.2.1 Influence of the ODPA-to-Cd mole ratio.....	79
5.3.2.2 Influence of the Cd-to-S mole ratio	83
5.3.2.3 Influence of the precursor concentration	84
5.3.2.4 Influence of the precursor injection process	85
5.3.2.5 Influence of the different ligands on Cd-complexing.....	86
5.3.2.6 Time-dependent shape evolution studies.....	89
5.3.2.7 Potential applications and scale-up issues.....	91
5.4 Conclusions.....	93
Chapter 6 Dynamical Study of Growth Mechanism for Monodisperse CdS Nanowires.....	94
6.1 Introduction.....	94
6.2 Experimental Section.....	96

6.3 Results and Discussion.....	96
6.4 Conclusions.....	106
Chapter 7 Controlling Growth of CdSe Nanowires through Surfactants Optimization.....	108
7.1 Introduction.....	108
7.2 Experimental Section.....	110
7.2.1 Materials	110
7.2.2 Synthesis of CdSe nanocrystals	110
7.3 Results and Discussion.....	111
7.3.1 Phase analysis.....	111
7.3.2 Morphological studies.....	114
7.3.2.1 Influence of different ligands on Cd-complexing	114
7.3.2.2 Influence of different ligands on Se-complexing	116
7.3.2.3 Influence of the reaction temperature.....	119
7.3.2.4 Influence of the precursor concentration	121
7.3.2.5 Influence of the precursor injection process.....	123
7.3.2.6 Time-dependent studies	124
7.4 Conclusions.....	127
Chapter 8 Controlled Synthesis of CdSe and CdTe Multi-block Heteronanostructures (HNSs).....	129
8.1 Introduction.....	129
8.2 Experimental Section.....	131
8.2.1 Materials	131
8.2.2 Synthesis of CdSe and CdTe multi-block HNSs	132
8.2.3 Characterization	132
8.3 Results and Discussion.....	133
8.4 Conclusions.....	141
Chapter 9 Hybrid Photovoltaic Devices.....	143
9.1 Introduction.....	143
9.2 Experimental Section.....	144
9.2.1 Materials	144
9.2.2 Device fabrication	144
9.2.3 Device characterization	146
9.3 Results and Discussion.....	146
9.3.1 CdS/MEH-PPV hybrid solar cells.....	146
9.3.2 CdSe/P3HT hybrid solar cells.....	150
9.3.3 HNSs/P3HT hybrid solar cells.....	154
9.4 Conclusions.....	159
Chapter 10 Conclusion and Future Directions.....	162
10.1 Thesis Conclusions.....	162
10.2 Future Directions.....	167
References	170
Appendix I: List of Publications.....	177

List of Figures

Fig. 2.1.	(a) Scheme of VLS growth of Si whisker. (b) Binary phase diagram of Au-Si. (c) Scanning electron microscopy (SEM) image of Si nanowires prepared by following ablation of a Au target in the presence of silane at 450 °C.....	10
Fig. 2.2.	(a) Schematic illustration showing the growth of a 1D nanocrystal through SLS growth. TEM images of (b) PbSe nanowires and (c) Au/Bi nanocrystals attached to the end of PbSe nanowires synthesized by SLS method.....	12
Fig. 2.3.	(a) A phase diagram for water/oil/surfactant system. (b) Schematic illustration showing the formation of a cylindrical reverse micelle in an organic solvent. TEM images of (c) CdS nanorods prepared in AOT + lecithin reverse micelles system and (d) hydroxyapatite (HAP) nanorods using mixtures of triblock copolymer, pluronic P123 and tween-60.....	14
Fig. 2.4.	SEM image of CoPt nanowires prepared via the hydrothermal method.....	17
Fig. 2.5.	The set-up for the synthesis using hot coordinating/ noncoordinating solvents method.....	18
Fig. 2.6.	TEM images of cadmium chalcogenide nanocrystals with different shapes prepared by hot coordinating solvents method. (a) CdSe dots, (b) CdSe rice grains, (c) CdSe rods, (d) CdTe tetrapods and (e) CdS nanowires.....	19
Fig. 2.7.	(a) Device representation and (b) band diagram of P3HT-PCBM organic solar cells.....	23
Fig. 2.8.	(a) Device representation and (b) band diagram of dye-sensitized solar cells.....	24
Fig. 2.9.	(a) Device representation of CdSe nanorods/P3HT hybrid solar cells. (b) The external quantum efficiencies (EQEs) of 7 nm diameter CdSe nanorods with lengths 7, 30 and 60 nm. (c) Solar cell characteristics of this 7 x 60 nm CdSe nanorods device illuminated with simulated air mass (AM) 1.5 Global light.....	26
Fig. 2.10.	TEM images of (a) CdSe and (b) CdTe nanorods. Scale bar, 40 nm. (c) An energy diagram of two materials. (d) SEM image of a typical spin-cast film. The film edge of this about 100 nm is shown for contrast with the silicon substrate. Scale bar, 1 µm.....	28
Fig. 3.1.	Chemical structure of AOT.....	30
Fig. 3.2.	Typical XRD pattern of as-prepared CdSe nanocrystals with $R=5.0$, $S=5.2$ (a) and JCPDS hexagonal CdSe pattern (b)	36
Fig. 3.3.	TEM images of as-prepared CdSe nanocrystals with different R values: (a) $R=8.5$, (b) $R=6.7$ and (c) $R=5.0$, respectively.....	37
Fig. 3.4.	TEM images of as-prepared CdSe nanocrystals with different S values: (a) $S=4.0$, (c) $S=7.8$ and (c) $S=11.4$	40
Fig. 3.5.	TEM images of as-prepared CdSe nanocrystals with different concentration: (a) 1.39 mmol/ml and (b) 5.56 mmol/ml.....	41
Fig. 3.6.	(a) HRTEM image of single CdSe crystal and (b) bright field image of single nanorod with diffraction pattern (inset).....	43
Fig. 3.7.	The EDAX spectrum of the as-prepared CdSe nanocrystals.....	43
Fig. 3.8.	FT-IR spectra of (a) AOT and (b) as-prepared CdSe nanocrystals.....	44

Fig. 3.9.	(a) UV-Vis absorption and (b) PL excitation spectrum of the as-prepared CdSe nanocrystals.....	45
Fig. 3.10.	Different colour observed for samples taken at different time after injecting the second precursor (1 [#] to 9 [#] : 0.5, 1, 2, 4, 6, 8, 15, 30 and 60 min)	46
Fig. 3.11.	TEM images of samples after different reaction time: (a) 1 min, (b) 5 min, (c) 30 min, (d) 1 h and (e) 6 h, respectively.	48
Fig. 3.12.	Yield of nanocrystals as a function of reaction time.....	50
Fig. 3.13.	Size distribution of nanorods under optimum conditions. Average length: 63.85 nm (diameter: 20 nm), STDEV: 19.6 and size distribution: 0.31. (Note: above data are based on 330 nanorods.)	50
Fig. 4.1.	Typical XRD patterns of as-prepared CdSe nanocrystals with 4mmol AOT and 5ml hydrazine hydrate (a) and JCPDS hexagonal CdSe pattern (b).....	56
Fig. 4.2.	TEM images of the CdSe nanocrystals with fixed the amount of hydrazine hydrate (5 ml) and varied the amount of AOT: (a) 1 mmol, (b) 4 mmol and (c) 8 mmol.....	58
Fig. 4.3.	TEM images of the CdSe nanocrystals with fixed AOT amount (4mmol) and varied hydrazine hydrate amount: (a) 2.5 ml, (b) 5 ml and (c) 10 ml.....	60
Fig. 4.4.	(a) HRTEM image, (b) TEM image of single CdSe nanorod with diffraction pattern (inset) and (c) the EDAX spectrum of the as-prepared CdSe nanocrystals. (d) AFM height image of CdSe nanorods. The scanning area is 2 μm x 2 μm	63
Fig. 4.5.	(a) UV-Vis absorption spectrum, (b) PL spectra of 35 dots and (c) the corresponding confocal microscopic image of CdSe nanorods.	65
Fig. 4.6.	Raman spectrum of CdSe nanorods.....	66
Fig. 4.7.	TEM images of nanocrystals after (a) 1 h, (b) 2 h, (c) 3h, (d) 5 h and (e) 10 h reaction.	69
Fig. 5.1.	Typical XRD patterns of (a) 600 nm long as-prepared CdS nanowires, (b) shorter nanowires (150 nm in length), (c) nanorods (14 nm in length) and (d) JCPDS hexagonal CdS pattern...	76
Fig. 5.2.	(a) Bright-field image of CdS nanowires, (b) dark-field image of the same CdS nanowires using the CdS 002 reflection and (c) the diffraction pattern of the same area. The positions of the reflections for hexagonal CdS (CdS H JCPDS card no. 41-1049), cubic Fm3m CdS (21-0829) and cubic $\bar{F}4_3\text{m}$ CdS (89-0440) are marked. (d) The EDAX spectrum of the as-prepared CdS nanowires.....	78
Fig. 5.3.	(a) HRTEM image of a CdS nanowire, (b) an FFT of the HRTEM image showing the indices and (c) high resolution image looking down the axis of a bent nanowire.....	79
Fig. 5.4.	TEM images of CdS nanowires with ODPa-to-Cd mole ratios of (a) 1:1, (b) 1.5:1, (c) 2:1, (d) 3:1 and (e) 4:1.....	80
Fig. 5.5.	TEM images of CdS nanowires synthesized with Cd-to-S mole ratios of (a) 1:1.5 and (b) 1:0.5.....	84
Fig. 5.6.	TEM images of CdS nanocrystals synthesized with: (a) a single precursor injection and (b) multiple injections with an interval of greater than 5min.....	85
Fig. 5.7.	Chemical structures of three phosphonic acids with varying linear alkyl chain lengths.....	87
Fig. 5.8.	TEM images of CdS nanocrystals synthesized with: (a) HPA and (b) DDPA ligands. (c) UV-Vis absorption spectra of nanocrystals produced with different ligands.....	88

Fig. 5.9.	TEM images showing the temporal evolution of the CdS nanowires after (a) 5 min, (b) 15 min, (c) 30 min, (d) 1 h and (e) 2 h. (f) Graph showing the change in the average length of the CdS nanowires over time. (g) UV-Vis absorption (solid line) and PL emission spectrum (dotted line) of CdS nanowires obtained during nanowire growth.....	89
Fig. 5.10.	TEM images of the active layer of proposed hybrid solar cells with nanowire loadings of (a) 1:1 and (b) 1:3 by volume in a P3HT matrix.....	92
Fig. 6.1.	(a) The UV-Vis absorption spectra of CdS nanocrystals (after injection 10, 30, 40, 50, 60, 70 and 95 min) with the absorption intensity change at 308 nm and the 1 st exciton absorption around 440 nm, (b) the expanded scale absorption spectra and (c) the color change of solution vs time.....	98
Fig. 6.2.	TEM images of tiny dots before attachment.....	98
Fig. 6.3.	FT-IR spectra of pure TOP, TOP-S complexes, CdS nanocrystals after injection 10, 60 and 95 min	100
Fig. 6.4.	TEM images of CdS: (a-c) nanorods ((b) partially enlarged (a)), (d-e) nanowires and (f) nanotubes.....	103
Fig. 6.5.	TEM images of nanowire “etched” by electron beam. (a) to (c) are observed at increasing time.....	106
Fig. 7.1.	Typical XRD patterns of CdSe nanocrystals with different dimensions: (a) nanowires (220 x 8 nm), (b) long nanorods (83 x 9 nm), (c) short nanorods (20 x 7 nm) and (d) JCPDS hexagonal CdSe pattern.....	112
Fig. 7.2.	(a) HRTEM image, (b) diffraction pattern of a CdSe nanowire, (c) the EDAX spectrum of the as-prepared CdSe nanowires and (d) AFM height image of CdSe short nanowires. The scanning area is 1 μm x 1 μm	113
Fig. 7.3.	TEM images of CdSe nanocrystals synthesized with different ligands for Cd at 310 °C: (a) HPA, (b) DDPA and (c) ODP. The ligand used for Se is TOP.....	115
Fig. 7.4.	Chemical structures of ligands for Se-complexes.....	116
Fig. 7.5.	A comparison of the steric effect with different ligands on Se-complexes.....	118
Fig. 7.6.	TEM images of CdSe nanorods synthesized with DDPA and (a) TBP or (b) TPP ligands. (c) HRTEM images of single hexagonal CdSe disk. (d) UV-Vis absorption spectra of nanocrystals synthesized with TBP, TOP and TPP ligands.....	119
Fig. 7.7.	TEM images of CdSe nanocrystals synthesized with DDPA at (a) 250 °C, (b) 280 °C, (c) 340 °C and (d) HRTEM image of a spheroidal structure.	121
Fig. 7.8.	TEM images of CdSe nanowires synthesized using DDPA and with varying precursor concentrations (in comparison with the concentration used for synthesizing sample shown in Fig. 7.4b): (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.....	122
Fig. 7.9.	Scheme showing how various reaction parameters affect the growth of nanocrystals.....	124

Fig. 7.10.	Time-dependent TEM images of CdSe nanorods (a) 2 min after the 3 rd injection, (b) 7 min after the 4 th injection and (c) 30 min after the 4 th injection. (d) Time-dependent UV-Vis absorption spectra of CdSe nanocrystals.....	126
Fig 8.1.	Thin film XRD patterns of CdTe nanorods and CdTe/CdSe multi-block HNSs after the 2 nd and 3 rd injection are compared with the JCPDS hexagonal CdTe and CdSe patterns.....	133
Fig. 8.2.	TEM images of CdTe/CdSe multi-block HNSs synthesized (a) CdTe nanorods, (b) after the 2 nd injection and (c) after the 3 rd injection.....	135
Fig. 8.3.	HRTEM images of single CdTe/CdSe HNS: (a) tri-block, (b) multi-block linear extension and (c) branch point.....	137
Fig. 8.4.	High angle annular dark-field (HAADF) image of HNSs.....	138
Fig. 8.5.	(a) HAADF image of the rod used for the EELS line scan. The trace of the line scan can be seen as a series of black dots along the rod starting near the top of the image. (b) EELS line scan from the rod shown in (a). The values plotted are the measured areas of the Cd M ₄₅ edge at 404 eV (solid line), the Te M _{4,5} edge at 572 eV (dotted line) and the Se L _{2,3} edge at 1436 eV (dashed line) at each point, scaled to a maximum value of 1. Negative edge areas are due to noise in the background subtraction calculation. The image and line scans were taken using an accelerating voltage of 120 kV to reduce electron beam damage. (c) Diagram showing the growth sequence after each precursor injection.....	139
Fig. 8.6.	(a) UV-Vis absorption and (b) PL spectra of as-prepared nanocrystals after the series of secondary precursors have been injected.....	140
Fig. 9.1.	(a) Schematic energy level diagram for HNSs and P3HT showing the charge transfer of electrons to CdTe, then CdSe and holes to P3HT and (b) TEM image of a network formed by concentrated CdSe nanowires only.....	144
Fig. 9.2.	TEM image of a blend film of CdS nanowires/MEH-PPV with 70% CdS nanocrystals loading.	147
Fig. 9.3.	UV-Vis absorption spectra of CdS nanocrystals, MEH-PPV and CdS nanowires/MEH-PPV blend thin film.	148
Fig. 9.4.	I-V curves of PV devices of (a) CdS nanorods/MEH-PPV and (b) CdS nanowires/MEH-PPV in the dark (dotted line) and under illumination of 100 mW cm ⁻² (solid line).	148
Fig. 9.5.	TG curves of TOPO, ODPA and CdS nanocrystals before ligand exchange, after the 1 st and 2 nd ligand exchange, respectively.....	150
Fig. 9.6.	TEM images of CdSe nanorods with different aspect ratios range from 3 to 15. The TEM images show the samples of different dimensions: (a) 7 nm x 20 nm, (b) 7 nm x 60 nm and (c) 9 nm x 140 nm.....	151
Fig. 9.7.	UV-Vis absorption spectra of (a) CdSe in solution form of different lengths (1) 140 nm and (2) 60 nm and (b) of pure P3HT film (dashed line), CdSe film (dotted-dashed line) and CdSe - P3HT film made of 140 nm nanorods (black) and 60 nm nanorods (red).....	151
Fig. 9.8.	TEM images of P3HT and CdSe nanorods blend films with 90% nanorod loading formed by (a) 7 x 60 nm and (b) 9 x 140 nm nanorods.....	152

Fig. 9.9.	(a) I-V curves of P3HT/CdSe hybrid solar cells made of different CdSe nanorod lengths: 140 nm (solid line) and 60 nm (dashed line) and (b) relative EQE of the devices made of 140 nm (solid line) and 60 nm (dashed line), respectively.....	153
Fig. 9.10.	(a) TEM image of the blend film of HNSs/P3HT with (a) 50% and (b) 70% HNSs loading.	156
Fig. 9.11.	TG curve of HNSs nanocrystals after ligand exchange.....	156
Fig. 9.12.	(a) UV-Vis absorption and (b) PL spectra of P3HT, HNSs nanocrystals and HNSs/P3HT blend thin film.....	157
Fig. 9.13.	I-V curve of PV devices in the dark (dotted line) and under illumination of 100 mW cm ⁻² (solid line).....	158
Fig. 10.1.	A summary of three synthesis methods for shape control.....	167

List of Tables

Table 2.1.	A comparison of the different generation solar cells.....	21
Table 3.1.	Summary for the influence of the parameters on morphology (Reverse micelles).....	51
Table 4.1.	Summary for the influence of parameters on morphology (Hydrothermal).....	70
Table 4.2.	A comparison between the reverse micelle and the hydrothermal methods.....	71
Table 9.1.	PV characteristics of the best performed devices fabricated using different CdSe nanorod lengths under simulated solar spectrum with AM 1.5 filter at an intensity of 0.85 suns.....	152

List of Schemes

Scheme 3.1.	Proposed model for CdSe nanocrystal formation in the reverse micelles: (a) the nucleation and growth of spherical particles, (b) further growth of nanorods (Ostwald ripening), (c) intraparticle ripening (resulting in a decrease in the aspect ratio of the nanocrystals).....	46
Scheme 4.1.	Proposed model of the process of nanocrystal formation in reverse micelles assisted by hydrothermal method: (a) Fusion and exchange of the contents within the cores and re-dispersion of the reverse micelles before heated up, (b) Nucleation and growth of spherical and rodlike nanocrystals with heating and pressure before micelles collapsed, (c) Further growth of nanorods provided by directional aggregation of smaller particles including shorter rods and nuclei after micelles collapsed.....	68
Scheme 6.1.	Scheme of CdS nanowire formation.....	101

Abstract

In recent years, the synthesis of one-dimensional (1D) nanocrystals has attracted considerable interest. The morphologies of the 1D nanocrystals studied include rods, wires, belts and tubes whose lateral dimensions fall within the 1 to 100 nm range. Their potential applications are related to their size- and shape-dependent physicochemical and optoelectronic properties. 1D cadmium chalcogenide nanocrystals have become important potential building blocks for new electronic and optical nanodevices. As the electronic and optical properties are dependent on the crystal dimensions, the issue of how to control the growth of 1D cadmium chalcogenide nanocrystals is of prime importance and this issue remains one of the most challenging issues to address in both chemistry and materials science. This is one of the motivations behind this study.

In this work, three catalyst-free and solution-based methods were used for the synthesis of 1D cadmium chalcogenide nanocrystals. These methods are the reverse micelle method, the hydrothermal method and the hot coordinating solvents method. Using both the reverse micelle method and the hydrothermal method, we have successfully synthesized CdSe nanorods. We found that the reverse micelle method has better morphological control than the hydrothermal method, but the latter has both the higher crystallinity and yield. Using the hot coordinating solvents method, good size distribution, controllable growth and an aspect ratio as high as 170 has been achieved. This is significant because in the past fifteen years, this method has only been able to generate low aspect ratio nanorods (less than 20). Contrary to the existing mechanisms, an oriented attachment mechanism was observed and proposed in this study. We also attempted to synthesize CdSe nanowires using the same method. Although this method has been successful in producing cadmium selenide (CdSe) nanodots, nanorods and tetrapods, it remains a challenge to obtain nanowires. After systematically varying the parameters, we were able to gain some understanding in the growth of anisotropic nanocrystals. CdSe nanowires with a length of 220 nm and a diameter of 8 nm were successfully synthesized.

Using the same method, a novel 1D multi-block heteronanostructures (HNSs) nanocrystal were successfully prepared and studied. Our study may help in the understanding of the growth of more complex functional nanomaterials. Furthermore, the successful formation of these structures is essential for future applications of semiconductor nanocrystals in nanoscale devices.

Finally, the PV properties of devices containing polymer and 1D nanocrystals blends have been studied. This is the next motivation behind this study to enhance the performance of solar cells. Three types of hybrid solar cells have been successfully processed from solution by blending polymer and nanocrystals. The best hybrid cells combination is CdSe nanorods and poly(3-hexyothiophene) (P3HT). Under air mass 1.5 solar conditions and an ambient test environment, the best performing device, made of 140 nm-long-CdSe nanorods and P3HT, showed a short-circuit current density, an open-circuit voltage, a fill factor and a power conversion efficiency (PCE) of -3.436 mA/cm^2 , 0.490 V, 0.504, and 0.85%, respectively. This study also showed that with increasing aspect ratio, the performance of the devices also increases.

Chapter 1: Introduction

1.1 Motivation

One-dimensional (1D) nanocrystals (also known as nanoparticles), such as nanorods, nanowires, nanobelts and nanotubes, exhibit remarkable physical and chemical properties that make them attractive building blocks for electronic, mechanical, optical and life sciences applications. [1 - 5] In recent years, 1D nanocrystals have become the focus of intensive research due to their unique applications in mesoscopic physics and nanoscale devices. [6 - 9] Cadmium chalcogenide, which is a narrow band gap materials (bulk: $E_g=2.5$ eV for cadmium sulfide (CdS), $E_g=1.75$ eV for cadmium selenide (CdSe) and $E_g=1.45$ eV for cadmium telluride (CdTe) at 300K), has a high optical absorption coefficient and represents one of the most important group II-VI semiconductors. [10, 11] These materials have been widely used in electronic and optical areas. Currently, 1D cadmium chalcogenide nanocrystals have become important potential building blocks for new electronic and optical nanodevices such as laser, [12] transistor, [13] light-emitting diodes [14] and photovoltaic (PV) [15, 16] devices. As the electronic and optical properties of nanocrystals are dependent on the dimensions of these crystals, the issue of how to control the growth of 1D cadmium chalcogenide nanocrystals is one of the most challenging issues in chemistry and materials science.

Over the past decade, significant progress had been made in the control of nanocrystals properties, such as size distribution, uniformity and shape. [17 - 22] A variety of methods had been employed to produce 1D cadmium chalcogenide nanocrystals. These methods include the chemical vapor deposition (CVD) growth, the thermal evaporation, the vapor-liquid-solid (VLS) growth, the solution-liquid-solid (SLS) growth, the super-fluid-

Chapter 1: Introduction

liquid-solid (SFLS) growth, the microemulsion method, the templates-based growth, the sol-gel process, hydrothermal/solvothermal process, the sonochemical process and the hot coordinating/noncoordinating solvents method. Amongst these methods, the solution-based methods are the most attractive because they have several advantages in the synthesis of 1D nanocrystals with the following properties: [6, 7, 16, 17]

- 1) High crystallinity: Although their growth temperatures are comparatively low (less than 350C), nanocrystals are highly crystalline as shown by the high resolution transmission electron microscopy (HRTEM) results presented in the later chapters (such as in Chapter 3, 4 5, 7 and 8). This is due the low cohesive energy between the atoms which is related to the melting point of the material. Since size of the nanocrystals go down to 2-3 nm, the melting point of the material can be halved.
- 2) Good dispersibility: Usually, the surface of nanocrystals is capped with organic ligands either by covalent bonding or physical attachment. These ligands provide the nanocrystals with good dispersibility in common organic solvents due to steric stabilization and also prevent them from oxidation. The surface chemistry of nanocrystals can also be altered via ligand exchange process to give them either hydrophilic or hydrophobic characteristics.
- 3) Good shape-controlled growth: The growth kinetics of the resulting materials can be controlled by controlling the reaction conditions such as the type of reagents, the reaction temperature, the concentration, the type of surfactants and/or ligands.
- 4) New nanostructures: There are flexibility in the nanostructures obtainable using solution-based methods. These methods provided some of the first examples of the synthesis of nanocrystals with tetrapod, v-shape, y-shape, t-shape and other “higher order” morphologies.

Chapter 1: Introduction

In this study, our first motivation is to synthesize 1D cadmium chalcogenide nanocrystals with good size distribution and controllable growth using solution-based synthesis methods. First, we synthesized nanocrystals using reverse micelle and hydrothermal methods because these two methods have the possibility of producing 1D nanocrystals on top of other advantages such as simple process, comparative low reaction temperature and low cost compared with VLS or hot coordinating solvents method. [20, 23] Using these methods, we synthesized CdSe nanorods with reasonable morphological control but the aspect ratio of these nanorods were less than 5 (refer to Chapter 3 or ref 24). There is a large size distribution in CdSe nanorods synthesized. We proposed a possible reason, which is due to reduced control over the nucleation and growth stages. The stability of the micelles in the presence of other components is poor. The details will be presented in Chapter 3. In the hydrothermal method (refer to Chapter 4 or ref 25), we proposed that before the micelles collapsed due to an increase in both pressure and temperature, the nucleation and growth of the spherical and rodlike nanocrystals within micelles is to some extent controlled by the micellar shape. After the micelles collapsed, further growth was provided by directional aggregation of the smaller spherical crystals and shorter rods. In the latter process, there is less control. This is the reason for poor size distribution and morphology control of nanorods in the hydrothermal method. The details on the hydrothermal synthesis will be presented in Chapter 4.

To gain better control in the nucleation and growth of the nanocrystals, the hot coordinating solvents method was used. This method has successfully generated 0D and low aspect ratio (less than 20) 1D cadmium chalcogenide nanocrystals due to the separation of the nucleation and growth stages. [26 - 30] The good crystal quality and control over the morphologies of the nanocrystals synthesized have made this method very important in the development of light-emitting diodes and solar cells. [10 - 16]

Chapter 1: Introduction

However, it remains a challenge to obtain 1D nanocrystals with a high aspect ratio (more than 20) and controllable growth using this method. [31] Thus, we think it is possible to produce high aspect ratio nanocrystals if we can optimize the parameters that favor the formation of high aspect ratio nanocrystals via systematic investigation in order to achieve a good balance between nucleation and growth.

The second motivation behind this study is to incorporate these 1D nanocrystals into PV devices to enhance the performance of these cells while reducing the production costs. 1D nanocrystals are preferable to 0D, 2D, or sintered nanocrystals in PV application, because they naturally provide a directed path for electrical transport by reducing the number of interparticle hopping events. Furthermore, 1D nanocrystals are readily dispersed in polymer matrixes from solution compared to 2D nanocrystals. Non-silicon based PV devices have the potential to play an important role in meeting the electric power needs in this century at low cost. If the cost of these PVs can be made to be comparable to other conventional energy generator methods, the potential for such system is tremendous. [32] Recent progress had been made in the use of organic materials, organic/inorganic hybrid materials and inorganic nanocrystals for PV applications. [8, 15, 33 - 35] There is an increase in the power conversion efficiency (PCE) in these types of solar cells. However, despite recent advances, the PCE of these solar cells is significantly lower than that of their Si-based counterparts due to low mobilities, poor separation and transport of the electrons/holes and the lack of complete percolation pathway in electron acceptor materials. [34, 36] Hybrid solar cell was fabricated using inorganic nanocrystals embedded in organic matrices. The reason of not using pure nanocrystals solar cells is that it is difficult to form a dense nanocrystal layer. A less dense layer would result in more chance for recombination due to high trap densities and a low carrier transport in the device. [15] On the other hand, the reason of

Chapter 1: Introduction

not using pure organic solar cell is low electron mobilities due to the presence of electron traps such as oxygen. [8] This type of solar cells has the following advantages: [8, 15, 37, 38]

- 1) The optical band of inorganic nanocrystal can be tuned by both material selection and size control.
- 2) Inorganic nanocrystals can both improve the electron transport capability due to high mobility (at least two orders of magnitude higher than that of organic materials) and provide a substantial interface for charge transfer due to their size.
- 3) In general, organic materials have extremely high optical absorption efficiency, which offers the possibility for the producing a very thin film solar cells. On top of this, there is also a wide range of material candidates ranging from small molecules to polymers for solar cell applications. [33, 36]
- 4) Inorganic nanocrystals with higher aspect ratio will give a better chance for charge separation in the cells and the transport of charges will be improved. Using high aspect ratio nanocrystals will provide a better possibility of forming a network of inorganic crystals in the polymers during spin-coating. This gives rise to a more continuous pathways for charge to travel.
- 5) Devices can be solution processable, light in weight and flexible.

1.2 Objectives

The overall objectives of this study are:

- 1) Use new routes to synthesize 1D cadmium chalcogenide nanocrystals with good size distribution, high aspect ratio and controllable growth, including hydrothermal, reverse micelle and hot coordinating solvents methods.
- 2) Synthesize novel 1D nanocrystals such as the multi-block heteronanostructures (HNSs).

Chapter 1: Introduction

- 3) Study the structure, composition, morphology, surface status and optical properties of 1D cadmium chalcogenide nanocrystals by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), electron energy-loss spectroscopy (EELS) line scans, Fourier transform infrared (FT-IR), Raman spectroscopy, ultraviolet-visible (UV-Vis) and photoluminescence (PL).
- 4) Investigate the nucleation and growth mechanism for each system.
- 5) Incorporate the 1D nanocrystals into PV device and study the optical and electronic properties of resulting devices.

1.3 Organization of Thesis

The main content of this thesis comprises ten chapters, which are arranged and based on author's papers (Chapter 3, 4, 5 and 8) and drafts to be published (Chapter 6, 7 and 9). In Chapter 1, the motivations behind this study are first presented. This includes a brief introduction of 1D cadmium chalcogenide nanocrystals and the advantages of solution-based synthesis methods. The objectives for this work are also provided.

In Chapter 2, a review of the literature is presented. Several methods for synthesizing 1D nanocrystals will be introduced. Their advantages and disadvantages will also be discussed. On top of that, an overview of the PV development and the current technologies of several different third generation solar cells will also be presented.

In Chapter 3 and Chapter 4, a microemulsion method at moderate temperature (100 °C) and a novel reverse micelle assisted hydrothermal method for synthesizing CdSe nanorods will be presented and discussed. The nucleation and growth mechanisms relating to these systems are also proposed based on the observations. A comparison

Chapter 1: Introduction

between these two methods will also be presented at the end of Chapter 4.

In Chapter 5, 6, 7 and 8, the discussion will be focused on the used of hot coordinating solvents method for the synthesis of three 1D nanocrystals. The main focus are the growth of monodisperse CdS nanowires in Chapter 5; the growth mechanism studies for monodisperse CdS nanowires in Chapter 6; the growth of nearly monodisperse CdSe nanowires in Chapter 7, and the growth of CdSe and CdTe multi-block HNSs in Chapter 8. The structure, composition, morphology, optical properties, surface state and growth mechanisms of these nanocrystals are investigated.

In Chapter 9, the PV applications of these 1D nanocrystals will be presented. Three types of hybrid solar cells are processed from solution by blending polymer and nanocrystals. They are HNSs/ poly(3-hexyothiophene) (P3HT), CdS/poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene](MEH-PPV) and CdSe/P3HT hybrid solar cells. The study on the optical and electronic properties of the devices will be presented.

Finally, conclusions and recommendations for future research will be presented in Chapter 10.

Chapter 2: Literature Review

In recent years, the synthesis of 1D nanocrystals, such as rods, wires, belts and tubes whose lateral dimensions fall within the range of 1-100 nm, has attracted considerable interest. [2, 3, 18] This is due to their novel size and shape-dependent physicochemical and optoelectronic properties. These properties make them attractive building blocks for electronic, optical and life sciences applications. [1 - 5] 1D nanostructure is thought to be a good model system to study the dependence of electrical, optical and mechanical properties on dimensional and quantum confinement. [6 - 8] To date, many methods have been employed to synthesize 1D nanocrystals. They can be roughly classified into two approaches: top-down approach and bottom up approach. The top-down approach involves sculpting bulk materials into nanoscale using advanced nanolithographic techniques, such as electron-beam or focused-ion-beam (FIB) writing, proximal-probe patterning and X-ray or soft electron-beam lithography. [2, 39] This approach has been proven to be successful for generating nanostructures and be especially useful in the microelectronic industry. It has shown a remarkable miniaturization possibility, where even smaller, even faster electronics and computing systems is achievable. However, there is a limitation in the development of these techniques into practical routes for large-scale nanodevice production. This is due to the technological and economical reason. [20, 22] For example, in the photolithography process, the critical dimension of devices is ultimately limited by the wavelength of the light. [40]

In contrast, the bottom-up approach, analogous to the way that nature uses proteins and other macromolecules to built complex biological systems, may prove to be a suitable solution to the technological challenges as the devices reduce in size. [17, 22] This is because this approach makes use of synthesis and then subsequent assembly to reach

Chapter 2: Literature Review

dimensions that is far beyond of the limit of top-down technology. The starting species can be an atom, a molecule or a nanocluster which will naturally rearrange into more complex assemblies due to the interaction energies between the species. [40]

This review begins by presenting the synthesis of 1D nanocrystals using several bottom-up synthesis methods and comparing these methods. Following that, the discussion on the PV development --- the current technologies of several third generation solar cells are presented. Four types of third generation solar cells: organic, dye-sensitized, organic/inorganic hybrid and inorganic nanocrystals solar cells will be introduced as well as the advantage and disadvantages of these cells are compared.

2.1 Synthesis Methods for 1D Nanocrystals

In the past decades, a variety of methods has been employed to synthesized 1D nanocrystals. These methods include CVD growth, thermal evaporation, VLS growth, SLS growth, supercritical-fluid-liquid-solid (SFLLS) growth, microemulsion, templates-based growth, sol-gel process, hydrothermal/solvothermal, sonochemical process and hot coordinating/noncoordinating solvents. [17, 18, 22] Solution-based methods such as hydrothermal, microemulsion and hot coordinating solvents have several advantages, such as the ability to encourage high crystallinity, good dispersibility and well shape-controlled growth as mentioned in Chapter 1. [7] In the following sections, we will discuss about one vapor phase synthesis method-VLS and focus on four solution-based synthesis methods, namely SLS, microemulsion, hydrothermal and hot coordinating/noncoordinating solvents.

Chapter 2: Literature Review

2.1.1 Vapor-liquid-solid (VLS) method

VLS method was first discovered in 1964 by Wagner and Ellis in Bell Labs. [41] They used small Au particles as catalysts to grow crystalline Si whiskers from vapor sources such as SiCl_4 or SiH_4 . [17] The process for Si whisker growth is shown schematically in Fig. 2.1a. In the process, the Au particles are heated above the eutectic temperature (363 °C at Au:Si ratio of 4:1) of Au and Si in the presence of a vapor-phase source of the Si. This vapor is produced from the reaction between SiCl_4 and H_2 at a temperature above 800 °C. Without the assistance of catalysts, this vapor results in a liquid droplet of the Au and Si alloy. The Au-Si phase diagram is shown in Fig 2.1b. The continuous refurbishing of Si in the vapor phase into the liquid alloy results in an over-saturation of the liquid AuSi, leading to nucleation and growth of the Si whiskers.

Fig. 2.1. (a) Scheme of VLS growth of Si whisker. (b) Binary phase diagram of Au-Si. (c) Scanning electron microscopy (SEM) image of Si nanowires prepared by following ablation of a Au target in the presence of silane at 450 °C.

Seed particles for VLS are obtained by heating a thin film of Au and making use of the surface tension to form small molten droplets on the substrate. [17] Due to thermodynamic limitations, the diameter of the resulting Au particles ranges from hundreds of nanometers to microns. [42] The whiskers grow only in the areas activated by the Au catalysts, and their diameters are mainly affected by the size of the catalysts.

Chapter 2: Literature Review

Due to this reason, Wagner, Ellis and others could not obtain Si whiskers with sizes within the confinement regime of many important systems. [43] The solution to this problem eluded material scientist for nearly 30 years. [7] In the late 1990s, breakthroughs were made in Japan [44] and later in US. Lieber *et al.* [45] showed that laser ablated catalyst particles could be used to grow high quality 1D quantum wires with narrow diameters as shown in Fig. 2.1c. [42] This is because laser ablated catalyst method could overcome thermodynamic limitations on the size of nanocrystalline catalysts. Later, chemically synthesized spherical nanocrystal catalysts were used to activate 1D nanocrystal growth in VLS-based growth. [46] Thus, the VLS growth made great progress in producing 1D nanocrystals with uniform crystalline structures for different materials systems such as semiconductors, oxide, nitride, etc. [7] However, it seems to be impossible to apply VLS to grow 1D metal nanocrystals. [2, 17] Another disadvantage of this method is the necessity to use a metal catalyst that may contaminate the nanocrystals and thus potentially result in a change in their properties. [17] Furthermore, this method has other drawbacks, such as high temperature, high vacuum requirement, and large size distribution in the final products. [2, 20]

2.1.2 Solution-liquid-solid (SLS) method

In 1995, Buhro *et al.* developed a SLS growth method for the synthesis of highly crystalline 1D nanocrystals at relatively low temperatures ($<350\text{ }^{\circ}\text{C}$). [47] The schematic of this method is shown in Fig. 2.2a. In a typical procedure, metal catalysts (such as Bi, Ga and Au), that are extremely small in size and readily activated at low temperatures, are used. [2, 7] The reactants are generated by decomposing organometallic precursors. These reactants diffuse onto the metal catalysts to form supersaturated alloy droplets. As the diffusion of precursors onto the catalyst seeds increases, the supersaturated pure solid nanocrystal was achieved.

Chapter 2: Literature Review

This method can generate single-crystalline 1D nanocrystals with lateral dimensions of 10-100 nm and lengths up to several micrometers. [2] In some case, ultra-thin nanowires with diameters of 2-3 nm have been reported. [48] Nanowires with such small diameters cannot be readily synthesized using the traditional VLS method. [17] 1D semiconductor nanocrystals (single component, binary and ternary) obtained by this method include Si, Ge, III-V group, II-VI group and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ materials. [7] Fig. 2.2b-c shows TEM images of PbSe nanowires and Au/Bi nanocrystals attached to the end of PbSe nanowires, respectively. [49] Several parameters can affect the morphology of 1D nanocrystals such as the catalyst nanocrystals size, the amount of catalyst, the precursor concentration, the type of metal coordinating ligand and the growth temperature. [7] Currently, for the synthesis of II-VI nanowires, such as CdSe nanowires, the reaction reagents used is same as that of the hot coordinating solvents method (We will discuss in the later sections). The only difference is that this method employed catalysts to activate the growth. Similar to VLS, the necessity to use a metal catalyst may contaminate the 1D nanocrystals and thus potentially result in changes to their properties. [17] Furthermore, the size distribution of these nanocrystals is larger than that synthesized using the hot coordinating solvents method.

Fig. 2.2. (a) Schematic illustration showing the growth of a 1D nanocrystal through SLS growth. TEM images of (b) PbSe nanowires and (c) Au/Bi nanocrystals attached to the end of PbSe nanowires synthesized by SLS method.

Chapter 2: Literature Review

2.1.3 Microemulsion method

The term - “microemulsion” was introduced by Schulman *et al.* in 1958. [50] It means that a thermodynamically stable dispersion of two immiscible liquids, one polar such as water or glycols and the other non-polar hydrocarbon such as *n*-heptane. [51] The dispersion is stabilized by surfactants. The microemulsion consists of two phases: dispersed phase and continuous phase. In general, the phase behavior of the ternary system is affected by variables such as the concentration of the surfactant, temperature, and the molar ratio between water and surfactant. A phase diagram for water/oil/surfactant system at constant pressure and temperature is shown in Fig. 2.3a. When the concentration of the surfactant is high enough, the system forms a single phase regardless of water-to-oil ratio. On the water rich side of the phase diagram, oil in water microemulsions or direct micelles are formed. In this case, oil swollen micelles are dispersed in water. On the oil rich side of the phase diagram, water in oil microemulsions or reverse micelles are formed. In contrast, oil-in-water microemulsions refer to swollen micelles dispersed in oil. These micelles are also known as reverse micelles. We will mainly discuss about this type of microemulsion. In the intermediate region of the phase diagram, bicontinuous microemulsions are possibly formed (see Fig. 2.3a). [80] Reverse micelle system provides a suitable reaction media for the synthesis of nanocrystals. It is because that these water droplets are dispersed in a continuous oil phase and stabilized by surfactant molecules at the water-oil interface. These surfactant-covered water droplets provide a unique environment for the formation of nanocrystals. They will not only act as microreactors for reactions but also prevent the aggregation of crystals because the surfactants could be adsorbed or attached on the crystal surface when nanocrystals fill the whole water droplet. [52] When the concentration of surfactants reaches a critical value, surfactant molecules automatically organize into cylindrical

Chapter 2: Literature Review

micelles as shown in Fig. 2.3b. These anisotropic structures can be used as soft templates to control the formation of 1D nanocrystals in a chemical reaction. [21, 23]

Fig. 2.3. (a) A phase diagram for water/oil/surfactant system. (b) Schematic illustration showing the formation of a cylindrical reverse micelle in an organic solvent. TEM images of (c) CdS nanorods prepared in AOT + lecithin reverse micelles system and (d) hydroxyapatite (HAP) nanorods using mixtures of triblock copolymer, pluronic P123 and tween-60.

Based on this principle, several groups have reported the synthesis of metallic, [53 - 55] semiconductor [56, 57] and magnetic [58] 1D nanocrystals. For example, Simmons *et al.* demonstrated the synthesis of CdS nanorods in reverse micelles using a combination of two surfactants: sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and phosphatidylcholine (lecithin) as shown in Fig. 2.3c. [57] Wu *et al.* synthesized ZnS nanowires by reacting Zn^{2+} with S^{2-} in a reverse micelle system. [59]

Chapter 2: Literature Review

Alternatively, block copolymer can also be used to synthesize 1D nanocrystals. [2] Block copolymer consists of two or more chemically distinct segments or blocks joined end-to-end by a covalent bond. [60] Due to the incompatibility between the chemically distinct blocks, block copolymer undergoes a similar phase separation as that of oil and water. [2] Under appropriate conditions, such as with the proper ratio of each segment, the block copolymer can form well-defined cylindrical micelles. [2] Different regions in such a well-defined structure can be selectively modified with precursors through physical adsorption or chemical coordinating and thus making block copolymer a possible system for the synthesis of 1D nanocrystals. For example, Karanikolos *et al.* reported the synthesis of ZnSe nanorods and nanotubes in a aqueous phase of a poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer/water/p-xylene ternary system. [61] Recently, Feng *et al.* synthesized hydroxyapatite (HAP) nanorods using mixtures of triblock copolymer (Pluronic P123) and tween-60 as the templating agents. [62] The nanorods are shown in Fig. 2.3d.

As there is an abundant selection of surfactants and block copolymers, the range of nanocrystals that can be synthesized using this method is potentially very broad. [2, 7, 63] On top of that, this method has the advantage of being a simple process, requiring comparatively low reaction temperature and low cost. [64] Of course, there are some drawbacks relating to this method. The size distribution of the nanocrystals is not that good due to less control during the nucleation and growth stages. Besides, this method has low yield and results in nanocrystals with low crystallinity. [2]

2.1.4 Hydrothermal method

Hydrothermal or solvothermal method has been proven to be a powerful tool for the synthesis of 1D nanocrystals. [6, 20] In a typical hydrothermal reaction, precursors with

Chapter 2: Literature Review

fixed molar compositions of a compound are mixed in an organic or aqueous solvent with the addition of reducing reagents, surfactant or other capping agents. [6] The mixture is then heated at moderate temperature in an autoclave. One advantage of hydrothermal or solvothermal method is that most materials can be made soluble in appropriate solvent by heating and pressurizing the system close to its critical point. [2, 20] This allows many inorganic nanocrystals to be synthesized at temperature substantially below those required by traditional solid-state and vapor-phase reactions. On top of that, the morphologies can usually be controlled by varying the reaction parameters, including change in the type of solvent, surfactant, capping agent and the reaction temperature. [65] This method has been used to prepare various 1D nanocrystals such as metal, magnetic and semiconductor materials. For example, Heath *et al.* first reported using this method to prepare single crystal Ge nanowires by reducing GeCl_4 or phenyl- GeCl_3 with sodium in an alkane solvent. [66] This method was later exploited extensively by several groups to produce 1D nanocrystals such as rods, [67] wires [68] and tubes. [69] Zhang *et al.* produced magnetic CoPt alloy nanowires by direct decomposition of platinum acetylacetonate and cobalt carbonyl compound in ethylenediamine solvent (refer to Fig. 2.4). [70] They reported that the CoPt alloy nanowires obtained by this method have a tunable diameter of 10 - 50 nm and a length along the longitudinal axis of up to several microns, depending on the crystallization temperature and the reaction time. Despite the fact that this method seems to be versatile in producing 1D nanocrystals in terms of the diversity of materials synthesized, there are several disadvantages related to this method. [2] The disadvantages include poor control in the morphology during the reaction and the difficulty in observing the growth of the crystal. Therefore, a fundamental understanding of the reaction and growth mechanism during hydrothermal growth is ambiguous at this moment. [7]

Fig. 2.4. SEM image of CoPt nanowires prepared via the hydrothermal method.

2.1.5 Hot coordinating/noncoordinating solvents method

This method was pioneered by Murray *et al.* in 1993 [26] and later developed by Alivisatos and co-workers around 2000s [5, 28, 71] and other groups. [29, 72 - 78] Using this method, it is possible to separate the nucleation stage from the growth stage during the synthesis and obtain 0D or low aspect ratio 1D nanocrystals with a narrow size distribution, at least for II-VI semiconductors. This method opens a new generation of nearly monodisperse nanocrystals. The protocol has been modified by several groups in the past fifteen years. [5, 28, 71 - 78] However, the general synthetic scheme remains the same: a solution containing precursors is injected into a flask of coordinating solvents which may contain precursors and heated above 300°C using a heating mantle. The reaction is carried out under an inert gas (nitrogen (N₂) or argon (Ar)). [79] The set-up used for the synthesis is shown in Fig. 2.5.

In practice, the metal source used in this synthesis can be an organometallic precursor (such as dimethylcadmium (CdMe₂) or metal oxide (such as cadmium oxide (CdO)). [7] Chalcogen precursors introduced can be phosphine-based species such as trioctylphosphine sulfide (TOPS), selenide (TOPSe) and telluride (TOPTe) which are prepared by dissolving elemental powders into trioctylphosphine (TOP). [7] The solvents

Chapter 2: Literature Review

and/ or surfactants can be long alkyl chains of phosphines (or acids), phosphine oxides, amides or amines, nitrogen-containing aromatics and carboxylic acids.

Fig. 2.5. The set-up for the synthesis using hot coordinating noncoordinating solvents method. [80]

Usually, trioctylphosphine oxide (TOPO) can be used as the coordinating agent, while octadecene (ODE) is used as the noncoordinating agent. [7, 80] The choice of the coordinating solvents/surfactant (or the mixture of surfactants) has very different effect on the particular reaction. [79] If solvents or surfactants coordinate too strongly, they will prevent nanocrystals from growing and are therefore not suitable. Conversely, a weak coordinating surfactant would result in large crystals and aggregation effects. In addition, bulky surfactants, such as triphenylphosphine (TPP), may limit growth and result in small crystals, whereas less bulky surfactants, such as hexylphosphine, result in bigger crystals. [79] On top of this, the precursor concentration, injection process, cadmium-to-surfactant mole ratio, cadmium-to-chalcogenide mole ratio as well as the reaction temperature can also affect the growth of nanocrystals. [5, 17 - 19] Currently, existing mechanisms for the formation of 1D nanocrystals are the effective monomer, [19, 81] the selective adsorption, [29, 73, 82, 83] size distribution focusing [84] and

Chapter 2: Literature Review

oriented-attachment models. [80, 85] However, in some special cases, the growth cannot be explained by any of these models. [6] Thus, the exact mechanism of formation 1D nanocrystals is still unknown. [6]

Fig. 2.6. TEM images of cadmium chalcogenide nanocrystals with different shapes prepared by hot coordinating solvents method: (a) CdSe dots, (b) CdSe rice grains, (c) CdSe rods, (d) CdTe tetrapods and (e) CdS nanowires.

The main advantages of this method are highly controllable morphology, controllable aspect ratio and good size distribution. Some examples are shown in Fig. 2.6. [8, 19, 82, 83] This method can also be extended to synthesize III-V semiconductors, such as InP, [86] InAs, [87] and metal oxides. [88 - 90] This method is also suitable for the synthesis of metal nanocrystals, especially ferromagnetic nanocrystals (they are promising candidate for the next generation magnetic storage media). [58, 91] The drawbacks of this method are the requirement for good high temperature control, high cost compared to microemulsion or hydrothermal/solvothermal methods and the difficulty to get high aspect ratio nanocrystals. [31, 79, 83, 92]

2.2 Third Generation Photovoltaic (PV) Devices

A PV device or solar cell is a device that converts solar energy into electricity. The development of PV devices can be classified into three generations (refer to Table 2.1). [32, 93 - 95] First generation solar cells consists of large-area, high efficiency and single junction devices (such as using single crystal silicon wafers). The production of such solar cells involved high energy and labor inputs, thus resulting in difficulty to reduce the production costs. The second generation solar cells, which has been under intense development from the 1990s to the early 2000s, required lower cost for production and has lower but reasonable efficiency compared to the first generation solar cells. Alternative techniques, such as CVD and electroplating, were used to prepare the thin films and these techniques reduced the process temperature and cost significantly. [93, 95] The most popular materials used are amorphous silicon (A-silicon), polycrystalline silicon, CdTe and copper indium gallium selenide (CIGS). The disadvantages of this generation of solar cells are the lower efficiency compared with silicon solar cells. The reasons include the lack of interpenetrating network, the poor charge separation and transport. [34, 36]

Third generation solar cells aims to enhance the poor electrical performance of the second generation solar cells while reducing the production costs further. There are a few approaches, including multi-junction PV cells, tandem cells, nanostructured cells and hot carrier cells. [96] Furthermore, organic solar cells, dye-sensitized solar cells, organic/inorganic hybrid solar cells and all-inorganic nanocrystals solar cells have also become popular in the third generation solar cells due to their low cost and short energy payback time. The big difference between these solar cells and the previous generation solar cells is that they do not rely on a traditional p-n junction to separate photogenerated

Chapter 2: Literature Review

charge carriers. [8, 32, 36] In the following sections, the development, the current technologies and the potential of these third generation cells will be presented.

Table 2.1. A comparison of the different generation solar cells.

Generation	Type/Mater.	Advantages	Disadvantages
First Generation	Silicon	Broad spectral absorption range A quite high efficiency High carrier mobilities Large area	Requirement of the expensive manufacturing technologies Requirement of a highly energy intensive process The price is high compared to the power output Very pure silicon is needed
Second Generation	A-silicon, Poly-silicon, CdTe, CIGS	Lower manufacturing costs; Allows fitting panels on light or flexible materials, even textiles Reduced mass Reduced process temperature Very good light absorption(CIGS)	Lower efficiency than silicon cells Amorphous silicon is not stable Increased toxicity Poor charge separation/transport
Third Generation	Organic solar cells	Solution processable, lots of candidates, flexible, low temperature.	Degradation effects due to environmental effects, high band gap, low mobility
	Grätzel cells	Flexibility, easy to process, high efficiency and low cost	Suffer from degradation of the electrodes from the electrolyte
	Hybrid solar cells	Printable nanocrystals on a polymer film and improved conversion efficiency potentially) and combining advantages of both organic and inorganic materials	Potential degradation problems similar to polymer cells and interfacial problem
	All-inorganic nanocrystal solar cells	Share all of the primary advantages of organics, also retain the broadband absorption and superior transport properties of traditional semiconductors.	Efficiency is lower compared with silicon (wafer-based) solar cells

2.2.1 Organic solar cells

In the late 1970s, Heeger, MacDiarmid and Shirakawa pioneered the work on organic electronics and organic PV. [97] Three polymers were used in their work: polyacetylene, perylene and phthocyanine. [98] Specifically, organic solar cells are solar cells that made

Chapter 2: Literature Review

use of organic molecules or conjugated polymers as the active layer of the device. In the past decades, organic solar cells research has attracted both scientific and economic interest due to a rapid increase in the PCE. This is achieved through the introduction of new materials, the improvement in materials engineering and the new device structure. [33]

It is well known that some organic materials, such as dyes or organic molecules and conjugated polymers, can show p- or n-type semiconducting properties. [99] These materials have an extremely high optical absorption efficiency, which offers the possibility for the production of very thin film solar cells (well below 1 μm). This permits a device to be made with very small amount of materials. Besides this advantage, there are unlimited number of possibilities for the type of materials to be used - ranging from small molecules ($<10^4$ molecular weight) to polymers ($>10^6$ molecular weight). [100] The other advantages are the ease in scaling up, the low-temperature processes involved and consequently the low production cost and the short energy pay-back time. [33, 36, 101]

The concept of organic solar cells has also been through several “generations” - from single layer, to bilayer and then to the current bulk heterojunction concept. [33] The bulk heterojunction structure was introduced to resolve the issue relating to the short exciton diffusion which is considered to be a serious bottleneck in organic solar cells. Due to the short exciton diffusion length, the photogenerated excitons do not have enough time to reach a donor-acceptor interface to dissociate into free charge carriers and hence resulting in charge recombination. This is a significant factor limiting the cell efficiency. To get around this problem, Heeger and co-workers made use of the concept of interpenetrating networks with fullerene derivatives (i.e. C_{60}). [102] Another way to

Chapter 2: Literature Review

solve this issue of the short diffusion length is to use stratified layers that is made up of donor–acceptor blends. [103] A schematic for this kind cell architecture and the band diagram of P3HT-phenyl C₆₁-butyric acid methyl ester (PCBM) organic solar cells are shown in Fig. 2.7.

Fig. 2.7. (a) Device representation and (b) band diagram of P3HT-PCBM organic solar cells.

Before 1999, only modest solar conversion efficiency of up to 1% was achieved. Since then the efficiency has increased rapidly. Lucent Technologies reported that with the use of molecularly flat-layered systems based on molecular organic single crystals made of iodine or bromine doped pentacene, gives rise to efficiency of up to 3.3% under AM 1.5 illumination. [104] A PCE of 5.15% for a 1.02 cm² cell fabricated by Konarka was tested at the National Renewable Energy Laboratory (NREL). [105] The device structure used was glass/ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/polymer:PCBM/aluminum (Al). For these cells to become commercially viable, the efficiency will have to increase further. On top of that, these organic materials are generally sensitive to ultraviolet radiation, have low mobility and have to be operated at a lower temperature. [36]

2.2.2 Dye-sensitized solar cells

Dye-sensitized solar cells, also known as photoelectrochemical cells or Grätzel cells, are alternative to the p–n junction PV devices. [106] It was invented by O'Regan and Grätzel

Chapter 2: Literature Review

in the early 1990s. [107] The major advantage of the concept of dye sensitization is that the conduction mechanism is based on a majority carrier transport. [99] This is as opposed to the minority carrier transport in conventional inorganic cells. In such solar cells, the functional element responsible for light absorption (the dye) is separated from the charge carrier transport material. This means that the bulk or surface recombination of the charge carriers in the TiO_2 cannot happen. The scheme of a dye sensitized cell and its band diagram are shown in Fig. 2.8.

Fig. 2.8. (a) Device representation and (b) band diagram of dye-sensitized solar cells.

The dye molecules are adsorbed onto the surface of TiO_2 crystals. Upon photoexcitation of the dye molecules, electrons are injected very efficiently from the excited state of the dye into the conduction band of the TiO_2 . The dye is subsequently reduced by a redox electrolyte which is a mixture of an organic solvent and an redox couple iodide/triiodide. The redox electrolyte is also a media of the charge transport between the counter electrode and the dye molecules. Thus, it is a fast regenerative photoelectrochemical process. [99] In addition to TiO_2 , other wide band gap oxides such as ZnO , SnO_2 and Nb_2O_5 have also been investigated for this type of solar cells. [108, 109] They are all relatively easy to process. Currently, this type of cell is being developed into large area and low cost solar cells. [110] This type of solar cell has surprisingly high efficiency. A PCE of 11.1% for a 0.2 cm^2 dye-sensitized cell was fabricated by Sharp and tested at NREL. [111]

Chapter 2: Literature Review

There are still some disadvantages relating to these solar cells. The most important issue is that both the stability over the time and the temperature range are reduced when the cells are used under outdoor conditions. [99] Although it could be shown that intrinsic degradation can be considerably reduced, the behavior of the liquid electrolyte under extreme conditions is still unknown. [112] Recently, a significant effort has been taken to replace the liquid electrolyte by a solid-state glass electrolyte. However, this solution limits the shape of the cells to a flat design and may impact the practical applications. [99] For successful commercialization of these cells, the encapsulation/sealing, the coloration and the electrolyte filling have to be transferred into fully automated lines. [113]

2.2.3 Organic/inorganic hybrid solar cells

Many conjugated polymers have extremely low electron mobilities, typically below $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ due to the presence of electron traps such as oxygen. [114] An alternative to a purely organic cell may be the use of hybrid materials consisting of inorganic nanocrystals embedded in organic matrices. The advantages of this type of solar cells have been presented in Chapter 1. [8, 15, 37, 38] Fig. 2.9a shows a scheme of a CdSe nanorods/P3HT hybrid solar cell. In this case, CdSe nanorods are used as the electron transport material and P3HT (in its regioregular form) is an effective hole transport material. P3HT has demonstrated to have the highest field effect hole mobilities observed in polymers so far. [8, 15, 115] The best cells showed 1.7% PCE and an external quantum efficiency (EQE) of 55% under simulated solar light (AM 1.5) (refer to Fig. 2.9b and c). [8] They found that as the aspect ratio of the nanorods increases from 1 to 10, an EQE enhancement by a factor of approximately 3 times should come from the substantial improvement of charge transport. They also found that longer nanorods were oriented partly in the direction of the direction of electron transport and can penetrate through a large portion of the devices whereas shorter nanorods or dots are less effective.

Chapter 2: Literature Review

This suggested that increasing aspect ratio could potentially enhance the charge transfer and further improve the performance of these devices. [8, 15]

Fig. 2.9. (a) The device structure of CdSe nanorods – P3HT hybrid solar cells. (b) The external quantum efficiencies (EQEs) of 7 nm diameter CdSe nanorods with lengths 7, 30 and 60 nm. (c) Solar cell characteristics of this 7 X 60 nm CdSe nanorods device illuminated with simulated air mass (AM) 1.5 Global light.

The branched CdSe structures (tetrapods) have potential advantages in such systems because it is possible for them to be oriented perpendicular to the substrate within the film. It is because unlike rods, these tetrapods are unable to lie flat within the plane of the film. [116] Sun *et al.* have reported higher efficiencies (PCE = 2.8% and EQE = 52%) obtained from CdSe tetrapods blended with poly(phenylene vinylene) (PPV) derivatives. [116] Besides CdSe nanocrystals, the other inorganic materials that are used for this type

Chapter 2: Literature Review

of solar cells are copper indium diselenide (CuInSe_2), CdS, CdTe, ZnO, indium selenide (InSe) and carbon nanotube (CNT); while other organic materials used besides P3HT includes PPV derivatives and PCBM. [10, 117]

Organic/inorganic hybrid solar cells have some drawbacks. Although organic materials offer strong potential for cost reduction compared with conventional solar cells, they have limited spectral absorption and low carrier mobilities, which will result in reduced device efficiency. [118] Using inorganic nanocrystals for electron transport can enhance the performance of semiconductor polymer or organic solar cells, the ultimate limitations of these hybrid systems may still be dictated by the low mobility and environmental sensitivity of their organic phase. Moreover, the interfacial problem between organic and inorganic may also affect the lifetime of the cells. [16]

2.2.4 All-inorganic nanocrystals solar cells

A solar cell that is fabricated using only nanocrystals has been thought to be doable theoretically. [119, 120] Inorganic nanocrystals not only share all of the primary advantages of organics—scalable and controlled synthesis, an ability to be processed in solution and a decreased sensitivity to substitutional doping, but also retain the broadband absorption and superior transport properties of traditional PV semiconductors. [121, 122] Alivisatos and co-workers reported a bilayer solar cell based on CdSe and CdTe nanorods (refer to Fig. 2.10). [16] They designed their inorganic solar cells around the same electron-donor-and-acceptor concept used in organic solar cells. A thin layer of electron-rich CdTe nanocrystals is first deposited on top of a conductive glass and followed by a thin layer of electron-poor CdSe nanocrystals. The best performing solar cells showed a PCE of 2.9% under AM 1.5 light condition.

Chapter 2: Literature Review

Very recently, they reported a Cu_2S dots and CdS nanorods solar cells with 1.6% PCE on both conventional glass substrate and flexible plastic substrates. [123] However, the research into this type of solar cells is still in its infancy. Work should be focused on understanding the nature of the donor-acceptor heterojunction that is responsible for the current generation in the cells and increasing the efficiency if these quantum systems could be electronically coupled for practical use. [32, 117]

Fig. 2.10. TEM images of (a) CdSe and (b) CdTe nanorods. Scale bar, 40 nm. (c) An energy diagram of two materials. (d) SEM image of a typical spin-cast film. The film edge of this about 100 nm is shown for contrast with the silicon substrate. Scale bar, 1 μm .

Chapter 3: Synthesis and Characterization of CdSe Nanorods Using a Novel Microemulsion Method at Moderate Temperature

3.1 Introduction

The synthesis of 1D semiconductor nanocrystals in a controllable fashion has attracted considerable attention in recent years. CdSe, which is a narrow band gap material with energy bandgap of 1.75 eV at 300 K, [11] is one of the most important group II-VI semiconductors. This material has been widely used for photoelectronic devices. [124] In the past decade, a great deal of research has been done on controlling the size, shapes and crystal structures of CdSe nanocrystals because their electrical and optical properties are strongly related to their morphologies. Many methods have been used for the preparation of nanorods. Alivisatos and co-workers have developed a high temperature (around 300 °C), non-aqueous based method using organometallic precursors to control the shapes of CdSe nanocrystals. [5] This method can generate nearly monodisperse CdSe nanorods due to the separation of nucleation and growth stages. Several other shapes of CdSe nanocrystals, such as rod-, tetradrod- and tetrapod-, have also been prepared by carefully controlling the nucleation and the growth rate in a mixed surfactants system. [71, 28] There are some disadvantages relating to this organometallic synthesis method. [125] The temperature for the synthesis is high and the nanocrystals produced has poor reproducibility. On top of this, extremely dangerous reactants (e.g., CdMe₂) are used. Another drawback of this method is the high cost compared to microemulsion method. [93] Recently, some changes were made to this process such as the replacement of CdMe₂ with CdO. However, the complicated procedures involved in this method and the requirement for accurate temperature control at such high temperature is still a concern.

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

Peng *et al.* first employed sodium selenite (Na_2SeO_3) as Se source in their synthesis where Na_2SeO_3 is reduced to highly reactive Se by hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). They found that at 140 °C, CdSe with a mixed morphology of both branch-shaped fractals and nanorods was produced mainly, and at 180 °C, the products are mainly CdSe nanorods. [126] Chen *et al.* used a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) via hydrothermal method at 180 °C to synthesis CdSe nanorods. They used the same precursor and reducing agent as Peng *et al.* [67] However, to the best of our knowledge, there has been less work carried out on the study of the synthesis of CdSe nanorods at moderate temperature. [127] In the hydrothermal work, they also synthesized nanocrystals in the micelles and dispersed them with the aid of ultrasound at low temperature. Both nanorods and spherical particles coexist in the products.

Fig. 3.1. Chemical structure of AOT.

In this study, an anionic surfactant, AOT (refer to Fig. 3.1), and a reducing agent, hydrazine hydrate, are used in a water-in-oil microemulsion synthesis route for CdSe nanorods at the moderate temperature of 100 °C. AOT is an anionic surfactant with double alkyl chain and because of its long tail group, it can be used to form a reversed micelle system. The morphology of the nanocrystals synthesized by this route are typically spherical. However, Pileni *et al.* have synthesized copper nanorods with a combination of AOT and hydrazine hydrate by carefully controlling the water content at

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

a constant hydrazine hydrate concentration. [128] According to the phase diagram, [129] the current system employed is on the *n*-heptane-rich side. Therefore reverse micelles are formed in the synthesis. In our case, water droplets with two precursors, Na₂SeO₃ and Cd(NO₃)₂, are dispersed in the *n*-heptane separately and stabilized by a shell formed by AOT. The stability of these micelles is greatly enhanced due to the high concentration of AOT and the existence of hydrazine hydrate. The concentration of AOT in this system is far above the CMC, which is 0.0025 mmol/ml. [130] The concentration of AOT will determines the type of micelles formed and the concentration of hydrazine will affect the reducing behavior and templating structure. It was found by several groups that hydrazine hydrate is not only a reduction agent, but also acts as a component of the templating agent in the formation of CdTe and a nickel nanorod structure. [131, 132] Besides, it also can prevent oxidation of CdSe nanocrystals after preparation due to its reducing capability. [133] However, the detail of the mechanism is still unclear at this time. In this study, we attempt to study the mechanism of growth for these crystals at low temperature. In order to monitor the change in the reaction in this chapter, two molar ratios were considered:

$$R = [\text{H}_2\text{O}]/[\text{AOT}]$$

$$S = [\text{hydrazine hydrate}]/[\text{AOT}]$$

By varying the molar ratio of *R*, *S* and the precursor concentration, the size and morphology of CdSe nanocrystals can be controlled at moderate temperature. Based on the experimental results, the mechanism for the formation of CdSe nanocrystals have been proposed in the final part of this chapter.

3.2 Experimental Section

3.2.1 Materials

Cadmium nitrate-tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%) was purchased from Merck. Both Na_2SeO_3 (99%) and AOT (96%) were purchased from Sigma-Aldrich. Hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98%) and *n*-heptane ($\text{CH}_3(\text{CH}_2)_5\text{CH}_3$, 98%) was purchased from Kanto Chemical Co. Inc. and Lab-scan, respectively. All chemicals employed in this study were used without further purification and/or treatment unless mentioned. Dionized water was used in all experiments.

3.2.2 Synthesis of CdSe nanocrystals

In this synthesis, a series of *R* and *S* value were studied. The *R* value ranges from 5.0 to 8.5, while the *S* value ranges from 4.0 to 9.0. In a typical synthesis, where *R* = 5.0, while *S* = 5.2, and the molar ratio of $[\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}] / [\text{Na}_2\text{SeO}_3]$ is equal to 1:1, the amount of reactants and the procedure for the synthesis are as follows: 10 mmol of AOT was dissolved in 50 ml of *n*-heptane in a three-necked flask which is attached with condenser and a septum plus valves. The mixture was deaerated by bubbling N_2 initially, at room temperature. 0.45 ml of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ aqueous solution (2.78 mmol/ml) was injected into the solution while the system was being stirred and heated. When the temperature of the solution reached around 100 °C, a mixture of 2.55 ml of hydrazine hydrate (52.4 mmol), and 0.45 ml Na_2SeO_3 aqueous solution (2.78 mmol/ml) was added into the solution using a syringe. The mixture was added over a duration of 30 to 45 sec. The whole reaction took place under N_2 environment and the solution was refluxed while being stirred constantly for about 6 h. The color of the final solution changed rapidly from yellow to orange, to red and then to deep dark red which indicate the synthesis of the CdSe nanocrystals has been successful. After the reaction was completed, the deep

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

dark red precipitate was washed repeatedly with dionized water and ethanol to remove any ions that may still be present in the sample. Finally, the product was dried overnight in a vacuum oven at 60 °C to remove the remaining water from the sample.

3.2.3 Characterization

1. Transmission electron microscopy (TEM)

TEM is a method of producing 'image' from a specimen by illuminating the specimen with electrons in a high vacuum and detecting the electrons that are transmitted through the specimen. In practice, TEM images are generated in two stages. In the first stage, specimen is scattered by an incident electron beam. This scattered radiation goes through an objective lens which focused it to form a primary image. In the second stage, the primary image is subsequently magnified by additional lenses to form a highly magnified final image. In the first stage, the objective lens generates a diffraction pattern at its back focal plane. The diffraction pattern is the Fourier transform of the scattered electron wave. That means that the primary image is the Fourier transform of the diffraction pattern. This two steps process forms the basis of image formation during HRTEM. In this study, TEM and SAED studies were carried out using a JEOL 2010 microscope fitted with a LaB₆ filament using an acceleration voltage of 200 kV. TEM samples were prepared by placing one or two drops of the nanocrystals in the ethanol solution onto carbon-coated copper grids.

2. X-ray Diffraction (XRD)

X-ray scattering technique is a family of non-destructive analytical techniques. Tests are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization and wavelength or energy. XRD can be used to characterize the crystallographic structure, crystallite size (grain size) and

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

preferred orientation in polycrystalline or powdered solid samples. In this study, powder XRD patterns were recorded using a Shimadzu LabX-XRD-6000 X-ray diffraction instrument at a scanning rate of $4^{\circ} \text{ min}^{-1}$ with 2θ ranging from 10 to 80° , using $\text{CuK}\alpha$ radiation ($\lambda=0.1542 \text{ nm}$) radiation at 40 kV and 60 mA . Thin film XRD studies were carried out in a Rigaku DMAX 2200 using $\text{Cu K}\alpha$ radiation at a scanning rate of $1^{\circ} \text{ min}^{-1}$ with 2θ ranging from 10 to 80° 40 kV and 40 mA .

3. Energy dispersive analysis of X-ray (EDAX)

Energy dispersive X-ray spectroscopy (EDAX or EDS) is an analytical technique. It is used for the elemental analysis or chemical characterization of a sample. This technique relies on the interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being strike with charged particles. The composition of the as-prepared CdSe nanocrystals was also determined by EDAX, which was attached on a JEOL 6360 scanning electron microscopy (SEM).

4. UV-Vis and PL characterizations

The UV-Vis absorption and PL spectra of the nanocrystals were obtained using a Shimadzu UV2501PC spectrophotometer and a Shimadzu RF-5301 PC fluorometer, respectively. The excitation wavelength for PL was 475 nm . All the optical measurements were performed at room temperature under ambient conditions.

5. Fourier transform infrared (FT-IR)

Fourier transform infrared (FT-IR) works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. In practice, a molecule exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to this molecule. During FTIR analysis, a spot on the sample is exposed to a modulated IR beam. The sample's transmittance and reflectance of the infrared rays at different frequencies are translated

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectrum is then analyzed and matched with known signatures of identified materials in the FTIR database. FT-IR can provide information about the chemical bonding or molecular structure of materials regardless of organic or inorganic materials. FT-IR spectra were recorded in the range $400\text{--}4000\text{ cm}^{-1}$ using a Perkin-Elmer (Spectrum GX) spectrometer.

The facilities used in the rest of this study were the same as those in this chapter unless mentioned.

3.3 Results and Discussion

3.3.1 Phase analysis

A typical XRD pattern of the as-prepared CdSe nanocrystals and JCPDS of hexagonal CdSe pattern are shown in Fig. 3.2a and 3.2b. All the reflection peaks of the prepared CdSe nanocrystals can be indexed to hexagonal CdSe with lattice constants of $a=4.264\text{ Å}$ and $c=7.014\text{ Å}$ (JCPDS file No.08-0459, $a=4.299\text{ Å}$ and $c=7.010\text{ Å}$). In addition, the strong and sharp diffraction peak ($2\theta=25.5^\circ$) suggests that the extended crystalline domain along the c -axis of the hexagonal lattice. XRD analysis revealed no impurities such as Se in the sample.

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

Fig. 3.2. Typical XRD pattern of as-prepared CdSe nanocrystals with $R=5.0$, $S=5.2$ (a) and JCPDS hexagonal CdSe pattern (b).

3.3.2 Morphologies studies

The morphologies of the CdSe nanocrystals were characterized using TEM. The morphologies of the CdSe nanocrystals were mainly affected by the water to AOT molar ratio (R), hydrazine hydrate to AOT molar ratio (S) and precursor concentration.

3.3.2.1 Influence of the water to AOT molar ratio (R)

It is well known that the size of water droplets in the microemulsion is mainly dependent on the molar ratio of water to surfactant (R). [132, 134] In this study, at a constant S value of 5.2, changing R value will change both the size of the nanocrystals and the final morphology of nanocrystals formed. TEM images of the CdSe nanocrystals with different R value are shown in Fig. 3.3a-c. When the R value is greater than 6.7, the morphology of nanocrystals is mainly dendritic with a size that is more than 200 nm (refer to Fig. 3.3a). With the decrease of R value to 6.7, both nanorods and dendrites are formed (refer to Fig. 3.3b).

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

Fig. 3. 3. TEM images of as-prepared CdSe nanocrystals with different R values: (a) $R=8.5$, (b) $R=6.7$ and (c) $R=5.0$, respectively.

When the R value is further decreased to 5.0, a mainly rodlike structure was obtained, but the diameter of the nanocrystals remained fairly constant (refer to Fig. 3.3c). Eicke *et al.* found that at low R values ≤ 10 , the water is strongly bound to the AOT surfactant polar head groups and exhibits unique properties different from bulk water. [135] At higher R values, free water is predominant in the swollen reverse micelles. However, in this study, since the R value is less than 10, the formation of dendritic nanocrystals may not be due to the presence of free water inside the micelles. The reason for the presence of a dendritic structure at comparably low R values may be due to the destabilization of

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

the shape of the micelles or phase transition caused by the addition of a large amount of reducing agent to the reverse micelles. This process leads to a drastic change in the self-organization of surfactant molecules. [23] When R decreases to a particular value, these reverse micelles formed are stabilized by sufficient AOT. The change in the size of the nanocrystals is related to the change in the size of micelles due to changes in R . In general, with a decrease in molar ratio of water to AOT, the size of the micelle should decrease. However in this synthesis, the crystal growth is not totally constrained by the micelles as they grow. Referring to Fig. 3.3a – c, the actual size of the nanocrystals is obviously bigger than the mean diameter of the micelles measured by acoustic spectroscopy, neutron scattering and X-ray scattering methods by other groups. [136] In these cases, the system was based on the classic three components system: *n*-heptane, water and AOT. However, in our study, other factors such as the reducing reaction and the presence of an excess of hydrazine hydrate also play important roles in the nanocrystal growth and further affect the size and shape of nanocrystals. [21] Based on the above results and discussion, we can conclude that the appropriate molar ratio R effectively decreased the yield of dendritic particles and favored the formation of nanorods. From this study, the optimum value for R is 5.0 and this value was used for the next study.

3.3.2.2 Influence of the hydrazine hydrate to AOT molar ratio (S)

As mentioned in the introduction, S is the molar ratio of hydrazine hydrate to AOT. This is another key parameter for the control of the morphology of the nanocrystals. In this study, the amount of surfactant was kept constant while the amount of hydrazine hydrate was changed to investigate the effect of hydrazine hydrate on the morphology of the nanocrystals. TEM images of the CdSe nanocrystals with different S value are shown in Fig. 3.4a-c. It is found that with the increase in the amount of hydrazine hydrate, the length of the nanorods increases, while the width of nanorods remains constant.

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

When the S value is less than 5.2, for example when $S=4.0$, the nanostructure formed is a mixture of dendrites and rods (refer to Fig. 3.4a). When the S value is increased to $S=5.2$, nanorods are formed (refer to Fig. 3.3c). With the increase in the amount of hydrazine hydrate to $S=7.8$ (refer to Fig. 3.4b), the diameter of rods remains constant, while the length of the rods increases. At high S value, the total amount of hydrazine not only provides reduced Se^{2-} for the reaction with Cd^{2+} , but it also affects the structure and size of the micelles in the solution. Hydrazine hydrate may increase the micelles size slightly because it contributes to the changes of stabilization and template structure of the aqueous phase in the system due to the addition of a very large amount of hydrazine to the reverse micelle solution. [137] If the S value is increased further, the morphology and the stability of the micelles are totally changed. Hence, there are dendritic nanocrystals with long arms formed at high S value (refer to Fig. 3.4c). This is due to the micelle morphology being disturbed by the high concentration of hydrazine hydrate. If S is increasing further, the stability of the colloids could be destroyed in the presence of an excess of electrolyte (hydrazine hydrate). [138] Therefore, we conclude that the molar ratio of hydrazine hydrate to AOT is an effective factor in controlling the formation of rodlike nanocrystals and preventing the formation of dendritic CdSe nanocrystals. This observation is also similar to Li *et al.* [131] and Ni *et al.* [132] who have synthesized ZnTe and nickel nanorods, respectively using hydrazine hydrate as a reducing agent. For this system, the optimum S value for the formation of nanorods was found to be 5.2, when R is equal to 5.0.

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

Fig. 3.4. TEM images of as-prepared CdSe nanocrystals with different S values: (a) $S=4.0$, (b) $S=7.8$ and (c) $S=11.4$.

3.3.2.3 Influence of the precursor concentration

The precursor concentration is another factor that influenced the formation of CdSe nanorods. With fixed R and S value, changing the two precursor concentrations is found to change the morphology of the nanocrystals substantially. TEM images of the CdSe nanocrystals with different concentration are shown in Fig. 3.5a and b. As seen in the earlier experiment section, at $R=5.0$ and $S=5.2$, when the precursor concentration is 2.78 mmol/ml, the nanocrystals formed are rodlike structure (refer to Fig. 3.3c). The length of nanorods is about 64 nm and diameter is about 20 nm. When the precursor concentration

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

is reduced by half, both rod and dendritic structure are produced (refer to Fig. 3.5a). This phenomenon is not what we expected. In the previous studies, as the precursor concentration was increased, the morphology of the nanocrystals changed from spherical, short rods to long rods, and then to branched rods. [19, 74] The growth of the branched nanocrystals required even higher monomer concentration than that of rods. [74, 139]

Fig. 3.5. TEM images of as-prepared CdSe nanocrystals with different concentration: (a) 1.39 mmol/ml, (b) 5.56 mmol/ml.

The reason of the formation of a dendritic structure at low concentration may be the low speed of nanocrystal nucleation and growth which is affected by the concentration of precursors. [126] When the precursor concentration is doubled (compared to the baseline concentration of 2.78 mmol/ml), the length of the rodlike nanocrystals becomes shorter, and diameter increase slightly as shown in Fig. 3.5b. This is contrary to the general observations that high precursor concentration could promote anisotropic growth and result in high aspect ratio.[19, 74] The possible reason for the formation of lower aspect ratio at higher precursor concentration is due to the higher number of nuclei present at the initial stage of the reaction. These nuclei consumed most of the monomer at the same time and hence led to a lower monomer concentration after nucleation. The remaining low monomer concentration cannot sustain the anisotropic growth regime for a long time,

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

resulting in lower aspect ratio nanocrystals. A further increase in the precursor concentration showed little influence on the shape of the nanocrystals. Therefore, the concentration is not a key factor in controlling nanocrystal growth. Other factors, such as the molar ratio of water to AOT (R), and hydrazine hydrate to AOT (S), play more important role in the formation of the nanocrystals as discussed above.

3.3.3 Crystallography of nanocrystals

HRTEM images and electron diffraction patterns of nanocrystals synthesized in these systems are shown in Fig. 3.6a and b inset. Fig. 3.6a is a typical HRTEM image of a single nanorod and the lattice fringes can be observed. The lattice planes are indicative that the as-prepared nanostructure has a relatively well-crystallized single crystal. This result confirms that the nanorod is a single crystal. The spacing of the planes corresponds to the spacing of the planes in bulk wurtzite CdSe structure. The interplanar distance is about 0.35 nm. The value is close to the (001) lattice spacing of wurtzite CdSe formed. These results indicate the nanorod growth along the [001] direction is preferred, which is in agreement with the results from other groups. [67] The compositional analysis of as-prepared CdSe nanocrystals using EDAX is shown in Fig. 3.7. The average atomic percentages for Cd and Se are 48.1% and 51.9%, respectively. This EDAX spectrum confirmed that the nanocrystals are indeed composed of Cd and Se with no impurities, such as the sodium ions.

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

Fig. 3.6. (a) HRTEM image of single CdSe crystal and (b) bright field image of single nanorod with diffraction pattern (inset).

Fig. 3.7. The EDAX spectrum of the as-prepared CdSe nanocrystals.

3.3.4 Spectra analysis of nanocrystals

The FT-IR spectra of a pure AOT and as-prepared CdSe nanocrystals in the frequency range 600–4000 cm^{-1} are shown in Fig. 3.8. All the observed bands can be attributed to the functional groups of AOT and hydrazine hydrate. The band at 1046 cm^{-1} is due to the absorption of the SO_3^- group in AOT, [140] whereas the bands at 1602 and 3250 cm^{-1} corresponds to the bending vibration of NH_2 and stretching vibration of N–H group of

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

hydrazine hydrate respectively. [142, 143] From the spectra, it is can be seen that both the AOT and the hydrazine hydrate were present in the sample. We can conclude that the AOT and the hydrazine hydrate were adsorbed on the surface of CdSe nanocrystals because these samples were washed completely.

Fig. 3.8. FT-IR spectra of (a) AO and (b) as-prepared CdSe nanocrystals.

3.3.5 Optical Characterization

Fig. 3.9a and b show the UV-Vis absorption and PL spectra of the CdSe nanorods. It can be seen that there is a broad peak in the UV curve, which centers around 595 nm. As the rods grow longer, the long axis (the direction along the length of the rods) grows beyond the confinement regime, and the excitation peak only depends on the short axis (diameter) of the rods. This is the reason for the red-shift of the excitation peak. The PL spectrum in Fig. 3.9b shows two bands. The broad band with maximum intensity at 620 nm came from band-edge emission and the narrow red band near 713 nm which is caused by surface states. [140] The broad peak in the PL spectrum, from 525 nm to 700 nm is due to the size distribution of the nanocrystals, while the red band from 700 - 730 nm is thought to be due to the surface defects. This situation is not expected. To improve the adsorption and PL of the nanocrystals, ligand exchange should be carried out to

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

replace the AOT on the surface with other ligands such as pyridine or to anneal the nanocrystals at high temperature to remove any surfactant before the device fabrication. The improvement to the surface quality is especially important in applications such as PV application where the charge separation occurs at the interface. In ethanol, after half and hour of ultrasonic treatment, the nanocrystals solution was found to be stable for two hours.

Fig. 3.9. (a) UV-Vis absorption and (b) PL excitation spectrum of the as-prepared CdSe nanocrystals.

3.3.6 Growth Mechanism

To study how the growth of the crystals progresses, a growth mechanism is carried out for molar ratios $R=5$ and $S=5.2$. As mentioned earlier, once a mixture of hydrazine hydrate and Na_2SeO_3 aqueous solution was added into the AOT capped Cd^{2+} solution, the color of solution changed rapidly from yellow to orange and to red in the first 7-8 min (refer to Fig. 3.10). Subsequently, the color of the solution changes to dark red and deep dark red as the reaction progresses. The above phenomenon indicates the nucleation and growth of nanocrystals (refer to Scheme 3.1a-c). In this reaction, Se source was derived from the reduction of Na_2SeO_3 by hydrazine hydrate. [67, 126] The modified chemical reaction between two precursors and hydrazine hydrate for this reaction is:

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

Initial phase of the reaction involves the gradual reduction of Na_2SeO_3 to Se and then to Se^{2-} by the hydrazine hydrate present in the micelles at that temperature. [67, 126] Due to the Brownian motion, [23] these micelles with reduced Se^{2-} will collide with micelles containing Cd^{2+} and CdSe nucleates in the newly formed micelles (refer to Scheme 3.1a). They are spherical at this stage. The shape of nanocrystals is less influenced by the templating structure at this moment because they are small.

Fig. 3.10. Different colour observed for samples taken at different time after injecting the second precursor (1[#] to 9[#]: 0.5, 1, 2, 4, 6, 8, 15, 30 and 60 min).

Scheme 3.1. Proposed model for CdSe nanocrystal formation in the reverse micelles: (a) the nucleation and growth of spherical particles, (b) further growth of nanorods (Ostwald ripening), (c) intraparticle ripening (resulting in a decrease in the aspect ratio of the nanocrystals).

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

With prolonged reaction, the diameter of these spherical nanocrystals increased because these micelles tend to collide with each other frequently, resulting in fusion and exchange of the contents within the cores and re-dispersion of the reverse micelles. [23] As mentioned earlier, the micelles are made up of a combination of AOT and hydrazine hydrate. Because all nanocrystals were constrained in the nanoreactors, they grow into larger nanocrystals along a certain orientation under the direction of its crystal structure and are affected by the micelle shape. Similar explanations were given by Pileni *et al.* to account for the formation of nanodisks by the addition of a very large amount of hydrazine to a reverse micellar solution (refer to Scheme 3. 1b). [21, 142] When the precursor in the individual micelle is nearly used up, further growth of the initially produced rod-like nanocrystals is provided by Ostwald ripening where the smaller nanocrystals will start shrinking while larger ones will be growing due to intermicellar exchange processes. [23] In the constrained space of a micelle, the dissolution of small nanocrystals such as the spherical and/or rod-like particle will refurnish larger nanocrystals with new monomers, this leads to the growth of the larger particle. However, Ostwald ripening is partially prevented by the presence of a surfactant. Hence, once the smaller particles were depleted, intraparticle ripening phenomena starts to happen. This meant that the monomer migrated from the long sharp tip at the end of the nanorods to the surface of the nanocrystals within micelles resulting in an increase in the diameter. Similar behavior was observed by Peng *et al.* previously during the synthesis of CdSe nanorods by hot coordinating solvents method. [5] This process leads to an increase in the diameter and a decrease in the aspect ratio of the nanocrystals (refer to Scheme 3. 1c). To proof that this proposed mechanism is true, we will next look at the time dependent studies of the nanocrystals.

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

To study the growth process of these nanorods, we stop the reaction at different times. Fig. 3.11a-e are the TEM images of five samples reacted for: 1 min, 5 min, 30 min, 1 h, and 6 h after injecting a mixture of hydrazine hydrate and Na_2SeO_3 aqueous solution. Fig. 3.11a and b show small spherical nanocrystals produced in the initial reaction process and grew in three dimensions, which correspond to Scheme 3.1a. After 1 min of the reaction, the nanocrystals formed were spherical with a diameter of about 4 nm. When the reaction was extended to 5 min, the spherical particles had grown to a diameter of 9 nm. Looking at the yield in Fig. 3.12, there is very little increase in the weight of the products. At this stage, Ostwald ripening may be happening which resulted in the growth of the initially produced nanocrystals with little increase in the weight. As the reaction progressed (30 min), these nanocrystals grew into a rod-like structure along the direction of its crystal structure and the micelles is formed by the combination of AOT and hydrazine hydrate (refer to Fig. 3.11c and Scheme 3.1b). The diameter and length of nanocrystals are about 11 nm and 45 nm respectively.

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

Fig. 3.11. TEM images of samples after different reaction time: (a) 1 min, (b) 5 min, (c) 30 min, (d) 1 h and (e) 6 h, respectively.

After the reaction has proceeded for 1 hour, the diameter and length of nanocrystals increased to about 15 nm and 75 nm respectively, as shown in Fig. 3.11d and this step corresponded to Scheme 3.1b. The yield has dropped slightly, this may be due to some of the particles redissolving due to the instability generated by the shape of the crystals. After 1 hour, these nanorods are still not at their optimum dimension. After 6 hours, the morphology of the nanocrystals changed significantly due to the intraparticle ripening phenomena. This process leads to an increase in the diameter of the nanocrystals and a decrease in their aspect ratio (refer to Scheme 3.1c and Fig. 3.11e). The length of the final nanorods is slightly shorter while the diameter increases greatly at the reaction has

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

been going on for 1 hour. It can be seen clearly that the long sharp ends of nanocrystals have disappeared when comparing Fig. 3.11d and e. This is because higher energy is required to maintain a sharp tip and therefore as the reaction progressed, due to intra-particle ripening, the tip blunts and hence the resulting nanorods have more uniform diameters. The diameter of nanocrystals increases from 15 nm at 1 hour to 20 nm after 6 hours and the aspect ratio of the nanocrystals decreases from 5 at 1 hour to 3.3 for the final products. The length of the nanocrystals after 6 hours reaction decreases to about 64 nm (refer to Fig. 3.13).

Fig. 3.12. Yield of nanocrystals as a function of reaction time.

Fig. 3.13. Size distribution of nanorods under optimum conditions. Average length: 63.85 nm (diameter: 20 nm), STDEV: 19.6 and size distribution: 0.31. Note: above data are based on 330 nanorods.

3.4 Conclusions

In summary (also refer to Table 3.1), hexagonal CdSe nanorods were successfully synthesized using a novel microemulsion method at a moderate temperature. Hydrazine

Chapter 3: Synthesis of 1D CdSe via Reverse Micelle Method

hydrate is not only acting as a reduction agent but also as one of the templating agent that favors the formation of a rodlike structure. The morphologies of the as-prepared nanocrystals can be controlled by the amount of AOT and hydrazine hydrate. A relatively large size distribution of the CdSe nanocrystals synthesized using this method is still a concern. In the last part of this chapter, a possible nucleation and growth mechanism was presented and this mechanism was substantiated by TEM observations of the nanocrystals. This low temperature synthesis method provides an alternative method to synthesis CdSe nanorods. These CdSe nanorods capped with anionic surfactant (AOT) also provide a possibility for the nanocrystals alignment under electric-field assistance or self-assembly in solution which may be useful for PV applications.

Table 3.1. Summary for the influence of the parameters on morphology (Reverse micelles)

	Parameters	Morphology	Diam. (nm)	Aspect ratio	Remark
<i>R</i> effect	$R=8.5, S=5.2$	Mainly dendritic	n/a	n/a	The size is more than 200 nm and with multiple arms.
	$R=6.7, S=5.2$	Both nanorods and dendrites	For rod: 20	For rod: 3.0	The size is about 100 nm for dendrites with less arm than that of the $R=8.5, S=5.2$ group.
	$R=5.0, S=5.2$	Mainly rods	20	3.2	Well controlled growth
<i>S</i> effect	$R=5.0, S=4.0$	Both nanorods and dendrites	n/a	n/a	The size is from several ten nm to few hundreds nanometer and with less arm than that of the $R=5, S=11.4$ group.
	$R=5.0, S=7.8$	Mainly rods	20	5	Well controlled growth
	$R=5.0, S=11.4$	Dendritic with long arms	n/a	n/a	The size is from 100 nm to several hundreds nanometer and with multiple arms.
Conc. effect ($R=5.0, S=5.2$)	1.39 mmol/ml	Mainly dendritic	n/a	n/a	The size is about 200 nm with multiple arms.
	2.78 mmol/ml	Mainly rods	20	3.2	Well controlled growth
	5.56 mmol/ml	Mainly rods	29	2.4	With small spherical particles

Chapter 4: Synthesis and characterization of 1D CdSe by a novel reverse micelle assisted hydrothermal method

4.1 Introduction

A variety of methods has been employed to synthesize semiconductor nanorods in recent years. These methods include the hot coordination solvents method using TOPO and TOP, [5] the hydrothermal or solvothermal method [67, 126] and the micelle or reverse micelle method. [24, 141] The electrical and optical properties of nanocrystals are affected by the chemistry involved in their synthesis. Bottom-up approaches such as those using surfactants or micelles as the regulating agents are very effective for the synthesis of 1D nanostructure because of their high efficiency, controllability, simplicity and versatility. Hydrothermal techniques have been widely applied for the synthesis of conventional and advanced materials. The advantages of this method include the relatively low temperature required for processing, the possibility of controlling particle morphology and the good crystallinity of the products. These have been discussed in Chapter 2.

In our previous studies (refer to Chapter 3 or [24]), we showed that at a moderate temperature (100 °C), with a combination of an anionic surfactant, AOT and a reducing agent, hydrazine hydrate, it is possible to control the morphology of the nanocrystals. [24] The mechanism for the formation of CdSe nanorods is the phase transition due to the addition of a very large amount of hydrazine hydrate to the reverse micelle solution during the reaction. In this study, we attempt to synthesize 1D CdSe nanocrystals using a combination of the reverse micelle and the hydrothermal method. We aim to combine the advantages of good crystallinity with controlled growth using both these methods. We

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

were surprised to note that when we followed our previous protocol to prepare CdSe nanocrystals (refer to Chapter 3 or [24]), we obtained a mixture of spherical and hexagonal nanosheets. The changes in the reaction conditions are as follows.

(1) The different mole ratio of water to surfactant (R) results in a different phase structure. In our previous study, R was less than 10. It is possible that the nucleation and growth occurred inside the reverse micelles. Nanocrystals grow in size along certain orientations directed by their crystal structure and are affected by the shape of the micelles, which is in turn controlled by both AOT and hydrazine hydrate concentration. However, in this study, the R value is more than 130 which is likely to favor the formation of cylindrical reverse micelles. As this synthesis was carried out at elevated pressure and temperature, there is no way to confirm the structure of the micelles. According to Kawabata *et al.*, the bending modulus of the monolayer of ionic surfactants becomes more flexible with increasing temperature but increasing pressure has an opposite effect on the modulus. This corresponds to an increase in the head-head repulsion with increasing temperature and an increase in the tail-tail attraction with increasing pressure. [145] This helps in turn to stabilize the micelles at elevated temperature and pressure. These newly formed micelles will affect the initial nucleation and growth of the nanocrystals.

(2) The concentration of precursors for this study (0.25 mmol/ml) is significantly lower than in the previous study (2.78 mmol/ml). In general, anisotropic growth of nanocrystals along a certain axis occurs readily at a high monomer concentration. In this study, it is possible to produce nanorods at a lower precursor concentration. It can be seen that the hydrothermal method is an effective method for synthesizing anisotropic nanocrystals at a lower concentration of precursors.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

(3) The phase behavior and growth mechanisms are different at elevated temperature and pressure. In our previous study, we proposed that the mechanism for the formation of CdSe nanorods is a phase transition due to the addition of a very large amount of hydrazine hydrate to the reverse micelle solution during the reaction. In the last part of this chapter, a mechanism for the formation of 1D CdSe nanocrystals will be proposed.

4.2 Materials and Methods

4.2.1 Materials

The chemicals used in this chapter are the same as those described in the previous chapter, section 3.2.1.

4.2.2 Synthesis of CdSe Nanocrystals

In a typical synthesis, the molar ratio of $[\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ to $[\text{Na}_2\text{SeO}_3]$ was maintained at 1:1. 4 mmol of AOT was dissolved in 22 ml of *n*-heptane in a two-necked flask which was fitted with a septum and valves. The mixture was deaerated by bubbling N_2 through it at room temperature. 5 ml of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ aqueous solution (0.25 mmol/ml) was injected into the solution while the system was constantly stirred. After the solution was stirred for about half an hour, a mixture of 5 ml of hydrazine hydrate and 5 ml of Na_2SeO_3 aqueous solution (0.25 mmol/ml) was prepared under a N_2 environment and added to the solution using a syringe. After the precursors were well-dispersed in the cylindrical reverse micelles, the final solution was transferred to a 45 ml Teflon-lined autoclave. The autoclave was filled to 70% of its total volume, sealed in a stainless steel bomb, heated up to at 180 °C and held that temperature for 10 h. After the reaction was completed, the autoclave was allowed to cool to room temperature and the black

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

precipitate formed was then washed repeatedly with deionized water and ethanol to remove any ions that may still be present in the sample. Finally, the product was dried overnight in a vacuum oven at 60 °C.

4.2.3 Characterization

1. Raman spectroscopy

Raman spectroscopy is a technique used to study vibrational, rotational and other low-frequency modes in a system. It depends on inelastic scattering of monochromatic light from a laser in the visible, near infrared or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, leading to the energy of the laser photons being shifted up or down. The shift in energy provides information about the phonon modes. In this study, Raman and PL spectra were recorded using a triple monochromator Raman system (Witec R300) equipped with a charge-coupled device (CCD) camera for multichannel detection. The Raman experiments were performed using a 633 nm diode laser and the PL spectra using a 488 nm laser. The resolution of the Raman spectra was 2 cm^{-1} and the confocal microscope 300 nm. All the measurements were performed at room temperature. The samples were prepared by casting a dilute solution containing the nanocrystals onto a Si substrate and drying under flowing N_2 .

2. Atomic Force Microscope (AFM)

Atomic Force Microscope (AFM) is a technique for imaging, measuring and manipulating specimen at the nanoscale from angstroms to 100 microns. The information is generated by touching the surface with a mechanical probe or tip. The probe or tip usually made of piezoelectric elements is held several nanometers above the surface using a feedback mechanism. Using this mechanism, surface–tip interactions on the scale of nano Newtons is measured. Changes of tip height are used to produce a topographic

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

image of the surface. AFM images were obtained with a Digital Instrument Dimension 3100 atomic force microscope under ambient conditions. Test was carried out in the tapping mode with an optical readout using Si cantilevers.

4.3 Results and Discussion

4.3.1 Phase analysis

A typical XRD pattern from the as-prepared CdSe nanocrystals and the positions of the X-ray peaks for hexagonal CdSe are shown in Fig. 4.1a and b. All the diffraction peaks from the CdSe nanocrystals are consistent with the wurtzite structure of CdSe with measured lattice constants of $a=4.212 \text{ \AA}$ and $c=6.907 \text{ \AA}$ (these can be compared to the lattice constants of wurtzite CdSe-from JCPDS file No.08-0459: $a=4.299 \text{ \AA}$ and $c=7.010 \text{ \AA}$). In addition, the strong and sharp diffraction peak at $2\theta=25.8^\circ$ suggests that the crystals are elongated along the c -axis. The sharp diffraction peaks also indicate that the products are highly crystalline. XRD analysis revealed no impurities such as Se and SeO_3 in the sample.

Fig. 4.1. Typical XRD patterns of as-prepared CdSe nanocrystals with 4 mmol AOT and 5 ml hydrazine hydrate (a) and JCPDS hexagonal CdSe pattern (b).

4.3.2 Morphological studies

4.3.2.1 Influence of the amount of AOT

The structure and morphologies of the CdSe nanocrystals were characterized using TEM. The morphologies of the CdSe nanocrystals were mainly affected by the amount of AOT, the amount of hydrazine hydrate and the reaction temperature. It is well known that the size of the water droplets in the microemulsion is mainly dependent on the molar ratio of water to surfactant. [132, 134] If the chemical reaction is carried out inside the constrained environment provided by the surfactant, it will serve as a molecular-scale template to limit the initial growth.

There are many examples in the literature where the size and shape of the synthesized nanocrystals correlate with the size and shape of the organized template. [57, 146 - 148] However, recently Pileni *et al.* proposed that reverse micelles can only ensure the homogeneous growth of the nuclei to nanocrystals with similar shapes but a rather large number of exceptions are seen for anisotropic shapes, such as copper and silver nanodisks which they synthesized. [23] They further proposed that the effect of the surfactant on nanocrystal growth is negligible. However, our previous studies showed that the morphology of the CdSe nanocrystals could be controlled by the amount of AOT and hydrazine hydrate in the reverse micelles. Therefore, in this study we changed the amount of AOT (keeping the amount of hydrazine hydrate and water constant) to study whether the amount of AOT is a key parameter in the growth of the 1D CdSe nanocrystals. TEM images of the CdSe nanocrystals prepared using different amounts of AOT are shown in Fig. 4.2a-c. When the amount of AOT is less than 4 mmol, both nanorods and dendrites are formed (refer to Fig. 4.2a). When the amount of AOT is increased to 4 mmol, mainly rod-like crystals were obtained with a diameter of 43 ± 6

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

nm and an aspect ratio of 3.7 ± 0.6 (refer to Fig. 4.2b). When the amount of AOT is increased to 8.0 mmol, the length of the nanorods remains at 3.7 ± 0.6 , but the diameter of the rods increases to 49 ± 17 (refer to Fig. 4.2c). With increasing AOT, the distribution of both the length and the diameter of the nanocrystals becomes worse. This result disagrees with the findings of Pileni *et al.* as mentioned above.

Fig. 4.2. TEM images of the CdSe nanocrystals with fixed the amount of hydrazine hydrate (5 ml) and varied the amount of AOT: (a) 1 mmol, (b) 4 mmol and (c) 8 mmol.

The formation of a dendritic structure at low AOT concentration could be due to a phase transition or thermal/pressure induced shape change of the micelles. Kitchens *et al.*

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

found that increasing either the temperature or the pressure induces a shape fluctuation and increases the intermicellar exchange of micelles. [149] During nucleation and initial growth, the newly formed nuclei within these destabilized cylindrical micelles have no spatial constraint from the surfactant shell. Thus, multiple facets can grow on the nuclei after the reverse micelles have collapsed under the extreme temperature and pressure, resulting in a dendritic structure.

When the amount of AOT is increased above a certain value (such as 4 mmol), stable reverse cylindrical micelles are formed as there is now sufficient AOT to stabilize the micelles. This observation is in good agreement with our previous work, although in that case, the amount of AOT required to form stable reverse micelles was slightly higher than for the current system. [24] This is because the reverse cylindrical micelles can now exist at lower concentrations due to the elevated temperature and pressure. Thus, the newly formed nuclei grow within the stable cylindrical micelles resulting in nanorods. The change in the size of the nanocrystals is also related to the change in the amount of AOT. In general, as the amount of AOT is increased, the size of the micelles should decrease if the amount of water is fixed. However, for this study, further increasing the amount of AOT leads to an increase in the diameter of the nanorods. It has been shown that AOT will restrict the growth of the nanocrystals along their length. This observation is similar to that made by Jain *et al.* [23] who synthesized tin oxide via a hydrothermal method and found that the addition of AOT results in a nanocrystal morphology transition from rod-like to spherical. As a result, we can conclude that the amount of AOT is one of the key factors that control the formation of nanorods. The optimum amount of AOT to ensure that there is only nanorods in the final product is 4 mmol and this value was used in the subsequent studies.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

4.3.2.2 Influence of the amount of hydrazine hydrate

The amount of hydrazine hydrate is another key parameter in controlling the morphology of the nanocrystals. We thus investigated the effect of hydrazine hydrate on the morphology of the nanocrystals while keeping the amount of AOT fixed at 4 mmol. TEM images for the CdSe nanocrystals synthesized with different amount of hydrazine hydrate are shown in Fig. 4.3a-c. When the amount of hydrazine hydrate is less than 2.5 ml, the nanostructure formed is comprised of short rods with a large size distribution (refer to Fig. 4.3a).

Fig. 4.3. TEM images of the CdSe nanocrystals with fixed AOT amount (4 mmol) and varied hydrazine hydrate amount: (a) 2.5 ml, (b) 5 ml and (c) 10 ml.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

When the amount of hydrazine hydrate is increased to 5 ml, nanorods with a diameter of 43 ± 6 nm and an aspect ratio of 3.7 ± 0.6 are obtained (refer to Fig. 4.2b and Fig. 4.3b).

It is found that when the amount of hydrazine hydrate is increased up to 5 ml, the length of the nanorods increases, while their diameter remains around 43 nm. Thus the amounts of hydrazine hydrate and AOT have different roles in the growth of nanorods. Hydrazine hydrate restricts their diameter while AOT restricts their length. We believe this is because the different compounds accumulate on different crystal faces during nucleation and growth. Hydrazine not only provides reduced Se^{2-} for the reaction with Cd^{2+} , but it also affects the morphology of the micelles in the solution. Hydrazine hydrate may increase the micelle size slightly because it contributes to the changes in the template structure in the aqueous phase due to the large amount of hydrazine added to the reverse micelle solution. [137]

On top of that, Clint *et al.* proposed that hydrazine may react with AOT to form an imine dimmer. This so-called ‘polymerisation’ of the surfactant may help to improve the stability of the cylindrical reverse micelles and nanorods formed therein. [150, 151] After the reaction, a strong smell was detected which may be due to the formation of the imine dimmer. If the amount of hydrazine hydrate is increased to 10 ml, the size distribution of the rods becomes poor (refer to Fig. 4.3c). It is thought that the stability of the colloids could be destroyed in the presence of an excess of electrolyte (hydrazine hydrate). [138] Therefore, we conclude that the amount of hydrazine hydrate is another factor in controlling the formation of nanorods. This agrees with other groups who have synthesized metal and semiconductor nanorods or nanowires using hydrazine hydrate as both a reducing and a templating agent that favors the formation of a rod-like structure. [131, 132, 137, 141, 152] For our system, the optimum amount of hydrazine hydrate for the formation of nanorods is 5 ml, when 4 mmol of AOT is used.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

4.3.2.3 Influence of the reaction temperature

We now consider the effect of the reaction temperature on the formation of CdSe nanorods. With the amount of AOT and hydrazine hydrate fixed as above, decreasing the reaction temperature to 100 °C results in both spherical and dendritic structures. Peng *et al.* proposed that when the reaction temperature is lowered to 100 °C, the rate and range of movement of the precursor is decreased, therefore more nuclei will be formed in the solution during the nucleation process. [126] With a prolonged reaction time, some of these newly formed nuclei grow to form thin CdSe rods with the CdSe monomers, and at the same time, these randomly moving nuclei collided and merged with each other to form dendritic structures as suggested by the diffusion-limited aggregation model. [126, 153] In general, the exact mechanism cannot be conclusively determined because of the possibility of the presence of the reverse micelles at least at the start of the reaction and these micelles may or may not be present as the reaction progressed. The detailed growth mechanism for the system based on the observations will be proposed and discussed later (section 4.3.6).

4.3.3 Crystallography of nanocrystals

HRTEM images and electron diffraction patterns of nanocrystals synthesized at 180 °C are shown in Fig. 4.4a and b. The lattice fringes observed indicate that the nanorod has the characteristic of a single crystal, and the 0.35 nm spacing is consistent with (001) wurtzite CdSe. [67] Fig. 4.4a shows that the length of the nanorod is along the [001] direction which is in agreement with our XRD data and also the results from other groups. [29, 67, 74, 126] Compositional analysis of the as-prepared CdSe nanocrystals using EDAX shows that Cd and Se have a ratio of 1:1 and that no other elements, such as sodium, are present (see Fig. 4.4c). In an attempt to observe the 3D shape of individual nanocrystals, AFM scans were carried out. An AFM height image of CdSe nanorods is

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

shown in Fig. 4.4d. It can be seen that at the left-bottom corner of the image, many rods stacked and aggregated together. At the right-top corner of the image, there are several nanorods aggregated on the substrate. Based on nanorods at this region, we can roughly tell that nanorods have a 3D structure. The diameter and aspect ratio are around 60 nm and 4 respectively.

Fig. 4.4. (a) HRTEM image, (b) TEM image of single CdSe nanorod with diffraction pattern (inset) and (c) the EDAX spectrum of the as-prepared CdSe nanocrystals. (d) AFM height image of CdSe nanorods. The scanning area is $2\ \mu\text{m} \times 2\ \mu\text{m}$.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

4.3.4 Optical characterization

Fig. 4.5 shows the absorption spectra, the luminescence spectra and a confocal microscopic image of the as-prepared CdSe nanorods. It can be seen from Fig. 4.5a that there are broad weak peaks in the UV curve centered at around 673 nm. These broad peaks are due to the size distribution and differences in morphologies of the nanocrystals. In an attempt to observe the photoluminescence properties of individual nanocrystals, confocal photoluminescence measurements were carried out on the samples using an excitation wavelength of 488 nm. The resulting PL spectra from 35 individual dots and a confocal microscopic image of the CdSe nanorods are shown in Fig. 4.5b and c. The average peak in the PL spectra is centered at around 699 nm. We cannot see the individual nanorods in this image because the resolution of the confocal microscope is limited to 300 nm. We observed a blue-shift of 15 nm in the PL spectra when compared to the PL peak from the bulk wurtzite CdSe which is centered at 716 nm due to quantum confinement. The deviation of these peaks is about 15 nm, which may be due to the different surface states of these nanorods. It is also thought that the strong PL intensity from the CdSe nanorods can be attributed to their high crystallinity [154, 155], which is in good agreement with the XRD patterns discussed earlier and the presence of good surface states on the nanorods, which effectively prevent the CdSe nanorods from having carrier-quenching defects and non-radiative traps. [156] The as-prepared CdSe nanocrystals remain stable for at least one year, as shown by the absence of any changes in their PL spectra. We believe this stability is due to the presence of hydrazine hydrate on them which can prevent the oxidation of CdSe nanocrystals due to its reducing capability. [133] All these PL peaks are significantly red-shifted from the absorption peaks due to the Stokes shift which increases with decreasing nanocrystal diameter and increasing morphological complexity. [157]

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

Fig. 4.5. (a) UV-Vis absorption spectrum, (b) PL spectra of 35 dots and (c) the corresponding confocal microscopic image of CdSe nanorods.

4.3.5 Raman spectroscopy

A room temperature Raman spectrum of the CdSe nanorods (Fig. 4.6) shows the phonon frequencies of the longitudinal optical (LO) and its overtone (2LO) modes of CdSe to be 203.4 and 407.8 cm^{-1} respectively. This blue-shift of the LO and 2LO peaks can be compared to the wave numbers for bulk CdSe of 210 and 418 cm^{-1} respectively [158] and is frequently observed for CdSe nanocrystals. [156, 159, 160] The as-prepared CdSe nanorods have diameters that exceed 40 nm, so quantum confinement of the phonon motion due to the size effect is negligible, and therefore size is unlikely to contribute significantly to this spectra shift.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

Fig. 4.6. Raman spectrum of CdSe nanorods.

In their study of this spectra shift, Zhang *et al.* [156] and Venugopal *et al.* [154] thought that lattice contraction is the real reason for this peak shift when they studied free-standing CdSe quantum dots and CdSe nanobelts and sheets. Their X-rays results are consistent with these peak shifts. However, there is no obvious difference when we compare the interplanar spacing of our samples with that of standard hexagonal CdSe thin film (JCPDS file No. 08-0459, $d=0.351$ nm). It is possible that the surface tension experienced during surface reconstruction when the nanocrystals grow is the reason for the lattice contraction and this contraction occurs mainly on the surface. [156] Prominent size dependencies (~ 5 -20 nm in diameter) of the blue-shift due to lattice contraction and of the red-shift caused by quantum confinement have also been observed by Scamarcio *et al.* in Raman spectra of ternary $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals. [159] In their case, the blue-shift dominates. This also supports the theory that the blue-shift of Raman scattering peaks in the CdSe nanorods comes from a lattice contraction.

4.3.6 Growth mechanism

A time dependent TEM study of the synthesized CdSe nanorods is shown in Fig. 4.7. Very little reducing reaction took place before the solution was heated. This experiment was carried out for more than 6 h at room temperature and no visible color change was

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

seen over this period. Color change is usually an indication of a reducing reaction taking place in this system. Once the mixture of hydrazine hydrate and aqueous Na_2SeO_3 solution was added with constant stirring into the AOT capped Cd^{2+} solution, AOT formed cylindrical reverse micelles together with the hydrazine hydrate. These micelles with hydrazine hydrate and Na_2SeO_3 aqueous solution will collide with micelles containing Cd^{2+} and re-disperse the contents in the micelles (refer to Scheme 4.1a). When the solution was transferred to an autoclave and heated up, the reaction began and nucleation and growth occurred. The detailed chemical reaction between the two precursors and the hydrazine hydrate has been presented in section 3.3.6. [67, 126] With increasing temperature, the speed of reduction from SeO_3^{2-} to Se^{2-} by hydrazine hydrate in the micelles accelerated. If Cd^{2+} is present within the same micelle, then nucleation will happen (refer to Scheme 4.1b). Otherwise, CdSe nuclei were formed in the reorganized micelles when these micelles collided with micelles containing Cd^{2+} due to Brownian motion. Fig. 4.7a shows a mixture of small spherical and very short rod-like nanocrystals (less than 20 nm in length) produced in the initial reaction process.

With prolonged reaction time, cylindrical reverse micelles are gradually destroyed due to the elevated temperature and pressure in the autoclave. The larger rod-like nanocrystals cannot be suspended in the solution for further growth and precipitate to the bottom of the autoclave capped by surfactants. Further growth of the initially produced nanocrystals is provided by directional aggregation of smaller particles including shorter rods and nuclei (refer to Scheme 4.1c and Fig 4.7b-e). [161] These tiny particles re-dissolve and aggregate in a directional manner along the *c*-axis of its crystal structure. This process results in the formation of larger nanocrystals and is affected by the surface absorption and desorption of both hydrazine molecules and AOT molecules on the nanorod. [21] Similar explanations were given by Cao *et al.* to account for the formation

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

of nanofibers using the reverse micelles assisted hydrothermal method. [161 - 163] In that case, they proposed that the ultrahigh aspect-ratio nanofibers are formed by aggregation growth rather than in the water droplets of the reverse micelles due to low water content environment. The R value in their study is about 10. In our case, the R value is more than 130. It is possible that in the initial reaction stage, both nuclei and some short rods are formed before the reverse micelles collapsed due to the extreme reaction conditions. However, we noticed that Kong *et al.* proposed that the formation of α -CoMoO₄ nanorods/nanowhiskers happened within reverse micelles under hydrothermal conditions. [164] Because the autoclave is a closed opaque system under high temperature and high pressure, it is not feasible to dynamically monitor the phase transition during the reaction process. Therefore, the detailed mechanism is still unclear at this moment.

Scheme 4.1. Proposed model of the process of nanocrystal formation in reverse micelles assisted by hydrothermal method: (a) Fusion and exchange of the contents within the cores and re-dispersion of the reverse micelles before heated up, (b) Nucleation and growth of spherical and rodlike nanocrystals with heating and pressure before micelles collapsed, (c) Further growth of nanorods provided by directional aggregation of smaller particles including shorter rods and nuclei after micelles collapsed.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

Fig. 4.7. TEM images of nanocrystals after (a) 1 h, (b) 2 h, (c) 3h, (d) 5 h and (e) 10 h reaction.

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

4.4 Conclusions

In summary (refer to Table 4.1), 1D wurtzite CdSe nanorods with a diameter of 43 ± 6 nm and an aspect ratio of 3.7 ± 0.6 have been successfully synthesized through a novel reverse micelle assisted hydrothermal method at a relatively low temperature. The morphologies of the as-prepared nanocrystals can be controlled by the amount of AOT, the amount of hydrazine hydrate and the reaction temperature. It is proposed that AOT restricts the growth of the length and hydrazine hydrate restricts the growth in the diameter during the reaction. It is thought that AOT and hydrazine hydrate tend to accumulate on different crystal faces during the nucleation and growth process.

Table 4.1. Summary for the influence of parameters on morphology (Hydrothermal)

	Parameters	Morphology	Diameter (nm)	Aspect ratio	Remark
AOT amount (N₂H₄ = 5 ml)	AOT=1 mmol	Mainly dendritic	n/a	n/a	The size is more than 600 nm and with multiple arms.
	AOT=4 mmol	Mainly nanorods	60	3.3	Well controlled growth
	AOT=8 mmol	Spherical, rod and dendritic	n/a	n/a	Less control.
N₂H₄ amount (AOT = 4 mmol)	2.5 ml	Short rods	20	5	Poor size distribution
	5 ml	Mainly rods	43 ± 6	3.7 ± 0.6	Better controlled growth
	10 ml	Spherical, rods	20	1 - 5	Poor size distribution
Temp. (AOT=4 mmol, N₂H₄=5ml)	180 ° C	Mainly rods	43 ± 6	3.7 ± 0.6	Better controlled growth
	100 ° C	Dendritic and spherical.	n/a	n/a	Less control.

At higher temperature, the chances of micelle collisions increase and hence nanorods can be formed in the reverse micelles. Confocal photoluminescence mapping of the

Chapter 4: Synthesis of 1D CdSe by Hydrothermal Method

individual nanorods shows the presence of strong PL intensity which is due to both high crystallinity and the good surface states of the nanocrystals. Raman spectra measurements show a blue-shift of both the LO and 2LO phonon peaks which may come from a lattice contraction of the CdSe nanorods. Finally, a possible nucleation and growth mechanism was discussed based on time-dependent studies. This relatively low temperature synthesis method provides an alternative method to synthesize CdSe nanorods and also can be extended to prepare other 1D metal or semiconductor nanocrystals. These CdSe nanorods have potential to be used for electronic and optical nanodevices fabrication.

In addition, a comparison between the reverse micelle and the hydrothermal methods is shown in Table 4.2. Overall, it can be seen that the reverse micelle method has better morphological control than the hydrothermal method, but the latter gives the higher crystallinity and yield.

Table 4.2. A comparison between the reverse micelle and the hydrothermal methods

	Reverse micelle	Hydrothermal
AOT and N₂H₄	$R < 10$. More AOT, less N ₂ H ₄ . Nucleation and growth occurred inside the reverse micelles.	$R > 130$. Less AOT, more N ₂ H ₄ . Favor the formation of cylindrical reverse micelles. These newly formed micelles will affect the initial nucleation and growth of nanocrystals.
Concentration	2.78 mmol/ml. Anisotropic growth occurs at a high monomer concentration.	0.25 mmol/ml. Produce nanorods at a lower precursor concentration.
Affect factors	R , S and the precursor concentration.	The morphologies can be affected by the amount of AOT, hydrazine and reaction temperature.
Growth mechanism	1. A phase transition due to the addition of a very large amount of hydrazine hydrate to the reverse micelle solution during the reaction. 2. Cylindrical micelles.	1. Before micelles collapsed, nucleation and growth of spherical and rodlike nanocrystals within micelles. 2. After micelles collapsed, further growth provided by directional aggregation of smaller particles including shorter rods and nuclei.
Overall	1. Better control in morphology. 2. A relative narrow size distribution. 3. Low yield (80%).	High crystallinity and yield (>90%). Less control in morphology. A fundamental understanding on the growth mechanism is ambiguities.

Chapter 5: Growth of Monodisperse CdS Nanowires in Solution

5.1 Introduction

Semiconductor nanowires exhibit physical properties that make them attractive building blocks for electronic, optical and life sciences applications. [3, 4, 9, 165, 166] One such application is germanium or silicon nanowire field-effect transistors (FETs) which have recently been reported to have high hole/electron mobilities, large on-currents, large I_{ON}/I_{OFF} ratios, and good sub-threshold swings. [167 - 169] These novel transistors are attracting attention due to their potential applications in electronics and biomolecular detection. Furthermore, these nanowires can be assembled to make three-dimensional (3D) multifunctional electronics, such as electromechanical and resistance-change memory devices based on the layer-by-layer assembly method. [170, 171]

Current strategies for producing higher aspect ratio nanowires have mainly made use of the VLS method which benefits from catalyst activation of one end of the nanowire. [172] Growth of nanowires via VLS often suffers from the requirements of high temperature, special conditions and complex procedures. In general, the size and aspect ratio distribution of these nanowires are difficult to control. [48] Solution growth of nanowires provides an alternative strategy for generating 1D nanowires. Recent years, SLS method has been proven to be a useful approach to produce semiconductor nanowires. [173 - 175] This method has several advantages, including ease of control of the mean diameters, the narrow diameter distributions and the comparably low reaction temperature ($< 400\text{ }^{\circ}\text{C}$). [173, 176] However, this method also requires the catalyst activation at the beginning of growth which is similar to the VLS method. Hydrothermal methods have been found to be more effective when compared to the low temperature

Chapter 5: Growth of Monodisperse CdS Nanowires

solution route for low cost and large volume production of anisotropic nanocrystals. [25, 177, 178] For example, Peng *et al.* employed ammonium as a complexing agent for cadmium ions to synthesize CdSe nanocrystals through a hydrothermal method. [126] They found that at 180 °C, mainly CdSe nanowires with diameters of 20–100 nm and lengths ranging from tens of nanometers to one micrometer were produced. However, this method has poor control over the size and shape of the nanowires produced. Alivisatos and co-workers developed a high temperature (around 300 °C), non-aqueous based method using organometallic precursors to control the shapes of CdSe nanocrystals. [5] This method can generate nearly monodisperse CdSe nanorods due to the separation of the nucleation and growth stages. CdSe rods and tetrapods have also been prepared in a mixed surfactant system. [5, 71] This method has not only been used to synthesize CdS, CdSe and CdTe nanocrystals, but has also been extended to the synthesis of ZnS and ZnSe nanocrystals as well as core/shell rods (or dots) of CdSe/CdS/ZnS and quantum dot-quantum well structures. [27, 30] The crystal quality and control over the morphologies of the nanocrystals synthesized have made this method very important in the development of light-emitting diodes and solar cells. [8, 179] Very recently, Kang *et al.* reported their research on preparing CdS nanowires using tetradecylphosphonic acid (TDPA) as a ligand where they mainly studied the effect of temperature on the morphology of the nanowires. [84] Although nanorods have been prepared for close to 10 years using the hot coordinating solvents method, only Kang *et al.* [84] reported the successful synthesis of nanowires using a catalyst-free and solution-based synthesis method. Catalyst-free, solution-based synthesis methods are much cheaper and easier to scale up to industrial proportions than those other methods for the synthesis of nanowires. In our systematic investigation of nanowire formation, we determined the optimum parameters for the synthesis to maintain a good balance

Chapter 5: Growth of Monodisperse CdS Nanowires

between nucleation and growth. These conditions favor the formation of nanowires with high aspect ratio in our systems.

As discussed earlier, solution synthesis methods are more commonly used to prepare nanostructures with low aspect ratio such as rods and dots. In this study, we report a general method to prepare very long monodisperse CdS nanowires using solution synthesis. As well as the reaction temperature, we also investigate the effect of the reactant ratio (ODPA-to-Cd mole ratio), the precursor ratio (Cd-to-S mole ratio), the precursor concentration, the precursor injection process and the type of ligand on the morphology of the nanowires.

5.2 Experimental Section

5.2.1 Materials

TOPO (99%) and P3HT were purchased from Sigma-Aldrich. TOP (90%) and CdO (99.95%) were purchased from Fluka. HPA (hexylphosphonic acid, 100%), DDPA (dodecylphosphonic acid, 100%), ODPA (octadecylphosphonic acid, 100%) and sulphur (99%) were purchased from Polycarbon Inc. and Chemicon, respectively.

5.2.2 Synthesis of CdS nanowires

The CdS nanowires were prepared using a modified Peng's procedure for cadmium chalcogenide nanocrystals. [74] A 128 mg of CdO, 0.668 g of ODPA (0.500 g DDPA or 0.232 g HPA) and 3.00 g 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 N₂ and the temperature was gradually raised to 330 °C to dissolve the CdO. After the CdO was dissolved and Cd-complexes formed, the

Chapter 5: Growth of Monodisperse CdS Nanowires

solution turns colorless. When the temperature was lowered to 310 °C, a solution of 32 mg sulphur in 2.0 g TOP was injected by multiple injections (4 times at 2 min intervals). After the injection of sulphur, 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 procedure to clean the products was as follows: (1) the nanowires were initially purified by precipitating the particles with excess ethanol and discarding the supernatant after centrifuging twice. (2) The precipitate was then dispersed in toluene. The solution obtained was centrifuged at 9500 rpm for 30 min. The precipitate that settled at the bottom of the tube was discarded. (3) The supernatant containing the nanowires was washed twice with toluene/ethanol and re-dissolved in toluene for further characterization and application.

5.2.3 Characterization

The excitation wavelength for the PL test was 350 nm. Thin film XRD studies were carried out in a Rigaku DMAX 2200 using Cu K α radiation.

5.3 Results and Discussion

5.3.1 Phase Analysis

Typical XRD patterns of the as-prepared CdS nanowires (600 nm in length), shorter nanowires (150 nm in length), nanorods (14 nm in length) and the positions of the X-ray peaks for hexagonal CdS from the JCPDS are shown in Fig. 5.1. All the reflection peaks of the CdS nanocrystals, to within experimental error, can be indexed using hexagonal CdS (JCPDS card no. 41-1049).

Chapter 5: Growth of Monodisperse CdS Nanowires

Fig. 5.1. Typical XRD patterns of (a) 600 nm long as-prepared CdS nanowires, (b) shorter nanowires (150 nm in length), (c) nanorods (14 nm in length) and (d) JCPDS hexagonal CdS pattern.

In addition, the strong and sharp (002) diffraction peak suggests that the crystalline domains are extended along the *c*-axis. Comparison of XRD patterns for nanowires and nanorods reveals that the nanowires exhibit a sharper (002) peak compared to the rods due to their length. However, when comparing the XRD pattern of our CdS nanowires with that of Kang *et al.*, [84] we found that our (002) peaks for both nanowires and nanorods are both more intense and sharper when compared to theirs. Our results are more reasonable in supporting the assumption that the nanowires grow along the *c*-axis. This analysis is consistent with the results from other groups who have synthesized CdS nanorods and nanowires. [74, 180 - 182] This growth orientation will be supported by high resolution TEM and SAED studies which will be discussed latter. In contrast to the nanorods, the nanowires exhibit several diffraction peaks with reduced intensity (particularly the (102) and (103) peaks). This is related to the fact that the nanowires

Chapter 5: Growth of Monodisperse CdS Nanowires

readily self-assemble along certain directions and lie in the plane of the substrate during the XRD measurement process.

Bright-field and dark-field TEM images of the nanowires suspended on a holey carbon film are shown in Fig. 5.2 along with a diffraction pattern of the same area. The bright-field image (Fig. 5.2a) shows that the nanowires are long and have a uniform diameter. It can also be seen that they self-assemble into groups of parallel nanowires. The dark-field image (Fig. 5.2b) was taken with the CdS 002 reflection and shows that the nanowires are mainly single crystal. The diffraction pattern (Fig. 5.2c) shows the preferential orientation of the CdS nanowires with the strong 002 reflection along the length of the nanowires. The positions of the reflections for hexagonal CdS, cubic $Fm\bar{3}m$ CdS and cubic $F\bar{4}3m$ CdS are marked and it can be seen that the positions of the diffraction rings match those of hexagonal CdS, in agreement with the XRD results of Fig. 5.1a.

Fig. 5.3a is a high resolution image of one nanowire showing this region to be single crystalline with no stacking faults. The measured interplanar spacing of the lattice fringes along the length of the nanowire is about 0.332 nm, corresponding to the (002) lattice plane spacing of wurtzite CdS (0.336 nm). Fig. 5.3b is a diffractogram from Fig. 5.3a with spots marked corresponding to the 002 and 100 lattice fringes indicating that the zone axis is [010]. Note the similarity between the diffractogram and the diffraction pattern from a group of nanowires shown in Fig. 5.2c indicating that the nanowires are all in similar orientations. A lattice image taken looking along the length of a nanowire at a point where the nanowire is bent is shown in Fig. 5.3c. From this image, the hexagonal structure of the nanowire is clear confirming the [001] growth direction. All these results suggest that the CdS nanowires grow along the c-direction with defect free

Chapter 5: Growth of Monodisperse CdS Nanowires

single crystals and that the crystal structure is the wurtzite CdS structure suggested by the XRD results discussed earlier. The compositional analysis of as-prepared CdS nanowires using EDAX is shown in Fig. 5.3d. The average atomic percentages for Cd and S are 47.1% and 52.9%, respectively. This EDAX spectrum confirmed that the nanocrystals are indeed composed of Cd and S with no impurities.

Fig. 5.2. (a) Bright-field image of CdS nanowires, (b) dark-field image of the same CdS nanowires using the CdS 002 reflection, and (c) the diffraction pattern of the same area. The positions of the reflections for hexagonal CdS (CdS H JCPDS card no. 41-1049), cubic $Fm\bar{3}m$ CdS (21-0829) and cubic $F\bar{4}3m$ CdS (89-0440) are marked.

Chapter 5: Growth of Monodisperse CdS Nanowires

Fig. 5.3. (a) HRTEM image of a CdS nanowire, (b) an FFT of the HRTEM image showing the indices and (c) high resolution image looking down the axis of a bent nanowire. (d) The EDAX spectrum of the as-prepared CdS nanowires.

5.3.2 Morphological studies

5.3.2.1 Influence of the ODPA-to-Cd mole ratio

In this study, we found that the ligand-to-Cd mole ratio was a key factor that affects the morphology of the CdS nanocrystals in addition to the reaction temperature as found by other groups. [84] A series of experiments was performed with different ODPA-to-Cd mole ratios at fixed initial concentration of Cd and Cd:S precursor ratio. TEM images of the CdS nanocrystals are shown in Fig. 5.4.

Chapter 5: Growth of Monodisperse CdS Nanowires

Fig. 5.4. TEM images of CdS nanowires with ODPA-to-Cd mole ratios of (a) 1:1, (b) 1.5:1, (c) 2:1, (d) 3:1 and (e) 4:1.

If the ODPA-to-Cd mole ratio was less than 1, the solution would not turn colorless indicating that no reaction has taken place. This was still the case even after holding the

Chapter 5: Growth of Monodisperse CdS Nanowires

solution at 330 °C for more than one hour. When the ODPA-to-Cd ratio was increased to 1:1, a mixture of short rods and dots (Fig. 5.4a) was formed. The rods have a diameter of about 3.5 nm and length of about 15 nm. If the ratio was increased to greater than 1 but less than 2:1, the color of the Cd-complex solution became lighter than when the ratio was 1:1, but still the solution did not turn totally colorless completely. The morphology of the nanocrystals synthesized was similar to that when the ratio was 1:1, but the length of the rods had increased to 40 nm while the diameter remained constant (Fig. 5.4b). When the ratio was increased to 2:1, the solution turned colorless after 20 min at 330 °C. The crystals formed were mainly nanowires with a monodisperse diameter of 3.5 nm while their length had increased to 600 nm (Fig. 5.4c). The general trend was that the aspect ratio increased as the ODPA-to-Cd mole ratio increased up to the mole ratio of 2:1, as shown in Fig. 5.4a-c.

It was assumed by several groups that 2 mol of phosphonic acid is required to dissolve 1 mol of CdO so that all the cadmium ions formed complexes with the phosphonic acid. [29, 83, 183] A modified balanced chemical equation for this reaction is

Therefore, when the ODPA-to-Cd mole ratio is less than 2 (refer to Eq. 5.1), CdO cannot be completely decomposed to form a colorless Cd-complex solution at the reaction temperature. This results in a lower monomer concentration and hence decreases the growth rate of the CdS nanocrystals. It is thought that anisotropic growth of the nanocrystals requires a high monomer concentration after the nucleation stage. [27] Therefore, we only get a mixture of short nanorods and dots when the ODPA-to-Cd mole ratio was equal to 1.5 (refer to Fig. 5.4b). We noticed that Shieh *et al.* synthesized CdS,

Chapter 5: Growth of Monodisperse CdS Nanowires

CdSe and CdTe nanodots and nanorods with a mole ratio of TDPA-to-Cd equal to 1.73, which is close to 2 (there is an error in their calculation of the amount of TDPA in their supporting material). [75] They only managed to produce short nanorods (less than 100 nm) with a poor size distribution using a similar method. The main reason is possibly due to the mole ratio of TDPA-to-Cd that they used.

When the ODPA-to-Cd mole ratio was increased to 3, nanowires with different lengths ranging from 10 nm to 400 nm and a larger diameter of 3.7 nm were obtained as shown in Fig. 5.4d. It was also found that the reaction speed was slower. If the mole ratio was further increased to 4, the reaction generated short nanowires mixed with a significant amount of short rods (Fig. 5.4e). These nanowires had diameters of approximately 5 nm and lengths up to 300 nm. The length of the short rods ranged from 10 to 80 nm while their diameter was roughly the same as the nanowires. The reaction speed was significantly slower. This observation is different from the results of Peng *et al.* where they studied the effect of the TDPA-to-Cd mole ratio on the morphology of CdSe nanocrystals. [29] They found that the growth rate of rods with the TDPA-to-cadmium ratio higher than 2 is significantly faster. In the synthesis of CdTe tetrapod-branch nanocrystals, Manna *et al.* thought that the presence of more phosphonic acid per Cd decreases the reactivity of the Cd precursor and so the driving force for its addition to the crystal, leading to a slower growth rate for a given Cd concentration. [83]

Chapter 5: Growth of Monodisperse CdS Nanowires

Recently, the Alivisatos and co-workers proposed that the concentration of phosphonic acid affects the cleavage of the alkylphosphine chalcogenide bond (refer to Eq. 5.2). [183] This process is supposed to result in the formation of a semiconductor monomer, and this cleavage rate affects both crystal nucleation and growth. We tentatively assume that the reason for the decrease in the reaction speed in our reactions is probably due to cadmium being more coordinated with ODPa and hence reducing the accessibility of the phosphine for the Cd. This leads to a reduction in the cleavage rate of the P=S double bond, leading to a relatively lower concentration of monomer and further affecting the nucleation and the growth rate of anisotropic nanocrystals. Furthermore, we think that the rate at which P=S is broken is a vital factor in affecting the morphology of nanocrystals in this system. We also attempted to synthesize CdSe nanowires using the same method but we only managed to obtain nanorods with diameters of 10 nm and lengths of 40 nm. The reason for this is due to the faster cleavage rate of P=Se than P=S which results in more nuclei and hence more rapid depletion of the monomers. [183] As a result, the rods had no more precursor to grow into nanowires.

5.3.2.2 Influence of the Cd-to-S mole ratio

The Cd-to-S mole ratio was another important factor that influenced the morphology of the resulting nanocrystals. It was found that decreasing the Cd-to-S mole ratio can lead to a decrease in the highest aspect ratio of the nanowires (refer to Fig. 5.5a). A similar observation has been made by other groups. [74, 83] A possible explanation is that the more sulphur precursor present in the initial stage (lower Cd-to-S mole ratio), the faster the nucleation process occurs, and more nuclei are formed during nucleation. This results in a lower monomer concentration after nucleation. [74] This change is more significant as the Cd-to-S mole ratio is decreased further. Anisotropic growth is due to the presence of a high monomer concentration after the nucleation stage. [19] The remaining low monomer concentration cannot sustain the anisotropic growth regime for a long time,

Chapter 5: Growth of Monodisperse CdS Nanowires

resulting in a lower aspect ratio and a poor length distribution, ranging from 10 nm to 200 nm as shown in Fig. 5.5a. When we increased the initial Cd-to-S mole ratio to 1:0.5, we obtained a mixture of tiny particles and nanowires with different lengths (refer to Fig. 5.5b). This shows that these tiny particles are still in their early growth stage due to the earlier depletion of the monomer which is limited by the amount of S.

Fig. 5.5. TEM images of CdS nanowires synthesized with Cd-to-S mole ratios of (a) 1:1.5 and (b) 1:0.5.

5.3.2.3 Influence of the precursor concentration

The precursor concentration is another factor that influenced the morphology of CdS nanowires. With the ODPA-to-Cd mole ratio fixed at 2:1 and the total amount of TOPO and ODPA fixed at 3.668 g, changing the two precursor concentrations was found to change the morphology of the nanocrystals substantially. When the precursor concentration was reduced by half, shorter nanowires were produced. The length of the nanowires ranged from 50 to 150 nm and the diameter was 3.4 nm. These results show that the growth of longer nanowires requires a higher precursor concentration than the growth of shorter ones. [74] When the precursor concentration is doubled, the reaction yields shorter nanowires mixed with short rods and dots. This result is not what we expected. In previous studies, when the precursor concentration was increased, the

Chapter 5: Growth of Monodisperse CdS Nanowires

morphology of the nanocrystals changed from spherical, short rods to long rods and then to branched rods. [19, 74] A higher precursor concentration may result in longer or branched nanowires. The reason for the formation of shorter nanowires mixed with short rods and dots at high concentration in our case may be due to the higher number of nuclei at the initial stage of the reaction. The speed of nucleation and growth is accelerated by increasing the precursor concentration. [74] These nuclei grow to larger crystals by consuming the semiconductor monomers. [183] With the depletion of the monomers, the final nanocrystals have different lengths.

5.3.2.4 Influence of the precursor injection process

As discussed above, the monomer concentration at the initial stage of the reaction is an important factor because it can affect the rate of nucleation and growth. In this study, we investigated the effect of the precursor injection process on the morphology of the nanocrystals while keeping other parameters constant. It was found that different final nanocrystal morphology was obtained when a single injection process was used instead of multiple injections.

Fig. 5.6. TEM images of CdS nanocrystals synthesized with: (a) a single precursor injection and (b) multiple injections with an interval of greater than 5 min.

Chapter 5: Growth of Monodisperse CdS Nanowires

A single injection generates short, 1D nanocrystals as shown in Fig. 5.6a. Their length ranged from a few tens of nanometers to 200 nm, and their diameter was 3.7 nm. This is because the single injection introduced all the sulphur monomer at once, resulting in more nuclei during nucleation than when there are multiple injections. These nuclei consumed most of the monomer at the same time and hence led to a lower monomer concentration after nucleation. The remaining low monomer concentration cannot sustain the anisotropic growth regime for a long time, resulting in a lower aspect ratio nanocrystals as we discussed earlier. When multiple injections at 2 min intervals are carried out, the nanocrystals formed are nearly monodisperse nanowires with very high aspect ratios (refer to Fig. 5.4c). We did not observe significant difference in diameter between single and multiple injections that was reported by Peng *et al.* [74] They found a 1.8 nm difference in their experiments. The reason for the increase in aspect ratio using multiple injections is that multiple injections regularly replenish the monomer concentration and hence provide a relatively stable growth environment with high monomer concentration. [5, 29, 74] In this case, after the nucleation, the presence of a high monomer concentration can maintain the anisotropic growth regime for a long time, resulting in a higher aspect ratio. Further increases of the interval between multiple injections can lead to a great decrease in the aspect ratio of the nanocrystals as shown in Fig. 5.6b, where there is a mixture of nanorods with varying lengths but monodisperse diameter. Although these longer interval multiple injections still periodically top up the available monomer, a variable growth environment and relative low monomer concentration due to nucleation and growth between the longer intervals. This variable growth environment was not able to ensure anisotropic growth of the nanocrystals to high aspect ratio.

5.3.2.5 Influence of the different ligands on Cd-complexing

Chapter 5: Growth of Monodisperse CdS Nanowires

We also investigated the effect of different ligands on the morphology of nanocrystals while keeping the other parameters constant. Three different phosphonic acids are used as ligands in the reaction and their chemical structures are as shown in Fig. 5.7. We found that the phosphonic acids with longer alkyl chains, such as ODPA, are better at controlling the morphology of the nanocrystals than those with shorter alkyl chains, such as DDPA and HPA. It was found that the shorter alkyl chain phosphonic acid - HPA can only generate nanoneedles with a rough surface. The diameter was around 7 nm and the length was around 150 nm. It can be seen that the control of the morphology was poor as shown in Fig. 5.8a.

Fig. 5.7. Chemical structures of three phosphonic acids with varying linear alkyl chain lengths.

When DDPA and ODPA are used, mostly nanowires are formed as shown in Fig. 5.8b and Fig. 5.4c. There is still a slight difference between the nanowires synthesized using DDPA and ODPA. Fig. 5.8b shows that the morphology of the nanocrystals synthesized using DDPA is less well-controlled compare to those synthesized using ODPA. The product synthesized using DDPA is a mixture of short rods, branches and nanowires. The reason for the poor control over the nanocrystals morphology offered by phosphonic acids with shorter alkyl chains, such as HPA and DDPA, is the higher reactivity of the Cd-ligand complexes. [74] The reactivity of Cd-ligand complexes affects the P=S cleavage kinetics and the nucleation/growth rate of the anisotropic nanocrystals. [183] Furthermore, complexes with lower reactivity allow the monomers to adjust their position on the surface of the nanocrystal before the binding occurs. [74] Therefore, Cd-

Chapter 5: Growth of Monodisperse CdS Nanowires

ODPA complexes which provides both a low diffusion rate and low reactivity, are good candidates for generating nearly monodisperse and high aspect ratio CdS nanowires. This may be the reason for the low monodispersity and the varied morphology of CdS nanocrystals synthesized by Kang *et al.* [84]

Fig. 5.8. TEM images of CdS nanocrystals synthesized with: (a) HPA and (b) DDPA ligands. (c) UV-Vis absorption spectra of nanocrystals produced with different ligands.

Fig. 5.8c shows the UV-Vis spectra of nanocrystals synthesized using HPA, DDPA and ODPA ligands. The absence of a sharp peak in the spectrum from the nanocrystals synthesized using HPA is due to the poor size distribution of the nanocrystals as shown in Fig. 5.8a. The strong sharp peaks in the spectrum from nanocrystals synthesized using DDPA and ODPA indicate that their diameter is nearly monodisperse. The slight shift in

Chapter 5: Growth of Monodisperse CdS Nanowires

the absorption peak from 456 nm for nanocrystals synthesized using DDPA to 464 nm for that synthesized using ODPA indicates that the diameter of the nanowires has increased slightly.

5.3.2.6 Time-dependant shape evolution studies

To study the growth of these nanowires over time, aliquots were taken from the reaction flask at different times, cast onto the copper grids and examined in the TEM (Fig. 5.9a-e). It is clearly seen that the length of the nanowires increased significantly while the diameter increased only slightly during the first 2 h of reaction (refer to Fig. 5.9f).

Chapter 5: Growth of Monodisperse CdS Nanowires

Fig. 5.9. TEM images showing the temporal evolution of the CdS nanowires after (a) 5 min, (b) 15 min, (c) 30 min, (d) 1 h and (e) 2 h. (f) Graph showing the change in the average length of the CdS nanowires over time. (g) UV-Vis absorption (solid line) and PL emission spectrum (dotted line) of CdS nanowires obtained during nanowire growth.

Tiny nanoclusters can be observed in Fig. 5.9a and b. Their existence is an indication of the high monomer concentration present in the reaction. [74] A high monomer concentration supports 1D growth for the formation of long nanowires. These nanoclusters gradually decrease as the reaction time is extended due to dissolution. However, some tiny clusters are still present even after 2 h. Apart from the nanowires, a small quantity of branched structures can also be seen in Fig. 5.9a-e. These structures are often observed in the synthesis of II-VI anisotropic nanocrystals. [28, 29, 74, 75] This is

Chapter 5: Growth of Monodisperse CdS Nanowires

because of the presence of multiple facets on the nucleating crystal that can grow at high monomer concentration.

Fig. 5.9g shows the UV-Vis absorption and PL spectra of the CdS nanowires during nanocrystal growth. It can be seen that the absorption band becomes sharper during the reaction, which indicates that the diameter gradually become more monodisperse throughout the growth. The slight shift in the absorption peak indicates that the diameter of the nanowires increased slightly during the reaction. As the nanowires grow longer, the long axis (length direction) grows beyond the confinement regime, and the excitation peak only depends on the short axis (diameter) of the nanowires. This causes a red-shift in the emission peak. The sharp and narrow peak in the PL spectra also indicates that the samples has uniform diameter. With increasing reaction time, the PL peak shifts to a longer wavelength as the diameter of the CdS nanowires increases and becomes broader and less symmetrical due to near band-edge emission.

5.3.2.7 Potential applications and scale-up issues

After half and hour ultrasonic treatment, nanowires after cleaning can be stable in toluene for several hours. The nanowires were found to be stable for a few months. There was no change in their UV-Vis and PL spectra. The possible reason is due to the presence of ODPa on them. A remarkable feature of the synthesis reported here is that the CdS nanowires exhibit a higher degree of dispersibility than nanorods of the same diameter. These highly dispersible nanowires have the potential to be processed into devices, such as solar cells and transistors, more readily. The nanowires can easily form an interconnected network in a conducting polymer thin film when prepared using spin-coating. This is ideal for preparing the active layer of solar cells (refer to Fig. 5.10a-b). It is thought that an active layer with a more intimate mixture can increase the amount of

Chapter 5: Growth of Monodisperse CdS Nanowires

interaction between the conducting polymer chain and inorganic crystals. [34] This network structure can help in the exciton separation, the diffusion of free charges and the charge collection efficiency. [33] The PV applications of the monodisperse nanowires will be presented in Chapter 9.

In addition, nanowires with such small diameters (less than 5 nm) are ideal for the fabrication of nanowire MOSFETs to study true 1D transport at room temperature. [167] Such MOSFETs provide a larger voltage margin to observe true one-dimension carrier conduction compared with larger diameter nanowires. Furthermore, these high quality nanowires can be used as building blocks for memory and logic devices. [3, 170, 171, 184, 185]

In terms of scale-up of the synthesis, it should be readily to be scaled-up. The potential problems in the large scale production of these nanowires is the optimizing the precursor injection process, stirring speed and the precursor concentration.

Fig. 5.10. TEM images of the active layer of proposed hybrid solar cells with nanowire loadings of (a) 1:1 and (b) 1:3 by volume in a P3HT matrix.

5.4 Conclusions

In summary, monodisperse CdS nanowires were successfully synthesized in solution. It was found that the mole ratio of ODPA-to-Cd is one key factor in determining the morphology of the CdS nanocrystals in addition to the reaction temperature. We also found that the precursor ratio (Cd-to-S mole ratio), the precursor concentration and the precursor injection process can affect the morphology of the nanowires. In addition, it was found that Cd-ODPA complexes have both a low diffusion rate and a low reactivity compared to Cd-HPA or Cd-DDPA complexes. This makes ODPA a good candidate for generating nearly monodisperse and high aspect ratio nanowires. The possible growth mechanism of these monodisperse nanowires will be dynamically studied and proposed in Chapter 6. One remarkable feature of the CdS nanowires is their dispersibility. These highly dispersible CdS nanowires have the potential to be readily processed into devices, such as solar cells and transistors. Furthermore, our monodisperse nanowires could be aligned using an electric-field or self-assembled in solution for nanoelectronic applications.

Chapter 6: Dynamical Study of Growth Mechanism for monodisperse CdS Nanowires

6.1 Introduction

In 1993, Murray *et al.* pioneered a method to synthesize nearly monodisperse cadmium chalcogenide semiconductor nanodots. [26] Their synthesis is based on the pyrolysis of organometallic precursors by injection into a hot coordinating solvent. It is known as the hot coordinating (non-coordinating) solvents method. This method opens up a new generation of nearly monodisperse nanocrystals synthesis. Their protocol has been modified by several groups in the past 15 years. [5, 28, 29, 71, 74 - 79] For example, Alivisatos and co-workers synthesized nearly monodisperse II-VI nanodots, nanorods and tetrapods as well as core/shell rods and quantum dot-quantum well structures in a mixed surfactants system. [5, 28, 71, 83, 172] The good crystal quality and the excellent control over the morphologies of the nanocrystals synthesized have made this method very important in the development of light-emitting diodes [179, 186 - 190] and solar cells. [8, 38, 117] Currently, the growth mechanisms for the morphologies obtained were mainly discussed based on the size distribution focusing, [85] the selective-adsorption of surfactants on different crystallographic faces [29, 74, 83, 84] and the effective-monomer models. [19, 82] These theories can explain the formation of nanodots, nanorods and branches in this system very well. However, there are few reports in the literature where the formation mechanism of anisotropic nanocrystals under similar reaction conditions cannot be explained using the above models. [6] For example, Cozzolli *et al.* reported their synthesis of ZnSe nanodots, nanorods and branches using a monosurfactant amine system. [81] The formation of different morphologies, ranging from dots to a range of complex architectures, is controlled by the injection rate and the temperature conditions.

Chapter 6: Growth Mechanism for CdS Nanowires

It is because these conditions will allow the nucleation and growth of ZnSe nanocrystals to switch between the wurtzite and the zinc blend structures. Cho *et al.* synthesized PbSe nanowires in multicomponent surfactant mixtures. [86] In this case, the author showed that the formation of PbSe nanowires can be explained using an oriented attachment mechanism due to the presence of dipole moment in the nanodots.

In the previous studies (refer to Chapter 5 or [191]), we showed that CdS nanowires with a monodisperse diameter of 3.5 nm and a length of about 600 nm were successfully synthesized using hot coordination solvents method (refer to Fig. 5.2c and 5.9e). The chemicals and reaction conditions are similar to that of Peng and co-workers [29, 74] and Alivisatos and co-workers. [5, 83] We proposed that the ODPa-to-Cd mole ratio is a key factor in controlling the morphology of the nanocrystals because it affects both the cleavage rate of the P=S double bond and the nucleation/growth rate of the anisotropic nanocrystals. Through systematic investigation, we determined the optimum parameters for nanowire formation. In our case, nanowires were formed because the growth condition used was able to maintain a good balance between nucleation and growth. The detailed growth mechanism for these monodisperse nanowires was not clear at that moment. We were not able to agree with Kang *et al.* on the formation mechanism of CdS nanowires in similar reaction conditions. [84] They proposed a selective-adsorption model for their CdS nanowire formation based on HRTEM analysis. Their proof is that the seeding site can be either a zinc blende or wurtzite structure, while the wire is in a wurtzite structure; hence the nanowires formation is thought to be a kinetic-driven growth. Alternatively, in recent years, the oriented attachment mechanism was introduced to explain the formation of 1D nanocrystals. It refers to the phenomenon where the formation of the nanowires is driven by preferential attachment of dot-shaped nanocrystals along a given crystal orientation due to the dipole moment or the reduction

Chapter 6: Growth Mechanism for CdS Nanowires

of surface tension through the elimination of surfaces via attachment. [6, 31, 155, 192, 193] This growth mechanism was first reported in 1998 by Penn *et al.* to study TiO₂ crystal growth. [192] Since then, several systems with similar growth mechanism have been observed, including ZnO nanorods [194], CdSe [31, 155], CdTe [155] and PbSe [86] nanowires. Recently, Cao *et al.* synthesized CdS nanowires using hydrothermal method. [195] Instead of Ostwald ripening mechanism, which is thought to be the main mechanism for crystal growth, they proposed the oriented attachment mechanism to explain the formation of these nanowires.

6.2 Experimental Section

TBP (tributylphosphine) was purchased from Fluka. 2 g of TBP was used to dissolve 32 mg sulphur. Details of the other chemicals used and the synthesis method for CdS nanowires used in this study are the same as those described in Chapter 5.

6.3 Results and Discussion

In this study, we employed a shorter alkyl chain ligand of sulphur, TBP, to study the effect of sulphur complexing agent (we used TOP as sulphur complexing agent previously). It was found that TBP could greatly slow down the reaction. We found that similar situation also applies to the growth of CdSe nanowires (using TBP, aspect ratio of 28 was achievable – to be discussed in Chapter 7) using similar method. This observation is different from that of several groups. [75, 82, 196] For example, Yu *et al.* [82] and Washington II *et al.* [196] studied the influence of chain length of phosphines on the growth of CdSe and CdTe nanocrystals. They found that the reactivity of TOP is lower than that of TBP. They proposed that the possible reasons are (1) differences in the polarizability of R₃P-X (R=C₄H₉ or C₈H₁₇ and X=Se or Te) bond due to changes in the

Chapter 6: Growth Mechanism for CdS Nanowires

orbital hybridization in the R_3P and (2) the steric effect. TOP with longer chains has a higher degree of steric effect than that of TBP. This results in a decrease in packing density and thus a lower reaction rate for TOP. [196] However, they also acknowledged that these conclusions need further investigation due to poor reproducibility. We think that the difference in the reaction rate cannot be explained by the steric effect. We proposed that the difference in reaction rate is due to a higher binding energy of butyl chain (from TBP) than that of octyl chain (from TOP) which may prevent $P=X$ ($X=S$ or Se) double bond broken. Further studies are required to resolve this issue.

In this chapter, I will show that the growth mechanism of CdS can be better understood through both absorption studies and also morphological studies. The time-dependent optical properties of the nanocrystals are shown in Fig. 6.1a and b. It can be seen that there are three obvious peaks in the absorption spectra. The first peak is centered at 308 nm first started to appear at 30 min and disappeared after 70 min. It was proposed that the existence of a sharp peak at 308 nm is an indication of the presence of CdS clusters containing 17 Cd atoms (Cd_{17}) which size is about 0.8 nm. [197 - 199] They are commonly known as the magic sized nanoclusters which have a tetrahedron close-shell configuration with a zinc blend core. This kind of structure is thought to have the permanent dipole moment. [200] The second obvious peak is located at around 440 nm (refer to Fig. 6.1b). It can be seen that the peak intensity and peak center are gradually increasing and red shifting. The change in intensity of these two peaks is shown in the inset in Fig. 6.1a. It can be seen that the appearance of these two peaks is nearly simultaneous. This means that the nucleation and growth occurred at nearly the same time. The appearance of the peak 430 nm at 30 min after the last injection is due to the growth of previously formed nanoclusters (also refer to Fig. 6.1c). The size of these

Chapter 6: Growth Mechanism for CdS Nanowires

nanoclusters gradually increases as the reaction progressed. It changes from unobservable using TEM to about 3.5 nm in size (refer to Fig. 6.2).

Fig. 6.1. (a) The UV-Vis absorption spectra of CdS nanocrystals (after injection 10, 30, 40, 50, 60, 70 and 95 min) with the absorption intensity change at 308 nm and the 1st exciton absorption around 440 nm, (b) The expanded scale absorption spectra and (c) the color change of solution vs time.

Fig. 6.2. TEM images of tiny dots before attachment (50 min after 4th injection).

As the reaction progressed, the peak intensity at 308 nm reaches a maximum while the 1st exciton absorption at around 440 nm gradually becomes stronger and sharper. It is due

Chapter 6: Growth Mechanism for CdS Nanowires

to the development of larger nanoclusters at the expense of the magic sized nanoclusters. [29] The peak at 308 nm gradually becomes weaker and vanishes when reaction is carried on to 70 min. It is because of the reduction in the cleavage of alkylphosphine chalcogenide which is thought to generate semiconductor monomers. [183, 201] The nucleation of these semiconductor monomers gave rise to the magic sized nanoclusters. Beside, in Fig. 6.1b, an obvious broad peak at around 380 nm is due to the second excitation (1s-1p) absorption. [202, 203] This peak gradually red shifted from 370 nm after 50 min to 385 nm after 95 min with the development of the 1st exciton absorption peak. The gradually increasing intensity and decreasing width of the 1st and 2nd exciton absorption peaks is another indication of the monodispersity of the diameters of the nanocrystals as the growth progresses. [29, 74, 75, 78, 79, 196, 203]

In an attempt to study the cleavage of the P=S bond, FT-IR is used. FT-IR spectra of pure AOT, TOP-S complexes, CdS nanocrystals after injection 10, 60 and 95 min in the frequency range 400–2000 cm⁻¹ are shown in Fig. 6.3. It can be seen that the difference between pure TOP and TOP-S complexes spectrum is the presence of the vibration at around 598 cm⁻¹. The presence of a strong band at 598 cm⁻¹ in the spectrum of TOP-S complexes is due to the presence of R₃P=S. [204] This confirms that TOP and S formed a double bond after stirring at room temperature. In practice, after adding the yellow sulphur powder into TOP, the mixture becomes a colorless solution within one hour. The maximum peak shifting from 598 cm⁻¹ for TOP-S complexes to 575 cm⁻¹ in the CdS nanocrystals may indicate that the cleavage happens as indicated in the spectrum. Furthermore, the peak intensity of this region also decreased when comparing the spectra of after injection 10, 60 and 95 min. This results also suggest that the cleavage of P=S bond happened which is in good agreement with the results of Liu et al. [183] A weak band still exist even after 95 min. It is possible due to incomplete reaction in this system.

Chapter 6: Growth Mechanism for CdS Nanowires

The conversion of this reaction is about 30%. [193] A band at $1456 - 1470 \text{ cm}^{-1}$ is due to CH_2 vibration which can come from alkyl chain(s) of TOP, TOPO or ODPA. Three strong bands at 1174 , 1107 and 993 cm^{-1} are due to the $\text{P}=\text{O}$ stretching in TOPO. [204] TOPO comes from two sources. One is generated by the oxidation of TOP during reaction [183], the other part is added before reaction (please refer to section 5.2.2).

Fig. 6.3. FT-IR spectra of pure TOP, TOP-S complexes, CdS nanocrystals after injection 10, 60 and 95 min.

Based on the observations discussed above, we proposed a four stages growth mechanism for CdS nanowires (refer to Scheme 6.1). The first stage is the formation of CdS semiconductor monomers due to the cleavage of $\text{P}=\text{S}$ bond. Recently, Liu *et al.* studied the molecular mechanism of the precursor evolution in the synthesis of group II-VI semiconductor nanocrystals using NMR spectroscopy and mass spectrometry. [183] They found that the cleavage of alkylphosphine chalcogenide is the likely reaction leading to the formation of semiconductor monomers. Surfactants, such as ODPA, are responsible for the cleavage.

Chapter 6: Growth Mechanism for CdS Nanowires

Scheme 6.1. Schematic of CdS nanowire formation.

The second process is the nucleation of these semiconductor monomers to produce magic sized nanoclusters. In general, the nucleation is a very fast step and takes place once the semiconductor monomers are produced. The third process is the Growth I stage as discussed above. This proposed mechanism is different from that proposed by Pradhan *et al.* [31] They thought that the prewire aggregation or pearl-necklace-shaped nanowires (2.1 ± 0.3 nm) were formed by the aggregation of the magic sized nanoclusters (1-2 nm for CdSe). However, in our case, the size of magic sized nanoclusters (0.8 nm) [202] is much less than the diameter of nanowires (3.5 nm). Thus it is possible that there is a growth stage for these magic sized nanoclusters. We called these big nanoclusters as nanodots. The size of these nanodots is about 3.5 nm in diameter (refer to Fig. 6.2).

The crystal structure of these nanodots can be either zinc blende or wurtzite, while the wire has a wurtzite structure. [19, 84, 86, 155] In a similar study, Cozzoli *et al.* proposed that the wurtzite phase which is more stable than in the zinc blende structure can originate from three paths: zinc blende-wurtzite phase transition, direct wurtzite nucleation and wurtzite growth on zinc blende. [81] A sudden phase transition from zinc blende to wurtzite is possible if the nanocrystals reach a critical size. [74, 81] The last step is the growth of nanowires with oriented attachment and the recrystallization of the nanodots.

Chapter 6: Growth Mechanism for CdS Nanowires

Although it is impossible to directly observe the formation of nanowires in this case, several indirect observations during the growth of the nanowires suggested that monodisperse nanowires are formed by the oriented attachment. For example, the formation of CdS nanorods and nanowires is observed in the initial stage of reaction (refer to Fig. 6.4a-e) and the formation of CdS nanotubes is observed during the ligand exchange process in pyridine where the excess stabilizing surfactants have been partially removed (refer to Fig. 6.4f).

In Fig. 6.4a, it can be seen that nearly every rods are accompanied with dots of similar diameter. Some of the dots aggregate at the ends of the rods. In order to see the morphology of these short rods clearly, the circled area in the Fig. 6.4a was enlarged (refer to Fig. 6.4b). We can see that the diameter of these short rods is not uniform and these nanorods have an uneven shape at this moment. They might have just undergone the process of oriented aggregation and about to undergo recrystallization. At this stage, these nanodots firstly share a common crystallographic orientation, followed by the joining of these nanodots at a planar interface. [192, 195] This mechanism is contrary to Ostwald ripening mechanism which is thought to be the main manner for crystal growth in the past. Peng *et al.* previously found that Ostwald ripening happens at a lower concentration than that of intraparticle ripening. [29] The diameter and aspect ratio of these short rods are 3 nm and around 6 respectively. Fig. 6.4c shows nanocrystals that has been through a longer reaction time. It can be seen that even after aggregation and fusion, the rough surface on the nanorods and difference in contrast are still observable which implied that the recrystallization process is slow. The diameter and aspect ratio of these short wires are 3.3 nm and around 18 respectively.

Chapter 6: Growth Mechanism for CdS Nanowires

Fig. 6.4. TEM images of CdS nanorods: (a) 50 min after 4th injection, (b) partially enlarged (a), (c) 70 min after 4th injection. (d) 95 min after 4th injection, (e) nanowires and (f) nanotubes.

Fig. 6.4d shows that after the reaction carried on for three hours, these previously formed short wires grow longer via attachment of nanoclusters. The maximum length of them is

Chapter 6: Growth Mechanism for CdS Nanowires

about 800 nm. The diameter and aspect ratio are 3.5 nm and around 170 respectively. However, we can see that there still exist some nanoclusters and short rods. That means that the oriented attachment is a slow process. With the number or the concentration of nanoclusters decreased after long reaction time, the chance for them to grow any further decreases. The growth of these nanoclusters or short nanorods remain at their initial stage. Fig. 6.4e shows that even on well-formed nanowire, oriented attachment can still take place. An interesting observations made looking at these TEM samples is that the longer the reaction time, the fewer the number of nanodots attached to the short nanorods or nanowires. These results are consistent with that of Cao et al. [195] It further proves that the growth of nanowires followed the oriented attachment mechanism. In addition, other groups found that after partially removing stabilizing agents, nanowires or nanorods can be formed from tiny nanocrystals due to the induced dipole moment. [86, 192] Interestingly, in this study, we observed the formation of CdS nanotubes in pyridine during ligand exchange process after partially removing the stabilizing agents (refer to Fig. 6.4f).

We proposed that these previously formed nanodots or magic-sized nanoclusters slowly self-aggregate into a complex geometry during a long reaction time (4 days) and low temperature (60 °C). This is supposed to be another proof of oriented attachment. These observations are similar to that of several other groups. For example, Pradhan *et al.* and Tang *et al.* separately reported the formation of CdTe and CdSe nanowires by oriented attachment. [31, 155] The difference between these nanowires formation is in the growth mechanism proposed. Pradhan *et al.* thought that the reason for CdSe nanowires formation is due to the loosely associated nanoclusters and the chemically fused fragments, while Tang *et al.* thought that it is due to the dipole moment. They proposed that the cubic, zinc blend CdTe nanocrystals formed chainlike aggregates because of

Chapter 6: Growth Mechanism for CdS Nanowires

induced dipole-dipole interactions at the early stages of nanowires formation and then slowly recrystallized into hexagonal, wurtzite CdTe nanowires. This growth mechanism is similar to our case. Regardless of whether CdS nanodots formed from magic sized nanocluster are zinc blende or wurtzite structures, they have been reported to have dipole moment. [200] Thus, it is possible that these magic sized nanoclusters aggregate due to dipole-dipole interactions, and then go through a recrystallization under high temperature (310 °C) during reaction and finally transform into wurtzite CdS nanowires. These nanowires are confirmed to have wurtzite structure through XRD and HRTEM analysis. (refer to Chapter 5 or [191])

A more convincing evidence of the formation mechanism is another observation made during the TEM studies (refer to Fig. 6.5 a-c). It can be seen that some of the initially formed short nanowires are broken into segments when exposed to the electron beam for extended time. After several minutes, some dots gradually disappeared and others grow slightly bigger due to recrystallization. Such a reversible change supports that before the phase transition, nanodots aggregated together due to dipole-dipole interactions. These dots can be zinc blende (less stable) or wurtzite structure (more stable) as discussed above. [81] When exposed to the electron beam, the unstable short nanowires (that have not undergo recrystallization) are etched and break into short segments. Because this etching process is slow, some of the dots/short segments formed have time to recrystallize and become bigger initially. This observation is more direct and reliable than the study carried out by other research group. [31] In their study, they used both ultrasonic and annealing to study indirectly the growth mechanism of CdSe nanowires.

Chapter 6: Growth Mechanism for CdS Nanowires

Fig. 6.5. TEM images of nanowire “etched” by electron beam. (a) to (c) are observed at increasing time.

6.4 Conclusion

In summary, the formation mechanism for monodisperse CdS nanowires is presented in this study. The formation of nanowires can be divided into four stages. They are the formation of CdS semiconductor monomer, the nucleation of magic sized nanoclusters, the further growth of these nanoclusters to nanodots and finally the oriented attachment and recrystallization of nanodots. UV-Vis and TEM images are used to support this proposed mechanism. Other evidence that support this mechanism is the effect of electron beam on the nanowires. Some of the nanowires were etched under electron

Chapter 6: Growth Mechanism for CdS Nanowires

beam exposure and give rise to dots/short segments. During oriented attachment, the phase transition of nanodots from zinc blende structure to wurtzite structure takes place. This proposed mechanism can be proven by the previous study showing that the nanowires are wurtzite structure (confirmed by XRD, SAD and HRTEM analysis discussed in Chapter 5.) These studies reinforced our proposed new growth model for 1D CdS nanocrystals when synthesized using the hot coordinating solvents method.

Chapter 7: Controlling Growth of CdSe Nanowires through Surfactants Optimization

7.1 Introduction

In recent years, significant progresses have been made in controlling nanocrystal properties, such as size, shape, size/shape distribution and optical quality using the hot coordinating solvents method. [5, 6, 26, 29, 71, 75 - 79] With all of these improvements, CdSe nanocrystals has become one of the most well studied materials in terms of overall control in its morphology and properties. [82] Despite the success in producing high-quality CdSe nanodots, [26] nanorods, [5, 6, 29] tetrapods, [83] as well as quantum dot-quantum well structures, [30] it is still a challenge to synthesize nanowires in a controllable manner using this method. [31] There are several other methods that can be used to synthesize nanowires in solution, including SLS, hydrothermal/solvothermal, oriented attachment process. For example, SLS method has been proven to be a useful approach for producing nanowires in recent years. [173 - 175] This method has several advantages, including narrow diameter distributions and a comparatively low reaction temperature ($<350\text{ }^{\circ}\text{C}$). [173, 176] However, there are several disadvantages related to this method that has been discussed in Chapter 2.

Due to the degree of control that is offered by 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 nanorods reached a length of 50 nm, their uniformity along the growth direction became poor and branching

Chapter 7: Controlling Growth of CdSe Nanowires

was often observed. [6, 31, 205] Recently, Kang *et al.* [84] and our group (refer to Chapter 5 or [191]) 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, respectively. In that study, we optimized the parameters which favor the formation of high aspect ratio nanocrystals via systematic investigation. It was proposed that the reason of formation of nanowires is due to a good balance between nucleation and growth. CdSe nanorods produced following the same method were short and this was proposed to be due to the faster cleavage rate of P=Se than 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 has reduced substantially. It is critical for high precursor concentration to be maintained for anisotropic growth. Thus, we think it is possible to produce CdSe nanowires if we can manipulate the cleavage rate of P=Se and Cd-complexes via changing their ligands to achieve a good balance between nucleation and growth. After investigating the effect of the type of ligands both for Cd-complexes and Se-complexes, the reaction temperature, the precursor concentration and the precursor injection process on the morphology of the nanocrystals, the nanowires with a length of 220 nm and a diameter of 8 nm were successfully synthesized.

High aspect ratio semiconductor nanorods or nanowires are potential building blocks for electronic, optical and life sciences applications owing to their attractive physical properties. [3, 4, 6 - 9] One such application is PV cells. It is because high aspect ratio nanorods or nanowires can easily form an interconnected network in the conducting polymer thin film for efficient charge transport. The solubility of these nanowires in polymer is also an important aspect to consider. Research found that an active layer with a more intimate mixture can increase the amount of interaction between the conducting

Chapter 7: Controlling Growth of CdSe Nanowires

polymer chain and semiconductor nanorods or nanowires. [34] Such hybrid network structure as the active layer for photovoltaic application is thought to improve efficiency of exciton separation, charge diffusion and collection. [33]

7.2 Experimental Section

7.2.1 Materials

Selenium (99.99%) and TPP (95%) were purchased from Kanto Chemicals Inc. and Tokyo Kasei Kogyo Co. Ltd. respectively. Other chemicals used in this study are the same as those in Chapter 5 and Chapter 6.

7.2.2 Synthesis of CdSe nanocrystals

In a typical synthesis, 128 mg of CdO, 0.500 g DDPA (0.668 g of ODPa or 0.232 g of HPA) and 3.0 g 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 N₂ 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 78 mg selenium in 2.0 g of TOP (2.0 g of TBP or 2.0 g of TPP which is heated up to 200 °C due to its high boiling point) was injected by multiple injections (4 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 and application.

7.3 Results and Discussion

7.3.1 Phase Analysis

Typical thin film XRD patterns of the as-prepared CdSe nanocrystals with different dimensions and the positions of the X-ray peaks for hexagonal CdSe from the JCPDS are shown in Fig. 7.1. It can be seen that all reflection peaks of the CdSe nanocrystals can be indexed using hexagonal CdSe (JCPDS card No. 08-0459). In addition, it is found that in these three cases, some lines of reflections are enhanced while others are suppressed compared to the bulk wurtzite CdSe pattern (refer to Fig. 7.1d). These changes likely arise from the substrate-induced nanocrystal orientation. [7] This phenomenon has been observed with CdSe, [205] and CdTe [206] nanowires. Grebinski et al. and Kuno et al. proposed that in an X-ray diffractometer, regardless of powder or thin film XRD, only planes parallel to the surface produce strong diffraction lines. [7, 205] They assumed that these one-dimension (1D) nanocrystals lie nearly flat on the substrate during sample preparation. The samples are prepared by drop casting the nanocrystalline solution onto the substrate. As the solvent dried, these nanocrystals are packed and aligned. In the case of a wurtzite CdSe 1D nanocrystals with a [001] growth axis, only planes parallel to this axis reflect strongly and can be observed in the patterns. [7, 205] Therefore, planes which contribute significantly to the XRD patterns are (100), (110) and (200) planes as shown in Fig. 7.1. With the increasing aspect ratio, the intensity of (100) and (110) reflections becomes stronger. However, we proposed that on top of above substrate-induced orientation assumption, another probable reason for these absent or suppressed reflections is likely that they are more sensitive to stacking faults. That is to say the diffraction from planes other than the (001) planes may be reduced because of the presence of the stacking faults. As the wires grow longer, the (001) reflections are the least affected by stacking faults. The possibility of the higher aspect ratio nanocrystals to

Chapter 7: Controlling Growth of CdSe Nanowires

lie flat on the substrate is high. In the case of the short rods, not all the rods lie flat on the substrate and hence the (100) reflections is seen to be stronger compared to the other reflections for the shorter rods than the nanowires.

Fig. 7.1. Typical XRD patterns of CdSe nanocrystals with different dimensions: (a) nanowires (220 x 8 nm), (b) long nanorods (83 x 9 nm), (c) short nanorods (20 x 7 nm) and (d) JCPDS hexagonal CdSe pattern.

HRTEM image and diffraction pattern of a single CdSe nanowire is shown in Fig. 7.2a and b. The lattice fringes show that the nanowire has the characteristic of a single crystal. The 0.35 nm spacing is consistent with (001) lattice plane spacing of wurtzite CdSe. This results also indicate that the growth of nanowire is preferred along the [001] direction, which is in agreement with results from other groups. [26, 29, 74, 84, 85] In this study, even these HRTEM images do not show any defects, some stacking faults and branches are still often observed during the TEM testing. The compositional analysis of as-prepared CdSe nanocrystals using EDAX is shown in Fig. 7.2c. The atomic percentages for Cd and Se are 53% and 47%, respectively. This EDAX spectrum confirmed that the nanocrystals are indeed composed of Cd and Se with no impurities. In order to observe

Chapter 7: Controlling Growth of CdSe Nanowires

the 3D shape of individual nanocrystals, AFM scans were carried out. An AFM height image of CdSe short nanowires is shown in Fig. 7.2d. We can see that lots of individual nanowires randomly lied on the substrate. We are not able to know the exactly height (diameter) of these nanowires because it nearly arrives the resolution limit of AFM. However, we can measure that the width (also diameter) of these nanowires is about 8 nm which is good agreement with TEM testing.

Fig. 7.2. (a) HRTEM image, (b) diffraction pattern of a single CdSe nanowire, (c) the EDAX spectrum of the as-prepared CdSe nanowires and (d) AFM height image of CdSe short nanowires. The scanning area is 1 μm x 1 μm .

7.3.2 Morphological studies

7.3.2.1 Influence of different ligands on Cd-complexes

In the past, the major role of surfactants such as phosphonic acids, phosphines, amines and carboxylic acids has popularly been believed to be the selective adhesion to certain nanocrystals surface, as well as controlling monomer solubility. [81] Recent studies show that these surfactants are also ultimately responsible for cleavage of the phosphorus chalcogenide double bond. [183] This process is supposed to lead to the formation of semiconductor monomers, while the rate of this cleavage affects crystal nucleation and growth. Based on these findings, we will study the influence of different ligands on Cd- and Se-complexes, respectively.

We first investigated the effect of different ligands for Cd-complexes on the morphology of nanocrystals. In this study, three different phosphonic acids are used as ligands for Cd-complexes in the reaction. Their chemical structures are shown previously in Fig. 5.7. 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, have better control in morphology of the nanocrystals than those with shorter alkyl chains, such as HPA. HPA produces nanocrystals with morphologies ranging from dots, rods to branches. The diameter of these nanocrystals was not uniform along the growth direction. This ligand hence has very poor control on the morphologies of the nanocrystals (refer to Fig. 7.3a).

Chapter 7: Controlling Growth of CdSe Nanowires

Fig. 7.3. TEM images of CdSe nanocrystals synthesized with different ligands for Cd at 310 °C: (a) HPA, (b) DDPA and (c) ODPA. The ligand used for Se is TOP.

Using DDPA and ODPA, nearly monodisperse nanorods are formed as shown in Fig. 7.3b and c, respectively. The diameter of the nanocrystals synthesized using both DDPA and ODPA is equal to 9 nm. The length of nanorods synthesized using DDPA is 83 nm and using ODPA, we obtained nanorods with length of about 41 nm. The morphology of the nanocrystals synthesized using DDPA is well-controlled compare with those synthesized using ODPA. This result is not as we expected and is different from that of the CdS nanowires case which we reported previously (refer to Chapter 5 or [191]). Previous studies showed that the reactivity of Cd-ligand complexes affects the P=S

Chapter 7: Controlling Growth of CdSe Nanowires

cleavage kinetics and the nucleation/growth rate of anisotropic nanocrystals. [183] Complexes with lower reactivity allow the monomers to adjust their position on the surface of the nanocrystals before the binding occurs. [74] 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 seen from Fig. 7.3, DDPA help to generate the highest aspect ratio nanorods. Hence, there is at least on other factor that also affects the growth. We think that the rate at which P=Se is broken is possible to be another factor affecting the morphology of the nanocrystals. It is reported that the cleavage rate of P=Se is faster than that of P=S [183, 191] 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 P=E (E=S and Se) also affects balance between nucleation and growth. A good balance will favor the formation of the nanocrystals with a higher aspect ratio. In the following, we will study the effect of different ligands on the nanocrystal morphology when using DDPA as a Cd-complexes ligand.

7.3.2.2 Influence of different ligands on Se-complexes

Comparing with Cd-complexes, the different ligands for Se-complexing were found to have strong effect on the morphology. Three different phosphines are used as ligands for Se-complexes in the reaction and their chemical structures are shown in Fig. 7.4.

Fig. 7.4. Chemical structures of ligands for Se-complexes.

Chapter 7: Controlling Growth of CdSe Nanowires

In this study, it was observed that the time taken for the color of the solution with TBP=Se to change is slower by several minutes compared to that taken by the solution containing TOP=Se. The color for the solution containing TBP=Se went from red after the 2nd injection, to brown after the 3rd injection, then to dark brown after the 4th injection. For the solution containing TOP=Se, the changes take place between the 1st and 2nd injection. This difference in reaction speed between TBP complexed solution and TOP complexed solution was also found to be the case during CdS nanowires synthesis which has been proposed in Chapter 6. In that study, we proposed that the difference in the reaction rates cannot be explained by the steric effect because the octyl group offers even larger steric hindrance to the cleavage of the P=X (X = S or Se) bond compared to the butyl group. It is very likely that TBP=X has a stronger binding energy compared to TOP=X because the octyl group is less stabilizing to the P=X bond compared to the butyl group. Thus, the steric effect can not be used to explain the reaction rate difference between TOP and TBP.

On the other hand, the difference in reaction rate is readily observed when using TPP. During the synthesis, the color change for TPP is significantly slower (around 30 min) than those using TOP and TBP as ligands. During the cleavage, its three benzene rings will prevent alkylphosphonate attack to (TPP=Se)-Cd. Fig. 7.5 shows a schematic on how the proposed attack may take place in the presence of the three different ligands. The scheme was first proposed by Liu et al. [183]. We proposed that this difference is due to the steric effect. The reason will be presented as below.

Chapter 7: Controlling Growth of CdSe Nanowires

Fig. 7.5. A comparison of steric effect with different ligands on Se-complexes.

Fig. 7.6a-b shows TEM images of nanocrystals grown with TBP and TPP ligands. Using TBP, nanorods formed are mainly 43 nm in length and 5 nm in diameter. Comparing with the nanocrystals produced by TOP ((refer to Fig. 7.4b), both the length and diameter are reduced by nearly half for those synthesized using TBP. However, the aspect ratio of the nanocrystals are close. This is due to the effect of TBP on both the facets contributing to the short axis and the long axis of the nanocrystals. Using TPP, a mixture of dots, short rods, triangle rods and hexagonal disks is obtained as shown in Fig. 7.6b. It can be seen the less control over morphology using TPP. Fig. 7.6c shows HRTEM image of a hexagonal disk. The reason of different morphology of these nanocrystals when using TBP, TOP and TPP likely arises from the different cleavage rate of P=Se. Lower cleavage rate such as TPP and TBP results in lower CdSe monomer concentrations in the initial stage. This did not favor an anisotropic growth with a higher aspect ratio. [5, 29, 74] Thus, it was found that DDPA and TOP as ligands both for Cd- and Se-complexes can achieve a good balance between nucleation and growth. This kind of combination will be used to explore the possibility of the synthesis of CdSe nanowires.

Fig. 7.6d shows the UV-Vis absorption spectra of the nanocrystals synthesized using TBP, TOP and TPP ligands, respectively. A red-shift in the absorption peak from 636 nm using TBP, to 677 nm using TOP and then around 685 nm using TPP indicates that the

Chapter 7: Controlling Growth of CdSe Nanowires

diameter of the nanocrystals has increased. The relative broad peak for TPP is due to its poor size distribution and difference in morphology of the nanocrystals (refer to Fig. 7.6b).

Fig. 7.6. TEM images of CdSe nanorods synthesized with DDPA and (a) TBP or (b) TPP ligands. (c) HRTEM images of a single hexagonal CdSe disk. (d) UV-Vis absorption spectra of the nanocrystals synthesized with TBP, TOP and TPP ligands.

7.3.2.3 Influence of the reaction temperature

The reaction temperature was found to be another factor affecting the cleavage rate. It is because regardless of growth mechanism, the cleavage of P=Se double bond is a thermodynamic process. [183, 196] In the previous studies, it is found that the required

Chapter 7: Controlling Growth of CdSe Nanowires

reaction temperature for 1D CdSe nanocrystals (260 – 290 °C) is lower than that of CdS nanocrystals (300 – 315 °C). [75, 84, 183, 191] Contrary to the findings, we observed that decreasing the reaction temperature can lead to a decrease in the highest aspect ratio of the nanorods (refer to Fig. 7.4b and Fig. 7.7a-b). The diameter of nanorods synthesized at 250 °C and 280 °C is 3.3 nm and 6 nm, while the length for them is 10-30 nm and 64 nm. As shown in Fig. 7.4b, 1D CdSe nanocrystals synthesized at 310 °C are 9 nm in diameter and 83 nm in length. The morphology of these nanocrystals is well-controlled compared to those synthesized at lower temperature. In addition, the surface of CdSe nanorods synthesized at lower temperature (250 °C and 280 °C) is less uniform than that at 310 °C. The temperature dependence of aspect ratio can be seen as another form of the concentration dependence. [74, 196] As mentioned above, the cleavage is a thermodynamic process and affected by temperature. Lower reaction temperature results in lower cleavage rate and lower monomer concentrations in the solution. As a result, lower monomer concentrations do not favor anisotropic growth which requires a presence of a high monomer concentration after the nucleation stage. [74]

When the reaction temperature is increased to 340 °C, nanorods with a diameter of 16 nm and a length of 42 nm are obtained. The aspect ratio of nanorods is decreased. It is because although 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. This provides the monomers less time to adjust their position on the surface of the nanocrystal before the binding occurs. Thus, the morphology of nanocrystals is less controlled (refer to Fig. 7.7c). In addition, there exist some sphenoid structures which are indicated by the dotted circles in Fig. 7.7c. This structure feature is observed after the 2nd injection (refer to Fig. 7.7d). When the reaction goes on, the diameter increases and the tip becomes

Chapter 7: Controlling Growth of CdSe Nanowires

blunt due to an intraparticle ripening. [19] Thus, in this study, it is found that the reaction temperature of 310 °C is an optimum condition for high aspect ratio growth which may favor a good balance between nucleation and growth.

Fig. 7.7. TEM images of CdSe nanocrystals synthesized with DDPA at (a) 250 °C, (b) 280 °C, (c) 340 °C and (d) HRTEM image of a sphenoid structure.

7.3.2.4 Influence of the precursor concentration

In this study, with fix the total amount of reactants fixed at 5.706 g, changing the two precursor concentrations was found to change the aspect ratio of the nanocrystals substantially. When the precursor concentration is doubled, the reaction yields nanowires with nearly monodisperse diameter of 8 nm and a length of 220 nm (refer to Fig. 7.8a).

Chapter 7: Controlling Growth of CdSe Nanowires

These results showed that in order for the growth of longer nanowires, a higher precursor concentration is required compared to the growth of shorter ones (refer to Fig. 7.4b). [5]

Fig. 7.8. TEM images of CdSe nanowires synthesized using DDPA and with varying precursor concentrations (in comparison with the concentration used for synthesizing sample shown in Fig. 7.4b): (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.

However, a further increase in the precursor concentration showed adverse effect on the distribution of the length, diameter and the aspect ratio of the nanocrystals. The length of the nanocrystals ranged from 20 to 300 nm and the diameter was ranging from 5 to 12 nm (refer to Fig. 7.8b). 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. [19, 74] A higher precursor concentration should result in either longer or branched anisotropic nanocrystals. This is true for increasing precursor concentration by two times (compared to the baseline concentration of 0.18 mol/kg) in our case. But it does not work when the concentration is increased by three times.

Chapter 7: Controlling Growth of CdSe Nanowires

The overall precursor concentration that we are working with when the concentration was increased three times (0.53 mol/kg) is higher than that used by other group (0.43 mol/kg). [74] It is possible that due to the difference in the reactants (for example, they used ODPa or TDPA as Cd complexing agent and TBP mixed with TOP as Se complexing agent) and the injection conditions (for example, the injection and growth temperature of their studies are at 350 °C and 300 °C) between our experiments and that of other groups. It was found by several groups that the injection process can also affect the nanocrystal morphology. We will discuss this effect in the next section. However, we think the reason for the formation of a mixture of nanowires and nanorods at even higher concentration may be due to a higher number of nuclei at the initial stage of the reaction. (refer to Chapter 5 or [191]) The speed of nucleation and growth can be accelerated by increasing the precursor concentration. [74] A fast nucleation and growth speed may lead to less time for monomers to arrange themselves before binding on the surface of the nanocrystals as we discussed in Chapter 5. Thus the morphology of nanocrystals in increasing the concentration three times is less well-controlled.

7.3.2.5 Influence of the precursor injection process

In this work, we studied the effect of injection process on the morphology of the nanocrystals under twice precursor concentration conditions. It was found that there is no obvious difference in the morphology between continuous injection for 16 min and multiple injections (4 times x 2 min interval x 2 min injection duration). The length of the nanorods is about 220 nm and their diameter is around 8 nm (not shown). However, when the injection interval is increased to 4 min or even longer, the length of nanocrystals is decreased while diameter is kept constant. The nanorods are obtained with length around 170 nm and poor size distribution. The long interval multiple refurnishing monomer was not able to maintain a high monomer concentration in the solution which is thought to be prerequisite for the anisotropic growth with a high aspect

Chapter 7: Controlling Growth of CdSe Nanowires

ratio. [5, 19] Thus, the optimum conditions for the growth of CdSe nanowires are using DDPA and TOP as precursors' ligands with twice the baseline concentration and multiple injections at short intervals or continuous injection process.

A summary of the effect of the various reaction parameters on the growth of nanocrystals is shown in Fig. 7.9. (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. [183] 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. [19, 29, 74] (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.

Fig. 7.9 Scheme showing how various reaction parameters affect the growth of nanocrystals.

7.3.2.6 Time-dependent studies

A time-dependent study of growth of CdSe nanocrystals is shown in Fig. 7.10. It can be seen that after the 3rd injection of TOP=Se, nanoneedles are formed which are 75 nm in

Chapter 7: Controlling Growth of CdSe Nanowires

length and 6.5 nm in diameter (refer to Fig. 7.10a). As more precursors were subsequently injected and reaction progressed, these nanoneedles grew longer and slightly thicker. At 7 min after the 4th injection, the length of the nanowires grew to 220 nm and their diameter increased to 8 nm. This observation is consistent with literatures. [29, 74, 85] At 30 min after the 4th injection, the length and diameter of nanorods grew to 85 to 230 nm and 9 nm respectively as shown in Fig. 7.10c. An increase in the diameter and a decrease in the aspect ratio of nanorods are due to intraparticle ripening, which means that the monomer migrated from the long sharp end to the side of the nanorods. [24, 83] Similar behavior was often observed during the synthesis of other II-VI group nanorods using this method. [5, 24, 29, 74, 83] It is proposed that a balance between the kinetic and the thermodynamic growth regimes strongly affects the final morphology of the nanocrystals. [18] Anisotropic growth of nanocrystals along their c-axis is favored under a kinetic growth regime if a high precursor concentration is present. Based on above time-dependent TEM images, we can deduce that the most widely accepted model - effective monomer model which is proposed by Peng et al. to explain the shape evolution of CdSe nanocrystals. [5, 19, 74] According to this model, the growth of anisotropic nanocrystals mainly depends on the effective monomer concentration. Thus, these nanocrystals go through three stages and they are 1D growth stage, 3D growth stage and 1D to 2D ripening stage as the effective monomer concentration decreases. However, in some cases, we observed that the nanocrystals may follow oriented attachment mechanism. There are many tiny nanodots accompany the nanorods. With the new precursor injected, these tiny nanodots grew and attached to the previously formed nanorods (not shown). As the reaction continues, these dots fused and became part of the nanocrystals. [195] The most possible reason for the oriented attachment is the presence of dipole moment in these CdSe nanodots. [31, 155]

Chapter 7: Controlling Growth of CdSe Nanowires

Fig. 7.10. Time-dependent TEM images of CdSe nanorods (a) 2 min after the 3rd injection, (b) 7 min after the 4th injection and (c) 30 min after the 4th injection. (d) Time-dependent UV-Vis absorption spectra of CdSe nanocrystals.

Fig. 7.10d shows UV-Vis absorption spectra of the CdSe nanocrystals at different stages of growth. It can be seen that there are two obvious peaks observed in the absorption spectra after the 3rd injection 2 min. 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. [74, 155] These clusters are commonly known as the magic sized nanoclusters and they have a tetrahedron close-shell configuration with a zinc blend core. [6, 19, 207] As the reaction progressed, the peak intensity at 349 nm is gradually decreased. It almost completely vanishes 7 min

Chapter 7: Controlling Growth of CdSe Nanowires

after the 4th injection. This change tells us that previous formed CdSe clusters (Cd_{17}) have been converted to larger or more complicated nanoclusters. The second peak, namely the 1st exciton absorption, is located at around 650 - 690 nm. Its intensity is gradually increasing and the peak center is red-shifting as the reaction processed. This shift is consistent with the increase in diameter of the nanorods.

7.4 Conclusions

In summary, nearly monodisperse CdSe nanowires with a diameter of 8 nm and a length of 220 nm were successfully synthesized using catalyst-free solution-based method. The effects of ligand type for both Cd- and Se-complexes, the reaction temperature, the precursor concentration and the precursor injection process on nanocrystal morphology were systematically studied. Varying these parameters can change the morphology of nanocrystals from short rods to wires. It was found that the morphologies of the nanocrystal 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 $\text{P}=\text{Se}$ is broken is another key factor affecting the morphology of the nanocrystals. It was found that TOP as the ligand for Se-complexes can well match with DDPA as the ligand for Cd-complexes. This is because a good balance is achieved using them which favor the anisotropic growth with higher aspect ratio. It is also found that the decreasing 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 increased in the precursor concentration results in the increased both in branching of the nanocrystals and in size distribution. The effect of these reaction parameters on the growth of CdSe nanowires is also summarized. The time-dependent

Chapter 7: Controlling Growth of CdSe Nanowires

morphological and optical studies imply that the most widely accepted model – 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 transistors and PV cells. The later one will be presented in Chapter 9.

Chapter 8: Controlled Synthesis of CdTe and CdSe Multi-block Heteronanostructures (HNSs)

8.1 Introduction

As showed previously in Chapter 5 - 7, we have successfully synthesized 1D cadmium chalcogenide nanocrystals with good size distribution, controllable growth and high aspect ratio using hot coordinating solvents method. On top of being able to control anisotropy in growth for binary compounds, it is also possible to extend this solution-based synthesis method to synthesize heteronanostructures (HNSs). In this study, we attempt to synthesize a novel CdTe and CdSe multiple-block HNSs using this method.

HNS dots or rods represent a convenient approach to the development of nanoscale building blocks, because they combine inorganic parts with different functionalities in the same particle. [83, 208] Such a structure can restrict the movement of charge carriers (electrons or holes) and force them into quantum confinement leading to a set of discrete energy levels at which the carriers can exist. [11] It was found by Peng *et al.* that HNSs have rise times and biexponential decays longer than those of nanorods with similar dimensions. In PV applications longer charge carrier or recombination lifetimes are desirable because more charge can be transferred. [209] Furthermore, the proximity between the different blocks may be an advantage from the charge separation point of view. Blocks based on semiconductor nanorods will exhibit a lower lasing threshold, emit linearly polarized light and also give rise to improve PCE for PV applications. [8, 12, 210, 211] The formation of these structures is essential for the future applications of semiconductor nanocrystals in nanoscale devices and at the same time, this is important in the exploitation of the properties of nanomaterials. However, the strategies currently

Chapter 8: Controlled Synthesis of HNSs

employed to connect quantum dots or rods mainly involve the use of an organic coupling agent. [212, 213] These methods have limited control over the coupling conditions and the geometry and complexity of the assemblies. [172]

As an alternative to the organic coupling method, a great deal of research has been done on the direct synthesis of heterostructure nanorods or nanowires using VLS, [214] SLS [215] or CVD. [216] Dick *et al.* synthesized multiple branched GaP nanotrees via the VLS method with the aid of gold aerosol nanocrystal catalyst activation. [214] Wu *et al.* developed a hybrid pulsed laser ablation-CVD (PLA-CVD) process for the synthesis of block-by-block Si/SiGe heteronanowires. [216] However, there are some disadvantages related to these methods. One disadvantage is that there is little control over the dimensions of the heteronanowires; their diameters can vary by several hundred nanometers and they often have a polycrystalline structure with less ideal interfaces. [216] On top of that, these methods require expensive high vacuum equipment and/or catalysts.

Alternatively, the growth of colloidal elongated nanocrystals from homogeneous solutions seems reasonable due to its controllable growth and simplicity. These methods include the micelle or reverse micelle method, [24, 144] the hydrothermal method [25, 126] and the hot coordinating solvents method. [11, 83, 172, 191, 210] In these methods, especially the hot coordinating solvents method, has potential to synthesize relatively complicated heterostructures. In the past years, research on the heterostructures including core/shell, linear and 3D heterostructure makes great progress. Several groups have actively investigated this kind of configuration. [27, 217 - 223] For example, Milliron *et al.* synthesized several cadmium chalcogenide heterostructure nanocrystals with linear and branched topologies using this method. [172] Very recently, Korgel and co-workers

Chapter 8: Controlled Synthesis of HNSs

synthesized CdTe/CdSe/CdTe heterostructures nanorods by sequential reactant injection. [224] They further studied the coalescence and interface diffusion of prepared heterostructure nanorods. [225]

Although several groups have reported that a linear CdSe block followed by CdTe extensions heterostructures, [172, 221, 222, 224 - 226] the growth of linear CdTe block followed by CdSe extensions is rarely reported to date. Moreover, the possibility of forming increasingly complex structures, such as multi-block HNSs, opens the door to more complex 1D materials and devices exploiting the unique properties of nanomaterials. In this study, we aimed to synthesize a multi-block CdTe and CdSe HNS using the hot coordinating solvents method by sequential injection of two different precursors-TOPTe and TOPSe. This is the first attempt to synthesize multiple block HNSs with this configuration. This investigation may help in the building up more complex functional nanoscale devices and nanomaterials because the multi-step procedure allows a level of control and flexibility.

8.2 Experimental Section

8.2.1 Materials

Tellurium (99.9%) and lauroyl peroxide (97%) were purchased from Sigma-Aldrich and Lancaster, respectively. Other chemicals used in this study are the same as those in Chapter 5 and Chapter 7. Two stock precursor solutions were prepared. For the first stock solution (TOPTe), 127.6 mg Te powder was dissolved into 2.0 ml TOP by heating to 80 °C. For the second stock solution (TOPSe), 78.6 mg Se powder was dissolved into 1.5 ml TOP at room temperature.

Chapter 8: Controlled Synthesis of HNSs

8.2.2 Synthesis of CdSe and CdTe multi-block HNSs

The HNSs were prepared using a modification of Peng's procedure for cadmium chalcogenide nanocrystals. [74] Firstly, CdTe nanorods were synthesized in a mixture of 1.98 g Cd-ODPA complexes (0.2054 g CdO, 0.8928 g ODPA and 0.88 g TOPO) and 2.02 g TOPO aged overnight at 350 °C. After the temperature was stabilized at 330 °C, half of the 1st stock solution (TOPTe) was injected in two injections. We call this the 1st injection. After four minutes of reaction, 0.8 ml of the 2nd stock solution (TOPSe) was gradually injected into the above solution using another two injections and we called this the 2nd injection. The reaction was carried on for an additional five minutes. The other half of the 1st stock solution (TOPTe) was injected into the above solution using two injections and we called this the 3rd injection. The reaction was stopped after seven minutes. The nanocrystals were purified by precipitating the particles from toluene with excess ethanol. The nanocrystals for EELS studies were etched with lauroyl peroxide to remove the ligands and to some certain extent the surface of the nanocrystals. [227]

8.2.3 Characterization

TEM was carried out using a monochromated FEI Titan electron microscope with a field emission gun using acceleration voltages of 120 kV and 300 kV. TEM samples were prepared by dropping one or two drops of the HNSs solution onto carbon-coated copper grids. EELS and high angle annular dark field (HAADF) were used to study the chemical composition along the length of the HNSs. In EELS test, sample is exposed to electron beam with a known narrow range of kinetic energies. Some of electrons will undergo inelastic scattering. This process will result in energy loss and paths deflecting. The amount of energy loss can be measured through an electron spectrometer and interpreted

Chapter 8: Controlled Synthesis of HNSs

in terms of the reason of the energy loss. The energy loss can reveal the composition of the sample.

8.3 Results and Discussion

Thin film XRD patterns from CdTe nanorods and the CdTe/CdSe multi-block HNSs are shown in Fig. 8.1. The pattern of the CdTe nanorods indicates the presence of the hexagonal structure. In addition, the strong and sharp diffraction peak at $2\theta = 23.7^\circ$ suggests that the crystals are extended along the c -axis. By comparing the diffraction pattern of the CdTe nanorods prepared after the first injection with that of bulk hexagonal CdTe, it was found that the pattern of the CdTe nanorods shows a high degree of distortion in the intensity ratios due to shape anisotropy which leads to an enhancement of the reflections associated with crystalline domains along the c -axis. [5]

Fig 8.1. Thin film XRD patterns of CdTe nanorods and CdTe/CdSe multi-block HNSs after the 2nd and 3rd injection are compared with the JCPDS hexagonal CdTe and CdSe patterns.

The diffraction patterns for CdTe/CdSe HNSs after the 2nd injection show that the HNSs have the same structure as CdTe and CdSe but with slightly different lattice parameters. For example, three new peaks of hexagonal CdSe at faces (110), (103) and (200) are

Chapter 8: Controlled Synthesis of HNSs

present. Meanwhile, the original peaks of CdTe nanorods are kept such as (002) and (110) as shown in Fig. 1. This suggests that CdSe is growing on CdTe epitaxially rather than as separate crystals, which is in good agreement with the HRTEM and EELS line scan analysis shown later. The (002) peak becomes broadened and shifted slightly due to the smaller lattice parameter of CdSe. After the 3rd injection, these peaks at faces of (110), (103) and (200) become less sharp and the (002) peak becomes even broader and shifts slightly. It comes from the effect of Te precursor injection. The slight shift of the (002) peak in XRD patterns and the shift in the optical absorption of the HNSs which will be discussed later tell us that there are at most a few monolayers of CdSe on the sides of the previously formed HNSs. [172, 228] Therefore, we conclude that hexagonal CdSe and CdTe blocks grow on the ends of the previously formed CdTe blocks after the secondary injection.

Representative TEM images showing evolution in size and shape of CdTe/CdSe HNS are shown in Fig. 8.2. A comparison between the TEM images of samples taken before and after the 2nd injection (Fig. 8.2a and b) indicates that the mean length of the nanorods increases without any significant change in diameter upon growth of the secondary material. Different facets of a crystal have different atomic arrangements which affect the ability of a surfactant to coordinate. This results in different surface energies and therefore a variation in the growth rates on different facets. Cadmium chalcogenide nanocrystals can grow anisotropically as rods or into more complex shapes, such as branched structures in the presence of a high monomer concentration. [5, 28, 29, 74] When these wurtzite structure materials grow in the presence of suitable surfactants, the lateral non-polar facets have much lower growth rates than the basal polar facets, therefore the nanocrystals grow preferentially along their unique *c*-axis. [208] The higher

Chapter 8: Controlled Synthesis of HNSs

reactivity of the ends of such nanorods provides a higher possibility to nucleate a second material on these locations. [172, 220]

Fig. 8.2. TEM images of CdTe/CdSe multi-block HNSs synthesized from (a) CdTe nanorods, (b) after the 2nd injection and (c) after the 3rd injection.

In Fig. 8.2b, there are CdSe branches or irregularities growing at the ends of some of the CdTe nanorods. It is thought that the topology of each block is determined by the initial growth phase of the nucleating material. [74] The main reason for the branching after the 2nd injection is the presence of stacking faults [5] although the high monomer concentration may be another reason. [229 - 231] It is shown in Fig. 8.2c that the length of the HNS rods formed initially increases while the diameter increases only very slightly after the 3rd injection. The previously formed tip or branch is the main location

Chapter 8: Controlled Synthesis of HNSs

for further growth. It is shown that the newly added precursor (Te) prefers to grow on one tip of the previously formed HNSs. *Ab initio* pseudopotential calculations based on small CdSe wurtzite nanocrystals suggested that the difference in the reactivity of the various facets is due to differences in the passivating strength of the surfactant molecules. [208, 232] This difference exists even between the two polar facets perpendicular to the *c*-axis. In our case, the high reactivity of the ends of the CdTe/CdSe HNS is still maintained because the length of HNSs gradually increases with the new injections. The diameter increased very slightly perhaps due to either Ostwald ripening as the precursors in the solution gradually become depleted or the formation of a core-shell heterostructure due to overgrowth or ion exchange. [172, 225]

To study the crystal structure, HRTEM was used to characterize the synthesized rods and branched HNSs as shown in Fig. 8.3. From Fig. 8.3a and b it can be seen that the rods consist of a single crystal but contain stacking faults. The branched particles have original wurtzite CdTe rods as shown in Fig. 8.3c. The structure of the interface area between the CdTe and CdSe is still unclear at this moment. A previous study by Milliron *et al.* showed that zinc blende core and wurtzite branches of CdTe grew on the original wurtzite CdSe rods. [172] In this study, it is found that stacking faults are commonly found at the interfaces between the two materials. A probable reason for the presence of stacking faults at the interface is the large mismatch between the CdTe and the CdSe lattices. [229]

Chapter 8: Controlled Synthesis of HNSs

Fig. 8.3. HRTEM images of single CdTe/CdSe HNS: (a) tri-block, (b) multi-block linear extension and (c) branch point.

To confirm chemically that the rods synthesized do have CdSe and CdTe blocks, both HAADF imaging and EELS line scans were carried out. EELS is different from the energy dispersive analysis of X-ray spectroscopy (EDAX) reported by other groups. [172, 214, 221, 224, 225] EELS is not affected by stray scattering and secondary fluorescence that are a problem with EDAX, so EELS has a higher spatial resolution (about 1 nm). In a HAADF image the brightness is a function of the atomic weight of the elements present and the sample thickness. If the sample has uniform thickness, any difference in brightness along the length of a single particle should correspond to differences in elemental composition. From Fig. 8.4 it can be seen that there is a variation of the intensity along the length of the rods. But because of the variation in the

Chapter 8: Controlled Synthesis of HNSs

thickness of the rods, it is not possible to conclusively say that there is a composition change along the HNSs.

Fig. 8.4. High angle annular dark-field (HAADF) image of HNSs.

In order to determine whether the rods are indeed made up of separate CdTe and CdSe blocks, we collected EELS line-scans along the length of a number of HNSs. For EELS line-scans a small probe is scanned along the rod and an energy loss spectrum taken at a number of points along the length of the rod. From each energy loss spectra the ratio of Te to Se can be determined from the areas under the respective edges. An EELS line-scan from one of the rods is shown in Fig. 8.5. We see from Fig. 8.5b that the rod is Te rich at the centre, while towards the end of the rod, especially at the left end, the rod is Se rich. Because the rods are very thin the EELS edge areas are quite noisy with the noise level increasing towards the ends of the rods where the thickness is lowest, hence the variability of the measured Se and Te concentrations along the length of the rods. Of the rods we analyzed, most were CdTe with a high Se concentration at one end, and a few (such as the one shown in Fig. 8.5b) showed high Se concentrations at both ends.

Chapter 8: Controlled Synthesis of HNSs

Fig. 8.5. (a) HAADF image of the rod used for the EELS line scan. The trace of the line scan can be seen as a series of black dots along the rod starting near the top of the image. (b) EELS line scan from the rod shown in (a). The values plotted are the measured areas of the Cd M_{45} edge at 404 eV (solid line), the Te $M_{4,5}$ edge at 572 eV (dotted line) and the Se $L_{2,3}$ edge at 1436 eV (dashed line) at each point, scaled to a maximum value of 1. Negative edge areas are due to noise in the background subtraction calculation. The image and line scans were taken using an accelerating voltage of 120 kV to reduce electron beam damage. (c) Diagram showing the growth sequence after each precursor injection.

The Te rich composition at the centre of the rods corresponds to the first injection of the Te precursor. As we move away from the centre of the rod the Se concentration increases, corresponding to the second injection of the Se precursor. As we move towards the end of the rods, the Te concentration should increase again although we did not see any evidence for this. It is likely that the etching process may have removed some material from the ends of the rods. A diagram of the growth of the HNS after each precursor injection is shown in Fig. 8.5c.

Chapter 8: Controlled Synthesis of HNSs

HNSs represent unique systems due to the ability to tune the optical and electronic properties by varying the chemical composition of their components and the length of each block. [208] The absorption and PL spectra of HNSs after the second injection are shown in Fig. 8.6. The UV-Vis absorption and photoluminescence of CdTe nanorods immediately after the 1st injection is easily observed (refer to Fig. 8.6a). The appearance of higher order features in the absorbance spectra and the sharp exciton peak indicate that the CdTe nanorods are nearly monodisperse in size and shape. [75]

Fig. 8.6. (a) UV-Vis absorption and (b) PL spectra of as-prepared nanocrystals after the series of secondary precursors have been injected.

With the addition of the secondary precursor, the optical absorption of HNSs becomes weak and eventually disappears from the spectra and the peak shifts slightly to longer wavelengths. If the length of the 1D nanocrystals is bigger than the Bohr exciton diameter but the diameter of the nanocrystals is less than the Bohr exciton diameter, then the size-dependent shift in the optical spectra is solely related to the energy level quantization from the nanocrystal's diameter. [5, 233] Therefore, the shift in the spectra indicates that a thin shell has formed on the HNS rods (also refer to Fig. 8.2 b-c). [172] The lack of distinctive sub-band gap tails on the optical absorption spectra, which is observed from type-II core-shell quantum dots or core-shell tetrapods is due to the same reason discussed above. [172, 234] The absence of photoluminescence after the 2nd

Chapter 8: Controlled Synthesis of HNSs

injection (refer to Fig. 8.6b) indicates that the secondary precursors significantly modify the electronic structure of the initial CdTe rods. [11, 172]

However, the real reason for the luminescence quenching in the HNSs is unclear at this moment. Milliron *et al.* and Peng *et al.* proposed that the high degree of charge separation occurring at the interfaces quenches the luminescence in the optical analysis. [11, 172] Halpert *et al.* thought that since the carriers are spatially well separated, recombination occurs primarily through nonradiative pathways involving surface trap states. [221] This process makes the luminescence absent in the PL spectra of CdSe/CdTe nanobells. Saunders *et al.* thought it via electron-hole recombination in both the CdSe block and across the CdSe | CdTe heterojunction after spatial separation of them. [224] Although several models are proposed to this system, [11, 221, 224, 226] the fully understanding of the dynamics of exciton traps, charge separation and recombination is still on the way, especially for single HNS.

8.4 Conclusion

We have reported the growth of CdTe/CdSe multi-block HNSs using the hot coordinating solvents method. In this study, it was found that the newly added precursor preferred to contribute to growth at the tips of previous formed nanocrystals. This is because in the presence of suitable ligands, the lateral non-polar facets of wurtzite structure materials have much lower growth rates than the basal polar facets, therefore the nanocrystals grew preferentially along their unique *c*-axis. HRTEM, HAADF, EELS line scans and XRD were used to examine the chemical composition and the structure of these HNSs. HNSs feature is different from that of previously established reports in which the linear CdSe block is followed by CdTe extensions. This study may help in

Chapter 8: Controlled Synthesis of HNSs

understanding the growth of more complex functional nanomaterials. Furthermore, the successful formation of these structures is essential for future applications of semiconductor nanocrystals in nanoscale devices.

Chapter 9: Hybrid Photovoltaic Devices

9.1 Introduction

As discussed in Chapter 1 and 2, hybrid solar cells have attracted much attention as candidates for generating clean and renewable power. [8, 15, 37, 38] This type of solar cells offers several advantages, including high mobility, tunable absorption spectra and extremely high optical absorption coefficient. In addition, they are solution processible, light weight and is flexible. To date, nanodots, nanorods and tetrapod-shaped nanocrystals have been used as electron acceptors in hybrid solar cells. [8, 15, 37, 117, 228, 235, 236] The scheme of a hybrid solar cell was shown in Fig. 2.9a. A hybrid solar cell composed of a conjugated polymer and CdSe / CdTe multi-block HNSs has recently been highlighted as one of the desired materials for potential PV applications. The different polarities that CdSe and CdTe blocks possessed can help in the separation of the carriers (electrons and holes) when the electrons jump over the band gap into the conduction band. [11, 172, 228, 237] Fig. 9.1a shows a schematic energy level diagram for HNSs and P3HT. It can be seen from the comparison made on the different energy levels alone that the charge carriers in this blend will have a better chance to be separated than that those in the CdSe nanorods and P3HT blend.

Before investigating HNSs/P3HT hybrid solar cells, hybrid solar cells made using CdS and CdSe and conjugated polymer were fabricated and their properties were studied. The reason for these hybrid solar cells work is because recent studies done by other groups suggested that increasing the aspect ratio of the nanocrystals can enhance the charge transfer, improve the absorption and improve the performance of these devices. [8, 15] The possibility of forming a network in the polymer can be achieved during spin-coating

Chapter 9: Hybrid Photovoltaic Devices

using high aspect ratio nanocrystals (refer to Fig. 5.10). In Fig. 9.1b, a network of pure CdSe nanowires is shown when a concentrated nanocrystal solution is dropped on the copper grid. This further supports the above assumption. In the following, the studies of hybrid solar cells composed of CdS/MEH-PPV, CdSe/P3HT and HNSs/P3HT will be presented.

Fig. 9.1. (a) Schematic energy level diagram for HNSs and P3HT showing the charge transfer of electrons to CdTe, then CdSe and holes to P3HT and (b) TEM image of a network formed by concentrated CdSe nanowires only.

9.2 Experimental Section

9.2.1 Materials

MEH-PPV and P3HT were purchased from Sigma-Aldrich and Rieke Metal, Inc. PEDOT:PSS was purchased from Bayer AG. Nanocrystals used in this study are synthesized using the methods discussed in Chapter 5, Chapter 7 and Chapter 8 and their properties are also presented in these previous chapters.

9.2.2 Device fabrication

After synthesis, the nanocrystals are usually covered with phosphonic acid (ODPA or DDPA) which can be detrimental to the conduction properties at the interface. Hence to

Chapter 9: Hybrid Photovoltaic Devices

improve the surface properties, the nanocrystals were dispersed in 20 ml pyridine and stirred under reflux at 60 °C for 4 days, allowing for ligand exchange. Nanocrystals were then precipitated with *n*-hexane and redissolved in pyridine. The above procedures were then repeated. After ligand exchange, hybrid solar cells were fabricated using a structure consisting of ITO/PEDOT:PSS/polymer: nanocrystals blend/Al layers as shown in Fig. 2.9a.

For HNSs/P3HT and CdS/MEH-PPV hybrid cells: ITO-coated glass substrates (Kintec Co., 7 ohm/sq) were cleaned by ultrasonication in detergent, de-ionized water, acetone and isopropyl alcohol for 15 min each. A layer of PEDOT:PSS was spin-coated onto the etched ITO glass and annealed at 120 °C for 20 minutes. The nanocrystals and polymer were mixed in pyridine and stirred overnight before use. The mixture consisted of 70% nanocrystal loading was spin-coated on top of the PEDOT:PSS and dried at 130 °C for 30 minutes. Finally, Al (cathode) was evaporated on top of the film.

For CdSe/P3HT hybrid cells, ITO-coated glass substrates (Kintec Co., 7 ohm/sq) were cleaned using similar procedure as mentioned above. However, after that, ozone plasma cleaning for 2 min was conducted. This step aims to form O-H bond on the ITO surface which helps in the formation of uniform PEDOT :PSS layer and also remove organic contamination from the ITO surface. A layer of PEDOT:PSS was spin-coated and annealed at 120 °C for 20 min. Nanocrystals were first dispersed in a solvent mixture of chloroform and pyridine. Fixed amount of P3HT solution (in chloroform) was added into the solution afterwards to form a blend that consists of 90 wt% of CdSe nanocrystals in P3HT and a chloroform-to-pyridine ratio of 9:1. The partial concentrations of CdSe and P3HT were 14.4 mg ml⁻¹ and 1.6 mg ml⁻¹, respectively. The P3HT and CdSe blend solutions were ultrasonicated for at least 30 min

Chapter 9: Hybrid Photovoltaic Devices

before use. Active layers were spin-coated in a N₂ glove box at various spin rates. Al was deposited on the P3HT:CdSe active layer in vacuum at a pressure lower than 3×10^{-6} mbar to form devices with an area of 0.07 cm². After the electrode deposition (Al), all devices were annealed at 150 °C for 30 min on a hotplate in the N₂ glove box.

9.2.3 Device characterization

The ligand content of nanocrystals were measured using a TA instruments Q500 thermogravimetric Analyzer (TGA). The samples were measured over a temperature range from ambient to 650 °C at the rate of 10 °C min⁻¹ under N₂ atmosphere, with a gas flow of 60 ml min⁻¹. Photocurrent measurements were carried out using a 150 W xenon lamp (Newport model 66902) with an AM 1.5 filter. The optical power used for the measurement is 100 mW cm⁻². Current–voltage measurements (I–V curve) were carried out using a Keithley 2400 source measurement unit and the measurement was conducted in the ambient atmosphere. EQE measurements were conducted using a light source from a mechanically chopped 150 W Xenon-lamp based solar simulator directed into Newport Cornerstone™ 260 1/4M monochromator. The calibration for the measurement was done using a Hamamatsu calibrated silicon cell and the samples were measured using the Oriel Merlin™ digital lock-in radiometry system. The film thicknesses were determined using the KLA Tencor Alpha-Step IQ surface profiler.

9.3 Results and Discussion

9.3.1 CdS/MEH-PPV hybrid solar cells

As mentioned early, it has been proposed that increasing the aspect ratio of the nanocrystals can enhance the charge transfer and hence further improve the performance of these hybrid solar cells. [8, 15] The CdS nanowires synthesized in this work exhibit a

Chapter 9: Hybrid Photovoltaic Devices

high degree of dispersibility and have an aspect ratio as high as 170. They are thus good candidates for improving the efficiency of PV devices.

Fig. 9.2 is a TEM image showing our nanowires in a polymer matrix (also refer to Fig. 5.10). It can be seen that the nanowires formed an interconnected network. It is thought that an active layer with a more intimate mixture can increase the amount of interaction between the conducting polymer chain and inorganic crystals. [34] This network structure can help in the exciton separation, the diffusion of free charges and the charge collection efficiency. [33] Thus the aim of this work is to compare the hybrid solar cells performance made from using both nanorods and nanowires blended with MEH-PPV. The main reason for choosing MEH-PPV in this study is due to the band alignment consideration. [235, 238, 239]

Fig. 9.2. TEM image of a blend film of CdS nanowires/MEH-PPV with 70% CdS nanocrystals loading.

Fig. 9.3 shows the UV-Vis absorption spectra from thin film blends of CdS nanocrystals/MEH-PPV and CdS nanowires/MEH-PPV. It can be seen that the absorption range of the thin film blend is wider than that of the pure MEH-PPV ($\lambda=500$ nm). This indicates that CdS nanocrystals and MEH-PPV have complementary absorption spectra in the visible region. [235] Fig. 9.4 also shows that the blend film has a good absorption capability. I-V curves from CdS nanowire and nanorod devices are

Chapter 9: Hybrid Photovoltaic Devices

presented in Fig. 9.4a and b. It is surprising that the open-circuit voltage (V_{oc}) measured for the devices made using nanorods is 1.17 V whereas the devices with the nanowires has a V_{oc} of 1.24 V. A possible reason may be the difference in the amount of ligands remaining for the shorter and longer wires is slightly which will be discussed later based on the TGA results.

Fig. 9.3. UV-Vis absorption spectra of CdS nanocrystals, MEH-PPV and CdS nanowires/MEH-PPV blend thin film.

Fig. 9.4. I-V curves of PV devices of (a) CdS nanorods/MEH-PPV and (b) CdS nanowires/MEH-PPV in the dark (dotted line) and under illumination of $100 mW cm^{-2}$ (solid line).

Compared with the nanorod blend, there is a two-fold increase in short-current density (I_{sc}) found for the CdS nanowire blend. This resulted in a three-fold improvement in the overall PCE for the nanowire blend from 0.01% to 0.03% under $100 mW cm^{-2}$ illumination. This result is consistent with Huynh *et al.*'s proposal that increasing the aspect ratio of the nanocrystals can enhance the charge transfer and improve the

Chapter 9: Hybrid Photovoltaic Devices

performance of the devices. [8, 15] It was also found that in our study that when the optical power is decreased to 50 mW cm^{-2} , the efficiencies of both devices are increased by 1.8 times. Despite the good absorption spectrum for our devices as shown in Fig. 9.3, the efficiency reported here is lower than that reported by others using the same materials. [238, 239] For example, Kang *et al.* reported an efficiency of 0.6% with well-aligned CdS nanorods/MEH-PPV solar cells. [238] Very recently, Wang *et al.* reported an even higher efficiency of 1.17% using multi-armed CdS nanorods/MEH-PPV solar cells. [239] The main reason for the comparably low efficiency of devices is low I_{sc} . In general, I_{sc} is affected by optical absorption properties, the thickness of active layer, the interface and band-gap matching of the materials. [33, 240]

Fig. 9.5 shows TG curves of TOPO, ODPa and CdS nanocrystals before ligand exchange, after the 1st and 2nd ligand exchange, respectively. It can be seen that the ligand capped nanocrystals is mainly ODPa, not TOPO as reported previous by other group. [15] The ligand exchange is found to be an efficient way to remove ODPa on the surface of nanocrystals. After the 1st ligand exchange with pyridine, the ligand content decreases from 59% to 42% in weight as shown in Fig. 9.5. In this study, we found even after the 2nd ligand exchanges, there is still about 29% ODPa in the nanocrystals. These ODPa can be either attached on the nanocrystals or existed as unreacted Cd-ODPa complexes mixed with the nanocrystals. It was reported that the conversion of trialkylphosphine chalcogenide is about 80% under anhydrous conditions. [29, 183] We further studied the spectra response of devices and found that the maximal EQE value is about 3% (at 490 nm) for the devices based on CdS nanowires/MEH-PPV. The relatively low EQE can tell us the efficiency of charge transport is poor. [8] In order to improve the performance, we need to improve the surface state of the nanocrystals. Small molecular organics such as ODPa can trap charge carriers, thus reducing the efficiency of charge

Chapter 9: Hybrid Photovoltaic Devices

separation and transportation. [8, 228] The future work could focus on optimizing parameters such as annealing conditions and the nanocrystal loading.

Fig. 9.5 TG curves of TOPO, ODPa and CdS nanocrystals before ligand exchange, after the 1st and 2nd ligand exchange, respectively.

9.3.2 CdSe/P3HT hybrid solar cells

In this study, our focuses are on the 1D CdSe nanocrystals with different lengths and P3HT hybrid solar cells. Although there are studies done on short CdSe nanorods previously, [8, 15] none has focused on the PV properties made of CdSe nanorods with higher aspect ratio. In addition, an alternative co-solution preparation method to obtain better dispersion of the nanocrystals is also being explored.

As mentioned above, it is believed that increasing the length of CdSe nanorods may result in an improvement of device performances because of enhanced charge transport. [8, 15, 241] Fig. 9.6 shows TEM images of CdSe nanorods synthesized with different aspect ratios, ranging from 3 to 15. Longer rod length leads to a higher packing density and hence provides a better pathway for charge transport.

Chapter 9: Hybrid Photovoltaic Devices

Fig. 9.6. CdSe nanorods with different aspect ratios range from 3 to 15. The TEM images show the samples of different dimensions: (a) 7 nm x 20 nm, (b) 7 nm x 60 nm and (c) 9 nm x 140 nm.

Fig. 9.7a and b show the UV-Vis absorption spectra of the different length CdSe nanorods in solution form and P3HT:CdSe films spin-coated on quartz, respectively. UV-Vis absorption of P3HT film and CdSe film are also shown in Fig. 9.7b. P3HT-CdSe film has complementary absorption at region from 400 nm to 700 nm. It was observed that in both absorption spectra there is a slight red shift of the absorption profile for 9 nm by 140 nm CdSe nanorods due to a larger diameter. [8] In addition, CdSe nanorods with a higher aspect ratio also show a strong and wide range absorption.

Fig. 9.7. UV-Vis absorption spectra of (a) CdSe in solution form of different lengths (1) 140 nm and (2) 60 nm and (b) pure P3HT film (dashed line), CdSe film (dotted-dashed line) and P3HT-CdSe film made of 140 nm nanorods (black) and 60 nm nanorods (red).

TEM images of P3HT:CdSe films fabricated from the mixtures are shown in Fig. 9.8a and b for 7 nm x 60 nm and 9 nm x 140 nm nanorods, respectively. CdSe nanocrystals used in this study contain less than 5% organic residue after two rounds ligand exchange

Chapter 9: Hybrid Photovoltaic Devices

processes based on the TGA results. At a high nanocrystal loading (90 wt%) and concentration, CdSe nanorods form network and provide a percolation pathway for the charges to transport. [15, 241] In the bulk heterojunction concept, this network structure increases the donor-acceptor interfaces and hence allows easier exciton dissociation. [242] The film thickness of active layer of the devices is about 70 nm measured by surface profiler. Their PV properties, such as I_{sc} , V_{oc} , fill factor (FF) and PCE of the devices fabricated from 20 nm, 60 nm and 140 nm long CdSe nanorods, are compared and shown in Table 9.1. The results are in good agreement with those of Huynh *et al.* They observed that with increasing aspect ratio of nanorods, the performance of devices increases. [8, 15, 241]

Fig. 9.8. TEM images of P3HT and CdSe nanorods blend films with 90% nanorod loading formed by (a) 7 x 60 nm nanorods and (b) 9 x 140 nm nanorods.

Table 9.1. PV characteristics of the best performed devices fabricated using different CdSe nanorod lengths under simulated solar spectrum with AM 1.5 filter at an intensity of 0.85 suns.

Rod length (nm)	PCE (%)	I_{sc} (mA/cm ²)	V_{oc} (V)	FF
20	0.438	-1.938	0.49	0.461
60	0.533	-2.431	0.505	0.434
140	0.849	-3.346	0.490	0.504

Note: The thickness of all these films is about 70 nm as mentioned in the main text.

Although film with longer rods seems to be absorbing slightly better as shown in Fig. 9.7b, the increment in I_{sc} can be attributed to better charges transport via long CdSe rod, which reduces the electron hopping frequencies from rods to rods. The I-V

Chapter 9: Hybrid Photovoltaic Devices

characteristics of the devices are shown in Fig. 9.9a. The best performing device, made of 140 nm-long-CdSe nanorods, showed a I_{sc} , V_{oc} , FF and PCE of -3.436 mA/cm^2 , 0.490 V, 0.504, and 0.85%, respectively. This performance is improved as compared to the devices made of 60 nm nanorods which record an efficiency of 0.53%.

Relative short-circuit EQE spectra for P3HT-CdSe blend film composed of 140 nm and 60 nm-long-nanorods are shown in Fig. 9.9b. Compared to the film formed by 60 nm CdSe nanorods, a slight red shift is observed for devices made of 140 nm nanorods due to the larger diameter of CdSe nanorods. P3HT strongly absorbs light from wavelength of 450 nm to 650 nm, whereas, the band edge of the absorption for CdSe is at 700 nm. It is observed that the EQE response of the devices is higher at 400 nm. This can be attributed to response from CdSe nanorods. Film with thickness of 70 nm is not optimal for P3HT absorption; however, we still can observe at 500 nm, there is a step in the spectra which is corresponding to P3HT.

Fig. 9.9. (a) *I-V* curves of P3HT/CdSe hybrid solar cells made of different CdSe nanorod lengths: 140 nm (solid line) and 60 nm (dashed line) and (b) relative EQE of the devices made of 140 nm (solid line) and 60 nm (dashed line), respectively.

Huynh *et al.* proposed that a binary solvent mixture can achieve a range of optimal solvent ratio for P3HT-CdSe blends. [15] However, CdSe nanorods have limited solubility in chloroform especially in the case of longer rods and at the same time

Chapter 9: Hybrid Photovoltaic Devices

pyridine is a poor enough solvent for P3HT that it will cause P3HT to precipitate. [15] Therefore we tried to prepare the blend solution using an alternative method. CdSe nanorods were dissolved in pyridine and P3HT was dissolved in chloroform separately. A mixed amount of solution was extracted from both stocks and mixed together to achieve a 90 wt% CdSe loading in P3HT and a chloroform to pyridine ratio of 4.17. It was found that using this solution preparation method, the PCE of the devices made with the 60 nm CdSe nanorods is 0.62%, whereas the PCE is 0.30% when using the method stated in experimental section or that of Huynh *et al.* [8, 15] It can be seen that the PCE improves more than 100% when using our method. For the devices made with the 140 nm nanorods, the performance of the devices made from both preparation methods does not show any significant difference. It is believed that CdSe nanorods disperse better in pure pyridine than in binary solvent. Films that were casted from the combined solution after ultrasonication have a larger donor-acceptor interfacial area. This promotes exciton dissociations and therefore increases device performance. However, as the aspect ratio increases, there is a larger tendency for the nanorods to aggregate side-by-side. [243] The dispersion stability of nanocrystals in the mixtures will be affected. Although this preparation method aids the dispersion of nanocrystals, the drawback is the limited concentration of CdSe stock solution we can prepare. This results in a lower chloroform-to-pyridine ratio of the final solutions (4.17:1).

9.3.3 HNSs/P3HT hybrid solar cells

As shown in Fig. 9.1a, P3HT has both higher LUMO and HOMO compared with CdTe and CdSe. When excitons were generated by the photons adsorbed in P3HT, they diffused to the interface of HNSs and P3HT, electrons transfer from P3HT to CdTe and then CdSe, whereas holes jump to P3HT from CdTe. The charge separation and transfer are easier when using a combination of P3HT and HNSs compared to that of MEH-PPV

Chapter 9: Hybrid Photovoltaic Devices

and HNSs combination due to the energy level matching between P3HT and the HNSs. This is the reason why we choose P3HT, not MEH-PPV for this study. In general, in hybrid solar cells, 1D nanocrystals with high aspect ratio readily form a continuous network and hence, provide the percolation pathway for the charge to move towards the electrode. [15] Fig. 9.10 shows TEM images of HNSs in P3HT matrix at different HNSs loading. Both TEM images show that the HNSs after ligand exchange are well-dispersed in the P3HT matrix. It can be seen that the network structure of films with a 70% nanocrystals loading is better than that of with 50% nanocrystals loading. However because the length of HNSs is short (about 40 nm), there may still be some interconnectivity issues between the rods even when the nanocrystals loading is 70%. To have a complete study of the effect of nanocrystals loading on the performance of devices, we also attempted to increase the nanocrystals loading up to 90%. Although, the network structures are supposed to be improved with the addition of nanocrystals, we did not found that the performance of the devices increases as the nanocrystals loading increased. The possible reason for poor performance of the devices is the presence of organic residues on the nanocrystals which may result in charge quenching and higher interfacial resistance. This is confirmed by the TGA test that showed the ligand content is about 30% by weight in the HNSs as shown in Fig. 9.11 The weight loss before 400 °C is due to the decomposition or the evaporation of small molecules, such as pyridine, ODPA and TOPO, whereas after 750 °C, the weight loss is due to the decomposition of HNSs nanocrystals.

Chapter 9: Hybrid Photovoltaic Devices

Fig. 9.10 TEM images of the blend film of HNSs/P3HT with (a) 50% and (b) 70% HNSs loading.

Fig. 9.11. TG curve of HNSs nanocrystals after ligand exchange.

The light absorption and charge separation properties of the blended film of P3HT and HNSs were investigated using absorption and photoluminescence spectroscopy. Fig. 9.12a shows the UV-Vis absorption spectra from thin film of P3HT, HNSs and HNSs nanocrystals/P3HT blends. It can be seen that the absorption range of the thin film blend is slightly wider than that of the pure P3HT ($\lambda=520$ nm). This indicates that HNSs nanocrystals and P3HT have complementary absorption spectra in the visible region from 350 nm to 700 nm. [235] Thus, the blend films can harvest the visible sunlight

Chapter 9: Hybrid Photovoltaic Devices

more efficiently. The UV-Vis absorption spectra also show that the blend film has a good absorption capability. Good adsorption of sunlight but poor device performance tells us that the sunlight adsorption ability of the devices is not the only reason that affects the device performance. Fig. 9.12b shows the PL spectra of from thin film of P3HT, HNSs and HNSs nanocrystals/P3HT blends. As mentioned previously (Section 8.3), PL quenching in the HNSs nanocrystals occur very readily but the exact reason for this quenching is still under investigation at this moment. In this study, we found that the addition of the HNSs nanocrystals in the polymer results in a significant PL quenching of the polymer (P3HT). The possible reason of this quenching is that the photoinduced charge transfer occurred between P3HT and HNSs nanocrystals. [228]

Fig. 9.12. (a) UV-Vis absorption and (b) PL spectra of P3HT, HNSs nanocrystals and HNSs/P3HT blend thin film.

Fig. 9.13b shows the I-V curve from hybrid PV devices with the architecture - ITO/PEDOT:PSS/P3HT+HNSs/Al in the dark (dotted line) and under illumination of AM 1.5, 100 mW cm^{-2} (solid line) in an ambient environment. It can be seen that the blend devices show a small rectification ratios in the dark as well as significant leakage currents. [38] There also exists a low shunt resistance which can be observed from the voltage dependence of the current density around the I_{sc} . We further studied the annealing effect on the performance of devices. Unfortunately, we did not observe any

Chapter 9: Hybrid Photovoltaic Devices

obvious improvement in PCE before annealing and after anneal at 130 °C for 30 min. This method is previously found to be an effective way in improving the performance of the devices. [8, 15, 33] In this study, the best performing devices showed I_{sc} , V_{oc} and FF of $6.5 \mu A cm^{-2}$, 0.53 V and 0.23, respectively. The PCE is 0.011%.

Fig. 9.13. *I-V curve of PV devices in the dark (dotted line) and under illumination of $100 mW cm^{-2}$ (solid line).*

The efficiency of this device is lower than that reported from other multiple-branched heterostructure rods/P3HT [228] and CdSe nanorods/P3HT devices. [8, 117] The possible reasons for this are as follows. (1) The presence of organic residues in the nanocrystals may results in charge quenching. (2) The charge readily recombines before it is able to reach the electrodes because the length of each block of HNSs is too short, meaning that there is a lack of interconnectivity between the rods. Efficient charge separation and good transport along HNSs are essential for cells performance. [11, 117] For future study, if the length of each block could be increased to around 50 nm and the total length of the HNSs could be extended about 250 nm, the chance of charge separation and transport will be improved. This will also help to form a network between the polymer and the HNSs during spin-coating. However, the length of nanorods cannot

Chapter 9: Hybrid Photovoltaic Devices

be extreme long. It is because although it will help to improve 1D transport characteristic, nanorods become difficult to be dispersed.[15] In addition, Zhong *et al.* thought that the holes generated in the CdTe block would impede electron transportation along the HNS networks in the disordered hybrid system when they studied the hybrid heterostructures/P3HT solar cells. [228] (3) The defects in the nanocrystals such as stacking faults and surface defects which are formed during anisotropic growth can also trap the charge carriers, thus reducing the efficiency of charge separation and transportation. [172, 228] Huynh *et al.* and Gur *et al.* minimized the surface defects and improved carrier transport in the devices by annealing and sintering treatment. [15, 16] Huynh *et al.* found that the heat treatment could both remove of interfacial pyridine and bring nanorods closer. They proposed that the aggregation of nanorods in the film is likely to improve electron transport between nanorods. After sintering nanocrystal film, Gur *et al.* found that the photoconductivity of devices is increased by two orders of magnitude.

9.4 Conclusions

In summary, three types of hybrid solar cells have been successfully fabricated from solution with a different blending polymer and nanocrystals. They are CdS/MEH-PPV, CdSe/P3HT and HNSs/P3HT hybrid solar cells. The PV properties of these devices were studied. It was found that the best hybrid cells combination is CdSe nanorods and P3HT. The hot coordinating solvents method provides a high degree of control over size and shape in CdSe nanocrystals. By optimizing nanorod length used in the hybrid solar cells, the distance on which electrons are transported directly through the blend films is also changed. It was found that using high aspect ratio CdSe nanocrystals, the 1D transport characteristics are improved. This can be seen when comparing 60 nm and 140 nm

Chapter 9: Hybrid Photovoltaic Devices

nanorods. In addition, the organic residues in the CdSe nanocrystals is lowest after ligand exchange which can help to decrease the chance of charge quenching in the surface of nanocrystals before charge transport to polymer. On the other hand, P3HT is an effective hole transport polymer in its regioregular form which enables the good transport characteristics of CdSe to work in the devices. Furthermore, the good dispersibility of both materials in mixture solvents is also useful to tune exciton dissociation and electron transport via optimizing the nanocrystals concentration in the polymer matrix and the length of nanocrystals.

The following is a summary of our findings for the respective hybrid solar cells.

1). CdS/MEH-PPV hybrid solar cells: The efficiency of these devices increased from 0.01% to 0.03% when nanowires instead of nanorods were used. This result proves that increasing the aspect ratio of the nanocrystals can enhance the charge transfer and further improve device performance. The main reason for their comparably low efficiency comes from their low I_{sc} . Future work could focus on improving the surface states of the nanocrystals as well as optimizing parameters such as annealing conditions and the nanocrystal loading.

2). CdSe/P3HT hybrid solar cells: CdSe nanorods with different lengths and P3HT hybrid solar cells were being studied. It was found that the efficiency of PV devices, made of CdSe nanorods with higher aspect ratio, has been improved. The best performing device, made of 140 nm-long-CdSe nanorods, showed a I_{sc} , V_{oc} , FF and PCE of -3.436 mA/cm², 0.490 V, 0.504, and 0.85%, respectively. The PCE of device showed an improvement as compared to the devices made of 60 nm nanorods, whose PCE is 0.53% and increases more than 60%. These results are in good agreement with the studies done by other research groups. As mentioned above, an alternative method for

Chapter 9: Hybrid Photovoltaic Devices

the preparation of the solution was also explored, where CdSe nanorods were dissolved in pyridine and P3HT was dissolved in chloroform, separately. It was found that the PCE of the devices, made of 60 nm CdSe nanorods, increases more than 100% when prepared by this method (0.62%) as compared to the preparation methods used by other research groups (0.30%). However, there is no significant effect in PCE for those made using 140 nm nanorods. A possible reason is that as the aspect ratio increases, there is a larger tendency for the nanorods to aggregate side-by-side which will affect the dispersion stability of nanocrystals in the mixtures.

3). HNSs/P3HT hybrid solar cells: The I_{sc} , V_{oc} and FF of the devices are $6.5 \mu A cm^{-2}$, 0.53 V and 0.23, respectively. The PCE of the best performing device is 0.011% under illumination of AM 1.5, $100 mW cm^{-2}$ in an ambient environment. The main reasons for their comparably low efficiency arise from the presence of organic residues in the nanocrystals, recombination of the charges before they are able to reach the electrodes, as well as organic residue capped around HNSs which may lead to charge quenching. Increasing the length of these structures so that a network of HNSs can be formed as well as removing the surface ligands may help to improve cell efficiency.

Chapter 10: Conclusions and Future Directions

10.1 Thesis Summary

Cadmium chalcogenide, which is a narrow band gap material (bulk: $E_g=2.5$ eV for CdS, $E_g=1.75$ eV for CdSe and $E_g=1.45$ eV for CdTe at 300K), has a high optical absorption coefficient and represents one of the most important group II-VI semiconductors. These materials have been widely used in electronic and optical areas. In recent years, the synthesis of 1D nanocrystals, such as rods, wires, belts and tubes whose lateral dimensions fall within the range of 1-100 nm, has attracted considerable interest. This is due to their novel size and shape-dependent physicochemical and optoelectronic properties. For example, 1D cadmium chalcogenide nanocrystals have become important potential building blocks for new electronic and optical nanodevices such as laser, transistor, light-emitting diodes and PV devices. As the electronic and optical properties of nanocrystals are dependent on the dimensions of crystals, the issue of how to control the growth of 1D cadmium chalcogenide nanocrystals is of prime importance and remains one of the most challenging issues in chemistry and materials science. This is the first motivation behind this study.

With the motivation, we have successfully synthesized 1D cadmium chalcogenide nanocrystals with three catalyst-free solution-based methods. They are reverse micelle, hydrothermal and hot coordinating solvents methods. In Chapter 3 and Chapter 4, a reverse micelle method at moderate temperature (100 °C) and a novel reverse micelle assisted hydrothermal method for synthesizing CdSe nanorods have been presented and discussed. Two different nucleation and growth mechanisms relating to these systems have also been proposed. In Chapter 3, we showed that at a moderate temperature

Chapter 10: Conclusions and Future Directions

(100 °C), with a combination of an anionic surfactant, AOT and a reducing agent, hydrazine hydrate, it is possible to control the morphology of the nanocrystals. It is found that hydrazine hydrate not only acts as a reduction agent but also as one of the templating agent that favors the formation of rodlike structure. The mechanism for the formation of CdSe nanorods is the phase transition due to the addition of a very large amount of hydrazine hydrate to the reverse micelle solution during the reaction. It has been proposed that the formation of CdSe nanorods happened inside these micelles which are mainly affected by the amount of AOT and hydrazine hydrate.

In Chapter 4, it has been shown that the phase behavior and growth mechanisms under hydrothermal conditions are different with those in reverse micelle method due to at elevated temperature and pressure. Proposed model of nanocrystals formation are: (a) fusion and exchange of the contents within the cores and re-dispersion of the reverse micelles before heated up, (b) nucleation and growth of spherical and rodlike nanocrystals with heating and pressure before micelles collapsed, (c) further growth of nanorods provided by directional aggregation of smaller particles including shorter rods and nuclei after micelles collapsed. This process results in the formation of the larger nanocrystals and is affected by the surface absorption and desorption of both hydrazine molecules and AOT molecules on the nanorods.

In this work, a hot coordinating solvents method with good size distribution, highly controllable morphology and highly reproducibility has been employed to synthesize CdS nanowires (Chapter 5 and 6), CdSe nanowires (Chapter 7) and HNSs (Chapter 8).

In Chapter 5 and 6, CdS nanowires with a monodisperse diameter of 3.5 nm and length of about 600 nm were successfully synthesized and studied. The focus of Chapter 5 is on the synthesis of CdS nanowires. It was found that the mole ratio of ODPa-to-Cd is one

Chapter 10: Conclusions and Future Directions

key factor in determining the morphology of the CdS nanocrystals in addition to the reaction temperature. We also found that the precursor ratio (Cd-to-S mole ratio), the precursor concentration and the precursor injection process could affect the morphology of the nanowires. ODPa was found to be a good candidate for generating nearly monodisperse and high aspect ratio nanowires due to having a low diffusion rate and a low reactivity as compared to Cd-HPA or Cd-DDPA complexes. In Chapter 6, the growth mechanism for monodisperse CdS nanowires has been dynamically studied. Contrary to existing mechanisms proposed for 1D nanocrystal growth for CdS, an oriented attachment mechanism was proposed. UV-Vis and TEM images are used to support this proposal.

In Chapter 7, nearly monodisperse CdSe nanowires with a diameter of 8 nm and length of 220 nm that are successfully synthesized were presented. After systematically investigating the effects of ligand type for both Cd- and Se-complexes, reaction temperature, precursor concentration and precursor injection process on nanocrystal morphology, the optimum conditions for nanowire formation are proposed. The use of DDPA and TOP as complexing ligands for Cd and Se respectively and the doubling the precursor concentration is the optimum condition for the nanowire formation. A good balance is achieved using them which favor the anisotropic growth with higher aspect ratio. Contrary to previous findings, we found that a high reaction temperature (310 °C) favors a higher aspect ratio nanocrystal growth compared to a lower temperature (250 °C or 280 °C). Doubling the precursor concentration can greatly increase the aspect ratio of nanocrystals from 9 using the baseline concentration to 28 for twice the concentration. The nearly monodisperse CdSe nanowires with high dispersibility can be potentially used in devices such as photovoltaic cells and transistors.

Chapter 10: Conclusions and Future Directions

In Chapter 8, we have reported the growth of CdTe/CdSe multi-block HNSs. Using this method, we grow CdSe at each end of CdTe nanorods and then grow CdTe at the ends of the CdSe/CdTe/CdSe rods. This kind of structural feature is different from that of previously established reports in which the linear CdSe block is followed by CdTe extensions. HRTEM of the heterostructure shows that the CdSe and CdTe rich parts of the nanorods both have the wurtzite crystal structure and that stacking faults are common. EELS line scans accompanied with optical analysis (UV-Vis and PL) and thin film XRD of the prepared nanocrystals were also used to confirm the formation of HNSs. This study may help in understanding the growth of more complex functional nanomaterials and the successful formation of these structures is essential for future applications of semiconductor nanocrystals in nanoscale devices.

Finally, the PV properties of devices containing polymer and 1D nanocrystals blends have been studied. With the goal of enhancing the performance of solar cells, three types of hybrid solar cells have been successfully processed from solution with a different blend of a polymer and nanocrystals. They are CdS/MEH-PPV, CdSe/P3HT and HNSs/P3HT hybrid solar cells. CdS/MEH-PPV and HNSs/P3HT hybrid solar cells showed comparable low efficiencies. Several reasons are proposed, such as charge recombination and poor surface states (organic residues). CdSe/P3HT hybrid solar cells showed the best performance because the organic residues are lowest in the CdSe nanocrystals, good energy level matching between CdSe and P3HT, and well-optimized nanocrystals concentration and length. It is found that the PCE, made of CdSe nanorods with a higher aspect ratio, has been improved. The best performing device, made of 140 nm-long-CdSe nanorods, showed a I_{sc} , V_{oc} , FF and PCE of -3.436 mA/cm^2 , 0.490 V, 0.504, and 0.85%, respectively.

Chapter 10: Conclusions and Future Directions

In summary, three catalyst-free and solution-based methods were used to synthesize 1D cadmium chalcogenide nanocrystals. These methods are hydrothermal, reverse micelle and hot coordinating solvents methods. A summary of these methods for shape control is shown in Fig 10.1. Using both the reverse micelle method and the hydrothermal method, we have successfully synthesized CdSe nanorods with reasonable morphological control but the aspect ratio of these nanorods were less than 5. We found that the reverse micelle method has better morphological control than the hydrothermal method, but the latter has both the higher crystallinity and yield. Using the hot coordinating solvents method has achieved good size distribution, highly controllable morphology and an aspect ratio as high as 170 for CdS nanowires. In addition to CdS nanowires, CdSe nanowires were also successfully synthesized using this method after systematically investigating the effects of several parameters on the crystal morphology. Furthermore, using the same method, a novel 1D nanocrystal, multi-block HNSs, has been successfully prepared and studied by growing CdSe at each end of CdTe nanorods and then growing CdTe at the ends of the CdSe/CdTe/CdSe rods. The structure, composition, morphology, surface status and optical properties of 1D cadmium chalcogenide nanocrystals are characterized by XRD, TEM, HRTEM, SAED, EELS line scans, FT-IR, Raman spectroscopy, UV-Vis and PL. The nucleation and growth mechanism for each system were proposed. Finally, the PV properties of device containing blends of polymer and nanocrystals have been studied. The best performing device was made of 140 nm-long-CdSe nanorods and P3HT which showed the PCE of 0.85%. It also found that with increasing aspect ratio of nanocrystals, the PCE of these devices increased. The PCE increased more than 60% when using nanorods which were 140 nm instead of 60 nm long. It is possible due to an enhancement of charge transport and formation of percolation networks.

Chapter 10: Conclusions and Future Directions

Fig. 10.1. A summary of three synthesis methods for shape control.

10.2 Future Directions

This work has shown that the synthesis of 1D cadmium chalcogenide nanocrystals via three solution-based methods is highly probable: reverse micelle, hydrothermal and hot coordinating solvents. Using the hot coordinating solvents method has achieved good size distribution, controllable growth and an aspect ratio as high as 170 for CdS nanowires and 28 for CdSe. This is significant because in the past fifteen years, this method has only been able to generate low aspect ratio nanorods (less than 20). In addition, contrary to existing mechanisms proposed for 1D nanocrystal growth, such as the effect monomer model and the selective adhesive model, an oriented attachment mechanism was proposed for the growth of monodisperse CdS nanowires. Nevertheless,

Chapter 10: Conclusions and Future Directions

future studies are needed in several areas to corroborate as well as to extend this study.

Several recommendations for future research are as follows:

- 1) Study the growth mechanism of CdSe nanowires. Although we proposed the oriented attachment mechanism for the formation of monodisperse CdS nanowires, the question remains as to its suitability for CdSe nanowires formation. This is because the reaction rate of two systems is very different. Thus, the formation mechanism for CdSe nanowires may not have enough time for oriented attachment due to its very high reaction rate. Is it possible to explain the growth mechanism of CdSe nanowires by the previous proposed mechanisms such as the size distribution focusing, the selective-adsorption of surfactants on different crystallographic faces or the effective-monomer models? Further studies are needed to solve this issue for the formation of CdSe nanowires.
- 2) Understand the transport mechanism of the electron/hole carriers and how the confinement of photons within a single 1D cadmium chalcogenide nanocrystal affects the transport of charges as well as the optical properties, such as absorption and PL quenching of HNSs at different temperature ranges. Proposed equipments or methods are spatially and temporally resolved femtosecond or attosecond near-field spectroscopy, multi-mode scanning probe microscope (SPM), ultrahigh vacuum scanning tunneling microscope at liquid helium temperature (UHV-LT STM) and computer controlled optical characterization equipment to obtain PL imaging, bright field imaging and time-resolved PL spectroscopy.
- 3) Extend these methods to synthesize high quality 1D nanocrystals such as III-V or copper indium chalcogenide (CuInX_2 , with $X = \text{S, Se and Te}$) semiconductor nanocrystals. In addition, synthesize other HNSs such as CdS/CdSe heteronanowires with a higher aspect ratio for the PL quenching study.

Chapter 10: Conclusions and Future Directions

- 4) Optimize the parameters for these hybrid solar cells, especially for CdSe/P3HT and CdS/MEH-PPV. This is because they have shown a direct relationship between the PV performance and the aspect ratio. In addition to this, investigate other organic materials including small molecules or conjugated polymers for the hybrid solar cells in order to further improve their performance.
- 5) Explore the potential of single 1D nanocrystals synthesized as solar cells and nanoelectronic power sources. This study may demonstrate a possibility of self-powered functional nanoelectronic systems, which are assembled by integrating multiple stacked nanowire PV elements with nanoelectronic, photonic and biological sensing devices.
- 6) Align 1D nanocrystals by alignment techniques such as the electric field, the fluid flow and the Langmuir-Bodgett (LB) technique or soft templating such as block copolymer (polystyrene-block-poly(4-vinylpyridine (PS-P4VP))), in order to get large-scale well-ordered nanocrystal arrays. These assembled nanocrystal arrays have the potential to be used in nanoscale devices and circuits to replace conventional silicon-based devices that have almost arrived their scale-down limit.

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Appendix I: List of Publications

List of Publications

1. **L. F. Xi**, Y. M. Lam. Controlling Growth of CdSe nanowires through Ligand Optimizion. *Chem. Mater.* 2009, 21, 3710 – 3718.
2. **L. F. Xi**, C. Boothroyd, Y. M. Lam. Controlled synthesis of CdSe and CdTe Multi-block Heteronanostructures. *Chem. Mater.* 2009, 21, 1465 – 1470.
3. **L. F. Xi**, W. X. W. Tan, K. S. Chua, C. Boothroyd, Y. M. Lam. Synthesis of monodisperse CdS nanowires and their photovoltaic applications. *Thin Solid Film.* 2009, 517, 6430 – 6434.
4. **L. F. Xi**, W. X.W. Tan, C. Boothroyd, Y. M. Lam. Understanding and controlling the growth of monodisperse CdS nanowires in solution. *Chem. Mater.* 2008, 20, 5444 - 5452.
5. **L. F. Xi**, Y. M. Lam. Y. P. Xu, L. J. Li. Synthesis and characterization of 1D CdSe by a novel reverse micelles assisted hydrothermal method. *J. Colloid Interface Sci.* 2008, 320, 491 - 500.
6. Y. M. Lam, L.X. Song, Y. C. Moy, **L. F. Xi**, C. Boothroyd. Controlled chemical stabilization of self-assembled PS-P4VP nanostructures. *J. Colloid Interface Sci.* 2008, 317, 255 - 263.
7. **L. F. Xi**, Y. M. Lam. Synthesis and characterization of CdSe nanorods using a novel microemulsion method at moderate temperature. *J. Colloid Interface Sci.* 2007, 316, 771 - 778.
8. **L. F. Xi**. Y. M. Lam. Dynamical study of growth mechanism for monodisperse nanowires. *Chem. Mater.* (In preparation)
9. J. Y. Lek, **L. F. Xi**, Y. M. Lam. The effect of the aspect ratio on the performance of CdSe/P3HT hybrid solar cells. *Solar Energy Mater. Solar Cell.* (In preparation).