DESIGN, SYNTHESIS, CHARACTERIZATION, AND PHOTOVOLTAIC APPLICATIONS OF CONJUGATED POLYMER HYBRIDS CONTAINING COORDINATIVELY BINDED SEMICONDUCTING NANOCRYSTALS

A DISSERTATION IN
Chemistry
and
Pharmaceutical Sciences

Presented to the Faculty of the University of Missouri-Kansas City in partial fulfillment of the requirements for the degree

DOCTOR OF PHILOSOPHY

by

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2014
ORGANIC-INORGANIC HYBRIDS CONTAINING ORGANIC CONJUGATED POLYMERS AND INORGANIC SEMICONDUCTING NANOCRYSTALS

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University of Missouri-Kansas City, 2014

ABSTRACT

Organic-inorganic hybrids containing organic conjugated polymers and inorganic semiconducting nanocrystals are fascinating optoelectronic materials which may combine the advantages of both worlds. This dissertation aims at developing rod-coil diblock copolymers with semiconducting nanoparticles coordinatively bound to the coil block. A mechanochemical process has been shown to be a viable and economical approach to prepare uncapped composition tunable semiconducting nanocrystals including CdSe$_x$S$_{1-x}$, Cd$_x$Zn$_{1-x}$S, and CdSe$_x$Te$_{1-x}$. The resulting II-IV nanocrystals are chemically homogenous with average sizes lower than ~10 nm, and show a linear lattice parameter-composition relationship. The CdSe$_x$S$_{1-x}$ and Cd$_x$Zn$_{1-x}$S series show close-to-linear relationship between the bandgap energy and the composition. The ternary CdSe$_{0.25}$Te$_{0.75}$, CdSe$_{0.5}$Te$_{0.5}$ and CdSe$_{0.75}$Te$_{0.25}$ nanocrystals show strong absorption in the NIR range presumably due to both optical bowing effect and Te induced crystal defects.

Colloidal CdSe nanocrystals have also been prepared by wet chemical methods with organic capping ligands. Three rod-coil diblock copolymers (DCPs) of the modified poly(3-hexylthiophene)-polystyrene (P3HT-PS) type with different phosphorus-containing
functional groups for binding to inorganic nanoparticles have been designed and synthesized. Their corresponding P3HT-PS-CdSe nanocomposites were prepared by ligand-exchange with chemically prepared CdSe nanocrystals. Solid state absorption and fluorescence measurements indicate that the electronic energy states of the polymers are affected by CdSe. Solar cell devices of the three hybrids showed high open circuit voltages of 1.13~1.40 V and improved power conversion efficiencies over devices of the corresponding P3HT-PS diblock copolymers without cluster attachment. The improvement of the PCE is believed to be brought by intimate contact between the P3HT and the CdSe, which enhances the initial charge separation. The device performance is however hampered by the low nanoparticle loading.

Carbon nanoparticles (CNPs) with average sizes around 40–60 nm can also be prepared by the high energy ball milling process. The CNPs was utilized as an interfacial layer between TiO$_2$-coated ZnO nanorod arrays and P3HT polymer. They are found to form close and intimate contacts with both TiO$_2$ through carboxylic acid binding and P3HT polymer presumably by way of π–π interaction. The resulting hybrid solar cells showed the highest photocurrent ever reported among the similar type of device.

This abstract of 346 words is approved as to form and content.
The faculty listed below, appointed by the Dean of the School of Graduate Studies have examined a dissertation titled “Design, Synthesis, and Characterization of Inorganic Semiconductor Nanocrystal-Conjugated Polymer Hybrid Materials and Their Application in Photovoltaic Devices”, presented by Shaohua Li, candidate for the Doctor of Philosophy degree, and certify that in their opinion it is worthy of acceptance.

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CONTENTS

ABSTRACT .................................................................................................................................................. iii

LIST OF ILLUSTRATIONS .......................................................................................................................... x

LIST OF TABLES .......................................................................................................................................... xvii

ACKNOWLEDGMENTS ................................................................................................................................. xviii

Chapter

1. INTRODUCTION .................................................................................................................................. 1

1.1. Inorganic semiconductor nanocrystals-conjugated polymers hybrid semiconductors .......................................................... 1

1.2. Inorganic semiconductor nanocrystals ................................................................................................. 3

1.2.1. Quantum confinement effect ........................................................................................................ 3

1.2.2. II-VI semiconductors ..................................................................................................................... 6

1.3. Conjugated Polymers .......................................................................................................................... 10

1.4. SNC-CP Hybrid Systems and Their Applications .............................................................................. 12

1.5. Research Objectives .......................................................................................................................... 18

2. PREPARATION OF UNCAPPED TERNARY SEMICONDUCTING NANOCRYSTALS BY MECHANICAL ALLOYING .......................................................... 23

2.1. Introduction ........................................................................................................................................ 23

2.1.1. Mechanical Alloying .................................................................................................................... 23

2.1.2. Types of high-energy ball milling equipments .............................................................................. 25

2.1.3. Mechanical Alloying in Preparation of Composition Tunable Semiconductor Nanocrystals .................................................................................................................. 29
2.2. Results and Discussions ................................................................. 31
  2.2.1. Structural Evolution during Mechanical Alloying ......................... 31
  2.2.2. Microstructures of Uncapped and Capped Ternary Nanocrystals ...... 42
  2.2.3. Microstructures of Capped CdSe\textsubscript{x}S\textsubscript{1-x} Nanocrystals in Na\textsubscript{2}S or Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{3} Aqueous Solutions ......................................................... 48
  2.2.4. Composition Dependent Optical Properties of Uncapped Nanocrystals ..... 50
  2.2.5. Raman Properties of Capped CdSe\textsubscript{x}Te\textsubscript{1-x} .......................... 58

2.3. Conclusions ................................................................................. 61

2.4. Experimental Section ................................................................. 62

3. SYNTHESIS OF PHOSPHORUS-CONTAINING POLYSTYRENE AND POLY-3-HEXYLTHIOPHENE-POLYSTYRENE DIBLOCK COPOLYMERS ...... 64
  3.1. Atom Transfer Radical Polymerization ............................................. 64
  3.2. Synthesis of Phosphorus-Containing Styrene Monomer .................... 66
  3.3. Preparation of Polystyrene Containing Phosphonate and Phosphine Oxide Groups by Free Radical Polymerization ........................................ 72
  3.4. Preparation of Polystyrene Containing Phosphonate and Phosphine Oxide Groups by ATRP ................................................................. 75
  3.5. Preparation of Polystyrene with Phosphonic Acid Groups ................. 78
  3.6. Syntheses of P3HT-PS Diblock Copolymers ................................... 80
  3.7. Experimental Section ................................................................... 92

4. PHOSPHINE CONTAINING DIBLOCK COPOLYMER BINDING TO CHEMICALLY PREPARED NANOCRYSTALS AND THE RELATED DEVICE STUDIES ............................................................... 99
  4.1. Introduction ................................................................................. 99
  4.2. Direct Synthesis of Cdse Nanocrystal with PS-3 as both the Acid and the Binding Ligand by Wet Chemical Approach ................................. 101
4.3. Preparations of TOPO-Capped Cdse NCs by Wet Chemical Approach .......... 103
4.4. Preparation of DCP-Cdse Nanocomposites through Ligand Exchange ........... 105
4.5. Photovoltaic Devices Fabrication and Evaluation Based on the DCP-Cdse Nanocomposites ........................................................................................................ 123
4.6. Conclusions ........................................................................................................ 128
4.7. Experimental Section ......................................................................................... 128

5. PREPARATION OF CARBON DOTS BY BALL MILLING AND RELATED ORGANIC-INORGANIC HYBRID PHOTOVOLTAIC DEVICES STUDIES ...... 133
5.1. Introduction ........................................................................................................ 133
5.2. Preparation of Water-Soluble Carbon Nanoparticles by High-Energy Ball Milling ................................................................................................................. 136
5.3. Growth of TiO$_2$-Coated ZnO Nanorods on ITO Glass, Treatment with Water-Soluble CNPs, and Fabrication of HSCs ......................................................... 144
5.4. Conclusions ........................................................................................................ 155
5.5. Experimental Section ......................................................................................... 156

REFERENCES ........................................................................................................ 158

VITA ......................................................................................................................... 173
### ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Electron energy levels of single atom/molecule, semiconductor nanocrystal, and bulk material</td>
<td>5</td>
</tr>
<tr>
<td>2. The absorption and pictures of colloidal CdSe nanocrystals prepared of different reaction times</td>
<td>8</td>
</tr>
<tr>
<td>3. Schematic description of hot injection synthesis of colloidal SNCs</td>
<td>9</td>
</tr>
<tr>
<td>4. A few typical conjugated polymers</td>
<td>11</td>
</tr>
<tr>
<td>5. NC-CP hydrids preparation approaches, including direct mixing, ligand exchange, direct grafting and direct NC growth</td>
<td>18</td>
</tr>
<tr>
<td>6. Single-point(a) and multi-point(b) attachment of CPs onto the NC surface</td>
<td>19</td>
</tr>
<tr>
<td>7. Self-assembled DCPs creating electron/hole transporting pathway with NC hybrids</td>
<td>21</td>
</tr>
<tr>
<td>8. Demonstration of the breakage of powders between two agitated balls: (a) compaction of particles, (b) deformation and agglomeration of particles, and (c) release of particles and balls</td>
<td>24</td>
</tr>
<tr>
<td>9. (a) SPEX 8000 mixer/mill in the assembled condition. (b) Stainless steel vial set consisting of the vial, lid, gasket, and balls</td>
<td>26</td>
</tr>
<tr>
<td>10. (a) Fritsch Pulverisette P-5 four station mechanical ball mill. (b) Schematic description of the ball movement inside the milling vial</td>
<td>27</td>
</tr>
<tr>
<td>11. (a) Model 1-S attritor. (b) The inside arrangement of the attrition ball mill</td>
<td>28</td>
</tr>
<tr>
<td>12. XRD patterns of the as-milled CdSe$<em>{0.5}$S$</em>{0.5}$ products</td>
<td>32</td>
</tr>
<tr>
<td>13. XRD patterns of the as-milled mixture of 0.5Cd+0.5Zn+S after milling</td>
<td>33</td>
</tr>
<tr>
<td>14. XRD patterns of the as-milled Cd$<em>{0.5}$Zn$</em>{0.5}$S compound</td>
<td>35</td>
</tr>
<tr>
<td>15. XRD patterns of the as-milled CdSe$<em>{0.5}$Te$</em>{0.5}$ products</td>
<td>37</td>
</tr>
</tbody>
</table>
16. XRD patterns of CdSe$_{1-x}$S$_x$ nanocrystals ball-milled for 40 h
17. XRD patterns of Cd$_{1-x}$Zn$_x$S nanocrystals ball-milled for 40 hours
18. XRD patterns of 40h ball-milled CdSe$_x$Te$_{1-x}$ nanocrystals
19. HRTEM images of the uncapped CdSe$_{0.5}$S$_{0.5}$ nanocrystals
20. HRTEM images of the 40h as-milled Cd$_{0.5}$Zn$_{0.5}$S nanoparticles
21. HRTEM images of small CdTe0.5Se0.5 nanocrystals dispersed in ethanol solution
22. HRTEM images of aggregated CdSe$_{0.5}$Te$_{0.5}$ nanocrystals
23. HRTEM images of CdSe$_{0.5}$S$_{0.5}$ nanocrystals dispersed in a Na$_2$S/Na$_2$SO$_3$ aqueous solution
24. UV-Vis absorption spectra of uncapped CdSe$_{x}$S$_{1-x}$ nanocrystals
25. Relationship of the bandgap energy (a) and the lattice parameter (b) versus the mole fraction of sulfur in the CdSe$_{x}$S$_{1-x}$ nanocrystals
26. UV-vis absorption spectra of 40h as-milled Cd$_{1-x}$Zn$_x$S ($x=0$–1) nanocrystals
27. Dependence of lattice cell volumes (a) and band gap energies (b) of Cd$_{1-x}$Zn$_x$S nanocrystals on the Zn content
28. UV-Vis absorption spectra of uncapped CdSe$_x$Te$_{1-x}$ nanocrystals
29. Raman spectra of CdSe$_x$Te$_{1-x}$ ($x=0$–1) nanocrystals
30. a) UV-Vis-NIR absorption and b) Raman spectra of (a) pure CdSe NCs and (b) a physical mixture of CdSe NCs and 5% Te metal
31. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of diethyl vinylbenzyl phosphonate
32. $^{13}$C NMR spectrum (CDCl$_3$, 400MHz) of diethyl vinylbenzyl phosphonate
33. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of diethyl vinylbenzyl phosphonate
34. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of dioctyl vinylbenzyl phosphine oxide
35. $^{13}$C NMR spectrum (CDCl$_3$, 400MHz) of dioctyl vinylbenzyl phosphine oxide
36. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of dioctyl vinylbenzyl phosphine oxide ....... 72
37. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-1 .................................................. 74
38. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-2 .................................................. 74
39. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-1 synthesized by ATRP ............ 77
40. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-2 synthesized by ATRP ............ 77
41. $^1$H NMR spectra (CDCl$_3$, 400MHz) of PS-1 and PS-3 ........................................ 79
42. $^1$H NMR spectra of vinyl-terminated P3HT, hydroxyethyl-terminated P3HT, and bromoester-terminated P3HT macroinitiator ............................................................ 82
43. $^1$H NMR spectra of P3HT macroinitiator and P3HT-PS-1, 2, 3 .................................. 85
44. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-1 ........................................ 86
45. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-1 ........................................ 86
46. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-2 ........................................ 87
47. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-2 ........................................ 87
48. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-3 ........................................ 88
49. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-3 ........................................ 88
50. MALDI-TOF MS spectra of (a) Vinyl-terminated P3HT and (b) bromoester-terminated P3HT .......................................................... 90
51. GPC chromatograms of P3HT macroinitiator and P3HT-PS-1, 2, 3 .................... 91
52. The absorption spectra of CdSe/PS-3 composites by direct synthesis ................. 102
53. The absorption and fluorescence spectra of colloidal CdSe NCs ......................... 105
54. FT-IR spectra of P3HT-PS-1,2,3 and P3HT-PS-CdSe-1,2,3 ................................. 108
55. HRTEM images of (a) P3HT-PS-CdSe-1, (b) P3HT-PS-CdSe-2, (c) and (d) P3HT-PS-CdSe-3 .......................................................... 110
56. EDX result of P3HT-PS-CdSe-1 samples ................................................................. 112
57. EDX result of P3HT-PS-CdSe-2 samples ................................................................. 113
58. EDX result of P3HT-PS-CdSe-3 samples ................................................................. 114
59. Normalized UV-visible absorption spectra of pure P3HT and P3HT-PS-1,2,3 samples in chloroform solutions (solid lines) and as thin films (dashed lines) .................. 116
60. Normalized UV-visible absorption spectra of P3HT-PS-CdSe-1,2,3 samples in chloroform solutions (solid lines) and as thin films (dashed lines) .................. 116
61. Normalized fluorescence spectra of pure P3HT and P3HT-PS-1,2,3 samples in chloroform solutions (solid lines) and as thin films (dashed lines) .................. 118
62. Normalized fluorescence spectra of P3HT-PS-CdSe-1,2,3 samples in chloroform solutions (solid lines) and as thin films (dashed lines) .................. 118
63. Cyclic voltammograms of pure CdSe nanocrystal samples ........................................ 121
64. Cyclic voltammograms of P3HT-PS-1,2,3 and P3HT-PS-CdSe-1,2,3 samples ...... 122
65. Solar cell device architecture of the P3HT-PS-CdSe-1,2,3 samples ............................... 123
66. Absorption spectra of P3HT-PS-CdSe-1, P3HT-PS-CdSe-2, and P3HT-PS-CdSe-3 in chloroform solutions (solid lines) and as thin films (dashed lines) .................. 124
67. Current density–voltage (J–V) curves (empty: dark; filled: illuminated) of the solar cells of glass/ITO/PEDOT:PSS/P3HT-PS-CdSe/Ca/Al ........................................... 127
68. SEM images of as-milled (a) and water-soluble (b) CNPs ........................................ 137
69. TEM images of as-milled (a) and water-soluble (b) CNPs ........................................ 138
70. XRD diffraction patterns of (a) water-soluble, (b) as-milled CNPs, and (c) pure graphite ......................................................................................................................... 140
71. FT-IR spectrum of water-soluble CNPs ................................................................. 141
72. Absorption of water-soluble CNPs ............................................................................ 142
73. Fluorescence spectra of water-soluble CNPs ......................................................... 143
74. Reduction cyclic voltammogram of CNPs in aqueous solution ................................... 144
75. ZnO nanorods on ITO glass substrate .......................................................... 146
76. Cross-section of ZnO nanorods on ITO glass substrate ................................. 146
77. TiO$_2$–ZnO nanorods on ITO glass substrate .................................................. 147
78. Cross-section of TiO$_2$–ZnO nanorods on ITO glass substrate ...................... 147
79. TiO$_2$–ZnO-C dots nanorods on ITO glass substrate ...................................... 148
80. Cross-section of TiO$_2$–ZnO-C dots nanorods on ITO glass substrate .......... 148
81. Cross-section TiO$_2$–ZnO–P3HT nanorods on ITO glass substrate ................. 149
82. Cross-section of TiO$_2$–ZnO–Carbon dots-P3HT nanorods on ITO glass substrate .. 149
83. Device structure of the solar cells of ITO/ZnO/ZnO–TiO$_2$–CNP/P3HT/Au........... 150
84. Energy level diagram of the solar cells of ITO/ZnO/ZnO–TiO$_2$–CNP/P3HT/Au... 151
85. Absorption spectra of the films of ZnO–TiO$_2$, ZnO–TiO$_2$–CNP, ZnO–TiO$_2$/P3HT and ZnO–TiO$_2$–CNP/P3HT on ITO glass substrates......................................................... 152
86. J–V characteristics (empty: dark; filled: illuminated) of the photovoltaic devices of ITO/ZnO–TiO$_2$/P3HT/Au and ITO/ZnO–TiO$_2$–CNP/P3HT/Au ........................ 153
ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ATRP mechanism</td>
<td>65</td>
</tr>
<tr>
<td>2. The structure of modified styrene monomer with diethyl phosphonate (a) and dioctyl phosphine oxide (b) groups</td>
<td>66</td>
</tr>
<tr>
<td>3. Preparation of diethyl vinylbenzyl phosphonate</td>
<td>67</td>
</tr>
<tr>
<td>4. Preparation of dioctyl vinylbenzyl phosphine oxide</td>
<td>68</td>
</tr>
<tr>
<td>5. Preparation of phosphine-containing polystyrene by free radical polymerization with AIBN as the initiator</td>
<td>73</td>
</tr>
<tr>
<td>6. Preparation of polystyrene with diethyl phosphonate groups by ATRP</td>
<td>75</td>
</tr>
<tr>
<td>7. Preparation of polystyrene with dioctyl phosphine oxide groups by ATRP</td>
<td>76</td>
</tr>
<tr>
<td>8. Preparation of polystyrene with phosphonic acid groups by hydrolysis</td>
<td>78</td>
</tr>
<tr>
<td>9. Synthesis of the P3HT-PS DCPs by ATRP</td>
<td>81</td>
</tr>
<tr>
<td>10. Synthesis and ligand exchange of the CdSe NCs with P3HT-PS DCPs</td>
<td>106</td>
</tr>
</tbody>
</table>
TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Molecular weights of P3HT macroinitiator and P3HT-PS-1, 2, 3 from both MS/\textsuperscript{1}H-NMR calculation and GPC results</td>
<td>92</td>
</tr>
<tr>
<td>2. Steady-state UV-visible absorption and fluorescence data of P3HT, P3HT-PS-1,2,3 and P3HT-PS-CdSe-1,2,3</td>
<td>119</td>
</tr>
<tr>
<td>3. Frontier Energy levels of P3HT-PS-CdSe-1,2,3 determined from CV and calculated driving forces associated with the potential electron and hole transfer processes (ET and HT) at P3HT/CdSe interface</td>
<td>121</td>
</tr>
<tr>
<td>4. Parameters of the Photovoltaic Cells under AM 1.5 G 1-Sun (100 mW/cm\textsuperscript{2}) Illumination</td>
<td>127</td>
</tr>
</tbody>
</table>
I would like to express my deepest appreciation and thanks to my advisor and the committee chair, Dr. Zhonghua Peng, for providing me of the opportunity to perform my research work in his group. His constant guidance and persistent help in not only my experimental techniques, but more importantly in the spirit of exploration in regard to research and scholarship, has always been the most valuable part of my experience and my life. It is he who directs me in establishing the eagerness of discovery, the rigorous working attitude, and the motivation in scientific investigation. This dissertation would not have been possibly done without his continuous assistance and support.

I would also like to thank my committee members, Dr. Jerry Dias, Dr. Nathan Oyler, Dr. James Murowchick and Dr. Kun Cheng for supporting my research work and review my dissertation.

I would like to express my gratitude to my colleges and friends who provide inestimable assistance and effort to support my work. I’m really thankful for Dr. Andrew Keightley at the School of Biological Sciences, UMKC for helping us with MALDI-TOF mass measurements. I would like to thank Dr. Vladimir Dusevich at the School of Dentistry, UMKC for SEM and TEM measurements. I’m very much grateful to Dr. Clarissa Wisner and Dr. Nicholas Leventis at the Department of Chemistry, Missouri University of Science and Technology for assisting us with the HRTEM measurements. I specially wish to express my earnest thanks to Dr. James Murowchick at the School of
Geosciences, UMKC. Not only has been supporting me as my committee member, he has also been paying great effort in helping and teaching me with XRD and SEM measurements.

I must express my thanks to all my past and present group members: Dr. Mahuya Bagui, Mr. Jeffrey Hsu, Dr. Sanjiban Chakraborty, Dr. Ching-En Chou, Dr. Tanmoy Dutta, Dr. Guolong Tan, Dr. Yong Li, Ms. Jin Lu, Mr. Kuldeep Shetye and Mr. John Oster. I would have not been able to achieve my accomplishments without their kindness help and support. I want to thank all the staff of the Department of Chemistry: Ms. Josephine Maningat, Ms. Florence Middleton, Ms. Michael Sykora, Mr. John Whitchurch and Ms. Kathy Garrison.

Finally, I would like to express my deepest gratitude to my mom and dad for their priceless love and encouragement. Their support has always been my source of strength to face all the difficulties. Last but not least I want to thank my beloved girlfriend Kathryn Cheng for her sincerely love and effort which are the most valuable part of my life.
Dedicated to my beloved
CHAPTER 1

INTRODUCTION

1.1. Inorganic semiconductor nanocrystals-conjugated polymers hybrid semiconductors

With the world facing fossil energy crisis and serious environmental issues, many genius scientists focus their research effort on seeking for green, sustainable, and environmental friendly materials and energy sources. A great number of ideas and innovations, such as solar cells,\textsuperscript{1-4} light-emitting diodes (LEDs),\textsuperscript{5-7} sensors,\textsuperscript{8-10} and photocatalysis,\textsuperscript{11,12} have been invented and put into practice. Most of these applications are indeed based on various types of semiconductors. To date, hundreds types of semiconducting materials, including both inorganic and organic, have been extensively developed and studied. Inorganic semiconductors have long been demonstrated with great values in electronic, photovoltaic and electroluminescent applications.\textsuperscript{13,14} As an example, silicon-based solar cells are the most well developed ones with energy conversion efficiency as high as 25\%,\textsuperscript{15} and these cells with efficiency of 15–18\% have already been commercialized over the past decade.\textsuperscript{16} Metal oxides, such as titanium dioxide and zinc oxide, have been utilized as photocatalysts for the purposes of photocatalytical water splitting and photodecomposition of pollutes in water waste.\textsuperscript{17}

Specially, inorganic semiconductor nanocrystals show highly pure and adjustable photoluminescence, which make them attractive materials in biosensors, bio-labeling and light emitting applications.\textsuperscript{18-20} They exhibit the unique size-dependent optical and electrical properties, and can be prepared in a wide range of approaches including both “top-down” and “bottom-up” approaches. A top-down approach involves breakage of
large particles into nano-sizes by means of electron beam or laser/x-ray, such as molecular beam epitaxy (MBE), ion implantation, e-beam lithography, and X-ray lithography. The bottom-up approach involves preparation of nanocrystals from molecular precursors, such as hot-solution methods, sol-gel approach, microwave-assisted approach, electrochemical methods, vapor-deposition, and sputtering, etc. By means of changing starting precursors, NCs with various chemical compositions and structures (e.g. core-shell structure) can be simply prepared.

Organic semiconductors, e.g. conjugated polymers, are as well remarkable for their easily tunable band gap and energy levels by such as chemical modifications of their functional groups. Organic semiconductors generally have very high absorption efficiency and relatively high charge mobility, thus only an ultra-thin film of these materials is needed in applications which certainly can lower the production costs. They also exhibit strong photoluminescence and electroluminescence. As a result, they are widely applied in all types of optical and electronical applications, such as solar cell, organic LED, transistors and others.

Apparently, there is always a continuous demand on developing semiconducting materials with better physical, mechanical, electrical and optical performances. More and more attention has been paid on hybrid inorganic-organic semiconductors, which is beneficial in both of their mechanical and optoelectronic properties. As an example, a number of inorganic-organic hybrid solar cells has been designed and fabricated with expectation of high flexibility, low-cost, and high absorption with simple techniques. Inorganic semiconductor nanocrystals (SNCs)-conjugated polymers (CPs) hybrid
semiconductors are among the best of inorganic-organic semiconductors. During the past two decades, a vast type of SNC-CP hybrid materials has been synthesized and studied with improved physical, chemical, optical and electronical properties and enhanced device performances. The benefit brought by SNC-CP hybrid materials is that both the energy levels of the SNC and the CP can be easily tuned by material preparation and chemical modification. It is well known that the band gap energy of semiconducting nanoparticles depends on a few factors: their elemental composition, sizes of the particle, crystallinity and defects. Modification of the SNCs in their crystal size, shape and structure will certainly affect their band gaps. For conducting polymers, Chemical modification of both polymeric backbones and their side groups will affect the conjugation, in which case, the HOMO and LUMO levels of the polymer will be changed. Manipulation of the energy levels of both SNCs and CPs can results in proper alignment in the hybrids which is crucial for enhancement of charge separation/transfer rate on the interface of the two species. Such an enhancement will be essential in improving their device performances.

1.2. Inorganic semiconductor nanocrystals

1.2.1. Quantum confinement effect

Inorganic semiconductors with crystal sizes less than 10nm show tremendous different properties from their bulk materials. They exhibit noteworthy size-dependent optical properties due to the quantum confinement effect. In a semiconductor, when the
electron is excited to the conduction band by an external energy source, a hole will be created in the valance band. Such a formed electron-hole pair has a certain size which is generally specified as the Bohr radius defined by this equation:

\[ \alpha_B = \alpha_H * \varepsilon_r \frac{m_0}{\mu} \]

Here \( \alpha_H = 0.053 \text{ Å} \), which is the Bohr radius of hydrogen atom. \( \varepsilon_r \) is the relative dielectric constant, \( m_0 \) is the mass, and \( \mu \) is the reduced mass which can be expressed as this:

\[ \mu = \frac{m_e^* * m_h^*}{m_e^* + m_h^*} \]

Here \( m_e^* \) is the effective mass of the electron and \( m_h^* \) is the effective mass of the hole.

When the size of the inorganic semiconductor nanocrystal is smaller the exciton Bohr radius, the nanocrystal will behave differently and will show the quantum confinement effect. In this case, the energy levels of the exciton are delocalized over the whole nanocrystal. The energy bands are continuous in a bulk semiconductor, but now they are degenerated into discrete energy levels in a semiconductor nanocrystal. As demonstrated in Figure 1, the bandgap energy of SNCs will become smaller if the size getting larger but within the quantum confinement range. Consequently, their optical
properties, like the absorption and photoluminescence energy, will change dependently on the sizes of the SNCs.

![Figure 1. Electron energy levels of single atom/molecule, semiconductor nanocrystal, and bulk material.](image)

The theoretical calculation of bandgap energy of SNCs was initially done by Brus et. al. with CdS and CdSe as examples. He used the “effective mass approximation” in the calculation, which considered the spherical confinement of exciton inside the SNCs.
The effective mass of electron and hole was used instead of the true mass, and the bandgap energy of SNC can be expressed by the following equation:

\[ E_g^n = E_{g}^{bulk} + \frac{\hbar^2}{8R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.786e^2}{4\pi\varepsilon_0\varepsilon_r R^2} \]

Here \( E_{g}^{bulk} \) is the band gap energy of the bulk material, \( R \) is the radius of the nanocrystal, \( m_e^* \) and \( m_h^* \) is the effective mass of the electron and hole, \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) is the relative permittivity, and \( e \) is the electronic charge. It clearly demonstrated that the band gap energy is dependent to the material itself and to the size of the nanocrystal. Using Brus’s theory, the emission energy of SNC can be calculated as:

\[ \Delta_E = E_g^n + \frac{\hbar^2}{8R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \]

Here \( \Delta_E \) is the emission energy of SNC. This equation elegantly demonstrated the dependence of the emission energy with the band gap energy \( E_g^n \) and the particle size. Clearly, by means of tuning of nanoparticles’ composition and size, engineering of their optical and electronical properties can be accomplished.
1.2.2. II-VI semiconductors

Inorganic Semiconductor nanocrystals can be generally classified into IV (Ge, Si), II-VI (e.g. CdS, CdSe, CdTe, ZnS, ZnSe), III-V (e.g. InP, InAs, GaN, GaAs), and IV-VI (e.g. PbS, PbSe) semiconductors depending on their elemental compositions. Among all types of SNCs, particular attention has been paid in II-VI semiconductors. These nanosized compounds are well known for their easy preparation with high crystalline quality, high luminescence quantum yields with impressive color purity (narrow emission bandwidth), and great stability.\textsuperscript{36-38} Based on their band gap structures, their absorption/emission range normally lies in the UV-Visible range, making them attractive materials in applications of photovoltaic devices and light-emitting diodes.

II-VI semiconductor nanocrystals, similar to other types of SNCs, show strong size-dependent absorption and photoluminescence properties. As an example, Figure 2 displayed the absorption and pictures of colloidal CdSe nanocrystals of different preparation times. The sizes of the CdSe nanocrystals are getting larger when the reaction time is increased. It can be clearly observed that the absorption peaks of the CdSe NCs shift to the longer wavelength when their sizes are increased. The shift of the peak is due to the aforementioned quantum effect. The increase of the crystal size results in decline of the bandgap energy, which will show longer wavelength absorption.
Figure 2. The absorption and pictures of colloidal CdSe nanocrystals prepared of different reaction times. Samples from left to right: 22sec, 35sec, 51sec, 1min, 2min, 3min, 4min, 5min, and 8min.

One of the most developed bottom-up synthetic approaches of II-VI semiconductor nanocrystals, named “hot injection method”, was first developed by Murray and his co-workers in 1993. He synthesized monodisperse CdE (E=S, Se, Te) nanocrystals by quick injection of an organometallic anion precursor solution into a hot solution (300 °C) of a cadmium cationic precursor dissolved in trioctylphosphine oxide (TOPO). Once injected, the organometallic precursors will react fast and form CdSe nanocrystals in a short time. During the reaction, a great number of nucleation centers are generated discretely, followed by a steady growth of the atom precursors on the nuclei. As
the nucleation step is fast, no more nucleation site will form in the following crystal growth step. That leads to a rather narrow size-distribution of the final NCs. The as-prepared NCs possess pure photoluminescent color with quite high quantum yields, and can be synthesized with desirable size, shape, and size distribution by careful control of the synthetic conditions (e.g., temperature, reaction time, ratio of precursors).

Figure 3. Schematic description of hot injection synthesis of colloidal SNCs.
The compounds such as phosphine oxides, amines, and carboxylic acids, which are normally referred as “ligands”, are playing very important role in wet chemical preparation of NCs.\textsuperscript{40} These ligands play two key roles during the reaction: 1) reaction solvent and 2) binding ligand to bring the insoluble quantum dots into hydrophobic organic solutions. For example, TOPO and alkyl amines/carboxylic acids are usually used in CdSe NC preparation by hot-injection method. After the injection of the anion precursor the crystal growth start, and as the CdSe nanocrystals gradually grow to a certain size (~5 nm), these ligands turn to cap the whole surface of the nanocrystals to prevent and stop the already-formed NC from further growth. The ligands play an important role in keeping the stability of NCs from aggregation; however, they are often insulating materials which make it detrimental for applications involving charge transfer in and/or out of the NCs.\textsuperscript{41}

1.3. Conjugated Polymers

Conjugated polymers are conductive or semiconductive due to containing of large \(\pi\)-conjugate systems.\textsuperscript{25} They are generally referred of three types: no heteroatom containing in the backbones, nitrogen heteroatom containing, and sulfur heteroatom containing. The first type include Poly(fluorene)s, polyphenylenes, polypyrrenes, polyazulenes, polynaphthalenes, PPV, Poly(acetylene)s (PAC). The second type contains
poly(pyrrole)s (PPY), polycarbazoles, polyindoles, polyazepine, polyanilines (PANI). The third types contains poly(thiophene)s (PT), poly(p-phenylene sulfide) (PPS).

Figure 4. A few representative conjugated polymers.

A single π-conjugate molecule contains elementary molecular orbital which are referred as highest occupied molecular orbital, HOMO and lowest unoccupied molecular
orbital, LUMO. A conjugated polymer can be considered as a combination of multiple π-electron molecular orbital of the monomers. Degeneration of the molecular orbital favors in electron delocalization, which certainly lower the energy gap between the HOMO and LUMO. The electrons in conjugated polymers can be excited to LOMO, leaving holes in the HOMO. Such formed electron-hole pairs are called excitons. The formation of excitons brings semiconductivity to the conjugated polymers. The unique properties of conjugated polymers lay in their tailorable electron energy levels through chemical modifications. The addition of electron donating/withdrawing groups on the backbone or side of the main chain could affect the electron energy state of the HOMO and LUMO of the whole conjugate system so as to affect its energy levels.

1.4. SNC-CP Hybrid Systems and Their Applications

SNC-CP hybrids were most prepared by simple physical mixing. Many of physically-mixed nanocomposites containing NCs of various type (e.g. CdS, CdSe, CdTe, CdSe<sub>1-x</sub>Tex, TiO<sub>2</sub>, and ZnO) and structure (e.g. quantum dots, nanorods, tetrapods, and nanowires), and different CPs (e.g. P3HT, MEH-PPV), have been studied in solar cell applications and showed good device performances. This method, however, presents major limitation in lack of sufficient charge interaction between the CP and SNC mainly due to the relatively large amount of insulating binding groups on the SNC surfaces. In this dissertation, more attention is paid on the better design of creating intimate contact between SNCs and CPs. This design are beneficial as
The CPs are brought closer to the NCs where charge transfer would be enhanced, and the polymers can act as capping/spacing agents for NCs to prevent them from aggregation. A couple of methods, including ligand exchange and/or directly coupling/grafting of conducting polymers onto the surface of the NCs, were developed by introducing binding functional groups at the end of the conducting polymer chain or on the NC surface. They are discussed with details in this dissertation.

The most easy and convenient way of preparing NC-CP nanocomposites is through direct growth of NCs inside the polymer matrix. In this approach, the SNCs will be grown directly inside the CP matrix under careful control of the growth conditions. A. Watt et. al. first grew lead sulfide (PbS) nanocrystals within MEH-PPV by a one-pot method. No additional ligands were used in this approach; the PbS NCs were synthesized simply by directly mixing of sulfur precursor with lead acetate in a MEH-PPV solution. CdSe NCs in a P3HT solution were prepared in a similar manner by S. Dayal and his coworkers. The as-synthesized CdSe-P3HT nanocomposites showed good solubility in common organic solvents and was suitable for device fabrication. C. H. Lai and his coworkers prepared ZnO NCs within a solution of various alkylethoxy-modified polythiophene analogues, including poly(3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene) (P3MEEHT), poly((3-hexyloxy)thiophene) (P3HOT), poly(3-((2-methoxyethoxy)methyl)thiophene) (P3MEMT), and poly(3-[2-(2-ethoxyethoxy)ethoxy]thiophene) (P3EEET). The as-prepared ZnO nanoparticles were found to be uniformly dispersed in the P3EEET polymer matrix. CdS NCs with various geometrical features were also prepared in P3HT matrix by H. C. Liao and his
coworkers.\textsuperscript{68} Solar cell devices with as high as 2.9% power conversion efficiency were fabricated with these CdS-P3HT nanocomposites. Direct growth of NCs can also be achieved by thermal decomposition of molecular precursors with in CP films, such as CdS-P3HT and ZnO-P3HT hybrids.\textsuperscript{69-72}

Direct NC growth approaches benefit for its simple experimental preparation manner, and it can create a high-intimately contacted interface between the NCs and CPs. It can also eliminate of the usage of organic ligands which are usually insulators. Both of the intimate contact and the elimination of insulating ligands promote higher charge separation rate on the interface, which is beneficial in achieving high efficient solar cells. Although it seems to be a promising and simple way to prepared NC-CP nanocomposites with ligand free, this approach comprises a major limitation of difficulty in control of the size, shape, and size distribution of the NCs.\textsuperscript{73} Other types of preparation approaches thus draw attention, including ligand exchange and direct grafting methods.

Ligand exchange method has been extensively applied for surface modification and functionalization of NCs.\textsuperscript{74,75} NCs are typically surface-covered by ligands, however, they are not tightly connected to each other through chemical bond(s). The ligands are generally attached to the NCs with a dynamic absorption/desorption equilibrium, and can be readily removed and/or replaced by other ligands in the surrounding environment. The equilibrium process of ligands binding to the NCs can be expressed as the following equations:\textsuperscript{74}
Adsorption rate: \( \frac{d\theta}{dt}_a = k_a (1 - \theta)[L] \)

Desorption rate: \( \frac{d\theta}{dt}_d = k_d \theta \)

Here \( \theta \) stands for the surface ligand coverage and can be given as:

\[
\theta = \frac{[ML]}{[M] + [ML]}
\]

Here \( M \) refers to the potential bonding sites on the surfaces of NCs, and \( L \) refers to the free ligand concentration in solutions. The bond state is referred to ML. The dynamic equilibrium of adsorption can be expressed \( M + L \rightarrow ML \), and the equilibrium of desorption as \( ML \rightarrow M + L \).

The ligand coverage percentage on the surface of the NCs is apparently depending on the rate constant \( k_a \) and \( k_d \) value. Several factors could also affect the surface coverage, including the absorption affinity and the steric hindrance of the functional groups on the binding ligand. Generally, the affinity of functional groups can be arranged in the following order (from strong to weak): phosphoric acid > carboxyl acid > alkyl thiols > phosphine oxide > amines > hydroxyl. Stronger binding groups would create more stable colloidal NCs while weak ligand show potential of falling from the surface of NCs, resulting a trend of NC aggregation.
Ligand exchange preparation of NC-CP hybrids can be carried out by either directly exchange of the original ligand on NCs with CPs, or replaced the original ligand first by weak ligand (typically pyridine, Py) then exchange with the CPs. In both cases, CPs containing bindable functional groups are generally required for the adsorption. As examples, Frechet et. al. prepared amino-terminated P3HT composite with CdSe nanorods by ligand exchange.\textsuperscript{76} CdSe were synthesized by wet-chemical methods, followed by ligand exchange with pyridine then with the amino-ended P3HT. They obtain a PCE of as high as 1.4% for the resulting photovoltaic device. They also prepared CdSe NCs hybrid materials with phosphonic acid-terminated P3HT by a similar approach.\textsuperscript{77} Nanocomposites of polythiophene with terminal carbodithioic acid groups and CdSe NCs were reported through ligand exchange approach by C. Querner and his coworkers.\textsuperscript{78} A rod-coil triblock copolymer with multidentate amine binding groups were also attached to CdSe NCs by C. Fang et. al.\textsuperscript{79} Other research works included attachment of -COOH end-functionalized P3HT onto the surface of metal oxides NCs, such as TiO\textsubscript{2} NCs.\textsuperscript{80}

NCs are generally prepared before attachment of CPs in ligand exchange approaches, which ensures the growth of NCs is well controlled in order to obtain high crystal quality, narrow size distribution and low crystal defects. However, ligand exchange method do suffer from a few drawbacks: 1) The process requires multi-step treatment which is more complicate than other methods; 2) when NCs original ligand are replaced with new CPs, it usually end up with insufficient coverage.\textsuperscript{81} This will result in aggregation of NCs in the composites.
The direct grafting approach of CPs onto the surface of NCs was developed to overcome these shortcomings. This approach requires the NCs to be surface-covered by bifunctional ligands either through directly chemical preparation or ligand exchange. Typical bifunctional ligands contain a binding group at one end, and a functional group at the other end which are suitable to couple with end-functionalized CPs. The bifunctional ligands here serve both as the coordinating ligand and as the coupling reagent with the CPs. Hybrid materials of CdSe nanorods, quantum dots and ZnO NCs have also been binded with end-functionalized P3HT. The binding group utilized here included phosphonic ester, phosphine oxide and phosphonic acid. In a typical approach, NCs were first prepared by wet chemical synthesis followed by ligand exchange with bromophenyl phosphine oxide. The arylbromide end group was then coupled with vinyl-terminated CPs (e.g. P3HT, PPV) to form the nanocomposites.
Figure 5. NC-CP hydrids preparation approaches, including direct mixing, ligand exchange, direct grafting and direct NC growth.

1.5. Research Objectives

In this dissertation, a type of inorganic semiconductor nanocrystal-diblock copolymer (SNC-DCP) hybrid systems based on “coil-rod” type of conducting polymers is presented to fulfill the target. The coil block of the copolymer will contain multiple functional groups on the side of the polymer backbone to serve as the binding ligand. The
rod block of the copolymer will be conjugated conducting polymer as electron donor/acceptor and transporter.

This design gives us several unique features: 1) The coil block serves as binding ligands which will solubilize the SNCs, prevent them from aggregation, and bring the SNCs close to the conducting polymer (the rod block). It will be structure flexible to match the surface landscape on SNCs. This can ensure multiple ligands to bind with the SNCs, and thus the binding will be magnified due to stronger attracting force between the SNC and the polymer, which will result in a more stable hybrid system. 2) The conducting...
polymer as the rod block will be electron donor/acceptor and charge carrier in such a design. As a closer distance between the SNC and the polymer is expected due to the strong binding force, a higher electron-hole pair dissociation rate can be expected on the interface, and this design should be beneficial for photovoltaic applications. 3) In a diblock copolymer, the two constituent blocks will preserve distinct structural and chemical features while the whole polymer maintaining microscopic phase separation. Various synthetic approaches make adjustment of the properties for each block possible, and that can lead an effective control over domain functionality. As shown in Figure 7, the rod block in the copolymer turn to stack together due to the π-π interaction between the polymer backbones, and this π-π stacking will promote a phase separation of the two distinct blocks. All SNCs attached to the coil block are expected to stay in same regions while the rigid conducting polymer will form other regions. A spontaneous domain separation is expected under this design when the composites are treated under annealing, which will create effective charge transport pathways in it and result in higher charge transfer efficiency.
The objectives of this dissertation are to synthesize SNC-diblock copolymer nano composites, study their self-assembly behavior in both solution and as solid films, explore their electronic and optical properties, and evaluate their performances as photovoltaic materials and water-splitting photocatalysts. Both coil-coil and rod-coil diblock copolymers will be synthesized. One of the coil block will contain binding ligands such as phosphoric acids, phosphonates, carboxylic acids, or pyridyl groups. The rod block is either PPV or P3HT. For the SNCs, we will initially focus on CdSe one of the most extensively studied systems. We will develop modified wet chemical routes for its synthesis. We will also explore its synthesis using mechanical alloying.

The specific research objectives are: 1) Explore the preparation of SNCs using mechanical alloying and study the compositional, structural, and optical properties of the
resulting SNCs, 2) Develop synthetic approaches to the preparation of polymers containing phosphonates or phosphine oxides, 3) Prepare coil-coil and rod-coil diblock copolymers (DCP) containing phosphonates or phosphine oxides in the coil block, 4) Synthesize DCP-SNC composites through physical mixing (mechanical alloying or ultrasonication of the SNC-DCP mixture, 5) Prepare DCP-SNC nanocomposites using DCP as the acid and binding ligand for simultaneous SNC synthesis and hybrid formation, 6) Study the compositional, structural, morphological properties using NMR, IR, X-ray, SEM, and TEM techniques, 7) Study the optical properties, in particular the fluorescence quenching efficiency and dynamics, 8) Evaluate the photovoltaic device performances of the resulting nanocomposites.
CHAPTER 2

PREPARATION OF UNCAPPED TERNARY SEMICONDUCTING NANOCRYSTALS BY MECHANICAL ALLOYING

(The main content of this chapter was published in Journal of Applied Physics 2011, 110, 124306 entitled “Preparation of uncapped CdSe₁₋ₓSₓ semiconducting nanocrystals by mechanical alloying” and in Journal of Electronic Materials 2013, 42, 3373-3378 entitled “Preparation of uncapped CdSe₁₋ₓTe₁₋ₓ nanocrystals with strong near-IR tunable absorption” as research articles.)

2.1. Introduction

2.1.1. Mechanical Alloying

Mechanical alloying is a process of simultaneously blend and attrition of two or more powder elements into homogeneous single composition compound. This process usually involves “ball milling”, where multiple milling balls and substances constantly impact each other and thus attrition take place. Mechanical alloying is beneficial in fulfilling multiple purposes: 1) continuously grinding results in reduction of particle size, 2) solid-state chemical reaction occurring in the process of mixing multiple elements to form chemical homogeneous alloys, 3) changing of physical properties of the mixtures, such as density, shape, surface topography/morphology and crystal structures. Mechanical alloying was first developed by John Benjamin et. al. at the Paul D. Merica Research Laboratory of the International Nickel Company (INCO) in 1966, who originally used a shaker mill with relatively high speed to prepare nickel-chromium-aluminum-titanium alloy. In 1981 and 1983, Y±Co and Ni±Nb intermetallic
compound was synthesized by milling of elemental Y/Co and Ni/Nb metal powders. These research works established the foundation of potential alloy preparation process by ball milling. Since then, mechanical alloying has been applied in synthesizing various types of metal alloys, ceramics and polymers.

The major driving force of particle size reduction and alloy formation is from the impaction of the milling media. During the milling process, milling balls constantly impact each other, and the collision energy would be absorbed by the particles trapped between two milling balls. The detailed process is depicted in Figure 8. It generally involves three steps: at first, the large particles are compacted and break into smaller and irregularly shaped particles. After that, the two milling balls are continually forced to get close to each other, resulting in elastic and plastic particle deformation. In the third stage, the milling balls are bouncing back due to the elastic impaction, causing further fracture and deformation of the particles. 95
Figure 8. Demonstration of the breakage of powders between two agitated balls: (a) compaction of particles, (b) deformation and agglomeration of particles, and (c) release of particles and balls. Figures are redrawn based on ref. 95.

The Griffith theory specifically demonstrated the fraction stress of the ball impaction during the milling process.\textsuperscript{96} It can be described by this equation:

$$\sigma_F \approx \sqrt{\frac{\gamma E}{c}}$$

Here $\sigma_F$ is the fracture stress, $c$ is the length of the fracture, $E$ is the modulus of elasticity, and $\gamma$ is the surface energy of the milled substance. Particle fracture will be induced when the stress equals or larger than the atom cohesion force of the milled
materials. As the milling process continues, the reduction of particle size will reach a limit: the fracture resistance will increase as the length of the fracture are reduced, due to the decrease in particle size.

2.1.2. Types of high-energy ball milling equipments

A few types of mechanical alloying instruments have been developed and applied in performance. They process different milling arrangement, capacity, production efficiency and other characteristic properties.

SPEX Shaker mills are one of the high-energy ball milling equipments that have most been used for laboratory and research practices. It contains one vial with a few milling balls made in same media. When the machine operates, it will be controlled by an electric motor to move back and forth in a very high frequency. In this process, the milling balls constantly impact the milled samples. The machine is operated at amplitude of 5cm and a rotation speed of 1200 rpm. Typical load of samples is 10~20 g. The vial is well secured and sealed to prevent the air interference and loss of samples. A couple of various milling media of the vials/balls have been developed, including stainless steel, hardened steel, zirconia ceramic, agate, plastic, silicon nitride, methacrylate and others.
Planetary ball mills are favorable mechanical alloying equipments due to its higher loading capacity of samples (Figure 10). A few hundred grams of samples can be milled each time. When it is operated, the milling vials on a rotating support disk moves in planet-like rotation instead of shaking. The vials themselves are also spin on a contrary direction in their own axes. In that case, the samples are actually being grinded and milled under combined centrifugal force from both the rotating support disk and the vial. There are usually two or four vial sets in one machine. Their milling energy is generally lower than the shaker mills.
Attritor mills are designed and operated in a very simple manner. It contains a stationary tank, a large number of milling balls and a rotating drum impeller. When the machine runs, the vertical drum rotates at a relatively high speed (~250 rpm) which forcing the milling balls grinding and agitating. Grinding forces of the powders are from the impact between balls, between balls and wall, and between balls and impellers, all due to the energized ball movement by the impeller. The powder sample loadings are usually very large: from 0.5 to 40kg product can be prepared each time. The limitation is that the particle size distribution of the products is not narrow enough comparing to the previous two methods.
Other ball milling equipments include the rod mills, vibrating frame mills, and others which are operated at various sample capacity, rotation speed and temperature.

2.1.3. Mechanical Alloying in Preparation of Composition Tunable Semiconductor Nanocrystals
Composition-tunable semiconducting nanocrystals (also called alloyed quantum dots) are appealing nanomaterials not only because they exhibit size-dependent optical properties due to the quantum confinement effect but also because they offer an additional means in bandgap engineering through composition tuning. A large number of semiconducting alloyed quantum dots have been reported, some of them exhibiting superior properties over their parent nonalloyed counterparts and finding applications from photostable blue-emitting to near IR-emitting diodes, from ion sensors to solar cell. The majority of these alloyed quantum dots are prepared by solution chemical processes where one or multiple capping agents are needed to solubilize the growing nanoparticles and prevent their aggregation. Although the appealing advantage of the wet chemical approach lies in its remarkable control in the size, shape and size distribution of the resulting nanoparticles, it suffers from some drawbacks: The process requires careful control of reaction temperature and reaction time, and it is difficult to scale up; the resulting alloyed nanocrystals may lack composition homogeneity due to varied reactivity and/or solubility of the competing components, and the as-prepared nanocrystals are ligand-capped which are beneficial for luminescence properties but may be detrimental for applications involving charge transfer in and/or out of the nanoparticles as the capping agents are often insulating organic materials. There is, thus, a need of a complementary synthetic approach which is easily scalable, allows facile composition tuning, and leads to homogeneous nanoparticles without capping groups.

High energy ball milling (HEBM) has been demonstrated to be an effective top-down physical approach to generate ligand-free nanoparticles with sizes smaller than 10
nm. With higher attrition energy being absorbed by the milling media, the particle sizes can be reduced down to nanometer range. HEBM has been applied successfully to prepare semiconductor nanocrystals such as CdS, CdSe, CdTe, PbSe, CuS, ZnO, and CuIn0.75Ga0.25Se2, etc. Mechanical alloying approach in preparation of nanocrystals is favored in a couple of advantages, including: 1) various combinations of elemental reactants make easy preparation of composition tunable nanocrystals with a simple setup. 2) Low operation temperature. The reaction temperature of HEBM is normally less than 100 °C. 3) Large product quantity. Nanocrystals can be prepared in scale of grams by HEBM which is much more than other approaches (usually in mg scale). 4) Nanocrystals prepared in this manner are capping-agent free, which can ensure a high purity of the products.

In this contribution, we show for the first time that simple mechanical alloying (MA) can be used to prepare uncapped ternary CdSe_{x}S_{1-x}, Cd_{x}Zn_{1-x}S and CdSe_{x}Te_{1-x} nanocrystals through the entire composition range.

2.2. Results and Discussions

2.2.1. Structural Evolution during Mechanical Alloying

Structural evolution of CdSe_{x}S_{1-x}, Cd_{x}Zn_{1-x}S and CdSe_{x}Te_{1-x} nanocrystals were studied by X-ray diffraction measurements. During the mechanical alloying, sets of samples at different milled times were removed and their XRD pattern were collected and compared. The results are shown in Figure 12-15.
The elemental Cd, Se, and S diffraction peaks of the CdSe_{0.5}S_{0.5} sample completely disappeared after milling for 1h, confirming that the conversion of Cd+0.5Se+0.5S elemental mixture to CdSe_{0.5}S_{0.5} alloy is completed. The results are shown in Figure 12. As the mechanical alloying process was carried on, the relative intensity of the (101), (102), and (103) diffraction peaks decreases while the rest of the peaks are gradually broadened. The as-milled CdSe_{0.5}S_{0.5} is assigned with a wurtzite structure, where the related diffraction peaks can be indexed to the lattice planes (100), (101), (002), (102), (110), (103), (112), and (201). The structure of the 40 h as-milled CdSe_{0.5}S_{0.5} nanocrystals can still be assigned to the wurtzite structure since the diffraction peaks from lattice planes of (101) and (103) still remain in the XRD pattern. Meanwhile, the X-ray diffraction pattern also indicates the existence of minor amount of products in the “zinc blende” structure. An overlap in diffraction patterns of the two different crystal structures can be observed: the diffraction peaks from \{111\}, \{220\}, and \{311\} lattice planes of the “zinc blende” structure overlap with those from \{002\}, \{110\}, and \{112\} lattice planes of the wurtzite structure. The broadening of the peaks shows the effect of the finite crystallite sizes, as similar broadening effects have also been observed on wet-chemical prepared CdSe nanocrystals. Both of the clean diffraction pattern and the broadening effects clearly indicates that pure CdSe_{0.5}S_{0.5} nanocrystals have been successfully prepared.
Figure 12. XRD patterns of the as-milled CdSe$_{0.5}$S$_{0.5}$ products after (a) 60 min, (b) 2 h, (c) 5 h, (d) 10 h, (e) 20 h, and (f) 40 h of ball milling.

Figure 13 shows X-ray diffraction patterns of 0.5Cd+0.5Zn+S sample in the early stages of the mechanical alloying process. Within the initial one hour of ball milling process, dominant diffraction peaks from elemental Cd, Zn and S can be cleanly seen in the spectrum, indicating that no obvious chemical reactions have occurred. However, all elemental diffraction peaks started to disappear in the 2h sample and completely gone in the 5h sample. Again, this shows the mechanochemical reaction of $0.5\text{Cd}+0.5\text{Zn}+\text{S} \rightarrow \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ has been completed in 5h. There is apparently a rather long induction period
for this particular reaction. The final Cd$_{0.5}$Zn$_{0.5}$S crystals are in the wurtzite structure after 5h of ball milling, and all diffraction peaks can be indexed to the lattice planes (100), (101), (002), (102), (110), (103), (112), (201), as shown in Figure 13a.

Figure 13. XRD patterns of the as-milled mixture of 0.5Cd+0.5Zn+S after milling for (a) 15 min, (b) 30 min and (c) 60 min.

When the mechanical alloying process was kept on after 5 hours, the intensity of the diffraction peak corresponding to the (100) lattice plane in wurtzite structure decreased significantly, while diffraction peaks of the (101), (102), (103) lattice planes
disappeared almost completely. Further prolonging the ball milling time did not cause any further noticeable change. The dominant diffraction peaks of those samples after extended ball milling are assigned to the \{111\}, \{200\}, \{220\}, and \{311\} lattice planes in the zinc blende structure, as shown in Figure 14. Apparently, the crystal structure of the as-milled \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S} alloys transformed from the wurtzite structure at 2 hour’s ball milling to a zinc blende structure after 5 hour or longer ball milling. The crystal phase transition is presumably caused by the local high pressure exerted by the milling balls. Such a phase transition is similar to the high pressure induced structural transformation in \text{CdSe} nanocrystals.\textsuperscript{108} The dominant phase of the final product is the cubic zinc blende structure. It is worth noting that the hexagonal phase was reported to be the major phase of a ball-milled \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S} NC.\textsuperscript{115} Short ball milling time (25 min ~ 160 min) was used there and likely the hexagonal to cubic phase transition was not yet completed. Since the diffraction peak from the (100) lattice planes, albeit weak, nonetheless clearly remains in the XRD pattern of even the 40h as-milled \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S} NCs, the existence of small amount of NCs in the wurtzite structure cannot be excluded. It should be noted that the diffraction peaks from the \{111\}, \{220\}, and \{311\} lattice planes of a zinc blende structure overlap with those from the \{002\}, \{110\}, and \{112\} lattice planes, respectively, of a wurtzite structure. The reasonably clean diffraction patterns in Figure 14 show that pure \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S} nanocrystals have been successfully fabricated through mechanical alloying \text{Cd}, \text{Zn} and \text{S} elemental powders for more than 5 hours. No elemental powders or other impurity are visible in the XRD patterns. The excessive broadening of the \{111\}, \{220\} and \{311\} diffraction bands reflects the finite size broadening effect.

35
Figure 14. XRD patterns of the as-milled \( \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S} \) compound, which were ball milled for (a) 2 hours, (b) 5 hours, (c) 10 hours, (d) 20 hours and (e) 40 hours.

Similar XRD measurements were carried out for the mechanical alloying of \( \text{Cd}+0.5\text{Se}+0.5\text{Te} \) samples. The dominant elemental diffraction peaks in the spectrum of the 15 min ball-milled sample can be clearly observed, such as lattice planes (002), (100), (101) and (102) of cadmium crystals and (101) of tellurium crystals (Figure 15a). The elemental peaks decreased in intensity and disappeared eventually after 5 h of ball milling as the mechanical alloying process continues. This indicates the mechanochemical
reaction of Cd+0.5Se+0.5Te→CdSe$_{0.5}$Te$_{0.5}$ was complete in 5h, similar to the CdSe$_{0.5}$S$_{0.5}$ sample. In the meantime, diffraction peaks corresponding to the (111), (220), and (311) lattice planes of CdSe$_{0.5}$Te$_{0.5}$ compound in the “zinc blende” structure gradually emerged. A nice XRD spectrum is collected for the CdSe$_{0.5}$Te$_{0.5}$ samples ball milled for 40 h, with all the major diffraction peaks showing and can be assigned to the lattice planes (111), (220) and (311) in a cubic structure (zinc blende).

Figure 15. XRD patterns of the as-milled CdSe$_{0.5}$Te$_{0.5}$ products after (a) 15 min, (b) 30 min, (c) 1 hours, (d) 5 hours, (e) 10 hours, (f) 20 hours and (g) 40 hours of ball milling. The XRD patterns of elemental Cd (ICCD PDF#00-005-0674) and Te (ICCD PDF#00-036-1452) crystals are also shown for comparison.
XRD patterns of CdSe<sub>x</sub>S<sub>1-x</sub>, Cd<sub>x</sub>Zn<sub>1-x</sub>S and CdSe<sub>x</sub>Te<sub>1-x</sub> (x=0~1) nanocrystals, all after 40 h of HEBM, are shown in Figure 16-18. A continuous lattice contraction can be observed for all three types of products with increasing mole ratio of sulfur in the CdSe<sub>x</sub>S<sub>1-x</sub>, zinc in the Cd<sub>x</sub>Zn<sub>1-x</sub>S and selenium in the CdSe<sub>x</sub>Te<sub>1-x</sub> compounds. For all three groups of samples, a linear relationship is found between the lattice spacing and the component concentration, indicating that the Vegard’s law is followed here. This is also a proof of the formation of homogeneous ternary alloys instead of heterogeneous mixtures of separate binary nanocrystals, as in which case a superposition of the peaks of pure binary nanocrystals are expected. The crystal structure type evolves as well in addition to changes in lattice spacing.

For CdSe<sub>x</sub>S<sub>1-x</sub> samples, their crystal structure change from the dominating “zinc blende” structure of CdSe to wurtzite structure of CdS. The ternary CdSe<sub>x</sub>S<sub>1-x</sub> nanocrystals with x = 0.25, 0.5 and 0.75 show intermediate crystal structural features between CdSe and CdS. All these three ternary samples show a mix of wurtzite and “zinc blende” structures. In the XRD patterns of CdSe<sub>0.25</sub>S<sub>0.75</sub> and CdSe<sub>0.5</sub>S<sub>0.5</sub> nanocrystals, the existence of diffraction peaks of (101) and (103) lattice planes suggests that they mostly pursue the features of a wurtzite structure. Meanwhile, the XRD pattern of CdSe<sub>0.75</sub>S<sub>0.25</sub> indicates mostly a “zinc blende” structure. CdSe<sub>x</sub>S<sub>1-x</sub> nanocrystals reported by wet chemical synthesis also have similar mixed crystal structures 20 or a pure “zinc blende” structure3, however, the CdSe<sub>x</sub>S<sub>1-x</sub> nanocrystals in “zinc blende” structure throughout showed very
little difference in lattice spacing when their chemical composition changed. In our case, the lattice spacing of the CdSe_{1-x}S_{1-x} nanocrystals prepared by mechanical alloying changes significantly and linearly with various chemical composition.

Figure 16. XRD patterns of CdSe_{1-x}S_{x} nanocrystals ball-milled for 40 h.

XRD patterns of Cd_{1-x}Zn_{x}S (x=0–1) NCs with different Cd to Zn mole ratios have been studied. All those Cd_{1-x}Zn_{x}S NCs (x = 0, 0.25, 0.5, 0.75, 1) were ball milled for 40 hours. As shown in Figure 17, the as-milled CdS NCs have the wurtzite structure while the ZnS NCs show the zinc blend structure. The ternary Cd_{1-x}Zn_{x}S NCs (x=0.25, 0.5,
0.75), however, exhibit intermediate structural features with both crystal structure forms coexistent. The Cd$_{0.75}$Zn$_{0.25}$S NCs are wurtzite structure dominant since the diffraction peaks of the (100), (102) and (103) lattice planes are clearly visible in the XRD pattern (Figure 17b). Cd$_{0.5}$Zn$_{0.5}$S and Cd$_{0.25}$Zn$_{0.75}$S NCs, on the other hand, are predominantly the zinc blende structure as indicated by the disappearance of diffraction peaks of (101), (102) and (103) lattice planes of wurtzite structure (Figure 17c,d). Although both wurtzite and zinc blende structures are found in the ternary ball-milled NCs, they are clearly chemically homogenous alloys instead of heterogeneous mixtures of separate CdS and ZnS nanocrystals, in which case a superposition of the peaks of pure CdS and pure ZnS would be expected. As the Zn content increases, one sees a continuous lattice contraction. A linear relationship is found between the lattice spacing and the cation composition (x), indicating that the Vegard’s law is followed and again the formation of homogeneous alloys. Both the chemical composition and varied lattice spacing may contribute to the modulation of the nanocrystal’s bandgap energies.
Figure 17. XRD patterns of Cd_{1-x}Zn_{x}S nanocrystals ball-milled for 40 hours, (a) CdS; (b) Cd_{0.75}Zn_{0.25}S; (c) Cd_{0.5}Zn_{0.5}S; (d) Cd_{0.25}Zn_{0.75}S; (e) ZnS; Grey indices are corresponding to wurtzite structure, while black ones to zinc blende structure.

Figure 18 shows XRD patterns of CdSe_{x}Te_{1-x} nanocrystals with different mole ratios of Se to Te, all ball milled for 40h. The XRD peaks are normalized with respect to the (111) peak intensity. All samples show prominent XRD patterns of the “zinc blende” structure with a continuous lattice contraction as the molar ratio of Se in the CdSe_{x}Te_{1-x} compounds increases. Using CdSe and CdTe as end members, the Te compositions in the three alloys were calculated from the X-ray diffraction peaks\(^{41}\) to be in the range of 0.77-0.83, 0.48-0.56, and 0.18-0.26 for CdSe_{0.25}Te_{0.75}, CdSe_{0.5}Te_{0.5}, and CdSe_{0.75}Te_{0.25}, respectively, which are reasonably close to the initial element loading ratios. It should be noted that a small but clear peak at around 26°, which is believed due to the (101) plane
diffraction of elemental Te crystals, is observed for the CdSe$_{0.25}$Te$_{0.75}$, CdSe$_{0.5}$Te$_{0.5}$ and CdSe$_{0.75}$Te$_{0.25}$ samples. This peak appears at the same position for all three ternary samples and the intensity of this peak increases in the prior compound order.

Figure 18. XRD patterns of 40h ball-milled CdSe$_x$Te$_{1-x}$ nanocrystals where $x = 0$ (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e).

2.2.2. Microstructures of Uncapped and Capped Ternary Nanocrystals

Nanocrystals prepared by mechanical alloying tend to aggregate together to form larger particles. The repeated fracturing and welding process of the particles trapped
during collision of ball milling causes the aggregation of the particles. Nanometer grains are single crystalline while those aggregated big particles are polycrystalline. HRTEM images often give us such morphological views of aggregated nanoparticles, which are composed of nanocrystal grains.

Figure 19 shows two HRTEM images of as-milled CdSe$_{0.5}$S$_{0.5}$ nanocrystals dispersed in ethanol by ultrasonication. Lattice fringes are clearly seen in these images, indicating that the products were highly crystalline. The inset in Figure 19 is the fast Fourier transformation (FFT) pattern of particle A, from which the zone axes of the particle were identified to be wurtzite structure in [01$\overline{2}$] orientation. The lattice fringes are assigned to the {01$\overline{1}$}, {20$\overline{2}$1}, and {2$\overline{1}$0} lattice planes in the wurtzite structure. These results are consistent with the conclusion drawn from XRD diffraction patterns. The uncapped nanocrystals are mostly aggregated with a few individual nanocrystals shown at the edge of the carbon frames. Most of the particles show small sizes with diameters around 5 nm. Bigger particles (6–20 nm), however, are also observed. Most of these nanocrystals exhibit only one-dimensional lattice fringes, making it hard to identify the structure and orientation of these CdSe$_{0.5}$S$_{0.5}$ nanocrystals. On the other hand, {111} lattice planes in the “zinc blende” structure share the same lattice spacing with {0002} lattice planes in the wurtzite structure. As stated earlier, the existence of some CdSe$_{0.5}$S$_{0.5}$ nanocrystals in the “zinc blende” structure again cannot be excluded.
Figure 19. HRTEM images of the uncapped CdSe_{0.5}S_{0.5} nanocrystals.

Figure 20 shows high resolution transmission electron microscopy (HRTEM) images of Cd_{0.5}Zn_{0.5}S NCs, ball milled for 40 hours. Lattice fringes are clearly seen in these images, indicating that the ball-milled alloys are highly crystalline. Consistent with XRD studies, the majority of the NCs are found to have the zinc blende structure but NCs with the wurtzite structure can also be identified. For example, particles A, B, C, E, and F circled in Figure 4 all have the zinc blende structure, while particle D is identified as a wurtzite structure. The lattice fringes of particles A, B and C are assigned to the \{111\} and \{200\} lattice planes of zinc blende structure. The spacing for \{111\} lattice plane in these zinc blende Cd_{0.5}Zn_{0.5}S nanoparticles is determined to be 3.139±0.015 Å in the fast Fourier transformation (FFT) reciprocal space. The lattice spacing of particle D is determined to be 2.007 Å, which is much smaller than those of other particles and is consistent with the spacing of (110) lattice planes of a wurtzite Cd_{0.5}Zn_{0.5}S unit cell. The
inset shows the FFT pattern of particle E, from which the zone axes of the particle were identified to be zinc blende structure in [011] orientation. The lattice fringes are assigned to \{111\}, \{200\} and \{311\} lattice planes. Small particles (4~10 nm) are dominant in these HRTEM images. Larger particles (10-20 nm) are also randomly observed.

Figure 20. HRTEM images of the 40h as-milled Cd_{0.5}Zn_{0.5}S nanoparticles.
Figure 21 shows the HRTEM images of as-milled CdSe$_{0.5}$Te$_{0.5}$ nanocrystals dispersed in ethanol by ultrasonication. Even though most of the as-milled nanocrystals tend to aggregate together, one can still easily pick out small individual nanocrystals, marked by red circles, with sizes of 3-8 nm. Both images share the same scale bar. It can be seen that the small particle in the inset image of Figure 21 exhibits only one dimensional lattice fringe of \{111\} lattice plane, the structure of which is assigned to the fcc zinc blende one. The one dimensional lattice fringes of other particles can be assigned to the \{111\} lattice plane of CdSe$_{0.5}$Te$_{0.5}$ nanocrystals with zinc blende structure as well, consistent with the conclusion drawn from XRD diffraction patterns.

Figure 21. HRTEM images of small CdTe$_{0.5}$Se$_{0.5}$ nanocrystals dispersed in ethanol solution.
Figure 22 shows HRTEM images of aggregated CdSe$_{0.5}$Te$_{0.5}$ nanocrystals. The majority of nanocrystals have their sizes centralized within the range of 2-8 nm, while a small number of aggregated particles with size around 30 nm are also observed. Fast Fourier transformations (FFT) of several individual nanocrystals were carried out in order to identify the crystalline structure of the CdSe$_{0.5}$Te$_{0.5}$ nanocrystals as well as the phase composition. The inset images in Figure 22 demonstrate fast Fourier transformation of three individual nanocrystals being marked as A, B and C. These FFT images show structural features of individual nanocrystals in the reciprocal space. Each spot in FFT image (reciprocal space) corresponds to one lattice plane in real space. The index of each lattice plane corresponding to the diffraction spot has been labeled in these FFT images. Lattice fringes of \{111\}, \{200\} or \{131\} can be clearly seen in the images. Particles A, B and C are all determined to be zinc blende structure (cubic) in [011] orientation from their FFT images in reciprocal space.
2.2.3. Microstructures of Capped CdSe\textsubscript{x}S\textsubscript{1-x} Nanocrystals in Na\textsubscript{2}S or Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{3} Aqueous Solutions

The as-milled CdSe\textsubscript{x}S\textsubscript{1-x} nanocrystals can be dispersed in Na\textsubscript{2}S or Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{3} aqueous solutions, forming clear solutions with color ranging from colorless (CdS) to yellow (CdSe\textsubscript{0.5}S\textsubscript{0.5}) and to red (CdSe). The nanoparticles are likely capped by HS, the
major anionic form of the Na$_2$S solution, which helps to disperse the nanoparticles into the solution. The resulting solutions exhibit excellent stability without color changes after being set at ambient conditions for months. The CdSe$_{0.5}$S$_{0.5}$ aqueous solution was dropped on a holey carbon TEM grid, and its HRTEM images are shown in Figure 23. Contrary to the severe aggregation observed in the HRTEM images of uncapped nanocrystals, the HS capped CdSe$_{0.5}$S$_{0.5}$ nanocrystals are well separated. The size of the particles ranges from 2 to 7 nm (average around 4 nm) and is reasonably uniform. The lattice fringes of a single particle are clearly seen (inset of Figure 23(b)).

Figure 23. HRTEM images of CdSe$_{0.5}$S$_{0.5}$ nanocrystals dispersed in a Na$_2$S/Na$_2$SO$_3$ aqueous solution (black dots are nanocrystals and bridge-like branches are carbon frames).
2.2.4. Composition Dependent Optical Properties of Uncapped Nanocrystals

The optical spectra of the as-milled uncapped nanocrystals were measured using a Shimadzu UV-3600 UV-VISNIR spectrophotometer with an ISR3100 Integrating Sphere attachment which allows the direct measurement of powder samples. The powder samples were pressed into a round hole (10 mm) within a sample holder, which were then put into an integrating sphere mounted in an UV-3600 spectrophotometer. The reflectivity of the alloyed nanocrystals was measured through the integrating sphere. The reflectivity was then converted to absorbance by the Kramers-Kronig transformation.

Figure 24 shows the UV-vis-NIR spectra of the alloyed CdSe$_x$S$_{1-x}$ ($x=0\sim1$) nanocrystals. All five samples were milled for 40 h and thus have similar sizes and size distributions. The color of the CdSe$_x$S$_{1-x}$ powders changes from black, dark red, red to yellow when $x$ value increases. All five samples show optical spectra typical of semiconductors. The absorbance is very small (less than 0.2 cm$^{-1}$) when photon energies are lower than the bandgap energy of the semiconductor nanocrystals. However, when photon energies are higher than the bandgap energy, the absorbance steeply increases. This reflects the intrinsic band structure of as-milled CdSe$_x$S$_{1-x}$ nanocrystals and is similar to the absorption spectra of bulk semiconductors. No absorption peaks are observed, contrary to what is often seen in the solution optical spectra of CdSe$_x$S$_{1-x}$ nanocrystals prepared by wet chemical methods.30 It should be noted that the solution optical properties of nanocrystals are very sensitive to capping agents (or ligands) and solvents. Thus, the solution spectra of capped nanocrystals may not reflect their intrinsic band
structure. As clearly shown in Figure 24, the absorption edges shift towards shorter wavelengths when the mole fraction of sulfur increases.

Figure 24. UV-Vis absorption spectra of uncapped CdSe$_x$S$_{1-x}$ nanocrystals. The inset shows the plots of $a^2E^2$ versus E, where a is the absorption coefficient and E is the photon energy.

To extract the bandgap energies, a direct gap model using a linear fit to a plot of $a^2E^2$ versus E in the region of interest is carried out, where a is the absorption coefficient in cm$^{-1}$ and E is the photon energy in eV. The plots are shown in the inset of Figure 24, based on which the bandgap energies were obtained by linearly extrapolating the steep
a^2E^2 edges to zero absorption. The obtained bandgap energies are plotted in Figure 25a, which clearly shows that the bandgap energy increases with increasing mole fraction of sulfur in the CdSe_{1-x}S_x nanocrystals. The data indicate that the relationship of the bandgap energy with the mole fraction x is slightly off linear and can be better fitted by the following quadratic equation:

\[ E_g(x) = 1.521 + 0.413x + 0.251x^2 \text{(eV)} \]

This yields a bowing parameter of 0.25, lower than the bulk bowing constant of 0.3 and the bowing constant (0.29) reported for CdSe,S_{1-x} nanocrystals prepared by pyrolytic solution processes, indicating lower nonlinearity (better linearity) between bandgap and composition. It is worth noting that the bandgap energies of the as-milled CdSe and CdS nanocrystals are about 0.2 eV lower than the reported values of bulk CdSe (1.74 eV) and CdS (2.53 eV) crystals, presumably due to the differences in crystal structures. For example, the bulk CdSe crystal is wurtzite structure while the ball-milled CdSe is mostly “zinc blende” structure. While the bandgap varies in a slightly off-linear fashion with composition, the lattice parameter changes linearly as shown in Figure 25b. Clearly, the lattice contracts when Se is substituted by a smaller sized S. The lattice contraction changes the valence band structure of the CdSe,S_{1-x} nanocrystals and thus should be responsible for the widening of the bandgap. The linear relationship between the lattice parameter and the composition and the near-linear relationship between the
bandgap energy and the composition indicate that the lattice parameter and the bandgap energy of the alloyed CdSe$_x$S$_{1-x}$ nanocrystals can be rationally designed and engineered.

Figure 25. Relationship of the bandgap energy (a) and the lattice parameter (b) versus the mole fraction of sulfur in the CdSe$_x$S$_{1-x}$ nanocrystals.

Figure 26 shows UV-vis-NIR spectra of the alloyed Cd$_{1-x}$Zn$_x$S ($x = 0 \sim 1$) nanocrystals. All five samples have been ball milled for 40 hours, so that they have similar sizes and size distributions. As shown in Figure 26, there is a steep drop in absorbance at wavelengths around the band gap energy, which is typical for direct semiconductors. The absorbance is very small when photon energy is lower than the band gap energy.
However, when the photon energy is higher than the band gap energy, the absorbance increases sharply and steeply. This reflects the intrinsic band structure of as-milled \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) \( (x=0\sim1) \) nanocrystals, and is similar to absorption spectra of bulk semiconductors. As clearly shown in Error! Reference source not found., the absorption edge shifts towards shorter wavelengths when the mole fraction of zinc increases.

Figure 26. UV-vis absorption spectra of 40h as-milled \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) \( (x=0\sim1) \) nanocrystals, (a)ZnS, (b)\( \text{Cd}_{0.25}\text{Zn}_{0.75}\text{S} \), (c)\( \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S} \), (d)\( \text{Cd}_{0.75}\text{Zn}_{0.25}\text{S} \), (e)CdS.
To extract the band gap energies, a direct gap model using a linear fit to a plot of $\alpha^2E^2$ versus $E$ in the region of interest is carried out, where $\alpha$ is the absorption coefficient in cm$^{-1}$ and $E$ is the photon energy in eV. The plots are shown in the inset of Figure 27, based on which the band gap energies were obtained by linearly extrapolating the steep $\alpha^2E^2$ edges to zero absorption. The obtained band gap energies are plotted in Error! Reference source not found.a (red curve), which clearly shows that the band gap energy increases with increasing mole fraction of Zinc in the Cd$_{1-x}$Zn$_x$S NCs. The data indicate that the relationship of the band gap energy with the mole fraction $x$ is clearly nonlinear and can be well fitted by the following quadratic equation:

$$E_g(x)=2.179+0.448x+0.491x^2 \text{ (eV)} \quad (1)$$

Figure 27. Dependence of lattice cell volumes (a) and band gap energies (b) of Cd$_{1-x}$Zn$_x$S nanocrystals on the Zn content.
This yields a bowing parameter of 0.49, very close to the average bowing constant (0.45) reported in the literature for ternary CdZnS alloys. The bandgap energies of the as-milled Cd$_{1-x}$Zn$_x$S alloys vary from 2.18 eV (CdS) to 3.12 eV (ZnS) in a nonlinear fashion when x changes from 0 to 1.

As mentioned earlier, the lattice contracts when the Zn content in the alloy increases. As shown in Figure 27b, the unit cell volume decreases linearly with the mole fraction x of zinc in Cd$_{1-x}$Zn$_x$S NCs. The magnitude of the contraction of the Cd$_{1-x}$Zn$_x$S unit cell is 27% when Cd atoms are fully replaced by Zn atoms (or x value varies from 0 to 1), which is much larger than that of ball-milled CdSe$_{1-x}$S$_x$ where the lattice contracts only about 11%. The much larger difference in ionic size between Zn$^{2+}$ and Cd$^{2+}$ than that between S$^{2-}$ and Se$^{2-}$ may account for the larger cell contraction. The lattice contraction changes the band structure of the nanocrystals and thus should be responsible, at least partially, for the widening of the bandgap.

Figure 28 shows the UV-vis-NIR spectra of the alloyed CdSe$_x$Te$_{1-x}$ (x = 0~1) nanocrystals. All five samples were milled for 40 h and thus have similar sizes and size distributions. The color of the five CdSe$_x$Te$_{1-x}$ powders is all black. The CdSe and CdTe samples show optical spectra typical of semiconductors: a steep drop in absorption at wavelengths around the bandgap energy. This reflects the intrinsic band structure of as-milled nanocrystals, and is similar to the absorption spectra of bulk semiconductors. The alloyed CdSe$_{0.25}$Te$_{0.75}$, CdSe$_{0.5}$Te$_{0.5}$ and CdSe$_{0.75}$Te$_{0.25}$ samples, however, show very
different optical properties: no clear absorption band edge is observed and strong absorption extends beyond 1400 nm. As the percentage of selenium increases in CdSe$_x$Te$_{1-x}$ nanocrystals, the absorbance in the NIR range increases. It is known that both bulk CdSeTe alloys and chemically prepared CdSeTe quantum dots with wurtzite crystal structures exhibit a nonlinear relationship between the band gap energy and its composition, called “optical bowing”, and it has been reported that the band gap of the CdSeTe alloys can be substantially lower than those of both binary CdSe and CdTe. The “optical bowing” effect has been attributed to a local structural ordering which arises due to differences in ionic size, electro-negativity and lattice constants of different alloyed components. While similar mechanism may be in play in our ball-milled systems, our ball-milled samples show some distinct, unique and previously unseen features: first, the absorption extends to much longer wavelengths; second, there is no clear band edge and the spectrum resembles those of indirect semiconductors;$^{117,118}$ third, the absorbance in the NIR range continues to increase when the Se content is as high as 75%. It is apparent that the local structural ordering, or more broadly the theoretical model developed by Zunger and coworkers on the observed “bowing effect”$^{119}$ is not sufficient to account for the unprecedentedly strong and broad NIR absorption of our ball-milled samples.
2.2.5. Raman Properties of Capped CdSe\textsubscript{x}Te\textsubscript{1-x}

To gain insight into the unusual NIR absorption of the ball-milled alloys, their Raman spectra were collected. As shown in Figure 29, longitudinal optical (LO) and transverse optical (TO) phonons, labeled as LO\textsubscript{1}/TO\textsubscript{1} for CdTe-like and LO\textsubscript{2}/TO\textsubscript{2} for CdSe-like, are observed between 130-220 cm\textsuperscript{-1}. The peaks between 330-430 cm\textsuperscript{-1} are second order LO phonons. Similar to bulk CdSeTe samples, the Raman spectra of ball-milled CdSe\textsubscript{x}Te\textsubscript{1-x} (x = 0.25, 0.5, 0.75) alloys show both the LO\textsubscript{1} and LO\textsubscript{2} bands,\textsuperscript{120} indicating the coexistence of two components. As the percentage of Se in the CdSeTe
nanocrystals increases, the intensity of LO$_1$ peaks decrease while LO$_2$ peaks gradually become dominant. Meanwhile, a clear Te vibrational peak at 122 cm$^{-1}$ is observed in the as-milled CdSe$_x$Te$_{1-x}$ ($x = 0.25, 0.5, 0.75$) samples. The intensity of this peak increases when the content of Se in the CdSe$_x$Te$_{1-x}$ nanocrystals increases. These results indicate the existence of a small amount of tellurium metal in the three alloyed CdSe$_x$Te$_{1-x}$ samples, which is in accordance with XRD results.

Figure 29. Raman spectra of CdSe$_x$Te$_{1-x}$ ($x = 0$–1) nanocrystals.
To find out whether Te metal cluster exists as CdSe$_x$Te$_{1-x}$ crystal defects, or as an independent component in a physical mixture, the UV-vis-NIR absorption and Raman spectra of a physical mixture containing ball-milled CdSe nanocrystals and 5% Te metal were measured and are shown in Figure 30. Unlike ball-milled ternary CdSeTe samples, the physical mixture of CdSe/Te shows no NIR absorption, which indicates at least indirectly that the strong NIR absorption of the three alloyed samples are not due to the existence of Te metal as a physical mixture, but rather as defects of the CdSe$_x$Te$_{1-x}$ crystals. It has been reported that small amount of Te impurities in bulk CdTe can lead to rather strong defect bands which are lower in energy than the bound excitons.\textsuperscript{121} We believe that defect bands arising from local Te clusters are the major contributor to the ternary alloys’ NIR absorption although the regular “optical bowing” mechanism may play a role as well.
2.3. Conclusions

In summary, pure and homogeneous \( \text{CdSe}_x\text{S}_{1-x}, \text{Cd}_x\text{Zn}_{1-x}\text{S} \) and \( \text{CdSe}_x\text{Te}_{1-x} \) nanocrystals \((x=0\text{--}1)\) nanocrystals have been successfully prepared by HEBM of the corresponding elemental powders. The chemical composition of the resulting ternary
nanocrystals can be conveniently controlled by the initial loading of the various elements. The average size of the nanocrystals falls below 10 nm after 40 h of ball milling. The crystal structure of CdSe$_x$S$_{1-x}$ ($x=0$~$1$) evolves gradually from zinc blend type (CdSe, $x=1$) into wurtzite structure (CdS, $x=0$) as the sulfur content increases. For the Cd$_x$Zn$_{1-x}$S samples, the crystal structure evolves gradually from wurtzite structure (CdS, $x=0$) to zinc blend type (ZnS, $x=1$) as the zinc content in the ternary alloy increases. In the meantime, the unit cell volume of all three ternary nanocrystals contracts linearly, indicating that the resulting nanocrystals are chemically homogenous, and the bandgap energies of the ternary compounds can be tuned by chemical compositions.

For the CdSe$_x$Te$_{1-x}$ nanocrystals ($x=0$~$1$), although the as-milled CdSe and CdTe nanocrystals show typical optical behavior of direct semiconductors, the ternary CdSe$_{0.25}$Te$_{0.75}$, CdSe$_{0.5}$Te$_{0.5}$ and CdSe$_{0.75}$Te$_{0.25}$ nanocrystals show strong absorption in the NIR range presumably due to both optical bowing effect and Te induced crystal defects, which is confirmed by Raman spectroscopy. These results have opened an exciting prospect that the simple mechanical alloying approach can be utilized to prepare uncapped composition-tunable semiconducting nanocrystals of ternary, quaternary, or even more complicated chemical compositions. Such ternary nanocrystals are appealing materials for photovoltaic, thermoelectric and NIR-sensitive photodetector applications.

2.4. Experimental Section
A sample preparation procedure of CdSe\(_{x}\)S\(_{1-x}\) nanocrystal is given here and Cd\(_x\)Zn\(_{1-x}\)S and CdSe\(_x\)Te\(_{1-x}\) nanocrystals are synthesized by the same approach. In a typical process, a raw powder mixture of 15g total weight of high purity cadmium (99.99%), selenium (99.99%), and sulfur (99.99%) powders in the desired atomic ratio was sealed in a stainless steel vial, together with stainless balls, under inert atmosphere. The ball milling process of the mixture was carried out in a SPEX 8000M Mixer/Mill using a ball-to-powder mass ratio of 10:1. The milling balls with different diameters of 4–12 mm were used. At different time intervals, small amount of samples were taken out of the vial for structural and property characterizations.

Crystal structure characterizations were carried out by X-ray diffraction measurements on a Rigaku Miniflex powder X-ray diffractometer (Cu K\(_\alpha\), 35kV 15mA, Ni filter), and JEOL 2100F high resolution transmission electronic microscopy (HRTEM) was used to record TEM images. The Raman spectra were collected on an EZRaman-N benchtop Raman spectrometer (Enwave Optronics, Inc., Irvine, CA). The excitation wavelength is set at 785 nm with a 300mW diode laser. The optical spectra of the as-milled powders were measured using a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer with an ISR3100 Integrating Sphere attachment.
CHAPTER 3
SYNTHESIS OF PHOSPHORUS-CONTAINING POLYSTYRENE AND POLY-3-HEXYLTHIOPHENE-POLYSTYRENE DIBLOCK COPOLYMERS

3.1. Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) stands for one of the best studied living radical polymerization methods based on the fast dynamic exchange equilibrium between a relatively small scale of active propagating radicals and a large amount of dormant species. The key feature of such a reaction appreciates a fast initiation step followed by slow propagation step in the polymerization. Not only realizing high degree of polymerization with narrow molecular weight distribution, more importantly, ATRP allows end-functionalization of polymer chain with complex architectures and high compatibility of variety of functional groups. The active chain-end functional initiator allows formation of block copolymers with well control in polymer chain length.

ATRP is achieved with a transition metal catalyst, a multidentate ligand (L), and a counter ion (e.g. halogen) species. The polymerization is started from the one-electron oxidation of the transition metal complex through the reversible cleavage of the alkyl halide initiator, R-X. This process forms a higher oxidation state of the transition metal with combination of the halogen atom X, and meanwhile generates an active radical from the associated halogen elimination. A rate constant $k_a$ is followed for this activation step. Polymer propagation occurs from the addition of the dormant monomers to the intermediate radicals, of which the rate constant is $k_p$. The active radical can also react
with the higher oxidation state metal complex to form the initiative deactivated species with a rate constant of \( k_d \), or they can be terminated by other radicals and disproportionate with a rate constant of \( k_t \). In most cases of well-controlled ATRP, this termination can be drastically diminished to a very low level. As ATRP mainly depends on the fast reversible oxidation-reduction equilibrium between the metal complex and the alkyl halide, the active radical species only stay for short time during polymer propagation. The low exposure time of radicals ensures much lower termination rate.\(^{135}\)

![Scheme 1. ATRP mechanism](image)

If the assumption of fast equilibrium between the activator and deactivator was applied and the contribution of termination turned out to be insignificant, the polymerization rate can be expressed by the following equation:

\[
R_p = k_p [M][P^*] = k_p K_{eq}[M][RX]/([Mt^n/L]/ [Mt^{n+1}X/L])
\]
Here $K_{eq} = k_a / k_d$ which stands for the equilibrium rate of the activation/deactivation.

Clearly, the ATRP reaction rate was controlled by both the concentration of persistent radical ($M_{n+1}^aX/L$) and the activator ($M^i/L$). By modification of transition metal catalyst, binding ligands, initiator functional group/structure and polymerization conditions, controlled molecular weights and polydispersities can be obtained.

3.2. Synthesis of Phosphorus-Containing Styrene Monomer

The first goal in this design is to prepare phosphorus-containing styrene monomer and carry out their polymerization under ATRP conditions as for concept-demonstration before the actual synthesis of the DCPs. Three types of binding groups are selected here, including diethyl phosphonate, dioctyl phosphine oxide, and phosphonic acid. As a result, two modified styrene monomers will be prepared: diethyl vinylbenzyl phosphonate (M1) and dioctyl vinylbenzyl phosphine oxide (M2), as displayed in Scheme 2.

![Scheme 2. The structure of modified styrene monomer with diethyl phosphonate (a) and dioctyl phosphine oxide (b) groups.](image-url)
These two compounds are prepared through the Arbuzov reaction. Both monomers were synthesized from p-vinylbenzyl chloride as the starting compound. In preparation of M1, p-vinylbenzyl chloride was first treated with NaI for overnight where a substitution of –Cl with –I would occur. As iodine is a better leaving group than chlorine, it can be readily react with triethyl phosphite to generate diethyl vinylbenzyl phosphonate through a substitution reaction. The product is a colorless liquid which can be purified by a flash column chromatography with CH$_2$Cl$_2$.

![Scheme 3. Preparation of diethyl vinylbenzyl phosphonate.](image)

The synthesis of M2 is in a similar but easier manner. By reaction of the starting compound with dioctyl phosphine oxide under a basic condition it formed dioctyl vinylbenzyl phosphine oxide. In this reaction, an aqueous solution of 30% NaOH was used as the base. Since the compound will only be soluble in organic solutions, tetrabutylammonium hydrogen sulfate (TBAHS) was used here as the phase transfer
Recrystallization by hexane generated the product as white solid. The product is soluble in Chloroform, THF and acetone, but not soluble in hexane and methanol.

The structure of the two modified styrene monomers are determined by $^1$H-NMR, $^{13}$C-NMR, and $^{31}$P-NMR spectra. The spectra are displayed in Figure 31-36. Both compounds displayed proton peaks from both the aromatic region and from the ethylene group on the side chain of the phosphonate group. For M1, the proton on the aromatic ring showed two doublet peaks at $\sim$7.36 and $\sim$7.25 ppm, while the proton on the double bond showed two doublet peaks at 5.75/5.70 ppm and 5.24/5.21 ppm, and a quadruplet peak at 6.72-6.65 ppm. The proton peaks at 4.01 and 1.23 ppm are assigned from the phosphonate group, which confirms the structure of the product. The $^{31}$P-NMR peak of this compound is found at 21.27 ppm. For M2, the proton on the aromatic ring showed similar two doublet peaks at 7.37/7.35 ppm and 7.19/7.17 ppm, while the proton on the double bond
also showed two doublet peaks at 5.75/5.70 ppm and 5.24/5.22 ppm, and a quadruplet peak at 6.72-6.65 ppm. The proton peaks from the methylene group on the phosphine oxide group are appeared to be a doublet at 3.12/3.08 ppm, and the proton peaks of the alkyl chain on the phosphine oxide group are observed from 1.70-0.87 ppm. The $^{31}$P-NMR peak of this compound is found at 46.99 ppm.

Figure 31. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of diethyl vinylbenzyl phosphonate.
Figure 32. $^{13}$C NMR spectrum (CDCl$_3$, 400MHz) of diethyl vinylbenzyl phosphonate.

Figure 33. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of diethyl vinylbenzyl phosphonate.
Figure 34. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of dioctyl vinylbenzyl phosphine oxide.

Figure 35. $^{13}$C NMR spectrum (CDCl$_3$, 400MHz) of dioctyl vinylbenzyl phosphine oxide.
3.3. Preparation of Polystyrene Containing Phosphonate and Phosphine Oxide Groups by Free Radical Polymerization

The synthesis of the modified polystyrene with phosphine-containing side groups are carried out through regular free radical polymerization reactions. The synthetic scheme is displayed in scheme 5. A regular free radical polymerization condition was applied in all reactions. Both pure styrene and the aforementioned phosphorous-containing styrene monomer were used in the polymerization with a set molar ratio of 9:1 between them. Azobisisobutyronitrile (AIBN) was used as the initiator and toluene was used as the
solvent. Overnight reaction at 80 ºC afforded polystyrene with the desired side groups. Both of the as-prepared polymers showed good solubility in chloroform, THF and acetone but are not soluble in methanol.

Scheme 5. Preparation of phosphine-containing polystyrene by free radical polymerization with AIBN as the initiator.

$^1$H-NMR spectra were taken to confirm the structure of the polystyrene with phosphorous-containing side groups (Figure 37, 38). After polymerization, broad peaks at 7.08 ppm and 6.56–6.46 ppm can clear be seen, which are assigned to the aromatic protons of the polystyrene. For PS-1 sample, the $^1$H-NMR spectra show proton signal at 3.93 ppm and 3.03 ppm which are corresponding to phosphonate groups. Proton signals from alkyl groups, both on styrene and on phosphonate side groups, are also observed at 1.82, 1.41 and 1.15 ppm. For PS-2 sample, the $^1$H-NMR spectra display proton signal at 3.09 ppm corresponding to phosphine oxide groups, and also at 1.84–0.89 ppm which are from the alkyl groups. The $^1$H-NMR results effectively confirm the polymerization of styrene together with the modified styrene monomers are successful.
Figure 37. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-1.

Figure 38. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-2.
3.4. Preparation of Polystyrene Containing Phosphonate and Phosphine Oxide Groups by ATRP

In order to demonstrate the strategy of the preparation of DCPs, ATRP of the modified styrene monomers were also carried out. The synthetic scheme of both modified styrene is displayed in scheme 6 & 7. A typical ATRP condition was applied in all reactions, where CuBr was used as the catalyst, N,N,N’,N’,N’”-pentamethyldiethylenetriamine (PMDETA) as the ligand, Methyl 2-bromopropionate (MBP) as the initiator. No solvent was used in the preparation of polystyrene with diethyl phosphonate groups as both of the reactants are liquid and ATRP are expected to process efficiently. For the preparation of polystyrene with dioctyl phosphine oxide groups, p-xylene was used as solvent. Both reactions were carried out for 24 h at 110 ºC which afforded the desired polystyrene with side groups.

![Scheme 6. Preparation of polystyrene with diethyl phosphonate groups by ATRP.](image-url)
Scheme 7. Preparation of polystyrene with dioctyl phosphine oxide groups by ATRP.

$^1$H-NMR spectra of the two polystyrene with phosphorous-containing side groups were taken to confirm the structure, and the results are displayed in Figure 39 and Figure 40. The broad aromatic proton signals at ~7.07 and ~6.55 ppm confirms the formation of polystyrene. Similar to the polystyrene prepared by free radical polymerization, proton signal at 3.96 ppm and 3.04 ppm which are corresponding to phosphonate groups are observed for PS-1 sample, and proton signals at 2.98 ppm corresponding to phosphine oxide groups can be seen for PS-2 sample. This effectively proves the feasibility of carrying out ATRP on the modified styrene monomers.
Figure 39. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-1 synthesized by ATRP.

Figure 40. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of PS-2 synthesized by ATRP.
3.5. Preparation of Polystyrene with Phosphonic Acid Groups

The polystyrene with phosphonic acid groups (PS-3) was prepared by hydrolysis of the polystyrene with diethyl phosphonate groups (PS-1), as displayed in scheme 8.\textsuperscript{137} The conversion of diethyl phosphonate group into phosphonic acid groups involved hydrolysis reaction through treatment with bromotrimethylsilane (TMSBr) and methanol. During the reaction, a substitution of the ethyl group with the TMS group was occurred. Further treatment with methanol replaces the TMS group, which is a good leaving group, with hydroxyl group. This reaction afforded the target polystyrene with phosphonic acid side groups (PS-3).

![Scheme 8. Preparation of polystyrene with phosphonic acid groups by hydrolysis.](image)

\textsuperscript{1}H-NMR spectra were taken of the polystyrene with phosphonic acid side groups in DMSO-d6 deuterated solvent. It can be seen that after hydrolysis, the aromatic proton signals do not change much (7.11, 6.53 ppm). The proton signals originally at 3.03 ppm which is the proton of the methylene group between the styrene and the phosphonate, are
down-shifted to 2.82 ppm. New peak with strong intensity at 4.01 ppm is observed which is believed corresponding to the protons of phosphonic acid groups. The product shows limited solubility in both non-polar solvent such as CH₂Cl₂ and polar solvent such as methanol, but can be readily dissolved in a 1:1 mixture of CH₂Cl₂ and methanol, or polar solvent with high boiling point such as DMF and DMSO. Both the ¹H-NMR and the amphiphilicity of the product indicates the successful conversion of hydrophobic phosphonate groups into hydrophilic phosphonic acid groups on the polystyrene.

Figure 41. ¹H NMR spectra (CDCl₃, 400MHz) of PS-1 and PS-3.
3.6. Syntheses of P3HT-PS Diblock Copolymers

The detailed syntheses and structures of the P3HT-PS diblock copolymers is shown in Scheme 9. The diblock copolymer was prepared by atom-transfer radical polymerization (ATRP) of the modified styrene monomer under a typical ATRP condition with referring to the literature reports. Here, a subsequential bromoester-terminated P3HT was used as macroinitiator. The P3HT macroinitiator were prepared based on literature reported procedures as displayed in scheme 9. The 3-hexylthiophene monomer was carried out through a Grignard metathesis polymerization (GRIM) and terminated with vinyl ending groups. Followed treatment with 9-BBN and H$_2$O$_2$ afforded hydroxyethyl-terminated P3HT. By reacting with 2-bromopropionyl bromide, bromoester-terminated P3HT was obtained which would serve as the macroinitiator of the ATRP reaction.
Scheme 9. Synthesis of the P3HT-PS DCPs by ATRP.

$^1$H-NMR spectra of 2,5-dibromo-3-hexylthiophene, vinyl-terminated P3HT, and the P3HT macroinitiator were displayed in Figure 42. The pure 2,5-dibromo-3-hexylthiophene shows sharp peaks corresponding to the proton on the thiophene ring (~6.75 ppm) and on the hexyl chain (~2.50, 1.52, 1.27, 0.90 ppm). After polymerization and termination with vinyl group, the proton peaks of the thiophene ring (~6.98 ppm) and on the hexyl chain (~2.76, 1.71, 1.45, 1.27, 0.90 ppm) moved to higher proton shift and became broadened, indicating the formation of P3HT polymers. Small but observable doublet peaks at ~6.80, ~5.51/5.47 and ~5.12/5.09 ppm can be seen which proves the attachment of vinyl ending groups. The final reaction afforded the P3HT macroinitiator with bromoester end groups. In the $^1$H-NMR spectrum, the proton signals of the vinyl groups are disappeared. New peaks at ~4.35, ~3.11, and ~1.83/1.82 ppm are observed.
which correspond to the bromoester end group, indicating the successful preparation of the P3HT macroinitiator.

Figure 42. $^1$H NMR spectra of vinyl-terminated P3HT, hydroxyethyl-terminated P3HT, and bromoester-terminated P3HT macroinitiator.
The preparation of the DCPs was carried out under regular ATRP conditions where CuBr and PMDETA were used as the catalyst and ligand. Three types of DCPs with different functional groups and/or molecular weight were prepared by modifying the functionalized styrene monomers and/or by changing of the monomer/initiator molar ratio. For P3HT-PS-1, pure styrene and diethyl vinylbenzyl phosphonate were both used as monomers with their molar ratio set to be 1:1, and the ratio between \([M]:[I]:[\text{CuBr}]:[\text{ligand}]\) was 100:1:1:6. For P3HT-PS-2, pure styrene and dioctyl vinylbenzyl phosphine oxide were used as monomers with their molar ratio set to be 1:1, and the ratio between \([M]:[I]:[\text{CuBr}]:[\text{ligand}]\) was 100:1:1:6. For P3HT-PS-3, same monomers including pure styrene and dioctyl vinylbenzyl phosphine oxide were used with their molar ratio set to be 4:1, and the ratio between \([M]:[I]:[\text{CuBr}]:[\text{ligand}]\) was changed to be 250:1:20:120. All three reactions successfully afforded DCPs with excellent solubility in chloroform and THF, and they are moderately soluble in acetone. The partial solubility of DCPs in acetone also indirectly indicated the formation of the polystyrene block, as the P3HT macroinitiator was not soluble in acetone. The partial solubility should be brought by the addition of the polystyrene block, which has the functional groups containing long alkyl chains and could promote the improvement of the solubility.

\(^1\)H-NMR spectra of P3HT-MI and all three DCPs are displayed in Figure 43. After ATRP, clear aromatic proton signals from both P3HT (~7.02 ppm) and the attached polystyrene (~6.97, 6.52 ppm) can be observed. More importantly, the spectra show proton signal at 3.96 ppm and 3.04 ppm corresponding to phosphonate group for P3HT-PS-1, and 3.09 ppm corresponding to phosphine oxide group for P3HT-PS-2 and P3HT-
PS-3. This clearly illustrate that the ATRP reactions proceed well with phosphonate- or phosphine oxide-modified styrene monomer. Comparing to P3HT-PS-1 and P3HT-PS-2 samples, P3HT-PS-3 shows much higher in intensity of the proton peaks of the styrene (the aromatic peaks), which indicates a relatively higher amount of styrene repeating units in P3HT-PS-3. This is reasonably in accordance with the reaction setup, where larger amount of monomers were applied and results in higher molecular weight of P3HT-PS-3. While the signals are broad and most are significantly overlapped, one can still identify certain signals which are characteristic to each repeating unit. For example, signals marked as 1, 2 and 3 in Figure 2 can be attributed to the 3-hexylthiophene unit. The phosphonate or phosphine oxide-functionalized styrene units give distinct signals marked as a, b, c, d and e. The phenyl protons (α,β) of styrene are overlapped with those of M₁ or M₂ (a & b). Based on the integration of the characteristic signals, one can calculate the diblock copolymer compositions. For P3HT-PS-1, using the integration ratio of well resolved signals 3 and c (4:1), one can calculate the average number ratio of M₁:M_{thiophene} unit in the diblock copolymer to be ~1:5. With P3HT and M1 compositions in the DCP known and using the integration of the aromatic signals (either a/1/α or b/β or both), one can calculate the average number ratio of M_{styrene}:M_{thiophene} in the DCP to be ~1:3. For the other two DCPs, well-resolved signal 2 was used as the reference for the P3HT block. Based on the integration of signals 3/e and 2, one can calculate the number of protons corresponding to proton e, and thus the number of repeating unit M₂. Once the P3HT and M₂ compositions in the DCP are known, the integration ratio of the aromatic signals versus that of 2 can be used to calculate the number of styrene repeating unit. Following
these procedures, the average number ratio of $M_2$:$M_{\text{styrene}}$:$M_{\text{thiophene}}$ repeating units in P3HT-PS-2 and P3HT-PS-3 are found to be $\sim 0.8:1:2$ and $\sim 1:4:1$, respectively.

Figure 43. $^1$H NMR spectra of P3HT-PS-1, 2, 3.
Figure 44. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-1.

Figure 45. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-1.
Figure 46. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-2.

Figure 47. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-2.
Figure 48. $^1$H NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-3.

Figure 49. $^{31}$P NMR spectrum (CDCl$_3$, 400MHz) of P3HT-PS-3.
The molecular weight and the polydispersity of the P3HT-MI and the three DCPs were determined by MALDI-TOF and Gel permeation chromatography (GPC), and the results are showed in Figure 50 and Figure 51. The MALDI of the vinyl-terminated P3HT sample shows major peaks which are corresponding to the P3HT block with hydrogen or vinyl as ending groups on one side, and hydrogen or bromo group on the other side. However, the relative intensity of hydrogen-terminated P3HT are much lower than that of the vinyl-terminated P3HT, indicating a majority of vinyl-terminated P3HT existence in the product. Figure 51b shows the MALDI of P3HT-MI, where the molecular weight of the most dominant peak was determined to be 2253.46. The mass spectra of P3HT with vinyl ending group (most dominant peak at 2101.45) and that of the P3HT-MI display a difference of 152.01, which is close to the mass of the 2-bromopropionic acid group (~151.95). This is clear evidence of the formation of the bromoester-terminated P3HT macroinitiator. The degree of polymerization (m) is calculated to be 14 based on the average molecular weight of 2,338 determined from MALDI results. Based on the integration of the characteristic signals calculated by $^1$H NMR, the average molecular weight of P3HT-PS-1, P3HT-PS-2 and P3HT-PS-3 are calculated to be 3640, 5038 and 12355, respectively.
Figure 50. MALDI-TOF MS spectra of (a) Vinyl-terminated P3HT and (b) bromoester-terminated P3HT. Expanded spectra in both insets showing sets of peaks corresponding to P3HTs with different terminate group.
GPC results of the P3HT-MI and the three DCPs are shown in Table 1. Determined from both $^1$H-NMR and GPC results, the polymer propagation rate are relatively lower for P3HT-PS-1 and P3HT-PS-2, both of which are under the condition with $[M_0]$:[$I$] = 100:1. When the $[M_0]$ to $[I]$ ratio was increased to 250:1 while the amount of CuBr catalyst was also enlarged, the polystyrene block was prolonged. The results gave $M_n$s of 4975, 5499, and 14822 for P3HT-PS-1, P3HT-PS-2 and P3HT-PS-3, respectively, which are consistent with the calculated $M_n$s based on MALDI and $^1$H NMR. The coil block compositions in all three DCPs reasonably match the monomer loading ratios with styrene only in slight excess, indicating that $M_1$ and $M_2$ have similar reactivity to the styrene monomer.

![Figure 51. GPC chromatograms of P3HT macroinitiator and P3HT-PS-1, 2, 3.](image-url)
Table 1. Molecular weights of P3HT macroinitiator and P3HT-PS-1, 2, 3 from both MS/\textsuperscript{1}H-NMR calculation and GPC results.

<table>
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<th>[M\textsubscript{0}]:[I]:[CuBr]:[Ligand]</th>
<th>PT-MI</th>
<th>P3HT-PS-1</th>
<th>P3HT-PS-2</th>
<th>P3HT-PS-3</th>
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<td>2338</td>
<td>3640</td>
<td>5038</td>
<td>12355</td>
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\(M_n\) calculated by MALDI and \textsuperscript{1}H-NMR

<table>
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<th>(M_n)</th>
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<th>5499</th>
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<td>7256</td>
<td>7282</td>
<td>21167</td>
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<td>1.46</td>
<td>1.32</td>
<td>1.42</td>
</tr>
</tbody>
</table>

All other characterization of DCPs are discussed in chapter 4, including FT-IR spectroscopy, CV measurements, and absorption/fluorescence spectroscopy.

3.7. Experimental Section

**Materials.** All chemicals were purchased from Aldrich or Acros and were used without additional purification unless otherwise noted. \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and \textsuperscript{31}P spectra were recorded in CDCl\textsubscript{3} on a Varian INOVA 400 MHz FTNMR spectrometer. All samples were referenced to the deuterated solvents for the \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra.
measurements, while triphenylphosphine (TPP) was applied as internal standard of the $^{31}$P NMR measurements. GPC measurements were performed on a Tosoh Ecossec HLC 8320GPC system equipped with a differential refractometer, light scattering detector, UV detector, and styragel column with THF as the mobile phase. The instrument was calibrated by the use of five polystyrene standards ranging from 8000 to 90,000 in $M_n$.

**Diethyl (4-Vinylbenzyl)phosphonate (M1).** $p$-Vinylbenzyl chloride (2.15 g, 14.1 mmol) was first stirred with NaI (10.5 g, 70.4 mmol) in acetone solution (40 mL) overnight. Ether (30 mL) was added to the reaction mixture, which was then washed three times with deionized water (100 mL). The formed vinylbenzyl iodide was collected by removing the organic solvents under vacuum, which was then stirred with triethylphosphite (2.34 g, 14.1 mmol) at room temperature for 12 h. The side product (iodoethane) was removed by rotary evaporation, and column chromatography purification of the product on silica gel with dichloromethane as the eluent afforded diethyl(4-vinylbenzyl)phosphonate as pale yellow liquid (3.34 g, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.36 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 10.4$ Hz, 2H), 6.69 (dd, $J = 10.8$ Hz, 18.0 Hz, 1H), 5.73 (d, $J = 17.6$ Hz, 1H), 5.22 (d, $J = 17.6$ Hz, 1H), 4.11-3.92 (m, 4H), 3.14 (d, $J = 21.6$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 135.7, 135.6, 130.8, 129.2, 125.8, 113.1, 61.4, 33.5, 32.2, 15.8; $^{31}$P NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 21.2.

**Dioctyl (4-Vinylbenzyl)phosphine Oxide (M2).** The mixture containing $p$-vinylbenzyl chloride (0.152 g, 1 mmol), dioctyl phosphine oxide (0.220 g, 0.8 mmol), (TBA)$_2$SO$_4$ (29 mg), toluene (3 mL) and 30% NaOH (1.2 mL) was stirred for 24 h.
organic phase was washed with water, and the product was precipitated by adding hexane. Recrystallization of the precipitates from hexane afforded the title product as white solids (0.312 g, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.36 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 10.4$ Hz, 2H), 6.68 (dd, $J = 10.8$ Hz, 17.6 Hz, 1H), 5.72 (d, $J = 17.6$ Hz, 1H), 5.23 (d, $J = 10.8$ Hz, 1H), 3.10 (d, $J = 14.4$ Hz, 2H), 1.6-1.5 (m, 8H), 1.4-1.2 (m, 20H), 0.87 (t, $J = 6.8$ Hz, 6H); $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 136.2, 131.8, 129.6, 129.0, 126.6, 113.4, 35.7, 32.2, 30.9, 28.8, 27.3, 26.7, 22.5, 21.4, 14.0; $^{31}$P NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 47.0.

**Synthesis of PS-1 and PS-2 by ATRP.** Both polystyrene with diethyl phosphonate and dioctyl phosphine oxide groups were prepared through ATRP. CuBr was used as catalyst and PMDETA was used as ligand. In a typical polymerization process, CuBr (17.2 mg, 0.12 mmol, 1 eq), PMDETA (124 mg, 0.72 mmol, 6 eq), and styrene (900 mg, 8.64 mmol, 72 eq) together with diethyl vinylbenzyl phosphonate (244 mg, 0.96 mmol, 8 eq) were added to a dry round bottom flask. The reaction mixture was degassed by three freeze-pump-thaw cycles, and then filled with N$_2$ gas. Methyl 2-bromopropionate (MBP, 40 mg, 0.24 mmol, 2 eq) as the initiator was added, and the reaction mixture was stirred at 110 °C for 24 h under N$_2$ protection. No additional solvent was added as the reaction monomer was in liquid form. After allowing the reaction mixture cooled to room temperature, CH$_2$Cl$_2$ (5 mL) was added and the mixture was poured into hexane (30 mL) to precipitate the product. The green precipitate was collected, redissolved in THF and let run through a short neutral Al$_2$O$_3$ column to remove the catalyst. The solution was then dried under vacuum and washed with methanol for a few times. The solid product was
then dried to afford the pure polymer PS-1. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta/\text{ppm} = 7.07\) (br), 6.56–6.47 (br), 3.95 (br), 3.04 (br), 2.1–1.1 (br).

For the preparation of polystyrene with dioctyl phosphine oxide group, CuBr (3 mg, 0.02 mmol), PMDETA (21 mg, 0.12 mmol), and styrene (176 mg, 1.7 mmol) together with dioctyl phosphine oxide (117 mg, 0.3 mmol) were dissolved in p-Xylene (2 mL) to a dry round bottom flask. The reaction mixture was degassed by three freeze-pump-thaw cycles, and then filled with N\(_2\) gas. MBP (6.7 mg, 0.04 mmol) was added as the initiator. The reaction mixture was stirred at 110 °C for 24 h under N\(_2\) protection. The product was purified by similar method as mentioned above and afforded PS-2. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta/\text{ppm} = 7.06\) (br), 6.55 (br), 3.59 (br), 3.44 (br), 2.98 (br), 2.0-1.1 (br), 0.88 (br).

**Polystyrene with Phosphonic Acid Oxide Groups (PS-3).** Polystyrene with diethyl phosphonate groups (PS-1) were used in the reaction. PS-1 (1.40 g) were dissolved in dry CH\(_2\)Cl\(_2\) (30 mL) under N\(_2\) protection. Trimethylsilyl bromide (1.84g, 12 mmol) was added dropwise, and the reaction mixture was stirred for 24h at room temperature. The reaction mixture was then evaporated in vacuo to remove most of the solvents. Methanol (100 mL) was added to the volatile, and the suspension was stirred overnight at room temperature. The solvent were then evaporated to afford the polystyrene with phosphonic acid groups (PS-3). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta/\text{ppm} = 7.04\) (br), 6.53 (br), 4.00 (br), 3.44 (br), 2.90 (br), 2.1-1.1 (br), 0.88 (br).

**Poly(3-hexylthiophene) Macroinitiator (P3HT-MI).** Vinyl-terminated P3HT was synthesized using a one-pot Grignard metathesis polymerization (GRIM). 2,5-Dibromo-3-hexylthiophene (0.57 g, 1.75 mmol) was stirred in 2 mL of dry THF under
nitrogen protection while tert-butylmagnesium chloride (1.0 M in anhydrous THF, 1.75 mL, 1.75 mmol) was added dropwise over a period of 20 min. The resulting mixture was stirred at r.t. for additional 2 h. After diluted with THF (20 mL), the solution was added [Ni(dppp)Cl₂] (18 mg, 0.036 mmol) and the reaction was continued for 30 min before vinylmagnesium bromide (1.0 M in anhydrous THF, 0.87 mL, 0.87 mmol) was added. After another 30 min, the solution was poured into methanol. The precipitates were collected by filtration and purified by Soxhlet extraction with methanol and hexane to give the vinyl-terminated P3HT in 21.0% yield. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 6.96 (br), 6.80 (m), 5.49 (d, J = 16.8 Hz), 5.11 (d, J = 11.2 Hz), 2.78 (br), 1.68 (br), 1.5-1.3 (br), 0.89 (br).

Preparation of hydroxyethyl-terminated P3HT: 0.5 mL of 9-BBN in THF (0.5 M, 0.25 mmol) was added dropwise into a THF (20 mL) solution of P3HT-V (0.52 g, 0.022 mmol, Mₙ ≈ 2400) at r. t. under N₂. The reaction mixture was stirred at 40 ºC for 24 h, followed by the slow addition of a 30% NaOH solution (0.5 mL). The reaction was continued for another 15 min at r.t. before a 33% aqueous solution of hydrogen peroxide (1 mL) was slowly added. The resulting mixture was stirred for 24 h at 40 ºC and was then poured into methanol. The polymer precipitates were collected by filtration, washed with methanol several times and dried to give P3HT-OH in 94% yield. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 6.96 (br), 3.84 (t, J = 5.6 Hz), 3.47 (s), 3.02 (t, J = 6.4 Hz), 2.78 (br), 1.69 (br), 1.5-1.3 (br), 0.89 (br).

Preparation of bromoester-terminated P3HT: A sample of 2-bromopropionyl bromide (1.5 mL, 12 mmol) was added dropwise into a solution containing P3HT-OH
(0.49 g, 0.02 mmol), triethylamine (2 mL, 14.7 mmol) and anhydrous THF (20 mL) at room temperature under N₂. After being stirred at 40 °C for 24 h, the solution was poured into methanol. The polymer precipitates were collected by filtration and purified by Soxhlet extraction with methanol and hexane. Yield: 96%. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 6.96 (br), 4.35 (m), 3.11 (t, J = 7.2 Hz), 2.78 (br), 1.83 (d, J = 6.8 Hz), 1.68 (br), 1.5-1.3 (br), 0.89 (s).

**P3HT-PS-n (n=1,2,3):** All three DCPs were prepared by ATRP. In a typical polymerization process, CuBr, PMDETA (ligand), and styrene (M) together with the modified styrene monomer (M1 or M2) were added to dry p-xylene. The reaction mixture was degassed by three freeze-pump-thaw cycles, and then filled with N₂ gas. A degassed solution of P3HT-MI in p-xylene (1 mL) was then added, and the reaction mixture was stirred at 110 °C for 24 h under N₂ atmosphere. For P3HT-PS-1, styrene and M1 were used as monomers with a molar ratio of 1:1. For P3HT-PS-2, and P3HT-PS-3, styrene and M2 were used as monomers with a molar ratio of 1:1 and 4:1, respectively. The mole ratio of [M]total:[P3HT-MI]:[CuBr]:[PMDETA] was set to be 100:1:1:6 for P3HT-PS-1 and P3HT-PS-2, while 250:1:20:120 for P3HT-PS-3. After cooled to room temperature, a minute amount of THF was added to the dark-red solution. The solution was then passed through a short neutral Al₂O₃ column to remove the copper catalyst. The eluent was poured into methanol and the resulting precipitates were collected by centrifugation. The collected polymers were redissolved in THF and reprecipitated from methanol to give the corresponding diblock copolymers.
P3HT-PS-1 (23%): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.02 (br), 6.97 (s), 6.50 (br), 3.96 (br), 3.04 (br), 2.79 (br), 1.84 (br), 1.69 (br), 1.4-1.1 (br), 0.90 (br). $^{31}$P NMR (CDCl$_3$, 400 MHz): $\delta$/ppm = 22.1.

P3HT-PS-2 (17%): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.02 (br), 6.96 (s), 6.43 (br), 3.10 (br), 2.78-2.60 (br), 2.0-1.1 (br), 0.88 (br). $^{31}$P NMR (CDCl$_3$, 400 MHz): $\delta$/ppm = 48.1.

P3HT-PS-3 (22%): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.05 (br), 6.97 (s), 6.52 (br), 3.09 (br), 2.79 (br), 2.3-1.2 (br), 0.89 (br). $^{31}$P NMR (CDCl$_3$, 400 MHz): $\delta$/ppm = 46.0.
CHAPTER 4
PHOSPHINE CONTAINING DIBLOCK COPOLYMER BINDING TO CHEMICALLY PREPARED NANOCRYSTALS AND THE RELATED DEVICE STUDIES

4.1. Introduction

Poly(3-hexylthiophene-2,5-diyl) (P3HT), as a benchmark photovoltaic material, is one the most extensively utilized hole-conducting conjugated polymers in HSCs.\textsuperscript{141,142} Its combination with a wide selection of nanostructured (nanoparticles, nanocrystals (NCs), quantum dots, nanowires, nanorods, nanosheets, nanoporous structures, etc.) inorganic semiconductors such as Si,\textsuperscript{143} CdS,\textsuperscript{43,144} CdSe,\textsuperscript{45,145} CdTe,\textsuperscript{49} CuInSe\textsubscript{2},\textsuperscript{146} PbS,\textsuperscript{147} TiO\textsubscript{2},\textsuperscript{148} and ZnO,\textsuperscript{33,149} has been studied in solar cell devices. These HSCs capitalize on the exclusive advantages of both the conjugated polymer and the inorganic semiconductors, and enjoy success not only because of the value adding properties of the resulting hybrids which can combine solution processability of P3HT with the high charge carrier mobility of the inorganic semiconductors, but also due to the prospect of possible synergistic effects. For example, an HSC combining P3HT and an electron accepting semiconductor may exhibit significantly enhanced photoinduced charge separation efficiency due to fast electron dissipation through the semiconductor network.

However, P3HT/inorganic semiconductor HSCs are commonly fabricated by using simple physically mixed composites which make it challenging to realize the required mesoscopically phase-separated interpenetrating, bicontinuous networks with intimate electronic coupling between P3HT and the inorganic component for high-performing HSCs. What’s more, because of the drastic structural and property differences
between those two components, the phase separation of P3HT and inorganic semiconductor is almost inevitable, which eventually limits the performance and long-term stability of the resulting devices.\textsuperscript{150} To improve the compatibility and to ensure intimate contact between the two components as well as the structural stability of the blend films, researchers have developed quite a few viable methods such as surface modification on the inorganic component or the attachment of inorganic-binding ligands to the organic component. It favors in lowering the surface energy of nanoparticles thus improving the interfacial interactions and help facilitate electron injection across the heterojunction. This approach, however, suffers from photodegradation of the dye molecules and lack of morphology control. Compared to the above methods, a more ultimate solution is to covalently or coordinately link the two components through chemical bonds. These methods are beneficial in forming intimate contact between the polymer and the inorganic nanoparticles thus will improve the charge separation. Even though different covalently or coordinately linked nanocomposites have been synthesized or fabricated, thus far no related solar cell devices have been reported.

Rod-coil diblock copolymers (DCPs) are ultimate systems where the two constituent blocks preserve distinct structural and chemical features while the whole polymer maintaining microscopic phase separation.\textsuperscript{151–153} Due to the chemical and structural nature of individual blocks and intermolecular forces between blocks, such as amphiphilicity, flexibility, $\pi$-$\pi$ interaction and hydrogen bonding, they can form microscale or nanoscale structures including micelles and core-shell type of nanoparticles. As a result, they are widely studied and demonstrated in application of drug delivery,\textsuperscript{154}
lithographic masks,\textsuperscript{155} photonic and optoelectronic materials.\textsuperscript{156,157} Studies of rod-coil DCPs with inorganic nanocrystal hybrids in solar cell applications, however, are still limited and can be improved.\textsuperscript{158-160}

In this design we report detailed synthesis, optical studies and devices performance of three “coil-rod” type of modified poly(3-hexylthiophene)-polystyrene (P3HT-PS) diblock copolymers and their corresponding P3HT-PS-CdSe nanocomposites in solar cell applications. The rod block is P3HT which will be the photoactive component, and the coil block is polystyrene which is chemically-modified with phosphorus-containing functional groups. Such a design with multidentate ligands on the PS chain is beneficial in amplifying the affinity between the CdSe nanocrystals and DCPs. The stronger binding interaction can create a more intimately contact between the polymer and nanoparticles\textsuperscript{161,162} thus a higher charge transfer rate can be expected. The optical properties of the nanocomposites, including FT-IR and UV/FL, are carefully studied and discussed. The related solar cells are well evaluated with improved performances comparing to similar devices of pure diblock copolymers.

4.2. Direct Synthesis of CdSe Nanocrystal with PS-3 as both the Acid and the Binding Ligand by Wet Chemical Approach

To test the binding capability of polystyrene with sidegroups as the capping agents, CdSe nanocrystals were synthesized directly within the PS-3 solutions by the wet chemical approach. Cd\textsuperscript{2+} cationic precursor were prepared by reacting of cadmium oxide
with the PS-3 in a NMP solutions. The formed Cd cationic precursors are soluble in NMP and form a clear solutions. The formation of CdSe nanocrystals were archeived by quick injection of Se anionic precursor in TOP solution. The reaction were monitored by UV/Vis absorption of small amout of reaction mixtures (0.2mL) taken out at different time intervals and diluted with CHCl₃. The results are displayed in Figure 52.

Figure 52. The absorption spectra of CdSe/PS-3 composites by direct synthesis. The inset shows the images of the composites of different reaction times in chloroform solutions.
The initial reaction mixture was clear before the injection of selenium precursors, and was recorded as sample S0. Reaction time was recorded immediately after injection, and the solution became change to red-brown color after ~1min. Samples were taken out at 32 s, 2 min 51 s, 5 min 1 s, 7 min 55 s, 10 min, 15 min, 20 min, 30 min and 1 h. It can be seen from the inset of Figure 53 that as reaction continued, the solution became darker in color, indicating CdSe NCs with larger sizes were formed. As a result, the absorption edge extended to longer wavelengths. Although CdSe NCs seems to be formed, however, no identified peaks are observed in the absorption spectra of NCs. This must be due to the relatively broad size-distribution of the formed NCs. The broad distribution of the size of NCs shows that the PS-3 polymer can be binded to NCs as capping agent, however they are lack of control to the NC formation. Additionally, the reaction time were much longer comparing to that of TOPO/HDA-capped CdSe NCs. This can be explained by the more stronger affinity of Cd\textsuperscript{2+} ions to the polymer, which slows the NC formation. In conclusion, the direct formation of CdSe NCs in a polymer solution seems to be processbale, but severy problems lies in its uncontrollable size distribution. As a result, an alternative approach which is the ligand-exchange method, were applied to form the CP-NC nanocomposites.

4.3. Preparations of TOPO-Capped Cdse NCs by Wet Chemical Approach

TOPO/HDA-capped colloidal CdSe nanocrystals were synthesized through the well-demonstrated hot-injection method in order to afford nanocrystals with highly purity,
good crystallinity and narrow size distribution. Stearic acid (SA), hexadecylamine (HDA), and TOPO were used here as the capping agents during CdSe NC formation. The UV-Vis spectrum and fluorescence spectrum of the as-prepared CdSe NCs was recorded to identify the optical properties and the energy gap of the nanocrystals. The absorption peak of colloidal CdSe NCs in a chloroform solution was found at 563 nm and the fluorescence peak was at 580 nm. The band gap energy of CdSe NCs can be determined by the absorption onset value by the following equation:

\[
E_{\text{bandgap}} = \frac{\hbar \times C}{\lambda} = \frac{1240}{\lambda} \text{(eV)}
\]

The value of the absorption onset was determined to be 592 nm, and the band gap energy was calculated to be 2.09 eV. The as-prepared CdSe NCs in chloroform solution showed orange color and displayed a bright yellow fluorescent color when excited by a UV lamp with light wavelength of 365 nm, as displayed in Figure 53. The color purity of both the solution absorption and fluorescent again confirmed its good crystalline quality with narrow size distribution.
Figure 53. The absorption and fluorescence spectra of colloidal CdSe NCs. The inset show the images of the as-prepared CdSe NCs in chloroform solution and the bright yellow fluorescent when excited by a UV lamp with light wavelength of 365 nm.

4.4. Preparation of DCP-Cdse Nanocomposites through Ligand Exchange

The ligand-exchange process was favorable in preparation of DCP-CdSe nanocomposites with good NC quality, as the NCs can be synthesized separately. The scheme of this process is displayed in scheme 10. The aforementioned chemically-prepared colloidal CdSe NC was applied in the ligand exchange process. Before capping of the CdSe NCs with the DCPs, the original TOPO, SA and HDA ligands on the surface
of them need to be removed and replaced with pyridine (py). In this case, pyridine is a less strong capping ligands, thus it can remain on the NC surfaces to keep them stable but also can be readily removed as an intermediate ligand. This process was carried out by constant stirring of the TOPO/HDA-capped CdSe NCs in excess pyridine at 90 °C for 24h. Pyridine slowly replaced the original ligands during the treatment, and the pyridine-capped CdSe can be precipitated out with hexane.

The pyridine-capped CdSe NCs were then exchanged with the DCP(s) in a THF solution again to form the DCP-CdSe nanocomposites as demonstrated in Scheme 10. The exchange process was carried out by ultrasonication where the energy would promote the remove of the pyridine and the attachement of the DCP. The nanocomposites were washed with acetone and methanol to remove excess pyridine and other impurities. The as-prepared DCP-CdSe nanocomposites after ligand exchange show good solubility and processability in chloroform and THF which makes it favorable for device fabrication.

![Scheme 10. Synthesis and ligand exchange of the CdSe NCs with P3HT-PS DCPs.](image)

106
The formations of the DCP-CdSe nanocomposites were determined by FT-IR, TEM and SEM-EDX analysis. Figure 54 shows the FT-IR spectra of the DCPs and the DCP-CdSe nanocomposites. For all DCPs, the IR absorption at 2960~2860 cm⁻¹ (C–H stretching) and 1730~1600 cm⁻¹ (aromatic C=C stretching) can be clearly observed. The characteristic absorption peak of P=O stretching appears at around 1250~1260 cm⁻¹, indicating the existence of phosphonate or phosphine oxide groups on the polymer chains. The IR absorptions of DCP-CdSe nanocomposites, however, show differences: The peaks corresponding to the P=O stretching are either shifted (P3HT-PS-1&2) or reduced (P3HT-PS-3). This is believed to be due to the interaction between the phosphorus-containing functional groups and the NCs, which indicates intimate contacts exist between the two species.
Figure 54. FT-IR spectra of P3HT-PS-1,2,3 and P3HT-PS-CdSe-1,2,3.
Figure 55 shows the high-resolution TEM images of three DCP-CdSe nanocomposites. CdSe nanocrystals with distinct crystalline lattice fringe can be clearly observed in all three composite samples, and the average size of them is ~5 nm. The inset in Figure 55d showed the fast Fourier transformation (FFT) pattern of P3HT-PS-CdSe-3 nanocomposite, from which the crystallinity of the CdSe NC was confirmed. The CdSe NCs appeared to be brighter than the DCP in P3HT-PS-CdSe-1 TEM image but darker in P3HT-PS-CdSe-2 and P3HT-PS-CdSe-3 samples. This should be due to the different phosphorus functional group on the DCP side chains. As can be seen from all images, the CdSe nanocrystals are uniformly distributed among all DCP substrates. However, they show aggregation to some extent especially in P3HT-PS-CdSe-3 samples. This is reasonable as the DCPs are different from small ligands: the multidentate ligands contained by the DCPs are supposed to bind stronger to NCs; instead of covering NCs on their surface, they could attract NCs from different direction and thus form thin molecular layers in between NCs. As a result, the NCs could be brought close to each other. The lattice fringe spacing of the CdSe NCs is measured to be 0.385 nm and is consistent with the lattice spacing of CdSe NCs with Wurzite structure.
Figure 5. HRTEM images of (a) P3HT-PS-CdSe-1, (b) P3HT-PS-CdSe-2, (c) and (d) P3HT-PS-CdSe-3. The inset in figure 5d displays the fast Fourier transformation (FFT) pattern of the nanocrystals in P3HT-PS-CdSe-3.

The content of CdSe nanocrystals in the P3HT-PS-CdSe nanocomposites is examined by EDX analysis. The sample was placed on an aluminum stub by drop-casting.
of chloroform solution of the composites and dried under vacuum. All weight ratios of the two components were calculated based on the weight ratio between sulfur and cadmium. The weight ratio of Polymers to CdSe are estimated to be 18:1, 19:1 and 27:1 for P3HT-PS-CdSe-1,2,3. The result indicates that a relatively low amount of CdSe nanocrystals are indeed coordinated with the diblock compolymers through ligand exchange. It needs to be noted that some region of the nanocomposite samples showed no Cd component, indicating the relatively low amount and partial aggregation of CdSe in the composites.
Figure 56. EDX result of P3HT-PS-CdSe-1 samples. The weight ratio between P3HT-PS-1 and CdSe was calculated to be ~18:1.
Figure 57. EDX result of P3HT-PS-CdSe-2 samples. The weight ratio between P3HT-PS-2 and CdSe was calculated to be ~19:1.
Figure 58. EDX result of P3HT-PS-CdSe-3 samples. The weight ratio between P3HT-PS-3 and CdSe was calculated to be ~27:1.

Solution and film absorption measurements of all DCPs and DCP-CdSe nanocomposites were carried out to study their optical properties at low concentration and at solid state (Figure 59, 60). All three DCPs show almost identical absorption spectra with a strong peak at 444nm in solution similar to that of pure P3HT. After CdSe NCs
attachment, besides the absorption peak of P3HT segment at 442–446 nm, an extra small absorption hump at 578–580 nm can be observed for all DCP-CdSe nanocomposites as displayed in the inset of Figure 60. This absorption is similar to that of pure CdSe NCs (563 nm) in solution, indicating that the NCs had been successfully brought to the solutions. The DCPs films show a broad absorption peak at 483–492 nm with a shoulder at 587–592 nm, over 40 nm red-shifted compared to that of their solution spectra. Such extent of redshifts is common for P3HT-containing DCPs due to the inter-P3HT chain π-stacking in the thin solid films.\textsuperscript{163} It is however worth noting that the extent of the redshifts for the DCPs is less than that for pure P3HT film (Figure 59) because of the introduction of non-conjugated PS segments of different type/length in the polymer chain which interference somehow the inter-P3HT chain π-stacking. After the attachment of CdSe NCs, the absorption of all DCP-CdSe nanocomposites further red-shifted to 496–511 nm. This may be due to the aggregation of CdSe NCs, as can be seen from the TEM images shown in Figure 56, which may have restored the P3HT packing order to different extent in the thin solid films.
Figure 59. Normalized UV-visible absorption spectra of pure P3HT and P3HT-PS-1,2,3 samples in chloroform solutions (solid lines) and as thin films (dashed lines).

Figure 60. Normalized UV-visible absorption spectra of P3HT-PS-CdSe-1,2,3 samples in chloroform solutions (solid lines) and as thin films (dashed lines). The inset is the expanded absorption of the P3HT-PS-CdSe solutions which show the hump absorption of CdSe NCs.

The fluorescence emission spectra of DCPs and HDCPs in chloroform solutions and as solid films have been studied (Figure 61 & 62). When excited at 440 nm, all DCP
and HDCP solutions show nearly identical fluorescence emission spectra and comparable fluorescence quantum yields (~0.065). The typical narrow emission of CdSe NCs was not discernable in the emission spectra of the hybrids, most likely overshadowed by the broad emission of P3HT segments. The lack of fluorescence quenching indicates that the energy/electron transfer from the photoexcited P3HT chromophores to the CdSe NCs is inefficient in dilute solutions. In solid state, the three DCPs show very different emission spectra. While films of P3HT-PS-1 and P3HT-PS-2 both gave an emission maxima at 636 nm, the maximum emission wavelength of P3HT-PS-3 film is only 576 nm, less than 10 nm red-shifted over its solution emission spectrum. As explained earlier, the π-stacking of P3HT in P3HT-PS-3 is not the driving force for the DCP self-assembly but rather the interaction among the much longer PS blocks, which accounts for its much less red-shifted emissions. The binding of CdSe NCs to the PS block resulted in starkly different changes in their films’ fluorescence emissions. While the binding of CdSe NCs leads to negligible change in the film emission spectrum of P3HT-PS-2, the emission spectra of P3HT-PS-1 are blue shifted by 21 nm while those of P3HT-PS-3 are red-shifted by 34 nm after CdSe NCs were coordinated. The relative sizes of the P3HT block and the PS block change from P3HT dominant (P3HT-PS-1) to comparable (P3HT-PS-2) to PS dominant (P3HT-PS-3). The different size disparity in the three DCPs likely gives rise to their different emission changes in responding to CdSe NC binding. It is noted that the film emission spectra of the three HDCPs do not differ as much as those of the three DCPs do. Binding with CdSe NCs significantly alters the interactions among PS blocks. The ligand-cluster coordination is much stronger than other non-covalent intereactions existed in the
HDCPs, such as $\pi-\pi$ stacking and alkyl chain interdigitation. It is thus reasonable to assume that it is the NC-binded PS block dictates solid state aggregation for all three hybrid DCPs, regardless of their initial PS block sizes, making all three hybrid DCPs with comparable solid state optical properties.

Figure 6.1. Normalized fluorescence spectra of pure P3HT and \textbf{P3HT-PS-1,2,3} samples in chloroform solutions (solid lines) and as thin films (dashed lines).

Figure 6.2. Normalized fluorescence spectra of P3HT-PS-CdSe-1,2,3 samples in chloroform solutions (solid lines) and as thin films (dashed lines).
Table 2. Steady-state UV-visible absorption and fluorescence data of P3HT, P3HT-PS-1,2,3 and P3HT-PS-CdSe-1,2,3.

<table>
<thead>
<tr>
<th></th>
<th>Absorptiona (nm)</th>
<th>Emissionb (nm)</th>
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<tr>
<td></td>
<td>solution</td>
<td>film</td>
</tr>
<tr>
<td>P3HT</td>
<td>444</td>
<td>506</td>
</tr>
<tr>
<td>P3HT-PS-1</td>
<td>444</td>
<td>491</td>
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<tr>
<td>P3HT-PS-CdSe-3</td>
<td>442</td>
<td>580</td>
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</table>


The HOMO/LUMO energy levels of the CdSe NCs, DCPs and HDCPs were studied by cyclovoltammetry (CV) measurements. Films of the TOPO/HDA-capped CdSe NCs, DCPs and HDCPs were prepared by drop-casting their solutions onto a Pt-disc working electrode. After drying under the flow of Argon, the CV measurements of all samples were run under identical conditions. As shown in Figure 63, the cyclic voltammogram of pure CdSe NCs shows a clear reversible reduction wave with a half cell potential of −1.13 eV (vs Fc/Fc⁺), from which the LUMO energy level of CdSe NCs can be estimated to be ~−3.67 V. There is no oxidation wave observed during the anodic scan. All DCPs and HDCPs show a similar reduction wave onsetting around −2.3 eV and a semireversible oxidation wave onsetting at 0.3 eV (vs Fc/Fc⁺), both of which are
attributed to the P3HT block (Figure 64). Careful comparison shows that redox processes in HDCPs are all less reversible than those in DCPs. At a lower negative potential, all three HDCPs show a small but clear reduction hump with a peak potential around −1.1 eV. This hump is missing in the voltammograms of the three DCPs and can thus be attributed to the CdSe NCs. The observation of the reduction process of CdSe NCs in the HDCPs not only confirms the successful incorporation of the NCs in the HDCPs, but also indicates that those incorporated NCs are susceptible to electron transfers. Based on the redox onset potentials, one can calculate the HOMO and LUMO levels of the P3HT block to be −5.1 eV and −2.51 eV, respectively. The driving forces for potential charge transfer between the P3HT moiety and the CdSe NCs can be estimated by the Rehm–Weller equation,

\[
\Delta G = e[E_{ox}(D) - E_{red}(A)] - E_g - C \quad (1)
\]

where \(\Delta G\) is the free energy change (in eV) associated with the photoinduced charge transfer process, \(E_{ox}(D)\) and \(E_{red}(A)\) are the oxidation potential of the donor (P3HT) and the reduction potential of the acceptor (CdSe NCs), respectively, \(E_g\) is the bandgap of the donor or acceptor, and \(C\) is the Coulomb term which is \(ca.\) 0.06 eV in acetonitrile.\(^{46}\) The free energy change associated with the electron transfer process from the excited P3HT moiety to the LUMO of the CdSe NCs is calculated to be −1.22 eV, while the free energy change associated with the hole transfer process from the excited CdSe NCs to the HOMO of the P3HT moiety is calculated to be −0.72 eV. The large negative free energy changes indicate that the charge transfer at the P3HT/CdSe NC interface is thermodynamically feasible.
Figure 63. Cyclic voltammograms of pure CdSe nanocrystal samples.

Table 3. Frontier Energy levels of P3HT-PS-CdSe-1,2,3 determined from CV and calculated driving forces associated with the potential electron and hole transfer processes (ET and HT) at P3HT/CdSe interface.

<table>
<thead>
<tr>
<th></th>
<th>Ered (V)</th>
<th>Eox (V)</th>
<th>ELUMO (eV)</th>
<th>EHOMO (eV)</th>
<th>EgCV (eV)</th>
<th>ΔG (ET) (eV)</th>
<th>ΔG (HT) (eV)</th>
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<tbody>
<tr>
<td>P3HT-PS-CdSe-1</td>
<td>-2.39</td>
<td>0.26</td>
<td>-2.41</td>
<td>-5.06</td>
<td>2.65</td>
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<td>2.60</td>
<td>-1.69</td>
<td>-1.18</td>
</tr>
<tr>
<td>P3HT-PS-CdSe-3</td>
<td>-2.38</td>
<td>0.33</td>
<td>-2.42</td>
<td>-5.13</td>
<td>2.71</td>
<td>-1.62</td>
<td>-1.00</td>
</tr>
</tbody>
</table>
Figure 6. Cyclic voltammograms of P3HT-PS-1,2,3 and P3HT-PS-CdSe-1,2,3 samples.
4.5. Photovoltaic Devices Fabrication and Evaluation Based on the DCP-Cdse Nanocomposites

To evaluate the photovoltaic properties of the hybrid diblock copolymers, regular photovoltaic cells with the configuration of glass/ITO/PEDOT:PSS/P3HT-PS-CdSe/Ca/Al as illustrated in Figure 65 were fabricated. In general, the solar cells were fabricated by spin-coating the DCP-CdSe nanocomposite solutions on top of ITO/PEDOT:PSS followed by the deposition of Ca/Al electrodes. Due to the very rough surface of the spin-coated thin films, a very thick Ca layer (45 nm) was adopted which is reported to significantly elevate the work function of Al and consequently provides a much higher electrical field for the active layer.

Figure 65. Solar cell device architecture of the P3HT-PS-CdSe-1,2,3 samples.

Figure 66 displays the absorption spectra of P3HT-PS-CdSe-1,2,3 in chloroform solutions and annealed films on top of the PEDOT:PSS thin film on ITO glasses. The
annealed thin films of P3HT-PS-CdSe-1,2,3 show broad spectral coverage with an absorption peak at ~412nm (for P3HT-PS-CdSe-1,3) or ~485 nm (for P3HT-PS-CdSe-2) with broad shoulder peak (~600 nm) extended to over 700nm. Among the three DCP-CdSe nanocomposites, the P3HT-PS-CdSe-2 film shows the most intense absorption in the visible range. This is a result of balanced interactions of multi-segments/components, i.e. P3HT, PS, and CdSe NCs, in the nanocomposite thin films upon thermal annealing.

Figure 66. Absorption spectra of P3HT-PS-CdSe-1, P3HT-PS-CdSe-2, and P3HT-PS-CdSe-3 in chloroform solutions (solid lines) and as thin films (dashed lines). Note that the thin films were fabricated on PEDOT:PSS/ITO glass substrates and were thermally annealed at 120 °C for 10 min in dark prior to the optical studies.
Figure 67 shows the $J$–$V$ curves of the solar cells, while Table 4 summarizes their $J$–$V$ characteristics, including open circuit voltage ($V_{OC}$), short circuit current density ($J_{SC}$), fill factor (FF), and power conversion efficiency (PCE). Good $V_{OC}$s of 1.40, 1.39, and 1.13 V are observed for the devices of P3HT-PS-CdSe-1, P3HT-PS-CdSe-2 and P3HT-PS-CdSe-3, respectively. The $V_{OC}$s of P3HT:CdSe blends fall usually in the range of 0.55 to 0.80 V depending on the size, structure and morphology of the CdSe component. Referring to the energy level diagrams of the P3HT block and the CdSe nanocrystals in the present cases, the theoretical $V_{OC}$ values for ideal devices with proper percolation should approximately be 0.78, 0.67, 0.85 V, for P3HT-PS-CdSe-1,2,3 respectively (according to the semiempirical equation: $V_{OC} = [\text{LUMO(A)} – \text{HOMO(D)}]/e – 0.30$ V). The outstanding $V_{OC}$s suggest that CdSe component in these DCPs didn’t contribute to the $V_{OC}$. This observation is consistent with the TEM images of the films of the three composites where the CdSe nanocrystals are scattered, isolated from each other and almost entirely covered by the polymers. The relatively higher degree of aggregation of CdSe NCs in P3HT-PS-CdSe-3 is believed to the cause of its relatively lower $V_{OC}$ as part of them may have contributed to the charge separation. P3HT-PS-CdSe-2 gives a much higher $J_{SC}$ of 1.042 mAcm$^{-2}$ comparing to that of P3HT-PS-CdSe-1 (0.217 mAcm$^{-2}$) and P3HT-PS-CdSe-3 (0.119 mAcm$^{-2}$). This is partially due to the most prominent absorption of P3HT-PS-CdSe-2 thin films in the visible range (Figure 66). The long alkyl chains in the binding group in P3HT-PS-CdSe-2 are believed to induce this higher $J_{SC}$ as they would promote the intimate contact between the DCP and CdSe component through the alkyl-alkyl interaction, which would be more favorable during the charge
transportation. Although same long alkyl chains are also present in P3HT-PS-CdSe-3, it suffers from the longer insulating PS block which will prevent efficient charge transportation. The three DCP-CdSe samples give close FF of 0.125, 0.118, and 0.158. This is a result of the non-uniform morphology of the films which is hard to control under the current experimental situations (spin coated from chloroform solutions). While the devices of P3HT-PS-CdSe-1 and P3HT-PS-CdSe-3 give PCE of 0.038 and 0.021%, respectively, the PCE of device of P3HT-PS-CdSe-2 is 0.17% which is about 17 times higher than that of pure P3HT-PS solar cells (~0.01%) fabricated under the same situation. Although the CdSe components are most likely covered by the DCPs and do not contribute much to the $V_{OC}$, they apparently benefit in forming the intimate contact with the P3HT components. The CdSe NCs contributes significantly to promote the charge transportation in P3HT films and thus notably improves the $J_{SC}$ and the PCE of the solar cells.
Figure 67. Current density–voltage ($J$–$V$) curves (empty: dark; filled: illuminated) of the solar cells of glass/ITO/PEDOT:PSS/P3HT-PS-CdSe/Ca/Al. The illuminated curves were measured under AM 1.5 G 1 sun (100 mW/cm$^2$) illumination. For clarity, the inset in (c) shows the illuminated $J$–$V$ curves of the devices with the $J$-axis plotted in log-scale.

Table 4. Parameters of the Photovoltaic Cells under AM 1.5 G 1-Sun (100 mW/cm$^2$) Illumination.

<table>
<thead>
<tr>
<th>active material $^{a,b}$</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-PS-CdSe-1</td>
<td>1.40</td>
<td>0.217</td>
<td>0.125</td>
<td>0.038</td>
</tr>
<tr>
<td>P3HT-PS-CdSe-2</td>
<td>1.39</td>
<td>1.042</td>
<td>0.118</td>
<td>0.170</td>
</tr>
<tr>
<td>P3HT-PS-CdSe-3</td>
<td>1.13</td>
<td>0.119</td>
<td>0.158</td>
<td>0.021</td>
</tr>
</tbody>
</table>

$^{a}$ With device structure of glass/ITO/PEDOT:PSS/P3HT-PS-CdSe/Ca/Al. $^{b}$ Devices were fabricated with thermal annealing treatment at 120 °C for 10 min.
4.6. Conclusions

In conclusion, three types of P3HT-PS diblock copolymers with phosphorus-containing side groups were synthesized through ATRP reaction. Modifications of the ratio of the monomers to the P3HT macroinitiator afforded DCPs with different molecular weight which is characterized by GPC and MALDI-TOF measurements. Nanocomposites of the DCPs and CdSe nanocrystals were prepared by ligand-exchange method and were confirmed by FT-IR, TEM and EDX measurements. While the solution absorption and fluorescence of the nanocomposites showed not much difference compared to that of pure DCP samples, the absorption and fluorescence peaks drastically shifted in the solid state, indicating aggregation of either P3HT component and/or CdSe component occurred to different extent in the P3HT-PS-CdSe-1,2,3. The energy levels of all samples were studied by CV measurements which proved them to be suitably lined up for PV devices. Devices of the three nanocomposites were fabricated with high $V_{oc}$ of 1.13~1.40 V, and PCEs of 0.17% was obtained for devices of P3HT-PS-CdSe-2, which is around 17 times higher than the PCE of pure P3HT-PS devices. The intimate contact between the P3HT and the CdSe components is believed to significantly enhance the charge transportation in P3HT films which remarkably improves the $J_{sc}$ and the PCE.

4.7. Experimental Section

**Materials.** All chemicals were purchased from Aldrich or Acros and were used without additional purification unless otherwise noted. FT-IR spectra were recorded on a
Shimadzu IRAffinity-1 Fourier transform infrared spectrophotometer. TEM images were taken using a FEI TECNAI F20 200 kV super twin lens transmission electron microscope in standard TEM mode. CV studies were performed with a BAS Epsilon EC electrochemical station, using a Pt working electrode of 1.6mm in diameter, a silver wire as the reference electrode and a Pt wire as the counter electrode under argon protection. A 0.1 M tetra-n-butylammonium hexafluorophosphate solution in acetonitrile was used as supporting electrolyte. Cabibration of the potential was carried out by a ferrocene/ferrocenium (Fc/Fc⁺) redox couple whose absolute energy was assigned as −4.80 eV vs vacuum. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated by HOMO = −(E_{ox}^{onset} + 4.80) (eV) and LUMO = −(E_{red}^{onset} + 4.80) (eV), respectively. UV/Vis absorption spectra were collected on a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescence spectra were measured with a Shimadzu RF-5301PC spectrofluorophotometer. Fluorescence quantum yields for solution were calculated with quinine sulfate in 1N H₂SO₄ (φₚ ≈ 0.58) as the standard.

**Synthesis of CdSe Nanocrystals with PS-3 as the both acid and binding ligand by wet chemical approach.** To a 3-necked bottle flask fitted with a thermometer and a condenser, cadmium oxide (0.0523 g, 0.407 mmol) and PS-3 (0.3850 g, ~0.08 mmol) were added to a NMP solution (8 mL) under N₂ atmosphere. The mixture was heated to 150 °C for about 30 min, when the brownish CdO gradually dissolved and the solution became colorless. The solution was further heated to ~220 °C with constant stirring. A solution of selenium (0.0685 g, 0.86 mmol) in TOP (1.08 g, 3.86 mmol) was quickly
injected into the reaction flask. At various time intervals, aliquots of reaction mixture (0.2 mL) were collected and diluted in a chloroform (3 mL) solution. The diluted solutions were examined with UV/FL to study its optical properties. The final product was precipitated out by adding methanol. The precipitated nanocrystals were redissolved with CHCl₃ and reprecipitated with methanol again to afford pure hybrids.

**Synthesis of HDA/TOPO-capped CdSe Nanocrystals by hot-injection method.**

CdSe nanocrystals were prepared according to well-demonstrated wet chemical method. To a 3-necked bottle flask, cadmium oxide (0.0512 g, 0.399 mmol) and stearic acid (2.4308 g, 8.54 mmol) were added under N₂ atmosphere. The mixture was heated to 150 °C for about 30 min, when the solid-brownish mixture gradually liquefied and became colorless. The solution was cooled to room temperature, and trioctylphosphine oxide (TOPO, 5.028 g, 13.0 mmol) and 1-hexadecylamine (HDA, 6.149 g, 25.5 mmol) was added to the flask. The flask was fitted with a thermometer and a condenser, and heated to ~310 °C with constant stirring. A solution of selenium (0.331 g, 4.20 mmol) in TOP (4.28 g, 11.5 mmol) was quickly injected into the reaction flask, and the solution temperature dropped to ~270 °C. The reaction was continued at 270 °C for 3 min, and then was removed from the heating mantle and let cooled to ~60 °C. Chloroform (30 mL) was added to dissolve the nanocrystals which were then precipitated out by adding acetone. The precipitated nanocrystals were redissolved with CHCl₃ and reprecipitated with acetone two additional times. Pure HDA/TOPO capped CdSe nanocrystals were collected and dried under vacuum.
Preparation of DCP-CdSe nanocomposites by Ligand Exchange. The as-prepared CdSe nanocrystals (100 mg) were dissolved in pyridine (10 mL), followed by stirred for 12 h at 90 °C. During the process, the HDA and TOPO ligands on the CdSe NC surface would be replaced by pyridine. After cooled down to room temperature, hexane was added to the solution and pyridine-capped CdSe nanocrystals were precipitated and collected by centrifuge. This process was repeated two additional times. Clean pyridine-capped CdSe nanocrystals were collected and dried with a stream of nitrogen gas. For the ligand-exchange with the diblock copolymer, pyridine-capped CdSe nanocrystal powder (10 mg) was added to a solution of DCP (20 mg) in THF (5 mL), and the suspension was treated by ultrasonication for 3h. The mixture was cooled to room temperature and passed through a 0.45 μm filter, where the undissolved pyridine-capped CdSe nanocrystals were removed. Acetone was added to the clear solution and the precipitated DCP-CdSe nanocomposites were collected by centrifuge. The precipitated nanocomposites were further washed with methanol and acetone for a few times. The nanocomposites can be readily redissolved in THF and chloroform for further studies.

Photovoltaic Devices Fabrication and Characterization. Indium tin oxide (ITO) coated glass (Delta Technologies; sheet resistance, 8–12 Ω/square) was used as substrates. Under the protection of Magic tapes, the ITO side of each substrate was patterned by etching with aqua regia vapor. The patterned ITO glass substrates were cleaned in an ultrasonic bath sequentially by hot detergent, water, deionized water, toluene, acetone, and isopropyl alcohol, and then dried by compressed air. Cleaned ITO substrates were treated with UV ozone for 45 min before use. Highly conductive poly(3,4-
ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Heraeus Precious Metals; Clevios P VP AI4083) thin layer was spin-coated (4000 RPM, 30 s) onto the ITO substrates from an aqueous solution. The PEDOT:PSS thin films were dried at 120 °C for 45 min on hotplate in air. The P3HT-PS-CdSe-1, P3HT-PS-CdSe-2, and P3HT-PS-CdSe-3 solutions were prepared in chloroform with concentration of 5 mg mL\(^{-1}\). The above solutions were passed through 0.45 μm filters and spin-coated on top of the PEDOT:PSS layers at 400 RPM for 30 s. The devices were transferred to glove box and thermally annealed at 120 °C for 10 min in dark. Subsequently, electrodes including 45 nm thick Ca and 100 nm thick Al were deposited on the top by thermal evaporation under high vacuum (< 2 × 10\(^{-6}\) mb) through a shadow mask. The active area of 0.14 cm\(^2\) of the devices was defined by the overlap area of the ITO and the deposited Ca/Al electrodes. Current–voltage characteristics of the solar cells were measured using a Keithley 2400 Source Meter. The thickness of the films was measured with a Tencor Alphastep 200 automatic step profiler.
5.1. Introduction

Carbon nanoparticles (CNPs) are a type of carbon allotropes that shows special and valuable physical, chemical and optical properties. CNPs including graphene and graphite nanodots have gathered tremendous research attention in recent years. They are generally less than 100nm in size, are of graphite type structures or amorphous carbon in their cores, and will contain abundant hydroxyl and carboxylic acid groups on their surfaces. The large number of surface hydrophilic functional groups brings excellent water solubility to these nanoparticles. Apart from their large surface area, high carrier mobility, excellent thermal, chemical, and photo-stability, superior mechanical flexibility, low toxicity and inexpensive production cost, CNPs also show exciting new properties such as strong excitation-dependent emission and/or up-converted photoluminescence induced by the quantum confinement and edge effects. These merits meet important requirements for applications particularly in bioimaging, photovoltaics and solid-state lighting.
Interestingly, CNPs were first discovered at 2004 in a purification process of single-walled carbon nanotubes (SWCNTs) by electrophoresis. A great number of synthetic methods, including electrochemical synthesis, combustion/thermal/hydrothermal/acidic oxidation, microwave/ultrasonic synthesis, laser ablation/passivation, have been developed for CNPs preparation. CNPs have been synthesized by electrochemical oxidation of graphitic column electrode, including graphene and graphite rod, in various electrolytes e.g. phosphate solution, ionic liquid (IL), NaOH/EtOH and even pure water. In a combustion/thermal/hydrothermal/acidic oxidation method, small carbon nanoparticles from either carbon soot or hydrothermal treatment of carbon-containing materials or precursors were prepared first, followed by surface oxidation with HNO3 to obtain water-soluble CNPs. Microwave/ultrasonic pyrolysis treatment of carbohydrate, e.g. glycerol, glycol, glucose, and sucrose, have also been used to prepare CNPs.

CNPs were widely studied as bioimaging probes and bio-sensors for a variety of biological agents, e.g. DNA, nitrite sensing, sensors for phosphate, glucose, and metal ions. The major rationale of these applications are from their excellent water solubility with high fluorescence and good bio-compatibility. Apart from that, CNPs were also used in photocatalysis applications, including TiO₂/C-dots, C-dots/ZnO, C-dots/Fe₂O₃, C-dots/Ag/Ag₃PO₄, and C-dots/Cu₂O composite. These composites showed better photocatalytic efficiency due to the absorption and charge transfer from CNPs to composites. CNP thin layers were as well utilized in LED devices as good light
converter since they usually exhibit relatively high fluorescent quantum yield for being a more economical resource.\textsuperscript{200,201}

Applications of CNP in photovoltaic devices, however, are still limited by far. Colloidal graphene quantum dots with green luminescence was applied as the electron acceptor materials in P3HT-based and MEH-PPV-based thin film solar cells with energy conversion efficiency as high as of 1.28\%\textsuperscript{202} C-dots-sensitized nanocrystalline TiO2 solar cell have also been fabricated with a short circuit current density ($J_S$) of 0.53 mA cm\textsuperscript{2} and an open-circuit voltage ($V_O$) of 0.38 V were produced with a fill factor (FF) of 0.64 for a power conversion efficiency of 0.13\%\textsuperscript{203}

In the present work we developed a new synthetic route involving high-energy ball-milling of graphite powders followed by acidic oxidation for the synthesis of CNPs. This method is favorable in large-scale production of CNPs with an easy experimental approach and low cost. A more significant innovation of this work is the expansion of CNPs in hybrid solar cell applications. CNPs are expected to perform good absorption of sun light and charge transportation properties as electron acceptors. Ideally it could replace the expensive PCBM in hybrid solar cells with a much lower production cost. The CNPs prepared by HEBM were studied in such as solar cell applications. An effective interfacial engineering approach on structurally stable TiO2-coated ZnO nanorods with water-soluble carbon nanoparticles (CNPs) for the fabrication of efficient HSCs are propose and demonstrate. The incorporation of CNPs serves the HSCs with five key features: (i) surface passivation of the inorganic nanorods to facilitate the full infiltration of conjugated polymers and the formation of intimate contact/electronic coupling, (ii)
relay of electrons as both donor and acceptor, (iii) complementary light absorption, (iv) down-converted emission that is harvestable to conjugated polymers, e.g. P3HT, and (v) reduction of inter-rod distance to better address the intrinsic short exciton diffusion length of conjugated polymers.

5.2. Preparation of Water-Soluble Carbon Nanoparticles by High-Energy Ball Milling

In this research, a new approach of preparation of carbon nanoparticles with diameter of less than 100 nm was developed by HEBM treatment of graphite powders at ambient conditions for 40 h. During this process, large graphite particles were constantly charged and welded into nano-sized particles. The as-milled graphite powder was treated with nitric acid for surface oxidation, and this reaction afforded water-soluble CNPs. The acid oxidation creates abundant -COOH groups on the CNP surface which brings in the good water solubility.

The as-synthesized CNPs were characterized by multiple techniques. Scanning electron microscopy (SEM) and Transmission electron microscopy images of water soluble CNPs were collected and displayed in Figure 68 and 69. The SEM images clearly show the difference between the as-milled CNPs and the water-soluble CNPs. As displayed in Figure 68a, the as-milled CNPs severely aggregated together, forming large type of clusters. Even so, small particles with sizes less than 100nm can still be identified. The aggregation of particles is very reasonable due to the high surface energy of nanoparticles, as similar phenomena are also observed in HEBM-prepared CdSeS
nanocrystals. After the acid treatment, CNPs are well dispersed in aqueous solution and show no signs of aggregation, as displayed in Figure 68b. This obviously indicates formation of –COOH groups on CNP surfaces: abundant –COOH groups brings the high water solubility and prevent them from aggregation.

Figure 68. SEM images of as-milled (a) and water-soluble (b) CNPs. The inset of figure (b) is the CNP size distributions.

The TEM images of the as-milled CNPs and the water-soluble CNPs show little but observable differences (Figure 69). For the as-milled CNPs, even though small particles with diameters less than 100nm can be observed, most of them tend to form large pieces of flake-shaped particles with sizes bigger than 200 nm. The water-soluble CNPs,
however, have much smaller average sizes which is around 50 nm. Both SEM and TEM measurements show that most of the CNPs are nearly spherical in shape and have a relatively uniform diameter of ca. 40–60 nm.

Figure 69. TEM images of as-milled (a) and water-soluble (b) CNPs.
The XRD patterns of water-soluble CNPs, as-milled CNPs and pure graphite sample are measured to study the crystalline evolvement of CNPs (Figure 70). A pure graphite sample shows a typical XRD pattern with a sharp and clear peak at ~ 26.7° which is close to its theoretical value (Figure 70c). The sample after ball milling, however, shows both a sharp peak at ~ 26.7° which corresponding to the graphite and a broad peak with a sharp tip at ~ 25.8° (Figure 70b). This appearing broad peak is presumably due to the destruction of the graphite crystalline, which is expected to be caused by the extensive impaction and welding during the HEBM process. The broadness of the peak indicates formation of nanocrystalline in the milled samples. The XRD pattern of the CNPs (Figure 70a) shows a broad (002) peak centered at ~25°, which is similar to the as-milled graphite particles and is very close to that of electrochemically synthesized graphene quantum dots.
The acidic oxidation process has introduced many active sites along the surface of CNPs as further confirmed by FT-IR spectroscopic study. Strong characteristic vibrational modes with frequencies at 1575, 1335, and 3350 cm\(^{-1}\) corresponding to C=O, C–O, and O–H stretchings, respectively, were observed in FT-IR spectrum of the CNPs (Figure 71),
implying that the CNPs contain large amounts of –COOH groups at their surface. The large quantity of COOH groups at the CNP surface is important as they bring the high water solubility to the CNPs, which ensure them with better solution processability. They also guarantee a firm, intimate grafting of the CNPs at TiO$_2$ surface in the proposed HSC devices.

Figure 71. FT-IR spectrum of water-soluble CNPs.

The optical properties of CNPs were explored in aqueous solution by both absorption and fluorescence spectroscopies. Rather than a long tail exceeding 600 nm and showing decreasing absorptivity along with increasing wavelength, no well-defined peaks
were seen from UV-vis absorption spectrum of the CNPs (Figure 72). This is consistent with previously reported results for those CNPs of similar size.\textsuperscript{172} Like CNPs prepared by many other methods, the down-converted emission spectra of presently prepared CNPs show a notable excitation-dependent feature. During the fluorescence test, the excitation wavelength was steadily increased from 300 nm to 550 nm with intervals of 25 nm. Upon excitation at 300 nm, the CNPs show a main emission peak at \(\sim 515\) nm (Figure 73). The main emission peak is progressively red-shifting to as far as 576 nm as the excitation wavelength was increased. During the same time, the fluorescence intensity first increases and then decreases with the highest emission intensity obtained at \(\sim 529\) nm (with excitation at 475 nm) which falls into the yellow luminescence region and is harvestable to conjugated polymers (i.e. within the major absorption range of such as P3HT).

Figure 72. Absorption of water-soluble CNPs. The insets display the color of the CNPs in aqueous solution and under UV light of 365 nm.
Figure 73. Fluorescence spectra of water-soluble CNPs. The excitation wavelength are set to be (from left to right): 300, 325, 350, 375, 400, 425, 450, 475, 500, 525, 550 nm. The inset shows the normalized fluorescence spectra of CNPs which displays the excitation-dependent emission.

The electrochemical property of CNPs was investigated both as thin film and in aqueous solution using cyclic voltammetry (CV) measurement, and the results are displayed in Figure 74. Same with electrochemically synthesized graphene quantum dots, there are no obvious redox peaks observed during CV scans for the CNP film. The CNPs in aqueous solution however displayed a quasi-reversible reduction/reoxidation process in the negative potential region. Referenced to K₄Fe(CN)₆, the lowest unoccupied molecular orbital (LUMO) energy level of CNPs was determined to be −4.00±0.02 eV from its onset reduction potential. This makes CNPs suitable for either electron donor or electron acceptor or both applications in solar cells.
5.3. Growth of TiO$_2$-Coated ZnO Nanorods on ITO Glass, Treatment with Water-Soluble CNPs, and Fabrication of HSCs

The fabrication of proposed HSCs starts with the growth of TiO$_2$-coated ZnO nanorods. The coating of a thin layer of TiO$_2$ on ZnO surface is believed to be able to significantly improve the interface quality and thus promote the charge injection. In this work, the hydrothermally grown oriented ZnO nanorods with inter-rod distance of from several tens to a couple of hundreds of nanometers are estimated to be ~800 nm long and averagely 80–100 nm in diameter (Figure 75,76). Figure 77 & 78 shows the SEM images
of the ZnO nanorods with a thin layer of TiO$_2$ (several tens of nanometers thick) coated on them. The thin layer of TiO$_2$ covered both the ZnO nanorod surface and the inter-rod space.

The TiO$_2$-coated ZnO nanorods (referred as ZnO-TiO$_2$ thereafter) were further treated with the aforementioned CNPs (see the Experimental section). As shown in Figure 79 & 80, a layer of CNPs was uniformly attached to the surface of TiO$_2$. As is known, it is an open challenge to construct ordered ZnO nanorod scaffold with uniform and perfect inter-rod distance (20–40 nm) by the hydrothermal method. The coating of TiO$_2$ has reduced the inter-rod distance to some extent, however, showing a broad distribution ranging from several tens to over a couple of hundreds of nanometers, they are still not optimal in terms of inter-rod distance. The grafting of CNPs on TiO$_2$ surface has another time reduced the inter-rod distance by several tens to over a hundred nanometers (doubling the diameter of the CNPs), making the CNP-modified ZnO-TiO$_2$ (referred as ZnO-TiO$_2$-CNP thereafter) more suitable for HSC applications. Furthermore, the introduction of CNPs onto the TiO$_2$ surface has significantly changed the surface energy of the inorganic framework, providing a more compatible interface to facilitate the full infiltration of P3HT. This is confirmed by the SEM images of the ZnO-TiO$_2$ and ZnO-TiO$_2$-CNP after the coating of P3HT (Figure 81,82). As seen in Figure 81 & 82, a densely packed and fully-infiltrated P3HT phase and an intimate contact between the organic and inorganic components were realized in the presence of the CNP layer, both of which are demanding requirements for high-performing HSCs.
Figure 75. ZnO nanorods on ITO glass substrate.

Figure 76. Cross-section of ZnO nanorods on ITO glass substrate.
Figure 77. TiO$_2$-ZnO nanorods on ITO glass substrate.

Figure 78. Cross-section of TiO$_2$-ZnO nanorods on ITO glass substrate.
Figure 79. TiO$_2$-ZnO-C dots nanorods on ITO glass substrate.

Figure 80. Cross-section of TiO$_2$-ZnO-C dots nanorods on ITO glass substrate.
Figure 81. Cross-section TiO$_2$-ZnO-P3HT nanorods on ITO glass substrate.

Figure 82. Cross-section of TiO$_2$-ZnO-Carbon dots-P3HT nanorods on ITO glass substrate.
After the deposition of Au as contact on top of the P3HT layer, solar cells with the new device structure as shown in Figure 83 were thus fabricated. The energy level diagram of the solar cells is shown in Figure 84. The HOMO level of the CNPs (−4.00±0.02 eV) is perfectly aligned with both the LUMO level of P3HT (−3.2 eV) and the conduction band (CB) edge of TiO₂ (−4.2 eV), which ensures the possibility of both efficient exciton dissociation at the P3HT/CNP interface and efficient electron extraction. In such a device, P3HT acts as electron donor, CNPs acts as electron acceptor, while the ZnO-TiO₂ works as electron collector and transporter.

Figure 83. Device structure of the solar cells of ITO/ZnO/ZnO–TiO₂–CNP/P3HT/Au.
Figure 84. Energy level diagram of the solar cells of ITO/ZnO/ZnO–TiO2–CNP/P3HT/Au.

Figure 85 shows the absorption spectra of the fabricated films. By comparing the absorption spectra of ZnO-TiO2 and ZnO-TiO2-CNP, the supplementary effect of CNP in absorption can be clearly seen. After P3HT was coated onto either the ZnO-TiO2 or ZnO-TiO2-CNP, the characteristic absorption peaks of P3HT can be obviously identified. It is noted that the absorption of P3HT is more prominent in ZnO-TiO2-CNP than in ZnO-TiO2. This is consistent with the observations from SEM images shown in Figure 78-82.
Figure 85. Absorption spectra of the films of ZnO–TiO$_2$, ZnO–TiO$_2$–CNP, ZnO–TiO$_2$/P3HT and ZnO–TiO$_2$–CNP/P3HT on ITO glass substrates.

Figure 86 shows the current density–voltage ($J$–$V$) curves of the ZnO-TiO$_2$/P3HT and ZnO-TiO$_2$-CNP/P3HT solar cells. The open circuit voltage ($V_{OC}$), short circuit current density ($J_{SC}$), fill factor (FF), and power conversion efficiency (PCE, $\eta$) of the two types of cells are compared in Table 1. Without any interfacial treatment, the ZnO-TiO$_2$/P3HT solar cell performed poorly, showing even much lower $V_{OC}$ and $J_{SC}$ than those of our recently reported equivalent solar cells in which the TiO$_2$ surface was treated by regioregular poly[3-(3-carboxypropyl)thiophene-2,5-diyl] before the coating of P3HT.$^{[18]}$ This result is however consistent with what we observed in Figure 81 & 82 which showed that a large fraction of the inter-rod space was not filled by P3HT and only a small portion
of the ZnO-TiO$_2$ surface was isolatedly covered by P3HT without forming the desired interconnected P3HT phase. Modification of the TiO$_2$/P3HT interface by the grafting of a layer of CNPs on TiO$_2$ dramatically improved the device performance. The $V_{OC}$ of the device with ZnO-TiO$_2$-CNP increased from 0.05 to 0.22 V, and the $J_{SC}$ drastically increased by more than six folds to a remarkable value of 8.69 mA cm$^{-2}$. These resulted in a PCE of 0.68%, an over 30-fold improvement compared to the CNP-free equivalent devices.

Figure 86. J–V characteristics (empty: dark; filled: illuminated) of the photovoltaic devices of ITO/ZnO–TiO2/P3HT/Au and ITO/ZnO–TiO2–CNP/P3HT/Au.
Theoretically, the $V_{OC}$ of heterojunction solar cells is directly related to the energy level difference between the HOMO of donor and the LUMO of acceptor$^{204}$ which is, referring to the energy level diagram shown in Figure 84, $(-4.0 \text{ eV}) - (-5.2 \text{ eV}) = 1.2 \text{ eV}$. This corresponds to a large theoretical $V_{OC}$ of ~0.9 eV for the present solar cells. Many factors of course such as nanoscopic local morphology, donor/acceptor ratio, etc. can affect the realization of the theoretical $V_{OC}$ in real solar cells.$^{204}$ While the mechanism is awaiting discovery, it is possible that the relatively broad size distribution of the CNPs is responsible for the low $V_{OC}$ because the energy level of CNPs has been found to be size dependent by comparing the results of ourselves with others’. Even though the as-synthesized CNPs are averagely 40-60 nm in diameter, there still exist very small sized CNPs in the material which might have been selectively adsorbed by the TiO$_2$ in, for example, the porous grid especially after the outmost surface is covered by bulky CNPs with relatively large size. Effort is being made towards the optimization of the device performance particularly in $V_{OC}$ by the development of different sized CNPs with narrow size distribution for the HSCs of this type.

The outstandingly high $J_{SC}$ has exclusively provided a sound proof for that the CNPs having large surface area and high electron mobility can effectively afford high-quality exciton separation interfaces and electron transporting media. The PCE of 0.68% is low compared to those of many all-organic solar cells of polymer:fullerene blends, however, it is close to the highest reported efficiency of $0.74 \pm 0.02\%$ for ZnO nanorod based HSCs despite the absence of device optimization in this primary study. More importantly, considering the very high $J_{SC}$ obtained by this type of solar cells, it is
envisioned that if the theoretically very high $V_{OC}$ is realized upon optimization, very high power conversion efficiency will be achieved.

5.4. Conclusions

In summary, we have demonstrated a highly effective interfacial engineering approach on TiO$_2$-coated ZnO nanorods with water-soluble carbon nanoparticles (CNPs) for the fabrication of high-photocurrent HSCs. Ball milling of graphite powder followed by acidic oxidation produces CNPs with average particle size of 40-60 nm exhibiting a yellow luminescence and having a LUMO level of $\sim$4.0 eV. The grafting of CNPs onto the TiO$_2$ surface significantly enhances the compatibility of TiO$_2$-coated ZnO nanorods with P3HT. With energy levels of the components perfectly aligned, the un-optimized HSCs show remarkably high photocurrent of 8.69 mA cm$^{-2}$ and efficiency of 0.68% that is close to the highest reported efficiency for ZnO nanorod based HSCs. The large deviation of real $V_{OC}$ from the theoretically very high one is ascribed to relatively broad size distribution of CNPs. Development of different sized CNPs with narrow size distribution is in progress, and HSCs of the present type with high $V_{OC}$ and thus high efficiency is expected. Carbon is one of the most abundant elements in the earth’s crust and many of its allotropes and derivatives including fullerenes, carbon nanotubes, graphenes, etc. have played leading roles in the revolution of the organic-based photovoltaics. We expect that our endeavor can further the advancement of CNPs in
photovoltaic applications, and hope that our findings will motivate other researchers as well to explore further in the very filed and achieve commercializable HSCs.

5.5. Experimental Section

**Preparation of CNPs.** Graphite powders (< 20 μm, Sigma-Aldrich) were placed into a stainless steel vial together with milling balls of different diameters (4–12 mm) in glove box. The powder to ball mass ratio was set to be 1:10. The vial was then sealed and the ball milling was carried out for 40 h. As-milled powders (20 mg) were placed in 5M HNO$_3$ (15 mL) followed by reflux for 18 h in N$_2$. The reaction mixture was then centrifuged at 3000 rpm for 10 min. The top clear dark brown-colored solution was collected, to which 5M NaOH solution was added dropwise until pH reached 7~8. The mixture was filtered to remove iron impurities introduced during the ball milling. Dialysis was then performed on the solution with a Float-A-Lyzer G2 dialysis device (approximate Molecular weight cut off 100-500 Daltons) to remove the salt(s). The resulting solution was evaporated under reduced pressure and the black powders were collected.

**Fabrication and Characterization of HSCs.** TiO$_2$-ZnO films were prepared by the following procedures: The TiO$_2$-ZnO films were heated to 80 °C, immersed into CNP solution (0.5 mg mL$^{-1}$) in H$_2$O/EtOH (1/1, v/v) and kept at room temperature overnight. The films were taken out, flushed with H$_2$O/EtOH mixture (1/1, v/v) and dried by compressed air and then under vacuum at 50 °C for 6 h. P3HT solution (30 mg mL$^{-1}$) in 1,2-dichlorobenzene was heated at 50 °C with stirring for 14 h and passed through a 0.45
μm filter. The P3HT film was deposited by spin coating the P3HT solution onto the TiO2-ZnO-CNP films at 600 rpm for 1 min. The films were annealed at 140 °C for 1 h under nitrogen atmosphere. Finally, a 120 nm thick Au layer was deposited onto the P3HT layer by thermal evaporation under high vacuum (< 2 × 10⁻⁶ MB). Current–voltage characteristics of the devices were measured using a Keithley 2400 source meter. The devices were illuminated with an Oriel xenon arc lamp solar simulator with an AM1.5 filter at an intensity of ~100 mW cm⁻². \( J_{SC}, V_{OC} \), and maximum output power density \( (J_{max}V_{max}) \) were derived from the \( J-V \) curves. The PCE was calculated by \( \eta = J_{SC}V_{OC}FF/P_{in} \), where \( P_{in} \) is the incident power density and FF is given by \( J_{max}V_{max}/J_{SC}V_{OC} \).
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158


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1. Li, Shaohua; Li, Yong; Wisner, Clarissa; Leventis, Nickolas; Peng, Zhonghua. “Synthesis, Optical Properties and Photovoltaic Applications of Rod–Coil Diblock Copolymers with CdSe Nanocrystals Coordinately Attached to the Coil Block.”, Manuscript in revision.

2. Li, Shaohua; Tan, Guolong; Murowchick, James B.; Wisner, Clarissa; Leventis, Nickolas; Xia, Ting; Chen, Xiaobo; Peng, Zhonghua. “Preparation of uncapped

3. Li, Yong; Li, Shaohua; Jin, Lu; Murowchick, James B.; Peng, Zhonghua. “Carbon nanoparticles as an interfacial layer between TiO$_2$-coated ZnO nanorod arrays and conjugated polymers for high-photocurrent hybrid solar cells.”, *RSC Advances* **2013**, 3, 16308-16312.

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