Synthesis and Characterization of Colloidal Metal and Photovoltaic Semiconductor Nanocrystals

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ABSTRACT

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Mutalifu Abulikemu

Metal and semiconducting nanocrystals have received a great deal of attention from fundamental scientists and application-oriented researchers due to their physical and chemical properties, which differ from those of bulk materials. Nanocrystals are essential building blocks in the development of nanostructured devices for energy conversion. Colloidal metals and metal chalcogenides have been developed for use as nanocrystal inks to produce efficient solar cells with lower costs. All high-performing photovoltaic nanocrystals contain toxic elements, such as Pb, or scarce elements, such as In; thus, the production of solution-processable nanocrystals from earth-abundant materials using environmentally benign synthesis and processing methods has become a major challenge for the inorganic semiconductor-based solar field. This dissertation, divided into two parts, addresses several aspects of these emerging challenges.

The first portion of the thesis describes the synthesis and characterization of nanocrystals of antimony sulfide, which is composed of non-scarce and non-toxic elements, and examines their performance in photovoltaic devices. The effect of various synthetic parameters on the final morphology is explored. The structural, optical and morphological properties of the nanocrystals were investigated, and Sb$_2$S$_3$ nanocrystal-based solid-state semiconductor-sensitized solar cells were
fabricated using different deposition processes. We achieved promising power conversion efficiencies of 1.48%.

The second part of the thesis demonstrates a novel method for the in situ synthesis and patterning of nanocrystals via reactive inkjet printing. The use of low-cost manufacturing approaches for the synthesis of nanocrystals is critical for many applications, including photonics and electronics. In this work, a simple, low-cost method for the synthesis of nanocrystals with minimum size variation and waste using reactive inkjet printing is introduced. As a proof of concept, the method was used for the in situ synthesis of gold nanoparticles as a model system. Relatively monodisperse gold nanoparticles were produced. The size and shape of gold nanoparticles can be controlled by the gold precursor and surfactant concentration in the ‘ink.’ This approach can be extended to the synthesis of other nanocrystals and is thus a truly impactful process for the low-cost synthesis of materials and devices incorporating nanocrystals.
ACKNOWLEDGMENTS

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<th>Abbr.</th>
<th>Description</th>
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<tbody>
<tr>
<td>3MPTMS</td>
<td>3-mercaptopropyl(trimethoxysilane)</td>
</tr>
<tr>
<td>AuCl$_3$</td>
<td>Gold chloride</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper indium gallium diselenide</td>
</tr>
<tr>
<td>CIJ</td>
<td>Continuous inkjet</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DOD</td>
<td>Drop-on-demand</td>
</tr>
<tr>
<td>DSSCs</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EDT</td>
<td>1, 2-ethanedithiol</td>
</tr>
<tr>
<td>ETM</td>
<td>Electron transport materials</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorinated Tin oxide</td>
</tr>
<tr>
<td>HAuCl$_4$.3H$_2$O</td>
<td>Gold chloride trihydrate</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HRSEM</td>
<td>High-resolution scanning electron microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>------------</td>
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<tr>
<td>HTM</td>
<td>Hole-transporting materials</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin oxide</td>
</tr>
<tr>
<td>Li-TFSI</td>
<td>Lithium-bis(trifluoromethanesulfonyl)imide</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular-beam-epitaxy</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic-chemical-vapor-deposition</td>
</tr>
<tr>
<td>MPA</td>
<td>3-mercaptopropionic acid</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystal</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>NR</td>
<td>Nanorod</td>
</tr>
<tr>
<td>OA</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>ODE</td>
<td>1-Octadecene</td>
</tr>
<tr>
<td>OLA</td>
<td>Oleylamine</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>PbS</td>
<td>Lead sulfide</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaics</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
</tr>
<tr>
<td>PYSA</td>
<td>Photoemission Yield Spectrometry in air</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>RIP</td>
<td>Reactive inkjet printing</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>Sb(OAc)₃</td>
<td>Antimony (III) acetate</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>Antimony(III) oxide</td>
</tr>
<tr>
<td>Sb₂S₃</td>
<td>Antimony sulfide</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>Antimony (III) chloride</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene</td>
</tr>
<tr>
<td>SSSCs</td>
<td>Semiconductor-sensitized solid state</td>
</tr>
<tr>
<td>TBACl</td>
<td>Tetra-butyl ammonium chloride</td>
</tr>
<tr>
<td>TBAI</td>
<td>Tetra-butyl ammonium iodide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TMS</td>
<td>Bis(trimethylsilyl) sulfide</td>
</tr>
<tr>
<td>TOP</td>
<td>Triocylphosphine</td>
</tr>
<tr>
<td>TOPO</td>
<td>Triocylphosphine oxide</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zinc Sulfide</td>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>min.</td>
<td>Minute</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celcius</td>
</tr>
<tr>
<td>Å</td>
<td>Ångstrom, 10-10</td>
</tr>
<tr>
<td>Eg</td>
<td>Energy gap</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density-voltage</td>
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Introduction

1.1 Motivation

Nanostructured materials are materials with at least one external dimension in the size range from approximately 1-1000 nanometers. Metal and semiconductor materials with dimensions on the order of nanometers have been used in the plasmonic,\textsuperscript{1} photovoltaics\textsuperscript{2-8} and water-splitting fields.\textsuperscript{9} Due to the large surface areas and energies of nanostructured nanomaterials, their physical and chemical properties differ from those of their bulk counterparts.\textsuperscript{10} Both top-down and bottom-up synthetic methods have been used to prepare nanostructured materials.\textsuperscript{11} Top-down techniques refer to solid-state physics-based methods for preparing nanostructured materials, such as molecular-beam-epitaxy, metal organic-chemical-vapor-deposition, milling and attrition. Bottom-up approaches generally refer to the preparation of nanomaterials in solution and include hot injection, hydrothermal, sol-gel and templating methods. These approaches are versatile synthetic methods that offer various shapes and different sizes of nanomaterials. Compared to the top-down approach, the bottom-up approach generates fewer defects on the surface of the nanomaterial.\textsuperscript{11}
Photovoltaic technologies that convert sunlight into electricity may make a large contribution toward solving global energy challenges. Copper indium gallium diselenide $^{12}$ is one of the most efficient and stable thin-film semiconductors for use in photovoltaic applications. Traditionally, the CIGS absorber layers in these solar cells are deposited using physical vapor deposition methods, such as co-evaporation and co-sputtering. Greater than 20% efficiency has been achieved for CIGS$^{13}$ prepared using co-evaporation at the lab scale. Due to the operational complexity and expensive maintenance associated with high-vacuum processes, high-throughput, high-yield processing using non-vacuum deposition methods is a promising route to versatile thin-film deposition. Non-vacuum deposition methods have a number of attractive features, such as low cost, high material utilization, and scalability to large-area manufacturing. Widespread commercialization of thin-film PV technology can be readily realized using solution-processing techniques.

Solution-processed ternary and quaternary semiconductor nanocrystals have already achieved 15.2% efficiency in lab tests (Table 1). Thus, methods for the wet chemical preparation of ternary and quaternary semiconductor nanocrystal nanoparticles with narrow size distributions and well-controlled stoichiometries that are more environmental friendly and stable are of substantial interest.

Solution-processed metal, binary, ternary and quaternary nanocrystals have attracted considerable attention for applications in optoelectronic devices$^{2-8,13-15}$ due to their shape-and size-dependent optical and electronic properties, which differ from those of their bulk counterparts. Various shapes of metal nanoparticles
Table 1.1. Solar cell performance of solution-processed binary and Cu-based chalcogenides

<table>
<thead>
<tr>
<th>Materials/Device architecture</th>
<th>Open-circuit voltage $V_{oc}$ (mV)</th>
<th>Short-circuit current density $J_{sc}$ (mA/cm²)</th>
<th>Fill Factor FF</th>
<th>Power Conversion Efficiency $\eta$ (%)</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$ZnSn(S,Se)$_2$ Glass/Mo/CZTSSe/CdS/ZnO/ITO/Ni-Al</td>
<td>430</td>
<td>31.2</td>
<td>53.9</td>
<td>7.23</td>
<td>NCs, N$_2$H$_4$ capped</td>
<td>19</td>
</tr>
<tr>
<td>Cu$_2$ZnSnS$<em>x$Se$</em>{4-x}$ Glass/Mo/CZTSSe/CdS/ZnO/ITO/Ni-Al</td>
<td>513.4</td>
<td>35.2</td>
<td>69.8</td>
<td>12.6</td>
<td>Thin film, N$_2$H$_4$ solvent</td>
<td>20</td>
</tr>
<tr>
<td>Cu(In$<em>x$Ga$</em>{1-x}$)(S,Se)$_2$ Glass/Mo/CIGS/CdS/ZnO/ITO/Ni-Al</td>
<td>623</td>
<td>32.6</td>
<td>75</td>
<td>15.2</td>
<td>N$_2$H$_4$ solvent</td>
<td>21</td>
</tr>
<tr>
<td>CuIn(S,Se)$_2$ Glass/Mo/CIS/CdS/ZnO/ITO/Ni-Al</td>
<td>550</td>
<td>29.8</td>
<td>73</td>
<td>12.2</td>
<td>N$_2$H$_4$ solvent</td>
<td>22</td>
</tr>
<tr>
<td>CuInS$_2$ FTO/TiO$_2$/CIS/ZnS/Cu$_2$S</td>
<td>586</td>
<td>20.65</td>
<td>58.1</td>
<td>7.04</td>
<td>QDs</td>
<td>23</td>
</tr>
<tr>
<td>CuInSe$_2$ Glass/Mo/CIS/CdS/ZnO/ITO/Ni-Al</td>
<td>280</td>
<td>25.8</td>
<td>39</td>
<td>3.2</td>
<td>NCs</td>
<td>24</td>
</tr>
<tr>
<td>PbS QDs ITO/ZnO/PbS/Au</td>
<td>555</td>
<td>24.2</td>
<td>63.8</td>
<td>8.55</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>PbSe QDs ITO/Zn$_1$-$x$Mg$_x$/PbSe/Mo3/Au</td>
<td>482</td>
<td>22</td>
<td>35</td>
<td>3.7</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Sb$_2$S$_3$ FTO/m-TiO$_2$/Sb$_2$S$_3$/PCPDTBT/Au</td>
<td>711</td>
<td>16.1</td>
<td>65</td>
<td>7.5</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Sb$_2$Se$_3$ FTO/d-TiO$_2$/Sb$_2$Se$_3$/Au</td>
<td>520</td>
<td>10.3</td>
<td>42.3</td>
<td>2.26</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Bi$_2$S$_3$ ITO/PbS+Bi2S3/Ag</td>
<td>400</td>
<td>24.2</td>
<td>50</td>
<td>4.87</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>CdSe FTO/TiO$_2$/CdSe/Na$_2$S/ZnO</td>
<td>538</td>
<td>16.86</td>
<td>39</td>
<td>3.53</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>CdTe ITO/CdTe/ZnO/Al</td>
<td>684</td>
<td>25.8</td>
<td>71</td>
<td>12.3</td>
<td></td>
<td>8</td>
</tr>
</tbody>
</table>
(NPs) have potential applications in photovoltaic cells\textsuperscript{14,16,17} and catalysis.\textsuperscript{9} Metal NPs in PV cells can enhance light absorption due to plasmonic effects, which boost the efficiency of PV cells. Inorganic semiconducting NCs (Table 1.1) are appropriate light harvesting layers in PV cells due to the tunability of their band gaps and size-dependent optical properties and are advantageous\textsuperscript{18} over organic light harvesters because of their high electron and hole mobility, high light absorption efficiency and long-term stability. The In-based materials is not sustainable, due its earth scarcity and other non-toxic binary chalcogenide materials like Bi\textsubscript{2}S\textsubscript{3} and Sb\textsubscript{2}Se\textsubscript{3} (Table1.1) usually gave lower V\textsubscript{oc}, due to their lower band gap. Similarly, CdTe is nor favorable, owing to toxicity of cadmium and scarcity of tellurium.

Semiconductor materials with band gaps of approximately 1.4 eV that are less toxic and prepared from earth-abundant materials are desirable for PV applications. Various inorganic semiconductor nanocrystals\textsuperscript{18} have been prepared for use in low-cost, high-efficiency solar cells and have attracted widespread interest in the scientific and industrial communities for solar cell applications due to their advantageous properties compared to dye molecules and organic semiconductors.\textsuperscript{25} Metal nanoparticles are also widely used in PV cells as electrodes and incorporated into active layers to enhance light absorption. In addition, to fabricate cheaper and flexible PV devices on a large scale, solution-based deposition techniques, such as roll-to roll and inkjet printing, must replace current deposition methods for electrodes such as sputtering or evaporation. Synthesis and deposition techniques with minimal material waste that employ
heavy-metal-free (Pb, Cd, etc.) earth-abundant (without In, Ga, etc.) semiconductors have received considerable attention. Thus, we would like to propose the synthesis and characterization of Au and photovoltaic Sb$_2$S$_3$ semiconducting nanocrystals. My proposed work is divided into two parts:

1. The development of a systematic colloidal synthesis method for lead-free, earth-abundant Sb$_2$S$_3$ NCs, the characterization of the effects of the shape, size and phase of Sb$_2$S$_3$ NCs, and the fabrication of solution-processed PV cells using these as-synthesized NCs.

2. The development of a cost-effective, rapid, in situ reactive inkjet printing synthetic method for synthesis of monodisperse gold nanoparticles.

1.2 Organization of Thesis

This thesis is organized as follows:

Chapter 2 focuses on understanding nanomaterials, the quantum confinement effect, and the methods used for ligand exchange and its importance for solar cells, as well as the surface plasmonic properties of metallic nanoparticles and the physics of intrinsic and extrinsic semiconductors. The hot injection synthesis method and reactive inkjet printing are generally described. We then provide a brief review of different generation solar cells and their prevalence. We also explain the device structure and operating principles of inorganic nanostructured materials widely used in solid-state dye-sensitized solar cells and hybrid solar cells.
Chapter 3 describes the synthesis of various shapes of Sb$_2$S$_3$ using different antimony and sulfur sources and characterizes the structural, morphological and optical properties of as-prepared Sb$_2$S$_3$ NCs. The effects of temperature, reaction time, different capping agents, and foreign ions on the shape and crystallinity of NCs are discussed.

Chapter 4 presents the performance results of PV devices using as-prepared Sb$_2$S$_3$ NCs, including an introduction of the device fabrication process, a discussion of the effect of different deposition techniques, and the effect of different HTMs on the device performance.

Chapter 5 introduces a novel technique for synthesizing monodisperse Au NPs on solid substrates by reactive inkjet printing and discusses the effects of Au precursor and reducing agent concentration, different printing sequences, and different gold precursors on the shape and monodispersivity of Au NPs. A comparison is presented between RIP and bath synthesis methods of Au NPs.

Chapter 6 provides a summary of the results and an outlook for future work.
REFERENCES


Chapter 2

Background Knowledge

In this chapter, we generally discuss nanomaterials, the quantum confinement effect, the hot injection synthesis method, and reactive inkjet printing and provide a general overview of three generations of solar cells. In addition, we discuss the importance of ligand exchange and surface passivation methods for solution-processed nanocrystals to be used for optoelectronic devices and generally categorize the performance of different types of ligands. Moreover, we shed light on the principles and device structures of semiconductor-sensitized solar cells and the architecture of hybrid solar cells, in which nanocrystals are widely used.

2.1 Nanomaterials

Nanostructured materials are defined as materials with at least one spatial dimension in the size range of approximately 1-1000 nanometers.\(^1\) \(^2\) By decreasing the size of a material, its surface area and surface energy are greatly increased, which may result in different physical and chemical properties from those of its bulk counterpart. Nanostructured materials have zero-, one-, and two-dimensional nanostructures based on their dimensionality.\(^3\)

Top-down and bottom-up synthetic methods have been used to prepare nanostructured materials \(^1\) \(^2\) \(^4\). Top-down techniques refer to the solid-state physics methods of making nanostructured materials, such as MBE, MOCVD,
milling and attrition.\textsuperscript{2, 4} The bottom-up approach refers to nanomaterials made in solution, such as hot injection, hydrothermal, sol-gel and templating.\textsuperscript{1, 2, 4} This approach is a versatile synthetic method used to produce various shapes and sizes of nanomaterials. Compared to the top-down approach, the bottom-up approach generates fewer defects on the surface of the nanomaterials.\textsuperscript{1}

The most attractive properties of nanomaterials to be used for solar cell devices are not only their solution processability but also their size and their tunable optical and electronic properties.\textsuperscript{4-12} The photoluminescence and absorption peaks of nanomaterials can be tuned by simply changing their size and composition. These qualities make nanomaterials very promising for photovoltaic,\textsuperscript{8-11} catalysis and light-emitting diode applications.\textsuperscript{12} In addition, the light absorption coefficient can be enhanced by the preparation of self-assembled nanoparticles.\textsuperscript{13}

### 2.2 Quantum Confinement Effect

When the size of as-synthesized nanocrystals is below the Bohr radius of the material, the electronic excitation feels the presence of the particle boundaries, which leads to changes in their energy spectra.\textsuperscript{4, 6, 14} This phenomenon is called the quantum confinement (size) effect, and nanoscale materials that exhibit the quantum confinement effect are known as quantum dots.\textsuperscript{4, 6, 14}
Figure 2.1. (a) Energy bands of a bulk semiconductor showing the continuity of the conduction and valence bands separated by a bandgap, \( E_g \). (b) For QDs, such continuity is broken, and discrete atomic-like states become available with energies determined by the size of the QD material. (c) Comparison of absorption spectra between a bulk semiconductor (curved line) and a QD nanocrystal (vertical bars).\(^4\)

The energy gap in QDs can be controlled by the size of the QDs (Figure 2.1b), and the band gap in QDs increases with decreasing size.\(^4\) The continuous energy bands of the bulk material collapse into discrete, “atomic” energy levels due to the
quantum confinement effect with decreasing size (Figures 2.1a and c). The blue shift or red shift of the emission and absorption spectra of QDs can be controlled by size. This quality makes QDs very promising materials for photovoltaics and light-emitting diodes.

2.3 Hot Injection Synthesis

Many synthetic techniques have been developed to synthesize metal and inorganic semiconducting NCs. In general, the methods can be divided into two categories: vacuum-based methods and solution-based methods. Vacuum-based methods such as molecular beam epitaxy, metal organic chemical vapor deposition and vapor-liquid-solid require a high vacuum condition to form NPs, which makes operation complex and expensive. Solution-based methods such as hot injection, hydrothermal and sol-gel methods are inexpensive and quite easy to operate as well as easy to use to functionalize the surface of the as-prepared NPs and scale up. Thus, it is believed that widespread commercialization of PV technology based on NPs can be readily realized based on solution-based methods.

In 1993, the Bawandi group reported the synthesis of cadmium chalcogenide semiconductor NCs using metal–organic precursors in hot coordinating solvents; this method is known as the hot injection method. This synthesis protocol was later optimized and extended to other semiconductor NCs and quantum dots and tailored to synthesize various shapes of NCs. This method produces high-quality monodisperse NCs.
The concept of this method\textsuperscript{4,14,16} is based on the studies of La Mer and Dinegar. La Mer's mechanism for the stages of nucleation and growth of monodisperse colloidal particles is illustrated in Fig. 2.2a. The nucleation is started immediately after the precursor is quickly injected into a hot solvent by forming a supersaturated solution. Growth is subsequently started, and there is no nucleation once the concentration of supersaturation is below the nucleation threshold concentration. Growth will stop when the concentration of the growth species reaches the
equilibrium concentration (saturation). During Ostwald ripening, larger NCs or QDs grow at the expense of smaller NCs or QDs.

Monodisperse NCs are obtained if all nuclei are formed at the same time and there is no nucleation after growth starts.\(^1,4\) The size of NCs can be controlled by time, temperature or the ratio of precursor concentration to stabilizing surfactant (capping agent).\(^4\) The selective use of capping agent(s) \(^{20,21}\) or the addition of foreign ions \(^{22}\) leads to changes in the shape of the NCs.

### 2.4 Ligand Exchange

Most nanocrystals prepared by the colloidal method are capped by insulating long-chain organic ligands, and the space between nanocrystals is determined by the capping ligand.\(^4,14,23\) Thus, surfaces play a key role in determining NCs’ structural and optical properties and electron mobility.\(^23\) Controlling the surfaces is critical to controlling the physical and chemical properties that make NCs unique compared to their epitaxial QD counterparts.\(^23\)

NCs stabilized by long-chain organic ligands (oleylamine, oleic acid and trioctyl phosphine oxide) show good chemical stability, but their highly insulating nature hinders charge transport.\(^{23-25}\) It is difficult to completely remove organic ligands, and attempts to do so may degrade the properties of NCs through the formation of multiple surface dangling bonds and mid-gap charge-trapping states.\(^{26}\) Annealing of NCs may be one effective way to remove long-chain ligands, but it may lead to sintering, which can destroy the properties of NCs or QDs. Some work has been carried out to stabilize NCs by short-chain and cross-linking ligands in solution, but
it is difficult to fabricate uniform films due to their poor colloidal stability and susceptibility to oxidation. To overcome these issues, a solid-state ligand exchange technique was proposed using short-chain ligands such as 1, 2-ethanedithiol$^{27}$ and 3-mercaptopropionic acid.$^{28}$ and this method greatly improved carrier mobility and transport. A 5.1% power conversion efficiency$^{28}$ was obtained for MPA-treated PbS QD solar cells.

Talapin et al. reported$^{24, 25}$ that the conductivity of NCs films significantly increased when the surface of the NCs was capped by metal chalcogenide inorganic ligands (please refer to Table 2) instead of organic ligands. Thus far, there has been no report on optoelectronic devices treated by metal chalcogenide inorganic ligands. Recently, Sargent et al.$^{30}$ demonstrated PbS QD solar cells treated by halide inorganic ligands, which increased the power conversion efficiency of the PbS QD-based solar cell by up to 6%. The authors claimed that halide ligands offer better surface passivation over short-chain organic ligands. Hybrid ligand QDs sequentially treated by halide ligands and short-chain organic ligands such MPA and passivated PbS-based solar cells were fabricated, and a 7% improvement in efficiency$^{31}$ was obtained. A hybrid ligand (multiple-liganding) strategy can be more effective than a single ligand class through better surface passivation and elimination of trap states for electron-hole recombination. Subsequently, devices with a bottom layer of a PbS QD film treated by halide ligands and a top layer of a PbS QD film treated by EDT were introduced, and their efficiency reached 8.85%.$^{32}$

**Table 2.1.** Different types of surface ligands used in nanocrystals and nanocrystal solids (based on the worth of Talapin group$^{23}$)
<table>
<thead>
<tr>
<th>Ligand type</th>
<th>Molecular structure</th>
<th>Interparticle spacing</th>
<th>Function, characteristics, typical examples</th>
</tr>
</thead>
</table>
| Molecules with a single head group and a long hydrocarbon chain           | ![Molecules](image1) | >1.5 nm               | • Most commonly used ligands for NCs synthesis  
• Form a stable colloidal solution  
• Hydrophobic surface  
• Form highly insulating NC solids, σ ~ 10^-12 –10^-19 S cm^-1 |
| Short-chain molecules with a single head group                             | ![Short-chains](image2) | 0.3-1 nm              | • Treatment of NC in solid or ligand-exchange in solution  
• Decreased colloidal stability  
• Improved electronic transport compared to long-chain ligands  
• Solar cell based on PbS QDs showed 5.1% efficiency |
| Cross-linking molecules with two end groups                                | ![Cross-linking](image3) | 0.3-1 nm              | • Mainly prepared by treating NC solids  
• Solar cells based on PbS and PbSe NC solids showed power conversion efficiencies up to 2.1% |
| Metal chalcogenide complexes                                               | ![Metal chalcogenide](image4) | ≥0.5 nm               | • High conductivities of ~ 200 S cm^-1 in Au-Sn₂Se₆⁴⁺ NC solids  
• Hydrophilic surface  
• Prepared via solution phase ligand exchange  
• Complete removal of original organic ligands |
More importantly, the devices were air-stable. Thus, short-chain organic ligands and halide ligands can decrease electron transport loss, enhance conductivity and increase carrier mobility in NC-based solar cells by decreasing the space between NCs, improving the surface passivation of NCs and eliminating trap states. It is believed that the power conversion efficiency of NC-based solar devices may be further enhanced by introducing new ligands and improving the liganding strategy.33

2.5 Surface Plasmon of Metal Nanoparticles

A schematic representation of the creation of a surface plasmon oscillation is provided in Figure 2.3. Under an external electric field, there is a displacement of the negative charges (free electrons) from positive charges (positive charges are assumed to be immobile), causing a net charge difference at the nanoparticle boundaries.34, 35 This effect provides a linear restoring force to the system. As a result, a dipolar oscillation of the electrons is created that is in resonance with the incident light, and this phenomenon is the surface plasmon oscillation.34, 35 To create a surface plasmon, there should be coupling between an electromagnetic
wave and the metal nanostructure.\textsuperscript{34, 35} There is no surface plasmonic function of metal nanoparticles without incident light.

There is normally a plasmon in bulk metal surfaces, but it cannot be excited by ordinary plane-wavelength light due to a mismatch between the plasmon dispersion relation and that of the photon.\textsuperscript{34, 35}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_3}
\caption{Schematic representation of the creation of a surface plasmon in metallic nanoparticles due to the interaction of electromagnetic radiation with the metal sphere. A dipole is induced, which oscillates in phase with the electric field of the incoming light.\textsuperscript{34}}
\end{figure}

\section*{2.6 Physics of Semiconductors}

When atoms approach to form crystals, the energy levels divide into separate but closely spaced levels due to atomic interactions, which lead to a continuous energy band.\textsuperscript{36, 37} The lower band is known as the valence band, and the upper band is known as the conduction band. The gap between two bands is defined as the band
gap. At the temperature of absolute zero, the valence band of a semiconductor is full of electrons, and the conduction band is empty.\textsuperscript{36-38} Electrons in the valence band start to vibrate with increasing temperature, and some bonds may be broken by stimulus vibrating. Electrons from the valence band may move into the conduction band, which is known as thermal generation (Figure 2.4). Once electrons leave the valence band, there are empty electronic states (missing electrons) in the valence band, called holes. Holes are also carriers in a semiconductor, and they represent positively charged particles.

A semiconductor is an important component of optoelectronic devices, and it is used as a light-absorbent layer in photovoltaic cells. When a semiconductor is excited by a photon and the energy of the photon is higher than the band gap of the semiconductor, the electrons from the valence band are excited into the

![Energy band diagram of a semiconductor. At 0 K, the VB is full with all of its valence electrons.\textsuperscript{36}](image)
Figure 2.5. A photon with energy greater than $E_g$ can excite an electron from the VB to the CB.\textsuperscript{36}

Figure 2.6. Energy band diagrams for (a) intrinsic, (b) n-type and (b) p-type semiconductors. In all cases, $np=n_i^2$.\textsuperscript{36}
conduction band and form electron-hole pairs (Figure 2.5). The band gap of a semiconductor is an important parameter in solar cells.

A semiconductor with electron-hole pairs that are mainly generated by thermal excitation is called an intrinsic semiconductor.\textsuperscript{36-38} Generally, intrinsic semiconductors are purely crystalline, and the number of electrons (n) and number of holes (p) are equal (n=p=n_i). This does not mean that there are no impurities, but electron-hole pairs generated from impurities are negligible in the intrinsic semiconductor.\textsuperscript{36} The carrier concentration of the intrinsic semiconductor is inversely proportional to the band gap, and the conductivity of the intrinsic semiconductor is proportional to temperature. The Fermi level of an intrinsic semiconductor is in the middle position between the valence and conduction bands, as shown in Figure 2.6a.\textsuperscript{36-38}

Adding impurities into a semiconductor will result in an excess of electrons or holes compared to its undoped counterpart, and this doped semiconductor is called an extrinsic semiconductor.\textsuperscript{36, 38} Electron-hole pairs are mainly generated by the dopant in an extrinsic semiconductor at moderate temperatures. For example, a small amount of a pentavalent element such as, P, or Sb can be doped into a pure silicon (Si) semiconductor crystal. Phosphorous (P) has five valence electrons, and Si has four. The four valance electrons of P form a covalent bond with Si, and the fifth electron that is loosely bound to the P atom is easily ionized even at room temperature. Thus, this electron becomes a conduction electron with a negative charge, creating excess electrons compared to undoped Si crystals. The pure intrinsic Si semiconductor then becomes an n-type semiconductor, and the P is
called a donor atom. The Fermi level of an n-type semiconductor is close to the conduction band, and the energy band diagram is illustrated in Figure 2.6b. The majority carrier of an n-type semiconductor is an electron.

Group III atoms such as boron (B), aluminum (Al) and gallium (Ga) can also be introduced into a pure Si crystal as a dopant. The Group III elements have three valence electrons, and Si has four. The Group III elements can attract electrons from Si, which generates a hole. There will be excess holes in the Si crystal, making it a p-type semiconductor. The dopant is called an electron acceptor. In a p-type semiconductor, holes are the majority carrier. The band diagram of a p-type semiconductor is shown in Figure 2.6c. When an n-type semiconductor and p-type semiconductor are brought together, a p-n junction is formed that has a built-in potential under thermal equilibrium. The p-n junction can separate the photon-produced electron-hole pairs, and this is the basic principle of most conventional photovoltaic devices.

The physical properties of semiconductor nanocrystals, such as mechanical strength and melting point, are different from their bulk counterparts because of their large surface to volume ratio.

2.7 Reactive Inkjet Printing

Inkjet printing is a form of non-vacuum digital printing with high throughput and high yield relative to vacuum-based processes (such as sputtering, evaporation, and physical vapor deposition and solution-based processes (such as spin coating, dip coating and electrophoretic deposition). Inkjet printing has a number of
attractive features, including its low cost, high material utilization, and scalability to large-area manufacturing. In our proposed work, inkjet printing is used as a synthesis tool for the in situ formation of Au NPs on a silicon or glass substrate directly from commercially available precursors.

Inkjet printing is a versatile technique with which to fabricate materials on a given substrate with substantially reduced and material usage as well as real-time patterning of printed materials. In general, inkjet printing is divided into two categories\textsuperscript{39}: continuous inkjet (CIJ) printing and drop-on-demand (DOD) inkjet printing.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{inkjet_categories.png}
\caption{Categories of inkjet technology. a) Continuous, b) piezoelectric and c) bubble jet.\textsuperscript{42}}
\end{figure}
CIJ is widely used for coding and marking applications. DOD is categorized into bubble jet DOD and piezoelectric DOD based on droplet production. Bubble jet DOD involves a vapor bubble that is heated, creating an expanded bubble that results in the formation of an acoustic wave, which forces a droplet out of the chamber. In the piezoelectric DOD method, an external bias expands or contracts a piezoelectric crystal chamber, creating a pressure wave that forces the fixed quantity of ink to expand and exit through a nozzle. Temperature-sensitive biological samples or very-low-viscosity inks can be printed by piezoelectric DOD. Reactive inkjet printing 43, 44 is the mixing or reaction in situ of one droplet of reactant with a second reactant on a substrate. This technique gives more accuracy to synthesis materials with good stoichiometry due to its controlled picoliter volume.

2.8 Nanostructured Solar Cells

In this section, a brief history of solar cells and a general overview of the status and prosperity of three generations of solar cells will be briefly provided, and the device architectures and working principles of inorganic nanocrystal semiconductors and semiconductor-sensitized and hybrid solar cells will be discussed.

2.8.1 General Overview of Different Solar Cells

Producing clean energy at a reasonable cost using renewable energy technology is an important task for the 21st century to reduce emissions of carbon dioxide from
fossil fuels, including coal, oil, and natural gas. Solar cells are an emerging renewable energy technology that can provide clean and sustainable energy.

A solar cell directly converts sunlight into electric energy. A semiconductor with a band gap of approximately 1.4 eV is used as a light absorber. The energy conversion involves the creation of an electron-hole pair (exciton) upon the absorption of light (photon) in the active semiconductor layer, charge separation, charge transport and charge collection. In most solar cell devices, a p-n junction is used for charge separation due to its built-in potential \(^{38}\).

Since the first discovery of the photoelectrochemical (PEC) phenomenon by Henri Becquerel (Becquerel, 1839), \(^{38}\) who discovered photocurrent and photovoltage.

![Figure 2.8. Efficiency table of different types of solar cells.](image)
produced by sunlight acting on silver chloride-coated platinum electrodes in various electrolytes, and the first silicon solar cell with 4% power conversion efficiency fabricated by scientists at Bell Labs (1954), many photovoltaic materials have been tested, many new materials have been synthesized, and several photovoltaic device architectures have been fabricated. The progress of several types of solar cells is shown in the timeline in Figure 2.8. The highest efficiency obtained by single crystal GaAs is over 44%, and quantum dot solar cells give the lowest efficiency is about 8.5%. Generally, solar cells can be divided into three generations.\textsuperscript{45}

The first generation consists of crystalline silicon-based solar cells. This cell has shown the highest module efficiency among single-junction devices, and it dominates the solar market. A 25%\textsuperscript{45} power conversion efficiency can be obtained at the lab scale, and this result approaches the theoretical Schockley–Queisser limit efficiency of 31%\textsuperscript{46} for single-junction solar cells. Despite the low cost of silicon itself, the fabrication cost of a defect-free, high-purity silicon wafer is great. It is very difficult to further decrease the cost of a crystalline silicon module.

The second generation includes thin-film solar cells.\textsuperscript{45} Copper indium gallium diselenide, cadmium telluride (CdTe), and amorphous silicon-based thin materials are representatives of the second generation of solar cells. Among these cells, the efficiencies of CIGS and CdTe are 19.6% and 18.3%, respectively. CdTe is not favored due to the toxicity of Cd and Te, and large-scale production of CIGS remains difficult due to the scarcity of In and Ga. Recently, solution-processed copper zinc tin sulfide (CZTS) \textsuperscript{47} showed very promising results (over 12%), and
scientists throughout the world are actively working on enhancing the efficiency of CZTS thin-film solar cells due to its abundance and environmental benignancy.

Third-generation solar cells include dye-sensitized solar cells, inorganic semiconductor-sensitized solar cells, organic solar cells, quantum dot solar cells and halide perovskite solar cells. The advantages of this type of solar cell include low temperature processability, solution processability, inexpensive large-scale production using cheaper fabrication methods such as roll-to-roll printing, not requiring a thick absorber layer, and the capability of fabricating flexible photovoltaic devices. Currently, most of the research activities on third-generation solar cells are being done in the laboratory, and the third generation solar cells are hoped to be commercialized once their efficiency, cost and stability are comparable with other solar cells available on the market.

2.8.2 Semiconductor-Sensitized Solar Cells

Dye-sensitized solar cells were invented by O'Regan and Grätzel (1991), and DSSCs have shown great potential for the next generation of low-cost and high-efficiency solar cells. The device architecture and working principles of DSSC are illustrated in Figure 2.9. Generally, DSSCs contain conducting glass electrodes coated with compact and mesoporous TiO₂ film, a dye molecule, an iodide/triiodide redox couple as hole-transporting materials, and a platinized conducting glass electrode. DSSCs have reached 12% efficiency and are now commercially available. In terms of long-term stability and the safety of the liquid electrolyte, the large-scale production of DSSCs seems risky for commercial applications. Thus,
solid-state DSSCs are fabricated using a solid hole conductor such as Spiro-OMeTAD. However, the efficiency of these cells is less than that of other DSSCs due to the lower mobility of solid HTM, a faster recombination at the interface and the poor pore filling of solid HTM into the nanopores of the nc-TiO$_2$ layers. In addition, QDs and inorganic semiconductor-sensitized solid state sensitized solar cells, also known as extremely thin absorber (ETA) cells, have been fabricated to utilize the advantages of solution-processed QDs and inorganic semiconductors over dye molecules due to their high absorption coefficient, large intrinsic dipole moment.

**Figure 2.9.** Device architecture of a liquid electrolyte dye-sensitized solar cell. A photogenerated electron is injected from the dye into the CB of the mesoporous oxide semiconductor, and the electron passes through the metal oxide film to the TCO-coated glass working electrode. A hole is transferred to the redox electrolyte, and the dye molecule is regenerated by the redox electrolyte, which is itself reduced to original state at the platinized counter-electrode by electrons passed through the external circuit.\textsuperscript{38}
convenient band gap tunability, multiple exciton generation, and good stability. Currently, QDs and inorganic semiconductor-sensitized solar cells have reached 8% and 7.5% power conversion efficiencies, respectively.

Generally, SSSCs have two types of architectures (Figure 2.10): porous and columnar. The porous structure offers a large surface area and can accommodate a large amount of absorber. The advantages of columnar architecture are that it can offer a sizeable surface enlargement with no grain boundaries along the transport path, relieves the mass transport problem at the vicinity of the absorber and HTM and reduces the backward recombination in absorber–photoelectrochemical cells.

The cells consist of a thin absorber layer between the electron and hole transporter materials. They have a wide band gap, and transparent materials are used as electron transporter layers, such as TiO$_2$ and ZnO. TiO$_2$ is widely used in mesoporous architecture-based solar cells, and several synthesis and processing methods have been examined, such as the sol-gel technique, spray pyrolysis, screen printing and spin coating. These techniques are chosen based on demands. Screen printing gives a thicker film and spin coating a relatively thinner film. There are two types of HTM: organic and inorganic HTM. Inorganic HTM is favored due to its long-term stability and price, and the most common HTMs are listed in Table 2.2.
Figure 2.10. Typical SSSC cell architecture. The interfaces between the absorber and electron and hole transport layers are structured, usually in porous (Figure 2.10a) or columnar (Figure 2.10b) form.

and the VB edge of hole transporter defines the maximum photovoltage that the cell can generate. If the value of $\Delta E_c$ and $\Delta E_v$ is approximately 0.2-0.3 V, the contact of the The operating principle of SSSCs is illustrated in Figure 2.11. $E_{F,n}$

Table 2.2. Some of the most commonly used HTMs in SSSCs or ETA-solar cells.

<table>
<thead>
<tr>
<th>HTM</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cul (gamma phase)</td>
<td>3.1</td>
</tr>
<tr>
<td>CuSCN</td>
<td>3.4</td>
</tr>
<tr>
<td>CuAlO$_2$</td>
<td>3.54</td>
</tr>
<tr>
<td>NiO</td>
<td>3.0</td>
</tr>
<tr>
<td>PEDOT:PSS function</td>
<td>5.2 (work function)</td>
</tr>
<tr>
<td>Spiro-OMeTAD function</td>
<td>4.9 - 5.22 (work function)</td>
</tr>
<tr>
<td>P3HT</td>
<td>2</td>
</tr>
</tbody>
</table>
and $E_{F,p}$ represent the majority carrier quasi-Fermi level of electron and hole conductor materials in the cell, respectively. The potential difference $3,38$ between the CB edge of electron transporter absorber layer with the electron and hole conductor is considered ideal. Electronically speaking $38$, SSCs are $p$-$i$-$n$ junction solar cells. Normally, the minority carrier diffusion lengths of the $i$-layer are short. Electron-hole pairs (carriers) photogenerated by incoming light in the absorber (i) layer are dissociated into free carriers by an electric field. The dissociated electrons are injected into the conduction band of an electron transporter (normally wide band gap oxide materials) and the holes into the valence band of HTM. The separated charges then transport to their respective contacts through transporter layers. One of disadvantages of this design is that there may be a slightly higher series resistance due to the poorer conductivity of the absorber layer relative to the doped layer.$^{38}$

SSCs$^3$ are divided into two types: three-component and two-component SSCs. Three-component cells include an inorganic semiconductor absorber layer and electron and hole transporters, whereas two-component cells include absorber and electron transporters. In this cell, the absorber layer has a hole-conductor function. Up to now, 8% and 5% power conversion efficiencies have been obtained for three- and two-component cells, respectively.$^3$
2.8.3 Hybrid solar cells

Polymer semiconducting materials\textsuperscript{50-55} have certain advantages over inorganic semiconductor materials, including good solubility in organic solvents and low-cost manufacturing methods. However, photo-generated excitons in polymer are strongly bound by Coulombic force due to its lower dielectric constant.\textsuperscript{55} Nevertheless, inorganic semiconducting NCs have lower binding energy and can be synthesized in various shapes (i.e., spherical, rod and tetrapod). These different-shaped NCs give different performances in solar cell devices. Hybrid solar cells combine the advantages of photovoltaic-organic and inorganic materials.
Thus, hybrid solar cells are one of the strategies used to boost solar cell efficiency with lower cost. A bulk hetero-junction organic/inorganic-inorganic hybrid solar cell is prepared by blending polymer and inorganic semiconductor NCs or different inorganic semiconductor NCs (or QDs) on a given substrate.

Hybrid solar cells are divided into two device structures: bi-layer and bulk heterojunction cells. Their device architectures are illustrated in Figure 2.12. In bi-layer cells, there is only a single interface layer, and the exciton diffusion length of conjugated polymers is shorter (approximately 10 nm); thus, the efficiency of generating free carriers is not high. However, the efficiency can be enhanced by increasing the interfacial area in bulk heterojunction cells.

![Figure 2.12. Schematic prototype of (a) bi-layer heterojunction (b) bulk heterojunction hybrid solar cell architectures.](image)

The working principle of organic-inorganic hybrid solar cells is illustrated in Figure 2.13. The sunlight is absorbed by the donor layer, which generates an exciton (electron-hole pair). The excitons then diffuse to the interfacial area, where
they dissociate into free carriers. The holes and electrons are transported and collected on the respective electrodes. Some excitons may also be generated in the acceptor layer.

Figure 2.13. Schematic illustration of the working principle of hybrid solar cells.\textsuperscript{52}
REFERENCES


47. Liu, W.; Mitzi, D. B.; Yuan, M.; Kellock, A. J.; Chey, S. J.; Gunawan, O., 12% Efficiency CuIn(Se,S)2 Photovoltaic Device Prepared Using a Hydrazine Solution Process†. *Chemistry of Materials* 2009, 22 (3), 1010-1014.


Chapter 3

Colloidal Synthesis and Characterization of Various Shapes of Sb$_2$S$_3$ Nanocrystals

3.1 Introduction

Binary chalcogenide semiconductors$^{1-7}$ have exhibited great potential for solar energy conversion due to their solution processability, band gap tunability, good light absorption efficiency, and simple composition. Most binary chalcogenide semiconductors have quantum confinement effects$^8$ when their size is smaller than their Bohr radius. This quantum confinement results in optical and electrical properties that differ from those of their bulk counterparts.

PbS QD-based solar cells (Table 3.1) are the most efficient binary chalcogenide-based solar cells, but the commercialization of lead-based solar cells is undesirable due to environmental and health concerns. After PbS QD-based solar cells, antimony sulfide (Sb$_2$S$_3$)-based solar cells exhibit the highest (Table 3.1) efficiency.

Sb$_2$S$_3$ $^{9-12}$ is a direct band gap semiconductor with a band gap of 2.2 eV as amorphous orange Sb$_2$S$_3$ and 1.7 eV as crystalline black Sb$_2$S$_3$, supporting
potential applications in solar cells,\textsuperscript{3, 13-24} optical data storage,\textsuperscript{11} lithium batteries \textsuperscript{25} and supercapacitors.\textsuperscript{26} Sb\textsubscript{2}S\textsubscript{3} has been used in high-performance semiconductor-sensitized solar cells as a light harvester due to its high light absorption coefficient. Sb\textsubscript{2}S\textsubscript{3} can form stable complexes with bifunctional hole-transporting materials in SSSCs,\textsuperscript{18} and this feature is important for high-efficiency semiconductor-sensitized inorganic-organic hetero-junction solar cells. The Haque group\textsuperscript{27} reported polymer-inorganic semiconductor hybrid solar cells using Sb\textsubscript{2}S\textsubscript{3} as a light-harvesting and electron-transporting component. Sb\textsubscript{2}S\textsubscript{3} can be used as an electron transporter for PV cells with other hole transporters, such as Sb\textsubscript{2}Se\textsubscript{3}, PbS, P3HT or perovskite.

\textbf{Table 3.1.} Solar cell performance of different solution-processed binary chalcogenides.

<table>
<thead>
<tr>
<th>Material/device structure</th>
<th>Open-circuit voltage $V_{oc}$(mV)</th>
<th>Short-circuit current density $J_{sc}$(mA/cm$^2$)</th>
<th>Fill factor FF</th>
<th>Power conversion efficiency $\eta$(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS QDs ITO/ZnO/PbS/Au</td>
<td>555</td>
<td>24.2</td>
<td>63.8</td>
<td>8.55</td>
<td>1</td>
</tr>
<tr>
<td>PbSe QDs ITO/Zn$_{1-x}$Mg$_x$O/PbSe/Mo3/Au</td>
<td>482</td>
<td>22</td>
<td>35</td>
<td>3.7</td>
<td>2</td>
</tr>
<tr>
<td>Sb2S3 FTO/m-TiO2/Sb2S3/PCPDTBTAu</td>
<td>711</td>
<td>16.1</td>
<td>65</td>
<td>7.5</td>
<td>3</td>
</tr>
<tr>
<td>Sb$_2$Se$_3$ FTO/d-TiO2/Sb$_2$Se$_3$/Au</td>
<td>520</td>
<td>10.3</td>
<td>42.3</td>
<td>2.26</td>
<td>4</td>
</tr>
<tr>
<td>Bi2S3 ITO/PbS+Bi2S3/Ag</td>
<td>400</td>
<td>24.2</td>
<td>50</td>
<td>4.87</td>
<td>5</td>
</tr>
<tr>
<td>CdTe ITO/CdTe/ZnO/Al</td>
<td>684</td>
<td>25.8</td>
<td>71</td>
<td>12.3</td>
<td>7</td>
</tr>
</tbody>
</table>
Various shapes of Sb$_2$S$_3$ NCs have been synthesized using hydrothermal, solvothermal,\textsuperscript{31-34} polyol,\textsuperscript{35} and chemical vapor transport reactions\textsuperscript{36} and chemical bath deposition.\textsuperscript{11} There has been one report\textsuperscript{37} on the synthesis of Sb$_2$S$_3$ nanowires using the hot injection method, but no systematic studies of the synthesis of amorphous and crystalline Sb$_2$S$_3$ NCs using colloidal hot injection methods have been reported, and there are no reports on solar cell devices based on Sb$_2$S$_3$ NCs. Here, we aim to develop systematic colloidal synthesis schemes for Sb$_2$S$_3$ NCs and study the effect of precursors, temperature and time on the formation of Sb$_2$S$_3$ NCs. In addition, we will explore their application in SSSCs.

3.2 Properties of Sb$_2$S$_3$

Sb$_2$S$_3$ is a weakly polar semiconductor, and it is a good photoconductor. The lattice of Sb$_2$S$_3$ is orthorhombic, and there are 4 molecules per unit cell. Sb$_2$S$_3$ belongs to the Pbnm space group.\textsuperscript{38}

The structure of Sb$_2$S$_3$ includes two infinite ribbons (Sb$_4$S$_6$)$_n$ along the c axis, each of which is made of two types of chains. The ribbons are weakly bound in the b direction.\textsuperscript{34,38} In the b axis, the shortest interatomic distances between the ribbons are approximately 1.5 times larger than those in the ribbon, which enables easy cleavage in the (010) plane (Figure. 1).\textsuperscript{34,38}
Figure 3.1. Structure of Sb$_2$S$_3$; projection of one ribbon in the (010) plane along the [0(-1)0] direction.

Table 3.2. The physical properties of Sb$_2$S$_3$.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (T=300K)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>11.299 Å</td>
</tr>
<tr>
<td>C</td>
<td>11.310 Å</td>
</tr>
<tr>
<td>B</td>
<td>3.8389 Å</td>
</tr>
<tr>
<td>Band gap</td>
<td>Amorphous (~2.0 eV)</td>
</tr>
<tr>
<td></td>
<td>Crystalline (~1.65 eV)</td>
</tr>
<tr>
<td>Dielectric constant [$\varepsilon_{(\infty)}$]</td>
<td>9.5 (T=320 K)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>~2.7-2.75</td>
</tr>
</tbody>
</table>
3.3 Synthesis of Sb$_2$S$_3$ NCs

3.3.1 Materials

Antimony (III) chloride (SbCl$_3$, 99.99%), antimony (III) acetate (Sb(OAc)$_3$, 99.99%), antimony(III) oxide (Sb$_2$O$_3$, 99%), tris(dimethylamido)antimony, lead oxide (PbO, 99.5%), oleic acid (OA), 1-octadecene (ODE, 90%), oleylamine (70%), trioctylphosphine (TOP, 97%) trioctylphosphine oxide (TOPO, technical grade, 90%), anhydrous toluene, anhydrous methanol, acetone(99.5%), bis(trimethylsilyl) sulfide (TMS, 98%), and elemental sulfur were purchased from Sigma-Aldrich.

3.3.2 Synthesis Procedure of Sb$_2$S$_3$ NCs

1. A total of 1 mmol SbCl$_3$, 6 ml oleic acid and 8 ml ODE were loaded into a 3-neck round-bottom flask, which was purged with N$_2$ and vacuum for 5 minutes, then heated to 150°C under vacuum for 1 h.

2. Then, the vacuum was replaced with a N$_2$ environment, and the flask was heated to 180°C. A total of 1.5 mmol TMS in 5 ml ODE was then injected into the flask, and the temperature was decreased to 100°C. Aliquots were taken at different times.

3. The as-synthesized NCs were washed with chloroform and ethanol by centrifuging and redispersed in toluene.

This is Standard Synthesis Protocol 1.

3.3.3 Description of Characterization Tools
**UV-Vis spectroscopy:** UV-Vis spectra of Sb$_2$S$_3$ NCs film on glass were acquired using double beam JASCO V-670 (Data interval: 1 nm and Scan speed 400nm/min.) spectrometer.

**PXRD:** all samples of Sb$_2$S$_3$ NCs is measured by PXRD using Brucker-D8 advance.

**TEM and EDS:** The TEM analysis was performed to study the morphology, crystal structure, and the elemental composition of samples. TEM-analysis of the samples was also performed by employing FEI Company’s TEM of model TitanG$^2$ 80-300 CT that was equipped with field-emission-gun and an X-ray EDS detector from EDAX, Inc. It is imperative to note that the TEM specimens were prepared by placing a small amount of samples on the holy-carbon coated copper (Cu) grids of 300 mesh-size. Moreover the analysis was carried out by the operating the microscope at beam energy of 300 keV and thus several low as well as high- magnification electron micrographs from various locations were acquired during the analysis. In addition SAED and EDS were also recorded to investigate the crystal structure and elemental composition of the samples, respectively. The entire TEM data acquisition and the proceeding image-analysis was carried out in the Digital Micrograph of version GMS 1.85 from Gatan, Inc.

### 3.4 Results and Discussion of Sb$_2$S$_3$ NCs Synthesized using Antimony Chloride Precursor

#### 3.4.1 Synthesis of Different Phase Sb$_2$S$_3$ NCs using Antimony (III) Chloride Sources
The synthesis procedure is described in Section 3.3.2. After the injection of TMS solution (TMS in ODE solution was prepared in a glove box, and ODE was degassed before use) at 180°C, the reaction temperature was set to 100°C. Before injection, the solution in the flask was a clear yellowish color, which immediately turned to orange after injection. The first aliquot was taken 90 s after the injection. The solution was quenched by cold anhydrous toluene and then washed 3 times with a mixture of acetone and methanol. The final product was redispersed in toluene and kept in a glove box for further characterization.

PXRD, TEM, HRTEM, SAED and UV-Vis spectroscopy were performed to characterize its structural, morphological, compositional and optical properties. The powder of as-synthesized NCs was dried under vacuum, and PXRD was performed. The PXRD of the

![Figure 3.2. PXRD of as-synthesized orange Sb$_2$S$_3$ NCs.](image)
Figure 3.3. UV-Vis spectroscopy of a film of orange color Sb$_2$S$_3$ NCs on a glass substrate.

As-synthesized NCs is shown in Figure 3.2, and the results indicate good agreement with the standard database value of pure, weakly crystalline Sb$_2$S$_3$.

To characterize the optical properties of the as-synthesized orange NCs and to determine their band gap, a Sb$_2$S$_3$ NC film was prepared on a clean glass substrate, as shown in Figure 3.3. The absorption onset in Figure 3.3 started at 770 nm, but it was weak. The band gap of the amorphous NCs was calculated to be approximately 630 nm, or 1.97 eV.
TEM, HRTEM and SAED measurements were carried out to determine the shape, size and crystallinity of as-synthesized NCs. The TEM images (Figure 3.4a and b) show that the particles are connected in a chain-like structure and are spherical in shape. The average size of the NCs is approximately 30 nm (Figure 3.4c). The SAED pattern indicates that the NCs are weakly crystalline. Based on the color of the NCs and the results of the PXRD and SAED, the as-synthesized NCs are weakly crystalline Sb$_2$S$_3$ NCs.
The EDS spectrum was carried out to determine the stoichiometry of NCs, and the atomic percentage ratio of Sb to S was found to be 42:58, as shown in Figure 3.5, indicating that the NCs are slightly sulfur-rich. After injection of the TMS solution at 180°C, the reaction temperature was gradually decreased to 100°C. After approximately 30 minutes, the orange color of the solution started to change into a black color. The reaction was stopped.

![EDS Spectrum](image)

**Figure 3.5.** EDS spectrum of the as-synthesized orange color Sb$_2$S$_3$ NCs.
Figure 3.6. PXRD of crystalline Sb$_2$S$_3$ NCs.

Figure 3.7. UV-Vis spectroscopy of a crystalline film of Sb$_2$S$_3$ NCs on a glass substrate.
Figure 3.8. a) and b) TEM, c) HRTEM (scale bar is 10 nm), and d) corresponding FFT pattern of Sb$_2$S$_3$ NCs.

after 90 minutes and immediately cooled down to RT using an ice bath. The washing process was the same as for the amorphous NCs, and the final product was similarly redispersed in toluene and stored in a glove box for further characterization. The PXRD in Figure 3.6 shows that the as-prepared NCs are very crystalline and comprise a pure phase. This finding is further confirmed by the standard database of Sb$_2$S$_3$. The as-synthesized NCs were deposited on a clean
glass substrate to measure their optical properties and band gap, and the film is shown in Figure 3.7. The absorption onset of the NC film started at 830 nm, and its band is approximately 1.63 eV, which is close to the band gap of bulk crystalline Sb$_2$S$_3$.

The TEM images (Figures 3.8a and b) show that the as-synthesized NCs have an urchin-like nanostructure composed of many nanorods. The HRTEM images (Figure 3.8c) indicate that the Sb$_2$S$_3$ NCs are highly crystalline, with an NR diameter of approximately 15 nm. The high crystallinity of these NCs is further affirmed by SAED (Figure 3.8d). We were able to control the shape and phase of Sb$_2$S$_3$ NCs simply by controlling the reaction time, when using SbCl$_3$ as an antimony source. The EDS spectrum of crystalline NCs confirmed that the crystalline phase is stoichiometric, with an atomic ratio of Sb to S of 40:60.
3.4.2 The Sulfur Sources’ Effect on the Morphology of Sb$_2$S$_3$ NC
Figure 3.10. TEM and SAED images of as-synthesized Sb$_2$S$_3$ NCs using elemental sulfur in oleylamine as the sulfur source and SbCl$_3$ as the antimony source. a-b) 90s after injection, c-d) 90 minutes after injection, e-f) twice injection of sulfur source (90 min.)

Controlling the shape of colloidal NCs by the reactivity of the precursors has received considerable attention due to its versatility and simplicity. The synthesis of different shapes of semiconductor NCs has great technological potential due their shape-dependent optical and electrical properties. Guo et al. comprehensively studied the effect of sulfur and selenium sources on the shape of cadmium chalcogenide NCs, and they found that sulfur or selenium precursors with a lower reactivity lead to progressively slower nucleation and higher selectivity for anisotropic growth, all the way from dots to pods to tetrapods.

Elemental sulfur was dissolved in degassed oleylamine (1 mol elemental S in 3 ml oleylamine) and stored in a glove box as a stock solution. A total of 1.5 mmol sulfur stock solution was injected instead of the TMS solution, and all other conditions remained unchanged. Similar to the previous experiment, two aliquots were taken at 90 s and 90 minutes following the injection, and the same cleaning process was used. The TEM and SAED images of NCs synthesized for 90 s are shown in Figures 3.10a and b. The as-synthesized NCs are of a spherical shape and are connected in a chain structure. The average size is approximately 18 nm, smaller than comparable NCs synthesized using TMS solution. The color of the as-synthesized NCs is orange, and they are weakly crystalline. After approximately 40 minutes, the orange color of the solution in the flask started to change to black. The reaction was stopped after 90 minutes, and the solution was cooled to RT
using an ice bath. Figures 3.10c and d show that the morphology is that of highly crystalline nanorods. However, there are some antimony NCs on the surface of the Sb$_2$S$_3$ NCs, suggesting that the SbCl$_3$ was reduced to Sb by the oleylamine. Another experiment with a second injection of the sulfur source was performed to obtain pure Sb$_2$S$_3$ NRs. During the experiment, a 0.75 mmol sulfur stock solution was injected once the orange color of solution started to change into black after the initial injection of the 1.5 mmol sulfur stock solution. The TEM images (Figures 3.10e and f) indicate that there are no Sb NCs on the surface of the NRs. The

![Figure 3.11. a and b) TEM, c) scanning TEM, d and f) EDS of as-synthesized NCs using elemental sulfur in ODE.](image)

**Figure 3.11.** a and b) TEM, c) scanning TEM, d and f) EDS of as-synthesized NCs using elemental sulfur in ODE.
reactivity of the elemental S in oleylamine is lower than in TMS, which may lead to the anisotropic growth of Sb$_2$S$_3$ NCs.

Elemental S in ODE was used as a sulfur source because it is stable in air. The stock solution was prepared by dissolving 1 mmol S in 6 ml ODE under nitrogen at 200°C for 1 h. Two rounds of experiments were carried out: one in which the reaction temperature was decreased to 100°C after the injection of the 1.5 mmol sulfur source and another in which the reaction temperature was maintained at 180°C following the injection. In both cases, there was no formation of NCs. Another experiment was carried out at 220°C, with the solution maintained for 90 minutes at that temperature. We only obtained black NCs, and could not obtain orange NCs by this method. This outcome may be due to the lower

Figure 3.12. POXRD of Sb NPs obtained in place of Sb$_2$S$_3$ NCs.
reactivity of elemental sulfur in ODE. Guo et al.\textsuperscript{40} reported that there was no formation of CdS NCs when diphenyl disulfide was used as a sulfur source. The TEM and EDS measurements shown in Figure 3.11 indicate that the as-synthesized NCs is composed of crystalline Sb$_{2}$S$_{3}$ with an NR-like morphology. There are Sb NCs on the surface of the Sb$_{2}$S$_{3}$ NCs.

In the last round, 1 mmol elemental S was dissolved in 3 ml TOP, and experiments were carried out on the reaction. The PXRD (Figure 3.12) confirmed that the NCs were composed of pure Sb, in agreement with other reports.\textsuperscript{42} This outcome may be due to the reduction of SbCl$_{3}$ by TOP.

### 3.4.3 TOPO's Role in The Morphology of Sb$_{2}$S$_{3}$ NCs

TOPO \textsuperscript{43-48} is a common ligand for the synthesis of monodisperse highly luminescent NCs. TOPO is a bulky, weakly bonding ligand, and it can act as a solvent and a phosphorus source. It is widely believed that TOPO is a ligand that can be used to obtain small (≤4 nm) cadmium chalcogenide NCs with a narrow size distribution.\textsuperscript{43} Our goal in obtaining smaller crystalline Sb$_{2}$S$_{3}$ NCs is to fabricate a high-quality film for solar cell applications. We expected long-alkyl chain TOPO to yield slower particle growth due to its strong steric hindrance force and strong metal binding capability, which may affect the urchin-like rod growth by changing the relative growth rates of different crystal faces.\textsuperscript{48} Therefore, TOPO was chosen to examine whether monodisperse crystalline Sb$_{2}$S$_{3}$ NCs could be
Figure 3.13. The effect of TOPO on the morphology of Sb$_2$S$_3$ NCs.

obtained.

A total of 3.5 mmol TOPO was added to the reaction flask, and all other conditions were the same as in the standard reaction protocol. After 90 minutes of reaction time, TEM was employed to observe TOPO’s effect on the morphology of the NCs. There were some small NCs, which are the irregularly shaped crystalline NCs shown in Figure 3.13. Hence, the addition of TOPO did not succeed in obtaining small NCs of the desired quality.
3.4.4 Temperature Effect on the Growth Kinetics and Shape of \( \text{Sb}_2\text{S}_3 \) NCs

Figure 3.14. TEM, HRTEM and SAED images of \( \text{Sb}_2\text{S}_3 \) NCs, where the TMS solution was injected at 140°C.

The injection and NC growth temperature can affect the size, shape, monodispersity, and phase of NCs.\(^{48}\) Several experiments were carried out to explore the effect of temperature on the size and morphology of \( \text{Sb}_3\text{S}_2 \) NCs as well as on the reaction kinetics of the formation of \( \text{Sb}_2\text{S}_3 \) NCs.

TMS solution was injected at 140°C, and all other conditions were the same. An orange aliquot was taken 90 s after the injection, and a second one was taken after 90 minutes, with a mixture of orange and black colors. We took a third aliquot after 2 h, which had a completely black color. The TEM image (Figure 3.14a) of the first
aliquot indicates that it is composed of spherical amorphous Sb$_2$S$_3$ NCs, and TEM and HRTEM images (Figures 3.14b and c) of the second aliquot show that the as-synthesized NCs are a mixture of amorphous and crystalline Sb$_2$S$_3$. The TEM, HRTEM and SAED (Figures 3.14d-f)

![TEM and SAED images of Sb$_2$S$_3$ NCS, with an injection temperature of 230°C and a reaction time of just 90 s.](image)

**Figure 3.15.** TEM and SAED images of Sb$_2$S$_3$ NCS, with an injection temperature of 230°C and a reaction time of just 90 s.

confirmed that the third aliquot formed pure crystalline Sb$_2$S$_3$ NCs. The diameter of the NRs was smaller than that of the crystalline Sb$_2$S$_3$ NCs obtained when the
injection temperature was 180°C. Thus, the lower injection temperature affected the diameter of the NRs and the kinetics of formation of the crystalline Sb$_2$S$_3$ NCs.

To further quantify the effect of a high injection temperature, TMS solution was injected at 220°C. The TEM and SAED images (Figure 3.15) of an aliquot of as-synthesized NCs, taken 90 s after the injection, indicate that the NCs consist of amorphous and crystalline Sb$_2$S$_3$. After the TMS injection, the solution color immediately changed to orange and subsequently started to change to black. The shape of the crystalline Sb$_2$S$_3$ NCs was irregular, resembling a nanobelt structure. This finding further demonstrates how injection temperature affects the morphology and kinetics of formation of Sb$_2$S$_3$ NCs.

In another trial, TMS solution was injected at 100°C, and this temperature was maintained throughout the reaction. It took more than 2.5 h to form completely black NCs. Thus, it takes a longer time to form crystalline Sb$_2$S$_3$ NCs if the TMS solution is injected at a lower temperature. The diameter of the crystalline NCs (Figure 3.16b) is larger than for the NCs injected at 140°C or 180°C.

We also designed another experiment to grow Sb$_2$S$_3$ NCs at a higher growth temperature. In this experiment, TMS solution was injected at 140°C, and the reaction temperature was maintained at 140°C. Highly crystalline Sb$_2$S$_3$ NCs were obtained, as shown in Figures 3.17a-c. Compared to NCs grown at the lower temperature (100°C), the diameter of the NRs was larger.

Based on these experiments carried out at different nucleation (injection) and growth temperatures (Figures 3.16 and 3.17), it can be concluded that lower
nucleation (injection) temperatures lead to lower monomer concentrations and can yield larger-size nuclei, whereas larger particles can be obtained by higher growth temperatures as the rate of monomer addition to existing particles is enhanced. In addition, there is a high chance of Ostwald ripening at higher temperatures.\textsuperscript{48}

\textbf{Figure 3.16.} TEM and HRTEM images of Sb\textsubscript{2}S\textsubscript{3} NCs with TMS solution injected at different temperatures and left for different reaction times. After the injection, the temperature of all was reduced to 100°C. a) 100°C, 90 s; b) 100°C, 3 h; c) 140°C, 90 s; d) 140°C, 2 h; e) 180°C, 90 s; f) 180°C, 90 s; g) 230°C, 90 s; h) and i) 230°C, 90 min.
Figure 3.17. Comparison of the growth of Sb$_2$S$_3$ NCs at different temperatures. TEM and HRTEM images of Sb$_2$S$_3$ NCs, a-c) injection and growth at 140°C, d-f) injection at 140°C and growth at 100°C.

3.5 Synthesis and Characterization of Sb$_2$S$_3$ NCs using Antimony Acetate and Oxide Precursors

Acetate and oxide precursors $^{49}$ of metals are widely used to synthesize NCs and QDs by the hot injection method due to their easy formation of complexes with coordinating organic ligands, moderate decomposition temperatures and solubility in most common coordinating and non-coordinating ligands.

3.5.1 Synthesis of Sb$_2$S$_3$ NCs using Antimony Acetate
A total of 1 mmol Sb(OAc)$_3$, 6 ml of oleic acid and 8 ml of 1-octadecene (ODE) were loaded into a 3-neck round-bottom flask that was purged with N$_2$ and under vacuum for 5 minutes. The flask was then heated to 150°C under vacuum for 1 h, after which the vacuum was replaced with a N$_2$ that was heated to 180°C. The sulfur source (1.5 mmol TMS in 5 ml ODE) was then injected into the flask, and the solution was slowly cooled to 100°C before being incubated for different lengths of time. The as-synthesized NCs were washed with chloroform and ethanol by centrifugation before being redispersed in a non-polar organic solvent. This methodology is referred to as Standard Reaction Protocol 2.

3.5.2 Characterization of Sb$_2$S$_3$ NCs Synthesized using Acetate and Oxide Antimony Precursors at Different Temperatures and Times

Figure 3.18. TEM and SAED images of Sb$_2$S$_3$ NCs synthesized with different reaction times using Sb(OAc)$_3$ precursor. a) 90 s, b) 90 minutes.
TEM and SAED images are shown in Figure 3.18. The color of both solutions was orange, indicating that they were both composed of weakly crystalline Sb$_2$S$_3$ NCs. The as-synthesized NCs were well separated with a spherical shape and an average size of approximately 125 nm. The size of the NCs did not change significantly after 90 minutes of reaction time.

![Figure 3.18. TEM and SAED images of Sb$_2$S$_3$ NCs synthesized using Sb$_2$O$_3$ precursor for different times. a) 90 s, b) 90 minutes.](image)

Similarly, Sb$_2$S$_3$ NCs were synthesized using Sb$_2$O$_3$ instead of Sb(OAc)$_3$, with the other conditions the same as in Standard Synthesis Protocol 2. The TEM images (Figure 3.19) show that the as-synthesized NCs are spherical in shape, with an average size of approximately 100 nm, smaller than for NCs synthesized using Sb(OAc)$_3$. SAED (Figure 3.19b insert) confirmed that the NCs synthesized for 90 minutes were weakly crystalline. In both cases, the experiments were continued overnight, but the orange color did not change. It is known that crystalline chain-like NRs are formed when SbCl$_3$ is used as an antimony precursor.
To see the effect of temperature on the morphology of NCs, the temperature was maintained at 180°C. After 1.5 h of reaction time, the orange color of the NCs started to change to black, and the reaction was stopped after 2 h. The TEM, HRTEM and SAED images (Figure 3.20) indicate that the as-prepared NCs were highly crystalline and composed of large NRs with a diameter larger than 200 nm.

Figure 3.20. TEM, HRTEM and SAED images of crystalline Sb$_2$S$_3$ NCs synthesized using oxide (a and b) and antimony acetate precursors (c and d).
3.5.3 Chlorine Ion’s Effect on The Morphology of Sb$_2$S$_3$ NCs

Morphology is a key parameter in the design of novel nanomaterials with controlled functional properties.$^{50,51}$ Foreign ion effects on the morphology of metal and semiconductors NCs have been observed.

As noted above we could not obtain highly crystalline black Sb$_2$S$_3$ NCs when antimony acetate or oxide were used as an antimony source under the same reaction conditions. We suspected that this effect may be due to the role of chlorine ions.$^{50}$ Zhao et al.$^{50}$ reported that they were able to obtain octapod iron oxide NPs by adding NaCl solution in water to the reactant. To study this effect, different amounts of 3 and 6 mmol NaCl in 0.5 ml H$_2$O were added to the mixture of Sb(OAC)$_3$, oleic acid and ODE, with the other conditions and details of the procedure the same as in Standard Reaction Protocol 2. The reaction was carried out at different time lengths, but all of the as-synthesized NCs were orange Sb$_2$S$_3$ NCs. The TEM and SAED images (Figures 3.21a and b) indicate that there is weak crystallinity in the product, with some spherical NCs of both large and small sizes. The reason that NaCl did not induce a morphology change is that chlorine ions may not participate in the metal-organic complex in this reaction due to water's miscibility with oleic acid and ODE.

For a follow-up trial, TABCl was chosen as a chlorine source, and 3 mmol TABCl was added to the mixture of Sb(OAC)$_3$, oleic acid and ODE, with other conditions and details of the procedure the same as in Standard Protocol 2. The orange color started to change to black half an hour after the TMS injection, and the second
$\text{Sb(OAc)}_3 + \text{NaCl}$

90 S

$\text{Sb(OAc)}_3 + \text{TBACl}$

90 min.
Figure 3.21. TEM, HRTEM and SAED images of Sb$_2$S$_3$ NCs synthesized in the presence of different chlorine sources.

A aliquot was taken after 90 minutes of reaction time. The TEM, HRTEM and SAED images (Figures 3.21c-f) reveal that amorphous and crystalline Sb$_2$S$_3$ NCs were obtained. The shape of the amorphous NCs is chain-like spherical, whereas the shape of the crystalline NCs is chain-like NRs with a diameter of approximately 20 nm. We were therefore able to control the morphology of Sb$_2$S$_3$ NCs by adding a proper chlorine source, i.e., TBACl. TBACl has a good solubility in the mixture of oleic acid and ODE at an elevated temperature.

3.5.4 Synthesis of Well-Separated Sb$_2$S$_3$ NRs through Multiple Injections of Sulfur Source

In this section, we describe the effect of other sulfur sources and coordinating ligands on the morphology of Sb$_2$S$_3$ NCs.

Figure 3.22. Images of Sb$_2$S$_3$ NCs synthesized using elemental sulfur in oleylamine as a sulfur source. a) TEM, b) HRTEM.
A total of 1 mmol of elemental sulfur was dissolved in 3 ml oleylamine and maintained as a stock solution. An aliquot of 1.5 mmol sulfur stock solution was injected at 220°C, with the other conditions the same as in Standard Reaction Protocol 2. The samples taken after 90 minutes were characterized by TEM, and the images (Figure 3.22) reveal that

![Images of Sb$_2$S$_3$ NCs synthesized using oleylamine and elemental sulfur in oleylamine as a coordinating ligand and sulfur source, respectively. a) TEM, b) Scanning TEM, c) EDS.](image)

**Figure 3.23.** Images of Sb$_2$S$_3$ NCs synthesized using oleylamine and elemental sulfur in oleylamine as a coordinating ligand and sulfur source, respectively. a) TEM, b) Scanning TEM, c) EDS.
the product is highly crystalline, with large NCs resembling nanobelts. These results suggest that larger NCs are produced when the injection temperature is increased.

A total of 1 mmol elemental sulfur was dissolved in 3 ml oleylamine and was kept as a stock solution. An aliquot of 1.5 mmol sulfur stock solution was injected at 220°C, and the same amount of oleylamine (6 ml) was used as a coordinating ligand instead of oleic acid. Other conditions were the same as in Standard Reaction Protocol 2. A brown solution was obtained after 90 minutes of reaction time, which persisted for longer reaction times. The TEM images (Figure 3.23a) show the presence of well-separated Sb$_2$S$_3$ NRs, together with some Sb NPs (Figures 3.23b and c). For this reason, a second 0.75 mol sulfur source was injected 30 minutes after the first injection to eliminate pure Sb NPs, and the reaction was stopped after 90 minutes. The TEM and HRTEM images (Figure 3.24) reveal that well-separated Sb$_2$S$_3$ NRs were obtained. Compared to the results obtained in Section 3.4.2, the NRs were more uniform and smaller, and the ink stability was much better.

Another experiment was carried out to synthesize Sb$_2$S$_3$ NCs through multiple injections of a sulfur source in the presence of TOPO to obtain smaller NCs due to the strong steric hindrance of the TOPO. As a result, irregularly shaped Sb$_2$S$_3$ NCs (Figure 3.25) were obtained with some pure Sb NPs.
Figure 3.24. Images of Sb$_2$S$_3$ NRs obtained through multiple injections of a sulfur source. a) TEM, b) HRTEM.

Figure 3.25. a and b) TEM and c) HRTEM images of Sb$_2$S$_3$ NCs synthesized through multiple injections of a sulfur source in the presence of TOPO.
3.6 Synthesis of Sb-Rich and Stoichiometric Sb$_2$S$_3$ NCs using Tris(dimethylamido)antimony

It is critical to select a suitable starting molecular precursor for the design of a new synthesis of uniform NCs.$^{52}$

The synthesis of highly crystalline uniform small (<20 nm) colloidal InSb, Bi$_{1-x}$Sb$_x$, and Sb NCs has been reported using a hot injection method with tris(dimethylamido)antimony $^{53-55}$. Our goal is to obtain small crystalline Sb$_2$S$_3$ NCs for use in the preparation of a uniform film at room temperature for the fabrication of Sb$_2$S$_3$-based solar cells.

![Figure 3.26. TEM and SAED images of Sb-rich Sb$_2$S$_3$ NCs.](image)

3.6.1 Synthesis of Sb$_2$S$_3$ NCs using Tris(dimethylamido)antimony

A total of 10 ml oleylamine was loaded into a 3-neck round-bottom flask, which was purged with N$_2$ and vacuum for 5 minutes, heated to 120°C under vacuum, and maintained under these conditions for 1 h. The vacuum was then filled with N$_2$, which was then heated to 220°C. Then, 1 mmol tris(dimethylamido)antimony in 2
ml ODE and 1.5 mmol TMS in 2 ml ODE were injected at the same time into the flask, and the temperature was maintained for 10 minutes before being cooled to RT. The as-synthesized NCs were washed with chloroform and ethanol by centrifuging before being redispersed in toluene.

### 3.6.2 Characterization of As-Synthesized Sb$_2$S$_3$ NCs

After the reaction, the color of the solution was brown, and TEM, SAED and EDS measurements were performed. TEM images (Figure 3.26) reveal that the NCs are spherical in shape with an average size of 50 nm, and SAED (Figure 3.26b insert) indicates that the product is weakly crystalline. The EDS spectrum (Figure 3.27) confirms that the as-synthesized NCs are Sb-rich Sb$_2$S$_3$, the ratio of Sb to S is 64:36. Even with a longer reaction time, the product was still Sb rich.

![Figure 3.27. EDS spectrum of Sb-rich Sb$_2$S$_3$ NCs](image)

Another experiment was conducted to obtain stoichiometric Sb$_2$S$_3$ NCs. A total of 3 mmol TMS solution was injected, and the other conditions were the same as in
the previous synthesis procedure. The TEM image (Figure 3.28a) reveals that the NCs are a mixture of Sb$_2$S$_3$ NCs and Sb NPs. The experiment was carried out again in the presence of 10 ml oleic acid instead of oleylamine to avoid the reduction of the antimony amide precursor by oleylamine. The TEM image (Figure 3.28b) shows that the as-synthesized NCs are still a mixture of Sb$_2$S$_3$ NCs and Sb NPs.

![Figure 3.28. TEM images of antimony sulfide NCs synthesized with an excess of TMS in the presence of a) oleylamine, b) oleic acid.](image)

### 3.7 Synthesis of Sb$_2$S$_3$ NCs through Cation Exchange

#### 3.7.1. Basic Principles of Cation Exchange

Ion exchange is an alternative to the conventional hot injection method for the synthesis of novel nanomaterials and nanostructures not accessible by conventional synthesis. $^{56-58}$
Cation exchange is a versatile chemical transformation method. It is critical to understand the thermodynamic requirements for the process to occur.\textsuperscript{56, 58, 59} The process of cation exchange is illustrated in Figure 3.29. This effect can be achieved through simple mutual diffusion with another cation.

One important thermodynamic consideration is the solubility of the cations in the starting nanomaterials.\textsuperscript{56, 57} The cation exchange process may proceed once the cations are fully dissolved in the solution medium. Most transformation reactions are conducted in polar solvents.\textsuperscript{56, 57} The thermodynamic favorability of a cation exchange reaction can be determined by the relative solubility difference between the solubility of the reactants and products in solution.\textsuperscript{57} Thus, the exchange reaction will proceed if the solubility of ions in a solid is higher than the solubility of the product.\textsuperscript{57} Thermodynamically speaking, the solubility product (Ksp) of an ionic solid is defined as an equilibrium constant between
Figure 3.30. The relative order of the solubility products of various metal chalcogenides.$^57$

We can see from Figure 3.30 that the solubility of antimony chalcogenides is lower than that of lead chalcogenides. Thus, the cation exchange from PbS to Sb$_2$S$_3$ is favorable, whereas the reverse reaction is unfavorable. We designed a cation
exchange reaction from PbS QDs to Sb$_2$S$_3$ NCs with the goal of obtaining smaller Sb$_2$S$_3$ NCs.

![UV-Vis spectrum of as-synthesized PbS QDs.](image)

**Figure 3.31.** UV-Vis spectrum of as-synthesized PbS QDs.

### 3.7.2 Synthesis and Characterization of PbS QDs

The lead oleate complex 60 was prepared by dissolving 0.45 g PbO in 3 ml oleic acid and 6 ml ODE under vacuum at 100°C overnight. The 4.5 ml lead oleate complex and 15 ml ODE were then heated to 120°C under vacuum and kept at this temperature for 1 h. The reaction temperature was then decreased to 115°C, and 0.15 ml TMS in 10 ml ODE was injected before cooling to RT over a 60 minute
period by deactivating the heating mantle. The as-prepared QDs were washed by chloroform and methanol and dispersed in toluene.

![TEM image of as-synthesized PbS QDs.](image)

**Figure 3.32.** TEM image of as-synthesized PbS QDs.

UV-Vis spectrum and TEM were employed to characterize the as-synthesized PbS QDs. The UV-Vis absorption spectrum (Figure 3.31) indicates that the PbS QDs have a strong absorption peak at 960 nm. The TME image (Figure 3.32) reveals that the as-synthesized PbS QDs are very uniform, with an average size of approximately 5.5 nm.
3.7.3 Synthesis of $\text{Sb}_2\text{S}_3$ NCs through Cation Exchange

1. A total of 3 mmol of PbS QDs was dissolved in 6 ml toluene to produce Stock Solution A, with a brown-black color.

2. A total of 2 mmol SbCl$_3$ was dissolved in 10 ml methanol to produce Stock Solution B, which is a colorless solution.

Figure 3.33. UV-Vis absorption spectrum of $\text{Sb}_2\text{S}_3$ NCs obtained by cation exchange reaction from PbS QDs.

3. Stock Solution A was added dropwise into Stock Solution B at room temperature, and the color changed quickly from brown-black to yellowish orange.
The reaction scheme is shown in Figure 3.34, and this reaction occurred very quickly. After the reaction, the color of the solution was yellowish orange, which is indicative of the formation of Sb$_2$S$_3$ NCs. The product was washed with chloroform and ethanol by centrifuging, and the NCs were redispersed in toluene for further characterization. UV-Vis absorption spectrum, TEM and EDS measurements were carried out to characterize the NCs after the ion exchange reaction.

$$3\text{PbS} + 2\text{SbCl}_3 \rightarrow \text{Sb}_2\text{S}_3 + 3\text{PbCl}_2$$

**Figure 3.34.** Ion exchange reaction from PbS QDs to Sb$_2$S$_3$ NCs.

![](image)

**Figure 3.35.** TEM images of Sb$_2$S$_3$ NCs obtained by cation exchange reaction from PbS QDs, a) lower resolution TEM, b) higher resolution TEM.

The UV-Vis absorption spectrum (Figure 3.33) indicates that the absorption onset begins approximately 650 nm, and its band gap is approximately 1.97 eV. These results are similar to those of the weakly crystalline Sb$_2$S$_3$ NCs synthesized by hot
injection. The size of the individual NCs was below 20 nm, with a chain-like structure revealed by TEM images (Figure 3.35). The EDS spectrum (Figure 3.36) confirmed that the NCs were composed of pure Sb$_2$S$_3$ NCs, without any lead or other elements, and the atomic percentage ratio of Sb to S was 40.67 to 59.33.

Figure 3.36. EDS spectrum of Sb$_2$S$_3$ NCs obtained by cation exchange reaction from PbS QDs.
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Chapter 4

Fabrication of Solid-State Dye Sensitized Solar Cell-Based Sb$_2$S$_3$ NCs

4.1 Introduction

Dye-sensitized$^{1-5}$ solar cells have received considerable attention due to their cost-effective fabrication and reasonable efficiency compared with conventional solar cells. This structure of these devices comprises$^5$ mesoporous titania, a light harvester and a hole conductor (transporter). Once an electron-hole pair is generated in the light-harvesting material, it is rapidly transferred to the mesoporous TiO$_2$ and the hole conductor. In most DSSC architectures, dye molecules and a liquid electrolyte containing a regenerative redox couple are used as the light harvester and hole conductor, respectively. The liquid electrolyte used in DSSCs may hinder its large-scale commercialization due to safety and scalability concerns. Thus, there is increasing interest in completely solid-state sensitized solar cells.$^6,7$

Antimony sulfide$^{8-22}$ is a potential material for use in low-cost solar cells because of its relatively high abundance on earth, low toxicity and strong light absorption coefficient. In addition, it is not only a light harvester but also an electron transporter, which means that Sb$_2$S$_3$ can form a p-n junction cell and bulk hetero-
junction hybrid device with solution processable organic and inorganic semiconducting light absorbing materials, such as P3HT and PbS QDs.

Sb$_2$S$_3$ is widely used in solid-state SSSCs, and different synthetic methods and deposition techniques have been used to obtain Sb$_2$S$_3$ on mesoporous TiO$_2$ (Table 4.1). Based on the extensive literature review shown in Table 4.1, there are no

**Table 4.1.** Solar cell performance of Sb$_2$S$_3$-based photovoltaic devices.

<table>
<thead>
<tr>
<th>Synthesis method/device structure</th>
<th>Open-circuit voltage $V_{oc}$ (mV)</th>
<th>Short-circuit current density $J_{sc}$ (mA/cm$^2$)</th>
<th>Fill factor FF</th>
<th>Power conversion efficiency $\eta$ (%)</th>
<th>Hole transporting material(s)/surface treatment</th>
<th>Ref.</th>
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<td>3.3</td>
<td>Cobalt redox+P3HT</td>
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<td>36.2</td>
<td>0.94</td>
<td>P3HT</td>
<td>19</td>
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</table>
reports on the fabrication of solid-state SSSCs using as-synthesized Sb$_2$S$_3$ NCs in ink. There is a report on the surface treatment of Sb$_2$S$_3$ but no report on the surface functionalization of the surfaces of TiO$_2$. We believe that surface functionalization of TiO$_2$ with (3-mercaptopropyl)trimethoxysilane can improve the uniformity of Sb$_2$S$_3$ films on TiO$_2$ surfaces and may further facilitate electron transfer between Sb$_2$S$_3$ and TiO$_2$. We would like to fabricate completely solid-state SSSCs using ink containing as-synthesized Sb$_2$S$_3$ NCs.

4.2 History of Sb$_2$S$_3$-Based Solar Cell Research

Early work on Sb$_2$S$_3$-based solar cells dates to 1992, when Savadogo et al. made photoelectrochemical cells with 0.8% and 2.0% efficiencies under 40 mW/cm$^2$ illumination for amorphous and crystalline Sb$_2$S$_3$, respectively.$^{23}$ A year later, n-Sb$_2$S$_3$/p-Si heterojunction solar cells$^{24}$ were reported with 1.03% efficiency, and 5.19% efficiency was obtained using silicotungstic acid. In the following year, a Sb$_2$S$_3$-sensitized TiO$_2$ solid state cell was fabricated with an IPCE of 88% at 420 nm; the cell efficiency was not reported.$^{25}$

The first work on Sb$_2$S$_3$-based solid state sensitized solar cells that presented the device efficiency was reported by Yafit et al.$^{26}$ in 2009. A power conversion efficiency of 3.37% under a full sun was obtained, and nonporous TiO$_2$ and CuSCN were used as the electron and hole transporters, respectively. The Sb$_2$S$_3$ is deposited on TiO$_2$ using a CBD method. In 2010, the Gratzel group reported Sb$_2$S$_3$ SSSCs with a 3.1% efficiency using spiro-OMeTAD as the hole conductor.$^{18}$ Subsequently, 5.09%$^9$ and 6.3%$^{10}$ efficiencies were obtained by the Gratzel and
Seok groups, who used P3HT and a mixture of P3HT and PCBM as the hole conductor, respectively. In that year, a 7.5% efficiency\textsuperscript{14} was obtained via surface passivation of Sb$_2$S$_3$ by thioacetamide using PCPDTBT polymer as the hole transporter. In those works, the Sb$_2$S$_3$ is deposited on TiO$_2$ using the CBD method.

In 2013, low-temperature, solution-processed SSSCs were reported.\textsuperscript{19} In this work, the researchers synthesized single precursor antimony ethyl xanthate, and they made a paste to fabricate films using this precursor. After depositing a film on meso-porous TiO$_2$, the precursor is thermally decomposed. These devices yielded efficiencies of 0.98%, and this approach is a promising method to fabricate large-scale Sb$_2$S$_3$-based solar cells despite its low performance.

4.3 Preparation of Sb$_2$S$_3$ NCs and TiO$_2$-Based Pastes and Hole Transporting Material Solutions

4.3.1 Chemicals and Materials

TiO$_2$ paste (Dyesol 18NR-T), home-made Sb$_2$S$_3$ NCs, hydrochloric acid, zinc powder, titanium isopropoxide (99.999% purity), thioacetamide, spiro-OMeTAD(98%), TiCl$_4$, P3HT(99.9%), lithium-bis(trifluoromethanesulfonyl)imide, 4-\textit{tert}-butylpyridine, tert-Butanol, distilled water, isopropanol, \textit{N,N}-dimethylformamide ,1-thioglycerol, EDT, TBAI, methanol, acetonitrile, toluene, chlorobenzene, ethanol, Au, FTO glass and kapton tape were purchased from Sigma-Aldrich. All solvents are anhydrous.

4.3.2 Preparation of Titanium Isopropoxide and TiO$_2$ Paste Solution
Preparation of titanium isopropoxide solution for the TiO$_2$ compact layer\textsuperscript{27, 28}: 35 µL of a 2 M HCl solution is mixed with 5 ml of anhydrous ethanol, and the mix solution is placed in an ice bath for a while. Then, 370 µL of a titanium isopropoxide solution is added dropwise into the HCl, which contains ethanol. The final solution should be transparent. The TiO$_2$ paste solution \textsuperscript{28} is prepared by dissolving 1 g TiO$_2$ in 3.5 g isopropanol and stirred vigorously until fully dissolved.

![Figure 4.1. Optical images of the as-prepared Sb$_2$S$_3$ NCs paste.](image)

**4.3.3 Preparation of the Hole Transporting Materials Solution**

First, a Li-TFSI stock solution is prepared by dissolving 170 mg of LiTFSI in 1 M acetonitrile. Then, a spiro solution\textsuperscript{27, 29} is prepared by dissolving 80 mg of spiro-OMeTAD in 28.5 µL of 4-tert-butanol and 30 µL of the Li-TFSI stock solution in 1
ml of DMF. Similarly, the P3HT-based hole transporting solution is prepared by dissolving 15 mg of P3HT in 15 µL of the Li-TFSI stock solution and 7.5 µL of 4-tert-butanol.

4.3.4 Preparation of Sb$_2$S$_3$ NCs Based Paste

First, 0.5 g of dried amorphous Sb$_2$S$_3$ NCs are dissolved in 15 ml of toluene, and the solution is ligand exchanged with 2 ml of 1-thioglycerol under vigorous stirring in a glove box overnight. Then, the solution is washed with the toluene and acetone mixture 3 times and centrifuged. The ligand exchange process is repeated a second time, and the NCs are cleaned again. Finally, the pasted is prepared by dispersing the ligand exchanged Sb$_2$S$_3$ NCs in 3 ml of tert-butanol and 1.5 ml of isopropanol.$^{30}$ The paste is sonicated and stirred overnight before use.

4.4 Fabrication of the Sb$_2$S$_3$ NC-Based Solid-State Semiconductor Sensitized Solar Cells

4.4.1 Substrate Patterning and Cleaning

FTO glass is patterned by etching with Zn powder and a 2 M HCl solution. Then, the etched FTO is cleaned with DI H$_2$O by sonication for 20 minutes and rinsed with DI H$_2$O. This process is repeated with acetone and isopropanol, and the substrate is dried with nitrogen. The substrate undergoes an oxygen plasma treatment for 15 minutes to remove the last traces of organic residues prior to the deposition of the compact TiO$_2$ layer.

4.4.2 Device Fabrication Process
The prepared titanium isopropoxide solution is deposited on the clean and patterned FTO using a spin coater at 2000 RPM for 30 s, and the substrate is then annealed at 500°C for 30 min to form a compact TiO₂ film. The as-prepared TiO₂ paste is spin coated onto the compact TiO₂-coated FTO at 2500 RPM for 30 s. After this step, the substrate is annealed at 550°C for 1 h to form a mesoporous TiO₂ layer. After the formation of the mesoporous TiO₂ layer, the sintered TiO₂ film is treated with a 0.02 M TiCl₄ solution in water at 70°C for 10 min. The film is rinsed with DI H₂O, dried with nitrogen after the treatment and sintered at 500°C for 30 min. Finally, the film undergoes an oxygen plasma treatment for 5 min to remove traces of organic residues.

Figure 4.2. Illustration of the device fabrication process of the Sb₂S₃-NC-based SSSCs.

The surface of the TiO₂ film is functionalized with 3-MPTMS to improve the contact between the TiO₂ film and the Sb₂S₃ film. The TiO₂ film is immersed in a 5%
(volume ratio) MPTMS toluene solution and refluxed at 90°C for 3 h in a glove box. The functionalized TiO$_2$ film is rinsed with toluene. The diluted Sb$_2$S$_3$ NCs paste in isopropanol (1:1 by volume ratio) is spin coated on the TiO$_2$ film at 3500 RPM for 30 s. Then, the film is dip coated in a TBAI solution (10 mg/ml in methanol) for 30 s, followed by three spin steps with methanol. After an iodide treatment, the film is then treated with drops of 2% (v/v in acetonitrile) EDT at 2000 RPM and rinsed with acetonitrile at the same rotating speed. The spin coating sequence from the Sb$_2$S$_3$ paste to the EDT treatment is repeated one more time. The ligand-exchanged Sb$_2$S$_3$ film is annealed at 300°C for 30 min under vacuum.

A sulfurization using a TA solution (0.01 g/ml, DMF) is applied to the annealed Sb$_2$S$_3$ film for further surface passivation. To facilitate the efficient penetration of the TA solutions into the pores of the mp-TiO$_2$, DMF is dropped onto the Sb$_2$S$_3$ film and spin coated at 2000 RPM for 60 s. Then, the TA solutions are spin coated on the DMF-treated Sb$_2$S$_3$ film at the same rotating speed as the DMF spin coating. Finally, the samples are annealed at 290 °C in a glove box for 1 min.

The as-prepared hole transporting solution is spin coated on the Sb$_2$S$_3$ film at 2000 RPM for 45 s in air. Then, the film is kept in air overnight. Finally, a 100-nm-thick Au contact is thermally evaporated.

**4.5 Measurements of the Ionization Potentials of the As-Synthesized and Annealed Sb$_2$S$_3$ Nanocrystals**

To determine the edges of the VB and CB of the as-synthesized and annealed Sb$_2$S$_3$ NCs, Photoemission Yield Spectrometry in air is used to measure the...
ionization potentials of the Sb$_2$S$_3$ NCs. PYSA$^{33-36}$ is a technique that can measure the work functions of metals and the ionization potentials of semiconductors on conductive substrates in air at very high resolution.

Its operating principles are illustrated in figure 4.3. Deep UV light is used as a light source. The UV light hits the sample, and electrons are emitted from the sample. Then, those emitted electrons pass through two grids (quenching and suppressor grids) whose voltages are kept at 80 and 100 V, respectively, and they enter the counter.$^{33}$ A counter discharge is then initiated by an incident electron, which induces a pulse.

**Figure 4.3.** Illustration of PYSA operating principles.

across the series resistance.$^{33}$ The counter pulse is amplified and drives a quenching circuit and a suppressor, both of which contain one-shot multivibrators.
to produce positive and negative square pulses, respectively. The counter pulse is also fed into a scaling circuit equipped with a rate meter.\textsuperscript{33, 36}

The as-synthesized Sb\textsubscript{2}S\textsubscript{3} and annealed Sb\textsubscript{2}S\textsubscript{3} NCs are deposited on the cleaned FTO via dip coating. Then, the films are ligand exchanged with EDT to improve the conductivity of the film. Subsequently, the ionization potentials of the samples are measured. The UV intensity is 10.1 nW during the measurements, and the results are shown in figures 4.4-4.6. The values of the edges of the CB and VB of the Sb\textsubscript{2}S\textsubscript{3} NCs are described in table 4.2. The band gap of the bulk crystal is reported to be approximately 3.7 eV, and the edge of the VB maximum is 5.4 eV. The edge of the CB minimum is 3.7 eV. Uda and Eastman\textsuperscript{37, 38} compared the values of the work functions of several metals measured in air and ultra-high vacuum. The values of the work functions of the metals measured in air are lower than the values measured in ultra-high vacuum, and the difference ranges from 0.15 eV to 0.9 eV. In most cases, the difference is approximately 0.3 eV. If we account for this difference, the absolute values of the positions of the VB and CB shift to larger values. Then, their values are comparable with those obtained in other reports. The Bawendi group found that the absolute value of the band edge of the VB and CB of EDT-treated PbS QDs is lower than that of PbS QDs treated with other ligand due to the Pb-thiol-carbon interaction, which produced different surface dipole moments.\textsuperscript{32} Thus, the EDD treatment of the Sb\textsubscript{2}S\textsubscript{3} NCs may be one of the factors that affects the positions of the VB and CB. However, the values must be verified using other techniques, such as UPS.
Figure 4.4. PYSA of weakly crystalline orange Sb$_2$S$_3$ NCs on FTO.

Figure 4.5. PYSA of annealed Sb$_2$S$_3$ on FTO at 300°C for 30 min.
Figure 4.6. PYSA of the as-synthesized, crystalline Sb$_2$S$_3$ NCs on FTO.

Table 4.2. The values of the band gaps, ionization potentials, and positions of the VBs and CBs of Sb$_2$S$_3$ NCs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Band gap (eV)</th>
<th>Ionization potential (eV)</th>
<th>The edge of Max. VB (eV)</th>
<th>The edge of Min. CB (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange Sb$_2$S$_3$ NCs</td>
<td>2.15</td>
<td>5.42</td>
<td>-5.42</td>
<td>-3.27</td>
</tr>
<tr>
<td>Annealed Sb$_2$S$_3$</td>
<td>1.59</td>
<td>5.0</td>
<td>-5.0</td>
<td>-3.41</td>
</tr>
<tr>
<td>Black Sb$_2$S$_3$ NRs</td>
<td>1.64</td>
<td>5.15</td>
<td>-5.15</td>
<td>-3.51</td>
</tr>
</tbody>
</table>

4.6 Characterization of the Photovoltaic Parameters of Sb$_2$S$_3$-Based Solar Cells

In this section, the characterization of Sb$_2$S$_3$-NC-based SSSCs fabricated using spin coating and dip coating methods are described.

4.6.1 Optical Images of Sb$_2$S$_3$ Film Fabricated via Spin Coating
In earlier sections, we discussed how to prepare Sb$_2$S$_3$-NC-based pastes. Sb$_2$S$_3$ films are fabricated using these pastes with spin coating and a doctor blade. The as-prepared Sb$_2$S$_3$ paste is diluted in isopropanol (1:1 in V/V) and sonicated for half an hour before spin coating.

*Figure 4.7.* A Sb$_2$S$_3$ film deposited on TiO$_2$-coated FTO using spin coating.
**Figure 4.8.** A $\text{Sb}_2\text{S}_3$ film deposited on TiO$_2$-coated FTO using spin coating after 30 min of annealing at 300°C.

**Figure 4.9.** A $\text{Sb}_2\text{S}_3$ film deposited on TiO$_2$-coated FTO using a doctor blade.
Figure 4.10. A Sb$_2$S$_3$ film deposited on TiO$_2$-coated FTO using a doctor blade after 30 min of annealing at 300°C.

A uniform Sb$_2$S$_3$ film is obtained from both the spin coating and scalpel techniques (Figures 4.7 and 4.9). After annealing at 300°C for 30 min, the film obtained from the scalpel method peeled off, perhaps due to its thickness (Figure 4.10). The film fabricated using spin coating is uniform after annealing (Figure 4.9). Thus, the spin speed used in the spin coating Sb$_2$S$_3$-based SSSCs devices affects the thickness and roughness of the film.
Figure 4.11. The device architecture of the FTO/d-TiO₂/meso-TiO₂/Sb₂S₃/Spiro-OMeTAD/Au.

4.6.2 Device Architecture and J-V Characteristics of Sb₂S₃-Based SSSCs Fabricated using the Spin Coating Method

The device fabrication process is described in section 4.4.2, and the device architecture is shown in figure 4.11. The cross section-SEM image (Figure 4.12) indicated that the Sb₂S₃ layer is quiet uniform and its thickness is about 500nm. A Spiro-OMeTAD solution is used as the HTM in this device, and the J-V (Oriel PV
system) characteristics of the as-fabricated device are measured using a solar simulator under 1 sun.

Figure 4.12. Cross section-SEM image of as-fabricated device.
The J-V curve of the as-fabricated device (Figure 4.13) indicated that a 1.13% power conversion efficiency is obtained, and the short circuit current is 7.84 mA/cm², the opencircuit voltage is 349 mV and the fill factor is 41.45%, which the best device performance is obtained using the spin coating technique. Without TA treatment, the PCE of the device is below 1%, and the film quality of HTM is crucial for the device performance. In addition, the device must be exposed to sufficient O₂ to increase the conductivity of the Spiro-OMeTAD after HTM deposition.

The band alignment and operating principles of the as-fabricated device are illustrated in figure 4.14 (the materials CB maximum edge positions of TiO₂, Sb₂S₃,
and Spiro and work function of Au is measured by PYSA). In short, the photon is absorbed by the Sb$_2$S$_3$

![Diagram](image)

**Figure 4.14.** Band alignment and operating principles of Sb$_2$S$_3$-based SSSCs.

absorber layer, and electron-hole pairs are generated and quickly separated into free electrons and holes. Then, the electrons are injected into the CB of the electron transport TiO$_2$, and the holes are injected into the VB of the hole
transporter. Next, the electrons and holes are collected at the front and back contacts, respectively. There are quasi-Fermi levels between the absorber layer and the ETM and the absorber and the HTM. The potential difference between the quasi-Fermi levels defines the maximum open circuit voltage that this device can generate.

4.6.3 Fabrication of Sb$_2$S$_3$ Films by Dip Coating

Dip coating is another low-cost method to deposit absorbing layers in PV cells. More uniform films can be obtained by dip coating. The TiO$_2$ coated film is functionalized by 3-MPTMS to uniformly deposit Sb$_2$S$_3$ on the top of the TiO$_2$ film. The dip coating process is shown in figure 4.15, and this process is performed under mild stirring in the glove box. The Sb$_2$S$_3$ NCs are dispersed in anhydrous toluene, and the concentration of the solution is 15 mg/ml. The thickness of the film can be controlled by the dip coating time at a particular concentration.

Optical images of Sb$_2$S$_3$ NCs film deposited on TiO$_2$-coated FTO are shown in figures 4.16 and 4.17, and they are uniform both before and after annealing. The deposition of Sb$_2$S$_3$ is not uniform after 3-MPOTMS functionalization of the surface of the TiO$_2$ film.
Figure 4.15. Dip coating process of orange color Sb$_2$S$_3$ NCs on TiO$_2$ coated FTO.

Figure 4.16. Dip coated Sb$_2$S$_3$ NCs on TiO$_2$ coated FTO for 2 h.
Figure 4.17. The Sb$_2$S$_3$ film deposited on the TiO$_2$-coated FTO by dip coating after 30 min of annealing at 300°C.

4.6.4 The J-V Curve of the Sb$_2$S$_3$ NC-Based SSSCs Solar Cells

Sb$_2$S$_3$ NCs are deposited on TiO$_2$-coated FTO using the dip coating technique, and Sb$_2$S$_3$-based SSSCs are fabricated. The device fabrication process is the same as the device fabricated using spin coating, except for the deposition of the Sb$_2$S$_3$ NCs: The Sb$_2$S$_3$ film is dipped into a 5% EDT solution in acetonitrile (V/V) for 60 s. Then, it is dipped into acetonitrile for 90 s, and this process is called one cycle. The cycle is repeated 3 times.

The J-V curve of the as-fabricated device is shown in figure 4.18. Compared with the device fabricated using spin coating, the fill factor (48.27%), open circuit voltage (425 mV) and PCE (1.38%) are enhanced, and the short circuit current (6.74 mA/cm$^2$) is decreased. A higher shunt resistance is obtained in this device,
which means that the current leakage is decreased. The dip coating produces a more uniform film, and the film conductivity increases accordingly. These factors lead to an increase the FF and \( V_{oc} \), and, ultimately, enhance the PCE of the device.

![Figure 4.18](image)

**Figure 4.18.** The J-V curve of FTO/d-TiO₂/meso-TiO₂/Sb₂S₃/Spiro-OMeTAD/Au (dip coating).

4.6.5. Characterization of ZnS-Passivated Sb₂S₃-NC-based Solid-State Sensitized Solar Cells

The device efficiency can be increased by decreasing the surface defects through coating thin layer inorganic semiconductor on the surface of absorber layer.³⁹ To improve the surface passivation of the absorber layer in PV cells, a thin layer of ZnS is coated. Thus, we introduce this ZnS coating on the surface of Sb₂S₃ after annealing.
Figure 4.19. PL of Sb$_2$S$_3$ NCs and ZnS-coated Sb$_2$S$_3$ NCs film on a glass substrate.

First, a 0.1 M zinc acetate dehydrate and 0.1 M sodium sulfide hydrate solution is prepared in water.$^{39}$ The annealed Sb$_2$S$_3$ film is dipped into the zinc acetate dehydrate and sodium sulfide hydrate solution for 60 s. After each dipping, the film is dipped into water and dried under a clean nitrogen flow. The PL (NT-TMD Entegra Spectra) measurement is performed for Sb$_2$S$_3$- and ZnS-coated Sb$_2$S$_3$ NC films on a glass substrate. The PL results (Figure 4.19) showed that the PL intensity is significantly enhanced after the ZnS surface treatment, which indicates that the surface defects are decreased due to better surface treatment. This result may leads to increased device efficiency.
A PV device is fabricated with a ZnS coating. In the device process, Sb$_2$S$_3$ NCs are deposited on meso-TiO$_2$ using dip coating, and the film is annealed and treated with ligands as described above. Then, ZnS is coated, and the other procedures are the same as before. The J-V curve (Figure 4.20) of the as-fabricated device indicates that the PCE, J$_{sc}$ and FF are increased. Thus, a 1.48% PCE is obtained with a ZnS coating.
REFERENCES


Chapter 5

**In-Situ Synthesis of Gold Nanoparticles on Solid Substrates via Reactive Inkjet Printing**

5.1 Introduction

Interest in colloidal NPs is increasing due to their size- and shape-dependent optical and electronic properties as well as potential applications in electronic and energy-harvesting devices \(^1\) to \(^5\) and flexible electronics.\(^6\)

Due to their resistance to oxidation, Au NPs been applied in various applications, such as plasmonic solar cells,\(^7\), \(^8\) electrochemical detection,\(^9\) electrodes,\(^10\) and fingerprint detection.\(^11\) Solution-processed, organic halide perovskite or inorganic-semiconductor-based solar cells can be fabricated into flexible photovoltaic devices with large areas to decrease the cost and increase the utilization of photovoltaic devices in everyday life. To realize low-cost, flexible solar cell with large areas, solution-processing production techniques, such as roll-to roll, spray and inkjet printing, should replace vacuum or sputtering for electrode deposition.\(^12\)

Various methods have been used to deposit Au NPs on a substrate. Inkjet printing
is particularly attractive because it offers significantly reduced, more efficient materials usage and real-time patterning of printed NPs.\textsuperscript{13, 14}

Au NP colloidal solutions (ink) are prepared prior to use in inkjet deposition.\textsuperscript{10} The preparation of Au NPs involves synthesis using various wet chemical methods, purification, and final preparation as a stable Au NP ink by dispersion in an appropriate organic solvent for use in printing. This process thus involves two steps: a complicated, lengthy synthetic process and the printing process. We would like to demonstrate to synthesis Au NPs using reactive inkjet printing and a unique solvent-precursor system directly on the substrate. This approach is advantageous because it is rapid and cost-effective for large-scale fabrication and provides on-demand, facile integration of Au NPs into solid-state devices. This method may enable \textit{in situ} assembly of Au NPs linked to organic and inorganic materials to fabricate hetero-structured nanomaterials with tailored functionality. Moreover, \textit{in situ} synthesis of these particles will facilitate their growth inside porous host materials without a pore size limitation. The \textit{in situ} preparation of relatively uniform Au NPs directly on a substrate using RIP has not been reported. We would like to demonstrate the effect of precursors, printing sequence and solvents on the formation of these particles. We believe that this approach can also be applied for the preparation of other metal or semiconductor NPs (including QDs).

\section*{5.2 Properties of Gold Metal}
Gold nanoparticles has many applications, such as plasmonic solar cells, corrosion, chemical and biological sensing. Its crystal structure is a face center cubic (Figure 5.1) and it is very good conductor. Its physical properties is described in Table 5.1.

**Table 5.1.** The values of some physical properties of gold.\(^{15}\)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>FCC</td>
</tr>
<tr>
<td>Density</td>
<td>19.3 g/cm(^3)</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>196.97</td>
</tr>
<tr>
<td>Atomic number</td>
<td>79</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>0.407nm</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>2.44</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>79GPa</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>314.1W/(m.K) at 273K</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>(2.05 \times 10^{-5}) Ω.cm at 273K</td>
</tr>
</tbody>
</table>
5.3 Experimental and Measurement

5.3.1 Chemicals and Materials
HAuCl₄·3H₂O (≥99.9%), HAuCl₄·xH₂O (99.999%), AuCl₃ (99%), Oleylamine (≥70%, technical grade), DMSO, DMF, 1, 2-Dichlorobenzene, Toluene, Absolute ethanol (96%), Acetone, Isopropanol, DI water, Silicon wafer and microscopic glass. All chemical are purchased from Sigma-Aldrich.

5.3.2 Inkjet Printing Process

Substrate cleaning: All substrates were cleaned thoroughly by first rinsing them with deionized water then sonicating for 10 min in acetone, ethanol, and isopropanol, respectively, followed by drying with nitrogen at each step.

Inkjet printing parameters: The printer used in this experiment is piezoelectric drop-on-demand inkjet printer purchased from Fujifilm Dimatix with the model number Dimatix Materials Printer DMP-2800. The Dimatix Materials Printer cartridge used gives 10-pL droplet volume droplets, with diameter of less than 22-um. The cartridge is placed at 0.25-mm height above the substrate, at room temperature. The print head consist of 16 nozzles, with 254-um spacing on single line. The nozzles voltage was calibrated between 6-9 volts, since the inks viscosity was relatively low. The inks were printed using a square matrix shape with 30-um spacing between drops.

Printing process: The sequential printing process involves printing from cartridge A, on silicon (100) surface, containing the dispersion solvent and capping agent (1,2-dichlorobenzene and oleylamine in 10:1 ratio), followed by printing of the gold
precursor (0.12 mmol HAuCl₄·3H₂O in DMSO (10 ml)) from cartridge B, at the same location of drops deposited by cartridge A. The substrate was then placed in an oven at 120 °C for 3 hours. The printing was also carried out in reverse order.

5.3.3 Description of Characterization Tools

**Surface tension:** This was measured at 22.6°C using Kruss Tensiometer, k100MK2/SF/C, and contact angle was measured at room temperature using Kruss EasyDrop Contact Angle System.

**SEM characterization:** SEM Nova NANO 600 was used to characterize the as-synthesized Au NPs on silicon substrate without any conductive film coating.

**TEM characterization:** The sample for cross section TEM analysis was prepared by focused ion beam (FIB, Helios 400s, FEI) with lift-out method. The lamellar was thinned with Ga ion beam (30 kV, 0.28 nA) and cleaned at 2 kV and 47pA. We used Titan ST 300kV (FEI) for HRTEM imaging.

![A schematic description of in situ synthesis of Au NPs via reactive inkjet printing.](image)

**Figure 5.2. A schematic description of in situ synthesis of Au NPs via reactive inkjet printing.**

This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, Angewandte Chemie 2014, 126 (2), 430-433.
5.4 Synthesis and Characterization

5.4.1 Results and Discussion of As-Synthesized Average Particles 8 nm Au Nanoparticles via Reactive Inkjet Printing

The detailed printing process is described in the experimental section. The surface tension and contact angle of solution prepared for printing is measured to know the wettability and printability of solutions. The surface tension of the solvent system in this cartridge A was measured as 29.68 mN/m, and the contact angle with Si- wafer surface as 28.60°. The surface tension of the cartridge B was measured as 43.88 mN/m and a contact angle with Si-wafer as 35.75°. A schematic representation of the in-situ formation of Au NPs process via RIP is shown in Figure 5.2. To start the synthesis, cartridge A prints the solvent pL droplets on a pre-cleaned silicon substrate followed by cartridge B, printing on top of the previous droplets under same printing parameters and room temperature condition. The printing pattern before heat treatment is shown in Figure 5.3, and the printed droplets are quiet well-aligned. The printed substrate was then placed for 3h in an oven at 120 °C resulting in the formation of Au NPs on the substrate surface. SEM image (inset of Figure 5.3) revealed the formation of densely packed NPs inside the printed droplets upon completion of the reaction and drying. The diameter of the Au NPs was ca. 8 ± 2 nm, as indicated by HRSEM (Figure 5.4) and TEM (Figure 5.5). HRTEM revealed that the Au NPs had a spherical geometry with clear lattice fringes, indicating the highly crystalline nature of these particles (Figure 5.5). The lattice spacing was
This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, Angewandte Chemie 2014, 126 (2), 430-433.

**Figure 5.3.** Optical image of printed pattern of drops on silicon substrate. Bottom right-hand inset is an SEM image of one of the heat-treated droplets in the printed array. Heat treatment was carried at 120 °C for 3 hours.\(^\text{16}\)

**Figure 5.4.** HRSEM image of the Au NPs synthesized on a silicon substrate after completion of the post-printing heat treatment.\(^\text{16}\)
This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, Angewandte Chemie 2014, 126 (2), 430-433.

**Figure 5.5.** HRTEM image of Au NPs after heat treatment of droplets printed on a silicon substrate.\(^\text{16}\)

![HRTEM image of Au NPs](image)

**Figure 5.6.** a) Thin film XRD, and b) EDS of Au NPs formed on silicon substrate upon heat treatment of printed droplets.\(^\text{16}\)

![XRD and EDS plots](image)

2.35 Å and 2.03 Å, as determined by HRTEM. These spacings correspond to the (111) and (002) planes of the face-centered cubic phase of Au.\(^\text{17}\) Additional evidence of the crystallinity of the RIP Au NPs is given by XRD data presented in figure 5.6a. To determine the chemical composition of the as-prepared NPs, EDS analysis was performed. The results (Figure 5.6b) confirmed the presence of Au without any impurities on the substrate surface.
The UV-Vis absorption spectrum showed a peak at 602 nm, corresponding to Au NPs (Figure 5.7). The shoulder observed at approximately 536 nm corresponds to the intrinsic plasmon resonance of isolated Au NPs.\textsuperscript{18}

Oleylamine acts as a capping agent and a reducing agent.\textsuperscript{19,22} The reduction process involves two steps: a partial reduction of Au\textsuperscript{3+} to Au\textsuperscript{+} through the formation of oleylamine-AuCl, followed by a slow reduction of Au\textsuperscript{+} to Au. The continuous supply of Au from the oleylamine-AuCl complex has been reported to cause the nucleation and growth of Au

\begin{center}
\includegraphics[width=0.7\textwidth]{figure5.7.png}
\end{center}

\textbf{Figure 5.7.} UV-Vis spectrum of Au NPs synthesized via RIP on a glass substrate.\textsuperscript{16}
This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, Angewandte Chemie 2014, 126 (2), 430-433.

Figure 5.8. SEM images of Au NPs formed on silicon substrate upon heating. In this case, reverse printing sequence was used (i.e., precursor was printed first). Bottom right-hand inset is an SEM image of one of the heat-treated droplets in the printed array.

However, in the present case, Au NPs were formed. Although the details of nanoparticle growth and assembly are still fully understood at this moment, we suspect that the effects of solvent polarity and temperature, the relatively fast reduction at higher temperature, and the limited pL volume available play a major role in the process under these experimental conditions. DMSO and 1,2-dichlorobenzene were selected as solvents due to their comparatively higher viscosities and higher boiling points with acceptable surface tension. Due to its higher solubility, the Au precursor forms a stable solution in DMSO, and thus high-concentration solutions can be formed. Another advantage of this solvent system...
Figure 5.9. SEM image of Au NPs printed on silicon substrate (after printing, the substrate was placed in oven for 3h at 100 °C).

is that DMSO and 1,2-dichlorobenzene are miscible, which is very important because oleylamine is not miscible with DMSO. DMSO also acts as an anti-solvent soon after the formation of nanoparticles capped by oleylamine, which may also be a factor in the formation of relatively ordered Au NPs over the substrate surface, as shown in Figure 5.4. The printing process was also carried out in a reverse sequence (first by printing precursor ink followed by solvent ink, Figure 5.8). In this case, the resultant nanoparticles were not relatively uniform in size or as highly crystalline as those obtained from the straight printing sequence describe above. This may be due to the lower contact angle of the precursor on
silicon and glass substrates. In addition, experiments performed with different growth times and temperatures (Figure 5.9) revealed no significant change in the formation or the size of the Au NPs.

Figure 5.10. SEM images of Au NPS synthesized in different solvent systems.

5.4.2 Solvent and Concentration Effect on the Size and Morphology of Gold NPs

Solvent is one of key factors to have an effect on size, shape and mono-dispersivity of metal NPs. Thus, solvent effect is also taken into consideration during our work.
To demonstrate the impact of a judicial choice of solvent system, three other solvent systems were used: 1) gold precursor in water and oleylamine in ethanol (Figure5.10a), 2) gold in DMF and oleylamine in toluene (Figure5.10b), and 3) gold in a mixture of ethanol/toluene (1/10) and oleylamine in toluene (Figure5.10c). The results indicate that gold precursor in DMSO and oleylamine in dichlorobenzene is by far the most suited solvent system for RIP synthesis of Au NPs with acceptable size uniformity on a given substrate surface. We suspect the main reasons behind this are the higher surface tension (water) and lower boiling point of ethanol and toluene. The Au NPs obtained by ethanol/1,2-dichlorobenzene solvent system
This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, *Angewandte Chemie* 2014, 126 (2), 430-433.

(Figure 5.11) showed noticeable broad size distribution as compared to that obtained from DMSO/1,2-dichlorobenzene system.

![SEM image of Au NPs formed upon post printing heat treatment of silicon substrate.](image)

**Figure 5.12.** SEM image of Au NPs formed upon post printing heat treatment of silicon substrate. The gold precursor concentration in this case was increased to 0.4 mmol in DMSO.\(^{16}\)

The shape and size of Au NPs can be controlled by concentration of Au precursor and reducing agent. A considerable change in the shape of the NPs was noticed (Figure 5.12) when the concentration of gold precursor was increased from 0.12 mmol to 0.4 mmol in DMSO, consistent with previous reports.\(^{24, 25}\)

By increasing the concentration of the Au precursor and oleylamine, Au NPs with an average diameter of ca. 25 nm can be obtained on a silicon substrate following
a heat treatment step similar to that described previously (Figure 5.13). More importantly, the pattern of printed drops after heat treatment is quiet-well aligned without printing inside confined space. This patterned Au NPs may found applications in palsmonic solar cells.

![SEM image of printed drops after heat treatment at 120 °C for 3 h. The inset is a magnified image of a typical dried droplet on the substrate showing the formation of Au NPs. For this image, the concentration was 2 mmol AuCl4.3H2O in 10 ml of DMSO and 3 ml of oleylamine in 10 ml of 1,2-dichlorobenzene, resulting in NPs of greater diameter compared to those in Figure 5.3.]

**Figure 5.13.** SEM image of printed drops after heat treatment at 120 °C for 3 h. The inset is a magnified image of a typical dried droplet on the substrate showing the formation of Au NPs. For this image, the concentration was 2 mmol AuCl4.3H2O in 10 ml of DMSO and 3 ml of oleylamine in 10 ml of 1,2-dichlorobenzene, resulting in NPs of greater diameter compared to those in Figure 5.3.\(^\text{16}\)

**5.4.3 Gold precursor’s Effect on the Monodispersivity of Gold NPs**

To examine the Au precursor’s effect on size or size distribution of as-synthesized Au NPs, AuCl\(_3\) is employed as an Au precursor. Other solvents, reducing agent
This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, *Angewandte Chemie* 2014, 126 (2), 430-433.

**Figure 5.14.** SEM images of Au NPs formed on silicon substrate upon heat treatment after printing. a) solvent ink is printed first, then precursor ink is printed at the same position and b) precursor ink was printed first, followed by printing of solvent ink over the same location as printed precursor droplets. Here AuCl$_3$ was used as gold precursor.

and concentration is same as of HAuCl$_4$.3H$_2$O, and it is printed in straight and reverse way. The use of AuCl$_3$ resulted in a broad size distribution (Figure 5.14).

At this time, we are unable to ascertain the reasons for such behaviour in size distribution.

**5.4.4 Comparison of Average Size of Au NPs Prepared Reactive Inkjet Printing and Conventional Bath Method**

To clarify the advantages of RIP method over conventional bath method, Au NPs is synthesized in the flask with same concentration used for RIP. The nanoparticles synthesized via RIP is compared with the nanoparticles synthesized by the traditional colloidal method in a flask. The flask method resulted in the formation of Au NPs with diameters of ca. 15 ± 2 nm (Figure 5.15), whereas the RIP approach
resulted in nanoparticles with diameters of ca. 8 ± 2 nm (Figure 5.4). This size difference could be due to the highly controlled pL volume of the inkjet-printed droplets, as opposed to the relatively larger volume in the flask.

![TEM image of Au NPs synthesized using the colloidal method in a flask. The size distribution is shown in the inset.](image)

**Figure 5.15.** TEM image of Au NPs synthesized using the colloidal method in a flask. The size distribution is shown in the inset.\(^\text{16}\)

### 5.5 Printable Non-Particle Ink for the Synthesis of Gold Nanoparticles via One-Step Reactive Inkjet Printing

Au NPs have received a great deal of interest due to their unique optical and physical properties at nano level. Nowadays, Au NPs are being used for a wide number of applications in different fields of science and technology, such as solar cells\(^1,\)\(^4\) and biology.\(^{26}\) The interesting properties of Au NPs have incited a
considerable amount of research to improve nanoparticle synthesis and to develop scalable processes. In our previous methods, we developed an in situ method synthesis relatively monodispersed Au NPs on solid substrate via RIP, and it is two–step printing process.

To make the process simpler, a simple and easy one step method for the deposition of Au nanoparticles by inkjet printing is developed. Au NPs were synthesized and deposited in situ directly from an ink containing gold precursor in oleylamine. Au NPs were printed.

Figure 5.16. Microscopic image of inkjet printed drops of ink containing 0.18 mmol solution of HAuCl₄.xH₂O on silicon, with 75mm drop spacing, inset showing ink waveform.
This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, Angewandte Chemie 2014, 126 (2), 430-433.

Figure 5.17. (a) SEM image of printed pattern of drops after heat treatment at 120 °C for 2 hours (b) SEM image of a single drop (c) SEM of Au nanoparticles within a drop (d) UV-Vis spectrum of printed Au NPs on a glass substrate.

separately from two inks containing different HAuCl₄·xH₂O concentrations. The reason of choosing HAuCl₄·xH₂O as a gold precursor, instead of other gold precursors, it has better solubility in oleylamine over others. Au NPs were printed separately from two inks containing different HAuCl₄·xH₂O concentrations. The first ink (A) contained 0.18 mmol of HAuCl₄·xH₂O whereas the second ink (B) contained 0.09 mmol of HAuCl₄·xH₂O. Each ink was prepared by dissolving the respective amount of the gold precursor in 10 ml of oleylamine by vigorously
stirring at room temperature until a clear solution was obtained. Oleylamine acts as dispersion solvent, capping agent and also as a reducing agent. The solutions were then filtered (pore size 0.45 µm) to remove any possible agglomeration that might clog the nozzle, and then directly loaded in the cartridge for printing. The cartridges were then used immediately for printing. The substrate cleaning and inkjet printing process parameters is described in experimental section.

Figure 5.18. SEM of Au nanoparticles within a drop printed on silicon glass after heat treatment (method 2).

The micro-patterns printed on the substrate were controlled by optimizing the shape of the droplet ejected from the cartridge using a proper waveform applied to the piezoelectric actuator. The patterns from ink (A) were printed on the silicon

This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, Angewandte Chemie 2014, 126 (2), 430-433.
substrates with 75 µm drop spacing, as shown in Figure 5.16, using a single jet. The drops were printed with high uniformity on large scale with an average drop diameter of 56 µm on the substrate. The printed silicon substrates were then heated in an oven at 120˚C for 2 h (method 1). Also ink (A) was printed on silicon substrate at room temperature and the printed substrate by this method was heated initially at 50 ºC for 30 hrs and then at 100 ºC for another 30 hrs to study the effect of heat treatment temperature and time on the size and shape of nanostructures (method 2).

Figure 5.19. SEM of Au nanoparticles within a drop printed on silicon substrates prepared by using 0.09 mmol solution of HAuCl₄·xH₂O as an ink after heat treatment at 120 ºC for 2 hours.
The SEM image of printed pattern of drops on silicon substrate prepared by method 1 is shown in Figure 5.17a. The drops which were uniform in size before the heat treatment (Figure 5.16) are no more uniform after the heat treatment. Also the pattern of drops has changed from straight rows to distorted rows which may have happened due to the change in surface tension by heating. The shape of drops remains spherical and free from any coffee ring effect. Figure 5.17b shows an image of a single drop containing clusters of Au NPs while Figure 5.17c is a high resolution SEM image showing the assembly of monodispered Au NPs inside the drop. The average diameter of these NPs is 22 nm. The absorption spectrum in Figure 5.17d of as-synthesized Au NPs on glass substrates shows an absorption peak around 620 nm, and the peak broadening may be due to the coupling of electromagnetic waves of nanoparticles.²⁷

The Au NPs (Figure 5.18) prepared by method 2 showed no significant difference in the size but the shape of nanoparticle is a little bit distorted. Therefore it is easy to conclude that the heating temperature or the heating time showed no noticeable effect on the growth of nanoparticles in this case.

The printed silicon substrates from ink (B) by method 1 produced NPs (Figure 5.19) which showed noticeable shape distortion of the particles as compared to those prepared from ink (A) (Figure 5.17c). The printed substrate from ink (B) by method 2 showed considerable change in the size and shape of nanoparticles. The SEM image (Figure 5.20) showed the shaped nanostructures instead of spherical nanoparticles. The mixed shape nanostructures comprise of cubes, rectangles and some rods. It is worth noting that no shaped structures were obtained at higher
concentration of gold precursor (ink A). Thus, the shape of Au nanostructures depends on the precursor concentration, heat treatment temperature and time in this case. We have issue to reproduce these structure. However, it is demonstrated that the capability of inkjet printing method over conventional method to produce different shape of NPs. Further studies are needed to understand the effect of various parameters on the growth, shape and size of these nanostructures.

Figure 5.20. SEM image of Au nanosheets printed on silicon substrates prepared by using 0.09 mmol solution of HAuCl₄.xH₂O as an ink after heat treatment using method 2.
REFERENCES


This chapter is based on “In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing”, *Angewandte Chemie* **2014**, *126*(2), 430-433.


Chapter 6

Conclusion and Outlook

The most important aims of this thesis project were to develop the colloidal hot injection synthesis protocol to synthesize shape- and phase-controlled Sb$_2$S$_3$ NCs and to demonstrate their application for solar cells as a light harvester as well as to demonstrate the applicability of reactive inkjet printing technology in the synthesis of nanoparticles directly on a solid substrate using commercially available precursors. This perspective dominates the following discussion of the results, including providing plausible explanations for the obtained results and discussing the limitations of the applied methods.

6.1 Synthesis and Characterization of Sb$_2$S$_3$ Nanocrystals for Solid-State Semiconductor Solar Cells

6.1.1 Conclusion

A synthesis protocol was established for novel, nanostructured, Sb$_2$S$_3$ NC photovoltaic materials, and their structural, morphological and optical properties were characterized. The main achievement was the development of a colloidal, hot-injection synthetic protocol that enables the production of various shapes of Sb$_2$S$_3$ NCs for inks for use in the fabrication of low-cost, environmentally friendly
PV cells. Moreover, different antimony and sulfur sources and the effects of foreign ions on the shape and crystallinity of Sb$_2$S$_3$ NCs were examined. In addition, a cation-exchange experiment was performed to obtain smaller Sb$_2$S$_3$ NCs using PbS QDs.

A Sb$_2$S$_3$ NC paste was prepared for the first time to obtain better films via spin coating. Sb$_2$S$_3$ NC-sensitized solid-state solar cells were fabricated, and a maximum power conversion efficiency of 1.13% was obtained. More importantly, the surface functionalization of TiO$_2$ with 3MPTMS was introduced to improve Sb$_2$S$_3$ NC film uniformity and facilitate electron transfer from Sb$_2$S$_3$ to TiO$_2$. To elucidate the band structure of NC films and further enhance the efficiency of these solar cells, PYSA measurement was performed to define the positions of the valence and conduction bands of the as-prepared and annealed Sb$_2$S$_3$ NC films.

Dip coating is another low-cost method to deposit absorbing layers in PV cells. More uniform films can be obtained by dip coating. Sb$_2$S$_3$ NC-based SSSCs were fabricated via dip coating, which exhibit higher efficiencies (1.38%) and fill factors compared to devices fabricated using spin coating.

The most important result of this project is the first-time colloidal hot injection synthesis of Sb$_2$S$_3$ NCs and the demonstration of Sb$_2$S$_3$ NC-based SSSCs devices. The results achieved in this project will encourage other researchers to fabricate Sb$_2$S$_3$-based low-cost and environmental friendly solar cells and explore other Sb$_2$S$_3$ NC-based photovoltaic device architectures through optimizing synthesis methods to obtain smaller crystalline Sb$_2$S$_3$ NCs.
6.1.2 Future Work and Outlook

**Figure 6.1.** Device structure using Sb$_2$S$_3$ NCs as light harvesting and electron transporting materials a) Bilayer all inorganic solar cells, a) Bilayer organic-inorganic hybrid solar cells.

**Figure 6.2.** Device structure using Sb$_2$S$_3$ NCs as light harvesting and electron transporting materials a) Bulk hetero-junction inorganic-organic hybrid solar cells, b) Bulk hetero-junction all inorganic solar cells.
One limitation of our synthesis work is that we could not obtain sub-20 nm crystalline well-separated stoichiometric Sb$_2$S$_3$ NPs. This shortcoming limits the utilization of Sb$_2$S$_3$ NCs in low-temperature processed solar cell device architectures. Sub-20 nm crystalline well-separated stoichiometric Sb$_2$S$_3$ NPs can be obtained through the initial synthesis of small (≤10 nm) Sb NPs and then transformed into Sb$_2$S$_3$ NPs by adding sulfur. In this case, a strong bind ligand is needed to prevent the formation of chain-like Sb$_2$S$_3$ NCs.

The as-synthesized Sb$_2$S$_3$ NRs (including hyperbranched NRs) and annealed NCs can act as a light-harvesting and electron-transporting component in PV cells. Moreover, the hyperbranched NCs have advantages with regard to electron–hole separation and transport. The wide band gap electron transport semiconductor oxide materials (TiO$_2$ ~3.2eV, ZnO$_2$ ~3.3eV) cannot absorb solar light in the visible region. Compared to these materials, n-type Sb$_2$S$_3$ NCs can increase light absorption in the PV cells. Thus, future work will include the fabrication of bilayer (p-n junction) and bulk hetero-junction organic/inorganic-inorganic devices to utilize the advantages of organic and inorganic materials for PV cells. The device architectures are shown in Figures 6.1 and 6.2.

6.2 *In situ* Synthesis of Gold Nanoparticles on Solid Substrates via Reactive Inkjet Printing

6.2.1 Conclusion
The main ambition of this project was to investigate a reactive inkjet printing method with commercially available inks to synthesize Au NPs directly on a solid substrate. By using a judicial choice of solvents and reducing agent, a simple and versatile *in situ* synthesis of Au NPs with a narrow size distribution on solid substrates via reactive inkjet printing has been demonstrated. We can control the size and shape of the Au NPs by controlling the concentrations of the gold precursor and oleylamine. In addition, the effects of different gold precursors, different solvents and reverse printing on the size distribution of as-synthesized Au NPs were investigated. HAuCl$_4$.3H$_2$O gold precursor, DMSO and 1, 2-dichlorobenzene solvents as well as reducing agent oleylamine comprise the best material system with which to synthesize relatively monodisperse Au NPs. Another advantage of this system is the broad range of Au precursor inks that can be prepared due to the high solubility of HAuCl$_4$.3H$_2$O gold precursor in DMSO. We believe that this approach can be further developed and adopted as a low-cost, reliable, high-throughput method for the preparation of various types of nanoparticles on a variety of substrates.

Additionally, oleylamine-capped Au NPs with an average diameter of 22 nm were successfully synthesized using printable non-particle ink via one-step inkjet printing. The effects of precursor concentration as well as heat treatment temperature and time on the size and shape of nanostructures were also investigated. At higher precursor concentrations, the heating temperature or time did not affect the size or shape of nanostructures, whereas at lower precursor
concentrations, the heating temperature and time showed a significant effect on the size and shape of nanostructures.

6.2.2 Future Work

To fabricate all solution-processable solar cell devices, Au NPs will be integrated into solar cell devices as an electrode according to our method. With this approach, large-scale solution-processable and flexible solar cell modules can be fabricated to decrease the cost of solar cell fabrication. Moreover, this technique can minimize the waste of Au during deposition.

Another important task is to increase the conductivity of Au NPs prepared by RIP, enabling the integration of Au NPs prepared by RIP for solar cells devices to be compatible with Au deposited by conventional methods. Solid-state ligand exchange and plasma cleaning can increase the conductivity of Au NPs.

The alignment of printed pattern after heat treatment is not well-aligned. We may get well-aligned pattern through printing on confined space. That makes the pattern gold NPs on substrate more attractive for application in plasmonic solar cells and other opto-electronic devices.