EARTH-ABUNDANT METAL CHALCOGENIDES: SYNTHESIS, INTERFACE MODIFICATION, AND APPLICATIONS IN ENERGY CONVERSION DEVICES

BY

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A Dissertation Submitted to the Graduate Faculty of

WAKE FOREST UNIVERSITY GRADUATE SCHOOL OF ARTS AND SCIENCES

in Partial Fulfillment of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

Physics

May, 2017

Winston-Salem, North Carolina

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DEDICATION AND ACKNOWLEDGEMENT

I would like to express my appreciation for those who have guided and supported me through my doctoral education. In particular, I would like to thank my advisor Dr. David Carroll for imparting his ingenious and optimistic research approach upon me. Also, I want to thank Dr. Carroll for always being patient, supportive and encouraging for me to explore and realize all my wild research ideas, I cannot become the independent thinker and researcher as I am today without the trust or freedom he gave to me.

I would like to thank the people on my thesis committee: Dr. Richard Williams, Dr. Daniel Kim-Shapiro, Dr. Scott Geyer, and Dr. K. Burak Üçer, for your kindly help and advice in the past several years. I greatly appreciate the help of Dr. Williams, who has helped me to understand mechanism behind optical systems, and provided insight thoughts about our ongoing perovskite luminesce project. I am extremely thankful for Dr. Geyer for all the great collaborations between our groups and the fruitful discussions regarding the surface chemistry of nano system. Thank Dr. Kim-Shapiro and Dr. Üçer for joining my defense, reading my dissertation, and providing valuable suggestions for my research.

The people that I met in Carroll’s group have all been unique and my time with them has been rewarding. I would especially like to thank Dr. Yuan Li and Dr. Huihui Huang. They are not only great colleagues who helped me over the years, but also amazing friends for lifetime. Special thanks must go to Dr. Corey Hewitt whose brilliance and dedication is unmatched, without him our facilities could not run so smoothly. Additional thanks go to my friend Dr. Qi Li and Jiajie Xiao whose camaraderie and wit are sorely missed. I am going to miss Wake Forest because of people like them make it special.
Finally, I would like to thank my family. Even though I am thousands of miles away from home, their love and care is always surrounding me. The sacrifices my parents made for my sister and me will never be forgotten. I thank them for their endless support.
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<th>Description</th>
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<tbody>
<tr>
<td>MC</td>
<td>Metal chalcogenide</td>
</tr>
<tr>
<td>CZTS</td>
<td>Cu₂ZnSnS₄</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole-transporting layer</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron-transporting layer</td>
</tr>
<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
<td>Short-circuit current</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>TE</td>
<td>Thermoelectric</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystal</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin-film transistor</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna ab initio simulation package</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
</tr>
<tr>
<td>OLA</td>
<td>Oleylamine</td>
</tr>
<tr>
<td>BBT</td>
<td>Butanethiol</td>
</tr>
<tr>
<td>HXT</td>
<td>Hexanethiol</td>
</tr>
<tr>
<td>DDT</td>
<td>Dodecanethiol</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>TOPO</td>
<td>Octylphosphine oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared spectroscopy</td>
</tr>
<tr>
<td>MCC</td>
<td>Metal chalcogenide complexes</td>
</tr>
<tr>
<td>EDS/EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space charge limited current</td>
</tr>
<tr>
<td>AcAc</td>
<td>Acetylacetone</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark plasma sintering</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b’] dithiophene)-alt-4,7(2,1,3-benzothiadiazole)]</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>MOE</td>
<td>2-methoxyethanol</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped tin oxide</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>tBt</td>
<td>tert-Butylthiol</td>
</tr>
<tr>
<td>IPCE</td>
<td>incident photon to current efficiency</td>
</tr>
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Abstract

Metal chalcogenides (MCs) have attracted significant attention in a variety of energy devices for the wide range of properties that MCs can offer by combining different metal cations and chalcogen anions. However, the most common MCs used for photovoltaic and thermoelectric devices all consist rare or toxic elements which rises criticism on their candidacy as a solution for future sustainable energy. The focus of this work is to develop low-cost solution methods to synthesize non-toxic earth-abundant MC materials Cu$_2$ZnSnS$_4$ (CZTS) and Sb$_2$S$_3$ for thin-film solar cells and thermoelectric generator. By tweaking the surface chemistry of CZTS nanocrystals, we fabricated CZTS thin-films with high carrier mobility and large grain size without involving hazardous procedure. We also derived ligand-free nanostructured CZTS from aerogel for the first time, and explored its potential application for thermoelectric generator. At last, we’ll show you a planar heterojunction Sb$_2$S$_3$ solar cell with an efficiency of 4.2% fabricated via a simple sol-gel method. Combined with interface modification, we achieved a record-breaking power conversion efficiency 5.3%.
Chapter 1 . General Introduction

Background

The motivation for this work comes from global warming that threaten the human society. According to a recent study (Figure 1-1), the positive correlation between CO$_2$ emission and temperature anomaly suggests that we must reduce our consumption of fossil fuels. On the other hand, the depletion of fossil fuel will become more apparent in the next decades. Based on above understanding, it is important to find sustainable and viable alternative energy sources that support the speed development of world’s economy, industry, and technology. Among all renewable energy technologies, photovoltaic and thermoelectric have attracted the most attention because of the capability of producing electricity without moving part, and the potential of providing enough electrical energy to support entire human society. However, nowadays renewable energy only consists a very small portion of our energy usage. The major reason beyond the inferior efficiencies, is that for many of those devices, mass pollution was created during the fabrication (Figure 1-2). Therefore, the task of my PhD research was to tackle the energy crisis by developing environment-friendly techniques to fabricate low-cost and earth-abundant materials for photovoltaics and thermoelectrics.
Figure 1-1 Correlation between global average temperature anomaly and CO$_2$ annual mean concentration. Data from Earth System Research Laboratory of U.S. National Oceanic and Atmospheric Administration

Figure 1-2 Schematic illustration of the production process of silicon solar cells. The hazardous chemical and pollution involved in the process are labeled red.
Brief Working Principle of Energy Conversion Devices

Thin-Film Photovoltaics

Figure 1-3 Schematic diagram of the work principle of solar cell. Current is generated from excitons (electrons and holes) excited by incident light flowing directed by the potential slope built by a p-n junction from semiconductors.

A solar cell is a semiconductor device that directly converts light into electricity. The most essential component of a solar cell is the p-n junction created from a layer of absorber and another layer of semiconductor with the opposite conduction ability (Figure 1-3). When the photon in the incident light beam with higher energy than the band gap of absorber, electro-hole pairs are created, and separated by the built-in electric filed in the space charge region of the p-n junction, then finally collected by electrodes.

Traditional silicon solar normally requires a thick absorber layer with a thickness > 100 μm\cite{1} to achieve a high efficiency as the result of poor absorption coefficient of silicon. In contrast, modern 2nd generation solar cells as known as thin-film solar cells utilizing
novel absorber materials with high absorption coefficient, so a very thin layer with a thickness ranging from hundreds of nanometers to several micrometers can sufficiently absorb almost all the incident sun light. A common thin-film solar cell has more layers beyond a simple p-n junction in order to facilitate charge extraction (Figure 1-4).

Figure 1-4 A typical structure of Sb$_2$S$_3$ thin-film solar cell. P-n junction forms between p-type Sb$_2$S$_3$ and n-type TiO$_2$. An extra hole transport layer (HTL) is added beyond the p-n junction to provide a better hole collection for top Ag electrode.

The most important measurement of solar cells is the power conversion efficiency (PCE) $\eta$ given by

$$\eta = \frac{V_{oc}J_{sc} \times FF}{P_{in}}$$

$Eqn. \ 1-1$

Where $V_{oc}$ is open-circuit voltage, $J_{sc}$ is the short-circuit current, FF is fill factor and $P_{in}$ is the energy density of incident light. All those parameters can be easily measured from the photo current density – voltage (J-V) characteristics except $P_{in}$. $P_{in}$ depends on the light condition, and for the standard terrestrial spectra of AM1.5G which simulating the sun light density at earth’s sea level, $P_{in} = 100 \text{ mW/cm}^2$. A typical J-V curve is shown in Figure 1-5.
Voc and Jsc are the intercepts on V and J axis respectively. And FF can be calculated with following equation:

\[ FF = \frac{P_{\text{max}}}{V_{\text{oc}} \times J_{\text{sc}}} \]

*Eqn. 1-2*

Where \( P_{\text{max}} \) is the largest product of \( J \times V \) could be found on the curve.

Figure 1-5 J-V curve of a solar cell under illumination. The green square area represents the maximum power from this cell, and the blue square area is the product of \( V_{\text{oc}} \times J_{\text{sc}} \)

Solar cell is basically a diode, so its J-V curve follows the conventional diode law with an extra current generated by light:
\[ J = J_0 \left[ \exp \left( \frac{qV}{n k T} \right) - 1 \right] - J_L \]

Eqn. 1-3

\( J_0 \) is the smallest saturation current density, \( k \) is Boltzmann’s constant, \( T \) is the temperature in Kelvin, \( q \) denotes the elementary charge, \( n \) is the ideality factor for diode and \( J_L \) is the light induced current. For a short circuit conditions the \( J_{sc} \) is equal to \( J_L \) when the solar cell has a small series resistance, so sometime \( J_L \) term in above equation is replace by \( J_{sc} \). Setting the net current to 0, open-circuit voltage \( V_{oc} \) can be described by following equation:

\[ V_{oc} = \frac{n k T}{q} \ln \left( \frac{J_L}{J_0} + 1 \right) \]

Eqn. 1-4

As we can see \( V_{oc} \) depends on light-generated current and saturation current. Normally, \( J_L \) has small variation while \( J_0 \) can change in orders of magnitude, so \( V_{oc} \) mostly depends on saturation current which reflect the internal exciton recombination in the solar cell. So, \( V_{oc} \) is the simplest direct indication of the amount of recombination in the device when optimizing the device design.

**Thermoelectric Generator**

Thermoelectric (TE) generator is known to convert thermal energy directly to electricity originates from the discovery of Thomas J. Seebeck in 1821 that a temperature gradient across a material creates a voltage. The efficiency of a thermoelectric material is determined by dimensionless figure of merit defined as,
In which $\sigma$ is electrical conductivity, $T$ is the absolute temperature in Kelvin, $\kappa$ is thermal conductivity and $S$ is Seebeck coefficient which is a measure of the magnitude of an induced thermoelectric voltage in response to the temperature difference across the material. A large Seebeck coefficient, high electrical conductivity, and a small thermal conductivity therefore are necessary for achieving an efficient TE device. In general, materials having a ZT value close to one could be considered as a good TE material. However, in order to compete with other widely used power generation methods, a ZT > 3 is desired.

The efficiency $\eta$ of a TE material is given by

$$\eta = \eta_c \times \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c / T_H}$$

Where $T_c$ and $T_H$ are the temperatures of the cold and hot ends respectively. $\eta_c = 1 - T_c / T_H$ represents the maximum Carnot efficiency. Assuming at room temperature, with a temperature difference of 100K, i.e. $T_c = 300K$ and $T_H = 400K$, in order to get an efficiency of 10% which is the minimum expectation for competing with traditional power sources, we need a $ZT > 3.7$. However, the best TE materials to-date still have a $ZT < 0.5$. The major reason behind this low ZT is that while a high ZT requires opposite trends of $\sigma$, $S$, and $\kappa$, but they are interdependent. The relationship between $\sigma$ and $\kappa$, given by carrier concentration ($n$), carrier charge ($e$), carrier mobility ($\mu$) and Lorenz number is:
\[ \sigma = ne\mu \]
\[ k = k_L + L\sigma e \]

_Eqn. 1-7_

From above equation, we can see that \( \sigma \) and \( \kappa \) have positive correlation, preventing them move in opposite direction, therefore resulting a low ZT limits the wide application of TE materials.

**Earth Abundant Metal Chalcogenides**

Metal chalcogenide is a chemical compound consisting of at least one chalcogen anion (S, Se, Te) and at least one metal cation. Metal chalcogenide semiconductors have attracted much attention because of the vast combinations of metal cation and chalcogen anion that offers tremendous amount of materials with a wide range of characteristics for different applications like fuel cell systems,\(^{[2]}\)[\(^{[3]}\) photovoltaic\(^{[4]}\)[\(^{[5]}\)[\(^{[6]}\)[\(^{[7]}\)[\(^{[8]}\), thermoelectric (TE) generators\(^{[9]}\)[\(^{[10]}\), Li-ion batteries\(^{[11]}\), and supercapacitors\(^{[12]}\).

Particularly, for photovoltaic the most popular metal chalcogenides are PbS(Se), CdTe, and CuIn\(_x\)Ga(1-x)Se\(_2\) (CIGS) while for TE there are BiTe-based, PbTe-base, and SiGe-based materials. For all above metal chalcogenides, they are not ideal for commercialization and wide application as the result of consisting expensive, rare or toxic elements. Therefore, earth-abundant materials with low-toxicity should be developed for more sustainable future renewable energy technologies. In this section I will provide a brief review of two novel earth-abundant metal chalcogenides with potential applications for photovoltaic or TE.
**Copper-Zinc-Tin-Sulfide/Selenide (CZTSSe)**

CZTSSe is an emerging candidate to further the development of thin-film solar cell and thermoelectric. It has a structure originated from ZnS by replacing Zn with Cu and In then replacing In with Zn and Sn (Figure 1-7). It offers a high absorption coefficient of $\sim 10^4$ cm$^{-1}$ with a tunable bandgap from 1.0 to 1.5 eV which matches appropriately with solar spectrum.\(^{[13]}\) Also, as a quaternary chalcogenide, it has a naturally distorted structure due to the diverse types of interior bonding. This structure can scatter phonons effectively and lead to a low thermal conductivity which enables CZTS to be a potential TE material. Besides the performance, the major advantage of CZTSSe is that it solely consists of low-cost earth abundant elements. Figure 1-6 shows the abundance and cost of each element in CZTS as compared with some elements that are used in current commercialized thin-film photovoltaic materials. Also, the production quantities of CZTS elements are in large quantities which allows the CZTS-based solar industry to grow.
Figure 1-6 Global production of elements used for photovoltaics. (top) Occurrence in the Earth’s crust and current costs of some of the elements relevant to thin-film photovoltaics. Note that logarithmic scales have been used for both y axes. (bottom) \(^{[14]}\)
Antimony Sulfide (Sb$_2$S$_3$)

Despite CZTSSe is the most successful example in earth-abundant chalcogenides for photovoltaic having an impressive 12.6% power conversion efficiency\textsuperscript{[15]}, its quaternary nature causes a very small region on phase diagram as shown in Figure 1-8 indicating the low reproductivity of pure CZTSSe which limits the further improvement for CZTSSe devices. This limitation has already started to emerge as we have noticed the record efficiency of CZTSSe solar cell has kept static since 2014.\textsuperscript{[15]} On contrast, simple binary materials can effectively avoid the complexity of phase and defect control as encountered in CZTSSe. There are several binary earth-abundant absorbers such as FeS$_2$,\textsuperscript{[16]} SnS\textsuperscript{[17]} have been intensively studied for decades, however, their efficiencies have dawdled substantially behind.
Figure 1-8 The calculated chemical-potential stability diagram of Cu$_2$ZnSnS$_4$ in a 2D Cu-rich plane (the stable 3D region is inset). All values are in eV. The volume of the stable region is small, and a deviation outside this space will cause the formation of impurities of CuS, ZnS, SnS, or Cn$_2$SnS$_3$. [18]

Antimony trisulfide (Sb$_2$S$_3$) is a binary chalcogenide with orthorhombic crystal structure. It is a layered compound consisting of parallel 1D (Sb$_4$S$_6$)$_n$ ribbons stacked together by van der Waals forces which makes it a member of low-dimensional van der Waals material. [19][20] It has high absorption coefficient in visible range (≈1.8 × 10$^5$ cm$^{-1}$ at 450 nm), air/moisture-stability, and a direct band gap of 1.7eV which is close to the prime bandgap for solar cell (~ 1.5 eV), making it a very promising material for photovoltaic. [21][22][23][24][25] Besides the simple binary structure, elements in Sb$_2$S$_3$ are both cheap and relatively abundant in earth. The cost and abundancy of Sb and S are compared with elements in most commercially successful thin-film photovoltaic materials CdTe and CIGS are shown in Figure 1-9. Apparently, Sb and S have higher storage than Te and lower price than In and Ga. In conclusion, antimony trisulfide has outstanding physical properties
for solar cell, a low-cost, non-toxic, and earth-abundant nature, which makes it a promising candidate for future low-cost and environment-friendly energy solution.

Figure 1-9 (top left) lattice structure of Sb$_2$S$_3$. Comparison of the cost (top right) and abundancy (bottom) of elements in Sb$_2$S$_3$, CIGS, and CdTe solar cells. Elements price from Wolfram Alpha Knowledgebase, July 2011 estimates.
Reference


Mater. Interfaces 2014, 6, 2836.
Chapter 2. Surface Modification Enabled Carrier Mobility Adjustment in CZTS Nanoparticle Thin Films


Authors: Wenxiao Huang, Qi Li, Yonghua Chen, Yingdong Xia, Huihui Huang, Chaochao Dun, Yuan Li, and David L. Carroll.

I initiated this project, designed experiments and took the major role in the data collecting and manuscript preparation. Qi Li performed all the simulations.

Abstract

As the essential building blocks of many electronic devices, solid state thin-films are attracting extensive interest. Soluble nanocrystals (NCs) make it possible to develop robust, low-cost, large-scale fabrication methods for thin-films. However, the organic surface ligands normally used to stabilize the NCs make those thin-films a NC–ligand complex which may possess varied electrical performance compared to a single component system. Previous models could only estimate the charge transportation characteristics in those films quantitatively by considering the capping ligands as a barrier of charges from inter-particle hopping. In this work, we demonstrated that starting from first principles density functional theory, the carrier mobility in a CZTS NC–ligand complex can be determined quantitatively, and guided by this model, we developed a low-cost, low-temperature technique to fabricate CZTS thin films which have a carrier mobility of up to 10.9 cm²/(VS).
Introduction

Semiconductor thin films are the fundamental building blocks for rapidly growing fields involving thin-film-transistors (TFTs), solar cells, and transparent electrodes. While many fabrication methods have been developed, semiconductor nanocrystals (NCs) substantially reduce the cost of thin-film electronic and photovoltaic device fabrication because the soluble NCs ‘ink’ can be applied to large-scale, low-cost fabrication techniques such as drop casting, dip casting, spin coating, spray casting, and inkjet printing. However, to avoid aggregation caused by their high surface area, the NCs are normally stabilized by organic insulating capping ligands, which introduce a major obstacle in improving the electronic performance of these thin films. To get rid of these organic ligands, many thin-film preparations employ high-temperature annealing; during this aggressive procedure, defects occur in the film formation due to high weight losses, and the high annealing temperature limits the choices of substrate. Otherwise, removing the surface capping ligands requires a hazardous and toxic procedure involving hydrazine. Therefore, searching for a new low-cost method to improve the NCs thin film electrical performance becomes worthwhile.

One solution is to modify the surface of the NCs by exchanging the long chain insulating ligands with new shorter ligands. Past studies have revealed that the charge transport in a PbSe NC-ligand system can be considered as a series of incoherent tunneling transitions between neighboring NCs, using the ligand monolayer as the tunneling barrier. In these previous models, carrier mobility is determined by the site energies, exchange coupling energy between two NCs, and average barrier width. However, given
that those parameters are difficult to determine experimentally, these models can only analyze them qualitatively.

In this work, we studied Cu2ZnSnS4 (CZTS) NC-ligand systems. Instead of describing the ligand as an individual tunneling barrier for charge hopping, we coupled it with the NCs and studied how the surface modification influenced the electron structure and the effective mass of charges in this NC-ligand complex. This allowed us to determine the carrier mobility quantitatively.

The kesterite material CZTS possesses promising characteristics to be a conventional absorber for thin film solar cells with the added benefits of being low-cost, non-toxic, and comprised of earth-abundant elements. Various techniques have been developed for the preparation of CZTS thin films, such as sulfurization followed co-sputtering\cite{5}, chemical vapor deposition (CVD)\cite{6}, electrodeposition\cite{7}, and hydrazine based solution processing\cite{8}, which leads to the current highest performing CZTS solar cells (>11% efficiency)\cite{9}. Nevertheless, the non-vacuum, low-toxic preparation of CZTS inks could produce low-cost thin films with superior homogeneous composition. Also, the traditional CZTS ink technique requires a high-temperature procedure which has the same issues that other solution-based NC devices have confronted, but with additional drawbacks: Sn losses through desorption of SnS from CZTS due to high vapor pressure of SnS\cite{10} leads to impurity and defects, and sulfur diffusion into the molybdenum back contact forms MoS2 and yields secondary phases at the CZTS|Mo interface, lowering the performance\cite{11}. Therefore, the theoretical investigation on CZTS NC-ligand systems would not only help us anticipate the electrical performance but also guide us to develop a low-temperature surface modification process that solves the above issues.
**Result and Discussion**

To reveal the origin of how the ligands cap the CZTS NCs and further influence carrier transport in NC-ligand systems, a method based on first principles density functional theory (DFT) is proposed below:

Compared to the bulk material, NC thin films are a complex of organic ligands and nanoparticles. This distinct structure causes great differences between the charge transport features of neighboring particles. Instead of considering the NCs and ligands separately, the CZTS nanoparticles are coupled with different ligands to perform electronic structure calculations for the surface states of CZTS nanoparticles in order to determine the effective mass and then further derive the carrier mobility.

The crystal structure of kesterite CZTS is tetragonal, space group $I\bar{4}$ (No.82 of the International Tables of Crystallography). Our ab initio calculations are carried out in the projector-augmented wave framework in Vienna ab initio simulation package (VASP)$^{[12]}$ $^{[13]}$. We employ both hybrid functionals (HSE06$^{[14]}$ and PBE0$^{[15]}$) and compare the results to the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation$^{[16]}$. The mixing factor is 0.25 for both hybrid functionals. The plane wave kinetic cutoff energy is 300 eV. A self-consistency convergence criterion of $1 \times 10^{-6}$ eV is used for all calculations and the structures (crystal and crystal-ligand) are relaxed until all force components are less than 0.01 eV/Å. The bulk properties of ideal kesterite CZTS are calculated with the primitive cell of 8 atoms. A $\Gamma$-centered $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh is applied for all three functionals. Results are listed in the supporting material. The
GGA results underestimate the band gap and HSE06 has the closest result to the experimental data. This tendency is also found in Ref. \[17\].

Figure 2-1 Relaxed surface structures of keresite CZTS ligand complex systems for 4 different ligands with varying lengths. The whole unit cell contains a 48 atom supercell arranged along the X axis and ligands on both ends. The anions of the ligands are bonded with the copper ion of CZTS.

For the crystal-ligand system simulation, we chose oleylamine (OLA) and a few alkanethiols (1-butanethiol (1-BTT), 1-hexanethiol (1-HXT), and 1-dodecanethiol (1-DDT)), ligands with different chain lengths. OLA is a common ligand used in CZTS NCs synthesis. The alkanethiols have stronger bonding between CZTS NCs than OLA does, so the alkanethiols are potentially capable of exchanging with the surface ligand of OLA-capped CZTS NCs. We first create a non-polarized surface (110) which is favorable to the
ligand. This is done by using two new basis vectors ($\vec{T}_1, \vec{T}_2$) on the x-y plane of the 16 atom tetragonal conventional cell, where $\vec{T}_1 = \vec{a}_1 - \vec{a}_2$ and $\vec{T}_2 = \vec{a}_1 + \vec{a}_2$ and $\vec{a}_1$ and $\vec{a}_2$ are the two original basis vectors in the (100) and (010) directions, respectively, while the basis vector in z-direction is unchanged. In Figure 2-1, $\vec{T}_1, \vec{T}_2$ are defined as the new X and Y axes, respectively. A supercell is created by stacking three new unit cells in the X direction. Then we remove one hydrogen atom from the amino or thiol group of the ligand molecules and bond the sulfur or nitrogen atom with a copper atom on both sides of the supercell, which are two (110) surfaces of kesterite CZTS. This selection is based on the fact that the Cu$^{+}$ existing in bulk CZTS can still provide one more electron to bond with the sulfur or nitrogen atoms of the ligands.

Calculations on the CZTS-ligand complex structure are performed with traditional GGA-PBE functional theory. Although the energy gap calculated from GGA-PBE is not correct, we apply the idea of “scissors operator” [18] and trust the shape of the conduction bands which directly lead to band edge effective masses [19]. The k-point sampling is scaled with the size of the new cells. All atoms are relaxed with the same criteria stated above, and the relaxed structures at the surfaces are shown in Figure 2-1. As expected, the sulfur and nitrogen atoms from the ligand molecules are bonded most closely with the copper ion of CZTS. In order to simulate the mobilities, we calculated the effective mass at the conduction band minimum. Simulation of electron-phonon scattering time is shown in the supporting material. The overall mobilities are calculated as the average of the mobilities in the X, Y, and Z directions.
<table>
<thead>
<tr>
<th></th>
<th>1-BTT</th>
<th>1-HXT</th>
<th>1-DDT</th>
<th>OLA</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_{xx}(m_e))</td>
<td>33.96</td>
<td>46.79</td>
<td>67.94</td>
<td>163.75</td>
<td>0.35</td>
</tr>
<tr>
<td>(m_{yy}(m_e))</td>
<td>0.97</td>
<td>2.25</td>
<td>6.73</td>
<td>21.37</td>
<td>0.35</td>
</tr>
<tr>
<td>(m_{zz}(m_e))</td>
<td>1.07</td>
<td>2.77</td>
<td>7.52</td>
<td>23.38</td>
<td>0.22</td>
</tr>
<tr>
<td>(\mu\ (cm^2/V\cdot s))</td>
<td>7.08</td>
<td>2.94</td>
<td>1.05</td>
<td>0.34</td>
<td>40.6</td>
</tr>
</tbody>
</table>

Table 2-1 Simulated band masses and mobilities for four CZTS-ligand systems, \(m_{xx}, m_{yy}, m_{zz}\) are band masses in the X, Y, and Z directions, respectively. Overall mobilities are obtained by averaging mobilities in these directions.
Figure 2-2 Carrier mobility versus ligand length, from the aspects of theoretical value (red sphere) and experimental statistics (blue hole) with mean (black square).
As a result, we combined the electronic structure calculations with the analytical formula for electron-phonon scattering of the NC-ligand complex systems and simulated the electron mobilities quantitatively. The results are listed in Table 2-1 and shown in Figure 2-2. Due to the fact that the band masses along the X axis are the largest, we can deduce that carrier transport along the ligand molecules is less efficient than transport on the CZTS-ligand surfaces. The band masses on the Y and Z axes have relatively close values. Furthermore, they are also controlled by the length of the ligand molecules. As a general tendency, longer ligands lead to increasing effective masses at the conduction band minimum and hence sharply decreasing mobility. Inspired by our simulation result, and in order to verify this phenomenon and experimentally calculate mobility, we developed a low-temperature, low-cost technique for CZTS NCs thin-film fabrication. OLA-capped CZTS NCs with size 15~25 nm were synthesized as other literature has described\textsuperscript{[20]}. Then the OLA, bonded to NC surfaces, was replaced by 1-BTT, 1-HXT, and 1-DDT in solution, followed by spray casting onto ITO substrates to make NC thin films (Figure 2-3).
Figure 2-3 Ligand exchange process followed by thin-film fabrication and corresponding molecular image of ligands

This ligand exchange has been identified via Thermogravimetric Analysis (TGA) and FT-IR (Fourier Transform Infrared Spectra). Since the C-S bond is not sensitive in infrared spectra measurement, the existence of N-H bond was studied: clearly the N-H peaks disappeared after ligand exchange, revealing that the alkanethiols completely replaced the OLA (see Figure 2-4(B)). Besides, as shown in Figure 2-4(A), 1-butanethiol, 1-hexanethiol, 1-dodecanethiol, and OLA-capped NCs contain 3.36%, 4.04%, 5%, and 23.32% organic ligands in total weight of NCs, respectively, indicating that ligands with shorter chains could reduce the amount of insulator in the NC thin films. Also, with the noticeable difference of weight percentage, we can conclude that there are weight losses during the ligand exchange process. With a solutionless ligand exchange method, the weight loss happens during the film formation and leaves many cracks[21]. The SEM image in Figure
2-5 shows that with solution ligand exchange followed by spray casting, we can fabricate condensed homogeneous films without noticeable cracks. Since the NCs still retain their solubility after the ligand exchange, this is a suitable method for large scale fabrication.

Figure 2-4 (A) TGA data for different ligand capped CZTS NCs at a constant heating rate of 5°C min⁻¹ under argon flow. The samples were retained at 140°C for 30min to avoid the influence of excess solvent. Before measurement, samples were dried in vacuum for 24h. (B) FT-IR of NCs capped by different ligands showing that the N-H stretching (blue circle) and N-H bending (red circle) peaks vanished in thiol ligands-NCs system which indicates that after ligand exchange, OLA is replaced by alkanethiols.
Figure 2-5 SEM images of CZTS films with different ligands, and the scale bar has a length of 1µm

We fabricated the hole-only devices with structure Glass/ITO/CZTS/MoO3/Al since CZTS is p type material. Experimentally, the current-voltage relationship was collected using a Keithley 236 source-measurement unit. The carrier mobility (hole) was then extracted from the J-V characteristics through approximation of the space charge limited current (SCLC) in Eqn. (1) \[22\]

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon \mu_0 \exp \left(0.89 \beta \sqrt{V / d} \right) \frac{V^2}{d^3}
\]  

(1)
V is the applied voltage, d is the thickness of the film, \( \mu_0 \) is the mobility, \( \varepsilon_0 \) is the permittivity of free space, and \( \varepsilon = 6.7 \) is the dielectric constant\[23\]. Eqn. (2) gives the efficiency \( \beta \)[22], where \( T \) is the temperature in calculation.

\[
\beta = \frac{1}{K_B T} \left( \frac{q^3}{\pi \varepsilon_0 \varepsilon} \right)^{1/2}
\]  \tag{2}

The experimental results are superimposed onto Figure 2-2. Although the lengths of the ligands (1nm–3nm) are much smaller than the diameter of the CZTS NCs (15–25 nm), changing those lengths dramatically influences transportation of carriers in the film. Shifting from OLA to 1-BTT, the carrier mobility improves by a factor of 29. More generally, the mobility increases exponentially while the ligand chain length decreases linearly, which agrees with reported PbSe systems\[4\]. Not only is the trend consistent with our calculations, but also, the measured values have great agreement with our theoretically calculated values. In other words, the agreement in Figure 2-2 exemplifies both the qualitative and quantitative validity of our model. Additionally, by developing this low-cost, low-temperature technique we were able to achieve a top mobility of 10.9 cm\(^2\)/Vs, which is comparable with that of reported high-temperature processes\[24][25][26][27\].

**Conclusion**

In summary, we reported a novel theoretical method to quantitatively estimate the carrier mobility in a NC-ligand complex, and we demonstrated both experimentally and theoretically that simple surface modification could remarkably change the carrier transportation characteristics in the NC thin film. In the CZTS NC-ligand system, we showed that the carrier mobility increases exponentially with decreasing ligand length because the carrier’s effective mass is significantly influenced by the capping ligands.
Based on this understanding, we developed a low-cost, low-temperature solution method to fabricate condensed homogenous CZTS thin films. With this method, we illustrated that with the shortest ligand adopted in this report, the carrier mobility of a CZTS thin film could be increased to 10.9 cm²/(VS), which is a 29-fold increase compared to the original OLA-capping NC thin film. It is also pertinent to note that further improvement in carrier mobility would be expected through utilizing ligands which are even shorter than 1-BTT.

In conclusion, the present findings proved the importance of the surface state of the NCs in the thin-film device, as it enabled us to adjust the carrier mobility through a simple surface modification of the NCs.

**Experimental Section**

*CZTS NCs synthesis:* The typical synthesis routine was adopted from a former report\(^{[20]}\). The amounts of Cu, Zn, and Sn precursors are chosen to obtain Cu-poor, Sn-rich NCs which have better photovoltaic performance. Generally, 1.332 mmol of copper(II) acetylacetonate, 0.915 mmol of zinc acetylacetonate, and 0.75 mmol of tin(IV) bis(acetylacetonate) dibromide are dissolved in 10 ml of oleylamine (OLA) and then transferred into a two neck flask connected to a Schlenk line. After the solution is degassed by heating to 135°C under vacuum and purged with argon several times, the temperature is raised to 225°C. In another flask, 0.16 g S powder is dissolved in 5 ml OLA and purged with argon for 30 min and then quickly injected into the 225°C precursor mixture. The color of the solution turns dark brown immediately and finally black after holding the temperature at 225°C for 25 minutes. Removing the heating mantle lets the solution cool down to 80°C where 40 mL methanol is added. The NCs are isolated from the supernatant
by centrifugation at 5000 rpm for 10 min, and precipitation is dispersed in 15 mL toluene followed by adding 30 mL methanol and centrifuging to remove residual OLA twice. Eventually, NCs are redispersed in 20 mL toluene to form a stable ink.

X-ray diffraction (XRD) was employed to ensure the composition homogeneity of the NC powder. The XRD result (Figure 2-6) shows the peaks are matching well with JCPDS database and previous reports on stoichiometric CZTS NCs.

![XRD result of synthesized CZTS NCs](image.png)

Figure 2-6 XRD result of synthesized CZTS NCs. Red is experimental data while black line represents standard JCPDS data.

**Ligand exchange:** As synthesized ink is divided into four 5 mL portions, 0.5 mmol of 1-butanethiol (1-BTT), 1-hexanethiol (1-HXT), and 1-dodecanethiol (1-DDT) are added into three portions respectively. The mixtures are allowed to stir for 5 hours. Then the excessive ligands are removed by triple washing with toluene and methanol under centrifuge.
Eventually, NCs with different organic ligands are dried under argon for further use.

**Film fabrication:** Different ligand stabilized CTZS NCs are dispersed in 15 mL toluene separately. Formed inks are then sprayed cast onto ITO substrates (2cm×2cm) at a constant temperature of 180°C with a spray speed controlled at 1 ml/min and a nitrogen flow pressure of 10 psi. For I-V characterization, 5 nm Molybdenum oxide (MoO3) and 200nm Aluminum electrodes were then deposited with a 3mm×3mm mask via thermal evaporation at the pressure of 10^{-6} torr.

**Characterization:** Current voltage characteristics were collected using a Keithley 236 source-measurement unit. The morphology and thickness were measured by the Scanning Electron Microscope (JEOL, JSM-6330F).

**Simulation Parameters:** Relaxed bulk material properties and simulation of electron-phonon scattering rates (reciprocal of scattering time).

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_\infty$</th>
<th>$\varepsilon_s$</th>
<th>$\sigma_d$ (eV)</th>
<th>$c_s$ (m/s)</th>
<th>$1/\tau_{LO^+}$ (1/s)</th>
<th>$1/\tau_{LO^-}$ (1/s)</th>
<th>$1/\tau_{LA^+}$ (1/s)</th>
<th>$1/\tau_{LA^-}$ (1/s)</th>
<th>$\hbar \omega_{LO}$ (meV)</th>
<th>$\hbar \omega_{LA}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTS</td>
<td>6.7</td>
<td>9.3</td>
<td>17.2</td>
<td>1046</td>
<td>0</td>
<td>$1.3 \times 10^{13}$</td>
<td>$8.5 \times 10^{13}$</td>
<td>$6.6 \times 10^{13}$</td>
<td>41.3</td>
<td>8.3</td>
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</table>

Table 2-2 Calculated parameters used in electron-phonon interaction, high frequency dielectric function $\varepsilon_\infty$, static dielectric function $\varepsilon_s$, deformation potential $\sigma_d$, effective sound velocity $c_s$, LO phonon emission rate $1/\tau_{LO^+}$, LO phonon absorption rate $1/\tau_{LO^-}$, LA phonon emission rate $1/\tau_{LA^+}$, LA phonon absorption rate $1/\tau_{LA^-}$, LO and LA phonon energy $\hbar \omega_{LO}$ and $\hbar \omega_{LA}$ are listed.
<table>
<thead>
<tr>
<th>Functional</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>E_g (eV)</th>
</tr>
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<tr>
<td>GGA-PBE</td>
<td>5.467</td>
<td>10.997</td>
<td>0.975</td>
</tr>
<tr>
<td>HSE06</td>
<td>5.446</td>
<td>10.858</td>
<td>1.430</td>
</tr>
<tr>
<td>PBE0</td>
<td>5.440</td>
<td>10.846</td>
<td>2.151</td>
</tr>
<tr>
<td>Expt.</td>
<td>5.434 [15]</td>
<td>10.834</td>
<td>1.4-1.6 [15]</td>
</tr>
</tbody>
</table>

Table 2-3 Calculated lattice parameters and band gap with different functionals.
Reference


Chapter 3 . Hydrazine-free Surface Modification of CZTSe Nanocrystals with Inorganic Ionic Ligand

A revised version was published on The Journal of Physical Chemistry C 118 (51), 30302-30308

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I initiated this project, designed the experiments, conducted the proof-of-concept research, involved in the manuscript preparation, but took the minor role of collecting data for the manuscript

Abstract

The optoelectronic properties of semiconductor nanoparticles (NPs) depend sensitively on their surface ligands. However, introducing certain organic ligands to the solution-synthesized CZTSe NPs unfavorably suppresses the interaction among those NPs. These organic ligands prevent the NPs from dissolving in water and create an insulating barrier for charge transportation, which is the key property for semiconductor devices. In our study, by adopting Na$_2$S to displace the associated organic ligands on Cu$_2$ZnSnSe$_4$(CZTSe), we obtained high solubility NPs in an environmentally friendly polar solvent as well as excellent charge transport properties. Because of the inorganic ligand S$^{2-}$ around CZTSe NPs, thin films can be easily fabricated by solution processing out of benign solvents like water and ethanol. After annealing, a homogeneous CZTSSe absorbing layer without carbon point defects was obtained. As the S$^{2-}$ effectively facilitates the electronic coupling in nanocrystal thin films, carrier mobility of the surface-engineered CZTSe enhances from 4.8 to 8.9 cm$^2$/Vs. This raises the possibility for engineering chalcogenide materials by controlling the surface properties during the fabrication process.
Introduction

Inorganic Nanoparticles (NPs), such as CdSe/CdTe \(^1\), Cu\(_2\)ZnSnSe\(_4\) (CZTSe) \(^2\), metal oxide \(^3\) etc., are believed to possess promising potentials as high efficiency photovoltaic (PV) \(^1\)[4], thermal-electrical materials \(^2\), light emitting diodes \(^3\). Although each type of Nanocrystal holds its own size dependent properties, the charge carrier transportation is dominated by their inter-particle medium \(^5\)[6][7]. It is therefore fundamentally important to engineer the surface properties of NPs to achieve high transport properties as well as ease of processing. As is well known, the essential function of the coordinating solvents (i.e. ligand, surfactant etc.) in the solution-based methods is to prevent aggregation and increase stability of the inorganic NPs \(^8\). However, as these organic additives unfavorably suppress the interaction of neighboring NPs by introducing an insulating barrier, lager amount of ligands bounded to the NPs surface are detrimental to the electronic coupling between adjacent NPs. Moreover, the ligands introduced density of undesirable surface defects once the NPs are made into thin films that can become significant traps to lower the semiconductor device property, especially after annealing at high temperature. Considerable efforts have been done to overcome such problem after introducing organic ligands to NPs, for example, the surface modification approach using smaller capping molecules, including both organic short alkyl chain molecules \(^9\)[10][11][12] and inorganic capping agents \(^5\)[6][7][13]. These methods have achieved varying degree of success in terms of attaining a high disperse state and acquiring enhanced electronic communication. Nonetheless, the involved hydrazine is explosive, pyrophoric and carcinogenic, which becomes the major drawback when it comes to the wide applications.
Chalcogenide PV based on Cu$_2$ZnSnS$_4$ (CZTS) and CZTSe, as one of the most promising NPs that can be used as an absorbing layer in high efficiency thin film solar cells [4][14][15][16][17], has achieved power conversion efficiencies (PCE) as high as 12.6% [4]. One commonly utilized method to fabricate CZTS/CZTSe device involves the colloidal nanoparticle ink, followed by non-vacuum deposition [15][18][19]. However, the above-mentioned issue will again become a big concern for depositing those NPs into thin film for solar cell. Specially, the CZTS/CZTSe NPs adopted large organic surface ligands like oleylamine (OLA), oleic acid or octylphosphine oxide (TOPO) as capping/stabilizing reaction solvents. Those ligands lead to poor transport property due to the insulating nature and possible defect after high temperature sintering that could kill the device performance. Moreover, those organic ligands would only allow the NPs to dissolve in hexane and toluene solvent that are highly toxic. Thus, further improvements in charge transport, conductivity and lower in toxicity to fabricate the CZTS/Se absorbing thin film is urgently needed and this will require new ligand to be developed for this material system.

It has been reported that sodium could significantly improve the PCE of CZTS/CZTSe solar cell device [20][21] by increasing the carrier density and elongating the carrier lifetime. In this paper, by taking advantage of sodium as well as reducing the amount of long hydrocarbon molecules at surface of NPs, we used Na$_2$S to implement the chemical modification of CZTSe NPs. It is worthy mention that Na$_2$S serves several purposes: (I) imparts the water solubility by adhering S$^2-$ to the NC surface and provides colloidal stabilization without introducing foreign toxic metal ions (II) acts as a functional ligand since it produces sulfur anion which is believed to generate CZTSSe after
annealing (III) provides electronic communication between the NPs, and enhances the carrier mobility (IV) increases the charge carrier concentration and minority lifetime by incorporating proper amount of Na⁺. Hydrophilic CZTS/CZTSe NPs fully dissolvable in Water/Ethanol/Formamide were obtained. The toxicity of these NPs was determined to be around 10 mg/L. Because of the presence of sulfur without carbon, considerable enhancement of carrier mobility $\mu$ up to (8.9 cm²V⁻¹s⁻¹) was achieved. As the commercial photovoltaic relies strongly on high carrier mobility and efficient transport of charge carrier, it is therefore reasonable to predict that CZTSSe based PV devices might be fabricated by using the present engineered all-inorganic CZTSe. Also, this surface charged NPs could be utilized for electrostatically driven self-assemble when combing with two oppositely charged species.

**Result and Discussion**
Figure 3-1 Schematic illustration of ligand exchange process to produce all inorganic nanocrystals and subsequent sprayed CZTSe thin film. The chemical modification process is performed under room temperature.

The ligand exchange process of OLA displacement with Na$_2$S was illustrated in Figure 3-1. Compared with the long length of OLA-capped NPs, the S$^2-$ capped NPs is considered to be nearly “naked”. Moreover, in comparison to the NPs capped with short alkyl chain molecules $^{[9][10][11]}$, the present S$^2-$ capped NPs is less sensitive to oxidation and thermal degradation. After ligand exchange, the surface of CZTSe NPs was negatively charged, which procedures the stable dispersion of NPs in polar solvent by introducing the electrostatic repulsion. It is shown that the Nanocrystals dispersions ability is closely related with the solvent dielectric constant $\varepsilon^{[22]}$. The higher the value of $\varepsilon$ is, the better the solubility of NPs. Hydrophilic S$^2-$ capped CZTSe NPs we synthesized are fully dissolvable in various polar solvents, including Formamide ($\varepsilon$=111), Water ($\varepsilon$=80.1) and Ethanol ($\varepsilon$=24.5), which are stable for at least 1-2 weeks in the air. This enables thin film formation by solution processing, such as spray coating, in wide variety of solvents. At the same time, all S$^2-$ attached CZTSe NPs lost solubility in nonpolar solvents. Upon thermal annealing, the deposited all-inorganic NPs could form crack-free thin film since there is less/no volume reduction that associated with organics decomposition. Because of the presence of sulfur, CZTSSe thin film was believed to form after annealing. Thus, the implement of bi-functional S$^2-$ ligand is expected to yield enhanced chemical and optoelectronic properties of the resulting CZTSe NPs.
Figure 3-2 TEM and HRTEM Photographs of colloidal solutions. TEM images of CZTSe (a) Capped with original organic ligands OLA in hexane. (c) Capped with inorganic ligands S²⁻ in water. (b) and (d) are the corresponding HRTEM showing the crystal structure in each NC, respectively.

The all-inorganic CZTSe nanoparticle is dissolvable in kinds of hydrophilic solvents. The crystal structures and morphology of the CZTSe NPs before and after ligand exchange are characterized by using TEM, as shown in Figure 3-2. Before ligand exchange, all the NPs show the pebble-like shapes, with the average particle size around 20 nm. Also, a high resolution TEM (HRTEM) image of the regular lattice fringes indicates that the NPs are highly crystalline, with characteristic inter-planar distance of ~0.3 nm from (112) plane of kesterite CZTSe phase. After ligand exchange, there are no apparent crystal structure or shape variations. While the size distribution remains almost unchanged, it is shown that the inter-particle distance is reduced to the extent that slight agglomeration even happens.
It is expected that the decrease of the inter-particle distance can eliminate the influence of the insulating barrier, which might promote the electronic coupling in nanocrystal solids.

Figure 3-3 FTIR and TGA for CZTSe NPs capped with long chain organic ligands OLA (red line) and with short inorganic ligands Na$_2$S (black line). (a) FTIR illustrates the absence of C=H stretch and C-H stretch absorption in the surface modified CZTSe after ligand exchange. The FTIR spectra were normalized to the amount of absorbing materials and curves are offset vertically for clarity. (b) TGA indicates weight loss as low as 15% after ligand exchange.

The efficacy of ligand exchange was further studied by Fourier Transform Infrared spectroscopy (FTIR) and Thermogravimetric Analysis (TGA). Figure 3-3(a) shows the FTIR spectra of dried CZTSe:OLA and CZTSe:Na$_2$S NPs. The intensity of characteristic C-H stretch at 2800-3000 cm$^{-1}$ that is ascribed to OLA is dramatically reduced after chemical modification, demonstrating that ligand exchange strategy using Na$_2$S effectively eliminates carbon from the NPs. The completeness of the ligand exchange were similar to those using metal chalcogenide complexes (MCC) $^{[23]}$, but without any toxic solutions. TGA is also performed, as shown in Figure 3-3(b), which indicates weight loss as low as 15% compared with the high value of 30% before ligand exchange. The higher mass loss
of CZTSe:OLA nanoparticles is caused by the decomposition of bulk OLA molecules. Therefore, it is predictable that the concentrated CZTSe: Na$_2$S solutions have the ability to remove the organic ligand. It is noteworthy that even the engineered all-inorganic CZTSe loss 15% of its original mass. One of the reasons is the partial decomposition of CZTSe (or CZTSSe) under the annealing process, which is,

$$2 \text{Cu}_2\text{ZnSnSe}_4 \rightarrow 2 \text{Cu}_2\text{Se} + 2 \text{ZnSe} + 2 \text{SnSe} + \text{Se}_2 \text{(gas)}.$$ 

Without supplying the additional Se vapor pressure, CZTSe power will decompose, leading to the loss of small amounts of vapor products $^{[24]}$.

XPS analysis is used to study the valence state of all elements in the as-synthesized hydrophilic CZTSe NPs, as shown in Figure 3-4. According to the peak splitting, valence states of Cu, Zn, Sn and Se are determined as Cu$^+$, Zn$^{2+}$, Sn$^{4+}$ and Se$^{2-}$, as expected. At the same time, the inorganic ligand S is found to be in S$^{2-}$ state $^{[25]}$. The average composition of the nanocrystals was determined by EDS (Figure 3-5). We take Tin as the basis such that the composition takes the form Cu$_x$Zn$_y$Sn$_{1.0}$Se$_z$. Considering the $\pm 2\%$ uncertainty, the average elemental composition data was Cu$_{1.9}$Zn$_{1.2}$Sn$_{1.0}$Se$_{5.0}$ before ligand exchange. After surface engineered, however, the elemental composition data changes into Cu$_{2.0}$Zn$_{1.3}$Sn$_{1.0}$ (Se$_{0.63}$S$_{0.37}$)$_{4.6}$. The annealing treatment with glass cover did not alter the compositional notably, which is consistent with the previous literature $^{[26]}$. The elements ratio with Cu/(Zn+Sn)=0.86~0.87, and Zn/Sn=1.2~1.3 that deviated from the stoichiometry, is exact in the range that could perform the highest solar cell efficiency $^{[18]}$$^{[27]}$. Also, the ratio of Se/(S+Se) is determined to be 0.67 here. It has been reported that the grain size of pure CZTS is smaller than CZTSe, which means CZTSe has less grain
boundary scattering. At the same time, because the atomic scattering factor for Se is higher than that of S, the CZTSe has a higher atomic scattering ability. Se-rich CZTSSe compounds is verified to optimize these two factors \cite{4}\cite{28}, which can also be obtained by the present surface engineering process.

![XPS spectra of CZTS_e: Na_2S NCs, showing Cu 2p, Zn 2p, Sn 3d, Se 3d and S 2p states.](image)

*Figure 3-4 XPS spectra of CZTS_e: Na_2S NCs, showing Cu 2p, Zn 2p, Sn 3d, Se 3d and S 2p states.*
Figure 3-5. EDS of CZTSe before (a) and after (b) ligand exchange ligand, giving the composition of $\text{Cu}_{1.9}\text{Zn}_{1.2}\text{Sn}_{1.0}\text{S}_{5.0}$ and $\text{Cu}_{2.0}\text{Zn}_{1.3}\text{Sn}_{1.0}(\text{Se}_{0.63}\text{S}_{0.37})_{4.6}$, respectively.

The thin film morphology is studied before and after $\text{S}^2^-$ modification by SEM in Figure 3-6. Thin films of $\text{S}^2^-$ capped CZTSe nanocrystals were prepared by spray-coating nanocrystal solutions (Ethanol) onto glass with ITO, and then annealed at a relative low temperature 350 °C for 30 min. To protect side reaction that relates to metal oxides $^{[31]}$, care was taken to ensure no oxygen remains in the annealing process. Also, in order to prevent the decomposition of CZTSe as suggested by the TGA data, thin film of CZTSe capped with $\text{S}^2^-$ was place under a small glass cover $^{[26]}$. As there is no additional decomposition or related volume contraction for the engineered CZTSe, the fabricated
dense semiconductor thin film could prevent defects like cracking and voids in the annealed process, as can be seen from Figure 3-6. Compare with Figure 3-6(b) and Figure 3-6(d), although both cases show certain growth of the grain size, it is confirmed that the NPs become much more compacted without voids in the vertical directions for the engineered CZTSe thin film. The disappearance of the insulating organic ligands and subsequently carbon point-defect would create a more conductive film.

Figure 3-6 Cross sectional SEM of CZTSe:OLA and CZTSe:Na$_2$S thin film before and after annealing (under 350 °C). (a) CZTSe:OLA before annealing (b) CZTSe:OLA after low temperature annealing (c) CZTSe:Na$_2$S before annealing (d) CZTSe:Na$_2$S after low temperature annealing.
To confirm the crystal structure for the synthesized nano-crystals, we run X-ray diffraction and Raman spectrum on the respective thin film. Figure 3-7(a) shows the XRD diffraction patterns of the as-fabricated and surface engineered nanoparticles-based thin films before annealing, which correspond to CZTSe (JCPDS No.70-8930). To gain further insight into the potential impurities like ZnS and Cu₂SnS₃, Raman spectra of the deposited CZTSe thin film before and after ligand exchange were obtained, as shown in Figure 3-7(b). Both patterns show Raman peaks at 81, 174, 196 and 235 cm⁻¹ that are attributed to $E_{\text{LO}}$ symmetry modes, two minor $A$ modes, the main $A$ mode and $B_{\text{LO}}$ symmetry modes, respectively. This is in great agreement with previous experimental [13] and simulated [32][33] results. Therefore, either XRD or Raman measurement shows detectable secondary phases. Also, XRD and Raman results do not reveal noticeable crystal changes, confirmed that the ligand exchange did not change the structure of CZTSe NPs.
Figure 3-8 XRD of CZTSe:OLA and CZTSe:Na$_2$S thin film after annealing.

Figure 3-8(a) shows the XRD patterns for the annealed CZTSe:OLA and CZTSe:Na$_2$S deposited thin film. After annealing, diffraction peaks become sharper compared with XRD patterns before thermal treatment, suggesting the formation of crystalline quaternary semiconductors. The sharp peaks of the CZTSe:OLA thin films was confirmed to be $2\theta$=27.3°, 45.2° and 53.4°, which corresponds to the diffraction plane (112), (204)/(220) and (312), respectively. On the other hand, Figure 3-8(b) and (c) illustrates the enlargement of $2\theta$ angles around the respective peaks. After annealing, the diffraction peaks of CZTSe:Na$_2$S shift to a higher values of $2\theta$, corresponding to smaller lattice spacing. This is because of the integration of attached S atoms into the original CZTSe, the lattice parameters will decreases as expected. This result suggests that the binding negatively charged S$^{2-}$ ions were attached to CZTSe NC surface. After annealing, reaction between S$^{2-}$ and CZTSe NPs was triggered, which leads to the formation of CZTSSe.
Chemical modification of NPs surface is significantly important to the development of solar materials since the surface ligand has strongly relationship with the electrical communication. In order to get at least relative information about the electrical property, the hole-only device with structure Glass/ITO/CZTSe/MoO₃/Al was fabricated. It was known that the carrier mobility can be exacted from the J-V characteristics through approximation of the space charge limited current (SCLC) \(^{[34]}\) by

\[
J = \frac{9}{8} \varepsilon_0 \mu_0 \exp(0.89 \beta \left(\frac{V}{d}\right)^{1/2}) \left(\frac{V}{d}\right)^2
\]

Where \(\mu_0\) is the carrier mobility, \(V\) the applied voltage, \(d\) the thickness of the film, \(\varepsilon_0\) \((\varepsilon_0 = 8.8541872 \times 10^{-12} \text{ m}^{-1} \text{kg}^{-1} \text{s}^4 \text{A}^{-2})\) the permittivity of free space, \(\varepsilon\) the dielectric constant of CZTSe \((\varepsilon = 8.6 \ ^{[35]}\) which determines \(\beta\) by

\[
\beta = \frac{1}{k_B T} \left(\frac{q^3}{4\pi \varepsilon_0 \varepsilon}\right)^{1/2}
\]

Where \(k_B\) denotes the Boltzmann constant, \(T\) the temperature, \(q\) is the elementary charge.

Since the deposited post-ligand exchanged NPs produce crack-free thin film after annealing, a striking improvement of carrier mobility in CZTSe:Na₂S was achieved up to 8.9 from 4.8 cm²/(Vs) for CZTSe:OLA, suggesting the better transport property of carriers to across from absorber layer to electrode without recombination.

**Conclusion**

A facile and versatile ligand exchange strategy to modify the surface properties of CZTSe NPs by using none-toxic solvent Na₂S was demonstrated. This approach benefits from the combination that Na₂S not only could remove the long ligand but also change the
NPs chemical composition to obtain the desired CZTSSe NPs. A nearly Carbon-free surface CZTSe NPs that can be fully dissolved in hydrophilic media was obtained. It is found out that Na$_2$S (I) has the ability to provide colloidal stabilization of the CZTSe NPs by adhere $S^2-$ to the surface. (II) Could provide facile electronic communication between the NPs and enhance the mobility of CZTSe thin film. (III) Enables NPs being sintered at relatively low temperature while retain the efficient interparticle transport. The developed approach can potentially improve the performance of CZTSe-based photovoltaic.

**Experimental Section**

*General Information:* Copper (II) acetylacetonate (98+ %), Zinc acetylacetonate (98%), Tin (IV) bis (acetylacetonate) dichloride (98%), Selenium powder (99.7%), Oleylamine (OLA, 70%), Trioctylphosphine oxide (TOPO, 99%), Sodium borohydride (NaBH$_4$, 98%) and Sodium sulfide none-hydrate (Na$_2$S, 98%) were used as received.

*Synthesis of CZTSe NPs:* CZTSe NPs were synthesized by hot injection method according to literature $^{[36]}$. The amounts of Cu, Zn, and Sn precursors are chosen to obtain Cu-poor, Sn-rich NCs which have better photovoltaic performance. Generally, 0.7012 mmol of copper(II) acetylacetonate, 0.4321 mmol of zinc acetylacetonate, and 0.375 mmol of tin(IV) bis(acetylacetonate) dibromide are dissolved in 6 ml of oleylamine (OLA) and transferred into a two-neck flask connected to a Schlenk line. After the solution is degassed and purged with argon several times at 135°C, the temperature is raised to 325°C. In another flask, 2.64 mmol Se powder is dissolved in 6 ml OLA and purged with argon for 30 min. Here, Se power is reduced by 1.6 mmol NaBH$_4$ with the assist of ultra-sonication in presence of OLA. At the same time, 20 mmol of TOPO was purged with argon and keep the temperature to be 325°C. The precursor mental mixture and Se dissolved OLA were
injected TOPO simultaneously. The color of the solution turns dark brown immediately and finally black after holding the temperature at 325°C for 5 minutes. After that, the heating mantle was removed to cool down the solution to room temperature where 40 mL methanol is added. The NCs are isolated from the supernatant by centrifugation at 5000 rpm for 5 min, and precipitation is dispersed in 15 mL hexane followed by adding 30 mL methanol and centrifuging to remove residual OLA at least three times. Eventually, NCs are dispersed in 10 mL hexane to form a stable ink.

**Ligand Exchange of CZTSe NPs:** 10 mL (~30 mg/mL) CZTSe NPs dispersion in hexane was combined with 0.55 g Na₂S that is fully dispersive in 45 mL Formamide. The ligand exchange process was performed by vigorously stirring the resulting mixture overnight. All the heterogeneous reaction was carried out under ambient condition. After ligand exchange, the solution was allowed to separate into organic (upper) and inorganic (bottom) layers, as shown in Figure 1. The surface modified NPs were then precipitated by adding 10 mL Isopropanol and centrifuging to remove the supernatant that contains hexane. To purify the NPs and remove the excessive Na⁺, 2 mL deionized water were added to redisperse the NPs. The aqueous media was subsequently sonicated for 3 minutes. This purification process was repeated for at least three times to remove any trace of insoluble materials.

**Thin film Fabricating:** The ligand stabilized CTZSe NCs capped with OLA and S²⁻ are dispersed in 15 mL Hexane and Ethanol respectively. The fabricated inks are then sprayed cast onto ITO substrates (2cm×2cm) at a constant temperature of 150 °C with a spray speed controlled at 1 ml/min. For J-V characterization, 5 nm Molybdenum oxide (MoO₃) and 150
nm Aluminum electrodes were deposited with a 3mm×3mm mask via thermal evaporation at the pressure of $10^{-8}$ Torr.

**Characterizations:** The synthesized NCs and spray coated thin films were analyzed by XRD using Cu Kα radiation (Bruker D2 Phaser) and Raman Spectroscopy. Transmission electron microscope (TEM, FEI Tecnai G2) was used to confirm the unchanged size and shape of the engineered all-inorganic CZTSe NCs. The degree of ligand exchange (presence and absence of the capping ligands) was characterized by Fourier transform infrared (FT-IR, PerkinElmer) spectroscopy and Thermogravimetric analysis (TGA, Q600 SDT thermal analysis machine). TGA was conducted at a heating rate of 5 °C/min under N₂. The element composition was analyzed by energy dispersive X-ray spectroscopy (EDS). Current voltage characteristics were collected using a Keithley 236 source-measurement unit. The morphology and thickness were measured by the Scanning Electron Microscope (JEOL, JSM-6330F).
Reference


Chapter 4 . Ligand-free Cu$_2$ZnSnS$_4$ Derived from Chalcogel for Thermoelectric Application

Ready to submit to Chemical Communication

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I initiated this project, designed the experiments, and took the major role of data collection and manuscript preparation.

Abstract

Cu$_2$ZnSnS$_4$ (CZTS) as an earth-abundant thermoelectric material has also been approved to have potential application in thermoelectric. The typical method of fabricating CZTS and its analogues for thermoelectric application is wet-chemistry synthesis of nanoparticles then subsequent consolidation into nanostructured bulk materials. However, nanoparticles are normally covered by insulating organic ligands which needs removal by hazardous chemical before consolidation. Here, we demonstrated a new method to fabricate CZTS from chalcogel without any organic ligands involved. This chalcogel CZTS needs much lower consolidation temperature and pressure to achieve an improved electrical conductivity without copper-doping. Meanwhile the balanced performance in Seebeck coefficient collectively results in an improved power factor at room temperature comparing with the nanocrystals counterparts.
**Introduction**

Thermoelectric (TE) devices have been widely recognized as a promising technology to transfer waste heat directly into electrical energy. Currently, the most common thermoelectric materials including BiTe-based, PbTe-based, and SiGe-based materials, all consist of expensive or toxic elements which limit the real-life TE application. In the search of low-cost environment-friendly TE materials, Cu$_2$ZnSnS$_4$ (CZTS) has attracted researchers’ attention. CZTS is an earth-abundant, nontoxic p-type wide-band-gap (~1.5 eV) semiconductor with excellent photovoltaic performance\cite{1}. As a quaternary chalcogenide, it has a naturally distorted structure due to the diverse types of interior bonding. This structure can scatter phonons effectively and lead to a low thermal conductivity\cite{2} which enables CZTS to be a potential TE material.

The typical successful method of fabricating CZTS and its analogues for thermoelectric application is wet-chemistry synthesis of nanoparticles then subsequent consolidation into nanostructured bulk materials with hot-press\cite{3} \cite{4} \cite{5} or spark plasma sintering\cite{6}. Though the interfaces of nanoparticles provide efficient energy filtering and phonon scattering to enhance the thermoelectric performance, they also nest insulating organic ligands which obstruct the charge transportation\cite{7}. Therefore, the surface of synthesized nanoparticles must be cleaned before packing. Since the cleaning process always implicates energy consuming treatment\cite{8} or toxic and explosive chemicals\cite{3} \cite{6} \cite{9}, it limits CZTS for wide thermoelectric application.

Chalcogel is a new class of aerogels with three-dimensional random networks and highly accessible nanoscale pores. In this study, we demonstrate that SnS$_4^{4-}$ anions and Cu$^{2+}$, Zn$^{2+}$ cations can crosslink into a large CZTS chalcogel network while all the
unwanted ions from each precursor are dispersed in the interconnected pores and can be easily removed by a solvent (Figure 4-1 A). The ligand-free nature of the obtained CZTS chalcogel allowed us to fabricate a thermoelectric generator without the need to pre-remove surface ligands with hazardous chemicals. We characterized the thermoelectric performance of the CZTS chalcogel and showed a higher power factor compared with reported nanoparticle-based CZTS.

**Result and Discussion**

Figure 4-1 (A) The scheme of synthesizing CZTS chalcogel. Photographs of (B) CZTS wet gel, the inset shows a piece of wet gel placed on a flat surface, (C) CZTS gel after drying and grinding into powders, (D) A plate pressed from dried CZTS gel powder with a hydraulic presser at room temperature
CZTS chalcogel is synthesized by a solution method as schematically illustrated in Figure 4-1(A). In general, the precursor solutions were prepared according to the stoichiometric ratio: Cu(II) acetylacetonate (Cu(AcAc)), Zn acetylacetonate (Zn(AcAc)), and Na₄SnS₄ with a ratio of 2:1:1 were dissolved in formamide separately, then the Cu and Zn precursors were mixed before slowly adding into Na₄SnS₄ solution. Due to the crosslinking between SnS₄⁴⁻ anion and Cu²⁺/Zn²⁺ cations, the viscosity of the mixed solution gradually increased and eventually solidified to a monolithic black jelly-like wet gel with some mechanical strength as shown in Figure 4-1B. For the gelation reaction to succeed in resulting a chalcogel, the precursor should engage in a gradual self-assembly process; therefore Cu(AcAc) and Zn(AcAc) were used to slowly react with anionic thiosaltanate clusters of SnS₄⁴⁻ to form a network rather than precipitates. Other metal precursors with high reactivity, such as acetates or halides of copper and zinc will result in precipitation. After the formation of the gel network, byproduct Na(AcAc) and impurities are soluble and distributed in the accessible pores, they can be removed by a solvent exchange which was carried out by washing the gel with ethanol. After performing this process several times, a pure Cu-Zn-Sn-S network can be obtained. The resulting product is dried in vacuum for 24h, ground into powders, and then pressed into a thin circular plate with a manual hydraulic presser at 10MPa and room temperature (Figure 4-1C-D). The pressed sample has a density about 4.3g/cm³ which is 94% of the theoretical value.
Figure 4-2 Electron micrographs of (A) pressed CZTS plate before annealing, (B)(C) after 350C annealing in nitrogen. (D) Powder X-ray diffraction patterns for dried CZTS gel before and after annealing. (E) Thermogravimetric analysis of dried CZTS gel powders in nitrogen.

The morphology of the obtained CZTS gel plate was examined with scanning electron microscopy (SEM). Figure 4-2A shows that the hydraulic pressed dried gel exhibits the nature of packed nanoparticles (NPs) with monodispersed size around 20nm. After annealing in nitrogen at 350°C for 30 minutes, a condensed material with large grains formed (Figure 4-2B-C). This micrometer-size grain is over 20 times larger than that of the previously reported hot-pressed[3] [4] or spark plasma sintered[6] colloid counterparts even though they were fabricated at a much higher temperature (> 400°C) and pressure (50~60MPa). The improved grain size is due to the ligand-free nature of our CZTS gel.
because it is known that the carbon contents on the surface of CZTS/Se nanoparticles can hinder the growth of grain during annealing\textsuperscript{[10]} \textsuperscript{[11]} \textsuperscript{[12]}. Analysis of the morphology highlights some important points. First, our sample can be processed at relatively lower temperature. In addition to saving energy, a lower temperature can also avoid Sn loss through desorption of SnS at high temperature (\( > 400^\circ C \)), impeding the control of sample composition and morphology\textsuperscript{[13]}. Second, organic ligands contribute to a large portion of the weight in traditional colloid-packed samples. For typical CZTS nanoparticles synthesized with oleylamine as surface ligands, the weight proportion of ligands could be more than 20\%.\textsuperscript{[7]} Volume loss originating from the vaporization of organic ligands demands a simultaneous high pressure and high temperature process which requires expensive equipment and increases the cost of fabrication. However, with our ligand-free CZTS gel, we eliminated the ligands induced volume loss and adapted to a simple two-step fabrication that separates the pressing and annealing procedures while still achieving a condensed morphology. The small volume loss was verified by thermogravimetric analysis showed in Figure 4-2E. Only 5\% weight loss is observed at the annealing temperature (350\(^\circ C\)), and only 6\% at 600\(^\circ C\) which is similar to those surface-cleaned CZTS nanoparticles\textsuperscript{[12]} \textsuperscript{[14]}.

The x-ray diffraction (XRD) pattern of the pressed thin plate as shown in Figure 4-1D can be indexed as pure crystalized Cu\(_2\)ZnSnS\(_4\). However, we found that before annealing the CZTS gel presented an amorphous character. As an evidence, in contrast to the sharp peaks of the annealed sample, the peaks of unannealed sample are broader and less structured. The amorphous structure is due to the formation mechanism of CZTS chalcogel: SnS\(_4^{4-}\) anions and Cu\(^{2+}\)/Zn\(^{2+}\) cations crosslinked at 70\(^\circ C\) in solution with
randomized directions, therefore the formed gel network was not as ordered as crystalized CZTS. But after annealing at 350°C, the gel became highly ordered crystal with sharp XRD peaks. The annealed sample was characterized by EDX, giving the composition of Cu$_{1.4}$Zn$_{0.9}$Sn$_{1.0}$S$_{3.3}$ which deviated from the precursor ratio of Cu:Zn:Sn:S = 2:1:1:4. To explain the nonisometric result, the possible reason besides decomposition during annealing is that solvent exchange process might have extracted some loose bonded ions because the wet gel was not a robust structure and finally resulted a copper and sulfur poor product.

![Figure 4-3](image)

Figure 4-3 (A) Temperature-dependent electrical conductivity and Seebeck coefficient of the CZTS gel plate. (B) Plot of power factor. The inset shows the dimension of the sample, the locations of four probes, and the direction of the temperature gradient used during the TE measurements.

With the growing market of portable and wearable electronics devices, lightweight thermoelectric generators have become a promising power source for said devices. While all previous researches on CZTS and its derivatives were focused on bulk materials in high
temperature region, we decided to explore the potential thermoelectric application of low-volume CZTS thermoelectrics derived from chalcogel in the low to room temperature region. Thermoelectric generator was fabricated by cutting a thin (0.4 mm) rectangular-shape sample from an annealed plate following the dimensions shown in Figure 4-3B. With a temperature gradient applied in the direction of the sample’s long edge, the temperature-dependent electrical conductivity and Seebeck coefficient were measured by the steady four-probe method from 100K to 300K as shown in Figure 4-3A. The Seebeck coefficient \( S \) of the thin sample derived from annealed CZTS chalcogel increased from +159 to +246 \( \mu \text{V/K} \), and the positive values indicate a p-type conduction. The electrical conductivity increased from 2.0 S/m to 46.0 S/m. The electrical conductivity and Seebeck coefficient combined to yield the power factor given by \( \sigma S^2 \) as shown in Figure 4-3B. Table 4-1 compares the room temperature thermoelectric performance between the CZTS chalcogel based sample fabricated in this work and other reported CZTS thermoelectrics. The power factor is 2.78 \( \mu \text{W/mK}^2 \) at room temperature, which is lower than the product synthesized from solid-state reaction with pure element powders but much higher than the nanoparticle-based materials with or without copper-doping. Comparing with the non-doped CZTS NPs, chalcogel CZTS has an elevated electrical conductivity which can be expected from the much larger grain size in our chalcogel-based samples. However, the large grain size also reduces the Seebeck coefficient because the small sized grains can provide vast grain boundaries to scatter the low-energy carriers thereby the average energy per carrier is increased. For the Cu-doped CZTS NPs, though the electrical conductivity is significantly enhanced by increased carrier concentration\(^{[15]}\), it has the typical opposite trend of lower Seebeck coefficient and higher electrical conductivity; thus in combination the power
factor is still low. Though neither $S$ nor $\sigma$ is outstanding in the comparison, the chalcogel CZTS benefits from the balanced performance in both categories to achieve a higher power factor than the NPs counterparts.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S$</th>
<th>$\sigma$</th>
<th>Power Factor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTS (NPs + SPS)</td>
<td>457</td>
<td>2.1</td>
<td>0.42</td>
<td>[6]</td>
</tr>
<tr>
<td>Cu-doped CZTS (NPs + SPS)</td>
<td>66</td>
<td>405</td>
<td>1.76</td>
<td>[6]</td>
</tr>
<tr>
<td>CZTS (Solid-state reaction + SPS)</td>
<td>331</td>
<td>34</td>
<td>3.73</td>
<td>[15]</td>
</tr>
<tr>
<td>Chalcogel CZTS</td>
<td>246</td>
<td>46</td>
<td>2.78</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 4-1 Comparison of room temperature performance (300K) of reported CZTS thermoelectrics and the chalcogel CZTS based device fabricated in this work.

**Conclusion**

To conclude, for the first time we demonstrate that ligand-free CZTS can be derived from chalcogel. Comparing with previously reported NP-based methods, our procedure is performed with much lower temperature and pressure, doesn’t involve any toxic or explosive chemicals, and thereby is more environment friendly. This is also the first report on the thermoelectric properties of chalcogenides made from chalcogel. The annealed CZTS chalcogel showed micrometer grain size and superior power factor compared to the condensed nanoparticle counterparts.

**Experimental Section**

*Synthesis of tin sulfur precursor Na$_4$SnS$_4$·14H$_2$O*: This precursor was prepared according to literature procedures with slight modification$^{[16]}$. An amount of 14.4g (60 mmol) of
Na₂S·9H₂O was dissolved in 50 mL H₂O with stirring. Then, 7.9g (15 mmol) of SnCl₄·5H₂O was dissolved in H₂O and added dropwise to the Na₂S solution with continuous stirring. The solution was kept at 45°C over night before adding into 250 mL methanol and stirring for 5 h. The solution was then stored in a refrigerator for 48 h before the white precipitated crystals were collected by centrifugation and purified by acetone at least three times. The final product was store in vacuum for 24 h before use.

![XRD of as-synthesized Na₄SnS₄·14H₂O](image)

**Figure 4-4 XRD of as-synthesized Na₄SnS₄·14H₂O**

*Synthesis of Cu₂ZnSnS₄ chalcogel:* An amount of 1 mmol of Na₄SnS₄·14H₂O was dissolved in 10 mL formamide. Then 1 mmol of Zn (acetylacetonate) and 2 mmol of Cu(II)(acetylacetonate) were dissolved in 15 mL formamide in a separate vial. The Zn/Cu precursor solution was slowly added into the tin sulfur precursor solution with stirring. A cloudy suspension may appear but would dissolve quickly with vigorous stirring. The precursors were completely dissolved, and the solution was placed in a 70°C sand bath for
3 days or until forming a monolithic wet gel. The remaining solvent was decanted. The gel was then soaked in ethanol and mechanically broken down to form a slurry. After 12 h, the slurry was centrifuged, the supernatant was discarded. This process was repeated for 3 times, then the gel is dried in vacuum for 24 h. The volume of gel reduced dramatically after drying.

*Fabrication of thermoelectric device:* Dried CZTS chalcogel was manually ground into fine black powder with mortar. Then 250 mg powder was pressed into a circular plate with a hydraulic presser with a pressure of 10 MPa for 10 min at room temperature. The plate was then annealed at 350°C in a tube furnace with nitrogen gas for 30 min.

*Thermoelectric characterization:* The thermoelectric properties of the annealed CZTS chalcogel plate were measured on a custom-built apparatus shown in *Figure 4-5*. A typical 4-probe technique was used to measure the electrical conductivity based on the following formula:

\[
\sigma = \frac{1}{R} \cdot \frac{l}{S} \cdot \left(\frac{\ln 2}{\pi}\right)
\]

R is the measured 4 probe resistance, l is the length and S is the cross section of the sample. The standard correction term was introduced due to the finite dimensions of the probes and boundaries of the sample\(^{[17]}\). The Seebeck coefficient was measured by heating one copper block and simultaneously measuring ΔT and the thermoelectric voltage generated. This system was calibrated using a standard constantan sample, including the subtraction of the contribution from the gold-plated voltage probes.
Figure 4-5 Experimental setup for measuring thin film (S) electrical conductivity $\sigma$ and Seebeck coefficient. S is suspended between copper blocks Cu1 and Cu2 mounted to an insulating Teflon stage M. $\sigma$ is measured by a 4-probe method using electrodes $V_+$, $V_-$, $I_+$, $I_-$. Seebeck is measured by heating copper block Cu1 via heater H to create $\Delta T$, and measuring VTE across $V_+$, $V_-$. $\Delta T$ is measured by Si diode thermometers Th and Tc. The whole assembly is inserted into a vacuum chamber via transfer rod R where T can be controlled from 20K to 290K.
Reference


Chapter 5. Fabrication of planar heterojunction Sb$_2$S$_3$ solar cells with 4.2% efficiency via a non-toxic sol-gel route

In preparation to submit to Solar Energy Materials & Solar Cells

Author: Wenxiao Huang, Ismail Borazan, Huihui Huang, Junwei Xu, Wei Zhou, Jiwen Liu, Chang Lu, David L. Carroll

I initiated this project, designed the experiments, and took the major role of data collection and manuscript preparation

Abstract

To replace the conventional chemical bath deposition method which is time-consuming and has a high impurity level, a non-toxic sol-gel deposition method is introduced to fabricate planar heterojunction Sb$_2$S$_3$ solar cell. Combing a specially designed segmented heating schedule during the annealing process, uniform Sb$_2$S$_3$ thin-film is achieved and results efficient photovoltaic devices. The most efficient device exhibits an open-circuit voltage of 0.63 V, a short-circuit current of 13.7 mA/cm$^2$, and a fill factor of 47%, yielding a power conversion efficiency of 4.22% under AM1.5G illumination.
Introduction

As a competitive alternative to silicon-based solar cells, thin-film photovoltaics have advantages of low cost, high efficiency, light weight and flexibility. Varies metal chalcogenides have showed impressive performance as absorbers: Copper indium gallium (CIGS), cadmium telluride (CdTe), and copper zinc tin sulfur (CZTS) have achieved efficiency of 20.4%, 19.6% and 12% respectively. However, the toxicity of Cd and the scarcity of In and Te restrict the mass production of CdTe and CIGS, while the complexity of CZTS as a quaternary material limits the formation of pure-phase CZTS. Therefore, seeking earth-abundant, low-cost, low-toxic materials with simple binary system is a long-standing object for photovoltaic research.

Among all current binary earth-abundant absorbers, antimony chalcogenides such as Sb$_2$S$_3$ and Sb$_2$Se$_3$ hold great potential for high-efficient, low-cost, low-toxicity thin film solar cells. Particularly for Sb$_2$S$_3$, it has a reported direct band gap around 1.7 eV, high absorption coefficient, and high carrier mobility. However, regardless of its potential as an efficient photovoltaic material, the device efficiency remains limited to less than 10% because of impurity phases, deep trap sites, and the dominant energy-loss channel caused by strong electron–phonon interactions.

The most extensively studied and common method for depositing Sb$_2$S$_3$ is chemical bath deposition (CBD). It is utilizing simple equipment and techniques based on an aqueous reaction of SbCl$_3$ and Na$_2$S$_2$O$_3$. However, the experimental parameters are hard to control precisely for generating high-quality film. In another hand, even all the conditions are controlled perfectly, impurities such as Sb$_2$O$_3$, SbOCl, and Sb(OH)$_3$, are inevitably formed. These impure phases may act as deep trap states causing electron/hole
recombination. Recently, atomic layer deposition (ALD) has been reported to achieve a condensed pure-phase Sb$_2$S$_3$ film for high efficient planar solar cell with efficiency of 5.77%. However, even ALD lead to a better performance and reproducibility, its slow growth rate, requirement for sophisticated equipment limit its practical application. Therefore, it is essential to develop alternative techniques for depositing pure-phase Sb$_2$S$_3$ at low-cost is highly desirable for potential mass production.

Recently, a metal-thiourea complex sol-gel method has been reported to fabricate various metal chalcogenide$^{[1]}$ $^{[2]}$. This method can be easily performed by spin-casting metal-thiourea precursor solution onto substrate followed by annealing to achieve a thin-film with high purity. Recently, Choi et al. reported a meso-structured Sb$_2$S$_3$-sensitized solar cell fabricated from SbCl$_3$ – thiourea complex solution and achieved an impressive 6.4% efficiency with PCPDTBT as hole transporting material.$^{[3]}$ However, the viability of such method for fabricating planar heterojunction Sb$_2$S$_3$ solar cells is still unclear. On the contrary to its meso-structured counterpart, a planar heterojunction geometry needs less processing steps, allows easier upscale, and has more defined interfaed for modification due to its simplicity. However, planar structure also results in much less interface area demanding higher film quality of consequently thicker absorber films.

In this report, we demonstrated the fabrication of planar heterojunction Sb$_2$S$_3$ solar cells using a Sb-thiourea sol-gel method. Combined with an optimized segmented annealing process, a uniform micro-structured Sb$_2$S$_3$ thin-film without deep trapping state was achieved. Using this technique, allowed us to fabricate planar Sb$_2$S$_3$ solar cell with a high efficiency of 4.22% under standard AM1.5G.
Result and Discussion

Figure 5-1 Schematic illustration of the fabrication process of planar Sb$_2$S$_3$ solar cell with non-toxic sol-gel route

The fabrication of planar Sb$_2$S$_3$ solar cell from non-toxic sol-gel is schematically illustrated in *Figure 5-1*. In general, the Sb-thiourea sol-gel precursor solution was prepared by dissolving SbCl$_3$ and thiourea in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) or 2-methoxyethanol (MOE) with an optimized ratio of Sb:S = 1:1.75 to guarantee a stoichiometric final product without impurity. Then the precursor was spin-casted onto the FTO substrate coated with a compact TiO$_2$ electron transport layer (ETL), followed by annealing on hotplate at 140°C for 5 minutes until the color of the film turned from colorless to orange. The deposition of sol-gel precursor was repeated to achieve a desired thickness. Then the substrate was place on hotplate to anneal at 340°C for 10 – 15 minutes. When the temperature was increasing, the color of the Sb$_2$S$_3$ film started to darken,
and turned black around 240°C. After annealing, a layer of Poly(3-hexylthiophene-2,5-diyl) (P3HT) was spin-casted to form the hole transporting layer (HTL) prior to evaporating a 150nm thick silver as top electrodes.

Figure 5-2 SEM image of the Sb$_2$S$_3$ film casted on TiO$_2$ layer (A) annealed at 140°C and (B) 340°C, (Inset) EDX measurement of the annealed film. Scale bars = 1µm, the inset pictures showed the photographs of corresponding films. (C) TGA and heat flow of dried Sb$_2$S$_3$ sol-gel precursor. (D) Tauc plot of 340°C annealed film. (E) XRD patterns of the Sb$_2$S$_3$ film and standard pattern (ICSD-99794) is included for reference. (F) XPS Sb 3d spectra of Sb$_2$S$_3$ obtained from sol-gel process

The properties including morphology, band gap, lattice structure and chemical state of fabricated Sb$_2$S$_3$ film were studied by scanning electron microscopy (SEM), Uv-vis absorption spectra, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) respectively (Figure 5-2). The morphology of the Sb$_2$S$_3$ film during different annealing stages is shown in Figure 5-2AB. After first annealing at 140°C (Figure 5-2A), clusters of
amorphous Sb$_2$S$_3$ formed, presenting an orange color$^{[4]}$. Those clusters aggregated and expanded after second annealing at 340°C, transformed into crystallized Sb$_2$S$_3$ islands with strong absorption in visible light range (Figure 5-2B). Due to the lattice mismatch induced dewetting, this island-like morphology is very common and extensively reported for Sb$_2$S$_3$ films growing on TiO$_2$ substrate$^{[4]}$ $^{[5]}$ $^{[6]}$. The annealing procedure was optimized according to the thermal gravimetric analysis (TGA) of dried sol-gel precursor. As shown in Figure 5-2C, the thermal decomposition reaction of the precursor started around 200°C and the weight% decreased gradually to 40% when the temperature reached 340°C which was picked as the final annealing temperature for our Sb$_2$S$_3$ film. Also, the heat flow curve has a deep valley around 250°C indicating the crystallization of Sb$_2$S$_3$ which agrees with our observation of the color change during annealing. It’s noteworthy that the crystallization happens in the region of rapid weight decreasing, which has significant impact to the film morphology and therefore the performance of planar structured solar cells. We found that if the temperature increased too fast in the second annealing, macroscopic inhomogeneity could be observed by eyes on the crystalized Sb$_2$S$_3$ film. Therefore, to obtain a uniform film, in the second annealing either a low temperature ramping rate (< 2°C/min) or a segmented annealing method should be adopted. In a segmented annealing, the hotplate is held at 240°C for 5 min or until the film turned black before the temperature is increased to 340°C.

With this segmented annealing method, highly reproducible homogenous films can be achieved and the influence of ramping rate is negligible. The chemical composition of the final product was determined to be Sb$_2$S$_{3.03}$ by EDX (Energy-dispersive X-ray spectroscopy), and the optical band gap was calculated as 1.75 eV (Figure 5-2D) which is
similar to reported values. The XRD pattern of the film in Figure 5-2E confirmed a phase-pure, orthorhombic Sb$_2$S$_3$ film and no other phases were produced in the reaction. One of the major drawbacks of CBD Sb$_2$S$_3$ film is that the formation of Sb$_2$O$_3$ is inevitable. Sb$_2$O$_3$ as an impurity, it has a conducting band minimum locating within the band gap of Sb$_2$S$_3$ causing exciton recombination. To check the impurity of sol-gel derived Sb$_2$S$_3$, XPS measurement was conducted on the surface of Sb$_2$S$_3$ thin-film deposited on the compact TiO$_2$ layer. As shown in Figure 5-2F, very narrow peaks for Sb 3d orbit is observed. Different chemical states of Sb are analyzed by deconvolution of the XPS peaks and it shows very small amount of Sb$_2$O$_3$ phase. In contrast, normally Sb$_2$O$_3$ phase consists more than 50% of the surface states of CBD Sb$_2$S$_3$ thin film$^{[7]}$ $^{[8]}$.

Figure 5-3 (A) J-V curve of the planar Sb$_2$S$_3$ solar cells with different layers of Sb$_2$S$_3$. (B) The dependence between Sb$_2$S$_3$ film thickness and the number of layers

To optimize the thickness of the Sb$_2$S$_3$ layer for the solar cells, devices with different layers of Sb$_2$S$_3$ were fabricated. The thickness of the Sb$_2$S$_3$ grew linearly along with the number of depositions, and for each layer the Sb$_2$S$_3$ thickness is estimated to be
107nm (Figure 5-3B). The J-V curves of the fabricated devices were measured under an illumination of 100 mW/cm² (Figure 5-3A), and the photovoltaic parameters are summarized in Table 5-1. As we can see, the total power conversion efficiency (PCE) increases when the number of Sb₂S₃ layers increased from 1 to 2, then dramatically dropped when the thickness further increased, therefore the prime number of Sb₂S₃ depositions is 2 corresponding to a thickness around 200 nm. This result agrees with the estimated carrier diffusion length of Sb₂S₃ thin film (180±60 nm)[9]. When the film thickness is equal or less than diffusion length, excitons can be extracted efficiently, therefore devices with 1 and 2 Sb₂S₃ layers both have decent performance, and the device with thicker film has better efficiency due to the improved photon absorption. However, when the number of Sb₂S₃ layers is 3 or above, then the film has a thickness greater than 300 nm which is beyond the carrier diffusion length, therefore the exciton recombination increases and causes deteriorated Voc and Jsc due to the insufficient charge extraction.

Table 5-1 Summary of the device performance for planar Sb₂S₃ solar cell with different thickness of Sb₂S₃ layer

<table>
<thead>
<tr>
<th>Sb₂S₃ layers</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.53</td>
<td>8.93</td>
<td>38.9</td>
<td>1.82</td>
</tr>
<tr>
<td>2</td>
<td>0.47</td>
<td>11.35</td>
<td>39.5</td>
<td>2.11</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>4.49</td>
<td>42.7</td>
<td>0.88</td>
</tr>
</tbody>
</table>
The performance of the device was further improved by fine-tuning the fabrication parameters. The champion device was fabricated under the conditions of 80 nm thick compact TiO$_2$, 2 layers of Sb$_2$S$_3$ with a total thickness ~ 200 nm, and P3HT HTL deposited from a 15mg/mL solution. The photocurrent density – voltage (J-V) curve of the champion device is presented in Figure 5-4. The champion device has a Voc of 0.63V, FF of 48%, Jsc of 13.7 mA/cm$^2$, and in combination a PCE of 4.22%. The average PCE is 3.23±0.45% calculated from 27 devices fabricated in 3 batches, and the PCE distribution is shown in Figure 5-4B. The performance of the champion device is also compared with the best planar heterojunction Sb$_2$S$_3$ solar cells to-date in Table 5-2. Though the efficiency of our sol-gel processed device is still lower than that of the ALD processed counterpart, it presented the highest efficiency in the solution processed category, demonstrating the sol-gel route is a competitive approach towards high efficiency planar heterojunction Sb$_2$S$_3$ solar cell.
Figure 5-4 (A) J-V curve of the champion device. The inset chart summarized the photovoltaic performances. (B) PCE distribution of 26 devices fabricated with optimal parameters.

Table 5-2 Comparison of power conversion efficiency (PCE) of best reported planar structured Sb2S3 solar cells with P3HT HTL to our device

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Method</th>
<th>Device Structure</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5]</td>
<td>CBD</td>
<td>TiO2/Sb2S3/P3HT/Ag</td>
<td>4.06%</td>
</tr>
<tr>
<td>[7]</td>
<td>ALD</td>
<td>TiO2/ALD-Sb2S3/P3HT/Au</td>
<td>5.77%</td>
</tr>
<tr>
<td>[10]</td>
<td>CBD</td>
<td>SnO2/Sb2S3/P3HT/Au</td>
<td>2.49%</td>
</tr>
<tr>
<td>[11]</td>
<td>CBD</td>
<td>TiO2/Sb2S3/CuSCN/Au</td>
<td>2.50%</td>
</tr>
<tr>
<td>This Work</td>
<td>Sol-gel</td>
<td>TiO2/Sb2S3/P3HT/Ag</td>
<td>4.22%</td>
</tr>
</tbody>
</table>

Conclusion

In conclusion, we demonstrated a simple Sb-thiourea sol-gel method for fabrication of planar heterojunction Sb2S3 solar cell. Using this method combined with an optimized
segmented annealing technique, we successfully deposited Sb$_2$S$_3$ thin-film without impurity. The most efficient device we obtained via this approach exhibited a high efficiency of 4.22% measured under AM 1.5G condition.

**Experimental Section**

*Substrate preparation:* The FTO coated glass substrates were purchased from Sigma-Aldrich with sheet resistance of 13 $\Omega$/sq. The substrate was cleaned with acetone, methanol, and isopropanol in sonication for 15 min successively, then O$_2$ plasma treated for 15 min. The compact TiO$_2$ layer was prepared by spin-casting a solution of 15% w.t. of titanium butoxide polymer in 1-butanol at 3000 rpm for 40 seconds, followed by sintering on a hot plate at 500°C for 30 min.

*Sb$_2$S$_3$ film deposition:* Sb$_2$S$_3$ film was deposited by spin-casting Sb-thiourea complex solution. 1.2 mmol SbCl$_3$ and 2.1 mmol of thiourea were dissolved in 1 ml dimethylformamide (DMF) and stirred for 1 h then filtered with 0.45 $\mu$m syringe filter. 150 $\mu$L of the solution was spin-coated on to the 1 by 1 inch substrate with 3000 rpm for 60 s and then annealed at 140°C for 5 min or until the color of film turned orange in a N$_2$ filled glovebox. This processed was repeated to achieve a desired thickness. After the last 140°C annealing, the temperature of hotplate was increased to 240°C then kept for 5 min or until the color of Sb$_2$S$_3$ film turned black, followed by annealing at 340°C for another 10 - 15 min.

*Solar Cell Fabrication:* For the fabrication of devices, the hole-transporting layer was deposited on the top of Sb$_2$S$_3$ layer by spin-casting a solution with 15mg/mL poly(3-hexylthiophene-2,5-diyl) (P3HT) in chlorobenzene, at 2000 rpm for 60 s in glovebox followed by annealing on hotplate at 140°C for 5 min. Then Ag (100 nm) was evaporated
on top of P3HT layer as top electrode.

*Solar Cell Testing:* For measuring the performance of the solar cells, simulated AM 1.5 sunlight was generated with a class AAB solar simulator. It was calibrated to 100 mW cm$^{-2}$ irradiance. The solar cells were sealed in a plastic box with only the light incident face exposed to ensure no light can enter the device from the side. The solar cells were also masked with a metal aperture defining the active area of 4 mm$^2$. The IPCE spectrum were measured using a power source (Newport 300 W Xenon lamp, 66920) with a monochromator (Newport Cornerstone 260) and a multimeter (Keithley 2001).
Reference


Chapter 6. Efficient Solution-processed Planar Sb$_2$S$_2$ Solar Cell via Multifunctional Interface Engineering

In preparation to submit to *Advanced Functional Materials*

Author: Wenxiao Huang, Junwei Xu, Bing Han, Huihui Huang, Linqi Shao, David L. Carroll

*I initiated this project, designed the experiments, took the major role in collecting all the data and preparing the manuscript.*

**Abstract**

Compared with meso-structured architecture, a planar heterojunction solar cell has less interfaces for carrier recombination, more defined layers for easy optimization, and allows simplified fabrication procedures. However, despite the advantages provided by planar heterojunction, the efficiency of planar Sb$_2$S$_3$ solar cell has lagged significantly compared with its meso-structured counterparts. Planar devices suffer from island-like morphology of the Sb$_2$S$_3$ layer resulting from the dewetting, creating contact between hole- and electron-transporting layers, leading to a decreased open-circuit voltage and fill factor. Here we demonstrate a simple solution method to introduce a self-assembled layer of small molecule tert-Butylthiol (tBt) to the exposed surface of electron transporting layer to block the leaking current by shutting off the shunt path. We also discovered that tBt hindered carrier recombination by passivating the surface trapping states of Sb$_2$S$_3$. Combining with the improved interaction between Sb$_2$S$_3$ and hole transporting layer, all parameters including open-circuit voltage, short-circuit current, and fill factor are improved. Using this multifunctional interface engineering technique, we achieved a record-breaking efficiency of 5.3% for solution processed planar heterojunction Sb$_2$S$_3$ solar cell.
Introduction

Thin-film solar cells based on inorganic absorbers permit high efficiency and stability. Among all those absorber candidates, van der Waals material Sb₂S₃ has attracted extensive attention because of its suitable band gap (1.2eV ~ 1.7 eV), strong optical absorption\([1]\), a high dielectric constant for frequencies in the visible range, non-toxic, low-cost and earth-abundant constituents, and the ability to inhibit dangling bonds at grain boundary\([2]\). Currently state-of-art Sb₂S₃ solar cells adopt the structure of solid-state dye-sensitized solar cell: absorber layer deposited on mesostructured TiO₂ electron transport layer in combination with organic hole transport layer (HTL) on top. However, it is challenging to fill the nanostructured TiO₂ layer with Sb₂S₃ and subsequently by hole transport materials (HTM). Incomplete coverage could lead to tri-phase interfaces acting as charge recombination centers.

In contrast, a planar heterojunction cell has simplified structure requiring less steps to fabricate, is easier to upscale, and potentially has a higher open circuit voltage because of the reduced interface carrier recombination. Also, a planar structure has more defined layers and interfaces, which is a prerequisite for separated optimization of individual layers of solar cell. For the fast developing of lead halides perovskite solar cell, planar heterojunction devices have already been shown to have similar or superior performance comparing with their mesostructured counterparts.\([3]\) For planar Sb₂S₃ solar cell, the highest efficiency of 4.06% in solution processed device was reported by Zimmermann et.al.\([4]\). However, this performance is much lower than the state-of-art solution processed mesostructured devices which have already achieved an efficiency over 6% \([5]\ [6]\ [7]\). Recently, Kim et.al. fabricated highly reproducible and efficient planar Sb₂S₃-based
devices with atomic layer deposition (ALD), to achieve an efficiency up to 5.77%,[8] but the high cost and low fabrication speed of ALD makes it not viable for industrialization. Therefore, high efficient planar devices should be realized by a low-cost solution-based process.

The deficient performance of solution processed planar Sb$_2$S$_3$ solar cell is majorly originated from the morphology of Sb$_2$S$_3$ layer. Since planar devices have well defined layers and interfaces, the film morphology is essential. Due to the lattice mismatch between TiO$_2$ and Sb$_2$S$_3$, the reported Sb$_2$S$_3$ films produced by different methods including CBD,[4] hydrazine-based deposition[9], recently reported in situ solid-gas reaction,[7] and our sol-gel deposition, all exhibit dewetting issue that rather than forming continuous film without pin holes, it develops separated Sb$_2$S$_3$ islands and leaves uncovered TiO$_2$ domains. The exposed TiO$_2$ surface allows HTL to directly contacts with TiO$_2$ electron transporting layer (ETL). This contact decreases the shunt resistance ($R_{sh}$) by creating a path for the leaking current. It’s known that reduced $R_{sh}$ will decrease fill factor (FF) and open-circuit voltage (Voc) thus the efficiency of the solar cell decreases. Though this island morphology impaired the photovoltaic performance, the complete transparent region between islands enable the potential application for neutral color semitransparent solar cell which are commercially desired for integrating solar cells into windows. [10]

As such, we demonstrate a simple wet-chemical technique to introduce a self-assembled tert-Butylthiol (tBt) electrical blocking layer onto the exposed TiO$_2$ surface to shut off the shunt path, therefore both Voc and FF are simultaneously increased. In addition, X-ray photoelectron spectroscopy (XPS) revealed that tBt also passivated trapping states of Sb$_2$S$_3$/HTL interface, depressed the exciton recombination, promoted charge transfer,
and therefore increased the short-circuit current Jsc. In combination, by introducing tBt as a multifunctional modifier we present a planar Sb$_2$S$_3$ solar cell with a 5.3% efficiency which is the highest of solution processed planar devices to-date and comparable to state-of-the-art mesostructured devices.

**Result and Discussion**

![Figure 6-1](image)

Figure 6-1 (A) AFM image representing the morphology of Sb$_2$S$_3$ thin film on top of TiO$_2$. (B) Roughness profile of the Sb$_2$S$_3$ thin film. (C) SEM image of the cross section of a planar Sb$_2$S$_3$ solar cell device. (D) Structure of tert-Butylthiol molecule used for interface modification. (E) Sketch of a planar Sb$_2$S$_3$ solar cell with self-assembled tBt blocking layer between Sb$_2$S$_3$ islands.

Sb$_2$S$_3$ layer was fabricated by spin-cast Sb-thiourea sol-gel solution onto compact TiO$_2$ layer followed by annealing in N$_2$ filled glovebox for 10 min at 340°C. The morphology of as synthesized Sb$_2$S$_3$ film was first examined by atomic force microscopy (AFM) as shown in Figure 6-1A. The Sb$_2$S$_3$ islands with gaps between them can be clearly
seen. The surface roughness profile was extracted from the AFM image to estimate the dimension of the islands and gaps (Figure 6-1B). The size of an individual Sb$_2$S$_3$ domain is measured to be several hundred nanometers while the spacing is about 160nm. For better exciton extraction, the thickness of the Sb$_2$S$_3$ layer was kept around 200 nm, which is in the range of the carrier diffusion length (120 ~ 240 nm). [11] A full planar device has a structure of Glass/FTO/TiO$_2$/Sb$_2$S$_3$/poly(3-hexylthiophene-2,5-diyl) (P3HT)/Ag as shown in Figure 6-1E and a scanning electron microscopy (SEM) image of the cross section of a full device is shown in Figure 6-1C. The cross section showed that a layer of P3HT coats the islands of Sb$_2$S$_3$ while infiltrating the gaps between them creating shunt paths. To shut off the shunt path, commercially available small molecule tert-Butylthiol (tBt) was employed as a surface modifier by dissolving in tBt in 1-butanol with an optimized concentration of 2%v.v followed by spin-casting to the surface of Sb$_2$S$_3$ layer prior to the deposition of P3HT as HTL. Due to the strong bonding between the thiol group and Ti, a self-assembled electron blocking layer was formed by tBt on the exposed TiO$_2$ interfaces between the Sb$_2$S$_3$ domains as shown in Figure 6-1E.

The photovoltaic performances of planar Sb$_2$S$_3$ solar cells before and after applying tBt modification were measured under illumination with a light intensity of 100 mW cm$^{-2}$. The corresponding parameters of the champion device are shown in Figure 6-2, and the statistical performance is summarized in
Table 6-1. As expected, the fill factor and shunt resistance of the champion device increased dramatically from 47% to 56% and 129 Ω cm$^2$ to 459 Ω cm$^2$ respectively while Voc and Jsc slightly improved for about 5%. In combination, the overall power conversion efficiency was significantly increased for 3.3% to 5.3%, which is the highest for solution-processed planar devices to our best knowledge. From the incident-photon-to-current-efficiency (IPCE) spectrum of Figure 6-2B, the integrated Jsc is 14.7 mA/cm$^2$ which agrees well with that measured by the J-V curve. Those improvements can also be observed in
Table 6-1. It’s noteworthy that the tBt-Sb$_2$S$_3$ devices have an average PCE of 4.0% which is already similar to the highest efficiency of reported solution-processed device.\textsuperscript{[4]}

Figure 6-2 Photovoltaic performances of the champion devices in both tBt-modified and non-modified categories. (A) The J-V characteristics with parameters summarized in inset chart. (B) IPCE spectrum of the champion tBt-Sb$_2$S$_3$ planar device.
Table 6-1 Average photovoltaic performances of tBt-modified and non-modified devices

<table>
<thead>
<tr>
<th>No. of Devices</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBt</td>
<td>45</td>
<td>0.63±0.03</td>
<td>12.9±1.2</td>
<td>0.49±0.04</td>
</tr>
<tr>
<td>pristine</td>
<td>25</td>
<td>0.60±0.03</td>
<td>12.3±1.6</td>
<td>0.44±0.02</td>
</tr>
</tbody>
</table>

To elucidate the mechanisms behind the improvement, we investigated the effects of tBt modification. First, we utilized Fourier transform infrared spectroscopy (FT-IR) to verify the attachment of tBt on the TiO₂ surface. A thin-film of TiO₂ was deposited on glass substrate prior to performing the tBt treatment. Before the FT-IR measurement, the samples were rinsed with 1-butanol then stored in vacuum at 60°C for 12 hours to eliminate the influence of loosely attached molecules. We showed that in Figure 6-3A, the stretch vibration peaks associated with C-H group could be observed within the 2850 cm⁻¹ – 2950 cm⁻¹ range on modified TiO₂ sample, suggesting that tBt successfully bond to the exposed TiO₂ surface. The current-voltage (I-V) characteristics before and after applying tBt treatment to the TiO₂ surface were measured to assure the insulating effect of tBt blocking layer. Two simple sandwich-structured devices were fabricated by stacking treated or non-treated TiO₂ layer between FTO and silver electrodes as shown in Figure 6-3B. To eliminate variation in resistance induced by thickness of TiO₂, those two devices were fabricated from the same chip by cutting it into two devices after TiO₂ deposition. It is clear that the self-assembled tBt layer effectively blocked the charges so that the current flow through a tBt modified TiO₂ is smaller than the pristine one. Meanwhile, for Figure 6-3A
we must notice that tBt molecules bonded to the surface of Sb₂S₃ islands as well, so a thin barrier layer was also created at the interface of Sb₂S₃ and P3HT hindering the charge extraction which contradicted with our improved Jsc.

Figure 6-3 (A) FT-IR of tBt treated TiO₂, Sb₂S₃ films and a non-treated control sample with both Sb₂S₃ and TiO₂. (B) The I-V characteristic of TiO₂ thin film with and without tBt modification

To understand this paradox, the surface states of Sb₂S₃ before and after tBt modification were investigated by X-ray photoelectron spectroscopy (XPS) without plasma etching. Figure 6-4AB shows the XPS spectra of Sb 3d peaks. The deconvolution shows two chemical states representing Sb₂S₃ and Sb₂O₃. The spectrum indicates the existence of Sb₂O₃ at the surface of Sb₂S₃ layer in both pristine and treated samples. Even Sb-thiourea complex solution used to fabricate those films was believed to produce Sb₂S₃ thin-film with high purity, however, in a nanoscale system there exist vast grain boundaries nesting dangling bonds, which makes the surface of film vulnerable to oxidization. Sb₂O₃ is harmful to the device’s performance⁶⁸ by forming deep trapping states: its conduction
band sitting in the band gap of Sb$_2$S$_3$, and the excitons will be trapped in those deep states, causing recombination, before being collected by ETL. Also, the wide band gap of Sb$_2$O$_3$ creates energy barrier, deteriorating the hole extraction at Sb$_2$S$_3$/P3HT interfaces (Figure 6-4C). By integrating the peaks in XPS spectrum, we estimated the concentration of Sb$_2$O$_3$ phase. Before tBt treatment, Sb$_2$O$_3$ consisted 33% of the film, and it decreased to 14% after the modification. Therefore, tBt modification reduced the interface trapping states by passivate the Sb$_2$O$_3$ phase. Furthermore, the increased Sb$_2$S$_3$ component at the interface may provide a better connection to the P3HT because the neighboring thiophene moieties can chelate with Sb$_2$S$_3$ by breaking the weak van der Waals Sb-S bonds.$^{[12]}$ The water contact angle of the TiO$_2$/Sb$_2$S$_3$ surface is also measured, showing that a more hydrophobic surface was generated by tBt due to its claw-like alkyl chain (Figure 6-4). Considering the non-polar nature of P3HT molecule, a hydrophobic surface will promote the adhesion between P3HT and Sb$_2$S$_3$ therefore may enhance the charge transportation. Another possible source of the improved Jsc could be the band bending induced by surface dipoles because tBt as an electron donor can elevate the HOMO/LUMO at the surface of metal chalcogenides without affecting the band gap.$^{[13]}$ This effect can be expected in Sb$_2$S$_3$ as well, and the elevated energy level creates surface dipoles at the Sb$_2$S$_3$/P3HT interface, promoting hole extraction while inhibiting electron transferring backwards into HTL. As a tradeoff, though tBt attaching to the Sb$_2$S$_3$ surface creating an energy barrier deteriorate the charge transfer, it also reduced the carrier recombination, improved the Sb$_2$S$_3$/P3HT interaction, and possibly enhanced the carrier extraction via surface dipoles. In combination, it improved Jsc along with Voc and FF.
Figure 6-4 XPS spectra of Sb 3d in (A) primitive Sb$_2$S$_3$ and (B) tBt-modified Sb$_2$S$_3$. (C) the flat band-diagram of planar Sb$_2$S$_3$ solar cell with Sb$_2$O$_3$ impurities at the interface creating deep trapping states and blocking hole transportation. (D) Water contacting angle of primitive and tBt-modified Sb$_2$S$_3$ surface.
Table 6-2 Comparison of power conversion efficiency (PCE) of best reported meso- and planar structured Sb$_2$S$_3$ solar cells with P3HT as HTM to our tBt treated devices.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Type</th>
<th>Device Structure</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>[4]</td>
<td>Planar</td>
<td>TiO$_2$/Sb$_2$S$_3$/P3HT/Ag</td>
<td>4.1%</td>
</tr>
<tr>
<td>[8]</td>
<td>Planar</td>
<td>TiO$_2$/ALD-Sb$_2$S$_3$/P3HT/Au</td>
<td>5.8%</td>
</tr>
<tr>
<td>[14]</td>
<td>Planar</td>
<td>SnO$_2$/Sb$_2$S$_3$/P3HT/Au</td>
<td>2.5%</td>
</tr>
<tr>
<td>[15]</td>
<td>Planar</td>
<td>TiO$_2$/Sb$_2$S$_3$/CuSCN/Au</td>
<td>2.5%</td>
</tr>
<tr>
<td>This Work</td>
<td>Planar</td>
<td>TiO$_2$/Sb$_2$S$_3$/P3HT/Ag</td>
<td>5.3%</td>
</tr>
</tbody>
</table>

**Conclusion**

In summary, we demonstrated an efficiency enhancement by introducing small molecule tBt as a multifunctional surface modifier to Sb$_2$S$_3$ film on TiO$_2$ substrates. In this treatment, tBt bonded to exposed TiO$_2$ domains creating a self-assembled charge blocking layer thus improved Rsh, Voc, and FF. In addition, tBt also passivated the trapping states on the Sb$_2$S$_3$/P3HT interface, provided a better interaction at the interface, then boosted the charge extraction. We have achieved a remarkable 5.3% PCE for solution processed planar Sb2S3 solar cell which represents the highest efficiency to-date, and comparable to the best mesostructured device (
Table 6-2). This low-cost and easily scalable interface treatment paved the way toward a high efficiency planar Sb$_2$S$_3$ solar cell.
Reference


Curriculum Vitae

Wenxiao Huang

EDUCATION

2010 - 2017  
**Wake Forest University**, Winston Salem, NC  
*Ph.D. in Physics, M.S. in Computer Science*

2005 - 2009  
**University of Science and Technology of China**, Hefei, China  
*B.S. in Applied Physics*

RESEARCH

2010 - 2017  
**Ph.D. Researcher**  
**Wake Forest University**, Winston Salem, NC, USA

- **Nanoscale System and Interfaces**
  - Modeled the carrier transportation characters within an organic-inorganic complex. Based on the model, improved the carrier mobility of Cu$_2$ZnSnS$_4$ (CZTS) nanocrystal thin-film by 21 folds via interface modification
  - Invented a method to utilize inorganic ions as surface ligand and in-situ dopant for nanocrystals, decreased the fabrication temperature of CZTS thin-film from traditional 540°C to 350°C while avoid involving toxic chalcogenide gases
  - Synthesized ligand-free CZTS from chalcogel for thermoelectrics

- **Photovoltaic**
  - Designed a solution-based technique to build planar heterojunction Sb$_2$S$_3$ solar cell, achieved an efficiency 30% higher than that of the best previously reported device
  - Designed an algorithm to optimize the grading profile for graded bandgap solar cell
  - Developed a hardware/software platform to automatically collect, process and visualize solar cell measurement data

- **Perovskite LED**
  - Synthesized color tunable 2-D organometallic perovskite nanoplate
  - Built OLED based on inorganic perovskite active layer
  - Discovered giant oscillator strength in cesium-lead-bromide perovskite, expanded the understanding of quantum confinement and bright luminescence of inorganic perovskites

2009 - 2010  
**Research Assistant**  
**National Center for Nanoscience Nanotechnology**, Beijing, China

- Synthesized varies metal and semiconductor nanoparticles
- Utilized electron microscopy and spectroscopy to study the self-assembly dynamics of various nanostructures
SKILLS

- **Materials Characterization**: XPS, XRD, TGA, FT-IR, SEM, TEM, AFM
- **Thin-Film Deposition**: Sputtering, Thermal Evaporating, Spin-Casting, Blade-Casting
- **Device Fabrication**: Thin-film Solar Cell, LED/OLED
- **Programming**: Python (with Numpy, Pandas, Matplotlib), Java, C, MySQL, PHP, LabVIEW, MATLAB
- **3D Modeling**: Blender, SketchUp

SELECTED PUBLICATIONS & PATENT


Wenxiao Huang, D. R. Onken, Y. Li, C. Hewitt, D. L. Carroll. Ligand-free Cu$_2$ZnSnS$_4$ Derived from Chalcogel for Thermoelectric Application. *Ready to submit*

Wenxiao Huang, I. Borazan, H. Huang, J. Xu, C. Lu, D. L. Carroll. Fabrication of planar heterojunction Sb$_2$S$_3$ solar cells with 4.2% efficiency via a non-toxic sol-gel. route. *In preparation*

Wenxiao Huang, J. Xu, B. Han, H. Huang, L. Shao, D. L. Carroll. Efficient Solution-processed Planar Sb$_2$S$_3$ Solar Cell via Multifunctional Interface Engineering. *In preparation*

C Dun, Wenxiao Huang, H Huang, J Xu, N Zhou, Y Zheng, H Tsai, W Nie, etc. Hydrazine-free Surface Modification of CZTSe Nanocrystals with All-Inorganic Ligand. *The Journal of Physical Chemistry C 118.51(2014), 30302-30308*


