SYNTHESIS AND LIGAND ENGINEERING OF COLLOIDAL METAL CHALCOGENIDE NANOPARTICLES FOR SCALABLE SOLUTION PROCESSED PHOTOVOLTAICS

by

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Abstract

As global population continue to rise, the demand for energy is slated to increase substantially. To combat climate change, large amounts of renewable energy will be needed to feed this growing demand. Of renewable energy sources, photovoltaics are well positioned to meet this increasing demand due to the immense abundance of solar energy incident on earth. However, existing energy intensive, low throughput, and costly manufacturing techniques for photovoltaics may pose a barrier to continued large scale implementation.

Solution processing has emerged as a promising photovoltaics fabrication technique with high throughput, high materials utilization, and lower cost than existing vacuum-based methods. Thin film photovoltaic materials such as $Cu(In,Ga)(S,Se)_2$ and CdTe have both been fabricated using various solution processing methods. Of the various solution processing routes, colloidal metal chalcogenide nanoparticles have demonstrated promise as a hydrazine-free route for the solution processing of high efficiency $Cu(In,Ga)(S,Se)_2$ solar cells. However, conventional solution processing with colloidal nanoparticles has long suffered from anionic and carbonaceous impurities, stemming from legacy synthesis methods. The work in this dissertation aims to solve these issues through the development of novel synthetic methods, ligand engineering, and ultimately improved scalability through slot-die coating.

Typical colloidal syntheses rely on the use of metal salts as precursors such as metal halides, nitrates, acetates, and so forth, where the anions may incorporate and alter the electrical properties of the targeted nanomaterials. In this work, the recent advances in amine-thiol chemistry and its unique ability to solubilize many metal containing species are expanded upon. Alkylammonium metal thiolate species are easily formed upon addition of monoamine and dithiol to elemental Cu, In, Ga, Sn, Zn, Se, or metal chalcogenides such as Cu_2S and Ag_2S. These species were then used directly for the synthesis of colloidal nanoparticles without the need for any additional purification. The metal thiolate thermal decomposition pathway was studied, verifying that only metal chalcogenides and volatile byproducts are formed, providing a flexible route to compositionally uniform, phase pure, and anionic impurity-free colloidal nanoparticles including successful syntheses of In_2S_3, $(In_xGa_{1-x})_2S_3$, $CuInS_2$, $CuIn(S_xSe_{1-x})_2$, $Cu(In_xGa_{1-x})S_2$, Cu_2ZnSnS_4, and $AgInS_2$.

However, further impurities from deleterious carbonaceous residues originating from long chain native ligands were still a persistent problem. This impurity carbon has been observed to hinder grain formation during selenization and leave a discrete residue layer between the absorber layer and the back contact. An exhaustive hybrid organic/inorganic ligand exchange was developed in this work to remove tightly bound oleyalmine ligands through a combination of microwave-assisted solvothermal pyridine ligand stripping followed by inorganic capping with diammonium sulfide, yielding greater than 98% removal of native ligands via a rapid process. Despite the aggressive ligand removal, the nanoparticle stoichiometry remained largely unaffected when making use of the hybrid ligand exchange. Scalable blade coating of the ligand exchanged nanoparticle inks from non-toxic dimethyl sulfoxide inks yielded remarkably smooth and crack free films with RMS roughness less than 7 nm. Selenization of ligand exchanged nanoparticle films afforded substantially improved grain growth as compared to conventional non-ligand exchanged methods yielding an absolute improvement in device efficiency of 2.8%. Hybrid ligand exchange nanoparticle-based devices reached total-area power conversion efficiencies of 12.0%.

While extremely effective in ligand removal, ligand exchange pathways increase process complexity and solvent usage substantially, which may limit the cost advantage solution processing aims to provide. Further synthesis improvement was developed through a ligand exchange free, direct sulfide capped strategy. Using sulfolane as a benign solvent, $CuInS_2$ nanoparticles with thermally degradable thioacetamide ligands were synthesized using thermal decomposition of isolated metal thiolates from Cu_2S and In precursors. Through gentle thermal treatment, these ligands decomposed into non-contaminating gaseous byproducts leaving carbon free nanoparticle films without the need for ligand exchange.

With the development of virtually contamination free colloidal nanoparticle inks, focus was shifted to scalability using slot die coating. Unlike typical lab-scale coating techniques such as spin coating, slot die coating is a widely used industrial coating technique with nearly 100% materials utilization, and high throughput roll-to-roll compatibility. A custom lab-scale slot-die coater was used to rapidly proof coating conditions, which were rapidly analyzed for uniformity using absorbance scanning in conjunction with profilometry. A cosolvent chlorobenzene/dichlorobenzene ink was developed to yield highly uniform, crack free thin films from non-ligand-exchanged $Cu(In,Ga)S_2$ nanoparticles, which were finished into devices with champion total are efficiencies of 10.7%. To the best of our knowledge, this represents the first report of slot die coated $Cu(In,Ga)(S,Se)_2$ photovoltaics. The methods presented in this work offer a pathway towards low impurity, high efficiency, scalable solution processed $Cu(In,Ga)(S,Se)_2$ photovoltaics to enable low cost renewable energy.