ABSTRACT

Miskin, Caleb K. Ph.D., Purdue University, May 2016. Solution-Processed Solar Cells via Nanocrystal Inks and Molecular Solutions. Major Professor: Rakesh Agrawal.

On February 15, 2008 the National Academy of Engineering unveiled their fourteen grand challenges of engineering for the 21st century. At the top of the list and voted by the public as the most important challenge was the thrust to *make solar energy economical*. My research has been dedicated to solving this millennial challenge by developing routes to high-efficiency, solution-processed photovoltaics (PV) for low-cost and low-energy manufacturing.

My research has primarily advanced two methods for solution processed PV. In one method, semiconducting nanocrystals are synthesized and then suspended in an appropriate solvent to form an ink. The ink is then applied to a substrate by a variety of high-throughput methods such as spray coating or doctor blading and then annealed to form a polycrystalline absorber layer for solar energy. I have applied this method with great success to Cu_2ZnSnS_4, a promising earth-abundant, non-toxic semiconductor. A challenge with this material is its propensity to form binary and ternary undesired phases. Using advanced nano-characterization techniques, my colleagues and I have been able to determine the spatially resolved composition of these nanoparticles and have found them to be highly non-uniform. As a result, I developed synthesis techniques aimed at controlling the nucleation and growth of this material to improve nanocrystal compositional homogeneity. Though particles produced in this work still exhibit some non-uniformities, they are greatly improved. When combined with optimized fabrication techniques, I have been able to advance the efficiency of nanocrystal ink based solar cells of CZTS from 7.2 to 9.0 percent in our lab.

Another promising route to solution-processed PV is by directly coating molecular precursor solutions (rather than first forming nanocrystals) and annealing the coating to form the polycrystalline solar absorber layer. Unfortunately, a major challenge is that many metals, metal salts, and chalcogens that would be useful precursors to such films have poor solubility in organic solvents compatible with roll-to-roll manufacturing techniques. Interestingly, we have found that mixtures of commonly available thiols and amines are able to dissolve at room temperature and pressure a host of metals and salts that are otherwise insoluble in either solvent by itself. In this work, I have primarily focused on CdTe—which has been by far the most successful technology in terms of production cost ($/peak watt) and energy payback time for thin-film solar cells. In this research thrust I demonstrate for the first time the fabrication of CdTe thin-films via a solution-processed molecular precursor approach by dissolving $CdCl_2$ and Te in ethylenediamine and 1-propanethiol. The films are formed by spin-coating ultra-thin layers of the solution and then annealing each layer until a ~1-2 μm thick film is achieved. I have achieved 0.5% efficient devices by this method. As amine-thiol mixtures have the potential to leave residual sulfur in these films, other novel solvent systems are presented as future work.

While amine-thiol mixtures are excellent solvents for many materials, they do not dissolve lead chalcogenides with ease. I leverage this to develop room-temperature synthesis routes to PbS, PbSe, PbTe, and PbS_xSe_{1-x} nanoparticles. This is achieved by mixing a lead salt dissolved in thiol-amine with a chalcogen dissolved in thiol-amine at room temperature. We find that when particles produced in this manner are pressed into pellets, they show comparable thermoelectric performance to more complicated and energy intensive synthesis techniques. Ultimately, we wish to enable the use of these particles in room-temperature fabricated quantum dot solar cells. This requires the synthesis of highly monodisperse, stable colloids and is the subject of future work. .