THE CHEMISTRY OF SOLUTION PROCESSED PHOTOVOLTAICS: SYNTHESIS APPROACHES FOR METAL CHALCOGENIDE SEMICONDUCTORS

by

Jonathan Turnley

With climate change creating the need for renewable energy sources to replace fossil fuels, solar energy technologies are primed to dominate the energy sector. And while photovoltaics have improved significantly in recent decades, continued evolution of this technology requires research into new fabrication techniques and new materials. The solution processing of metal chalcogenide semiconductors offers an opportunity to fabricate photovoltaics in a low-cost and high-throughput way. However, for this methodology to make a commercial impact a variety of challenges around the fundamental chemistry and materials science need to be addressed. Furthermore, while solution processing has been applied heavily to the $Cu(In,Ga)(S,Se)_2$ family of materials, these techniques can also open doors for emerging materials like $Cu_2ZnSnSe_4$, $Ag_2ZnSnSe_4$, and $BaZrS_3$.

In solution processed $Cu(In,Ga)(S,Se)_2$ devices, researcher have generally started with a $Cu(In,Ga)S_2$ film that is then selenized to form the final $Cu(In,Ga)(S,Se)_2$ material. However, this process has been connected to the formation of a problematic “fine-grain” layer. To solve this issue, the molecular precursors from amine-thiol chemistry were modified to produce soluble molecules with metal selenium bonding. This enabled direct solution deposition of $CuInSe_2$ films that could be processed without forming a fine-grain layer.

Reactive dissolution chemistry (or “alkahest” chemistry) is useful for solution processing because it can enable the direct use of metal or metal chalcogenide precursors, bypassing the potential impurities from metal salt precursors. However, the commonly used amine-thiol reactive solvent system is better suited to making metal sulfides than metal selenides because the thiol acts as a sulfur source. To address this limitation, a new alkahest based on alkylammonium polyselenide solutions was developed which could reactively dissolve a wide range of metals, metal chalcogenides, and metal oxides. This generalizable chemistry enabled the synthesis of a wide range of binary and multinary metal chalcogenides including $Cu(In,Ga)Se_2$, $Cu_2ZnSnSe_4$, and $Ag_2ZnSnSe_4$.

Emerging metal chalcogenide semiconductors composed of earth-abundant and non-toxic elements that can exhibit strong optoelectronic properties and high stability are a target of significant interest. Chalcogenide perovskites like $BaZrS_3$ and $BaHfS_3$ are an intriguing option to satisfy these requirements but have rarely been studied because of synthesis difficulties, historically being made by solid-state reactions or the sulfurization of oxides around 1000 °C. Here a solution-based approach that only requires moderate temperatures of 550-575 °C was developed utilizing a hybrid ink containing soluble metal thiolates and nanoparticulate metal hydrides.

The hybrid ink was an important proof of concept that chalcogenide perovskites could be synthesized at these moderate temperatures. However, it relies on complex and difficult to handle precursors. A simpler route would be to use air-stable precursors to make an oxide perovskite and subsequently sulfurize the material. However, this route has historically used excessively high temperatures. Therefore, a new surlfurization step was conceived based on thermodynamic arguments that includes both sulfur and hafnium-containing oxygen sink. This redesigned sulfurization enabled the conversion of $BaZrO_3$ into $BaZrS_3$ at temperatures around 575 °C.

Finally, an energy systems and economic analysis was performed to consider how photovoltaics might be incorporated into agricultural lands. This work showed that when compared with traditional photovoltaics or a PV Aglectric concept, using corn for ethanol is an inefficient way to generate both food and energy from a given unit of land.