

Sheets, Erik J. Ph.D., Purdue University, August 2015. The Solution-Based Synthesis of Semiconducting Phosphide Nanocrystals for Alternative Energy Applications. Major Professor: Rakesh Agrawal.

Abstract:

Semiconducting phosphide nanocrystals have great potential as earth-abundant and sustainable alternative energy materials. Applications focused on solar energy conversion are particularly promising for phosphides derived from Group II-VI and III-V materials with zinc-blende crystal structures. Currently, such materials are largely synthesized on the single crystallite scale, restricting their versatility in device fabrication and production. Exploiting their full potential requires developing novel nanocrystalline synthesis methods utilizing innovative solution-based chemistry. In doing so, optimization of physical and optical properties can be done in a scalable and timely fashion. Two semiconducting phosphide systems have been targeted: the group II-VI derivative  $\text{Cu}_3\text{PS}_4$  and the group III-V derivative  $\text{ZnSnP}_2$ . The solution-based processing of these materials on the nanoscale has resulted in the understanding of new reaction mechanisms, new product morphologies, and new material properties.

The field of solution-based phosphorus chemistry has evolved with the introduction of an in-situ phosphorus source,  $\text{P}_2\text{S}_5$  in trioctylphosphine (TOP). This chemistry has been successfully applied for the size and composition controlled synthesis of  $\text{Cu}_3\text{P}$  while indicating other transition metal phosphides of significant interest to the alternative energy community can be synthesized as well. Taking the  $\text{Cu}_3\text{P}$  system a step further, its use with decomposing thiourea has produced the intriguing semiconductor  $\text{Cu}_3\text{PS}_4$  whose properties have been characterized and potential in solar absorption demonstrated.

Furthermore,  $\text{ZnSnP}_2$  nanowires have been synthesized for the first time from a Zn-Sn alloy in TOP by solution-liquid-solid (SLS) growth. Purification of the synthesis product yielded extremely stable  $\text{ZnSnP}_2$  nanowires capable of withstanding concentrated nitric acid environments. The usefulness of  $\text{ZnSnP}_2$  as a solar absorption material has been demonstrated through photoelectrochemical measurements and initial device fabrication. The processing techniques established have opened the door for future alternative energy device optimizations as well as the development of other nanoscale transition metal phosphides.