Chemistry of Materials for Sustainability: From Halide Perovskites to Binary Metal Phosphides

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Our group is interested in the soft synthesis and chemical spectroscopy of optical nanomaterials. This talk will highlight some of our recent work in two areas:

Halide Perovskites: New Semiconductors for Energy Conversion. Halide perovskites are one the most interesting semiconductors for photovoltaics, with solar cells made of these materials approaching power conversion efficiencies of 25%. We were among the first to synthesize colloidal $APbX_3$ (A = methylammonium; X = I, Br) nanocrystals, and showed that, at the single particle level, they display shape-correlated PL emission across whole particles, with little photobleaching and very few off periods [1-3]. In addition, we introduced solid state NMR to probe the extent of alloying and phase segregation in mixed ion halide perovskites [4-5], which show superior performance and stability. Because ^{207}Pb chemical shifts are highly sensitive to local coordination, electronic structure, and vary linearly with halogen electronegativity and band gap, ^{207}Pb ssNMR gives the true chemical speciation of samples made by different methods. Nonstoichiometric dopants and amorphous phases are prevalent in samples made from solution, while a novel solid phase synthesis, starting from the parent, single-halide perovskites suppresses phase segregation [6-7]. Our observations are consistent with the presence of miscibility gaps and spontaneous spinodal decomposition in these materials at room temperature, underscoring how different synthetic procedures impact their composition, nanostructuring, and properties.

Binary Metal Phosphides: From Hydrogen Evolution to Nitrate Removal from Water. A better understanding of the chemistry of molecular precursors is useful in achieving more predictable and reproducible nanocrystal preparations [7-8]. Using commercially available organophosphite precursors, we have used a chemical reactivity approach to synthesize nickel and nickel phosphide nanocrystals with high selectivity (Ni, $Ni_{12}P_5$ and Ni_2P phases) [9]. Some organophosphites, such as $P(OMe)_3$ or $P(OiPr)_3$ transiently form zerovalent, metallic nickel; the latter is persistent with the bulky organophosphite $P(O\text{-}2,4\text{-}tBu_2C_6H_4)_3$. Along with other first row, transition metal phosphides, Ni_2P is a very active catalyst for the hydrogen evolution reaction, as well as for hydrodesulfurization, and other reforming reactions. Based on this information, we hypothesized that Ni_2P should be active in the reduction of oxyanions. Indeed, we have recently succeeded in using this material as a catalyst for the near ambient removal of nitrate from water [10].

1. Zhu *et al.* "Shape Evolution and Single Particle Luminescence of Organometal Halide Perovskite Nanocrystals." *ACS Nano* **2015**, *9*, 2948.
2. Rosales *et al.* "Lead Halide Perovskites: Challenges and Opportunities in Advanced Synthesis and Spectroscopy." *ACS Energy Lett.* **2017**, *2*, 906.
3. Freppon *et al.* "Photophysical Properties of Wavelength-Tunable Methylammonium Lead Halide Perovskite Nanocrystals." *J. Mater. Chem. C* **2017**, *5*, 118.
4. Rosales *et al.* "Persistent Dopants and Phase Segregation in Organolead Mixed-Halide Perovskites." *Chem. Mater.* **2016**, *28*, 6848.
5. Hanrahan *et al.* "Enhancing the Sensitivity of ^{207}Pb Solid-State NMR Spectroscopy for the Rapid, Non-Destructive Characterization of Organolead Halide Perovskites." *Chem. Mater.* **2018**, *30*, 7005.
6. Vela & Rosales, "Solvent-Free, Solid Phase Synthesis of Hybrid Lead Halide Perovskites with Superior Purity." U.S. Patent Application No. 15/854,596, December 26, 2017.
7. Guo *et al.* "Shape-Programmed Nanofabrication: Understanding the Reactivity of Dichalcogenide Precursors." *ACS Nano* **2013**, *7*, 3616.
8. Ruberu *et al.* "Molecular Control of the Nanoscale: Effect of Phosphine Chalcogenide Reactivity on CdS-CdSe Nanocrystal Composition and Morphology." *ACS Nano* **2012**, *6*, 5348.
9. Andaraarachchi *et al.* "Phase-Programmed Nanofabrication: Effect of Organophosphite Precursor Reactivity on the Evolution of Nickel and Nickel Phosphide Nanocrystals." *Chem. Mater.* **2015**, *27*, 8021.
10. Lin & Vela, To be communicated.