

Recent Progress in the Rappe Group: Bulk Photovoltaic Effect and Catalysis in Li-CO₂ Batteries

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In this poster we present some recent progress in research by the Rappe Group, a computational materials chemistry group at the University of Pennsylvania. We focus on the Bulk Photovoltaic Effect (BPVE), the generation of DC photocurrent in materials without inversion symmetry, and the catalytic activity of graphene-based cathodes in Li-CO₂ batteries, as well as the electronic structure methods used to calculate these phenomena.

Tight-binding models provide great insight and are a low-cost alternative to ab initio methods for calculation of a material's electronic structure. These models are used to calculate optical responses, including nonlinear optical effects such as the shift current in the bulk photovoltaic effect. The validity of tight-binding models is often evaluated by comparing their band structures to those calculated with DFT. However, we find that band structure agreement is a necessary but not sufficient condition for accurate optical response calculations. We compute shift current responses for a variety of tight-binding models of MoS₂, including both Slater-Koster and Wannier tight-binding models that treat the Mo 4*d* orbitals and/or S 3*p* orbitals. We also truncate hoppings in the Wannier function models to next-nearest neighbor, as is common in tight-binding models, in order to gauge the effect on optical response. We establish that both band structure agreement and wavefunction agreement are required to accurately model optical response.

The Li-CO₂ battery is a promising energy storage system with impressive theoretical specific energy and discharge capacity. Graphene-based single-atom catalysts (SAC) are among the most promising cathode catalysts, but these batteries continue to have high reaction barriers. Through DFT calculations, we identify improvements to the heavily studied FeN₄-SAC graphene catalyst, using solvation models to assess solvent impact. We propose enhancing the SAC by using a Ti metal center, which is found to stabilize high-energy intermediates in the reaction mechanism. This improvement is due to more active Ti 3*d* orbitals, identified with partial density of states calculations, and stronger bidentate interaction with adsorbates. Additionally, polar ligands show promising capability to modulate electron density of the SAC to induce favorable changes in adsorbate structure. These cathode materials are promising innovations for Li-CO₂ batteries and can help them reach their full potential as highly energy-dense storage systems.