**Rational Engineering of Binary Oxides and Semiconductors for Photocatalytic Applications**

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Photocatalytic materials are pivotal for the implementation of disruptive clean energy applications like conversion of H2O and CO2 into fuels and chemicals driven by solar energy. However, efficient and cost-effective materials able to catalyze the chemical reactions of interest when exposed to visible light are scarce due to the stringent electronic conditions that they must satisfy. Chemical and nanostructuring approaches are capable of improving the catalytic performance of known photoactive compounds, however the complexity of the synthesized nanomaterials and sophistication of the employed methods make systematic design of photocatalysts difficult. Here, we present the results of recent first-principles studies on binary oxides and semiconductors that have the potential to improve the systematic screening and rational design of photocatalytic materials1,2. First, we introduce an efficient multi-configurational supercell approach for estimating the mixing thermodynamics and structural and functional properties of semiconductor solid solutions, which takes into consideration the effects of configurational disorder and lattice vibrations on the free energy. The method is applied to (GaP)x(ZnS)1-x solid solutions with the finding that compositions x≈25, 50, and 75% render promising photocatalysts for water splitting under visible light. And second, we show that application of biaxial stress on semiconductor binary oxides can modify their optoelectronic and catalytic properties in a significant and predictable manner. In particular, upon moderate tensile strains CeO2 and TiO2 become suitable materials for photocatalytic conversion of H2O into H2 and of CO2 into CH4 under sunlight. The band gap shifts induced by biaxial strain are reproduced qualitatively by a simple analytical model that depends only on structural and dielectric susceptibility changes. Thus, compounds mixing and biaxial strain represent two promising routes for methodical screening and rational design of photocatalytic materials.

**References**

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