Computational screening of Transition metals doped on CdS photocatalyst for green hydrogen generation

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Hydrogen production and converting solar energy through photocatalysis into suitable fuels such as hydrogen has been established as an intriguing strategy to alleviate both energy crisis and environmental problems [1]. Several photocatalysts have been studied to assist solar visible-light during H_2O and H_2S photocatalysis processes [2]. In specific, cadmium sulfide (CdS), with a suitable band gap (around 2.4 eV) for visible light response, is the most widely studied experimentally for this purpose, whether as a pure photocatalyst or in conjunction with some suitable semiconductors. However, achieving higher quantum yields and selectivity still poses a great challenge in this field, making essential to understand how to improve the solar light utilization and conversion efficiency based on existing technologies and materials. Among these efforts, first principle Density Functional Theory (DFT) calculations can provide guidance to effectively select or design photocatalysts for improving hydrogen generation efficiency.

Therefore, in this contribution, we present and discuss results of the first computational screening study of single TM (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au)-doped CdS (TM@CdS) and selected dual TMs-doped CdS (TM1-TM2@CdS) focused on their stability and activity for hydrogen evolution of both H_2O and H_2S splitting reactions. We have performed spin polarized DFT-D3 calculations to gain a quantum-level understanding of the hydrogen evolution mechanism in these different catalytic surfaces, validated with measurements obtained from experiments and thermochemical computational approaches, while evaluating the stability and electronic structures of different CdS surfaces, as well as calculating the adsorption capacity for H_2S adsorption/splitting [6]. Results demonstrate that doping of TMs promotes the reduction of energy band and enhancement of impurity d-states near the Fermi level, resulting in more efficient photocatalytic activity. Activity analysis places Pt, Rh and Pd as optimal single metal doped to be used in TM@CdS catalysts for both H_2O and H_2S splitting reactions, with the lowest Gibbs free energy change of hydrogen adsorption, outperforming pristine CdS surface. Moreover, the dual co-catalysts decorated CdS photocatalysts show even better performance for hydrogen generation. The insights obtained from this work provide robust guidance on the designing of optimal HER catalyst candidates based on CdS for green hydrogen production.

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FIGURES

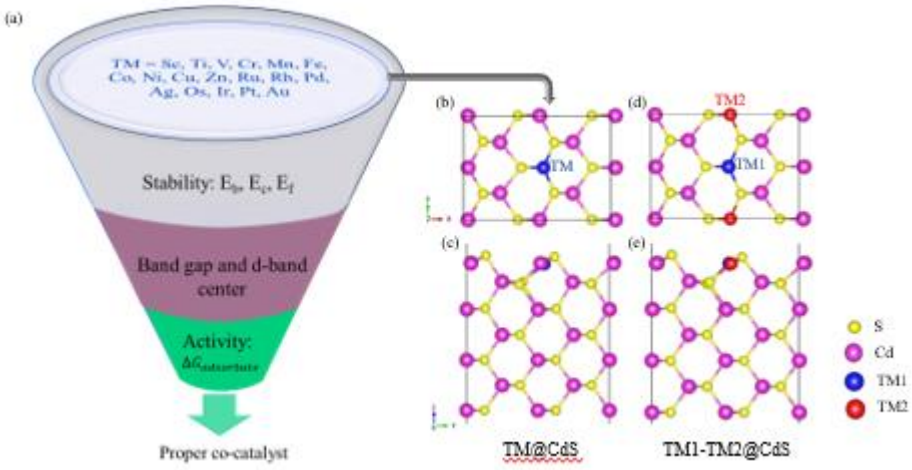

Figure 1: (a) Screening protocol for the discovery transition metal-doped CdS catalysts. (b) top view of an optimized TM@CdS configuration, (c) side view of an optimized TM@CdS configuration, (d) top view of optimized TM1-TM2@CdS configuration and (e) side view of optimized TM1-TM2@CdS configuration.