Multiscale Modelling of Two-dimensional Materials for Solar Water Splitting and Hydrogen Storage

Abstract of Thesis

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BY

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Abstract

In recent times, the increasing energy requirements resulting from technological advancements and population growth, coupled with the diminishing availability of traditional fuels, have prompted a search for alternative options, particularly in the field of transportation. Hydrogen fuel stands out due to its abundance from various sources, eco-friendliness with minimal emissions and high energy density. However, using hydrogen faces hurdles: cost-effective production and compact storage. This thesis addresses challenges by examining advanced two-dimensional (2D) nanomaterials for hydrogen production through water-splitting and devising a viable compact hydrogen storage medium using state-of-the-art density functional theory (DFT) simulations.

Our study delves into the hydrogen evolution reaction (HER) activity of pristine α-SiX (X=N, P, As, Sb, Bi), Ni anchored α-SiX (X=N, P, As, Sb, Bi) single-atom catalysts (SACs), pristine holey graphyne (HGY) and transition metals (Zr, Y, V, Sc, Mn, Co, Fe, Cr) anchored HGY SACs. This investigation is carried out through comprehensive dispersion corrected DFT simulations. Our results for the Gibbs free energy of H adsorption (ΔG_H) suggest that pristine form of α-SiX (X = N, P, As, Sb, Bi) and HGY monolayers are ineffective as catalysts for the HER activity. To enhance the HER activity, we have implemented a strategy of anchoring transition metals onto α-SiX (where X = N, P, As, Sb, Bi) and HGY monolayers in order to create SACs. Furthermore, we elucidate the alterations in the structural and electronic properties of α-SiX (X=N, P, As, Sb, Bi) and HGY monolayers due to anchoring with transition metals. This is achieved by considering orbital interactions, changes in band structures and partial density of states (PDOS) analysis. The significant bonding between Ni metal and 2D α-SiX (X = N, P, As, Sb, Bi) monolayers, as well as between transition metals and HGY monolayer, facilitated by p-d hybridization, enhances reactivity and conductivity. This is further attributed to a decrease in the band gap of the semiconducting α-SiX and HGY

monolayers. Our DFT finding predicts that Ni@α-SiX and Cr@HGY SACs emerge as highly efficient catalysts for HER, exhibiting remarkably low ΔG_H values of -0.04 eV and -0.05 eV, respectively. To validate their stability, we conducted extensive ab initio molecular dynamics (AIMD) simulations at 300K, affirming the integrity of Ni@α-SiX and Cr@HGY SACs at room temperature. Given the exceptional electrochemical performance for HER activity and stability of Ni@α-SiX and Cr@HGY SACs, they hold promise as viable catalysts for hydrogen production through the HER activity.

The dispersion corrected DFT simulations on pristine 2D orthorhombic diboron dinitride (o-B_2N_2) for HER activity show its limited suitability as a catalyst, as inferred from the ΔG_H calculation. However, the introduction of vacancy defects induces significant changes in the monolayer's structure and electronic properties, leading to the widening of the band gap from 0.66 eV to 0.99 eV in the case of the BN vacancy. Remarkably, the BN defected configuration exhibits ΔG_H close to zero compared to B and N defected as well as pristine configurations. This BN defect augmented HER activity by 77.34% in comparison to the pristine configuration at pH = 0. With the inclusion of C doping, the system's behavior transformed from a semiconductor to a metal. The ΔG_H of the C doped 2D o-B_2N_2 approached zero in both scenarios, signifying its suitability for HER. The C doping resulted in 86.71% boost in HER activity at the B site and 83.59% enhancement at the N site relative to the pristine configuration at pH = 0. This improvement was attributed to altered charge distribution following defect creation and C doping. Consequently, our findings propose that the metallic C doped 2D o-B_2N_2 could effectively act as an "electrocatalysts" for the HER activity within the pH range of 0 to 7. On the other hand, the BN defected 2D o-B_2N_2, characterized by 0.99 eV band gap, displays potential as a "photocatalyst" for HER activity at pH = 0. In addition, through AIMD simulations conducted at 300K, the structural integrity of 2D o-B_2N_2 with BN defects and C doping at room temperature is confirmed.

We explored the possibility of the pristine, defected and metals (including Na and K alkali metals; Be, Mg and Ca alkaline-earth metals and Sc, Ti, Y and Zr transition metals) decorated 2D o-B_2N_2 as a hydrogen storage medium through dispersion corrected DFT calculations. The findings indicate that the pristine, defected and metals Na, K, Be, Mg, Ca, Sc, Y and Zr decorated 2D o-B_2N_2 did not align favourably with the U.S. Department of Energy (DoE) requirements for an effective hydrogen storage medium. Nonetheless, promising results emerged from the Ti decorated 2D o-B_2N_2, suggesting its suitability as a hydrogen storage medium. Notably, the Ti atoms exhibited a strong and favourable bonding with the 2D o-B_2N_2, leading to a decrement in the band gap and an increase in conductivity. The adsorption energy for first hydrogen on the Ti decorated 2D o-B_2N_2 is -0.47 eV, satisfying the DoE's criteria. Furthermore, the charge donation from the Ti atom to the 2D o-B_2N_2 was observed through PDOS and Löwdin charge analysis. The two Ti decorated configuration demonstrated the capacity to bind a total of thirty-four hydrogen molecules, with average adsorption energy of -0.31 eV/H_2 and 396 K of desorption temperature. The calculated gravimetric storage capacity is 11.21%, notably surpassing the DoE's specified range. At a temperature of 396 K, our AIMD results convincingly demonstrate the excellent thermal stability of the Ti decorated 2D o-B_2N_2. As a summary, this research highlights the promising prospects of the Ti decorated 2D o-B_2N_2 as an efficient medium for high-capacity hydrogen storage.