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Effect of the CTF-1/Au(111) Interface in Enhancing Photocatalytic Water Splitting

Covalent Triazine Frameworks (CTFs) are a class of 2D organic materials that have attracted increasing attention over the past decade due to their high density of surface-active sites, efficient charge separation, fast carrier mobility, low recombination rates, chemical stability, and tuneable band gaps [1,2]. In this study, water splitting was investigated on both free-standing and gold-supported CTFs. We examined how the interaction between the CTF and the surface influences the electronic properties, reaction free energies, and the overall reaction mechanism. Although the physical interaction between the substrate and the film is often neglected in similar studies, it can play a crucial role in designing more efficient photoanodes and photocathodes. In this work, we apply the computational hydrogen electrode (CHE) approach [3] to study both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), computing the free energy changes associated with each elementary step on multiple active sites. All calculations are performed within the framework of periodic density functional theory. Our calculations show that the interaction between CTF-1 and the Au(111) surface modifies the potentials of the photogenerated hole (U_h) and electron (U_e). Specifically, U_h increases from 2.61 eV for the CTF-1 monolayer to 3.01 eV for CTF-1 supported on the gold surface, while U_e decreases from 0.99 eV to 0.39 eV. These results suggest that the interaction with gold could enhance the ability of the system to oxidize water, thereby improving the efficiency of the OER step. Meanwhile, U_e still retains sufficient potential to drive the HER. In addition, calculations performed for the OER and HER at pH = 0 reveal that the interface also affects the free energy changes of the involved reactions. Notably, we find that the minimum potential required to drive the OER decreases from 2.15 eV for the CTF-1 free monolayer to 1.39 eV for CTF-1 supported on gold. For the HER, a similar trend is observed, with the free energy change shifting from 0.3 eV to −0.1 eV. This study highlights the potential role of the interface in modulating the water-splitting reaction. The resulting insights into the reaction mechanism contribute to the rational design of more efficient photoanodes and photocathodes for solar-driven water splitting.

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