

***Ab-initio* study of excited states effects on CO₂ photo-reduction over Cu, TiO₂ and Cu doped TiO₂ surfaces.**

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Titanium dioxide has received significant attention in various applications over the past few decades, with photocatalysis being one of the most promising utilizations [1]. The rutile and anatase crystal phases have been studied extensively due to their favorable activity, but the brookite crystal phase has also garnered interest. However, the activation of TiO₂ is hindered by high charge recombination and high band gaps. To enhance its activity, methods such as doping, surface co-catalyst deposition, and defect integration have been employed.

Density functional theory (DFT) calculations were performed using VASP [2] with a 500 eV energy cut-off and the Perdew-Burke-Ernzerhof (PBE) functional, implemented within the projector augmented wave (PAW) method. A Hubbard correction and Grimme D3 correction were applied to account for strong Coulomb interactions and long-range dispersion forces, respectively. Saddle points were identified with NEB and refined using CI-NEB and dimer method.

While there has been a surge of theoretical investigations on the photocatalytic reduction of CO₂ in recent years, most models use ground state calculations that do not fully capture the essence of the photocatalytic process. In this study, the Δ SCF methodology [3] was applied to identify bottlenecks and reactivity of specific surfaces, where an electron was photo-excited from the valence band maxima (VBM) to the conduction band (CB), leaving a hole in the VB. The results for different surfaces, as well as the difference between ground state and excited state, were compared to determine the most efficient surfaces for CO₂ reduction.

The results indicate that metallic surfaces are unable to photo-reduce CO₂ as expected due to its conductive nature. On the other hand significant alterations to activation energies can be observed in the case of pristine anatase (101) and pristine rutile (110) surface. Finally the surface of pristine anatase (101) and pristine rutile (110) surface was decorated with four Cu atoms to further boost the activity. The results indicate that the activity is surface dependent, where excited states play a crucial role for a proper description of a photo-catalytic process.

References:

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