Computational study comparing the electronic properties of surface versus above surface dopant on (100) surface anatase

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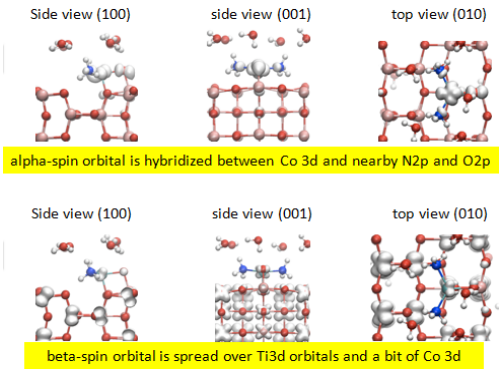
TiO_2 nanorods functionalized by cobalt ions at different exposed crystallographic faces are promising materials for photoelectrochemical water splitting.[1] This research is based on experimental studies of TiO_2 nanomaterials functionalized by a cobalt ion doping. Specifically, by studying the binding pattern, we hope to find a connection to the electronic properties. Computational studies can be a unique tool revealing details of surface chemistry, unavailable through direct measurements. On a much grander scale, it is our hope that this research will help steer research towards new photoelectrochemical solar cells.

Using unrestricted density functional theory, electronic properties are obtained for two open shell TiO_2 anatase thin film crystals doped in two ways: *surface* and *above surface*. The *surface doped* model replaces one surface titanium ion with a cobalt ion. Four water molecules are placed on the (100) surface, then geometry optimization results in cobalt coordinating with one oxygen from bulk, four oxygen from the surface, and an adsorbed H_2O.In the *above surface doped* model the cobalt ion coordinates with two surface oxygen atoms and is capped with two NH_3 ligands to have a tetrahedral coordinated dopant. Electronic structure calculations of charged models are completed to find the optimized oxidation state of the cobalt ion in each model.

Spin polarization is taken into consideration to calculate the density of states, optical absorption spectra, and partial charge densities. While the *surface doped* model does not show much difference between alpha and beta electrons in the density of states, the *above surface doped* model shows extreme differences. Specific open-shell features in electronic structure of *above surface doped* model are illustrated by analysis of partial charge densities of Kohn-Sham orbitals in the band gap energy range, shown in Figure 1 below. While the *surface* dopant readily forms hybrid orbitals with surrounding atoms, the *above surface* dopant results in orbitals which are much more isolated and little orbital mixing is noted. Future research will include molecular dynamics of ligand desorption upon a photoexcitation along with non adiabatic dynamics.

Figure 1: Partial Charge Densities of Kohn-Sham Orbital in Band Gap of *Above Surface* Model



1. Kang, W., et al., *Synthesis of brookite TiO 2 nanorods with isolated Co (ii) surface sites and photocatalytic degradation of 5, 8-dihydroxy-1, 4-naphthoquinone dye.* Journal of Materials Chemistry A, 2013.