Spin Resolved Nonradiative Relaxation Dynamics of Cobalt Doped TiO_2 Nanowire

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Abstract

Anatase nanowires, along with other TiO_2 nanomaterials, are widely studied for use in solar energy materials including photo electrochemical cells as a transparent conducting material [1-3]. Cobalt is known to induce the redox reaction of water into hydrogen and oxygen gases.[4]A cobalt doped anatase nanowire model (**Figure 1**) is studied for photocatalytic properties using spin unrestricted density functional. The cobalt ion is a surface substitutional dopant with two NH_3 neutral ligands, and the nanowire is surrounded by 123 water molecules to simulate an aqueous environment. Cobalt II and III oxidation state, both in low spin configuration, are of equal likelihood of occurring. Since substitutional cobalt doped TiO_2 is known to be ferromagnetic at room temperature with low doping concentrations [5], spin unrestricted calculations are a necessity. Spin unrestricted DFT with PBE functional and pseudopotentials is implemented to calculate ground state geometry and electronic properties. Spin unrestricted relaxation dynamics, including charge transfer, rates of electron/hole relaxation, and relaxation pathways, are calculated by nonadiabatic molecular dynamics and electronic couplings for spin up/down separately(Figure 2). The dopant is expected to show localized charge at the HO/LU energy levels indicating the possibility for photocatalytic activity, as well as provide information on how a doublet (Co 2+) state can alter relaxation dynamics compared to that of a singlet (Co 3+).

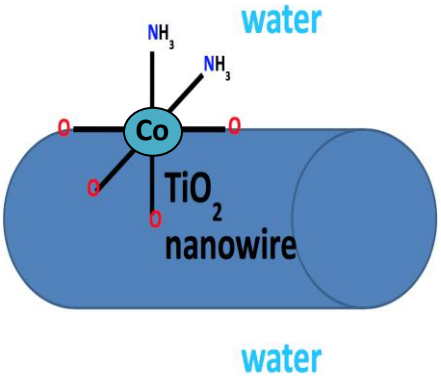

Figure 1A: Schematic of cobalt dopant in anatase nanowire

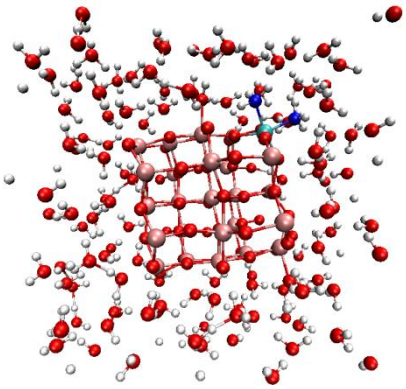

Figure 1B: Cobalt doped anatase nanowire model, surrounded by 123 H_2O molecules

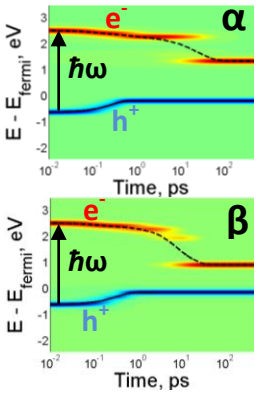

Figure 2: Spin unrestricted relaxation dynamics for spin up (top) and down (bottom) for the 3.3 eV transition. While rates of relaxation are similar, pathways differ.

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