Ab initio molecular dynamics of Ag, Ni, and Co doped titanium dioxide anatase (100) surface photoelectrochemical cell

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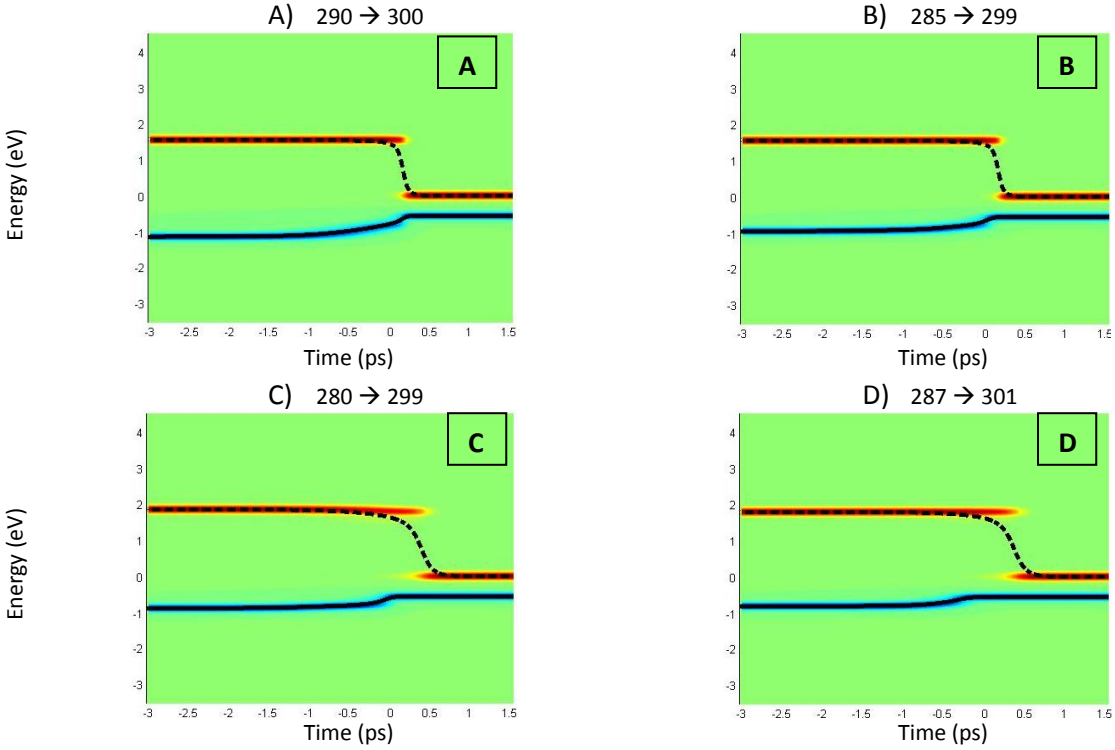
Using computational approaches, one is able to better understand electron transfer and specific atomistic behaviors in semiconductor materials; it is also more cost and time effective than experimental methods. If computed semiconductor characteristics show promise, experimentalists can synthesize and further examine the structure. Silver, nickel, and cobalt doped TiO_2 thin film surfaces increase photoelectric properties to induce H_2 production via redox reaction on water. The formulas used are $Ti_{32}O_{72}H_{16}$, $Ag_2Ti_{30}O_{72}H_{16}$, $Co_2Ti_{30}O_{72}H_{16}$ and $Ni_2Ti_{30}O_{72}H_{16}$ with the (100) crystallographic surface exposed and covered with a monolayer of water. Optimization is completed by DFT and PBE in VASP software. The density of states, absorption spectra, partial density of states, partial charge densities, molecular dynamics, and non adiabatic couplings are compared between doped and un-doped as the standard. Each dopant can be assigned to either a p- or n-type dopant based on energy differences. Specifically, ab initio molecular dynamic methods allow the study of state energy fluctuations and likely excitations between specific states as well as confirmation to whether the dopant is p- or n-type. The information can be used to show the mechanism of how doping the titanium dioxide nanocrystals facilitates photo induced charge transfer at the surfaces, which is useful in understanding photoelectrochemical water splitting.

Figure 1: Silver doped electron relaxation and hole cooling couplings for likely excitations



Above shows the four likely excitations of silver doped anatase (100) surface titanium dioxide. In each case, the hole is cooling faster than the electron relaxes. This is due to the energy differences when the processes occur as the hole has more states to cool to, but much smaller energy differences to overcome. The electron has fewer but larger energy differences to overcome and therefore takes longer.