

Surface Transition Metal Doped Anatase: A Study on Low Energy $d \rightarrow d$ Transitions

Stephanie Jensen, James D. Hoefelmeyer, Dmitri Kilin

Department of Chemistry, The University of South Dakota, 414 E. Clark Street, Vermillion, SD 57069

Titanium dioxide is an integral piece in dye sensitized solar cells (DSSC) as it efficiently transports both electrons and holes to respective electrodes, allowing for charge collection and current generation. While rutile is usually the most stable phase of TiO_2 , anatase is more stable below the nanoscale. Since thin films assist in easier charge separation and transport, TiO_2 in DSSCs are in the form of nano sized thin films and henceforth take the anatase phase.

A joint experimental and computational study of transition metal doped anatase is carried out with the following computational goals: 1) characterizing high wavelength transitions as either $p \rightarrow d$ or $d \rightarrow d$, 2) obtaining absorption spectra for comparison with experimental results, 3) performing ab initio molecular dynamics, and 4) obtaining non adiabatic thermalization rates of photoexcited electrons. The goal is to characterize the low energy transitions as metal to metal, which cannot be done in a laboratory; the thermalization rates will also indicate whether or not the material is well suited for photocatalysis applications. Materials are characterized to be bidentate with nearly 100% dopant coverage of the anatase surface. The computational models use a base anatase structure of $\text{Ti}_{32}\text{O}_{64}$ with two dopants providing 100% coverage on a (100) surface and either 2 NHCH_3 ligands for a tetrahedral coordinated metal or 4 for octahedral. DFT with PBE functional and PAW basis set in VASP is used for the calculations for both spin restricted and unrestricted calculations.

The cobalt doped model is depicted in **Figure 1**, where the two dopants have tetrahedral coordination and are bidentate to the anatase surface. **Figure 2** shows the computed absorption spectrum with an inset highlighting the low wavelength transitions. Peaks at 540 nm and 725 nm are the low energy peaks, which are due to the surface dopants. Looking into the peak at 540 nm, **Table 1** shows the major contributing orbital pairs of the peak are due to $d \rightarrow d$ transitions involving both Co and Ti 3d orbitals.

Figure 1:
Structure of cobalt doped anatase with NHCH_3 ligand (shortened form of oleylamine ligand used in experiment)

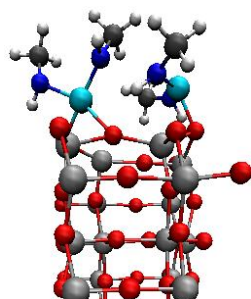


Figure 2:
Absorption spectrum of the model shown in Figure 1 with low energy peak spectrum inset

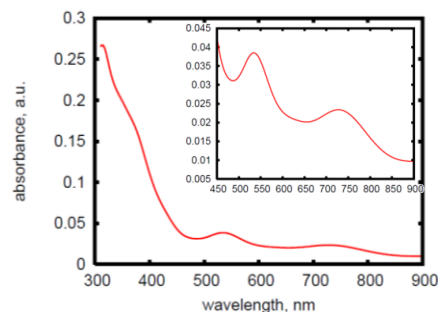


Table 1: Table of transitions (Trans) contributing to peak at 540 nm with highest oscillator strength (OS)

Trans	HO-78 \rightarrow LU+3	HO-47 \rightarrow LU+2	HO-5 \rightarrow LU+15	HO-5 \rightarrow LU+10	HO-15 \rightarrow LU+6
OS	0.156	0.138	0.118	0.112	0.107
λ (nm)	533	544	514	567	538
Donor	Co3d/N2p/O2p [†]	O2p/N2p*	Co3d*	Co3d*	Hybrid*
Acceptor	Co3d/N2p [†]	Co3d/N2p [†]	Ti3d*	Co3d/Ti3d [§]	Co3d/Ti3d [†]

* snapshot was taken at 0° angle

† snapshot was taken at 90°

§ snapshot was taken at 270°