

Electronic structure and hot carrier relaxation in wet <001> anatase TiO₂ nanowire

Shuping Huang, Dmitri Kilin

Department of Chemistry, University of South Dakota, Vermillion, SD 57069

A non-adiabatic excited state dynamics of <001> anatase TiO₂ nanowire (NW)¹ is investigated by combining density matrix formalism and *ab initio* electronic structure calculations.² A periodic boundary condition in the <001> direction is applied to a stoichiometric atomic model of anatase titania Ti₁₂₅O₅₀ while (100) and (010) faces are exposed to vacuum or to one monolayer of H₂O molecules. The electronic structures of the models are described by GGA-PBE³ and HSE06⁴ functionals with PAW potentials in VASP software and show an agreement to experiment [Figure 1]. Carrier dynamics is computed beyond the Born-Oppenheimer approximation using on-the-fly couplings. A time evolution of Kohn-Sham orbital populations is obtained for different electronic excitations. The analytical and numerical results on the electron relaxation show an agreement. The electron non-radiative relaxation to the bottom of conduction band involves Ti 3d orbitals, while the hole non-radiative relaxation to the top of valence band involves surface O 2p orbitals. TiO₂ NWs in vacuum and in aqueous environment exhibit different dynamics. In wet NWs, computed relaxation of electrons (holes) is approximately 2 (4) times faster when compared with the vacuum environment. The understanding of the relaxation pathways of photo-generated electron and hole is important for optimizing efficiency of materials for photovoltaics and photocatalysis applications.

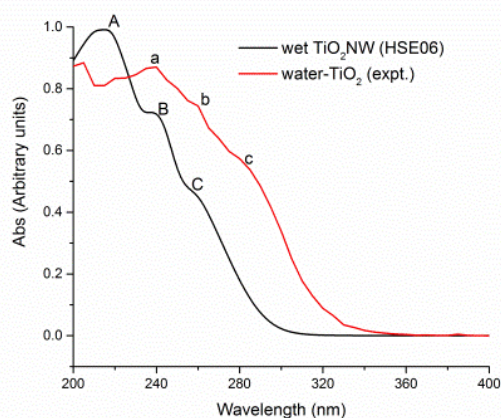


Figure 1 The calculated absorption spectra of wet TiO₂ NW and the experimental spectra of concentrated TiO₂ nanorod water solution.

¹ Huang, S.; Kilin, D. S. *Mol. Phys.* **2013**, <http://dx.doi.org/10.1080/00268976.2013.854932>

² Inerbaev, T.M.; Hoefelmeyer, J.D.; Kilin, D.S. *J. Phys. Chem. C* **2013**, *117*, 9673.

³ Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

⁴ Henderson, T. M.; Izmaylov, A. F.; Scalmani, G.; Scuseria, G. E. *J. Chem. Phys.* **2009**, *131*, 044108.