

Zooming in an excitonic solar cell: an ab initio investigation of the optically active site

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Metal-oxide nanoparticles (especially TiO₂, ZnO, SnO₂) may be sensitized to harvest visible radiation in working solar cells, upon molecular dye functionalization. However, at present the principles regulating interactions between the oxide layer and the rest of the photovoltaic (PV) cell are poorly understood. Indeed, upon molecular sensitization, semiconductor surface interacts with molecules in a wide range of possible scenarios, driving the formation of hybrid interfaces with specific spatial arrangement and novel electronic properties, and affecting both the light harvesting and the generation of the photovoltaic current. Another crucial point is the analysis of the oxide/electrode interactions that regulate the photogenerated charge transport through the oxide layer to the external collector and thus the final conversion efficiency of the solar cell.

By means of ab initio DFT calculations, we characterize the optoelectronic and transport properties of the main subsystems that form the active layer of a prototypical PV solar cell, based on dye/ZnO/AZO interfaces. Firstly, we present a first-principles study of the optoelectronic properties of a natural molecular sensitizer namely, cyanin (Cya) dye. In particular, we analyze the effects of both hydration and thermal dynamics on the optical properties of Cya in aqueous solution [1,2]. We combine Car-Parrinello molecular dynamics and time-dependent density functional theory (TDDFT) approaches to simulate the time evolution of UV-vis spectrum of the hydrated Cya molecule at room temperature [3]. Furthermore, we report on the functionalization of the non-polar ZnO(10-10) surface upon the adsorption of the chromophore linker, i.e. the catechol anchor group [4]. The resulting type-II staggered interface is recovered in agreement with experiments, and its origin is traced back to the presence of molecular-related states in the gap of metal-oxide electronic structure. A systematic analysis carried out for further catechol adsorbates allows us to identify the basic mechanisms that dictate the energy position of the gap states. Finally, we study the effects of aluminum doping on the electronic and optical properties of ZnO. We discuss the bandstructure and absorption properties of Al:ZnO (AZO) as a function of the dopant concentration, and compare with recent experimental data. Our results [5] support the formation of a transparent conductive oxide (TCO) compound up to an incorporation of Al of about 3% in substitutional Zn sites. We propose an explanation to the observed degradation of conductivity in terms of interstitial defects expected to occur at high doping concentrations, beyond the Al solubility limit.

[1] A. Calzolari, et al, J. Phys. Chem. A **113**, 8801 (2009).

[2] A. Calzolari, et al, J. Chem. Phys. **132**, 114304 (2010).

[3] O.B. Malciuglu et al, J. Am Chem. Soc., (2011), in press.

[4] A. Calzolari, et al, J. Am Chem. Soc. **133**, 5893 (2011).

[5] M. Bazzani, et al, Appl. Phys. Lett. **98** 121907 (2011).