

Level broadening and charge transfer on catechol-sensitized TiO₂ surfaces

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Sensitizing transition metal oxide surfaces with organic molecules has become an important step in the quest to harness and convert solar energy. For the prototypical case of a TiO₂ anatase surface sensitized with catechol, we present density-functional theory and time-dependent density-functional theory calculations showing how the optical absorption spectrum of the molecule is altered due to the attachment on the surface. Also, the charge transfer between catechol and surface is analyzed.

1. Introduction: One possible and promising alternative to silicon-based solar cells are so-called dye-sensitized solar cells (DSSCs) [1]. Desirable features like low cost raw materials and simple production processes in such devices make them attract attention and significant research efforts. However, DSSCs today still exhibit a much lower efficiency than conventional solar cells [2].

In a DSSC, dye molecules absorb the sunlight. These molecules are attached to the surface of a wide band-gap semiconductor. Often nanostructured TiO₂ is chosen as semiconductor material. Following the light absorption, the excited electrons of the dye can be transmitted into the conduction band of the semiconductor, from where they reach the front electrode. A redox couple, most of the time in an organic solvent, fills the hole left by the electron and thus reduces the oxidized dye back to its neutral state. The redox couple itself is regenerated at the back electrode, thereby closing the electric circuit.

From this description it is evident that a correct alignment of the energy levels of the adsorbed dye molecules with those of the semiconductor is crucial. The highest occupied molecular orbital (HOMO) of the dye must fall in the band-gap of the semiconductor, while the excited states of the dye must be in resonance with the conduction band.

The short-circuit current under illumination J_{sc} of the solar cell and the open-circuit voltage under illumination V_{oc} constitute its key physical parameters. In a DSSC J_{sc} is related to the optical gap of the dye and the efficiency of the conversion of electron-hole pairs. Similarly, the energy difference between the band edge of the conduction band (CB) of the semiconductor and the energy level of the redox couple determine V_{oc} . The choice of solvent and redox couple (e.g. iodide/triiodide (I^-/I_3^-)) determine the latter, while the CB band edge depends on several factors like the exposed surface, the dye, and the solvent [3]. The development of new and better DSSCs would profit from the calculation of V_{oc} in a realistic model, including electrolyte and surface imperfections. However, such a realistic description would necessitate very large computational cells to accommodate meaningful portions of (defected) surfaces and many solvent molecules. Such large systems are unfortunately still out of the scope of accurate first-principles calculations. In spite of this limitation, electronic structure calculations can nevertheless play an important role in the elucidation of elementary processes in such technological devices.

In this Letter, we focus on the electronic energy levels and optical absorption properties of the dye molecules and how these features are altered when the molecule is attached to a semiconductor surface. For our illustrations, we use a TiO₂ anatase (101) surface, which is the most widely studied semiconductor in the context of DSSCs. We choose the catechol molecule (1,2-dihydroxybenzene) as a prototypical organic molecule to be

adsorbed on the semiconductor surface. In fact, catechol has proven itself as an attractive ligand for functionalizations of many different substrates (including TiO₂) by providing a stable, versatile and effective surface modification, even in wet conditions [4].

Catechol is an often-used sensitizer in solar cells [5], in the photocatalytic oxidation of organic pollutants it serves as a model system [6], and it can scavenge radicals in biomolecular systems [7]. Furthermore, catechol as a functional group can effectively link complex polymers or bio-molecules in biomedical applications [8]. It is even used as a ligand in the formation of valence-tautomeric compounds for spintronic applications [9]. These favorable features are to a large extent thanks to catechol's anchoring mechanism via bidentate adsorption.

Here we show in such an idealized system consisting of catechol adsorbed to a defect-free anatase-101 surface how the optical absorption properties of the isolated molecule are modified by the presence of the surface and how the adsorption leads to charge-transfer between surface and adsorbate.

2. Methods: All calculations have been carried out in the framework of density functional theory (DFT) [10]. We have used the quantum-ESPRESSO (QE) suite of programs [11] which provides a unified framework for both ground-state and excited state computations. Within QE, the Kohn-Sham (KS) orbitals are represented using a plane-wave basis set. The ionic potentials due to the nuclei and the (clamped) core electrons are included using Vanderbilt's ultrasoft pseudopotentials [12]. The pseudopotentials from the standard QE distribution have been employed [13]. All calculations have been carried out using the Perdew-Burke-Ernzerhof (PBE) [14] semilocal functional.

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4 References

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