DFT and GW Calculations of the Electronic Structure for Thiophenes on TiO_2

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For the understanding of the photovoltaic processes in hybrid polymer-oxide structures it is essential an accurate theoretical prediction of the electronic properties of the system. In the case of polythiophene and TiO_2, a simple inspection of the band-edge alignment of the isolated materials, taken from experimental data, already indicates the possibility of efficient photovoltaic operation. However, it is not clear whether charger transfer is favored or even allowed, once it depends on the nature of the interface. Here we used *ab initio* Density Functional Theory (DFT) calculations to investigate the electronic properties of a model system composed by an infinite thiophene polymer on a TiO_2 (101)-anatase surface [1]. The DFT results show interface states extended through the materials, both in the valence and in the conduction bands, indicating there is an electronic coupling which favors charge transfer. This is the case of the states corresponding to the polymer LUMO and the valence band top (VBT) of TiO_2. According to this picture, an electron excited in the polymer and promoted to the LUMO could be transferred to the TiO_2, while by exciting an electron from the oxide VBT the hole left in this band could be transferred to the polymer layer. Nevertheless, the practically closed effective gap in the DFT band structure, due to the DFT underestimation of band gaps, demanded further inclusion of manybody corrections. G_0W_0 calculations were then performed for a simplified model of a thiophene molecule-TiO_2 system, and for the separated subsystems (molecule, polymer, and TiO_2 slab). From the results obtained we can estimate for the polymer-oxide system a restored wide gap between the polymer HOMO and the conduction band minimum of TiO_2, and a proper alignment of the conduction and valence band edges at the hybrid system interface, as needed for the photovoltaic application. We thank Daniele Varsano for help with the Yambo Code [2] and acknowledge support from FAPESP and CNPq.

Keywords: electronic structure, DFT, GW, thiophene, TiO_2, hybrid system, photovoltaics.

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