

A Concerted Investigation For Metal/Semiconductor Nanointerface: Interlayer Charge Transfer At Ag/TiO₂

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In the field of hybrid materials, suitably designed nanoheterojunctions enhance synergistic functionalities and allow to obtain “brave new materials” with physicochemical properties that are not simply the addition of the precursors’ ones, but are completely new, different, and sometimes unexpected. For these reasons, the use of them has paved the way toward promising applications in many fields, such as electrocatalysis, photocatalysis, electroanalysis, and environmental chemistry, impacting on the everyday life [1].

However, research on such systems is most often dominated by trial and error procedures, while a deep atomistic understanding of the phenomena inside the junction region driving appropriate design of the final device is missing. Here, a concerted theoretical and electrochemical investigation is proposed to gain insights into the important class of heterojunctions made by metal-semiconductor interfaces.

The presented case of study is the silver/anatase hybrid nanocomposite, a very promising material for advanced sensing applications [2]. Considering that in most cases titania semiconductors are useless in electroanalysis and silver is subject to fouling and oxidation/passivation, such broad outcomes were totally unexpected. Specifically, Ag/TiO₂ interphase provided the first photorenewable sensor device, pushing the limits in terms of accuracy, sensitivity, detection limits, and photoactivity [3]. Despite the ongoing research, a quantitative and comprehensive understanding of the physics behind this nanocomposite is still missing, thus preventing its full exploitation and the extension of the same paradigm to other systems and devices.

In particular, cyclic voltammetry and electrochemical impedance spectroscopy are used in combination with periodic plane-wave DFT calculations, giving comparable qualitative, but also quantitative results. We measure the exceptional electrochemical virtues of the Ag/TiO₂ junction in terms of current densities and reproducibility, providing their explanation at the atomic-scale level and demonstrating how and why silver acts as a positive electrode [4]. We theoretically estimate the overall amount of electron transfer toward the semiconductor side of the interface at equilibrium and suitably designed electrochemical experiments strictly agree with the theoretical charge transfer estimates. Moreover, photoelectrochemical measurements and theoretical predictions show the unique permanent charge separation occurring in the device, possible because of the synergy of Ag and TiO₂, which exploits in a favorable band alignment, in a smaller electron-hole recombination rate and in a reduced carrier mobility when electrons cross the metal-semiconductor interface. Finally, the hybrid material is proven to be extremely robust against aging, showing complete regeneration, even after one year [4].

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