A Concerted Electrochemical and Theoretical Investigation of the Ag/TiO_2 nano-heterojunction

L. Falciola, V. Pifferi, G. Di Liberto, L. Lo Presti, M. Ceotto

Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133-Milano, Italy
e-mail: luigi.falciola@unimi.it

Suitably designed nano-heterojunctions are able to enhance synergistic functionalities of different materials yielding to “brave new systems” with innovative and sometimes unexpected physicochemical properties [1]. However, the complete understanding of these devices has to be deeply studied. In this work, a concerted theoretical and electrochemical investigation is proposed to gain insights into a metal-semiconductor interface, namely that created by the silver/anatase hybrid nanocomposite, a promising material for advanced sensing applications [2]. In particular, it provided the first photorenewable and anti-fouling sensor device, enhancing the analytical limits in terms of accuracy, sensitivity, detection limits, and photoactivity [3]. Furthermore, the hybrid material is proven to be extremely robust against aging, showing complete regeneration, also after one-year storage.

The electrochemical/electroanalytical virtues of the Ag/TiO_2 junction were evaluated in terms of current densities and reproducibility, providing their explanation at the atomic-scale level and demonstrating how and why the final device can act as silver-cation positive electrode [4]. Moreover, Cyclic Voltammetry and Electrochemical Impedance Spectroscopy were used in combination with periodic plane-wave DFT calculations, giving comparable qualitative but also quantitative results. In particular, we theoretically estimated the overall amount of electron transfer toward the semiconductor side of the interface at equilibrium and suitably designed electrochemical experiments, which strictly agree with the theoretical charge transfer estimates. Moreover, photoelectrochemical measurements and theoretical predictions show the unique permanent charge separation occurring in the device [4].

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Additional information:

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- name and status (Mr./Mrs., Dr., Prof., etc) of the presenting author:
  Professor Luigi Falciola
- complete address for correspondence (e-mail, phone, postal address)
  Università degli Studi di Milano
  Dipartimento di Chimica
  via Golgi 19, 20133, Milano, Italy
  00390250314057
  Luigi.falciola@unimi.it
- accompanying persons (if any): name(s) and status
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