Supplementary Material (ESI) for Energy & Environmental Science

Photovoltaic performance of nanostructured ZnO sensitized with an indoline dye: a comparison between nanoparticulate films and electrodeposited nanowire arrays - Supporting Information

Elena Guillén[1], Eneko Azaceta[2], Laurie M. Peter[3], Arnost Zukal[4],

Ramón Tena-Zaera[2,*] and **Juan A. Anta[1,*]**

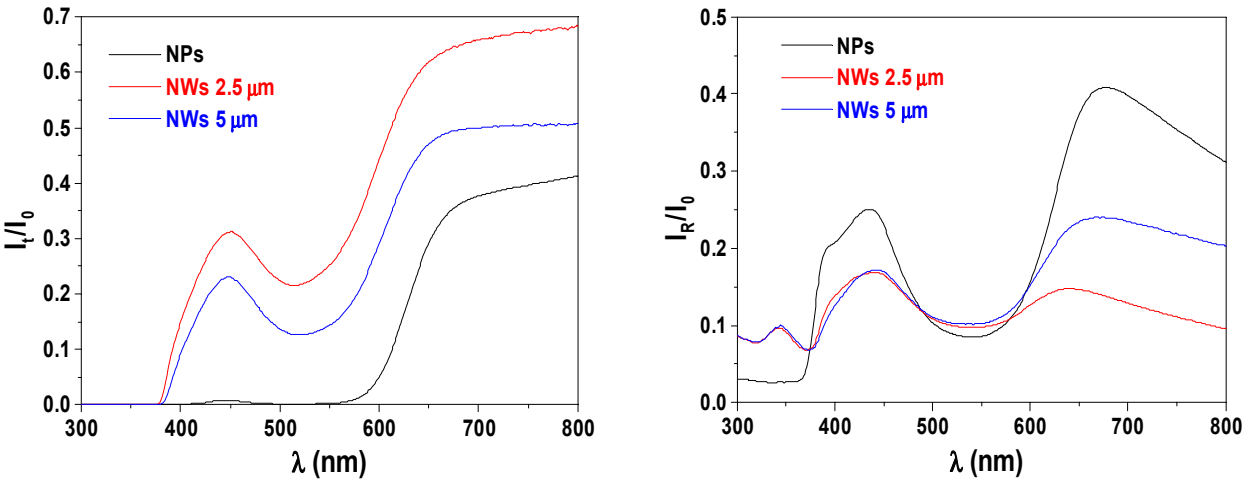
[1]Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, 41013 Sevilla, Spain

[2]New Materials Department, CIDETEC, Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastián, Paseo Miramón 196, Donostia-San Sebastián 20009, Spain

[3]Department of Chemistry, University of Bath, BA2 7AY, United Kingdom.

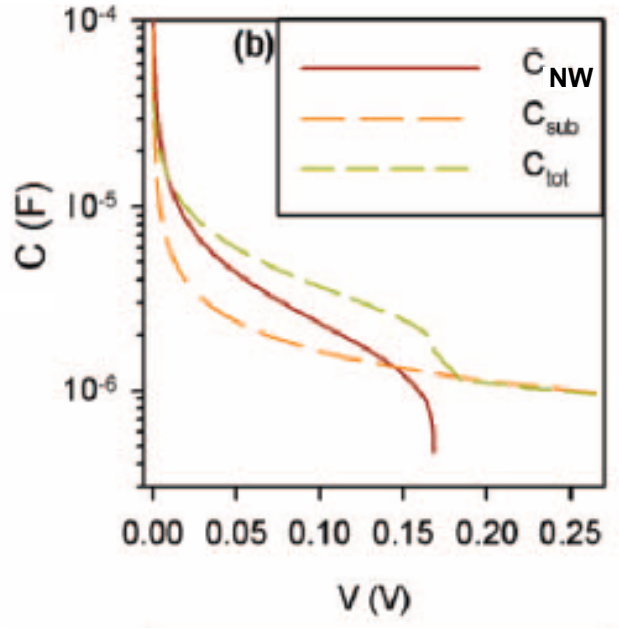
4 Department of Synthesis and Catalysis, J. Heyrovsky Institute of Physical Chemistry, v.v.i, Academy of Sciences of the Czech Republic, Dolejskova 3, CZ-18223-Prague 8

Figure S1. a) Transmittance and **b)** reflectance spectra of glass/SnO2:F/ZnO/D149 samples constituted of nanoparticles (black) and nanowire arrays (2.5 (red) and 5 µm (blue) in length).



Comments of the capacitance of the ZnO blocking layer.

Figure S2. The capacitance f the nanowire array and the blocking layer as a function of the potential.



(The figure has been taken from the reference 57 (figure 3b).)

The total capacitance of the samples is the sum of capacitance of the buffer layer plus the capacitance of the nanowires (because they are associated in parallel). In this sense the total capacitance is governed by the highest one, as can be seen in the graph this is the nanowire capacitance, except for the most positive potentials. Only when the nanowire capacitance is low enough to be comparable with the capacitance of the buffer layer, should the later one be taken into account.

Effect of back reaction on open circuit decay in case of non-linear kinetics

OCV decays were numerically simulated by solving the equation

$$\frac{dn_c}{dt} = \frac{I_{abs}}{d} - \frac{n_c^{\gamma}}{\tau_0} - \frac{j_{substrate}}{qd}$$

were n_c is the free electron density, I_{abs} is the absorbed photon flux, d is the film thickness, γ is the reaction order with respect to the free electron concentration and the current through substrate can be computed from the Tafel aproximation of the Butler-Volmer equation:

$$j_{substrate} = j_0 \exp\left(\frac{\alpha n q V}{k_B T}\right)$$

where j_0 is the exchange current density.

Figure S3. Simulation of OCV decay. It is showed that it is not possible to fit the NW response with γ = -0.456. A fit can be obtained using substrate shunting with an exchange current density of 10^{-8} A cm^2. However it must be born in mind that shunting may modify the electron density profile within the film at open-circuit, hence invalidating the application of the continuity equation above (that assumes a constant Fermi level within the film).