

Electronic Supporting Information

Quantum Dot-Sensitized Solar Cells Based on Directly Adsorbed Zinc Copper Indium Sulfide Colloids

Néstor Guijarro,^{*,†} Elena Guillén,[‡] Teresa Lana-Villarreal, and Roberto Gómez^{*}

Institut Universitari d'Electroquímica i Departament de Química Física, Universitat d'Alacant, Apartat 99,
E-03080 Alacant, Spain.

Present addresses:

[†]Laboratory for Molecular Engineering of Optoelectronic Nanomaterials, Institute of Sciences and
Engineering, École Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland.

[‡] Abengoa Research, C/ Energía Solar 1, Campus Palmas Altas, 41014, Sevilla, Spain

Email : nestor.guijarro@epfl.ch, roberto.gomez@ua.es

FAX : +34 965903537 ; Tel : +34 96590 3748

1.- Details of the synthesis of ZCIS colloidal QDs

Following the procedure reported by Nakamura et al.¹ with minor changes, 0.099 g of CuCl (Sigma-Aldrich, 98 %) and 0.22 g of InCl₃ (Sigma-Aldrich, 98 %) were dissolved in 6 ml of Oleylamine (Aldrich, Technical grade 70 %) by stirring and mild heating (*solution 1*), whereas 0.18 g of Zinc diethyldithiocarbamate (Aldrich 97%) were readily dissolved in 6 ml of Trioctylphosphine (Sigma-Aldrich) and 24 ml of Octadecene (Sigma-Aldrich, technical grade 90 %) (*solution 2*). Once the precursors were dissolved, both solutions were mixed and gently heated while monitoring the reaction temperature. An apparent change in the color of the dispersion from yellow to dark red was observed when the temperature rose from 115 °C to 140 °C. Higher temperatures led to dark brown solutions. All the samples studied in this work were obtained by stopping the reaction once the solution temperature reached 140 °C, by cooling down to ambient temperature the reaction flask (absorption and emission spectra recorded for different batches demonstrated reproducible results). All these processes were carried out under N₂ atmosphere and reagents were used without further purification. The as-prepared dispersions have proven to be stable in the dark for months, but washing procedures to remove the excess of reagents and by-products are required prior carrying out the described sensitization.

2.- Estimation of energy levels

The energy level of the sulfur/sulfide redox couple was obtained from the redox potential (-0.476 V vs SCE), by assuming that the potential of the standard hydrogen electrode corresponds to -4.44 eV in the vacuum scale.²

The location of the TiO₂ conduction band edge was determined by means of cyclic voltammogram (Figure 4) following a recently reported approach.³ The positions of the energy levels of the ZCIS QDs were estimated by combining photoelectrochemical and absorption measurements, as previously reported by some of us.³ The onset of absorbance spectrum of ZCIS dispersion indicates that the energy band gap of ZCIS colloids is 1.88 eV. Additionally, photocurrent transients as a function of the potential were performed to determine the position of the conduction band (CB) edge (Figure S1). More specifically, upon light absorption, photogenerated electrons are injected into the electron collector (FTO substrate), whereas holes are rapidly captured by sulfide ions. As expected, the photocurrent decreases as the potential becomes more negative (i.e. the Fermi level is shifted upward), until complete quenching at -1.22 V (vs. Ag/AgCl). We consider that complete quenching is attained when both the donor energy level of ZCIS QDs and the Fermi level of substrate match. Therefore, the CB of ZCIS QDs is located at -1.22 V (vs. Ag/AgCl/KCl (sat.)) or -3.42 eV vs. vacuum. It must be underlined that this is just an approximation for the location of the ZCIS QD CB, which may depend on the contacting media.

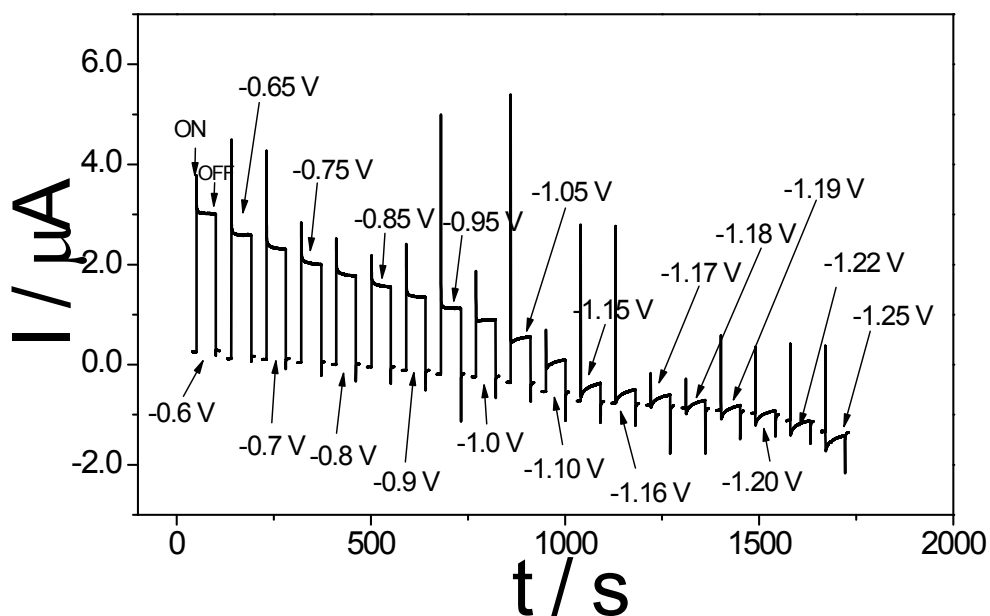


Figure S1. Photocurrent transients for a FTO/ZCIS electrode recorded at different applied potentials vs. Ag/AgCl (labeled). All transients were performed in an N_2 -purged 1 M Na_2S + 1 M NaOH electrolyte (irradiance: $48.0 \text{ mW} \cdot \text{cm}^{-2}$).

3.- References

1. H. Nakamura, W. Kato, M. Uehara, K. Nose, T. Omata, S. Otsuka-Yao-Matsuo, M. Miyazaki and H. Maeda, *Chem. Mater.*, 2006, **18**, 3330-3335.
2. S. Trasatti, *Pure & Appl. Chem.* 1986, **58**, 955-966.
3. N. Guijarro, T. Lutz, T. Lana-Villarreal, F. O'Mahony, R. Gómez, S. A. Haque, *J. Phys. Chem. Lett.* 2012, **3**, 1351-1356.