Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2018

Improving charge injection and charge transport in CuO-based *p*-type DSSCs – A quick and simple precipitation method for small CuO nanoparticles

Oliver Langmar[a], Carolina Ganivet[b], Peter Schol[a], Tobias Scharl[a], Gema de la Torre[b], Tomás Torres[b,c], Ruben D. Costa[a,d,] and Dirk M. Guldi[a,*]*

[a] Department of Chemistry and Pharmacy, Interdisciplinary Center for Molecular Materials, University of Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany;

[b] Universidad Autónoma de Madrid, c/Francisco Tomás y Valiente 7, 28049 Madrid, Spain;

[c] Instituto Madrileño de Estudios Avanzados (IMDEA)-Nanociencia c/ Faraday, 9, Cantoblanco, 28049 Madrid, Spain;

[d] Instituto Madrileño de Estudios Avanzados (IMDEA)-Materiales, c/Eric Kandel, 2, Tecnogetafe, 28906 Getafe, Madrid, Spain.

1. Synthesis

All reagents and starting materials were used as obtained from commercial sources.

CuO nanoparticles (NPs) were prepared according to a quick and simple precipitation route developed by Zhu *et.al.* which was slightly modified.[1] In detail, 150 ml of an aqueous 0.02M copper(II) acetate solution and 0.5 ml glacial acetic acid were mixed in a round-bottom flask and stirred for several minutes yielding a clear blue solution. Then, this solution was heated to 65°C under vigorous stirring and as soon as the target temperature was reached, 0.4 g of sodium hydroxide was swiftly added. The generation of copper(II) hydroxide was confirmed by the formation of a cloudy blueish precipitate that gradually transformed to copper(II) oxide indicated by a change in colour from blue to dark brown/black. Stirring at 65°C for 5-10 minutes led to the complete formation of the CuO-NPs. After cooling down to room temperature the product was collected and washed one time with distilled water and three times with ethanol. Drying overnight yielded the final product as a dark-brown/black powder ready for further use.

2. Photophysical, electrochemical and microscopic methods

Diffuse reflectance measurements were performed with a Cary 5000 (Varian) equipped with an integrated sphere; Spectralon was used as a reference. The bandgap energy (E_g) of the investigated CuO-electrodes was determined according to literature procedures.[2,3] Scanning electron microscopy (SEM) measurements were performed using a Zeiss Gemini 55 Ultra electron microscope while transmission electron microscopy (TEM) images were recorded on a Zeiss TEM 912 Omega. X-ray diffraction (XRD) assays were performed using a D8Advance (Bruker AXS) using a Cu Kα radiation source. Kelvin Probe Force Microscopy (KPFM) assays were performed with a JPK Nanowizard 4 atomic force microscope (AFM) equipped with a KPFM module and a Cr/Pt coated silicon cantilever probe (force constant 3 N/m, resonance frequency 75 kHz). A freshly cleaved highly oriented pyrolytic graphite sample (HOPG, ZYH 3.5° mosaic spread, µmasch) with a known work function of 4.65 eV was used as a reference to calculate the respective work function of the measured sample (Equation S1 and S2):[4]

$$\varphi_{Tip} = CPD_{HOPG} + \varphi_{HOPG} \tag{S1}$$

$$\varphi_{sample} = \varphi_{Tip} - CPD_{Sample} \tag{S2}$$

with φ being the respective work function of either the AFM tip, the HOPG reference or the sample under examination. While CPD is the contact potential difference between the tip and the respective sample, which was measured directly by the KPFM assays. Finally the obtained work function, which represents the Fermi-level energy (E_F) of the probed sample, is referenced against the normal hydrogen electrode (*vs* NHE).[5] BET N_2 absorption measurements were performed on powder samples of the respective CuO NPs using a Quantochrome Nova Station C. Nitrogen isotherms were measured at an relative pressure (P/P_0) from 0.05 to 0.27 at – 195.85 °C in liquid nitrogen. Measurements of film thicknesses were performed with the help of an OM DektakXT profilometer (Bruker).

3. Device preparation and analysis

Pastes of the synthesized and commercial (CAS No. 1317-38-0, 12 nm, Iolitec) CuO-NPs were prepared by diluting triacetin (Sigma-Aldrich), ethyl cellulose (Sigma-Aldrich) and the respective CuO powder in ethanol. After several days of stirring the well mixed suspension was ready for doctor blading. Prior to doctor blading, fluorine doped tin oxide glass slides (FTO, 8Ω/square, Pilkington, XOP Glass) were washed in an ultrasonic bath in solutions of acetone, tenside solution, water, and isopropanol, respectively for 15 minutes. After this washing protocol the slides were cleaned in an ozone lamp cleaner (Jelight company, Inc). The CuO-pastes were applied by doctor blading onto the FTO slides, with the help of a Scotch tape mask (total area of the electrodes was 0.2 cm^2). In the next step the as prepared films were baked at

300°C for 30 minutes before they were immersed into **ZnPc1** dye solutions ($c = 1 \times 10^{-4}$ M in ethanol) for one hour. Both of the aforementioned properties were optimized in previous studies.[3,6]

Final devices were assembled by pressing CuO electrodes and the Pt counter electrodes (5 mM H_2PtCl_6 in isopropanol on FTO baked at 400°C) with a Syrlin spacer (25 µm, Solaronix) at 150°C. The electrolyte (1 M LiI and 0.4 M I_2 in acetonitrile) was filled into the cell by two pre-drilled holes in the counter electrode before the cell was sealed with Syrlin foil and an additional glass slide.

The assembled *p*-type DSSCs were tested under dark and 1 sun AM 1.5 conditions. Photocurrent-voltage (J-V) curves were recorded with a PGSTAT30 potentiostat (Metrohm) in the range of -0.2 to 0.05 V with the counter electrode connected to the CuO and the working electrode connected to the platinum electrode. Five devices have been measured for the commercial and synthesized CuO-NPs each to ensure the reproducibility of our results. Electrochemical impedance spectroscopy (EIS) was measured under dark and 1 sun AM 1.5 conditions with the same potentiostat in the range of 100 kHz to 0.01 Hz. Linearity of the obtained EIS response was ensured by using a small amplitude of 10 mV. EIS measurements were performed starting at open-circuit conditions and then going down in 10 mV steps until short-circuit conditions have been reached. The iR-drop has been corrected with the following equation – Equation S3:[7,8]

$$V_{app} = V_f - JR_s \tag{S3}$$

With V_{app} being the applied voltage, V_f the potential related to the separation of Fermi levels, J the current density at V_f and R_s as the sum of r_s and R_{CE} extracted from the EIS measurements. All the obtained Nyquist plots have been fitted with the electrical circuit model shown in **Figure S2**, which has been widely used in the past for *p*-type DSSCs.[3,8] Intensity modulated photocurrent spectroscopy (IMPS) was measured using a PGSTAT30 potentiostat including a LED driver kit (Metrohm) and a costum build LED array consisting of five LEDs with an emission maximum at 630 nm (Luxeon Star). The amplitude of the bias light was set to 10% and all measurements have been performed under short-circuit conditions which could be varied by changing the illumination intensity of the LED array. Incident photon-to-current efficiency (IPCE) has been measured in the spectral range of 300 to 800 nm by illuminating the *p*-type CuO DSSCs with a xenon arc lamp over a Cornerstone 260 ¼ m Monochromator equipped with a Merlin digital radiometric lock-in-system.

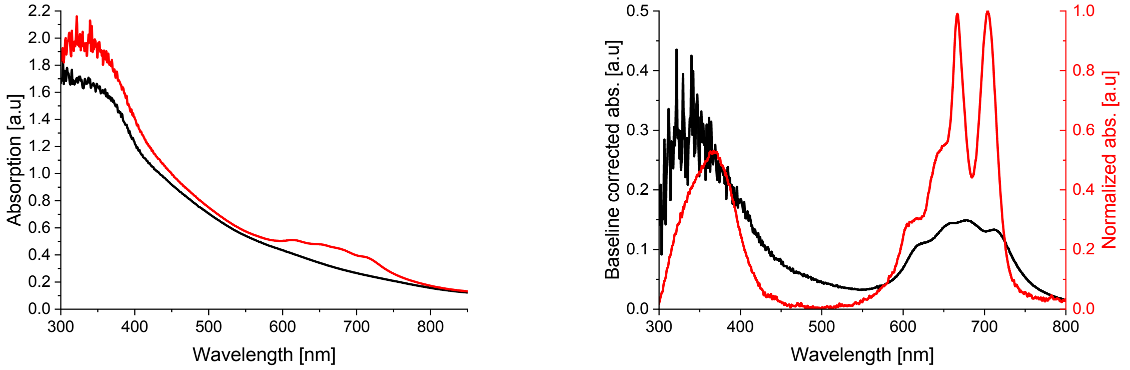

Figure S1: Left - Absorption spectra of non-sensitized (black) and **ZnPc1**-sensitized syn-CuO photocathodes (red) with comparable thicknesses. Right – Baseline corrected absorption spectrum of **ZnPc1**- and non-sensitized syn-CuO photocathodes (black) and normalized absorption spectrum of the **ZnPc1**-photosensitizer in solution (red). Slight variations in the high-energy region of the spectrum are due to light scattering of the CuO films and the FTO substrate.

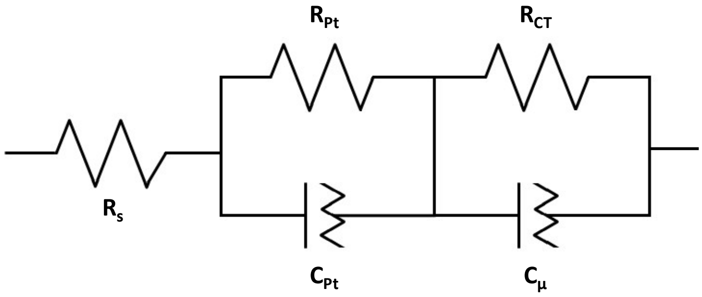

Figure S2: Electrical circuit model used for EIS data fitting

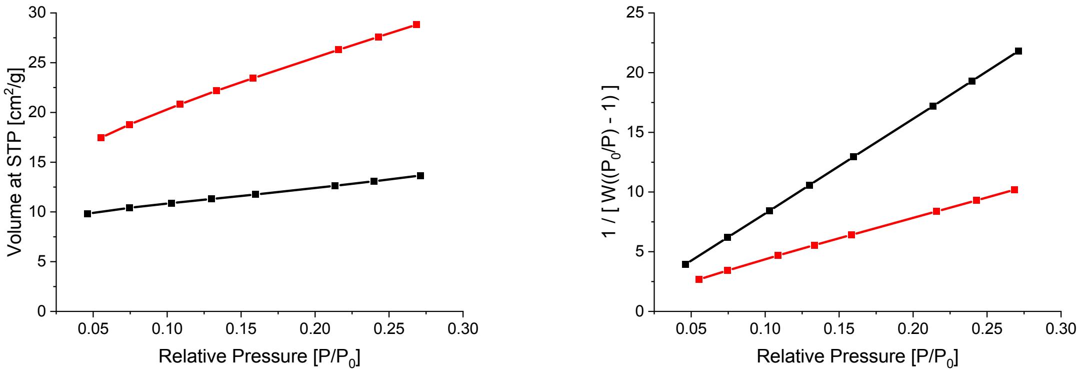

Figure S3: BET N_2 adsorption isotherms for the com-CuO (black) and syn-CuO (red) NP powder samples.

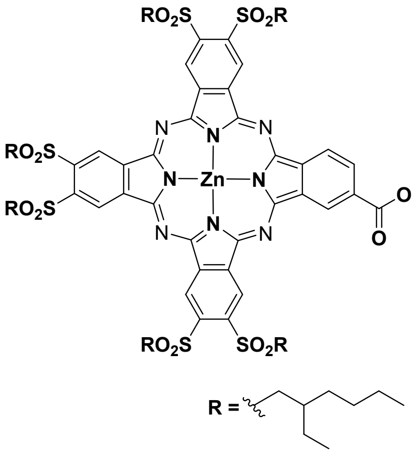

Figure S4: Structure of the electron accepting phthalocyanine **ZnPc1** that was used as photosensitizer.

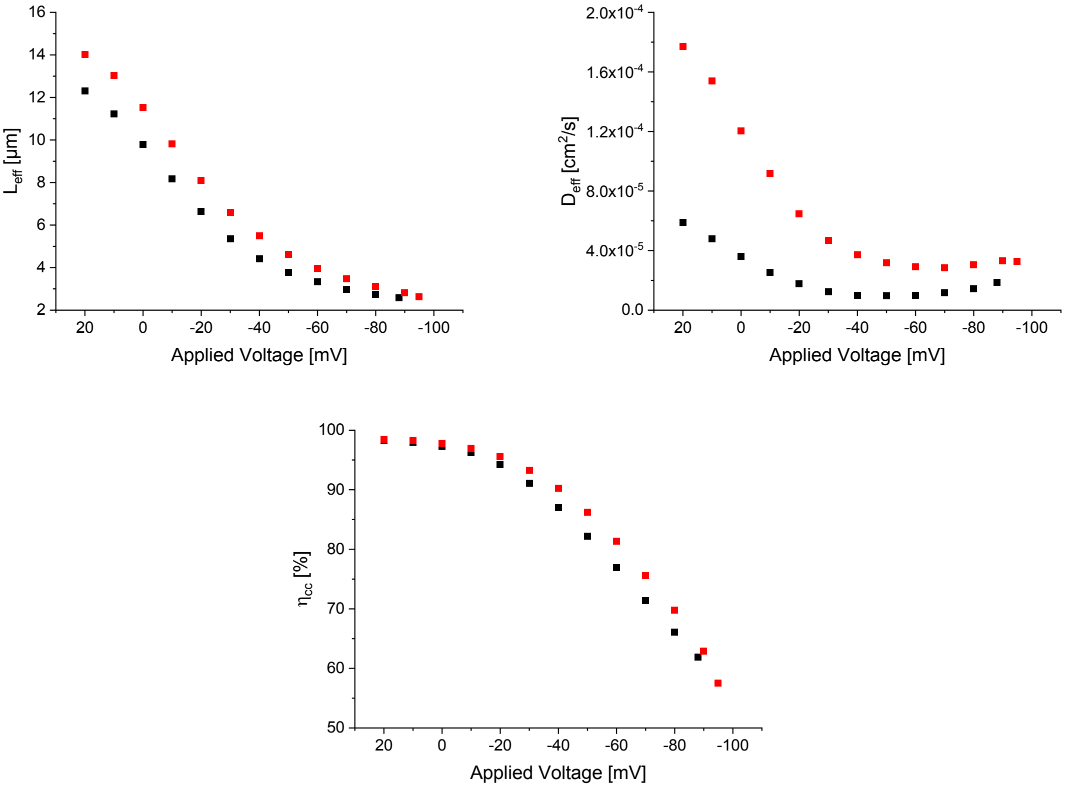

Figure S5: L_{eff} (top left), D_{eff} (top right) and η_{cc} (bottom) *vs* applied voltage for *p*-type DSSCs consisting of com-CuO (black) or syn-CuO (red) based photocathodes.

4. References:

1 J. Zhu, D. Li, H. Chen, X. Yang, L. Lu and X. Wang, *Mater. Lett.*, 2004, **58**, 3324–3327.

2 V. Kumar, S. K. Sharma, T. Sharma and V. Singh, *Opt. Mater. (Amst).*, 1999, **12**, 115–

119.

3 O. Langmar, C. R. Ganivet, A. Lennert, R. D. Costa, G. de la Torre, T. Torres and D. M. Guldi, *Angew. Chemie Int. Ed.*, 2015, **54**, 7688–7692.

4 W. Zhang and Y. Chen, *J. Nanoparticle Res.*, 2013, **15**, 1–7.

5 C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367–2371.

6 O. Langmar, C. R. Ganivet, G. de la Torre, T. Torres, R. D. Costa and D. M. Guldi, *Nanoscale*, 2016, **8**, 17963–17975.

7 F. Fabregat-Santiago, G. Garcia-Belmonte, I. Mora-Seró and J. Bisquert, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9083–9118.

8 Z. Huang, G. Natu, Z. Ji, M. He, M. Yu and Y. Wu, *J. Phys. Chem. C*, 2012, **116**, 26239–26246.