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SUPPORTING INFORMATION

for

Organic heterojunction photocathodes for optimized photoelectrochemical hydrogen peroxide production

Maciej Gryszel,*[1,2] Aleksandr Markov,[1,2] Mikhail Vagin[1,3] and Eric Daniel Głowacki[1,2]

[1]*Laboratory of Organic Electronics, ITN Campus Norrköping, Linköping University, 60221, Norrköping, Sweden*
[2]*Wallenberg Centre for Molecular Medicine (WCMM), Linköping University, Linköping, Sweden*
[3]*Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden*

E-mail: maciej.gryszel@liu.se

Experimental Methods

Materials:

N,N'-dimethyl perylene tetracarboxylicbisimide (PTCDI), Metal-Free Phthalocyanine (H_2Pc), and gold (99.99%, granules 1-3 mm) were supplied by BASF, TCI, and Testbourne respectively. Epindolidione (EPI) was synthesized according to published procedures. All pigments were purified by ×3 temperature-gradient sublimation before use. All other chemicals were obtained from Sigma-Aldrich and used without any purification.

Fabrication of photoelectrodes:

For fabrication of the photoelectrodes, as a conducting substrate, ITO-coated glass pieces (Kintec, 15 ohm/sq, 2.5 × 2.5 cm) were used, after cleaning by sequential sonication in acetone, isopropanol and DI water. Afterwards, the substrates were treated with UV-generated ozone for 30 minutes and placed in a stainless steel chamber, containing vapour of *n*-octyltriethoxysilane (OTS) for 2 h at 90 °C. After that time, substrates were washed with acetone, water and sonicated in acetone for 15 min. The OTS treatment was found to improve the adhesion of the organic semiconductor layer and prevent delamination, without any impact on photocurrent. The OTS treated substrates were covered with an adhesive foil shadow mask, exposing a central part of 2 × 2 cm size. Sublimation of organic pigment thin films was performed in an organic-designated, 2-source vacuum evaporation system (Moorfield) from resistively heated ceramic crucibles. The H_2Pc/PTCDI PN structures were prepared by consecutive evaporation of each pigment within one evaporation process. All organic evaporations were performed at a rate of 1-2 Å s^{-1} except EPI, evaporated at a rate of 7-9 Å s^{-1}. For Au evaporations (at a rate of 1 Å s^{-1} in all cases), samples were transferred to another, metal-designated vacuum evaporation system (Moorfield). Thickness of all layers (given in the table S1) were controlled by quartz crystal monitors during evaporation processes, tooling factors values were determined with Dektak 3ST profilometer beforehand.

Table S1. Thicknesses of layers in multi-layered organic photoelectrodes

Sample structure	**Thickness of corresponding layer [nm]**
H_2Pc	60
H_2Pc/PTCDI	60/60
H_2Pc/PTCDI/Au	60/60/5
H_2Pc/PTCDI/Au/PTCDI - *PN/Au/PTCDI*	60/60/5/30
H_2Pc/PTCDI/Au/EPI - *PN/Au/EPI*	30/30/5/100
EPI	200
2 × (H_2Pc/PTCDI/Au) + H_2Pc/PTCDI/Au/PTCDI - *3PN/Au/PTCDI*	2 × (30/30/2) + 30/30/5/30
H_2Pc/PTCDI/Au/H_2Pc/PTCDI/Au/PTCDI - *2PN/Au/PTCDI*	30/30/2 + 30/30/5/30
H_2Pc/PTCDI/Au/PTCDI - *1PN/Au/PTCDI*	30/30/5/30

Electrochemical characterisation:

Photoelectrochemical measurements of the photocathodes were performed in a three-electrode system, with a Pt coil as counter electrode, and the Ag/AgCl wire in 3 KCl as a reference electrode, with an Ivium technologies Vertex One potentiostat. All electrodes were placed in a Redox.me MM PEC H-CELL (Fig. S1) with two electrolyte chambers separated with nafion membrane, containing 10 ml of electrolyte in all cases. Active area of the sample mounted in the H cell is limited to 1.0 cm^2. As a light source, a tungsten halogen lamp (with FTO-coated glass filter to limit infrared heating) was used, after its calibration to a light intensity of 100 mW/cm^2 (1.00 sun). All samples were illuminated from the substrate side, *i.e* through the ITO. The cyclic voltammetry experiments were performed with the 2 mV/s scan rate within +0.3 V to -0.4 V range. The more positive polarization showed significant dark current, the more negative polarization caused a decrease in the sample photocurrent in the subsequent scans. The cathodic compartment was magnetically stirred (800 rpm) and constantly purged with oxygen during all measurements. In case of the measurements in two electrode arrangement, Pt coil counter electrode was replaced with Pt mesh placed close to the nafion membrane.

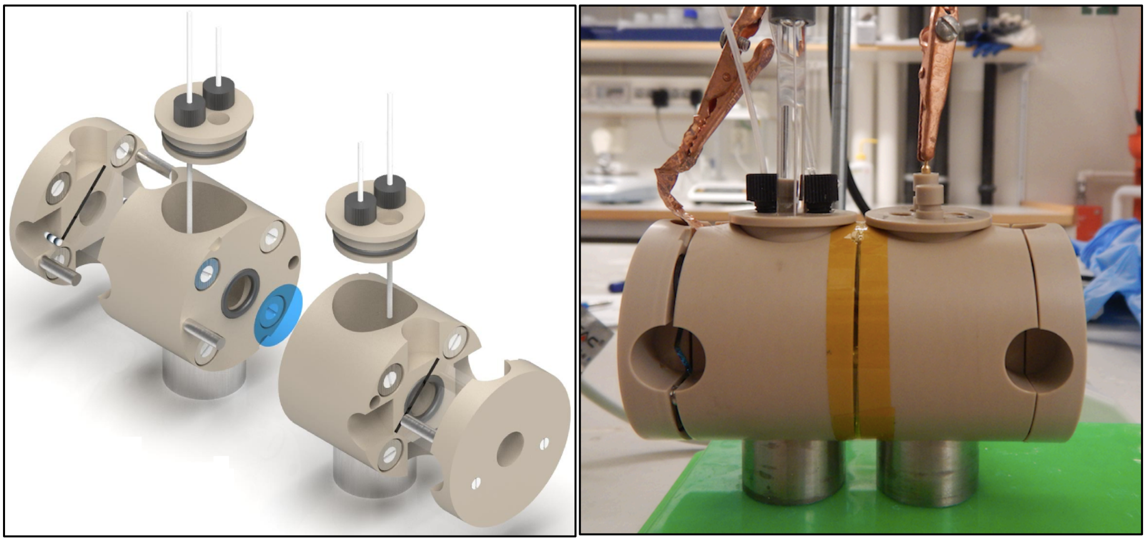

Fig. S1. The Redox.me MM PEC H-CELL photoelectrochemical H-cell used in all experiments in this work.

Photocathodes surface morphology characterization:

SEM images were taken with SEM Zeiss Sigma-500 at an acceleration voltage of 3 kV, using the in-lens secondary electron detector. For this purpose, uncovered areas of samples were contacted to the SEM stage using copper tape and placed in the microscope chamber. Before imaging, samples were washed with DI water and dried with stream of N_2.

Determination of the degradation of pigments in the photocathodes after 6h photoelectrolysis:

Light and electrolyte exposed areas of PN/Au/PTCDI and PN/Au/EPI samples, after 6 h of photoelectrolysis and subsequent UV-vis and SEM characterization, were separated from unused areas of the samples, wiped with cotton swab rinsed in acetone. The remaining active area of 1 cm^2 of multi-layer organic structures was dissolved in conc. H_2SO_4 (2.0 ml in case of the PN/Au/PTCDI, 1.0 ml in case of the PN/Au/EPI). The same was done for pristine unused samples, prepared along with 6 h-used samples beforehand as a reference. A UV-Vis spectrum of each solution was measured with a Synergy H1 Microplate reader (BioTek® Instruments, Inc.) using 96-Well Polystyrene flat bottom plates, allowing comparison of 6 h used with unused samples.

Determination of hydrogen peroxide concentration and Faradaic efficiency:

The quantification of the produced hydrogen peroxide was done spectrophotometrically by following the oxidation of 3,3′,5,5′-Tetramethylbenzidine (TMB) in the presence of horseradish peroxidase (HRP) and citric acid–phosphate buffer solutions. Values of absorbance were measured at 653 nm with Synergy H1 Microplate reader (BioTek® Instruments, Inc.) in 96-Well Polystyrene flat bottom plates. Depending on hydrogen peroxide concentration in the sample, aliquots of different volumes (1-5 μL) were taken and added to the corresponding volume of HRP/TMB/buffer solution, in every case giving 300 μL of the solution. The obtained absorbance values were recalculated to concentration values basing on calibration curve formulas ($R^2 > 0.998$ in every case). Faradaic efficiencies of the photoelectrolysis processes were determined basing on H_2O_2 concentration, electrolyte volume and theoretical molar amount of H_2O_2 generated (based on Faraday´s law and I=f(t) dependence).

Determination of the number of the transferred electrons per oxygen molecule by an experiment with rotating disc electrode:

RDE electrochemical experiments were performed with an Autolab type III bi-potentiostat (Autolab, EcoChemie, Netherlands). The RDE working electrode comprises a glassy carbon electrode (GCE, 5 mm diameter Pine Research Instrumentation Inc.) with 30 nm of PTCDI deposited by vacuum evaporation in the same way like all samples used in photoelectrochemical experiments (see *Fabrication of photoelectrodes* section). The rotating ring disk electrode setup has been utilized for the control of rotation speed. Linear sweep voltammetry data was acquired under different rotation speeds (Fig. S2) in oxygen-saturated 0.1 M KCl + 0.01 M HCl solution (pH 2). The experimental voltammograms were corrected by subtraction with the curve obtained on stagnant electrode in argon-saturated electrolyte in order to get rid of background processes. The transferred electron number (*n*) per oxygen molecule was calculated for the -0.5 V vs. Ag/AgCl bias by the Koutecký−Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B}\omega^{-1/2}$$

$$B = 0.62nFAD^{2/3}\nu^{-1/6}C$$

where i_k is the kinetic current (a current that would be observed in the absence of any mass transport limitations), ω is the electrode rotating rate (rpm), n is the transferred electron number, F is the Faraday constant (96,485 C mol^{-1}), A the electrode area (cm^2), D is the diffusion coefficient (1.9 10^{-5} cm^2 s^{-1} for oxygen in 0.1M KCl),[1] ν is the kinematic viscosity (0.0089 cm^2 s^{-1} for 0.1M KCl)[2] and C is the oxygen concentration (1.3×10^{-6} mol cm^{-3} in 0.1 M KCl at 298 K).[3] The constant 0.62 is adopted when the unit of rotation speed is rad/s. It was assumed that the active area of PTCDI-modified electrode is equal to the geometric area (0.19625 cm^2). Plotting the absolute value of the reciprocal current ($1/i$) against the reciprocal square root of the angular rotation rate ($\omega^{-1/2}$) yields a straight line with a slope B and an intercept equal to the reciprocal kinetic current ($1/i_k$). *I* values for 400 and 200 RMP are not included in calculations due to high noise level of the corresponding LSV plots. From the slope of the Koutecký-Levich plot (Fig. S2b), the number of the transferred electrons was estimated as 2.03.

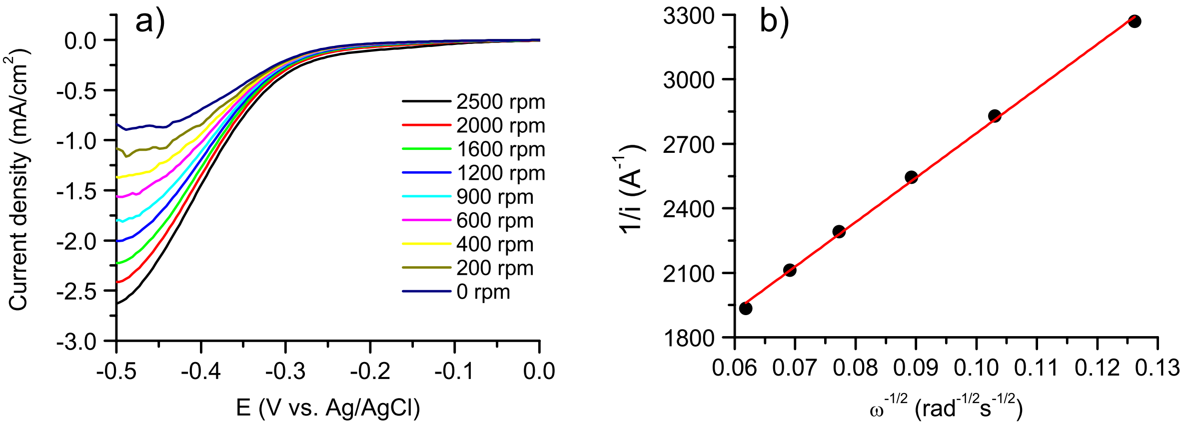

Fig. S2. (a) Linear sweep voltammograms obtained on PTCDI-modified RDE at various rpm in oxygen-saturated 0.1 M KCl + 0.01 M HCl (pH 2), scan rate 20 mV/s and (b) the corresponding Koutecký-Levich plot.

Impact of the catholyte stirring of the photocathode performance:

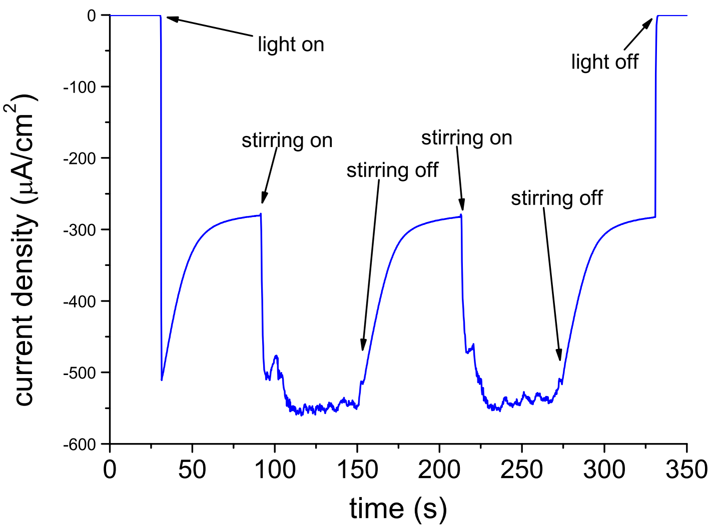

Fig. S3. Chronoamperometry experiment of the H_2O_2 photoevolution with the PN/Au/PTCDI device at pH 7, 0V vs. Ag/AgCl and magnetic stirring switched on/off in 60 s cycles shows the crucial role of the oxygen diffusion on the photocurrent value. The stirring effect is especially prominent for well-performing systems. For the photocurrent below 100 $\mu A/cm^2$ stirring has no impact on its value. Probably further photocurrent improvement could be achieved if the O_2 concentration in the electrolyte is increased by elevated gas pressure (according to Henry's law) but this remains beyond the capabilities of the setup used.

SEM images of the photocathodes:

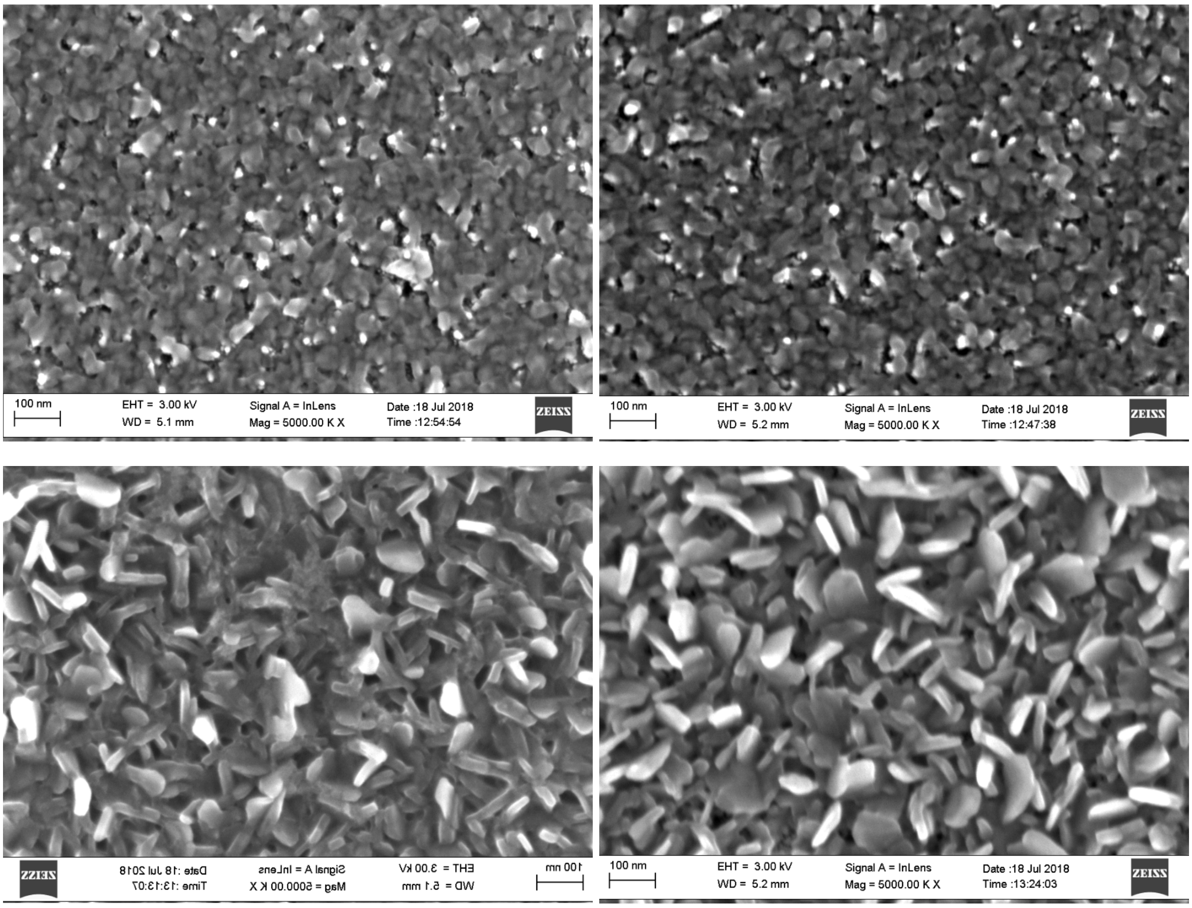

Fig. S4. SEM images of the photocathodes: a) PN/Au/PTCDI before 6 h photoelectrolysis, b) PN/Au/PTCDI after 6 h photoelectrolysis, c) PN/Au/EPI before 6 h photoelectrolysis, d) PN/Au/EPI after 6 h photoelectrolysis. In both cases, there is no difference in the shape and size of the nanocrystallites what proves that the morphology of the electrolyte/H_2O_2 synthesis catalyst interface does not significantly change over the course of the experiment.

References

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