Supporting Information

Precursor-approach in constructing 3D ITO electrodes for improved performance of Photosystem I-cyt *c* photobioelectrodes

Dmitri Ciornii*, Adrian Kölsch, Athina Zouni, Fred Lisdat*



Fig. S1 Surface enhancement as determined by cyclic voltammetry. Black line - flat FTO, blue dashed line - 15-layered 3D ITO (0.46 μ m latex beads have been used). Scan rate 30 mV s⁻¹, 5 mM KPP, pH 7.



Fig. S2 Photoamperometric measuerements at 15-layered 3D ITO electrodes at negative polarisation. **A**: 3D-ITO-PSI-cyt c (blue line). Red square is zoomed in **B**. **B**: 1 - 3D-ITO (black line), 2 - 3D-ITO-cyt c (red dashed line), 3 - 3D-ITO-PSI (green dashed line). Working buffer: KPP, 5 mM, pH 7, applied potential U = -0.2 V vs. Ag/AgCl (1M), light intensity: 100 mW cm⁻².



Fig. S3 Photoamperometric measurements at 15-layered 3D ITO electrodes at positive polarisation. 1 - 3D-ITO (black line), 2 - 3D-ITO-cyt c (red dashed line), 3 - 3D-ITO-PSI (green dashed line), 4 - 3D-ITO-PSI-cyt c (blue line). Working buffer: KPP, 5 mM, pH 7, applied potential U = +0.2 V vs. Ag/AgCl (1M), light intensity: 100 mWcm⁻².



Fig. S4 Cyclic voltammetry of 6-layered 3D ITO without (black dashed line) and with (red line) Q_0 (1.5 mM) in working buffer. Scan rate 100 mV s⁻¹, 5 mM KPP, pH 7.



Fig. S5 Photoamperometric experiments at 6-layered 3D ITO-PSI electrode prepared without cyt c. Black dashed line - working buffer 5 mM KPP, pH 7. Red line – upon addition of Q_0 (1.5 mM). Illumination with white light was between "On" and "Off" (100 mW cm⁻²).



Fig. S6 Emission spectrum of white light source used for photoelectrochemical experiments.



Fig. S8 SEM images of as-prepared 3D ITO electrodes by using different Latex Beads diameters. A - 0.46 μ m, B - 0.8 μ m, C - 1.1 μ m Latex Beads. Acceleration voltage 30 kV.



Fig. S9 Photocurrents as function of PSI concentration used for preparation of 3D-ITO-PSI-cyt *c* (0.46 μ m LB, 1.25 % Sn, 15layer arrangement, applied potential U= -0.2 vs Ag/AgCl, illumination 100 mW cm⁻². Working buffer: 5 mM KPP, pH 7, reference electrode Ag/AgCl (1M). In addition, the surface amount of cyt c is given. Here a slight decrease in photocurrent at high PSI concentration could be observed. This might become a limiting factor since a high amount of cyt c is necessary to wire PSI with the electrode surface.