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 µm latex beads have been used). Scan rate 30 mV s⁻¹, 5 mM KPP, pH 7.

**Fig. S2** Photoamperometric measurements 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 $Q_o$ (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. S7** Cyclic voltammetry experiments at 3D-ITO-PSi-cyt c (0.8 µm LB, 1.25 % Sn, 3 layer arrangement) and at different scan rates: 30 - 1500 mV s⁻¹. Working buffer: 10 mM KPP, pH 7, reference electrode Ag/AgCl (1M).

**Fig. S8** SEM images of as-prepared 3D ITO electrodes by using different Latex Beads diameters. A – 0.46 µm, B – 0.8 µm, C – 1.1 µm 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 µm LB, 1.25 % Sn, 15-layer 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.