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Supporting Information

Micropatterned Carbon-on-Quartz Electrode Chips for Photocurrent Generation from Thylakoid Membranes


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S1. Fabrication of the measurement holder

The components of the electrochemical measurement setup shown in Figure S1b were machined using a computer-numerically-controlled (CNC) Mini-Mill/3Pro micromilling system (Minitech Machinery Corporation, Norcross, GA, USA) by executing G-code generated by EZ-CAM17 Express software (EZCAM Solutions, Inc., New York, NY, USA) based on Autocad drawings (Autocad 2016 from Autodesk Inc., San Rafael, CA, USA). The following materials were used for fabrication of the components: 15 mm polycarbonate (Bayer MaterialScience AG, Leverkusen, Germany) for the top part (1) containing the oval measurement chamber (major/minor radius: 12.5/7.5 mm; opening to the electrode chip: Ø 8 mm; height of the oval chamber: 11.7 mm and a pocket with Ø 10 mm a height of 0.8 mm for the O-ring (2)); 5 mm poly(methyl methacrylate) (Röchling Technische Teile KG, Mainburg, Germany) for the middle part (5) containing the pocket for the electrode chip (3) and connecting wire (4); 10 mm aluminum for the metal bottom (6) supporting the assembly of the of the electrochemical cell; 31 mm Teflon® (supplied by Linatex A/S, Herlev, Denmark) for the connector of the light source (7). The O-ring (inner/outer Ø 8/10 mm) for sealing the measurement chamber was cut from 1 mm thick transparent RCT®SH-40 silicon sheet (Reichelt Chemietechnik GmbH, Heidelberg, Germany) using an Epilog Mini CO2 laser system (Epilog Laser, Golden, CO, USA).

Figure S1: (a) Wafer containing the 9 different chip patterns after pyrolysis. (b) Exploded view of the holder used in the electrochemical measurements.
S2. Characterization of electrode chips using cyclic voltammetry

The electrode chips were characterized using cyclic voltammetry in [Ru(NH$_3$)$_6$]$^{2+/3+}$, a reliable outer-sphere redox system$^{1,2}$ widely used for the characterization of carbon electrodes$^{3,4}$.

**Figure S2 a** shows cyclic voltammograms recorded using different electrode chip patterns at a scan rate of 10 mV s$^{-1}$. The anodic peak intensity varies by less than 20% between different chip patterns and by less than 10% for 3 chips of the same pattern.

**Figure S2 b** shows cyclic voltammograms recorded using a 20/40 chip and scan rates between 10 and 150 mV s$^{-1}$. At a scan rate of 10 mV s$^{-1}$, $\Delta E_p$ (the separation between the anodic and cathodic peak) is 93 mV. $\Delta E_p$ increases with increasing scan rates.

Figure S2: (a) Average results from cyclic voltammetry using different chip patterns in 1 mM [Ru(NH$_3$)$_6$]$^{2+/3+}$ at a scan rate of 0.01 V s$^{-1}$; (b) Cyclic voltammograms obtained with a 20 µm / 40 % electrode chip in 1 mM [Ru(NH$_3$)$_6$]$^{2+/3+}$ at scan rates between 0.01 and 0.15 V s$^{-1}$. E vs. Ag|AgCl$_{sat}$.

The influence of the presence of the thylakoid dispersion on the electrode was investigated using cyclic voltammetry. It is clear from **Figure S3** that the TM dispersion functions as a passivation layer on the electrode surface, leading to a faradaic current decrease. The anodic peak intensity decreases from 44.5±0.1 µA (in the absence of TMs) to 31.3±0.4 µA (in the presence of TMs).
Figure S3: Average results from cyclic voltammetry using 20 μm / 40% electrode chips in 1 mM [Ru(NH$_3$)$_6$]$^{2+/3+}$ at a scan rate of 0.01 V s$^{-1}$ with and without TMs on the electrode. The system was protected from light during the measurements. E vs Ag|AgCl$_{sat}$.

S3. Irradiance measurements

The irradiance of the lamp was measured in air, through the holder and through chips with different patterns. The lamp was set to supply 500 W m$^{-2}$ (measured through the holder), corresponding to 505 W m$^{-2}$ measured in air (1% dampening). Figure S4 shows the correlation between the measured irradiance and the transparent surface area percentages of different chips. As expected, the light passing through the chips is directly proportional to the transparent surface area. The slope of the linear regression shows an average loss in irradiance of less than 3% from the initial set value of 500 W m$^{-2}$.

Figure S4: Irradiance measured in the experimental setup through chips with different patterns vs. the open area fraction.
**S4. Baseline correction**

All chronoamperometric measurements were baseline-corrected using the OriginPro 9 software (OriginLab Corporation). The baseline was manually defined by selecting raw data values obtained in the absence of light (while the lamp was turned off). The baseline was then subtracted from the raw data. **Figure S5** shows the raw data, the baseline and the data after baseline correction for one amperometric measurement using a 20/40 electrode chip.

![Figure S5: Current-time trace for photocurrent collection from TMs using a 20 µm / 40% electrode chip and as mediator 1 mM [Ru(NH$_3$)$_6$]$_{3+}$ in PBS. E vs. Ag|AgCl sat. Raw data, the baseline and baseline-corrected data is shown. The light source was turned on and off every 100 s after the first 100 s, as indicated by the arrows.]

**S5. Control experiments without thylakoid membranes**

Control chronoamperometry experiments without TMs were performed. As shown in **Figure S6**, a negative current peak (< 0.5 µA) is measured when the light source is turned on in the absence of TMs. This could be attributed to a slight change in temperature in the system upon illumination.

Since control experiments do not show a current increase in the presence of light, the positive current peak from measurements with TMs can be attributed to photocurrent collection.

The experimental values for maximum currents were determined after baseline correction, by reading the measured current from amperometry 5 s after the first illumination pulse (for [Ru(NH$_3$)$_6$]$_{3+}$ as mediator) and 25 s after the first illumination pulse (for the Os redox polymer as mediator). The maximum currents and corresponding current densities measured with the different chip patterns for an irradiance of 500 W m$^{-2}$ are given in Table S1.

S-5
Table S1: Experimental values for maximum currents and current densities measured with the differently-patterned chips at an irradiance of 500 W m$^{-2}$. The carbon surface area used for the measurement is specified for every pattern.

<table>
<thead>
<tr>
<th>Pattern/(µm%/%)</th>
<th>C area/(cm$^2$)$^a$</th>
<th>I/(µA) with TMs + Ru$^{3+}$</th>
<th>Current density/(µA cm$^{-2}$) with TMs + Ru</th>
<th>I/(µA) with TMs + Os-RP</th>
<th>Current density/(µA cm$^{-2}$) with TMs + Os-RP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full opening</td>
<td>0</td>
<td>1.8 ± 0.2</td>
<td>3.6 ± 0.4</td>
<td>1.6 ± 0.3</td>
<td>3.2 ± 0.6</td>
</tr>
<tr>
<td>Full C</td>
<td>0.50</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>20/40</td>
<td>0.28</td>
<td>26.7 ± 0.4</td>
<td>53.2 ± 0.8</td>
<td>21.5 ± 0.3</td>
<td>42.8 ± 0.6</td>
</tr>
<tr>
<td>50/40</td>
<td>0.29</td>
<td>20.9 ± 0.3</td>
<td>41.6 ± 0.6</td>
<td>16.8 ± 0.1</td>
<td>33.5 ± 0.2</td>
</tr>
<tr>
<td>100/40</td>
<td>0.29</td>
<td>16.8 ± 0.2</td>
<td>33.5 ± 0.4</td>
<td>11.4 ± 0.3</td>
<td>22.7 ± 0.6</td>
</tr>
<tr>
<td>200/40</td>
<td>0.30</td>
<td>13.8 ± 0.3</td>
<td>27.5 ± 0.6</td>
<td>9.3 ± 0.2</td>
<td>18.5 ± 0.4</td>
</tr>
<tr>
<td>400/40</td>
<td>0.30</td>
<td>11.6 ± 0.3</td>
<td>23.1 ± 0.4</td>
<td>5.8 ± 0.5</td>
<td>11.6 ± 1</td>
</tr>
<tr>
<td>100/20</td>
<td>0.40</td>
<td>14.7 ± 0.2</td>
<td>29.3 ± 0.4</td>
<td>7.8 ± 0.2</td>
<td>15.5 ± 0.4</td>
</tr>
<tr>
<td>100/60</td>
<td>0.20</td>
<td>19.8 ± 0.4</td>
<td>39.4 ± 0.8</td>
<td>15.6 ± 0.3</td>
<td>31.1 ± 0.6</td>
</tr>
</tbody>
</table>

a) The total surface area in contact with the electrolyte is constant, with a value of 0.5 cm$^2$.

Figure S6: Current-time trace for photocurrent collection in the absence of TMs (control experiment) using a 20 µm / 40% electrode chip and as mediator 1 mM [Ru(NH$_3$)$_6$]$^{3+}$ in PBS. E = 0 V vs. Ag|AgCl$_{sat}$. The light source was turned on and off every 100 s after the first 100 s, as indicated by the arrows.

S6. The diffusion model and calculations

At t = 0 we assume the generated electrons to be uniformly distributed within a square surface of area $A = L^2$. We calculate the probability that during a time interval $\Delta t$ an electron has reached the sides of the square, given that it is absorbed the first time it hits the boundary of the region. We use the analytical expression of the exit probability for freely diffusing particles within a square with absorbing boundaries. For a particle located at $(x_0, y_0)$ at $t = 0$, the exit probability at $t = \Delta t$ is given by equation S1.
\[ P(x_0, y_0, L, \Delta t, D) = \]
\[ = \frac{16}{\pi^2} \times \left[ \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{(2n+1)^2\pi^2 \Delta t D}{L^2}\right) \cos\left(\frac{(2n+1)\pi x_0}{L}\right) \right] \times \left[ \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{(2n+1)^2\pi^2 \Delta t D}{L^2}\right) \cos\left(\frac{(2n+1)\pi y_0}{L}\right) \right] \]

\( \text{Equation S1.} \)

\( P(x_0, y_0, L, \Delta t, D) \) is integrated over the uniform electron distribution of the electrons generated at \( t = 0 \) to obtain the average exit probability (equation S2).

\[ \bar{P}(L, \Delta t, D) = \frac{1}{L^2} \int_{x_0=-L/2}^{x_0=L/2} dx_0 \times \int_{y_0=-L/2}^{y_0=L/2} dy_0 \times P(x_0, y_0, L, \Delta t, D) \]

\( \text{Equation S2.} \)

The maximum current measured using the chip, \( I_{\text{max}}(L) \), is related to the average exit probability as shown in equation S3:

\[ I_{\text{max}}(L, \Delta t, D, m, q) = m \times \bar{P}(L, \Delta t, D) + q \]

\( \text{Equation S3} \)

Where \( \Delta t \times D, m, \) and \( q \) are fitting parameters. The experimental current values for the devices with the two mediators (ruthenium complex and osmium redox polymer) are fitted to \( I_{\text{max}}(L, \Delta t, D, m, q) \). We obtain \( m = 16 \pm 1 \mu A \) for both data sets, whereas \( q \) is \( 10.3 \pm 0.5 \mu A \) for the Ru complex and \( 5 \pm 1 \mu A \) for the osmium redox polymer.

The fact that \( m \) has the same value for both mediators suggests that \( m \) could be related to \( Ne/\Delta t \), where \( N \) is the number of electrons transported in the system, and \( e \approx 1.602 \times 10^{-19} \) C is the elementary charge. The time-independent parameter \( q \) largely differs between the osmium redox polymer and \([\text{Ru(NH}_3)_6]^{3+}\), indicating that its value is affected by the efficiency of transfer from the thylakoid membrane to the mediator, or from the mediator to the electrode.

\textbf{Figure S7} shows the exit probability of electrons generated in the center of a square opening as a function of the distance between the photosynthetic reaction center, where the electrons are generated, and the electrode, where the electrons are collected. For both the ruthenium mediator and the osmium redox polymer, the exit probability starts decreasing significantly for distances above 10 \( \mu m \). For distances higher than 35 \( \mu m \), the exit probability approaches 0, which means that electrons generated further than 35 \( \mu m \) from the electrode surface have negligible contribution to photocurrent generation.
Figure S7: Exit probability of electrons generated in the center of an opening as a function of the distance between the photosynthetic reaction center, where the electrons are generated, and the electrode surface, where the electrons are collected. The distance represents the half-width of the opening. Data for both \([\text{Ru}(\text{NH}_3)_6]^{3+}\) and osmium redox polymer as mediators was obtained using the diffusion model.

A Jupyter Notebook (to reproduce calculations and Figure 4) is available as SI in native as well as HTML format.

References