Supplementary file

Room-Temperature Conversion of the
Photoelectrochemical Oxidation of Methane into
Electricity at Nanostructured TiO$_2$

*Yanir Kadosh, Eli Korin and Armand Bettelheim*

Department of Chemical Engineering, Ben Gurion University of the Negev, Be’er Sheva, Israel

*armandb@bgu.ac.il*
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Figure S1. Spectroscopic analysis of the TiO$_2$ nanotube arrays photoanode. (A) Raman spectrum and (B) Diffuse reflectance UV-Vis absorption spectrum of the anodized titania after annealing at 500 °C for 1 hour. Inset: Kubelka-Munk curve and band gap determination.

Figure S2. Zoom-in on the chopped light current-voltage curve. The plot presents the current density in the absence (Ar, dashed blue line) and presence of methane (solid red line). The spike-like feature is marked with a circle.
Table S1. Fitting parameters obtained by the equivalent circuit for the EIS data. The data were obtained for a TiO$_2$NTA photoanode (with NTA) and after peeling off the nanotube arrays (without NTA) at 0.3 V in the absence (Ar) and presence of CH$_4$ during illumination. Constant phase element (Q) and ideality factor (a) are used to describe nonideal capacitance behavior.

<table>
<thead>
<tr>
<th>Gas</th>
<th>R$_1$ [Ω]</th>
<th>C$_1$ [F]</th>
<th>R$_2$ [Ω]</th>
<th>Q$_2$ [S*sec$^a$]</th>
<th>a$_2$</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>With NTA</td>
<td>1244 ± 38</td>
<td>4.17E-3 ± 2.18E-4</td>
<td>45.8 ± 4.0</td>
<td>6.13E-4 ± 1.45E-4</td>
<td>0.809 ± 0.053</td>
<td>4.53E-05</td>
</tr>
<tr>
<td>Without NTA</td>
<td>1887 ± 85</td>
<td>2.62E-3 ± 4.1E-4</td>
<td>21.8 ± 4.9</td>
<td>1.15E-3 ± 4.06E-4</td>
<td>0.769 ± 0.050</td>
<td>1.69E-05</td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>With NTA</td>
<td>714 ± 22</td>
<td>4.37E-3 ± 2.5E-4</td>
<td>43.3 ± 3.9</td>
<td>8.39E-4 ± 1.76E-4</td>
<td>0.739 ± 0.049</td>
<td>1.43E-05</td>
</tr>
<tr>
<td>Without NTA</td>
<td>2086 ± 104</td>
<td>2.53E-3 ± 4.6E-4</td>
<td>20.1 ± 5.0</td>
<td>1.35E-3 ± 4.64E-4</td>
<td>0.760 ± 0.046</td>
<td>1.70E-05</td>
</tr>
</tbody>
</table>

Table S2. Redox potentials table.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E [V] vs. NHE (pH=0, 298K)$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_4 + 2H_2O$→$CO_2 + 8H^+ + 8e^-$</td>
<td>0.17</td>
</tr>
<tr>
<td>$CH_4 + 2H_2O$→$HCOOH + 6H^+ + 6e^-$</td>
<td>0.26</td>
</tr>
<tr>
<td>$CH_4 + H_2O$→$CO + 6H^+ + 6e^-$</td>
<td>0.26</td>
</tr>
<tr>
<td>$2CH_4$→$C_2H_6 + 2H^+ + 2e^-$</td>
<td>0.35</td>
</tr>
</tbody>
</table>
**Figure S3.** Trapping experiments. Photocurrents of TiO$_2$NTA in the absence (Ar, left) and presence (right) of methane in 0.05M H$_2$SO$_4$ under dark/light intervals of 100 s, with the additions of 200µM TBA (green), BQ (purple) and TEOA (black) as trapping agents.

**Figure S4.** CA at various biased potentials in the presence of methane in 0.05M H$_2$SO$_4$ at room temperature and under illumination intensity of 100 mW cm$^{-2}$. 
Faradaic efficiency calculation:

Since the PEC oxidation of methane was conducted in a batch mode, the faradaic efficiency (FE) of product “i” was calculated by:

$$Q_{\text{output, } i} = n_i * z * F$$

$$Q_{\text{input}} = \int_0^t I(t) \, dt$$

$$FE_i = \frac{Q_{\text{output, } i}}{Q_{\text{input, } i}} \times 100\%$$

where $Q_{\text{output, } i}$ is the charge involved in the production of product “i”, $Q_{\text{input}}$ is the total charge (C) generated by applying a specific potential for a period of time $t$ (sec), $n_i$ is the amount of product “i” generated in the reaction (mole), $z$ is the number of electrons transferred and $F$ is Faraday’s constant (96485 C mole$^{-1}$). The amount of each product “i” in the gas phase was calculated using a gas chromatograph (GC) calibration curve obtained by a known standard (SCOTTY). The concentration of the liquid products was derived by $^1$H-NMR.

Samples were prepared by 0.9 mL of the electrolyte after the experiment, 0.2 mL of D$_2$O and 0.05 mL 10mM of DMSO as an internal standard. Quantification was done by the ratio between the areas of the peak related to the product and the peak related to DMSO:

$$[\text{product "i"}] = \frac{n_{\text{DMSO}}}{V_{\text{sample}}} \cdot \frac{\text{area of product's peak}}{\text{number of protons in the product}} / \frac{\text{area of DMSO's peak}}{\text{number of protons in DMSO}}$$

The number of electrons for each product is presented in Table S3.
Table S3. Number of electrons involved in the formation of a specific product.

<table>
<thead>
<tr>
<th>Product</th>
<th>Transferred electrons per a product molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>8</td>
</tr>
<tr>
<td>CO</td>
<td>6</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>2</td>
</tr>
<tr>
<td>HCOOH</td>
<td>6</td>
</tr>
<tr>
<td>O₂</td>
<td>4</td>
</tr>
</tbody>
</table>

Figure S5. Gaseous products analysis. The gaseous products of the PEC oxidation of methane using TiO₂NTA were analyzed by GC for the headspace after 2 hours of electrolysis. The black dotted line represents the GC spectrum of a known standard (SCOTTY). Compounds marked with (*) were found in the headspace of the photoelectrochemical cell.
Figure S6. Gas chromatography calibration curves for carbon-based gaseous products.

Figure S7. Gas chromatography calibration curve for oxygen in the gas phase.
Figure S8. $^1$H-NMR spectra of the aqueous products. $^1$H-NMR (500MHz, in D$_2$O) spectra obtained in the half-cell configuration at applied potentials of: (a) 0.3, (b) 0.5, (c) 0.8, (d) 1 and (e) 1.3 V. The solution was analyzed after 2 hours of electrolysis. (f) $^1$H-NMR (500MHz, in D$_2$O) spectra obtained in the photo-fuel cell configuration. The solution from the anodic chamber was analyzed after an operation of 8 hours. The peaks at 2.72, 3.72 and 8.22 ppm correspond to DMSO, methyl hydroperoxide$^2$ (CH$_3$OOH) and formic acid, respectively.
Figure S9. Linear sweep voltammograms obtained with TiO$_2$NTA at different pH values. The curves were obtained at a scan rate of 5 mV s$^{-1}$ during illumination while purging Ar (blue) or CH$_4$ (red) to the solution at a flow rate of 20 mL min$^{-1}$. Higher current density is obtained in the absence of CH$_4$ at pH=13, which may indicate that the competitive water oxidation is more dominant at higher pH.

Figure S10. SEM top view image of the TiO$_2$ nanotube arrays photoanode after an 8 hours stability test of the photo-fuel cell.
**Gas phase photo-fuel cell (PFC)**

The membrane-electrode-assembly (MEA) was comprised of a Ti fiber felt photoanode (illuminated area of 0.23 cm$^2$), a Nafion membrane (Ion Power, Inc.) and a commercial Pt/C cathode (40% Pt on Vulcan XC-72 carbon, 2 mg cm$^{-2}$, ETEK). Prior to its use as a gas diffusion electrode, the Ti felt was anodized as described for the Ti foil. The nanotubes are characterized by a diameter and length of 60 ± 6 nm and 2.40 ± 0.04 μm, respectively (fig. S11). The membrane was pretreated as follows: cleaning and protonation in 3% H$_2$O$_2$ for 1 h at ~80°C, 1 h at ~80°C in deionized water and 2 h at ~80°C in 0.5M H$_2$SO$_4$, followed by rinsing and storing in deionized water at room temperature in the dark. Both photoanode and cathode were coated with 2 ml of 0.5% Nafion, were let to dry and were pressed over the membrane. Humidified methane and oxygen were fed to the photoanode and cathode, respectively, at a flow rate of 0.25 L min$^{-1}$. Prior to the polarization measurements, the PFC was maintained at open circuit for 20 min. Then, the potential was stepped down from open circuit to short circuit in 20 mV increments.

**Figure S11.** HRSEM images of the gas diffusion electrode – Ti fiber felt. Image (A) presents a bare felt while images (B, inset: higher magnification) and (C) present a top and side view of the obtained nanotube arrays of the anodized felt, respectively.
Figure S12. Polarization (blue) and power density (red) curves for the gas phase photo-fuel cell.

References