Supporting Information

Selective CO Production by Photoelectrochemical Methane Oxidation on TiO$_2$

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Experimental details

**Preparation of TiO$_2$ samples**

ALD TiO$_2$: TiO$_2$ was deposited on a 2.2 mm thick glass slide coated with fluorine-doped tin oxide conductive film (7 Ω/sq surface resistivity, Sigma-Aldrich) in a Cambridge nanotech (Savannah 100) system as previously reported. FTO coated glass substrate was cleaned in acetone, methanol, and deionized (DI) water. The reaction was performed at 275°C with a constant flow of N$_2$ (UHP, 99.999%, Airgas) at 20 sccm (background pressure ~1000 mTorr). Ti(i-PrO)$_4$ (99.999% trace metals basis, Sigma-Aldrich) served as the Ti precursor, and was heated to 75°C. DI H$_2$O at room temperature was used as the oxygen precursor. The pulse and purge time for Ti(i-PrO)$_4$ and H$_2$O was 0.1s & 5s, and 0.01s & 10s, respectively. The dependence of photocurrent density on TiO$_2$ thickness was discussed in the application of solar water splitting, the optimum TiO$_2$ thickness was ≈50 nm for planar devices corresponding with 3000 cycles growth. The ALD TiO$_2$ featured anatase (101) surface as previously reported.

Raman spectra confirmed the anatase phase of ALD TiO$_2$ (Figure S1), using an XploRA micro-Raman system (Horiba) with an excitation laser of 638 nm.

Commercial anatase TiO$_2$ and P25 TiO$_2$: Commercial anatase TiO$_2$ powder (Sigma Aldrich, 99.8% trace metal basis) or P25 TiO$_2$ powder (Evonik Industries, Aeroxide TiO$_2$ P25) was dispersed in ethanol to make a TiO$_2$ suspension solution with a concentration of 0.1 g/mL. The resulted solution was drop-casted on FTO substrate and followed a spin coating procedure at a rate of 2500 rpm. Then, the TiO$_2$ coated FTO substrate was annealed at 475°C in air for 3 h to remove the solvents and improve the adhesion between FTO substrate and TiO$_2$.

Electrode fabrication: As-prepared TiO$_2$ samples were scratched to expose conductive FTO surface, and connected with a Cu wire using Ag paste (MG Chemicals, 8331 Silver Conductive Epoxy Adhesive) and protected with non-conductive epoxy (Loctites 615 Hysol Epoxy Adhesive) to leave an electrode surface area of ca. 1.0 cm$^2$.

**Photoelectrochemical (PEC) characterizations**

PEC characterizations were carried out using a potentiostat/galvanostat (CH Instruments CHI604C) at room temperature (20°C) unless otherwise noted. A three-electrode configuration was employed, with TiO$_2$ coated FTO substrate as the working electrode, SCE (CH instruments) as the reference electrode and a Pt wire as the counter electrode. The three electrodes were sealed in a three-neck flask (15 mL) by rubber stoppers (with all possible leaking parts protected by parafilm and high vacuum grease). 1.0 M NaOH (ACS reagent, > 97.0%, pellets, Sigma Aldrich) was used as electrolyte with a pH value of 13.6. The electrochemical cell was purged with the gas of interest (CH$_4$, N$_2$ or CO) to remove the dissolved O$_2$ in the electrolyte for at least 30 min prior to measurements and maintain 1 atm of the gas in the headspace during measurements. In a typical cyclic voltammetry or linear sweep voltammetry, the voltage was swept from cathodic to anodic direction at a rate of 20 mV.s$^{-1}$. The light source for all data presented in this work was a ultra-violet light source with 254 nm wavelength (UVGL-55 Handheld UV Lamp, P/N 95-0005-05, 6
Watt, UVP LLC.). Front-side illumination was applied for all measurements.

**Products detection**

**CO detection:** Similar to a typical PEC measurement, a three-electrode configuration was employed, except that CH$_4$ (UHP, 99.99%, Airgas) or N$_2$ (UHP, 99.999%, Airgas) gas was encapsulated during bulk electrolysis with coulometry. The evolved CO in the headspace was sampled with a gastight syringe (100 µL) for product analysis using GC-MS (Shimadzu QP2010 Ultra, with Carboxen 1010 PLOT column). CO (UHP, 99.9%, Airgas) was used to calibrate the GC-MS.

**Carbonate detection:** Measuring the weight increase of carbonate precipitation after bulk electrolysis was used to quantify the carbonate formed in electrolyte. Prior to experiments, DI water was boiled to remove dissolved CO$_2$. After bulk electrolysis of ALD TiO$_2$ photoelectrode in the presence of CH$_4$ was finished, 10.0 mL of 1.0 M Ba(NO$_3$)$_2$ (ACS, > 99%, Alfa Aesar) was added to the electrolyte (also to fresh electrolyte as controlled experiment). No significant difference was obtained, suggesting the amount of carbonate product in the electrolyte was beyond the detection limit by this method.

Carbonate adsorbed on the TiO$_2$ surface was characterized by X-ray photoelectron spectroscopy (XPS) and attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR). XPS spectra in Figure S4 were obtained using K-alpha XPS (Thermo Scientific, Al Kα = 1486.7 eV), showing the carbonate formation on ALD TiO$_2$ surface only after PEC bulk electrolysis in the presence of CH$_4$. ATR spectra in Figure S7 were obtained using a Bruker ATR model Alpha spectrometer with diamond as the ATR crystal. ALD TiO$_2$ with different electrolysis history was placed on ATR plate with elastic pressing to improve the contact between the sample and the crystal. Acetone was used to clean the ATR substrates between each measurement. Air spectrum was measured as background. Data were collected using the Omnic software package. Each spectrum was collected with 32 scans at a 2 cm$^{-1}$ spectral resolution.

**O$_2$ detection:** The evolved O$_2$ by ALD TiO$_2$ was detected in situ using a Clark-type BOD oxygen electrode (Thermo Scientific 9708 DOP). For a typical experiment, the working electrode, the reference electrode, and the counter electrode were sealed in a three-neck flask by rubber stoppers (with all possible leaking parts covered by parafilm and high vacuum grease). CH$_4$ gas was purged in the electrolyte for at least 30 min and the headspace was protected by CH$_4$ gas to ensure an O$_2$ free environment. Once we removed the needle purging CH$_4$ gas into the electrolyte, and the oxygen sensor had been stabilized close to 0 ppm for a period time (5 min), the O$_2$ yield was read on a pH meter connected to the oxygen sensor.

**H$_2$O$_2$ detection:** After PEC electrolysis, 1 M HCl was used to adjust the pH of electrolyte to 2~2.5. Then 50 µL of the Mo catalyst was added into the solution and incubated for 3 min. Finally, 0.5 mL starch solution with concentration of 2 wt% was added to the solution. If there was H$_2$O$_2$, the
solution would turn blue.

**Calculations of efficiency and selectivity**
The product efficiency refers to Faradaic efficiency defined as the ratio between the charge corresponding to the amount of product (CO or O\(_2\)) evolved and the total charge consumed during the reaction. Because carbonate was only observed on the surface of TiO\(_2\) photoelectrode, its production efficiency was calculated by subtracting the efficiency of CO and O\(_2\) from unity. The CO selectivity refers to the percentage of CO Faradaic efficiency among the total charges other than O\(_2\) formation.
Since carbonate is subtracted from CO and O\(_2\), we consider the error bar of the carbonate efficiency of not statistically significant. In the manuscript, we used the following equation for standard deviation calculations:

\[ SD = \sqrt{\frac{\sum |x - \bar{x}|^2}{n}} \]

The calculated standard deviation represents the variation of our measurements on the product selectivity. From our calculations, we believe that our measurement is reasonably consistent and the trend of the data is reliable.

**Spectroscopic measurements**

**EPR spectroscopy:** A Bruker ELEXSYS E500 spectrometer equipped with a SHQ resonator was used for the EPR experiments. An Oxford ESR-900 continuous flow cryostat was used to measure spectra at 7.5 K. The EPR parameters used for recording the spectra are as follows: microwave frequency, 9.38 GHz; modulation frequency, 100 kHz; modulation amplitude, 19.95 G; microwave power, 5 mW; sweep time, 84 s; conversion time, 41 ms; time constant, 82 ms. Each spectrum was the average of two scans. Since the signal intensity is proportional to radical concentration, the quantity of Ti\(^{3+}\) was calculated and the results of three samples are listed in Table S3. The standard used was carefully weighed out 2,2-Diphenyl-1-picrylhydrazy (DPPH) standard (Analytical grade, Sigma Aldrich). The EPR spectrum of the standard was taken under identical conditions.

**Raman spectroscopy:** Raman spectra were obtained using a Horiba XploRA micro Raman system with excitation laser of 638 nm. Commercial anatase TiO\(_2\) (Sigma Aldrich, 99.8% trace metal basis) was employed instead of ALD anatase TiO\(_2\) film for more sufficient interaction with CH\(_4\); 3% H\(_2\)O-saturated CH\(_4\) was circulated and enclosed in a homemade quartz cell (Schematic S2). Spectra were collected under air, CH\(_4\)/H\(_2\)O and CD\(_4\) (99 atom% D, Assay 99%, Sigma Aldrich)/H\(_2\)O with/without illumination by UV light respectively (the same light source in PEC characterizations).

**ATR-FTIR spectroscopy:** ATR-FTIR spectra were recorded using a Bruker Vertex 70 FTIR spectrometer (Billerica, MA) equipped with an MCT detector (FTIR-16; Infrared Associates;
Stuart, FL). The TiO$_2$ coated FTO glass slide was pressed on the ATR Si prism crystal and the configuration is depicted in Schematic S3. The preparation of the Si crystal followed the procedure reported previously.\textsuperscript{3} Electrochemical experiments were carried out in a two-electrode configuration with a Pt foil (99.95%; BASi Inc.; West Lafayette, IN) as the reference/counter electrode. 0.10 M KNO$_3$ (99.999% trace metals basis, Sigma Aldrich) was used as the electrolyte at room temperature and it was purged for at least one hour by either N$_2$ (control experiment) or CH$_4$ before being added into the electrochemical cell. Figure S8 shows the linear sweep voltammogram (at a rate of 20 mV•s$^{-1}$) of ALD TiO$_2$ under light illumination in CH$_4$-saturated 1.0 M KNO$_3$ electrolyte in the FTIR set-up. To ensure steady-state conditions, the target potential was held at 0.3 V vs. internal Pt. The applied potential 0.3 V vs. internal Pt in Figure 4b would correspond to 0.9 V vs. RHE in a 3-electrode configuration. The appearance of specific adsorbed intermediates on the electrode is highly sensitive to surface heterogeneity, applied potential, and the amount of dissolved CH$_4$. Pressing of the working electrode against the IR transparent prism results in an electrochemical cell configuration that brings about uncertainties in the applied potential and unfavorable mass-transport conditions. As a result, while the three bands reported in Figure 4 were observed in multiple experiments, they did not always appear concurrently and/or with the same magnitude (Figures 4 and S13).

Each reported spectrum was collected at a 2 cm$^{-1}$ spectral resolution and a 40 kHz scanner velocity with 64 scans. The spectrum collected in the beginning of PEC bulk electrolysis was used as the reference, followed by the single beam spectrum collected at each corresponding time point. The change of optical density was calculated as follows,\[ \Delta \text{mOD} = -1000 \cdot \log \left( \frac{S_{\text{sample}}}{S_{\text{reference}}} \right). \]

**Computational methods**

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{4} The on-site Coulomb interaction was included using the DFT+U method described by Dudarev \textit{et al.}\textsuperscript{5} in VASP with a Hubbard parameter U=3.5 eV for the Ti atoms. Electron exchange-correlation was represented by the functional of Perdew, Burke and Ernzerhof (PBE) of generalized gradient approximation (GGA).\textsuperscript{6} The ion-electron interaction was described with the projector augmented wave (PAW) method.\textsuperscript{7} A cutoff energy of 400 eV was used for the plane-wave basis set. The anatase TiO$_2$ (101) surface was modeled with a three-layer thick slab with a 3 $\times$ 1 super cell. A vacuum layer of 15 Å along the z-direction was employed. The Brillouin zone was sampled by (3$\times$3$\times$1) Monkhorst-Pack k-point mesh. The top two TiO$_2$ layers of the slab together with the adsorbates were allowed to relax and the convergence threshold for structural optimization was set to be 0.025 eV/Å in force. The van der Waals interactions were included using the DFT-D3 method.\textsuperscript{8}

The change in Gibbs free energy ($\Delta G$) for the reaction steps was defined as $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$. $\Delta E$ can be directly determined by the DFT total energies. $\Delta E_{ZPE}$ and $\Delta S$ are the zero-point energy difference and the entropy difference between the products and the reactants, respectively.
T is the temperature, and 298.15 K was used in the present work.

Safety comment
No unexpected or unusually high safety hazards were encountered.
Figure S1. Raman spectra of ALD TiO$_2$ (Sample 1), commercial anatase TiO$_2$ (Sample 2) and P25 TiO$_2$ (Sample 3). Both Sample 1 (orange trace) and Sample 2 (pink trace) feature an anatase phase of TiO$_2$, Sample 3 (blue trace) feature the mix phases of anatase and rutile of TiO$_2$.

Figure S2. Linear sweep voltammogram of ALD TiO$_2$ in N$_2$ (blue trace) or CH$_4$ (orange trace)-saturated 1.0 M NaOH electrolyte at a rate of 20 mV.s$^{-1}$. 
**Figure S3.** Stability test of the photoelectrode. Conditions: 0.6 V vs. RHE; UV illumination at 0.1 mW/cm².

**Figure S4.** Cyclic voltammogram of ALD TiO₂ in CH₄ (orange trace) or CO (grey trace)-saturated 1.0 M NaOH electrolyte at a rate of 20 mV.s⁻¹.
Figure S5. Faradaic efficiency with error bars of CO and O₂ evolution from ALD TiO₂. The applied potentials for PEC bulk electrolysis were hold from 0.4 V to 1.2 V vs. RHE with 200 mV intervals, in CH₄-saturated 1.0 M NaOH electrolyte.

Figure S6. O 1s XPS spectra of (a) as-prepared ALD TiO₂ (b) ALD TiO₂ after PEC bulk electrolysis in the presence protection gas N₂ (c) ALD TiO₂ after PEC bulk electrolysis in the presence of CH₄.

In O 1s spectra shown (Figure S6a), as-prepared ALD TiO₂ photoelectrode shows two distinct features at 529.5 eV and 531.5 eV, representing lattice oxygen and surface hydroxyl groups, respectively. After PEC electrolysis under N₂, no significant difference was observed in Figure
S6b. By contrast, after PEC electrolysis under CH₄, new features arose at 532.2 eV and 533.5 eV in Figure S6c, which were ascribed to C-O and C=O formation.

Figure S7. ATR-FTIR spectra of ALD TiO₂ after PEC bulk electrolysis under N₂ (blue trace) and CH₄ (orange trace). A diamond ATR crystal was employed in this experiment.

Figure S8. Dependence of the product selectivity on light intensity. Here 100% intensity refers to 0.1 mW/cm² at λ=254 nm.
Figure S9. Product selectivity dependence on pH.

We carried out PEC bulk electrolysis ($V_{app} = 0.6 \text{ V vs. RHE}$) in 0.5 M H$_2$SO$_4$ (pH = 0.4), 0.1 M KNO$_3$ (pH = 7) and 1.0 M NaOH (pH = 13.6), respectively. Higher CO$_2$ selectivity was observed at lower pH. This could be due to better CO$_2$ desorption as a gaseous product at lower pH. We were able to detect CO$_2$ by GC-MS at pH 0.4 in 0.5 M H$_2$SO$_4$ and observed quantitative correlation of the detected products (CO, CO$_2$ and O$_2$) with the measured charges.

The peak at 1073 cm$^{-1}$ corresponds to the symmetric stretching mode of C=O in bidentate bicarbonate, and the peak at 1586 cm$^{-1}$ corresponds to the asymmetric stretching mode of C=O in bidentate bicarbonate.$^9$

Figure S10. An alternative pathway from intermediate 2 to 8. OH$^-$ would undergo nucleophilic attack on the carbon atom of intermediate 2, forming intermediate 7', which would undergo further
oxidation to 8 and finally to carbonate as the product.

Figure S11. Raman spectra of anatase TiO₂ without CD₄, with CD₄ under dark condition, and with CD₄ under illumination.

Isotope-labelling (CD₄) measurements, with distinct targeted Raman shift region of C-D stretching modes (1800 cm⁻¹ to 2500 cm⁻¹), are in excellent agreement with the above findings in CH₄. A manifest peak at 2101 cm⁻¹ was attributed to free CD₄ molecule, and the emerging peaks under illumination at 2094, 2083 and 2250 cm⁻¹ were assigned to adsorbed CD₄, symmetric stretching and asymmetric stretching mode in CD₃O, respectively.¹⁰ Surprisingly, an additional peak was observed at 1974 cm⁻¹ which is believed to represent the overtone of C-O stretching in CD₃O.¹¹ Taken together, the illumination-dependent peak evolution of surface-adsorbed CH₄ and CH₃O, and controlled isotope measurements validates our hypothesis that photoexcited TiO₂ at room temperature is active for C-H cleavage.
Figure S12. Linear sweep voltammogram (at a rate of 20 mV s⁻¹) of ALD TiO₂ under light (orange trace) or dark (grey trace) in CH₄-saturated 1.0 M KNO₃ electrolyte in the FTIR set-up.

Figure S13. FTIR spectra for up to 34 min after the illumination was started.

The peaks at 1763 cm⁻¹ and 2065 cm⁻¹ were observed up to 34 min after the initiation of the reaction, and the observation was stopped at 34 min artificially.
Figure S14. Gibbs free energy changes ($\Delta G$) for both CO and carbonate pathways.

Scheme S1. CH$_4$ under different conditions: (top left) w/light, w/electricity; (bottom left) w/light, w/o electricity; (top right) w/o light, w/o electricity; (bottom right) w/o light, w/electricity.

No CO production was observed in any following scenario: only anodic applied potential (lack of radical species upon 254 nm light illumination on TiO$_2$); infrared light illumination (less sufficient to excite charges in TiO$_2$); no applied potential (less efficient excited charges separation in TiO$_2$) either in aqueous or gas phase.
Scheme S2. Demonstration of the experimental set-up in *in situ* Raman measurement.

Scheme S3. Demonstration of the experimental set-up in *in operando* ATR-FTIR measurement.
Table S1. Comparison of carbonaceous products of ALD TiO$_2$ under different conditions.

| Feed gas | E (vs. RHE) | Light | Carbonaceous Product | Faradaic efficiency |
|----------|-------------|-------|----------------------|---------------------|
| CH$_4$   | 0.4 V       | 254 nm| CO, carbonate         | CO: 52.8 %          |
| CH$_4$   | 1.7 V       | off   | --                   | --                  |
| CH$_4$   | off         | 254 nm| --                   | --                  |
| CH$_4$   | 1.7 V       | 830 nm| --                   | --                  |
| N$_2$    | 0.4 V       | 254 nm| --                   | --                  |

Table S2. H$_2$ production on the cathode accounts for ca. 100% Faradaic efficiency, ruling out the possibility that H$_2$ oxidation contributes to the measured photocurrent.

|         | Trail 1 | Trail 2 |
|---------|---------|---------|
| Charge (µmol) | 3.06   | 21.54   |
| H$_2$ production (µmol) | 1.51   | 9.85    |
| FE (×100%)    | 98.9   | 91.5    |

Table S3. The concentration of Ti$^{3+}$ in ALD TiO$_2$ (Sample 1), commercial anatase TiO$_2$ (Sample 2) and P25 (Sample 3).

|         | ALD TiO$_2$ Sample 1 | Commercial anatase TiO$_2$ Sample 2 | P25 Sample 3 |
|---------|----------------------|-------------------------------------|--------------|
| Concentration of Ti$^{3+}$ | 32%                  | 0.008%                              | 0.08%        |

Table S4. Control experiments of H$_2$O$_2$ and CH$_4$ in 1 M NaOH under different experimental conditions.

| Experimental conditions       | CO (GC-MS) | Carbonate (FTIR) |
|-------------------------------|------------|------------------|
| TiO$_2$ w/light w/potential   | No         | No               |
| TiO$_2$ w/light w/o potential | No         | No               |
The additional control experiments included: 1. TiO$_2$ photoanode with H$_2$O$_2$ and CH$_4$ under illumination; 2. TiO$_2$ photoanode with H$_2$O$_2$ and CH$_4$ without illumination; 3. only H$_2$O$_2$ and CH$_4$ under illumination. None of these experiments yielded CO (as measured by GC-MS) or carbonates (as characterized by FTIR). These results prompted us to draw the following conclusions:

1. Under PEC conditions, H$_2$O$_2$ is likely oxidized more easily than CH$_4$. It implies that even if H$_2$O$_2$ (or other peroxide or superoxide) was indeed formed, it would likely be oxidized immediately before it could oxidize CH$_4$.
2. The results ruled out the possibility that CO production comes from the chemical reaction between H$_2$O$_2$ and CH$_4$.
3. The absence of CO or carbonate products suggests that CH$_4$ is unlikely to be activated by H$_2$O$_2$, under our reaction conditions, with or without light. This could be due to the ease of H$_2$O$_2$ oxidation by TiO$_2$. It could also be due to overoxidation of CH$_4$, as suggested by a reviewer. Taken as a whole, we consider that CH$_4$ activation is unlikely due to the intermediates of H$_2$O oxidation.
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