Supporting Information

Photoelectrochemical Homocoupling of Methane under Blue Light Irradiation

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Experimental details

Preparation of the WO₃/Ti fiber photoanode

Sintered Ti microfiber felt (diameter 20 µm, thickness 0.1 mm, porosity 67%, weight per unit area 14 mg cm⁻², Nikko Techno, Japan) was used as a three-dimensional conductive substrate for WO₃ electrode. The WO₃ electrode was prepared by solution-based dip coating and subsequent heat treatment at high temperature. First, ammonium metatungstate hydrate ((NH₄)₆[H₂W₁₂O₄₀]·6H₂O, 20.4 g, 80 mmol as WO₃) was dissolved in deionized water (40.0 g). Then, polyethylene glycol (PEG 20,000, average molecular weight 15,000–25,000, 10.0 g) was dissolved in the tungstate aqueous solution. The prepared solution was used to dip coat the Ti microfiber felt (submersion time 30 min, withdrawal speed 1000 µm s⁻¹, drying temperature 353 K, three cycles). The dip-coated Ti microfiber felt was calcined in air at 923 K for 2 h to transform the coated precursor into monoclinic WO₃. The thermal durability of Ti enabled the high-temperature calcination of the felt. The loading amount of WO₃ on the Ti microfiber felt was 10–13 mg cm⁻², which corresponds to 42–48 wt% WO₃. Such high loading was achieved because of the microporous structure of the felt substrate.

The obtained sample, denoted as WO₃/Ti fiber, was then modified with Nafion® perfluorosulfonic acid (PFSA) ionomer dispersion (5 wt% in lower aliphatic alcohols and water, contains 45 wt% water, Sigma–Aldrich Japan) to improve its proton conductivity. Nafion is made of chemically stabilized PFSA/PTFE copolymer in an acidic form. The Nafion ionomer dispersion was dropped on the surface and back side of the WO₃/Ti fiber sample at 20 µL cm⁻². The Nafion ionomer-coated WO₃/Ti fiber sample was then dried at 353 K for 30 min.
Preparation of the Pt/CB cathode

A carbon black-supported platinum catalyst (Pt/CB) was used as the cathode electrocatalyst (Pt loading 47 wt.%, TEC10E50E, Tanaka Kikinzoku Kogyo, Japan). Cathode catalyst ink was prepared by ultrasonically mixing the Pt/CB catalyst with deionized water, 1-propanol, 2-propanol, and Nafion ionomer dispersion. The weight ratio of Nafion to Pt was adjusted to 1.0. The cathode catalyst ink was painted onto a polytetrafluoroethylene (PTFE) film and then dried in a vacuum desiccator at room temperature overnight. The loading amount of Pt/CB catalyst in the ionomer-coated Pt catalyst film was approximately 0.1 mg of Pt cm\(^{-2}\).

Preparation of the membrane electrode assembly (MEA)

Nafion membrane N117 (typical thickness 183 µm, DuPont, USA) was used as a solid polymer electrolyte. The membrane is an electrical insulator and an excellent proton conductor at room temperature in a humidified environment. The ionomer-coated Pt catalyst film (5×5 cm) on a PTFE film was hot pressed onto an N117 membrane (8×8 cm) at 413 K and 15 kN for 8 min (1 min, eight times). After hot pressing, the PTFE film was peeled off, forming an assembled Pt catalyst electrode and membrane. The WO\(_3\)/Ti fiber electrode was hot pressed onto the opposite side of the MEA at 413 K and 15 kN for 8 min (1 min, eight times).

Photoelectrolysis reactor

The hot-pressed MEA was installed in a stainless-steel PEC flow reactor. The ionomer-coated Pt catalyst electrode was attached to wet-proofed Toray carbon paper (5×5 cm, Fuel Cell Store, USA) as a gas-diffusion layer. The fabricated gas-diffusion cathode was faced to a serpentine flow on a gold-coated copper block as a current collector. The WO\(_3\)/Ti fiber photoanode was attached
to a gold-coated current collector plate via a sintered stainless-steel microfiber felt (Nikko Techno, Japan). The current collectors contained four square holes (2×2 cm) that allowed 16 cm² of the WO₃ electrode to be exposed to the irradiated light. The gas diffusion photoanode faced onto an open chamber with a Tempax Float® borosilicate flat glass window. The MEA sandwiched between the two current collectors was covered by two stainless-steel plates with two holes that were used as gas inlet and exhaust tubes. Twelve screws were tightened to a torque of 3.0 N·m to hold the PEC membrane flow reactor together.

**Photoelectrolysis of CH₄**

The PEC reaction was carried out at room temperature (298 K) under atmospheric pressure (Figure S1). The feed gas containing CH₄, H₂O, and Ar with a volume ratio of 0–97/3/balance was passed through the photoanode compartment at a flow rate of 20 mL min⁻¹. The feed gas containing H₂O and Ar with a volume ratio of 3/97 was passed through the cathode compartment at a rate of flow of 20 mL min⁻¹. Water vapor was introduced by passing the gas feed through a bubbler filled with deionized water at room temperature. Reactants and products were analyzed by online GC-8A and GC-2014 gas chromatographs (Shimadzu, Japan) equipped with thermal conductivity detector (TCD; MS-5A column, Ar carrier), TCD (Shincarbon ST column, He carrier) and flame ionization detector (GS-CarbonPLOT column, N₂ carrier), and GS5100 auto gas samplers (GL sciences, Japan).

Visible light excitation was performed using 3-W blue light-emitting diode (LED) lamps (I_F = 800 mA, V_F = 3.8 V, OSB5XNE3C1S, OptoSupply, Hong Kong). The spectrum of the blue LED was measured using an i-trometer miniature back-thinned CCD spectrometer and FRC100 cosine corrector (B&W Tek, USA) (Figure S2). The irradiance was measured at the surface of the
photoanode using a 3664 optical power meter with a 9742 optical sensor (Hioki, Japan). Ultraviolet (UV) light excitation was performed using a 365-nm UV LED lamp ($I_F = 3000$ mA, $V_F = 4.0$ V, NS365L-7SMG, Nitride Semiconductor, Japan).

Electrochemical measurements of the PEC cell were performed in a two-electrode configuration using a VersaSTAT 3 potentiostat (Princeton Applied Research, USA). The applied cell voltage between the photoanode and cathode in the PEC reactor was typically set to 1.20 V. IPCE was calculated as the ratio of the number of electric charges to the number of incident photons.

$$\text{IPCE} = \frac{1240 \times I_{\text{photo}}}{\lambda \times I_0}$$

where $I_{\text{photo}}$ is the steady-state photocurrent density [mA cm$^{-2}$], and $I_0$ is the optical power of the incident monochromatic light [mW cm$^{-2}$] of wavelength $\lambda$ [nm]. Faraday efficiency (FE), also known as current efficiency, was calculated from the ratio of the electric current required for the formation of a product to the total electric current

$$\text{FE} = \frac{n_e \times F \times r(X)}{I_{\text{photo}}}$$

where $n_e$ is the number of electrons required to form a product, $F$ is the Faraday constant, $r(X)$ is the formation rate of product $X$. The $n_e$ value of $H_2$ is 2, because

$$2H^+ + 2e^- = H_2$$

The $n_e$ values of anodic reactions that produce $C_2H_6$, $O_2$, $CO$, and $CO_2$ are 2, 4, 6, and 8, respectively.

$$2CH_4 = C_2H_6 + 2H^+ + 2e^-$$

$$2H_2O = O_2 + 4H^+ + 4e^-$$

$$CH_4 + H_2O = CO + 6H^+ + 6e^-$$

$$CH_4 + 2H_2O = CO_2 + 8H^+ + 8e^-$$
Product selectivity on a per carbon basis was calculated from \( r(X) \) values. For example, assuming that the products converted from CH\(_4\) are C\(_2\)H\(_6\), CO, and CO\(_2\), the selectivity for C\(_2\)H\(_6\) can be expressed as follows.

\[
\text{C}_2\text{H}_6 \text{ selectivity} = \frac{2 \times r(\text{C}_2\text{H}_6)}{2 \times r(\text{C}_2\text{H}_6) + r(\text{CO}) + r(\text{CO}_2)}
\]

**Characterization**

Nitrogen adsorption isotherms at 77 K were recorded with a BELSORP-mini system (Bel Japan, Japan). Before the measurements, samples were outgassed at 473 K for 2 h. The \( S_{\text{BET}} \) was calculated using the Brunauer–Emmett–Teller (BET) equation for relative pressure between 0.05 and 0.30.

SEM images of WO\(_3\)/Ti fiber electrodes were observed on a JSM-7800F microscope (JEOL, Japan) with an operating voltage of 10 kV. The sample was directly deposited on carbon tape. High-magnification SEM observation was performed on S-5200 microscope (Hitachi, Japan) with an operating voltage of 5 kV. Before the high-magnification observation, the sample deposited on carbon tape was coated with Pt using an E-1030 ion sputter coater (Hitachi, Japan).

XRD measurements were carried out on a SmartLab diffractometer (Rigaku, Japan) using Cu K\(\alpha\) radiation at 40 kV and 20 mA. Laser Raman spectra were recorded on an NRS-5100 spectrometer (JASCO, Japan) using 532-nm green radiation. The spectrometer slit was set to give a spectral resolution of 1.1 cm\(^{-1}\).
Figure S1. Characterization of WO$_3$/Ti fiber. (a) Powder diffraction file (PDF) data for monoclinic and triclinic WO$_3$. XRD patterns of Ti microfibers and WO$_3$/Ti fiber. The patterns have been translated in the $y$-axis for clarity. Asterisks indicate the peaks assigned to hexagonal titanium (PDF#44-1294). $R$ indicates the peak attributed to the (110) reflection of rutile TiO$_2$ (PDF#21-1276). The rutile phase was formed in the thermally oxidized surface layer of the Ti microfibers. (b) Raman spectra of WO$_3$/Ti fiber and WO$_3$ powder (Aldrich #550086). Inset is an enlarged view of the lower intensity modes.
Figure S2. A system for photoelectrochemical activation of CH₄. (a) Process flow (FC: flow controller, TI: temperature indicator). (b) Photograph of the PEC reactor and LED lamp. (c) Spectral irradiance of the blue LED lamp, which had a center wavelength of 453 nm and full width at half maximum of 22 nm.
Figure S3. Effect of humidification on photoelectrolysis of 10 vol% CH₄ over a WO₃ photoanode at 1.2 V under pulsed blue light. The second run was performed without the supply of water vapor. (a) Current–time curve. (b) Time dependence of the formation rates of O₂, CO₂, and C₂H₆. (c) Data after PEC reaction for 2 h. Reaction conditions: 453-nm blue LED, irradiance 6.8 mW cm⁻², photoirradiation area 16 cm², applied voltage 1.2 V, flow rate 20 mL min⁻¹, temperature 298 K, pressure 0.1 MPa. Gas composition in the first and third runs: Ar/CH₄/H₂O = 87/10/3 for the photoanode, Ar/H₂O = 97/3 for the cathode. Gas composition in the second run: Ar/CH₄ = 90/10 for the photoanode, Ar = 100 for the cathode.
| Photocatalytic system                        | Reaction condition                                      | Products [a]                           | Quantum efficiency (%)                        |
|---------------------------------------------|---------------------------------------------------------|---------------------------------------|----------------------------------------------|
| Pt/TiO₂, Steam reforming of methane         | 300-W Xe lamp (λ < 385 nm), Flow reactor, Gas phase    | H₂, CO₂ (100%)                        | 0.6% at 365 nm, 2% at 254 nm                 |
| Ga₂O₃, NOCM [b]                            | 300-W Xe lamp (λ < 270 nm), Closed reactor, Gas phase  | H₂, C₂H₆ (86%), C₂H₄, C₃H₆, C₃H₈      | 0.01% at 220–270 nm                          |
| Ce³⁺/Al₂O₃, NOCM [b]                        | 300-W Xe lamp (λ < 330 nm), Closed reactor, Gas phase  | H₂, C₂H₆ (78%), C₂H₄, C₃H₆, C₃H₈      | Not reported (NR)                            |
| Zn⁺-zeolite, NOCM [b]                       | 150-W high pressure Hg lamp (λ < 390 nm), Closed reactor, Gas phase | H₂, C₂H₆ (~100%)                      | 0.55% at 300–400 nm                         |
| Ga³⁺-ETS-10, NOCM [b]                       | 150-W high pressure Hg lamp (λ < 350 nm), Closed reactor, Gas phase | C₂H₆ (>70%) without H₂               | NR                                           |
| Si-doped GaN nanowire, CH₄ to benzene       | 300-W Xe lamp (λ = 290–380 nm), Closed reactor, Gas phase | H₂, benzene (96%), toluene, C₂, C₃     | 0.72% at 290–380 nm                         |
| Pt/TiO₂, NOCM [b]                           | 4-W low pressure Hg lamp (λ = 254 nm), Semibatch reactor, Liquid phase | H₂, C₂H₆ (62%), CO₂                 | 4.7% at 254 nm                              |
| Pd/TiO₂, NOCM [b]                           | 4-W low pressure Hg lamp (λ = 254 nm), Semibatch reactor, Liquid phase | H₂, C₂H₆ (73%), CO₂                 | 2.8% at 254 nm                              |
| Au/ZnO nanosheet, NOCM [b]                  | 300-W Xe lamp full arc (Two lights of 320–400 and 400–800 nm), Closed reactor, Gas phase | H₂, C₂H₆                             | Energy conversion efficiency: 0.08%         |
| Ag/ZnO, Oxidation of CH₄ in air [10]        | 300-W Xe lamp full arc (UV-Vis), Flow reactor, Gas phase | CO₂                                   | 8% at 300–380 nm, 0.18% at 470 nm           |
| TiO$_2$ electrode, PEC oxidation of CH$_4$ $^{11}$ | 6-W low pressure Hg lamp ($\lambda = 254$ nm), Batch reactor, Liquid phase | CO (20–80%), O$_2$, carbonate | NR |
|-----------------------------------------------|-----------------------------------------------------------------|---------------------------------|----|
| WO$_3$ electrode, PEC coupling of CH$_4$ (This work) | 3-W blue LED lamps ($\lambda_{\text{max}} = 453$ nm), Flow reactor, Gas phase, 1.20 V | H$_2$, C$_2$H$_6$ (54%), CO$_2$ (42%), CO | 11% at 453 nm |

[a] The number in parenthesis shows the selectivity, C-based.
[b] NOCM: non-oxidative (dehydrogenative) coupling of methane, $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$.

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