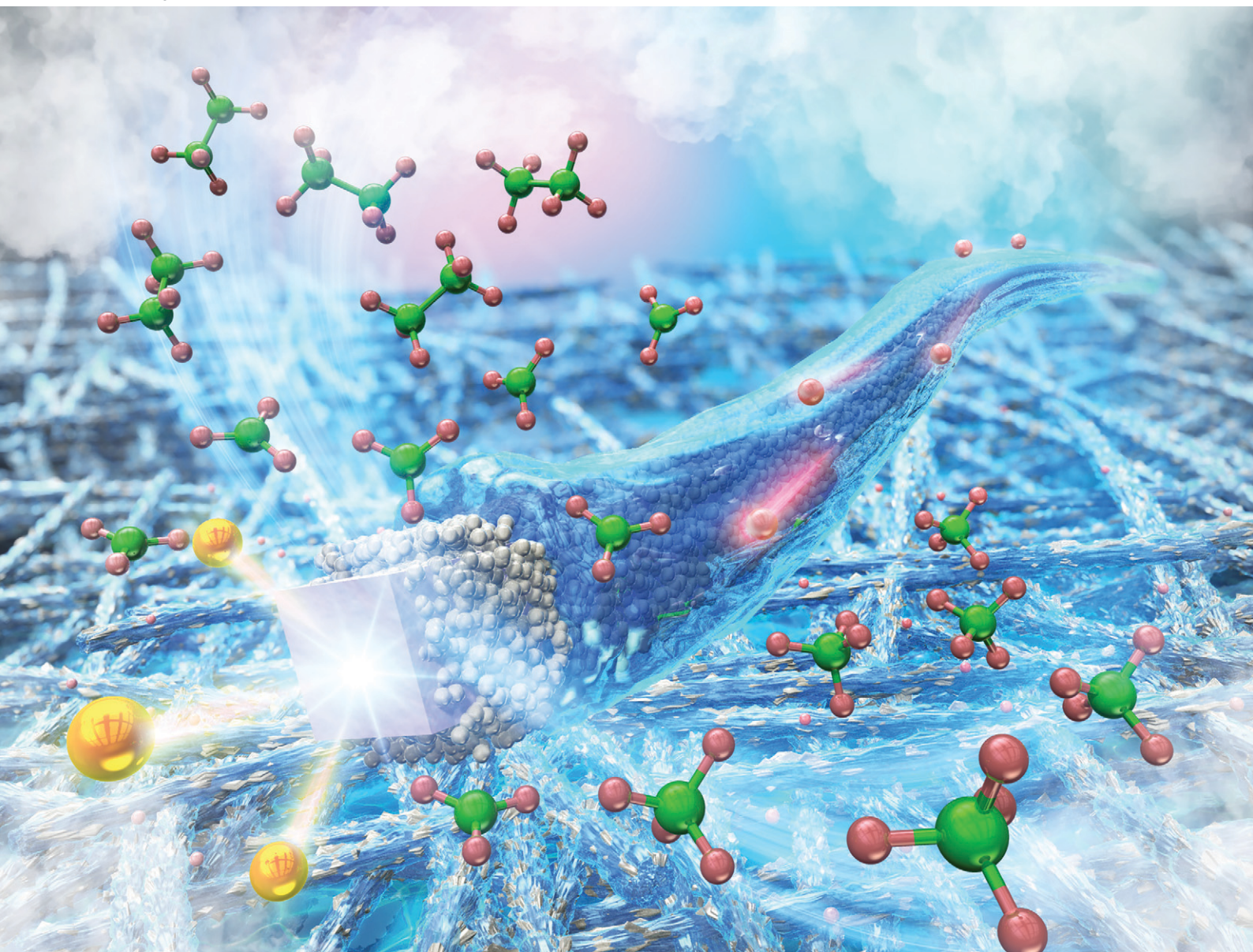


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**PAPER**

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## Photoelectrochemical C–H activation of methane to methyl radical at room temperature†

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Herein, we report a continuous gas-fed photoelectrochemical (PEC) system with a proton exchange membrane for CH<sub>4</sub> activation at ambient temperature and pressure. We found that both water splitting and steam reforming of CH<sub>4</sub> were induced over oxide photoanodes. When the CH<sub>4</sub> concentration was low, O<sub>2</sub> and CO<sub>2</sub> were formed on titanium oxide (TiO<sub>2</sub>) and tungsten trioxide (WO<sub>3</sub>) photoanodes under ultraviolet light irradiation. We also found that visible light enhanced CH<sub>4</sub> activation and ethane (C<sub>2</sub>H<sub>6</sub>) formation over the WO<sub>3</sub> photoanode. When the CH<sub>4</sub> concentration increased, O<sub>2</sub> formation was suppressed, with increasing production rates of CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and CO. Under optimised conditions, the selectivity of C<sub>2</sub>H<sub>6</sub> reached 57% on a carbon basis over the WO<sub>3</sub> photoanode under visible-light irradiation. The production of C<sub>2</sub>H<sub>6</sub> implies the formation of methyl radicals during the CH<sub>4</sub> gas-fed PEC process. We also demonstrated the PEC coupling of ethane to *n*-butane and the visible-light-induced oxidation of CH<sub>4</sub> without external bias.

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## Introduction

The catalytic conversion of CH<sub>4</sub> into value-added products is challenging because of its high stability and a large energy gap between its highest occupied and lowest unoccupied molecular orbitals.<sup>1,2</sup> Moreover, its electron affinity is low (−1.9 eV),<sup>3</sup> the ionization potential (12.6 eV) and the C–H bond dissociation energy (439 kJ mol<sup>−1</sup>) are high,<sup>4</sup> and the acidity is very weak (p*K*<sub>a</sub> = 56).<sup>5</sup> The dipole moment of CH<sub>4</sub> is zero because of its symmetric structure. Therefore, high-temperature processes are typically used for catalytic CH<sub>4</sub> conversion. However, a low-temperature catalytic process may be promising for achieving high selectivity. Photoelectrochemical (PEC) reactions at room temperature differ from conventional catalytic processes.<sup>6–10</sup>

There are three pathways that convert CH<sub>4</sub> into methyl radicals (<sup>•</sup>CH<sub>3</sub>), as shown in Fig. 1: electron transfer (ET), proton transfer (PT), and proton-coupled electron transfer (PCET). Among these reactions, ET (CH<sub>4</sub> = <sup>•</sup>CH<sub>4</sub><sup>+</sup> + e<sup>−</sup>, Δ<sub>r</sub>*G* = 1163 kJ mol<sup>−1</sup>) and PT (CH<sub>4</sub> = CH<sub>3</sub><sup>−</sup> + H<sup>+</sup>, Δ<sub>r</sub>*G* = 270 kJ mol<sup>−1</sup>) are extremely difficult to achieve. In contrast, PCET is more advantageous than stepwise transfer because the transfer of

H<sup>+</sup> and e<sup>−</sup> together can avoid the formation of high-energy chemical intermediates.<sup>11–13</sup> The Δ<sub>r</sub>*G* of PCET (CH<sub>4</sub> = <sup>•</sup>CH<sub>3</sub> + H<sup>+</sup> + e<sup>−</sup>) is 198.7 kJ mol<sup>−1</sup>. Thus, the potential of the <sup>•</sup>CH<sub>3</sub>/CH<sub>4</sub> couple is +2.06 V *versus* the standard hydrogen electrode (SHE).<sup>7</sup>

The potential to form <sup>•</sup>CH<sub>3</sub> is more negative than that for <sup>•</sup>OH/H<sub>2</sub>O (+2.38 V *vs.* SHE). These potentials are suitable for titanium oxide (TiO<sub>2</sub>) photocatalysts. Fig. 2a shows the band diagram of anatase TiO<sub>2</sub>, in which the valence band maximum (VBM) is located at approximately 3.0 V *vs.* SHE. Oxide semiconductors without partially filled d levels also exhibit a similar VBM.<sup>14</sup> Therefore, many semiconductor photocatalysts can activate CH<sub>4</sub> *via* the PCET mechanism. The nonoxidative coupling of methane (NOCM) is a well-known photocatalytic reaction (2CH<sub>4</sub> → C<sub>2</sub>H<sub>6</sub> + H<sub>2</sub>, Δ*G*<sub>298K</sub> = 68.6 kJ mol<sup>−1</sup>).<sup>15,16</sup>

However, the reported photocatalytic activities for NOCM are quite low.<sup>17–24</sup> In addition, TiO<sub>2</sub> can only use UV light as the band gap (*E*<sub>g</sub>) of anatase TiO<sub>2</sub> is 3.2 eV.<sup>25</sup>

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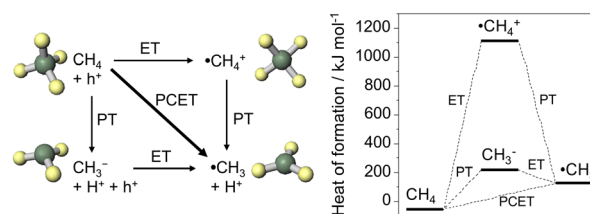
<sup>b</sup> Department of Chemical and Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135, Japan<sup>c</sup> Department of Biological Functions and Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka, 808-0196, Japan† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3cy00632h>

Fig. 1 Activation of CH<sub>4</sub> to methyl radical through electron transfer (ET), proton transfer (PT), and proton-coupled electron transfer (PCET). The heat of formation was calculated by MOPAC PM3.



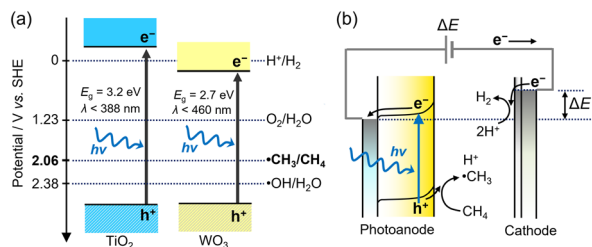


Fig. 2 (a) Energy band diagram of TiO<sub>2</sub> and WO<sub>3</sub>. (b) PEC process using photoanode and cathode under applied bias ( $\Delta E$ ).

The PEC process can overcome the following limitations of TiO<sub>2</sub> photocatalysis: low activity and lack of visible-light sensitivity (Fig. 2b). The external potential applied to the semiconductor electrodes improves the charge separation of the photoexcited carriers. Moreover, the applied voltage enables the use of visible light-responsive oxide semiconductors with a narrow  $E_g$  even though the conduction band minimum is too positive to induce the hydrogen evolution reaction (HER). Tungsten oxide (WO<sub>3</sub>) photocatalysts are theoretically inactive for NOCM accompanied by HER, but the PEC process enables the HER on the cathode by applying voltages between the two electrodes.

Herein, we investigate the PEC process for CH<sub>4</sub> activation using TiO<sub>2</sub> and WO<sub>3</sub> photoanodes.<sup>7–10,26,27</sup> We developed a continuous gas-flow PEC reactor using a proton exchange membrane (PEM) as a solid electrolyte.<sup>7,28–30</sup> The all-solid-state PEM-PEC cell is suitable for hydrophobic CH<sub>4</sub>, which is insoluble in water. The maximum concentration of CH<sub>4</sub> is only 0.0016 M in water while that of water is 55.5 M in liquid (Fig. 3).<sup>4</sup> However, in the case of humidified CH<sub>4</sub> gas, the saturated concentration of H<sub>2</sub>O(g) is 0.0013 M (3.16 kPa) at 25 °C, but the concentration of CH<sub>4</sub> is 0.041 M (101 kPa). We studied the probability of a gas-fed PEC process for CH<sub>4</sub> activation under both UV and visible-light irradiation.

## Results and discussion

### Photoanode materials and light wavelengths

CH<sub>4</sub> activation through PEC was tested using the PEM-PEC cell (Fig. S1 in ESI†) in a two-electrode system at 25 °C under

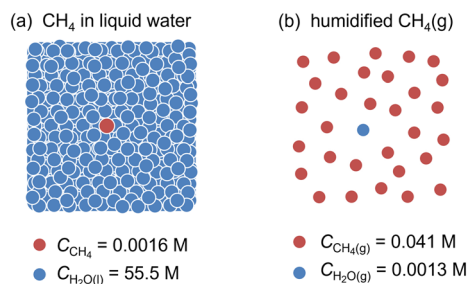


Fig. 3 (a) Molar concentrations of (a) dissolved CH<sub>4</sub> and H<sub>2</sub>O in liquid water, and (b) gaseous CH<sub>4</sub> and water vapor in humidified condition at 25 °C.

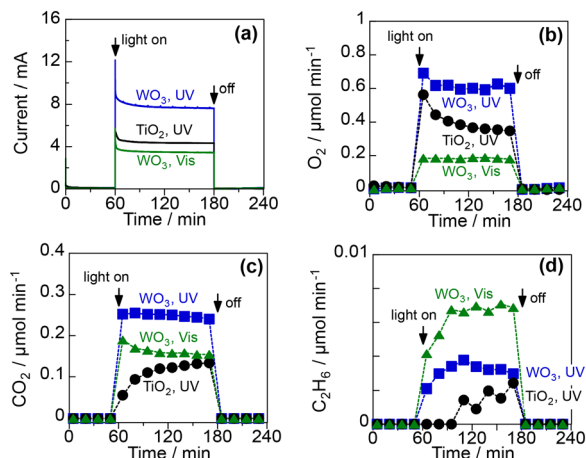


Fig. 4 PEC activation of 10 vol% CH<sub>4</sub> using WO<sub>3</sub> and TiO<sub>2</sub> photoanodes under UV light (6.5 mW cm<sup>-2</sup> at 365 nm) and visible light (6.8 mW cm<sup>-2</sup> at 453 nm): (a) the overall current at 1.2 V, (b) the rate of O<sub>2</sub> evolution, (c) the rate of CO<sub>2</sub> formation, and (d) the rate of C<sub>2</sub>H<sub>6</sub> formation on the photoanode side.

atmospheric pressure. Fig. 4 shows the time course of the PEC process using the TiO<sub>2</sub> and WO<sub>3</sub> photoanodes under a continuous flow of 10 vol% CH<sub>4</sub> and 3 vol% H<sub>2</sub>O(g) balanced with Ar. The cathode, which was separated from the photoanode using PEM, was a Pt/carbon electrocatalyst maintained under a humidified Ar flow. Humidification of the fed gases enhanced the proton conductivity of the PEM. The photoanode was irradiated with UV (365 nm) or blue light (453 nm). Before photoirradiation, the PEC system was kept in the dark to establish an adsorption-desorption equilibrium. Under irradiation, a good photocurrent response was observed for each condition when 1.2 V was applied between the photoanode and cathode catalysts (Fig. 4a). The incident photon-to-current conversion efficiencies (IPCE) at steady state were 19.8% and 11.3% for the WO<sub>3</sub> and the TiO<sub>2</sub> photoanodes, respectively, at 365 nm. The IPCE at 453 nm was 8.4% for the WO<sub>3</sub> photoanode. This high quantum efficiency suggests efficient charge separation in the space-charge layer formed by the applied potential.

O<sub>2</sub>, CO<sub>2</sub>, and a small amount of C<sub>2</sub>H<sub>6</sub> were obtained as products on the photoanodes (Fig. 4b–d). Carbon monoxide could not be analysed under these conditions because of its interference with the Ar diluent. The production of O<sub>2</sub> and CO<sub>2</sub> suggests that both water vapour and CH<sub>4</sub> were oxidised on the photoanodes. The Faraday efficiencies (FE) of O<sub>2</sub> and CO<sub>2</sub> were approximately 50% and 40%, respectively, under UV irradiation for both photoanodes (Table S1 in ESI†). The FE of O<sub>2</sub> decreased to 34% and that of CO<sub>2</sub> increased to 59% under visible-light irradiation of the WO<sub>3</sub> photoanode. The production rate of C<sub>2</sub>H<sub>6</sub> also increased when 453 nm visible light was used instead of 365 nm UV light. These results suggest that CH<sub>4</sub> oxidation to CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> is more plausible than water oxidation under visible-light irradiation. The production of C<sub>2</sub>H<sub>6</sub> implies that  $\cdot\text{CH}_3$  is generated by the PEC process; this is because the homocoupling of  $\cdot\text{CH}_3$  is

involved in the formation mechanism of  $C_2H_6$  in photo-Kolbe electrolysis.<sup>31–33</sup>

### Methane concentration and light intensity

Fig. 5 shows the effect of the concentration of  $CH_4$  fed into the  $WO_3$  photoanode under visible-light irradiation. The  $O_2$  evolution rate decreased significantly when the  $CH_4$  concentration increased to 50 vol%. The IPCE was 10.5%, and the FEs for  $O_2$ ,  $CO_2$ , and  $C_2H_6$  were 5.1%, 81.7%, and 4.9%, respectively (Table S2 in the ESI<sup>†</sup>). For the cathode catalyst, stoichiometric  $H_2$  evolution (FE of  $\sim 100\%$ ) was observed, indicating that the steam reforming of methane ( $CH_4 + 2H_2O_{(g)} \rightarrow CO_2 + 4H_2$ ) was mainly promoted in this PEM-PEC reactor. To the best of our knowledge, this is the first report of the gas-fed PEC steam reforming of methane, which is an uphill reaction ( $\Delta G_{298K} = 114 \text{ kJ mol}^{-1}$ ).<sup>15,16</sup> Notably, the purity of the evolved  $H_2$  can be sustained by the membrane separation from  $CH_4$  and the oxidised products. The  $H_2$  production rate, and thus the photocurrent, did not depend on the  $CH_4$  concentration, suggesting that the charge-separation efficiency was determined by the applied potential rather than the surface reactions.

Fig. 6 shows the PEC properties of the  $WO_3$  photoanode under the flow of 97 vol%  $CH_4$  and 3 vol%  $H_2O$  vapour.<sup>7</sup> When the light intensity is  $3.6 \text{ mW cm}^{-2}$ , the FEs of  $O_2$ ,  $CO_2$ ,  $CO$ , and  $C_2H_6$  were 1.5%, 72.3%, 8.3%, and 14.0%, respectively. The sum of the FE values was 96%, suggesting that unidentified products were limited, and no methanol was formed. The FE of  $C_2H_6$  was not very high because only two electrons were donated from  $CH_4$  to produce a  $C_2H_6$  molecule and eight electrons produced a  $CO_2$

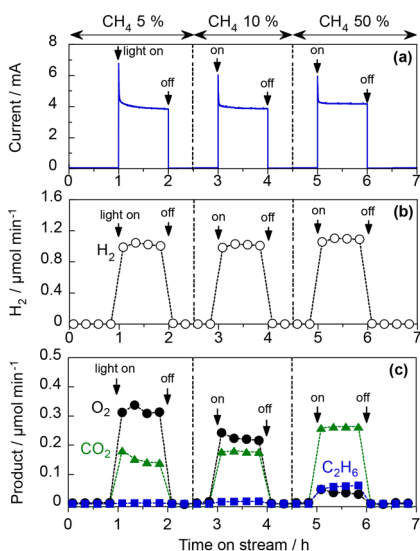


Fig. 5 Effect of  $CH_4$  concentration on the PEC reactions over the  $WO_3$  photoanode: (a) the overall current at 1.2 V, (b) the rate of  $H_2$  evolution on the cathode side, and (c) the rate of products formation on the photoanode side under visible-light irradiation ( $6.8 \text{ mW cm}^{-2}$  at 453 nm).

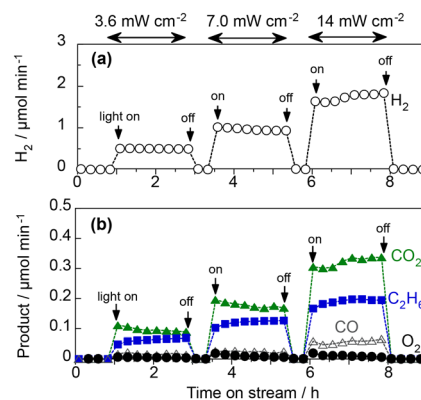


Fig. 6 Effect of light intensity on the activation of humidified  $CH_4$  using the  $WO_3$  photoanode under 453 nm irradiation at 1.2 V; (a) the  $H_2$  evolution rate on the cathode side and (b) the rates of product formation on the photoanode side.

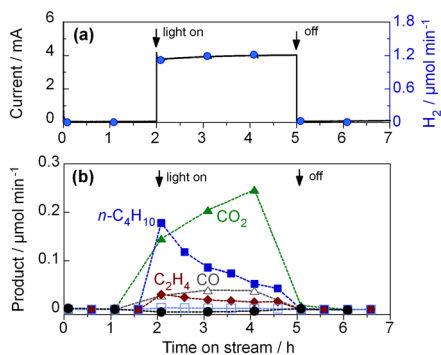
molecule. From the viewpoint of selectivity, the production rate of  $C_2H_6$  was comparable to that of  $CO_2$  at high  $CH_4$  concentrations and low light intensities. The  $C_2H_6$  selectivity on a carbon basis reached 57.4%, whereas the selectivities for  $CO_2$  and  $CO$  were 37.0% and 5.6%, respectively (Table S3 in the ESI<sup>†</sup>). This indicates that more than half of the PEC process can be explained by the dehydrogenative coupling of methane, similar to photocatalytic NOCM.<sup>7</sup>

The high  $C_2H_6$  selectivity implies the efficient formation of  $\cdot CH_3$  by the photogenerated holes of  $WO_3$ . When the concentration of the generated  $\cdot CH_3$  is high, homocoupling should easily occur to produce  $C_2H_6$ . In contrast, other side reactions of  $\cdot CH_3$  are promoted, thereby decreasing  $C_2H_6$  selectivity at low  $CH_4$  concentrations.

The production rates of  $CO_2$ ,  $CO$ , and  $C_2H_6$  increased with the incident light intensity (Fig. 6). This indicated that the products were formed *via* the photoexcitation mechanism. The  $C_2H_6$  selectivity gradually decreased from 57.4% to 49.1% when the irradiance intensity was changed from 3.6 to  $14 \text{ mW cm}^{-2}$ , implying that overoxidation is promoted when the concentration of holes is high at the semiconductor surface. Although the photocurrent fluctuated over time, which may have been affected by humidity, the  $WO_3$  photoanode repeatedly exhibited sufficient stability for several hours. We also did not confirm the degradation of the crystallinity of  $WO_3$  or the structure of the ionomer coated on the photoanode surface, as shown in X-ray diffraction patterns (Fig. S2<sup>†</sup>) and Fourier transform infrared spectra (Fig. S3<sup>†</sup>).

### PEC reaction mechanism

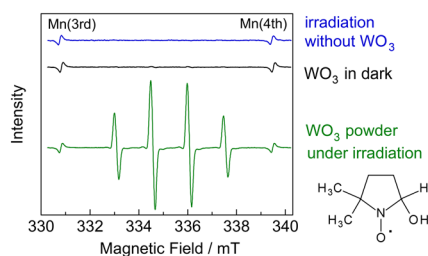
To further investigate the radical mechanism of the PEC process, we tested the PEC oxidation of  $C_2H_6$ .<sup>34</sup> Fig. 7 shows the time course of the  $C_2H_6$  activation on the  $WO_3$  photoanode. We detected *n*-butane as the product. The formation of *n*-butane suggests the occurrence of the



**Fig. 7** PEC activation of  $C_2H_6$  using  $WO_3$  photoanode under visible-light irradiation ( $6.8 \text{ mW cm}^{-2}$  at  $453 \text{ nm}$ ) at  $1.2 \text{ V}$ ; (a) the overall current and  $H_2$  evolution rate on the cathode side, and (b) the rates of product formation on the photoanode side.

homocoupling of ethyl radicals ( $C_2H_5 + C_2H_5 \rightarrow CH_3-CH_2-CH_2-CH_3$ ). We also detected the formation of ethylene, which could have been generated through intermolecular dehydrogenation ( $C_2H_6 + 2 h^+ \rightarrow CH_2 = CH_2 + 2H^+$ ). The FE of *n*-butane was 4.4%, and its selectivity was 39.7% (C-basis), as shown in Table S4 in the ESI†

To investigate the radical intermediates involved in the activation of  $CH_4$ , we conducted electron paramagnetic resonance (EPR) experiments using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a spin-trapping agent.<sup>35</sup> Photoirradiation was performed for  $WO_3$  powder dispersed in a 50 mM  $AgNO_3$  aqueous solution with  $CH_4$  gas. The silver cation acted as an electron acceptor for the photoexcited  $WO_3$ .<sup>36</sup> We observed four-line EPR signals ( $g = 2.0056$ ,  $A_N = 1.49 \text{ mT}$ ,  $A_H = 1.49 \text{ mT}$ ), which were consistent with the  $^{\bullet}DMPO-OH$  spin adduct, in the  $WO_3$  suspension after irradiation (Fig. 8). This implied that hydroxyl radical ( $^{\bullet}OH$ ) could form on the  $WO_3$  photoanode in the presence of water vapour. Therefore,  $^{\bullet}OH$  would be the active species for  $CH_4$  activation in the PEM-PEC system. In contrast, we could not detect a signal corresponding to the  $^{\bullet}DMPO-CH_3$  spin adduct, even in the presence of acetic acid and dimethyl sulfoxide. This suggests that spin trapping of  $^{\bullet}CH_3$  with DMPO is difficult in liquid water under our experimental conditions.



**Fig. 8** EPR spectra of an aqueous solution of DMPO and  $AgNO_3$  after 405 nm irradiation for 5 min without  $WO_3$  powder, aging in the dark with  $WO_3$  powder, and 405 nm irradiation for 5 min with  $WO_3$  powder. The standard  $Mn^{2+}$  marker shows signals at  $g = 2.0337$  (third line) and  $g = 1.9803$  (fourth line).

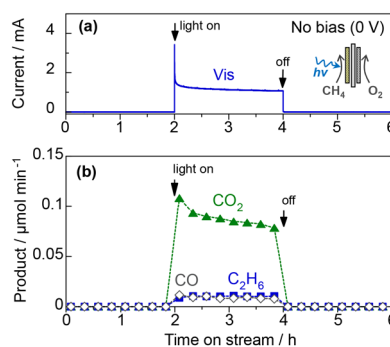
We also attempted a photo-Kolbe reaction using  $WO_3$  powder, 5 vol% acetic acid, and 50 mM  $AgNO_3$ .<sup>33,36</sup> The gaseous products obtained were  $CO_2$ ,  $CH_4$ , and  $O_2$  (Fig. S4 in ESI†). A trace amount of methanol was also formed in the aqueous solution. However,  $C_2H_6$  was not formed in the aqueous system, indicating the importance of the vapour-fed conditions in  $C_2H_6$  production.

The advantage of the gas-fed type reactor was also revealed by the gas flow rate dependence of  $C_2H_6$  formation (Fig. S5 in ESI†). The production rate of  $C_2H_6$  was very low at a gas flow rate of  $1 \text{ mL min}^{-1}$ . We realised that gas diffusion plays an important role in  $C_2H_6$  production in the PEM-PEC system because productivity increased at higher flow rates. The proposed reaction mechanism for the catalytic oxidative coupling of methane involves the coupling of  $^{\bullet}CH_3$  in the gas phase to form  $C_2H_6$ .<sup>2,37</sup> Similar to this mechanism, continuous flow facilitates the desorption of  $^{\bullet}CH_3$  from the surface of the  $WO_3$  photoanode and the formation of  $C_2H_6$ .

### Zero-bias PEC oxidation of methane

The photocatalytic oxidation of atmospheric  $CH_4$  to  $CO_2$  is another attractive reaction because the greenhouse gas effect of  $CH_4$  is over 30 times greater than that of  $CO_2$ . The complete oxidation of methane is an exergonic reaction ( $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$ ,  $\Delta G_{298K} = -801 \text{ kJ mol}^{-1}$ ),<sup>15,16</sup> but its high activation energy prevents the catalytic reaction at room temperature.

Fig. 9 shows the PEC oxidation of  $CH_4$  in the PEM-PEC reactor using the  $WO_3$  photoanode under blue-light irradiation at  $25 \text{ }^\circ\text{C}$ .  $CO_2$  formation by  $CH_4$  oxidation was confirmed without an external bias voltage. During the exergonic reaction, the oxygen reduction reaction ( $O_2 + 4H^+ + 4e^- = H_2O$ ,  $1.23 \text{ V vs. SHE}$ ) was promoted over the Pt/carbon catalyst in humidified air (Fig. 2a). The IPCE at zero bias was 2.5% at  $453 \text{ nm}$ , which was much higher than the quantum efficiency previously reported for photocatalytic systems.<sup>38,39</sup>



**Fig. 9** PEC oxidation of  $CH_4$  by the PEM-PEC reactor using the  $WO_3$  photoanode and Pt/carbon catalyst: (a) the overall current at zero bias, and (b) the rate of products formation on the photoanode side under  $453 \text{ nm}$  light irradiation ( $6.8 \text{ mW cm}^{-2}$ ).

## Experimental

### Preparation of photoanodes

Ti felt was used as the conductive substrate for the gas-diffusion photoanodes. The WO<sub>3</sub> electrode was prepared by dip coating with an aqueous solution of (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub> and polyethylene glycol; the electrode was then calcined at 923 K for 2 h.<sup>7,28,40</sup> The TiO<sub>2</sub> electrode was prepared by the anodization of Ti felt in ethylene glycol with 0.25 wt% NH<sub>4</sub>F and 10 vol% H<sub>2</sub>O at 50 V for 3 h.<sup>29,41,42</sup> The anodized Ti felt was calcined at 823 K for 1 h to crystallize into anatase TiO<sub>2</sub>. The photoanodes were modified using a Nafion ionomer dispersion (Sigma-Aldrich).

### PEM-PEC reaction

The PEC measurements were performed at 25 °C and 1 bar using an AMETEK VersaSTAT3 workstation. For the proposed all-solid-state cells, a Nafion N117 film (DuPont) was sandwiched between the photoanode and the cathode, which was composed of Pt/carbon (Tanaka Kikinzo Kogyo) and Toray carbon paper (Fuel Cell Store). The photoanode side was supplied with 20 mL min<sup>-1</sup> of humidified CH<sub>4</sub>/Ar or humidified CH<sub>4</sub> gas. The relative humidity was approximately 90% without liquid condensation. The cathode side was supplied with 20 mL min<sup>-1</sup> of humidified Ar gas. The geometric surface areas of the two electrodes were 25 cm<sup>2</sup>, whereas the irradiation area of the photoanode was 16 cm<sup>2</sup>. Photoirradiation was performed through a glass window using light-emitting diodes (LED). The peak wavelengths were 365 and 453 nm for the UV (Nitride Semiconductor) and blue LED (OptoSupply), respectively. The IPCE was calculated as follows:

$$\text{IPCE} = \frac{1240 j_{\text{photo}}}{\lambda I_0} \times 100\%$$

Here,  $j_{\text{photo}}$  is the photocurrent density,  $\lambda$  is the wavelength (nm), and  $I_0$  is the intensity of incident light.

### Product analysis

The gas products of the PEC reaction were analysed using gas chromatography (Shimadzu GC-8A and GC-2014). A thermal conductivity detector (TCD) equipped with a molecular sieve 5A column in an Ar carrier was used to quantify H<sub>2</sub> and O<sub>2</sub>. A TCD with a Shincarbon ST column in an He carrier was used to quantify CO and CO<sub>2</sub>. A flame ionisation detector with a GS-CarbonPLOT was used to detect alkane species.

The C<sub>2</sub>H<sub>6</sub> selectivity in carbon basis was calculated using the below equation:

$$S_{\text{C}_2\text{H}_6} = \frac{2r_{\text{C}_2\text{H}_6}}{r_{\text{CO}_2} + r_{\text{CO}} + 2r_{\text{C}_2\text{H}_6}} \times 100\%$$

Here,  $r_i$  is the production rate of each carbon-containing product determined by online GC and is referenced to the

calibration curves from the standard gas sample. The corresponding FE values are calculated as follows:

$$\text{FE} = \frac{n_i F r_i}{j_{\text{photo}}} \times 100\%$$

Here,  $n_i$  is the number of electrons involved, and  $F$  is the Faradaic constant. The  $n_i$  values for C<sub>2</sub>H<sub>6</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub> are 2, 4, 6, and 8, respectively.

### Characterization

X-ray diffraction patterns were recorded by a Rigaku SmartLab diffractometer using Cu K $\alpha$  radiation. Fourier transform infrared spectroscopy was performed on a Shimadzu IR Affinity-1 spectrometer in the attenuated total reflection mode. Electron paramagnetic resonance (EPR) spectra were recorded using a JES-X310 spectrometer (JEOL, Japan) at room temperature. The sample suspension was taken out by a quartz capillary tube with the two ends sealed by sealing compound for the EPR measurement.

## Conclusions

We studied the PEC activation of CH<sub>4</sub> over TiO<sub>2</sub> and WO<sub>3</sub> photoanodes in a gas-flow PEM-PEC system. We demonstrated that a WO<sub>3</sub> photoanode excited by visible light converts CH<sub>4</sub> into CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. At high CH<sub>4</sub> concentrations, the C<sub>2</sub>H<sub>6</sub> selectivity was above 50% on a carbon basis. Moreover, we found that WO<sub>3</sub> and visible light were more suitable than TiO<sub>2</sub> and UV light to form C<sub>2</sub>H<sub>6</sub>. When C<sub>2</sub>H<sub>6</sub> was used as the reactant, *n*-butane was formed, suggesting a radical coupling mechanism. The WO<sub>3</sub> photoanode showed an IPCE of 7.6% at 453 nm with an applied voltage of 1.2 V. The current efficiency of H<sub>2</sub> was nearly 100% in the cathode compartment, demonstrating that the PEM-PEC system is useful for steam reforming of methane and dehydrogenative methane coupling. Surprisingly, visible-light induced CH<sub>4</sub> oxidation was also efficiently promoted in the PEM-PEC system using humidified air, even under zero bias.

## Author contributions

Fumiaki Amano: conceptualisation, methodology, validation, visualisation, writing – review & editing, and supervision. Ayami Shintani: investigation visualisation, and writing – original draft. Tatsuya Sakakura and Yoshiyuki Takatsuji: investigation. Tetsuya Haruyama: validation and resources.

## Conflicts of interest

There are no conflicts to declare.

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