Supplementary Information

Photoelectrochemical C–H Activation of Methane to Methyl Radical at Room Temperature

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Table S1. PEC activation of 10 vol% CH_4 using WO_3 and TiO_2 photoanodes under UV light (365 nm) and visible light (453 nm) at 1.2 V

Sample	Wavelength / nm	%IPCE	Faraday efficiency (%)			
			O_2	CO_2	C_2H_6	Sum
WO_3	365	19.8	51.4	41.1	0.13	92.6
TiO_2	365	11.3	52.1	40.1	0.18	92.6
WO_3	453	8.4	34.3	58.9	0.66	93.9

Table S2. Effect of CH_4 concentration on the PEC reactions over WO_3 photoanode under visible light irradiation (453 nm) at 1.2 V

$\%CH_4$	%IPCE	Faraday efficiency (%)				Selectivity (%, C-basis)	
		O_2	CO_2	C_2H_6	Sum	CO_2	C_2H_6
5	9.7	52.4	46.8	0.2	99.4	96.5	3.5
10	9.7	35.8	59.1	0.7	95.5	91.8	8.2
50	10.5	5.09	81.7	4.9	91.7	67.8	32.2

Table S3. Effect of light intensity on the activation of humidified CH_4 using the WO_3 photoanode under visible light (453 nm) irradiation at 1.2 V

Irradiance [mW cm^{-2}]	Photoi [mA]	%IPCE	Faraday efficiency (%)						Selectivity (%, C-basis)		
			H_2	O_2	CO_2	C_2H_6	CO	Sum	CO_2	C_2H_6	CO
3.6	1.59	7.61	100	1.53	72.3	14.0	8.25	96.1	37.0	57.4	5.63
7.0	3.00	7.32	99.7	1.34	72.0	13.5	7.94	94.8	37.7	56.7	5.55
14.0	5.83	7.12	99.3	0.66	73.0	10.5	10.7	94.9	42.6	49.1	8.33

Table S4. PEC activation of C_2H_6 using WO_3 photoanode under visible light (453 nm) irradiation at 1.2 V

%IPCE	Faraday efficiency (%)								Selectivity (%, C-basis)				
	H_2	O_2	CO_2	*n*-C_4H_{10}	CO	C_3H_8	C_2H_4	Sum	CO_2	*n*-C_4H_{10}	CO	C_3H_8	C_2H_4
9.6	101	0.0	71.7	4.4	8.0	0.2	1.3	85.5	46.2	39.7	7.2	1.1	5.8

Table S5. PEC oxidation of CH_4 using PEM-PEC reactor using Pt/carbon catalyst and WO_3 photoanode under visible light (453 nm) irradiation at zero bias

%IPCE	Faraday efficiency (%)					Selectivity (%, C-basis)		
	O_2	CO_2	C_2H_6	CO	Sum	CO_2	C_2H_6	CO
2.5	0.0	94.4	3.2	7.0	105	73.2	19.6	7.2

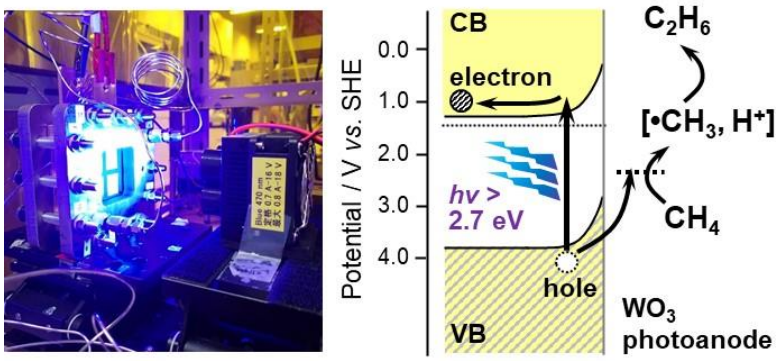

Figure S1. Proton exchange membrane photoelectrochemical (PEM-PEC) cell for activation of CH_4 gas without liquid electrolyte.

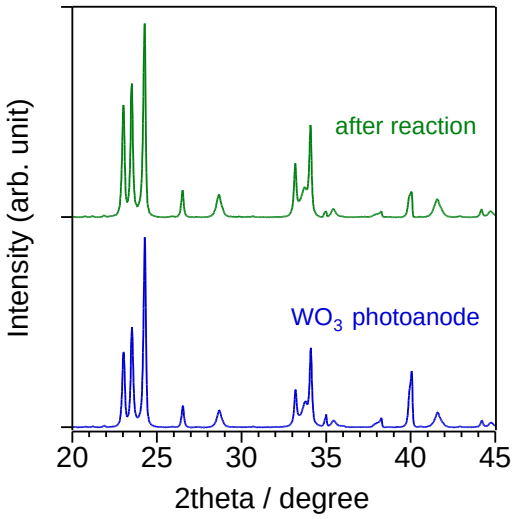

Figure S2. X-ray diffraction patterns of the WO_3 photoanode before and after the PEM-PEC reaction.

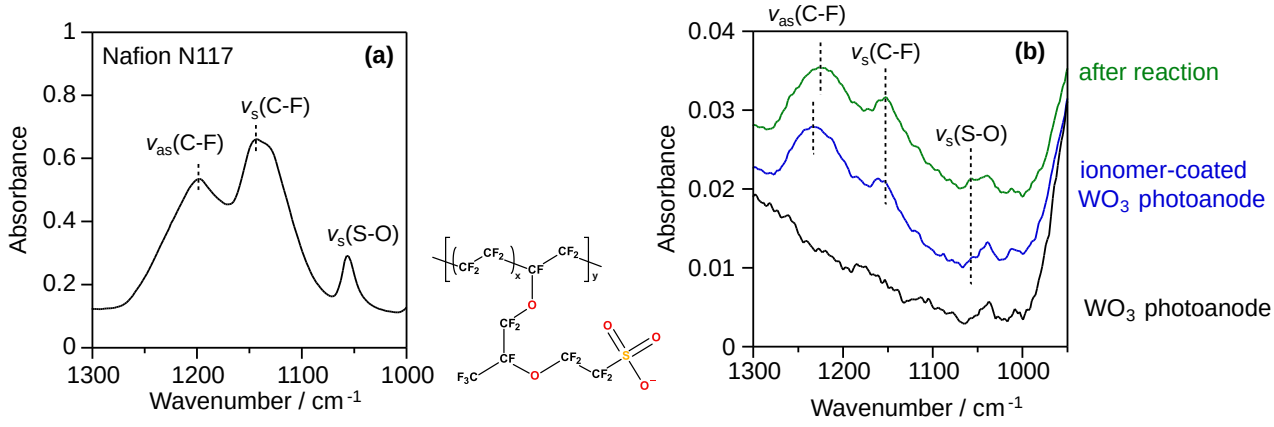

Figure S3. FT-IR spectra of (a) Nafion N117 membrane and (b) the WO_3 photoanodes: fresh, ionomer-coated, and the used samples.

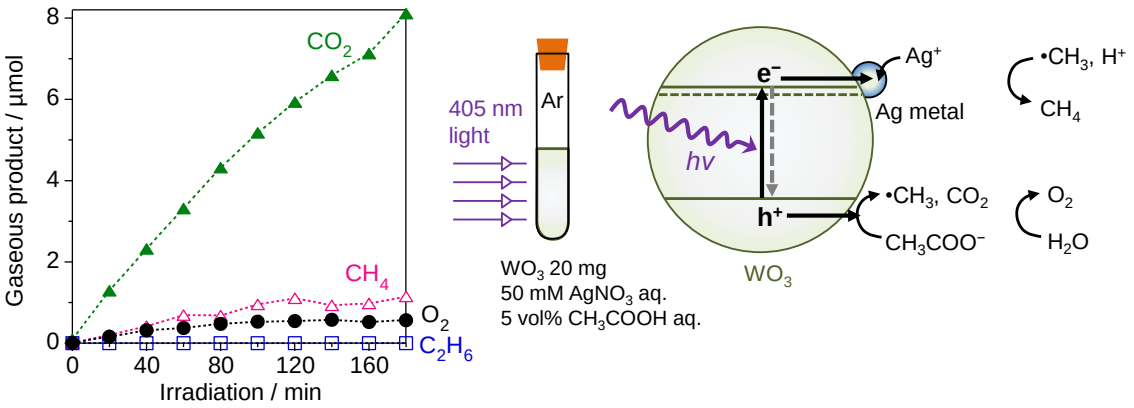

Figure S4. Photocatalytic decomposition of acetic acid over WO_3 powder in the presence of $AgNO_3$. 5 mL of an aqueous solution of 5 vol% CH_3COOH and 50 mM $AgNO_3$ was used for 20 mg WO_3 powder (Aldrich) under 0.1 MPa argon. 405 nm LED was used as a light source.

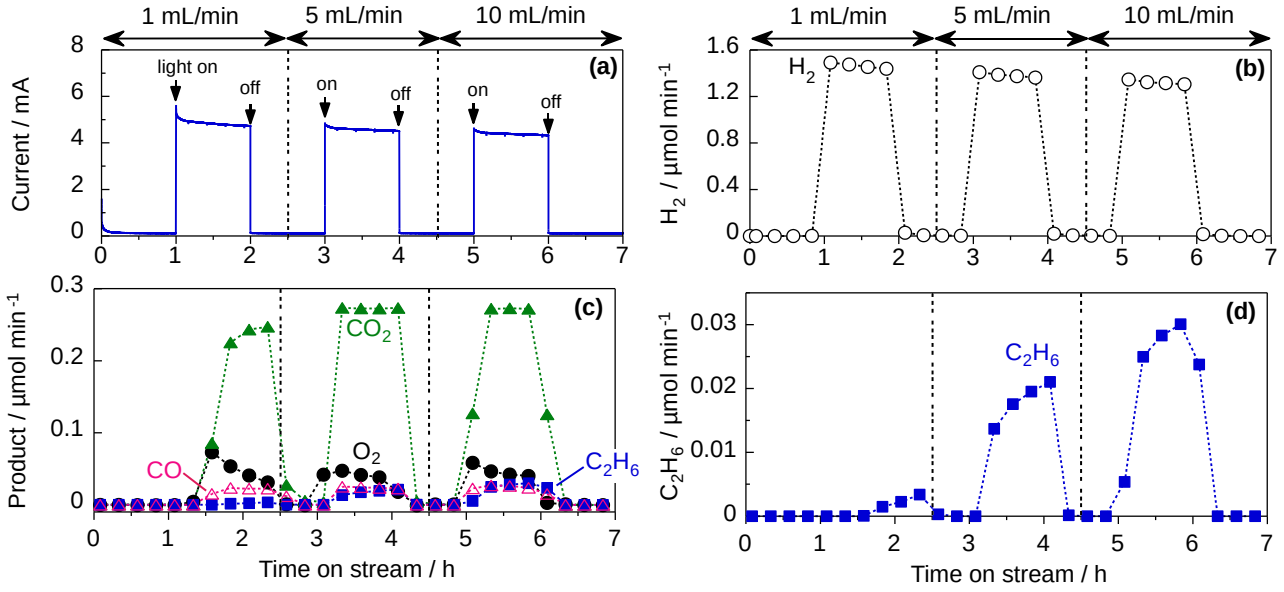

Figure S5. Effect of gas flow rate (1, 5, and 10 mL min^{-1}) on the PEC activation of CH_4 using the WO_3 photoanode under 453 nm irradiation at 1.2 V; (a) Photocurrent response, (b) the H_2 evolution rate on the cathode side, (c) the products formation rates on the photoanode side, and (d) the C_2H_6 production rate adopted from (c).