

Supporting Information

Gas-fed Photoelectrochemical Reactions Sustained by Phosphotungstic Acid as an Inorganic Surface Electrolyte

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Table S1. Vapor-fed PEC water splitting at 1.2 V (vs. Pt-CB) under visible light for 20 h^a

Photoanode	IPCE (%) ^c	H ₂ FE (%) ^d	O ₂ FE (%) ^e
PFSA/WO ₃ ^b	2.4	93.6	84.8
PWA/WO ₃ ^b	2.8	99.4	94.8

^a Wavelength 453 nm, Irradiance 12 mW cm⁻², and area 16 cm²

^b Surface electrolyte loading 5 wt%

^c Incident photon-to-current conversion efficiency, which was calculated by subtracting the dark current from the current density just before the light is turned off.

^d Faradaic efficiency of H₂ evolution on the cathode side

^e Faradaic efficiency of O₂ evolution on the photoanode side

Table S2. SEM-EDS analysis of the functionalized WO₃ photoanodes before and after the long-term vapour-fed PEC water splitting at 1.2 V (vs. Pt-CB) under visible light for 20 h ^a

Photoanode	Reaction	C (mass%)	O (mass%)	F (mass%)	S (mass%)	Ti (mass%)	W (mass%)
PFSA/WO ₃ ^b	Before	14.2	10.3	36.5	0.18	22.1	16.7
	After	9.3	17.5	18.5	0.13	21.8	32.8

Photoanode	Reaction	O (mass%)	P (mass%)	Ti (mass%)	W (mass%)
PWA/WO ₃ ^b	Before	29.0	0.29	25.8	44.9
	After	25.6	0.31	20.5	53.6

^a Wavelength 453 nm, Irradiance 12 mW cm⁻², and area 16 cm²

^b Surface electrolyte loading 5 wt%

Table S3. Gas-phase PEC methane conversion at 1.2 V (vs. Pt-CB) under visible light irradiation (Fig.7) ^a

Photoanode	IPCE (%)	H ₂ FE (%)	FE in photoanode (%)					Selectivity (% , C-basis)		
			O ₂	C ₂ H ₆	CO ₂	CO	Sum	C ₂ H ₆	CO ₂	CO
PFSA/WO ₃ ^b	6.3	99.5	15.7	8.6	63.2	2.7	90.2	50.5	46.7	2.8
PWA/WO ₃ ^c	7.1	101	2.5	10.5	71.3	9.2	93.9	50.0	42.3	7.6

^a Wavelength 453 nm, Irradiance 22 mW cm⁻², and area 2 cm²

^b PFSA loading 12 wt%

^c PWA loading 5 wt%

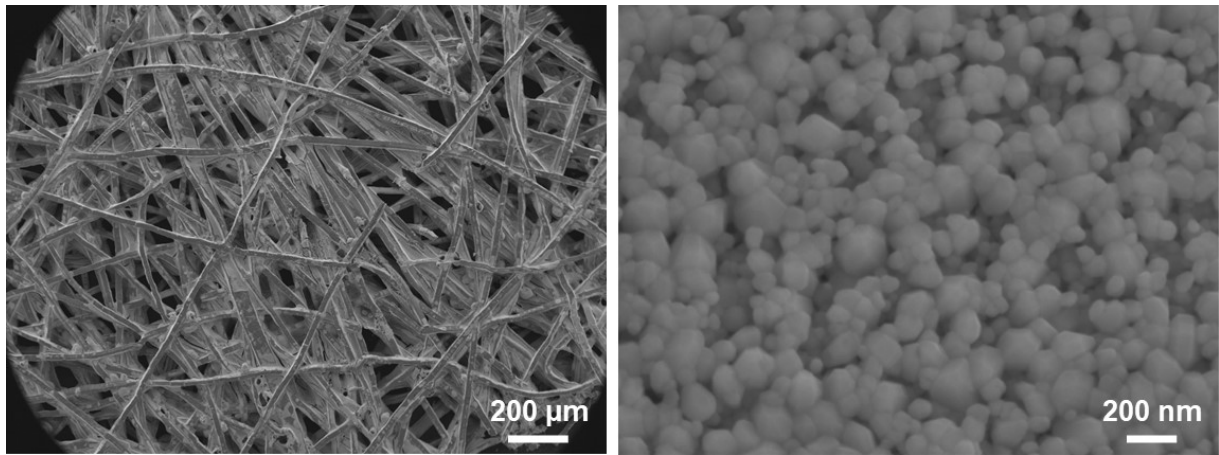


Figure S1. SEM images of the porous WO_3 electrode functionalized by PWA coating (PWA/ WO_3).

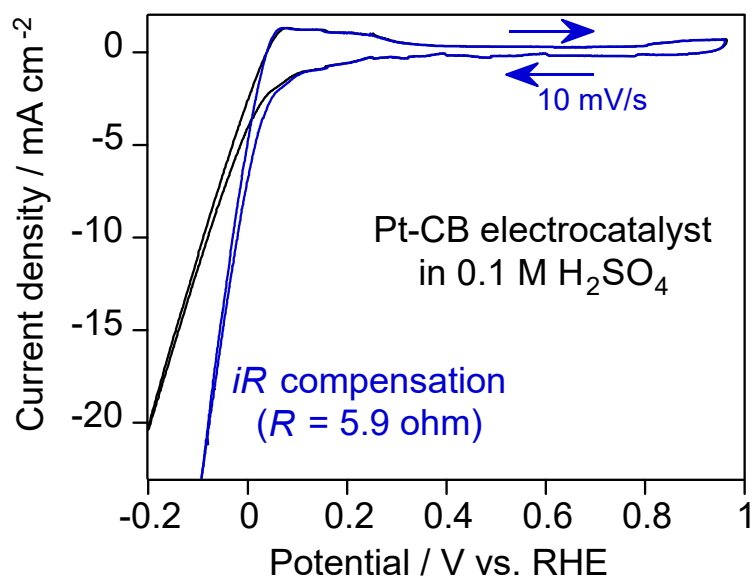


Figure S2. Cyclic voltammetry curves of the Pt-CB electrocatalyst in 0.1 M H₂SO₄ electrolyte (pH 1.0) at a scan rate of 10 mV s⁻¹ with and without *iR* compensation. The series resistance between the working and reference electrodes was measured by electrochemical impedance spectroscopy analysis.

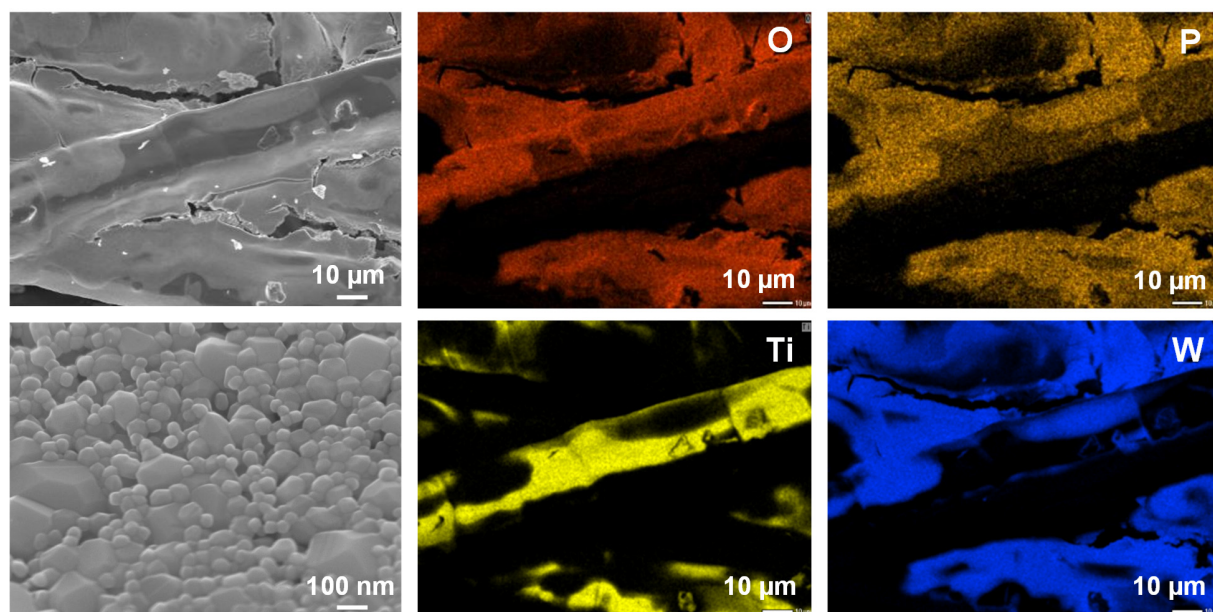


Figure S3. SEM-EDS mapping images of the PWA/WO₃ photoanode after the long-term vapour-fed PEC water splitting for 20 h.

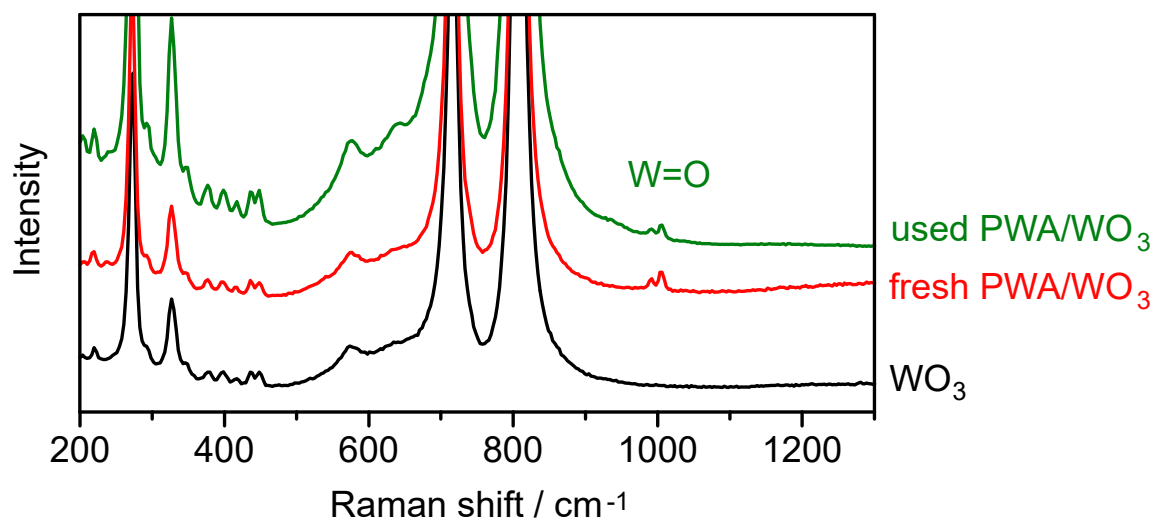


Figure S4. Raman spectra of (a) bare WO₃, (b) PWA/WO₃, and (c) PWA/WO₃ after the long-term vapor-fed PEC water splitting for 20 h.

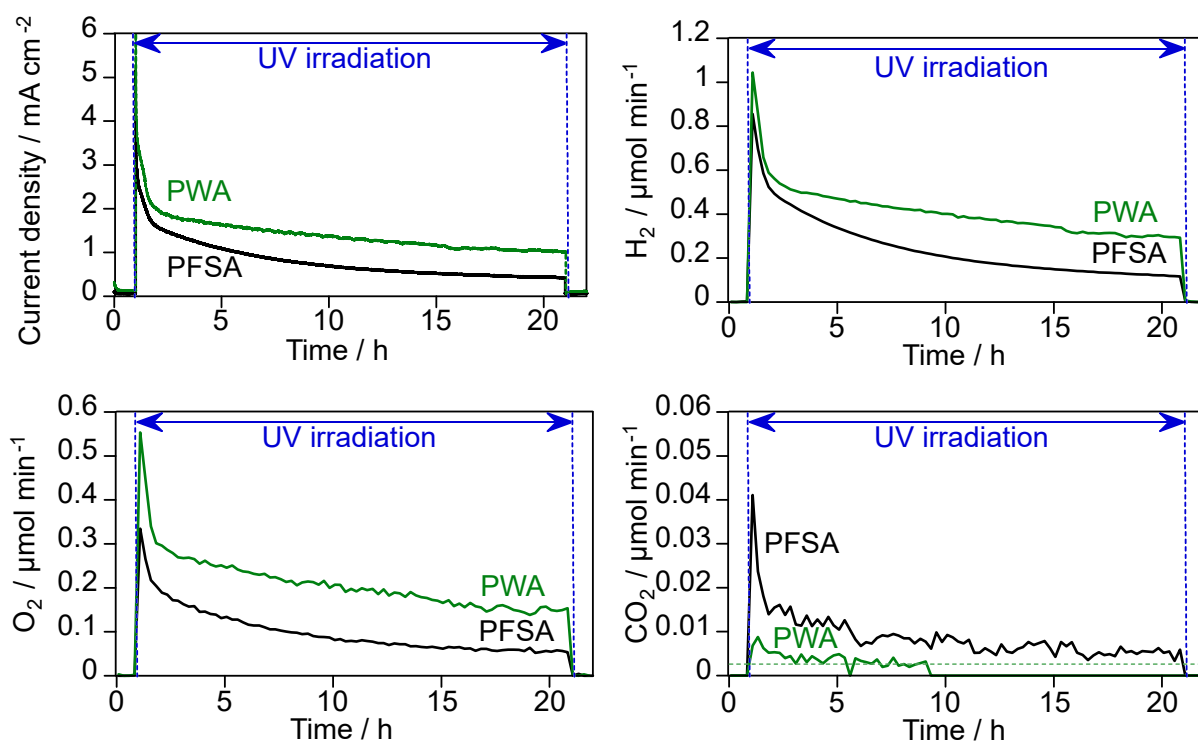


Figure S5. Vapour-fed PEC water splitting of PFSA/WO₃ and PWA/WO₃ photoanodes under UV light (wavelength 385 nm, irradiance 60 mW cm⁻², irradiation area 2 cm²) at an applied voltage of 1.2 V (vs. Pt-CB cathode). Carrier gas: Ar, Flow rate: 20 mL min⁻¹, Water vapour: 3 kPa, Temperature: 25 °C.