Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Photoelectrochemical Water Vapor Splitting Using an Ionomer-Coated Rutile TiO_2 layer on Titanium Microfiber Felt as an Oxygen-Evolving Photoanode

Fumiaki Amano,[ab] Hyosuke Mukohara,[a] Hiroki Sato,[a] and Teruhisa Ohno[b]*

[a] Department of Chemical and Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0135, Japan.

[b] Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

[c] Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan.

Corresponding Author

*Fumiaki Amano, E-mail: amano@kitakyu-u.ac.jp

Table S1. Results of PEC splitting of 3vol% water vapor by R650 | PEM | Pt/CB at 1.2 V under 365-nm UV light (40 mW cm^{-2}) for 20 h.

Irradiation / h	1	10	20
IPCE (%)	11.3	6.25	3.69
H_2 / μmol min^{-1}	6.7	3.7	2.2
O_2 / μmol min^{-1}	2.7	1.7	1.1
CO_2 / μmol min^{-1}	0.77	0.11	0.06
Faraday efficiency of H_2 (%)	101	101	103
Faraday efficiency of O_2 (%)	81	95	100

Table S2. EDS elemental analysis of a R650 electrode coated with Nafion ionomer before and after PEC water vapor splitting at 1.2 V for 20 h.

Sample	Ti (%)	O (%)	C (%)	F (%)
Before PEC reaction	15.7	26.1	19.4	38.8
After PEC reaction	22.7	47.7	10.1	19.6

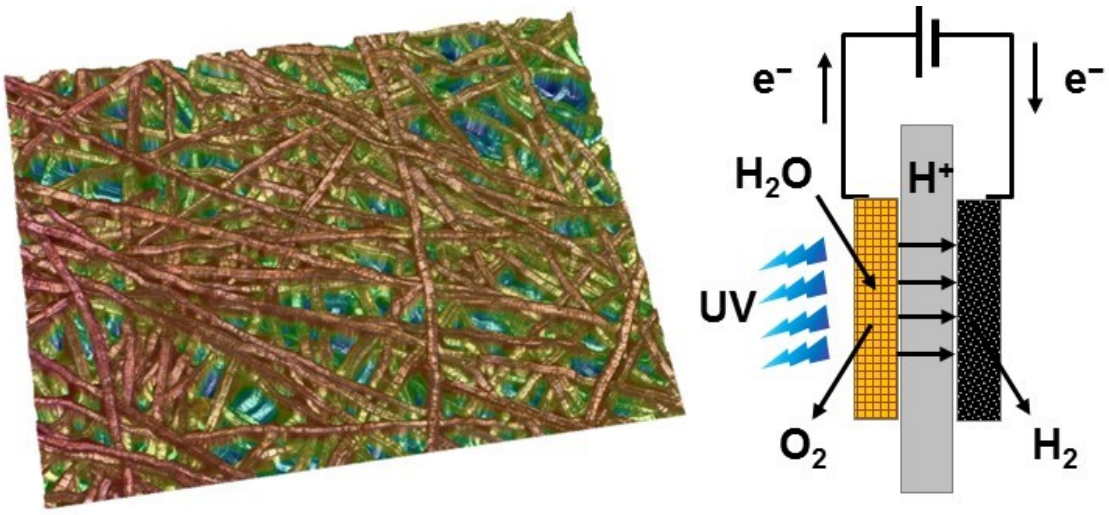

Figure S1. Rutile TiO_2 layer electrode on titanium microfibers for photoelectrochemical water vapor splitting into hydrogen (H_2) and oxygen (O_2) via a proton exchange membrane. Water was decomposed into O_2 and proton over the TiO_2 electrode under UV irradiation. The photoexcited electrons, which transfer to the counter electrode, reduce proton into H_2. The two electrodes are separated by the proton exchange membrane.

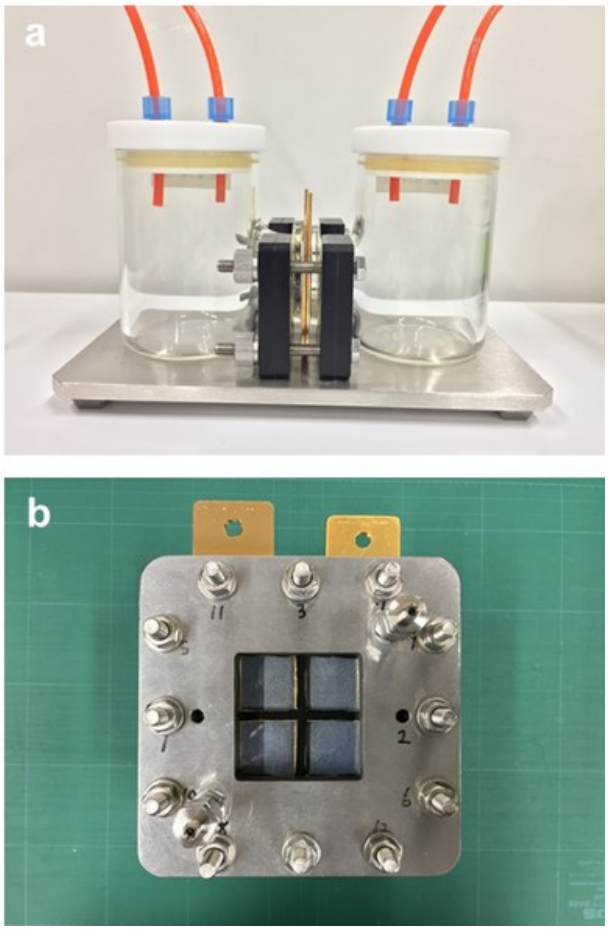

Figure S2. Experimental setups of the PEM-PEC system: (a) H-type dual-compartment glass reactor with a photoirradiation area of 2 cm^2 and (b) planar-type dual-compartment stainless-steel reactor with a photoirradiation area of 16 cm^2.

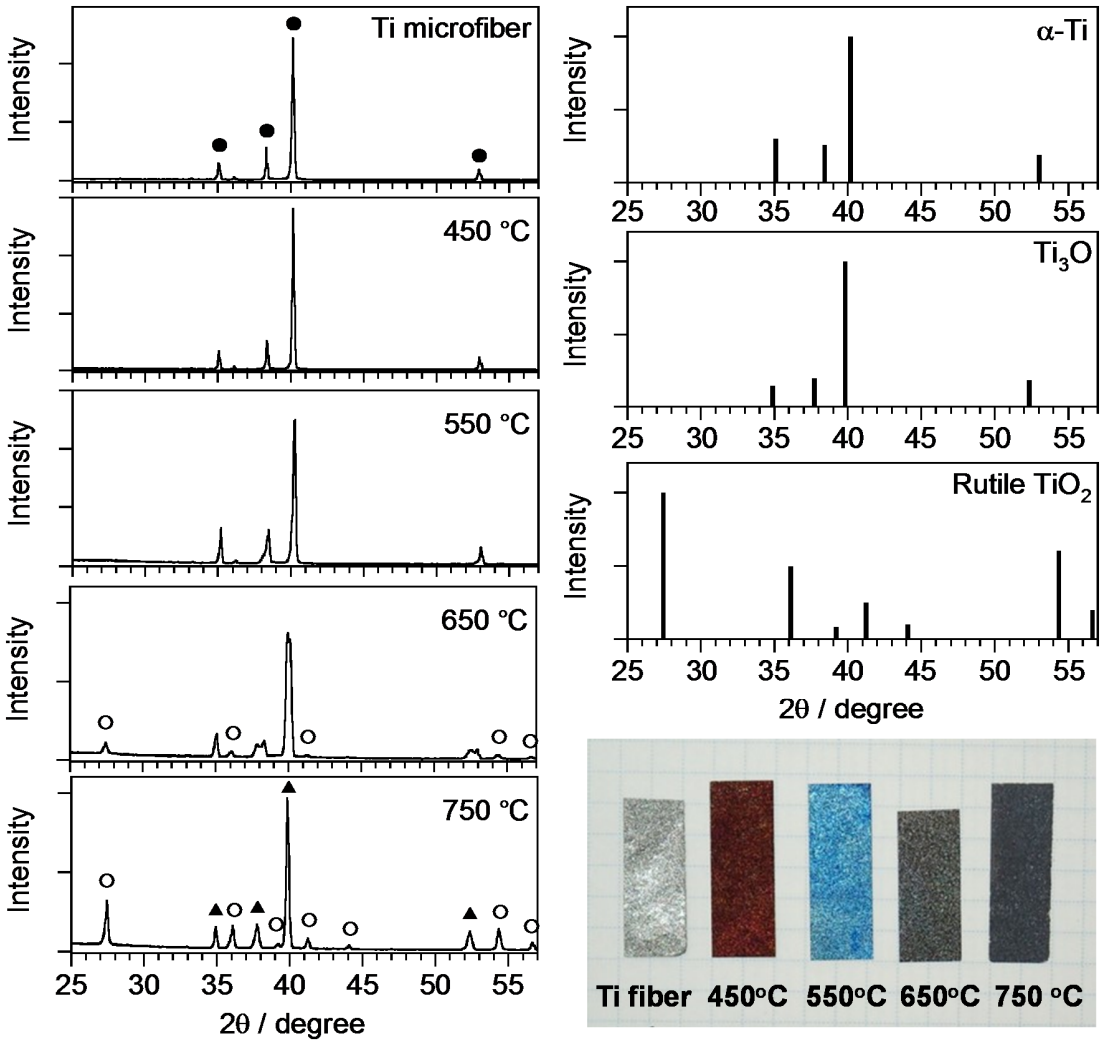

Figure S3. X-ray diffraction (XRD) patterns of titanium microfiber felts calcined at different temperatures (450, 550, 650, and 750 °C) for 2 h. The XRD data are taken from a Powder Diffraction File (PDF) provided by the International Centre for Diffraction Data (ICDD): hexagonal α-Ti (PDF 00-044-1294), hexagonal Ti_3O (PDF 01-073-1583) and rutile TiO_2 (PDF 00-021-1276). The closed and open circles indicate the peaks assigned to hexagonal α-Ti and rutile TiO_2. The closed triangles indicate the peaks assigned to hexagonal Ti_3O. When the microfiber was calcined at 750°C, the hexagonal Ti phase was converted to rutile TiO_2 and hexagonal Ti_3O.

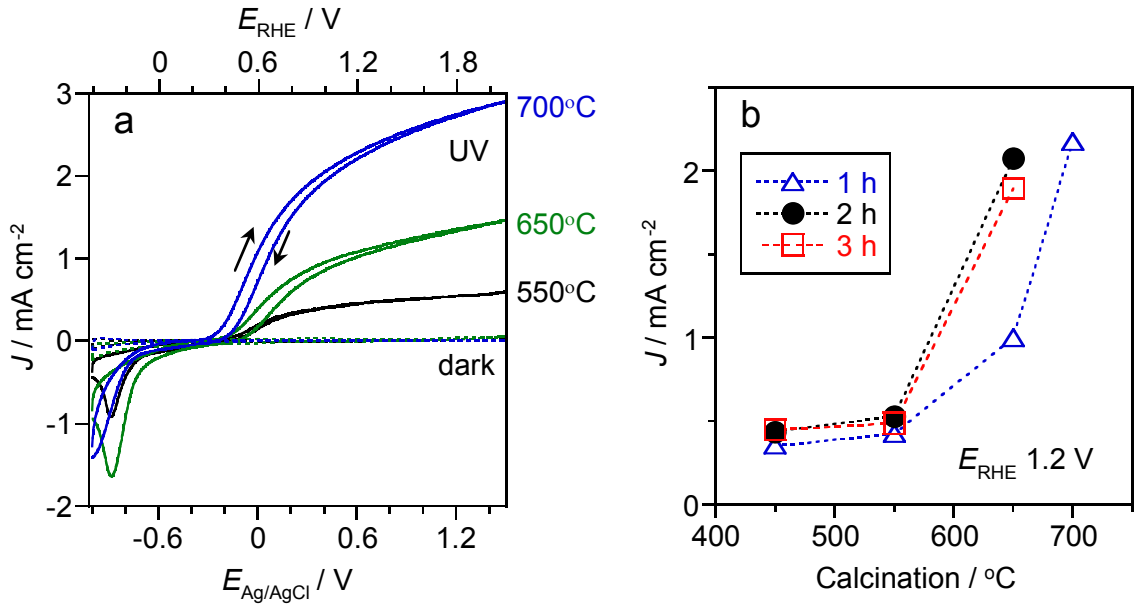

Figure S4. Photoelectrochemical (PEC) properties in pH 6.7 aqueous electrolyte under 365-nm UV irradiation (43 mW cm^{-2}). (a) Current density (J) vs. potential curves of Ti microfiber felt calcined at different temperatures for 1 h. The dashed and solid curves were obtained by cyclic voltammetry under dark and photoirradiation conditions, respectively. (b) Effect of temperature and duration (1, 2, and 3 h) in calcination treatment of titanium microfibers on the steady-state photocurrent density (J) at 1.2 V vs. RHE in chronoamperometry.

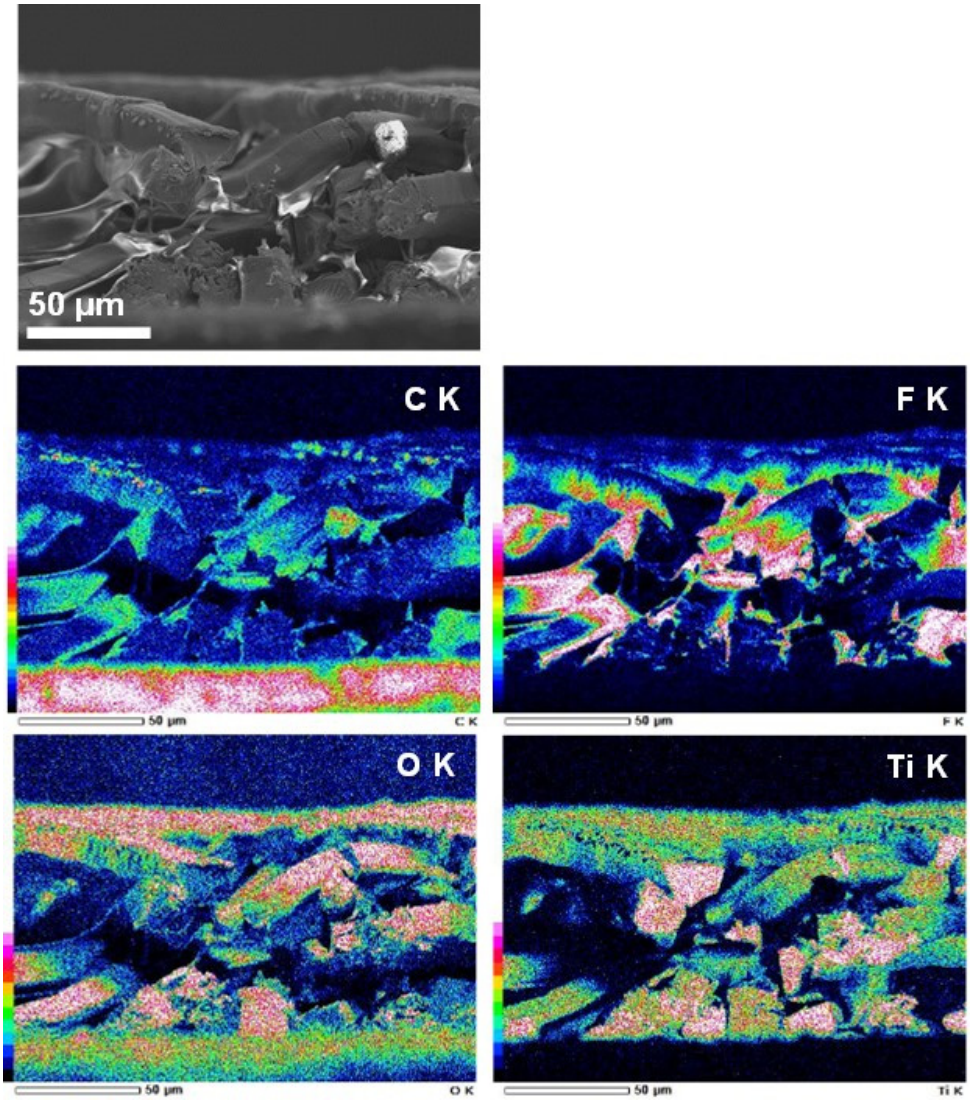

Figure S5. SEM image and EDS elemental (carbon, fluorine, oxygen, and titanium) mappings for the cross-section of the R650 microfiber felt with four coats of Nafion ionomer. The element concentration is indicated by the colour bar located at the left bottom of each map. Higher concentrations are red to white, whereas lower concentrations are blue to black.

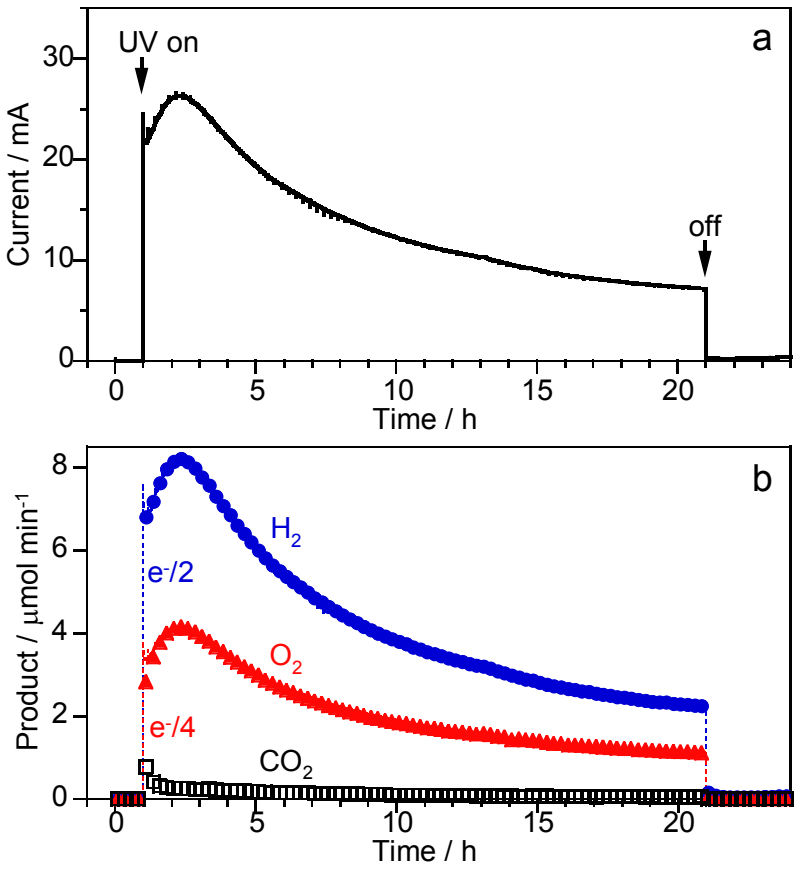

Figure S6. PEC water vapor splitting by ionomer-coated R650 | PEM | Pt/CB at 1.2 V under UV irradiation for 20 h. Reaction conditions: 365-nm UV LED, irradiance 40 mW cm^{-2}, photoirradiation area 16 cm^2, applied voltage 1.2 V, flow rate 20 mL min^{-1}, H_2O/Ar = 3/97, temperature 298 K, pressure 0.1 MPa, Nafion loading on R650 electrode 2.20 mg cm^{-2}.

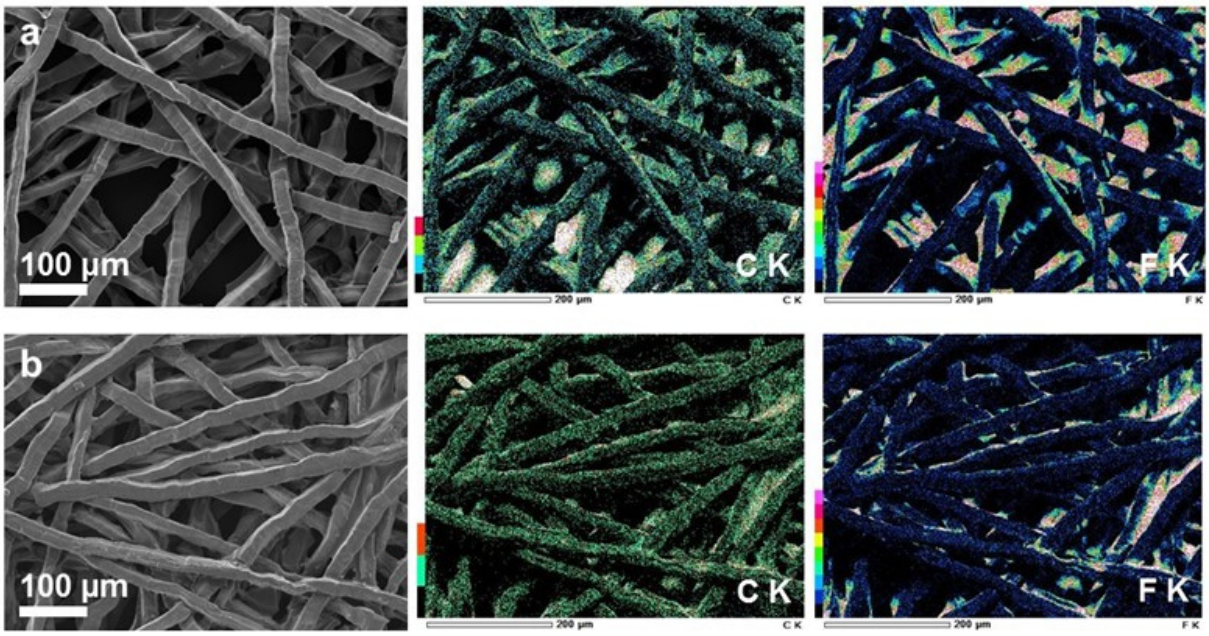

Figure S7. SEM images and EDS elemental (carbon and fluorine) mapping images of (a) the R650 electrode with four coats of Nafion ionomer and (b) the electrode after PEC water vapor splitting at 1.2 V under UV irradiation for 20 h.