Supporting Information

Co-dependency of TiO₂ underlayer and ZrO₂ top layer in sandwiched microwave-assisted Zr-Fe₂O₃ photoanodes for photoelectrochemical water splitting

Jun Beom Hwang,‡^a Mahadeo A. Mahadik,‡^a Periyasamy Anushkkaran,^b Sun Hee Choi,^c Weon-Sik Chae,^d Manish Kumar,^c H. M. Pathan,^e Hyun Hwi Lee,*^c and Jum Suk Jang*^{ab}

^a Division of Biotechnology, College of Environmental and Bioresource Sciences, Jeonbuk National University, Iksan 54596, Republic of Korea.

^b Department of Integrative Environmental Biotechnology, College of Environmental and Bioresource Sciences, Jeonbuk National University, Iksan 54596, Republic of Korea.

^c Pohang Accelerator Laboratory, POSTECH, Pohang 37673, Korea.

^d Daegu Center, Korea Basic Science Institute, Daegu 41566, Republic of Korea.

^eAdvanced Physics Laboratory, Department of Physics, Savitribai Phule Pune University, Pune 411007, India

*Corresponding authors.

E-mail addresses: jangjs75@jbnu.ac.kr (Jum Suk Jang), hhleec@postech.ac.kr (Hyun Hwi Lee)

‡Authors with equal contributions.

1.1 Experimental of Co-Pi electrodeposition

The three-electrode cells were fabricated with TZF2ZQ photoanodes as the working electrode, Pt mesh as the counter, and Ag/AgCl as the reference electrodes, respectively. The 0.5 mM cobalt nitrate in 0.1 M potassium phosphate solution was used as an electrolyte. The electrodeposition of Co–Pi on TZF2ZQ photoanodes was carried out at an applied potential of 0.9 V *vs*. Ag/AgCl, and a deposition time of 10 min.¹ Current densities were typically approximately 2–4 μ A/cm² during Co–Pi electrodeposition process.

1.2 Characterizations

The morphologies of the as-prepared photoanodes on the FTO substrate were examined using high-resolution scanning electron microscopy (HRSEM, Hitachi SU8230) at the Jeonju Center for Korea Basic Science Institution (KBSI). The crystal structure and the preferential orientation of the as-prepared α -Fe₂O₃ photoanodes were studied by a synchrotron X-ray diffraction (SR-XRD) at the BL5A materials science beamline at the Pohang Light Source II (PLS-II) in Korea. The X-ray wavelength was 0.1072 nm (11.57 keV), and the SR-XRD data were measured in a conventional theta-two theta measurement. Ultraviolet-visible diffuse reflectance (UV-DRS) spectra of as-prepared photoanodes were collected using a Shimadzu UV-vis-spectrophotometer (UV-2600). The energy bandgap of the photoanodes was determined using the Tauc method:²

$$(\alpha h\nu)^{1/n} = A(h\nu - Eg) \qquad (1)$$

where h is Planck's constant, ν is the photon frequency, α is the absorption coefficient, E_g is the bandgap, A is a proportionality constant, and n is an exponent dependent on the nature of electronic transitions (n = 2 for Fe₂O₃ indirect transitions). The structural and chemical information of the as-prepared samples was obtained using a transmission electron microscope (TEM, JEOL ARM-200F) operated at 200 kV, equipped with energy dispersive spectroscopy (EDS). The chemical state and elemental quantification of the as-synthesized samples were investigated using X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher Scientific K-Alpha spectrometer using a monochromatic AlK α X-ray source (hv = 1486.6 eV, 25 W, and 15 kV) at the Center for Research facilities at Kongju National University. X-ray absorption experiments were conducted on the 7D beamline of the Pohang Accelerator Laboratory (PLS-II, 3.0GeV) to understand the local structure in photoanodes. The fluorescence spectra were produced for the Fe K-edge ($E_0=7,112$ eV) on as-prepared photoanodes. The incident X-ray beam was detuned by 20% at 7112 eV to attenuate the flux from higher-order Bragg diffraction of Si (111) crystals in a monochromator, and its intensity was monitored with a He-filled IC Spec ionization chamber. The fluorescence signal from the sample was measured using a Lytletype detector combined with a passivated implanted planar silicon (PIPS) diode. The obtained spectra were background-removed and normalized using ATHENA in the IFEFFIT suite of programs.³ Time-resolved photoluminescence (TRPL) was carried out using a confocal microscope (MicroTime-200, Picoquant, Germany). A single-mode pulsed diode laser (LDH-P-C-470, Picoquant, Germany) with a 20 MHz repetition rate, ~30 ps pulse width, and 0.5 mW average power was used as an excitation source. A dichroic mirror (490 DCXR, AHF), a longpass filter (HQ500lp, AHF), and a single-photon avalanche diode (PDM series, MPD) were used to collect emission photons from the catalysts. The time-correlated single-photon counting (TCSPC) technique was used to count emission photons. TRPL images consisting of 200×200 pixels were recorded using the time-tagged time-resolved (TTTR) data acquisition technique. The acquisition time of each pixel was 2 ms. Exponential fitting for the PL decays (which were extracted from the TRPL images) with 8 ps temporal resolution was achieved by iterative leastsquares deconvolution fitting using the Symphotime-64 software (Ver. 2.2) using an exponential decay model, as follows:⁴

$$I(t) = \sum A_{i} e^{-t/\tau_{i}},(2)$$

Here, I (t) is the time-dependent PL intensity, A is the amplitude, τ is the PL lifetime, and i is 2. The average lifetime $\langle \tau \rangle$ is defined as follows:⁵

$$\langle \tau \rangle = \sum_{i} A_{i} \tau_{i}^{2} / \sum_{i} A_{i} \tau_{i}$$
(3)

1.3 Photoelectrochemical measurements

PEC studies were conducted with an Ivium CompactStat potentiostat (Ivium Instruments, Netherlands), using an electrochemical cell with a three-electrode system. The asprepared Fe_2O_3 photoanode, Hg/HgO (1 M NaOH), and Pt coil were employed as the working, reference, and counter electrodes, respectively. An aqueous solution of 1.0 M NaOH (pH 13.6) was used as the electrolyte throughout the PEC measurements. The photoanode was exposed to the light source (standard global solar light, AM 1.5G, 100 mW/cm²) with an active area of 1 cm², to perform photo-electrochemical measurements with front-side illumination. The potential was calculated against the reversible hydrogen electrode (RHE) by the following Nernst equation:⁶

$$E_{vs. RHE} = E_{vs. Hg/Hg0} + 0.059pH + E_{Hg/Hg0}$$
(4)
$$(E_{Hg/Hg0} = 0.095 V) \text{ at } 25 \text{ °C}$$

Current density-potential curves (J-V) were recorded in the range of 0.3 to 1.7 V vs. RHE with a scan rate of 50 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were carried out in 1 M NaOH electrolyte under visible light illumination conditions at 1.23 V vs. RHE over the frequency range of $(3x10^6)$ to $(5x10^{-1})$ Hz. The equivalent circuit used to fit the Nyquist plots consisted of the series resistance (R_s) , which mainly includes the sheet resistance of the FTO substrates, and two resistor-capacitor (RC) circuits. The current density according to PEC performance (J_{PEC}) can be described as follows:⁷

$$J_{H_20} = J_{abs} \times \eta_{bulk} \times \eta_{surface} \tag{6}$$

Here, J_{abs} is the photocurrent density if the absorbed photons are perfectly converted into current (*i.e.*, absorbed photon-to-current efficiency (APCE) = 100%). The value of $J_{H_2O_2}$ is measured for as-prepared photoanodes by adding 0.5 M H₂O₂ to 1 M NaOH electrolyte and is independent of the surface H₂O₂ oxidation kinetics (regarding $\eta_{surface} \approx 100\%$). Therefore, η_{bulk} and $\eta_{surface}$ can be calculated according to Equation (6) as

$$\eta_{surface} = J_{H_20} / J_{H_20_2} \dots \dots (7)$$

$$\eta_{bulk} = J_{H_2O_2} / J_{abs} \tag{8}$$

$$J_{abs} = \int_{300}^{600} \frac{1}{1240} \lambda P(\lambda) APCE(\lambda) d\lambda \qquad \dots \dots \dots (9)$$

where, ${}^{J_{H_2}o}$ is the photocurrent acquired from PEC water oxidation, ${}^{J_{H_2}o_2}$ is the photocurrent acquired from H₂O₂ oxidation, and P(λ) indicates the solar irradiance at the wavelength (λ). Intensity-modulated photocurrent spectroscopy (IMPS) measurements were performed on the same cell using a green light-emitting diode (LED, peak wavelength 520 nm) driven by a frequency-response analyzer. The light intensities were modulated with a depth of 10%, and the frequency was swept from 10 kHz to 0.1 Hz. The PEC solar hydrogen generation tests were carried out in a three-electrode cell at room temperature with an Ivium CompactStat potentiostat under standard global solar light (AM 1.5G, 100 mW cm⁻²). The Co-Pi/TZF2ZQ photoanode, a Pt wire, and a Hg/HgO (1.0 M NaOH) were utilized as working, counter, and reference electrodes, respectively. A blank test was conducted without irradiation of the photoanode before starting the experiment, showing no hydrogen/oxygen evolution. The evolved oxygen and hydrogen gases produced during PEC water splitting were quantified using a gas chromatography system equipped with a thermal conductivity detector (GC-TCD, Agilent 7820, U.S.A.) with a 5-Å molecular sieve column.⁸

Table S1. Comparative photocurrent density results of Fe_2O_3 photoanodes with underlayer/overlayer modifications at 1.23 V vs. RHE with previous studies.

Material	Deposition methods of underlayer/overlayer	Photocurrent (mA/cm ² at 1.23 V _{RHE})	Ref.
TiO ₂ /Fe ₂ O ₃	Layer-by-layer deposition	0.373	[9]
TiO ₂ /Fe ₂ O ₃	Spin-coating 0.614		[10]
SiO ₂ /Ti-Fe ₂ O ₃	Spin-coating 0.760		[11]
Ti ₃ C ₂ MXene/Fe ₂ O ₃	Drop-casting	1.30	[12]
ZrO ₂ /Fe ₂ O ₃	Spin-coating	1.00	[13]
Fe ₂ O ₃ /SnO ₂ /TiO ₂	Spin-coating deposition of SnO_2 and TiO_2	2.00	[14]
Fe ₂ O ₃ /Ferrous lactate	Spin-coating	1.44	[15]
Fe ₂ O ₃ /Graphene	chemical vapor deposition	0.75	[16]
Fe ₂ O ₃ /Graphene	chemical vapor deposition	1.64	[17]
Fe ₂ O ₃ /Ta ₂ O ₅	Atomic layer deposition	0.80	[18]
TiO ₂ /Zr-Fe ₂ O ₃ /ZrO ₂	Spin-coating deposition of TiO ₂ and dipping method of ZrO ₂	1.49	This study

Samples	f_{\min} (Hz)	Electron transport time (µs)
ZF2Q	668.3	238
TZF2Q	944.1	169
ZF2ZQ	1059	150
TZF2ZQ	1189	134

Table S2. Minimum imaginary component f_{min} (Hz) and electron transit time in the IMPS spectra for F2Q, ZF2Q, TZF2Q, ZF2ZQ, and TZF2ZQ photoanodes at 1.23 V vs. RHE.

 Table S3. PL lifetime parameters of the hematite photoanodes.

Sample	<i>A</i> ₁ (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	$A_{3}(\%)$	τ_3 (ns)	$< \tau >^{a)}(ns)$
ZF2Q	73.4	0.05	26.3	0.28	0.3	2.8	0.40
TZF2Q	71.2	0.06	27.9	0.33	0.9	3.7	0.91
ZF2ZQ	65.9	0.06	33.9	0.28	0.2	4.3	0.48
TZF2ZQ	70.9	0.06	28.8	0.28	0.3	3.5	0.46



Fig. S1 Schematics of experimental procedures of (a) F2Q, (b) ZF2Q, (c) TZF2Q, (d) ZF2ZQ, and (e) TZF2ZQ photoanodes.



Fig. S2 (a) UV-Vis absorbance spectra and (b) Tauc plot for F2Q, ZF2Q, TZF2Q, ZF2ZQ, and TZF2ZQ photoanodes, respectively.



Fig. S3 (a) XPS survey scan spectra, XPS spectra of (b) O 1s of ZF2Q, TZF2Q, ZF2ZQ, and TZF2ZQ photoanodes.



Fig. S4 Raman spectra of F2Q, ZF2Q, TZF2Q, ZF2ZQ and TZF2ZQ photoanodes.



Fig. S5 Photocurrent density–potential (J-V) curves under 1-sun standard illumination conditions of F2Q, ZF2Q, TZF2Q, ZF2ZQ, and TZF2ZQ photoanodes.



Fig. S6 (a) Photocurrent density–potential (*J*–*V*) curves under light with H₂O (solid lines) and with H₂O + H₂O₂ (dashed lines) under 1-sun standard illumination conditions, charge separation efficiencies (b) in the (η_{bulk}) and (c) on the surface (η_{surface}) of ZF2Q, TZF2Q, and TZF2ZQ photoanodes.



Fig. S7 (a) Representation of an equivalent circuit used for EIS data fitting, EIS fitted plots of (b) F2Q, (c) ZF2Q, (d) TZF2Q, (e) ZF2ZQ and (f) TZF2ZQ photoanodes at different applied potentials.



Fig. S8 Plots of equivalent circuit parameters (a) R_s , (b) R_1 , (c) R_2 , and (d) charge transfer efficiencies values measured at various applied potentials for the F2Q, ZF2Q, TZF2Q, ZF2ZQ, and TZF2ZQ photoanodes.

References

- (1) I. K. Jeong, M. A. Mahadik, J. B. Hwang, W. S. Chae, S. H. Choi and J. S. Jang, *J. Colloid Interface Sci.*, 2021, **581**, 751–763.
- (2) M. A. Lukowski, S. and Jin, J. Phys. Chem. C, 2011, 115, 12388-12395.
- (3) B. Ravel and B. Newville, J. Synchrotron Radiat., 2005, 12, 537-541
- (4) M. A. Mahadik, W. S. Chae, M. Cho and J. S. Jang, *Nanoscale*, 2020, 12, 19241– 19252.
- (5) G. W. An, M. A. Mahadik, G. Piao, W. S. Chae, H. Park, M. Cho, H. S. Chung and J. S. Jang, *Appl. Surf. Sci.*, 2019, **48**, 1–12.
- (6) X. Liu, X. Wang, X. Yuan, W. Dong and F. Huang, J. Mater. Chem. A, 2016, 4, 167– 172.

- (7) Y. S. Hu, A. Kleiman-Shwarsctein, A. J. Forman, D. Hazen, J. N. Park and E. W. McFarland, *Chem. Mater.*, 2008, **20**, 3803–3805.
- (8) M. A. Mahadik, H. S. Chung, S. Y. Lee, M. Cho and J. S. Jang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 12489–12501.
- (9) D. Wang, X. T. Zhang, P. P. Sun, S. Lu, L. L. Wang, Y. A. Wei and Y. C. Liu, *Int. J. Hydrog. Energy*, 2014, **39**, 16212–16219.
- (10) P. S. Shinde, M. A. Mahadik, S. Y. Lee, J. Ryu, S. H. Choi and J. S. Jang, *Chem. Eng. J.*, 2017, **320**, 81–92.
- (11) M. J. Kang and Y. S. Kang, J. Mater. Chem. A, 2015, 3, 15723–15728.
- (12) H. Ji, S. Shao, G. Yuan, C. Lu, K. Feng, Y. Xia, X. Lv, J. Zhong, H. Xu and J. Deng, *J. Energy Chem.*, 2021, **52**, 147–154.
- (13) A. Subramanian, A. Annamalai, H. H. Lee, S. H. Choi, J. Ryu, J. H. Park and J. S. Jang, ACS Appl. Mater. Interfaces, 2016, 8, 19428–19437.
- (14) S. H. Kimura, B. A. Williamson, S. Sathasivam, S. J. Moniz, G. He, W. Luo, D. O. Scanlon, J. Tang and I. P. Parkin, ACS omega, 2019, 4, 1449–1459.
- (15) X. Liu, H. Wang, W. Qiu, Q. Wu, H. Wang and S. Xue, Sol. Energy, 2022, 231, 897– 907.
- (16) M. P. Cardona, M. Li, W. Li, J. McCall, D. Wang, Y. Li and C. Yang, *Mater. Today Energy*, 2018, 8, 8–14.
- (17) S. A. Carminati, A. N. Barbosa, A. L. M. Freitas, F. L. Freire, F. L. Souza and A. F. Nogueira, J. Catal., 2019, 372, 109–118.
- (18) M. Forster, R. J. Potter, Y. Yang, Y. Li and A. J. Cowan, *ChemPhotoChem*, 2018, **2**, 183–189.