Supporting Information

Microwave Effects on Co-Pi Co-catalysts Deposited on α-Fe_2O_3 for Application to Photocatalytic Oxygen Evolution

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S1. Preparation and Characterization of α-Fe_2O_3 Thin Films

S1-1. Pulsed-Laser Deposition of α-Fe_2O_3 films

α-Fe_2O_3 and α-Fe_2O_3/Ta:SnO_2 bilayer films were grown on *c*-plane sapphire substrates by using pulsed-laser deposition (PLD). The α-Fe_2O_3 sintered ceramics target (3N) was purchased from High Purity Materials, Japan. The 3.0 mol% Ta-doped SnO_2 target was prepared by a conventional solid-state reaction method with Ta_2O_5 and SnO_2 powders (3N). The powders were mixed and pressed into a pellet. Then, it was sintered at 1200°C for 12h in air.

Prior to film growth, the *c*-plane sapphire substrates were annealed at 1100°C for 6 h in air to obtain step-and-terrace surfaces. The KrF excimer laser with a fluence of 0.9 J/cm^2 was utilized during film growth. The repetition rates of the laser were set at 5 Hz and 10 Hz for Ta:SnO_2 and α-Fe_2O_3 deposition, respectively. The pressure in the PLD chamber was adjusted to 1 mTorr with continuous flow of pure oxygen (6N). The growth temperature were set to 650°C and 700°C for Ta:SnO_2 and for α-Fe_2O_3, respectively. Thicknesses of both layers were approximately 60 nm. The Ta:SnO_2 layer was used as a bottom conductive electrode for photo-electrochemical (PEC) measurements. When α-Fe_2O_3 films were deposited on Ta:SnO_2 films, a part of the samples was covered with a stencil mask equipped in the PLD chamber to make electrical contact to the conductive layer of Ta:SnO_2 for PEC experiments.

(a) Bare α-Fe_2O_3 (b) Bare α-Fe_2O_3/Ta:SnO_2 bilayer

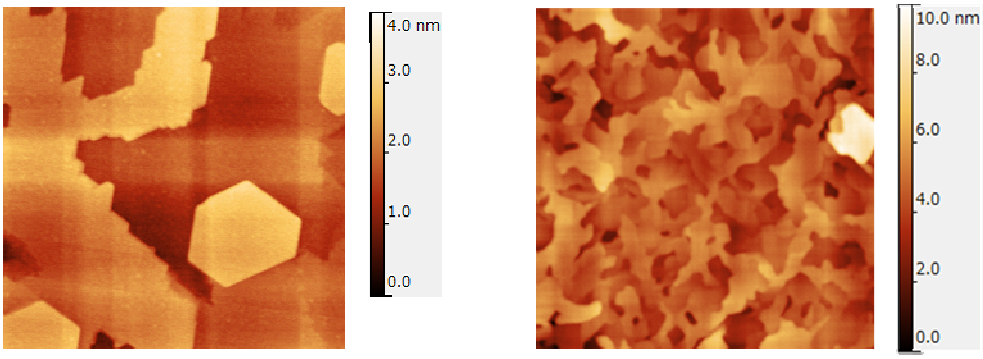

Figure S1 AFM images of as-deposited (a) α-Fe_2O_3 and (b) α-Fe_2O_3/Ta:SnO_2 bilayer films with scan area of 1 x 1μm.

S1-2. Characterization of As-deposited Fe_2O_3 Films

X-ray diffraction (XRD) measurements were performed using a X-ray diffractometer (SmartLab, Rigaku) equipped with monochromatic Cu Kα1 X-rays (λ = 1.54056 Å). The film thicknesses of the samples were characterized by Laue fringes in XRD patterns and a stylus profiler (Alpha-Step D-100, KLA-Tencor).

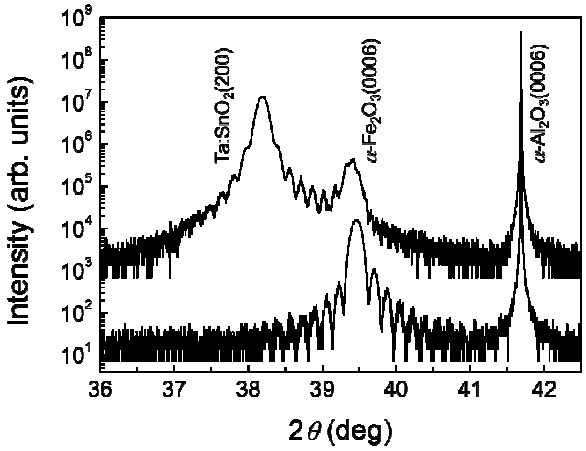

Figure S2 XRD patterns of α-Fe_2O_3 (bottom) and α-Fe_2O_3/Ta:SnO_2 bilayer (top) on *c*-sapphire substrate.

Table S1 Thickness of α-Fe_2O_3 and Ta:SnO_2 layers on *c*-sapphire substrate for each sample.

Sample	α-Fe_2O_3	α-Fe_2O_3/Ta:SnO_2
α-Fe_2O_3	57 nm	60 nm
Ta:SnO_2	-	61 nm

S2. Photo-chemical Deposition of Co-Pi Nanoparticles

Photo-chemical deposition of Co-Pi nanoparticles was performed on α-Fe_2O_3 and α-Fe_2O_3/Ta:SnO_2 bilayer substrates immediately after UV-ozone pre-treatment. Each substrate was immersed in a precursor aqueous solution (pH=7) containing $Co(NO_3)_2$ (0.5 mM) and potassium phosphate (0.1 M) in a quartz cell. Then the quartz cell was heated either by an oil bath or MW (5W). After the sample reached 97 ^oC, a UV light illumination (monochromatic UV at λ = 300 nm, 15 $\mu W/cm^2$) was applied from the top of the sample for 10 min. A single mode MW cavity (TE_{103} mode, 2.45 GHz) was utilized for MW irradiation supplied form a semiconductor MW generator (CHRONIX Inc.). The standing wave of TE_{103} was maintained by a plunger and three-stub tuner in order to minimize the reflection from the cavity. The solution temperature was accurately measured by an optical fiber thermometer (Anritsu Meter Co., Ltd.). Immediately after the deposition, the quartz cell was immersed into a water bath to quench the reaction, and then the samples were washed with deionized water three times and dried under reduced pressure overnight. The deposition time of 10 min was optimized for α-Fe_2O_3 substrate based on AFM observations.

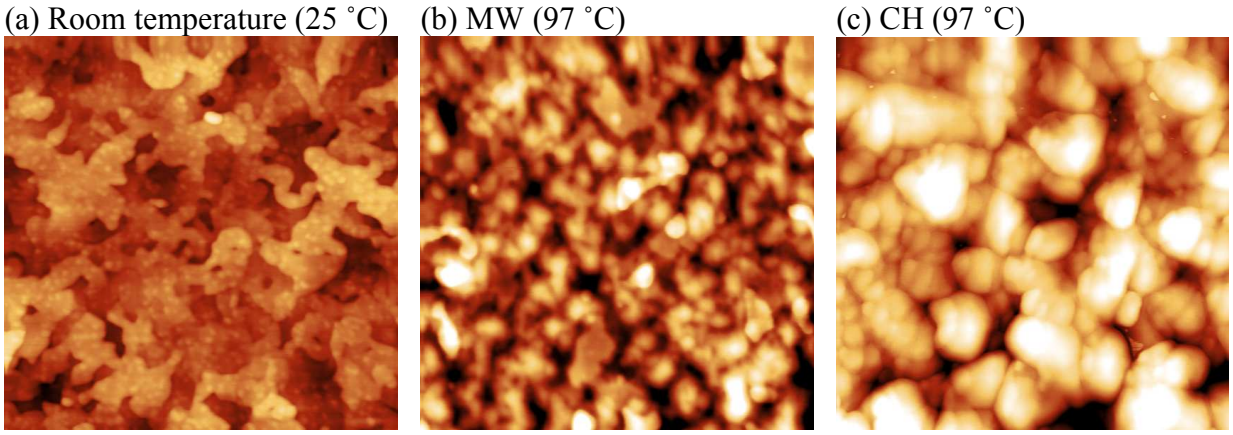

Figure S3 AFM images of Co-Pi deposited on Fe_2O_3/Ta:SnO_2 bilayer substrates with scan area of 1x1μm. Co-Pi were deposited at (a) room temperature, (b) 97 ˚C under MW irradiation, and (c) at 97 ˚C under CH.

S3. Characterization of Co-Pi Deposited Films

S3-1. Morphology Analysis of Co-Pi Co-catalysts by AFM

The morphology of the sample surface was examined by an atomic force microscopy (AFM). AFM images were collected by using NanoNaviReal s/NanoCute (SII NanoTechnology Inc.) operated under tapping mode. The cantilever has a silicon probe with a resonance frequency of 400~500 KHz and the tip radius of below 20 nm. All measurements were performed under ambient conditions. Since the lateral sizes of particles on the substrate are convoluted with the tip features, the height of observed particles on the surface was measured and determined as the particle diameter as discussed in the main section. The height analysis was performed by using a built-in software of the AFM system.

S3-2. Chemical Composition Analysis of Co-Pi Co-catalysts by XPS

X-ray photoelectron spectroscopy (XPS, Ulvac-Phi Inc. PHI VersaProbe II) data were obtained by using Al *Kα* radiation which provides the photons with 1486.6 eV and a photon flux of 50μW under detection pass energy of 23.5 eV. The peak fitting of the experimental data was performed by a combination of 70% Gaussian and 30% Lorentzian peaks after the linear background subtraction for Co 2p and P 2p core levels and Shirley background subtraction for Fe 2p core levels.

$$\text{Composition ratio } n_A/n_B = (I_A/I_B) \times (S_B/S_A) \quad \text{(S1)}$$

The composition ratio at the near-surface is given by semi-empirical formula (S1). I and S represent area and Scofield RSF respectively. X-rays penetrate deep beneath the surface of the sample about a few micrometers. However, since the photoelectrons that are directly ionized by X-rays have escaped without influence of inelastic scattering, only shallow information about several nanometers from the surface was examined by using XPS.

S4. Photo-electrochemical Characterization

Photo-electrochemical (PEC) characteristics in an electrolyte of 0.1 M NaOH aqueous solutions (pH = 13.0) were investigated for α-Fe_2O_3/Ta:SnO_2 bilayer samples with and without Co-Pi particles deposited in various conditions. An electrochemical cell with a standard three-electrode configuration was used for PEC measurements. An Ag/AgCl in 3 M NaCl (E^0 = 0.203 V at 25°C) and a platinum wire were the reference and counter electrodes, respectively. A 500 W Xe lamp was used as a light source passing through a quartz window in the PEC cell. The following electrochemical measurements were carried out with a potentio-galvanostat with frequency response analyzer (Princeton Applied Research, VersaSTAT 4). The current versus potential curves were measured by cyclic voltammetry at a rate of 50 mV/s. Electrochemical impedance spectroscopy (EIS) was performed in a 10 mV amplitude perturbation between 100000 and 0.01 Hz. The EIS Nyquist plot data were then fitted to the equivalent circuit simulated in Z-View software (Scribner Associates Inc.).

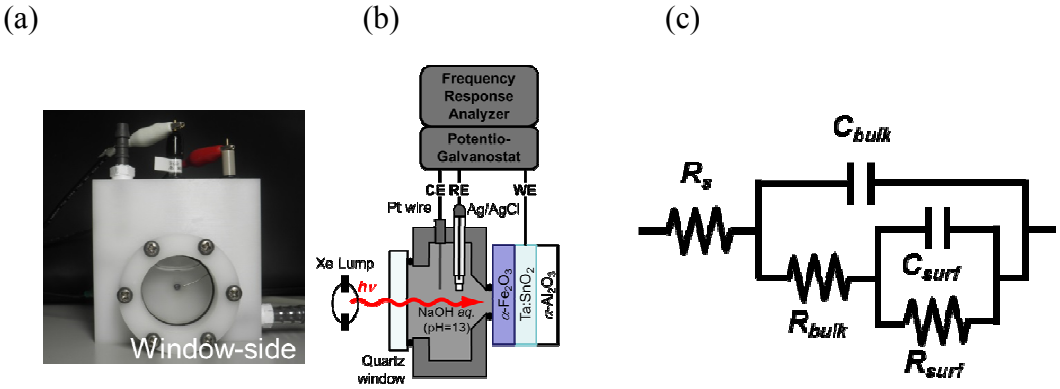

Figure S4 (a) Photo and (b) schematic of photoelectrochemical cell used for photocatalytic reactions and electrochemical measurements. (c) The transmission line model of photoelectrochemical cell applied to EIS analysis.

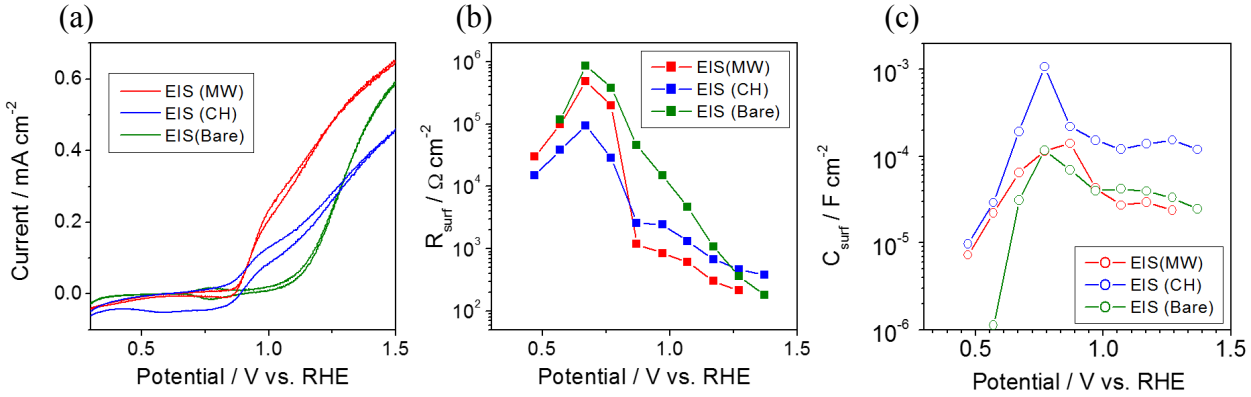

Figure S5 (a) Photocurrent, (b) surface resistance, and (c) surface capacitance component analyzed from the transmission line model of photoelectrochemical cell.

S5. Co-Pi/Fe_2O_3 Heating Properties by Microwave

To confirm the MW collaborational effect between Co-Pi nanoparticles and α-Fe_2O_3 substrate, α-Fe_2O_3 substrates with and without Co-Pi nanoparticles, and Co-Pi particles were irradiated with 10 W MW. The α-Fe_2O_3 substrate with Co-Pi nanoparticles was made by photodeposition that was carried out by immersing the substrate in a petri dish in 0.5 mM $Co(NO_3)_2$ and 0.1 M potassium phosphate electrolyte (pH 7). After the substrate was immersed in the precursor solution and illuminated by UV light from the top of the substrate for 10 min by using UV light (λ = 300 nm, 10 $\mu W/cm^2$) without heating. The Co-Pi particles were prepared by an electrodeposition of Co-Pi. A standard three-electrode setup in a cell was used for Co-Pi electrodeposition. The working electrode was 2 mm thick glass substrate with a fluorine doped tin oxide coating on one side (FTO, SOLARONIX SA). The counter electrode was platinum wire. The reference electrode was an Ag/AgCl electrode in KCl saturated solution. A bias of 1.29 V vs NHE was applied during deposition for 1 hour. After washing the surface with deionized (DI) water three times, the sample was dried under reduced pressure for 1 day. The synthesized Co-Pi layer on FTO substrate was peeled off by a slide glass. Then, the Co-Pi was grinded with a mortar. This 0.05 g powder Co-Pi was ultrasonically dispersed in 3 mL DI water for 30 min. For MW heating, all the Co-Pi dispersion liquid was drop deposited to the quartz substrate that was preheated at 423 K to form a circle having a diameter of 1 cm. MW cavity was built for TE_{103} single mode connected to 2.45 GHz semiconductor generator (Fuji Electronic Industrial Co., Ltd.). The resonance of TE_{103} mode was tuned after setting samples at MW electrical field maximum position by a three stub and a plunger under MW irradiation prior to each experiment in order to minimize the reflected power from the cavity. The center of sample surface temperature was measured by a CCD infrared thermographic camera (ARTCAM-320THERMO-WOM-TMC, Artray Co., Ltd.) and calibrated from each samples respectively depending on emissivity.

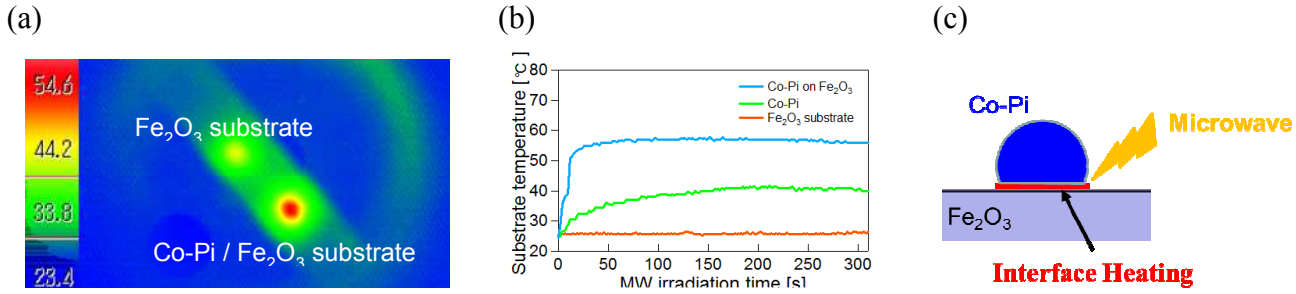

Figure S6 (a) Thermo-graphic images and (b) temperature increase measured by a thermos-graphic IR camera of each Co-Pi powder, Co-Pi/α-Fe_2O_3, and Fe_2O_3 substrate sample. (c) The schematic image of the interface heating of Co-Pi/α-Fe_2O_3 substrate.