Supporting Information

Crystalline IrO$_2$-Decorated TiO$_2$ Nanofiber Scaffolds for Robust and Sustainable Solar Water Oxidation

Won-Hee Ryu†, ‡ Yang Woo Lee†, § Yoon Sung Nam, † Doo-Young Youn, † Chan Beum Park, †,* and Il Doo Kim†,*

† Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Korea

Experimental Procedure

**Materials:** The acetone, ethanol, ethylene glycol (EG), chloroform, dimethylformamide (DMF), glacial acetic acid, titanium butoxide, polyvinylpyrrolidone (PVP, $M_w = 1,300,000$ and $10,000$), sodium persulfate (Na$_2$S$_2$O$_8$), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Ru(bpy)$_3$Cl$_2$·6H$_2$O), and iridium chloride hydrate (IrCl$_3$·xH$_2$O) used in this study were purchased from Sigma-Aldrich (MO, USA). Potassium hexachloroiridate (K$_2$IrCl$_6$) was purchased from Alfa-Aesar (MA, USA).

**Synthesis of IrO$_2$-nanoparticle-coated TiO$_2$ nanofiber:** TiO$_2$ nanofibers were prepared by an electrospinning technique. 1.2 g of PVP and 1 g of titanium butoxide were dissolved in a mixture of 6 mL of DMF, followed by an addition of 2 mL of chloroform and 0.2 mL of glacial acetic acid. The precursor solution was loaded in a syringe with a metal needle, and the electrospinning process was carried out with the following parameters: applied voltage, 12 kV; feeding rate, 1 mL hr$^{-1}$; needle size, 21 G; distance between the metal needle and collector, 15 cm; rotor speed, 200 rpm. TiO$_2$ nanofibers were obtained by annealing the as-spun mat at 500 °C for 3 h in air. The IrO$_2$-TiO$_2$ composite nanofiber was obtained by adding 144 mg of iridium acetylacetonate in chloroform with the same precursor solution and the same electrospinning condition described above. To prepare the 10 nm IrO$_2$ NPs decorated onto the TiO$_2$ NFs, Ir nanoparticles were synthesized by a polyol method as described in the literature.$^1$ After the Ir nanoparticles (1.5 mg/g, weight of Ir/Ir dispersed solution) were dispersed in ethanol, different concentrations of Ir colloidal solution (0.5 g and 3 g for low-content and high-content levels, respectively) were added to the TiO$_2$ nanofiber-dispersed ethanol solution. The solution was then stirred and evaporated at 85 °C overnight, after which the dried powder was annealed at 450 °C for 30 min. To prepare the 30 nm IrO$_2$ NPs decorated onto the TiO$_2$ NFs, a hydrous IrO$_2$ colloidal solution was prepared according to a method described in the literature. 250 mg of K$_2$IrCl$_6$ dissolved in 100 ml of D.I. water and 1 ml of 8.3 M NaOH solution was added. The solution was heated in an oil bath of 90 °C for 20 min. To remove the residual K$^+$ and Cl$^-$ impurities
from the IrO$_2$ colloidal solution, 0.05 g of PVP dissolved in 10 ml of an IrO$_2$ colloidal solution and 40 ml of acetone were added to precipitate the IrO$_2$/PVP complex. After several purification and precipitation steps, the precipitated IrO$_2$/PVP complex was dried at 85 °C overnight and then annealed at 450 °C for 30 min. To investigate the role of the scaffold, 10 nm IrO$_2$ NPs decorated onto SiO$_2$ NFs were prepared with the same method used for the 10 nm IrO$_2$ NPs decorated onto the TiO$_2$ NFs. 0.65 g of TEOS was dissolved in 1.35 g of ethanol and 2 g of 0.1 M HCl was then added. After stirring for 2 h., 6 g of DMF and 1 g of PVP were added and this was stirred for 12 h. An electrospinning process was carried out under the same conditions used for preparing the TiO$_2$ NFs described above. The obtained Si precursor/PVP composite nanofibers were calcined at 700 °C for 1 h. The obtained SiO$_2$ nanofibers were then dispersed in ethanol. Subsequently, an Ir colloidal solution (3 g) was added to the dispersed solution. The Ir NP/SiO$_2$ NF dispersed solution was stirred and evaporated in an oven at 85 °C overnight. The dried powder was annealed at 450 °C for 30 min.

**Characterization:** The morphology of the samples was examined using a transmission electron microscope (TEM, FEI Company, USA). The distribution of the elements was investigated by energy dispersive spectroscopy (EDS) mapping. All absorbance spectra were measured using a V/650 spectrophotometer (Jasco, Inc., Tokyo, Japan). The crystal structure of the samples was investigated using a D/MAX-RB powder x-ray diffractometer (Rigaku Co., Japan). An x-ray photoelectron spectroscopy analysis (XPS, Thermo, UK) was conducted using a sigma probe spectrometer equipped with an x-ray source (90 W) under an ultrahigh vacuum condition. The amount of IrO$_2$ decorated onto the TiO$_2$ or SiO$_2$ nanofibers was measured by inductively coupled plasma-auger electron spectroscopy (ICP-AES, POLY SCAN 61 E).

**Oxygen evolution measurement:** 20 mL of the reaction solution for photocatalytic water oxidation consisting of Ru(bpy)$_3$ (1 mM), Na$_2$S$_2$O$_8$ (5 mM), and 10 mg of catalyst in 80 mM sodium borate buffer (pH 8.0) was prepared. Light was irradiated onto the reaction solution using a Xe lamp (450 W) through a 420-nm cut-off filter. Oxygen measurements were carried out using a custom-made oxygen analysis system. To perform the recycling test, the precipitated nanofibers after the reaction were filtered, washed with distilled water and dried at RT.

**Electron-transfer reaction:** 1 mL of sodium citrate buffer (pH 5.3) containing Ru(bpy)$_3$ (1 mM) and Na$_2$S$_2$O$_8$ (5 mM) was filled into quartz vessels with a path length of 1 cm. The solution was irradiated using light from a Xe lamp for 15 seconds. After adding 10 μL of an aqueous catalyst solution containing 1 mg mL$^{-1}$ of catalyst, the absorbance at 620 nm was monitored for 1 min using a V/650 spectrophotometer (Jasco, Inc., Tokyo, Japan) in time-course measurement mode.

**Cyclic voltammetry:** The cyclic voltammetry tests were carried out using a three-electrode system. Samples were supported on a glassy carbon electrode by drop casting with 20 μL of 0.1 mg mL$^{-1}$ in a Nafion solution. The glassy carbon electrode (working electrode), Ag/AgCl (reference electrode) and Pt wire (counter electrode) were connected to a multi-channel potentiostat/galvanostat (WonATech,
Model WMPG1000, Korea) with a scan rate of 25 mV s \(^{-1}\) and with 80 mM sodium borated buffer (pH 8.0) used as the electrolyte.

Figure S1. STEM image and the corresponding element mapping of an IrO$_2$-TiO$_2$ composite NF
**Figure S2.** Experimental procedure for the purification of K⁺ and Cl⁻ containing an IrO₂ colloidal solution and the subsequent preparation of IrO₂ NPs (30 nm)
Figure S3. TEM image of the IrO$_2$ NPs (~10 nm) decorated onto the TiO$_2$ NF prepared using different Ir containing solutions: (a) low content (0.5 g) and (d) high content (3 g); element mapping of the IrO$_2$ NPs (~10 nm) decorated onto the TiO$_2$ NF prepared using different Ir-containing solutions: (b) low content and (e) high content; lattice fringes of the IrO$_2$ NPs (~10 nm) decorated onto a TiO$_2$ NF prepared using different Ir-containing solutions: (c) low content and (f) high content. We observed increasing amounts of IrO$_2$ NPs on TiO$_2$ NFs with an increase in the added amounts of Ir NPs in the TEM images (Figures S3a and S3d) and the corresponding mapping images (Figures S3b and S3e). The IrO$_2$ NP clusters were combined with a TiO$_2$ scaffold by atomic bonding and were well crystallized after a heat treatment (Figures S3c and S3f).
Figure S4. Graphic illustration of IrO$_2$ NPs (~10 nm) decorated onto the TiO$_2$ NF with different IrO$_2$ contents; (a) low, and (b) high, (c) IrO$_2$ NPs (~30 nm) decorated onto the TiO$_2$ NF.
Figure S5. X-ray diffraction patterns of the TiO$_2$ NF, the IrO$_2$-TiO$_2$ composite NF, the IrO$_2$ NPs (~30 nm) decorated onto the TiO$_2$ NF, and the IrO$_2$ NPs (~10 nm) decorated onto the TiO$_2$ NF with various IrO$_2$ contents: low (L) and high (H).
Figure S6. Time profile of the normalized concentration change ($C/C_0$) of Ru(bpy)$_3^{3+}$ determined from the absorbance change ($A/A_0$) at 670 nm. $C_0$ and $A_0$ denote the initial concentration and absorbance of Ru(bpy)$_3^{3+}$, respectively; (i) without a water oxidation catalyst and with (ii) the IrO$_2$ NPs (~30 nm) decorated onto the TiO$_2$ NF, and the IrO$_2$ NPs (~10 nm) decorated onto the TiO$_2$ NF with various IrO$_2$ contents: (iii) low (L) and (iv) high (H).
Figure S7. Cyclic voltammetry of (i) blank, (ii) IrO$_2$ NPs (~30 nm) decorated onto the TiO$_2$ NF, IrO$_2$ NPs (~10 nm) decorated onto the TiO$_2$ NF with various IrO$_2$ contents: (iii) low (L) and (iv) high (H) with a scan rate of 25 mV s$^{-1}$ in an 80 mM sodium borate (pH 8.0) buffer solution.

Figure S8. Cycling test of the evolved oxygen during repeated O$_2$ evolving testing of IrO$_2$/SiO$_2$ NF. The amount of oxygen which evolved during the repeated experiments was divided by the amount of the catalyst due to the unavoidable partial loss of the catalyst after the O$_2$ evolving test and subsequent filtration for the next recycling test.