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Supporting Information

Crystalline IrO_2-Decorated TiO_2 Nanofiber Scaffolds for Robust and Sustainable Solar Water Oxidation

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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 ($Na_2S_2O_8$), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2*6H_2O$), and iridium chloride hydrate ($IrCl_3 \cdot xH_2O$) used in this study were purchased from Sigma-Aldrich (MO, USA). Potassium hexachloroiridate (K_2IrCl_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_2IrCl_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), $Na_2S_2O_8$ (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 $Na_2S_2O_8$ (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 □L of an aqueous catalyst solution containing 1mg 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 uL 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.

[1]. Bonet, F.; Delmas, V.; Grugeon, S.; Urbina, R. H.; Silvert, P. Y.; Tekaia-Elhsissen, K. *Nanostruct Mater* **1999,** 11, (8), 127-1284

[Figure S1]

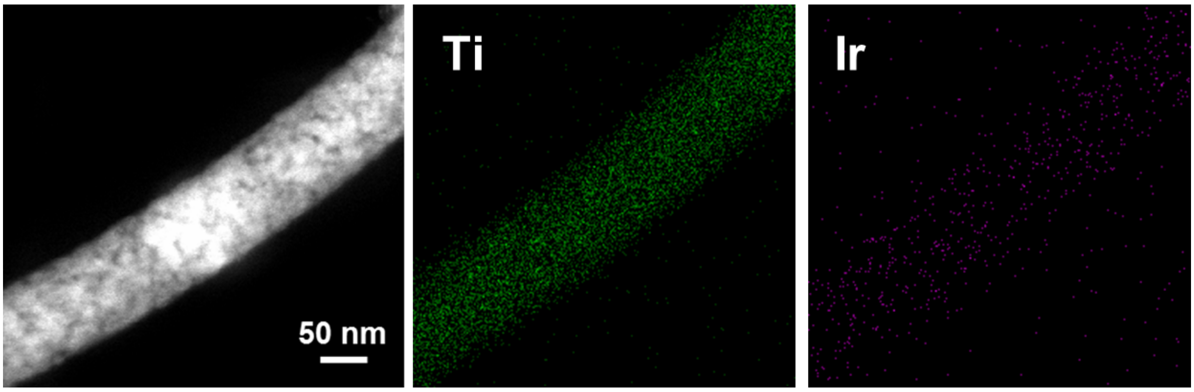

Figure S1. STEM image and the corresponding element mapping of an IrO_2-TiO_2 composite NF

[Figure S2]

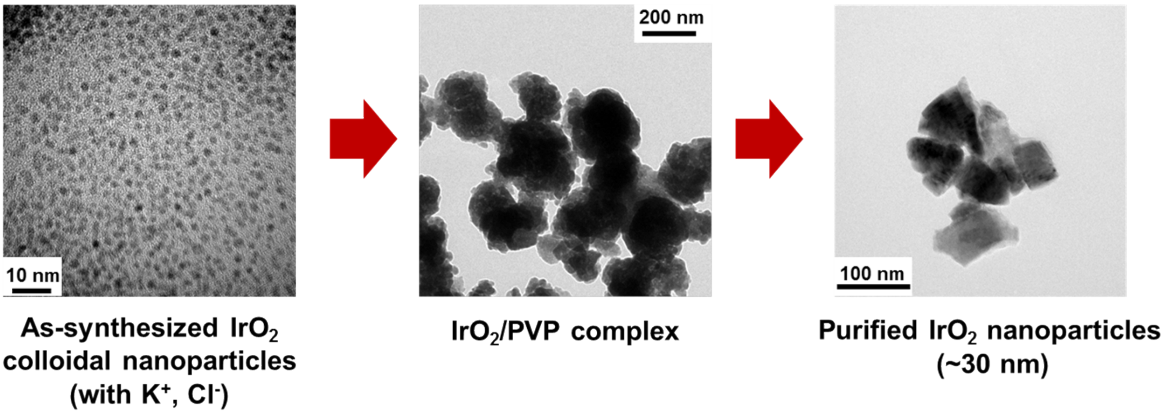

Figure S2. Experimental procedure for the purification of K^+ and Cl^- containing an IrO_2 colloidal solution and the subsequent preparation of IrO_2 NPs (30 nm)

[Figure S3]

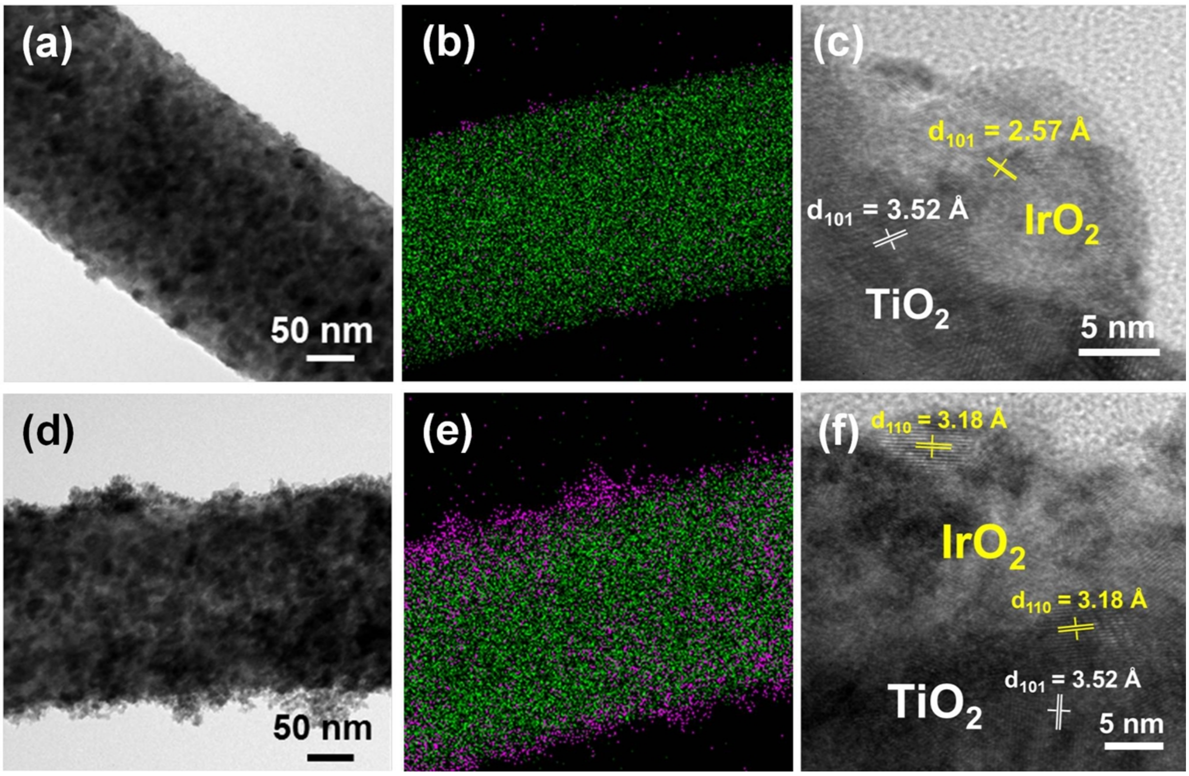

Figure S3. TEM image of the IrO_2 NPs (~10 nm) decorated onto the TiO_2 NF prepared using different Ir containing solutions: (a) low content (0.5 g) and (d) high content (3 g); element mapping of the IrO_2 NPs (~10 nm) decorated onto the TiO_2 NF prepared using different Ir-containing solutions: (b) 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 S2d) and the corresponding mapping images (Figures S2b and S2e). The IrO_2 NP clusters were combined with a TiO_2 scaffold by atomic bonding and were well crystallized after a heat treatment (Figures S2c and S2f).

[Figure S4]

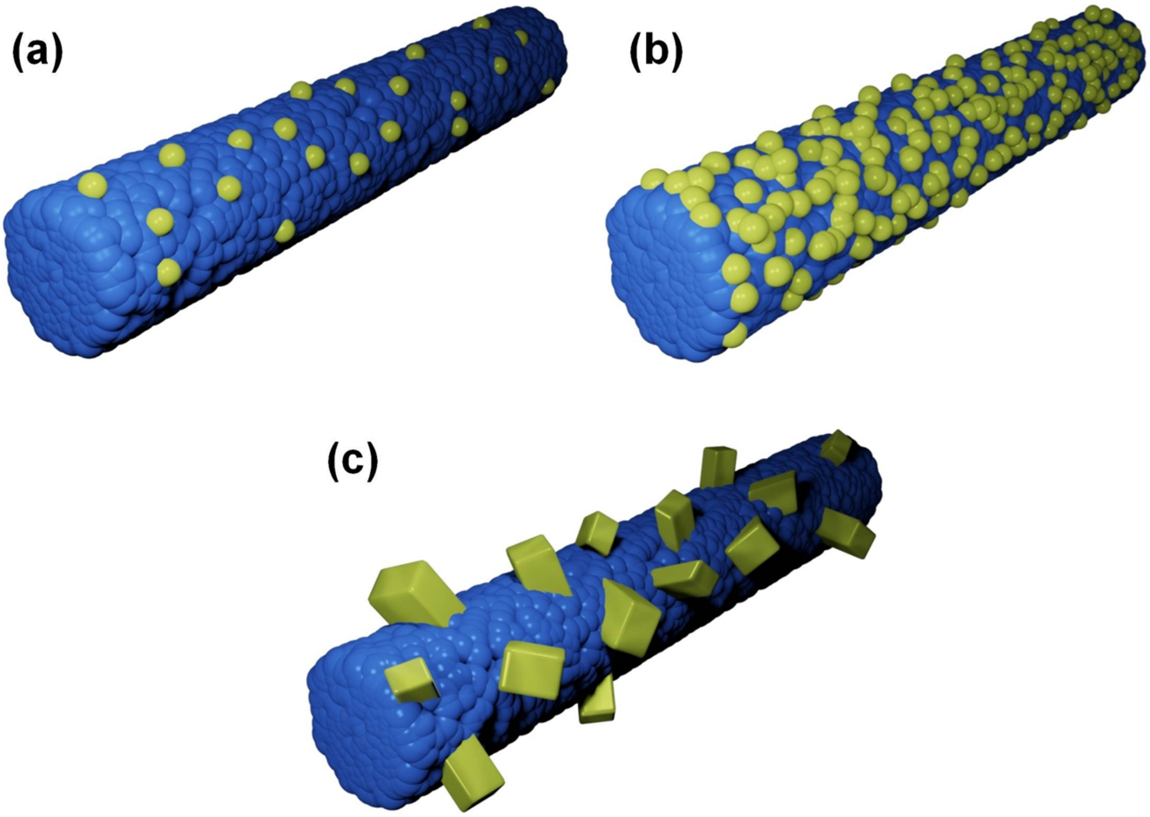

Figure S4. Graphic illustration of IrO_2 NPs (~10 nm) decorated onto the TiO_2 NF with different IrO_2 contents; (a) low, and (b) high, (c) IrO_2 NPs (~30 nm) decorated onto the TiO_2 NF.

[Figure S5]

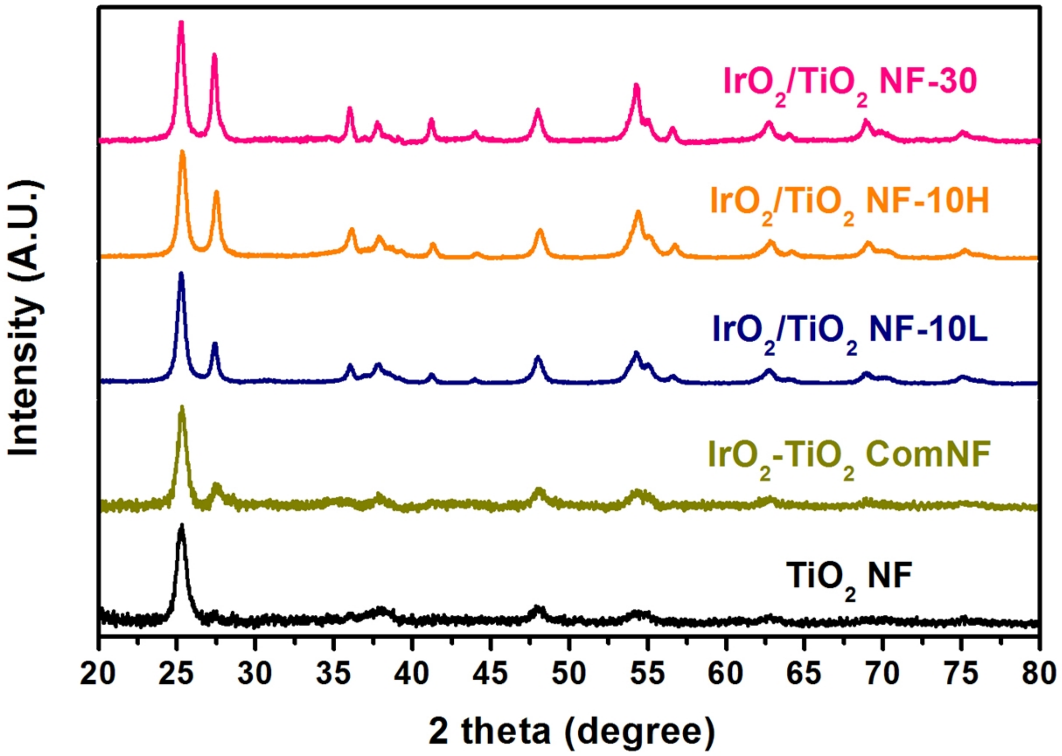

Figure S5. X-ray diffraction patterns of the TiO_2 NF, the IrO_2-TiO_2 composite NF, the IrO_2 NPs (~30 nm) decorated onto the TiO_2 NF, and the IrO_2 NPs (~10 nm) decorated onto the TiO_2 NF with various IrO_2 contents: low (L) and high (H)

[Figure S6]

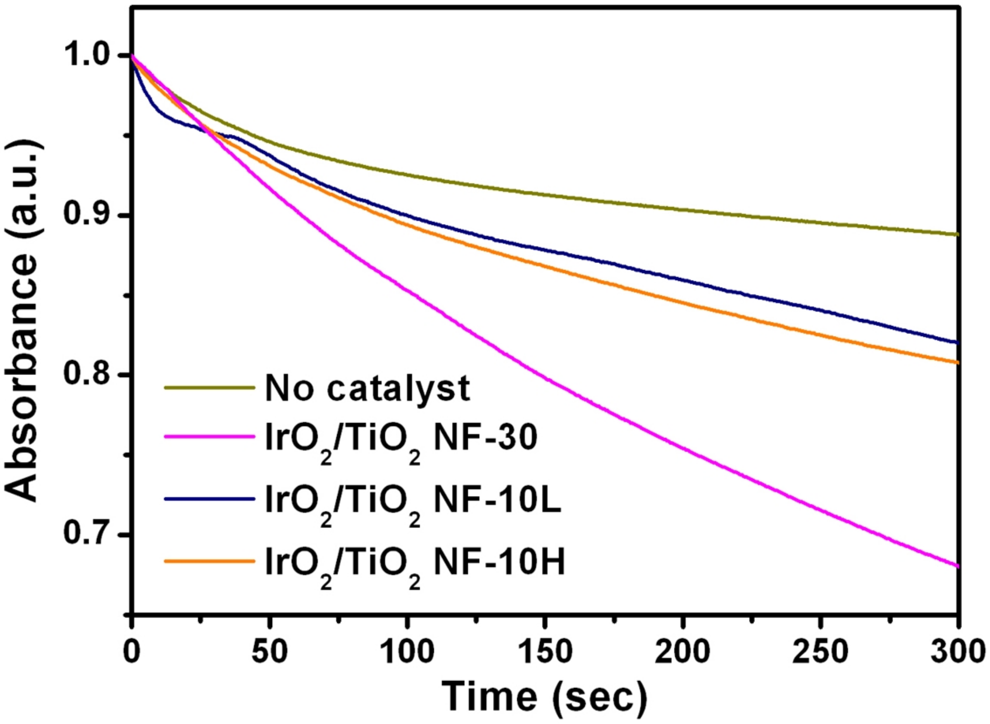

Figure S6. Time profile of the normalized concentration change (C/C_0) of $Ru(bpy)_3^{3+}$ determined from the absorbance change (A/A_0) at 670 nm. C_0 and A_0 denote the initial concentration and absorbance of $Ru(bpy)_3^{3+}$, respectively; (i) without a water oxidation catalyst and with (ii) the IrO_2 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]

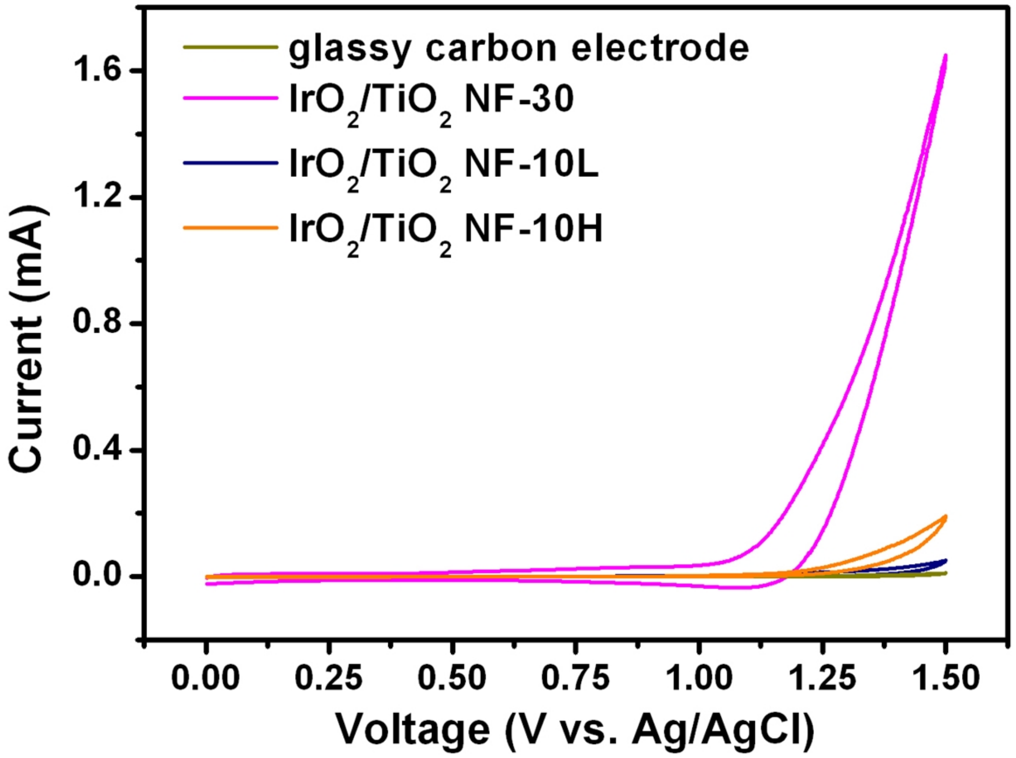

Figure S7. Cyclic voltammetry of (i) blank, (ii) IrO_2 NPs (~30 nm) decorated onto the TiO_2 NF, IrO_2 NPs (~10 nm) decorated onto the TiO_2 NF with various IrO_2 contents: (iii) low (L) and (iv) high (H) with a scan rate of 25 mV s^{-1} in an 80 mM sodium borate (pH 8.0) buffer solution

1. F. Bonet, V. Delmas, S. Grugeon, R. H. Urbina, P. Y. Silvert and K. Tekaia-Elhsissen, *Nanostruct Mater*, 1999, **11**, 1277-1284.

[Figure S8]

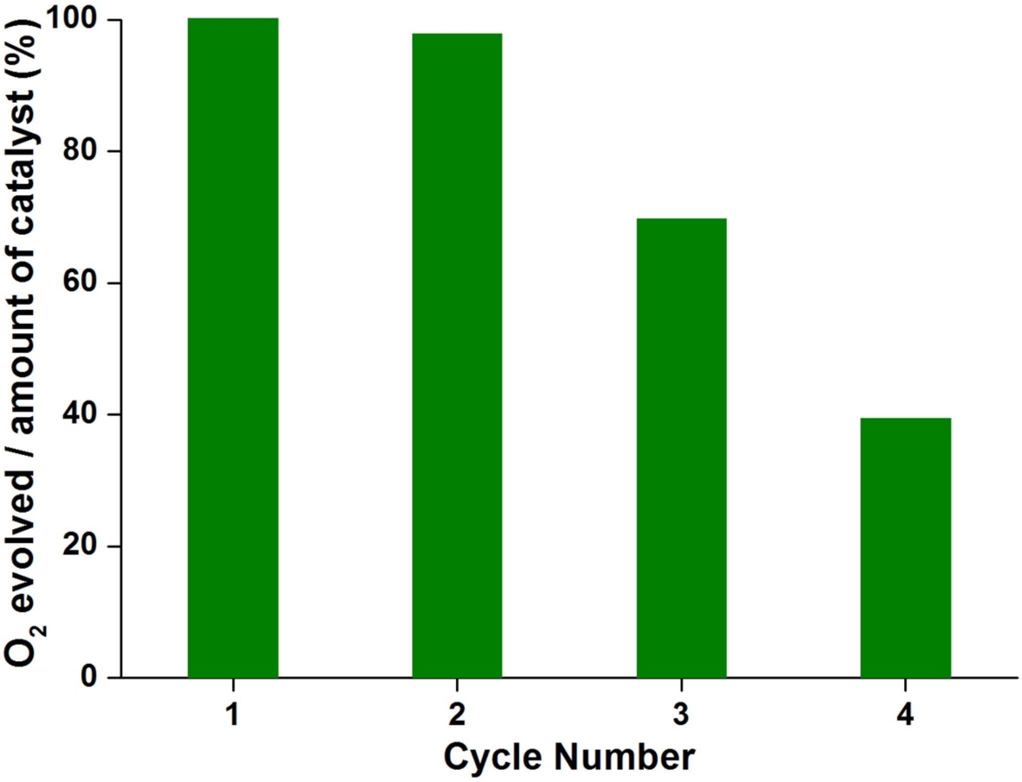

Figure S8. Cycling test of the evolved oxygen during repeated O_2 evolving testing of IrO_2/SiO_2 NF. The amount of oxygen which evolved during the repeated experiments was divided by the amount of the catalyst due to the unavoidable partial loss of the catalyst after the O_2 evolving test and subsequent filtration for the next recycling test