Supporting Information

Catalysis of Nickel Ferrite for Photocatalytic Water Oxidation Using $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$

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Experimental Method

Materials. All chemicals used for synthesis were obtained from a chemical company and used without further purification. Nickel(II) acetate tetrahydrate, nickel(II) chloride hexahydrate, cobalt(II) acetate tetrahydrate, iron(III) chloride hexahydrate, iron(II) sulfate heptahydrate, $Na_2S_2O_8$ and ethylene glycol (EG) were purchased from Wako Pure chemicals. Polyacrylamide (PAM) and Ag_2SO_4 were obtained from Sigma-Aldrich Co. $[Ru(bpy)_3]Cl_2$ was obtained from Tokyo Chemical Industry Co., Ltd. $[Ru(bpy)_3]SO_4$ was synthesized by adding one equivalent of Ag_2SO_4 to an aqueous solution of $[Ru(bpy)_3]Cl_2$. Purified water was provided by a Millipore MilliQ water purification system where the electronic conductance was 18.2 MΩ cm. $NiFe_2O_4$, NiO, Fe_2O_3, Fe_3O_4, Co_3O_4, $MnFe_2O_4$ and $MgFe_2O_4$ were synthesized by following reported methods.

Synthesis of $NiFe_2O_4$.[S1] To an aqueous solution (24 mL) containing $NiCl_2{\cdot}6H_2O$ (2.0 mmol, 0.46 g) and $Fe(NO_3)_3{\cdot}9H_2O$ (4.0 mmol, 1.62 g) was added KOH solution (2.0 M, 24 mL) with magnetic stirring in room temperature (RT). The mixture was then transferred into a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed tank was heated to and maintained at 160 ºC for 10 h in an oven and cooled to RT. The resulting brown precipitates were collected by filtration and washed with water and ethanol for more than 3 times, and finally dried in an oven at 60 ºC for 10 h.

Synthesis of NiO.[S2] To an aqueous solution (24 mL) containing $Ni(CH_3COO)_2{\cdot}4H_2O$ (5.0 mmol, 1.24 g) was added ethylene glycol (EG) (24 mL) with magnetic stirring to form a homogeneous in RT. The mixture was then transferred into a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed tank was heated to and maintained at 200 ºC for 3.0 h in an oven and cooled to RT. The resulting emerald green precipitates $[Ni(OH)_2]$ were collected by filtration and washed with water and ethanol for several times, and dried in a vacuum. NiO was prepared by calcination of the obtained $Ni(OH)_2$ in an oven at 300 ºC in air for 3.0 h.

Synthesis of Fe_2O_3.[S3] To an aqueous solution (30 mL) containing $FeSO_4{\cdot}7H_2O$ (1.0 M) was added NaOH (6.0 M) drop wisely to pH ~11 with magnetic stirring in RT. The mixtures were stirred vigorously for 1.5 h with bubbling air. The products were collected by filtration and washed with water several times, dried at 65 ºC.

Synthesis of Fe_3O_4.[S4] To an aqueous solution (40 mL) containing $FeCl_3{\cdot}6H_2O$ (2.0 mmol, 0.54 g) and sodium citrate (4.0 mmol, 1.176 g) was added ammonia (25%, 0.50 mL)

and polyacrylamide (PAM) (0.30 g) with vigorous magnetic stirring in RT. The mixtures were stirred vigorously for 0.50 h and then transferred into a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed tank was heated to and maintained at 200 °C for 12 h and cooled to RT. The solid product was collected by magnetic filtration and washed several times with deionized water and ethanol. The final product was dried in an oven at 100 °C for 10 h.

Synthesis of Co_3O_4.[S5] An aqueous solution of cobalt acetate (80 mM, 73 mL) was slowly added to an aqueous ammonia solution (25%, 7.3 mL) with vigorous stirring by a magnetic stirrer. After 20 min stirring, the obtained pale pink slurry was transferred to a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed tank was heated to and maintained at 350 ºC for 3.0 h in an oven and cooled to RT. The obtained particles were collected by filtration and washed with water for several times and dried at 65 ºC for several hours.

Synthesis of $MnFe_2O_4$.[S6] NaOH (3.0 g) was slowly added to an aqueous solution (40 mL) containing $FeSO_4 \cdot 7H_2O$ (5.0 mmol, 1.11 g) and $MnCl_2 \cdot 4H_2O$ (2.5 mmol, 0.40 g) at RT with magnetic stirring. The mixture was stirred vigorously for 30 min and then transferred into a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed tank was heated to and maintained at 200 °C for 5 h and cooled to RT. The solid product was collected by a magnet and washed several times with deionized water and ethanol respectively. The final product was dried at 100 ºC for 6 h.

Synthesis of $MgFe_2O_4$.[S7] $FeCl_3 \cdot 6H_2O$ (5.0 mmol, 1.25 g) and $MgSO_4$ (2.5 mmol, 0.30 g) was dissolved in ethylene glycol (40 ml), then CH_3COONa (3.6 g) and polyethylene glycol (1.0 g) were added to the solution. The mixture was stirred vigorously for 0.50 h and then transferred into a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed tank was heated to and maintained at 200 °C for 12 h and cooled to RT. The puce product was separated by centrifugation, washed several times with ethanol and finally dried at 60 ºC for 6 h

X-ray Diffraction. X-ray diffraction patterns were recorded by a Rigaku Ultima IV. Incident X-ray radiation was produced by Cu X-ray tube, operating at 40 kV and 40 mA with Cu K_α radiation of 1.54 Å. The scanning rate was 2 °/min from 10° to 80° in 2θ.

N_2 Adsorption for BET Surface Area Determination. Nitrogen adsorption-desorption at 77 K was performed with a Belsorp-mini (BEL Japan, Inc.) within a relative pressure range from 0.01 to 101.3 kPa. A sample mass of ~100 mg was used for adsorption analysis after

pretreatment at 120 ºC for ~1.0 h under vacuum conditions and kept in N_2 atmosphere until N_2-adsorption measurements. The sample was exposed to a mixed gas of He and N_2 with a programmed ratio and adsorbed amount of N_2 was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min).

X-ray Photoelectron Spectra. X-ray photoelectron spectra (XPS) were measured by a ULVAC-PHI ESCA5600. The incident radiation was Mg K_α X-ray (1253.6 eV) at 400 W and a charge neutralizer was turned on for acquisition. $NiFe_2O_4$ used for 1st run were collected by magnetic centrifugation and dried in vacuo. Iron and nickel oxides foil were prepared by calcinating each metal foils at 400 ºC for 2 h. The particles of $NiFe_2O_4$ before and after reaction were pressed on each copper foil and fixed on a stainless stage together with iron and nickel metals/oxides foil. The binding energy of each element was corrected by C 1s peak (284.8 eV) from residual carbon.

Transmission electron microscope (TEM). Transmission electron microscope (TEM) images of nanoparticles, which were mounted on a copper microgrid coated with elastic carbon, were observed by a JEOL JEM-2100 operating at 200 keV.

Photocatalytic Water Oxidation. Photocatalytic oxygen evolution was performed as follows. A iron- or nickel-based catalyst (0.050 – 1.0 g L^{-1}) was added to a phosphate buffer solution (50 mM, pH 8.0, 2.0 mL) containing $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (0.25 mM) flushed with Ar gas. The solution was then irradiated with a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a color filter glass (Asahi Techno Glass) transmitting λ > 420 nm at room temperature. Evolved oxygen gas in a headspace was quantified by a Shimadzu GC-17A gas chromatograph [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 19095PMS0, 30 m × 0.53 mm) at 313 K] equipped with a thermal conductivity detector.

Electrochemical Water Oxidation. Electrochemical water oxidation was performed on an ALS 630B electrochemical analyzer using a carbon paste electrode modified with 5% of a metal oxide catalyst as a working electrode, a saturated calomel reference electrode (SCE) and a Pt wire as a counter electrode. Linear sweep voltammograms were recorded by applying the voltage from 0 V to 1.5 V to the working electrode in a phosphate buffer (50 mM, pH 8.0) at room temperature with a scanning rate of 100 mV s^{-1}.

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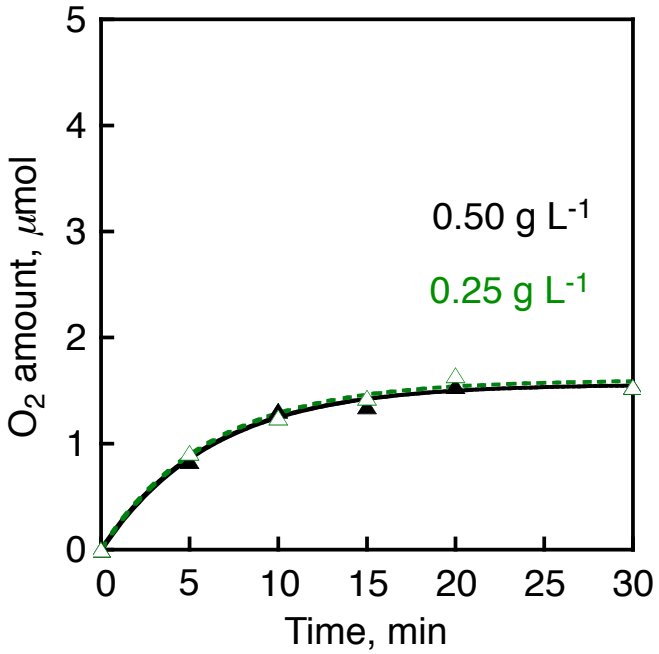

Figure S1. Time course of O_2 evolution under photoirradiation (Xe lamp, λ > 420 nm) with various concentrations of Fe_3O_4 [0.50 g L^{-1} (black, closed triangles), and 0.25 g L^{-1} (green, open triangles)] in an aqueous buffer solution (2.0 mL, pH 8.0) containing $[Ru(bpy)_3]^{2+}$ (0.25 mM) and $Na_2S_2O_8$ (5.0 mM).

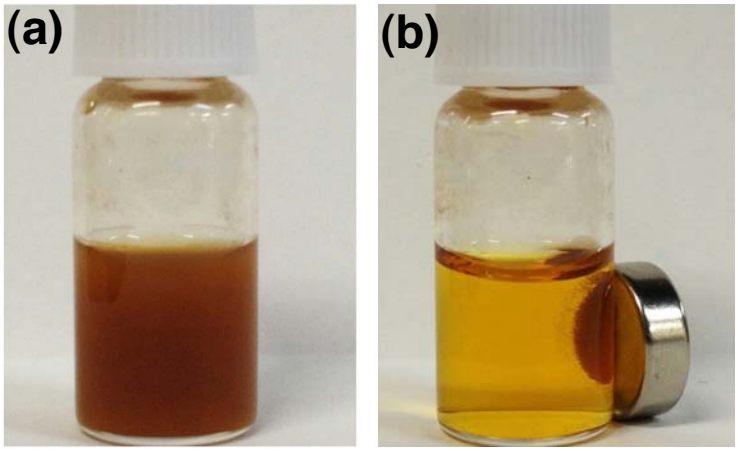

Figure S2. (a) $NiFe_2O_4$ is dispersed in a reaction solution. (b) $NiFe_2O_4$ is attracted to a magnet in the reaction solution.

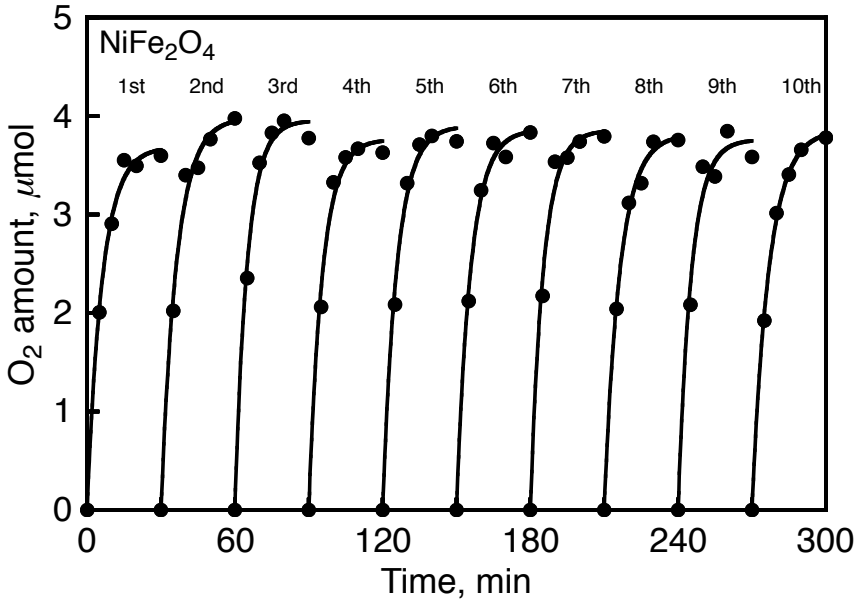

Figure S3. Time courses of O_2 evolution under photoirradiation (Xe lamp, $\lambda > 420$ nm) of a phosphate buffer solution (pH 8.0, 2.0 mL) containing $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (0.25 mM) with $NiFe_2O_4$ (0.50 g L^{-1}) at room temperature in 10 repetitive examinations.

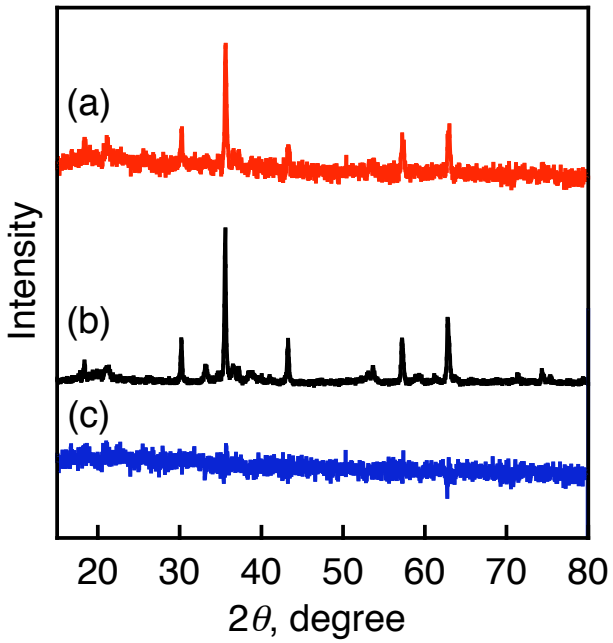

Figure S4. X-ray diffraction pattern of (a) $NiFe_2O_4$ after the catalytic reaction and (b) $NiFe_2O_4$ before the reaction. (c) Subtraction from spectrum (a) to spectrum (b). No peaks assignable to NiO or Fe_2O_3 were observed.

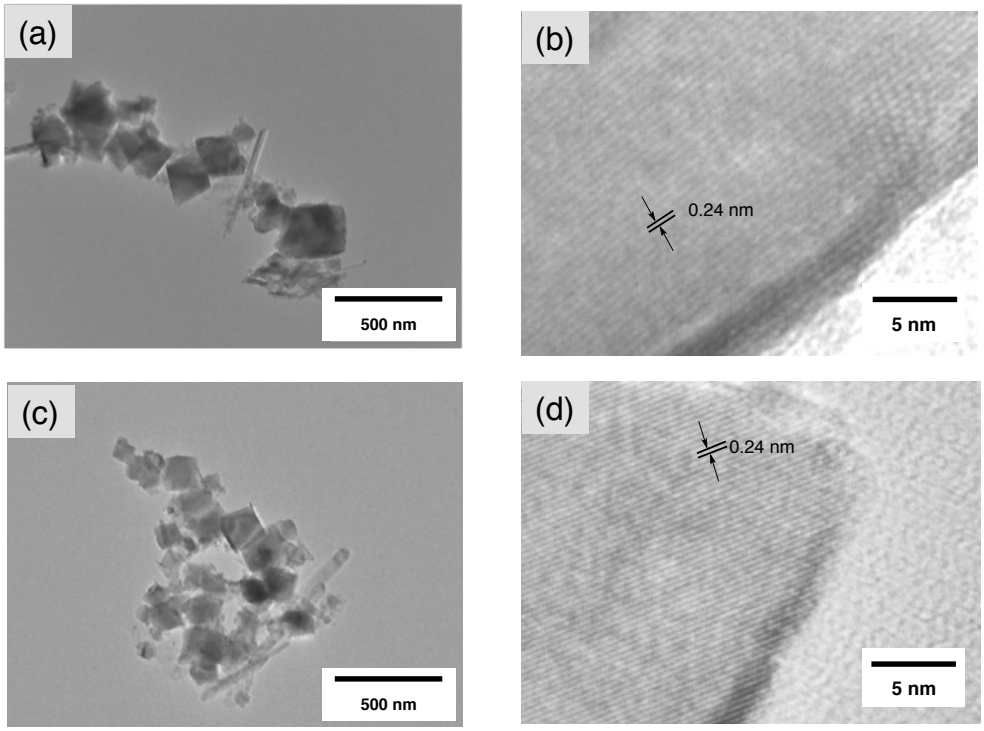

Figure S5. TEM images of (a, b) $NiFe_2O_4$ before the catalytic reaction and (c, d) $NiFe_2O_4$ after the reaction. No changes in morphology and lattice parameters were observed after the reaction.

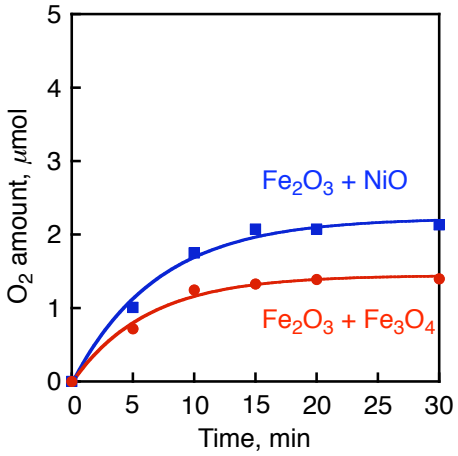

Figure S6. Time courses of O_2 evolution under photoirradiation (Xe lamp, $\lambda > 420$ nm) of a phosphate buffer solution (pH 8.0, 2.0 mL) containing $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (0.25 mM) with the addition of Fe_2O_3 (0.25 g L^{-1}) to NiO (0.25 g L^{-1}) or Fe_3O_4 (0.25 g L^{-1}) at room temperature.

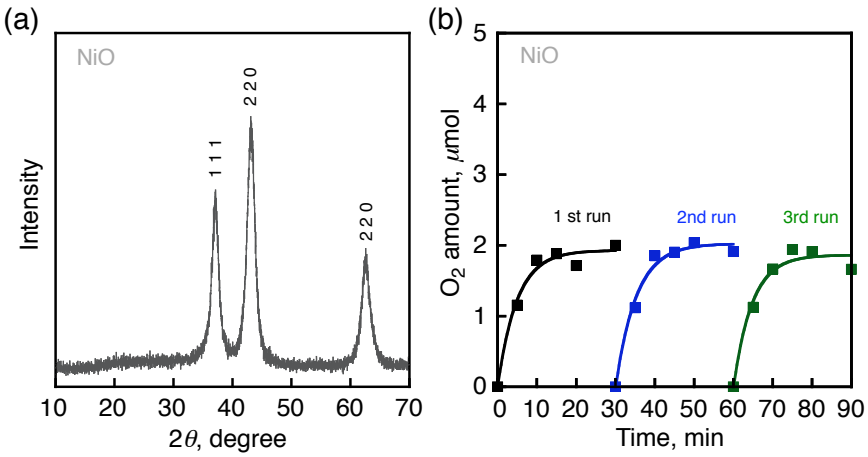

Figure S7. (a) Powder-XRD spectra of NiO catalysts. (b) Time courses of O_2 evolution under photoirradiation (Xe lamp, λ > 420 nm) of a phosphate buffer solution (pH 8.0, 2.0 mL) containing $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (0.25 mM) with NiO (0.50 g L^{-1}) at room temperature in three repetitive examinations.

Table S1. Overpotential of Various Catalysts for Electrochemical Water Oxidation

catalyst	onset potential, V (vs SCE)	pH	Standard potential, V (vs SCE)	overpotential, V	ref.
$NiFe_2O_4$	0.95	8.0	0.52	0.43	this work
Co phosphate	0.99	7.0	0.58	0.41	S8
CoO_x	1.01	8.0	0.52	0.49	S9
Ni borate	0.89	9.2	0.45	0.44	S10

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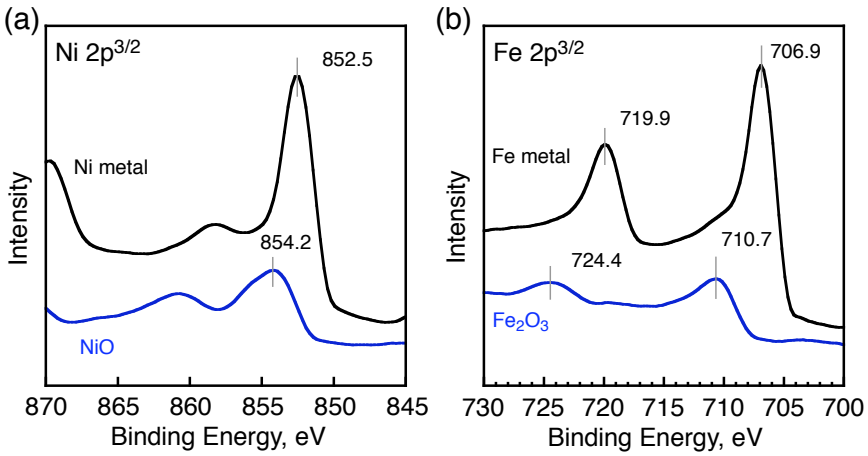

Figure S8. X-ray photoelectron spectra in the energy regions of (a) Ni 2p of an Ni metal foil (black) and NiO foil (blue) and (b) Fe 2p of Fe metal foil (black) and Fe_2O_3 foil (blue).