Electronic Supplementary Information

Bottom-up and top-down methods to improve catalytic reactivity for photocatalytic production of hydrogen peroxide from water and dioxygen with a ruthenium complex and water oxidation catalysts

Yusuke Isaka,^a Satoshi Kato,^a Dachao Hong,^a Tomoyoshi Suenobu,^a Yusuke Yamada^a and Shunichi Fukuzumi^{*abc}

 ^{a.} Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, SENTAN, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan
^{b.} Faculty of Science and Engineering, Meijo University, ALCA, SENTAN, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-0073, Japan
^{c.} Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea

Table of contents

	Pages
Experimental details	S3 – S5
Reference	S 5
Figs. S1 – S17	S6 – S22
Calculation of ratio of specific surface areas of NiFe ₂ O ₄	S23

Experimental section

Spectroscopic measurements in solution

¹H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer in D₂O solutions. The chemical shifts and relative integration signals were referenced by an external standard solution of 5.0 mM 3-(trimethylsilyl)propanoate-2,2,3,3- d_4 acid sodium salt (TSP) in D₂O sealed in a glass capillary. The UV-visible absorption spectra were recorded using a Hewlett Packard 8453 diode array spectrophotometer with a quartz cuvette (light-path length = 1.0 cm) at 298 K.

Synthesis of iridium hydroxide

Iridium hydroxide was synthesised according to the literature.^{S1,S2} The pH of an aqueous solution of H_2IrCl_6 was adjusted to ~10 by adding 5.0 M NaOH solution with vigorous stirring at 100 °C. After 1.0 h stirring, precipitates appeared were collected by centrifugation. Then, the precipitates were washed by water three times and dried *in vacuo* at room temperature and kept at 65 °C for 10 h.

Synthesis of [Ru^{II}(Me₂phen)₃]SO₄

Tris(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) sulfate ([Ru^{II}(Me₂phen)₃]SO₄) complex was synthesised according to the literature.^{S3} RuCl₃ (40 mg) was refluxed under N₂ overnight in ethanol/water (v/v 80/20) with 6 equiv. of ligand, Me₂phen, to form the red-orange [Ru^{II}(Me₂phen)₃]Cl₂ complex. After evaporation of the solvent, the product was readily precipitated from acetone with ether. The precipitate, [Ru^{II}(Me₂phen)₃]Cl₂, was added to water to be completely dissolved and Ag₂SO₄ (61 mg) solubilised in water was added to the solution. After stirring for 12 h, AgCl as precipitate was filtered off. An aqueous solution of (NH₄)₂SO₄ was added to the reaction solution to obtain crystalline product. ¹H-NMR (300 MHz, D₂O): δ (ppm) = 2.88 (s, 6H), 7.41 (d, *J* = 5.12 Hz, 2H), 7.90 (d, *J* = 5.12 Hz, 2H), 8.39 (s, 2H).

Synthesis of [(µ-Cl)(Co(Cp^{*})Cl)]₂

 $[(\mu-Cl)(Co(Cp^*)Cl)]_2$ was synthesised according to the literature.^{S4} Pentamethylcyclopentadiene (Cp^{*}, 25 mL) and *tert*-butyllithium (~1.7 M in *n*-pentane, 90 mL) were combined in an equimolar amount (1:1) in *n*-pentane at 203 K. The solution was stirred and slowly allowed to warm up to room temperature. After stirring for further 24 h at room temperature, a white suspension was filtered by an inert gas frit and pentamethylcyclopentadienyllithium (Cp^{*}Li) was filtered off. The anhydrous CoCl₂ (1.3 g) was added to the solution of Cp^{*}Li (1.4 g) in 20 mL of tetrahydrofuran. The

mixture was stirred for 3 h at room temperature until the brown solution became green-brown. Afterwards the solution was concentrated to a smaller volume under reduced pressure and extracted with 100 mL of *n*-pentane. The brown extracts were bubbled by CO gas for 30 min through the solution. Di- μ -chloro-bis[chloro(η^5 -pentamethylcyclopentadienyl)cobalt] ([(μ -Cl)(Co(Cp^{*})Cl)]₂) was obtained as a green powder.

Synthesis of [Co(Cp*)(bpy)(OH₂)]SO₄

[Co(Cp^{*})(bpy)(OH₂)]SO₄ was synthesised according to the literature.^{S4} [(μ -Cl)(Co(Cp^{*})Cl)]₂ (100 mg) in 20 mL of water was stirred with 1.5 equimolar amount of 2,2'-bipyridine (88 mg) for 1 h at room temperature under N₂. After filtering of free 2,2'-bipyridine, Ag₂SO₄ (120 mg) was added to the filtrate. After stirring for 12 h, AgCl as a precipitate was filtered off. An aqueous solution of (NH₄)₂SO₄ was added to the reaction solution to obtain crystalline product. ¹H-NMR (300 MHz, D₂O): δ (ppm) = 1.34 (s, 15H), 8.10 (t, *J* = 5.86 Hz, 2H), 8.43 (t, *J* = 8.06 Hz, 2H), 8.51 (d, *J* = 8.06 Hz, 2H), 9.85 (d, *J* = 5.50 Hz, 2H).

Synthesis of [Co(Cp^{*})(OH₂)₃]SO₄

 $[(\mu-Cl)(Co(Cp^*)Cl)]_2$ (180 mg) in 40 mL of water was stirred with 2.0 equimolar amount of Ag₂SO₄ (210 mg) for 22 h at room temperature under N₂. After filtering of AgCl as a precipitate, an aqueous solution of $(NH_4)_2SO_4$ was added to the reaction solution to obtain crystalline product.

Synthesis of [Ir(Cp^{*})((OH)₂bpy)(OH₂)(H₂O)]SO₄

[Ir(Cp^{*}){4,4'-(OH)₂-2,2'-bipyridine}(H₂O)]SO₄ ([Ir(Cp^{*})((OH)₂bpy)(H₂O)]²⁺) was synthesised according to the literature.^{S5} An aqueous solution (30 mL) of [Ir(Cp^{*})(H₂O)₃]SO₄ (400 mg, 0.84 mmol) and 4,4'-dihydroxy- 2,2'-bipyridine (160 mg, 0.84 mmol) was stirred at 40 °C for 12 h. The formed yellow crystals were collected by filtration to yield [Ir(Cp^{*})((OH)₂bpy)(H₂O)]SO₄. ¹H NMR (300 MHz, D₂O): δ (ppm) = 1.64 (s, 15H), 7.13 (dd, *J* = 6.4 Hz, 2.6 Hz, 2 H), 7.66 (d, *J* = 2.6 Hz, 2H), 8.70 (d, *J* = 6.4 Hz, 2H).

References

- 1 P. G. Hoertz, Y.-I. Kim, W. J. Youngblood and T. E. Mallouk, J. Phys. Chem. B, 2007, 111, 6845.
- 2 D. Hong, M. Murakami, Y. Yamada and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 5708.

- 3 C. Turro, J. M. Zaleski, Y. M. Karabatsos and D. G. Nocera, J. Am. Chem. Soc., 1996, **118**, 6060.
- 4 D. Hong, J. Jung, J. Park, Y. Yamada, T. Suenobu, Y.-M. Lee, W. Nam and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 7606.
- 5 D. Hong, M. Murakami, Y. Yamada and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 5708.



Fig. S1 Time course of H₂O₂ production under visible light irradiation ($\lambda = 450$ nm) of [Ru^{II}(Me₂phen)₃]²⁺ (100 µM) in the presence of Sc³⁺ (100 mM) and [Ir(Cp^{*})(H₂O)₃]²⁺ (1.0 mM) in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM). The reaction solution was pretreated by 20 h irradiation of visible light ($\lambda > 420$ nm) at room temperature prior to the reaction in order to produce Ir(OH)₃ nanoparticles *in situ*. The quantum efficiency was calculated from the slope of the black line.



Fig. S2 Time course of H₂O₂ production under photoirradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (200 µM) in the presence of Sc³⁺ (100 mM) and $[Ir(Cp^*)(H_2O)_3]^{2+}$ (1.0 mM) in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM). A solar simulator, in which the intensity was adjusted to 1.0 mJ cm⁻² s⁻¹ (AM1.5), was used as the light source. The solar energy conversion efficiency was determined from the slope of the black line.



Fig. S3 TEM images of Ir(OH)₃ nanoparticles formed after (a) 6 h, (b, c) 12 h and (d, e) 24 h irradiation of visible light ($\lambda > 420$ nm) of an aqueous solution containing [Ru^{II}(Me₂phen)₃]²⁺ (20 μ M) in the presence of [Ir(Cp^{*})(H₂O)₃]²⁺ (100 μ M) and Sc(NO₃)₃ (0.10 M) at 293 K in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM).



Fig. S4 X-ray photoelectron spectra in the energy regions of (a) Ir 4f and (b) O 1s of IrO₂ (blue), and Ir(OH)₃ (green) formed after visible light ($\lambda > 420$ nm) irradiation of [Ru^{II}(Me₂phen)₃]²⁺ (100 μ M) in the presence of [Ir(Cp^{*})(H₂O)₃]²⁺ (100 μ M) and Sc(NO₃)₃ (0.10 M) in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM) at 298 K for 40 h.



Fig. S5 TEM images of (a) nanoparticles derived from $[Ir(Cp^*)(H_2O)_3]^{2+}$ and (b) $Ir(OH)_3$ prepared from H_2IrCl_6 .



Fig. S6 Time courses of H_2O_2 concentration of aqueous suspensions containing 1000 μ M H_2O_2 and NiFe₂O₄ (0.17 g L⁻¹) in the absence (red) and presence (blue) of Sc(NO₃)₃ (0.10 M).



Fig. S7 Particles size and their distribution determined by DLS measurements of NiFe₂O₄ particles in an aqueous suspension at 298 K containing NiFe₂O₄ (0.17 g L⁻¹) in the presence of Sc(NO₃)₃ (0.10 M) in O₂-saturated H₂O (3.0 mL, $[O_2] = 1.2$ mM) under dark condition before (red) and after 24 h (orange), 48 h (green), 72 h (blue) and 240 h (purple).



Fig. S8 Particles size and their distribution determined by DLS measurement of $NiFe_2O_4$ (0.17 g L⁻¹) dispersed in water (red) and $NiFe_2O_4$ particles (0.17 g L⁻¹) in an aqueous HNO₃ (1.0 M) solution exposed to room light for 1 h (orange), 6 h (blue) and 15 h (purple) at 298 K.



Fig. S9 Particles size and their distribution determined by DLS measurements of $NiFe_2O_4$ (0.17 g L⁻¹) dispersed in water (black), and $NiFe_2O_4$ particles (0.17 g L⁻¹) in an aqueous HNO₃ (1.0 M) solution under dark conditions for 1 h (red), 6 h (orange), 12 h (green) and 24 h (blue).



Fig. S10 Particles size and their distribution determined by DLS measurements of NiFe₂O₄ (0.17 g L^{-1}) dispersed in water (black) and NiFe₂O₄ particles (0.17 g L^{-1}) in an aqueous solution containing Sc(NO₃)₃ [100 mM (blue), 10 mM (red), 1 mM (light blue), 0.1 mM (green)] for 12 h under room light at 353 K.



Fig. S11 Powder XRD patterns of NiFe₂O₄ (blue) and NiFe₂O₄ nanoparticles formed in an aqueous $Sc(NO_3)_3$ (10 mM) solution (red) after 12 h stirring at 353 K.



Fig. S12 UV-Vis spectrum of $[Fe^{II}(phen)_3]^{2+}$ (100 µM) as a reference (red), that of filtered and diluted supernatant of the aqueous solution in which NiFe₂O₄ nanoparticles were obtained (solution 1, green), that of solution 1 with 1,10-phenanthroline ligand (solution 2, blue) and that of solution 3 in which NADH added to solution 2 (black). The supernatant was obtained by filtering the reaction solution that was used to produce the NiFe₂O₄ nanoparticles. The reaction solution was obtained by stirring NiFe₂O₄ particles in an aqueous solution containing Sc(NO₃)₃ (10 mM) at 353 K for 12 h. The $[Fe^{II}(phen)_3]^{2+}$ solution did not show any change in UV-Vis spectra after addition of Sc(NO₃)₃ (1.4 mM) which was present in the other samples.



Fig. S13 TEM images of (a) NiFe₂O₄ and (b) NiFe₂O₄ nanoparticles formed after 12 h stirring in an aqueous $Sc(NO_3)_3$ (10 mM) solution at 353 K. The particles are aggregated due to their magnetism.



Fig. S14 Time courses of H₂O₂ production under visible light irradiation ($\lambda > 420$ nm) of an aqueous suspension containing [Ru^{II}(Me₂phen)₃]²⁺ (200 µM), Sc(NO₃)₃ (0.10 M) and NiFe₂O₄ nanoparticles (0.17 g L⁻¹) in various sizes [1300 nm (black), 620 nm (blue) and 91 nm (red)] in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM).



Fig. S15. Time course of H_2O_2 production under visible light irradiation ($\lambda = 450$ nm) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (200 μ M) in the presence of Sc³⁺ (100 mM) and NiFe₂O₄ (0.34 g L⁻¹) with diameter of 91 nm in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM). The quantum efficiency was calculated from the slope of the black line.



Fig. S16. Time course of H_2O_2 production under photoirradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (200 µM) in the presence of Sc³⁺ (100 mM) and NiFe₂O₄ (0.34 g L⁻¹) with diameter of 91 nm in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM). A solar simulator, in which the intensity was adjusted to 1.0 mJ cm⁻² s⁻¹ (AM1.5), was used as the light source. The solar energy conversion efficiency was determined from the slope of the black line.



Fig. S17 Time courses of H₂O₂ production in the presence of various sizes [1300 nm (black circle), 620 nm (green diamond), 120 nm (blue square) and 91 nm (red triangle)] of NiFe₂O₄ (0.17 g L⁻¹) and Sc(NO₃)₃ (100 mM) under visible light irradiation ($\lambda > 420$ nm) of [Ru^{II}(Me₂phen)₃]²⁺ (200 μ M) in O₂-saturated H₂O (3.0 mL, [O₂] = 1.2 mM). The original NiFe₂O₄ particle had diameter of 1300 nm. The 620 nm particles were recovered from the reaction suspension after 12 h visible light ($\lambda > 420$ nm) irradiation of [Ru^{II}(Me₂phen)₃]²⁺ (200 μ M) in the presence of Sc(NO₃)₃ (0.10 M) and NiFe₂O₄ (0.17 g L⁻¹). The 120 nm and 90 nm particles were obtained by treatment of NiFe₂O₄ in an aqueous Sc(NO₃)₃ solution at 80 °C for 6 h and 12 h, respectively. The initial rates of H₂O₂ production using NiFe₂O₄ with different diameters plotted in Figure 11 were determined from the slopes of the plots in Figure S12.

Calculation of specific surface areas based on particles sizes.

The volume of a true sphere with the diameter of $d(V_d)$ is given by eqn (S1).

$$V_{\rm d} = \frac{1}{6}\pi d^3 \tag{S1}$$

Surface area of such sphere (S_d) is given by eqn (S2).

$$S_{\rm d} = \pi d^2 \tag{S2}$$

When a true sphere with the diameter of D is divided into smaller true spheres with the diameter of d, the number of produced smaller true spheres (n) is given by eqn (S3).

$$n = \frac{V_{\rm D}}{V_{\rm d}} = \frac{D^3}{d^3} \tag{S3}$$

When larger true spheres with diameter of D are all divided into smaller true spheres with the diameter of d, given the number of the larger true spheres (N), the ratio (R) of total surface area of the larger true spheres to the total surface area of produced smaller true spheres is calculated by eqn (S4).

$$R = \frac{n}{N} \times \frac{S_{\rm d}}{S_{\rm D}} = \frac{\frac{D^3}{d^3} \times N}{N} \times \frac{d^2}{D^2} = \frac{D}{d}$$
(S4)

Assuming that the NiFe₂O₄ particles are true spheres, the ratio of specific surface areas of original 1300 nm particles to produced smaller particles with the diameter of d (nm) is given by substituting D = 1300 nm into eqn (S4) to give eqn (S5).

$$R = \frac{1300}{d} \tag{S5}$$