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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

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Hydrogen peroxide (H$_2$O$_2$) was produced from water and dioxygen using [Ru($^6$Me$_2$phen)$_2$]^{2+} (Me$_2$phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst and [Ir(Cp')(H$_2$O)$_2$]^{2+} (Cp' = $\eta^5$-pentamethylcyclopentadienyl) as a precursor of a water oxidation catalyst in the presence of Sc$^{3+}$ in water under visible light irradiation. TEM and XPS measurements of residues in the resulting solution after the photocatalytic production of H$_2$O$_2$ indicated that the [Ir(Cp')(H$_2$O)$_2$]^{2+} was converted to Ir(OH)$_3$ nanoparticles, which are actual catalytic species. The Ir(OH)$_3$ nanoparticles produced in situ during the photocatalytic production of H$_2$O$_2$ were smaller in size than that prepared independently from hydrogen hexachloroiridate (H$_2$IrCl$_6$), and exhibited higher catalytic reactivity for the photocatalytic production of H$_2$O$_2$. Photocatalytic production of H$_2$O$_2$ from water and dioxygen was also made possible when Ir(OH)$_3$ nanoparticles were replaced by nickel ferrite (NiFe$_2$O$_4$) nanoparticles, which are composed of more earth abundant metals than iridium. Size of NiFe$_2$O$_4$ nanoparticles became smaller during the photocatalytic production of H$_2$O$_2$ to exhibit higher catalytic reactivity in the second run as compared with that in the first run. NiFe$_2$O$_4$ nanoparticles obtained by the treatment of NiFe$_2$O$_4$ in an aqueous solution of Sc$^{3+}$ exhibited 33-times higher catalytic reactivity in H$_2$O$_2$-production rates than the as-prepared NiFe$_2$O$_4$. Thus, both of the bottom-up method starting from a molecular complex [Ir(Cp')(H$_2$O)$_2$]^{2+} and the top-down method starting from as-prepared NiFe$_2$O$_4$ to obtain nanoparticles with smaller size resulted in improvement of the catalytic reactivity for the photocatalytic production of H$_2$O$_2$ from water and dioxygen.

Introduction

The rapid and unsustainable use of fossil fuels has led to increased attention to development of zero-carbon emission fuels, particularly hydrogen, utilizing renewable energy sources.\textsuperscript{1-7} Solar energy is obviously the most abundant among renewable energy sources under consideration. Thus, extensive efforts have been devoted to produce hydrogen by water splitting (eqn 1), which is highly endergonic with the free energy change of

$$2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2 \quad \Delta G^\circ = 474 \text{kJ mol}^{-1} \quad (1)$$

$\Delta G^\circ = 474 \text{kJ mol}^{-1}$ which is provided by solar energy.\textsuperscript{8-12} In this case, however, a method for separating the simultaneously produced H$_2$ and O$_2$ remains to be developed to avoid possible explosion.\textsuperscript{13} In addition, the storage of hydrogen at reasonable energy density poses a technical and economic challenge due to its low volumetric energy.\textsuperscript{14,15}

In contrast to hydrogen, hydrogen peroxide (H$_2$O$_2$) is miscible in water, and therefore it can be an ideal energy carrier alternative to hydrogen, because H$_2$O$_2$ can be used as a fuel for one-compartment fuel cell.\textsuperscript{16-23} The output potential of a H$_2$O$_2$ fuel cell theoretically achievable is 1.09 V which is comparable...
with that of a hydrogen fuel cell (1.23 V).\textsuperscript{16-17} Thus, a combination of H\textsubscript{2}O\textsubscript{2} production using solar energy and power generation with a H\textsubscript{2}O\textsubscript{2} fuel cell provides an ideally sustainable solar fuel.\textsuperscript{16-17} It is desired to produce H\textsubscript{2}O\textsubscript{2} from H\textsubscript{2}O and O\textsubscript{2} (eqn (2)), which is highly endergonic with the free energy change of $\Delta G^\circ = 210$ kJ mol$^{-1}$.\textsuperscript{16}

$$2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{H}_2\text{O}_2 \quad \Delta G^\circ = 210 \text{ kJ mol}^{-1} \quad (2)$$

We have recently reported photocatalytic production of H\textsubscript{2}O\textsubscript{2} from H\textsubscript{2}O and O\textsubscript{2} by combining photoreduction of O\textsubscript{2} with a Ru photosensitiser and water oxidation with Ir(OH)$_3$ nanoparticles as water oxidation catalysts (WOCs) in the presence of Sc$^{3+}$ in water under visible light irradiation.\textsuperscript{24} In order to improve the photocatalytic reactivity of H\textsubscript{2}O\textsubscript{2} production from H\textsubscript{2}O and O\textsubscript{2}, it is required to employ more efficient WOCs. Extensive efforts have so far been devoted to develop efficient WOCs using transition metal complexes.\textsuperscript{25-45} In particular, a series of mononuclear iridium(III) complexes with $\eta^3$-pentamethycyclopentadienyl ligand (Cp*) have been reported to act as efficient WOCs, which are more active than rhodium complexes.\textsuperscript{36-49} The Cp* ligand is expected to provide an electron rich environment useful to stabilise reaction intermediates possessing high-valent oxidation state in the catalytic water oxidation by cerium ammonium nitrate, (NH$_4$)$_2$Ce(NO$_3$)$_6$, (CAN).\textsuperscript{46-49} Under the conditions of the catalytic water oxidation by CAN, however, the Cp* ligand of Ir complexes has been reported to be oxidised to produce IrO$_2$ or Ir(OH)$_3$ nanoparticles, which act as the actual reactive catalyst for water oxidation.\textsuperscript{50-54} The IrO$_2$ or Ir(OH)$_3$ nanoparticles have been reported to be more active than conventional IrO$_2$ prepared from H$_2$IrCl$_6$,55-61 Thus, in situ formation of a WOC provides a useful way to improve the catalytic reactivity for water oxidation.

We report herein the photocatalytic production of H\textsubscript{2}O\textsubscript{2} from H\textsubscript{2}O and O\textsubscript{2} using an Ir complex, [Ir(Cp*)(H$_2$O)$_3$]$^{2+}$, as a precursor of a water oxidation catalyst and [Ru($^{11}$Me$_2$phen)$_2$]$^{2+}$ (Me$_2$phen = 4,7-dimethyl-1,10-phenanthroline) as a homogeneous photocatalyst in the presence of Sc$^{3+}$ in water. The characterisation of the catalytically active species has revealed that [Ir(Cp*)(H$_2$O)$_3$]$^{2+}$ is converted to Ir(OH)$_3$ nanoparticles, which exhibit high catalytic reactivity for the photocatalytic water oxidation. Synthetic strategy for such Ir(OH)$_3$ nanoparticles from H$_2$IrCl$_6$ has not yet been established. Because Ir is a noble metal with limited natural supplies, it is desired to replace the noble metal in WOC by more earth-abundant metals such as Fe and Ni. In this context, we have also employed nanoparticles composed of earth abundant nickel and iron (NiFe$_2$O$_4$) instead of the Ir complex as a water oxidation catalyst for the photocatalytic production of H\textsubscript{2}O\textsubscript{2}. During the reaction, NiFe$_2$O$_4$ nanoparticles were formed from the corresponding as-prepared NiFe$_2$O$_4$. The effect of reaction conditions on the reactivity of the therein-formed nanoparticles from the Ir complex or NiFe$_2$O$_4$ is discussed in this paper.

**Results and discussion**

The photocatalytic production of H\textsubscript{2}O\textsubscript{2} was performed using [Ru($^{11}$Me$_2$phen)$_2$]$^{2+}$ as a photocatalyst for the two-electron reduction of O\textsubscript{2} and various Ir compounds as WOCs in the presence of Sc$^{3+}$ in distilled water as shown in Fig. 1a. Sc$^{3+}$ ion was reported to prohibit back electron transfer from O\textsubscript{2} to [Ru($^{11}$Me$_2$phen)$_2$]$^{2+}$ which is formed after photoinduced electron transfer to O\textsubscript{2} from an excited state of [Ru($^{11}$Me$_2$phen)$_2$]$^{2+}$ (vide infra).\textsuperscript{24} The initial rate of the H\textsubscript{2}O\textsubscript{2} production using [Ir(Cp*)(H$_2$O)$_3$]$^{2+}$ (red square in Fig. 1a) was 4.5 times faster than that using Ir(OH)$_3$ nanoparticles (blue circle in Fig. 1a) prepared from H$_2$IrCl$_6$ with the same amount of Ir. The rate of H\textsubscript{2}O\textsubscript{2} production using [Ir(Cp*)(H$_2$O)$_3$]$^{2+}$ was 4.4 times and 2.8 times higher than those using Ir(SO$_4$)$_2$ and [Ir(Cp*)(OH$_2$)bpyp(H$_2$O)$_3$]$^{2+}$ (bpyp = 4,4'-(OH)$_2$-2,2'-bipyridine), respectively. [Ir(Cp*)(H$_2$O)$_3$]$^{2+}$ had higher reactivity than Co complexes and a Co ion, which have been reported to act as highly active WOCs, as shown in Fig. 1b.\textsuperscript{62,63}

The quantum efficiency determined by using monochromatised light (450 nm) and solar energy conversion efficiency of the production of H\textsubscript{2}O\textsubscript{2} were determined to be 7.1 % and 0.063 %, respectively (Fig. S1† and Fig. S2†). The sigmoidal behaviour in the initial stage of the H\textsubscript{2}O\textsubscript{2} production with [Ir(Cp*)(H$_2$O)$_3$]$^{2+}$ (Fig. 2, green) indicates that [Ir(Cp*)(H$_2$O)$_3$]$^{2+}$ acts as a precatalyst to produce catalytically more active species during the photocatalytic production of H\textsubscript{2}O\textsubscript{2}.

The sigmoidal behaviour was more pronounced when the photocatalytic production of H\textsubscript{2}O\textsubscript{2} was performed at 278 K as shown in Fig. 2 (red circle), where the results at higher temperatures are compared. The initial rate of H\textsubscript{2}O\textsubscript{2} production increases with increasing temperature (Fig. 2), but the maximum H\textsubscript{2}O\textsubscript{2} concentration decreased because of enhanced decomposition of H\textsubscript{2}O\textsubscript{2}.

The formation of nanoparticles was observed by transmission electron microscopy (TEM) measurements. TEM

![Fig. 1](image_url)
images of the particles (Fig. S3†) showed that the diameters of the particles increase by extending the reaction time. The formation of nanoparticles was also confirmed by dynamic light scattering (DLS) measurements as shown in Fig. 3. The size of nanoparticles formed after 12 h photoirradiation at 278 K was 21 nm, whereas the size increased to 240 nm after 36 h photoirradiation. The large-size particles (450 nm) were obtained after 12 h photoirradiation at 333 K. Thus, the size of the particles depends on the photoirradiation time and temperature. During photocatalytic H₂O₂ production, the size of the nanoparticles (21 nm) increases to 240 nm after 36 h (Fig. 3a and 3b) and rate of the reaction decreases (Fig. 2, green line) under irradiation of visible light at room temperature. The deceleration of the reaction rate may be ascribed to the decrease in surface area of the nanoparticles with increasing the size of the nanoparticles. [Ir(Cp')(H₂O)]²⁺ has been reported to be efficiently oxidised by CAN, and TG/DTA and XPS measurements of nanoparticles produced after the water oxidation suggested that the nanoparticles were composed of Ir(OH)₆.¹¹ XPS measurements of the nanoparticles centrifugally recovered from the reaction solution after the H₂O₂ production reaction were performed for the energy regions of Ir 4f, O 1s and C 1s with reference to commercially available IrO₂ (Fig. S4†), which suggested that the formed nanoparticles are also composed of Ir(OH)₃. Since the binding energy of Ir 4f2/3 reflects the valence of Ir ions, the value was determined to be 61.9 eV for the Ir(OH)₃ nanoparticles, which is close to the reported value for Ir^{III} (62.0 eV).⁶² These values were significantly different from that for Ir^{II} (61.0 eV) or Ir^{IV} (63.7 eV).³⁸,⁶²,⁶⁷ The binding energy for O 1s of Ir(OH)₃ nanoparticles (531.9 eV) was shifted from that of IrO₂ (530.2 eV) due to OH moiety as reported previously.¹⁴ TEM images of the Ir(OH)₃ nanoparticles revealed that the size of the Ir(OH)₃ nanoparticles (10–20 nm) derived from [Ir(Cp')(H₂O)]²⁺ was smaller than that of Ir(OH)₃ (30–100 nm) derived from H₂IrC₁₆ (Fig. S5†). The higher catalytic reactivity of Ir(OH)₃ nanoparticles derived from [Ir(Cp')(H₂O)]²⁺ may result from the smaller size of the nanoparticles as compared with that derived from H₂IrC₁₆.

The dependence of the photocatalytic reactivity for H₂O₂ production on the concentration of [Ru²⁺(Me₂phen)]³⁺ was examined as shown in Fig. 4a. The photocatalytic reactivity decreased with decreasing the concentration of [Ru²⁺(Me₂phen)]³⁺, however, the highest TON based on [Ru²⁺(Me₂phen)]³⁺ was determined to be 898 after 94 h photoirradiation when the concentration of [Ru²⁺(Me₂phen)]³⁺ was reduced to 1.0 µM, which is much higher than that reported for the photocatalytic H₂O₂ production using Ir(OH)$_3$ as a WOC (307).²⁴

The dependence of the photocatalytic reactivity for H₂O₂ production on the concentration of Sc⁴⁺ was also examined as shown in Fig. 4b. The photocatalytic reactivity increased with increasing the concentration of Sc⁴⁺. This is because Sc⁴⁺ inhibits back electron transfer from O₂* to [Ru²⁺(Me₂phen)]³⁺, which is generated by photoinduced electron transfer from the excited state of [Ru²⁺(Me₂phen)]³⁺ to O₂ as reported previously.²⁴

The dependence of the photocatalytic reactivity of H₂O₂ production on concentration of [Ir(Cp')(H₂O)]²⁺ is shown in Fig. 4c. The highest TON based on [Ir(Cp')(H₂O)]²⁺ was determined to be 23 after 20 h photoirradiation when 50 µM of [Ir(Cp')(H₂O)]²⁺ was employed in the photocatalytic H₂O₂ production. The photocatalytic reactivity increased with increasing concentration of [Ir(Cp')(H₂O)]²⁺, but it decreased through the maximum value with further increase in concentration of [Ir(Cp')(H₂O)]²⁺ as shown in Fig. 4d. The
decrease in the rate of H₂O₂ production may result from the catalytic decomposition of H₂O₂ with [Ir(Cp*)(H₂O)₂]²⁺ as shown in Fig. 5a. When a high concentration of [Ir(Cp*)(H₂O)₂]²⁺ (e.g., 1000 μM) was employed in the photocatalytic production of H₂O₂, a part of [Ir(Cp*)(H₂O)₂]²⁺ may remain without the full conversion to Ir(OH)₃ nanoparticles. When a low concentration of [Ir(Cp*)(H₂O)₂]²⁺ was employed, all of [Ir(Cp*)(H₂O)₂]²⁺ may be oxidised to produce Ir(OH)₃ nanoparticles during the photocatalytic reaction. Formed Ir(OH)₃ nanoparticles are less reactive toward H₂O₂ decomposition as compared to [Ir(Cp*)(H₂O)₂]²⁺ (Fig. 5).

The conversion of [Ir(Cp*)(H₂O)₂]²⁺ to Ir(OH)₃ during the photocatalytic production of H₂O₂ may be associated with the oxidation of the Cp* ligand by O₂. The full oxidation of Cp* is expected to produce 10 equivalents of CO₂ and 8 equivalents of H₂O₂ (eqn (3)). During the photocatalytic production of H₂O₂,

\[
\text{C₁₀H₁₅} + 18\text{O}_₂ + \text{H}^+ \rightarrow 10\text{CO}_₂ + 8\text{H}_₂\text{O}_₂ \quad (3)
\]

CO₂ evolution was observed as shown in Fig. 6a. However, the yield of CO₂ based on eqn (3) is only 1 %. Thus, the Cp* ligand is only partially oxidised to CO₂. The amount of H₂O₂ that is expected to be produced from Cp* calculated based on eqn(3)

![Fig. 4](image4.png)

![Fig. 5](image5.png)

![Fig. 6](image6.png)
which oxidises water to form O₂ and [Ru⁴⁺(Me₂phen)₃]²⁺. Back electron transfer from O₂⁻ to [Ru⁴⁺(Me₂phen)₃]³⁺ and decomposition of H₂O₂ by NiFe₂O₄ are retarded in the presence of Sc³⁺ (vide supra, Fig. S6†). The photocatalytic production of H₂O₂ was performed using [Ru⁴⁺(Me₂phen)₃]²⁺ as a photosensitiser and NiFe₂O₄ as a WOC (Fig. 7a), which exhibited an induction period at the initial reaction time (black line in Fig. 7b). From the resulting solution, NiFe₂O₄ nanoparticles were recovered by centrifugation after 12 h photoirradiation and reused as WOCs. With the use of the recovered NiFe₂O₄ as WOC, the induction period was not observed (blue line in Fig. 7b). The diameter of nanoparticles measured by DLS decreased from 1300 nm to 620 nm after 12 h reaction as shown in Fig. 7c, suggesting that the induction period originates from the decrease in the diameter during the reaction.

In order to determine the conditions necessary for the size change of as-prepared NiFe₂O₄, DLS measurements of NiFe₂O₄ in an aqueous solution containing Sc³⁺ (100 mM) were performed under dark (Fig. S7†). The diameter of NiFe₂O₄ particle was decreased to 710 nm, which is in good agreement with the size observed for the particles in the reaction suspension, although the rate of the size change was significantly reduced to 1/20 of that under photoirradiation. This result indicates that the rate of the size change was accelerated with photoirradiation. Then, the size change of NiFe₂O₄ was also examined in an aqueous HNO₃ (1.0 M) solution (Fig. S8†) because Fe and Ni ions can be soluble in highly acidic solutions. However, the deceleration of the rate of the size change was also observed in the HNO₃ solution under dark conditions, as the diameter of NiFe₂O₄ did not change even after 24 h under dark conditions (Fig. S9†). These results indicate that the presence of Sc³⁺ is necessary for the size change, thus, dependence of the rate of the size change on the concentration of Sc³⁺ ranging from 0.1 to 100 mM was examined under room light at 353 K. The fastest size-decreasing rate was observed for an aqueous solution containing 10 mM of Sc³⁺ (Fig. S10†). Under the conditions, the size of formed nanoparticles became as small as 91 nm after 12 h (Fig. 8).

The nanoparticles were characterised by powder XRD to confirm that they kept the ferrite structure (Fig. S11†). It was also confirmed that the as-prepared NiFe₂O₄ was not dissolved to yield Fe ions by addition of phenanthroline and the reduced form of β-nicotinamide adenine dinucleotide disodium salt hydrate (NADH) as a reductant to the supernatant to produce [Fe²⁺(phen)]³⁻ which has strong absorption in visible region (λₘₘₙ = 508 nm, ε = 1.1 × 10⁴ M⁻¹ cm⁻¹) and therefore easy to be detected (Fig. S12†). It was also supported by the fact that NiFe₂O₄ nanoparticles used in the reaction solution were recovered by centrifugation in high yield (87%). TEM images of the NiFe₂O₄ particles manifested that the as-prepared NiFe₂O₄ has the form of aggregated smaller primary particles (Fig. S13†). The nanoparticles were formed by dissociation of the small particles that consist of a few primary particles as depicted in Scheme 2.

Photocatalytic production of H₂O₂ was performed using NiFe₂O₄ nanoparticles as the WOCs in the presence of [Ru⁴⁺(Me₂phen)₃]²⁺ and Sc³⁺ under visible light irradiation (λ > 420 nm) (Fig. 9a and Fig. S14†). The quantum efficiency determined by using monochromatised light (450 nm) and solar...
energy conversion efficiency were determined to be 2.7 % and 0.088 %, respectively, using NiFeO$_2$ nanoparticles with the diameter of 90 nm (Fig. S15† and Fig. S16†). To reuse the nanoparticles after H$_2$O$_2$ production ceased, an aliquot of an aqueous solution containing high concentration of [Ru($^{10}$Me$_2$phen)$_3$]$_2^+$ was added to the reaction suspension repeatedly, in which the amount of [Ru($^{10}$Me$_2$phen)$_3$]$_2^+$ added to the starting suspension at each run was calculated in terms of the concentration increasing of 200 $\mu$M. The concentration of H$_2$O$_2$ in the resulting suspension increased to as high as 3.3 mM, assuring the high stability of the nanoparticles as WOCs (Fig. 9b). The initial rate of H$_2$O$_2$ production was accelerated 22 times and 33 times when using NiFeO$_2$ nanoparticles with diameters of 120 nm and 91 nm, respectively, as compared to the as-prepared NiFeO$_2$ with a diameter of 1300 nm (Fig. 9a). This increase in reactivity could be due to simple increase in surface area, therefore, surface areas for nanoparticles were estimated from the respective diameters by eqn (S5)† and compared with respective initial rates of H$_2$O$_2$ production (Fig. 10). The linear relationship between surface areas and initial rates of H$_2$O$_2$ production observed in Fig. 10 indicates that the reactivity of each active site for water oxidation in the surface of NiFeO$_2$ remains unchanged irrespective of the particle size.

**Conclusions**

The reactivity of water oxidation catalysts for the photocatalytic production of H$_2$O$_2$ from H$_2$O and O$_2$ with [Ru($^{10}$Me$_2$phen)$_3$]$_2^+$ and Sc$^{3+}$ was improved by using [Ir(Cp')($^{10}$H$_2$O)$_2$]$^{2+}$ as a precatalyst, which was converted to Ir(III)$_2$ nanoparticles during the photocatalytic reaction, as compared with that using Ir(OH)$_3$ nanoparticles derived from H$_2$IrCl$_6$. The enhanced catalytic reactivity of Ir(OH)$_3$ nanoparticles results from the smaller size of nanoparticles produced in situ as compared with Ir(OH)$_3$ nanoparticles derived from H$_2$IrCl$_6$. The Cp$^*$ ligand of [Ir(Cp')($^{10}$H$_2$O)$_2$]$^{2+}$ was partially oxidised to CO$_2$ during the photocatalytic reaction and remaining organic residues may act as capping reagents to protect further aggregation of Ir(III)$_2$ nanoparticles. NiFeO$_2$ nanoparticles, which are composed of much more earth abundant metals than Ir, also acted as a water oxidation catalyst for the photocatalytic production of H$_2$O$_2$ with [Ru($^{10}$Me$_2$phen)$_3$]$_2^+$ in the presence of Sc$^{3+}$ in water. In this case, the size of NiFeO$_2$ nanoparticles decreased during the photocatalytic reaction to increase the catalytic reactivity of water oxidation. Thus, both a bottom-up method starting from a metal complex precatalyst ([Ir(Cp')($^{10}$H$_2$O)$_2$]$^{2+}$) to produce Ir(OH)$_3$ nanoparticles with small size and a top-down method starting from as-prepared NiFeO$_2$ to obtain smaller NiFeO$_2$ nanoparticles provide promising strategies to develop more efficient water oxidation catalysts for photocatalytic production of H$_2$O$_2$ from H$_2$O and O$_2$.

**Experimental section**

**Materials**

All chemicals commercially available were used without further purification unless otherwise noted. H$_2$IrCl$_6$·nH$_2$O (99.99%) was purchased from Furuya Metal. RuCl$_3$ (38.220 wt% Ru) was purchased from Tanaka Kikinzoku Kogyo K.K. 4,7-dimethyl-1,10-phenanthroline (Me$_2$phen, 98%), Ag$_2$SO$_4$ (99.9%) and (NH$_4$)$_2$SO$_4$ (99.9%) were supplied from Aldrich Chemicals. Pentamethyloctanediene was obtained from Kanto Chemical Co., Inc. Oxo[5,10,15,20-tetra(4-
pyridyl)porphinato]titanium(IV) ([TiO(tpyp)]) and NADH were supplied from Tokyo Chemical Industry Co., Ltd. (TCI). Sc(NO$_3$)$_3$·6H$_2$O (99.9%) was supplied from Mitsuwa Chemicals Co., Ltd. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore, Direct-Q 3 UV). [Ir(Cp)$^*$](H$_2$O)$_3$SO$_4$ was prepared by following the reported method.\(^{48}\)

**Synthesis of NiFe$_2$O$_4$**

NiFe$_2$O$_4$ was synthesized according to the literature.\(^{57,60}\) To an aqueous solution (24 mL) containing NiCl$_2$·6H$_2$O (2.0 mmol, 0.46 g) and Fe(NO$_3$)$_3$·9H$_2$O (4.0 mmol, 1.6 g) was added KOH solution (2.0 M, 24 mL) with magnetic stirring at 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 °C 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 °C for 10 h.

**Formation of NiFe$_2$O$_4$ nanoparticles**

Typically, an aqueous suspension (3.0 mL) containing Sc(NO$_3$)$_3$ and NiFe$_2$O$_4$ (0.50 mg) was stirred continuously for 3 h, 6 h or 12 h at 80 °C under room light to yield 220 nm, 120 nm and 91 nm nanoparticle respectively. The suspension was used for H$_2$O$_2$ production reaction after addition of [Ru$_2^3$(Me$_2$phen)$_3^2$]$_2$ and Sc(NO$_3$)$_3$. NiFe$_2$O$_4$ nanoparticles used as a sample for powder XRD measurements were prepared by immersing as-prepared NiFe$_2$O$_4$ (5.1 mg) in an aqueous solution (31 mL) of Sc(NO$_3$)$_3$ for 12 h. The resulting powder was collected by centrifugation and washed with water for 3 times. The yield of NiFe$_2$O$_4$ nanoparticle was 87%.

**Quantitative measurements of Fe$^{II}$ and Fe$^{III}$ ions**

An aqueous suspension containing as-prepared NiFe$_2$O$_4$ and Sc(NO$_3$)$_3$ was stirred at 80 °C for 12 h for formation of active NiFe$_2$O$_4$ nanoparticles as discussed in previous paragraph. After formation of NiFe$_2$O$_4$ nanoparticles, the supernatant of the suspension was examined for the presence of Fe$^{II}$ or Fe$^{III}$ ions. The filtered supernatant was diluted by water so that the solution may contain 300 mM of Fe ion if NiFe$_2$O$_4$ was dissolved completely. UV-Vis spectra were measured using a Hewlett Packard 8453 diode array spectrometer, for the diluted supernatant, the diluted supernatant in the presence of 1,10-phenanthroline (phen) (4.5 mM) and the diluted supernatant in the presence of phen (4.5 mM) and NADH (1.5 mM) to reduce Fe$^{III}$ that may have formed. Measured UV-Vis spectra were compared with the UV-Vis spectra of [Fe$^{II}$(phen)$_3$]$_2^{2+}$ (100 mM).

**Photocatalytic reactions**

[Ir(Cp)$^*$](H$_2$O)$_3$SO$_4$ or NiFe$_2$O$_4$ was introduced to distilled water (3.0 mL) containing [Ru$^{II}$(Me$_2$phen)$_3$]SO$_4$ and Sc(NO$_3$)$_3$ in a quartz cuvette with light path length of 1.0 cm. The solution was bubbled with oxygen gas for ~30 min. The solution containing photocatalyst was irradiated with a xenon lamp (USHIO Optical Module US-501XAMQ) through a cut-off filter (Asahi Techno Glass L42) transmitting $\lambda > 420$ nm at room temperature.

**Quantification of produced H$_2$O$_2$**

From spectroscopic titration with an acidic solution of [TiO(tpyp)$_2$]$_{10}^-$ complex (Ti-TPyP reagent), the amount of produced H$_2$O$_2$ was determined.\(^{30}\) The [TiO(tpyp)] complex (34 mg) was dissolved in 1.0 L of 50 mM hydrochloric acid and the solution was used as a Ti-TPyP reagent. An aliquot (e.g., 100 μL) of the reaction solution was diluted with water and 0.25 mL of the sample solution was mixed with 0.25 mL of 4.8 M perchloric acid and 0.25 mL of the Ti-TPyP reagent. After 5 min at room temperature, the mixture was diluted to 2.5 mL with water and used for the spectroscopic measurement. The absorbance at $\lambda = 434$ nm was measured by using a Hewlett Packard 8453 diode array spectrometer ($A_\lambda$). In the similar manner, a blank solution was prepared by adding distilled water in place of the sample solution in the same volume with its absorbance designated as $A_0$. The difference in absorbance was determined by following the equation: $\Delta A_{434} = A_\lambda - A_0$. Based on $\Delta A_{434}$ and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.\(^{30}\)

**Determination of the quantum yield**

Quantum yields (QYs) of the photocatalytic production of hydrogen peroxide ($\Phi$) were determined under irradiation of monochromatised light using a Shimadzu spectrofluorophotometer (RF-5300PC) through a band-pass filter transmitting $\lambda = 450$ nm, and estimated as

$$\text{QY} \text{ (})\%\text{) } = \left( \frac{2 \times R \times I}{\Phi} \right) \times 100$$

where $R$ (mol s$^{-1}$) and $I$ (einstein s$^{-1}$) represent the H$_2$O$_2$ production rate and the light intensity, respectively. Two photons are required for the electronic transition of [Ru$^{II}$(Me$_2$phen)$_3$]$_2^{2+}$ photosensitiser in order to produce a hydrogen peroxide through two-electron reduction of one molecule of oxygen. When all of the photons are fully utilized to produce hydrogen peroxide, QY reaches 100%. Therefore, the coefficient of the right-hand side in eqn (4) is 2 for this photocatalytic system. The total number of incident photons was measured by a standard method using an actinometer, potassium ferrioxalate, K$_3$[Fe$^{III}$(C$_2$O$_4$)$_3$], in H$_2$O at room temperature under photoirradiation of a Shimadzu spectrophotometer (RF-5300PC) through a band-pass filter transmitting $\lambda = 450$ nm (slit width of 5.0 mm) at room temperature. For the same quartz cuvette with light path length of 1.0 cm with 3.0 mL solution as used in the production of hydrogen peroxide experiments, the rate of photon flux of the incident light ($I$) was determined to be $7.40 \times 10^{-10}$ einstein s$^{-1}$.

**Quantification of evolved CO$_2$**

[Ir(Cp)$^*$](H$_2$O)$_3$SO$_4$ (100 μM) was added to distilled water (3.0 mL) containing [Ru$^{II}$(Me$_2$phen)$_3$]SO$_4$ (20 μM) and Sc(NO$_3$)$_3$.
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Notes and references
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