Electronic Supplementary Information for

Efficient Water Oxidation by Cerium Ammonium Nitrate with [Ir^{III}(Cp*)(4,4'-bishydroxy-2,2'-bipyridine)(H$_2$O)]$^{2+}$ as a Precatalyst

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Synthesis of Ir containing compounds

[Ir^{III}(Cp*){4,4'-(OH)$_2$-2,2'-bpy}(H$_2$O)]SO$_4$ (1) An aqueous solution (30 mL) of [Ir(Cp*)(H$_2$O)$_3$]SO$_4$ (400 mg, 0.84 mmol) and 4,4'-dihydroxy-2,2'-bipyridine (158 mg, 0.84 mmol) was stirred at 40 ℃ for 12 h. The formed yellow crystals were collected by filtration to yield **1** (400 mg, 75%). ^{1}H NMR (300 MHz, D$_2$O): δ = 1.64 ppm (s, 15H), 7.13 (dd, J = 6.4, 2.6 Hz, 2 H), 7.66 (d, J = 2.6 Hz, 2H), 8.70 (d, J = 6.4 Hz, 2H); ESI-MS: m/z = 515 [M–SO$_4$–H$_2$O–H]$^+$.

[Ir^{III}(Cp*){4,4'-(OMe)$_2$-2,2'-bpy}(H$_2$O)]SO$_4$ (2) An aqueous solution (30 mL) of [Ir(Cp*)(H$_2$O)$_3$]SO$_4$ (192 mg, 0.40 mmol) and 4,4'-dimethoxyl-2,2'-bipyridine (86 mg, 0.40 mmol) was stirred at 40 ℃ for 12 h. The formed yellow crystals were collected by filtration to yield **2** (223 mg, 85%). ^{1}H NMR (300 MHz, D$_2$O): δ = 1.67 (s, 15H), 4.11 (s, 6H), 7.41 (dd, J = 6.6, 2.2 Hz, 2H), 7.98 (d, J = 2.2 Hz, 2H), 8.90 (d, J = 6.6 Hz, 2H).

[Ir^{III}(Cp*)(4,4'-Me$_2$-2,2'-bpy)(H$_2$O)]SO$_4$ (3) An aqueous solution (30 mL) of [Ir(Cp*)(H$_2$O)$_3$]SO$_4$ (192 mg, 0.40 mmol) and 4,4'-dimethyl-2,2'-bipyridine (74 mg, 0.40 mmol) was stirred at 40 ℃ for 12 h. The formed yellow crystals were collected by filtration to yield **3** (202 mg, 81%). ^{1}H NMR (300 MHz, D$_2$O): δ = 1.67 (s, 15 H), 2.65 (s, 6H), 7.71 (dd, J = 5.9, 1.0 Hz, 2H), 8.36 (br, 2H), 8.93 (d, J = 5.9 Hz, 2H).

[Ir^{III}(Cp*){4,4'-(COOH)$_2$-2,2'-bpy}(H$_2$O)]SO$_4$ (4) An aqueous solution (30 mL) of [Ir(Cp*)(H$_2$O)$_3$]SO$_4$ (192 mg, 0.40 mmol) and 2,2'-bipyridine-4,4'-dicarboxylic acid (98 mg, 0.40 mmol) was stirred at 40 ℃ for 12 h. The formed yellow crystals were collected by filtration to yield **4** (205 mg, 75%). ^{1}H NMR (300 MHz, D$_2$O): δ = 1.70 (s, 15H), 3.7–3.4 (br, 2H), 8.29 (dd, J = 5.9, 1.7 Hz, 2H), 9.01 (d, J = 1.5 Hz, 2H), 9.27 (d, J = 5.9 Hz, 2H).

Iridium hydroxide (5) and iridium oxide (5') The pH of an aqueous solution of H$_2$IrCl$_6$ was adjusted to ~10 by adding 5.0 M NaOH solution with vigorous stirring at 100 ℃. After 1.0 h stirring, precipitates appeared were collected by a centrifugation. Then, the precipitates were washed by water three times and dried *in vacuo* at room temperature and kept at 65 ℃ for 10 h (**5**). Iridium oxide (**5'**) was obtained by calcination of iridium hydroxide (**5**) at 600 ℃ for 3 h.
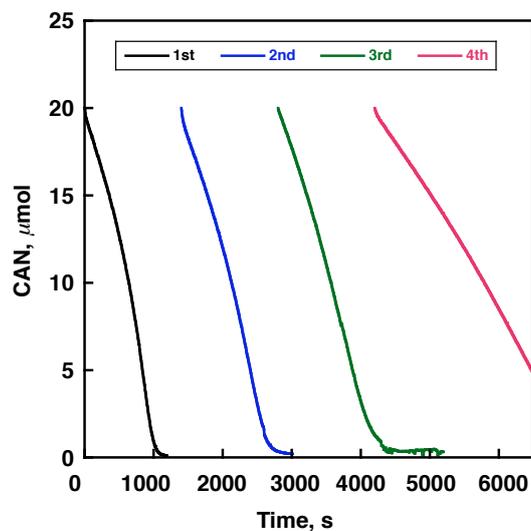
Fig. S1 Time course of concentration of CAN determined from the absorbance change at 420 nm in the catalytic water oxidation by CAN with the precatalyst **1** for repeated 4 cycles. The reaction solution (2.0 mL) contained 5.0 μM of **1**, 10 mM CAN and 0.10 M HNO$_3$.
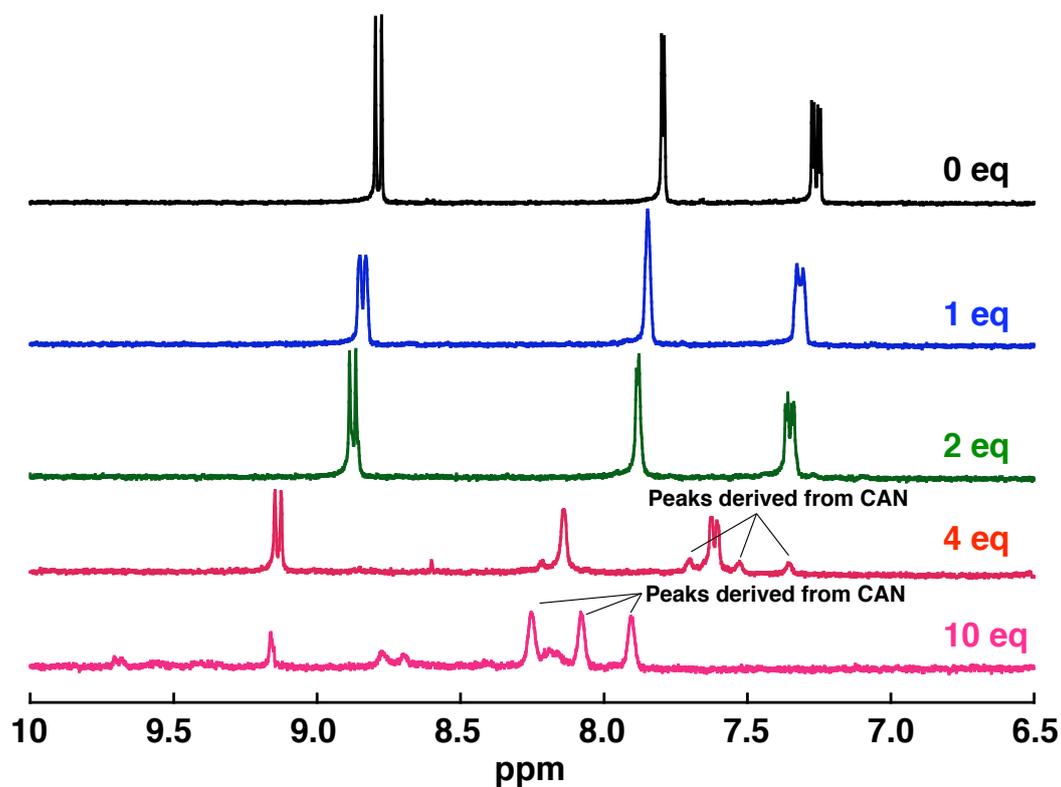

Fig. S2 ^{1}H NMR spectra (bpy region) of **1** (5.0 mM) in 0.1 M DNO$_3$ with 0 (black), 1 (blue), 2 (green), 4 (red) and 10 (pink) equiv. of CAN. TSP sealed in a glass capillary was used as an external standard.
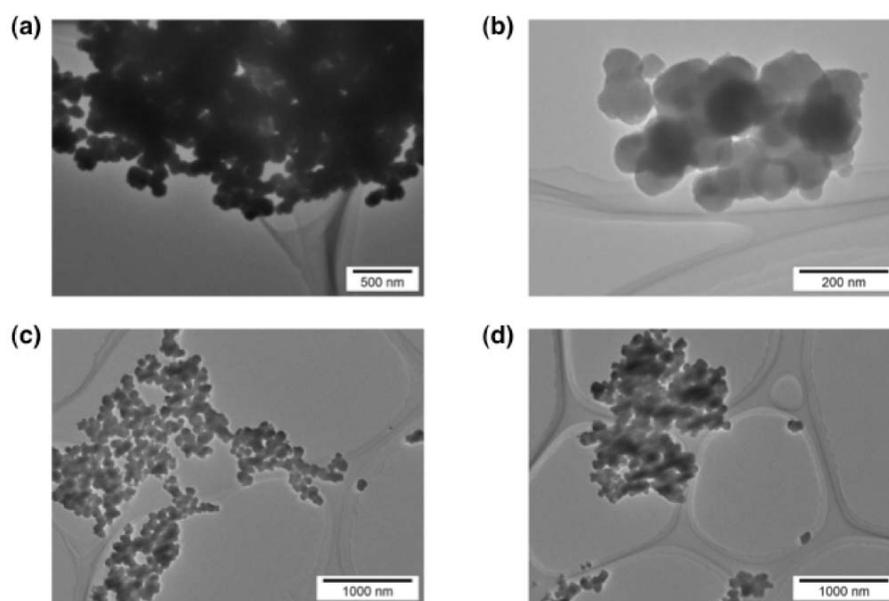
Fig. S3 TEM images at different magnifications (a-d) of iridium hydroxide (**5**) prepared by a conventional method.
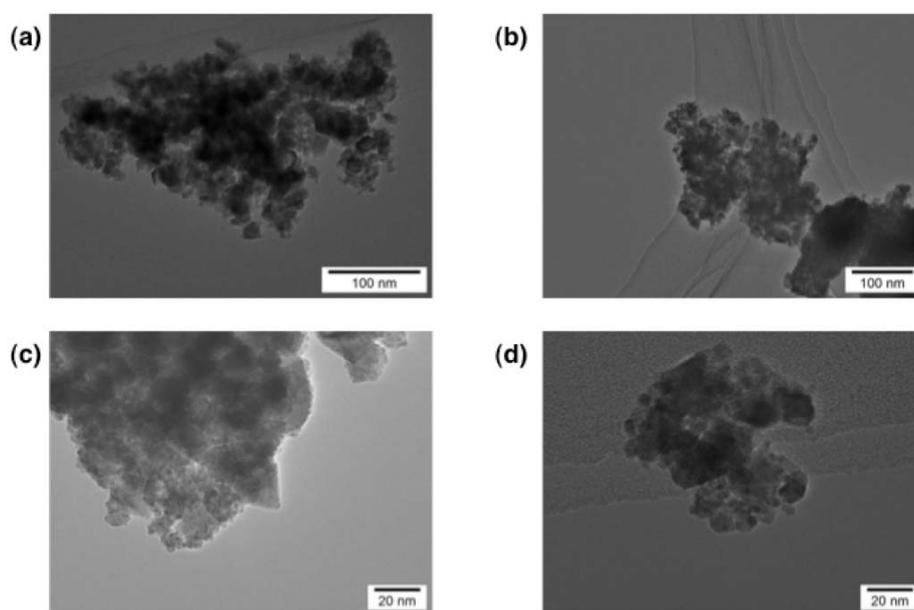

Fig. S4 TEM images at different magnifications (a-d) of iridium oxide (**5'**) prepared by a conventional method.
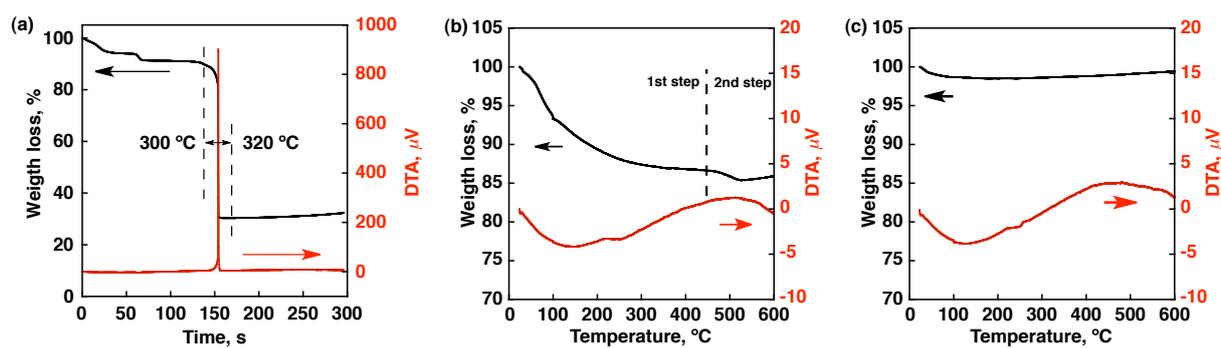
Fig. S5 TG/DTA data for (a) the Ir complex **1**, (b) iridium hydroxide (**5**), (c) iridium oxide (**5'**); TG curve (black) and DTA curve (red). The temperature increased from 25 °C to 100 °C (held at 100 °C for 10 min) and from 100 °C to 600 °C with a ramp rate of 2 °C / min.
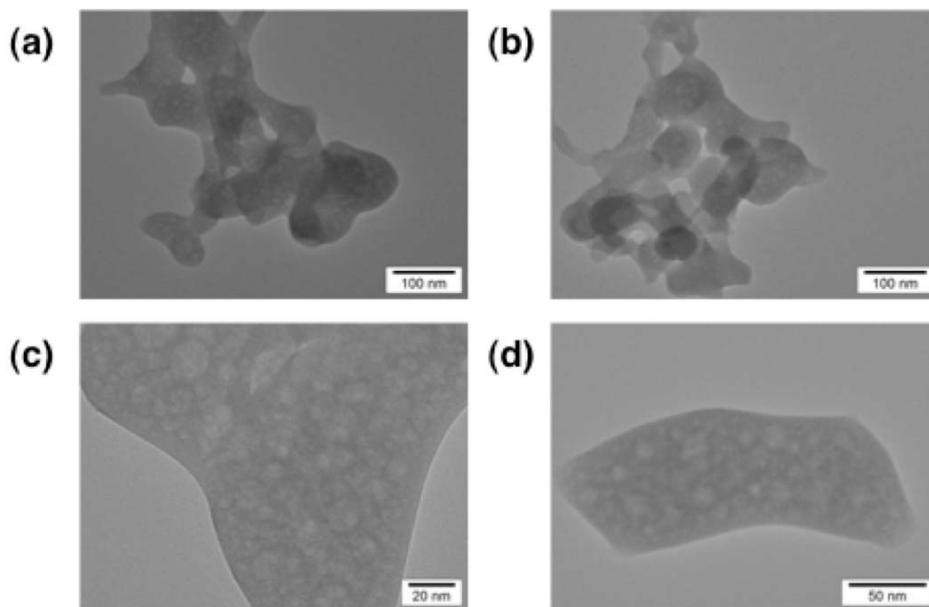

Fig. S6 TEM images at different magnifications (a-d) of the particles from $[IrCp^*(H_2O)_3]SO_4$ prepared by adding 10 equivalents of CAN to 2.0 mM of $[IrCp^*(H_2O)_3]SO_4$ in 0.10 M HNO_3.

Calculation of the numbers of Ir atoms on the particles surfaces

The numbers of surface Ir atoms were calculated by following equation.

$$N_s = [N_A \times (d / f_w)]^{2/3} \times \text{(number of Ir atoms in chemical formula)} \times \text{(catalyst weight)} \times \text{(SA)}$$

N_s : number of surface Ir atoms
N_A : the Avogadro's number
d : density of Ir-based metal oxide (IrO$_2$ for 11.7 g cm^{-3})
f_w: formula weight of Ir-based metal oxide
SA: BET surface area

	BET surface area (m^2 g^{-1})	number of surface Ir atoms in the reaction solution
Iridium hydroxide (**5**)	88	8.1×10^{17}
Iridium oxide (**5'**)	51	4.6×10^{17}