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Electronic Supplementary Information (ESI)

In situ formation of a molecular cobalt(III)/AgCl photocatalyst for visible-light water oxidation

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Experimental

Materials and reagents

$[Co(NH_3)_6]Cl_3$ (≥99.0%; Tokyo Chemical Industry Co.), $CoCl_2 \cdot 6H_2O$ (≥99.95%; Tokyo Chemical Industry Co.), $Co(NO_3)_2 \cdot 6H_2O$ (≥99.95%; Kanto Chemicals Co.), $AgNO_3$ (≥99.8%; Wako Pure Chemicals Co.), NaCl (≥99.5%; Kanto Chemicals Co.), hydrochloric acid (35.0–37.0%; Kanto Chemical Co.) and JRC-TIO-10 (Catalysis Society of Japan) were used without further purification. La_2O_3 (≥99.9%; Tokyo Chemical Industry Co.) was calcined in air at 1273 K for 2 h before use to remove residual hydroxide and/or carbonate phases. AgCl used for the photocatalytic reactions was prepared by adding $AgNO_3$ to a hydrochloric acid solution. $Na_2B_4O_7 \cdot 10H_2O$ (≥99.6%; Kanto Chemicals Co.), H_3BO_3 (≥99.5%; Kanto Chemicals Co.) and NaOH (≥95.0%; Kanto Chemicals Co.) were used to prepare an aqueous borate solution (0.50 M).

Characterization

XRD patterns were recorded on a Rigaku MiniFlex600 powder diffractometer equipped with a monochromated Cu Kα radiation source operated at 15 mA and 40 kV. UV–vis spectra were obtained using a spectrophotometer (V-670, JASCO). An integration sphere and spectraLon® (a reference) were used for diffuse-reflectance measurements.

Photocatalytic reactions

Photocatalytic O_2 evolution reactions were carried out using a gas closed-circulation system. In a typical experiment, a precatalyst (30 mg) such as $[Co(NH_3)_6]Cl_3$ was dissolved in an aqueous solution containing 5 mM $AgNO_3$ buffered at pH ~8 using 100 mg La_2O_3 in a top-irradiation reaction cell with a Pyrex window. When the reaction was conducted in an aqueous $Na_2B_4O_7$ solution, the pH of the reaction solution was adjusted by H_3BO_3 and/or NaOH. After the solution cell was degassed several times, ~3.3 kPa of Ar gas was introduced. The reaction cell was exposed to light from a 300 W Xe lamp (Ceramax, PE300BF) after the light passed through a water filter; an output current of 20 A was applied unless otherwise stated. The wavelength of the irradiation was controlled with a mirror (CM1) and a cutoff filter (L42, Y44, Y48, O54 or R60). The gases evolved by the reaction system were analysed by on-line gas chromatography (GL Science GC-3200).

For the $[Co(NH_3)_6]^{3+}/TiO_2$ combination, the reaction solution was prepared as follows. First, $[Co(NH_3)_6]Cl_3$ (30 mg; 112 μmol) and $AgNO_3$ (119 mg; 700 μmol), whose amounts were the same as those used under the standard condition, were reacted to form AgCl. The as-generated AgCl was filtered off, and a supernatant solution was obtained. Then, TiO_2 (50 mg) and La_2O_3 (100 mg) were added into the supernatant solution that contained $[Co(NH_3)_6]^{3+}$ and Ag^+ (and NO_3^-). The as-prepared suspension (140 mL) was used as the reaction solution.

The apparent quantum yield (AQY) for O_2 evolution was measured using the same reaction system, except for a MAX303 Xe lamp (Asahi Spectra Co.) used as the light source with a band-pass filter ($\lambda = 460$ nm), and was estimated as

$$\mathrm{AQY}(\%) = 4 \times R/I \times 100,$$

where R and I represent the O_2 evolution rate and the rate of incident photons, respectively. The total number of incident photons (ca. 16.6 mW) was measured using a calibrated Si photodiode.

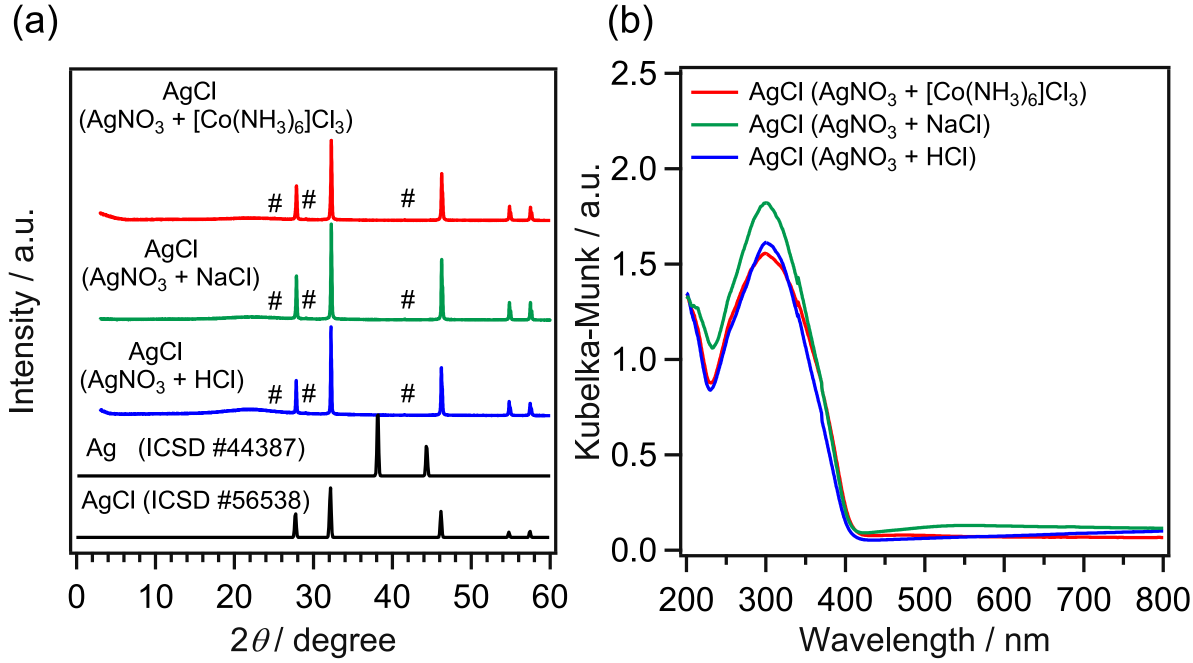

Fig. S1. (a) XRD patterns and (b) UV–visible diffuse-reflectance spectra of AgCl samples prepared by precipitation reaction using different precursors. The symbol # indicates unknown peaks.

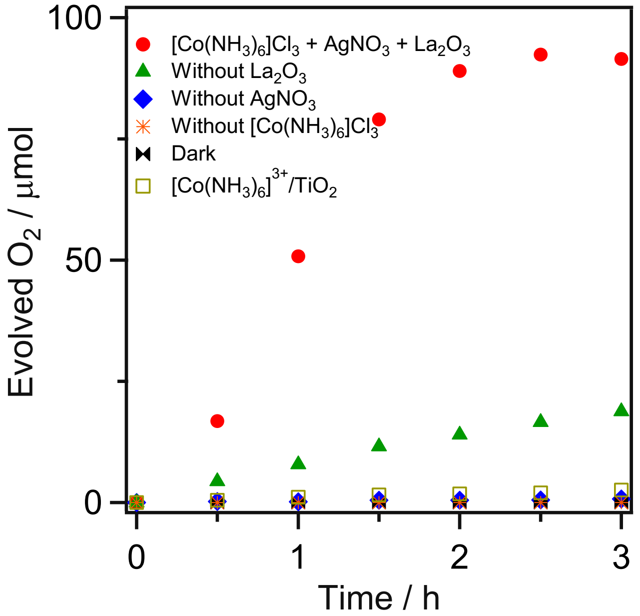

Fig. S2. Time courses of O_2 evolution over the $[Co(NH_3)_6]Cl_3$ system and systems in the absence of one of the components under visible light ($\lambda > 400$ nm). Reaction conditions: precatalyst, 30 mg; 5 mM aqueous $AgNO_3$ solution containing La_2O_3 (100 mg), 140 mL; light source, 300 W Xe lamp with a CM-1 mirror and a cutoff filter (L42).

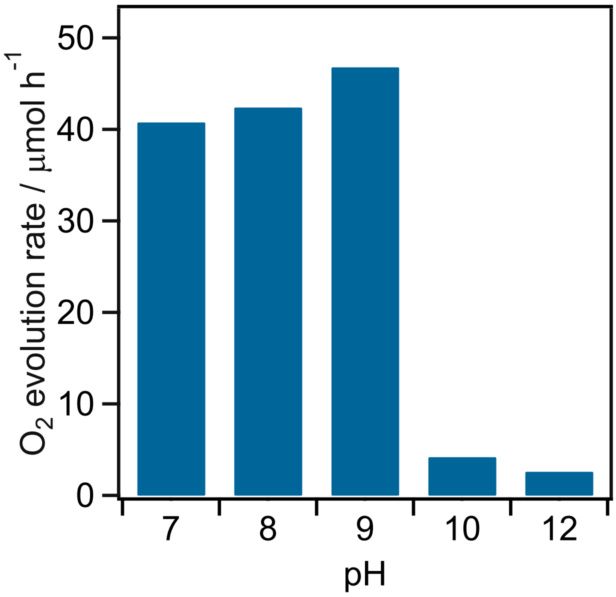

Fig. S3. Dependence of the rate of O_2 evolution over the $[Co(NH_3)_6]Cl_3$ system under visible light (λ > 400 nm) on the reaction pH. Reaction conditions: precatalyst, 30 mg; 5 mM aqueous $AgNO_3$ solution containing sodium tetraborate, 140 mL; light source, 300 W Xe lamp with a CM-1 mirror and a cutoff filter (L42).

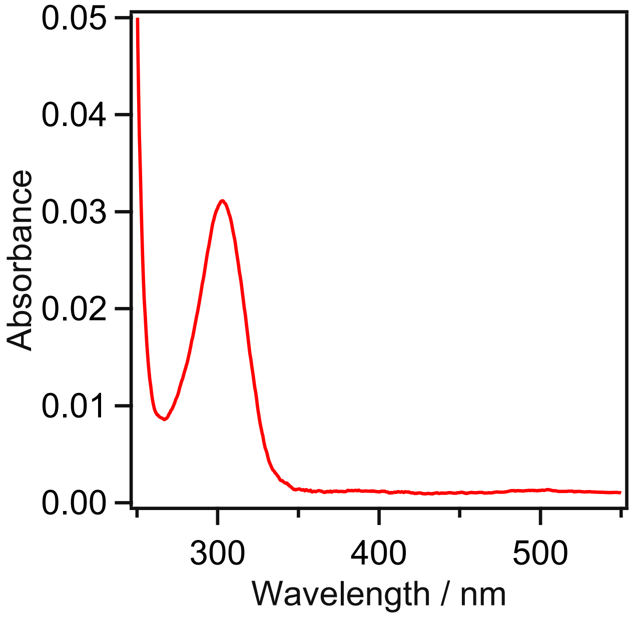

Fig. S4. UV-visible absorption spectrum of the supernatant solution (140 mL), which originated from an aqueous suspension containing $[Co(NH_3)_6]Cl_3$, $AgNO_3$, $Na_2B_4O_7 \cdot 10H_2O$ and NaOH (pH 10).

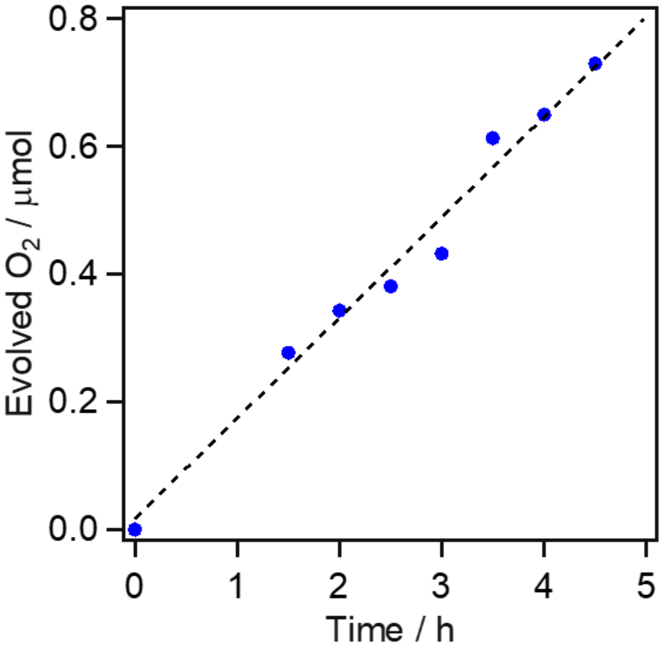

Fig. S5. Time course of O_2 evolution under monochromatized visible light (λ = 460 nm). Reaction conditions: precatalyst, $[Co(NH_3)_6]Cl_3$ (30 mg); 5 mM aqueous $AgNO_3$ solution containing La_2O_3 (100 mg), 140 mL; light source, 300 W Xe lamp with a band-pass filter.

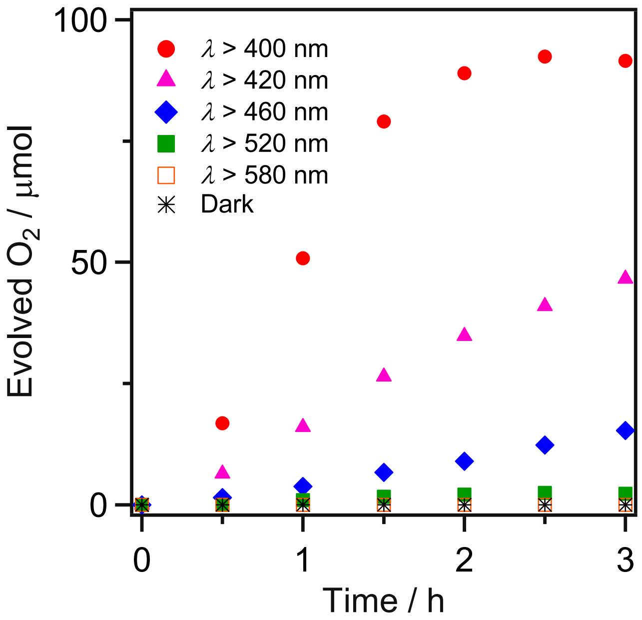

Fig. S6. Time courses of O_2 evolution over the $[Co(NH_3)_6]Cl_3$ system under visible light of different wavelengths. Reaction conditions: $[Co(NH_3)_6]Cl_3$, 30 mg; 5 mM aqueous $AgNO_3$ solution containing La_2O_3 (100 mg), 140 mL; light source, 300 W Xe lamp with a CM-1 mirror and cutoff filter (L42, Y44, Y48, O54 or R60).

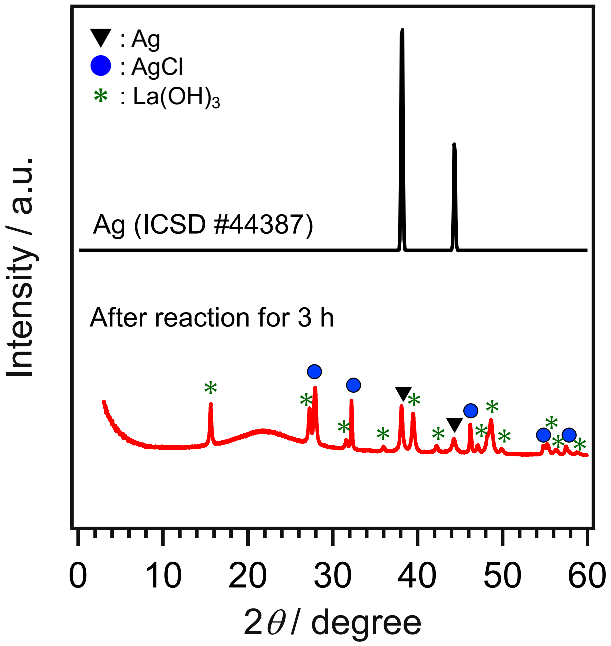

Fig. S7. XRD pattern of the obtained solid product after 3-h of reaction. Data for Ag reference is also shown. The generation of $La(OH)_3$ phase originates from hydrolysis of La_2O_3. $La(OH)_3$ and La_2O_3 are both insulators, which do not participate in any electron transfer event in the present photocatalytic system.

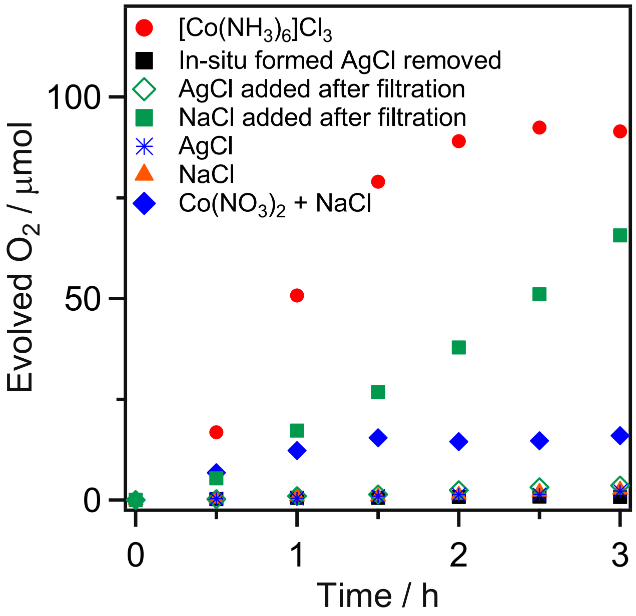

Fig. S8. Effects of the presence of AgCl in the reaction solution on the O_2 evolution activity ($\lambda > 400$ nm). Reaction conditions: precatalyst (20–30 mg); $[Co(NH_3)_6]Cl_3$ (30 mg), Homemade AgCl (50 mg), NaCl (20 mg), and $Co(NO_3)_2 \cdot 6H_2O$ (30 mg) + NaCl (20 mg); 5 mM aqueous $AgNO_3$ solution containing La_2O_3 (100 mg), 140 mL; light source, 300 W Xe lamp with a CM-1 mirror and a cutoff filter (L42).

Additional discussion on the photocatalyst deactivation. Although the decomposition of $[Co(NH_3)_6]Cl_3$ during the reaction appears to be one of the causes of the deactivation (Figs 2, S2, S6 and S8), we considered that the consumption of Ag^+ in the reaction solution is the main cause. The photocatalytic water oxidation reaction into O_2 using Ag^+ as an electron acceptor is described as

$$Ag^+ + e^- \rightarrow Ag$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

Therefore, 1 mol of O_2 molecules is formed from 4 mol of Ag^+ and the consumption of Ag^+ can lead to slower O_2 evolution. Given that 0.8 mM of $[Co(NH_3)_6]Cl_3$ and 5 mM of $AgNO_3$ in the 140 mL reaction solution react to stoichiometrically form AgCl, 364 μmol of Ag^+ remains in the solution and can produce 91 μmol of O_2. The total amount of O_2 evolved by the $[Co(NH_3)_6]Cl_3$ system was approximately 90 μmol, which corresponds to that expected from the reaction stoichiometry.

When 0.4 mM of $[Co(NH_3)_6]Cl_3$ was used for the photocatalytic reaction, the total amount of evolved O_2 exceeded that of $[Co(NH_3)_6]Cl_3$ (56 μmol), as shown in Fig. 9. This clearly shows the catalytic nature of this reaction.

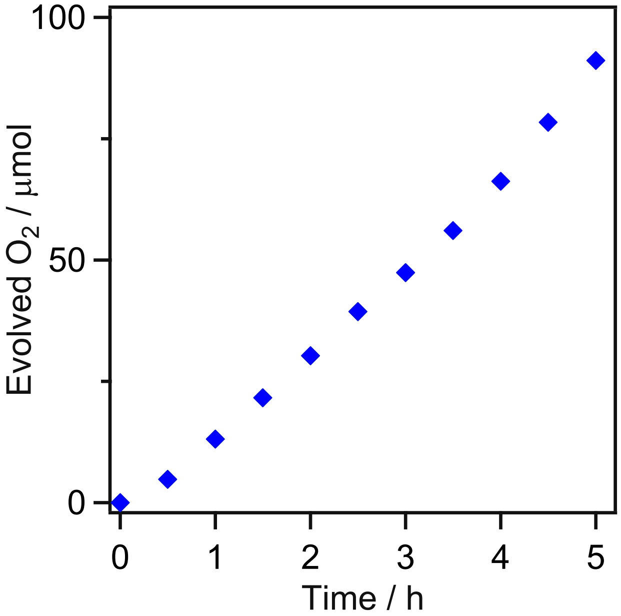

Fig. S9. Time course of O_2 evolution over the $[Co(NH_3)_6]Cl_3$ system under visible light ($\lambda > 400$ nm). Reaction conditions: $[Co(NH_3)_6]Cl_3$, 15 mg; 5 mM aqueous $AgNO_3$ solution containing La_2O_3 (100 mg), 140 mL; light source, 300 W Xe lamp with a CM-1 mirror and a cutoff filter (L42).