

Electronic Supporting Information

Efficient visible-light-driven water oxidation catalyzed by an all-inorganic copper-containing polyoxometalate

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Experimentals and calculation

Quantum yield calculation

Initial O₂ formation rate = 0.045 μmol.s⁻¹

Irradiation radius = 1 cm = 0.01 m

Photon flux = $\pi \times (0.01\text{m})^2 \times 1650 \mu\text{mol.m}^{-2}.\text{s}^{-1} = 0.527 \mu\text{mol.s}^{-1}$

$$\Phi_{\text{QY}}(\text{initial}) = 2 \times \frac{\text{initial O}_2 \text{ formation rate}}{\text{photon flux}} \times 100\%$$

$$= \frac{2 \times 0.045 \mu\text{mol} \cdot \text{s}^{-1}}{0.527 \mu\text{mol} \cdot \text{s}^{-1}} \times 100\%$$

$$= 17\%$$

Materials:

Purified water (18.2 MΩ cm) for the preparation of solutions was obtained from a Milli-Q system (Millipore, Direct-Q 3 UV), and all other chemicals and salts used were of the highest purity available from commercial sources.

Equipments and Apparatus

X-ray photoelectron spectra (XPS) were measured by ESCALAB250xi with X-Ray monochromatisation. Infrared spectra (2–4 wt% sample in KBr pellets) were recorded using a Bruker VERTEX 70v FT-IR spectrometer. UV-vis absorption spectra were recorded on Beijing Purkinje General Instrument Co.,Ltd. TU-1810 spectrophotometer equipped with a photomultiplier tube detector. Nanosecond transient absorption measurements were performed on an Edinburgh Instruments LP920-KS laser flash photolysis spectrometer, using an OPO laser source (OPOTEK Vibrant). Transient detection was obtained using a photomultiplier–oscilloscope combination (Hamamatsu R928P, Tektronix TDS3012C). The capillary electrophoretic were performed on Beckman, MDQ. equipped with a 32.karat 7.0 software. Dynamic light scattering (DLS) measurements were carried out using a Zatasizer Nano 3600 instrument (Malvern Instruments Ltd.). The post-reaction

solutions were evaluated three times consecutively.

The measurement of Quantum Yield

The quantum yields of O₂ evolution were determined for the photocatalytic water oxidation under the following conditions. A quartz flask containing a borate buffer solution (80 mM, pH 9.0, 15 mL) with **1** (20 μM), [Ru(bpy)₃]Cl₂ (1 mM) and Na₂S₂O₈ (5 mM) was irradiated by an interference filtered (Asahi spectra SV 490) from a LED source (420 < λ < 490 nm) described above. The photon flux of the incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum, 400-700 nm; sensitivity, 10-50 μV μmol⁻¹ m⁻² s⁻¹), affording a value to be 1650 μmol m⁻² s⁻¹.

Synthesis of [Ru(bpy)₃]Cl₂

Commercial RuCl₃·xH₂O is dried in an oven at 120 °C for 3 h. It is then finely ground in a mortar and returned to the oven for a further 1h prior to use. It is convenient to store the “dried” RuCl₃ at this temperature. “Dried” RuCl₃ (0.4 g, 1.93 mmol), 2, 2'-bipyridine (0.9 g, 5.76 mmol) and water (40 mL) are placed in a 100 mL flask fitted with a reflux condenser. Then sodium hypophosphite solution (2 mL) is added and the mixture heated at the boil for 30 min. During reflux, the initial green solution changes to brown and finally orange. It is filtered to remove traces of undissolved material and potassium chloride (12.6 g) added to the filtrate to precipitate the crude product. The solution and solid are then heated at the boil to give a deep red solution, which on cooling to room temperature yields beautiful, red plate-like crystals. These are filtered off, and air-dried. The yield is 0.9 g (63%). The product could be recrystallized from boiling water (~2.8mL·g⁻¹) and then air dried.

Synthesis of K₈-α-[SiW₁₁O₃₉] ligand

K₈-α-[SiW₁₁O₃₉] was synthesized according to reference.¹ Sodium metasilicate (2 g, 9 mmol) is dissolved with magnetic stirring at room temperature in 18mL of distilled water (Solution A). In a 250-mL beaker, containing a magnetic stirring bar, sodium tungstate (33 g, 0.1 mol) is dissolved in 54.5 mL of boiling distilled water

(Solution B). To the boiling Solution B, a solution of 4 M HCl (30 mL) is added dropwise in ~30 min, with vigorous stirring to dissolve the local precipitate of tungstic acid. Solution A is then added and, quickly, 9 mL of 4 M HCl is also added. The pH is ~5 to 6. The solution is kept boiling for 1 h. After cooling to room temperature, the solution is filtered if it is not completely clear. Potassium chloride (27 g) is added to the solution, which is stirred magnetically. The white solid product is collected on a sintered glass funnel (medium porosity), washed with two 9-mL portions of a KCl solution (~1 M) then washed with 9 mL of cold water, and finally dried in air (87 % yield).

Synthesis of $K_{10}[A-\alpha-SiW_9O_{34}]$ ligand

$K_{10}[A-\alpha-SiW_9O_{34}]$ was synthesized according to reference.² $K_8-\alpha-[SiW_{11}O_{39}]$ (10 g, 3.12 mmol) was dissolved in 100 mL of water at 50°C upon stirring. The solution was cooled to room temperature (solution A). A second solution was prepared by dissolving K_2CO_3 (2.58 g, 18.72 mmol) in 22 mL of water at room temperature. The solution of potassium carbonate was slowly added to the solution A. Then, the pH was ~9.4. After being stirred for 20 min, the solution was filtered if it was not completely clear (solution B). K_2CO_3 (8 g, 0.058 mol) was added to the solution B. The mixture was gently stirred for 2 h, and a white precipitate appeared slowly. The solid was collected by filtration through a fine frit, washed with a saturated KCl solution (6 mL), and dried in air (70 % yield).

Synthesis of **1**

1 was synthesized according to reference.³ A 0.50 g (0.16-mmol) sample of $K_{10}[A-\alpha-SiW_9O_{34}]$ was added with stirring to a solution of 0.076 g (0.44 mmol) of $CuCl_2 \cdot 2H_2O$ in 20 mL of a 0.5 M NaAc buffer (pH 4.8). This solution was heated to 80 °C for 30 min and then cooled to room temperature and filtered. Slow evaporation at room temperature resulted after about 1-2 weeks in green crystals that were filtered off and air-dried. Product yield: 0.26 g (60 %). Elemental analysis: found (calcd for **1**): K, 7.1 (7.0); Cu, 5.9 (5.7). FT-IR (KBr, cm^{-1}): 1009, 948, 913, 886, 811, 767, 695,

591, 540. The Cu 2p_{3/2} and Cu 2p_{1/2} binding energies of 932.8 and 952.5 eV for **1**.
UV-visible spectrum in 80 mM sodium borate buffer (pH 9.0) at 296 K: $\lambda = 790$ nm.

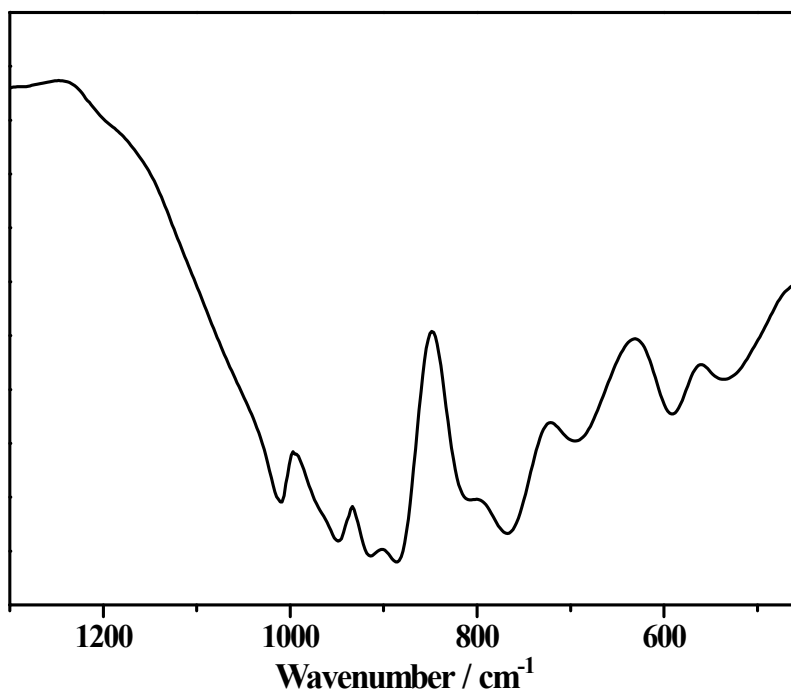


Fig. S1 FT-IR spectrum of **1**

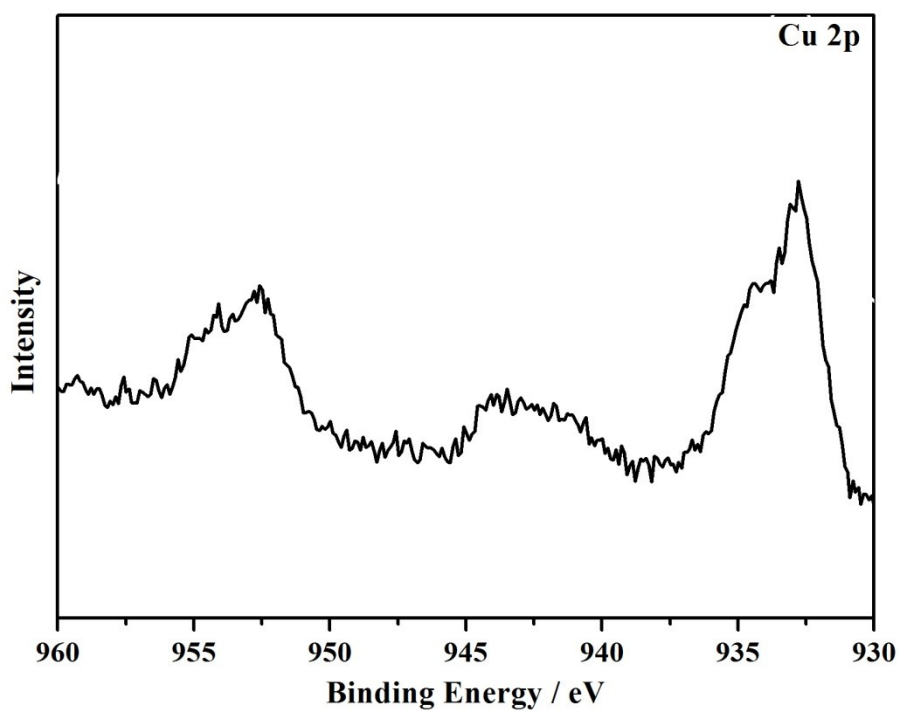


Fig. S2 X-ray photoelectron spectra of **1** showing the region of Cu 2p_{3/2} and Cu 2p_{1/2} peaks of **1**. The binding energy of each element was normalized to the C 1s peak (284.8 eV).

Synthesis of $[\{\text{Cu}_2(\text{H}_2\text{O})\text{SiW}_8\text{O}_{31}\}_2]^{12-}$

$[\{\text{Cu}_2(\text{H}_2\text{O})\text{SiW}_8\text{O}_{31}\}_2]^{12-}$ was synthesized according to reference.⁴ A 5-mL portion of acetonitrile solution containing 0.5 g (2.24 mmol) of CuBr_2 was dissolved in 20 mL of de-ionized water. The pH of this solution became 2.7 in 3 min. After stirring the solution, 2.0 g (0.67 mmol) of $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ was added, the solution was stirred for an additional 20 min, and the pH stabilized at 4.2. The undissolved residues were removed from solution by a medium frit and the filtrate (20 mL) was collected. A 10-mL portion of filtrate was transferred to a 50 mL beaker and to this, 0.225 g of sodium acetate and 1.5 mL of glacial acetic acid (forming 0.5 M HOAc/NaOAc buffer solution, pH = 4.2) were added. After stirring the solution for 5 min, 10 mL of ethylene glycol was added. The solution was stirred for an additional 5 min and then placed in a 30-mL beaker in a dark cabinet. Light blue, needle-like diffraction quality crystals of $[\{\text{Cu}_2(\text{H}_2\text{O})\text{SiW}_8\text{O}_{31}\}_2]^{12-}$ grew from this 1: 1 water: ethylene glycol mixed buffer solution after three days (53 % yield). FT-IR (KBr, cm^{-1}): 1013, 960, 907, 805, 746, 687, 625, 541, 529, 492.

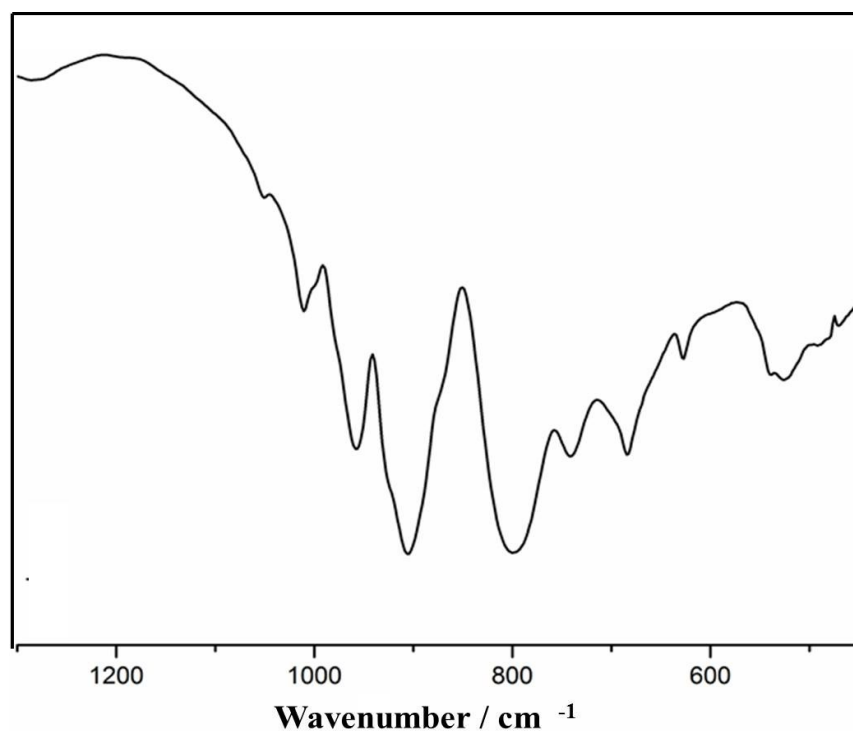


Fig. S3 FT-IR spectrum of $[\{\text{Cu}_2(\text{H}_2\text{O})\text{SiW}_8\text{O}_{31}\}_2]^{12-}$

Synthesis of $[\text{Cu}_4(\text{H}_2\text{O})_2(\text{OH})_4\text{Si}_2\text{W}_{16}\text{O}_{58}]^{8-}$

$[\text{Cu}_4(\text{H}_2\text{O})_2(\text{OH})_4\text{Si}_2\text{W}_{16}\text{O}_{58}]^{8-}$ was synthesized according to reference.⁵ 64 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.375 mmol) were dissolved in 20 mL of a 1 M NaCl solution (pH = 4.5) followed by the addition of 450 mg (0.15 mmol) of $\gamma\text{-SiW}_{10}$. The solution was stirred for 30 min at 50°C. Prism-like pale blue crystals were obtained after 2 weeks from the filtrate (40 % yield). FT-IR (KBr, cm^{-1}): 988, 946, 890, 836, 734, 684, 570.

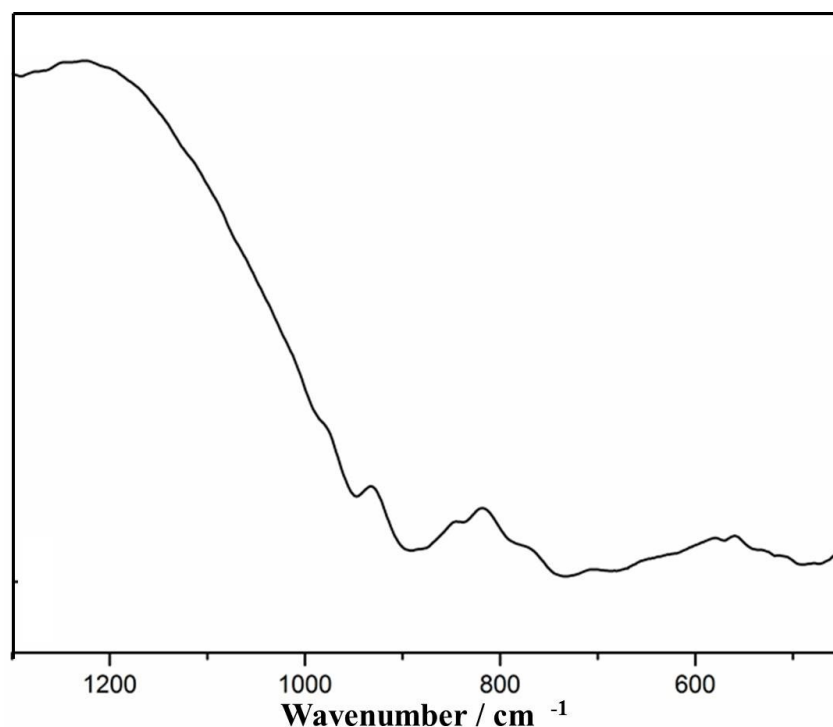


Fig. S4 FT-IR spectrum of $[\text{Cu}_4(\text{H}_2\text{O})_2(\text{OH})_4\text{Si}_2\text{W}_{16}\text{O}_{58}]^{8-}$

Synthesis of $[\text{Cu}_6\text{Cl}(\text{SbW}_9\text{O}_{33})_2]^{7-}$

$[\text{Cu}_6\text{Cl}(\text{SbW}_9\text{O}_{33})_2]^{7-}$ was synthesized according to reference.⁶ A 0.21 g (1.23 mmol) sample of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 20 mL of 0.5 M NaAc + HAc buffer solution (pH 4.8), and then 0.52 g (0.18 mmol) of $\text{Na}_9[\alpha\text{-B-SbW}_9\text{O}_{33}]$ was added with gentle stirring. The solution was heated to 80 °C for about 1 h and filtered after it had cooled to room temperature. Then 0.5 mL of 1.0 M KCl solution was added to the green filtrate. Slow evaporation at room temperature led to a green crystalline product after about 1 week (56 % yield). FT-IR (KBr, cm^{-1}): 938, 889, 845, 770, 734, 511.

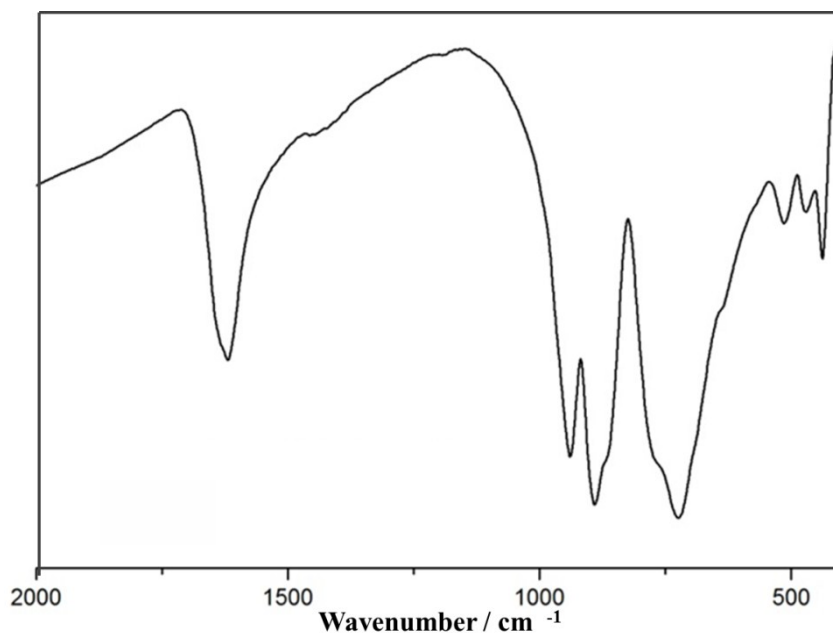


Fig. S5 FT-IR spectrum of $[\text{Cu}_6\text{Cl}(\text{SbW}_9\text{O}_{33})_2]^{7-}$

Synthesis of $[\text{Cu}_{20}\text{Cl}(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{P}_8\text{W}_{48}\text{O}_{184})]^{25-}$

$[\text{Cu}_{20}\text{Cl}(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{P}_8\text{W}_{48}\text{O}_{184})]^{25-}$ was synthesized according to reference.⁷ A sample of 0.10 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.60 mmol) was dissolved in a 1M LiCH_3COO buffer solution (20 mL) at pH 6.0, then 0.37 g $\text{K}_{28}\text{Li}_5[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}] \cdot 92\text{H}_2\text{O}$ (0.025 mmol) (synthesized according to ref 8) was added. This solution was heated to 80°C for 1 h and after cooling to room temperature it was filtered. The filtrate was allowed to evaporate in an open beaker at room temperature. After 1–2 days a blue crystalline product started to appear (28 % yield). FT-IR (KBr, cm^{-1}): 1002, 950, 902, 813, 769, 699, 538.

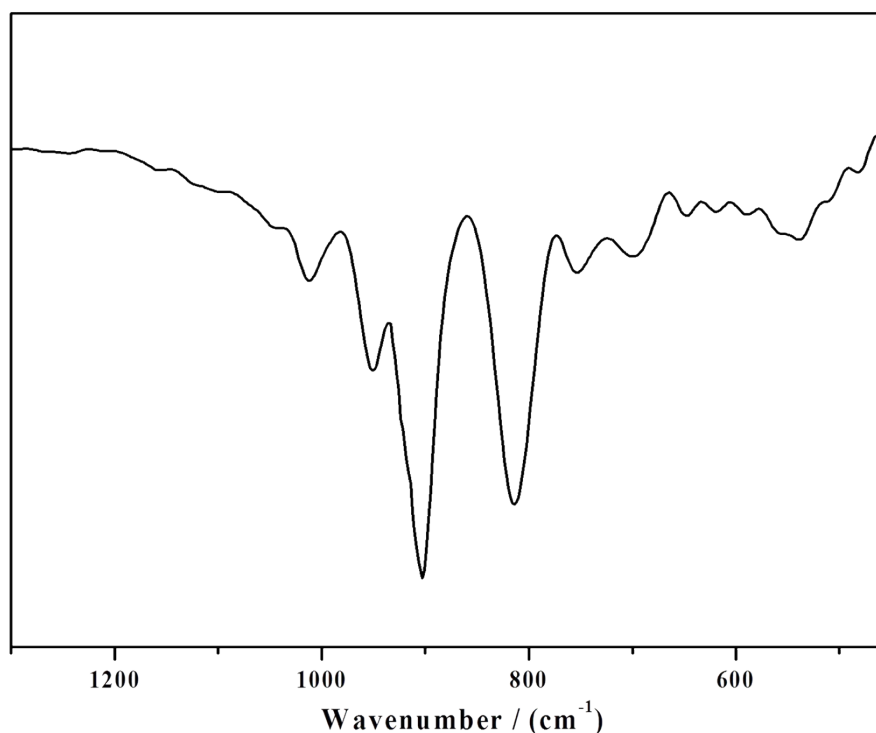


Fig. S6 FT-IR spectrum of $[\text{Cu}_{20}\text{Cl}(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{P}_8\text{W}_{48}\text{O}_{184})]^{25-}$

Laser flash photolysis

Nanosecond transient absorption measurements were performed on an Edinburgh Instruments LP920-KS laser flash photolysis spectrometer, using an OPO laser source (OPOTEK Vibrant). Transient detection was obtained using a photomultiplier-oscilloscope combination (Hamamatsu R928P, Tektronix TDS3012C). Kinetics of bleach recovery conditions: Excitation wavelength = 445 nm, analysis wavelength = 450 nm; 50 μM $[\text{Ru}(\text{bpy})_3]^{2+}$; 5 mM $\text{Na}_2\text{S}_2\text{O}_8$; 20 μM **1**; pH 9.0, 80 mM borate buffer.

Photocatalytic Water Oxidation

Photocatalytic water oxidation was performed as follows: the desired concentration of catalyst **1** (10–30 μM) was prepared by dissolving the appropriate amount of catalyst in a buffer solution (80 mM, pH 4.8–10.0 for borate buffer) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (0.25–1.5 mM) and $\text{Na}_2\text{S}_2\text{O}_8$ (1.0–7.5 mM). The above solution was deaerated by purging with Ar gas for 5 min in a flask (28 mL) sealed with a rubber septum (the total volume of the reaction solution was 15 mL). The reaction was then started by irradiating the solution with a LED light source (light

intensity 16 mW, beam diameter 2 cm) through a transmitting glass filter ($\lambda \geq 420$ nm) at room temperature. After each sampling time, 150 μL of Ar was injected into the flask and then the same volume of gas sample in the headspace of the flask was withdrawn by a SGE gas-tight syringe and analyzed by gas chromatography (GC). The O_2 in the sampled gas was separated by passing through a 2 m \times 3 mm packed molecular sieve 5A column with an Ar carrier gas and quantified by a Thermal Conductivity Detector (TCD) (Shimadzu GC-9A). The total amount of evolved O_2 was calculated based on the concentration of O_2 in the headspace gas. Contamination of the head-space with air was corrected by measuring the N_2 concentration present in the head-space (from the N_2 peak in the GC traces). The solution pH was monitored after the reaction by a METTLER TOLEDO FEP20 pH meter.

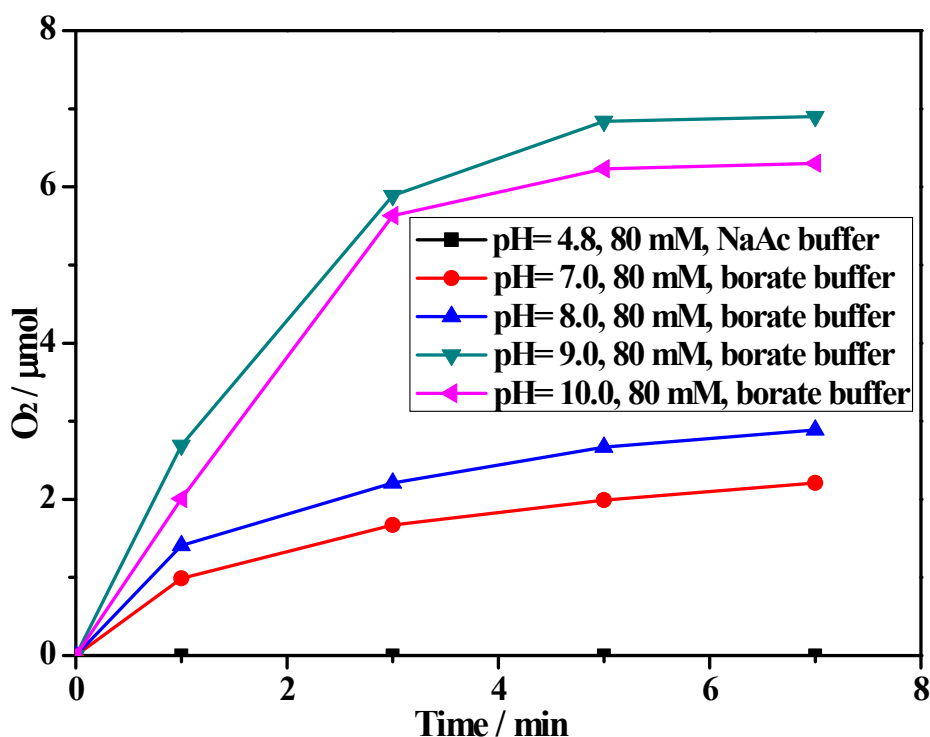


Fig. S7 Kinetics of O_2 formation in the photocatalytic system under various pH conditions. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 5.0 mM $\text{Na}_2\text{S}_2\text{O}_8$, 20 μM **1**, total reaction volume is 15 mL.

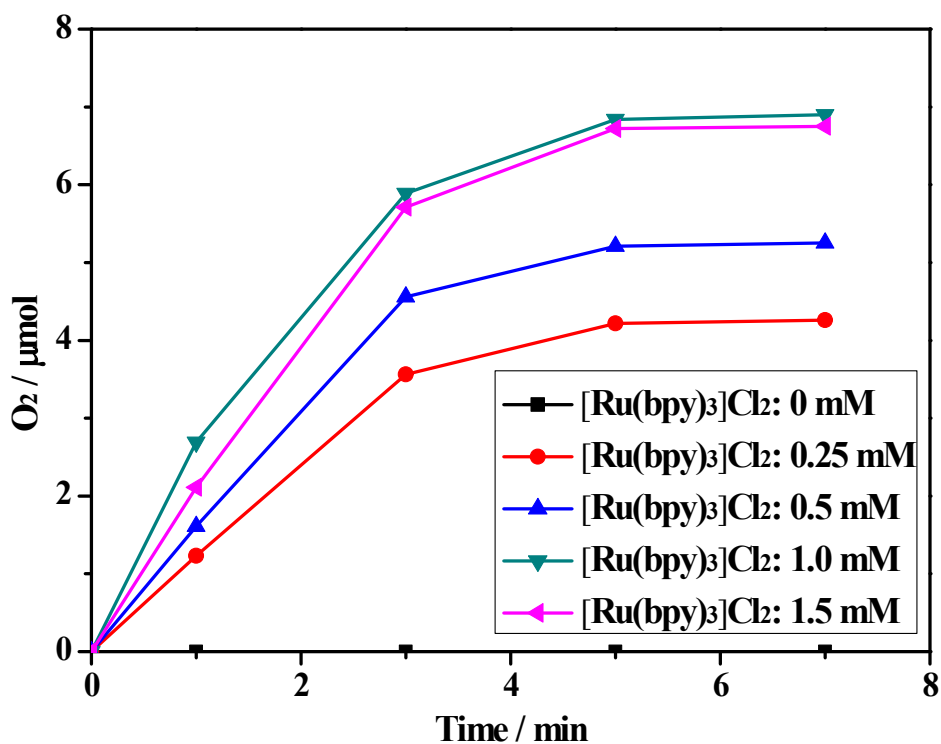


Fig. S8 Kinetics of O₂ formation in the photocatalytic system using different concentrations of [Ru(bpy)₃]Cl₂. Conditions: LED lamp ($\lambda \geq 420$ nm), 5.0 mM Na₂S₂O₈, 20 μ M **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

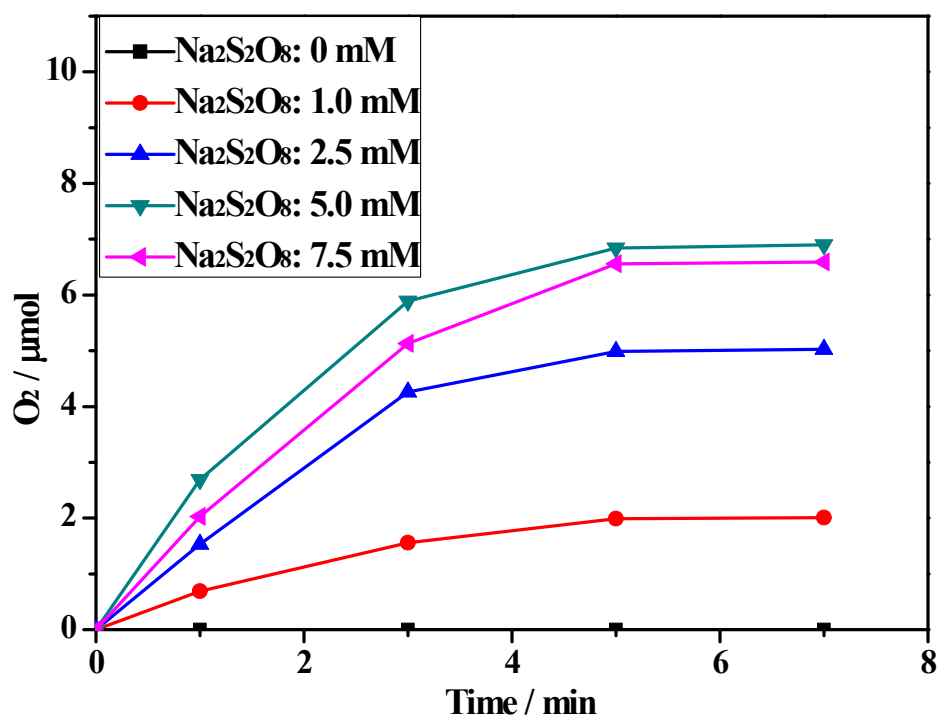


Fig. S9 Kinetics of O₂ formation in the photocatalytic system using different concentrations of Na₂S₂O₈. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 20 μ M **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

Table S1. TONs and O₂ chemical yields for water oxidation in the presence of 1^[a]

Entry	Concentration of catalysts (μM)	O ₂ yield ^[b] (%)	TON ^[c]	TOF ^[d] [s ⁻¹]	Φ_{QY} (initial) (%)
1	1	3.6	91	0.98	6
2	5	12.3	61	0.30	9
3	10	13.4	34	0.17	10
4	15	17.4	29	0.16	14
5	20	18.3	23	0.15	17
6	25	18.1	18	0.11	16
7	30	15.8	13	0.07	13

[a] Conditions: LED lamp ($\lambda \geq 420$ nm); 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL. [b] O₂ Yield = 2 × mole of O₂ per mole of Na₂S₂O₈. [c] TON = mole of O₂/mole of catalyst. [d] TOF_{initial} = mole of O₂/(mole of catalyst × 60 s), based on the amount of O₂ produced after 1 min of irradiation.

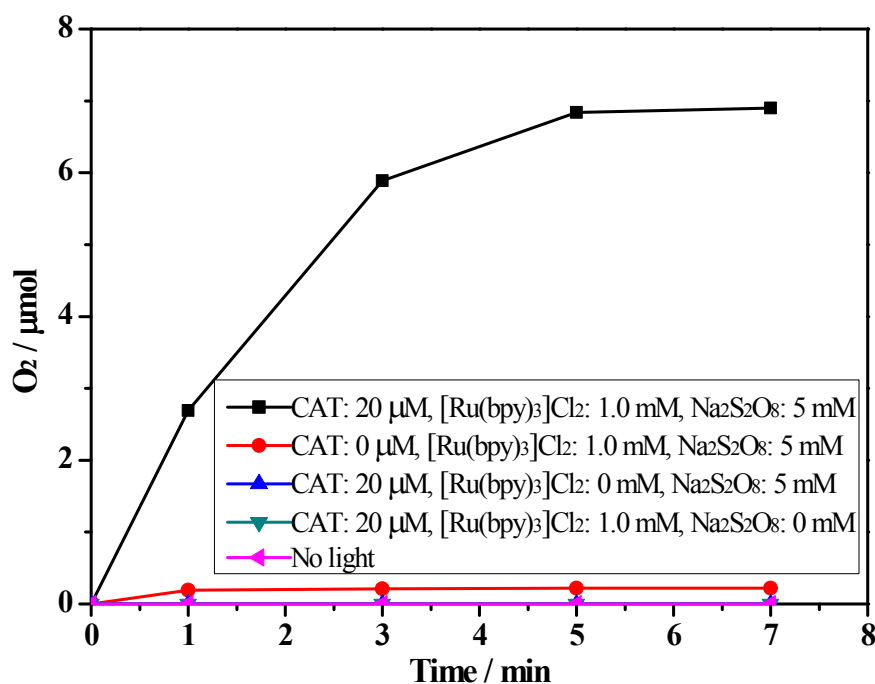


Fig. S10 Kinetics of O₂ formation in the photocatalytic system without 1 (red), [Ru(bpy)₃]Cl₂ (blue), Na₂S₂O₈ (blackish green) or light (pink).

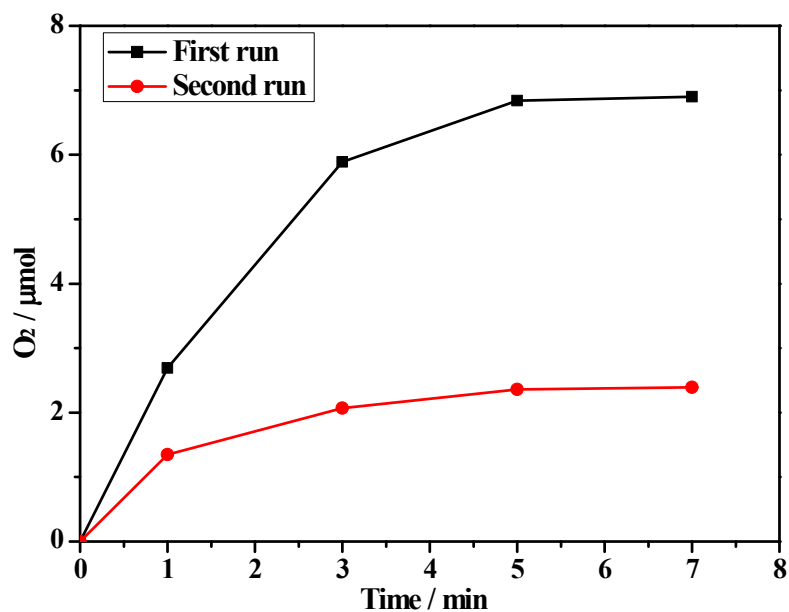


Fig. S11 O₂ formation kinetics of the first run and the second run. After completion of the first run, 17.8 mg Na₂S₂O₈ was added to the second run. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 20 μM **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

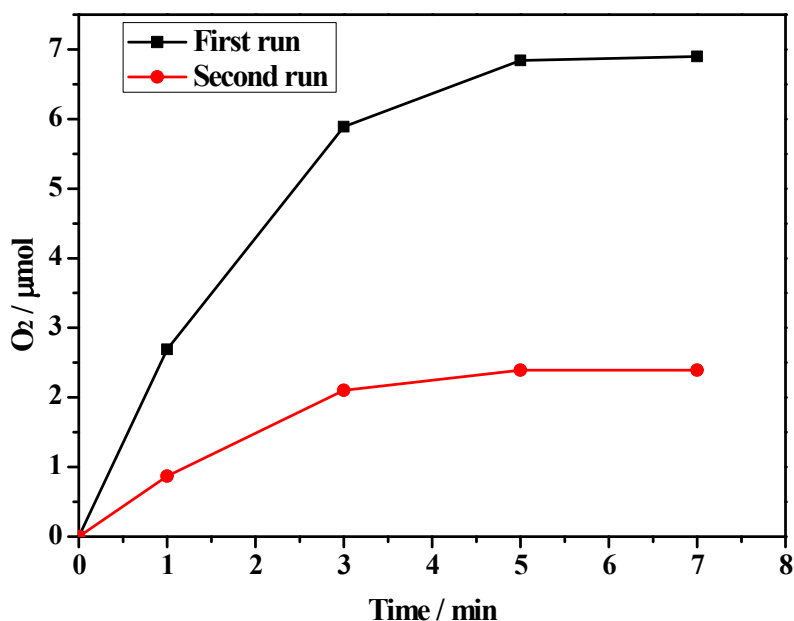


Fig. S12 O₂ formation kinetics of the first run and the second run. After completion of the first run, 5 mM Na₂S₂O₈ and 0.5 mM [Ru(bpy)₃]Cl₂ were added to the second run. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 20 μM **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

The amount of O₂ evolved is lower than that of the first run. In addition to Na₂S₂O₈ consumption and degradation of the photosensitizer, there are other reasons for the decrease of O₂ evolution over the reused catalyst, for example, the change of ionic strength, liquid electrolyte and the pH value of sodium borate buffer.

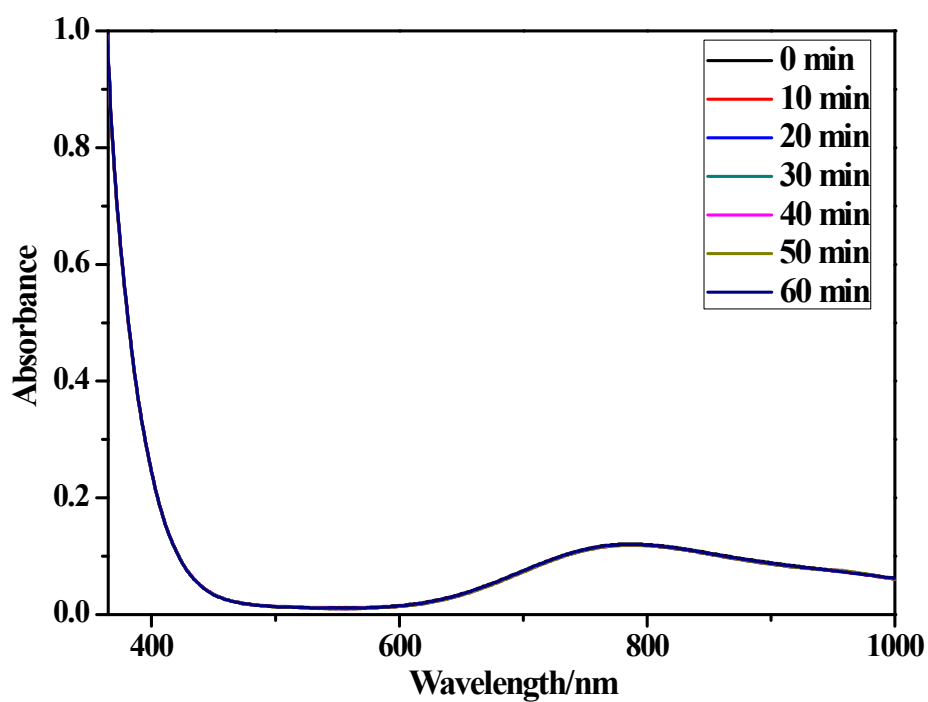


Fig. S13 UV-vis spectra of 2 mM **1** in pH 9.0, 80 mM sodium borate buffer solution.

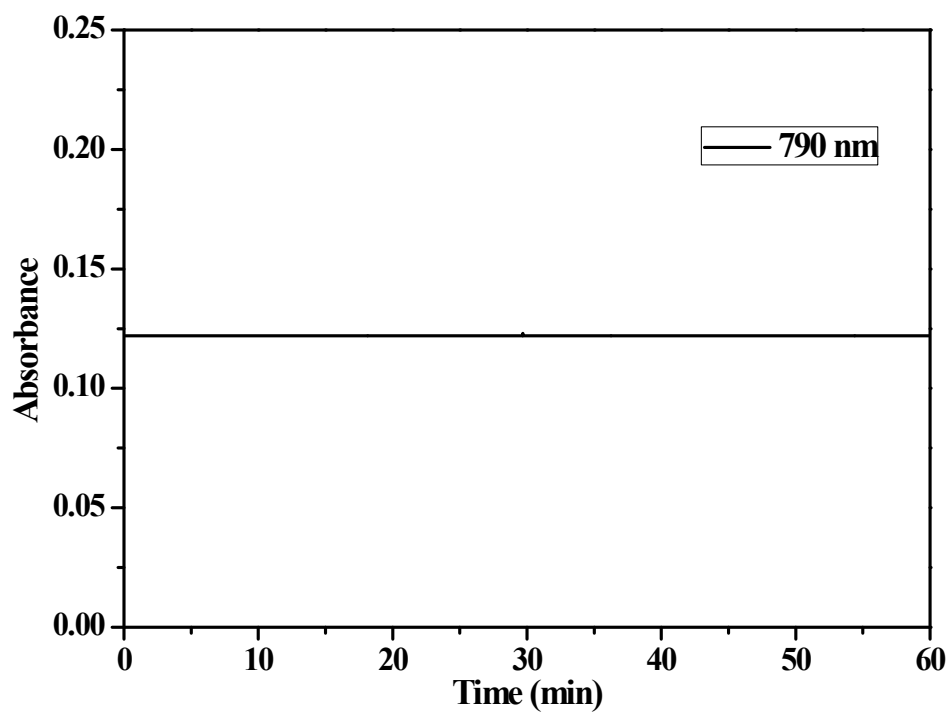


Fig. S14 Changes in UV-vis spectra of 2 mM **1** in 80 mM sodium borate buffer at pH 9.0.

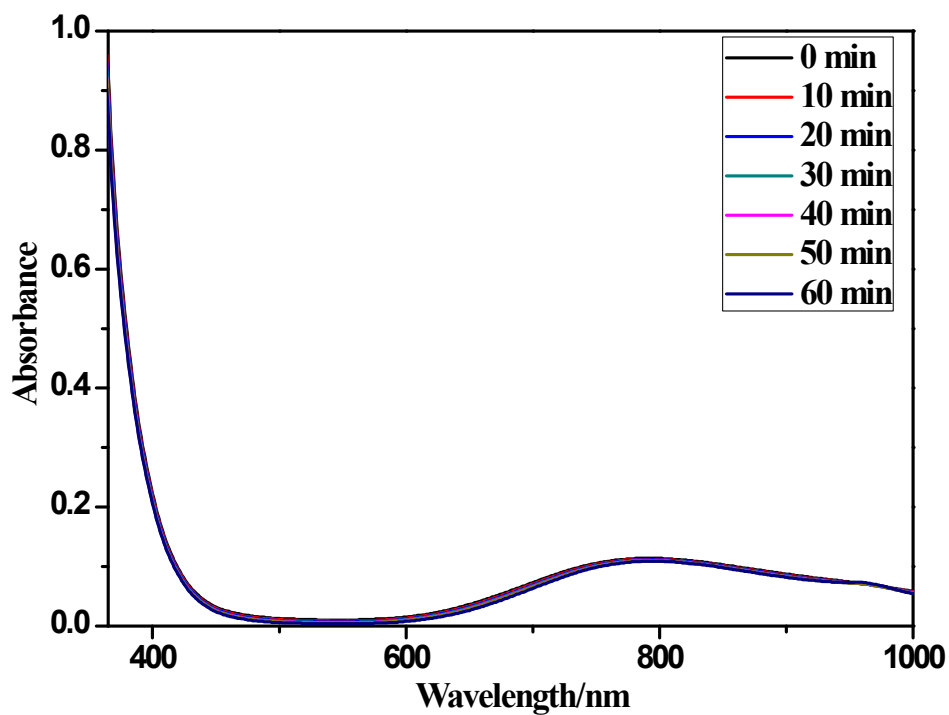


Fig. S15 Time-dependent UV-Vis spectra of **1** (2 mM) in the pH 9.0 sodium borate buffer solution (80 mM) with $\text{Na}_2\text{S}_2\text{O}_8$ (5 mM).

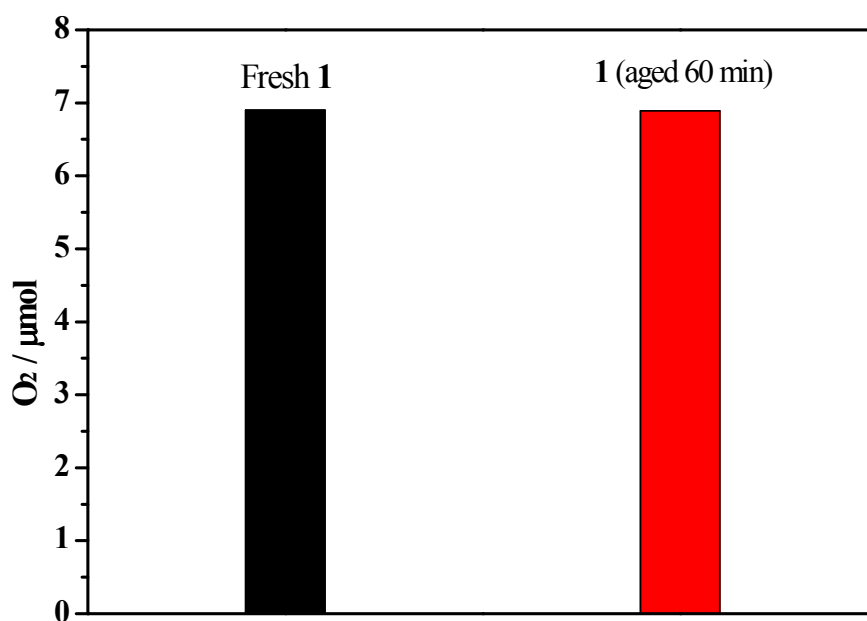


Fig. S16 O_2 evolution in the photocatalytic system using 20 μM of fresh (black) and 60 min aged **1** (red). Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 5.0 mM $\text{Na}_2\text{S}_2\text{O}_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

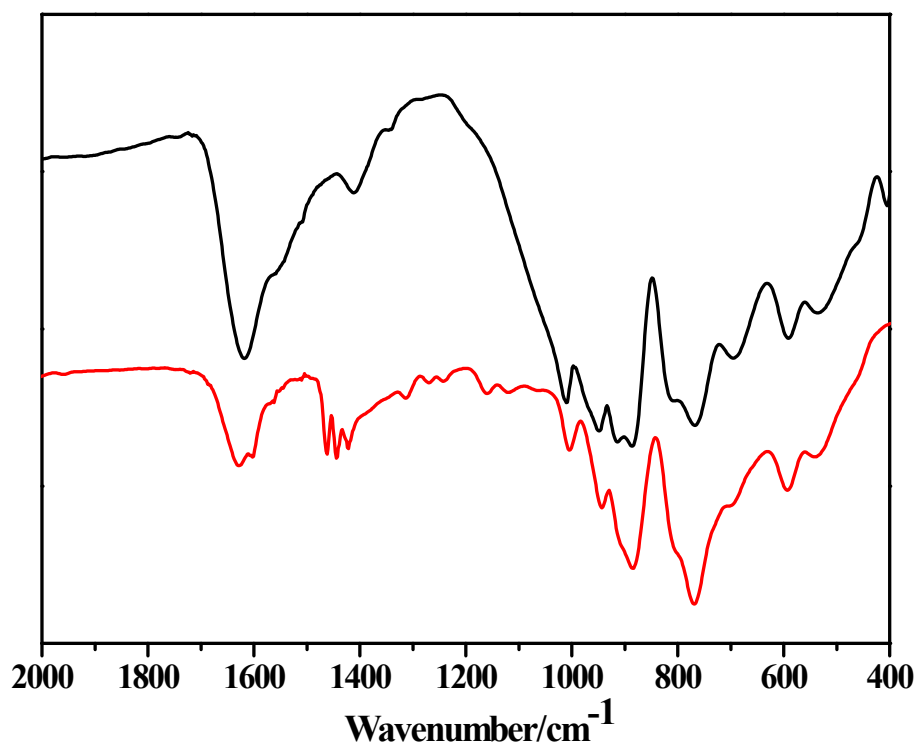
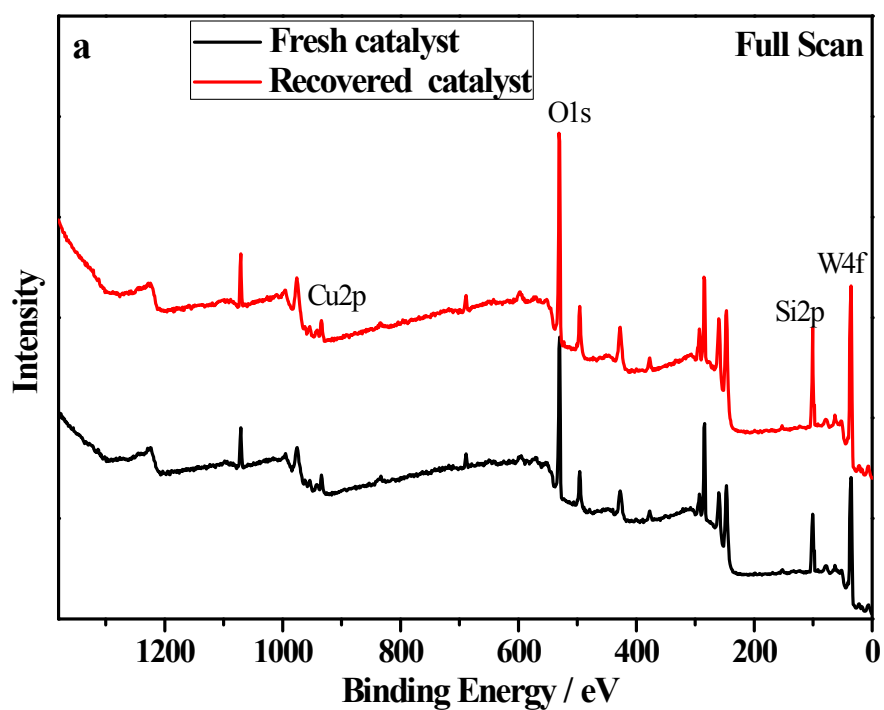
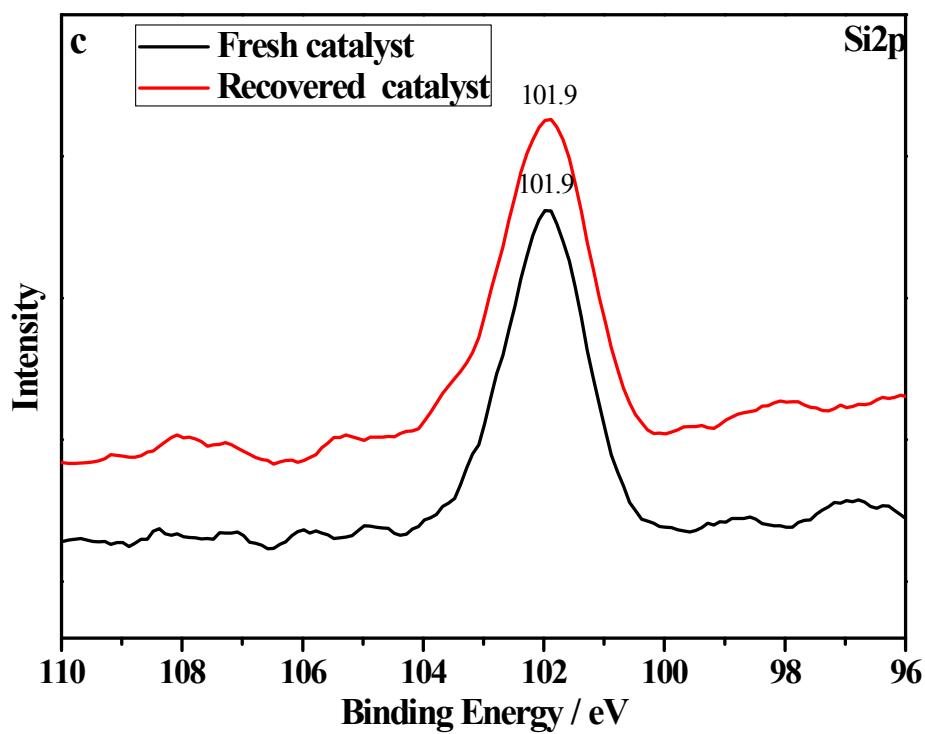
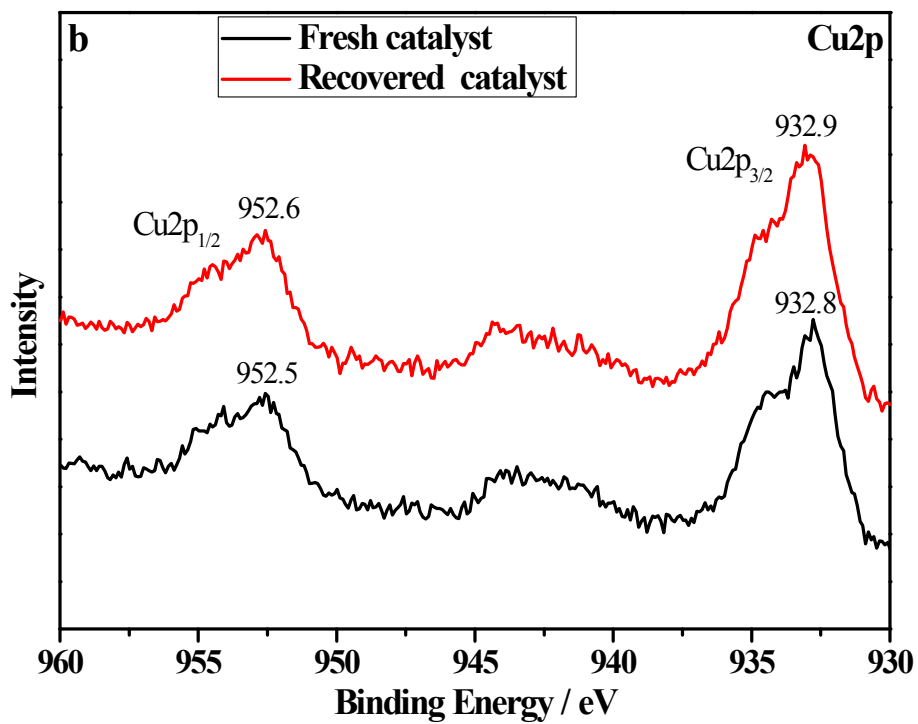


Fig. S17 FT-IR spectra of fresh **1** (black curve) and the recycled catalyst (red curve) obtained from the photocatalytic water oxidation solution using acetone.





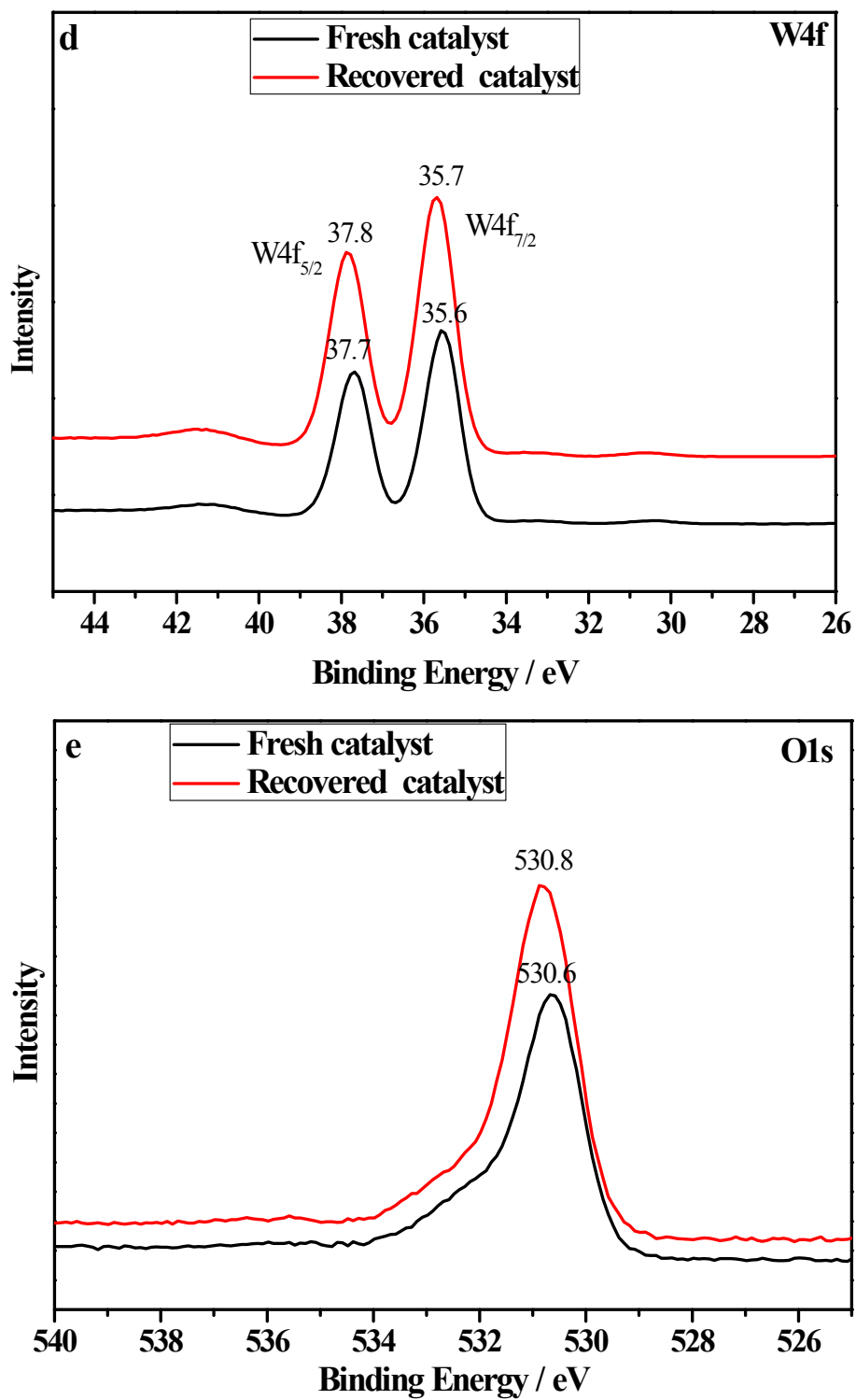


Fig. S18 X-ray photoelectron spectra of **1** before and after the reaction in the energy regions of (a) full scan, (b) Cu 2p, (c) Si 2p, (d) W 4f and (e) O 1s.

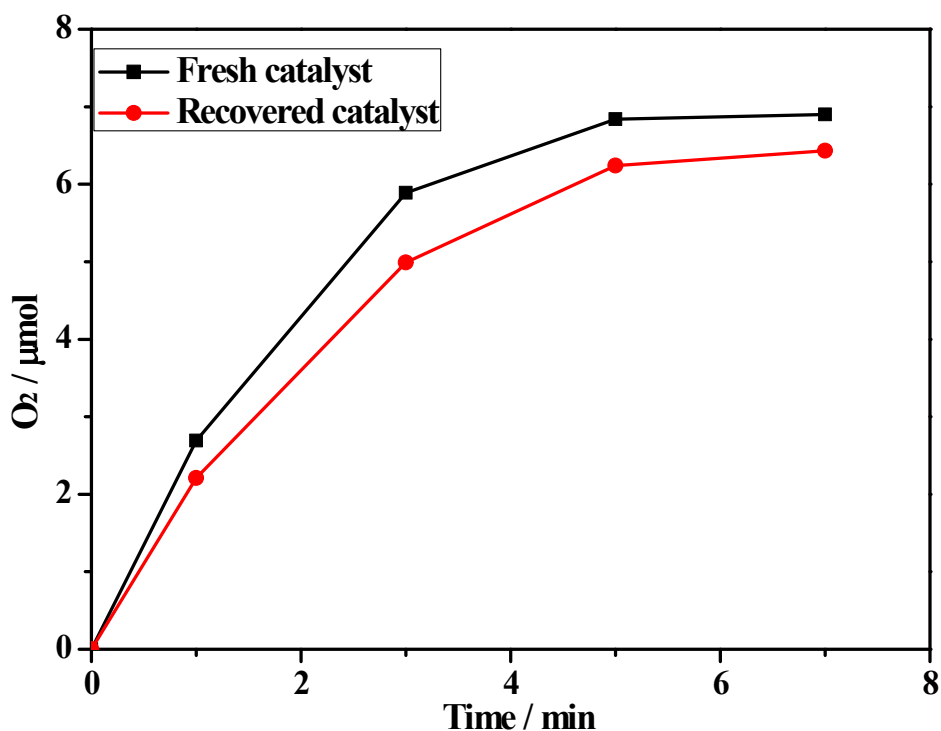


Fig. S19 Kinetics of O₂ formation in the photocatalytic system using fresh and recovered **1**. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 20 μ M **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

	Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm): 0.000	Peak 1: 0.000	0.0	0.000
Pdl: 0.000	Peak 2: 0.000	0.0	0.000
Intercept: 0.00	Peak 3: 0.000	0.0	0.000
Result quality Refer to quality report			

Size Distribution by Intensity

Record 11: 1

Fig. S20 DLS measurement of a water oxidation reaction solution of 20 μ M **1** in a 80 mM borate buffer solution (pH 9.0) with [Ru(bpy)₃]Cl₂ (1.0 mM), Na₂S₂O₈ (5.0 mM) after 7 min of irradiation.

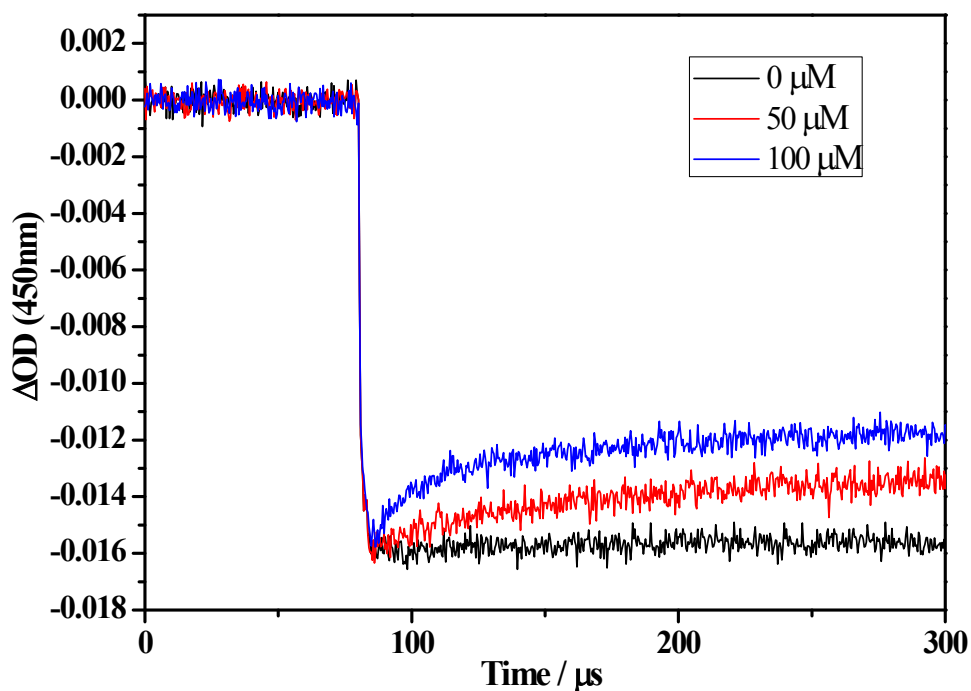


Fig. S21 Flash photolysis experiments (excitation at 445 nm) of 80 mM borate buffer (pH 9.0) solutions containing 50 μM [Ru(bpy)₃]Cl₂, 5 mM Na₂S₂O₈ and 0–100 μM **1**, measured at 450 nm.

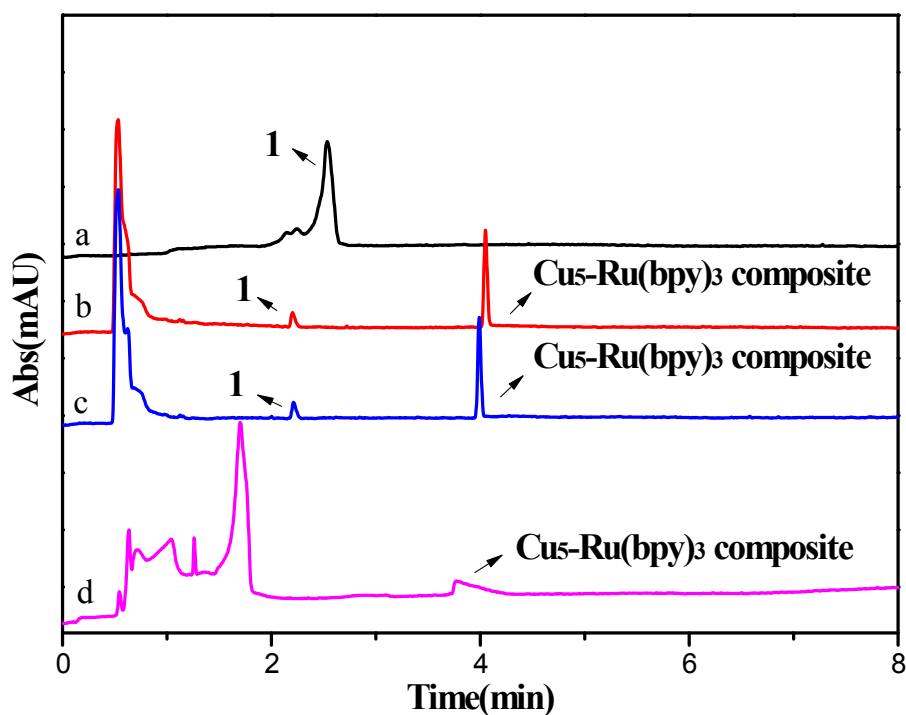


Fig. S22 An electropherogram for **1** (30 μM). (a): 30 μM of **1** in a 20 mM sodium borate buffer solution (pH = 9.0). (b): 30 μM of **1** in a 20 mM sodium borate buffer solution (pH = 9.0) containing [Ru(bpy)₃]Cl₂ (1.0 mM), Na₂S₂O₈ (5.0 mM) before illumination. (c): 30 μM of **1** in a 20 mM sodium borate buffer solution (pH = 9.0) containing [Ru(bpy)₃]Cl₂ (1.0 mM), Na₂S₂O₈ (5.0 mM) after 7 min of illumination. (d): the saturation liquor of Cu₅-Ru(bpy)₃ composite (sodium borate buffer solution, pH = 9.0).

Table S2. Inductively coupled plasma mass spectrometry for solution with 1

Entry	Aged time (h)	Concentration of [Ru(bpy) ₃]Cl ₂ (mM)	Concentration of Na ₂ S ₂ O ₈ (mM)	Element	Cu after extraction (μM)
1	1	0	0	Cu	0
2	0	1	5	Cu	1.1

Conditions: **1** (10 μM); in a 80 mM pH 9.0 borate buffer solution after 7 min of irradiation.

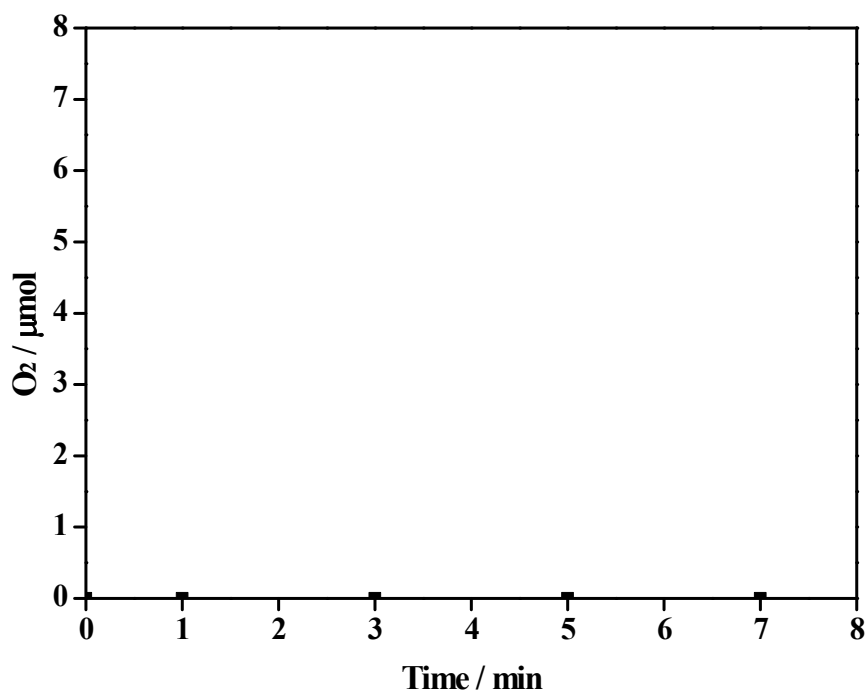


Fig. S23 O₂ Kinetics of O₂ formation in the photocatalytic system using 1.1 μM copper ions. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

No O₂ was detected in the exist of the 1.1 μM copper ions. Therefore, copper ions did not contribute to O₂ evolved.

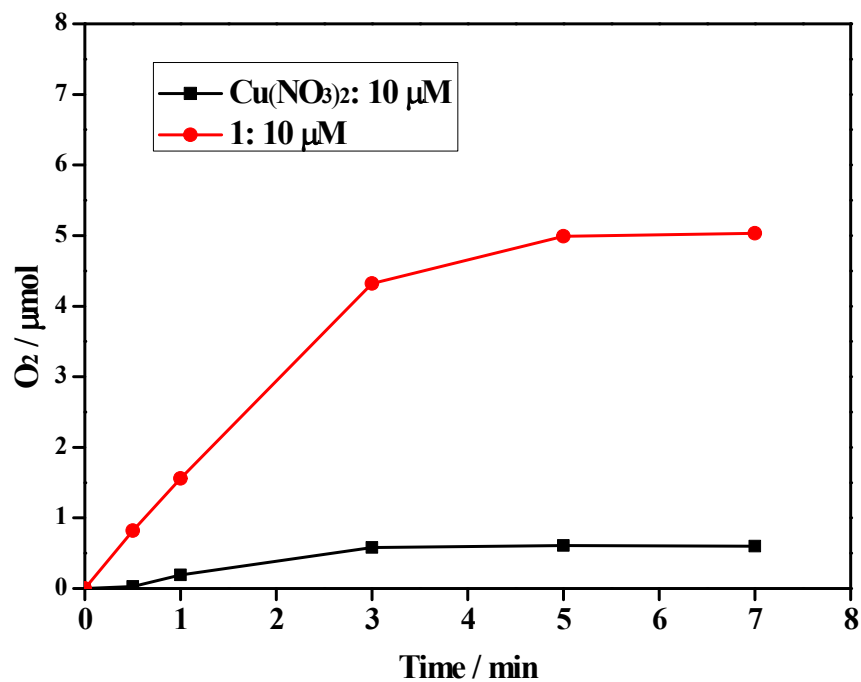


Fig. S24 Kinetics of O₂ formation in the photocatalytic system using 10 μM Cu(NO₃)₂ and 10 μM 1. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

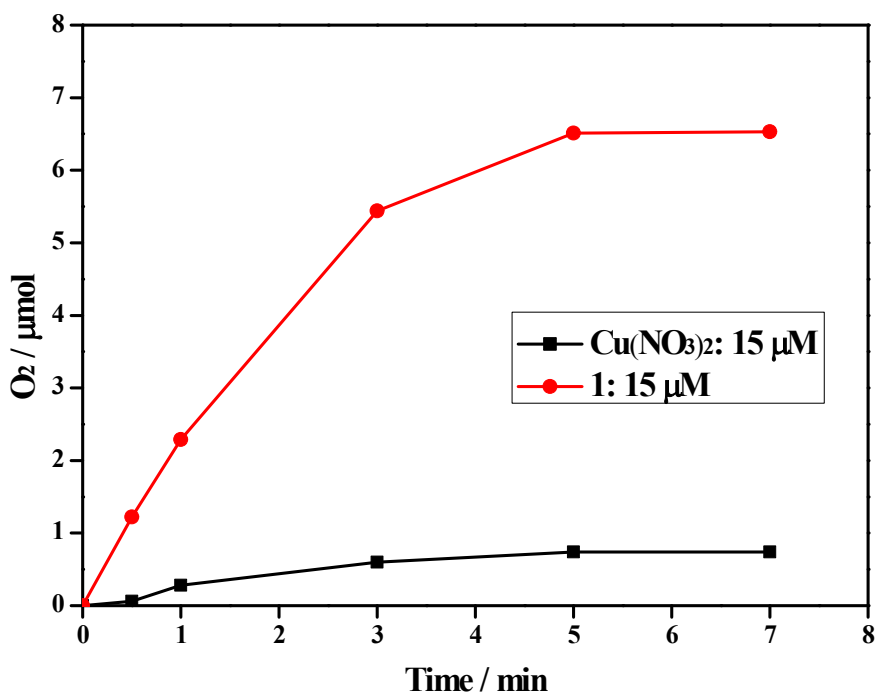


Fig. S25 Kinetics of O₂ formation in the photocatalytic system using 15 μM Cu(NO₃)₂ and 15 μM 1. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

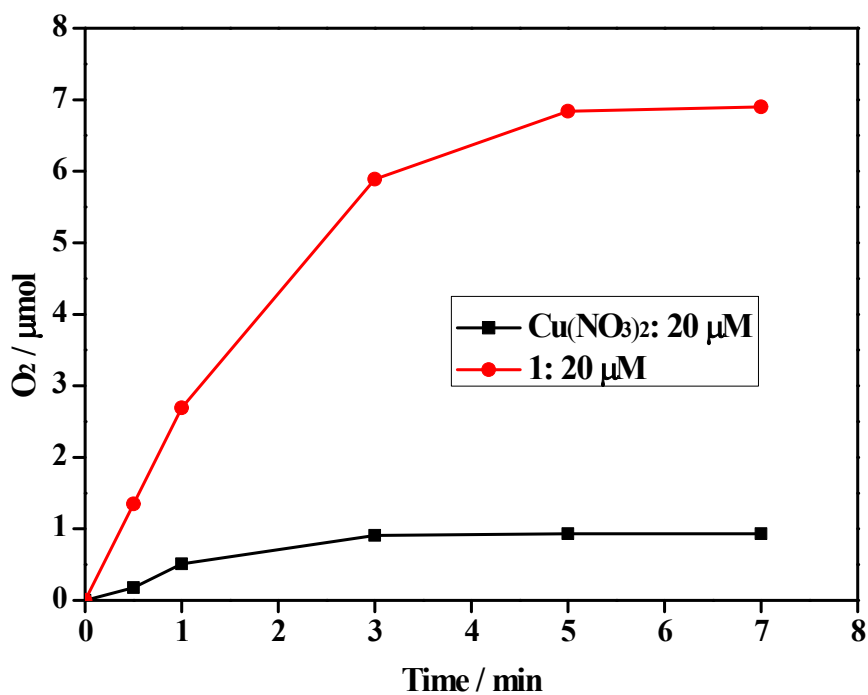


Fig. S26 Kinetics of O₂ formation in the photocatalytic system using 20 μM Cu(NO₃)₂ and 20 μM **1**. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

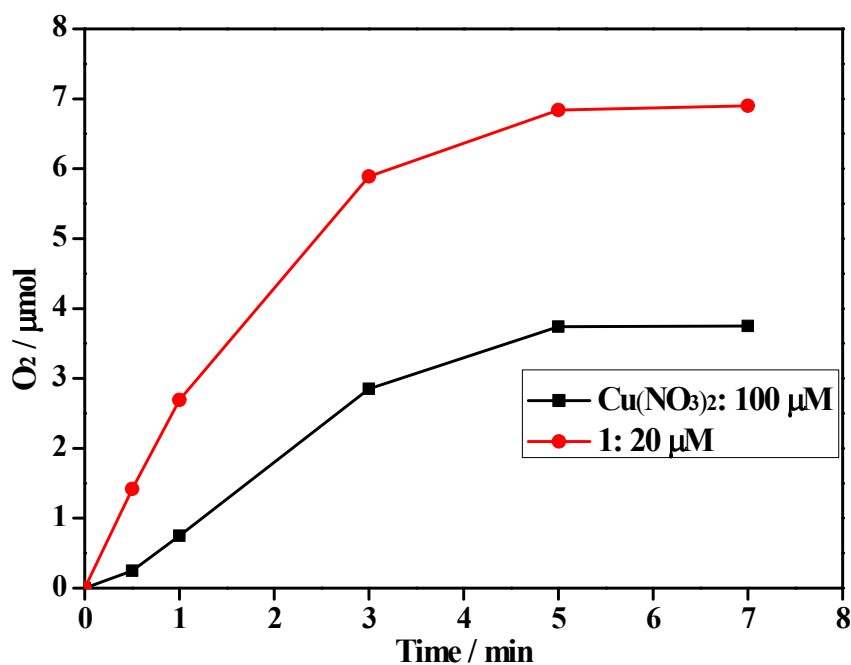


Fig. S27 Kinetics of O₂ formation in the photocatalytic system using 100 μM Cu(NO₃)₂ and 20 μM **1**. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

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