Republication Notice

This version of the ESI replaces the previous version that was published on 3rd May 2016. Details of the changes are included below. However, please see the corresponding Correction notice for more detailed information: *Chem. Commun.*, 2016, DOI: 10.1039/c6cc90561g.

The structural formula of the reported nickel-containing polyoxometalate has been revised to $[\{\beta\text{-}SiNi_2W_{10}O_{36}(OH)_2(H_2O)\}_2]^{12-}$, in line with that first reported by Kortz and co-workers (herein cited as ref. 2).

In order to better highlight the reproducibility of the catalytic water oxidation experiments, the authors wish to add that all catalytic runs were tested in triplicate. Error bars, which were omitted from the original figures, are therefore newly added to Fig. S26-30.

To further confirm that the observed catalytic activity can mainly be attributed to the anion **1**, rather than Ni^{2+} associated with the anion or free Ni^{2+}, data for free $NiSO_4$ is newly added to Fig. S34.

Further minor changes include an update to the caption for Fig. S32 to include the reaction conditions, the inclusion of a citation to the work of Kortz and co-workers in reference 2, meaning all subsequent references have been renumbered accordingly, and the addition of Fig. S37-39, which are photographic representations of the experimental set-up and some of the observed results.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

ChemComm Editorial Office

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Electronic Supporting Information

$[\{\beta\text{-SiNi}_2W_{10}O_{36}(OH)_2(H_2O)\}_2]^{12-}$: a robust visible light-driven water oxidation catalyst based on nickel-containing polyoxometalate

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Experimentals and calculation

Quantum yield calculation

Initial O_2 formation rate = 0.047 $\mu mol.s^{-1}$

Irradiation radius =1 cm =0.01 m

Photon flux = $\pi \times (0.01m)^2 \times 1750\ \mu mol.m^{-2}.s^{-1} = 0.549\ \mu mol.s^{-1}$

$$\Phi_{QY(initial)} = 2 \times \frac{\text{initial } O_2 \text{ formation rate}}{\text{photon flux}} \times 100\%$$

$$= \frac{2 \times 0.047\ \mu mol \cdot s^{-1}}{0.549\ \mu mol \cdot s^{-1}} \times 100\%$$

$$= 17\%$$

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 photomutiplier 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. The post-reaction solutions were evaluated three times consecutively.

The measurement of Quantum Yield

The quantum yields of O_2 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** (15 μM), $[Ru(bpy)_3]Cl_2$ (1 mM) and $Na_2S_2O_8$ (5 mM) was irradiated by an interference filtered (Asahi spectra SV 490) from a LED source ($420 < \lambda < 490$ 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}.

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 $[Ru(bpy)_3]^{2+}$; 5 mM $Na_2S_2O_8$; 0-100 μM **1**; pH 9.0, 80 mM borate buffer.

Photocatalytic Water Oxidation

Photocatalytic water oxidation was performed as follows. The desired concentration of catalyst (1–25 μM) was added to a buffer solution (80 mM, pH 4.8–10.0 for borate buffer) containing $[Ru(bpy)_3]Cl_2$ (1.0 mM) and $Na_2S_2O_8$ (5.0 mM). The above solution was deaerated by purging with Ar gas for 5 min in a flask (21 mL) sealed with a rubber septum (the volume of 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 irradiation time, 150 μL of Ar was injected into the flask and then the same volume of gas in the headspace of the flask was withdrawn by a SGE gas-tight syringe and analysed by gas chromatography (GC). The O_2 in the sampled gas was separated by passing through a 2 m × 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 from the concentration of O_2 in the headspace gas. Contamination of the head-space with air was corrected by measuring of N_2 present in the head-space (from the N_2 peak in the GC traces). The solution pH was measured after the reaction by a METTLER TOLEDO FEP20 pH meter.

Synthesis of $[Ru(bpy)_3]Cl_2$

Commercial $RuCl_3 \cdot xH_2O$ 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” $RuCl_3$ at this temperature. “Dried” $RuCl_3$ (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 $K_8[\beta\text{-}SiW_{11}O_{39}]$ ligand

$K_8[\beta\text{-}SiW_{11}O_{39}]$ was synthesized according to reference.[1] Sodium metasilicate (11 g, 50 mmol) is dissolved in 100 mL of water (Solution A). Sodium tungstate (182 g, 0.55 mol) is dissolved in 300 mL of water in a separate I-L beaker containing a magnetic stirring bar. To this solution, 165 mL of 4 M HCI is added in 1-mL portions over 10min, with vigorous stirring (there is a local formation of hydrated tungstic acid that slowly disappears). Then, Solution A is poured into the tungstate solution, and the pH is adjusted to between 5 and 6 by addition of the 4 M HCI solution (~ 40 mL). This pH is maintained by addition of small amounts of 4 M HCl for 100min. Solid potassium chloride (90g) is then added to the solution with gentle stirring. After 15min, the precipitate is collected by filtering through a sintered glass filter. Purification is achieved by dissolving the product in 850 mL of water. The insoluble material is rapidly removed by filtration on a fine frit, and the salt is precipitated again by addition of solid KCI (80 g). The precipitate is separated by filtration, washed with 2 M potassium chloride solution (2 portions of 50 mL), and air dried.

Synthesis of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ ligand

$K_8[\gamma\text{-}SiW_{10}O_{36}]$ was synthesized according to reference.[1] The potassium salt of the β isomer of undecatungstosilicate (15 g, 5 mmol), synthesized as described in the procedure in section F, is dissolved in 150 mL of water maintained at 25°C. Impurities in the $K_8[\beta\text{-}SiW_{11}O_{39}]$ salt (mainly paratungstate) give insoluble materials, which have to be removed rapidly by filtration on a fine frit. The pH of the solution is quickly adjusted to 9.1 by addition of a 2 M aqueous solution of K_2CO_3. The pH of the solution is kept at this value by addition of the K_2CO_3 solution for exactly 16 min. The potassium salt of the γ-decatungstosilicate is then precipitated by addition of solid potassium chloride (40 g). During the precipitation (10 min), the pH must be maintained at 9.1 by addition of small amounts of the K_2CO_3 solution. The solid is removed by filtering, washed with 1 M KCI solution, and air dried.

Synthesis of $[\{\beta\text{-}SiNi_2W_{10}O_{36}(OH)_2(H_2O)\}_2]^{12-}$ (1)

1 was synthesized according to reference.[2] 1.0 g $NiSO_4 \cdot 6H_2O$ was dissolved in 40 mL of a 0.5 M potassium acetate buffer (pH 4.8) followed by an addition of 4.8 g $K_8[\gamma\text{-}SiW_{10}O_{36}]$, resulting in a cloudy suspension. This solution was heated at 50 °C for 1 h and then was allowed to cool to room temperature. A 1.5 g amount of KCl was added, after several hours a yellow powder of the desired product was obtained by filtration. The crude product was dissolved in H_2O, and this solution was kept in a 50 mL beaker to allow slow evaporation at room temperature. After 3 weeks, yellow-green block crystals were isolated (45 % yield). Elemental analysis: found (calcd for **1**): Ni: 4.23. FT-IR (KBr, cm^{-1}): 988, 948, 889, 863, 800, 743, 700, 543, 519. The Ni $2p_{3/2}$ and Ni $2p_{1/2}$ binding energies of 932.8 and 952.5 eV for **1**. UV-visible spectrum of **1** in 80 mM sodium borate buffer (pH 9.0) at 296 K: $\lambda = 690$ nm.

Table S1 Crystal data and structure refinement for 1

Empirical formula	$H_{160}K_{20}Ni_{10}O_{228}Si_4W_{40}$
Formula weight	12644.74
Temperature/K	293(2)
Crystal system	N/A
Space group	$P2_1/n$
a/Å	20.5662(11)
b/Å	27.0389(6)
c/Å	20.6026(13)
α/°	90.00
β/°	118.757(8)
γ/°	90.00
Volume/$Å^3$	10043.8(9)
Z	2
$\rho_{calc}g/cm^3$	4.181
μ/mm^{-1}	24.283
F(000)	11320.0
Crystal size/mm^3	0.35 × 0.20 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.66 to 50
Index ranges	$-24 \leq h \leq 22$, $-32 \leq k \leq 23$, $-24 \leq l \leq 23$
Reflections collected	40588
Independent reflections	17186 [R_{int} = 0.0617, R_{sigma} = N/A]
Data/restraints/parameters	17186/324/1284
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0494, wR_2 = 0.1104
Final R indexes [all data]	R_1 = 0.0736, wR_2 = 0.1235
Largest diff. peak/hole / e $Å^{-3}$	3.00/-2.83

$^aR_1 = \Sigma||F0| - |Fc|| / \Sigma|F0|$; $^bwR_2 = \Sigma[w(F0^2 - Fc^2)^2]/\Sigma[w(F0^2)^2]^{1/2}$

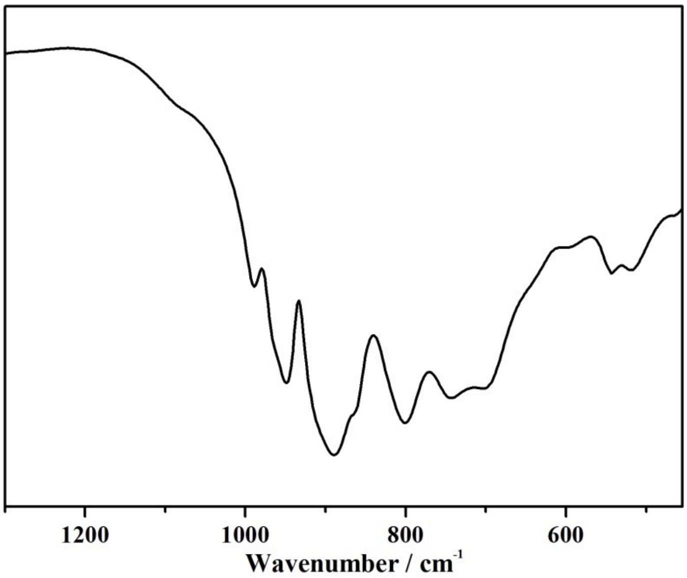


Fig. S1 FT-IR spectrum of **1**

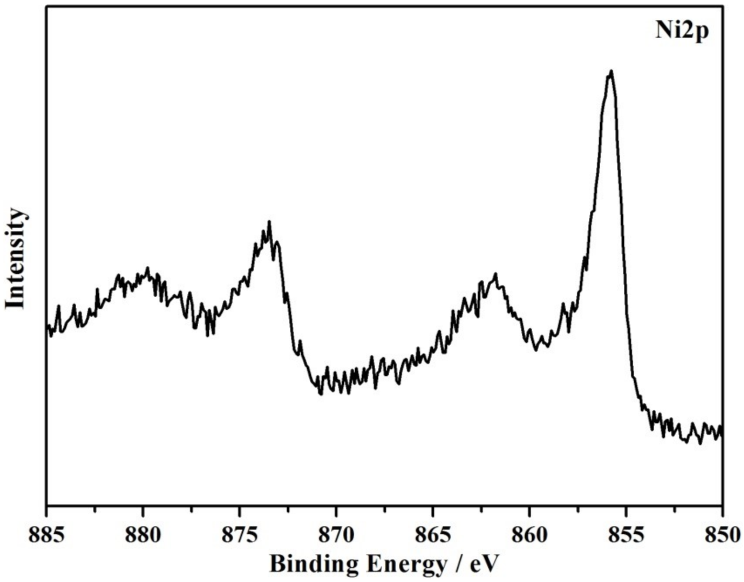


Fig. S2 X-ray photoelectron spectra of **1** showing the region of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks of **1**. The binding energy of each element was normalized to the C 1s peak (284.8 eV).

Synthesis of $[Na_2Ni_2(PW_9O_{34})_2]^{12-}$

$[Na_2Ni_2(PW_9O_{34})_2]^{12-}$ was synthesized according to reference.[3] $Na_2WO_4·2H_2O$ (5 g, 15.2 mmol) and Na_2HPO_4 (0.24, 1.7 mmol) were dissolved in 100 mL H_2O followed by an addition of $Ni(NO_3)_2·6H_2O$ (0.31 g, 1.1 mmol), resulting in a cloudy suspension. The pH was adjusted to 7.5 by dropwise addition of 6 M HCl, and a purple solution formed. The solution was heated at 90 °C for 1 h and then was allowed to cool to room temperature. Powdered KCl (0.6 g, 8.0mmol) was added, and the solution was left to slowly evaporate at room temperature. After several days, yellow-green needle crystals were formed (50 % yield). FT-IR (KBr, cm^{-1}): 1041, 1020, 955, 937, 906, 810, 745.

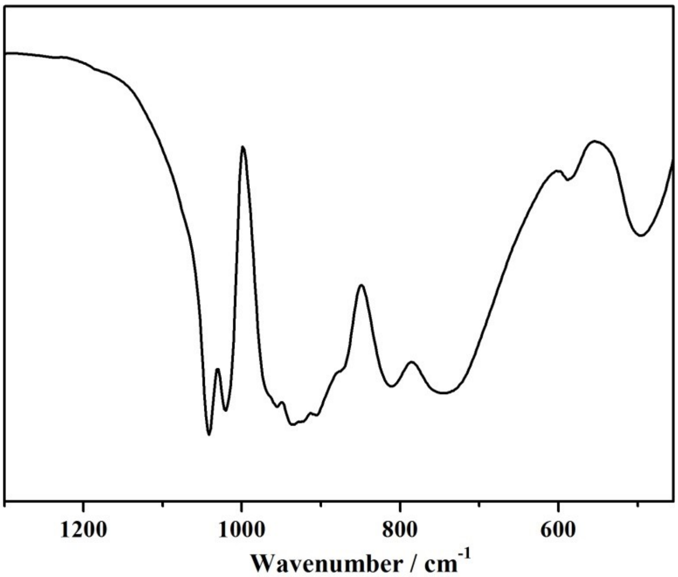


Fig. S3 FT-IR spectrum of $[Na_2Ni_2(PW_9O_{34})_2]^{12-}$

Synthesis of $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$

$[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ was synthesized according to reference.[4] The pH of an aqueous solution of 16.5 g (50 mmol) of $Na_2WO_4 \cdot 2H_2O$ and 0.78 g (5.5 mmol) of Na_2HPO_4 was adjusted to 7.9 with acetic acid. A solution containing 4.1 g (16 mmol) of $Ni(OOC\text{-}CH_3)_2 \cdot 4H_2O$ in 30 mL of H_2O was added to the first one. The resulting green solution (pH = 7.5) was refluxed for 2 h. A 4 g amount of Na_2HPO_4 was added, and the solution was refluxed again for 9 h and hot filtered. After adding 5 g of solid $K(OOC\text{-}CH_3)$, the resulting solution was allowed to cool at room temperature. After several hours small green needle-shaped crystals of the desired product were isolated by filtration and dried under vacuum. This product was recrystallized from hot water to obtain good-quality single crystals suitable for X-ray diffraction analysis (18 % yield). FT-IR (KBr, cm^{-1}): 1034, 1018, 959, 938, 891, 804, 723.

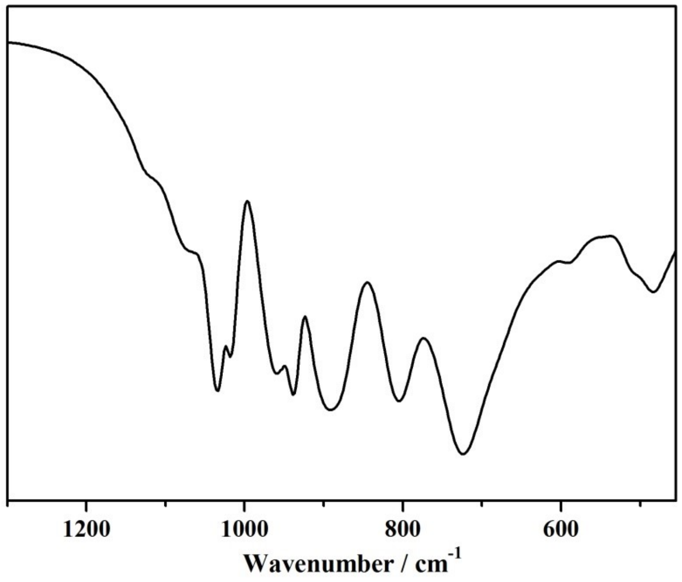


Fig. S4 FT-IR spectrum of $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$

Synthesis of $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$

$[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ was synthesized according to reference.[4] A solution of 5.53 g (22 mmol) of $Ni(OOC\text{-}CH_3)_2\cdot 4H_2O$ in 50 mL of water was added to 100 mL of an aqueous solution containing 33 g (100 mmol) of $Na_2WO_4\cdot 2H2O$ and 1.57 g (11 mmol) of Na_2HPO_4 with pH adjusted to 7.1 with acetic acid. The resulting yellow solution (pH = 6.9) was refluxed for 2 h and hot filtered, and then 4 g of $K(OOC\text{-}CH_3)$ was added to the filtrate while hot. After several hours a mixture of chunky small yellow crystals and powder of the desired product is obtained (58 % yield). FT-IR (KBr, cm^{-1}): 1039, 945, 899, 807, 726.

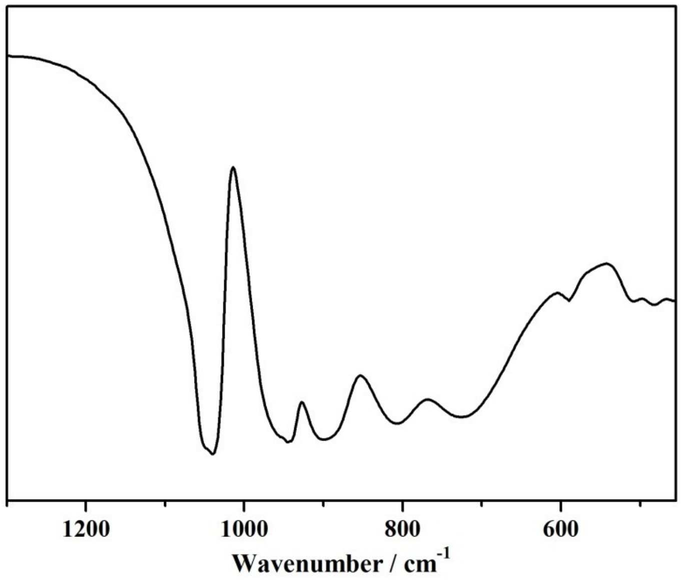


Fig. S5 FT-IR spectrum of $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$

Synthesis of $[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]^{7-}$

$[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]^{7-}$ was synthesized according to reference.[4] A solution of 2.49 g (10 mmol) of $Ni(OOC\text{-}CH_3)_2\cdot H_2O$ in 50 mL of water was added to 100 mL of an aqueous solution containing 9.87 g (33 mmol) of $Na_2WO_4\cdot H_2O$ and 0.425 g (3 mmol) of Na_2HPO_4 with pH adjusted to 6.5 with acetic acid. The resulting yellow solution (pH = 6.3) was refluxed for 2 h and hot filtered, and then 4 g of $K(OOC\text{-}CH_3)$ was added to the filtrate while hot. After several days small pale green needle-shaped crystals of the desired product were isolated by filtration and dried under vacuum (43 % yield). FT-IR (KBr, cm^{-1}): 1038, 941, 896, 809, 721.

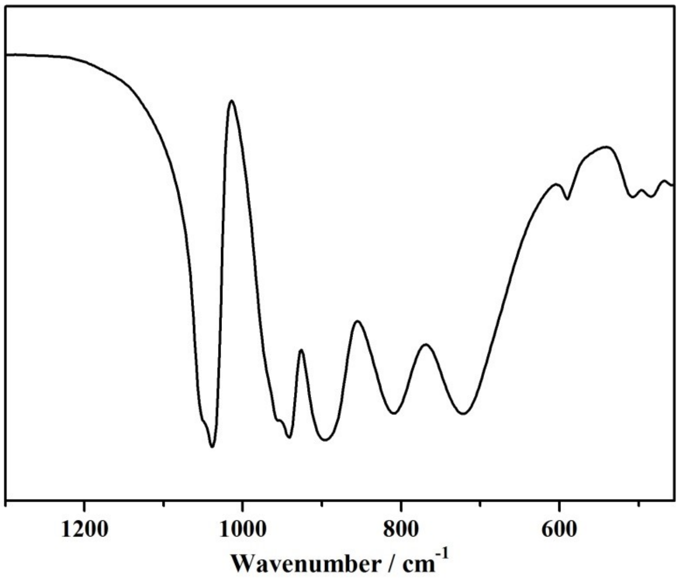


Fig. S6 FT-IR spectrum of $[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]^{7-}$

Synthesis of $[Na_3\subset\{Ni(H_2O)_4\}_6\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]^{15-}$

$[Na_3\subset\{Ni(H_2O)_4\}_6\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]^{15-}$ was synthesized according to reference.[5] Freshly prepared $K_{12}[H_2P_2W_{12}O_{48}]\cdot24H_2O$ (1.5 g, 0.38 mmol) was dissolved in 75 mL distilled water. Then 9.0 mL of 1.0 M $NiCl_2$ aqueous solution (9.0 mmol), 0.125 g of $Na_2WO_4\cdot2H_2O$ (0.38 mmol) and 1.0 g NaCl were added one by one with vigorously stirring. Then the pH value of the mixture was carefully adjusted to 1.0 with 4 M HCl solution. After an 8 h stirring, the solution was filtered. The filtrate was kept at room temperature for slow evaporation. Green block crystals was isolated after three weeks (35 % yield). FT-IR (KBr, cm^{-1}): 1090, 1011, 963, 952, 909, 787, 598, 562, 528.

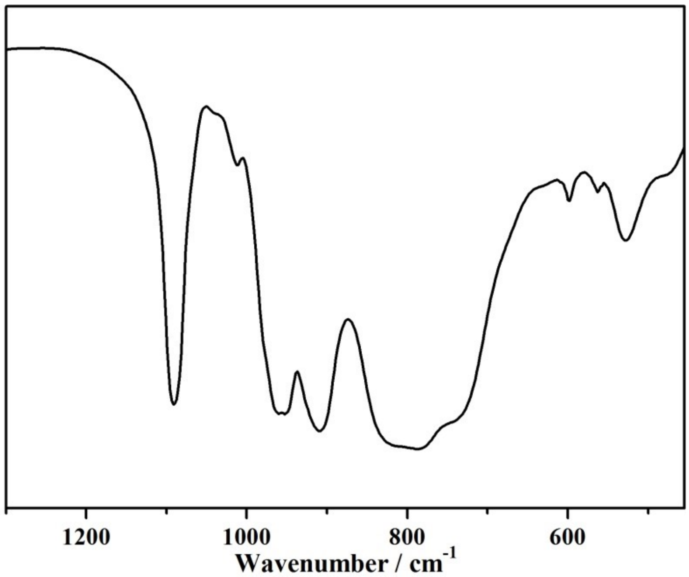


Fig. S7 FT-IR spectrum of $[Na_3\subset\{Ni(H_2O)_4\}_6\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]^{15-}$

Synthesis of $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$

$[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ was synthesized according to reference.[6] A 0.31 g (1.30 mmol) sample of $NiCl_2\cdot 6H_2O$ was added with stirring to 20 mL of a 1 M NaCl solution. Then 2.00 g (0.79 mmol) of $Na_9[A\text{-}PW_9O_{34}]\cdot 5H_2O$ was added in small portions over 5 min. The solution was heated to 60 °C for about 30 min in a water bath and then filtered. The green, clear filtrate (pH 6.9) was placed in a refrigerator (4 °C). After several months a mixture of green and yellow crystals had formed. The yellow crystals was isolated (2 % yield). FT-IR (KBr, cm^{-1}): 1038, 1023, 963, 940, 900, 739, 589, 491, 409.

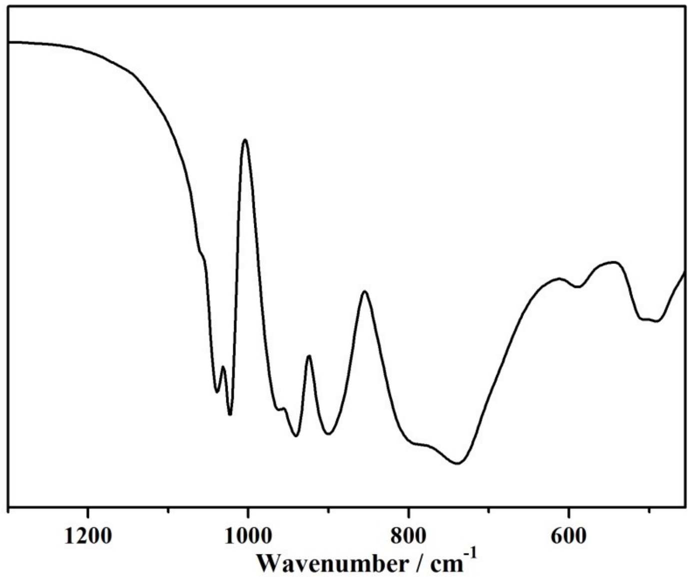


Fig. S8 FT-IR spectrum of $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$

Synthesis of $[Ni_{25}(H_2O)_2(OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]^{50-}$

$[Ni_{25}(H_2O)_2(OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]^{50-}$ was synthesized according to reference.[7] $NiCl_2 \cdot 6H_2O$ (0.3 g, 1.26 mmol) was dissolved in 40 mL of distilled water. $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}] \cdot 18H_2O$ (1.0 g, 0.34 mmol) was added and this mixture was stirred until a clear, green solution was formed. Then, $Na_3PO_4 \cdot 12H_2O$ (0.80 g, 2.1 mmol) and Na_2CO_3 (0.05 g, 0.47 mmol) were added successively, followed by the adjustment of pH of 8.0−9.0 with 255−325 µL of 4.0 M HCl (aq). The resulting green mixture was stirred for 2 h at 60−70 °C and the green precipitate was removed by filtration. The filtrate was kept in a 50 mL beaker to allow slow evaporation at room temperature. After 3 weeks, green block crystals were isolated, washed with cold distilled water, and air-dried (3 % yield). FT-IR (KBr, cm^{-1}): 1516, 1106, 986, 934, 889, 853, 806, 683, 588, 525.

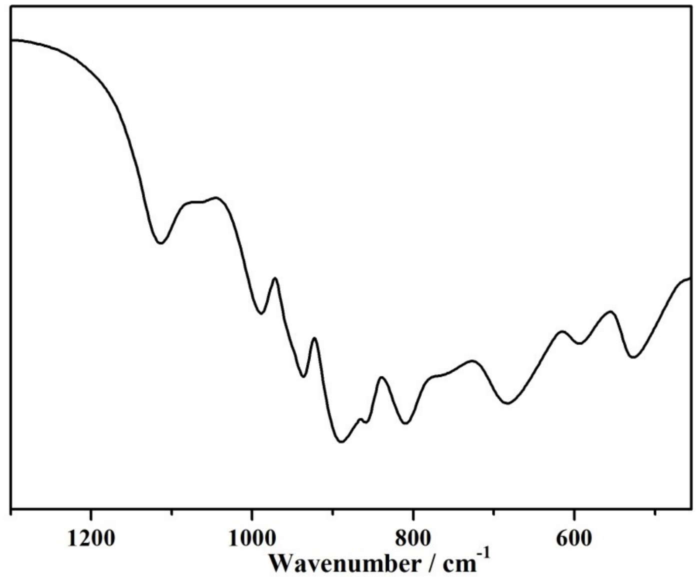


Fig. S9 FT-IR spectrum of $[Ni_{25}(H_2O)_2(OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]^{50-}$

Synthesis of $[Ni_5(OH)_6(OH_2)_3(Si_2W_{18}O_{66})]^{12-}$

$[Ni_5(OH)_6(OH_2)_3(Si_2W_{18}O_{66})]^{12-}$ was synthesized according to reference.[8] $Na_{10}[\alpha\text{-}SiW_9O_{34}]$ (1.5 g, 0.54 mmol) were added with stirring to 30 mL of deionized water, forming a turbid white suspension. The pH was adjusted to 6.8 with the dropwise addition of 1 M HCl, causing the suspension to dissolve into a solution. $NiCl_2{\cdot}6H_2O$ (320 mg, 1.35 mmol) was added to the stirring solution. The pH was 5.2 after addition and was adjusted using 1 M HCl if necessary. The solution was stirred, refluxed for two hours, cooled to room temperature, filtered, and then 20 mL of saturated KCl was added. The resulting solution was placed in an ice bath with stirring for an hour and the pale green precipitate that slowly formed over this time was collected via filtration. The crude product was recrystallized twice from minimal hot water. Slow evaporation over two days, green crystals were isolated, air-dried (10 % yield). FT-IR (KBr, cm^{-1}): 998, 946, 892, 798, 710, 637, 525.

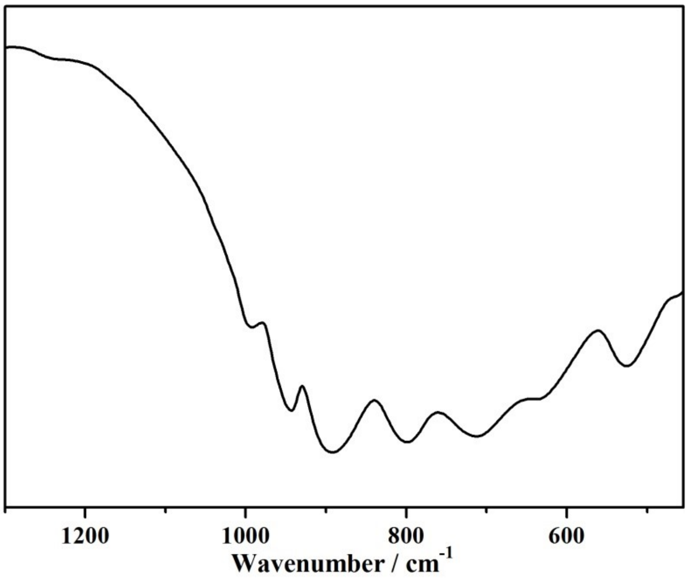


Fig. S10 FT-IR spectrum of $[Ni_5(OH)_6(OH_2)_3(Si_2W_{18}O_{66})]^{12-}$

Synthesis of $[Ni(H_2O)_2(\gamma\text{-}SiW_{10}O_{35})_2]^{10-}$

$[Ni(H_2O)_2(\gamma\text{-}SiW_{10}O_{35})_2]^{10-}$ was synthesized according to reference.[9] To 20 mL of a 1 M KCl solution were added simultaneously 0.078 g of $MnCl_2\cdot4H_2O$ (0.40 mmol) and 1.0 g of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ (0.36 mmol). The pH was then adjusted to 4.5 by the dropwise addition of a 0.1 M HCl solution. The resulting mixture was heated to 50 ◦C for 30 min, and then allowed to cool to room temperature and filtered. Slow evaporation of the filtrate resulted in dark brown crystals (28% yield). FT-IR (KBr, cm^{-1}): 1013, 960, 907, 805, 746, 687, 625, 541, 529, 492.

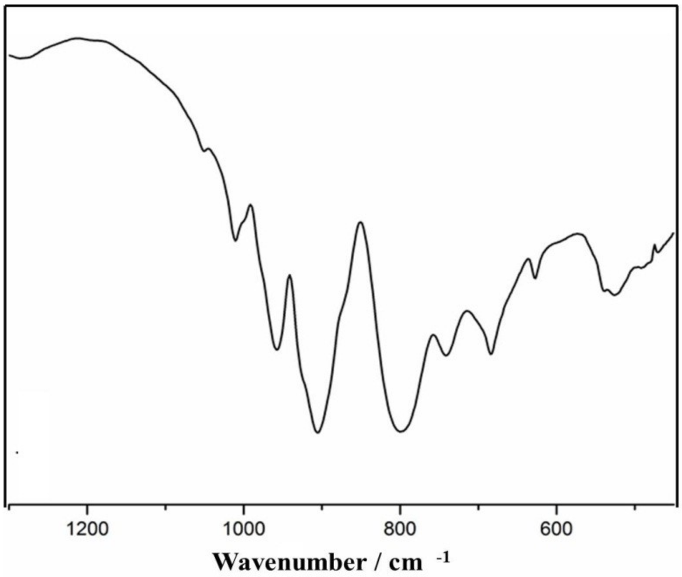


Fig. S11 FT-IR spectrum of $[Ni(H_2O)_2(\gamma\text{-}SiW_{10}O_{35})_2]^{10-}$

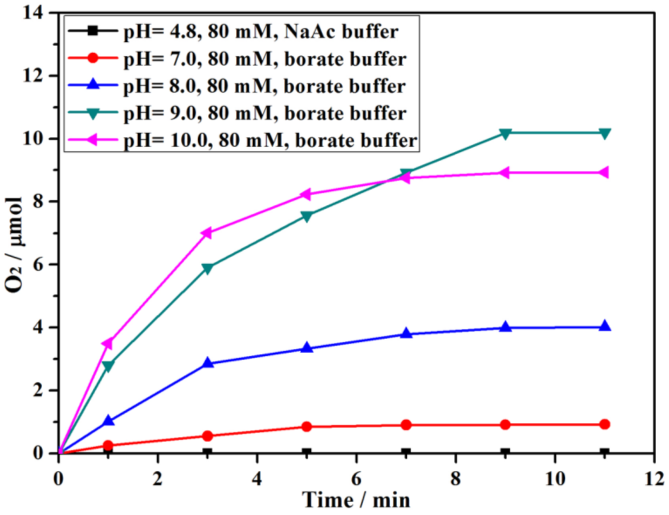


Fig. S12 Kinetics of O_2 formation in the photocatalytic system under various pH conditions. Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 15 μM **1**, total reaction volume is 15 mL.

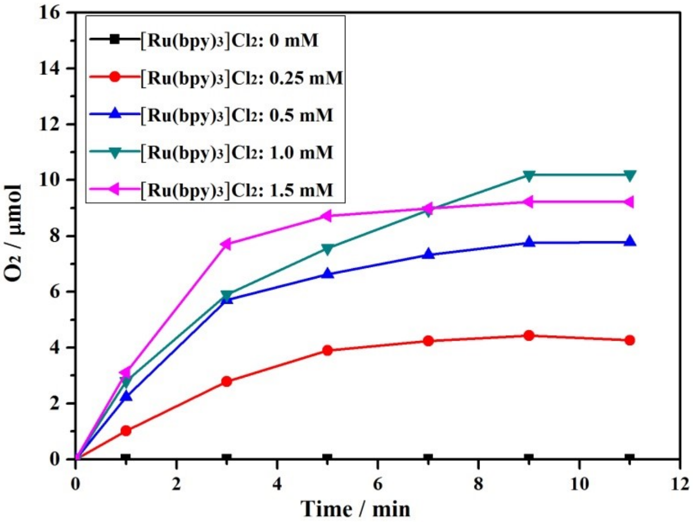


Fig. S13 Kinetics of O_2 formation in the photocatalytic system using different concentrations of $[Ru(bpy)_3]Cl_2$. Conditions: LED lamp (λ ≥ 420 nm), 5.0 mM $Na_2S_2O_8$, 15 μM **1** , 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

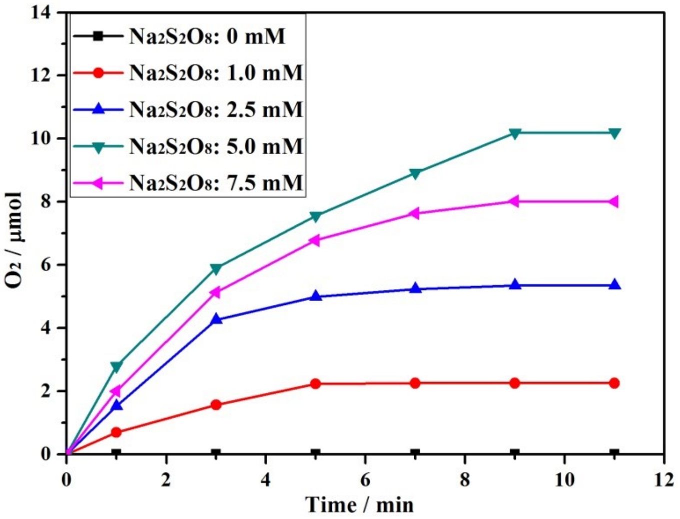


Fig. S14 Kinetics of O_2 formation in the photocatalytic system using different concentrations of $Na_2S_2O_8$. Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 15 μM **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

Table S2. TONs and O_2 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	13.3	335	1.7	9
2	5	13.9	70	0.3	10
3	10	22.1	55	0.2	11
4	15	27.2	45	0.2	17
5	20	26.6	33	0.1	15
6	25	16.9	17	0.1	13

[a] Conditions: LED lamp (λ ≥ 420 nm); 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL. [b] O_2 Yield = 2 × mole of O_2 per mole of $Na_2S_2O_8$. [c] TON = mole of O_2/mole of catalyst. [d] $TOF_{initial}$ = mole of O_2/(mole of catalyst × 60 s), based on the amount of O_2 produced after 1 min of irradiation.

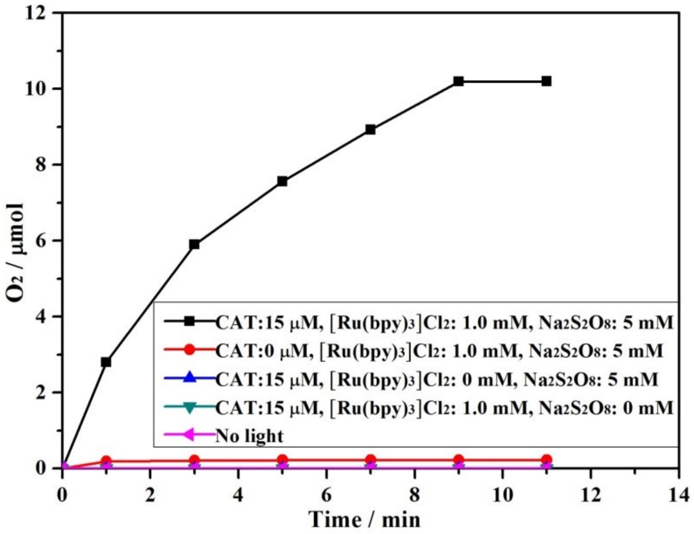


Fig. S15 Kinetics of O_2 formation in the photocatalytic system without **1** (red), $[Ru(bpy)_3]Cl_2$ (blue), $Na_2S_2O_8$ (blackish green) or light (pink).

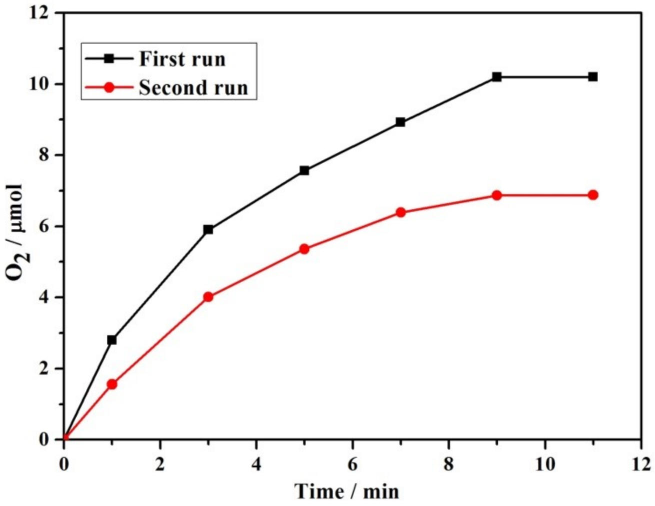


Fig. S16 O_2 formation kinetics of the first run and the second run. After completion of the first run, 17.8 mg $Na_2S_2O_8$ was added to the second run. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 15 µM **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

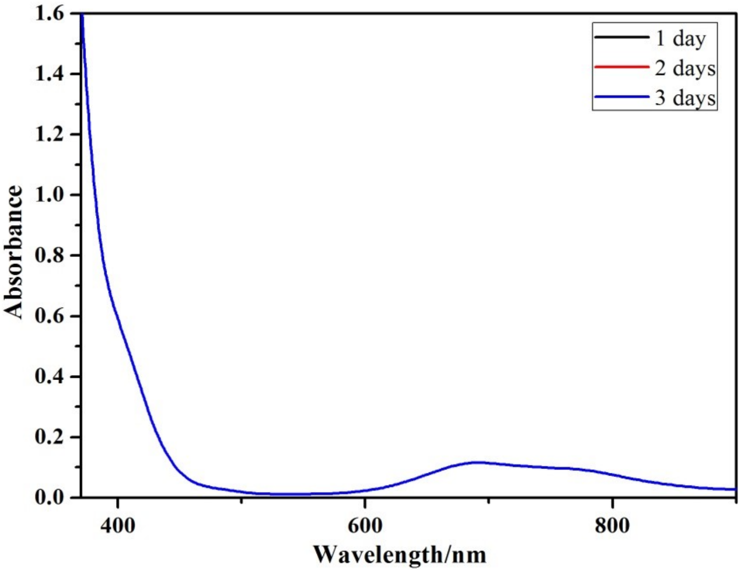


Fig. S17 Time-dependent UV-Vis spectra of 0.5 mM **1** in pH 9.0, 80 mM sodium borate buffer solution.

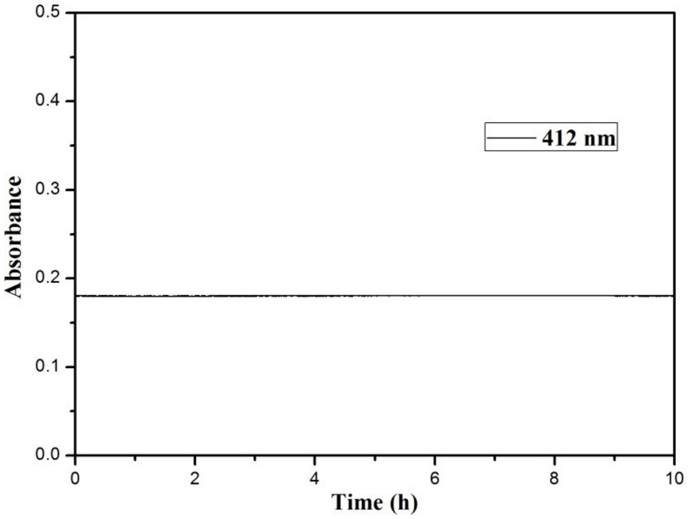


Fig. S18 Changes in UV-vis spectra of 0.5 mM **1** in 80 mM sodium borate buffer at pH 9.0.

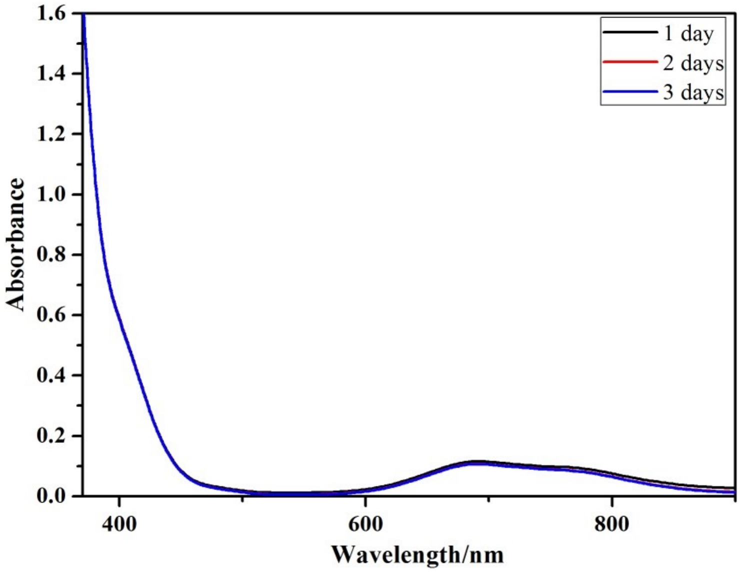


Fig. S19 Time-dependent UV-Vis spectra of **1** (0.5 mM) in the pH 9.0 sodium borate buffer solution (80 mM) with $Na_2S_2O_8$ (5 mM).

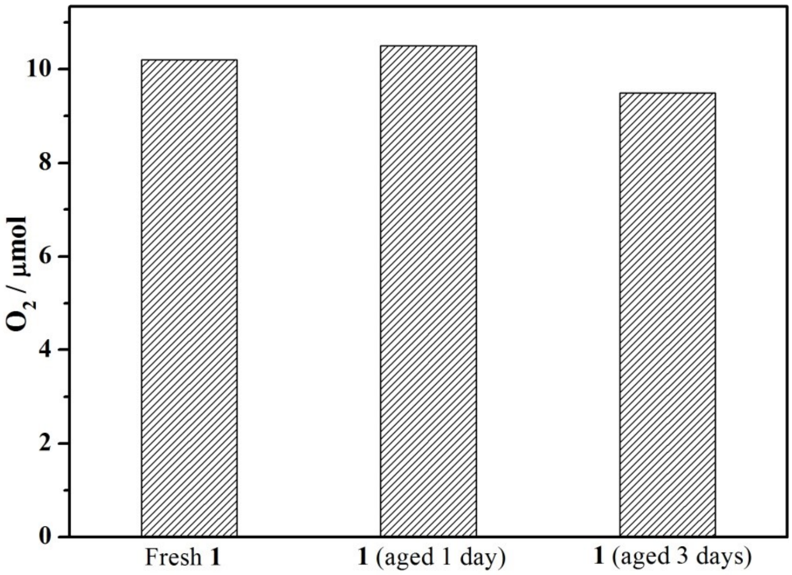


Fig. S20 O_2 evolution in the photocatalytic system using 15 μM of fresh, 1 day aged **1** and 3 days aged **1**. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

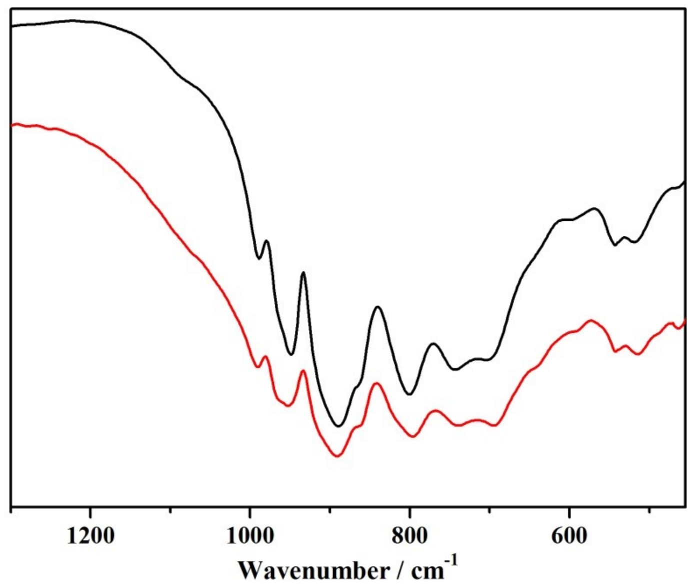
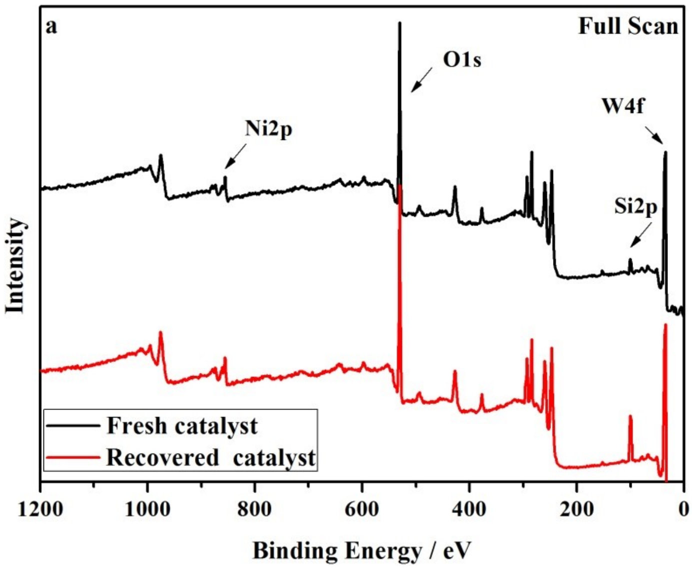
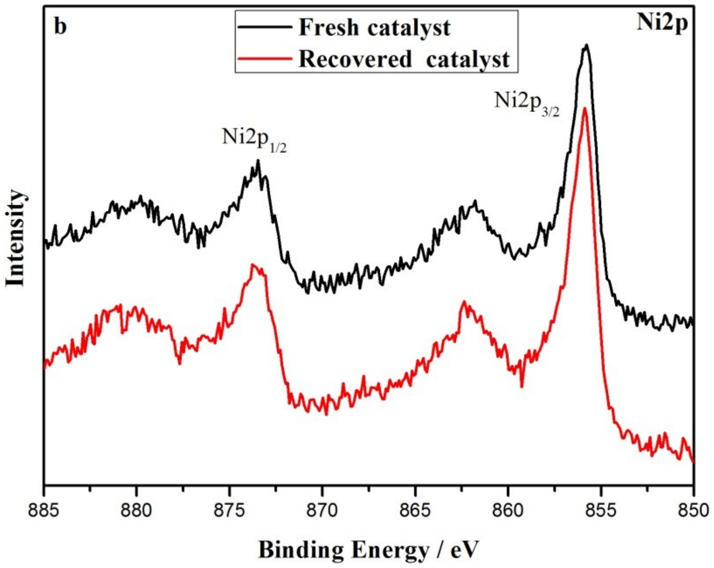
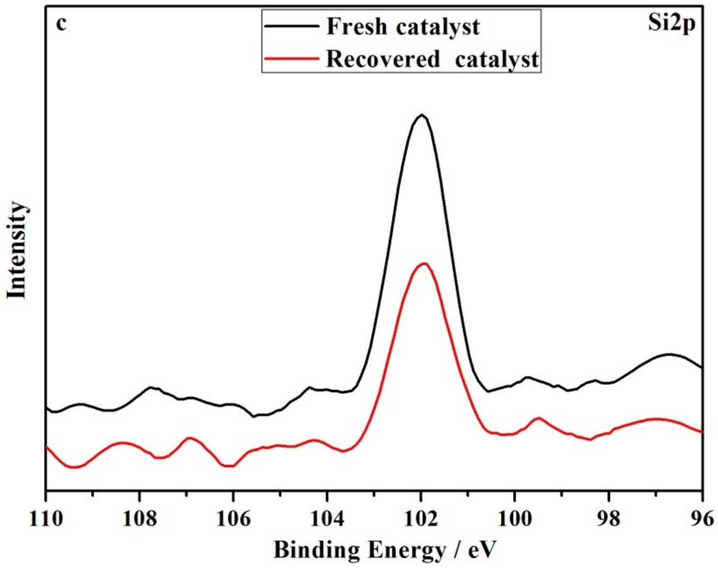
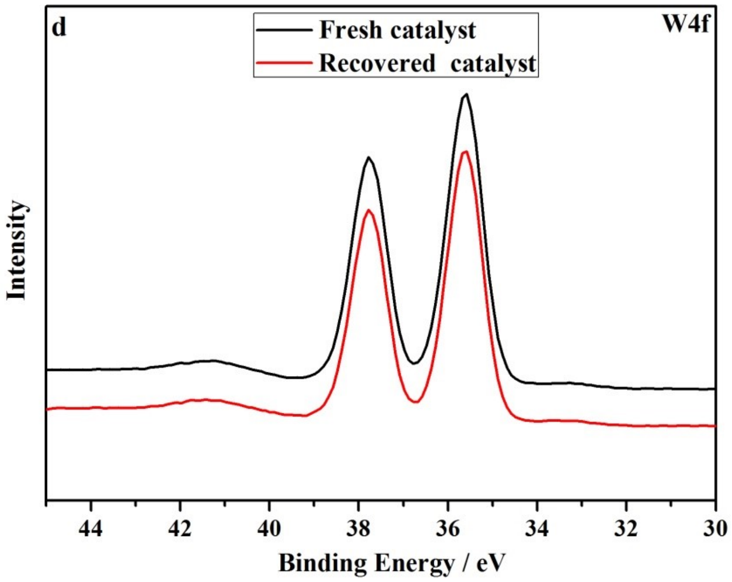


Fig. S21 FT-IR spectra of fresh **1** (black curve) and the recycled catalyst (red curve) obtained from the photocatalytic water oxidation solution using acetone.




b
Fresh catalyst
Recovered catalyst
Ni2p
Ni2p$_{3/2}$
Ni2p$_{1/2}$
Intensity
885
880
875
870
865
860
855
850
Binding Energy / eV


c
Fresh catalyst
Recovered catalyst
Si2p
Intensity
110
108
106
104
102
100
98
96
Binding Energy / eV


d
Fresh catalyst
Recovered catalyst
W4f
Intensity
44
42
40
38
36
34
32
30
Binding Energy / eV

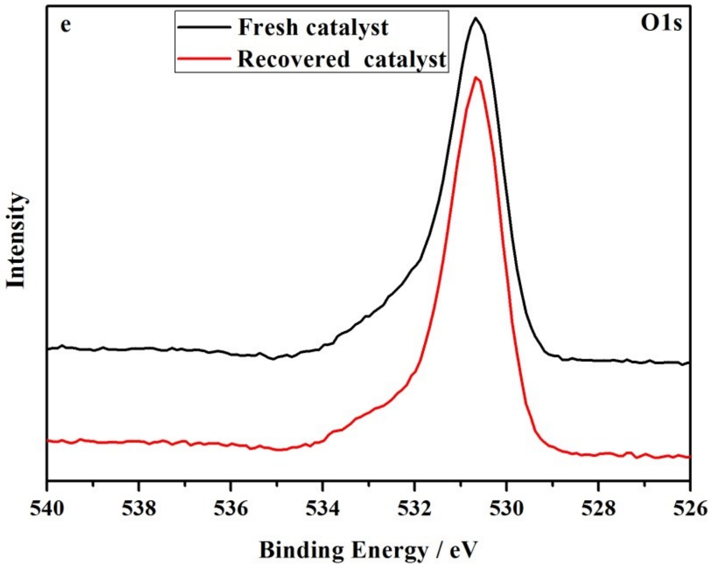


Fig. S22 X-ray photoelectron spectra of **1** before and after the reaction in the energy regions of (a) full scan, (b) Ni 2p, (c) Si 2p, (d) W 4f and (e) O 1s.

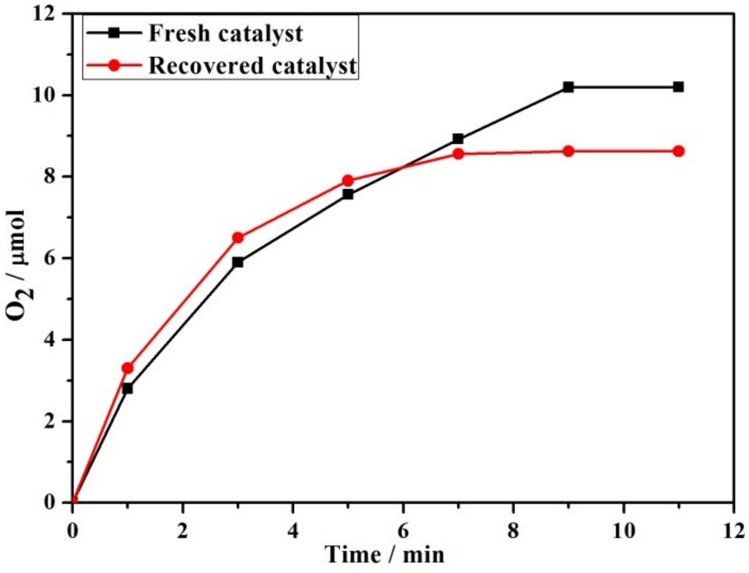


Fig. S23 Kinetics of O_2 formation in the photocatalytic system using fresh and recovered **1**. Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 15 μM **1**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

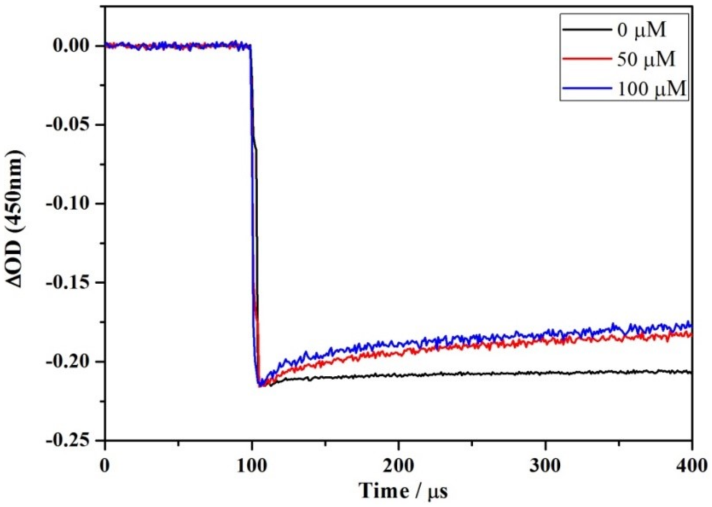


Fig. S24 Flash photolysis experiments (excitation at 445 nm) of 80 mM borate buffer (pH 9.0) solutions containing 50 μM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$ and 0−100 μM **1**, measured at 450 nm.

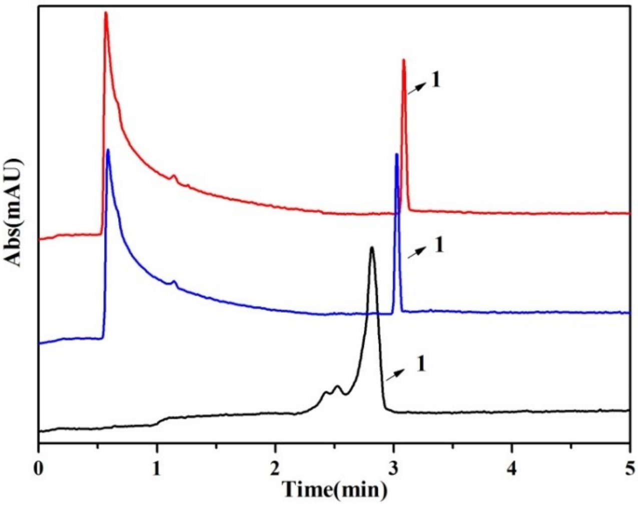


Fig. S25 An electropherogram for **1** (18 μM). Black line: 18 μM of **1** in a 20 mM sodium borate buffer solution (pH = 9.0). Blue line: 18 μM of **1** in a 20 mM sodium borate buffer solution (pH = 9.0) containing $[Ru(bpy)_3]Cl_2$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) before illumination. Red line: 18 μM of **1** in a 20 mM sodium borate buffer solution (pH = 9.0) containing $[Ru(bpy)_3]Cl_2$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) after 11 min of illumination. Experimental conditions for capillary electrophoresis: Fused-silica capillaries (50μm i.d., 365μm o.d., Hebei Yongnian Factory, China) with total length of 50.2 cm and effective length of 10 cm were used. The detection wavelength was set at 214 nm. The running buffer for CE separation was 20 mM sodium borate buffer (pH 10.0). The separation voltage was set at -20 kV. The sample was injected into the capillary (0.5psi, 3 s).

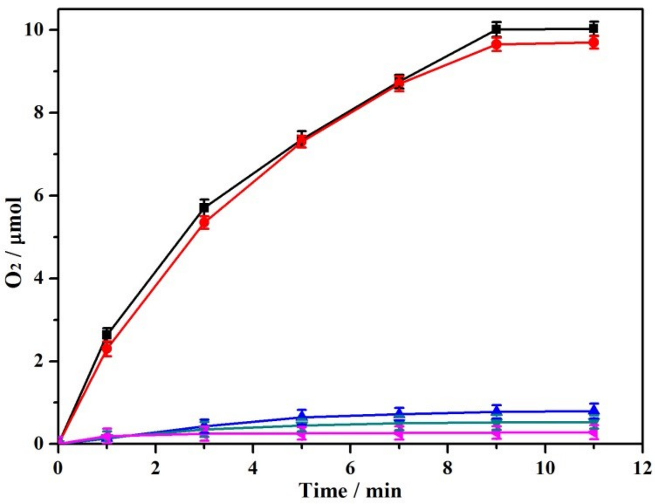


Fig. S26 Kinetics of light-driven catalytic O_2 evolution from water catalyzed by **1** in 80 mM sodium borate buffer at pH 9.0. Conditions: LED lamp (λ ≥ 420 nm), 5.0 mM $Na_2S_2O_8$, 1.0 mM $[Ru(bpy)_3]Cl_2$. Black line: 15 µM **1** without extraction by $THpANO_3$-toluene solution; Red line: extraction of the 15 µM **1** in sodium borate buffer by $THpANO_3$-toluene solution, followed by addition of 15 µM **1**, $[Ru(bpy)_3]Cl_2$ and $Na_2S_2O_8$; Blue line: extraction of the 15 µM **1** in sodium borate buffer by $THpANO_3$-toluene solution, followed by addition of 15 µM $NiSO_4$, $[Ru(bpy)_3]Cl_2$ and $Na_2S_2O_8$; Cyan line: complete extraction of the 15 µM **1** in sodium borate buffer with a $THpANO_3$-toluene solution, followed by addition of $[Ru(bpy)_3]Cl_2$ and $Na_2S_2O_8$ but no **1**. Magenta line: the reaction solution after the first run followed by extraction using a $THpANO_3$-toluene solution and addition of 17.8 mg $Na_2S_2O_8$.

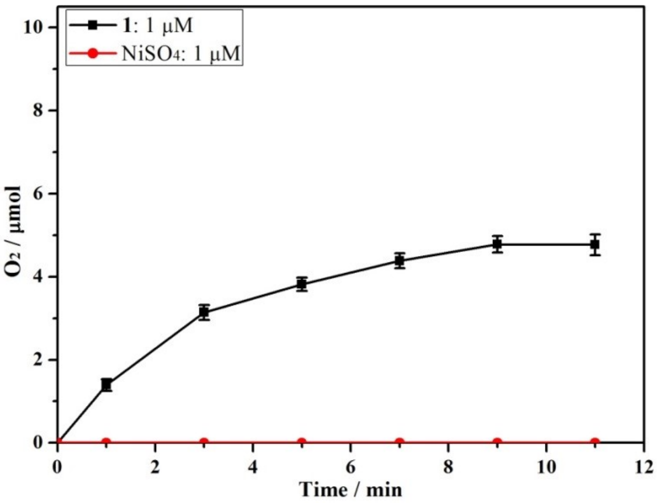


Fig. S27 Kinetics of O_2 formation in the photocatalytic system using 1 µM $NiSO_4$ and 1 µM **1**. Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

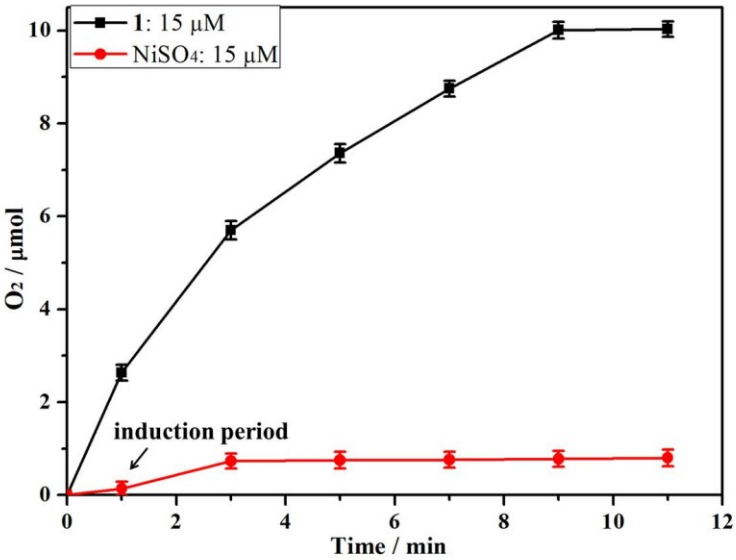


Fig. S28 Kinetics of O_2 formation in the photocatalytic system using 15 μM $NiSO_4$ and 15 μM **1**. Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

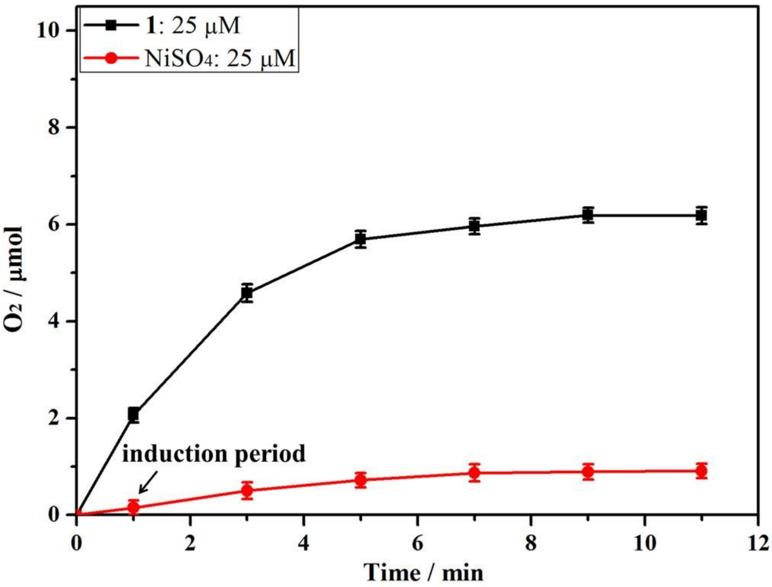


Fig. S29 Kinetics of O_2 formation in the photocatalytic system using 25 μM $NiSO_4$ and 25 μM **1**. Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

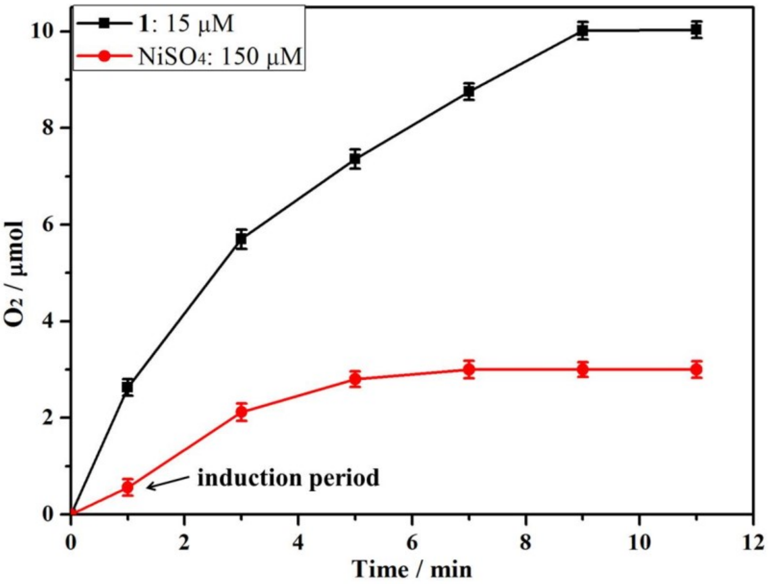


Fig. S30 Kinetics of O_2 formation in the photocatalytic system using 150 µM $NiSO_4$ and 15 µM **1**. Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

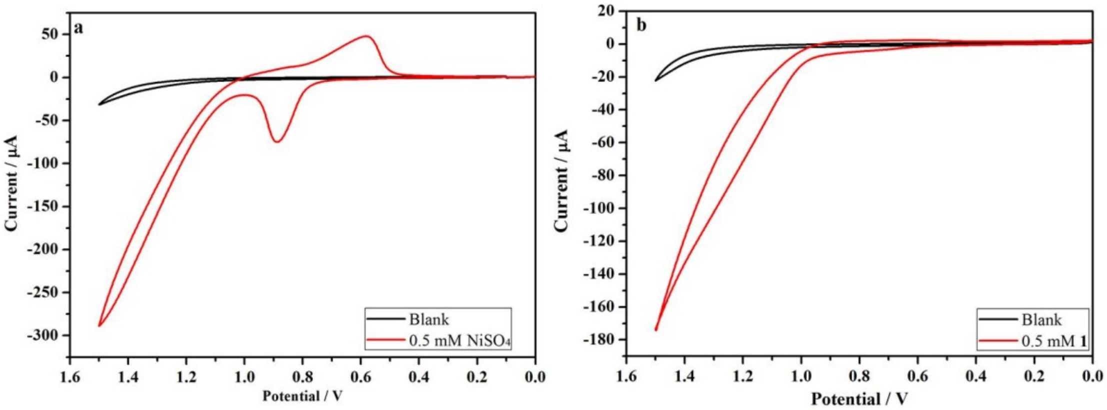


Fig. S31 (a) Cyclic voltammogram (CV) of 80 mM sodium borate buffer solution at pH 9.0 without $NiSO_4$ (black) and with 0.5 mM $NiSO_4$ (red). (b) Cyclic voltammogram (CV) of 80 mM sodium borate buffer solution at pH 9.0 without **1** (black) and with 0.5 mM **1** (red). Conditions: glassy carbon working electrode, Ag/AgCl (saturate KCl) reference electrode and Pt wire counter electrode; scan rate 25 mV/s.

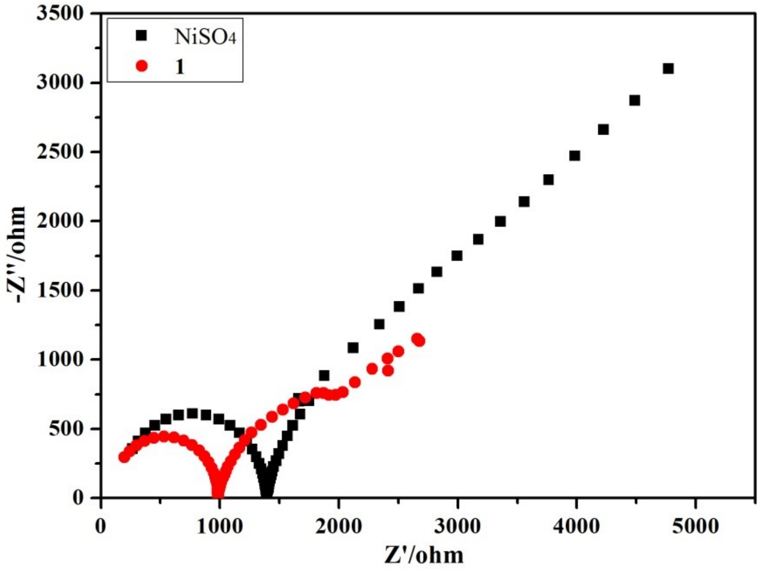


Fig.S32 Nyquist diagrams of electrochemical impedance spectroscopy (EIS) for $NiSO_4$ and **1**. Conditions: glassy carbon working electrode, Ag/AgCl (saturate KCl) reference electrode and Pt wire counter electrode, AC voltage with 5 mV amplitude in a frequency ranging from 100000 to 0.1 Hz in 80 mM borate buffer solution (pH=9.0).

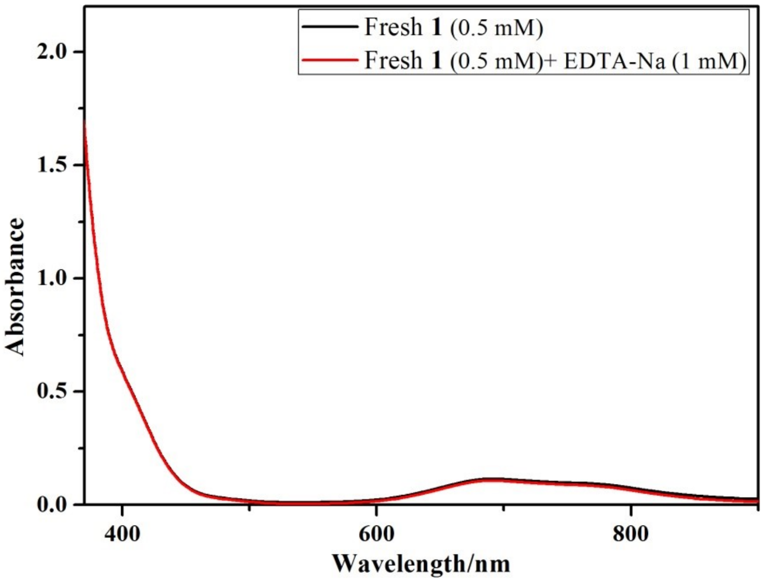


Fig. S33 Time-dependent UV-Vis spectra of 0.5 mM **1** with EDTA-Na in 80 mM sodium borate buffer at pH 9.0.

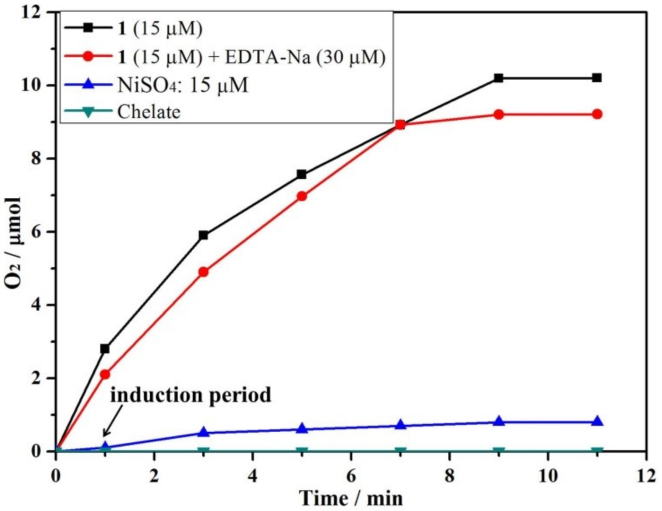


Fig. S34 Kinetics of light-driven catalytic O_2 evolution for: **1** (black line), **1** in the presence of EDTA-Na (red line), $NiSO_4$ (blue line) and chelate (dark cyan). Conditions: LED lamp (λ ≥ 420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

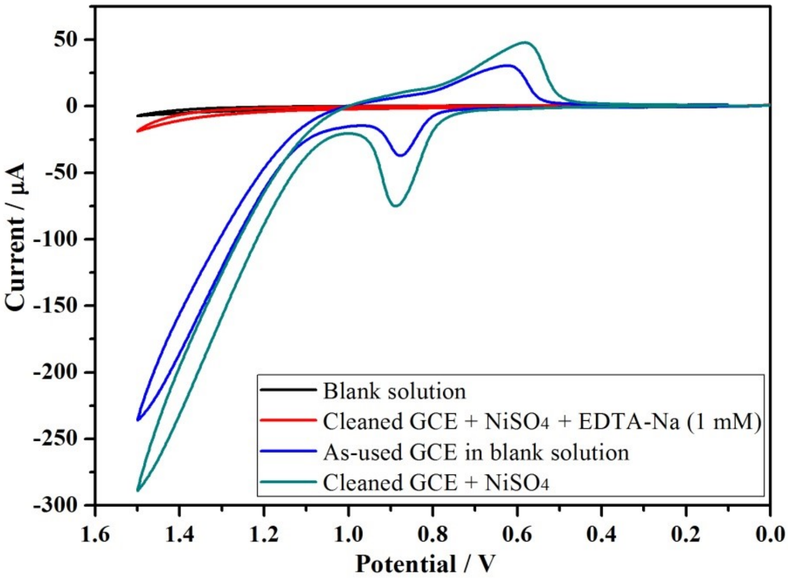


Fig. S35 CV curve of 0.5 mM $NiSO_4$ in 80 mM pH 9.0 borate buffer (dark cyan line) with cleaned glassy carbon electrode (GCE). Blue line shows the CV curve of the as-used GCE in 80 mM pH 9.0 borate buffer without $NiSO_4$. Red line shows the CV curve of 0.5 mM $NiSO_4$ in 80 mM pH 9.0 borate buffer with GCE in the presence of EDTA-Na. Black line shows the CV curve of cleaned GCE in 80 mM pH 9.0 borate buffer without $NiSO_4$ (i.e. blank solution). Conditions: glassy carbon working electrode, Ag/AgCl (saturate KCl) reference electrode and Pt wire counter electrode; scan rate 25 mV/s.

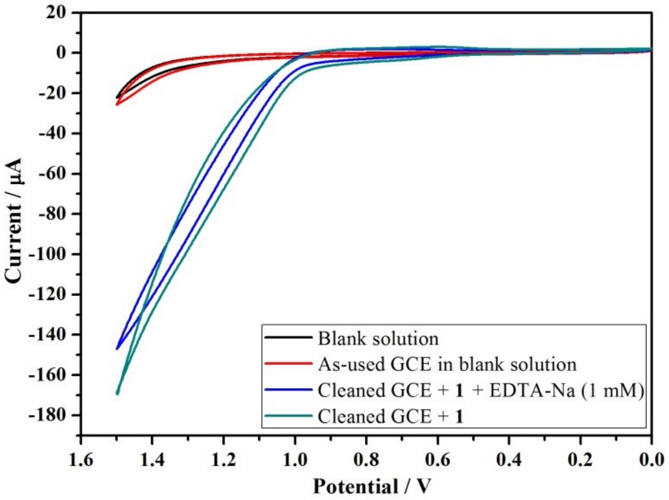


Fig. S36 CV curve of 0.5 mM **1** in 80 mM pH 9.0 borate buffer (dark cyan line) with cleaned glassy carbon electrode (GCE). Blue line shows the CV curve of 0.5 mM **1** in 80 mM pH 9.0 borate buffer with GCE in the presence of EDTA-Na. Red line shows the CV curve of the as-used GCE of the chelating reaction in 80 mM pH 9.0 borate buffer without **1**. Black line shows the CV curve of cleaned GCE in 80 mM pH 9.0 borate buffer without **1** (i.e. blank solution). Conditions: glassy carbon working electrode, Ag/AgCl (saturate KCl) reference electrode and Pt wire counter electrode; scan rate 25 mV/s.

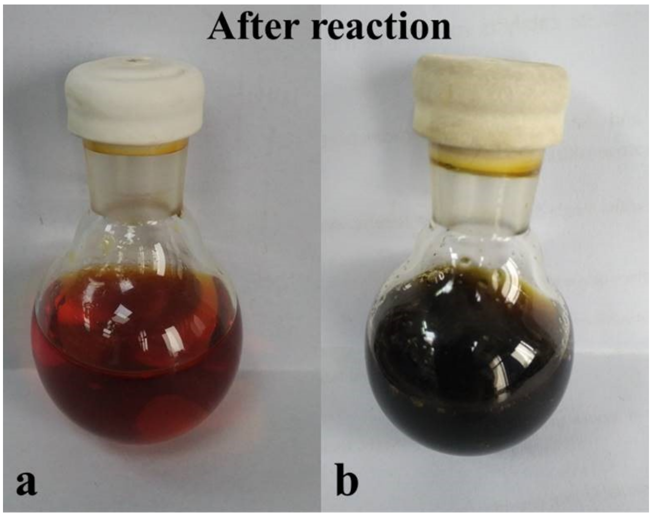


Fig S37 The pictures of water oxidation catalyzed by **1** (a) and $NiSO_4$ (b). Conditions: LED lamp (λ ≥ 420 nm), 15 μM $NiSO_4$ and 15 μM **1**, 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), the total reaction volume was 15 mL.

Fig S38 The experimental instruments for photocatalytic water oxidation.

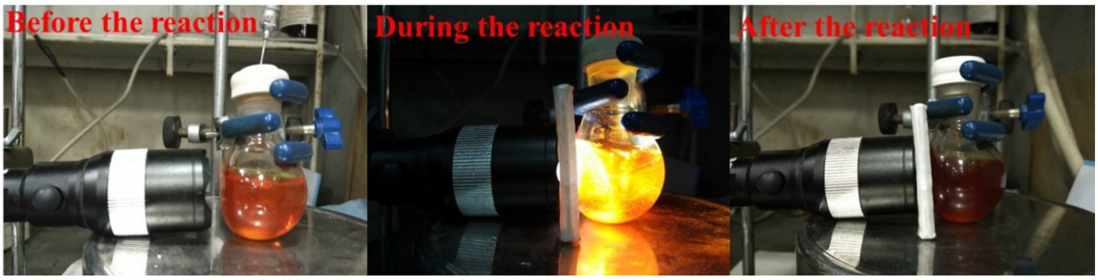


Fig S39 The enlarged reaction flask and light source during water oxidation process catalyzed by Ni_4 POM (**1**).

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