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 \([\beta\text{-SiNi}_2\text{W}_{10}\text{O}_{38}\text{(OH)}_2\text{(H}_2\text{O})_2]^{12-}\), 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

9th December 2016
Electronic Supporting Information

\[\{\beta-\text{SiNi}_2\text{W}_{10}\text{O}_{36}(\text{OH})_2(\text{H}_2\text{O})\}_2\}^{12-}: \text{a robust visible light-driven water oxidation catalyst based on nickel-containing polyoxometalate}\]

Li Yu\textsuperscript{a}, Yong Ding\textsuperscript{a,b,*}, Min Zheng\textsuperscript{a}, Hongli Chen\textsuperscript{a} and Junwei Zhao\textsuperscript{c}

\textit{a} Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China.

\textit{b} State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 10029, China.

\textit{c} Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004 (P. R. China)

* To whom correspondence should be addressed.

E-mail addresses: dingyong1@lzu.edu.cn
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 = $\pi \times (0.01 m)^2 \times 1750 \mu$mol.m$^{-2}.s^{-1} = 0.549 \mu$mol.$s^{-1}$

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

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

$= 17\%$

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. 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 \( \text{Ru(bpy)}_3 \text{Cl}_2 \) (1 mM) and \( \text{Na}_2\text{S}_2\text{O}_8 \) (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 \( \mu \text{V} \text{ mol}^{-1} \text{ m}^{-2} \text{ s}^{-1} \)), affording a value to be 1650 \( \mu \text{mol m}^{-2} \text{ s}^{-1} \).

**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 \( \mu \text{M} \) \( \text{Ru(bpy)}_3 \text{Cl}_2\); 5 mM \( \text{Na}_2\text{S}_2\text{O}_8\); 0-100 \( \mu \text{M} \) \( \text{I} \); pH 9.0, 80 mM borate buffer.

**Photocatalytic Water Oxidation**

Photocatalytic water oxidation was performed as follows. The desired concentration of catalyst (1–25 \( \mu \text{M} \)) was added to a buffer solution (80 mM, pH 4.8–10.0 for borate buffer) containing \( \text{Ru(bpy)}_3 \text{Cl}_2 \) (1.0 mM) and \( \text{Na}_2\text{S}_2\text{O}_8 \) (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 (\( \lambda \geq 420 \text{ nm} \)) at room temperature. After each irradiation time, 150 \( \mu \text{L} \) 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 \( \text{O}_2 \) 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 \( \text{O}_2 \) was calculated from the
concentration of O₂ in the headspace gas. Contamination of the head-space with air was corrected by measuring of N₂ present in the head-space (from the N₂ 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]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[β-SiW₁₁O₃⁹] ligand**

K₈[β-SiW₁₁O₃⁹] 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 HCl 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 HCl 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 KCl (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 K₈[γ-SiW₁₀O₃₆] ligand**

K₈[γ-SiW₁₀O₃₆] 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 K₈[β-SiW₁₁O₃₉] 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 K₂CO₃. The pH of the solution is kept at this value by addition of the K₂CO₃ 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 K₂CO₃ solution. The solid is removed by filtering, washed with 1 M KCl solution, and air dried.

**Synthesis of [[β-SiNi₂W₁₀O₃₆(OH)₂(H₂O)]₂]¹²⁻ (1)**

1 was synthesized according to reference.² 1.0 g NiSO₄·6H₂O was dissolved in 40 mL of a 0.5 M potassium acetate buffer (pH 4.8) followed by an addition of 4.8 g K₈[γ-SiW₁₀O₃₆], 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 H₂O, 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 2p₃/₂ and Ni 2p₁/₂ 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: λ = 690 nm.
Table S1 Crystal data and structure refinement for 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$\text{H}<em>{160}\text{K}</em>{20}\text{Ni}<em>{10}\text{O}</em>{228}\text{Si}<em>{4}\text{W}</em>{40}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>12644.74</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>N/A</td>
</tr>
<tr>
<td>Space group</td>
<td>$\text{P}2_1/\text{n}$</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>20.5662(11)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>27.0389(6)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>20.6026(13)</td>
</tr>
<tr>
<td>$\alpha$/°</td>
<td>90.00</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>118.757(8)</td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td>90.00</td>
</tr>
<tr>
<td>Volume/Å$^3$</td>
<td>10043.8(9)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$/g/cm$^3$</td>
<td>4.181</td>
</tr>
<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>24.283</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>11320.0</td>
</tr>
<tr>
<td>Crystal size/mm$^3$</td>
<td>$0.35 \times 0.20 \times 0.13$</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα ($\lambda = 0.71073$)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>6.66 to 50</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-24 \leq h \leq 22, -32 \leq k \leq 23, -24 \leq l \leq 23$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>40588</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>17186 ($R_{\text{int}} = 0.0617$, $R_{\text{sigma}} = \text{N/A}$)</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>17186/324/1284</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.036</td>
</tr>
<tr>
<td>Final R indexes [I $\geq$ 2σ (I)]</td>
<td>$R_1 = 0.0494$, $wR_2 = 0.1104$</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>$R_1 = 0.0736$, $wR_2 = 0.1235$</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å$^3$</td>
<td>3.00/-2.83</td>
</tr>
</tbody>
</table>

*R_1 = \Sigma ||F_0|| - |F_c|| / \Sigma |F_0|; wR_2 = \Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)]^{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$_2$Ni$_2$(PW$_9$O$_{34}$)$_2$]$^{12-}$

[Na$_2$Ni$_2$(PW$_9$O$_{34}$)$_2$]$^{12-}$ was synthesized according to reference.$^3$ Na$_2$WO$_4$·2H$_2$O (5 g, 15.2 mmol) and Na$_2$HPO$_4$ (0.24, 1.7 mmol) were dissolved in 100 mL H$_2$O followed by an addition of Ni(NO$_3$)$_2$·6H$_2$O (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, 8.0 mmol) 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.

![FT-IR spectrum](image)

**Fig. S3** FT-IR spectrum of [Na$_2$Ni$_2$(PW$_9$O$_{34}$)$_2$]$^{12-}$.

**Synthesis of [Ni$_9$(OH)$_3$(H$_2$O)$_6$(HPO$_4$)$_2$(PW$_9$O$_{34}$)$_3$]$^{16-}$**

[Ni$_9$(OH)$_3$(H$_2$O)$_6$(HPO$_4$)$_2$(PW$_9$O$_{34}$)$_3$]$^{16-}$ was synthesized according to reference.$^4$ The pH of an aqueous solution of 16.5 g (50 mmol) of Na$_2$WO$_4$·2H$_2$O and 0.78 g (5.5 mmol) of Na$_2$HPO$_4$ was adjusted to 7.9 with acetic acid. A solution containing 4.1 g (16 mmol) of Ni(OOC-CH$_3$)$_2$·4H$_2$O in 30 mL of H$_2$O was added to the first one. The resulting green solution (pH = 7.5) was refluxed for 2 h. A 4 g amount of Na$_2$HPO$_4$ was added, and the solution was refluxed again for 9 h and hot filtered. After adding 5 g of solid K(OOC-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.
Synthesis of $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_{9}\text{O}_{34})_2]$\textsuperscript{10-}

$[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_{9}\text{O}_{34})_2]$\textsuperscript{10-} was synthesized according to reference.\textsuperscript{4} A solution of 5.53 g (22 mmol) of Ni(OOC-CH\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 50 mL of water was added to 100 mL of an aqueous solution containing 33 g (100 mmol) of Na\textsubscript{2}WO\textsubscript{4}·2H\textsubscript{2}O and 1.57 g (11 mmol) of Na\textsubscript{2}HPO\textsubscript{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-CH\textsubscript{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\textsuperscript{-1}): 1039, 945, 899, 807, 726.
Synthesis of [Ni₃(H₂O)₅PW₁₀O₄₉H₂O]⁷⁻

[Ni₃(H₂O)₅PW₁₀O₄₉H₂O]⁷⁻ was synthesized according to reference.⁴ A solution of 2.49 g (10 mmol) of Ni(OOC-CH₃)₂·H₂O in 50 mL of water was added to 100 mL of an aqueous solution containing 9.87 g (33 mmol) of Na₂WO₄·H₂O and 0.425 g (3 mmol) of Na₂HPO₄ 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-CH₃) 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.
Synthesis of $[\text{Na}_3 \subset \{\text{Ni}(\text{H}_2\text{O})_4\}_6 \{\text{WO}(\text{H}_2\text{O})\}_3 \{\text{P}_2\text{W}_{12}\text{O}_{48}\}_3]^{15-}$

$[\text{Na}_3 \subset \{\text{Ni}(\text{H}_2\text{O})_4\}_6 \{\text{WO}(\text{H}_2\text{O})\}_3 \{\text{P}_2\text{W}_{12}\text{O}_{48}\}_3]^{15-}$ was synthesized according to reference.\textsuperscript{5} Freshly prepared $\text{K}_{12}[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}] \cdot 24\text{H}_2\text{O}$ (1.5 g, 0.38 mmol) was dissolved in 75 mL distilled water. Then 9.0 mL of 1.0 M $\text{NiCl}_2$ aqueous solution (9.0 mmol), 0.125 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (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\textsuperscript{-1}): 1090, 1011, 963, 952, 909, 787, 598, 562, 528.

**Fig. S6** FT-IR spectrum of $[\text{Ni}_3(\text{H}_2\text{O})_3\text{PW}_{10}\text{O}_{39}\text{H}_2\text{O}]^7-$. 
Synthesis of [Ni₃Na(H₂O)₂(PW₉O₃₄)₂]¹¹⁻

[Ni₃Na(H₂O)₂(PW₉O₃₄)₂]¹¹⁻ was synthesized according to reference.⁶ A 0.31 g (1.30 mmol) sample of NiCl₂·6H₂O was added with stirring to 20 mL of a 1 M NaCl solution. Then 2.00 g (0.79 mmol) of Na₉[A-PW₉O₃₄]·5H₂O 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. S7 FT-IR spectrum of [Na₃⊂{Ni(H₂O)₄}₆{WO(H₂O)}₃(P₂W₁₂O₄₈)₃]¹⁵⁻.
Synthesis of $[\text{Ni}_{25}(\text{H}_2\text{O})_2(\text{OH})_{18}(\text{CO}_3)_2(\text{PO}_4)_6(\text{SiW}_9\text{O}_{34})_6]^{50-}$

$[\text{Ni}_{25}(\text{H}_2\text{O})_2(\text{OH})_{18}(\text{CO}_3)_2(\text{PO}_4)_6(\text{SiW}_9\text{O}_{34})_6]^{50-}$ was synthesized according to reference.\textsuperscript{7} NiCl$_2$·6H$_2$O (0.3 g, 1.26 mmol) was dissolved in 40 mL of distilled water. Na$_{10}$[A-$\alpha$-SiW$_9$O$_{34}$]·18H$_2$O (1.0 g, 0.34 mmol) was added and this mixture was stirred until a clear, green solution was formed. Then, Na$_3$PO$_4$·12H$_2$O (0.80 g, 2.1 mmol) and Na$_2$CO$_3$ (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 $[\text{Ni}_{25}(\text{H}_2\text{O})_{18}(\text{OH})_2(\text{CO}_3)_2(\text{PO}_4)_6(\text{SiW}_{9}\text{O}_{34})_6]^{50^-}$.

**Synthesis of $[\text{Ni}_5(\text{OH})_6(\text{OH}_2)_3(\text{Si}_2\text{W}_{18}\text{O}_{66})]^{12^-}$**

$[\text{Ni}_5(\text{OH})_6(\text{OH}_2)_3(\text{Si}_2\text{W}_{18}\text{O}_{66})]^{12^-}$ was synthesized according to reference.\textsuperscript{8} $\text{Na}_{10}[\text{α-SiW}_{9}\text{O}_{34}]$ (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. $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ (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\textsuperscript{-1}): 998, 946, 892, 798, 710, 637, 525.
Synthesis of [Ni(H₂O)₂(γ-SiW₁₀O₃₅)₂]¹⁰⁻

[Ni(H₂O)₂(γ-SiW₁₀O₃₅)₂]¹⁰⁻ was synthesized according to reference.⁹ To 20 mL of a 1 M KCl solution were added simultaneously 0.078 g of MnCl₂·4H₂O (0.40 mmol) and 1.0 g of K₈[γ-SiW₁₀O₃₆] (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. S10 FT-IR spectrum of [Ni₃(OH)₆(OH₂)₃(Si₂W₁₈O₆₆)]¹²⁻

Fig. S11 FT-IR spectrum of [Ni(H₂O)₂(γ-SiW₁₀O₃₅)₂]¹⁰⁻
Fig. S12 Kinetics of O$_2$ formation in the photocatalytic system under various pH conditions. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)$_3$]Cl$_2$, 5.0 mM Na$_2$S$_2$O$_8$, 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 ($\lambda \geq 420$ nm), 5.0 mM Na$_2$S$_2$O$_8$, 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$_2$S$_2$O$_8$. Conditions: LED lamp ($\lambda \geq 420$ 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$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration of catalysts (µM)</th>
<th>O$_2$ yield$^b$ (%)</th>
<th>TON$^c$</th>
<th>TOF$^d$ [s$^{-1}$]</th>
<th>$\Phi_{QY}$(initial) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>13.3</td>
<td>335</td>
<td>1.7</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>13.9</td>
<td>70</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>22.1</td>
<td>55</td>
<td>0.2</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>27.2</td>
<td>45</td>
<td>0.2</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>26.6</td>
<td>33</td>
<td>0.1</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>16.9</td>
<td>17</td>
<td>0.1</td>
<td>13</td>
</tr>
</tbody>
</table>

$^a$ Conditions: LED lamp ($\lambda \geq 420$ nm); 1.0 mM [Ru(bpy)$_3$]Cl$_2$, 5.0 mM Na$_2$S$_2$O$_8$, 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$_2$S$_2$O$_8$. $^c$ TON = mole of O$_2$/mole of catalyst. $^d$ TOF$_{\text{initial}}$ = 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 O₂ formation in the photocatalytic system without I (red), [Ru(bpy)₃]Cl₂ (blue), Na₂S₂O₈ (blackish green) or light (pink).

Fig. S16 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 (λ ≥ 420 nm), 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 15 µM I, 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$_2$S$_2$O$_8$ (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$_2$S$_2$O$_8$, 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) Ni\textsubscript{2p} and Ni\textsubscript{2p}\textsubscript{1,2} components.
(c) Si\textsubscript{2p} components.
(d) W\textsubscript{4f} components.
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 ($\lambda \geq 420$ nm), 1.0 mM [Ru(bpy)$_3$]Cl$_2$, 5.0 mM Na$_2$S$_2$O$_8$, 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$_2$S$_2$O$_8$ 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$_2$S$_2$O$_8$ (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$_2$S$_2$O$_8$ (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\textsubscript{2} evolution from water catalyzed by 1 in 80 mM sodium borate buffer at pH 9.0. Conditions: LED lamp (\(\lambda \geq 420\) nm), 5.0 mM Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, 1.0 mM [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2}. Black line: 15 \(\mu\)M 1 without extraction by THpANO\textsubscript{3}-toluene solution; Red line: extraction of the 15 \(\mu\)M 1 in sodium borate buffer by THpANO\textsubscript{3}-toluene solution, followed by addition of 15 \(\mu\)M 1, [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}; Blue line: extraction of the 15 \(\mu\)M 1 in sodium borate buffer by THpANO\textsubscript{3}-toluene solution, followed by addition of 15 \(\mu\)M NiSO\textsubscript{4}, [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}; Cyan line: complete extraction of the 15 \(\mu\)M 1 in sodium borate buffer with a THpANO\textsubscript{3}-toluene solution, followed by addition of [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} but no 1. Magenta line: the reaction solution after the first run followed by extraction using a THpANO\textsubscript{3}-toluene solution and addition of 17.8 mg Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}.

**Fig. S27** Kinetics of O\textsubscript{2} formation in the photocatalytic system using 1 \(\mu\)M NiSO\textsubscript{4} and 1 \(\mu\)M 1. Conditions: LED lamp (\(\lambda \geq 420\) nm), 1.0 mM [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2}, 5.0 mM Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.
Fig. S28 Kinetics of O\textsubscript{2} formation in the photocatalytic system using 15 µM NiSO\textsubscript{4} and 15 µM 1.

Conditions: LED lamp (\(\lambda \geq 420\) nm), 1.0 mM [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2}, 5.0 mM Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

Fig. S29 Kinetics of O\textsubscript{2} formation in the photocatalytic system using 25 µM NiSO\textsubscript{4} and 25 µM 1.

Conditions: LED lamp (\(\lambda \geq 420\) nm), 1.0 mM [Ru(bpy)\textsubscript{3}]Cl\textsubscript{2}, 5.0 mM Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.
**Fig. S30** Kinetics of O₂ formation in the photocatalytic system using 150 µM NiSO₄ and 15 µM 1.

Conditions: LED lamp (λ ≥ 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. S31** (a) Cyclic voltammogram (CV) of 80 mM sodium borate buffer solution at pH 9.0 without NiSO₄ (black) and with 0.5 mM NiSO₄ (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 O₂ evolution for 1 (black line), 1 in the presence of EDTA-Na (red line), NiSO₄ (blue line) and chelate (dark cyan). Conditions: LED lamp (λ ≥ 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. S35** CV curve of 0.5 mM NiSO₄ 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 NiSO₄. Red line shows the CV curve of 0.5 mM NiSO₄ 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 NiSO₄ (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 NiSO₄ (b). Conditions: LED lamp (λ ≥ 420 nm), 15 μM NiSO₄ and 15 μM 1, 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈, 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 Ni₄ POM (1).

References
5 S. Yao, Z. Zhang, Y. Li and E. Wang, Dalton Trans., 2010, 39, 3884.