Supporting Information for:

Mesoporous Silica Supported Ruthenium Oxide Nanoparticulates as Efficient Catalysts for Photo-induced Water Oxidation

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**Figure S1.** The TEM image of NP2, where the circled area roughly corresponds to Figure 1b. With lower magnification and much shorter time of exposure under electron beam, a better ordering of nanoporous structure rendered, compared to that in Figure 1b.
Figure S2. Powder XRD patterns of NP2, NP1, RuCl$_3$-4% and commercial bulk RuO$_2$.
Figure S3. Reusability test of the reaction suspension in Figure 4. After the initial run 1-1 (same as Curve 1 in Figure 4) two subsequent runs were initiated by simply injecting concentrated Na$_2$S$_2$O$_8$ to the reaction system to reach its original concentration, without a step to separate NP2. The resulting data is shown as the curves 1-2 and 1-3. Compared to the original 1-1, re-initiated runs were clearly slower with lower oxygen yields, which is typically attributed to the oxidative decomposition of the photo-sensitizer.$^{1,2}$
**Figure S4.** Evaluation of the light scattering effect from SBA-15. Actinometry was done using K$_3$Fe(C$_2$O$_4$)$_3$ as Fe$^{3+}$ source. The stock solution (~0.15 M K$_3$Fe(C$_2$O$_4$)$_3$ in 0.05M H$_2$SO$_4$) was separated into two portions. To one of the portions SBA-15 was added at 3mg/mL. The other was used as control. Under irradiation with a LED light source (454 nm) the Fe$^{3+}$ is reduced to Fe$^{2+}$. This irradiation was done at time points of 0, 1, 2, 5, and 8 minutes. To assess the amount of Fe$^{3+}$ converted to Fe$^{2+}$, the samples were treated with an excess of 1,10-phenanthroline to form the easily detectable Fe(phen)$_3^{2+}$ complex. UV-Vis spectra were taken and the absorbance at 510 nm was used for concentration calculations. The results indicate that at longer irradiation times, scattering from SBA-15 will lead to a systematically low photon absorbance. It should be noted,
however, that the effective path of light during the water oxidation experiment is much shorter (~1 mm) compared to that from the actinometry experiment (~10 mm). This is due to the relatively high absorbance of the photosensitizer. Absorbances were recorded on a Jasco V-670 spectrophotometer.
Examples for the calculations of TOFs and O₂ yields.

(a) RuO₂/Y-zeolite reported by Lehn et al.³

The best RuO₂ catalyst is No. 2 sample in Table 1 of that paper. The conditions for the test were listed: 30 mL mixture containing $2.6 \times 10^{-2}$ M Co(NH₃)₅Cl²⁺ and $5.6 \times 10^{-4}$ M RuOₓ. The final production of O₂ was 1.52 mL and the rate of O₂ per mM metal was 2.71 mL/h.

In 30 mL suspension, 1 mM Ru metal equals $3 \times 10^{-5}$ mol RuOₓ. Applying ideal gas law again, the rate of O₂ production, 2.71 mL O₂/h/mM RuOₓ is equal to $1.09 \times 10^{-4}$ mol O₂/h/ mM RuOₓ, and so equal to $1.09 \times 10^{-4}$ mol O₂ / 60 min / $3 \times 10^{-5}$ mol RuOₓ = 0.0606 mol O₂ / mol RuOₓ / min. Multiplied with 4, the number of electrons transferred per generated O₂, the calculation leads to TOF of 0.24 min⁻¹.

Theoretical yield of O₂ = $2.6 \times 10^{-2}$ M Co(NH₃)₅Cl²⁺ × 0.03 L × [1 O₂ / 4 Co(NH₃)₅Cl²⁺] = 1.95 × $10^{-4}$ mol O₂. Applying ideal gas law, the actual production of O₂ (1.52 mL in the headspace) can be estimated as $6.11 \times 10^{-5}$ mol O₂. So the ratio of yield is $100\% \times 6.11 \times 10^{-5}$ mol / $1.95 \times 10^{-4}$ mol = 31%.

(b) RuO₂-Y catalyst reported by Das et al.⁴

Their best catalyst is RuO₂-Y, 200°C, in Table 1 of that paper. In the catalytic system, 0.200 g of [Co(NH₃)₅Cl]Cl₂, 0.050 g catalyst (Ru content: 2.96 wt%) plus the photosensitizer and buffering components were mixed in 40 mL water.
For the first 60 min, the rate was 0.67 mL O\textsubscript{2} / min / mmol of RuO\textsubscript{2}. Applying the ideal gas law at ambient conditions, the rate would be 0.0274 mol O\textsubscript{2} / min / mol RuO\textsubscript{2}. Multiplying it by 4, the TOF of 0.11 min\textsuperscript{-1} is obtained.

Theoretical production of O\textsubscript{2} can be similarly calculated as for Lehn’s sample: 2.00 \times 10^{-4} mol O\textsubscript{2}. The mole of RuO\textsubscript{2} is obtained by converting the weight of Ru in the catalyst: 0.05 g \times 2.96% / 101.07 g mol\textsuperscript{-1} Ru = 1.46 \times 10^{-5} mol Ru = 1.46 \times 10^{-5} mol RuO\textsubscript{2}. The produced O\textsubscript{2} at 150 min can be roughly estimated from the aforementioned molar rate of O\textsubscript{2} production: 0.0274 mol O\textsubscript{2} / min / mol RuO\textsubscript{2} \times 150 min \times 1.46 \times 10^{-5} mol RuO\textsubscript{2} = 6.00 \times 10^{-5} mol. So the percentage of conversion is 100\% \times 6.00 \times 10^{-5} mol / 2.00 \times 10^{-4} mol = 30\%. Because the generation of O\textsubscript{2} was nearly linear with respect to time (as observed in Figure 6 of that paper), this rough method does not lead to significant under-estimation of O\textsubscript{2} yield.

(c) Other TOFs, produced O\textsubscript{2} amounts of literature reports were either similarly calculated or directly obtained from the reports.
Additional calibration and calculation procedures for the analysis of O\textsubscript{2} production catalyzed by NP2, NP1, RuCl\textsubscript{3}-4\% and bulk RuO\textsubscript{2}.

(a) The calculation and calibration of TOF and O\textsubscript{2} production.

The O\textsubscript{2} sensor reads the concentration of O\textsubscript{2} in the headspace. Knowing the volume of the headspace (3.75 mL in most cases), applying ideal gas law, it was converted into moles of O\textsubscript{2} produced. The rest steps for the calculation of yield followed similar procedures as detailed for literature reports. Additional calibrations include the baseline correction and dissolved O\textsubscript{2} correction:

**Baseline subtraction.** The cuvette was sealed by a rubber septum, through which the needle tip of the O\textsubscript{2} sensor penetrated into the headspace. Generally, the light source was turned on when the tip of the sensor was fixed into the headspace for 1 h or longer. The light-on time was reset to \( t = 0 \). Due to the small leaking of the system that sometimes happened, the calibration of the baseline is necessary. A linear formula between detected O\textsubscript{2} concentration and elapsed time was fitted at the linear range before \( t = 0 \), and the actual produced O\textsubscript{2} after \( t = 0 \) was obtained by subtracting the detected value by the O\textsubscript{2} value calculated from the fitted baseline formula corresponding to the time \( t \).

**Dissolved O\textsubscript{2} calibration.** It is known that at 20 °C and 1 atm, air contains 20.9% volume portion of O\textsubscript{2} and the solubility of O\textsubscript{2} in water is \( 2.84 \times 10^{-4} \) M. Thus the distribution coefficient for O\textsubscript{2} in water and in the headspace was calculated as 0.0326:1. As we carefully measured the
headspace volume as 3.75 mL and the suspension was always 2.4 mL, the multiplier that convert
the detected \( \text{O}_2 \) amount to the real \( \text{O}_2 \) amount could be obtained as \( 1 + 0.0326 \times (2.4 \text{ mL} / 3.75 \text{ mL}) \)
\( = 1.021. \)

(b) The calculation of quantum efficiency (\( \Phi \)).

The photon influx was measured through a chemical actinometry method.\(^5\) Three parallel
measurements were conducted, and the calculated influx is \( 5.28 \times 10^{-6} \pm 0.02 \times 10^{-6} \text{ mol/min} \). The
number of absorbed photons was obtained by multiplying the influx with time \( t \). The rest
procedure for the calculation of cumulative \( \Phi \) was based on equation 2 in the main text.

The rate of \( \text{O}_2 \) production at time \( t \) was obtained via this equation:

\[
[(\text{moles of } \text{O}_2 \text{ produced at } t + 0.5 \text{ min}) - (\text{moles of } \text{O}_2 \text{ produced at } t - 0.5 \text{ min})] / 1 \text{ min}
\]

The 1 min range of sampling points significantly smoothened the curves of the rate of \( \text{O}_2 \)
production, and hence the curves of instantaneous \( \Phi \) in Figure 3b. The following step is described
in equation 3.

(c) The \( \Phi \) values for otherwise reported catalytic systems was either similarly calculated or
directly obtained from the reports.
References


