Supporting Information

For

Oxygen Evolution from Water Oxidation on Molecular Catalysts Confined in the Nanocages of Mesoporous Silicas

Bo Li,[a] Fei Li,[b] Shiyang Bai,[a] Zhijun Wang,[a] Licheng Sun,[b] Qihua Yang*[a] and Can Li*[a]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian 116023, China*

E-mail: yangqh@dicp.ac.cn; canli@dicp.ac.cn

[b] *State Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), Dalian 116024, China*

Experimental section

1. General material information

All chemicals were used as received unless otherwise stated. Pluronic P123 copolymer ($EO_{20}PO_{70}EO_{20}$) and pluronic copolymer F127 ($EO_{106}PO_{70}EO_{106}$) were purchased from Sigma Aldrich Company. Tetraethylorthosilicate (TEOS, AR) and cerium (IV) ammonium nitrate were purchased from Shanghai Chemical Reagent Company of the Chinese Medicine Group. Propyltrimethoxysilane (C3) was purchased from Meryer Chemical Technology Company. $Ru^{II}(bda)(pic)_2$, $Ru^{II}(pda)(pic)_2$ and mesoporous material SBA-16 were synthesized according to the literature.[S1-S3]

2. Characterization

N_2 physical adsorption was carried out on Micromeritics ASAP2020 volumetric adsorption analyzer. Before the sorption measurements, the samples were out gassed at 393 K for 6 h. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation of 0.15406 nm wavelength. UV/vis spectra were recorded on SHIMADZU UV-vis 2550 spectrophotometer for kinetic measurements. Transmission electron microscopy (TEM) was performed using a JEM-2010 instrument at an acceleration voltage of 100 kV. Ru contents were analyzed on Plasma-spec-II (Leeman, U.S.A.). The GC employed for O_2 detection is an Agilent Technologies Series 3000A micro GC equipped with thermal conductive detector and 5 Å molecular sieve column (12 mm/320 mm/10 m), using He carrying gas.

3. Estimation of the average number of molecular catalysts per cage

The calculation is based on the assumptions that the mesopore volume of SBA-16 is completely contributed by cages and each cage accommodates the same number of

$Ru^{II}(bda)(pic)_2$ molecules. The number of $Ru^{II}(bda)(pic)_2$ per cage (n) was calculated by the following equation:

$$\mathbf{n} = \frac{\mathbf{N_{Ru(1g)} \times 6.02 \times 10^{23}}}{\dfrac{\mathbf{V_{meso}}}{\frac{4}{3}\pi(\frac{D}{2})^3}}$$

$N_{Ru(1g)}$ is the mole of $Ru^{II}(bda)(pic)_2$ per gram of the solid catalyst.

$V_{meso.}$=$V_{total.}$-$V_{microp.}$, where V_{total} means the total pore volume, V_{meso} refers to the pore volume attributed by the mesopore and V_{microp} refers to the pore volume of the micropore.

D is cage size of SBA-16.

The estimation of the average number of $Ru^{II}(pda)(pic)_2$ in each cage is similar with that of $Ru^{II}(bda)(pic)_{2.}$

4. General procedure for oxygen evolution

In a typical run of water oxidation using $Ru^{II}(bda)(pic)_2$@SBA-16: a 100 mL flask was charged with the desired amount of $Ru^{II}(bda)(pic)_2$@SBA-16 (the Ru content for the catalytic system was 600 nmol) and evacuated for 30 min until no obvious background oxygen in the system was checked by GC. 18 mL Ce(IV) aqueous solution (0.5 M) purged with Ar for 2 h was injected to the flask through a septum cap.

In a typical run of water oxidation using homogenous $Ru^{II}(bda)(pic)_2$ catalyst: a 100 mL flask was evacuated for 30 min until no obvious background oxygen in the system was checked by GC. Then 600 μL $Ru^{II}(bda)(pic)_2$ (1 mM in acetonitirle) and 18 mL Ce(IV) aqueous solution (0.5 M) purged with Ar for 2 h were injected to the flask through a septum cap. The amount of evolved dioxygen was monitored by an oxygen sensor (Ocean Optics FOXY-OR125-G probe and Ocean Optics MFPF-100 fluorimeter) introduced in the neck of the flask. The oxygen sensor consists was connected to a PC, and the data were collected by the "TauTheta" Host Program and transfered to the percent of oxygen by a program named "OOISensors". GC was used to calibrate the end-point oxygen content which was converted to TONs.

The typical run of water oxidation using $Ru^{II}(pda)(pic)_2$ and $Ru^{II}(pda)(pic)_2$@SBA-16 were similar to the above procedures, only the amount of O_2 evolved was measured using an on-line gas chromatography.

REFERENCES

S1. L. Duan, A. Fischer, Y. Xu and L.Sun, *J. Am. Chem. Soc.*, 2009, **131**, 10397.

S2. L. Tong, L. Duan, Y. Xu, T. Privalov and L. Sun, *Angew. Chem. Int. Ed.*, 2011, **123**, 465.

S3. T. W. Kim, R. Ryoo, M. Kruk, K. P. Gierszal, M. Jaroniec, S. Kamiya and O. Terasaki, *J. Phys. Chem. B*, 2004, **108**, 11480.

Table S1. Textural properties of the solid catalysts $Ru^{II}(bda)(pic)_2$@SBA-16 with different Ru content and the performance in water oxidation.

Samples	Ru content[a] (wt%)	Surface area[b] (m^2/g)	Pore volume[c] (cm^3/g)	Pore size[d] (nm)	TOF[e] (s^{-1})	TON[f]
$Ru^{II}(bda)(pic)_2$@SBA-16	0.082	354	0.22	5.2	1.2	630
$Ru^{II}(bda)(pic)_2$@SBA-16	0.605	278	0.19	5.1	8.7	3300
$Ru^{II}(bda)(pic)_2$@SBA-16	0.920	251	0.19	5.1	8.0	3000

[a] Ru contents were determined by ICP. [b] BET surface area； [c] Pore volume, estimated at the relative pressure of P/P_0=0.99； [d] The pore size distribution calculated from the N_2 adsorption branch using the BJH method; [e] TOF was calculated based on O_2 evolved in the first two minutes. [f] TON was calculated based on O_2 evolved for 0.5 h.

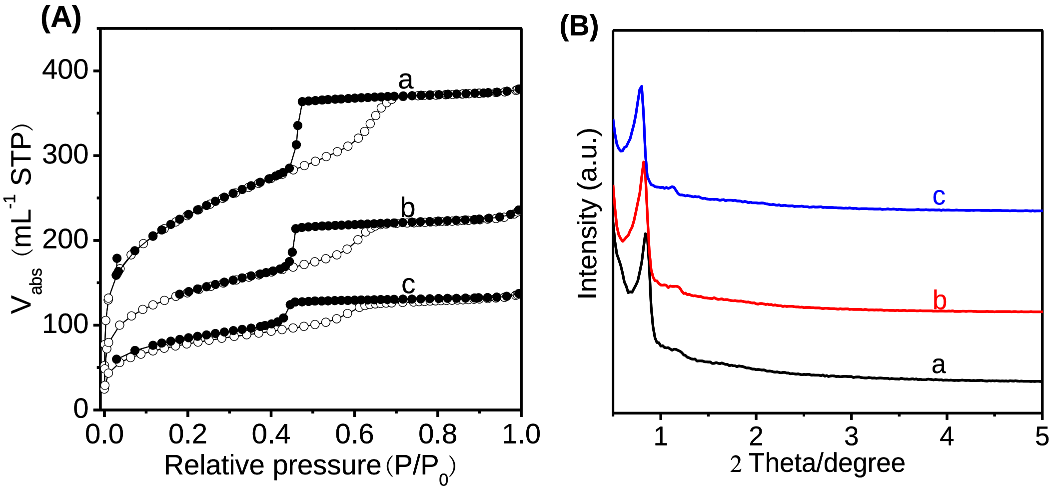
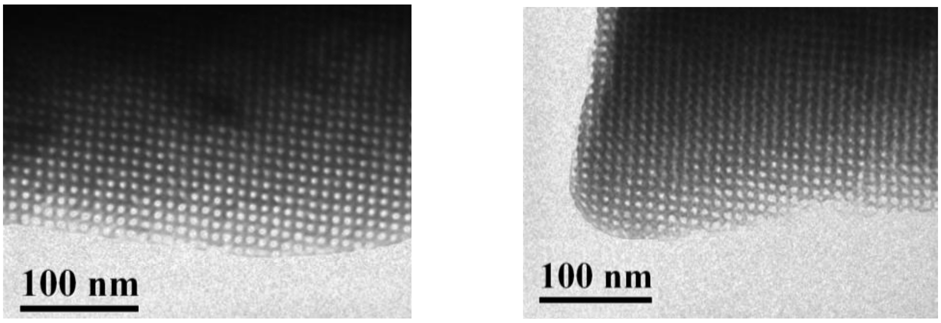


Fig. S1 N_2 sorption isotherms (**A**) and XRD (**B**) patterns of the samples: a. SBA-16; b. SBA-16-C3; c. $Ru^{II}(bda)(pic)_2$@SBA-16 (Ru, 0.605 wt%).



(A) SBA-16 (B) $Ru^{II}(bda)(pic)_2$@SBA-16

Fig. S2 TEM images of SBA-16 (**A**) and $Ru^{II}(bda)(pic)_2$@SBA-16 (Ru, 0.605 wt%) (**B**).

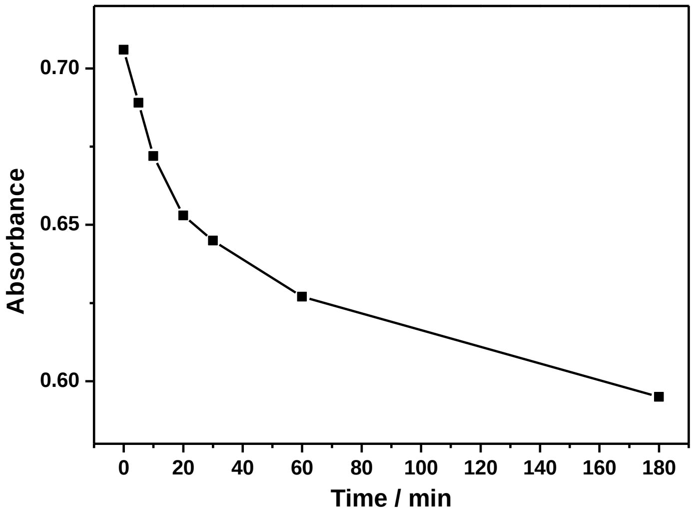


Fig. S3 Adsorption of Ce(IV) (1.5 mM, 5 mL) with SBA-16-C3 (50 mg) as a function of time measured by UV/vis spectroscopy (the absorbance change was monitored at 360 nm).

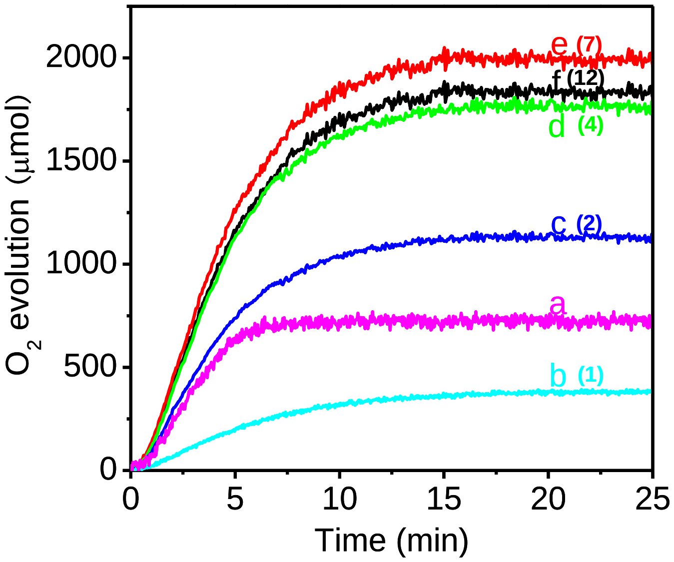


Fig. S4 Kinetics of oxygen evolution from homogeneous $Ru^{II}(bda)(pic)_2$ (**a**) and $Ru^{II}(bda)(pic)_2$@SBA–16 (**b–f**) with different number of $Ru^{II}(bda)(pic)_2$ molecules in each nanocage. The value in bracket is the number of $Ru^{II}(bda)(pic)_2$ molecules in each nanocage (the Ru amount in each catalytic system was 600 nmol; 0.5 M Ce(IV) aqueous solution, 18 mL). The O_2 evolved was measured by an O_2 sensor and calibrated by online-GC analysis.

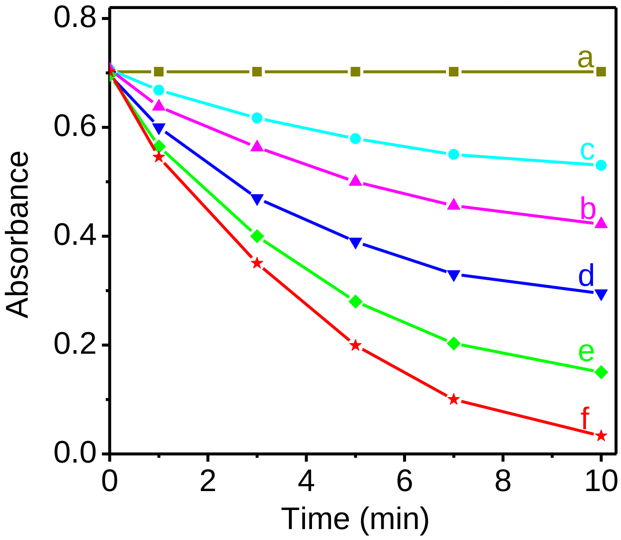


Fig. S5 UV/vis absorbance change of Ce(IV) (1.5 mM, 5 mL) monitoring at 360 nm as a function of time without catalyst (**a**) and in the presence of homogeneous $Ru^{II}(bda)(pic)_2$ (**b**) and $Ru^{II}(bda)(pic)_2$@SBA-16 with one (**c**), two (**d**), four (**e**), and seven (**f**) $Ru^{II}(bda)(pic)_2$ molecules in each nanocage (the Ru amount in each system was 5 nmol).

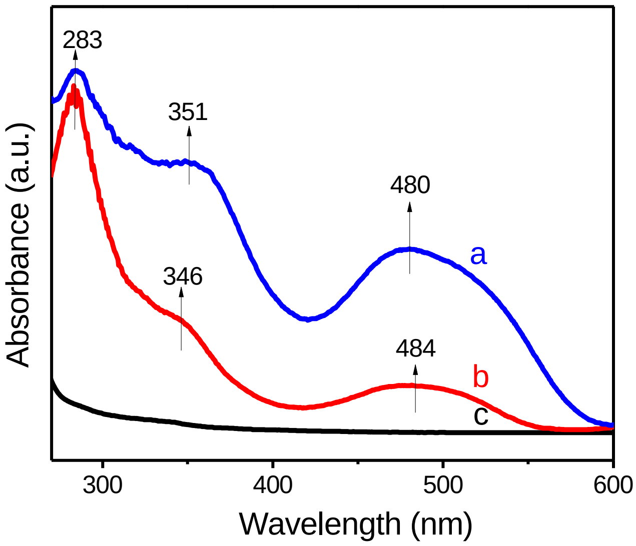


Fig. S6 UV/vis spectra of Ru^{II}(pda)(pic)$_2$@SBA-16 (Ru, 0.745 wt%) (a), Ru^{II}(pda)(pic)$_2$ in CH_2Cl_2 (b) and SBA-16-C3 (c).

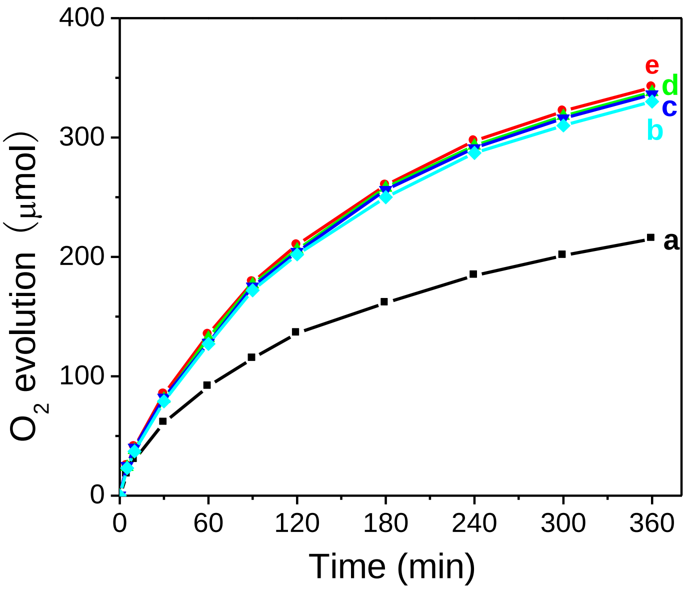


Fig. S7 The TON of oxygen evolution from homogeneous Ru^{II}(pda)(pic)$_2$ catalyst (**a**) and the solid catalysts Ru^{II}(pda)(pic)$_2$@SBA-16 with one (**b**), two (**c**), four (**d**), and eight (**e**) Ru^{II}(pda)(pic)$_2$ molecules in each nanocage (the Ru amount in each catalytic system was 600 nmol; 0.5 M Ce(IV) aqueous solution, 18 mL). The O_2 evolved was measured by online-GC.

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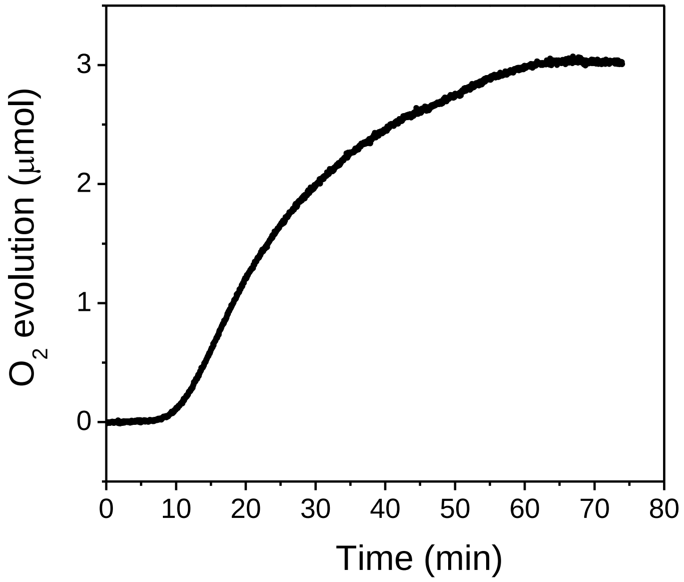

Fig. S8 The TON of oxygen evolution from SBA-16@Ru_2O (the Ru amount in each catalytic system was 600 nmol; 0.5 M Ce(IV) aqueous solution, 18 mL). The O_2 evolved was measured by an O_2 sensor and calibrated by online-GC analysis.