

Artificial Photosynthesis

Light-Harvesting Photocatalysis for Water Oxidation Using Mesoporous Organosilica

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Abstract: An organic-based photocatalysis system for water oxidation, with visible-light harvesting antennae, was constructed using periodic mesoporous organosilica (PMO). PMO containing acridone groups in the framework (Acd-PMO), a visible-light harvesting antenna, was supported with $[Ru^{II}(bpy)_{3}^{2+}]$ complex (bpy = 2,2'-bipyridyl) coupled with iridium oxide (IrO_x) particles in the mesochannels as photosensitizer and catalyst, respectively. Acd-PMO absorbed visible light and funneled the light energy into the Ru complex in the mesochannels through excitation energy transfer. The

Introduction

The oxidation of water in photosystem (PS) II is an important reaction that supplies electrons to PS I, in which NADPH (reduced nicotinamide adenine dinucleotide phosphate) is produced for CO_2 reduction.^[1] The oxygen-evolving complex in PS II is coupled with a light-harvesting antenna in order to promote the multi-electron reaction for water oxidation through concentration of the photon density of sunlight. Therefore, the construction of artificial photocatalysis systems linked with light-harvesting antennae is important.^[2]

Organic–inorganic hybrid nanoporous materials^[3] have attracted increasing attention in recent years as solid-state lightharvesting antennae and photocatalysts, because molecular chromophores and catalysts can be spatially distributed in their highly porous frameworks. We first reported the unique light-harvesting antenna properties of a periodic mesoporous organosilica (PMO), in which light energy absorbed by approximately 125 biphenyl groups in the framework was funneled to

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excited state of Ru complex is oxidatively quenched by a sacrificial oxidant ($Na_2S_2O_8$) to form Ru^{3+} species. The Ru^{3+} species extracts an electron from IrO_x to oxidize water for oxygen production. The reaction quantum yield was 0.34%, which was improved to 0.68 or 1.2% by the modifications of PMO. A unique sequence of reactions mimicking natural photosystem II, 1) light-harvesting, 2) charge separation, and 3) oxygen generation, were realized for the first time by using the light-harvesting PMO.

a single coumarin molecule in the mesochannel with almost 100% quantum efficiency.^[4] PMO was applied in the construction of a light-harvesting photocatalyst for CO₂ reduction by the fixation of a CO₂ reduction catalyst, a [Re(bpy)(CO)₃L] complex, in the mesochannels as a reaction center.^[5] Recently, there have been an increasing number of reports on the photocatalysis of metal–organic frameworks (MOFs). For example, Wang et al. reported photocatalytic CO₂ reduction, H₂ production, and Ce⁴⁺-driven water oxidation using MOFs with [Re(bpy)(CO)₃CI], [Ir(ppy)₂(bpy)], and Cp*Ir complexes in the framework, respectively.^[6] Fateeva et al. reported photocatalytic H₂ evolution using MOFs with a porphyrin unit in the framework.^[7] However, there is no report on water oxidation photocatalysis linked with a light-harvesting antenna for either PMOs or MOFs, despite its importance.

Here, we report the first organic-based photocatalysis system for water oxidation linked with a light-harvesting antenna, mimicking PS II. There are several homogeneous water oxidation photocatalysts, including an integrated system with molecular photosensitizers (typically $[Ru(bpy)_3]^{2+}$, bpy = 2,2'-bipyridyl) coupled to semiconductor nanoparticles ($IrO_2^{[8]}$ and $RuO_2^{[9]}$) and molecular catalysts^[10] (Ru, Ir, Fe, Co complexes). Because of the high efficiency, $[Ru(bpy)_3]^{2+}$ coupled with IrO_2 was selected for this study and was supported within the mesochannels of PMO containing acridone groups in the framework (Acd-PMO) as a visible-light harvesting antenna (Scheme 1). A unique sequence of reactions mimicking PS II, 1) light-harvesting, 2) charge separation, and 3) oxygen generation, was realized for the first time in this highly practical solid-state material.

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Scheme 1. Light-harvesting water-oxidation photocatalysis using the IrO_x/Ru -Acd-PMO and $S_2O_8^{2-}$ system.

Results and Discussion

Acd-PMO was prepared from 2,7-bis(triethoxysilyl)acridone precursor in the presence of C_{18} TMACI surfactant according to the method previously reported.^[4b] Acd-PMO has a highly ordered mesoporous structure (2d-hexagonal) and an organic–silica hybrid framework structure in which acridone groups are densely packed in the silicate network (Figure 1 a and b). A dif-



Figure 1. a) Structural model, and b) TEM image of Acd-PMO. c) Diffuse reflectance (broken line) and emission (solid line) spectra of Acd-PMO. d) Absorption (broken line) and emission (solid line) spectra of $[Ru(bpy)_3]^{2+}-C_4SC_3-Si(OEt)_3$ solution.

fuse-reflectance spectrum of Acd-PMO powder and an emission spectrum of the powder dispersed in CH₃CN showed an absorption edge at 450 nm and a fluorescence emission band at λ_{max} =525 nm (Figure 1 c). The fluorescence band was much longer in wavelength than that of the 2,7-bis(triethoxysilyl)acridone precursor solution (λ_{max} =412 nm in 2-PrOH) due to the densely packed structure of the acridone moiety in the framework. The emission spectrum was partially overlapped with the metal-to-ligand charge transfer (MLCT) absorption band of [Ru(bpy)₃]²⁺ complex (Figure 1 d), indicating that the excitation energy of the Acd groups can transfer to the Ru complex.

 $[Ru(bpy)_3]^{2+}$ complex was covalently attached on Acd-PMO by modification of the surface silanol groups (SiOH) with $[Ru(bpy)_3]^{2+}$ complex with alkylsilyl groups (Figure 2a). Acd-PMO powder was stirred in a CH_3CN solution containing



Figure 2. a) Fixation of $[Ru(bpy)_3]^{2+}$ complex in the mesochannels of Acd-PMO. b) N₂ adsorption isotherms, and c) NLDFT pore-size distribution curves for Acd-PMO, before (circle) and after (square) fixation of $[Ru(bpy)_3]^{2+}$ complex.

 $[Ru(bpy)_3]^{2+}-C_4SC_3-Si(OH)_3$ at 60 °C for 3 h. The use of triol species instead of nonhydrolyzed [Ru(bpy)₃]²⁺-C₄SC₃-Si(OEt)₃ was very effective at improving the fixed amount of [Ru(bpy)₃]²⁺ complex on Acd-PMO from 0.09 to 0.23 mmol g⁻¹, which were determined by UV/Vis spectra of the filtrates. The amount of the attached $[Ru(bpy)_3]^{2+}$ complex (0.23 mmol g⁻¹) was 7.1% of the total amount (3.24 mmolg⁻¹) of Acd groups in Acd-PMO. Figure 2b and c show nitrogen adsorption isotherms and nonlocal density functional theory (NLDFT) pore-size distribution curves for Acd-PMO before and after the attachment of [Ru(bpy)₃]²⁺ complex. The mean pore diameter of Acd-PMO decreased from 4.2 to 3.6 nm along with a decrease in surface area from 1126 to 882 m²g⁻¹ (Table S1 in the Supporting Information). α_s -Plot analysis of nitrogen adsorption isotherm for Ru-complex-attached Acd-PMO (Ru-Acd-PMO) showed that the inner surface area of the mesochannels (835 m²g⁻¹) was extremely large compared to the external surface area of Acd-PMO particles (47 $m^2 g^{-1}$). If all $[Ru(bpy)_3]^{2+}$ complexes were attached on the external surface of Acd-PMO particles, they could occupy only a small area of 0.36 nm² per [Ru(bpy)₃]²⁺ complex. The occupied area is not acceptable taking into account the diameter (1.2 nm) of almost spherical shape of $[Ru(bpy)_3]^{2+}$ complex. If $[Ru(bpy)_3]^{2+}$ complexes were attached on both the inner surface of the mesochannels and the external surface of Acd-PMO particles, the occupied area of one complex would be 6.4 nm². It is an acceptable value. The result suggests that $[Ru(bpy)_3]^{2+}$ complexes are attached within the mesochannels in addition to the external surface of Acd-PMO.

Diffuse reflectance and emission spectra of Ru-Acd-PMO are shown in Figure 3 a and b, respectively. The diffuse reflectance spectrum of Ru-Acd-PMO showed mainly two absorption bands at around 380 and 450 nm due to Acd groups and [Ru(bpy)₃]²⁺ complexes, respectively, which was confirmed by the comparison to the diffuse reflectance spectra of Acd-PMO and Ru-MPS (Ru complex-attached Acd-free mesoporous silica; Figure 3 a). The emission from Acd-PMO was almost completely quenched for Ru-Acd-PMO, while a new emission band due to phosphorescence of [Ru(bpy)₃]²⁺ appeared at λ_{max} =630 nm,

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Figure 3. a) Diffuse reflectance spectra of Ru-Acd-PMO (solid line), Acd-PMO (dotted line), and Ru-MPS (broken line). b) Emission spectra of Ru-Acd-PMO (solid line), Acd-PMO (dotted line), and Ru-MPS (broken line) dispersion in water (excited at 400 nm), and quenching behavior upon addition of $Na_2S_2O_8$ (broken arrows).

suggesting that efficient excitation energy transfer occurred from Acd groups to $[Ru(bpy)_3]^{2+}$ complexes (Figure 3 b). The almost complete quenching of the Acd emission is also strong evidence that $[Ru(bpy)_3]^{2+}$ complex is homogeneously distributed in the mesochannels of the Acd-PMO. If many $[Ru(bpy)_3]^{2+}$ complexes existed on the external surface of PMO particles, they could not completely quench the emission from Acd groups, especially those located in the center of the PMO particles because the particle size (1000 nm) is much larger than the critical quenching distance between donor and acceptor molecules (usually less than 10 nm).

The photocatalysis of water oxidation was evaluated for Ru-Acd-PMO loaded with IrO_x nanoparticles as a catalyst in the presence of $S_2O_8^{2-}$ as a sacrificial electron acceptor. The excited state $[Ru(bpy)_3]^{2+}$ is believed to be quenched by $S_2O_8^{2-}$ to produce $[Ru(bpy)_3]^{3+}$ and SO_4^{--} .^[11] The sulfate radical anion also reacts with $[Ru(bpy)_3]^{2+}$ to form a second $[Ru(bpy)_3]^{3+}$. Thus, one photon generates two $[Ru(bpy)_3]^{3+}$ species as shown Equation (1):

$$2 \left[\text{Ru}(\text{bpy})_3 \right]^{2+} + S_2 O_8^{2-} + h\nu \to 2 \left[\text{Ru}(\text{bpy})_3 \right]^{3+} + 2 SO_4^{2-}$$
(1)

The IrO_x nanoparticles were deposited on the pore surface of Ru-Acd-PMO by in situ photo-oxidation of prehydrolyzed IrCl₃ during the initial period of photocatalytic water oxidation. Ru-Acd-PMO powder was dispersed in a carbonate-buffered aqueous solution (pH 8.9) containing hydrolyzed IrCl₃ and a sacrificial oxidant (Na₂S₂O₈). The dispersion was placed in a Pyrex cell connected to a closed gas-circulation system. Ar gas was



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Figure 4. a) Time dependence of photocatalytic oxygen evolution from Ru-Acd-PMO (•) and a mixture of Acd-PMO and Ru-MPS (\odot) in a carbonate buffer solution (pH 8.9) under irradiation by 400 nm light in the presence of hydrolyzed IrCl₃ and Na₂S₂O₈ (31 mM). b) HAADF-STEM image of Ru-Acd-PMO after photoirradiation for 1.75 h.

charged into the line after repeated evacuations to remove air from the system. The time dependence of the photocatalytic water oxidation under irradiation of 400 nm monochromic light is shown in Figure 4. Oxygen was generated after an induction period of 1.25 h due to oxidation of the hydrolyzed IrCl₃ to form IrO_x nanoparticles. The amount of evolved oxygen leveled off after 10 h. A similar deactivation was reported previously for a homogenous photocatalysis system of $[Ru(bpy)_3]^{2+}$ and colloidal IrO₂, in which the amount of evolved oxygen leveled off within 1 h due to decomposition of $[Ru(bpy)_3]^{2+}$.^[8d] The almost linear kinetics for O₂ production reaction suggested that the oxidation reaction of the hydrolyzed IrCl₃ to IrO_x still continued after the start of the oxygen evolution. The amount of evolved oxygen (9.2 µmol) exceeded the amount of Ru and Ir atoms in the catalyst (4.6 and 5.6 µmol, respectively). The apparent quantum yield of the oxygen evolution was $\Phi^{\rm 400}_{
m O_2}\!=\!0.34\,\%$ for the initial linear region shown in Figure 4a.

The formation of IrO_x nanoparticles on Ru-Acd-PMO was confirmed by high-angle annular dark field (HAADF) scanning transmission electron micrograph (STEM) and X-ray absorption fine structure (XAFS) spectra. HAADF-STEM showed many white spots due to nanoparticles with diameters of 1-2 nm all over the Acd-PMO particles (Figure 4b). Energy-dispersive Xray spectroscopy (EDS) revealed that the regions with a large aggregation of white spots showed Ir-rich compositions (Ir/ Ru=4.1-4.3), while the other many regions had low Ir/Ru ratios of 0.80-0.88, indicating that the white spots consisted of mainly Ir species (Figure S1 in the Supporting Information). The ICP-AES analysis of IrO_x-deposited Ru-Acd-PMO showed that the amounts of Ir and Ru were 0.15 and 0.19 mmol g⁻¹, respectively. The ratio of Ir/Ru (0.79) is in good agreement with the Ir/Ru ratio (0.80-0.88) for many regions estimated by EDS. A XANES spectrum of IrO_x/Ru-Acd-PMO showed an Ir-L₃ edge peak at 11217.04 eV, an energy slightly lower than that of $Ir^{IV}O_2$ (11217.70 eV) but higher than that of $Ir^{III}CI_3 \cdot 3H_2O$ (11 216.38 eV), indicating a mixed valence of Ir^{III} and Ir^{IV} in $IrO_x/$ Ru-Acd-PMO. EXAFS spectra and their simulations suggested the complete absence of Ir-CI bonds (Figure S2 in the Supporting Information). The preservation of the ordered mesoporous structure for IrO,/Ru-Acd-PMO was confirmed for the sample prepared after photoirradiation for 1.75 h by XRD and

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 $\ensuremath{\mathsf{N}}_2$ adsorption isotherms (Figure S3 in the Supporting Information).

The tentative mechanism of photocatalysis for the IrO_x/Ru-Acd-PMO and S₂O₈²⁻ system is shown in Scheme 1. Acd-PMO absorbs 400 nm light and transfers the excitation energy to the $[Ru(bpy)_3]^{2+}$ complex. The excited state of the $[Ru(bpy)_3]^{2+}$ complex is oxidatively quenched by $S_2 O_8^{\ 2-}$ to form ${Ru}^{3+}$ species,^[12] which extracts an electron from IrO_x to oxidize water for oxygen production in the same manner reported in homogeneous water oxidation systems of [Ru(bpy)₃]²⁺, IrO₂ and $Na_2S_2O_8$.^[8] Although the $[Ru(bpy)_3]^{2+}$ complex can also absorb 400 nm light, the contribution is negligible because of the large ratio of Acd moieties to Ru complex in the catalysts (Acd/Ru = 14). As control experiments, some physical mixture systems were evaluated for photocatalysis of water oxidation. A physical mixture of Acd-PMO and Ru-MPS with a molar ratio of Acd/Ru = 16 showed no oxygen generation in the presence of the hydrolyzed IrCl₃ and Na₂S₂O₈ under irradiation at 400 nm, because 400 nm light was absorbed mainly by Acd-PMO, but not by Ru-MPS due to an inner-filter-effect (Figure 4a). Energy transfer did not occur from Acd groups to Ru complexes in this system, because they were separated in the different particles. However, only Ru-MPS without Acd-PMO generated oxygen at the same reaction conditions (Figure S4 in the Supporting Information), because Ru-MPS could directly absorbed 400 nm light. However, this system has no light-harvesting function owing to the absence of organic groups within the framework of MPS. Another physical mixture of Ru-Acd-PMO particles and IrO₂ nanoparticles also showed no oxygen generation in the presence of Na₂S₂O₈ under irradiation at 400 nm, because IrO₂ nanoparticles (the primary particle sizes are 10-30 nm, Figure S5 in the Supporting Information) could not be directly contacted with Ru complexes located in the mesochannels due to the smaller pore size (3.6 nm). The direct contact of Ru complex and IrO_x is important for oxygen production because the oxidative Ru³⁺ complex must extract an electron from IrO₂. The preferential quenching of the excited $[Ru(bpy)_3]^{2+}$ complexes rather than the Acd groups by $S_2O_8^{2-}$ was confirmed by the following quenching experiments. The emission of Ru-Acd-PMO (λ_{max} = 630 nm) was almost completely quenched in the presence of only 10 mм of Na₂S₂O₈, while the emission of Acd-PMO ($\lambda_{max} =$ 525 nm) was not completely quenched, even in the presence of 30 mm $Na_2S_2O_8$ (Figure 3 b). These observations demonstrate that the excited state of Acd groups is transferred to $[Ru(bpy)_3]^{2+}$ faster than quenching by $S_2O_8^{2-}$, and the excited state of $[Ru(bpy)_3]^{2+}$ is preferentially quenched by $S_2 O_8^{2-}$ to generate the oxidative Ru³⁺ species. These control and quenching experiments demonstrate the unique sequence of reactions for the IrO_x/Ru-Acd-PMO and $S_2O_8^{2-}$ system, 1) energy transfer from Acd to Ru^{2+} , 2) oxidative quenching of Ru^{2+} to Ru^{3+} by $S_2O_8{}^{2-}\!\!$, and 3) extraction of an electron from IrO_x by Ru^{3+} to catalyze water oxidation.

To improve the reaction quantum efficiency for water oxidation, the structures of IrO_x/Ru -Acd-PMO catalyst were modified by: 1) silica coating on the pore surface to prevent direct contact between Acd groups and IrO_x nanoparticles, and 2) the expansion of pore diameter from 4.2 to 10 nm to promote the smooth diffusion of molecules, such as $Na_2S_2O_8$.

The silica coating was carried out by TEOS vapor treatment of Acd-PMO. The TEOS-treated Acd-PMO was attached with Ru complex in the same manner (Ru-Acd-PMO(TEOS)). Ru-Acd-PMO(TEOS) showed a higher activity for water oxidation after a short induction period of 0.67 h than Ru-Acd-PMO, because unfavorable quenching of the excited state of Acd groups by IrO_x nanoparticles was suppressed (Figure 5 and Figure S6 in



Figure 5. Time dependence of photocatalytic oxygen evolution for Ru-Acd-PMO (\bullet), Ru-Acd-PMO(TEOS) (\bullet), Ru-Acd-PMO(10) (\blacktriangle) in a carbonate buffer solution (pH 8.9) under irradiation by 400 nm light in the presence of hydro-lyzed IrCl₃ and Na₂S₂O₈ (31 mM).

the Supporting Information). The reaction quantum efficiency was $\Phi_{O_2}^{400} = 0.68$ %, which was almost twice that of nontreated Ru-Acd-PMO ($\Phi_{O_2}^{400} = 0.34$ %). The almost half of the induction period (1.25 \rightarrow 0.67 h) was very reasonable because the activity for Ru-Acd-PMO(TEOS) was twice as much as that for Ru-Acd-PMO.

The pore expansion of Acd-PMO was carried out by the DMDA (*N*,*N*-dimethyldecylamine) treatment method (Figure S7 in the Supporting Information).^[13] The expanded Acd-PMO with a large mesopore (10 nm) was attached with Ru complex in the same manner (Ru-Acd-PMO (10)). Ru-Acd-PMO(10) showed a higher reaction quantum efficiency ($\Phi_{O_2}^{400} = 1.2\%$) for water oxidation under the same reaction conditions, with almost no induction period (Figure 5). The very short induction period is reasonably explained by the very high oxidation activity of Ru-Acd-PMO(10). It suggests that the diffusion of molecules in the channels is one of the crucial factors in determining the efficiency of photocatalytic reactions. These results suggest that further improvement of the reaction efficiency can be expected by optimization of the PMO structures.

Finally, a tracer experiment using $H_2^{18}O$ as a solvent for photocatalytic oxygen evolution was conducted to confirm that the produced oxygen originated from water. An evolved gas was quantitatively analyzed by GC-MS after irradiation by 400 nm light for 5 h of a dispersion of Ru-Acd-PMO(TEOS) powder in $H_2^{18}O$ containing hydrolyzed IrCl₃ and Na₂S₂O₈. The GC-MS spectra showed three peaks for ¹⁶O₂ (*m/z* 32), ¹⁶O¹⁸O (*m/z* 34), and ¹⁸O₂ (*m/z* 36) with ratios of 14, 5, and 80%, respectively in 4 µmol of totally evolved O₂ gas. This indicates

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that oxygen was evolved mainly by photocatalytic water oxidation.

Conclusion

In conclusion, a novel organic-based photocatalytic system for water oxidation including a coupled light-harvesting antenna to mimic PS II was constructed using PMO. PMOs have great potential as solid scaffolds for the construction of artificial photosynthesis systems, not only because of their unique light-harvesting antenna properties but also because they enable a high designability of reaction systems.^[14] The tunability of pore size in the large mesopore region (2–30 nm) for PMOs is of great merit in constructing efficient and highly functional photoreaction systems, such as those involved in natural photosynthesis.

Experimental Section

General measurement

The ¹H NMR and ²⁹Si NMR spectra of the solution samples were recorded on JEOL JNM-ECX400P and JEOL Lambda500 spectrometers, respectively. The electrospray ionization mass (ESI-MS) spectra were measured with a Micromass Q-TOF mass spectrometer. The UV/Vis diffuse reflectance (DR) spectra were recorded on a JASCO V-670 spectrophotometer with an integrating sphere unit (JASCO ISN-723). The longitudinal axes of the spectrum were converted using the Kubelka-Munk function from reflectance (% R) to K/S unit. The emission and excitation spectra were measured by a JASCO FP6500 spectrofluorometer. The nitrogen adsorption/desorption isotherms were measured using a Quantachrome Nova-3000e sorptometer at -196°C. Prior to the measurements, the samples were outgassed at 60°C for 4 h. The Brunauer-Emmett-Teller (BET) surface areas were calculated from a linear section of the BET plot ($P/P_0 = 0.05 - 0.2$). The DFT (density functional theory) pore diameter was calculated using a DFT kernel (N₂ at 77 K on silica, cylindrical pore, NLDFT equilibrium model). The powder X-ray diffraction (XRD) patterns were measured on a Rigaku RINT-TTR diffractometer with $\text{Cu}_{\text{K}\alpha}$ radiation (50 kV, 300 mA). The transmission electron microscopic (TEM) and high angle annular dark field (HAADF) scanning-TEM (STEM) observations were conducted using JEOL JEM-2000EX and JEM-2100F microscopes, respectively. For the observation, the powder samples were dispersed in ethanol after grinding with a mortar and deposited to a supporting grid. The inductively coupled plasma atomic emission spectrometry (ICP-AES) was conducted using a Rigaku CIROS 120EOP for quantitative analysis of heavy metals, Ru and Ir atoms. The measurements of X-ray absorption fine structure (XAFS), such as X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), were carried out for the Ir-L₃ edge at room temperature in the transmission mode at the BL33XU in SPring-8 (Hyogo, Japan).

Chemicals

All reagents and solvents were of highest commercial quality and were used without further purification. [Ru(bpy)₂Cl₂]-2H₂O was prepared according to the literature method.^[15] The organosilane precursors, 2,7-bis(triethoxysilyl)acridone^[4b] (BTEAD, (C₂H₅O)₃Si–C₁₃H₇NO–Si(OC₂H₅)₃, M_W = 519.75) and 4-[4-{3-(trimethoxysilanyl)-propylsulfanyl}butyl]-4'-methyl-2,2'-bipyridine^[16] (bpySi(OMe)₃,

 $(CH_3O)_3Si-C_3H_6-S-C_4H_8-C_{11}N_2H_9$, $M_W=420.65$) were purchased from Nard Institute, Ltd., Japan. The cationic surfactant, octadecyltrimethylammonium chloride $(C_{18}TMACI, C_{18}H_{37}N(CH_3)_3CI, M_W=$ 348.05) and *N*,*N*-dimethyldecylamine (DMDA, CH₃(CH₂)₉N(CH₃)₂, $M_W=185.36$) were purchased from TCI. The Acd-PMO powder^[4b] and MPS (mesoporous silica)^[17] were synthesized according to the literature. IrO₂ powder was purchased from Kojundo Chemical Lab. Co., Ltd.

Silica coating of Acd-PMO

In an airtight container, two vials separately containing the Acd-PMO powder (500 mg) and a tetraethoxysilane (TEOS) liquid (10 mL) were placed and evacuated through a cock at room temperature until bubbles slightly emerged in the TEOS liquid before the cock was shut. Then, the airtight container was heated at 120 °C for 12 h under stirring with magnetic stirrer bars. The obtained PMO powder was washed with EtOH and dried in vacuo. In order to convert residual Si–OEt bonds come from TEOS to Si–OH on the surface, the resultant powder was further treated with HCl for hydrolysis by stirring in an HCl (0.4 m) aqueous solution at room temperature, overnight, washed with water and dried under a vacuum.

Pore expansion of Acd-PMO

The as-made Acd-PMO powder containing C_{18} TMACI in the pores was prepared by the same method as the Acd-PMO powder^[4b] without post-pH adjustment and surfactant extraction (Acd-PMO; as-made, basic). The Acd-PMO (as-made, basic) powder (100 mg) was dispersed in an aqueous solution (2 mL) containing C_{18} TMACI (87 mM) and DMDA^[13] (370 mg, 2.00 mmol) was added. The mixture was heated with stirring at 165 °C for 24 h in a sealed sample tube (i.d. 10 mm). After being cooled to room temperature, the pH of the resultant suspension was adjusted to approximately 2. The powder recovered by filtration was stirred in EtOH (5 mg mL⁻¹) for surfactant removal to give Acd-PMO(10) as a pale yellow powder.

$[Ru(bpy)_3]^{2+}-C_4SC_3-Si(OEt)_3$

Ethanol (250 mL) solution containing [Ru(bpy)₂Cl₂]·2H₂O (500 mg, 0.96 mmol) and bpySi(OMe)₃ (500 g, 1.19 mmol) were refluxed under an Ar atmosphere for 24 h. After removal of the solvent under reduced pressure, the residue was redissolved in CH₂Cl₂ and shaken with the addition of saturated KPF₆ aqueous solution. The separated organic phase was isolated, washed with water three times, and dried with MgSO4. $[Ru(bpy)_3]^{2+}\text{-}C_4\text{SC}_3\text{-}\text{Si}(\text{OEt})_3$ as a red solid was recovered by solvent evaporation and was purified by reprecipitation with $\mathsf{CH}_2\mathsf{CI}_2\!/\mathsf{Et}_2\mathsf{O}$ three times and vacuum dried. ¹H NMR (400 MHz, [D₆]acetone, RT, TMS): $\delta = 8.79$ (d, J(H,H) = 8.2 Hz, 4H; bpy-3,3', bpy'-3,3'), 8.71 (dd, J(H,H) = 1.8 Hz, 2H; bpySi-3,3'), 8.18 (dddd, J(H,H) = 8.0, 8.0, 1.4, 1.4 Hz, 2H; bpy-4, bpy'-4), 8.17 (ddd, J(H,H) = 8.0, 8.0, 1.4 Hz, 2H; bpy-4', bpy'-4'), 8.05 (ddd, J(H,H) = 4.8, 0.9, 0.9 Hz, 1 H; bpy-6), 8.03 (ddd, J(H,H) = 4.1, 0.5, 0.5 Hz, 1H; bpy-6'), 8.03-8.00 (m, 2H; bpy'-6,6'), 7.86 (d, J(H,H) = 5.5 Hz, 1H; bpySi-6'), 7,83 (d, J(H,H) = 5.9 Hz, 1H; bpySi-6), 7.57 (dd, J(H,H) = 6.4, 1.4 Hz, 1 H; bpy-5), 7.55 (dd, J(H,H) = 5.5, 1.4 Hz, 1 H; bpy-4'), 7.57-7.52 (m, 2H; bpy'-5,5'), 7.43 (dd, J(H,H)=5.9, 1.8 Hz, 1H; bpySi-5'), 7.39 (ddd, J(H,H) = 5.9 1.6, 0.7 Hz, 1H; bpySi-5), 3.78 $(q, J(H,H) = 7.1 Hz, 6H; -Si-OCH_2CH_3), 2.88 (t, J(H,H) = 8.0 Hz, 2H;$ bpy-CH₂CH₂CH₂CH₂CH₂-S-), 2.56 (s, 3H; bpy-CH₃), 2.53 (t, J(H,H) =7.3 Hz, 2H; bpy-CH₂-), 2.50 (t, J(H,H) = 7.3 Hz, 2H; -S-CH₂CH₂CH₂-Si-), 1.81 (quintet, J(H,H) = 7.9 Hz, 2H; bpy-CH₂CH₂CH₂CH₂-S-), 1.63 (quintet, J(H,H) = 7.7 Hz, 4H; bpy-CH₂CH₂CH₂CH₂-S-CH₂CH₂CH₂-Si-),

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1.16 (t, J(H,H) = 6.8 Hz, 9 H; -Si-OCH₂CH₃), 0.68 ppm (t, J(H,H) = 8.2 Hz, 2H; -CH₂-Si-); see also Figure S8 in the Supporting Information; ²⁹Si NMR (99.4 MHz, [D₃]acetonitrile, RT, TMS): $\delta = -45.5$ ppm; HRMS (ES +): m/z: calcd for $C_{44}H_{54}N_6O_3RuSSi$ 438.1395; found 438.1355 [M-(PF₆)₂]²⁺ (see also Figure S9 in the Supporting Information); calcd for $C_{44}H_{54}F_6N_6O_3PRuSSi$ 1021.2432; found 1021.2455 [M-PF₆]⁺: elemental analysis calcd (%) for $C_{44}H_54F_12N_6O_3P_2RuSSi$: C 45.32, H 4.67, N 7.21, S 2.75; found: C 44.79, H 4.51, N 7.27, S 2.68.

Ru(bpy)₃-C₄SC₃-Si(OH)₃

A H₂O/MeOH (2:3 v/v, 10 mL) solution containing [Ru(bpy)₃]²⁺ -C₄SC₃-Si(OEt)₃ (50 mg, 0.043 mmol) was refluxed under Ar atmosphere for 2 h. [Ru(bpy)₃]²⁺-C₄SC₃-Si(OH)₃ was recovered as a red solid by evaporation of the resultant solution and dried under vacuum. The completion of the hydrolysis of $-Si(OEt)_3$ group was confirmed by a ¹H NMR measurement before the use for attachment treatment on surface of silica powders (Figure S8 in the Supporting Information).

Attachment of [Ru(bpy)₃]²⁺-C₄SC₃-Si(OH)₃ on PMOs and MPS

[Ru(bpy)₃]²⁺-C₄SC₃-Si(OH)₃ (50 mg) was dissolved in CH₃CN (10 mL) and added to Acd-PMO or MPS powder (100 mg). After dispersion by sonication, the resultant suspension was heated at 60 °C for 3 h in a sealed vial. The resultant orange-colored powder was recovered by filtration and dried under vacuum (Ru-Acd-PMO or Ru-MPS, respectively). The loaded amount of Ru complex for Acd-PMO or MPS was determined by absorbance measurements of the initial Ru complex solution and of the filtrate using the molar extinction coefficient ($\varepsilon = 16000 \text{ M}^{-1} \text{ cm}^{-1}$ at 445 nm) of [Ru(bpy)₂(dmb)]²⁺ (dmb = 4,4'-dimethyl-2,2'-bipyridine) in the CH₃CN solution.^[18]

Quenching experiments for Acd-PMO and Ru-Acd-PMO

PMO powder (1 mg) was dispersed in H_2O (5 mL) by sonication, and the suspension (1 mL, 200 mg L⁻¹) was mixed with a Na_2SO_4 aqueous solution (0.065 M, 3 mL). Emission spectra of the obtained suspension containing PMO powder (50 mg L⁻¹) and Na_2SO_4 (49 mM) were measured at room temperature under an Ar atmosphere. For the quenching experiment, the suspension (1 mL, 200 mg L⁻¹) was mixed with aqueous solution containing Na_2SO_4 (0.065 M, 3 mL) and $Na_2S_2O_8$ (0.013 or 0.039 M), and the emission spectra of the obtained suspension (PMO powder (50 mg L⁻¹), Na_2SO_4 (49 mM), and $Na_2S_2O_8$ (10 or 30 mM)) were measured under the same conditions.

Hydrolysis pretreatment of IrCl₃ for photodeposition of IrO_x particles

IrCl₃·3 H₂O (8 mg, 0.023 mmol) was heated in carbonate buffer solution (NaHCO₃ (0.1 м)/NaCO₃ (0.05 м), pH 8.9, 20 mL) with stirring at 60 °C for 2 h in the presence of Na₂S₂O₈ (47.6 mg, 0.20 mmol). The hydrolysis of IrCl₃ was confirmed by time-dependent UV/Vis/NIR spectra (Figure S10 in the Supporting Information). The spectra were measured using fivefold diluted solutions of aliquots. The obtained dark blue solution (5 mL) was diluted to 50 mL with water and kept at 4 °C, overnight, after addition of Na₂S₂O₈ (357 mg, 1.50 mmol). The resultant solution was used for the photocatalysis tests for water oxidation.

Photocatalysis for water oxidation

Ru-Acd-PMO powder (20 mg), Ru-MPS (75 mg) or a mixture of Acd-PMO (20 mg) and Ru-MPS (75 mg) powders, was dispersed in a hydrolyzed IrCl₃ solution (50 mL) containing sacrificial oxidant, Na₂S₂O₈ (31 mм). The suspension was introduced into a Pyrex vessel covered with a quartz cap equipped with a pit that reached the liquid surface in the vessel for insertion of an optical fiber. The vessel was connected to a closed gas circulation and evacuation system. Degassing under vacuum and purging with Ar gas (Taiyo Nippon Sanso 99.9%) were repeated three times to remove air from the reactor. Finally, Ar gas was introduced until the interior pressure reached 1 atm. Light from a 300 W xenon lamp (Asahi spectra, MAX-301) equipped with a mirror module and a bandpass filter (400 nm with half-width of 10 nm) was irradiated through the end of an optical fiber. The irradiated light intensity was monitored with a Molectron PowerMAX500AD power meter and adjusted to 9.8×10^{-8} einstein s⁻¹ with an ND filter. Apparent quantum efficiency of the oxygen evolution ($\Phi_{\Omega_2}^{400}$) was estimated according to Equation (2):

$$\begin{split} \varPhi^{400}_{O_2} &= (\text{rate of } O_2 \text{ evolution } [\text{mol s}^{-1}])/\\ (\text{irradiated-light intensity } [\text{einstein s}^{-1}]) \times 100 \end{split}$$

The reactor was kept at 20 °C in a thermostated water bath (Asone CB-15). The suspension was stirred with a magnetic bar, and the upper gas phase was pumped and circulated through the suspension during the photoreaction. A fraction (2.9 mL) of the gas phase (227.6 mL) after each of the irradiation times was sampled and analyzed using a Shimadzu GC-8A gas-chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a molecular sieve 5 Å (mesh 60/80, 2 m, i.d. 3 ϕ) column. For the tracer experiment using H₂¹⁸O as a reaction solvent, the reaction solution was scaled-down to 2 mL (see also the Supporting Information).

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- [1] a) Z. Liu, H. Yan, K. Wang, T. Kuang, J. Zhang, L. Gui, X. An, W. Chang, *Nature* **2004**, *428*, 287–292; b) Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **2011**, *473*, 55–60.
- [2] a) H. Inoue, T. Shimada, Y. Kou, Y. Nabetani, D. Masui, S. Takagi, H. Tachibana, *ChemSusChem* 2011, *4*, 173–179; b) J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, *Inorg. Chem.* 2005, *44*, 6802–6827; c) V. Balzani, A. Credi, M. Venturi, *ChemSusChem* 2008, *1*, 26–58.
- [3] a) N. Mizoshita, T. Tani, S. Inagaki, Chem. Soc. Rev. 2011, 40, 789–800;
 b) Y. Ishida, T. Shimada, D. Masui, H. Tachibana, H. Inoue, S. Takagi, J. Am. Chem. Soc. 2011, 133, 14280–14286; c) G. Calzaferri, Langmuir 2012, 28, 6216–6231; d) M. Yagi, M. Toda, S. Yamada, H. Yamazaki, Chem. Commun. 2010, 46, 8594–8596; e) C. A. Kent, B. P. Mehl, L. Ma, J. M. Papanikolas, T. J. Meyer, W. Lin, J. Am. Chem. Soc. 2010, 132,

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12767 – 12769; f) C. A. Kent, D. Liu, L. Ma, J. M. Papanikolas, T. J. Meyer, W. Lin, J. Am. Chem. Soc. **2011**, *133*, 12940 – 12943.

- [4] a) S. Inagaki, O. Ohtani, Y. Goto, K. Okamoto, M. Ikai, K. Yamanaka, T. Tani, T. Okada, *Angew. Chem.* 2009, *121*, 4102–4106; *Angew. Chem. Int. Ed.* 2009, *48*, 4042–4046; b) H. Takeda, Y. Goto, Y. Maegawa, T. Ohsuna, T. Tani, K. Matsumoto, T. Shimada, S. Inagaki, *Chem. Commun.* 2009, 6032–6034; c) N. Mizoshita, K. Yamanaka, T. Tani, H. Shinokubo, S. Inagaki, *Langmuir* 2012, *28*, 3987–3994.
- [5] H. Takeda, M. Ohashi, T. Tani, O. Ishitani, S. Inagaki, *Inorg. Chem.* 2010, 49, 4554–4559.
- [6] a) C. Wang, Z. Xie, K. E. deKrafft, W. Lin, J. Am. Chem. Soc. 2011, 133, 13445 – 13454; b) C. Wang, J. Wang, W. Lin, J. Am. Chem. Soc. 2012, 134, 19895 – 19908.
- [7] A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent, M. J. Rosseinsky, *Angew. Chem.* **2012**, *124*, 7558 7562; *Angew. Chem. Int. Ed.* **2012**, *51*, 7440 7444.
- [8] a) J. Kiwi, M. Grätzel, Angew. Chem. 1978, 90, 900–901; Angew. Chem. Int. Ed. Engl. 1978, 17, 860–861; b) A. Harriman, I. J. Pickering, J. M. Thomas, P. A. Christensen, J. Chem. Soc. Faraday Trans. 1 1988, 84, 2795–2806; c) M. Hara, T. E. Mallouk, Chem. Commun. 2000, 1903– 1904; d) M. Hara, C. C. Waraksa, J. T. Lean, B. A. Lewis, T. E. Mallouk, J. Phys. Chem. A 2000, 104, 5275–5280; e) M. Hara, J. T. Lean, T. E. Mallouk, Chem. Mater. 2001, 13, 4668–4675; f) N. D. Morris, M. Suzuki, T. E. Mallouk, J. Phys. Chem. A 2004, 108, 9115–9119.
- [9] a) R. Humphry-Baker, J. Lilie, M. Grätzel, J. Am. Chem. Soc. 1982, 104, 422-425; b) A. Harriman, M. Richoux, P. A. Christensen, S. Mosseri, P. Neta, J. Chem. Soc. Faraday Trans. 1 1987, 83, 3001-3014.
- [10] D. J. Wasylenko, R. D. Palmer, C. P. Berlinguette, Chem. Commun. 2013, 49, 218–227.

- [11] C. Besson, Z. Huang, Y. V. Geletii, S. Lense, K. I. Hardcastle, D. G. Musaev, T. Lian, A. Proust, C. L. Hill, *Chem. Commun.* **2010**, *46*, 2784–2786.
- [12] a) F. Bolletta, A. Juris, M. Maestri, D. Sandrini, *Inorg. Chim. Acta* **1980**, *44*, L175–L176; b) K. Henbest, P. Douglas, M. S. Garley, A. Mills, J. Photochem. Photobiol. A **1994**, *80*, 299–305.
- [13] a) A. Sayari, M. Kruk, M. Jaroniec, I. L. Moudrakovski, Adv. Mater. 1998, 10, 1376–1379; b) A. Sayari, Y. Yang, M. Kruk, M. Jaroniec, J. Phys. Chem. B 1999, 103, 3651–3658.
- [14] a) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Angew. Chem. 2006, 118, 3290–3328; Angew. Chem. Int. Ed. 2006, 45, 3216–3251; b) M. P. Kapoor, S. Inagaki, Bull. Chem. Soc. Jpn. 2006, 79, 1463–1475; c) K. Ariga, A. Vinu, J. Hill, T. Mori, Coord. Chem. Rev. 2007, 251, 2562–2591; d) S. Fujita, S. Inagaki, Chem. Mater. 2008, 20, 891–908; e) W. Wang, J. E. Lofgreen, G. A. Ozin, Small 2010, 6, 2634–2642; f) A. Mehdi, C. Reye, R. Corriu, Chem. Soc. Rev. 2011, 40, 563–574.
- [15] B. P. Sullivan, D. J. Salmon, T. J. Meyer, Inorg. Chem. 1978, 17, 3334– 3341.
- [16] a) J. V. Nguyen, C. Jones, J. Catal. 2005, 232, 276–294; b) J. V. Nguyen, C. W. Jones, Macromolecules 2004, 37, 1190–1203.
- [17] S. Inagaki, Y. Fukushima, K. Kuroda, J. Chem. Soc. Chem. Commun. 1993, 680-682.
- [18] P. A. Mabrouk, M. S. Wrighton, Inorg. Chem. 1986, 25, 526-531.

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FULL PAPER

Artificial Photosynthesis

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Light-Harvesting Photocatalysis for Water Oxidation Using Mesoporous Organosilica



The lining's on the wall: A photocatalysis system for water oxidation linked with a solid light-harvesting antenna was constructed using periodic mesoporous organosilica (PMO), mimicking photosystem II. The acridone-containing PMO absorbed visible light and funneled the light energy into $[Ru(bpy)_3]^{2+}$ complex fixed in the mesochannels. Oxygen was evolved on IrO_x nanoparticles deposited on the pore surface (see figure).