Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

for

Combination of visible-light responsive heterogeneous and homogeneous photocatalysts for water oxidation

Shunichi Fukuzumi,* Satoshi Kato and Tomoyoshi Suenobu

Experimental Section

Materials

Bi_2O_3 (99.9%) was purchased from Kishida Chemical. V_2O_5 (99%) was purchased from Nacalai Tesque. $RuCl_3$ (38.220 wt% Ru) was purchased from Tanaka Kikinzoku Kogyo. 4,7-dimethyl-1,10-phenanthroline (Me_2-phen, 98%), 5-chloro-1,10-phenanthroline (Cl-phen, 98%), tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate ($[Ru^{II}(bpy)_3]Cl_2 \cdot 6H_2O$), and pentaamminechlorocobalt(III) chloride ($[Co^{III}(NH_3)_5Cl]Cl_2$) were purchased from Aldrich Chemicals.

Preparation of $BiVO_4$ photocatalyst

The photocatalyst was prepared based on the published method by Kudo and co-workers.[1] Starting materials, 2.3 g of Bi_2O_3 and 0.9 g of V_2O_5 were vigorously stirred in a 1.0 M (mol dm^{-3}) aqueous acetic acid solution (50 mL) at room temperature for 11 days. The obtained $BiVO_4$ powder was repeatedly washed with distilled water to remove the acetic acid. The obtained $BiVO_4$ powder was calcined at 673 K for 5 h and used as prepared.

Characterization of $BiVO_4$ photocatalyst

Powder X-ray diffraction (XRD) patterns were recorded by a Rigaku Ultima IV. Measurements were performed under the supervision of Prof. Norimitsu Tohnai and Prof. Mikiji Miyata. Incident X-ray radiation was produced by Cu X-ray tube, operating at 40 kV and 40 mA with Cu $K\alpha$ radiation of 1.54 Å. A scanning rate was 4°/min from 5° to 50° in 2θ. Diffuse reflectance spectra were obtained using a UV-vis-NIR spectrometer (Shimadzu, UV-3100PC) equipped with integrated sphere unit (ISR-3100).

Preparation of ruthenium complexes

Ruthenium complexes were prepared according to the literature methods.[2-3] $[Ru^{II}(Me_2\text{-phen})_3]^{2+}$: $RuCl_3$ was refluxed under N_2 overnight in ethanol/water (v/v 80/20) with 6 equiv of ligand, Me_2-phen, to form the red-orange $[Ru^{II}(Me_2\text{-phen})_3]^{2+}$ complex. After evaporation of the solvent, the product was readily precipitated from acetone with ether. $[Ru^{II}(Cl\text{-phen})_3]^{2+}$: $RuCl_3$ was refluxed under N_2 overnight in ethanol/water (v/v 50/50) with 6 equiv of ligand, Cl-phen, to form the red-orange $[Ru^{II}(Cl\text{-phen})_3]^{2+}$ complex. After evaporation of the solvent, the product was readily precipitated from acetone with ether.

Photocatalytic reactions

$BiVO_4$ (3.0 mg) was dispersed in an aqueous sulfuric acid solution (pH 2.4, 3.0 mL) containing ruthenium complex ($[Ru^{II}(bpy)_3]^{2+}$, $[Ru^{II}(Me_2\text{-phen})_3]^{2+}$, or $[Ru^{II}(Cl\text{-phen})_3]^{2+}$) (20 μM) and $[Co^{III}(NH_3)_5Cl]^{2+}$ (1.0 mM) in a quartz cuvette (light path length = 1 cm). The solution was carefully deaerated by bubbling argon gas for ~30 min. The photocatalysts were irradiated with a xenon lamp (USHIO Optical Modulex SX-UID 501XAMQ) through a cut-off filter (Asahi Techno Glass L42) transmitting $\lambda > 420$ nm at room temperature. Alternatively, the photocatalysts were irradiated with a xenon lamp (Asahi Spectra MAX-302) through band-pass filters transmitting $\lambda = 420$, 450, 470, and 500 nm at room temperature. The emission spectrum of the xenon lamp is shown in Fig. S5. A small portion (100 μL) of the gas in a headspace was sampled via a gas-tight syringe and used for gas analysis. The amount of evolved oxygen gas was analyzed by a Shimadzu GC-17A gas chromatograph (Career gas: Ar; Column: HP-PLOT MoleSieve, 19095P-MS0, 0.530 mm, 30 m, Agilent Technologies Inc.; Column temp.: 40℃) equipped with a thermal conductivity detector (TCD temp.: 200℃).

Apparent quantum yield and quantum efficiency determination

Apparent quantum yield (AQY) and quantum efficiency (QE) of the photocatalytic oxygen evolution (Φ) were determined under irradiation of monochromatized light using a band-pass filter (ϕ25 96SA, Asahi Techno Glass, $\lambda = 450$ nm), and estimated as

$$\mathrm{AQY}(\%) = (4 \times R/I_1) \times 100 \tag{1}$$

and

$$\mathrm{QE}(\%) = (4 \times R/I_2) \times 100 \tag{2}$$

where R (mol s^{-1}) represents the O_2 evolution rate and I_1 and I_2 represent coefficients based on the rate of incident photons and that on the reacting surface, respectively. QE in eqn 2 is defined according to a recent paper.[4] In order to generate an oxygen molecule by four-electron oxidation of two molecules of water, four photons are necessary for the band-gap electronic transition in $BiVO_4$ semiconductor. When the total four photons are fully used for generation of an oxygen molecule, AQY reaches 100 %. Therefore, the coefficient of the right-hand side in eqn (1) is 4 for this photocatalytic system.[5] The total number of incident photons was measured by a standard method using an actinometer (potassium ferrioxalate, $K_3[Fe^{III}(C_2O_4)]_3$) in H_2O at room temperature under photoirradiation of a xenon lamp (Asahi Spectra MAX-302) through a band-pass filter transmitting $\lambda = 450$ nm at room temperature. For the same quartz cuvette (light path length = 1 cm) with 3.0 mL solution as used in the oxygen evolution experiments, the rate of photon flux of the incident light (I_1) was determined to be 3.67×10^{-8} einstein s^{-1}. In the same manner, the number of incident photons on reacting surface was determined by measuring the rate of photons transmitted through an aqueous sulfuric acid solution (pH 2.4, 3.0 mL) containing $[Ru^{II}(bpy)_3]^{2+}$ (20 μM) and dispersed $BiVO_4$ (3.0 mg) in a quartz cuvette (light path length = 1 cm). The ratio of the rate of transmitted photons to that of the total incident photons was measured by an illuminometer (T-10, Konica Minolta Sensing Inc.) and determined to be 63.2%. The rate of photon flux of the incident light on reacting surface (I_2) was calculated to be 1.35×10^{-8} einstein s^{-1}.

$BiVO_4$ (3.0 mg) was dispersed in an aqueous sulfuric acid solution (pH 2.4, 3.0 mL) containing $[Ru^{II}(bpy)_3]^{2+}$ (20 μM) and $[Co^{III}(NH_3)_5Cl]^{2+}$ (1.0 mM) in a quartz cuvette (light path length = 1 cm) and stirred by a magnetic stirrer (HERACLES-16G). The solution was carefully deaerated by bubbling with argon gas for ~30 min. The photocatalysts, i.e., $BiVO_4$ and $[Ru^{II}(bpy)_3]^{2+}$, were irradiated for 1 h with a xenon lamp (Asahi Spectra MAX-302) through a band-pass filter transmitting $\lambda = 450$ nm at room temperature with the rate of stirring at 1350 rpm. A small portion (100 μL) of the gas in a headspace was sampled via a gas-tight syringe and used for gas analysis. The amount of evolved oxygen gas was analyzed by a Shimadzu GC-17A gas chromatograph equipped with a thermal conductivity detector.

Emission spectral measurements

An aqueous sulfuric acid solution (pH 2.4, 3.0 mL) containing $[Ru^{III}(bpy)_3]^{3+}$ (20 μM) and $[Co^{III}(NH_3)_5Cl]^{2+}$ (0 - 10 mM) in a quartz cuvette (light path length = 1 cm) was carefully deaerated by bubbling with argon gas for ~30 min. Quenching experiments of the emission of $[Ru^{II}(bpy)_3]^{2+}$ were carried out on a Shimadzu spectrofluorophotometer (RF-5300PC). The excitation wavelength was $\lambda = 450$ nm. The monitoring wavelength was that corresponding to the maxima of the emission band at $\lambda_{max} = 600$ nm.

Spectral measurements for photoreactions

$BiVO_4$ (3.0 mg) was dispersed in an aqueous sulfuric acid solution (pH 2.4, 3.0 mL) containing $[Ru^{III}(bpy)_3]^{3+}$ (30 μM) in a quartz cuvette (light path length = 1 cm). The solution was carefully deaerated by bubbling argon gas for ~30 min. The photocatalysts were irradiated with a xenon lamp (Asahi Spectra MAX-302) through a band-pass filter transmitting $\lambda = 500$ nm at room temperature. A small portion (100 μL) of the gas in a headspace was sampled via a gas-tight syringe and used for gas analysis. After filtering the solution, the absorption spectral changes of the filtrate were measured using a Hewlett Packard 8453 diode array spectrophotometer.

Electrochemical measurement

Cyclic voltammetry measurement was performed on an ALS 630B electrochemical analyzer in a deaerated aqueous sulfuric acid solution (pH 2.4) containing 0.20 M KCl as a supporting electrolyte at 298 K. A conventional there-electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with a BAS polished alumina suspension and rinsed with acetone before use. The second-harmonic AC voltammetry measurement was performed on an ALS 630B electrochemical analyzer. The measured potentials were recorded with respect to the $Hg/HgCl_2$ (saturated KCl) reference electrode. Electrochemical measurements were carried out under an atmospheric pressure of Ar.

Bases for calculation of potentials in Scheme 1

The conduction band edge of $BiVO_4$ at the point of zero charge (pH$_{zpc}$) was predicted by

$$E_{CB} = X - E^{C} - 1/2\,E_g \qquad (3)$$

$$E_{VB} = E_{CB} + E_g \qquad (4)$$

where X is the absolute electronegativity of the semiconductor, expressed as the geometric mean of the absolute electronegativity of the constituent atoms, which is defined as the arithmetic mean of the atomic electron affinity ($BiVO_4$: 6.035) and the first ionization energy; E^c is the energy of free electrons on the hydrogen scale (~4.5 eV); and E_g is the band gap of the semiconductor (2.40 V).[6] The potential values obtained *versus* NHE were converted to those *versus* SCE by subtracting 0.24 V.

The oxidation potential of water to oxygen was predicted by Nernst equation;[7]

$$E\ (\text{V vs. NHE}) = 1.23 - 0.059\text{pH} \qquad (5)$$

The potential values obtained *versus* NHE were converted to those *versus* SCE by subtracting 0.24 V. The oxidation potential of the excited state of $[Ru^{II}(bpy)_3]^{2+}$ is given in ref. 8.

BET surface area determination

Nitrogen adsorption-desorption at 77 K was performed with a Belsorp-mini (BEL Japan, Inc.) within a relative pressure range from 0.01 to 101.3 kPa. A sample mass of about 30 mg was used for adsorption analysis after pretreatment at 393 K under vacuum conditions and kept in N_2 atmosphere until N_2-adsorption measurements. The sample was exposed to a mixture of He and N_2 with a programmed ratio and adsorbed amount of N_2 was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min). The number of physical adsorption sites on the surface of $BiVO_4$ powder was estimated from the N_2 adsorption BET surface area (2.53 m^2/g).

References

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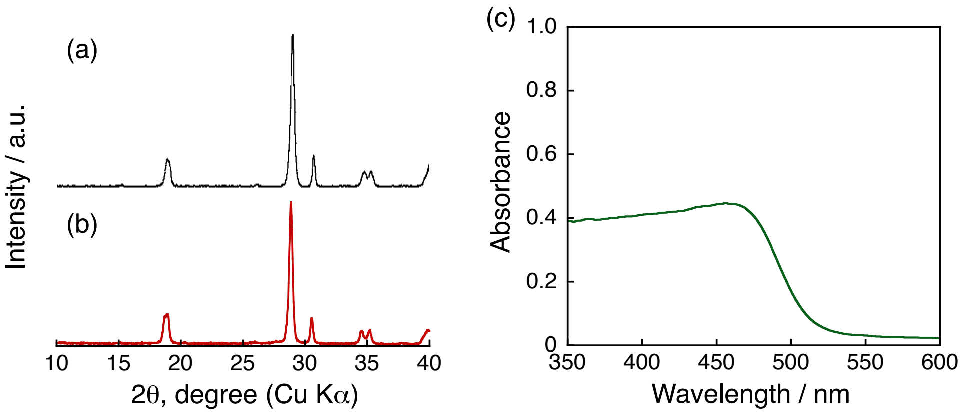

Fig. S1. XRD patterns of $BiVO_4$ (a) presented in reference 1 and (b) synthesized in this work. (c) UV-vis absorption spectrum of $BiVO_4$ (3.0 mg) dispersed in an H_2SO_4 aqueous solution (pH 2.4, 3.0 mL, 1 cm light-path length).

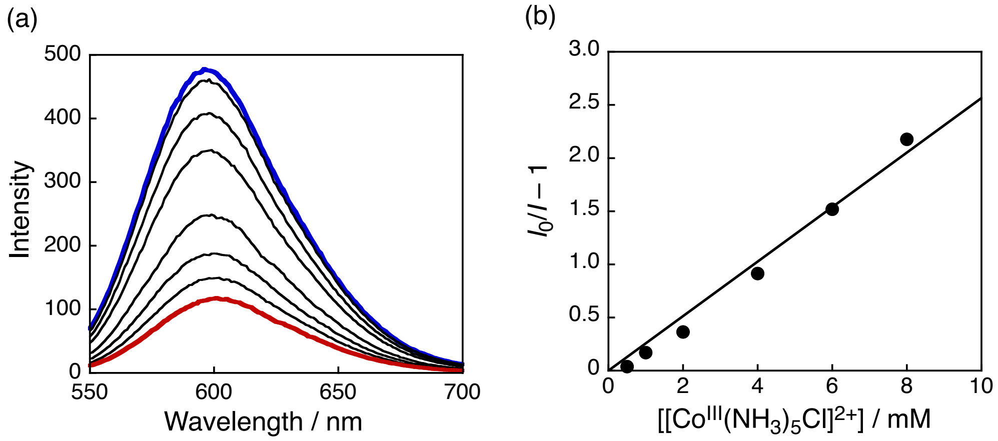

Fig. S2. (a) Emission spectra of $[Ru^{II}(bpy)_3]^{2+}$ (20 μM) in the absence and presence of $[Co^{III}(NH_3)_5Cl]^{2+}$ (blue: 0 mM, red: 10 mM) taken in a deaerated H_2SO_4 aqueous solution (pH 2.4). (b) Stern-Volmer plot for the emission quenching of $[Ru^{II}(bpy)_3]^{2+}$ by $[Co^{III}(NH_3)_5Cl]^{2+}$.

Comments.

The emission of $[Ru^{II}(bpy)_3]^{2+}$ is partially quenched by the oxidant $[Co^{III}(NH_3)_5Cl]^{2+}$ at the concentrations in Fig. 1 and Fig. 2 based on the data in Fig. S2 in ESI, which implies the efficiency of electron transfer from the excited state of $[Ru^{II}(bpy)_3]^{2+}$ to the oxidant can be enhanced by further increase in the concentration of the oxidant, however, the concentration higher than 1.0 mM resulted in the immediate formation of brown coloured precipitate in the photocatalytic water oxidation reaction, which interrupts the light absorption by the photocatalysts.

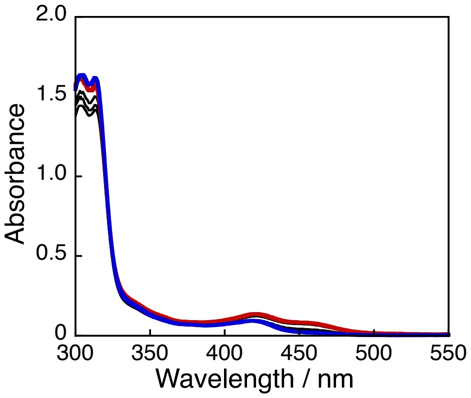

Fig. S3. UV-vis absorption spectral changes observed under visible light (λ = 500 nm) irradiation of the suspension (3.0 mL, pH 2.4) in the presence of $[Ru^{III}(bpy)_3]^{3+}$ (30 μM) without $BiVO_4$ (blue: 0 min, red: 30 min).

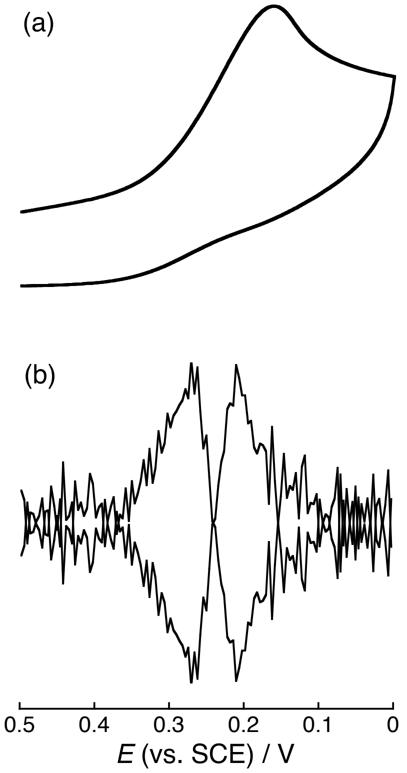

Fig. S4. (a) Cyclic voltammogram of $[Co^{III}(NH_3)_5Cl]^{2+}$ (2.0 mM) in a deaerated H_2SO_4 aqueous solution (pH 2.4) containing KCl (0.20 M). (b) Second-harmonic AC voltammogram of $[Co^{III}(NH_3)_5Cl]^{2+}$ (2.0 mM) in a deaerated H_2SO_4 aqueous solution (pH 2.4) containing KCl (0.20 M).

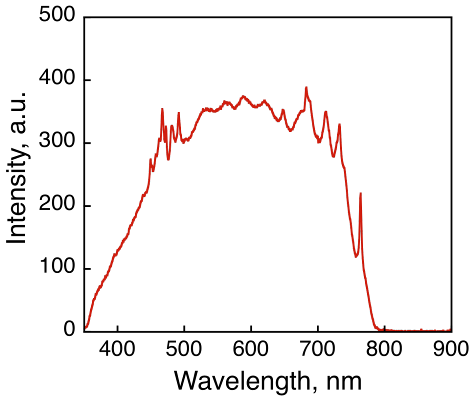

Fig. S5. The spectrum of a xenon lamp (Asahi Spectra MAX-302) used as a light source for the photocatalytic water oxidation reactions depending on the wavelength of the incident light (Fig. 4). The measurement has been done by using a multi-channel photodiode array spectrophotometer of an absolute PL quantum yield measurement system (Hamamatsu photonics Co., Ltd., C9920-02). The light intensities independently measured by a laser power meter (Ophir Optronics Ltd., model AN/2) at $\lambda = 450$, 470 and 500 nm were 32, 35 and 31 mW h^{-1}, respectively.

Reference

1. A. Iwase and A. Kudo, *J. Mater. Chem.*, 2010, **20**, 7536.