Supplementary Information

Role of Copolymerized Photosensitizer in Hydrogen-Generating Gel Systems

for Higher Quantum Efficiency

Kosuke Okeyoshi and Ryo Yoshida*

Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

TEL & FAX: +81 (0)3 5841 7112. E-mail: ryo@cross.t.u-tokyo.ac.jp

*To whom correspondence should be addressed.

(S1) Experimental details.

Materials. *N*-isopropylacrylamide (NIPAAm; Wako Pure Chemical Industries, Co., Ltd., Osaka, Japan) was purified by recrystallization from its toluene solution with hexane. Ruthenium(4-vinyl-4-methyl-2,2'-bipyridine)bis(2,2'-bipyridine)bis(chloride) (Ru(bpy)$_3$ monomer) was synthesized according to previous work.[1] Other reagents were used without further purification.

Preparation of Gels. Firstly, surfactant-modified Pt nanoparticles were prepared by the alcohol reduction method with chloroplatinic acid (H$_2$PtCl$_6\cdot$6H$_2$O) (Wako Pure Chemical Industries, Co., Ltd., JAPAN) (34 mg), anionic surfactant (S180A) (Kao Co., JAPAN) (380 mg)[2] as a protector and ethanol-water mixed solvent (30 mL / 30 mL). After centrifugation, the colloidal solution was concentrated and dispersed in water (6.0 mL). The diameter of the S180A-Pt nanoparticles was measured to be about 2-3 nm from transmission electron microscopy (TEM). Secondly, NIPAAm (414 mg), Ru(bpy)$_3$ monomer (86 mg), *N,N'*-methylenebisacrylamide as a cross-liker (12 mg), Pt-colloidal solution (100 µL), and *N,N,N',N'*-tetramethylenediamine (100 µL) as an accelerator were dissolved in ultrapure-water (10 mL). After this pre-gel solution was soaked in ice water in a nitrogen atmosphere for 30 min, ammonium persulfate (10 mg) as an initiator was mixed, and microgels were prepared by suspension polymerization using liquid paraffin as an oil phase at 4 ˚C over 6 hours. After gelation, they were thoroughly washed to remove unreacted compounds. The introduced Ru(bpy)$_3{}^{2+}$ in the gel was calculated by the absorption strength for the microgel suspension (1.4 mol%). The overall concentrations of copolymerized Ru(bpy)$_3{}^{2+}$, [Ru(bpy)$_3{}^{2+}$]$_{overall}$ in the suspension were determined by the UV-vis measurements. The diameters of the poly(NIPAAm-*co*-Ru(bpy)$_3$) microgels containing Pt nanoparticles in the swollen state just below the volume phase transition temperature (30 ˚C) in water were measured to be about 10 - 50 µm from optical microscopy observation.

Fluorescence Measurements. The microgel particles were observed by a fluorescence microscope (DFC360 FX, LEICA) equipped with a mercury lamp (ebq100, ISOLATED) and fluorescence imaging system (AF6000E, LEICA). A filter cube suitable for Ru(bpy)$_3{}^{2+}$ was used with the wavelength of excitation at 460 nm and emission at 600 nm. The fluorescence spectra were measured with a

spectrofluorometer (HITACHI, F-2500) with stirring at 30 ˚C. The wavelength of excitation was 460 nm.

Preparation of the gel systems for visible light irradiation. The poly(NIPAAm-*co*-Ru(bpy)$_3$) microgels containing Pt nanoparticles were soaked in the mixture of methylviologen (MV^{2+}) / ethylenediaminetetra acetic acid (EDTA). The microgel suspensions in the reaction cell (width: 10 mm, depth: 10 mm, height: *ca.* 50 mm) were stirred sufficiently in the dark for 1 day. After mixing, one side of the cell was irradiated by using a 500 W xenon lamp (UXL-500SX, USHIO) through an optical filter (460 ± 10 nm, ASAHI-BUNKO) and a window (10 mm × 20 mm). The input power was 7.0 mW. During the visible light irradiation, the microgel suspensions were stirred sufficiently at 30 ˚C. In anticipation of the complete system generating both hydrogen and oxygen, we carried out the visible light irradiation in a closed cell under an air atmosphere. At given times, the generated gas was collected and analyzed by gas chromatography (GC-8APT, SHIMADZU). The overall quantum efficiency of the H$_2$ generation was defined by the following equation:

$$\Phi_{H2} = \frac{\text{number of electrons for the } H_2 \text{ generation}}{\text{number of the absorbed photons}}.$$

The number of electrons for H$_2$ generation is two times the amount of the generated H$_2$ molecules. The number of the absorbed photons was measured by a power meter (UIT-250, USHIO).
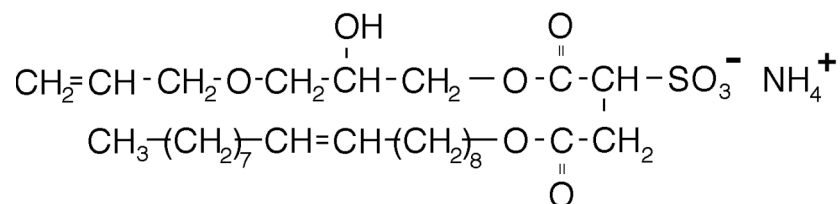
Figure S1 Chemical structure of the anionic surfactant: S180A.

(S2) Calculation for the local concentration of Ru(bpy)$_3^{2+}$ in gel.

$$[Ru(bpy)_3{}^{2+}]_{local} = [Ru(bpy)_3{}^{2+}]_{overall} \times \frac{V_{overall}}{V_{micogels}} \qquad (1)$$

$$[Ru(bpy)_3{}^{2+}]_{local,\,30°C} = \frac{[Ru(bpy)_3{}^{2+}]_{local,\,20°C}}{\dfrac{V_{30°C}}{V_{20°C}}} \qquad (2)$$

$$V_{microgels} = \frac{W_{microgel}}{W_{bulk}} \times V_{bulk} \qquad (3)$$

$[Ru(bpy)_3{}^{2+}]_{overall}$: Concentration of Ru(bpy)$_3^{2+}$ in the overall phase (the gel phase and the outer solution phase), determined by UV-vis measurements.

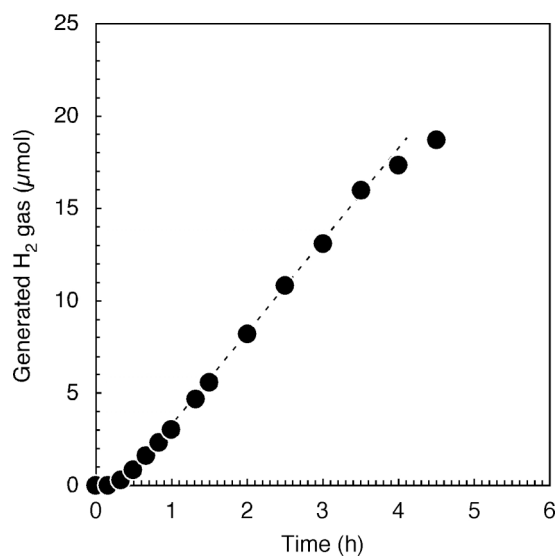$[Ru(bpy)_3{}^{2+}]_{local}$: Concentration of Ru(bpy)$_3^{2+}$ in the gel phase.

V: Volume of gel, determined by the swelling measurements.

W: Weight of gel.
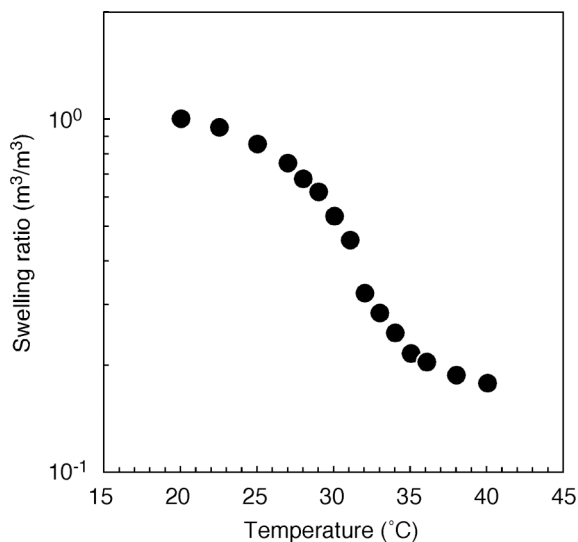
Figure S2 The equilibrium swelling ratio of the Pt nanoparticles-immobilized poly(NIPAAm-*co*-Ru(bpy)$_3$) gel in a mixture of [EDTA]$_0$ = 50 mM.

(S3) The duration time for the H$_2$ generation.

Figure S3 H$_2$ generation for the gel system and light irradiation at 30 ˚C. Total volume of the mixture: 3.0 mL. The microgel suspension was adjusted as $[Ru(bpy)_3^{2+}] = 5.0 \times 10^{-1}$ mM. Outer solution ($[EDTA]_0 = 50$ mM; $[MV^{2+}]_0 = 5.0$ mM).

References

[1]   (*a*) P. K. Gosh, T. G. Spiro, *J. Am. Chem. Soc.* 1980, **102**, 5543; (*b*) C. E. Williams, R. B. Lowry, J. B. Simon, T. Belt, *Inorg. Chim. Acta* 2001, **315**, 112.

[2]   (*a*) Y. Noguchi, K. Okeyoshi, R. Yoshida, *Macromol. Rapid Commun.* 2005, **26**, 1913; (*b*) K. Okeyoshi, T. Abe, Y. Noguchi, H. Furukawa, R. Yoshida, *Macromol. Rapid Commun.* 2008, **29**, 897.