Supplementary Information

Hydrogen Generating Gel Systems Induced by Visible Light

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

ryo@cross.t.u-tokyo.ac.jp

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

* To whom correspondence should be addressed.

(S1) Characterization of immobilized S180A-Pt NPs in gel.

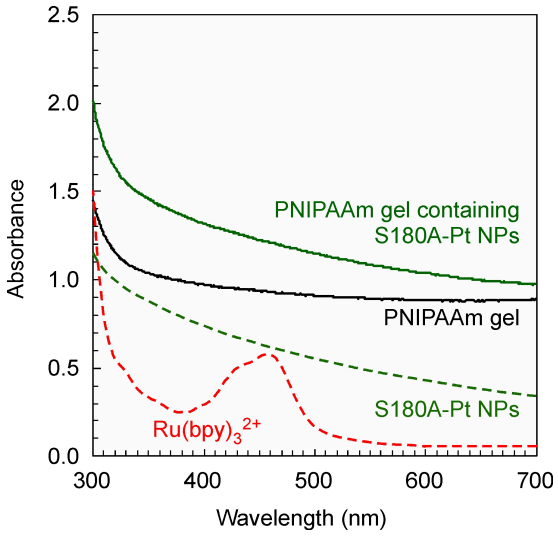

Fig. S1 The absorption spectra at 20 ˚C for the suspension of PNIPAAm microgel containing S180A-Pt NPs (20 mg) in water (3.0 mL) (green line), the suspension of PNIPAAm microgel (20 mg) in water (3.0 mL) (black line), S180A-Pt colloidal solution ([Pt] = 1.9×10^{-1} mM, green dotted line), and $Ru(bpy)_3^{2+}$ solution ($[Ru(bpy)_3^{2+}]_0 = 5.0\times10^{-2}$ mM, red dotted line).

For the PNIPAAm microgel suspension, the absorbance was almost constant at 400 ~ 700 nm. In the case of the PNIPAAm gel containing S180A-Pt NPs, the absorption spectra showed gentle curve with increasing absorbance. By comparing the slope of the curve with that of S180A-Pt colloidal solution, it was indicated that most of the Pt NPs was introduced into the gel. Assuming that all of the Pt NPs was introduced into the gel, the suspension contained 1.9×10^{-1} mM of Pt.

When the concentration of Pt is high, absorption by Pt causes difficulty in exciting $Ru(bpy)_3^{2+}$, which has absorption peak around 460 nm.

(S2) Characterization of copolymerized $Ru(bpy)_3^{2+}$ in gel.

Table S1 The concentrations of $Ru(bpy)_3^{2+}$ in preparation of the gels for the G2 systems.

$[Ru(bpy)_3^{2+}]_{pregel}$ (mM)	$[Ru(bpy)_3^{2+}]_{gel}$ ** (mM)	Overall concentration of $Ru(bpy)_3^{2+}$ in the G2 system, $[Ru(bpy)_3^{2+}]$ * (mM)
4.0×10^{-1}	2.7×10^{-1}	3.4×10^{-2}
5.7×10^{-1}	2.8×10^{-1}	5.0×10^{-2}
8.0×10^{-1}	5.5×10^{-1}	6.9×10^{-2}
1.6	8.3×10^{-1}	1.0×10^{-1}
3.2	1.8	2.3×10^{-1}
6.3	3.2	4.0×10^{-1}
1.3×10^{1}	6.4	8.0×10^{-1}

* Calculated by the absorption spectra of the G2 systems.

** Compensated by the swelling ratio of gels and the occupied volume of gel particles in the suspension at 20 ˚C.

Generally, about 50 ~ 70 % of $Ru(bpy)_3$ monomer in preparation was introduced in gel.

(S3) Characterization of copolymerized viologen in gel.

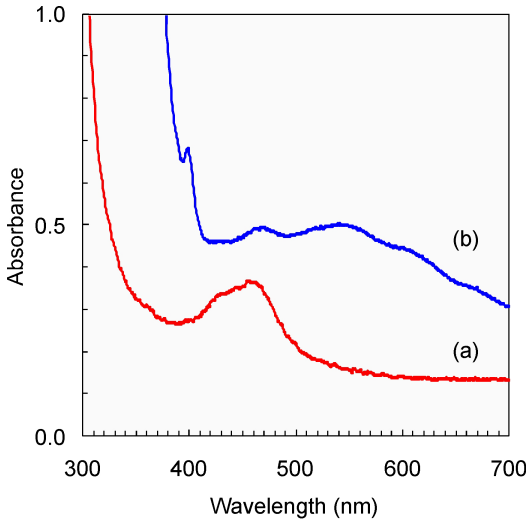

Fig. S2 Absorption spectra for (a) the microgel suspension of poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-viologen) gel containing Pt NPs (1.0 mg) in tris-HCl buffer solution (3.0 mL, 800 mM, pH7.4) at 20 ˚C and (b) the suspension when the viologen unit was reduced by $Na_2S_2O_4$ (40 mM).

The concentrations of the introduced Ru(bpy)$_3$ and viologen in the gel were calculated by the absorbance of the microgel suspension. From the absorbance at 460 nm originated from Ru(bpy)$_3$ at reduced state (Fig. S2(a)), [$Ru(bpy)_3^{2+}$] = 2.0×10^{-2} mM. From the absorbance at 535 nm originated from viologen at reduced state (Fig. S2(b)), [viologen] $\geq 2.2\times10^{-2}$ mM.

(S4) Duration time for the H_2 generation.

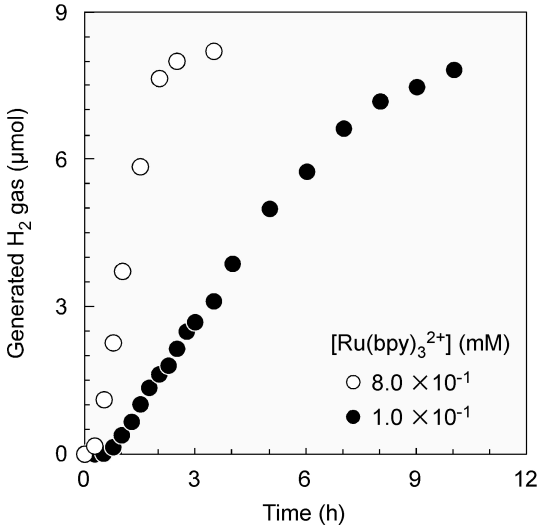

Fig. S3 H_2 generation for the microgel suspension using poly(NIPAAm-*co*-Ru(bpy)$_3$) gel containing Pt NPs at 20 ˚C under air atmosphere and light irradiation. The total volume of the mixture: 3.0 mL. The total amounts of gel particles: 20 mg. $[EDTA]_0$ = 50 mM; $[MV^{2+}]_0$ = 5.0 mM.

With an increase in the H_2 generating rate, the duration time for the H_2 generation became short. The duration time depends on the H_2 generating rate because the reaction stops when EDTA is completely consumed.