

Supporting Information

Photo-induced H₂ Evolution from Water via the Dissociation of Excitons in Water-Dispersible Single-Walled Carbon Nanotube Sensitizers

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EXPERIMENTAL

<General>

TEM measurements for the composites were conducted using a Hitachi S-5200. The specimens for the measurements were prepared by applying a few drops of the sample solution onto a holey carbon-coated copper grid (Ouken-Shoji 200-Abmesh), and then evaporating the solvent. The absorption data were recorded on a Shimadzu UV-3150 spectrophotometer using a standard cell with a path length of 10 mm. Atomic force microscopy (AFM) observation was carried out using a Seiko SPA 400-DFM and the samples for the observations were prepared by placing a drop of SWCNT aqueous solution on freshly cleaved mica, then allowing them to dry with a dryer. FT-IR spectra were recorded using Shimadzu IR Affinity-1. Raman spectra were obtained with a JASCO NRS-3100 Raman spectrometer using laser excitation at a wavelength of 488 nm. SWCNTs (HiPco) were purchased from Unidym Co. All other reagents were purchased from Kanto Kagaku Co., Ltd, Aldrich Chemical Co., and Tokyo Kasei Co., Ltd. All chemicals were used as received.

< Synthesis of poly(amidoamine) dendrimer(NH_3^+) >

A methanol solution (33 mL) of dendrimer(COOMe) (75 mg, 46 μ mol) was added dropwise to a stirred solution of ethylenediamine (7.38 mL, 110 mmol) at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for 3 days under a nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was reprecipitated from a methanol/diethyl ether (1/75) solution to produce dendrimer(NH_2), which was used for the following reaction without further purification. dendrimer(NH_2) (89 mg, 48 μ mol) was allowed to react with hydrochloric acid (0.38 mL, 1.0 mol/L) in methanol at room temperature for 1h under a nitrogen atmosphere. After removal of the solvent,

dendrimer having NH_3^+ terminals (81 mg, 37.4 μmol) was obtained as yellow oil in 78% yield.

Dendrimer(NH_2): ^1H NMR (300 MHz, D_2O) δ 1.15 (s, 36H), 1.39 (br, 12H), 2.28 (t, $J = 6.3$ Hz, 24H), 2.46 (br, 8H), 2.54-2.76 (m, 40H), 3.04-3.32 (m, 40H).

Dendrimer(NH_3^+): ^1H NMR (300 MHz, D_2O) δ 1.14 (s, 36H), 1.39 (br, 12H), 2.29 (t, $J = 6.3$ Hz, 24H), 2.46 (t, $J = 6.6$ Hz, 8H), 2.54-2.71 (m, 24H), 2.79 (q, $J = 8.7$ Hz, 16H), 3.03-3.34 (m, 40H); IR (KBr): 3400, 3252, 3080, 2930, 2855, 1659, 1551 cm^{-1} .

<Synthesis of Colloidal PVP-Pt>

An aqueous solution (10 mL) of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.034 g, 66 μmol) was dropped into poly(vinylpyrrolidone) (PVP, 0.320 g, $M_w = 40.000$ g/mol) in H_2O (20 mL) at room temperature. After diluting with H_2O (20 mL) and ethanol (50 mL), the solution was stirred under reflux conditions for 2 h. After the removal of solvents, the resulting precipitate was dissolved in H_2O (15 mL). After centrifugation at 15000 rpm for 13 h, a clear phase was collected to obtain a colloidal PVP-Pt.

<Hydrogen evolution>

Typically, an aqueous Tris-HCl buffer solution (3.5 mL, pH 7.5, 5 mM) of SWCNT/poly(amidoamine) dendrimer(COO^-) (0.125 mL), BNAH (38.6 mg, 1.8×10^{-4} mol, 1.20 mM) and methyl viologen dichloride (MV^{2+} , 92.4 mg, 3.6×10^{-4} mol, 2.40 mM) were dissolved in distilled water in a Pyrex reactor. The solution was diluted to a final volume of 150 mL with distilled water. It was degassed for five cycles and purged with Ar. Upon vigorous stirring, the solution was irradiated with a 300 W Xenon arc light (Ushio model UXL- 500 W) through the long-pass filter ($\lambda > 422 \pm 5$ nm: ASAHI SPECTRA CO, M. C.

422/10 nm 50 × 50) or band-pass filter (650 ± 6 nm: ASAHI SPECTRA CO, M. C. 650/12 nm 50 × 50). After a designated period of time, the cell containing the reaction mixture was connected to a gas chromatograph (Shimadzu, TCD, molecular sieve 5A: 2.0 m × 3.0 mm, Ar carrier gas) to measure the amount of H₂ above the solution.

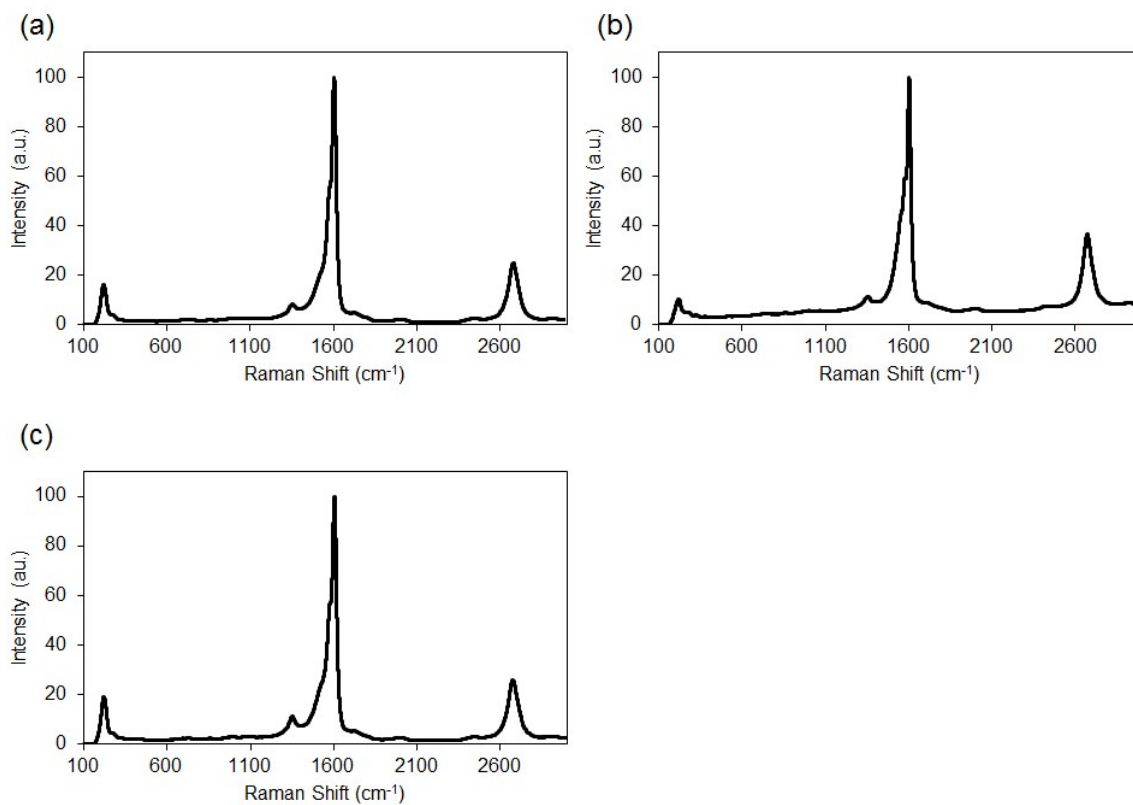
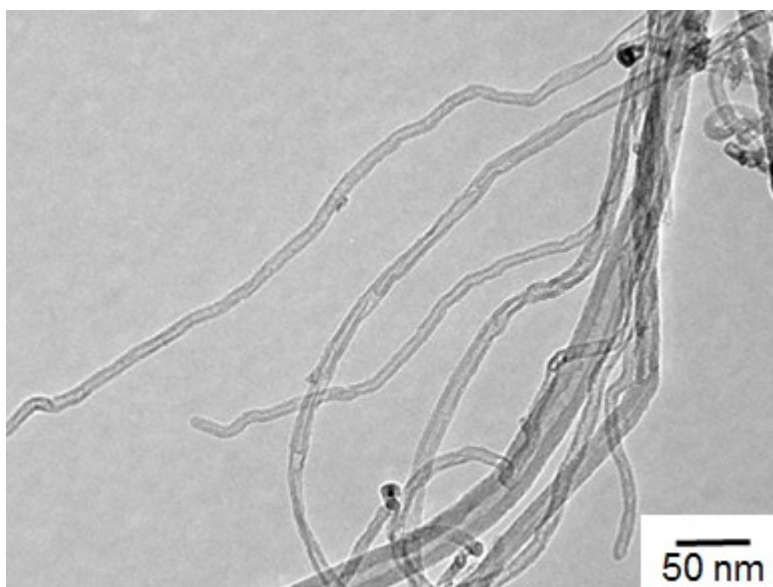


Fig. S1. Raman spectra of (a) SWCNT(HiPco-tube), (b) SWCNT/dendrimer(COO⁻), (c) SWCNT/dendrimer(NH₃⁺).

(a)



(b)

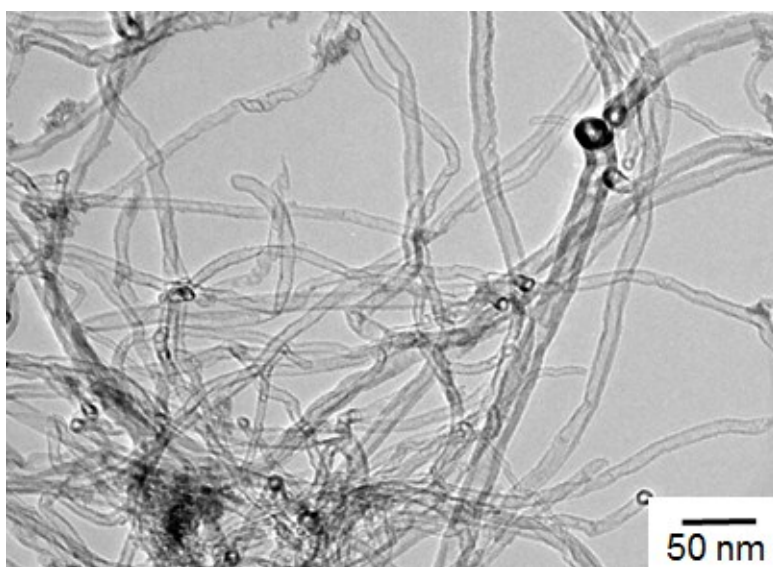


Fig. S2. TEM image of (a) SWCNT/dendrimer(COO^-), (b) SWCNT/dendrimer(NH_3^+).

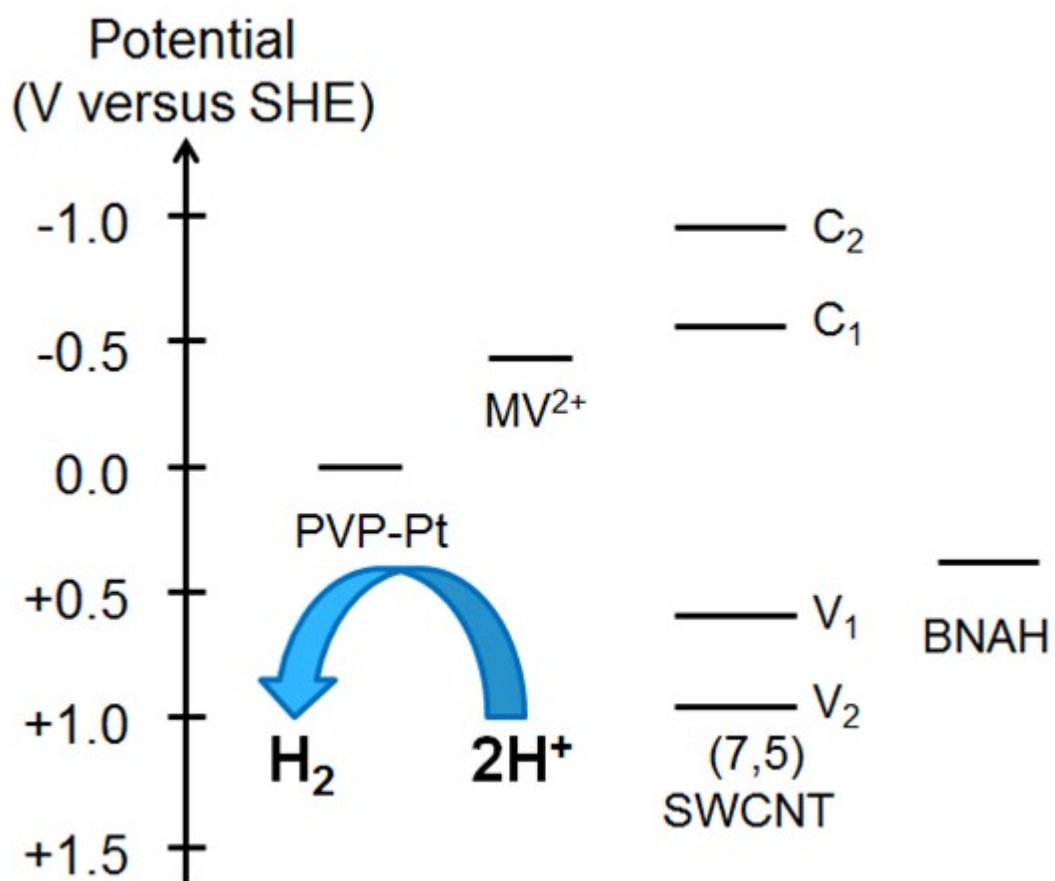


Fig. S3. Energy level diagram of the H₂ evolution system based on the SWCNT, (7,5)-tube.

<Evaluation of apparent quantum yields (AQYs) of H₂ evolution>

In a typical run, an aqueous Tris-HCl buffer solution (3.5 mL, pH 7.5, 5 mM) of SWCNT/dendrimer(COO⁻) (0.125 mL) or SWCNT/fullerodendron (0.25 mL), 1-benzyl-1,4-dihydronicotinamide (BNAH, 38.6 mg, 1.8×10^{-4} mol), methyl viologen dichloride (MV²⁺, 92.4 mg, 3.6×10^{-4} mol) and colloidal PVP-Pt (15 mL in H₂O, Pt atom content was 6.6×10^{-2} μmol) were dissolved in distilled water in a Pyrex reactor. The solution was diluted to a final volume of 150 mL with distilled water. It was degassed for five cycles and purged with Ar. Upon vigorous stirring, the solution was irradiated with a 300 W Xenon arc light (Ushio model UXL- 500 W) through the band-pass filter (650 ± 6 nm: ASAHI SPECTRA CO, M. C. 650/12 nm 50×50). After a designated period of time, the cell containing the reaction mixture was connected to a gas chromatograph (Shimadzu, TCD, molecular sieve 5A: 2.0 m \times 3.0 mm, Ar carrier gas) to measure the amount of H₂ above the solution. The apparent quantum yield (AQY) is defined as follows. $AQY = (\text{number of H}_2 \text{ generated} \times 2)/(\text{number of photons absorbed})$, which was evaluated from a change in power of the transmitted light, measured using a power meter (Photo-Radio meter Model HD 2302.0 coupled with the irradiance measurement probe LP 471 RAD having an exposure window diameter of 1.6 cm) placed behind the cell parallel to the irradiation cell face. Figure S4 (a) and (b) show plots of the total amount of H₂ produced versus time using SWCNT/dendrimer(COO⁻) or SWCNT/fullerodendron. A steady generation of H₂ ((a) 0.08 μmol/h, (b) 0.18 μmol/h) was observed upon photoirradiation ($\lambda = 650$ nm) during 6 h of irradiation after induction period due to a small amount of oxygen that could react with radical cation of methyl viologen (MV^{•+}).¹⁰ The AQY for the H₂ evolution were 0.03 (for SWCNT/dendrimer(COO⁻)) and 0.11 (for SWCNT/fullerodendron).

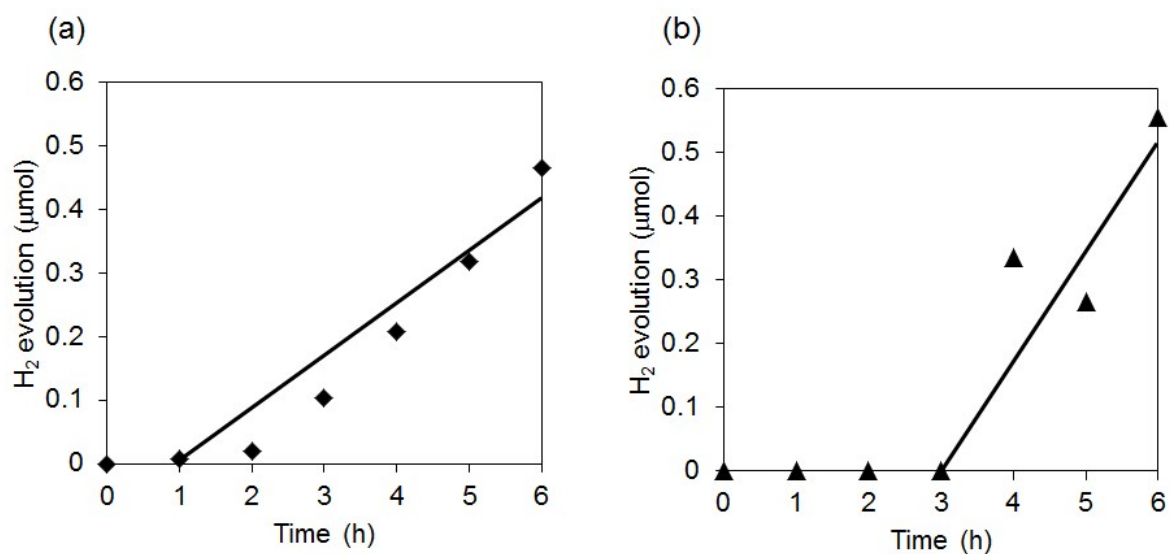


Fig. S4. Time dependencies of the H₂ evolution from water in the systems of (a) SWCNT/dendrimer(COO⁻) (◆) and (b) SWCNT/fullerodendron (▲). Conditions: [MV²⁺]₀ = 2.4 mM; [BNAH]₀ = 1.2 mM; [Tris-HCl buffer]₀ = 5.0 mM (pH = 7.5); [PVP-Pt]₀ = 740 mM, amount of solution = 150 mL, stirring vigorously at 25°C under Ar, upon exposure to a light of wavelength 650 nm monochromatic with a 300 W Xenon arc lamp.