Supporting Information

Incorporating a TiO$_x$ Shell in Single-Walled Carbon Nanotube/Fullerodendron Coaxial Nanowires: Increasing the Photocatalytic Evolution of H$_2$ from Water under Irradiation with Visible Light

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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/fullerodendron/TiO_x coaxial nanohybrids aqueous solution on freshly cleaved mica, then allowing them to dry with a dryer. FT-IR spectra were recorded using Shimadzu IR Affinity-1. Three-dimensional fluorescence spectra data were obtained using a spectrofluorometer (Shimadzu, NIR-PL system). SWCNTs (HiPco) were purchased from Unidym Co. Fullerodendron^1 and SWCNT/fullerodendron supramolecular nanocomposites^2 were prepared according to the reported procedure. All other reagents were purchased from Kanto Kagaku Co., Ltd, Aldrich Chemical Co., and Tokyo Kasei Co., Ltd., and were used as received.

<Preparation of SWCNT/fullerodendron supramolecular nanocomposites>

SWCNTs (HiPco: 1.0 mg) were placed in a water solution (10 mL) of the fullerodendron (25.5 mg, 0.01 mmol) and then sonicated with a bath type ultrasonifier (ULTRASONIC CLEANER vs-D100, 110 W, 24 kHz) at 17–25 °C for 1 h. After the suspension was centrifuged at 3000 g for 30 min, a black-colored supernatant dispersion, which included SWCNT/fullerodendron supramolecular nanocomposites and superfluous fullerodendron,
was collected. The SWCNT/fullerodendron nanocomposites were purified by dialysis for 3 days using dialysis tubing (SPECTRUM RC MEMBRANES Pro 4) to remove superfluous fullerodendron. The dialysis process was continued until the dialysate showed no absorption change at 258 nm in UV-vis spectra. This dialysate solution was used for further experiment as a stock solution of SWCNT/fullerodendron supramolecular nanocomposites.

<Synthesis of Colloidal PVP-Pt>

A colloidal PVP-Pt was prepared according to the reported procedure. An aqueous solution (10 mL) of H$_2$PtCl$_6$·6H$_2$O (0.034 g, 66 µmol) was dropped into poly(vinylpyrrolidone) (PVP, 0.320 g, Mw = 40,000 g/mol) in H$_2$O (20 mL) at room temperature. After diluting with H$_2$O (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$_2$O (15 mL). After centrifugation at 15000 ppm for 13 h, a clear phase was collected to obtain a colloidal PVP-Pt.

<Fabrication of SWCNT/fullerodendron/TiO$_x$ coaxial nanohybrids>

An aqueous solution of SWCNT/fullerodendron nanocomposites (250 µL: the content of SWCNT is 0.025 mg, 2.0 µmol as a C atom, and the content of fullerodendron is 0.042 mg, 1.64×10$^{-8}$ mol)* was diluted with water (750 µL). The pH was adjusted to pH 3 with HCl (1.0 N, 2.8 µL). After the stirring for 1 h, an EtOH solution of titanium tetra isopropoxide (3.51 mM, 20 µL, 7.4×10$^{-8}$ mol) was added to the solution at 0 °C and stirred at the same temperature for 48 h to obtain a dispersion of SWCNT/fullerodendron/TiO$_x$ coaxial nanohybrids.
*Estimated by TGA of the SWCNT/fullerodendron nanocomposites. The datum is shown in Fig. S7.

<Hydrogen evolution>

Typically, 150 mL of an aqueous solution consisting of SWCNT/fullerodendron/TiO$_x$ (1 mL), Tris-HCl buffer (3.5 mL in H$_2$O, pH 7.5, 5 mM), methyl viologen dichloride (92.4 mg, 359 µmol), 1-benzyl-1,4-dihydrnicotinamide (BNAH) (38.6 mg, 180 µmol), and a colloidal PVP-Pt (15 mL in H$_2$O, of which Pt atom content was 512 µmol) in a Pyrex reactor was degassed for five cycles and purged with Ar. Upon vigorous stirring at 25 ºC, that solution was irradiated with a 300 W Xenon arc light (Ushio model UXL 500 W) through the band-pass filter (450 ± 5 nm: ASAHI SPECTRACO, M. C. 450/10 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, Argon carrier gas) to measure the amount of H$_2$ above the solution. The apparent quantum yield (AQY) is defined as follows. AQY = (number of H$_2$ generated × 2)/(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.
Fig. S1. TEM image of SWCNT/fullerodendron/TiO$_x$ supramolecular nanohybrids.

Fig. S2. AFM image of SWCNT/fullerodendron/TiO$_x$ supramolecular nanohybrids.
Fig. S3. Raman spectra for SWCNT/fullerodendron (Gray line) and SWCNT/fullerodendron/TiO$_x$ (black line).

Figure S4. IR spectra of (i) SWCNT/fullerodendron, (ii) SWCNT/fullerodendron/TiO$_x$ and (iii) TiO$_x$. 
Figure S5. UV/Vis-NIR spectra of SWCNT/fullerodendron supramolecular nano-composites (red-line) and SWCNT/fullerodendron/TiO$_x$ coaxial nano-hybrids (black line).

Figure S6. SEM images of SWCNT/fullerodendron/TiO$_x$ coaxial nano-hybrids (a) for 1 day condensation, (b) for 2-day condensation, and (c) for 3-day condensation.
Figure S7. Thermogravimetric analysis plot of the SWCNT/fullerodendron supramolecular nano-composites and SWCNTs.

References

