SWCNT Photocatalyst for Hydrogen Production from Water upon Photoexcitation of (8, 3) SWCNT at 680-nm Light

Noritake Murakami1, Yuto Tango1, Hideaki Miyake2, Tomoyuki Tajima1, Yuta Nishina3, Wataru Kurashige4, Yuichi Negishi4 & Yutaka Takaguchi1

Single-walled carbon nanotubes (SWCNTs) are potentially strong optical absorbers with tunable absorption bands depending on their chiral indices ($n$, $m$). Their application for solar energy conversion is difficult because of the large binding energy ($>100$ meV) of electron-hole pairs, known as excitons, produced by optical absorption. Recent development of photovoltaic devices based on SWCNTs as light-absorbing components have shown that the creation of heterojunctions by pairing chirality-controlled SWCNTs with C60 is the key for high power conversion efficiency. In contrast to thin film devices, photocatalytic reactions in a dispersion/solution system triggered by the photoexcitation of SWCNTs have never been reported due to the difficulty of the construction of a well-ordered surface on SWCNTs. Here, we show a clear-cut example of a SWCNT photocatalyst producing H2 from water. Self-organization of a fullerodendron on the SWCNT core affords water-dispersible coaxial nanowires possessing SWCNT/C60 heterojunctions, of which a dendron shell can act as support of a co-catalyst for H2 evolution. Because the band offset between the LUMO levels of (8, 3)SWCNT and C60 satisfactorily exceeds the exciton binding energy to allow efficient exciton dissociation, the (8, 3) SWCNT/fullerodendron coaxial photocatalyst shows H2-evolving activity ($QY = 0.015$) upon 680-nm illumination, which is $E_{22}$ absorption of (8, 3) SWCNT.

Visible light-induced water splitting has received considerable attention in terms of solar energy conversion and hydrogen energy storage1–6. Although various semiconducting materials for H2-evolution photocatalysts have been reported7–9, examples of efficient H2 production using illumination wavelengths over 600 nm are very limited. For example, Domen and co-workers reported that g-C3N4 photosensitized by magnesium(II) phthalocyanine showed photocatalytic H2 production activity under visible light irradiation up to 700 nm, but with a rather low quantum efficiency (0.07% at 660 nm)10. Recently, Li and co-workers improved this phthalocyanine/g-C3N4 system by employing a highly asymmetric zinc(II) phthalocyanine derivative to achieve efficient photocatalytic H2 production with an apparent quantum yield (AQY) of 1.85% at 700 nm11. Because the main component of the solar spectrum consists of visible light ($400 < \lambda < 800$ nm), the unexplored region of visible light, from 600 nm to 800 nm, should be fully exploited by employing a new class of photocatalysts. Previously, we described the fabrication and efficient photoinduced electron transfer processes of single-walled carbon nanotube (SWCNT)/anthryl dendron12,13 and SWCNT/fullerodendron12,14 supramolecular nanocomposites, of which coaxial nanowire structures provide a photofunctional interface between the SWCNT core and the dendron shell. Since recent studies indicated that coaxial nanowire structures could improve carrier collection and overall efficiency with respect to bulk semiconductors of the same materials15, we have explored photosensitized hydrogen evolution from water under visible light irradiation (450 nm) using our coaxial supramolecular photosensitizers possessing a SWCNT core16, such as SWCNT/fullerodendron or SWCNT/fullerodendron/SiO2, in the presence of methyl viologen

1Graduate School of Environmental and Life Science; Okayama University; 3-1-1 Tsushima-Naka, Kita-ku, Okayama 700-8530, Japan. 2Graduate School of Sciences and Technology for Innovation; Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan. 3Research Core for Interdisciplinary Sciences; Okayama University, 3-1-1 Tsushima-Naka, Kita-ku, Okayama 700-8530, Japan. 4Department of Applied Chemistry; Faculty of Science Division I; Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. Correspondence and requests for materials should be addressed to Y.T. (email: yutaka@cc.okayama-u.ac.jp)
Results and Discussion

In order to obtain a photosensitizer/co-catalyst interconnecting system that exhibits H₂ evolution activity under irradiation of light of wavelengths over 600 nm, SWCNT/fullerodendron/Pt(II) coaxial nanohybrids having (6, 5), (7, 5), and (8, 3)SWCNT cores were fabricated by complexation between K₂PtCl₄ and SWCNT/fullerodendron supramolecular nanocomposites based on (6, 5)-enriched SWCNTs according to the literature procedure (Fig. 1)¹⁷. Complex formation between SWCNT/fullerodendron and platinum(II) can be monitored by the time course of UV-vis spectral changes during the reaction (Fig. 2a). Absorbance at 255 nm increased gradually up to 24 h because of ligand-to-metal charge transfer (LMCT) from the tertiary amine of the dendron moiety to Pt²⁺. From a comparison of the absorption bands (300–1200 nm) arising from the SWCNTs before and after the complexation, absorptions decreased slightly because the dispersion of the hybrids was diluted via the complexation process (Fig. 2b). However, the population of the chiralities, e.g., the ratio of absorptions at 570, 650, and 680 nm from the (6, 5), (7, 5), and (8, 3)SWCNTs, respectively, was not changed by the complexation.

Transmission electron microscopy (TEM) was used to characterize the photosensitizer/co-catalyst interconnecting system based on SWCNT/fullerodendron supramolecular nanocomposites (Fig. 3). The high-resolution TEM image in Fig. 3a reveals that the supramolecular nanocomposite exhibits nanofibrous morphology similar to that of HiPco/fullerodendron nanocomposites¹². Interestingly, tiny nanoparticles with a size of around 1 nm, which could be C₆₀, were observed on the surface of the nanowires with a thickness of 5 nm. After the complexation of Pt(II), we observed thicker branched fibrous morphology with a diameter of 7–13 nm (Fig. 3b). From these observations, we surmised that limited agglomeration of the SWCNT/fullerodendron supramolecular nanocomposites occurred after the treatment with K₂PtCl₄. However, the Pt(II) complex of SWCNT/fullerodendron is still dispersible in water. This finding is consistent with the results of atomic force microscopy (AFM) measurements (Supplementary Fig. 1). The height profiles reveal that the thickness of (6, 5)-enriched SWCNT/fullerodendron/Pt(II) (ca. 4.9 nm) is higher than that of (6, 5)-enriched SWCNT/fullerodendron (ca. 3.1 nm).

Figure 1. Fabrication of (6, 5)-enriched SWCNT/fullerodendron/Pt(II) coaxial photocatalyst. (a) Molecular structure of fullerodendron. (b) Schematic illustration of (6, 5)-enriched SWCNT photocatalyst having a Pt(II) complex on the shell.
In order to clarify the oxidation state of the shell-anchored Pt complexes, X-ray photoelectron spectroscopy (XPS) measurements of the (6, 5)-enriched SWCNT/fullerodendron/Pt(II) coaxial nanohybrids were conducted (Supplementary Fig. 2). The Pt(4f $5/2$) and Pt(4f $7/2$) peaks are present at 77.3 and 74.0 eV, respectively, which are consistent with the peaks of the Pt(II) complex of the poly(amidoamine) dendrimer reported by Crooks$^{27}$. Hence, we confirmed that coordination of the dendron units of SWCNT/fullerodendron with Pt(II) cause the formation of SWCNT/fullerodendron/Pt(II).

Figure 4 shows three-dimensional photoluminescence (PL) intensity mapping of SWCNT/fullerodendron and SWCNT/fullerodendron/Pt(II) in D$_2$O solutions. Before complexation of SWCNT/fullerodendron with K$_2$PtCl$_4$, three intense peaks can reasonably be assigned to (6, 5), (7, 5), and (8, 3) SWCNTs (Fig. 4a). Although (6, 5) SWCNT exhibited the strongest absorption among these chiralities (Fig. 2b), its PL intensity was weakest because strong bundles exclusively consisting of (6, 5) SWCNT were formed via rebanding process$^{28}$ of its enrichment procedure and were incorporated into the core of the SWCNT/fullerodendron supramolecular nanocomposite. In contrast, the PL intensities of (8, 3) and (7, 5) SWCNTs were very high owing to existence of the individual SWCNT at the core of the coaxial nanowires. Interestingly, after the formation of SWCNT/fullerodendron/Pt(II), quenching of PL emission from (6, 5) and (8, 3) SWCNTs was observed in contrast to the strong luminescence from (7, 5) SWCNT (Fig. 4b). An energy level diagram of the conduction bands (C1 and C2) and valence bands (V1 and V2) of different (n, m)SWCNTs along with the LUMO of C$_{60}$ and expected energy level of Pt(II) is shown in Fig. 5. Energy levels of SWCNTs$^{19}$ were corrected by the use of optical band-gap energies estimated by PL spectra, because PL peak positions are substantially red-shifted after the attachment of fullerodendrons on the lateral surface of SWCNTs$^{18}$. The LUMO level of C$_{60}$ was assumed using the reduction potential of fullerodendrimer (E$^{\text{red}}_{\text{red}}$ = −1.12 V vs Fe/Fe$^{3+}$)$^{29}$. The LUMO offset between SWCNTs and C$_{60}$ affects the efficiency of the electron transfer from SWCNTs to C$_{60}$$^{22}$. Because the C1 energy level of (7, 5) SWCNT is lower than that of (6, 5) and (8, 3) SWCNTs, PL emission quenching from (7, 5) SWCNT was not observed, which is in marked contrast to that from (6, 5) and (8, 3) SWCNTs.

In order to clarify the effect of chirality of SWCNTs on the efficiency of photocatalytic H$_2$ evolution, we investigated the photocatalytic activity of SWCNT/fullerodendron/Pt(II) upon chirality-selective photo-excitation by the use of monochromatic light irradiation at 570, 650, and 680 nm, which are the E$_{22}$ absorptions of (6, 5), (7, 5), and (8, 3) SWCNTs, respectively. In a typical experiment, 150 mL of aqueous solution of SWCNT/fullerodendron/
Pt(II) hybrids (SWCNT content 0.025 mg), Tris-HCl buffer (pH 7.5, 0.12 mM), and benzyldihydronicotinamide (BNAH; 1.2 mM), was exposed to monochromatic light (570, 650, or 680 nm) using a 300 W Xenon arc lamp with bandpass filters while being stirred vigorously at 25 °C. After the designated period, the gas phase above the solution was analyzed by gas chromatography. Figure 6 (a) shows plots of the total amount of H2 produced versus time using monochromatic light irradiation at 680 nm. A steady generation of H2 (0.083 μmol/h) was observed without an induction period or a decrease in activity during 6 h of irradiation. Compared with the H2 generated by the use of monochromatic light irradiation at 570 or 650 nm, 0.022 μmol/h (Fig. 6 (▲)) or 0.0065 μmol/h (Fig. 6 (◆)), respectively, the amount of H2 evolution under 680 nm irradiation was highest (0.083 μmol/h, Fig. 6 (◾)). Furthermore, in order to compare the efficiency of photocatalytic H2 evolution between (6, 5), (7, 5), and (8, 3) SWCNTs, we evaluated quantum yields by the use of monochromatic light irradiation at 570, 650, and 680 nm. The overall quantum yields for H2 evolution (QY = number of H2 molecules generated / number of photons absorbed) were 0.35% (for (6, 5) SWCNT/fullerodendron/Pt(II)), 0.17% (for (7, 5) SWCNT/fullerodendron/Pt(II)), and 0.06% (for (8, 3) SWCNT/fullerodendron/Pt(II)).

Figure 4. Individuality of SWCNT core of coaxial photocatalysts. (a,b) Three-dimensional fluorescence spectra of (6, 5)-enriched SWCNT/fullerodendron (a) and (6, 5)-enriched SWCNT/fullerodendron/Pt(II) (b). Before formation of the fullerodendron-Pt(II) complexes, the PL intensities of (8, 3) and (7, 5) SWCNTs were very high owing to existence of the individual SWCNT. After formation of the fullerodendron-Pt(II) complexes, quenching of PL emission from (6, 5) and (8, 3) SWCNTs was observed because of electron transfer from (6, 5) and (8, 3) SWCNTs to C60.

Figure 5. Energy level diagram of (6, 5)-enriched SWCNT/fullerodendron/Pt(II) coaxial photocatalyst system. Energy level diagram of conduction bands (C1 and C2) and valence bands (V1 and V2) of (8, 3), (7, 5), and (6, 5) SWCNTs, LUMO of C60, and expected energy level of Pt(II) complexes.
Preparation of photocatalyst solution. (6, 5)-enriched SWCNTs (1.0 mg) were placed in a water solution (10 mL) of fullerodendron (25.5 mg, 0.01 mmol) and then sonicated with a bath-type ultrasonic cleaner (Honda Electronics Co., Ltd., vs-D100, 110 W, 24 kHz) at 17–25 °C for 4 h. After the suspension was centrifuged at 3000 G for 30 min, a black supernatant dispersion, which included excess fullerodendrons and (6, 5)-enriched SWCNT/fullerodendron nanocomposites, was collected. The (6, 5)-enriched SWCNT/fullerodendron nanocomposite was purified by dialysis for 3 days using dialysis tubing (SPECTRUM RC MEMBRANES Pro 4) to remove excess fullerodendrons. The dialysis process was continued until the dialysate showed no change in absorption at 255 nm in UV-vis spectra. Then, 1.0 mL of the stock solution of (6, 5)-enriched SWCNT/fullerodendron nanocomposites was diluted with 19.0 mL of deionized water and used for the following experiment. The aqueous solution of (6, 5)-enriched SWCNT/fullerodendron nanocomposites was added to potassium tetrachloroplatinate(II) (0.28 mg, 0.68 μmol) in deionized water (0.28 mL) and stirred at 50 °C for 24 h to obtain a solution of (6, 5)-enriched SWCNT/fullerodendron/Pt(II) coaxial nanowires.
Hydrogen evolution. An aqueous solution of Tris-HCl buffer (3.5 mL, pH 7.5, 5 mM), (6, 5)-enriched SWCNT/fullerodendron/Pt(II) nanohybrids (5.0 mL), BNAH (38.6 mg, 1.20 mM), and deionized water (145 mL) in a Pyrex reactor 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 bandpass filters (570 nm, 680 nm: ASAHI SPECTRA CO, M. C.). After a designated period of time, the cell containing the reaction mixture was connected to a gas chromatograph (Shimadzu, TCD, molecular sieve 5 A: 2.0 mm × 3.0 mm, Ar carrier gas) to measure the amount of H2 above the solution. The apparent quantum yield (ΦH2) is defined as follows. ΦH2 = number of H2 molecules generated × number of photons absorbed, which was evaluated from a change in the power of the transmitted light, measured using a power meter (Photo-Radiometer Model HD 2302,0 coupled with an 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.

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Author Contributions
Y.T. conceived and designed the experiments. N.M., Y.T. and T.T. prepared the CNT photocatalyst samples and performed the experiments. H.M. observed TEM images. Y.N. performed XPS measurements. W.K. and Y.N. contributed 3D fluorescence spectra. Y.T., N.M. and T.T. wrote the paper. All the authors discussed the results and commented on the manuscript.
