Hot Electron Extraction in SWCNT/TiO₂ for Photocatalytic H₂ Evolution from Water

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Abstract: Single-walled carbon nanotube (SWCNT)/TiO₂ hybrids were synthesized using 1,10-bis(decyloxy)decane-core PAMAM dendrimer as a molecular glue. Upon photoirradiation of a water dispersion of SWCNT/TiO₂ hybrids with visible light (λ > 422 nm), the hydrogen evolution reaction proceeded at a rate of 0.95 mmol/h·g in the presence of a sacrificial agent (1-benzyl-1,4-dihydronicotinamide, BNAH). External quantum yields (EQYs) of the hydrogen production reaction photosensitized by (6,5), (7,5), and (8,3) tubes were estimated to be 5.5%, 3.6%, and 2.2%, respectively, using monochromatic lights corresponding to their E₂ absorptions (570 nm, 650 nm, and 680 nm). This order of EQYs (i.e., (6,5) > (7,5) > (8,3)SWCNTs) exhibited the dependence on the Cᵥ energy level of SWCNT for EQY and proved the hot electron extraction pathway.

Keywords: single-walled carbon nanotube; photocatalyst; hydrogen evolution; water splitting; hot electron extraction

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have attracted attention for their application as a photoelectric conversion material due to their outstanding solar light absorption property [1]. The optical absorption of semiconducting SWCNTs reveals sets of chirality-dependent absorption bands in the near-infrared and visible wavelength regions, which are labeled the first (E₁₁) and second (E₂₂) transitions, corresponding to the discrete energetic transitions of one-dimensional van Hove singularities [2]. The energy level of the second excited state (E₂ state) is higher than that of the first excited state (E₁ state). Hence, hot electron extraction directly from the E₂ state is effective to improve the performance of photovoltaics and photocatalysts based on SWCNT-light absorbers. However, regarding a SWCNT/C₆₀ heterojunction, which is often used in organic solar cells, the relaxation from the E₂ state to E₁ or ground states suppresses the hot electron extraction from SWCNT to C₆₀ [3]. As a result, the internal quantum efficiency (IQE) of SWCNT/C₆₀ solar cells depends on an energetic offset between the lowest molecular orbital (LUMO: Cᵥ) and the first state, of the nanotube and that of C₆₀ [4]. In other words, the IQE of SWCNT/C₆₀ solar cells is not affected by the energy level of the E₂ state (LUMO+1: Cᵥ) of SWCNTs, even upon E₂ photoexcitation with visible light. Recently, we developed SWCNT/C₆₀ photocatalysts that act as hydrogen evolution photocatalysts [5–9]. As in the case of SWCNT/C₆₀ solar cells, the external quantum yield (EQY) of the photocatalytic hydrogen production increased in the order (7,5)SWCNT (0.17%) < (6,5)SWCNT (0.35%) < (8,3)SWCNT (1.5%) with increasing LUMO energy levels of the SWCNTs, despite photoexcitation using E₂ absorption to generate the E₂ state [8]. Density functional theory (DFT) calculation has shown that E₂ excitation does not induce electron injection to C₆₀ in the (6,5)SWCNT/C₆₀ interface, although,
with $E_{11}$ excitation, ultrafast electron transfer ($\tau < 200$ fs) takes place from (6,5)SWCNT to C$_{60}$ [10]. These observations indicate that C$_{60}$ is not capable of extracting hot electrons from SWCNTs. On the other hand, Parkinson and co-workers fabricated SWCNT heterojunctions with atomically flat surfaces of TiO$_2$ and SnO$_2$, where higher-energy second excitonic SWCNT transitions produce more photocurrent [11]. Because of the continuum of states within the metal-oxide conduction band with a density that increases with increasing energy above the conduction band minimum, rates of carrier injection from E$_2$ of SWCNT to TiO$_2$ or SnO$_2$ are competitive with fast hot-exciton relaxation processes. In this context, the construction of similar photocatalytic systems is of interest in order to make photocatalytic reactions using SWCNTs more efficient. In this paper, we synthesized SWCNT/TiO$_2$ nanohybrids to demonstrate their photocatalytic activity for hydrogen evolution from water through the hot electron extraction from the E$_2$ state of SWCNT to TiO$_2$.

2. Materials and Methods

2.1. Reagents and Chemicals

SWCNTs were purchased from Sigma-Aldrich Co (St. Louis, MO, USA). TiO$_2$ was synthesized according to a previous report [12]. BDD-dendrimer(COOH) [13] and SWCNT/BDD-dendrimer(COOH) [14] were prepared according to our previous reports. All other reagents were purchased from Kanto Kagaku Co., Ltd. (Tokyo, Japan), Aldrich Chemical Co. (St. Louis, MO, USA), and Tokyo Kasei Co., Ltd. (Tokyo, Japan). All chemicals were used as received.

2.2. Characterization

The absorption data were recorded on a UV-3150 spectrophotometer (Shimadzu, Tokyo, Japan) using a standard cell with a path length of 10 mm. SEM measurements for the composites were conducted using a JEM-2100 (JEOL Ltd., Tokyo, Japan). Specimens for the measurements were prepared by applying a few drops of the sample solution onto a dedicated grid, and then evaporating the solvent. Raman spectra were obtained on a JASCO NRS-5100 (JASCO Co., Japan) using laser excitation at 532 nm.

2.3. Synthesis of SWCNT/BDD-Dendrimer(COOH) Nanohybrids

SWCNT/BDD-dendrimer(COOH) nanohybrids were synthesized as follows in accordance with the literature [14]. SWCNTs (1.0 mg) were added to a solution of BDD-dendrimer(COOH) (1.0 mg, 0.13 mM) in H$_2$O (5.0 mL) and then sonicated using a bath-type ultrasonifier (AS ONE Vs-D100, 24 kHz/31 kHz, 110 W) at a temperature below 25 $^\circ$C for 4 h. The centrifugation (3000 G) of the suspension for 30 min gave a stock solution of SWCNT/BDD-dendrimer(COOH) nanohybrids as a black-colored transparent supernatant.

2.4. Synthesis of SWCNT/TiO$_2$/Pt Hybrids

Here, 1.0 wt% Pt-loaded TiO$_2$ particles were prepared using the previously reported method [12]. The solid of TiO$_2$ (25 mg) was added to distilled water (22.5 mL), H$_2$PtCl$_6$ (0.66 mg, 1.28 $\mu$mol), and methanol (2.5 mL), and then irradiated by a 300 W Xe lamp (300 W, MAX-303, Asahi Spectra Co., M.C., without an optical filter) with stirring for 4 h at room temperature. After the irradiation, the gray solid was rinsed with methanol and dried under a vacuum. The SWCNTs were adsorbed onto TiO$_2$ by stirring the TiO$_2$/Pt (10 mg) in a mixture of SWCNT/BDD-dendrimer(COOH) nanohybrids (125 $\mu$L, SWCNT content 0.025 mg) in water (10 mL) at room temperature for 30 min and immersed overnight in the dark. After that, the supernatant was removed by decantation and the sample was dried and kept in the dark (denoted as SWCNT/TiO$_2$/Pt).

2.5. Photocatalytic Hydrogen Evolution Using SWCNT/TiO$_2$/Pt Hybrids

SWCNT/TiO$_2$/Pt (10 mg) and BNAH (38.6 mg, 180 $\mu$mol) were dissolved in deionized water (150 mL) in a Pyrex reactor. Upon vigorous stirring, the solution was irradiated with a 300 W Xenon arc light (300 W, MAX-303, Asahi Spectra Co., M.C., Tokyo, Japan)
through the cut-off filter ($\lambda > 422 \pm 5$ nm: Asahi Spectra Co., M.C., 25 $\varphi$) and bandpass filter ($\lambda = 570$ nm, 650 nm, 680 nm: Asahi Spectra Co., M.C., 25 $\varphi$). 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 m $\times$ 3.0 mm, Ar carrier gas) to measure the amount of H$_2$ above the solution (Figure S1).

3. Results and Discussion

Water-dispersible SWCNT/BDD-dendrimer nanohybrids were synthesized by the physical modification of SWCNTs with poly(amidoamine) dendrimer with a 1,10-bis(decyloxy)decane core and carboxy (–COOH) terminals, BDD-dendrimer(COOH) (Figure 1a) [12,13]. Pt-loaded TiO$_2$ mesocrystals (TiO$_2$/Pt) (25 mg) were prepared by a conventional photochemical deposition method [12]. The Pt loading on TiO$_2$ was confirmed by the hydrogen production activity (0.71 $\mu$mol/h·mg) under UV irradiation. To a water dispersion (10 mL) of TiO$_2$/Pt (10 mg), a solution of SWCNT/BDD-dendrimer(COOH) nanohybrids (125 $\mu$L, SWCNT content 0.025 mg) was added. The mixture was stirred for 30 min and immersed overnight in the dark. The solvent was removed by decantation to obtain SWCNT/TiO$_2$/Pt (Figure 1b). The amount of SWCNTs adsorbed on the TiO$_2$ surface was estimated to be 21 $\mu$g per 10 mg of TiO$_2$/Pt using the absorption spectrum of supernatant solution after the hybridization of SWCNTs with TiO$_2$ (Figure S2).

Figure 1. Fabrication of (a) the SWCNT/BDD-dendrimer(COOH) nanohybrids, and (b) SWCNT/TiO$_2$/Pt nanohybrids.

Figure 2 shows SEM images of TiO$_2$ and SWCNTs/TiO$_2$/Pt. The TiO$_2$ mesocrystals were plate-like structures with a particle size of 10 $\mu$m (Figure 2a), as previously reported [12]. The plate-like structure was retained after the attachment of SWCNT/BDD-dendrimer(COOH) nanohybrids to TiO$_2$ (Figure 2b). TiO$_2$ particles on the plate mesocrysts...
tals were stripped off by ultrasonic treatment during the Pt loading or SWCNTs attachment process. Although the amount of Pt and SWCNTs on the surface of the TiO$_2$ crystals was so small that they could not be observed by energy dispersive X-ray spectroscopy (EDX), HR-SEM images show the Pt nanoparticles and nanofibers on the TiO$_2$ mesocrystals (Figure S3). The SWCNTs/TiO$_2$/Pt exhibited a Brunauer–Emmett–Teller (BET) surface area of 54.7 m$^2$ g$^{-1}$.

![SEM images of TiO$_2$ and SWCNT/TiO$_2$/Pt.](image)

Figure 2. SEM images of (a) TiO$_2$ and (b) SWCNT/TiO$_2$/Pt.

The formation of SWCNT/TiO$_2$/Pt nanohybrids was confirmed by absorption, 2D excitation/emission, and Raman spectra. The absorption spectra of SWCNT/TiO$_2$/Pt (blue line) exhibit the characteristic absorption bands derived from SWCNTs that appeared at 400–700 nm (Figure 3). The absorption originating from (6,5)SWCNT ($\lambda_{\text{max}}$ 570 nm) along with a small shoulder at around 670 nm originating from (8,3) and (7,5)SWCNTs were observed, almost the same as that of SWCNT/BDD-dendrimer(COOH) (orange line). Two-dimensional excitation/emission spectra show the quenching of the fluorescence of SWCNTs after the hybridization with TiO$_2$/Pt due to photoinduced electron transfer from SWCNTs to TiO$_2$ (Figure S4).
Figure 3. Absorption spectra of SWCNT/TiO\(_2\)/Pt (blue line) and SWCNT/BDD-dendrimer(COOH) nanohybrids (orange line).

Figure 4 shows the Raman spectrum of the SWCNT/TiO\(_2\)/Pt hybrids. Raman shifts for the G band (1585 cm\(^{-1}\)), D band (1316 cm\(^{-1}\)), and G' band (2622 cm\(^{-1}\)) of the SWCNTs were observed, where the G/D ratio (3.30) did not change before or after the attachment of SWCNT onto TiO\(_2\), indicating that the sp\(^2\) carbon of SWCNTs was not changed to sp\(^3\) carbon. Peaks originating from the anatase crystal of TiO\(_2\) were observed at 403 cm\(^{-1}\) (B\(_{1g}\)), 517 cm\(^{-1}\) (A\(_{1g}\)), 156 cm\(^{-1}\), and 643 cm\(^{-1}\) (E\(_g\)) [15]. These observations indicate that SWCNTs are adsorbed on the surface of TiO\(_2\).

Figure 4. Raman spectrum of SWCNT/TiO\(_2\)/Pt hybrids.
Parkinson and co-workers reported that hot electron injection from the SWCNT \( E_{22} \) state to \( \text{TiO}_2 \) is more efficient than electron injection from the relaxed SWCNT \( E_{11} \) state at the SWCNT/\( \text{TiO}_2 \) heterojunction due to a higher density of states (DOS) at \( E_{22} \) than at \( E_{11} \) of SWCNTs and the continuum of states within the \( \text{TiO}_2 \) conduction band with a density that increases with increasing energy above the conduction band edge [11]. In marked contrast with SWCNT/\( C_{60} \) heterojunctions [3,10], hot electron extraction from the SWCNT \( E_{22} \) state (\( C_2 \)) is fast enough to compete with relaxation to the \( E_{11} \) state (\( C_1 \)) so that the relative photon conversion efficiency (RPCE) upon \( E_{22} \) photoexcitation is higher than that upon \( E_{11} \) photoexcitation. In this context, we expected photocatalytic hydrogen evolution from water using SWCNT/\( \text{TiO}_2/\text{Pt} \) nanohybrids via direct electron extraction from SWCNT \( E_{22} \) states (\( C_2 \)), of which the energy level diagram is shown in Figure 5. Higher-energy second excitonic SWCNT transition under visible-light irradiation leads to hot electron extraction from the SWCNT \( E_{22} \) state (\( C_2 \)) to the \( \text{TiO}_2 \) conduction band, followed by the electron migration to the Pt co-catalyst to induce the hydrogen evolution reaction. The remaining hole in the SWCNT valence bands (\( V_2 \)) is consumed by simultaneous hole migration to a sacrificial donor molecule, 1-benzyl-1,4-dihydronicotinamide (BNAH). The efficiency of the hydrogen evolution reaction is dominated by the efficiency of the hot electron extraction from SWCNT \( E_{22} \) to \( \text{TiO}_2 \), because the electron injection from the SWCNT \( E_{11} \) state (\( C_1 \)) to \( \text{TiO}_2 \) is relatively slow due to the small driving forces, although the hot-electron injection rate from \( C_2 \) to \( \text{TiO}_2 \) is competitive with hot-exciton relaxation processes, as described by Parkinson et al. [11].

![Energy-level diagram of the hydrogen evolution reaction using SWCNT/TiO2/Pt as a photocatalyst in the presence of BNAH as a sacrificial donor.](image)

Figure 5. Energy-level diagram of the hydrogen evolution reaction using SWCNT/\( \text{TiO}_2/\text{Pt} \) as a photocatalyst in the presence of BNAH as a sacrificial donor.

Figure 6 shows the time course of the photocatalytic hydrogen evolution reaction over SWCNT/\( \text{TiO}_2/\text{Pt} \) under visible-light irradiation (\( \lambda > 422 \text{ nm} \)). The hydrogen production rate of 9.5 \( \mu \text{mol/h} \) was observed (Figure 6, ●). The hydrogen evolution reaction continued until all of the sacrificial agent, BNAH, was consumed, and there was no induction period (Figure S5). In contrast, no production of hydrogen was detected using TiO\(_2/Pt\) without SWCNTs under the same conditions (Figure 6, ■), indicating that the SWCNTs act as photosensitizers and the hydrogen production reaction proceeds via electron extraction from SWCNTs on the surface of TiO\(_2\). To compare the electron-extracting ability of TiO\(_2\), commercially available P25 was used to synthesize SWCNT/TiO\(_2\)\((P25)/Pt\). Under the same reaction conditions, the hydrogen production rate of SWCNT/TiO\(_2\)\((P25)/Pt\) was 7.3 \( \mu \text{mol/h} \) (Figure S6), which is less active than that of SWCNT/TiO\(_2\)(mesocrystal)/Pt (9.5 \( \mu \text{mol/h} \)). The higher activity with TiO\(_2\) mesocrystals may be due to the suppres-
sion of charge recombination at the SWCNT/TiO$_2$ interface. A similar result using black phosphorous/TiO$_2$ (mesocrystal) interface was described by Fujitsuka and co-workers [16].

![Graph showing the amount of H$_2$ evolved over time](image)

**Figure 6.** Time course of H$_2$ evolution from water over SWCNT/TiO$_2$/Pt (blue line) and TiO$_2$/Pt (orange line) under visible-light irradiation ($\lambda > 422$ nm).

To obtain insight into this free-carrier generation process in the SWCNT/TiO$_2$ heterojunction, we compared the chirality dependence of EQY of the hydrogen evolution reaction using the SWCNT/TiO$_2$ heterojunction with that using SWCNT/C$_{60}$ upon E$_{22}$ photoexcitation of SWCNTs. In our previous reports [8,9], we found a commensurate reduction of EQY in the offset of the energy levels (driving force) between SWCNT C$_1$ and C$_{60}$ LUMO (Figure 7). (8,3)SWCNT shows the highest EQY among (6,5), (7,5), and (8,3)SWCNTs because of the electron transfer from SWCNT to C$_{60}$ after the relaxation from the SWCNT E$_{22}$ state to the SWCNT E$_{11}$ state, as in the case of SWCNT/C$_{60}$ solar cells. If the hot electron extraction from the SWCNT E$_{22}$ state to C$_{60}$ had occurred, the EQY would depend on the energy levels of SWCNT C$_2$, i.e., (6,5)SWCNT would represent the highest EQY, and (8,3)SWCNT would show the lowest EQY.

![Energy diagram](image)

**Figure 7.** Driving force of electron extraction using SWCNT/C$_{60}$ heterojunction from SWCNT E$_{22}$ state (left side) and SWCNT E$_{11}$ state (right side).
In this context, we investigated the photocatalytic activity of SWCNT/TiO$_2$/Pt upon chiral-selective photoexcitation using 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 an aqueous dispersion of SWCNT/TiO$_2$/Pt (10 mg) and 1-benzyl-4-dihydrionicotinamide (BNAH; 38.6 mg, 180 μmol/h) 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 8a (●) shows plots of the total amount of H$_2$ produced versus time using monochromatic light irradiation at 570 nm. A steady generation of H$_2$ (2.2 μmol/h) was observed without an induction period or a decrease in activity during 3 h of irradiation. Compared with the H$_2$ generated by the use of monochromatic light irradiation at 650 or 680 nm, 1.7 μmol/h (Figure 8a (■)) and 1.3 μmol/h (Figure 8a (▲)), respectively, the amount of H$_2$ evolution under 570 nm irradiation was the highest (2.2 μmol/h, Figure 8a (●)). The EQYs were in the same order as for the hydrogen production rate: 5.5% for (6,5) SWCNT > 3.6% for (7,5) SWCNT > 2.2% for (8,3) SWCNT. Notably, this order of EQYs is consistent with the energy levels of the second excitonic state (C$_2$) for (6,5), (7,5), and (8,3) SWCNTs, –3.30, –3.54, and –3.62 eV, respectively (Figure 9), and is the same as previous reports on the relative photon conversion efficiency (RPCE) of the SWCNT/TiO$_2$ heterojunction. This result indicated that the hot electron injection from the second excitonic state of SWCNTs to TiO$_2$ leads to a hydrogen evolution reaction in marked contrast to CNT photocatalyst based on the SWCNT/C$_{60}$ heterojunction, where the electron extraction from SWCNT to C$_{60}$ occurred after the inter-band transition from the E$_{22}$ state (C$_2$) to the E$_{11}$ state (C$_1$). Furthermore, the SWCNT/TiO$_2$/Pt photocatalyst exhibited higher EQYs than the previously reported SWCNT/C$_{60}$/Pt(II) photocatalyst. For example, upon 570 nm photoirradiation (E$_{22}$ absorption of (6,5) SWCNT), the EQY of SWCNT/TiO$_2$/Pt, 5.5%, is 16 times higher than that of SWCNT/C$_{60}$/Pt(II), 0.35%.

Figure 8. Time course of the H$_2$ evolution under irradiation at 570 nm (E$_{22}$ of the (6,5) SWCNT; ●), 650 nm (E$_{22}$ of (7,5) SWCNT; ■), and 680 nm (E$_{22}$ of the (8,3) SWCNT; ▲).
Figure 9. Energy level diagram of SWCNT/TiO2 heterojunctions. Gray bar reveals the conduction band of TiO2.

4. Conclusions

In summary, we have prepared a visible-light-responsive TiO2 photocatalyst, SWCNT/TiO2/Pt, by mixing TiO2/Pt and SWCNT/BDD-dendrimer nanohybrids. Since BDD-dendrimer can act as a molecular glue that does not suppress the electron transfer between SWCNT and TiO2, the photoinduced electron transfer from SWCNT to TiO2 proceeds very smoothly to form a charge-separated state (SWCNT+/TiO2−). The dependence on the C2 energy level of SWCNT for the EQY of the hydrogen evolution reaction upon E22 photoexcitation proved the hot electron extraction pathway. Interestingly, the EQYs are higher than those of the previous reports employing SWCNT/C60/Pt(II) as a photocatalyst because of the difference in the charge collection process where electron extraction takes place after the relaxation from the SWCNT E22 state to the SWCNT E11 state. Further studies on the SWCNT heterojunction with metal oxides to enhance the efficiency of the hot electron extraction pathway for solar hydrogen production are currently in progress in our laboratories.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12213826/s1, Figure S1: Photograph of closed circulation system used in a photocatalytic hydrogen evolution reaction; Figure S2: Absorption spectra of supernatant before/after the hybridization of SWCNTs with TiO2; Figure S3: HR-SEM images of SWCNT/TiO2/Pt using in-lens detector; Figure S4: Two-dimensional PL intensity maps of (a) SWCNT/BDD-dendrimer(COOH) nanohybrids and (b) SWCNT/TiO2/Pt; Figure S5: A time course of photocatalytic hydrogen evolution using SWCNT/TiO2/Pt under visible light irradiation (λ > 422 nm); Figure S6: A time course of H2 evolution from water over SWCNT/TiO2(P25)/Pt under visible light irradiation (λ > 422 nm).

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