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H_2-evolving SWCNT Photocatalysts for Effective Use of Solar Energy

Kiki Kurniawan, Noritake Murakami, Yuto Tango, Takumi Izawa, Kakeru Nishikawa, Ken Watanabe, Hideaki Miyake, Tomoyuki Tajima, Yutaka Takaguchi*

Graduate School of Environmental & Life Science, Okayama University
3-1-1 Tsushima-Naka, Kita-Ku, Okayama, 700-8530, Japan
Corresponding Author. Email: yutaka@cc.okayama-u.ac.jp

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Effective hydrogen evolution from water using SWCNT photocatalyst under near-infrared (NIR) light illumination was demonstrated. H_2 evolution reactions of 1.2 and 0.40 mmol/h were observed upon chirality-selective photoexcitation by the use of monochromatic light irradiation at 680 and 1000 nm, which are the E_{22} and E_{11} absorptions of (8,3) SWCNT, respectively, by the use of SWCNT/fullerodendron photosensitizer in the presence of a sacrifice donor, an electron relay, and a co-catalyst. Apparent quantum yields of this reaction were 0.17 (at 680 nm) and 0.073 (at 1000 nm), respectively. The result provides the first example of photocatalytic H_2 evolution reaction triggered by E_{11} photoexcitation of SWCNTs, and clearly shows the usefulness of SWCNTs in the light absorber for NIR light, which is the second main component of solar radiation.

From the view point of renewal energy resources to win the fight against global warming, there is increasing focus on the production of hydrogen from water using sunlight and photocatalysts because this water splitting reaction does not emit greenhouse gases [1]. For practical use of solar energy, visible- and near-infrared- (NIR) light driven photocatalysts are required to achieve useful and efficient H_2 production because approximately 85% of solar energy incident on the Earth's surface lies in the wavelength region between 400 and 1350 nm [2]. Although many researchers developed visible-light driven photocatalysts for the water splitting, the examples of efficient photocatalysts producing H_2 under NIR light illumination are quite rare [3].

Meanwhile, single-walled carbon nanotubes (SWCNTs) are potentially strong optical absorbers with tunable absorption bands depending on their chiral indices (n,m) [4]. But 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 [5]. 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 C_{60} is the key for high power conversion efficiency [6]. In contrast to thin film devices, photosensitizing reactions in a dispersion/solution system via photoinduced electron transfer triggered by the photoexcitation of SWCNTs are quite rare because of the difficulty of the construction of a well-ordered surface on SWCNTs. Recently, we developed water-dispersible coaxial nanowires possessing a SWCNT/C_{60} heterojunction that can be used for a photosensitizer to produce H_2 from water [7-9]. The photosensitizing property of SWCNT was firstly evidenced by chirality-selective photo-excitation by monochromatic light irradiation at 680 nm [9], which is E_{22} absorption of (8,3)SWCNT (Figure 1). Apparent quantum yield (AQY) of H_2 evolution reaction using (8,3)SWCNT/fullerodendron was estimated to be 1.5% at 680 nm. However, it still remains unclear whether E_{11} absorption in NIR region is effective for H_2 production or not. These circumstances prompt us to investigate the H_2 evolving efficiency of SWCNT photocatalysts under NIR light illumination. Here we describe the NIR-driven photocatalytic activity of SWCNT/fullerodendron nanohybrids.

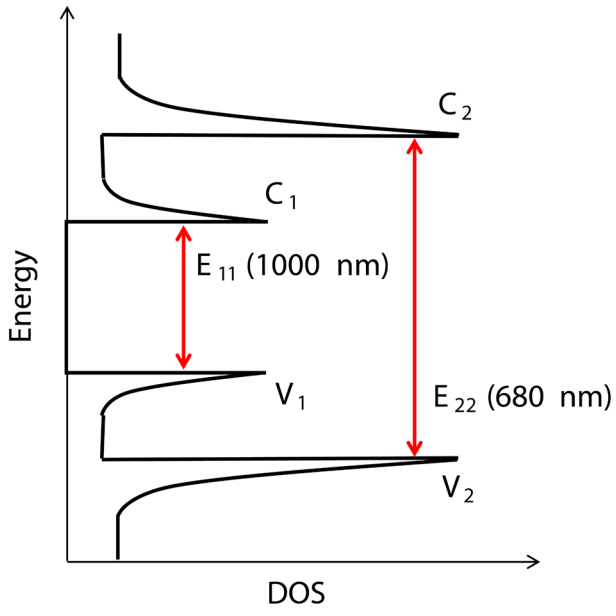

Figure 1. Electronic density of States (DOS) of (8,3) SWCNT.

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EXPERIMENTAL

Materials and methods

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. Samples for observation were prepared by placing a drop of the aqueous specimen on freshly cleaved mica, then allowing each drop to dry. (6,5)-enriched SWCNTs were purchased from Sigma-Aldrich Co. All other reagents were purchased from Kanto Kagaku Co., Ltd, Sigma-Aldrich Co., and Tokyo Kasei Co., Ltd. All chemicals were used as received. Fullerodendron was prepared according to the reported procedure [10].

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 supramolecular 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.

Hydrogen evolution

An aqueous solution of Tris-HCl buffer (3.5 mL, pH 7.5, 5 mM), (6,5)-enriched SWCNT/fullerodendron nanohybrids (5.0 mL), BNAH (38.6 mg, 1.20 mM), methyl viologen dichloride (MV^{2+}, 92.4 mg, 2.40 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 300 W Xenon arc lights (Ushio model UXL-500 W or Asahi Spectra MAX-303) through bandpass filters (680 nm or 1000 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 5A: 2.0 m × 3.0 mm, Ar 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 molecules generated × 2/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.

RESULTS AND DISCUSSION

SWCNT photocatalysts, SWCNT/fullerodendron nanohybrids, were prepared according to the literature procedure by the use of (6,5)-enriched SWCNTs (Figure 2) [11]. The formation of the nanohybrids was confirmed by absorption spectroscopy, Raman spectroscopy, three-dimensional photoluminescence (PL) intensity mapping, AFM observation. In the view point of a utility of NIR light for H_2 evolving photocatalytic system, the strong absorption band of SWCNT photocatalysts

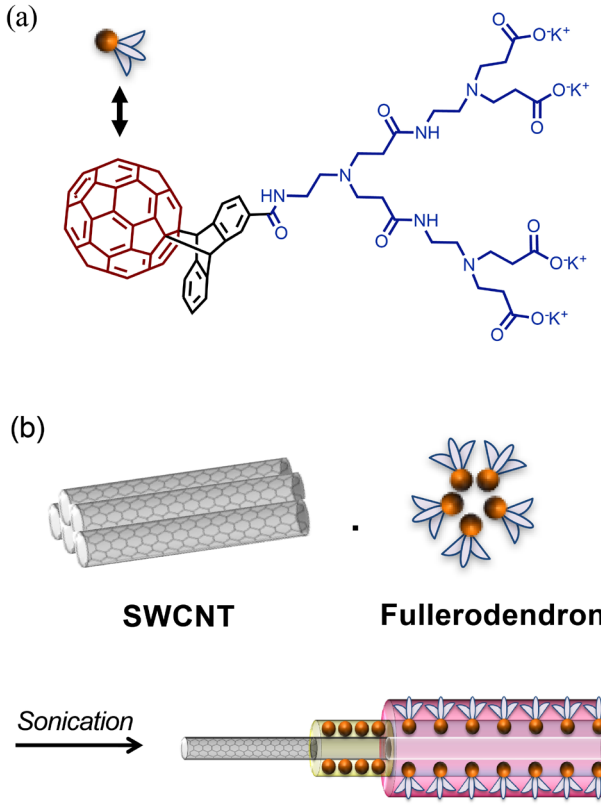

Figure 2. (a) Molecular structure of fullerodendron. (b) Sche-matic illustration of the fabrication of SWCNT/fullerodendron nano-hybrids (SWCNT photocatalysts).

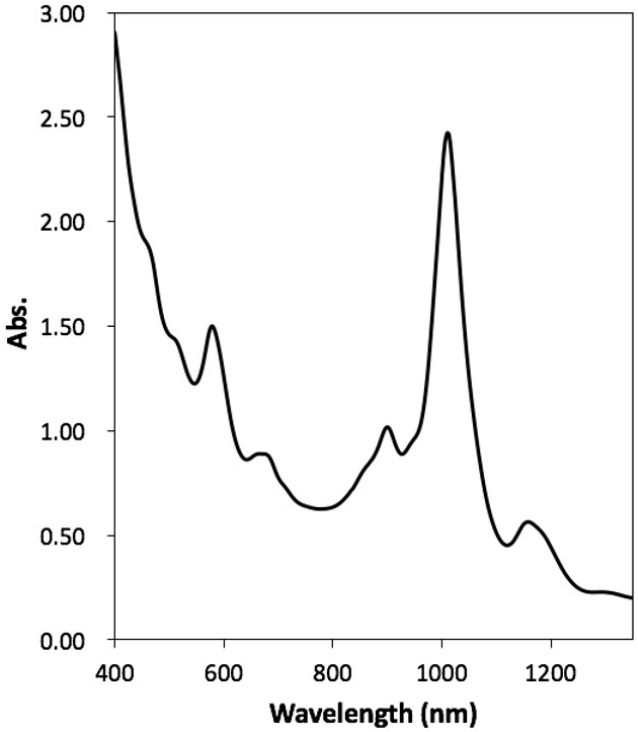

Figure 3. Absorption spectrum of SWCNT photocatalysts.

at 1000 nm, which is E_{11} absorption of (8,3)SWCNT, is on-target region of a light wavelength (Figure 3).

In order to clarify the H_2 production efficiency of SWCNT photocatalysts upon their E_{11} absorption in NIR region of the light, we investigated the photocatalytic activity of SWCNT/fullerodendron nanohybrids upon chirality-selective photoexcitation by the use of monochromatic light irradiation

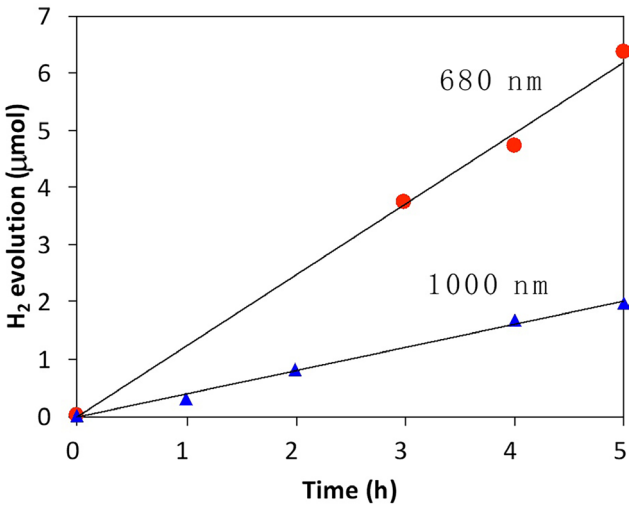

Figure 4. Time dependencies of Photocatalytic H_2 evolution from using SWCNT photocatalyst under monochromatic light at 680 nm (●) and 1000 nm (▲).

at 680 and 1000 nm, which are the E_{22} and E_{11} absorptions of (8,3)SWCNT, respectively. In a typical experiment, 150 mL of aqueous solution of SWCNT/fullerodendron hybrids (SWCNT content 0.025 mg), Tris-HCl buffer (pH 7.5, 0.12 mM), MV^{2+} (2.4 mM), and BNAH (1.2 mM), was exposed to monochromatic light (680 or 1000 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 4 (●) shows plots of the total amount of H_2 produced versus time using monochromatic light irradiation at 680 nm (E_{22} absorption of (8,3)SWCNT). A steady generation of H_2 (1.2 mmol/h) was observed without an induction period or a decrease in activity during 5 h of irradiation. Meanwhile, H_2 production rate upon irradiation at 1000 nm (E_{11} absorption of (8,3) SWCNT) was 0.40 mmol/h (Figure 4 (▲)). To compare the efficiency of photocatalytic H_2 evolution between two irradiation wavelengths, 680 and 1000 nm, we evaluated apparent quantum yields (AQYs) by the use of monochromatic light irradiation at 680 and 1000 nm. The AQYs for H_2 evolution (AQY = 2 × number of H_2 molecules generated / number of photons absorbed) were 0.17 at 680 nm and 0.073 at 1000 nm, respectively. Although E_{22} excitation of the SWCNT photocatalysts is more effective to produce H_2 from water, it is obvious that SWCNT/fullerodendron can act as photosensitizer by the use of E_{11} excitation of SWCNTs. The difference of AQYs between E_{11} and E_{22} excitations might be attributed to the exciton-exciton annihilation [12].

CONCLUSION

In summary, we demonstrated photocatalytic hydrogen evolution from water using SWCNT/fullerodendron nanohybrids with the help of a sacrifice donor (BNAH), an electron relay (MV^{2+}), and a co-catalyst (PVP-Pt). Upon chirality-selective photo-excitation by monochromatic light irradiation at 1000 nm (E_{11} absorption of (8,3) SWCNT), we provided the first clear-cut example of a H_2 evolution reaction owing to the E_{11} photoexcitation of SWCNT. It is notable that the AQY of 0.073 under 1000 nm irradiation for H_2 evolution reaction is the highest value under an illumination wavelength of over 1000 nm so far. Hence, SWCNT is promising for NIR light absorber that can be used for the core-component of coaxial nanowire photocatalyst. Further studies of SWCNT photocatalysts are in progress to make SWCNT photocatalysts more effective and useful under solar light irradiation.

Acknowledgements

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