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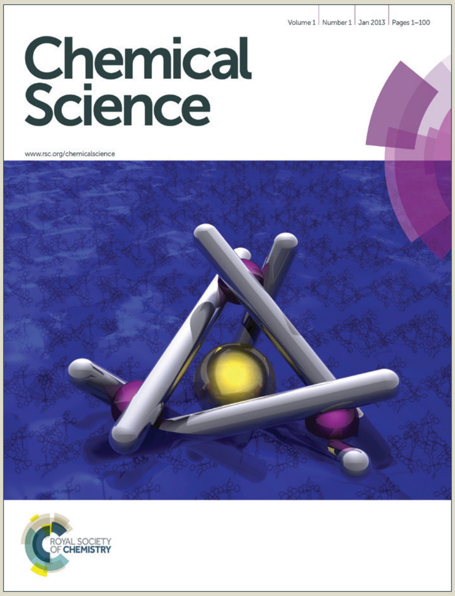

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Laser-induced pinpoint hydrogen evolution from benzene and water using metal free single-walled carbon nanotubes with high quantum yields †

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Metal-free photocatalytic hydrogen evolution occurred efficiently in benzene containing single-walled carbon nanotubes under laser irradiation at 532 nm with an extremely high turnover number of 2,000,000 and a high quantum yield of 130%. The rate of hydrogen evolution increased with increasing the laser intensity to exhibit the fourth-power dependence, suggesting that hydrogen was evolved via four-photon processes in which coupling of two radical anions derived from benzene is the rate-determining step and benzene radical anion is produced by electron transfer from benzene to the doubly excited state of single-walled carbon nanotubes, which requires two photons. Polymerisation of benzene was induced by the photogenerated $C_6H_6^{\bullet -}$, accompanied by hydrogen evolution, resulting in a leverage effect to increase the quantum yield of hydrogen evolution much larger than 25% expected for the four-photon process. Laser-induced hydrogen evolution also occurred in water containing single-walled carbon nanotubes. In contrast to the case of benzene, water was not oxidized but hydrogen evolution from water was accompanied by multi-oxidation of single walled carbon nanotubes. The yield of hydrogen based on one mole of single-walled carbon nanotubes with the 1.4 nm diameter and 1~5 mm length was determined to be 2,700,000%, when 27,000-electron oxidation of single-walled carbon nanotubes occurred to produce the polyhydroxylated product.

Introduction

Carbon nanomaterials have been widely studied for their potential applications as electrode materials for efficient energy conversion and storage.[1-5] Metal-free nanostructured elemental carbons and carbon-based composites have proven to be attractive alternatives to conventional metal-based catalysts for several important chemical reactions such as dehydrogenated reactions of aromatic compounds,[5-7] oxygenation[8] and Friedel-Crafts reactions.[9,10] However, their reactions were carried out under severe conditions to activate substrate molecules.

In particular, single-walled carbon nanotubes (SWCNTs) have been of great interest to researchers because of their unique structures and physical properties.[11-17] SWCNTs have been proposed as an advanced metal-catalyst support for electrochemical catalysis.[18–20] However, there is no report that SWCNTs itself is used as a photocatalyst under ambient conditions due to the poor photochemical and excited properties.

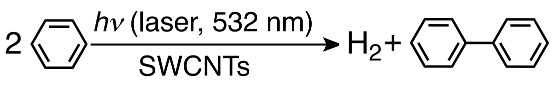
Catalytic hydrogen (H_2) evolution systems have been extensively studied because hydrogen is a clean energy source for the future, which should reduce dependence on fossil fuels and emissions of greenhouse gases in the long term.[21,22] In many cases, noble metals such as plutinum and semiconductors have been used as photocatalysts.[23-35] However, there is no report on photocatalytic metal-free H_2-evolution system using pure carbon alone as a photocatalyst.[36]

We report herein efficient H_2 evolution from benzene and benzene derivatives using metal free SWCNTs alone as a photocatalyst under visible laser light irradiation (532 nm) at room temperature under an atmospheric pressure with a high quantum yield of 130%. Efficient laser-induced hydrogen evolution was also observed from water with SWCNTs. The reaction mechanisms of laser-induced H_2 evolution from benzene and water with SWCNTs are clarified based on the oxidized products, deuterium kinetic isotope effects and the dependence of the rate of H_2 evolution on the laser intensity. This is the first example of laser-induced H_2 evolution with high quantum yields, paving a new way for pinpoint H_2 production with laser pulse, which may find various applications.

Results and discussion

1 Laser-induced photocatalytic hydrogen evolution from benzene with SWCNTs

Laser pulse irradiation (λ = 532 nm; 500 mW; 10 Hz) of an aerated benzene solution (2.5 mL) containing dispersed metal-free SWCNTs (0.15 mg) resulted in efficient hydrogen evolution. The amount of hydrogen evolved by laser irradiation for 2 h reached 100 μmol (2.2 mL). The quantum yield of hydrogen evolution was determined from the initial rate to be 34%. When benzene was replaced by deuterated benzene (C_6D_6), the deuterated hydrogen molecules such as D_2 and HD were also evolved efficiently (see Fig. S1 in the Supporting Information (SI)). The initial rate of hydrogen evolution was 21 μmol h^{-1} with 50 : 1 ratio for D_2 and HD, respectively. The KIE (kinetic isotope effect) value was determined from the slopes in Fig. 1 to be 2.4. These results indicate that the hydrogen source is benzene. The products derived from dehydrogenation of benzene were determined by the GC-MS and HPLC analyses to be biphenyl, terphenyls, and terphenylene (see Figs. S2 and S3 in SI). The stoichiometry to produce H_2 and biphenyl from benzene is given by eqn (1).



(1)

There is no evidence for functionalisation of SWCNTs by benzene under photoirradiation, which was observed by TG analyses (Fig. 2) because no weight loss from decomposition of functionalized molecule to SWCNTs was observed at low temperature. Thus, hydrogen was evolved via the condensation reaction of benzene in the photocatalytic reaction.

Hydrogen was also evolved in various aromatic solvents with electron withdrawing and donating substituent(s) (Fig. S4 in SI). The amounts of H_2 evolved are listed in Table 1. The highest catalytic activity was obtained in benzene. The catalytic turn over number (TON) is roughly estimated as (2.0 ± 0.5) × 10^6 per SWCNT for 2 h irradiation, calculated from the tube diameter and average length of SWCNTs with zig-zag structure used in this study.[37] When benzene was replaced by benzene-d_6, TON was decreased to (8.0 ± 2.0) × 10^5 per SWCNT. This value agrees with KIE of 2.4 determined from the initial rate of H_2 evolution as shown in Fig. 1.

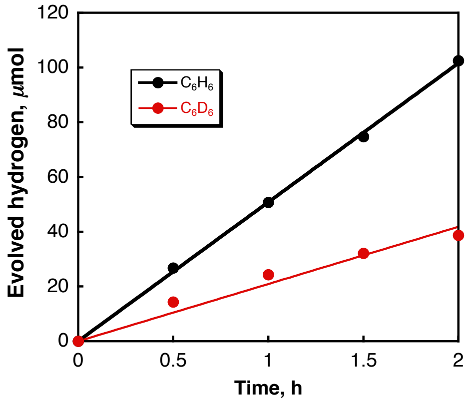


Fig. 1 Time courses of hydrogen evolution in deaerated benzene (black circles) and C_6D_6 (red circles) containing SWCNTs (0.060 mg mL^{-1}) under laser irradiation at 532 nm (50 mJ $pulse^{-1}$).

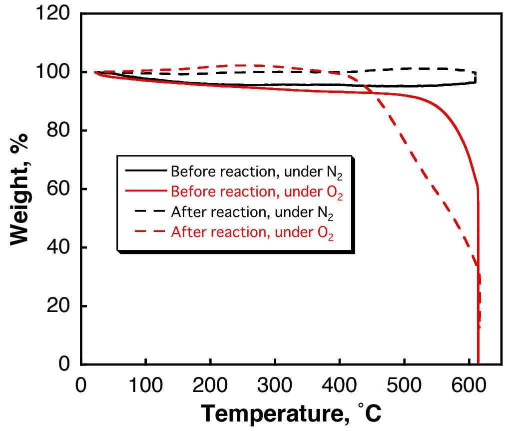


Fig. 2 TG curves of SWCNTs before and after laser light irradiation (H_2 evolution) in benzene observed under deaerated and aerated conditions.

Table 1 Amount of H_2 evolved in various solvents after laser irradiation for 2 h

Solvent	H_2 evolved,[a] μmol
benzene	100
mesitylene	71
toluene	66
p-xylene	60
chlorobenzene	54
benzonitrile	39
1,2-dimethoxybenzene	12

[a] Conditions: SWCNTs (0.15 mg) dispersed in deaerated solvent (2.5 mL). Excited at 532 nm (50 mJ $pulse^{-1}$).

Transmission electron microscope (TEM) measurements were performed to evaluate the transformation of SWCNTs before and after hydrogen evolution. The TEM images before photoirradiation (Figs. 3a and 3b) clearly exhibit tubular morphology. There is no inorganic impurity in the commercially available and highly purified SWCNTs used in this study (see Experimental Section). After hydrogen evolution, the tubular structure was partially changed to agnail structure and small clusters. However, tubular component still remains (Figs. 3c and 3d).

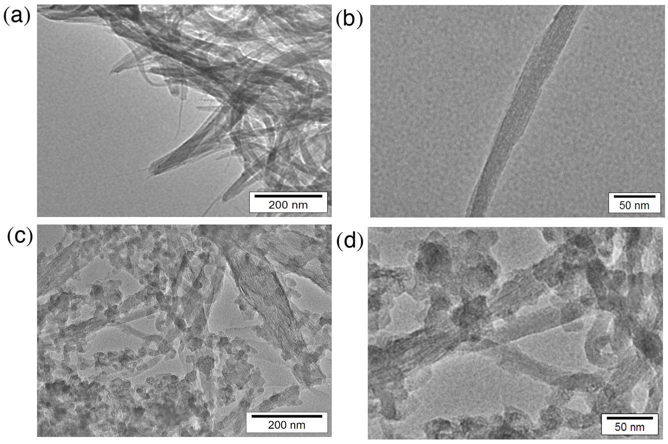


Fig. 3 TEM images of SWCNTs (a, b) before and (c, d) after laser photoirradiation (50 mJ $pulse^{-1}$, 10 Hz) for 2 h in deaerated benzene at 298 K.

The dependence of the rate of H_2 evolution on the laser intensity was examined using different laser power intensities at 532 nm (0 – 82 mJ pulse^{-1}). The initial rates of H_2 evolution are proportional to the fourth power of laser intensity as shown in Fig. 4. This suggests that a bimolecular reaction of two-photon absorbed species may be involved in the photocatalytic hydrogen evolution.

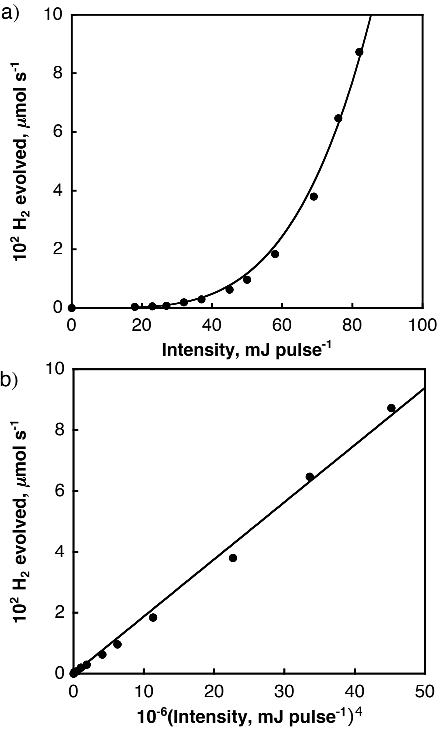
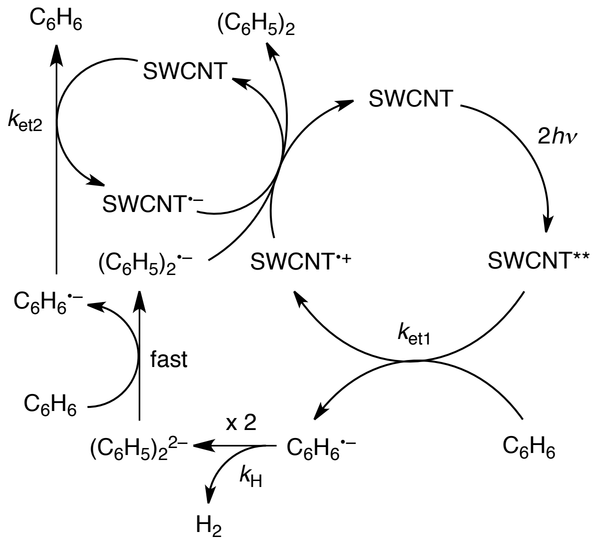


Fig. 4 (a) Plot of initial rate of H_2 evolved in deaerated benzene vs laser power intensity at 532 nm; (b) Plot of initial rate of H_2 evolved vs the fourth power of laser intensity.



Scheme 1

On the basis of above-mentioned results, the plausible photocatalytic mechanism for hydrogen evolution in benzene is shown in Scheme 1. SWCNT was excited by two photons to form doubly excited SWCNT (SWCNT**). SWCNT** can reduce benzene to produce benzene radical anion ($C_6H_6^{\bullet-}$) and the one-electron oxidized SWCNT ($SWCNT^{\bullet+}$) with the rate constant of k_{et1}. Dimerisation of $C_6H_6^{\bullet-}$ occurs associated with hydrogen evolution to produce biphenyl dianion [$(C_6H_5)_2^{2-}$] with the rate constant of k_H. Such hydrogen evolution via radical coupling of $C_6H_6^{\bullet-}$ has previously been reported for reduction of benzene with cesium nano carbon catalyst.[38] $(C_6H_5)_2^{2-}$ can reduce benzene to produce $C_6H_6^{\bullet-}$ and biphenyl radical anion [$(C_6H_5)_2^{\bullet-}$] in benzene.[39] Back electron transfer from $(C_6H_5)_2^{\bullet-}$ to $SWCNT^{\bullet+}$ results in formation of biphenyl [$(C_6H_5)_2$], accompanied by regeneration of SWCNT. On the other hand, $C_6H_6^{\bullet-}$ can reduce SWCNT to produce $SWCNT^{\bullet-}$ and C_6H_6 with the rate constant of k_{et2}. The charge recombination from $SWCNT^{\bullet-}$ to $SWCNT^{\bullet+}$ also regenerates SWCNT. The overall stoichiometry of the photocatalytic cycle in Scheme 1 agrees with eqn (1).

According to Scheme 1, the rate of hydrogen evolution is given by eqn (2). The rate of formation and decay of $C_6H_6^{\bullet-}$ is given by eqn (3). Assuming that $k_{et2}[SWCNT][C_6H_6^{\bullet-}]$ >>

$$d[H_2]/dt = k_H[C_6H_6^{\bullet-}]^2 \qquad (2)$$

$$d[C_6H_6^{\bullet-}]/dt = k_{et1}[SWCNT^{**}] - k_H[C_6H_6^{\bullet-}]^2 - k_{et2}[SWCNT][C_6H_6^{\bullet-}] \qquad (3)$$

$k_H[C_6H_6^{\bullet-}]^2$, the steady-state concentration of $C_6H_6^{\bullet-}$ is given by eqn (4). From eqn (2) and (4), the rate of hydrogen evolution is

$$[C_6H_6^{\bullet-}] = k_{et1}[SWCNT^{**}]/(k_{et2}[SWCNT]) \qquad (4)$$

rewritten by eqn (5). Because the concentration of SWCNT**

$$d[H_2]/dt = k_H\,[k_{et1}[SWCNT^{**}]/(k_{et2}[SWCNT])]^2 \qquad (5)$$

is proportional to the square of the laser intensity, the rate of hydrogen evolution is proportional to the fourth power of laser intensity as observed in Fig. 4b. The observed deuterium kinetic isotope effect on the photocatalytic H_2 evolution in Fig. 1 suggests that the C–H bond cleavage of $C_6H_6^{\bullet-}$ (k_H) is involved as the rate-determining step in the radical coupling for H_2 evolution in Scheme 1.

In Scheme 1, $C_6H_6^{\bullet-}$ produced by electron transfer from C_6H_6 to SWCNT** dimerizes to afford H_2 and $(C_6H_5)_2^{2-}$, followed by rapid electron transfer from C_6H_6 to $(C_6H_5)_2^{2-}$ to yield $C_6H_6^{\bullet-}$ and $(C_6H_5)_2^{\bullet-}$. The overall reaction of $C_6H_6^{\bullet-}$ with C_6H_6 to yield H_2 and $(C_6H_5)_2^{\bullet-}$ is shown in Scheme 2, where $(C_6H_5)_2^{\bullet-}$ can react further with C_6H_6 to produce terphenyl radical anion [$(C_6H_5(C_6H_4)C_6H_5)^{\bullet-}$] and H_2. The same type of reaction continues and the overall reaction is given by eqn (6). Thus, once one mol of $C_6H_6^{\bullet-}$ is produced *n* moles of hydrogen can be produced from *n* moles of benzene to form the radical anion of a benzene polymer [$(C_6H_5(C_6H_4)_{n-1}C_6H_5)^{\bullet-}$], which

$$C_6H_6 + C_6H_6^{\bullet-} \longrightarrow (C_6H_5)_2^{\bullet-} + H_2$$

$$C_6H_6 + (C_6H_5)_2^{\bullet-} \longrightarrow (C_6H_5(C_6H_4)C_6H_5)^{\bullet-} + H_2$$

$$\vdots$$

$$C_6H_6 + (C_6H_5(C_6H_4)_{n-2}C_6H_5)^{\bullet-} \longrightarrow (C_6H_5(C_6H_4)_{n-1}C_6H_5)^{\bullet-} + H_2$$

$$nC_6H_6 + C_6H_6^{\bullet-} \longrightarrow (C_6H_5(C_6H_4)_{n-1}C_6H_5)^{\bullet-} + nH_2 \qquad (6)$$

Scheme 2

may undergo charge recombination with $SWCNT^{\bullet+}$ to regenerate SWCNT.

According to Scheme 1, biphenyl is produced by the four-photon process when the maximum value of the quantum yield is 25%. However, the polymerisation of benzene induced by photo- generated $C_6H_6^{\bullet-}$ in Scheme 2 gains a leverage effect to increase the quantum yield of H_2 evolution much larger than expected from the four-photon process. Indeed, the highest quantum yield of formation of H_2 was determined to be 130% at the laser power of 82 mJ *per* pulse under the conditions in Fig. 2a, where the photon number of laser pulse was calibrated by ferrioxalate actinometry (see the experimental section in SI).[40]

The efficiency of the photocatalytic H_2 evolution is affected by substitution of the benzene ring with the electron donating or withdrawing substituents (Table 1). The efficiency of the photocatalytic H_2 evolution is the highest for benzene and the lowest for 1,2-dimethoxybenzene, because the substitution of the benzene ring may retard the radical coupling with hydrogen evolution in and the electron donating substituents (methoxy group) may slow down electron transfer to $SWCNT^{**}$ in Scheme 1.

Radical intermediates involved in photocatalytic H_2 evolution from benzene with SWCNTs were detected by ESR spectroscopy measured at 77 K as shown in Fig. 5. The observed ESR signal at the region of $g = 2.0025$ can be assigned to radical anions derived from benzene,[41] which are overwrapped with $SWCNT^{\bullet+}$.[42] The intensity of the ESR signal increased with increasing photoirradiation time because the stability of radical anions is expected to increase as the polymerisation of benzene in Scheme 2 proceeds.

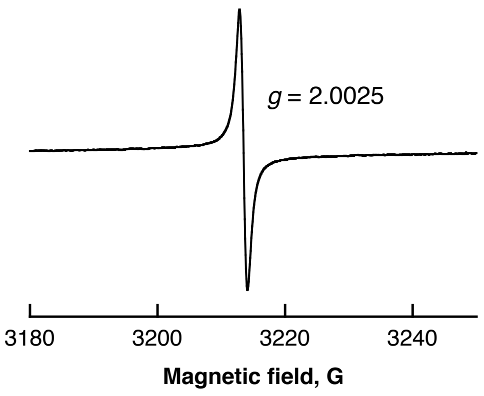


Fig. 5 ESR spectrum of a benzene glass containing SWCNTs (0.12 mg mL^{-1}) after laser pulse irradiation at 532 nm (40 mJ $pulse^{-1}$; 10 Hz) for 10 min at 77 K.

2 Laser-induced hydrogen evolution from water with SWCNTs

Hydrogen evolution also occurred in deaerated H_2O (2.5 mL) containing dispersed metal-free SWCNTs (2.0 mg) under Nd-YAG laser pulse irradiation (λ = 532 nm; 600 mW; 10 Hz) as shown in Fig. 6. The amount of evolved H_2 at 5 h reached 16.4 μmol, which is 2.7×10^4 times larger than the amount of SWCNT (0.6 nmol) calculated from the tube diameter and average length of SWCNTs with zig-zag structure used in this study. When H_2O was replaced by D_2O, the deuterated hydrogen molecules such as D_2 and HD were also evolved (see Fig. S5 in SI) and the KIE value was determined from the ratio of the H_2 evolution in H_2O *vs.* D_2O (Fig. 7) to be 1.9, which is somewhat smaller than the value in benzene. These results indicate that the hydrogen source of evolved H_2 is water.

In contrast to the case of benzene, no oxidized form of water (dioxygen or hydrogen peroxide) was produced after the

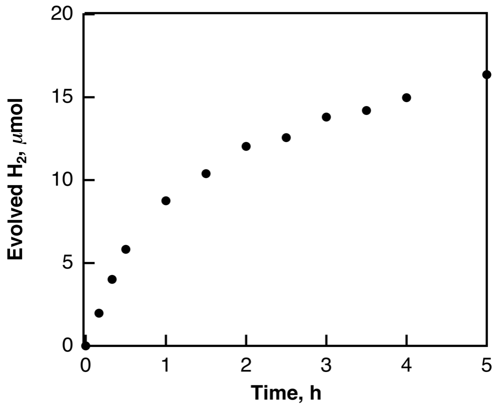


Fig. 6 Time course of hydrogen evolution in deaerated H_2O containing SWCNTs (0.80 mg mL^{-1}) under laser irradiation at 532 nm (60 mJ $pulse^{-1}$;10 Hz).

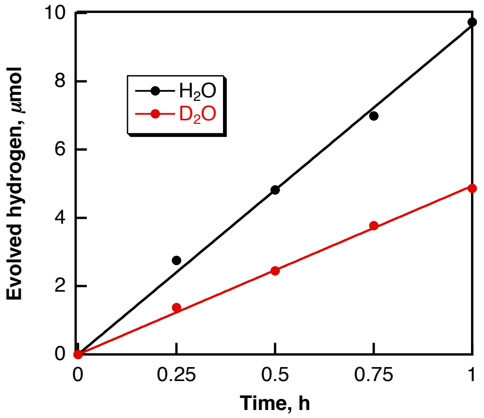


Fig. 7 Time courses of H_2 and D_2 evolution in deaerated H_2O (black circles) and D_2O (red circles), respectively, containing SWCNTs (0.80 mg mL^{-1}) under laser irradiation at 532 nm (60 mJ $pulse^{-1}$;10 Hz).

H_2 evolution (see Fig. S3 in SI). In such a case, SWCNTs may be oxidized, accompanied by the laser-induced H_2 evolution. The comparison of TEM images of SWCNTs before and after laser photoirradiation in H_2O (Fig. 8) indicates that the tubular morphology remained after the H_2 evolution by laser photoirradiation. The comparison of Raman of SWCNTs before and after laser photoirradiation of SWCNTs dispersed in deaerated H_2O is shown in Fig. 9. The G-band at 1590 and 1570 cm^{-1} decreased with appearance of D-band at 1340 cm^{-1}. The increased D/G ratio observed after the photoirradiation suggests that sidewall functionalisation of SWCNTs occurred.[43,44] The IR spectra was also suggests that SWCNTs were hydroxylated to exhibit O–H stretching vibrations at 3200–3600 cm^{-1} (Figs. S6 in SI).

The comparison of the weight loss of SWCNTs before and after the laser irradiation in H_2O observed in TG measurements (Fig. S7 in SI) also suggests that SWCNTs were hydroxylated. The number of OH groups of one SWCNT is estimated from the elemental analyses of SWCNTs before (C 96.81% and H 0.19%)[45] and after evolution of 16.4 μmol of H_2 (C 91.88% and H 0.60%) to be 18,000. Thus, the H_2 evolution is accompanied by the two-electron oxidation of SWCNT (attachment of two OH groups). The stoichiometry of the laser-induced H_2 evolution with SWCNTs in H_2O is given by eqn (7).

$$2H_2O \ + \ SWCNT \xrightarrow{h\nu} H_2 \ + \ SWCNT(OH)_2 \qquad (7)$$

The laser-induced H_2 evolution rate with SWCNTs in H_2O increases with increasing the amount of SWCNTs to reach a constant value as shown in Fig. 10. This shows sharp contrast with the case of the laser-induced H_2 evolution with SWCNTs in benzene, when the rate of H_2 evolution was independent of the amount of SWCNTs as discussed above based on Scheme 1. The pH dependence of the H_2 evolution rate was also examined as shown in Fig. 11, where the rate of H_2 evolution is rather independent of pH.

The overall stoichiometry agrees with that in eqn (7). EPR spectrum exhibits a radical intermediate in H_2 evolution with SWCNTs from water as shown in Fig. 12. The EPR signal was clearly observed at $g = 2.0030$ under laser irradiation at 77 K in

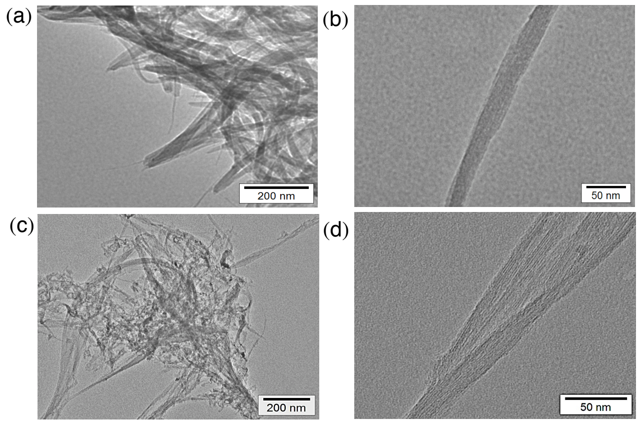


Fig. 8 TEM images of SWCNTs (a, b) before and (c, d) after laser photoirradiation (60 mJ $pulse^{-1}$, 10 Hz) for 2 h in deaerated H_2O at 298 K.

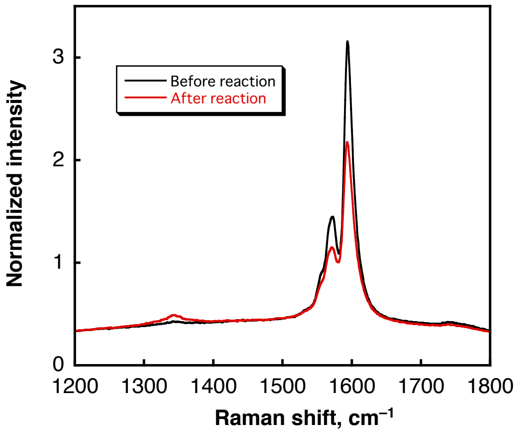


Fig. 9 Raman spectra of SWCNTs before laser irradiation (black line) and (b) SWCNTs obtained by laser light irradiation (λ = 532 nm; 60 mJ $pulse^{-1}$; 10 Hz) for 5 h in deaerated water (0.80 mg mL^{-1}, red line).

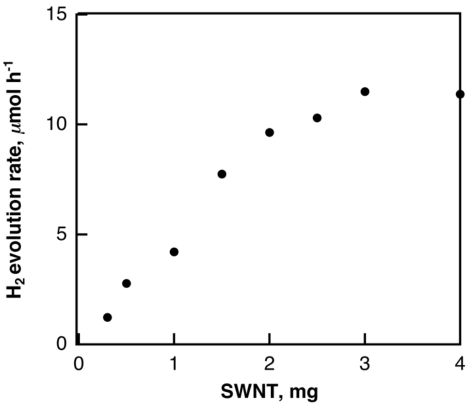


Fig. 10 Plot of rate of H_2 evolution in deaerated H_2O (2.5 mL) containing various amounts of SWCNTs under laser irradiation at 532 nm (60 mJ $pulse^{-1}$;10 Hz) vs amount of SWCNTs.

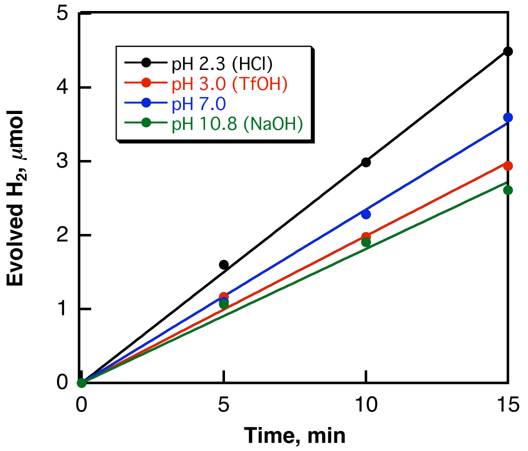


Fig. 11 Time courses of H_2 evolution in deaerated H_2O containing various amounts of SWCNTs (0.80 mg mL^{-1}) under laser irradiation at 532 nm (60 mJ $pulse^{-1}$;10 Hz) at various pHs.

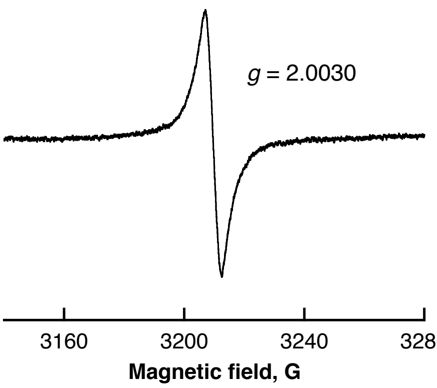


Fig. 12 ESR spectrum of a water glass containing SWCNTs (0.80 mg mL^{-1}) after laser pulse irradiation at 532 nm (60 mJ $pulse^{-1}$; 10 Hz) for 10 min at 77 K.

water glass containing SWCNTs. The g value is larger than the signal at $g = 2.0025$ observed in benzene (Fig. 5). Such a large g value indicates the existence of $SWCNT(OH)^{\bullet}$ as a radical intermediate due to the spin-orbit couplong of oxygen in the laesr-induced H_2 evolution with SWCNTs in water.

As the case of laser-induced H_2 evolution in benzene, the initial rates of laser-induced H_2 evolution in H_2O are proportional to the fourth power of laser intensity as shown in Fig. 13. This suggests that the doubly excited SWCNT (SWCNT**) and the subsequent bimolecular reaction are involved in the H_2 evolution. In the case of H_2O, solvated electron ($e^-(H_2O)$) may be produced by the reaction of SWCNT** with H_2O as shown in Scheme 3, where the bimolecular reaction of $e^-(H_2O)$ produces H_2 and two equiv. of OH^- as indicated by pulse radiolysis study of H_2O.[46-49] The OH^- may be attached to SWCNT to produce $SWCNT(OH)^-$, which is oxidized by the hole of $SWCNT^{\bullet+}$ to afford $SWCNT(OH)^{\bullet}$, which may disproportionates to yield the dihydoxylated SWCNT [$SWCNT(OH)_2$], accompanied by regeneration of SWCNT.

$$\mathrm{SWCNT} \xrightarrow{2h\nu} \mathrm{SWCNT^{**}}$$

$$\mathrm{SWCNT^{**}} + \mathrm{H_2O} \rightarrow \mathrm{SWCNT^{\bullet+}} + \mathrm{e^-(H_2O)}$$

$$\mathrm{2e^-(H_2O)} \rightarrow \mathrm{H_2} + \mathrm{2OH^-}$$

$$\mathrm{SWCNT} + \mathrm{OH^-} \rightarrow \mathrm{SWCNT(OH)^-}$$

$$\mathrm{SWCNT^{\bullet+}} + \mathrm{SWCNT(OH)^-} \rightarrow \mathrm{SWCNT} + \mathrm{SWCNT(OH)^{\bullet}}$$

$$\mathrm{2SWCNT(OH)^{\bullet}} \rightarrow \mathrm{SWCNT} + \mathrm{SWCNT(OH)_2}$$

Scheme 3

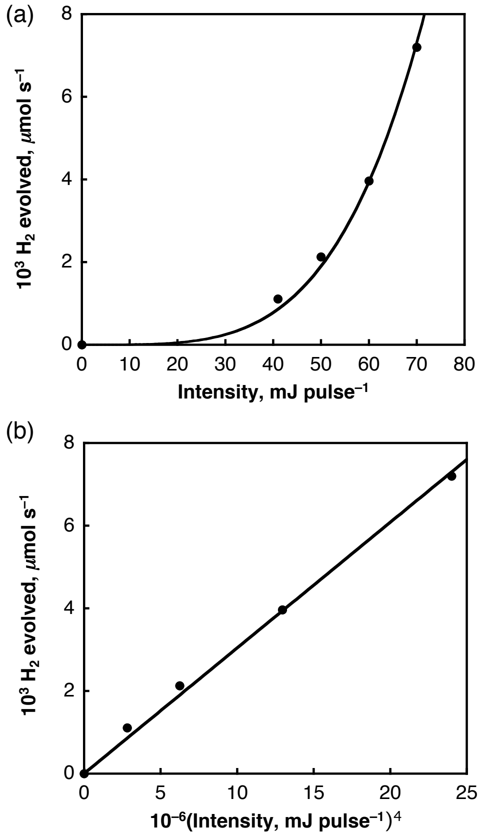


Fig. 13 (a) Plot of initial rate of H_2 evolved in H_2O vs laser power intensity at 532 nm; (b) Plot of initial rate of H_2 evolved vs the fourth power of laser intensity.

Conclusions

In conclusion, SWCNTs have been demonstrated to act as an efficient photocatalyst for H_2 evolution from benzene derivatives under laser irradiation. The TON was over 1 million based on one nanotube. The rate of H_2 evolution increased with increasing the laser intensity exhibiting the fourth-power dependence, because hydrogen was evolved via radical coupling of radical anions derived from benzene as the rate-determining step and benzene radical anion was produced by electron transfer from the doubly excited state of SWCNT to benzene, which requires two photons. The polymerisation of benzene induced by photogenerated $C_6H_6^{\bullet-}$ accompanied by H_2 evolution gains a leverage effect to increase the quantum yield of H_2 evolution as high as 130%, which is much larger than expected from the four-photon process (25%). Laser-induced H_2 evolution also occurred with SWCNTs in H_2O, exhibiting also the fourth-power dependence of the H_2 evolution rate. In this case, H_2 was evolved via the electron-transfer reduction of water by the doubly excited state of SWCNT, whereas SWCNT was oxidized to yield the dihydroxylated SWCNT. Metal-free laser-induced H_2 evolution from aromatic compounds and H_2O with SWCNTs found in this study paves a new way for efficient *pinpoint* hydrogen evolution, which may find various applications.

Experimental section

Materials

Chemicals were purchased from commercial source and used without purification. SWCNT (Synthetic method: arc plasma jet, diameter: 1.4 nm approximate length: 1 ~ 5 μm, percentage of carbon: >99%) was obtained from Meijo Nano Carbon, Japan. The solutions dispersed SWCNTs were prepared by ultrasonication (42 kHz, 125 W) for 5 min. Benzene was of spectral grade, obtained commercially and used without further purification. Deuterated benzene (C_6D_6, 99%) was obtained from Cambridge Isotope Laboratories, Inc., and used as received. Benzene was of spectral grade, obtained commercially and used without further purification. Benzonitrile was distilled over P_2O_5 in vacuo.[50] Mesitylene, *p*-xylene, chlorobenzene and 1,4-dimethoxybenzene were obtained commercially and used as received. Potassium ferrioxalate used as an actinometer was prepared according to the literature and purified by recrystallisation from hot water.[39] D_2 gas (99.5%) was commercially obtained from Sumitomo Seika Chemicals Co., Ltd. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore, Direct-Q 3 UV).

Reaction procedure

The photocatalytic hydrogen evolution was carried out by the following procedure. C_6H_6, C_6D_6 or benzene derivatives solutions (2.5 cm^3) containing SWCNT (0.15 mg) in a square quartz cuvette (10 mm i.d.) sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 5 min. The solution was then irradiated with a Nd:YAG laser (LS2134UTF) at λ = 532 nm with the power of 50 mJ $pulse^{-1}$ at room temperature. The gas in the headspace was analyzed using a Shimadzu GC–14B gas chromatograph (detector, TCD; column temperature, 50 °C; column, active carbon with 60–80 mesh particle size; carrier gas, N_2) to quantify the evolved hydrogen. The reaction solution was analyzed by a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 mass spectrometer to quantify produced biphenyl, and HPLC {detector, UV at λ = 280 nm (SPD-10A, Shimadzu); column, Shim Pack VP-ODS; eluent, CH_3CN: 0.40 mL min^{-1}, water: 0.10 mL min^{-1}} to qualify generated terphenyls. Hydrogen evolved in C_6D_6 after 2 h laser irradiation was detected using a Shimadzu GC-8A gas chromatograph [detector, TCD; column temperature, 77 K (liquid N_2); column, Hydro Isopack (2.0 m, 4.0 mm i.d., GTR TEC Co., Ltd.); carrier gas, Ne] to analyze H_2, HD and D_2 gases. In the case of measuring laser intensity dependence, a benzene solution (2.5 cm^3) containing SWCNT (0.15 mg) in a square quartz cuvette (10 mm i.d.) sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 5 min. The solution was then irradiated using a Nd:YAG laser (LS2134UTF) at λ = 532 nm with the various laser intensities (18 – 82 mJ $pulse^{-1}$) at room temperature. Amount of hydrogen evolved was analyzed at 10, 20 and 30 min using a Shimadzu GC–14B gas chromatograph.

Characterisation of SWCNT as a catalyst

Transmission electron microscope (TEM) images of SWCNT before and after 2 h laser irradiation (λ = 532 nm; 50 mJ $pulse^{-1}$; 10 Hz) in a benzene solution were measured using a JEOL JEM 2100 operating at 200 kV. TG data were recorded on a SII TG/DTA 7200 instrument. SWCNT, which were before and after reaction (~ 1 mg), were heated from 25 °C to 600 °C with a ramp rate of 2 °C min^{-1}. A certain amount of α-Al_2O_3 was used as a reference for DTA measurements. Raman spectra were obtained using a JASCO NR-1800 with a 514.5 nm Ar laser. IR spectra were recorded on a JASCO FT/IR-6200, using KBr pellets.

Quantum yield determinations

A standard actinometer (potassium ferrioxalate)[39] was used for the quantum yield determination of the hydrogen evolution from benzene with SWCNT. A square quartz cuvette (10 mm i.d.) that contained a benzene solution (2.5 cm^3) of SWCNT (0.15 mg) was irradiated using a Nd:YAG laser (LS2134UTF) at λ = 532 nm with the various laser power . Under the conditions of actinometry experiments, SWCNT absorbed essentially 100% incident light of λ = 532 nm. The light intensity of laser light of λ = 532 nm was determined as 6.5×10^{-9} einstein s^{-1} at 8.0 mJ $pulse^{-1}$. The photochemical reaction was monitored using a Shimadzu GC–14B gas chromatograph. The quantum yields were determined from amount of hydrogen evolved.

EPR measurements

The EPR spectra were measured on a JEOL X-band EPR spectrometer (JES-ME-LX) using a quartz EPR tube containing SWCNT (24 μg) dispersed in deaerated benzene (0.20 cm^3) by laser irradiation (λ = 532 nm; 40 mJ $pulse^{-1}$; 10 Hz) for 10 min at 77 K. The internal diameter of the EPR tube is 4.5 mm, which is small enough to fill the EPR cavity but large enough to obtain good signal-to-noise ratios during the EPR measurements. The amplitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The *g* values were calibrated with an Mn^{2+} marker.

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Notes and references

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† Electronic Supplementary Information (ESI) available: GC and HPLC analyses for products characterisation (Figures S1-S3 and S5), time course data of H_2 evolution in various solvents (S4), IR (S6), TG (S7) and experimental details (S8). See DOI: 10.1039/b000000x/

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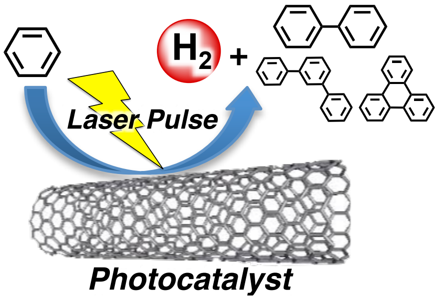
Graphical Abstract



Short Text for Graphical Abstract

Metal-free photocatalytic hydrogen evolution occurred efficiently in benzene containing SWCNTs under laser irradiation with an extremely high turnover number of 2,700,000 and a high quantum yield of 130%.