

# Synthesis of semiconducting SWNTs by arc discharge and their enhancement of water splitting performance with TiO<sub>2</sub> photocatalyst

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#### ABSTRACT

A feasible and scalable CO<sub>2</sub>-assisted arc discharge method was developed to directly synthesize single-walled carbon nanotubes (SWCNTs) with largely semiconducting species. Not only was electronic-type selectivity achieved on a large scale, with a semiconducting SWCNT (s-SWCNT) content of >90%, but also diameter selectivity was obtained, with a majority having diameters of >1.5 nm. The photo-catalytic water splitting performance of these SWCNTs with different ratios of s-SWCNTs to metallic single-walled carbon nanotubes (m-SWCNTs) was examined. The results show that, compared with m-SWCNTs, s-SWCNTs demonstrate a much better photocatalytic effect when used together with the common photo-catalyst TiO<sub>2</sub>.

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# 1. Introduction

Single-walled carbon nanotubes (SWCNTs) exhibit many fascinating electronic, chemical and mechanical properties with a wide range of applications [1]. SWNCTs can be semiconducting or metallic, depending on their geometrical structures. But the nature of as-prepared SWCNTs always comes as a mixture of metallic and semiconducting nanotubes, and this has been limiting their applicability for many proposed electronic devices. Therefore, it is highly demanded to obtain SWCNTs with a specific structural and electronic type. Post-treatment methods, including physical methods such as dielectrophoresis [2], gel chromatography [3] and density gradient ultracentrifugation [4] and chemical methods such as covalent [5–7] and noncovalent functionalization [8-10] have been employed to separate metallic SWCNTs (m-SWCNTs) and semiconducting SWCNTs (s-SWCNTs). Selective destruction of one type of nanotubes in a mixture

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is also carried out using gas-phase plasma treatment [11,12], light irradiation [13] or acid assisted microwave irradiation [14]. One of the main disadvantages for these post-treatment methods is that these methods always introduce significant defects on SWCNT structure, which causes their electronic and mechanical properties downgraded. Thus, it is highly demanded to obtain SWCNTs with desired structures at the stage of synthesis, that is, to synthesize SWCNTs with defined structures directly. Recently, great progress has been made using this approach, including selecting suitable carbon sources [15,16], plasma enhanced chemical vapor deposition (CVD) [17,18], ultraviolet (UV) irradiation during CVD [19], thermal annealing of the catalyst particles [20] and nanoengineering catalyst composites [21,22].

In this work, based on different reactivity of s-SWCNTs and m-SWCNTs, we have developed a feasible and scalable synthetic arcing method by introducing  $CO_2$  as a weak oxidant during the arc discharge process to directly react with

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m-SWCNTs. The results show that not only the selective growth of s-SWCNTs at large scale was achieved, but also the diameter distribution of these SWCNTs was narrowed. It was found that the semiconducting content, diameter and diameter distribution, electric conductivity as well as purity of the as-produced SWCNTs are all closely related to the concentration of CO<sub>2</sub> applied in the process. The high s-SWCNTs/ m-SWCNTs (S/M) ratio and diameter changes were also reflected in their photocatalytic water splitting.

## 2. Experimental

### 2.1. Synthesis of SWCNTs

The electric arc (EA) discharge apparatus and experimental conditions were similar to our work described earlier [23,24]. Consumable electrodes were 20 mm in diameter and 200–250 mm in length. All of the EA experiments were carried out under a flow He buffer gas mixed with 0–30 volume fraction (vol %) of  $CO_2$  at a total pressure of 530–550 Torr. Typical running time was 15 min, leading to the production of 1.2–6 g of as-prepared SWCNTs varied with different  $CO_2$  volume fractions, and very low yield of SWCNTs can be produced with  $CO_2$  higher than 40 vol % in the atmosphere.

### 2.2. Photoreaction

The photoreaction was carried out under Ar atmosphere in a quartz tube of 110 ml, maintaining the reaction mixture in suspension by a magnetic stirrer. A high-pressure mercury lamp (TMHHL 400 W GY-400) was used as the light source. The photo catalyst, a composite of  $TiO_2$  (Degussa P25)/SWCNTs, was synthesized as follows: 54 mg of Degussa P25 (P25) powder was added into a flask containing 51 ml Milli-Q water, and a series amount (varied from 0 to 30 wt.% of the weight of P25) of acid-purified SWCNTs [24] was put into 17 ml of methanol. Both the samples of SWCNT and P25 in the solvents were dispersed using ultrasonic bath, and then mixed together under ultrasonication again and pour into the quartz reaction tube. Prior to irradiation, the mixture was purged by Ar gas to degas air for ~30 min.

### 2.3. Characterization

UV-visible–NIR absorption spectra were collected on a Jasco V-570 spectrophotometer. Raman scattering studies were performed at room temperature with a Horiba Jobin Yvon LabRam HR800 spectrometer with 632.8 nm line from He–Ne laser and 514.5 nm line from an Ar<sup>+</sup> laser. Raman spectra were normalized by the G-band intensity and averaged from 6 random positions on each sample. Electrical conductivities were measured by a semiconductor parametric analyzer (Keithley 2612). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis was carried out using a NETZSCH STA 409PC in a mixture of 20% O<sub>2</sub> and 80% N<sub>2</sub>, with the heating rate of 2 K/min. Transmission electron microscopy (TEM) was performed using Philips T20ST electron microscope at acceleration voltage of 200 kV. The evolution amount of H<sub>2</sub> gas was measured with a gas chromatograph that uses a thermal conductivity detector (Shimadzu GC-9A).

### 3. Results and discussion

# 3.1. The effects of $CO_2$ concentration on the diameter control of SWCNTs

Depending on the volume fraction (vol %) of the CO<sub>2</sub> added in the atmosphere of He, a series of samples were obtained and denoted as  $C_0$  (represents pure He with 0 vol %  $CO_2$ ),  $C_{12}$ (12 vol %  $CO_2$  in the whole mixture of  $CO_2$  and He),  $C_{20}$ (20 vol % CO<sub>2</sub>), C<sub>25</sub> (25 vol % CO<sub>2</sub>), and C<sub>30</sub> (30 vol % CO<sub>2</sub>). Fig. 1a and b are typical high resolution transmission electron microscope (HRTEM) images of C<sub>0</sub> and C<sub>25</sub>, respectively. To evaluate the effect of CO<sub>2</sub> loading on SWCNT diameter distribution, a large number of HRTEM images were measured first. Based on these HRTEM image measurements, diameter distributions of each sample were obtained and showed in Fig. 1c (~150 SWCNTs measured for each sample). It was observed that the overall diameters of as-grown SWCNTs increased along with increasing of CO<sub>2</sub> volume fraction in the range from 0 to 25 vol %, but decreased from 25 to 30 vol %. Statistically, the diameters of over 80% SWCNTs synthesized at concentrations of CO<sub>2</sub> from 0 to 25 vol % is in a narrow range of  $1.3 \pm 0.3$ ,  $1.3 \pm 0.2$ ,  $1.4 \pm 0.2$ , and  $1.5 \pm 0.1$ , while extended to  $1.5\pm0.2\,nm$  in 30 vol % of  $CO_2,$  with the Gaussian means (d<sub>m</sub>) at 1.34, 1.35, 1.44, 1.52, and 1.48 nm, respectively, and the Full Width at Half Maximum (FWHM) of the Gaussian fit, which to some extent represents the diameter distribution, is 0.34, 0.27, 0.23, 0.22, 0.32 nm, respectively. These



Fig. 1 – Typical high resolution transmission electron microscope (HRTEM) images of (a) the pristine SWCNTs produced in pure He,  $C_0$  and (b) the pristine SWCNTs produced in 25 vol % CO<sub>2</sub>,  $C_{25}$ . (c) SWCNT diameter distributions of samples from  $C_0$  to  $C_{30}$ . Red solid lines show their Gaussian fits with means of 1.34, 1.35, 1.44, 1.52, and 1.48 nm, respectively; each sample was measured with 150 SWCNTs from their HRTEM images. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

results clearly indicate the trend that the diameters of SWCNTs increased with  $CO_2$  concentrations from 0 to 25 vol % and decreased then, and simultaneously, the distribution of diameters of these SWCNTs become narrowed first and then widened again from 25 to 30 vol %.

Similar trend was also observed from Raman spectra (Fig. 2). The diameters of SWCNTs were obtained using the semi-empiristic equation for the frequency of radial breathing mode ( $\omega_{\text{RBM}}$ ) of SWCNTs:  $\omega_{\text{RBM}} = 223.5/dt + 12.5$ , where dt is the diameter of SWCNT in nm and  $\omega_{\rm RBM}$  is the RBM frequency in cm<sup>-1</sup> [25]. To obtain more representative data from the view of statistical point for each sample, we averaged six individual Raman spectra, measured from six random different spots of the SWCNT sample. We can see clearly from Fig. 2a (excited with a laser line of 514.5 nm) and Fig. 2b (excited with a laser line of 632.8 nm) that the average diameters of SWCNTs gradually increased as the RBM bands downshifted from C<sub>0</sub> to C<sub>25</sub>, while decreased as the RBM peaks upshifted in C<sub>30</sub>. Estimated from the wavelength of the main RBM peaks using this equation, SWCNTs from  $C_0$  to  $C_{30}$  have main diameters of 1.27, 1.46, 1.49, 1.63 and 1.48 nm measured using the laser line of 632.8 nm, and 1.37, 1.44, 1.52, 1.67, 1.53 using the laser line of 514.5 nm, respectively. This is well in agreement with the above statistical analysis from HRTEM. Furthermore, there are more than two main peaks in the RBM regions of C<sub>0</sub>, however, after adding CO<sub>2</sub>, these main peaks gradually get narrowed. One interesting phenomenon we noted is that, with increasing of CO<sub>2</sub> in the synthesis, the D band (disorder band) in 1300  $\text{cm}^{-1}$  does not show a clear change, as observed with both two laser lines of 514.5 nm (Fig. 2a) and 632.8 nm (Fig. 2b).

The above data were summarized in Fig. 3. The average diameter of different samples obtained by TEM (Fig. 3a), as well as main diameters of SWCNTs gained from Raman with two laser lines, respectively (Fig. 3b and c), were all gradually enlarged with the increasing of  $CO_2$  concentration when below 25 vol %, and then, decreased from 25 to 30 vol %. In the mean time, the diameter distribution (in Fig. 3d) is narrowed down first and then broadened. This indicates that 25 vol % carbon dioxide is a relatively optimized condition, where SWCNTs with a lager diameter (>1.5 nm) but narrow diameter distribution can be produced.

# 3.2. The effects of CO<sub>2</sub> concentration on the electronic selectivity of s-SWCNTs

Raman scattering is a powerful tool, by which both the diameter-dependent resonance RBM located at a lower frequency and the tangential mode (G-band) at a higher frequency can provide important information about SWCNT structure characteristics [26]. Using Kataura plot, the ratios of m-SWCNTs and s-SWCNTs were studied with both 514.5 and 632.8 nm excitations [27]. The G-band feature for SWCNTs consists of two main components: one peaked at 1590 cm<sup>-1</sup> (G<sup>+</sup>) and the other one peaked at about 1570 cm<sup>-1</sup> (G<sup>-</sup>). The G<sup>-</sup> feature is associated with vibrations of carbon atoms along the circumferential direction of the SWCNT, and its peak shape is highly sensitive to whether the SWCNT is metallic (Breit–Wigner–Fano line shape) or semiconducting (Lorentzian line shape). Metallic SWCNTs can lead to downshift and broadening of the G<sup>-</sup> band peaks [28].

As well understood, Raman laser source with 632.8 nm resonates roughly equal population of both metallic and semiconducting SWCNTs for the diameter range from 1.2 to 1.8 nm, whereas the 514.5 nm laser excites semiconducting SWCNTs exclusively in this range [29,30] Indeed, as shown in Fig. 2a, no metallic species were detected in the RBM region for all samples when excited with 514.5 nm laser, this is also confirmed with the Lorentzian line shape (Fig. 2a) of the G<sup>-</sup> band. However, when excited with 632.8 nm laser radiation,



Fig. 2 – Raman spectra of samples prepared in different  $CO_2$  concentrations, from  $C_0$  to  $C_{30}$  (a) excited with a laser line of 514.5 nm and (b) excited with a laser line of 632.8 nm.



Fig. 3 – (a) Plots of average diameter by TEM, main diameters of different samples from Raman (b) with laser line of 514.5 nm, (c) with laser line of 632.8 nm, and (d) diameter distribution from the Gaussian fit described by FWHM, versus CO<sub>2</sub> volume fraction.



Fig. 4 – (a) RBMs and (b) relative G-band intensities of Raman spectra for pristine SWCNTs samples obtained, respectively, at a 632.8 nm excitation wavelength. (c) UV-visible–NIR absorption spectra of sodium dodecyl sulfate (SDS)-dispersed SWCNTs grown in different concentration of carbon dioxide normalized to the peak at 700 nm. The labels  $S_{11}$ ,  $S_{22}$  and  $S_{33}$  indicate the excitonic optical absorption bands for s-SWCNTs corresponding to the first, second and third one-dimensional van Hove singularities, respectively, and the  $M_{11}$  label corresponds to the first-order transition of m-SWCNTs.

C<sub>20</sub>

C<sub>25</sub>

C<sub>30</sub>

the SWCNTs prepared in the absence of CO<sub>2</sub> (C<sub>0</sub>) show multiple RBM bands in Fig. 4a along with a clear Breit-Wigner-Fano (BWF) line shape of G<sup>-</sup> band in Fig. 4b. Based on the revised Kataura plot, we assign the bands range from 120 to 160  $\mbox{cm}^{-1}$  to the semiconducting species (S33) and the bands range from 160 to  $230 \text{ cm}^{-1}$  to the metallic species (M<sub>11</sub>) [20,31,32]. As shown in Fig. 4a, the samples from  $C_{12}$  to  $C_{25}$ prepared in presence of CO<sub>2</sub> exhibit an enhanced intensity of the RBM band around 145 cm<sup>-1</sup> relative to the semiconducting band. Two metallic bands at 189 and 195 cm<sup>-1</sup> completely disappeared and the remained metallic band at around 165 cm<sup>-1</sup> was gradually suppressed with the increasing of CO<sub>2</sub> concentrations. This trend is further demonstrated in Fig. 4b, where the broad and asymmetric G<sup>-</sup> band, described as a BWF line shape and attributed to m-SWCNTs, almost vanished completely in C<sub>25</sub>. A much narrower G<sup>-</sup> band with a 35 cm<sup>-1</sup> up-shift is observed instead, providing further evidence for the substantial enrichment of s-SWCNTs in the 25 vol % CO<sub>2</sub> environment.

Using the areas of the peaks corresponding to s- and m-SWCNTs in Raman, we semi-quantitatively estimated [33] the ratio of the s- and m-SWCNTs under different arcing conditions. We set our pristine SWCNTs,  $C_0$ , which was produced in pure He, as the reference sample and assume that s-SWCNTs under such condition count 67% of the whole SWCNTs. RBM band peaks were first peak-fitted (Supplementary Information, Fig. S1) and then compared in area. The re-

Table 1 – Content of S-SWCN1s from Raman (632.8 nm) and UV-visible-NIR for as-produced SWCNTs.				
	Samples	Raman analysis	UV-visible-N	IIR analysis
		s-SWCNT content (%)	s-SWCNT content from S <sub>11</sub> /M <sub>11</sub> (%)	s-SWCNT content from S <sub>22</sub> /M <sub>11</sub> (%)
	C <sub>0</sub>	67	67	67
	C12	81	83	68

86

91

85

70

75

67

91

98

89

sults showed a same tendency as the above qualitative analysis, with the highest semiconducting percentage of >90% in sample  $C_{25}$ , where 25 vol %  $CO_2$  was used (Supplementary Information, Table S1).

We also performed UV-visible-NIR absorption [34] to estimate the semiconducting content in various SWCNT samples. Fig. 4c shows the UV-visible-NIR absorption spectra, normalized to the peak at 700 nm for better comparison, using SDS/D<sub>2</sub>O dispersed solutions of SWCNTs grown under different concentrations of CO<sub>2</sub>. Note the SWCNTs examined were all pristine SWCNTs without any chemical purification or treatment. The bands of S<sub>11</sub> (1400-2000 nm), S<sub>22</sub> (850-1200 nm) and S<sub>33</sub> (400-600) corresponds the first and second one-dimensional van Hove singularities, respectively, and the  $M_{11}$  (600–800 nm) band corresponds to the first-order transition of m-SWCNTs [32]. The broad band suggests that the samples for the spectra still contain SWCNT bundles. For sample C<sub>0</sub>, the peak envelopes, corresponding to intrinsic excitations of the  $S_{11}$ ,  $S_{22}$ , and  $M_{11}$  transitions, are clearly observed in the spectra, reflecting a mixture of semiconducting and metallic SWCNTs (Fig. 4c Co). However, as the concentration of  $\mbox{CO}_2$  increased from 0 to 25 vol %, the peaks of  $S_{11}$  and  $S_{22}$  are all simultaneously enhanced in intensity and narrowed in FWHM, and S33 become more obvious too, indicating an enrichment of semiconducting species and a narrowed chirality distribution. Similarly, the sample  $C_{30}$  showed a decrease in intensities for these semiconducting peaks, compared with that under 25 vol % CO<sub>2</sub> condition. These are all in well agreement with HRTEM and Raman results above.

We have also semi-quantitatively analyzed the semiconducting content for all samples based on their baseline-corrected UV-visible–NIR data (Supplementary Information, Table S2) [35,36]. Again, the sample  $C_0$  was set as the reference sample with a hypothetic S/M ratio of 2/1, corresponding to a semiconducting content of 67%. We estimated the semiconducting content based on two sets of data,  $S_{11}/M_{11}$  and  $S_{22}/M_{11}$  from the UV-visible–NIR absorption, respectively, and the results are summarized in Table 1, together with that from Raman. We found that these two sets of data both gave the same clear conclusion as the above qualitative analysis, that is, when the concentration of  $CO_2$  is increased from 0



Fig. 5 – (a) Photographs of films of SWCNTs deposited in He ( $C_0$ ), 20 vol % CO<sub>2</sub> ( $C_{20}$ ) and 25 vol % CO<sub>2</sub> ( $C_{25}$ ). Golden stripes above are post-deposited Au, and black layer below are deposited SWCNTs in glass substrates. (b) Current versus voltage (I–V) characteristics (with a normalized film thickness of 10  $\mu$ m).

to 25 vol %, the S/M ratio is increased simultaneously, while further increase of CO<sub>2</sub> concentration lead to a decrease in S/M ratio. However, they vary in the absolute degree of semiconducting enrichment, and results from  $S_{11}/M_{11}$  showed higher semiconducting contents than those from  $S_{22}/M_{11}$ . From this table, we can also see that the results from  $S_{11}/M_{11}$  are in better accordance with the Raman results.

Table 2 – Resistivity of in situ deposited films of SWCNTs.				
Films	Resistivity/(Ω cm)			
C <sub>0</sub> C <sub>20</sub> C <sub>25</sub>	2.10 4.01 151.2			

# 3.3. Conductivity of SWCNTs

We have also studied the conductivity of the SWCNTs produced under different conditions. The samples for the conductivity measurement were taken as films of SWCNTs, deposited in situ on glass substrates in the arcing chamber directly, and then Au stripes were deposited on the films (all with the same dimensional size of  $1 \times 2.5$  cm) as the electrodes (Fig. 5a) for measurement. Fig. 5b depicts the current–voltage (I–V) traces for those films, and the film thicknesses were normalized to 10 µm for comparison. As shown in Fig. 5b, the conductivities of the SWCNTs produced with higher CO<sub>2</sub> concentrations decreased significantly, indicating enriched s-SWCNTs under such conditions. For example, the average resistivity of the film  $C_{25}$  is about 151.2  $\Omega$  cm (Table 2), which is 72 times



Fig. 6 – (a) TGA analysis in a mixture of 20% O<sub>2</sub> and 80% N<sub>2</sub>, showing weight (solid lines) and DSC (dotted lines) with respect to temperature for the soot part of the pristine SWCNTs prepared with varying CO<sub>2</sub> concentrations in a He atmosphere. Heating rate is 2 K/min. Typical TEM of SWCNTs samples (b) C<sub>0</sub> (crossbar is 20 nm to better see amorphous carbons around SWCNTs), (c) C<sub>12</sub>, (d) C<sub>20</sub>, (e) C<sub>25</sub> and (f) C<sub>30</sub>, crossbars are 10 nm.

larger than that of  $C_0$  (2.10  $\Omega$  cm). This clearly is in line with the results observed from Raman and UV-visible–NIR.

### 3.4. Thermogravimetric analysis

Fig. 6a shows the TGA of the as-prepared SWCNTs grown under different concentrations of  $CO_2$ . The dotted line (DSC) shows two peaks at about 340 and 410 °C. The first peak is usually associated with amorphous carbon and the second one with SWCNTs [29,37]. The TGA results showed that, with the increasing ratio of  $CO_2$ /He, the first peak of the DSC decreases significantly, indicating that the production of SWCNTs have less amorphous carbon as the  $CO_2$  concentration increases, in agreement with that from TEM studies (Fig. 6b–f). We also noted that the metal catalyst impurity could be removed more easily for the SWCNTs produced with  $CO_2$ . This is probably due to the thick carbon layer coated around the metal catalyst being partially removed by  $CO_2$  in the synthesis process [34].



Fig. 7 – Plots of the evolution rate of  $H_2$  gas versus the SWCNT content to TiO<sub>2</sub>. The composite catalyst was prepared by blending of different loading of SWCNTs with TiO<sub>2</sub>. TiO<sub>2</sub> amount was kept at 54 mg for all cases. The P25/C<sub>25</sub> composite (red line with open circle) always gave higher  $H_2$  evolution rate than the P25/C<sub>0</sub> composite (blue line with open triangle) with the same SWCNT loading. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

# 3.5. Mechanism and discussion

There may be several reasons behind the selectivity observed in this work. Considering the oxidation feature of CO2 (Boudouard reaction (CO<sub>2</sub> + C  $\rightarrow$  2CO)), it is reasonable to assume that CO<sub>2</sub> would react selectively with some of the carbon material in the chamber. First, it has been well known that m-SWCNTs is more reactive than s-SWMTs, and SWCNTs with smaller diameters are more reactive than the SWCNTs with larger diameters, due to their more-abundant electroncharge density at the Fermi level or small radius of curvature that have higher strain in the C-C bonding configuration than their semiconducting or larger diameter counterparts [6,30,38]. Thus, m-SWCNTs or SWCNTs with smaller diameter may be etched away by  $CO_2$  in some extent. Second, considering the lower resistance of amorphous carbon to oxidation than that of SWCNTs, we believe that the Boudouard reaction (CO<sub>2</sub> + C  $\rightarrow$  2CO) likely occurring in the vicinity area of the EA acing might be the reason to reduce the amorphous carbon over-coated on SWCNTs and the metal particles. So it is reasonable to argue that CO<sub>2</sub> would burn away the amorphous carbon over-coated on the "poised" metal catalyst nano particles, which would increase the catalyst lifetime and also make the subsequent purification steps easier. Moreover, it looks like there is an optimized concentration of CO<sub>2</sub> for the selective growth, as plays an important role too. It was found that, only under certain critical value of CO<sub>2</sub> concentration (in our case 25 vol %), can the above different reaction activity of SWNTs dominate and lead to selective growth of s-SWNTs. Because, when the concentration of CO<sub>2</sub> further increased to above the critical value, even large diameter s-SWCNTs can be etched away by the abundant CO<sub>2</sub> in the atmosphere, thus the selectivity decreased as observed when 30 vol % CO<sub>2</sub> was used.

### 3.6. Photocatalytic water splitting

The unique electrical and electronic properties, wide electrochemical stability window, and high surface area render SWCNTs as scaffolds to anchor light-harvesting assemblies [39,40]. Recently, the composites of carbon nanotubes (CNTs) and TiO<sub>2</sub> have been reported to show photocatalytic enhancement [41,42], and several mechanism were proposed for this



Fig. 8 – (a) Photoinduced electron transfer between an excited  $TiO_2$  nanoparticle and SWCNT and charge equilibration. (b) One-dimensional density of states of semiconducting SWCNTs (red) and metallic SWCNTs (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

enhancement [43,44]. Among these studies, SWCNTs/TiO<sub>2</sub> are of greater importance since the electronic properties of SWCNTs are better defined than multiwalled CNTs, which will allow for better understanding of the proposed mechanisms. So far, no study has been done for the possible different behavior of semi and metallic SWCNTs in photocatalyst. With the scaled synthesis of different ratios for s-SWCNTs/ m-SWCNTs in hand, we thus prepared and used the composites of different SWCNTs,  $C_0$  and  $C_{25}$ , with a commercial TiO<sub>2</sub> (P25, Degussa) as the photocatalyst to study their water splitting performance. The composite photocatalyst was prepared using a simple blending method.

Fig. 7 shows the amount of hydrogen evolution under 1 h irradiation of UV-vis light. Firstly, for all different SWCNTs, with the increased loading of SWCNTs, the photo-catalytic activity of composites of TiO2/SWCNTs is at first increased and then decreased, in consistent with the literature [45]. Secondly, with the same loading of SWCNTs, the hydrogen evolution rate is always higher for the catalyst when using C<sub>25</sub> with more s-SWCNTs compared with the cases when using Co (Table S3). For example, with 10 wt.% loading, when the SWCNTs of C<sub>25</sub> was used, the hydrogen evolution rate reaches 2.0  $\mu$ mol h<sup>-1</sup>, 2.2 times of that when using C<sub>0</sub> (0.9  $\mu$ mol h<sup>-1</sup>). Note the hydrogen evolution rate is only 0.6  $\mu$ mol h<sup>-1</sup> when pure pristine P25 was used. Furthermore, the best performance using C25 happens at 10 wt.% SWCNT loading, and that for C<sub>0</sub> SWCNTs, it happens at 20 wt.% loading. These results clearly indicate that s-SWCNTs and m-SWCNTs have very different enhancement for the water splitting with TiO<sub>2</sub>, though both types of SWCNTs increase TiO<sub>2</sub> photocatalytic activity.

To understand the mechanism behind the enhancement of SWCNTs, an illustration of the electron transfer between a photoexcited TiO<sub>2</sub> nanoparticle and SWCNT is shown in Fig. 8a. After TiO<sub>2</sub> absorb photon, the generated excited electron and hole need to be separated and transferred to the surface of TiO<sub>2</sub>, to react with corresponding water or sacrificial agents. The work function of SWCNT bundles containing both s-SWCNTs and m-SWCNTs is about 4.8 eV [46]. When SWCNTs were added, charge transfer (electron) from TiO<sub>2</sub> conduction band ( $E_{CB} = 0.5 V$  versus normal hydrogen electrode (NHE)) to SWCNT conduction band ( $E_{CB} = 0.3$  V versus NHE) is therefore energetically favorable for all types of SWCNTs [47]. This would facilitate the overall charge separation and thus improve the water splitting efficiency. For the cases when s-SWCNTs were used, as shown in Fig. 8b, we argue that more allowable transitions from van Hove singularities of s-SWCNTs than m-SWCNTs between the conduction band and valance band of TiO<sub>2</sub> make s-SWCNTs more favorable for the charge transfer. Another possibility is that these van Hove singularities may work as mid-gap bands, causing the possible multi-electron-hole pairs (excitons) generation to occur, by absorption of single high energy photons in the UV region across these multiple low energy band gaps [48].

### 4. Summary

A  $CO_2$  assisted selective growth method for large diameter semiconducting enriched SWNTs was developed. It was found that the semiconducting content, diameter and diameter distribution, electric conductivity as well as purity of the

as-produced SWCNTs are all closely related to the concentration of the CO<sub>2</sub> applied in the method. When the concentration of  $CO_2$  is gradually increased from 0 to 25 vol %, the semiconducting content, their diameters and purity of the as produced SWCNTs are all gradually increased, while the diameter distribution narrowed down and the electric conductivity is simultaneously decreased. The produced SWCNTs in optimized condition show more uniform structure (>90% s-SWCNTs) with large diameter (>1.5 nm). The simplicity of this method, together with its large scale productivity, makes this method capable for some applications when s-SWCNTs are required or preferred. Photocatalytic water splitting results using these SWCNTs with TiO2 show that s-SWCNTs have much better photocatalytic enhancement than m-SWCNTs, probably due to different van Hove singularities of s-SWCNTs compared to m-SWCNTs.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2011.06.097.

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