

# Surface Modification of Single-Wall Carbon Nanotubes (SWCNTs) by Photo-Initiated Chemical Vapor Deposition (PICVD) Using Syngas

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## ABSTRACT

The commercial use of single-wall carbon nanotubes (SWCNTs) in biological applications can be limited by their cytotoxicity. Their inherent hydrophobicity has been identified as an important cytotoxic parameter, along with their high aspect ratio, size and surface energy, the latter of which needs to be modified for certain applications. To address the issue of surface energy, the primary objective of the present study is to add functional groups to the SWCNTs' surfaces to bring about superhydrophilic and superhydrophobic wetting properties. Functionalization by photo-initiated chemical vapour deposition (PICVD) is proposed, using syngas as an affordable and versatile gas precursor. Following PICVD surface treatment, water contact angle measurements show that a wide range of surface energy can be attained, ranging from superhydrophilic (<5°) to superhydrophobic (>150°) behaviour. X-Ray photoelectron spectroscopy (XPS) confirms the functionalization by oxygen containing groups.

**Keywords:** Carbon nanotubes, Photo-initiated chemical vapor deposition, Syngas, Functionalization, Surface energy.

## 1 INTRODUCTION

Carbon nanotubes (CNTs) have various properties such as high mechanical and electrical conductivity, remarkable thermal stability (up to 2800 °C under vacuum) [1, 2] and the highest Young's modulus among all different types of composites and nano-materials (higher than 1-5 TPa) [1, 3]. These individual properties make them promising candidates for a wide range of applications such as biotechnology, aerospace, biomedicine and tissue engineering, to name only a few. These materials have also shown potential to be used in bone applications due to their similarities with triple helix collagen fibrils in terms of size and shape (diameter of SWCNTs ranges between 0.7-1.5 nm) [4]. Not only do these materials promote the mechanical properties of biomaterials (polymers), but they also stimulate bone regeneration and, consequently, can accelerate the healing process [4]. Therefore, they may be effective for use in different bone substitutes, such as scaffolds and fillers.

Despite all the individual properties and potential for

biomaterials, CNTs have been also identified as cytotoxic when in contact with cells in several studies due to their inherent properties, such as their high aspect ratio, hydrophobicity, impurities and surface energy [5]. Inherent hydrophobicity and insolubility are the most challenging features that need to be addressed to resolve the cytotoxicity issues, as well as allow use in other fields. Various techniques have been reported to solve these problems such as surfactants, oxidation, sonication and functionalization [1], among which functionalization has been known as a promising approach [1].

Functionalization techniques can be classified into two groups: solvent chemistry and gas-phase methods. Solvent-based approaches suffer from multi-step and complex preparation methodologies [6]. It was also shown that these techniques damage the structure of CNTs [7]. Gas-phase surface modification techniques can be classified into several methods according to the energy source applied for reaction initiation including Plasma-enhanced Chemical Vapor Deposition (PECVD), Thermal-activated CVD (TACVD) and Photo-initiated CVD (PICVD). Among the current methods to functionalize nanomaterials, PICVD has been identified as the best method for this matter because of affordable cost due to the simple procedure, lack of vacuum, ability to adjust the desired degree of functionalization, near-atmospheric working pressure and high efficiency due to low energy consumption [6, 8]. The quality and quantity of deposition films can also be adjusted by operational parameter easily in comparison to other CVD techniques [9]. Both hydrophilic and hydrophobic surfaces can be produced easily on different geometries by this method by altering the precursor composition and operating pressure (+/-20 kPa with respect to atmospheric pressure) [8].

In this study, we propose an affordable and novel method, which is photo-initiated chemical vapor deposition (PICVD), to functionalize single wall carbon nanotubes (SWCNTs) developed at Polytechnique Montreal's Photochemical Surface Engineering Laboratory group (PhotoSEL).

## 2 MATERIALS AND METHODS

### 2.1 Materials

SWCNTs grown by radio frequency induction thermal plasma were purchased from Raymor-NanoIntegris

(Quebec, Canada); Hydrogen peroxide (3% (w/w)), Nitric acid (TraceMetal™ grade, 67% (w/w)), Methyl Alcohol ( $\geq 99.8\%$  (v/v)) and Ethyl Alcohol (90%  $\pm 1\%$  (v/v)) were purchased from Fisher Scientific (Montreal, Quebec). Syngas (CO (T-44) and H<sub>2</sub> (T-30) Air Liquide, chemically pure) and Argon (T-50, Air Liquide, 99.99%), was used as the functionalization precursor and deaeration inert gas, respectively. Two 96 cm-long UVC germicidal lamps (UVC germicidal lamps model of T-97505-80: Cole-Parmer Inc) were used for all experiments.

## 2.2 Purification Method for SWCNTs

To purify SWCNTs, the multi-step protocol developed by Kim et al. (2009) was followed [10]. Briefly, in the first step, raw-SWCNTs were annealed at 350 °C under in air for 1 h. In the second step, 301 mg of air-oxidized SWCNTs were refluxed in 270 mL of 7 M nitric acid for 6 h at 106 °C. The samples were then cooled at room temperature. In the third step, the samples were centrifuged at 3500 rpm for 15 minutes. Centrifugation was repeated 8 times. In each centrifugation period, supernatants were poured out and sediments were suspended with deionized water. In the fourth and final step, vacuum filtering through a 0.2  $\mu\text{m}$  pore size Millipore polycarbonate membrane was used to obtain bucky paper [10].

## 2.3 PICVD Setup

As shown in Figure 1, a PICVD reactor used consists of two UVC lamps with a peak emission wavelength at 253.7 nm and an intensity of  $8.02 \times 10^3 \mu\text{W}/\text{cm}^2$  at a distance of 4.5 cm, a 25 mm-diameter (internal) quartz tube reactor. A syringe pump was used for H<sub>2</sub>O<sub>2</sub> injection and Brooks (series 5850E) mass flow controllers were used to inject precursors (CO and H<sub>2</sub>). A centralized vacuum system was applied for working at sub-atmospheric pressure (down to -20 kPa).

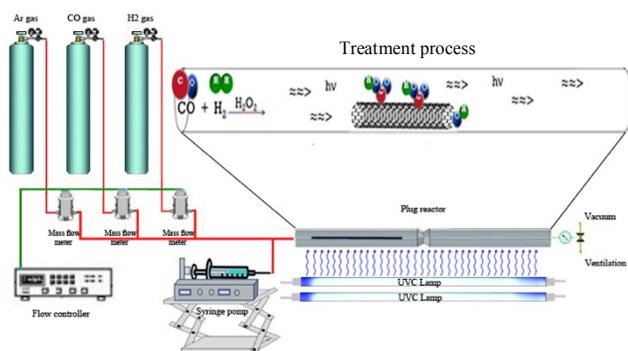


Figure 1: Schematic of PICVD setup.

## 2.4 Sample Preparation

15 mg of purified SWCNTs were dispersed in 10 mL of ethanol by bath sonication for 30 minutes (FS110, Fisher

Scientific, power level of 135 W). 400  $\mu\text{L}$  of dispersed SWCNTs were immediately deposited upon a glass substrate and placed in a vacuum oven for more than 3 h at a temperature of 100 °C to completely evaporate the ethanol.

## 2.5 Surface Modification

The method developed by Dorval Dion et al. has been used [8]. Accordingly, prepared samples were placed inside the quartz reactor. The reactor was closed and sealed. After passing argon for two minutes at a rate of 3 L/min in order to deaerate the reactor, CO and H<sub>2</sub> precursors (with the total flow rate of 27.4 sccm) were introduced at various ratios as per Table 1. H<sub>2</sub>O<sub>2</sub> was injected simultaneously via the syringe pump as radical photo-initiator (PI) at a rate of 1  $\mu\text{L}/\text{s}$ . According to the desired surface functionality, the process can be implemented under pressure (+20 kPa) or slight vacuum (-20 kPa). Hydrophilic surfaces are typically obtained under slight vacuum while hydrophobic surfaces are achieved under pressure (or +10 up to +20 kPa), based on previous work with copper [8]. The samples functionalized under pressure were positioned 82 cm from the inlet of the reactor while this distance for the samples functionalized under vacuum was 16 cm from the inlet of the reactor.

## 2.6 Experiment Design

Four independent variables, including precursor ratio (CO/H<sub>2</sub>), pressure, treatment time, and use of PI were studied. The experiments were carried out in both pressure (between +10 to +15 kPa) and slight vacuum (between -10 and -15 kPa) in an effort to achieve superhydrophobic and superhydrophilic surfaces, respectively. Table 1 shows different experimental conditions.

Exp#	H <sub>2</sub> flow (sccm)	CO flow (sccm)	Ratio (CO/H <sub>2</sub> )	H <sub>2</sub> O <sub>2</sub> (PI)	Pressure (kPa)	Time (Min)	CA After*
1	9.5	17.9	1.88	Yes	+10	60	153 $\pm$ 3°
2	9.5	17.9	1.88	Yes	-10	60	0°
3	9.5	17.9	1.88	Yes	+15	75	154 $\pm$ 2°
4	9.5	17.9	1.88	Yes	-15	75	2 $\pm$ 2°
5	9.5	17.9	1.88	No	+10	60	139 $\pm$ 5°
6	9.5	17.9	1.88	No	-10	60	115 $\pm$ 1°
7	9.5	21.4	2.25	Yes	+10	60	169 $\pm$ 5°
8	9.5	21.4	2.25	Yes	-10	60	70 $\pm$ 4°

\* After treatment by PICVD

Table 1: Experimental treatment conditions and effect on contact angle (CA). Experimental error shown represents standard deviation.

### 3 RESULTS AND DISCUSSION

#### 3.1 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM-JEOL model JEM2100F) was used to investigate the efficiency of purification protocol and morphology of SWCNTs. TEM grids used to characterize the samples were coated with a Lacey carbon film (D20040 Grids with formvar substrates mesh 400, metal Cu; D20045 Grids with formvar substrates mesh400, metal Ni-SOQUELEC International). Treated SWCNTs were dispersed in methanol (1 mg/mL). TEM grids were immersed in this suspension and, after drying, were placed in the TEM to be characterized. Figure 2 shows micrographs of SWCNTs before and after purification. As can be seen in Figure 2A, most of the impurities in raw-SWCNTs (R-SWCNTs) include amorphous carbon, catalytic metal nanoparticles and graphitic carbon while these impurities are significantly decreased after purification (Figure 2B).

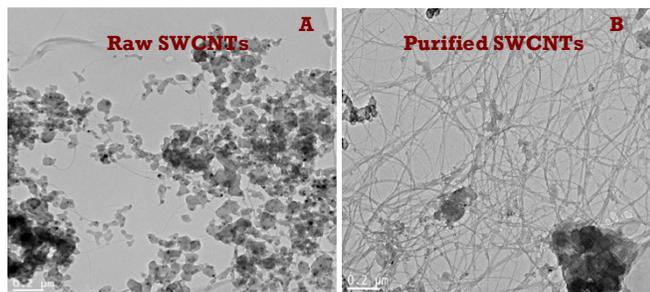


Figure 2: TEM image of A) R-SWCNTs, B) purified SWCNTs (P-SWCNTs).

#### 3.2 Contact Angle Measurement (CA)

Surface wetting was assessed through sessile drop contact angle measurements (tensiometer ODG 20AMP) by adding 2  $\mu$ l deionized water to surfaces covered with R-SWCNTs, P-SWCNTs and treated SWCNTs (T-SWCNTs) (Figure 3). The average contact angle of R-SWCNT and P-SWCNT samples was  $139\pm 2^\circ$  and  $79\pm 2^\circ$ , respectively while this value for T-SWCNTs under vacuum was less than  $5^\circ$  (Exp#2 and #4), proving the capability of PICVD to make SWCNT surfaces superhydrophilic. T-SWCNTs under higher pressure (Exp#1, #3 and #7) presented contact angle of more than  $159^\circ$  which shows ability of PICVD to make superhydrophobic surfaces (Table 1). By comparison of Exp#7 and #8, which had the ratio of 2.25, and Exp#5 and #6, we can understand that by increasing CO, the samples became more hydrophobic. The effect of PI ( $H_2O_2$ ) addition is readily observed by comparing Exp#5 and #6 (no PI) to Exp#1 and #2 (with PI): the desired effect on wettability requires the addition of PI.

In addition, T-SWCNTs which showed superhydrophilic

properties (CA lower than  $5^\circ$ ) were dispersed in deionized water (polar solvent) at a concentration of 0.05 g/mL. Superhydrophobic SWCNTs were similarly dispersed in toluene (non-polar solvent). After sonicating for 30 minutes in a water bath, the samples were allowed to settle. Untreated SWCNT samples from areas not reached by the PICVD treatment settled out, while true T-SWCNTs remained in suspension. Sediments were removed through decantation and the supernatants remained stable for 24 h. There was a significant difference between dispersion of T-SWCNTs and R-SWCNTs in water. T-SWCNTs under vacuum could easily disperse in water even by hand shaking, whereas R-SWCNTs could not disperse at all.

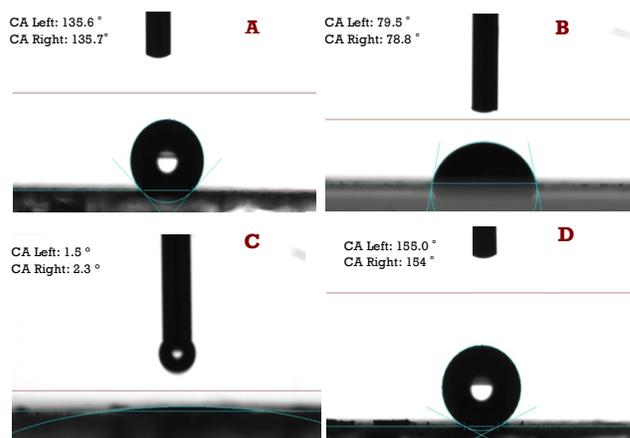


Figure 3: Contact angle measurement obtained by tensiometry A) R-SWCNT, B) P-SWCNT, C) T-SWCNT by PICVD under vacuum (Exp#4), D) T-SWCNT under pressure (Exp#3).

#### 3.3 X-Ray Photoelectron Spectroscopy (XPS)

Full surveys for all samples were obtained by X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 3 MKII) (Figure 4). Mg  $K\alpha$  is used as a source of X-ray with a pass energy of 100 eV and energy step size of 1.0 eV for survey scans. The relative atomic percent in XPS survey graphs, presented in the inset to Figure 4, show that ratio of oxygen to carbon of P-SWCNT increased compared to R-SWCNT. This increase was due to oxidation of SWCNTs by acid used for their purification [11]. This ratio was further increased in the case of T-SWCNT, which may be because of successful deposition of oxygen-containing groups on the SWCNT surface by PICVD. High resolution XPS data has been collected to obtain further information.

Figure 5 shows high-resolution C1s and O1s spectra of P-SWCNTs and T-SWCNTs, which were obtained by pass energy of 20 eV (Mg  $K\alpha$ ) and energy step size of 0.05 eV. The C1s fitting was performed as described by Yang and Sacher [12]. Sensitivity factor (SF) was used according to Wagner table for the mentioned elements. C1s peak in T-SWCNTs (Fig. 5B, Left column) can be deconvoluted into

6 components: A) 284.6 eV (35.7%), corresponding to C=C ( $sp^2$ ), B) 285.7 eV (5.1%), corresponding to C=C ( $sp^2$ ) with defect and C-C ( $sp^3$ , or possibly Fe-O-C), C) 286.5 eV (3.0%), assigned to C-O, D) 288 eV (2.1%), assigned to C=O and  $\pi \rightarrow \pi^*$  of C=C with defects, E) 289.0 eV (2.9%), corresponding to O-C=O, and F) 291.3 eV (1.4%), assigned to  $\pi \rightarrow \pi^*$  of C=C highly delocalized. O1s peak in T-SWCNTs (Fig. 5B, Right column) can also be deconvoluted into 3 components: A) 529.8 eV (29.2%), corresponding to O-Fe, B) 531.5 eV (16.8%), assigned to Fe-OH and O=C, and C) 533.0 eV (3.8%), corresponding O-C. According to the high resolution XPS, the real ratio of oxygen to carbon for R-SWCNTs, P-SWCNTs and T-SWCNTs were 0.03, 0.22 and 0.18, respectively. Based on these ratios, although oxygen functional groups increased, most of the oxygen was attached to Fe instead of carbon. Deposition of iron on the SWCNT surface can be attributed to the presence of iron pentacarbonyl in the CO tank [13].

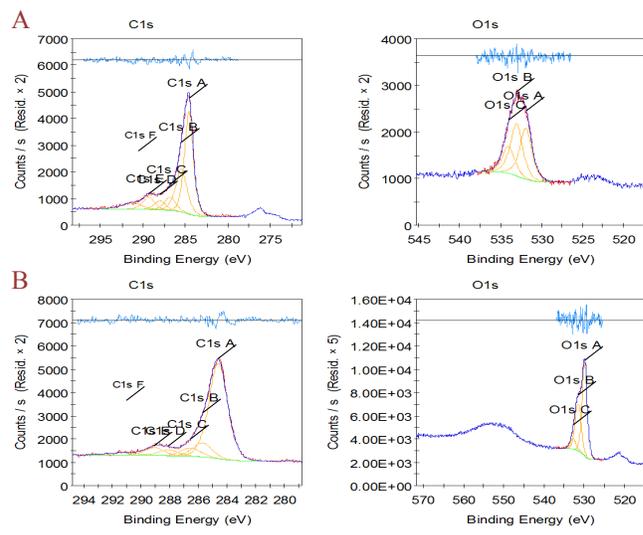


Figure 5: High resolution C 1s (left column) and O 1s spectra (right column) of (A) P-SWCNTs and (B) T-SWCNTs under vacuum.

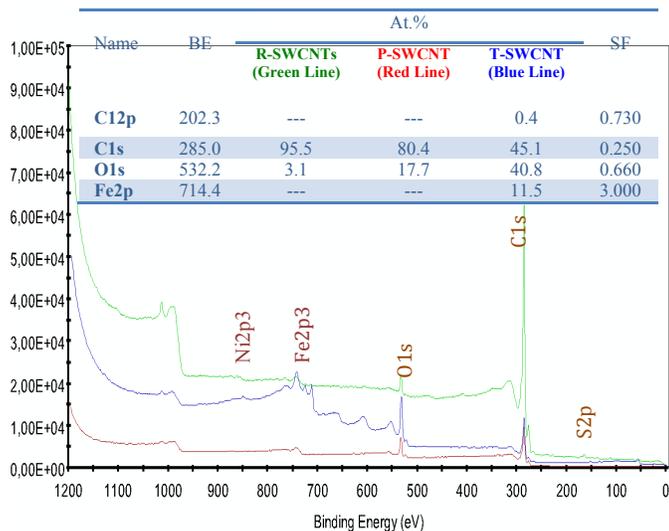


Figure 4: X-ray photoelectron spectroscopy (XPS) spectra for: Green Line) R-SWCNTs, Red Line) P-SWCNT and Blue Line) T-SWCNT.

### 3.4 Stability of T-SWCNTs

Instability of polymeric films, ageing, in which surface energy of materials reduced is one of the most important challenges for gas-phase functionalization methods [6]. Ageing is dependent on some parameters such as – absorption of contaminations, reorientation and reconstruction of dangling groups on the surface. This can increase the cytotoxicity of SWCNTs functionalized by the PICVD method over time. To investigate stability of modified surfaces, the contact angle for treated samples under vacuum and pressure was reassessed over time – hydrophobic samples remained at  $151 \pm 2^\circ$  after 7 days, while hydrophilic samples increased to  $5^\circ$ .

## 4 CONCLUSION

We successfully fabricated functionalized SWCNTs with both superhydrophilic and superhydrophobic behaviours using PICVD with a syngas precursor. We investigated functionalization physically and chemically by contact angle measurement and XPS, respectively. Both characterization demonstrated successful treatment and have validated the applicability of PICVD to form various oxygen-containing groups.

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