



# Total re-establishment of superhydrophobicity of vertically-aligned carbon nanotubes by CO<sub>2</sub> laser treatment

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## ABSTRACT

Total restitution of original superhydrophobicity of vertically-aligned multi-walled carbon nanotubes (VACNT) was achieved by CO<sub>2</sub> laser treatment. Superhydrophobic VACNT films obtained by microwave plasma chemical vapour deposition (MWCVD) were pre-treated with oxygen plasma to convert them in superhydrophilic films. Treatments with CO<sub>2</sub> laser at different powers were carried out on the superhydrophilic films for controlling of wettability. Changing in both surface energy and roughness of the VACNT films, was evaluated by contact angle measurement and atomic force microscopy images, respectively.

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## 1. Introduction

Liquid-repellent surfaces are attractive for microfluidic applications in biotechnology [1] and industry [2]. Various phenomena, such as surface contamination, oxidation and conduction, are expected to become controllable by the superhydrophobicity [3].

Superhydrophobic surfaces can be obtained by two ways: (a) creating roughness on a hydrophobic surfaces (contact angle >90°) [4–6], or (b) changing surface energy by attachment of chemical groups [7–10]. A surface is called hydrophilic when it is wettable by water or other polar liquids, while hydrophobic surfaces are wettable by non-polar substances.

Films made of vertically-aligned multi-walled carbon nanotubes (VACNT) produced by different techniques can present hydrophobic character. Li et al. [8] reported that the VACNT films coated with fluoroalkylsilane have a high contact angle with water (163.4°). Lau et al. also prepared a stable and superhydrophobic surface with a thin and conformal coating of polytetrafluoroethylene [5]. The effect of the roughness of VACNT films on the wettability is similar to lotus leaves, because of double structured roughness [8] and it has been theoretically explained by Patankar [11]. Cassie and Baxter [12] had to build a pattern with spatial regularity to achieve such characteristics. Therefore, nanotube aligning is considered an important factor for their superhydrophobicity, since they form surfaces with structured roughness.

In this work, we have produced superhydrophobic surfaces from superhydrophilic VACNT films, using CO<sub>2</sub> laser irradiance. This treatment, although it brings slight changes on the surface roughness, promotes the total re-establishment of the surface energy. The systematic study of the wettability with liquids of different polarities and by atomic force microscopy (AFM) pointed out that surface polarity of VACNT films is more important than roughness to warranty the superhydrophobicity of VACNT films.

## 2. Experimental details

Samples were produced as thin film, using a microwave plasma chamber at 2.45 GHz (MWCVD) [13]. The substrates were 10 mm Ti squares, covered by a 10 nm Ni layer, which was deposited from e-beam evaporator. The metallic layer was pre-treated to promote formation of nanoclusters, where VACNTs were nucleated. A pre-treatment was carried out during 300 s in plasma of N<sub>2</sub>/H<sub>2</sub> (10/90 sccm). After pre-treatment, CH<sub>4</sub> (14 sccm) was inserted in the chamber at 750 °C for 60 s. External heating by Ni–Cr heater (5.3 Ω m<sup>-1</sup> resistivity) under substrate holder was necessary to keep the substrate temperature. The chamber (reactor) was kept at a pressure of 40 × 10<sup>2</sup> Pa during whole deposition process. The samples were treated in a pulsed direct current (DC) oxygen plasma reactor [14] (oxygen pressure of 8 × 10<sup>3</sup> Pa, 700 V, during 120 s) to convert as-grown VACNT films to hydrophilic surfaces [15].

Superhydrophobic VACNT films were produced by irradiation of hydrophilic samples obtained by the oxygen plasma treatment [16,17] with CO<sub>2</sub> laser (Synrad Model J48). The laser beams was guided by 2 mirrors and irradiated selected areas of the sample, in N<sub>2</sub> atmosphere.

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**Table 1**  
Surface energy and viscosity parameters of the liquids used in the experiment.

Liquid probe	$\gamma$ (mJ m <sup>-2</sup> ) <sup>a</sup>	$\gamma^d$ (mJ m <sup>-2</sup> )	$\gamma^p$ (mJ m <sup>-2</sup> )	Viscosity (mPa s) <sup>a</sup>
Di-iodomethane	50.8	48.5	2.3	2.762
Polyethylene glycol (PEG)	48	29	19	21.81
Glycerol	63.4	37	26.4	1067.3
Water	72.8	21.3	51	1.00

<sup>a</sup> Values for surface tension and viscosity are all at 20 °C.

Laser irradiances of 15, 25, 35 and 50 kW cm<sup>-2</sup> were tested, with 20 scans at speed of 1 m s<sup>-1</sup> and beam diameter of 300 μm.

For evaluating the surface energy of as-grown and treated-VACNT films, the contact angle (CA) was measured by a Krüss Easy Drop system in sessile drop method, in atmospheric environment. Measures were taken immediately after liquid has been dropped, to avoid perturbation by evaporation. The average CA value was acquired by measuring at three different positions of each sample. A water droplet with a volume of ~3 μL was ejected from a dispensing needle and placed on top of the samples. The superhydrophobicity was identified when the water droplet did not adhere to the surface. The surface energy was evaluated by Owens and Wendt method [18]. According to this method, the polar and dispersive components of surface energy can be calculated from contact angles of liquids with different surface tensions and polarities with a surface. Table 1 shows the liquids used and their parameters of surface energy and viscosity [19,20].

The roughness of VACNT films was evaluated by a Nanoscope V Multimode atomic force microscope (AFM) in air. The AFM was used in tapping mode with an etched silicon probe ( $k = 50 \text{ N m}^{-1}$ ) at a scanning rate of 0.2 Hz. The root mean square roughness (Rrms) was taken from the surface topography of AFM images. Raman spectroscopy with excitation at 514.5 nm was performed with a Renishaw-2000 spectrometer, for all samples analyzed.

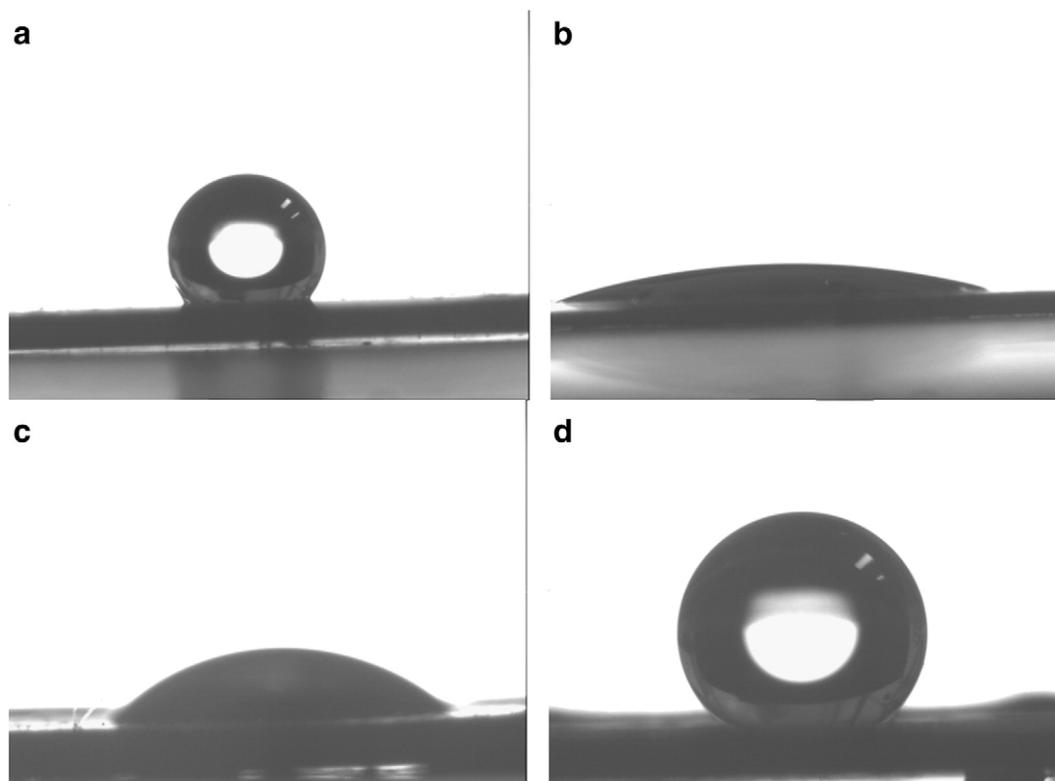
### 3. Results and discussion

Contact angle for de-ionized water was measured on the as-grown VACNT films, as well as samples treated with oxygen plasma, and after CO<sub>2</sub> laser irradiance. Fig. 1 shows photos of water droplets on each surface of VACNT films analyzed. As observed, the CA on as-grown VACNT was ~144° ± 6 (Fig. 1a), against ~7° ± 3 after oxygen plasma (Fig. 1b).

The large decreasing of CA with plasma etching is due to the attachment of oxygen-containing groups, such as (-C O, -COOH) [4,21]. This functional groups promote a chemical modification on nanotube surfaces, impelling a transition from hydrophobic to superhydrophilic characteristics. The oxidation of carbon nanotube surfaces by plasma is already known, as shown by the FTIR and TFD data of Naseh et al. [22]. The conversion of VACNT films to hydrophilic after air plasma was also shown by Tsung et al. [23]. Oxygen plasma etching of VACNT films promotes changes in surface energy of carbon films, mainly in polar component [24]. This result can be explained by high oxygen affinity with carbon. Fig. 1(c-d) shows the values of CA changes to 35.7 ± 4.2 (Fig. 1c) and to 142.2 ± 6.5 (Fig. 1d) degrees, after CO<sub>2</sub> laser irradiance of 15 kW cm<sup>-2</sup> and 50 kW cm<sup>-2</sup>, respectively. Fig. 1d shows the re-establishment of the superhydrophobic character of the VACNT.

Fig. 2 shows values of de-ionized water CA on as-grown and plasma-treated VACNT films after laser irradiance. The laser irradiance had low influence for as-grown samples, since the CA variation was smaller than for films with plasma treatment. However, there was a steady increase of the CA with the increase of laser power. On the plasma-treated samples, CA changing is huge, varying from superhydrophilic to superhydrophobic. This fact demonstrates a complete re-establishment of the superhydrophobicity of the VACNT.

More details of the effect of CO<sub>2</sub> laser irradiance were obtained with the analysis of other liquids. These results can be seen in Fig. 3, which shows the CA values for each liquid probe as the function of the increase of CO<sub>2</sub> laser irradiance on the surface of as-grown (Fig. 3a)



**Fig. 1.** Photos of water droplets on VACNT: (a) as-grown films (b) after oxygen plasma etching, (c) after oxygen plasma etching and CO<sub>2</sub> laser irradiance – 35 kW cm<sup>-2</sup>, and (d) after oxygen plasma etching and CO<sub>2</sub> laser irradiance – 50 kW cm<sup>-2</sup>.

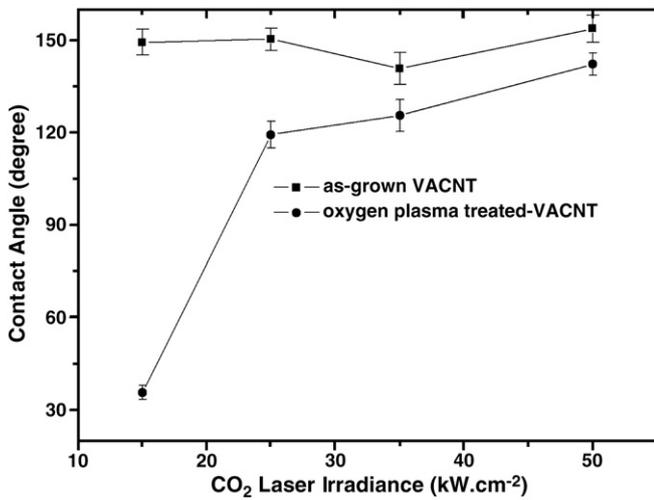


Fig. 2. Contact angle measured for water probe as function of CO<sub>2</sub> laser irradiance after laser treatment on (■) as-grown VACNT surface and (●) oxygen plasma-treated VACNT.

and oxygen plasma-treated (Fig. 3b) VACNT films. There are three different trends of CA, according to the liquid used. For water, CA was sensitive to the oxygen plasma treatment, while for non-polar liquids

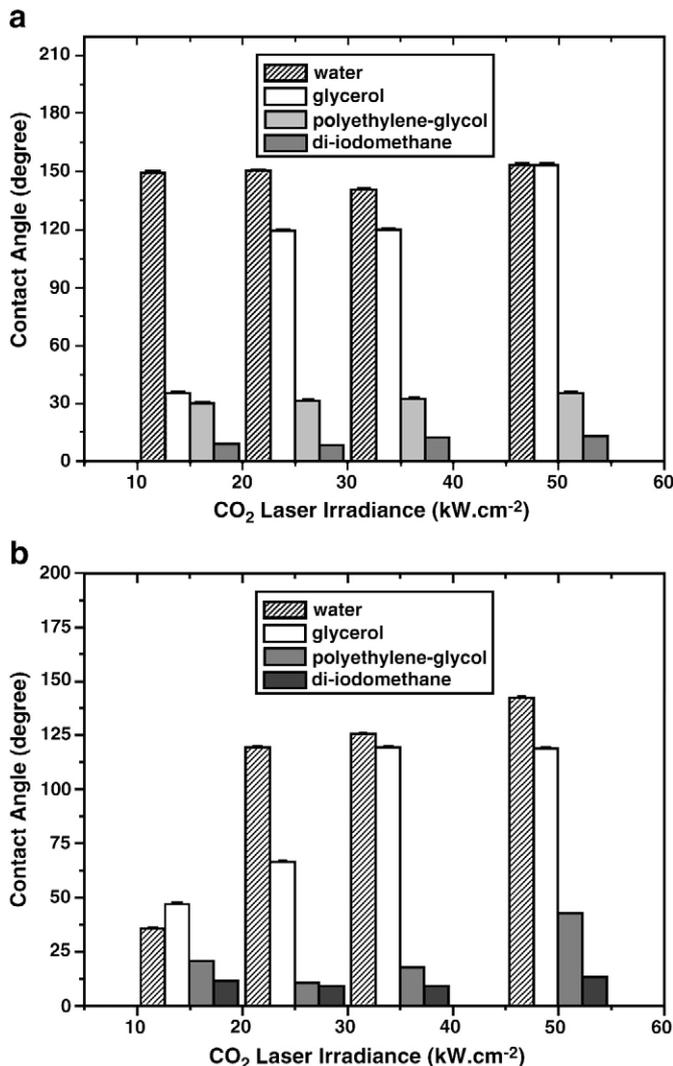


Fig. 3. Measurements of CA for different liquids as function as CO<sub>2</sub> laser irradiance for VACNT: (a) as-grown films (b) after oxygen plasma treatment.

(di-iodomethane) is not influenced neither by the plasma treatment or CO<sub>2</sub> laser treatment. The CA values with glycerol increase with laser irradiance but are less influenced by plasma treatment. The overall behavior for the polyethylene glycol is not conclusive. As observed, the main result is an increase in the CA for polar liquids with the increase of the laser irradiance, indicating an increase on the hydrophobicity [25,26] of VACNT films.

Despite the overall behavior of individual liquids shown in Fig. 3, a systematic study of the CA of polar and non-polar liquids on VACNT films has been performed to understand the effect of surface chemistry. A set of data composed of the CA with four liquids for each sample treated by laser was used to obtain Table 2. This table summarizes the calculations by Owens and Wendt [18] method, and it shows total surface energy ( $\gamma$ ) with their dispersive ( $\gamma^d$ ) and polar ( $\gamma^p$ ) components. We have obtained total surface energy values of 50.5 mJ m<sup>-2</sup>, and 64.7 mJ m<sup>-2</sup> for as-grown and plasma-treated VACNTs, respectively. The increase in the total surface energy of oxygen-treated VACNT films is mainly attributed to the increase in the polar component [27,28], but the dispersive component undergoes a significant reduction. As discussed by Nuriel et al. [30], the oxygen incorporation on CNT is responsible for this polar character. After CO<sub>2</sub> laser irradiance on the oxygen plasma-treated samples, polar component was progressively diminished, while dispersive component was increased. These results may indicate the removal of oxygen-terminated sites on VACNT surface, which loses its polar character. The re-establishment of the superhydrophobicity of VACNT surface was also demonstrated.

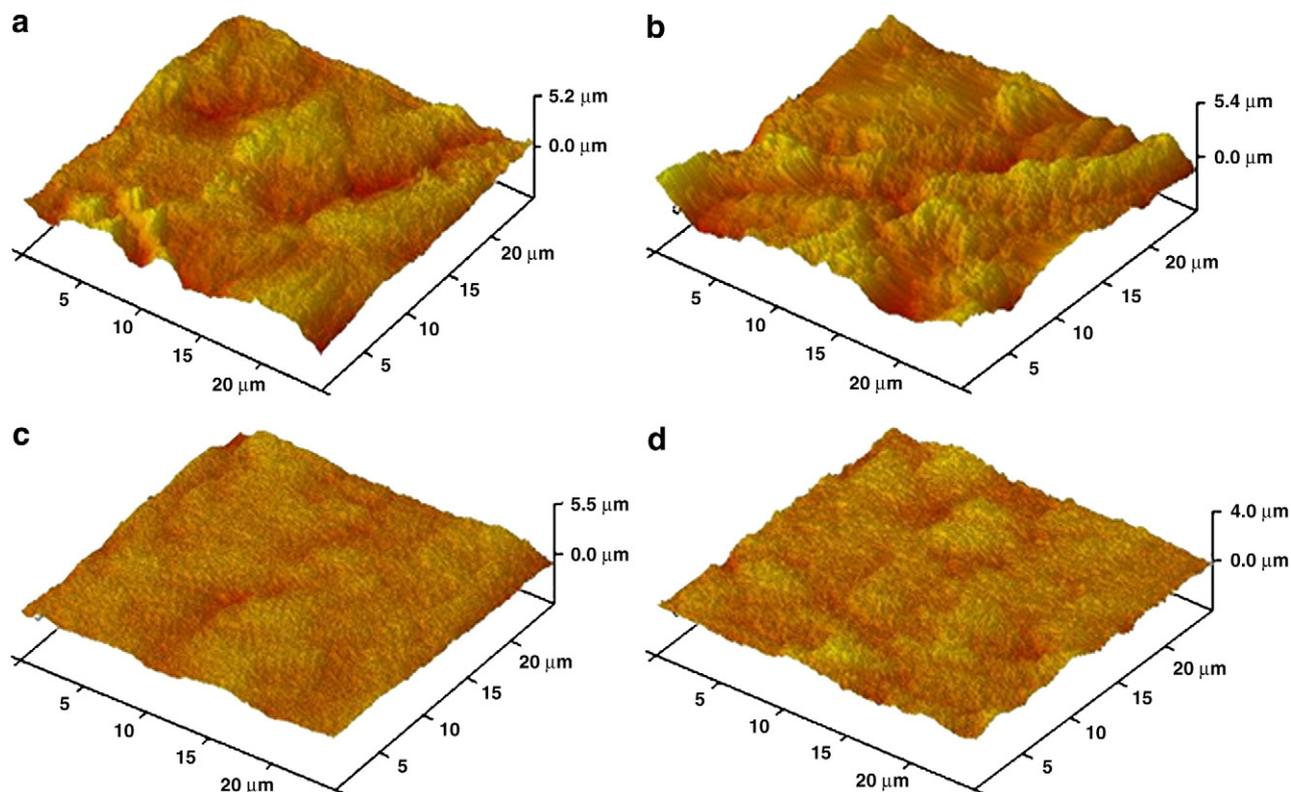
Raman spectra (shown elsewhere [31]) indicate that oxygen plasma treatment introduces defects on the VACNT films, since the  $I_D/I_G$  ratio and also the G line – full width at half maximum (FWHM) increases, compared to as-grown samples. On the other hand, CO<sub>2</sub> laser treatments promote its purification, since  $I_D/I_G$  ratio and also the G line FWHM decreases considerably, even compared to the as-grown samples. Ueda et al. [32] and Xiaodong et al. [33] have already shown CNT purification by CO<sub>2</sub> laser irradiation. The reduction of VACNT defects observed by Raman spectra may be correlated to the reduction of adsorbed impurities, mainly oxygen-terminated sites. Based on literature, surface roughness is important to determine the superhydrophobic character of VACNT. Therefore, the roughness of all samples was analyzed before being wet. AFM images were used to estimate the roughness (Rrms) of film surfaces, in a 20  $\mu$ m  $\times$  20  $\mu$ m area. Fig. 4 shows the AFM images of the VACNT films under study. Surfaces with roughness at nanometric scale are more hydrophobic than smooth surfaces, due to the reduced contact area between the water and solid [34–36].

Roughness values varied from 347 to 374 nm for as-grown VACNT (Fig. 4a) and plasma-treated (Fig. 4b), respectively. As expected, the surface roughness after plasma oxygen etching is higher than on as-grown VACNT, due to the bombardment of oxygen ions. After CO<sub>2</sub> laser treatment at 50 kW cm<sup>-2</sup>, as-grown and plasma-treated VACNT presented a roughness of 211 and 189 nm, respectively, as shown in Fig. 4(c–d). Surface roughness values obtained after oxygen plasma etching tends to increase depending on CO<sub>2</sub> laser irradiance. The

Table 2

Calculation of surface energy ( $\gamma$ ) of VACNT under study as function CO<sub>2</sub> laser irradiance, its polar ( $\gamma^p$ ) and dispersion ( $\gamma^d$ ) components from Owens and Wendt plot.

CO <sub>2</sub> laser irradiance (kW cm <sup>-2</sup> )	$\gamma$ (mJ m <sup>-2</sup> )		$\gamma^d$ (mJ m <sup>-2</sup> )		$\gamma^p$ (mJ m <sup>-2</sup> )	
	As-grown	Oxygen etching	As-grown	Oxygen etching	As-grown	Oxygen etching
0	50.5	64.7	48.7	24.7	1.8	40
15	51.2	50.7	43.7	44.9	7.5	5.8
25	47.5	52.3	44.6	44.5	3	7.8
35	49.7	50.1	46.5	46.5	3.2	3.6
50	49.5	50.9	47.2	49.2	2.3	1.7



**Fig. 4.** AFM topographic images of VACNT: (a) as-grown films; (b) after oxygen plasma etching, (c) after CO<sub>2</sub> laser irradiance – 50 kW cm<sup>-2</sup>, and (d) after oxygen plasma treatment and CO<sub>2</sub> laser irradiance 50 kW cm<sup>-2</sup>.

increase of surface roughness after oxygen plasma treatment is relatively small in comparison to the decrease obtained after CO<sub>2</sub> laser irradiance. In spite of this relatively small increase in roughness, plasma-treated samples became superhydrophilic, while the CO<sub>2</sub> laser treated samples keep or become superhydrophobic with a much smaller surface roughness.

The roughness after the surfaces wetting were not measured because they may be considered as a result of the wetting process. Even though as-grown and oxygen plasma-treated samples have very similar morphological characteristics before wetting (CNT height and density), the surface characteristics after wetting are completely different. As-grown samples show joining of CNT tips to form microscopic structures by the bending of nanotubes [29,37–39]. This is related in literature as a Cassie [11] to Wenzel [40] transition of the wetting character. Samples treated by oxygen plasma do not show nanotube bending, i.e., the water simply flows among them.

The surface aspect of samples treated by CO<sub>2</sub> laser after wetting have no resemblance with the bending observed on the as-grown samples, despite both are superhydrophobic. After laser, the nanotubes do not bend, they just do not wet. These non-bending characteristics may be related to a shortening of VACNT, since laser irradiance is also responsible for a reduction of nanotubes height. Evidently, the bending to form microstructured morphology is not necessary for superhydrophobicity.

Further studies are necessary to better understand the effect of the wetting process on the surface morphology after wetting. However these considerations indicate that VACNT structure after wetting is rather a result of wetting process than responsible for it. Further studies are necessary to better understand.

#### 4. Conclusion

Chemical modification and surface roughness of VACNT films treated with oxygen plasma etching and CO<sub>2</sub> laser irradiance were

investigated through contact angle measurements and AFM images, respectively. The oxygen plasma etching promotes chemical modification by alteration of polar surface component. This treatment favors the hydrophilic character, although the surface becomes rougher.

CO<sub>2</sub> laser was applied on modified surface, where it was observed a re-establishment of surface by decreasing of polar component of the surface energy, which confers superhydrophobic characteristics to the VACNT surface.

The CO<sub>2</sub> laser promotes a high rate of local heating, which may be able to evaporate oxygen terminations on surface. It is also responsible for a reduction of nanotubes' height. The laser irradiance, therefore, affects both roughness and contact angle.

Hence, CO<sub>2</sub> laser irradiation opens a great possibility for application of VACNT films as micro-fluidics devices because it allows total control of their wetting properties.

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