

# Oxygen functionalization of multiwall carbon nanotubes by Ar/H<sub>2</sub>O plasma treatment

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## ABSTRACT

To increase the applicability of multiwall carbon nanotubes (MWCNTs), oxygen-containing functional groups were introduced on the surfaces of MWCNTs by using microwave-excited Ar/H<sub>2</sub>O surface-wave plasma. X-ray photoelectron spectroscopy and Raman spectroscopy were used to determine dependencies of Ar/H<sub>2</sub>O gas partial pressure, treatment time and microwave power. The oxygen functionalization of MWCNTs by plasma can be achieved very rapidly, about 10 min. The C–O and O–C;O fractions firstly increase and then decrease with increasing Ar partial pressure. The C–O and O–C;O fractions increase with increasing microwave power from 400W to 700 W. A slight increase of the R (I<sub>D</sub>/I<sub>G</sub> ratio) value for the treated MWCNTs indicated disordering in the surface microstructure of MWCNTs coincident with the introduction of surface oxygen. The oxygen-containing groups introduced on the surfaces of MWCNTs by plasma treatment are hydrophilic. The dispersion of plasma treated MWCNTs is therefore improved.

Keywords: Carbon nanotubes, Plasma treatment, Oxygen functionalization

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## 1. Introduction

Carbon nanotubes (CNTs) [1] have led to many new technical developments and applications because of their high chemical stability, large surface area, and excellent mechanical strength. However, one of major obstacles for exploring CNT applications is their insolubility nearly in all solvents. A proper surface treatment of CNTs, on the other hand, can improve their independent dispersion capability, obtain a uniform and stable dispersion, and thus fully utilize the unique properties offered by CNTs. The easiest way to covalently attach chemical groups (e.g., carboxylic groups) is by oxidation, such as nitric ( $\text{HNO}_3$ ) and sulfuric ( $\text{H}_2\text{SO}_4$ ) acid oxidation [2,3], air oxygen [4,5], ozone oxidation [6,7], and plasma oxidation [8-12], leading to the formation of hydroxyl and carboxyl groups on the surfaces of the nanotubes. However, because of the rather harsh conditions involved, most oxidation reactions result in the opening of the nanotube tips, detrimental damage of their sidewalls, or both. It is important that these treatments are surface specific so that the bulk properties are preserved.

Since the 1960s, plasma technology has quickly evolved into a valuable technique to engineer surface properties without alteration of the bulk compositions [13]. Compared to other chemical modification methods, plasma treatment method has the advantages of shorter reaction time, non-polluting processing, and providing a wide range of different functional groups depending on plasma parameters. In the microwave excited surface-wave plasma (MW-SWP) system, plasma can be generated with high electron density and a low electron temperature, which allows uniform covalent functionalization of nanotubes at low temperature and does not easily destroy the integrity of CNT patterns at low temperature [14,15]. In our earlier reported [14,15], MWCNTs were successfully functionalized through a microwave discharge of ammonia and oxygen. Ar/ $\text{H}_2\text{O}$  MW-SWP was also used to treat MWCNT

surfaces in order to improve their dispersion capability in a polar medium of water [16]. Since proper surface hydrophilic groups were introduced onto MWCNT surfaces, it is expected that the plasma treated MWCNTs can provide strong affinity to liquid molecules, and hence self-disperse into the liquid medium and form a stable suspension without the aid of dispersing agents. Functionalization efficiency has relied on plasma parameters, such as plasma treatment time, pressure, power, etc.

This work is the extension of our earlier work [16]. Here, we estimated the effects of Ar /H<sub>2</sub>O mixture gas partial pressure, treatment time, and microwave power on the introduction of oxygen-containing groups onto the surfaces of MWCNTs by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

## **2. Experimental**

Plasma device for MWCNT treatment consists of a cylindrical stainless vacuum chamber with the diameter of 40 cm and the height of 40 cm (shown in Fig. 1). There is a 2.45 GHz microwave generator in the upper part of the chamber. An inlet for plasma gases is set up, and a rotary and turbomolecular pump system is connected to the chamber. The microwaves are guided through rectangular wave-guide and introduced into the chamber through slot antennas. The reflected microwave power was minimized by adjusting the E-H tuner. There was a 2.45 GHz microwave generator in the upper part of the chamber. MWCNT powder was placed in a glass beaker. The stage supporting the glass beaker was kept at a 15 cm distance from the plasma showering quartz plate. Firstly, MWCNTs were pretreated using Ar plasma for 5 min at a gas flow rate of 40 sccm, a microwave power of 700 W, and a pressure of 13.3 Pa. Ar plasma pretreatment is expected to activate the surfaces by bond breaking due to Ar-ion bombardment and to increase the reactivity of MWCNT surfaces [14-17]. And then MWCNTs were treated using Ar/H<sub>2</sub>O mixture gas plasma. Mixture

gas partial pressures were 13.3/0, 12.0/1.3, 10.0/3.3, 6.65/6.65, 3.3/10.0, 0/13.3 Pa, treatment times were 4, 7, 10, and 15 min, and microwave powers were 400 and 700 W, respectively. MWCNTs were characterized using X-ray photoelectron spectroscopy (XPS) carried out on an ESCA-3400 spectrometer (Shimadzu, Japan), and Raman spectroscopy carried out on an NR-1800 laser Raman spectrometer (JASCO, Japan)

### **3. Results and discussion**

#### *3.1. XPS analysis*

XPS analysis was performed to determine the chemical modification of MWCNTs before and after plasma treatment. Fig. 2 shows the influence of plasma treatment time on the contents of carbon and oxygen on MWCNT surfaces at Ar/H<sub>2</sub>O mixture gas partial pressure of 10.0/3.3 Pa and microwave power of 700 W. For MWCNTs before plasma treatment, oxygen atoms come from air contamination oxidation. From Fig. 2, it can be seen that the relative content of oxygen increases mainly during the first 4 min, and thereafter slightly increases. Thus, the oxygen functionalization of MWCNTs by plasma can be achieved very rapidly. This result is crucial because the treatment time is one of most important parameters for the industrial application of MWCNT treatment. After plasma treatment for 10 min at Ar/H<sub>2</sub>O mixture gas partial pressure of 10.0/3.3 Pa and microwave power of 700 W. The relative content of oxygen on the surfaces of MWCNTs can reach up to 31.0 at.%. Considering that XPS is a surface sensitive technology, probing about 5 nm deep into the material, one can estimate that about all the aromatic sites on the surfaces of MWCNTs are oxidized, and the surfaces of MWCNTs are coated with the oxygen-containing groups.

Fig. 3 shows the high resolution XPS C 1s spectra and O 1s spectra of MWCNTs before and after plasma treatment. The C 1s peaks are deconvolved into four component Gaussian peaks [16]: The main peak (1) at  $284.1 \pm 0.2$  eV corresponds to the  $sp^2$  hybridized graphite-like carbon atoms (C=C); Peak (2) centered at  $285.1 \pm 0.2$  eV is attributed to the  $sp^3$  hybridized carbon atoms (C-C); Peaks (3) at  $286.2 \pm 0.2$  eV, and (4) at  $288.9 \pm 0.2$  eV correspond to C-O (e.g., alcohol, ether), and O-C=O (e.g., carboxylic, ester) species, respectively. The quantitative analysis indicates that the Ar/H<sub>2</sub>O plasma treatment lead to decrease in the  $sp^2$  C=C component from 53.4% for the untreated MWCNTs to 37.2% for the Ar/H<sub>2</sub>O plasma treated MWCNTs, and also to increase in the C-O and O-C=O components from 4.8% and 1.9% for the untreated MWCNTs to 16.9% and 13.7% for the Ar/H<sub>2</sub>O plasma treated MWCNTs. Since the  $\pi$  bonds (C=C) in the  $sp^2$ -hybridized graphite-like carbon with the CNT lattice are active and chemical instability due to lack of rotation around C=C bonds and nonsaturation of C=C bonds, and therefore more susceptible to plasma attack [15]. This explains the decrease in the C=C fraction after plasma treatment. It is believed that radicals are first generated on the dissociated  $\pi$  bonds in C=C, which then further react with active OH radical originated from the deexcitation of the H<sub>2</sub>O. The O 1s peaks are deconvolved into two component Gaussian peaks [18,19]: Peaks (1) at  $532.7 \pm 0.2$  eV, and (2) at  $533.6 \pm 0.2$  eV correspond to C-O and O-C=O species, respectively. The ratio of peak area of O-C=O and C-O decreases from 2.56 to 1.22 after plasma treatment, indicating the increase in O-C=O component.

Relative contents fitted for the components forming the C 1s XPS spectra as a function of mixture gas partial pressure and microwave power are tabulated in Table 1. From Table 1, the C-O and O-C=O fractions firstly increases and then decreases with increasing Ar partial pressure. C-O and O-C=O fractions increases with increasing

microwave power from 400 W to 700 W. Optical emission spectroscopy (OES) was used for diagnostics of reactive plasmas. The emission spectra of Ar /H<sub>2</sub>O plasma are shown in Fig. 4. The most significant OH radical line in our experimental conditions is the 309.6 nm line, which corresponds to the deexcitation of the H<sub>2</sub>O. An OH radical can be created in plasma zone and other fractionation products (e.g. O\*, H\*) of the plasma may interact with the surface finally eliciting a surface-bound OH radical. The active OH radical is highly reactive and interacts with the non-activated and activated sites on the MWCNT surfaces. The OH radical may have a higher probability to form a covalent bond upon reaction with dangling bonds or defects. The introduction of oxygen-containing groups onto MWCNTs is mainly attributed to the existence of the active OH radical. Other fraction productions like O\*, H\* may also partially contribute to the introduction of oxygen-containing groups. Fig. 4 shows that the content of OH radical is enhanced with increasing microwave power. This explains the effect of microwave power on C-O and O-C=O fractions. The Ar addition enhances the content of OH radical. Pure H<sub>2</sub>O vapor gives unstable plasma and that phenomenon negatively affects the properties of the modified surfaces (inhomogeneous modification) and reproducibility of results. The Ar addition to the system makes plasma stable and makes properties of modified surfaces reproducible. Fig. 4 also shows that the content of OH radical first increases with increasing Ar gas partial pressure and thereafter decreases. This explains the effect of Ar/H<sub>2</sub>O mixture gas partial pressure on the C-O and O-C=O fractions.

### 3.2. Raman analysis

Fig. 5 shows the Raman spectra of MWCNTs before and after Ar/H<sub>2</sub>O plasma treatment as a function of mixture gas partial pressure. For the untreated MWCNTs, the G peak at 1572.8 cm<sup>-1</sup> is the E<sub>2g</sub><sup>(2)</sup> model corresponding to the movement in

opposite direction of two neighboring carbon atoms in a graphitic sheet, and it indicates the presence of crystalline graphitic carbon in MWCNTs. The D peak at approximately  $1345.9\text{ cm}^{-1}$  is an  $A_{1g}$  breathing mode. This mode is generally attributed to the defects in the curved graphite sheet,  $sp^3$  carbon, or other impurities. The  $R = I_D/I_G$  ratio, where  $I$  corresponds to the peak area of the Lorentzian functions, allows us to estimate the relative extent of structural defects. This ratio is 1.10 for the untreated MWCNTs. The enhancement of  $I_D/I_G$  for the plasma treated MWCNTs can be interpreted as being attributed to the microstructure of carbon sheets in tubes and the increasing of oxygen content. Compare to untreated MWCNTs, red shift of each peak position the plasma treated MWCNTs takes place, which can be caused by the increased disorder and defect density in the treated MWCNTs [20]. From Table 2, with pure  $H_2O$  plasma treatment,  $R$  values slightly increase due to the enhancement of surface defects and embedment of oxygen atoms. However, with increasing Ar gas partial pressure,  $R$  value appears to first increase, and then to decrease. This might be the result of the removal of some amorphous carbon layers,  $sp^3$  carbon, and other impurities. From XPS analysis, Ar/ $H_2O$  mixture plasma treatment enhances the oxygen fraction on the surfaces of MWCNTs. Slight increase of  $R$  values and red shift of peak positions of the treated MWCNTs indicate the changes in the surface structures of MWCNTs and the introduction of oxygen atoms.

### 3.3. Dispersion properties

Compared to the untreated MWCNTs, the MWCNTs after Ar/ $H_2O$  MW-SWP treatment have a very good dispersion in aqueous solution. After 20 days of settling time, all untreated and Ar plasma treated MWCNTs form aggregation at the bottom of bottle (Fig. 6 A and B). However, no aggregation forms in the suspension of MWCNTs after plasma treatment even after 20 days of settling time. (Fig. 6 C) The

oxygen-containing groups introduced on the surfaces of MWCNTs by plasma treatment are hydrophilic. The dispersion of plasma treated MWCNTs is therefore improved.

#### **4. Conclusion**

In summary, oxygen-containing functional groups were introduced on MWCNT surfaces by Ar/H<sub>2</sub>O MW-SWP treatment. The efficiency of oxygen-containing functional groups was dependent on treatment time, gas partial pressure, and microwave power. The C–O and O–C;O fractions firstly increase and then decrease with increasing Ar partial pressure. The C–O and O–C;O fractions increase with increasing microwave power from 400 to 700W. Slight increase of R values of the treated MWCNTs indicates the changes in the surface structure of MWCNTs and the introduction of oxygen atom. After Ar/H<sub>2</sub>O plasma treatment, the dispersion of MWCNTs was improved.

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Table 1. XPS analysis of MWCNTs before and after Ar/O<sub>2</sub> MW-SWP treatment as a function of mixture gas partial pressure and microwave power.

MWCNTs	C(%)	O (%)	sp <sup>2</sup> (%)	sp <sup>3</sup> (%)	C-O (%)	O-C=O(%)
Untreated MWCNTs	88.7	11.3	53.4	39.8	4.8	1.9
Ar/H <sub>2</sub> O 0/13.3 Pa, 700 W, 10 min	81.5	18.5	42.3	38.7	12.2	6.8
Ar/H <sub>2</sub> O 3.3/10 Pa, 700 W, 10 min	78.0	22.0	41.5	38.5	12.6	7.4
Ar/H <sub>2</sub> O 6.65/6.65 Pa, 700 W, 10 min	73.1	26.9	40.3	37.2	13.9	8.6
Ar/H <sub>2</sub> O 10/3.3 Pa, 700 W, 10 min	69.0	31.0	37.2	32.2	16.8	13.7
Ar/H <sub>2</sub> O 12/1.3 Pa, 700 W, 10 min	71.3	28.7	40.6	38.0	12.9	9.3
Ar/H <sub>2</sub> O 13.3/0 Pa, 700 W, 10 min	87.2	12.8	52.9	38.8	6.3	2.0
Ar/H <sub>2</sub> O 10/3.3 Pa, 400 W, 10 min	72.4	27.6	39.5	33.6	14.5	12.4

Table 2. Raman feature of of MWCNTs before and after Ar/O<sub>2</sub> MW-SWP treatment as a function of mixture gas partial pressure.

MWCNTs	<i>I<sub>D</sub></i> / <i>I<sub>G</sub></i>
Untreated MWCNTs	1.10
Ar/H <sub>2</sub> O 0/13.3 Pa, 700 W, 10 min	1.25
Ar/H <sub>2</sub> O 3.3/10 Pa, 700 W, 10 min	1.27
Ar/H <sub>2</sub> O 6.65/6.65 Pa, 700 W, 10 min	1.31
Ar/H <sub>2</sub> O 10/3.3 Pa, 700 W, 10 min	1.36
Ar/H <sub>2</sub> O 12/1.3 Pa, 700 W, 10 min	1.28
Ar/H <sub>2</sub> O 13.3/0 Pa, 700 W, 10 min	1.26

## Figure Captions

Fig. 1. Experimental setup.

Fig. 2. Influence of plasma treatment time on the relative contents of carbon and oxygen at Ar/H<sub>2</sub>O mixture gas partial pressure of 10.0/13.3 Pa and microwave power of 700 W.

Fig. 3. High resolution C 1s spectra and O 1s spectra of MWCNTs before (A, C) and after (B, D) plasma treatment for 10 min at Ar/H<sub>2</sub>O mixture gas partial pressure of 10.0/13.3 Pa and microwave power of 700 W.

Fig. 4. OES of Ar/H<sub>2</sub>O mixture gas, at microwave power 700 W, partial pressure 13.3/0 Pa (a), 0/13.3Pa (b), 3.3/10.0 Pa (c), 6.65/6.65 Pa (d), 10.0/3.3Pa (f), 12.0/1.3 Pa (g), and microwave power 400 W (f), partial pressure 10.0/3.3 Pa.

Fig. 5. Raman shift of MWCNTs after Ar/H<sub>2</sub>O MW-SWP treatment as a function of mixture gas pressure at microwave power 700 W, treatment time 10 min, and Ar/H<sub>2</sub>O mixture partial pressure: 0/13.3 Pa (a), 3.3/10.0 Pa (b), 6.65/6.65 Pa (c), 10.0/3.3 Pa (d), 12.0/1.3 Pa (f), and 13.3/0 Pa (g).

Fig. 6. Dispersion properties of MWCNTs (0.5 g/L in de-ionized water) before (A) and after plasma treatment for 10 min and microwave power of 700 W, pure Ar pressure of 13.3 Pa (B), Ar/H<sub>2</sub>O mixture gas partial pressure of 10.0/3.3 Pa (C), settling for 20 days.

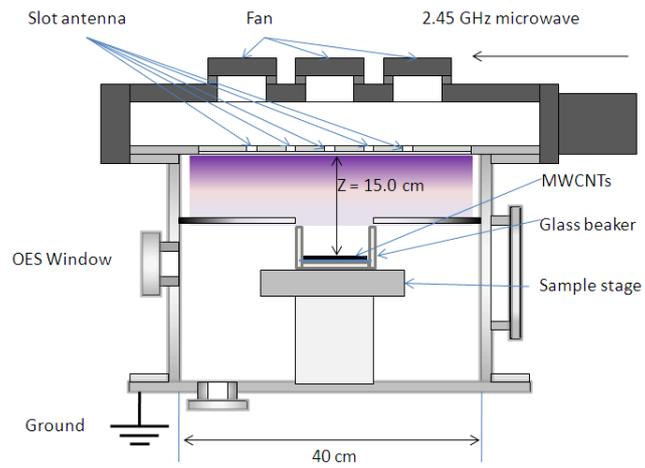


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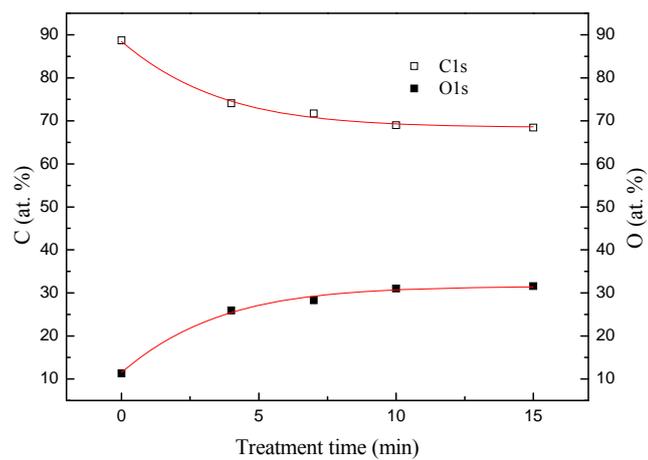


Fig. 2. Influence of plasma treatment time on the relative contents of carbon and oxygen at

Ar/H<sub>2</sub>O mixture gas partial pressure of 10.0/13.3 Pa and microwave power of 700 W.

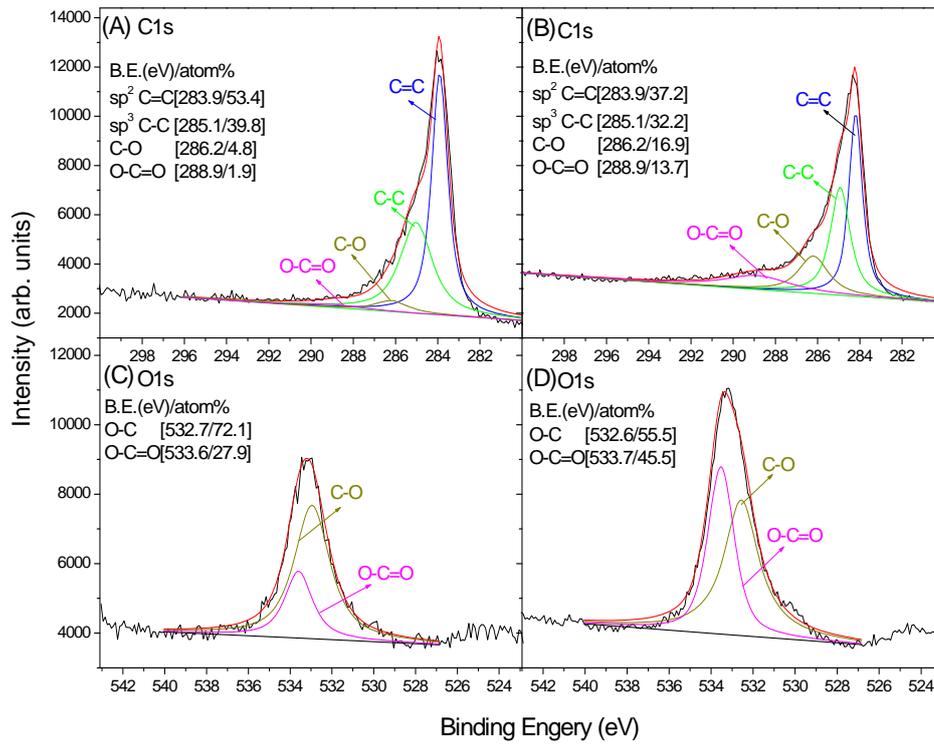


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microwave power of 700 W.

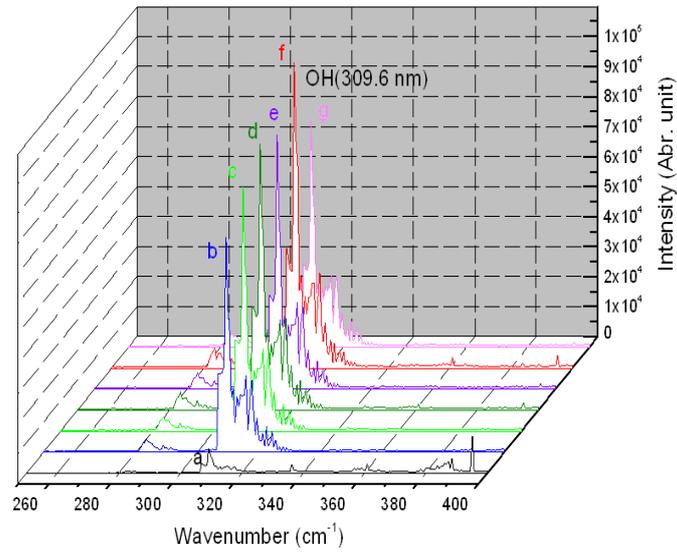


Fig. 4. OES of Ar/H<sub>2</sub>O mixture gas, at microwave power 700 W, partial pressure 13.3/0 Pa (a), 0/13.3Pa (b), 3.3/10.0 Pa (c), 6.65/6.65 Pa (d), 10.0/3.3Pa (f), 12.0/1.3 Pa (g), and microwave power 400 W (f), partial pressure 10.0/3.3 Pa.

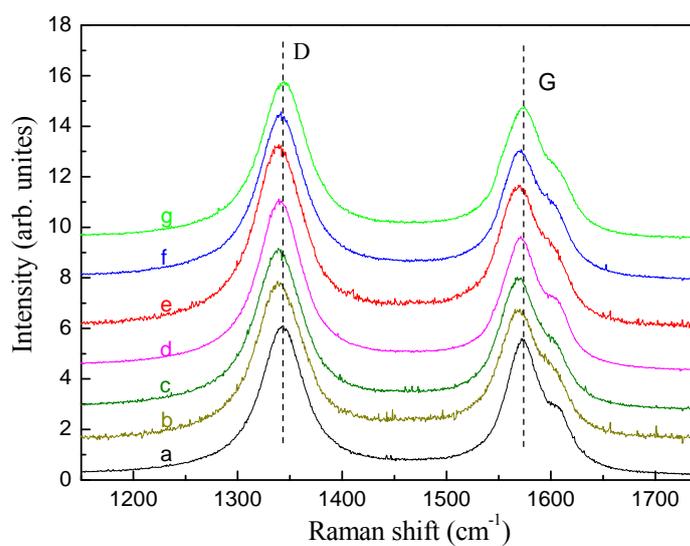


Fig. 5. Raman shift of MWCNTs after Ar/H<sub>2</sub>O MW-SWP treatment as a function of mixture gas pressure at microwave power 700 W, treatment time 10 min, and Ar/H<sub>2</sub>O mixture partial pressure: 0/13.3 Pa (a), 3.3/10.0 Pa (b), 6.65/6.65 Pa (c), 10.0/3.3 Pa (d), 12.0/1.3 Pa (f), and 13.3/0 Pa (g).



Fig. 6. Dispersion properties of MWCNTs (0.5 g/L in de-ionized water) before (A) and after plasma treatment for 10 min and microwave power of 700 W, pure Ar pressure of 13.3 Pa (B), Ar/H<sub>2</sub>O mixture gas partial pressure of 10.0/3.3 Pa (C), settling for 20 days.