

High frequency capacitively coupled RF plasma discharge effects on the order/disorder structure of PAN-based carbon fiber

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Abstract High-resolution confocal Raman microscopy was used to investigate the effects of nitrogen plasma on unsized high strength (HS) PAN-based carbon fiber surfaces. The fibers were treated by a high frequency (40.68 MHz) capacitively coupled single RF-PECVD reactor under different processing conditions (exposure times, RF powers and gas pressures). It was found that the order/disorder structure of the treated carbon fiber changed with different processing conditions. At low pressures, the degree of disordered structure increased with HF-RF power and process time. However, at high pressures, high-order structure ($IG/IT = 84.51\%$) was observed and almost no observable structural effects appeared at long treatment time. Also, the first-order Raman-band peaks (D and G) of the treated carbon fibers shifted. And, FWHM (wD/wG), intensity (ID/IG) and D-band relative integrated intensity (ID/IT) ratios increased with ordering whereas they decreased with disordering.

Author's contributions: All Authors, UG, SB and DA, carried out the experiments and characterizations, analyzed the data, and conceptualized the research. All authors read and approved the final manuscript.

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Introduction

In recent years, radio frequency plasma material processing has played an indispensable role in industrial areas [1]. Some of the applications in semiconductor manufacturing are etching (removing material from the surface), surface modification (making changes on the surface), cleaning (removing all possible undesirable residues), ashing (removing organic fragments from inorganic surfaces), and surface hardening (hardening the surface layer, without affecting the bulk properties of the material) [2]. In general, there are various methods of characterization and surface modification of the materials which are: mechanical, chemical, combustion and plasma treatment. Because the carbon fiber has only a few micrometers in diameter, it is difficult to use mechanical and combustion techniques as treatment methods. At the same time, since the popularity of chemical treatment is declining these days due to environmental pollution problems. As a result, it must be mentioned that the most convenient technique which can be used for surface modification of the carbon fibers is “plasma treatment” [3]. Furthermore, in addition to the environmental and economical benefits of the plasma glow discharges, it can maintain the properties of the mechanical bulk of carbon fiber.

In the previous literatures, the effect of the exposure time of the single RF plasma (13.56 MHz) discharge at constant gas pressure and RF power to the crystallite structure was investigated, and it was observed that the structure of carbon fibers was not changed under plasma discharge treatment [4–7]. However, by increasing the pressure and frequency of the source, the significant structural effects of plasma treatment can be seen [3].

Carbon fiber is an artificial material containing at least 90 % carbon by weight [8]. It is possible to obtain many

different carbon fibers using different polymeric precursor materials during manufacturing; for example, cellulose, rayon, polyvinyl chloride, pitch, and polyacrylonitrile (PAN) with different mechanical properties [9]. The pitch-based fibers have high modulus with a more-ordered (graphitic) crystalline structure, whereas PAN-based fibers have high strength with a more-disordered (non-graphitic, i.e., turbostratic) structure [8–11]. Thus, Raman spectroscopy is devoted as one of the very useful technique to understand the characteristics and the properties of untreated and treated carbon fibers. Raman (vibrational molecular) spectroscopy is one of the most important analytical techniques [2], whose workout mechanism depends on the laser light scattered inelastically from the surface of a substrate. The laser spectrum carries information about the modes (especially vibrational and rotational) of molecular interaction in the substrate [12, 13]. In previous studies, many Raman-band peaks were observed in the carbon fiber structure depending on the level of graphitization, laser power, laser excitation wavelength and precursor type [12, 14, 15]. But, there are two well-known Raman bands that mostly appeared in the range of 1,200–1,700 cm^{-1} spectrum, which are D (disordered) and G (ordered graphitic) bands [14]. The exact peak position of these two bands is: D-band at 1,330 cm^{-1} and G-band at 1,585 cm^{-1} [12]. The reason behind the existence of the G peak is the bond stretching of all pairs of sp^2 atoms in both rings and chains (symmetric E_2G vibration mode), while the D peak appears as a result of the breathing modes of sp^2 atoms in rings (symmetric A_1G vibration mode) [12, 14, 16]. And, the peak profile of these Raman lines is closely related to the structural properties of the analyzed carbon fiber. For example, the width of the G-band line is due to

the quantity of structural disorder [17], and changes in the peak locations are observed as a result of the applied strain [18]. In addition, the relative intensity ratio of the peaks (ID/IT and IG/IT) is essential to represent the amount of disorder in the carbon structure and crystallinity of carbon fibers [14, 17, 20]. The main objective of this study is to observe the structural effects of high frequency (40.68 MHz) capacitively coupled single RF nitrogen discharge on the unsized HS PAN-based carbon fiber surfaces using the Raman spectroscopy analyzing technique. It must be mentioned here that the nitrogen plasma treatments have not introduced new nitrogen functionality onto surfaces; but instead, have cleaned fiber surfaces of contaminants and successfully introducing C/N functionality into fiber surfaces. The functionalization occurs within the radio frequency (RF) plasma discharge by breaking the bonds of the fiber, and by creating reactive sites on the fiber chain which they are ready to react with active plasma species. The rapid integration of nitrogen to the surface causes formation of groups such as $\text{C}=\text{N}$, $\text{N}-\text{C}-\text{N}$, and amine groups in plasma [21, 22].

Experimental Setup

Plasma processing set-up as shown in Fig. 1 is basically composed of a stainless steel cylindrical chamber with the dimensions 500 × 400 mm, two-isolated (200 mm in diameter) identical aluminum electrodes, an automatic matching network, vacuum systems (rotary and Turbo pump, and high vacuum valves), a high band pass filter and RF generator. The distance between electrodes was fixed at 40 mm. High purity (99.995 %) nitrogen gas was used as an activation gas.

Fig. 1 The diagram of a high frequency capacitively coupled single RF-PECVD reactor

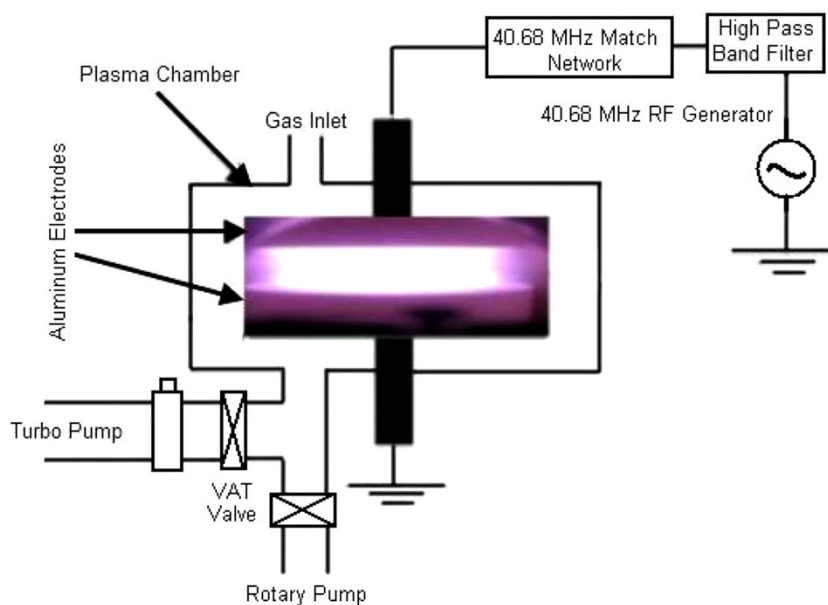
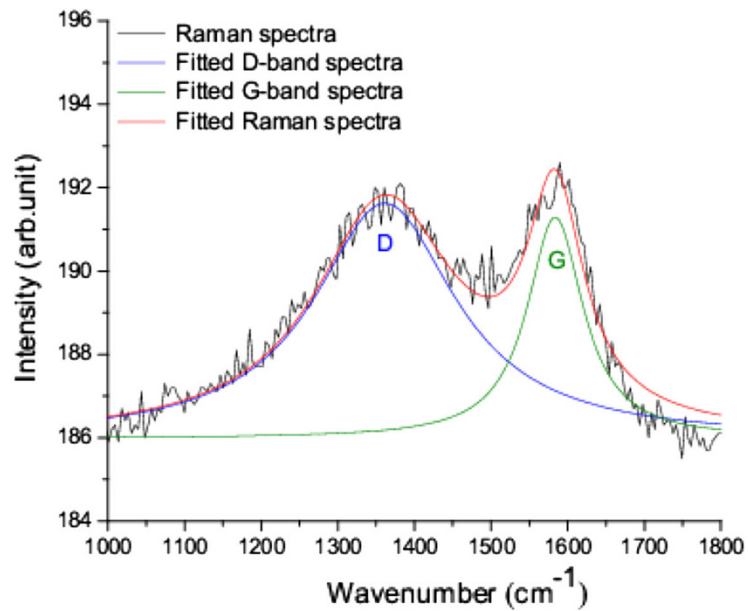


Fig. 2 Lorentzian multiple-peak-fitted Raman spectra of the treated fiber under treatment conditions 1 Torr, 200 W and 90 min



Parameters

	Value	Error
y0	185.9766009153	0.020109678915827
xc1	1361.3560585647	2.7396432958127
w1	224.78913251981	8.9948913289731
A1	1994.6011358473	67.437976893626
xc2	1583.7558688153	1.5979985433844
w2	88.712413833796	5.4648883444607
A2	741.26485535123	40.550973785746

Peaks

	Area	Center	Width	Height
1	1994.6011358473	1361.3560585647	224.78913251981	7.0797971121318
2	741.26485535123	1583.7558688153	88.712413833796	6.6669788137948

In the experimental design, a high frequency (40.68 MHz) RF source was connected to the top electrode with the automatic matching box and a high band pass filter whereas the bottom electrode was connected to the ground, as shown in Fig. 1. During plasma treatment, a non-conducting substrate (glass) with a 1-cm thickness was used as a sample holder on the lower electrode. In this study, different operational conditions were used for the treatment of the unsized carbon fiber: The HF-RF power varied between 50 and 200 W, the gas pressure between 0.3 and 1.0 Torr, and exposure time from 30 to 90 min. After the plasma treatment, the confocal Raman microscopy mode (alpha300 R) of a WITEC alpha300S scanning near-field optical microscopy (SNOM) instrument was used to characterize the surface structure of the untreated (as-received) and treated carbon fiber. This mode integrates an ultrahigh-throughput confocal microscope with an extremely

sensitive spectroscopy system for unrivaled resolution and chemical sensitivity. It supplies nondestructive Raman imaging with optical resolution down to 200 nm laterally, 500 nm vertically and spectral resolution down to 0.02 wavenumbers. 532 nm He-Ne laser with a power 100 mW has been used to excite all samples. Also, 25×, 50× and 100× Nikon objective lenses have been used to focus the laser beam onto the fiber surface. The laser light excites the surface by inducing vibrations of the chemical bonds within the samples. And, the spectrometer collects scattered lights from the surface after filtering, and sends them to the CCD camera detector connected to a powerful computer and a WITec special software system. The scanned Raman spectra started from 0 to 3,400 cm⁻¹ to detect the first-order D and G bands of the carbon fibers. The Origin Pro8 software program was used for data analyzing according to the Lorentz curve fitting [3, 18] model that is defined as:

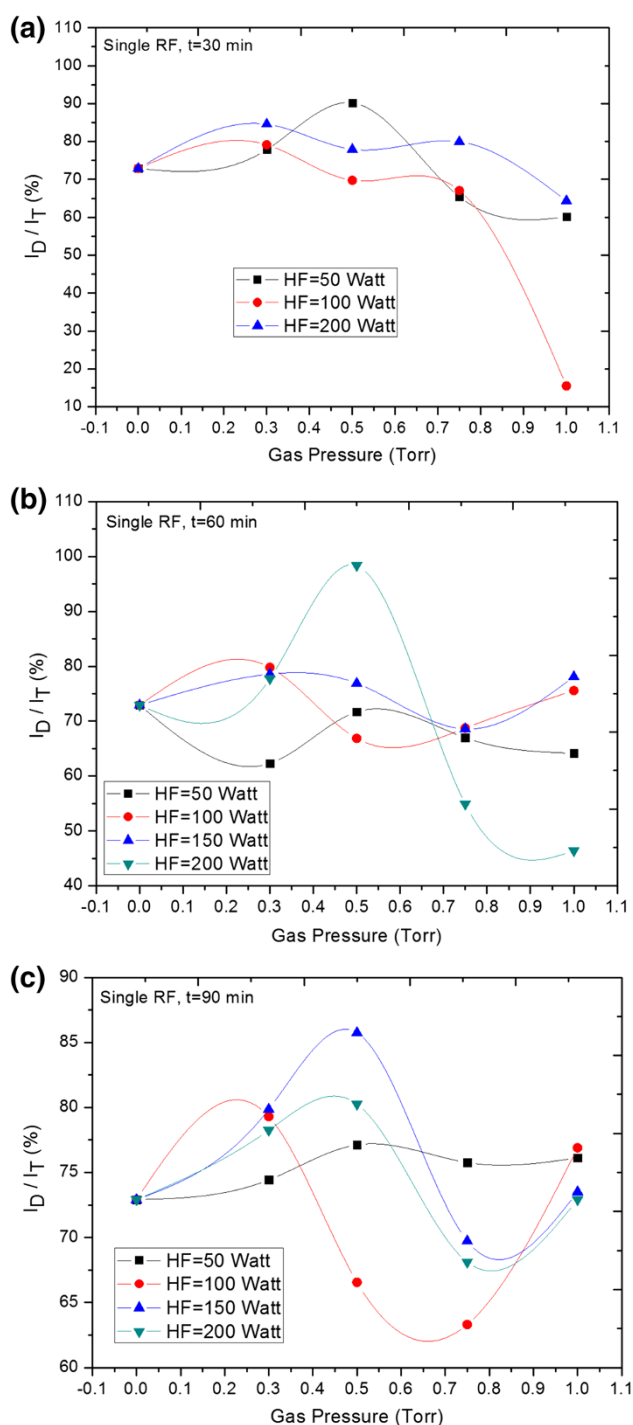


Fig. 3 Effects of gas pressure and HF-RF power on the order/disorder structure of the carbon fibers treated under different exposure times; **a** 30 min, **b** 60 min and **c** 90 min

$$y = y_0 + \frac{2A}{\pi} \frac{\omega}{4(x - x_0)^2 + \omega^2} \quad (1)$$

where y_0 is the baseline offset, A is the total area under the curve from the baseline, x_0 is the center of the peak and ω

Table 1 RF plasma processing treatment conditions of unsized PAN-based carbon fibers samples (a detail calculation is given in Table 2)

Sample	Power (W)	Pressure (Torr)	Time (min)
Disorder			
1	200	0.5	60
2	150	0.75	30
3	50	0.5	30
4	150	0.5	90
5	200	0.3	30
6	150	0.3	30
7	200	0.5	90
Order			
8	100	1	30
9	200	1	60
10	200	0.75	60
11	50	0.3	60
12	100	0.75	90
13	50	1	60
14	200	1	30

is the full width of the peak at half height (FWHM), since this fitting is usually preferred in the analysis of disordered carbon crystal [19]. Among these fitted parameters, the area (A) represents the integrated intensity of the peaks which can be used in the calculation of relative integrated intensity (curve area) ratios: ID/IT and IG/IT , where ID is the integrated intensity of the D-peak, IG is the integrated intensity of the G-peak and IT is total the integrated intensity of these two peaks ($ID + IG$). An example of fitted Raman spectra with its parameters is shown in Fig. 2.

Results and discussion

In this study, the effects of gas pressure, RF power and exposure time on the order/disorder crystalline structure of treated HS PAN-based carbon fibers were investigated. Furthermore, improvement of the interfacial properties of the treated fibers was examined by analyzing peak positions, widths and curve area ratios of the first-order Raman bands.

Crystalline structure

Effects of gas pressure and RF power

In short treatment time The degree of the disordered structure increases at low pressure, as in Fig. 3a, but, generally there is no observable effect of HF-RF power.

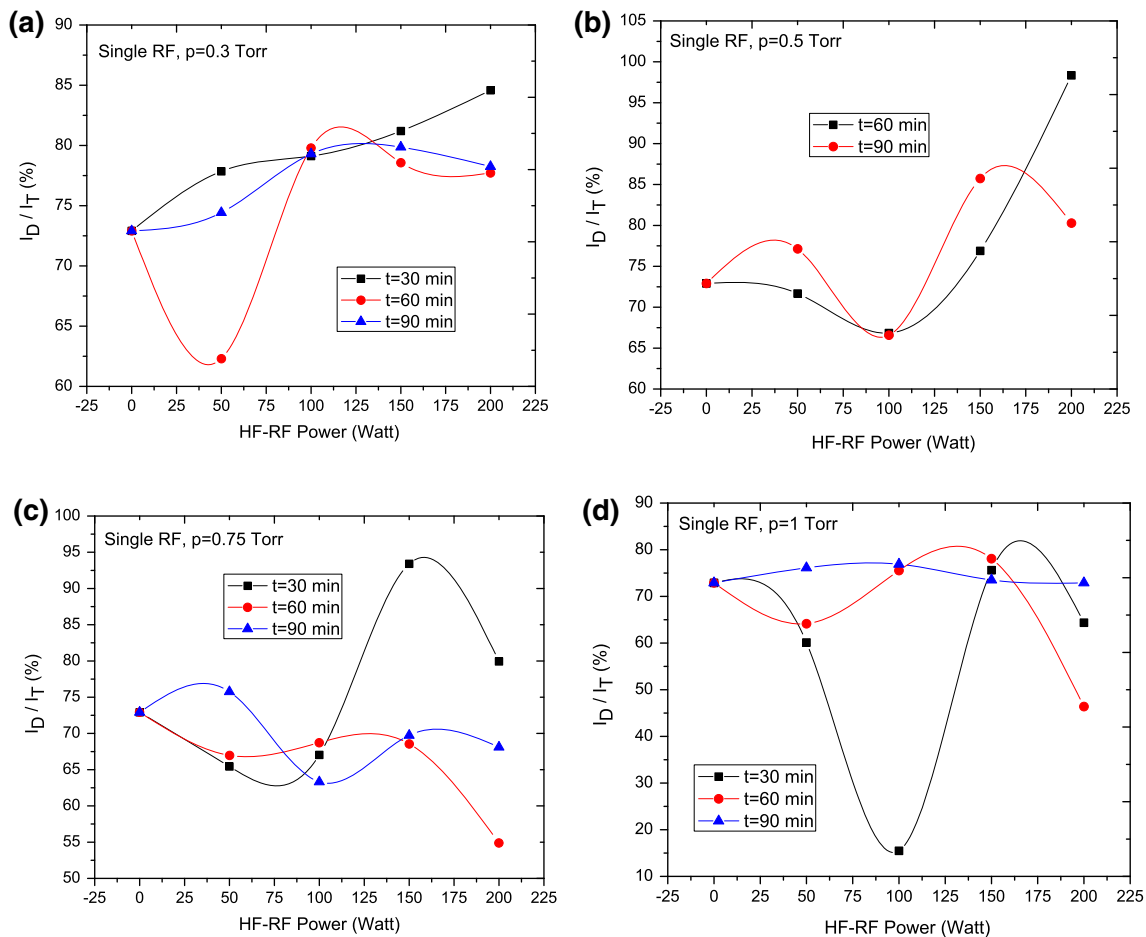


Fig. 4 Effects of HF-RF power and exposure time on the order/disorder structure of the carbon fibers treated under different gas pressures: **a** 0.3 Torr, **b** 0.5 Torr, **c** 0.75 Torr and **d** 1 Torr

However, at high pressure, the degree of ordered structure increases and the effect of power is seen by increasing pressure. Thus, the highest ordered structure (84.51 %) is obtained under the treatment condition 1 Torr and 100 W.

In long treatment time Figure 3b, c shows that the variations in the disordering and the effect of HF-RF power are almost the same as that of short treatment at low pressure. At high pressure, the effect of HF-RF power is clearly seen with pressure which disappears at long treatment time (90 min) at 1 Torr. The ordered degree of the treated fiber increases with increasing pressure except at 100 W. At 60 min and 200 W, the highest ordered ($I_G/I_T = 53.61\%$) structure was seen under treatment conditions 1 Torr. Meanwhile, the highest disordered structure ($I_D/I_T = 98.35\%$, as in Table 1) is obtained around 0.5 Torr. Generally, the degree of disordering increases with increasing the gas pressure (for pressure range <0.3 Torr) due to collisionless (non-Ohmic) electron heating whereas the degree of ordering increases with increasing pressure (> 0.3 Torr) because

of collisional (Ohmic) electron heating [20]. Because the transition point of the plasma from collisionless (alpha mode) collisional (gamma mode) which causes an increase of the number of energetic particles and nitrogen enrichment.

Effects of RF power and exposure time

At low gas pressure The degree of disordered structure increases with HF-RF power, as in Fig. 4a, b. Since HF-RF power increases the excitation and rotational temperatures of the neutral nitrogen gas which causes an increase in the density of the vibrational excited particles [23, 24]. These excited species destroy the basal plane of the fiber leading to an increase in the number of carbon atoms in the edge plane of the fiber that occurs in a high-level disordered structure [18, 25, 26]. In addition, a different molecular rearrangement can be observed in the carbon fiber structure with increasing the RF power and treatment time: carbon to nitrogen bonds have triple bonds ($C\equiv N$) at

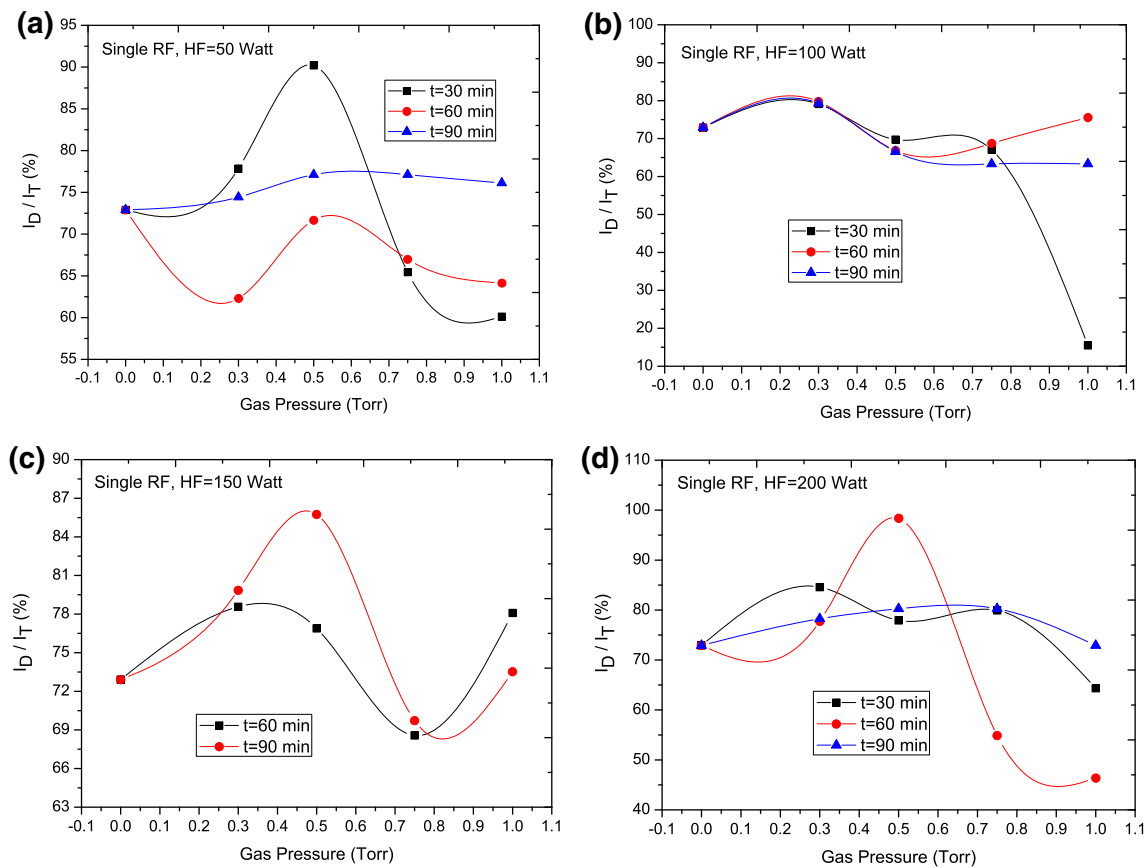


Fig. 5 Effects of gas pressure and exposure time on the order/disorder structure of the carbon fibers treated under different HF-RF powers: **a** 50 W, **b** 100 W, **c** 150 W and **d** 200 W

Table 2 Lorentz-fitted parameters of D and G Raman bands of untreated (as-received) and treated fibers listed in Table 2:

Carbon fiber	$x_o - D$ (cm^{-1})	$x_o - G$ (cm^{-1})	ω_D (cm^{-1})	ω_G (cm^{-1})	ω_D/ω_G	ID/IG	ID/IT (%)	ID/IT (%)
Untreated	1,362	1,584	225	89	2.53	2.69	72.91	27.09
Disorder								
Sample 1	1,437	1,560	926	68	13.72	59.46	98.35	1.65
Sample 2	1,388	1,566	603	96	6.27	14.17	93.41	6.59
Sample 3	1,367	1,562	527	97	5.44	9.19	90.19	9.81
Sample 4	1,355	1,560	384	96	4.01	6.01	85.74	14.26
Sample 5	1,350	1,572	335	77	4.35	5.49	84.58	15.42
Sample 6	1,365	1,589	293	84	3.50	4.32	81.20	18.80
Sample 7	1,349	1,561	298	103	2.89	4.07	80.26	19.74
Order								
Sample 8	1,351	1,560	4	16	0.25	0.18	15.49	84.51
Sample 9	1,353	1,560	41	33	1.26	0.87	46.39	53.61
Sample 10	1,359	1,554	92	64	1.42	1.22	54.88	45.12
Sample 11	1,354	1,562	160	86	1.86	1.65	62.30	37.70
Sample 12	1,350	1,554	151	86	1.76	1.73	63.31	36.69
Sample 13	1,355	1,558	161	89	1.82	1.79	64.15	35.85
Sample 14	1,353	1,560	168	87	1.93	1.81	64.36	35.64



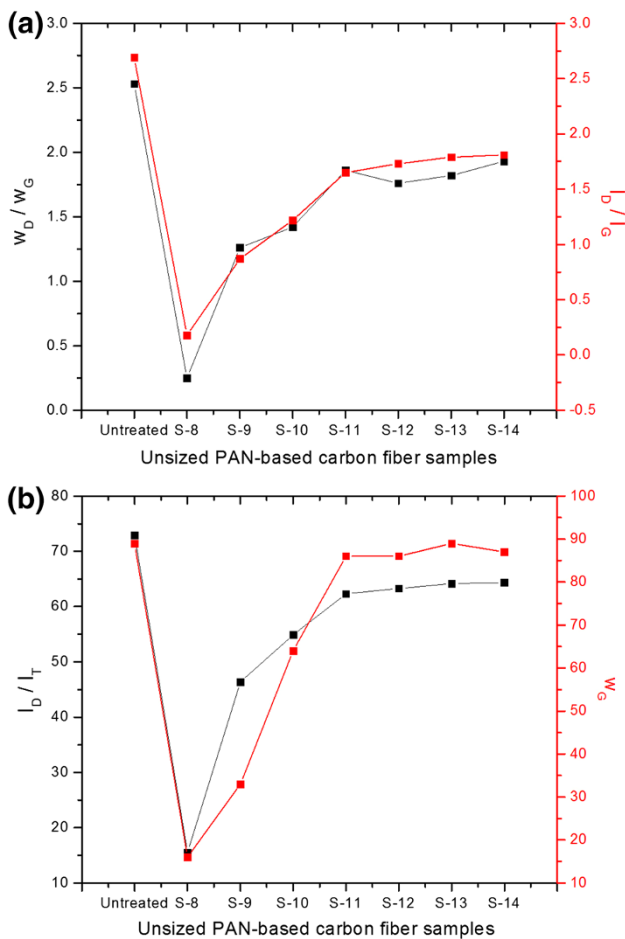


Fig. 6 **a** FWHM (w_D/w_G) and the integrated intensity (I_D/I_G) ratios, and **b** the relative integrated intensity (I_D/I_T) ratio and FWHM (G) of the high-ordered carbon fibers listed in Table 1. ('Sample' is abbreviated as "S")

30 min, but it can be changed to double bond (C=N) by increasing the exposure time. This result will be investigated in more detail in the future.

At high gas pressure From Fig. 4c, d, the degree of the ordered structure increases with HF-RF power only during short time treatment (30 min). But, there was almost no power effect on the structure during the ninety-minute treatment at 0.75 and 1 Torr.

Effects of gas pressure and exposure time

At low HF-RF power From Fig. 5a, b, at low HF-RF power (50 W) and with a short time treatment, the degree of disordering increases with low pressure whereas it decreases by increasing the pressure. Moreover, with a long-time treatment, the degree of ordering increases by increasing pressure. At HF-RF power (100 W), the treatment time effect is clearly seen with high gas pressure especially with a short process time. With a 90-min process

time, there is no pressure influence on the crystalline structure.

At high HF-RF power As shown in Fig. 5c, d, the level of disordering increases by decreasing the gas pressure. And, the crystalline structure of the carbon fibers treated for 60 min becomes more ordered with high pressure. Furthermore, the pressure effect of 90-min treatment time on the disordering structure decreases by increasing the high HF-RF power.

Interfacial properties

Since the obtained results are very complicated and require more detailed work, only samples which show an increment higher than 8 % of order/disorder crystalline structure have been selected at this stage of our work, as in Table 1, and fitted Raman-band parameters of these fibers are shown in Table 2.

According to previous Raman spectral analysis, central peak positions (x_o) of both Raman bands were shifted due to enharmonic distribution, decrease in bond modulus and increase in stress [12, 27, 28] and also increase in crystallite size. Moreover, FWHM (G) of the treated fibers decrease due to an increase in fiber modulus [8, 16, 17] and having more-ordered molecular structure. According to the low value of the FWHM (w_D/w_G) and the integrated intensity (I_D/I_G) ratios, it can be inferred that the tensile strain of the treated carbon fibers increase [10, 12, 16, 29]. Furthermore, the percentage increase in the relative integrated intensity ratio of G-band (or decrease in I_D/I_T) shows to a higher degree of graphitization, fiber modulus and crystallite size [4, 18, 29–31]. And, a similar relation between these Raman parameters can also be seen in Fig. 6. Therefore, it can obviously be inferred that tensile strain, fiber modulus and crystallite size of the high-ordered carbon fibers listed in Table 1 increase with nitrogen high-frequency RF plasma treatment under different processing conditions. Also, sample 8 (in Table 1) has the highest property and ordered structure due to crystallization [9, 17]. According to these results, it is very important to mention that there will be subsequent extensive measurement and analysis in future work.

Conclusion

In conclusion, this study points out that high-frequency capacitively coupled RF nitrogen plasma treatment processes have unexpected effects on structural ordering/disordering and some interfacial properties of the unsize HS PAN-based carbon fiber. Different structural changes were observed with different gas pressures, RF powers, and exposure times that are: (a) In short time treatment, the

amount of disordered structure increases with increasing HF–RF power at low pressure due to the increase in excitation and rotational temperatures of the neutral nitrogen molecular gas and also non-Ohmic electron heating. (b) In long time treatment, the degree of ordered structure increased with HF–RF power with high pressure due to Ohmic electron heating. (c) 90-min treatment is too long to observe structural changes at very high pressure, and interfacial properties of the carbon fibers were improved more with high pressure and high power.

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