EFFECT OF UV-OZONE TREATMENT ON PHYSICOCHEMICAL PROPERTIES OF MESOPOROUS HOLLOW CARBON NANOPARTICLES

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ABSTRACT: Carbon nanoparticles have been widely used in various applications. However, they are commonly known to have low dispersibility and chemical inertness which limit their practical ability in medical or biological area. Some studies have been performed to modify carbon nanoparticles such as carbon nanotubes using ultraviolet (UV)-Ozone system. However, little is known on the effects of such system towards other types of carbon nanoparticles such as mesoporous hollow carbon nanoparticles (MHCNs). Thus, in this study, improvement of MHCNs physiochemical properties have been studied using UV-Ozone treatment for the first time. The treatment was conducted in water as dispersant agent at ozone flowrate of 1.0 L/min and exposure time of 45 min. SEM images observed that MHCNs morphology and surface structure remain intact after the treatment. Observations on the dispersibility of MHCNs in phosphate buffered saline (PBS) solution shows that the dispersibility was improved compared to the untreated ones. This was supported by the low Z-average and PDI values of treated MHCNs obtained at ~400 nm and 0.2, respectively when compared to the untreated MHCNs which was obtained at 970 nm and 0.417, respectively. Thermogravimetric analysis (TGA) showed an increased in weight loss of treated MHCNs at the lower temperature compared to untreated MHCNs. Results from Fourier Transform Infrared (FTIR) showed an increase number of new functional groups that includes carboxylic acid group presence at the surface of treated MHCNs which contributes to the improvement of their dispersibility, thermal properties and chemical functionality. These findings opened a new possibility of using UV-Ozone treatment to improve physicochemical properties of MHCNs for medical area such as in drug delivery application in addition to their excellent storage and carrier system.

KEY WORDS: *Hollow carbon, Nanoparticles, Surface modification, UV/Ozone treatment, Dispersibility*

1. INTRODUCTION

Carbon nanomaterial possesses unique characteristics and properties by having nanoparticles in size. Mesoporous hollow carbon nanospheres (MHCNs) are one of many other carbon nanoparticles being developed in recent years [1-3]. MHCNs are among the

most studied nanoparticles along with carbon nanotubes (CNTs), graphene, carbon nanofibers and ordered mesoporous carbon nanoparticles [4]. Each of these carbon particles which is differentiated by their shape and morphology have their own capabilities and excel in different areas with greater efficiency due to high chemical and thermal stability, high surface area, large pore volume and good biocompatibility [4-6]. Meanwhile, MHCNs offer additional characteristics such as high payload, unique morphology, sustained release and tunable pore size and wall thickness [1, 7] which enable them to be used as the material for various applications not limited to biological area such as drug/protein delivery [6-8], bioimaging [9], supercapacitor [10], biomolecular sensing [11], support catalysts [12] and dye removal [13]. However, full capabilities of carbon-based nanoparticles are restricted since they are essentially chemically inert [6, 14] due to the absence/limited functional groups on the surface. Moreover, their original nature of low oxygen content is hydrophobic that repels polar molecules such as water which leads to poor solubility, particles aggregation and low dispersibility [8, 15, 16]. These limitations have become the major issues for their applications in biomedicine setting where further surface modification is needed prior to the application [16]. Hence, the step to modify carbon nanoparticle into a multifunctional and high-performance tool for biological applications is needed.

Surface functionalization of carbon nanoparticles is commonly utilized as an efficient solution to tune the surface wettability of the materials, impart biocompatible properties and add various specific functions [16-18] including through chemical grafting. Grafting molecules with targeted functional groups onto the surface functionalized carbon surface via covalent binding with oxygen or nitrogen based functional groups can be achieved to form stable interaction [16]. Several modification techniques have been employed to treat carbon nanoparticles which include oxidation, ozonolysis, plasma treatment and dehydrogenation [16]. The most common and widely used method is known as the acid treatment using a mixture of concentrated acid solutions to oxidize the carbon material [16, 19-23]. Surface treatment of carbon nanoparticles using conventional wet treatment method has been found to be able to modify their surface with oxygen functional group such as carboxylic acid and ester group and make them to be chemically active [16, 24]. Acid treatment can improve the hydrophilicity and degradability of carbon nanoparticles by introducing various functional groups such as carboxylic and ester groups on their surfaces where further modification can be accomplished. Unfortunately, the use of strong mixture of acids such as sulfuric acid and nitric acid proves to be fatal when the length and morphology of the carbon nanoparticles are adversely deformed due to surface etching [25, 26]. Moreover, this process requires harsh reaction conditions which also produce huge amount of acid waste to the environment [25, 27].

Herein, alternative oxidation approaches such as ozone, vapor-ozone or UV-Ozone have been developed as substitute method of modifying the carbon nanoparticles properties such as carbon nanotubes and graphene [25, 26, 28]. Among others, UV-Ozone treatment has gained popularity as it is a simple and environmentally friendly method which does not produce toxic acid wastes that can damage the environment with no adverse deformation on length and morphology of the nanoparticles [25]. To date, the improvement of carbon nanoparticles properties using UV-Ozone treatment has been under limited investigation for CNTs and graphene where organic solvents such as benzophenone and acetone [26] has been used as dispersant medium. Normally, carbon materials synthesis using different method shows different physicochemical properties. Following this, current study was carried out for the first time to study the effect of UV-Ozone treatment on MHCNs prepared previously by surfactant-free sequential heterogeneous nucleation pathway [1] in the

presence of water as dispersing agent. Chemical functionalities and dispersibility effect of treated MHCNs were investigated and further compared with UV-Ozone treated CNTs and carbon dendrite nanoparticles (CDNPs). The CDNPs were a modified form of MCHNs with similar hollow core but having rough surface structure. They were synthesized using the modified surfactant-free sequential heterogeneous nucleation pathway. It is suggested from this study that alternative strategy with UV-Ozone system to commonly used acid treatment could be used to modify MHCNs with improved biological advantages.

2. MATERIALS AND METHOD

2.1. Materials

The carbon nanoparticles involved in this experiment were mesoporous hollow carbon nanoparticles (MHCNs), carbon nanotubes (CNTs) and carbon dendritic nanoparticles (CDNPs). CDNPs were collected from the Laboratory of Advance Functional Nanomaterial, Australia Institute of Bioengineering Nanotechnology, University of Queensland and CNTs were purchased from Helix Material Solutions Inc., Texas, United States. All other chemicals including 95% tetrapropyl orthosilicate, 25 wt% ammonia solution for analysis, 99% resorcinol, absolute ethanol (analytical grade) and 37 wt% formaldehyde solution were purchased from Sigma Aldrich company.

2.2 MHCNs Synthesis

The MHCNs were prepared by previously described method by Nor and co-workers [7]. Tetrapropyl orthosilicate (TPOS, 3.46 mL, 12 mmol) was added to the solution containing ethanol (70 mL), water (10 mL), and ammonia solution (3 mL, 25 wt%) under stirring at room temperature. After 15 min, resorcinol (0.4 g) and formaldehyde (0.56 mL, 37 wt%) were added to the solution and the system was kept stirring for 24 hr to obtain as-synthesized composites. The as-synthesized solid products were collected by centrifugation and dried at 50 ℃ overnight. The as-synthesized products were further carbonized at 700 ℃ under an N_2 atmosphere. The silica templates were removed by hydrofluoric acid (HF, 10%) etching. The precipitates were further separated by centrifugation, washed with water and ethanol, and dried at 50 ℃ overnight.

2.3. Sample Pretreatment

Carbon nanoparticle samples must be cleaned and free from any impurities before UV-Ozone treatment. Before use, the nanoparticles were washed in ethanol solution by sonication to remove any contaminant present on the surface. After several washing cycles the solvent was removed by vacuum filtration and the nanoparticles were allowed to dry in oven at 80 °C overnight before being weighted prior to UV-Ozone treatment.

2.4. UV-Ozone Treatment

The UV-Ozone system for surface modification of the carbon nanoparticles was developed as reported in our previous study [29] except that the ozonizer was replaced with commercial ozonizer purchased from Absolute ozone Nano, Edmonton, Alberta, Canada. Pure supply of oxygen gas (O_2) was controlled by a flow rate meter at a constant standard working pressure of 20 psi. The O_2 gas was channeled to an O_2 inlet port lined with polytetrafluoroethylene (PTFE) gas tubing. Ozone was generated as the O_2 gas flows through an electrical discharge and channeled out through the outlet port to the Dresher bottle placed in a self-fabricated UV box. UV-C germicidal lamps (Sanyo Denki, Tokyo,

Japan) were mounted in the UV box. The lamps emit radiant energy of 254 nm wavelengths and constant radiation of 184.9 nm. Each sample of cleaned carbon nanoparticles were weighted by 5 mg. Weighted carbon nanoparticles were placed in the Dreschel bottle and were dispersed in 10 mL water solution by sonication. The Dreschel bottle was placed on an orbital shaker in the UV-Ozone machine setup under ambient air and was aerated with ozone (300 ppm) at flow rates of 1.0 L/min for 45 min. The samples were shaken at 180 rpm to obtain homogenous treatment. Additional two samples of MCHNs were also treated at a prolonged exposure time of 60 min at 1.0 L/min and at an increased flowrate of 1.5 L/min for 45 min.

2.5 Sample Characterization

The UV-Ozone treated samples in water solutions were filtered and dried at the room temperature before being analyzed. Scanning electron microscope (SEM, JSM 5600) operated at 15 kV was used to capture surface morphology of the untreated and treated MHCNs. For SEM measurement, the samples were prepared by adding the nanoparticles on the carbon tape. Thermogravimetric analysis (TGA) analysis was conducted at a heating rate of 10 °C/min to observe the thermal stability behavior of the samples in nitrogen through weight loss (%) measurement. Zetasizer (Nano-ZSP, Malvern) was used to determine the size and dispersibility behavior of the particles in PBS. The samples were dispersed in PBS solutions as a dispersant using water bath sonicator prior to measurement which were carried out at 25°C. FTIR (Thermo Scientific, Nicolet iS50) equipped with attenuated total reflectance (ATR) sampling device containing diamond at mid-IR was used to study the changes of chemical functional groups introduction on the samples surface before and after the treatment. Spectra from FTIR were acquired and processed using Omnic Software (Version 6.3.2). Lastly, digital images of the samples in water were captured to observe the stability of the nanoparticles in the PBS. The nanoparticles were initially dispersed in PBS using water bath sonicator and were leave in static condition before the images were taken at various time points.

3. RESULTS & DISCUSSION

3.1. Particle Morphology and Structure of the Samples

Scanning electron microscopy (SEM) images of the treated and untreated MHCNs were taken to study the effect of the treatment condition on the samples. Fig. 1A shows that the untreated MHCNs have smooth spherical morphology. Similarly, Fig. 1B shows that the treated MHCNs at a flowrate of 1.0 L/min for 45 min maintained their spherical morphology after treatment when compared to the untreated MHCNs. There were no obvious damages on the shapes and surface structure of the MHCNs with no reduction of the particle size of the MHCNs observed. The size of the nanoparticles was maintained at an average size of 300 nm as measured from the SEM images using ImageJ software. In contrary, a study by Najafi and co-workers discovered that acid treatment can severely damage the carbon particles morphology [25]. Hence, UV-Ozone treatment using water as dispersant agent proved to be an efficient method compared to acid treatment.

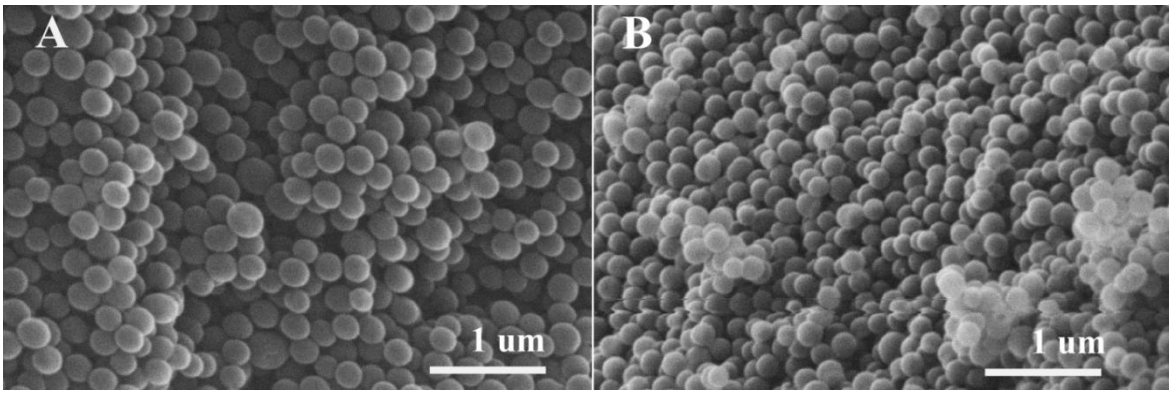

Fig. 1. SEM images at x25k magnification of (A) untreated MHCNs and (B) UV-Ozone treated MHCNs at flowrate of 1.0 $Lmin^{-1}$ for 45 min.

3.2. Chemical Functionalization of the Samples

Introduction of various functional groups on the carbon nanoparticles surfaces are said to improve the physicochemical behavior of the samples. By using FTIR, changes in functional groups present on the structure of nanoparticles were observed as in Fig. 2. Spectra obtained from Fig. 2 shows that newly formed peaks were introduced on the MHCNs after treated with UV-Ozone treatment. Black line representing the MHCNs-UT shows that there were peaks at 3272.53 cm^{-1} of hydroxyl group (O-H) and 1539.75 cm^{-1} of C=C groups. Meanwhile, red line representing the MHCNs treated at 1.0 L/min for 45 min shows shifted peaks at 3445.12 cm^{-1} representing the O-H group, 1716.02 cm^{-1} of C=O, 1622.09 cm^{-1} of C=O and 1241.04 cm^{-1} of C-O groups. Hence, UV-Ozone treatment on the MHCNs gave a high degree of functionalization, indicated by the high amount of oxygenated functional groups attached on their structures. This result was obtained because the MHCNs possess small amount of oxygen elements of about 7.1% [1] which were introduced during the synthesis of MHCNs which considered as defect side thus can be easily reacted with ozone molecules for further carboxylation formation. Meanwhile, the broad shoulder peaks of O-H stretches of terminal carboxylic group formation is associated with amorphous nature of MHCNs [1] which can easily forms a bond with air [26].

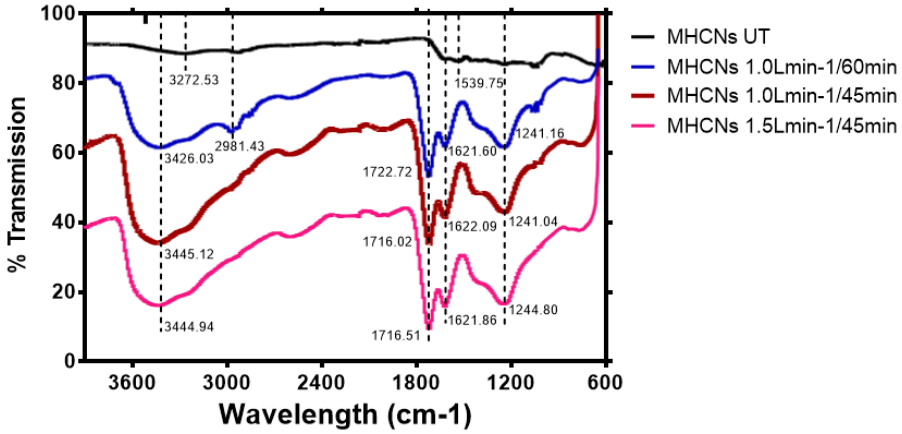

Fig. 2. FTIR spectra of untreated (UT) and treated MHCNs at different flowrates showing introduction of several functional groups after UV-Ozone treatment.

Two additional samples were added to see the effect of increasing treatment time and ozone flowrate on the intensity of the functional groups. Blue line representing MHCNs

treated at 1.0 L/min for 60 min shows introduction of peaks at 3426.03 cm^{-1} of O-H, 1722.72 cm^{-1} of C=O, 1621.60 cm^{-1} of C=O and 1241.16 cm^{-1} of C-O groups. Meanwhile, pink line representing MHCNs treated at 1.5 L/min for 45 min shows introduction of peaks at 3444.94 cm^{-1} of O-H, 1716.51 cm^{-1} of C=O, 1621.86 cm^{-1} of C=O, and 1244.80 cm^{-1} of C-O groups. Peaks at ~1600 cm^{-1} and ~1700 cm^{-1} corresponded to the stretching vibration of C=O from the carboxylic acid groups. Meanwhile, peak at ~3380 cm^{-1} corresponded to the stretching of O-H from phenol group. In addition, peak at ~1550 cm^{-1} corresponded to the stretching of C=C group. There are no huge difference in terms of functional group intensity when the treatment condition is prolonged to 60 min or when the flowrate is increased to 1.5 L/min except for the intensity of the O-H group which is slightly higher for the sample treated at 1.0 L/min for 45 min. This could be because of the treatment condition of 1.0 L/min for 45 min has successfully allowed all the defect sides to be reacted with the ozone molecules.

As a comparison, CNTs and CDNPs samples were also exposed to the UV-Ozone treatment and analyzed by FTIR. Fig. 3 shows the spectra for untreated and treated CNTs as well as untreated and treated CDNPs both at flowrate of 1.0 L/min for 45 min. From Fig. 3, it shows that no significant peak was observed on the structure of CNTs before and after UV-Ozone treatment except at around 2923 cm^{-1} representing the C-H group suggesting that the treatment condition is not sufficient enough to modify the chemical structure of the CNTs sample. It was previously reported that the CNTs can be chemically modified with UV-Ozone treatment in the presence of organic solvent (26). However, in the current study, water was used as the dispersant medium.

Meanwhile for CDNPs, new peaks were observed when compared to the untreated CDNPs (CDNPs UT). Green line representing CDNPs UT shows that there were peaks at 1557.67 cm^{-1} of C=C and 1184.36 cm^{-1} of C-O groups. Blue line representing CDNPs treated at 1.0 L/min for 45 min shows the introduction of new peaks at 3226.92 cm^{-1} of O-H and at 1713.10 cm^{-1} of C=O with increasing intensity of C=O and C-O functional groups at 1614.57 cm^{-1} and 1212.35 cm^{-1}, respectively. In conclusion, UV-Ozone treatment on CNTs shows no modification, while for CDNPs the treatment shows improvement on the degree of functionalization indicated by new peaks introduced on their structures. These results were obtained because CNTs has strong covalent C–C bond thus contained less or absence defect size which cannot reacts with atomic oxygen from the continuous dissociations of the oxygen molecules and the generation of ozone molecules for the carboxylation formation [26, 30]. In contrast, CDNPs were prepared by the same polymerization process as MHCNs with slight modification thus it is expected to perform similarly with MHCNs.

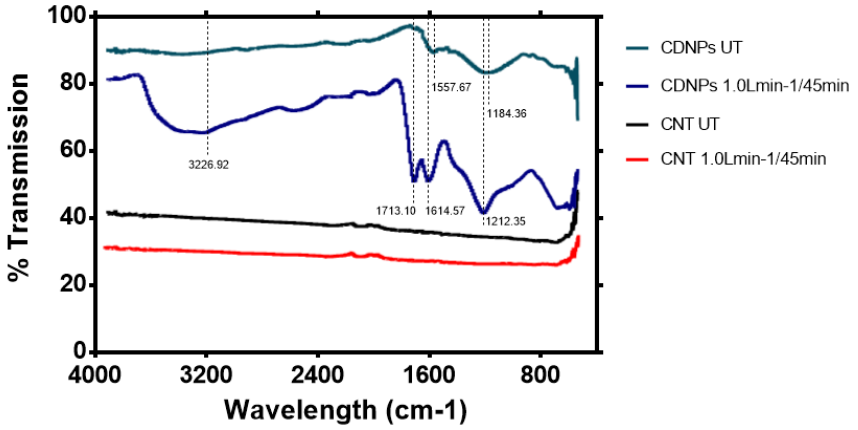

Fig. 3. FTIR spectra of untreated (UT) and treated CDNPs and CNTs showing introduction of several functional groups after UV-Ozone treatment.

3.3. Thermal Stability of Treated MHCNs

Degradation of carbon nanoparticles can be improved by both acid and UV-Ozone treatments. While acid treatment causes severe damage to the morphology of the particles [25], UV-Ozone treatment improvement in degradation can occur without them. Thermal stability study of the samples was performed to indirectly investigate the degradability property of the MHCNs. TGA study of the carbon nanoparticles in an inert atmosphere was also used for determination of functionalization degree. The test was performed with respect to the temperature of 25 °C to 750 °C at a rate of 10 °C/min under inert atmosphere condition. TGA result in Fig. 4 shows that the treated MHCNs undergoes thermal degradation initiated below 50 °C with a higher total mass loss of 2% compared to the untreated MHCNs showing improvement of sample degradability at low temperature after UV-Ozone treatment. Similarly, a rapid weight loss occurred from 50 °C to 470 °C with a total mass loss of 15% for the treated MHCNs which attributed to moisture removal as well decomposition of oxygenated surface functional groups such as carboxylic group [31] which is supporting the FTIR analysis result. It is also reported that oxidation of amorphous carbon residue at external surface of the treated MHCNs can occur in the presence of air due to lower oxidation temperature when carbon nanoparticles were induced with surface functional group.

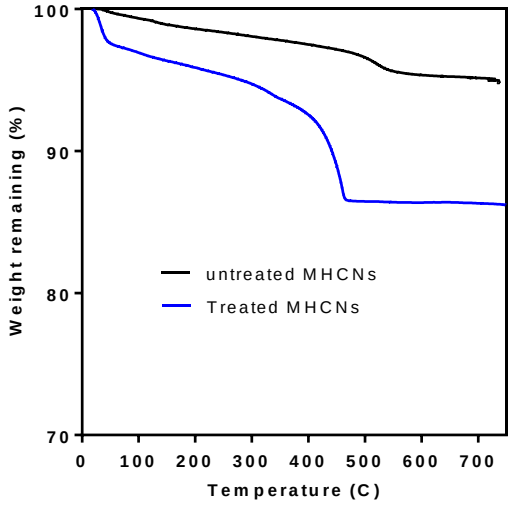

Fig. 4. TGA curves for untreated and treated MHCNs at 1.0 L/min for 45 min showing increase in weight loss (%) for treated MHCNs.

3.4. Dispersibility Study of MHCNs in PBS

Dispersion behavior of the treated and untreated MHCNs in PBS was conducted at static condition. An increase in dispersibility behavior of the nanoparticles in PBS is shown by digital images provided in Figs. 5A and 5B. The cloudy appearance of the mixture in Fig. 5B indicates the disperse behavior of the treated MHCNs at 1.0 L/min for 45 min even up to 24 hr as compared to untreated MHCNs which settled down almost immediately to the bottom of the vials. It is reported that introducing more polar groups on the surface is possible to modulate the surface wettability in which at the macroscopic level, leads to a better coupling with solvents or other materials [30]. Emergence of oxygen based functional groups after treatment makes the surface of carbon nanoparticles to be able to form hydrogen

bonds with water molecules thus increase their hydrophilicity and dispersibility in water. The surface wettability of samples can also improve material solubilization which is the precondition for using carbon-based nanostructures in biomedical applications. It was also observed that the color of treated MHCNs changed from black to dark brown after the UV-ozone treatment because of oxidation which introduced various functional groups on MHCNs surface. Improvement of dispersibility behavior of treated MHCNs in PBS is further supported by the data collected using Zetasizer analysis by measuring the size of the nanoparticles and value of the polydispersibility index (PDI).

Fig. 5. Digital images of nanoparticles dispersion in PBS of (A) untreated MHCNs and (B) treated MHCNs with increasing time under static condition.

Table 1: Zetasizer results for MHCNs samples of Z-average and PDI value

Sample	UT-MHCNs	1.0/45	1.0/60	1.5/4.5	UT(CNT)	TCNT
Z-avg [d.nm]	970	469	438	424	878	608
PDI	0.42	0.23	0.28	0.25	0.70	0.48

PDI value from Zetasizer analysis can be used to confirm particles dispersibility. PDI can be in the range of 0 to 1; whereas as the value approaches 1 is considered as polydispersed while approaching 0 is considered monodispersed. Meanwhile, Z-average value is the measurement of average diameter of nanoparticles. From results shown in Table 1, it can be seen that untreated MHCNs have a Z-average of 970 nm and PDI value of 0.417 which are higher compared to the treated MHCNs at 1.0 L/min for 45 min of Z-average value of 469 nm and PDI of 0.23. This data indicates a higher aggregation of untreated MHCNs compared to the treated MHCNs due to lack of oxygenated functional groups thus increasing hydrophobic property of the particles. The hydrophobic character of carbon-based materials is generally attributed to the non-polarity of the bonds formed by sp2 hybridized carbon atoms [30]. Prolonged treatment of MHCNs at 1.0 L/min for 60 min and increasing the flowrate to 1.5 L/min for 45 min show a minor effect towards the dispersibility behavior of the MHCNs with Z-average of 438 nm and PDI of 0.28 and Z-

average of 424 nm and PDI of 0.25 respectively. These results show that UV-Ozone treatment for MHCNs at 1.0 L/min for 45 min is sufficient to introduce polar functional group on the particles surface. As a comparison, Table 1 also shows that untreated CNTs have a Z-average of 877.8 nm and PDI values 0.7 which were higher compared to the treated CNTs samples indicating that dispersibility behavior of the CNTs samples slightly modified after the UV-Ozone treatment. However, the evidence was not obvious from the FTIR results. Overall, based on the results obtained it was proven that UV-Ozone treatment had the ability to improve the dispersion behavior of MHCNs in PBS solution.

4. CONCLUSION REMARKS

This study focuses on the improvement of physiochemical properties of MHCNs such as their degradation and dispersion ability in solution by using UV-Ozone surface treatment. It was observed that the UV-Ozone treatment did not damage the spherical morphology of the MHCNs when compared to the untreated one. Based on FTIR analysis it was found that the treatment has successfully introduced a number of surface functional groups such as carboxylic group on the structure of MHCNs which contributed to the improvement of particles degradability and dispersibility behavior in PBS compared to untreated MHCNs. Based on the results, it is suggested that prolonged exposure of the samples by 33% or increasing the flowrate of the ozone by 50% has little effect on the physicochemical properties of MHCNs when compared to the treatment at 1.0 L/min for 45 min. It is also found that current treatment conditions are not sufficient to induce defects on CNT surface. This study demonstrated that UV-Ozone treatment can improve physicochemical properties of MHCNs with only water as the dispersing medium at a shorter treatment time. The method offers a great opportunity to chemically modify the structure of the carbon nanoparticles using green solvent, simple steps and devices which provides economical alternative to the conventional approaches.

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