

Research Article

Water-Dispersible Multiwalled Carbon Nanotubes Obtained from Citric-Acid-Assisted Oxygen Plasma Functionalization

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A new and safe method has been developed to functionalize multiwalled carbon nanotubes (MWCNTs) with fewer surface defects, which significantly increases their dispersibility in water. MWCNTs are pretreated in pure ethanol by a supersonic homogenizer. Then, the mixture is dried and soaked in weak citric acid solution. Finally, the MWCNTs in the citric acid solution are treated with radio frequency (13.56 MHz) oxygen plasma. As a result, many carboxyl functional groups are attached onto the MWCNT surfaces and stable dispersion of the MWCNTs in water is obtained. The treatment conditions are optimized in this study.

1. Introduction

Water-dispersible carbon nanotubes (CNTs) have recently become of great importance owing to their promising chemical and physical properties. The most obvious benefits of these water-dispersible CNTs are their value in biochemistry and biomedical engineering, electronic technologies of films, plastic materials, and polymer composites [1, 2]. However, these applications are compromised by their poor dispersibility in water, because substantial van der Waals attractive forces between the CNTs aggregate them in solvents [3]. The most common method of improving their dispersibility in water is to functionalize their surfaces using hydrophilic oxygen-containing groups [4]. This is achieved by oxidizing CNTs by strong acids, such as refluxing in a mixture of sulfuric acid and nitric acid [5, 6], “piranha” solution (sulfuric acid-hydrogen peroxide) [7], boiling in nitric acid [8], or treating with oxidative gases, such as ozone [4, 9]. However, treatment under such harsh conditions clearly deviates from green chemistry and results in the opening of the tube tips [5], shortening of the tubes [7], and fragmentation of the sidewalls [8]. Therefore, their stability decreases and their integral properties change. Also, the acidic treatment often requires a long processing time and produces a large amount

of waste. To overcome these problems, alternative safer and easier functionalization methods should be considered.

In these respects, plasma processing is an advantageous technique when it is used in conjunction with conventional wet chemical methods. Plasma surface modification is particularly interesting because the method is flexible, rapid, contaminant-free, and relatively nondestructive [10, 11]. The excited species (ions, radicals, and electrons) and UV light within the plasma interact with the surfaces of CNTs and break the sp^2 -hybridized carbon (C=C) bonds creating the prime reaction sites [10–12]. A wide range of functional groups can then be introduced onto the surfaces of CNTs depending on the plasma production method, the source gas such as O_2 , N_2 , NH_3 , or H_2O , the input power, and the processing time [10–13].

In this study, we have attempted to modify multiwalled carbon nanotubes (MWCNTs) by three-step processing. MWCNTs are first supersonically mixed into ethanol to be deaggregated temporarily. Then, the mixture is dried and pretreated using citric acid solution. Finally, the MWCNTs in the solution are treated by the oxygen plasma including citric acid and water. This method is safer than the methods mentioned above as no hazardous reagents are used. The surfaces of the MWCNTs are chemically functionalized with carboxyl ($-COOH$) groups, and they can be easily dispersed

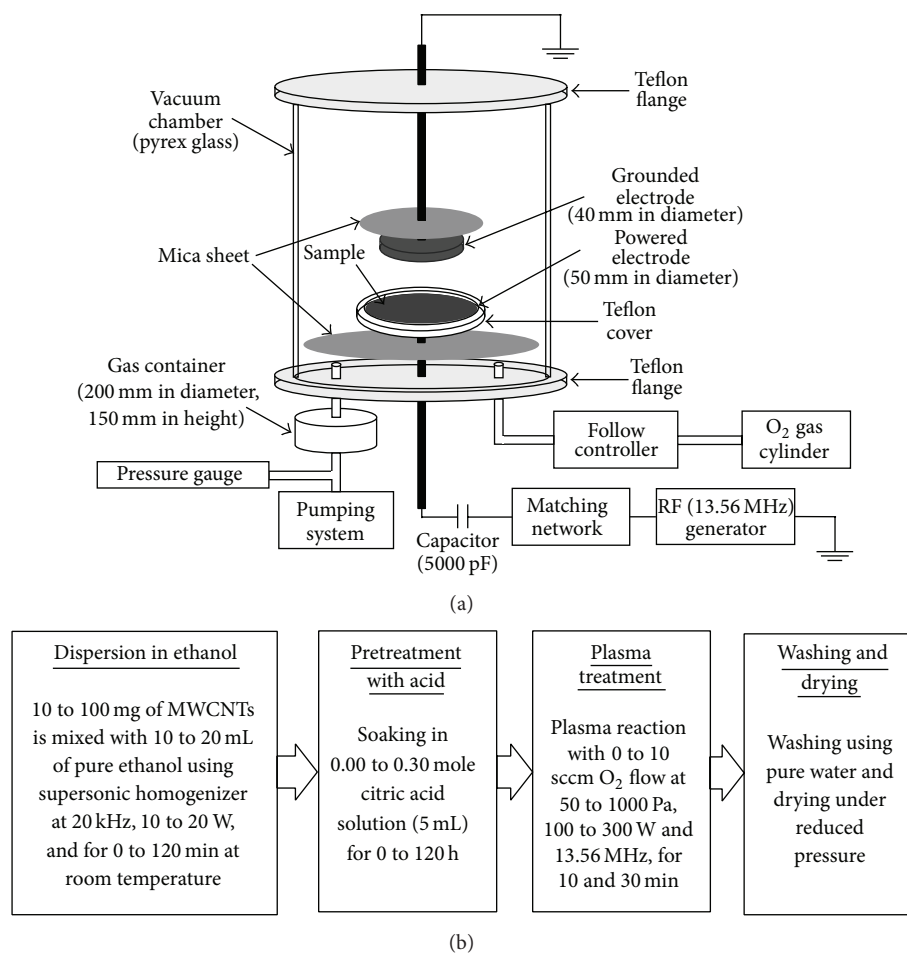


FIGURE 1: (a) Schematic diagram of the plasma reactor. (b) Flow chart of the functionalization process.

in water. Each step of the functionalization processes is optimized by varying the treatment parameters.

2. Experimental Setup and Method

A schematic setup of the plasma reactor and a flow chart of the functionalization process are shown in Figure 1. 10 to 100 mg of MWCNT powder (Sigma-Aldrich, outer diameter = 10 to 30 nm; inner diameter = 3 to 10 nm; length = 1 to 10 μm ; purity > 90%) is added to 10 to 20 mL of pure ethanol (Wako Pure Chemicals Co., purity > 95%) and sonicated at room temperature using a supersonic homogenizer (Sonics Vibra cell, VC 130, Sonic & Materials Inc., $f = 20$ kHz, 6.0 mm ϕ probe) at an input power of 10 to 20 W for 15 to 120 min. The suspension is dried under reduced pressure and soaked in 0.0 to 0.30 mole (5 mL) of citric acid (Wako Pure Chemicals Co., assay > 98%) solution for 0 to 120 h. The MWCNTs in the citric acid solution are then placed on the lower electrode (SUS, 50 mm ϕ) of the reactor, which is evacuated to ca. 400 Pa using a rotary pump at a very slow rate. When the wet phase starts to disappear, oxygen gas is introduced into the reactor at a rate of 0 to 10 sccm and the background chamber pressure is kept at about 400 Pa. Then the plasma reaction is carried out for 10 to 30 min by an RF input power

of $P_{\text{rf}} = 100\text{--}300$ W, $f = 13.56$ MHz. The reflected RF power is minimized (<20 W) by controlling the matching current during the plasma reaction. It is noted that when the samples become fully dried before starting the plasma reaction, they are less reactive for the oxygen plasma. However, when the plasma is started in the wet phase the water molecules and part of the citric acid molecules evaporate with the processing time but are considered to remain inside the chamber and in the gas container connected to the chamber, contributing to the functionalization process. After the treatment, the MWCNTs are washed at least three times using pure water (Wako Pure Chemicals Co., distilled water) and dried under reduced pressure at room temperature.

Fourier transform infrared (FT-IR) spectroscopy is used to measure the chemical groups attached onto the MWCNTs. Approximately 0.5 mg of a dried sample is dispersed in 1.0 mL of propanol, and the mixture is uniformly coated on a CaF₂ substrate (SIGMA KOKI Co., 20 mm diameter and 1 mm thickness), dried, and measured using an FT-IR spectrometer (Shimadzu Co., 8700, 100 scans averaged). The spectra presented in this report are obtained after base line correction.

To study the dispersion stability of the pristine, sonicated, and plasma-treated MWCNTs (hereinafter denoted

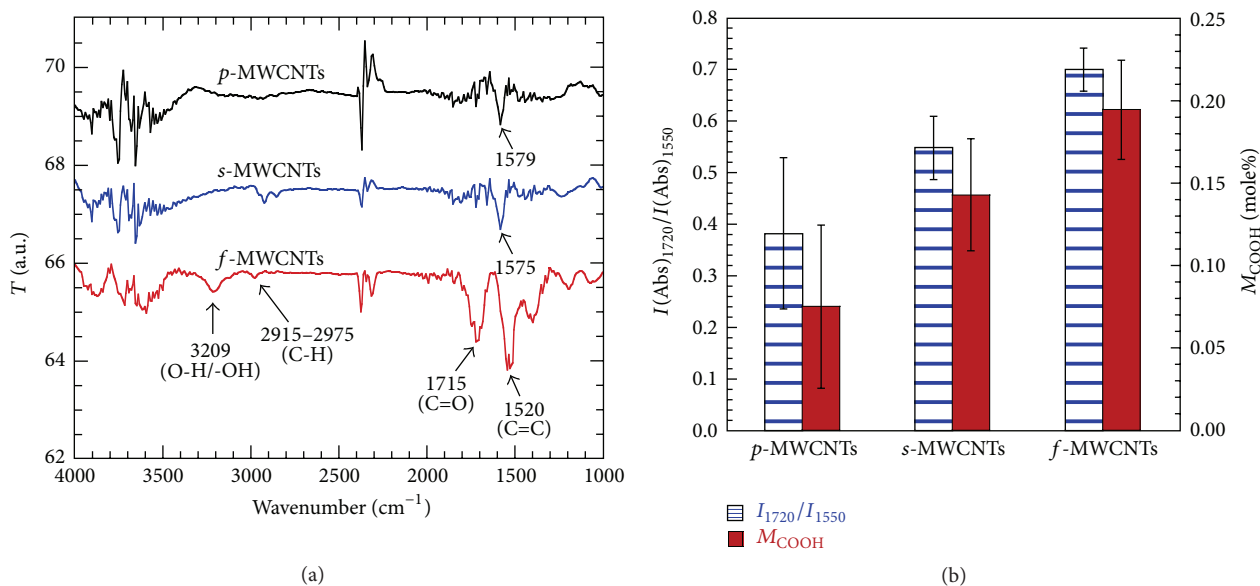


FIGURE 2: (a) FT-IR spectra for the *p*-MWCNTs, *s*-MWCNTs, and *f*-MWCNTs and (b) intensity ratios of the FT-IR absorbance peak at ca. 1720 to the most intense peak in the range 1520–1590 cm^{-1} and the content of carboxyl groups, M_{COOH} (mole%), estimated from the absorbance peak intensities at ca. 1720 cm^{-1} using the calibration curve drawn for benzoic acid.

by *p*-MWCNTs, *s*-MWCNTs, and *f*-MWCNTs, resp.), ca. 1.0 mg of the dried sample is mixed with 8.0 mL of pure water with a brief sonication for 2 min in a bath sonicator (IUCHI Japan, US-1, 110 W, 38 kHz) so that the MWCNTs are dispersed homogeneously. The dispersion stability is examined by a UV-visible spectrometer (JASCO Co., V-630). The sample is placed in a quartz cuvette ($1.0 \times 1.0 \times 4.5 \text{ cm}^3$) and time variation of absorbance (Abs) at a wavelength of 250 nm is measured for 4 h. Here the wavelength is chosen corresponding to the maximum absorbance region of the UV-visible spectra, because Beer's law of the linear relationship between the absorbance and concentration of the absorbing particles holds up to higher concentration in this region as compared to other regions [14]. The dispersion stability is also verified by mixing 20 mg of each sample in 10 mL of pure water with bath sonication for 2 min and then keeping the sample in a glass bottle undisturbed for more than one month.

The surface morphology of the samples is observed by a transmission electron microscope (TEM; HITACHI High Technology Co., H-7500), and the structural quality is measured by a Raman spectrometer (JASCO Co., NR-1800, $\lambda = 532 \text{ nm}$).

3. Results and Discussion

A variety of different techniques can be used to characterize the surface chemistry of CNTs after covalent functionalization [9, 12, 15, 16]. Among them FT-IR is widely used to ascertain the groups attached onto the functionalized CNTs [16, 17]. Therefore, FT-IR spectra of the *p*-MWCNTs, *s*-MWCNTs, and *f*-MWCNTs are measured. Usually, *p*-MWCNTs exhibit an almost featureless FT-IR spectrum because of the high transmittance of the π -electron

structure of symmetric carbons [18]. But in our case a small peak at approximately 1579 cm^{-1} is observed, which corresponds to C=C stretching vibration as shown in Figure 2(a) [16, 19]. *s*-MWCNTs do not show significant difference in the spectrum from that of the *p*-MWCNTs except for C–H stretching peaks at approximately 2925 to 2975 cm^{-1} , indicating an increase in the number of sp^3 carbon bonds [16, 17, 20]. These bonds are assumed to originate from the breakage of C=C bonds. A new clear peak appears at ca. 1720 cm^{-1} in the spectrum of *f*-MWCNTs as shown in Figure 2(a), which indicates the presence of C=O stretching bonds, and the broad band at ca. 3209 cm^{-1} corresponds to O–H/–OH bonds [18, 19]. Hence, it is conjectured that after the plasma treatment MWCNTs are functionalized and that hydrophilic carboxyl (–COOH) groups are attached onto the MWCNTs. Usually C=O stretching vibrations of the –COOH group are observed at 1740 cm^{-1} [8], but in our case the C=O vibration peak is shifted to ca. 1720 cm^{-1} , which suggests the abundance of –COOH groups on the MWCNTs after plasma treatment [21]. The peak at 1520 to 1590 cm^{-1} corresponds to the C=C graphitic stretching mode, which is infrared-activated by extensive sidewall functionalization [16, 21]. When *f*-MWCNTs are dispersed in water, the –COOH groups attached to the MWCNT surface are ionized to COO^- . As a result, the negative charges repel each other and the MWCNTs do not aggregate in the solvent. Thus, a stable dispersed solution is produced from the *f*-MWCNTs.

For the quantitative study of the attached groups different methods such as X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), chemical derivatization, or titration methods are used [9, 13, 15]. Each of these methods has strengths as well as limitations in finding the exact amount of the groups [22]. In this study, absorbance

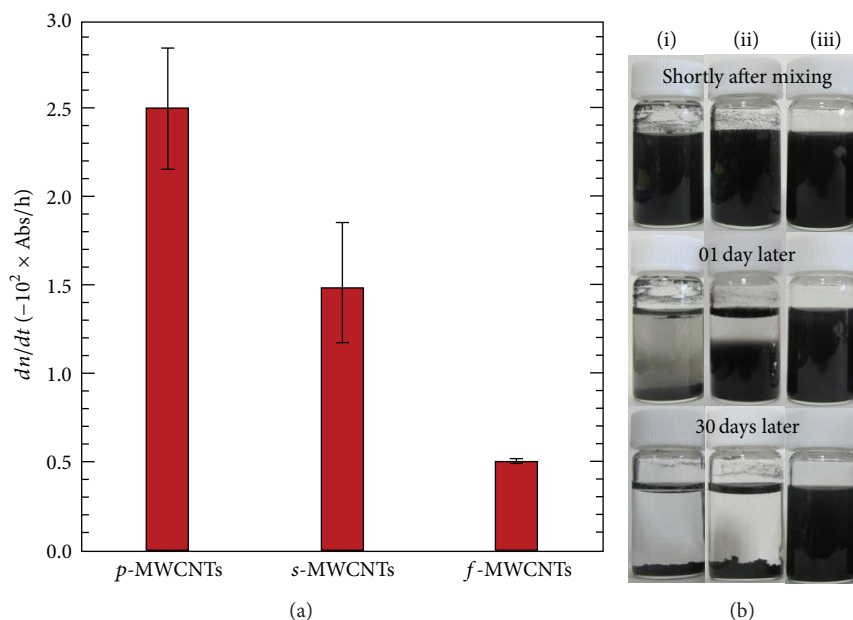


FIGURE 3: (a) Settling speed, dn/dt , calculated from the Abs (250 nm) versus $time$ graphs for the *p*-MWCNTs, *s*-MWCNTs, and *f*-MWCNTs. (b) Photographs of the dispersion of 20 mg of (i) *p*-MWCNTs, (ii) *s*-MWCNTs, and (iii) *f*-MWCNTs in 10 mL of pure water using 2 min of bath sonication.

intensity of the C=O stretching peak in the FT-IR spectra is considered to roughly estimate the quantity of $-\text{COOH}$ groups attached onto the MWCNT surfaces. For this, a calibration curve is drawn from the absorbance spectra of a set of benzoic acid ($\text{C}_6\text{H}_5-\text{COOH}$) solutions of different known concentrations. As $\text{C}_6\text{H}_5-\text{COOH}$ structure has only one $-\text{COOH}$ group in the benzene ring, the intensity of the C=O stretching bond is considered to be a measure of $-\text{COOH}$ content in the solution. The equation of the calibration curve is

$$y = 2.0963x, \quad (1)$$

where x is the molar concentration and y is the corresponding intensity of the absorbance peak at ca. 1720 cm^{-1} , indicating the C=O content of $-\text{COOH}$ groups [19]. Then, using the calibration curve, molar percentages of the $-\text{COOH}$ (M_{COOH}) attached onto the MWCNT surfaces are roughly estimated from the peak intensities of the absorbance data of the *p*-MWCNTs, *s*-MWCNTs, and *f*-MWCNTs at ca. 1720 cm^{-1} and are shown in Figure 2(b). The ratios of the peak intensity at ca. 1720 cm^{-1} and that of the intense peak in the range 1520 to 1590 cm^{-1} , I_{1720}/I_{1550} , are also calculated to confirm the content of $-\text{COOH}$ groups. It is observed that *p*-MWCNTs contain a small amount of $-\text{COOH}$, which may originate from their purification process. The content is slightly higher for *s*-MWCNTs, which may be due to the interaction of ethanol with MWCNTs under the cavitation forces in the sonication process. The significant increase in C=O content and the increase in I_{1720}/I_{1550} after the plasma treatment indicate the functionalization of MWCNTs. It is conjectured that during the acidic pretreatment, citric acid molecules become wrapped around the MWCNTs. From

the Raman spectra (described later), it is observed that the *p*-MWCNTs have defect sites on their structure. Therefore, there is a chance for the citrate ions to slowly attack the weak parts of the MWCNTs. As a result, some primary reaction sites may temporarily become functionalized. Besides, a large number of active sites are assumed to be generated on the surfaces of the MWCNTs from the attack of energetic ions and radicals produced during the plasma treatment. The oxygen ions and radicals are highly reactive and can form covalent bonds upon reacting with dangling bonds or defects [12]. The active sites then become attached to $-\text{OH}$ or $-\text{COOH}$ groups, which are generated from the fragmentation of the citric acid, water, and oxygen.

The surface functional groups increase the dispersion stability of MWCNTs. Hence, dispersion stability can be an indirect measure of the degree of MWCNT functionalization. UV-visible spectroscopy is used to study the dispersion stability of the treated samples in pure water. The absorption of UV-visible light is quantitatively highly accurate [14] and the change in absorbance with time can be interpreted as dispersion stability of MWCNTs in water. Because the absorbance of the solution is proportional to the concentration of the absorbing particles in the solvent [14], the settling speed (dn/dt), measured from the slope of the linear fitting of the Abs versus $time$ graph, would give the information about the amount of MWCNTs present in the optical path. Settling speed was observed to be used as a measure of studying the functionalized MWCNTs [23]. A decrease in dn/dt represents an increase in the dispersion stability of MWCNTs in the solvent.

The settling speeds (with error bars) of the *p*-MWCNTs, *s*-MWCNTs, and *f*-MWCNTs in water are shown in Figure 3(a), which are averaged from at least three times

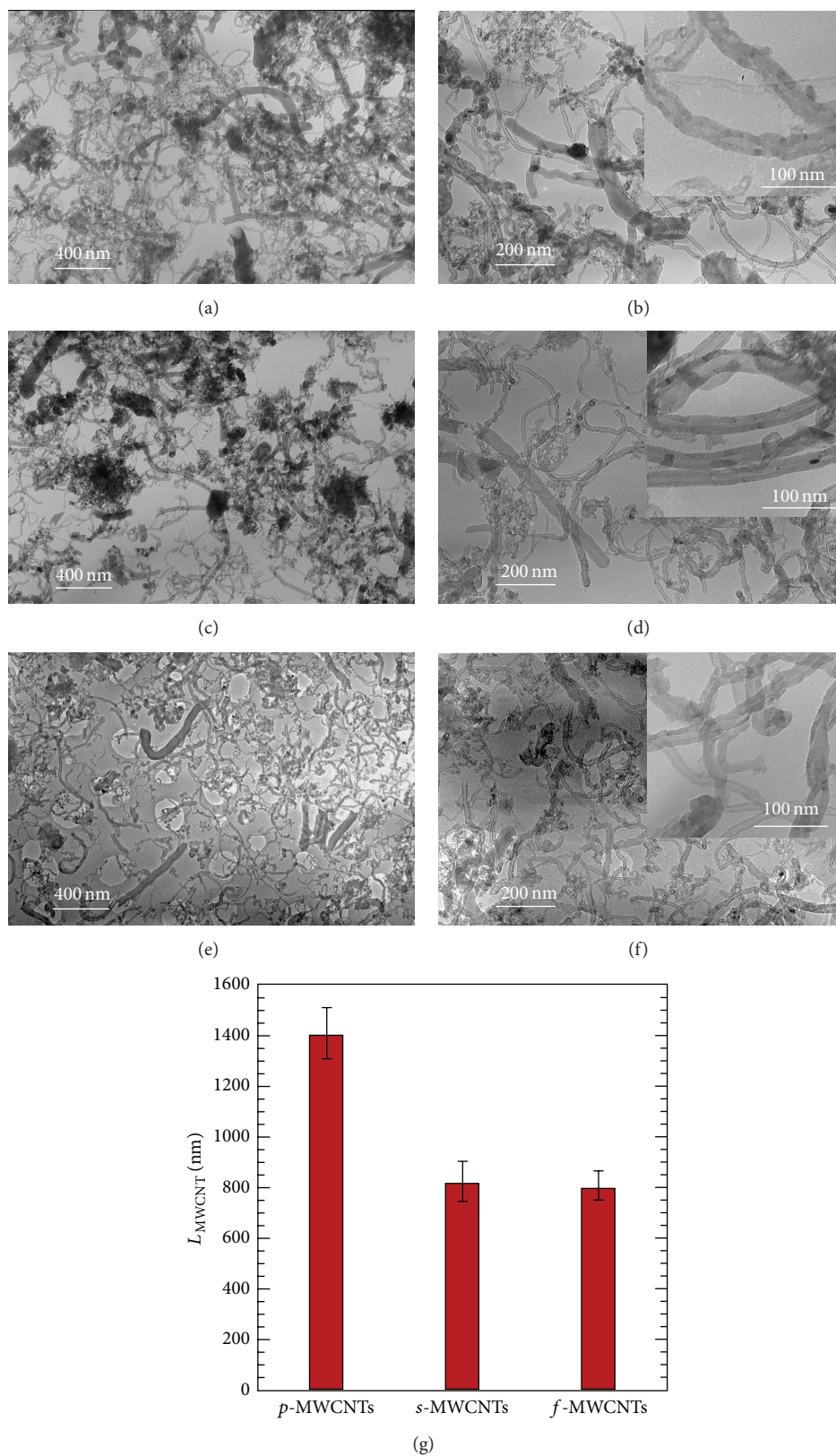


FIGURE 4: TEM images of the (a) and (b) *p*-MWCNTs, (c) and (d) *s*-MWCNTs, and (e) and (f) *f*-MWCNTs at different magnifications taken at an accelerating voltage of 100 kV. Insets of (b), (d), and (f) are showing higher magnification images. (g) Average MWCNT length (L_{MWCNT}) measured from more than 30 MWCNTs in each sample from several TEM images.

of the measurement. The lower value of dn/dt for the s -MWCNTs than for the p -MWCNTs indicates that the dispersibility is enhanced slightly by sonication. However, after the citric-acid-assisted plasma treatment, dn/dt becomes one-fifth that of the p -MWCNTs, which indicates the strong enhancement of dispersibility. The dispersion stability can also be observed in the optical photographs shown in Figure 3(b). It is observed that the f -MWCNTs produce a darker suspension than p -MWCNTs or s -MWCNTs, and the little change in the darkness even after a week indicates the higher dispersibility of f -MWCNTs. p -MWCNTs agglomerate soon after they are dispersed in water and form loose sediment on the container bottom. A part of the MWCNTs is assumed to be broken into shorter pieces during the supersonic treatment, and they are less likely to become entangled and aggregate [24]. As a result, the dispersibility of s -MWCNTs is improved. On the other hand, the f -MWCNTs disperse easily in water and the suspension remains stable for more than one month confirming the enhanced dispersibility.

The morphology of the MWCNTs is observed by TEM at each step of functionalization as shown in Figures 4(a)–4(e). The typical TEM images indicate that f -MWCNTs are more dispersed than p -MWCNTs and s -MWCNTs. Shortening of the MWCNT length is observed as a result of sonication, but almost no further shortening is observed after the subsequent plasma treatment. The plasma species only affect the surfaces of the MWCNTs and not the bulk [12]. No significant defects are observed on the sidewalls of f -MWCNTs in the TEM images of higher magnification, which suggest the preservation of structural integrity.

Raman spectrum is an important tool to study the CNT structure [25, 26] and is widely used to assess the amount of defects [16, 17]. Raman spectra of the p -MWCNTs, s -MWCNTs, and f -MWCNTs are presented in Figure 5, which are normalized and bodily shifted in the intensity axis. The defect induced D band appears at ca. 1350 cm^{-1} , which indicates the amount of disordered carbon in the CNT structure, and its intensity, I_D , corresponds to the degree of disorderiness. The G band at ca. 1600 cm^{-1} corresponds to the graphitic (ordered) carbon, and its intensity, I_G , corresponds to the amount of ordered carbon. Therefore, the ratio, I_D/I_G , is used to estimate the change in structural quality of CNTs after functionalization in different processes. Defect density corresponding to I_D/I_G for the p -MWCNTs, s -MWCNTs, and f -MWCNTs is observed to be 1.05 ± 0.02 , 1.06 ± 0.01 , and 1.08 ± 0.03 , respectively. The changes are very small, and also no distinct changes are observed in terms of the Raman shift. These suggest that the MWCNT structure and the chemical composition of the interior of the CNTs are almost unaffected by the ultrasonic and plasma treatments. This is also supported by the results of the TEM measurement.

On the basis of the above results, the basic functionalization scheme of the MWCNTs by the citric-acid-assisted oxygen plasma treatment is summarized in Figure 6. MWCNTs are long and web-like and remain strongly aggregated. When they are dispersed in ethanol by the supersonic treatment, ethanol molecules enter the aggregated parts of the MWCNTs and weaken the attractive forces between them. When the

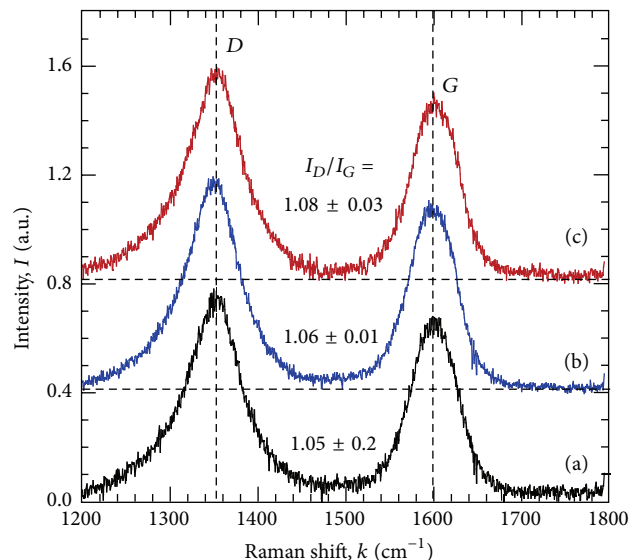


FIGURE 5: Raman spectra of the (a) p -MWCNTs, (b) s -MWCNTs, and (c) f -MWCNTs.

s -MWCNTs are placed in the citric acid solution, the citrate and hydronium ions attack their weak parts. During the plasma reaction, oxygen, water, and citric acid molecules or ions are fragmented to generate oxygen containing ions, radicals, and CO or CO₂, which react with the defect sites [12, 27, 28]. The CO and CO₂ are oxidized to form $-\text{COOH}$ groups and attach to the MWCNT surfaces [18]. Also, the attached $-\text{OH}$ groups are further oxidized to form $-\text{COOH}$ groups [17, 28]. These functional groups enable the MWCNTs to readily disperse in water due to hydrogen bonds formed between the carboxylic acid groups and water molecules [29]. The negatively charged surfaces of the CNTs repel each other and prevent them from coagulating. The polar interactions of the functional groups with the water molecules reduce the settling speed of the f -MWCNTs [29].

3.1. Optimization of the Functionalization Process. The dispersion stability depends on the degree of functionalization. Therefore, the settling speed shows qualitatively the content of functional groups attached to the MWCNT surfaces. Using this, optimal treatment conditions are sought for each step of the processes.

Sonication parameters play very important role in the dispersion of CNTs [30, 31]. To optimize the input sonication power, 10, 15, and 20 W are considered for the treatment of 30 mg of MWCNTs in 20 mL of pure ethanol for 60 min. For optimum treatment time, 30 mg of MWCNTs in 20 mL of ethanol is treated for 15, 30, 60, 90, and 120 min at an input power of 15 W. MWCNTs of 10, 30, 50, and 100 mg in 20 mL of pure ethanol are treated at 15 W for 60 min to optimize the amount in ethanol. Temperature of the mixture is kept constant by placing the flask containing the sample in a bath of ice water during the sonication to facilitate the equilibrium condition for the treatment [31]. The dn/dt is measured for all of these samples as described earlier and presented in

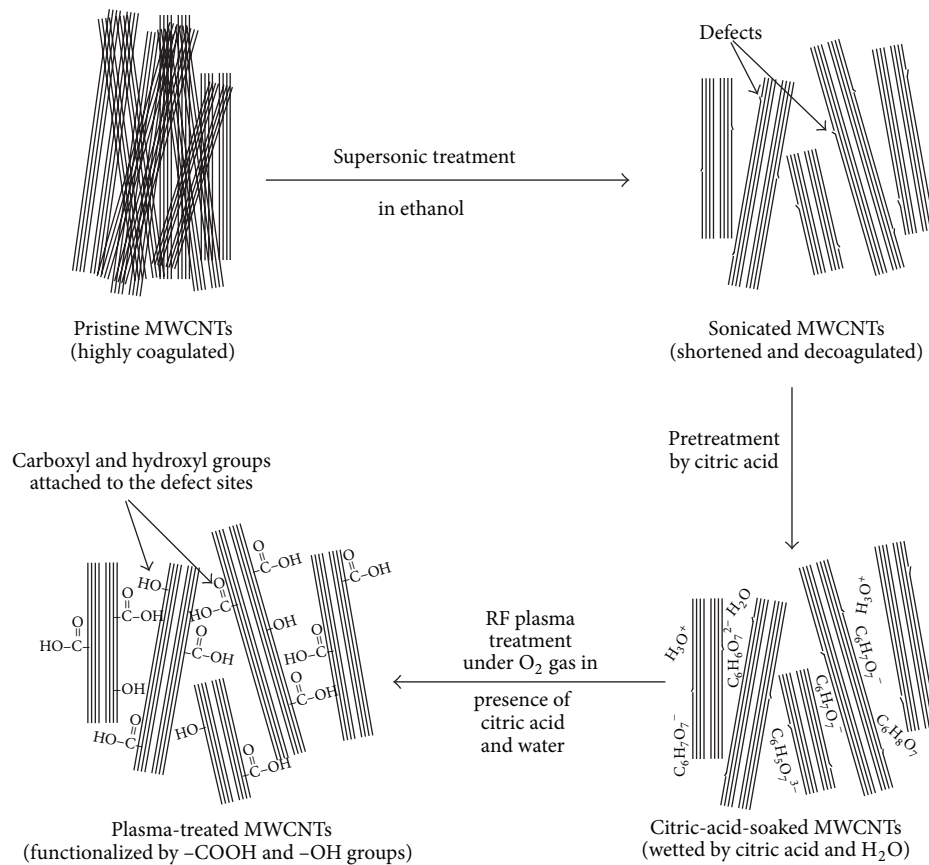


FIGURE 6: A model of the functionalization process of MWCNTs.

Figure 7(a), based on which it is observed that treatment of 30 mg of MWCNTs in 20 mL of ethanol at an input power of 15 W for 60 min is optimum for supersonic treatment.

The degree of plasma functionalization changes with the citric acid density and the soaking time. To optimize these, *s*-MWCNTs sonicated at optimum condition are placed in 5 mL of citric acid solution of 0.10, 0.15, 0.20, and 0.30 mole for 48 h. For optimum soaking time *s*-MWCNTs are soaked in 0.15 mole (5 mL) citric acid solutions for 0, 24, 48, and 120 h. After soaking, each sample is plasma treated for 15 min at 200 W with O₂ flow of 5 sccm. Then dn/dt is measured for these *f*-MWCNTs, which are presented in Figure 7(b). It is observed that soaking in 0.15 mole citric acid solution for ca. 48 h is optimum for citric acid treatment. Though dn/dt decreases for the samples soaked for longer time, 24 to 48 h is considered as sufficient, because after this the changes in the dn/dt are not so high.

To optimize the plasma reaction condition three different O₂ flow rates are considered (0, 5, and 10 sccm), at which the samples are plasma treated at a pressure of ca. 400 Pa and P_{rf} of 200 W for 15 min. Similarly, background pressure is varied from 50 to 1000 Pa for the treatment at P_{rf} = 200 W for 15 min with 5 sccm O₂ flow. RF power is varied as 100, 200, and 300 W at a pressure of 400 Pa with O₂ flow of 5 sccm and treatment time of 15 min. The treatment duration is varied as 10, 15, 20, and 30 min with O₂ flow

of 5 sccm and P_{rf} of 200 W with background pressure of 400 Pa. From the values of dn/dt for all these samples, which is shown in Figure 7(c), it is observed that 5 sccm O₂ flow, 400 Pa background pressure, 200 W RF power, and ca. 15 min treatment duration are optimum for the efficient functionalization. Plasma treatment without an O₂ flow is found to be less efficient. On the other hand, a higher O₂ flow rate (10 sccm) is also observed to deteriorate the functionalization. Higher RF power (300 W) is also observed to deteriorate the dispersion stability, which is assumed to be due to the dissociation of the functional groups to other groups. In the same way, 15 min of plasma treatment at 200 W has a more positive effect on functionalization than 10 min treatment and 20 or 30 min treatment results in no significant enhancement of functionalization. It is conjectured that after 15 min of treatment the plasma reaction reaches a saturation level, and therefore further treatment cannot improve the functionalization.

For clear results on the quantitative measurement of the attached groups XPS analysis is necessary, which will be done in the near future. As the plasma comes in from the upper side, surface part of the samples on the electrode may react more strongly than the inner part. Therefore, to obtain uniform functionalization, modification of the reactor configuration would be necessary, which is under active consideration.

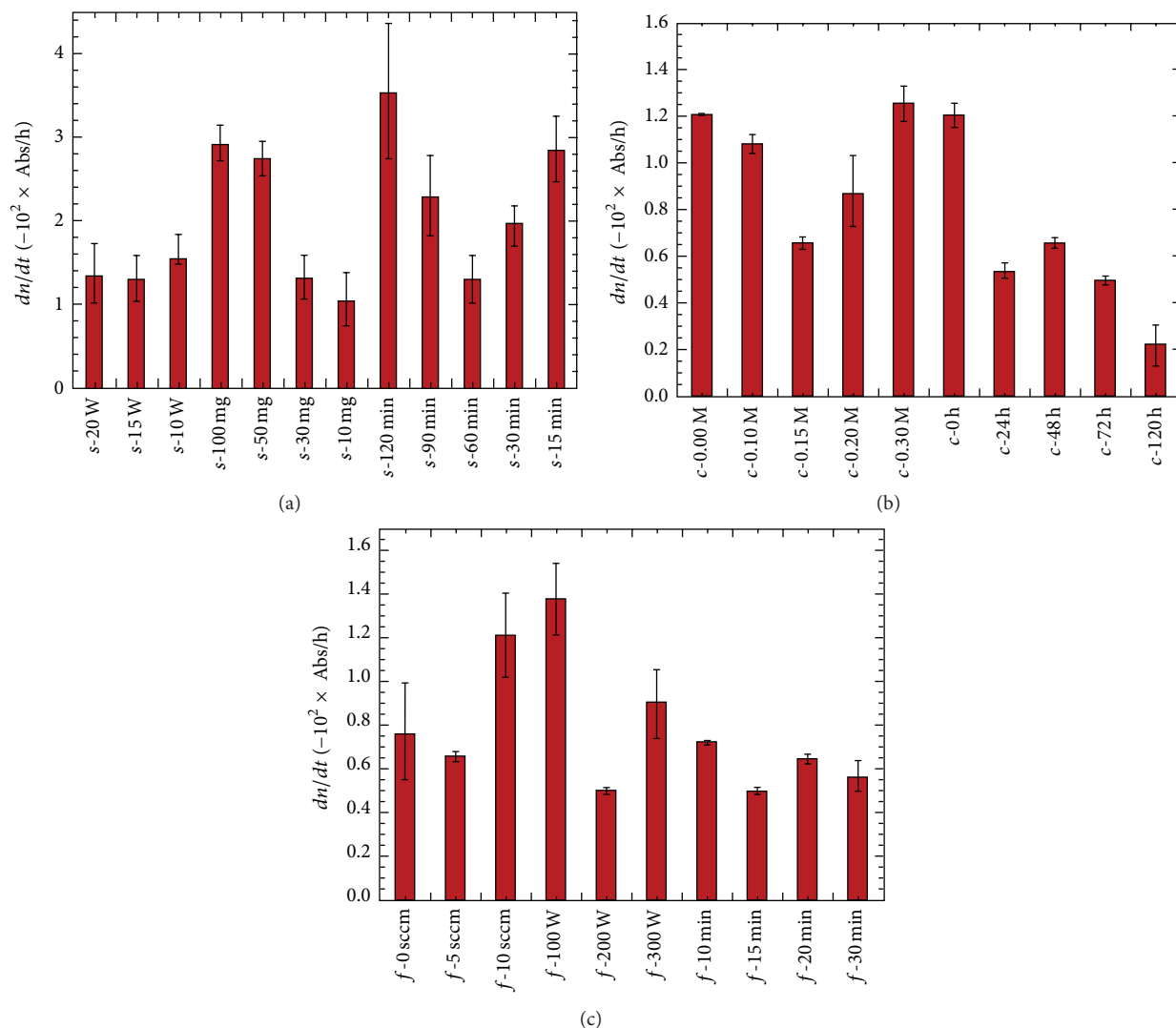


FIGURE 7: Settling speeds, dn/dt , measured (a) for the s-MWCNTs treated supersonically at different powers (10 to 15 W), different amounts (10 to 100 mg) in 20 mL ethanol, and different durations (15 to 120 min) at room temperature, (b) for the plasma treated samples soaked in different concentrations of citric acid (0.00–3.0 M), and for different durations (0 to 120 h) at room temperature, and (c) for the f-MWNTs plasma treated at different oxygen flows (0 to 10 sccm), RF power (100 to 300 W), and for different durations (10 to 30 min).

4. Conclusions

A new and safe method has been developed to functionalize MWCNTs. In the sequence of treatments, MWCNTs are pretreated in pure ethanol using a supersonic homogenizer, wetted using citric acid solution, and plasma treated using RF oxygen plasma. By the plasma reaction in the presence of citric acid, O_2 , and water vapor, plasma species interact with them to create many kinds of ions and radicals. They attack the MWCNT surfaces and activate a large number of sites to enhance the attachment of $-\text{COOH}$ groups onto their surfaces. These attached groups significantly enhance the dispersion stability of the MWCNTs in water. The structural integrity of the f-MWCNTs is conjectured to be preserved after plasma treatment, which is verified by the Raman and TEM measurements. The most suitable treatment parameters in this process are the sonication of 30 mg MWCNTs in 20 mL

ethanol at room temperature for 60 min at a probe power of 15 W, soaking in 0.15 mole (5 mL) citric acid solution for ca. 48 h, and plasma treatment for ca. 15 min at a pressure of ca. 400 Pa and an RF power of 200 W with ca. 5 sccm O_2 flow.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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