

Effects of ozone generated by dielectric barrier discharge on water-solubility of single-walled carbon nanotubes

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Abstract: This paper describes effects of ozone on water-solubility of single-walled carbon nanotubes (SWCNTs). Ozone was generated by dielectric barrier discharge (DBD) in air with the maximum concentration of 200 ppm. Water solubility of ozone-treated SWCNTs, which was evaluated by optical absorbance of the SWCNT suspension, increased with ozone treatment time. The dispersed SWCNT suspension was almost stable even after two months of the ozone treatment. FT-IR and Raman spectra measurements revealed that SWCNTs surface was functionalized with hydrophilic $-\text{COOH}$ group.

Key words: dielectric barrier discharge, ozone, single-walled carbon nanotubes, solubility

1. General

Single-wall carbon nanotubes (SWCNTs) own remarkable physical and chemical properties that might lead to a variety of potential applications. Since as-grown CNTs have very poor solubility and dispersibility in most solvents particularly in water, it is necessary to overcome this technical issue before realizing their industrial applications such as nano-scale electronic [1, 2], nano-sensors [3, 4] and reinforcement for materials [5]. Thus far, several approaches such as surfactant adsorption, polymer wrapping and charge repulsion have been taken to enhance the solubility [6-8].

Many approaches have been tried to carry out chemical functionalization of CNTs so far. Generally, chemical oxidation is the most common practice of surface modification, which enables the formation of oxygen-containing functional groups on the surface of CNTs [9]. For instance, acid oxidation has been extensively explored [10,11]. The present authors previously proposed a technique to prepare water-soluble CNTs using microplasma generated by a pulsed streamer discharge in water [12,13], which does not need any particular chemical agents or additives for CNTs solubilization. Ozone (O_3) oxidation also has been utilized extensively, for example in the eliminate of amorphous carbon in purification processes, for opening closed tips and sidewalls of nanotubes to maximize hydrogen uptake as well as to facilitate functionalization for achieving solubility [14].

In this work, we proposed a novel method of functionalization and water-solubilization SWCNTs using ozone generated by dielectric barrier discharge (DBD) in atmospheric air. DBD is well known as a useful method for generation of activate radicals and excited species such as O , H , O_3 , N_2^+ and OH , which are generated by dissociation and ionization of the ambient gases as a result of energy transfer from energetic electrons to the gas mole-

cules [15]. DBD-generated ozone has been applied on treatment of polluted water, decomposition of exhaust gas and surface modification [15-17]. However, little work has been done in relation to SWCNT functionalization and solubilization.

2. Experimental set-up

Fig.1 shows an experimental setup for the ozone treatment of SWCNTs using DBD generated in atmospheric air. Two parallel plane electrodes and a glass-dish as the dielectric were composed of DBD system. The lower (stainless-plate) electrode with diameter of 100 mm was covered by dielectric barrier and the upper (brass-plate) one with diameter of 40 mm was exposed in air. The gap between the upper and lower electrode was 2 mm. Sinusoidal high voltage of 60 Hz frequency and 20 kV amplitude (peak-to-peak value) was applied to the upper electrode so that stable DBD with many filament channels were generated between the dielectric barrier and the upper electrode. 10 mg SWCNTs (purchased from Sigma

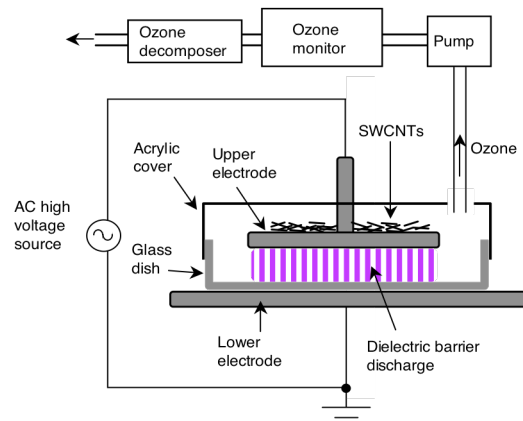


Fig.1 Experimental set-up for ozone treatment of SWCNTs using dielectric barrier discharge.

Aldrich Inc., USA, with purity of 60%) were placed on the upper side of upper electrode so that they could be exposed to DBD-generated ozone but not to electric field or plasma between the electrodes gap. During the DBD processing, ozone concentration was measured on a real time basis using a UV-ozone monitor (model PG-620MA, EBARA, Japan). After desired ozone treatment time, SWCNTs were collected from the DBD chamber and were suspended into 100 ml deionized water, followed by ultrasonication for 1 hour to get a suspension liquid with concentration of 0.1mg/ml.

Water solubility of SWCNTs was quantitatively evaluated by using a UV-visible absorption spectrophotometer (UV-160A, SHIMADZU, Japan) [12, 13]. The sample of suspension was ultrasonicated for 1 hour just before the absorbance measurement. The effective particle size was obtained by using nano particle size analyzer (SALD-7100, SHIMADZU, Japan). Trace amount of SWCNTs sample was supported on KBr plate for FT-IR analysis (FT-IR620, JASCO, Japan). The FT-IR spectrometer was sensitive to mid-infrared region from 4000 cm^{-1} to 500 cm^{-1} . Raman spectrum was obtained by using a Raman spectrometer (NRS-3100KK, JASCO, Japan) with an excitation length of 532 nm.

3. Results and discussion

3.1 Effects of ozone on water-solubility of SWCNTs

Fig.2 shows the typical appearance of SWCNTs suspension before and after DBD-generated ozone treatment. Before ozone treatment, SWCNTs were aggregated and precipitated at the bottom of bottle as shown in Fig. 2(a). While after 60 min of the ozone treatment, as shown in Fig. 2(b), the color of SWCNTs suspension became dark gray showing SWCNTs solubility was significantly increased by ozone treatment.

3.2 Relation between solubility of SWCNTs and ozone treatment time

The optical absorbance of SWCNTs suspension at the wavelength of 254 nm was measured by a UV-visible spectrometer. Fig. 3 shows temporal variations of SWCNTs suspension absorbance and ozone concentration with elapsed time after DBD onset. The ozone concentration quickly reached to 150 ppm within 10 min, then continued to increase gradually and nearly kept stable around 200 ppm after 60 min. The absorbance of SWCNTs suspension increased with elapsed time in a similar manner to the ozone concentration and reached the maximum in 60 min. With prolonged ozone treatment time over 60 min, the absorbance slightly decreased but nearly kept constant. These results suggest that SWCNT solubility can be attributed to high concentration ozone generated by DBD.

3.3 Long term stability of ozone-treated SWCNTs suspension

The absorbance of SWCNT suspension under various of ozone treatment time suspensions were measured again

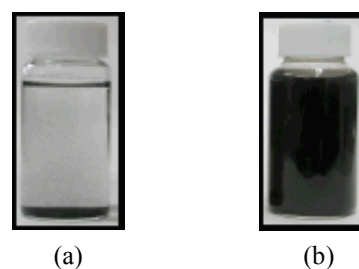


Fig. 2 SWCNTs after 1 h supersonication. (a) Before ozone treatment; (b) After 1 h ozone treatment

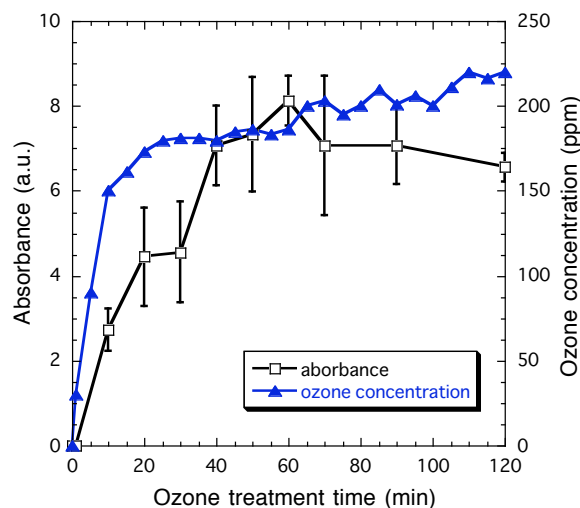


Fig. 3 Temporal variations of SWCNT suspension absorbance and ozone concentration with elapsed time after DBD onset.

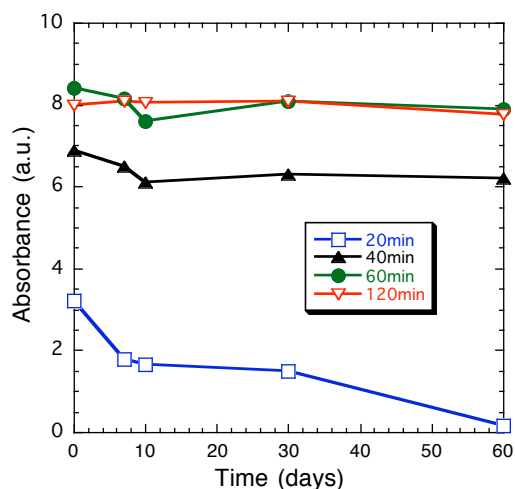


Fig. 4 Absorbance stability of SWCNTs suspension under different ozone treatment time.

after settling for 7 days, 10 days, one and two months in order to investigate the long term stability. Fig.4 shows that the stability of suspension increased by increasing ozone treatment time. The absorbance of SWCNTs under short ozone treatment (20 min) time decreased gradually day by day. On the contrary, the absorbance kept nearly

constant for 60 days when the ozone treatment time was longer than 40 min, meaning that most of SWCNTs were still dissolved in water without precipitation.

3.4 FT-IR spectra analysis

Fig.5 shows FT-IR spectrum of before and after ozone treatment of SWCNTs. No absorbance peak appears at 1385 cm^{-1} and 1580 cm^{-1} before ozone treatment. After ozone treatment, the peaks at 1385 cm^{-1} and 1580 cm^{-1} appeared, which correspond to the functional groups of COO^- [19]. The peaks became more intense with increasing ozone treatment time. In addition, appearance of a broad shoulder peak around 3250 cm^{-1} suggests OH groups on the SWCNTs sidewalls. FT-IR spectra analysis revealed that large extent hydrophilic group of COOH was introduced on the surface, which could be attributed to ozone oxidation effect. Li et al. [11] reported that ozone attacking on the $\text{C}=\text{C}$ double bond was responsible for the oxidation of carbon surface. $\text{C}=\text{C}$ would be firstly converted to C-OH which were then oxidized to C=O and COOH finally. Not only high concentration of ozone but also radicals such as O , H and OH generated by the dissociation and ionization of atmospheric air (with some moisture) during DBD treatment might react with sp^2 structure [20]. As a result, the chemical functional groups such as OH , C=O and COOH were finally formed on the sidewalls of SWCNTs after ozone treatment [11, 18]. All of these oxygen containing electron deficient groups caused repulsive force among SWCNTs bundles. In addition, because of these hydrophilic groups, SWCNTs have strong interaction with H_2O molecular. These mechanisms seem to be responsible for higher solubility and dispersibility of SWCNTs in water after ozone treatment.

3.5 Raman spectra analysis

To clarify the functionalization of SWCNTs after ozone treatment, Raman spectra analysis was taken for each sample. There are two feature peaks appear in the Raman spectra. One is the tangential (G) band at $1500\text{--}1650\text{ cm}^{-1}$, and the other at about 1330 cm^{-1} known as D-band. The intensity of G-band (I_G) indicates that graphitization degree of SWCNTs while intensity of D-band (I_D) indicates that structure defects of SWCNTs due to disordered sp^3 carbon materials. The intensity ratio of I_D/I_G has been widely used to evaluate the defects and carbon impurities with sp^3 bonds in SWCNTs [21]. It has also been pointed out that I_D/I_G ratio increases for more disordered carbon materials [22]. As depicted in Fig.6, I_D/I_G ratio increased with ozone treatment time, which might be another key evidence of sidewall functionalization with COOH , OH , and COO^- groups. It is also suggested that SWCNTs became more disordered after ozone treatment. For example, they could be shortened or morphologically damaged due to increased sp^3 -content on the sp^2 framework of SWCNTs sidewalls [22, 23].

3.6 Particle size analysis

Fig. 7 shows effective diameter of SWCNTs particles

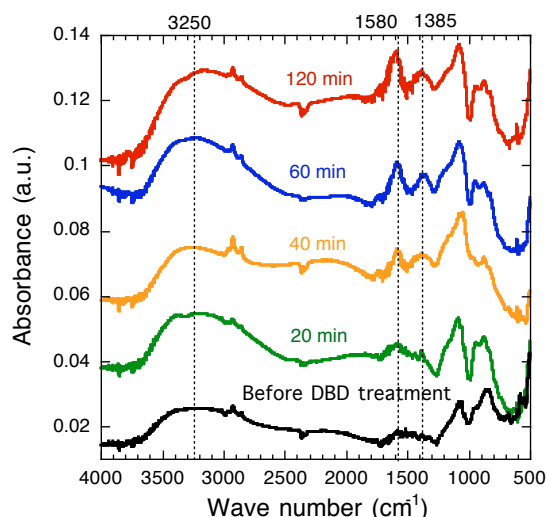


Fig. 5 FTIR spectra of SWCNTs before and after ozone treatment with various durations.

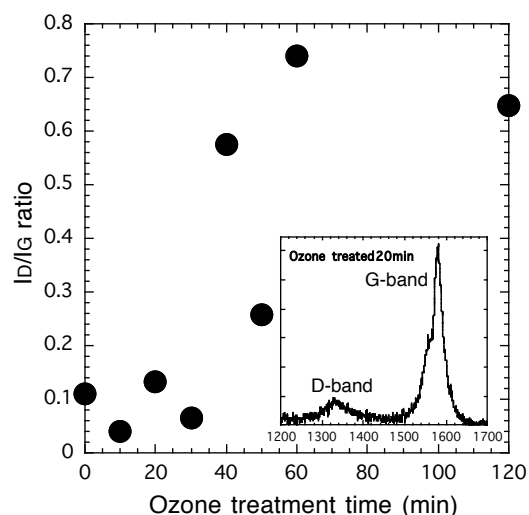


Fig. 6 I_D/I_G ratio of Raman spectra of SWCNTs treated by ozone for different time.

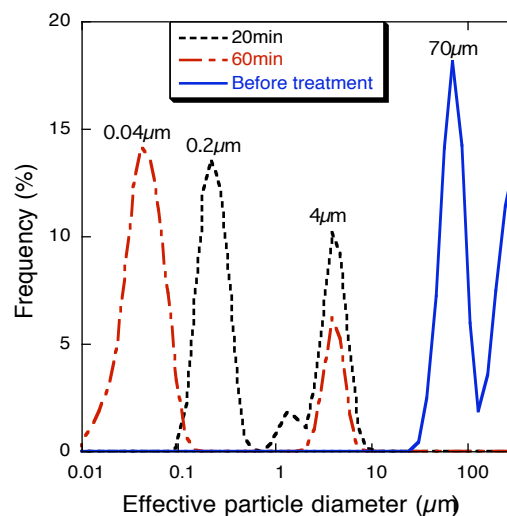


Fig. 7 Effective particle size of SWCNTs in water before and after ozone treatment.

(aggregates) suspended in water before and after ozone treatment. The effective diameter decreased from 70 μm to 0.2 μm after ozone treatment for 20 min. The particle size was further reduced to 0.04 μm for longer ozone treatment of 60 min. The smaller particle size implies that ozone treatment is responsible for higher water solubility as well as shorter length of SWCNT.

4. Conclusions

Water-solubilization SWCNTs were obtained by using high concentration ozone generated by DBD in atmospheric air. The ozone-treated SWCNTs were dissolved and dispersed in water for 2 months without precipitation. FT-IR and Raman spectra analysis revealed that hydrophilic functional groups, such as $-\text{OH}$, $-\text{C}=\text{O}$ and $-\text{COOH}$, were introduced on the surface of SWCNTs after ozone treatment.

5. Acknowledgement

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