

Low temperature oxidation of Fe-included single-walled carbon nanohorns in water by ozone injection to enhance porous and magnetic properties

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Abstract: This short communication reveals that the magnetic and porous properties of Fe-included single-walled carbon nanohorns (Fe-SWCNHs) can be improved via oxidation in water by injection of ozone at room temperature. Fe in Fe-SWCNHs is converted to ferrimagnetic Fe_3O_4 without producing paramagnetic Fe_2O_3 by this method. The specific surface area on the basis of the specimen mass can be doubled by this treatment together with significant increase of micro and meso pore volumes. Their magnetic susceptibility which is a determinant factor to magnetically drive the products in fluid can be increased by this ozone oxidation. The enhancement effects on the porous and magnetic properties of Fe-SWCNHs should be preferable to develop catalyst support or adsorption media which can be magnetically handled. The method proposed here is extremely safe and environmentally benign.

Key words: Carbon nanohorn; Nanoparticle; Ozone oxidation; Porous material

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1. Introduction

Single walled carbon nanohorns (SWCNHs) [1] considered to be carbon nanotube family materials have unique structures, and it is desired to develop the applications of SWCNHs based on their superior structural, physical and chemical properties. Among the important properties, the porous properties of SWCNHs can be significantly improved by a simple heat treatment in air, by which their surface area can be significantly expanded because the inner void of each closed-horn made of rolled graphene sheet can be available by opening small pores thereon [2, 3]. SWCNHs treated by this oxidation method may be useful for drug delivery [4], electroanalytical electrode [5], adsorbent [6,7], and catalyst support [8].

SWCNHs which include metallic nanoparticles can be synthesized by several methods. Among them, gas-injected arc-in-water (GI-AIW) method is suitable to synthesize SWCNHs including pure and alloy metal nanoparticles under controlled conditions [9]. Very recently, SWCNHs including magnetic Fe nanoparticles (Fe-SWCNHs) were synthesized by the GI-AIW method, and Fe nanoparticles in Fe-SWCNHs were successfully converted to ferrimagnetic Fe_3O_4 by oxidation in $\text{CO}_2\text{-N}_2$ mixture at 1000°C [10]. In this treatment, the porous properties of the carbonaceous part of Fe-SWCNHs was improved. The successful synthesis of the porous SWCNHs including Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4\text{-SWCNHs}$) can be a hopeful news because such $\text{Fe}_3\text{O}_4\text{-SWCNHs}$ can be useful for catalyst which can be easily recovered by a magnetic force. Nevertheless, a new method to synthesize $\text{Fe}_3\text{O}_4\text{-SWCNHs}$ in a low-cost and safe manner is desired to develop, which does not

require the temperature as high as 1000°C.

To give an answer to the above demand, a new method using ozone is proposed here. Diluted ozone can be cheaply prepared by using electric discharge or deep ultraviolet in oxygen-contained gas. Oxidative reactivity of ozone can be considered very high because the oxidation-reduction potential of $\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} + \text{O}_2$ is 2.07 V. Nevertheless, it can be expected that diluted ozone in water can have appropriate reactivity to mildly oxidize Fe-SWCNHs.

2. Experimental

In this study, Fe-SWCNHs were synthesized by the GI-AIW method using holey graphite electrodes. The detail of this method can be referred elsewhere [9,10]. In this method, graphite anode in which Fe wire is inserted into a co-axial hole on the anode is transferred into the hole on graphite cathode to generate DC arc discharge with 80 A (40 V). The electrode dimensions employed in this study are as follows: Diameter and length of the cathode = 20 mm and 50 mm. Diameter and depth of the hole drilled at the cathode bottom = 12 mm and 25 mm. Diameter of the anode = 6 mm. Diameter and depth of the hole drilled at the anode top = 2 mm and 70 mm. Diameter of Fe wire = 1.45 mm. While the arc discharge was generated, the both electrodes were submerged in water to realize rapid quenching of evaporated carbon and Fe, and N_2 was injected to the arc plasma zone inside the cathode hole at 10 L/min to make the reaction field inert. The anode was shifted toward the cathode at a constant speed of 1.8 mm/s to sustain the arc discharge. After the arc discharge was terminated, the powders floating on water was collected to use for the ozone oxidation experiment.

Ozone was synthesized using a silent-discharge type ozonizer (Tokyu Sharyo, SO-03UN-OX) from oxygen stream ($30 \text{ cm}^3/\text{min}$). The concentration of ozone in this oxygen stream was monitored by UV-absorption type ozone meter (Ebara Jitsugyo, UV Ozone Monitor Model-500) and this ozone concentration was constant at 80 g/m^3 . A glass-made filter funnel (tube inner diameter = 20 mm) was used to reserve water (50 cm^3). The ozone-contained oxygen was injected to this water through the glass filter to make bubbling so that ozone can be dissolved in water. From the solubility of ozone in water (Henry constant = 3500 atm^{-1} [11]), the concentration of ozone in water can reach 30 mg/L at the highest. Fe-SWCNHs (100 mg) were dispersed in this ozone-contained water to cause mild oxidation at room temperature. The duration for this ozone oxidation treatment was varied up to 5 h to investigate the influence of this treatment on the pore structures of carbonaceous part, structures of metallic particles, and magnetic properties of the post-treated Fe-SWCNHs. A thorough ozone oxidation treatment by taking 9 h was applied for Raman analysis.

3. Results and discussion

Here, all specimen treated by the ozone oxidation is referred to as Fe_3O_4 -SWCNHs because they contain Fe_3O_4 as explained later. The structures of the as-grown Fe-SWCNHs and treated Fe_3O_4 -SWCNHs were observed by a transmission electron microscope (TEM) (JEOL, JEM2010). The TEM images of the gas-grown Fe-SWCNHs and Fe_3O_4 -SWCNHs prepared with a treatment duration of 5 h are shown in Fig. 1. Here, no significant change in horn structures in carbonaceous part can be observed between Fe-SWCNHs and Fe_3O_4 -SWCNHs, suggesting that the carbonaceous horn

structures were not destroyed by this ozone treatment. It should be noted that the well-known oxidation in air at elevated temperature ($> 400^{\circ}\text{C}$) can easily destroy the horn structures unless the oxidation duration is strictly limited [10]. In contrast, the ozone oxidation here can preserve the horn structures stably.

Fe-SWCNHs and Fe_3O_4 -SWCNHs prepared by the ozone oxidation at varied duration were analyzed by X-ray diffractometer (XRD) (Rigaku, RINT2100). Fig. 2 shows the XRD patterns to reveal whether Fe in Fe-SWCNHs are oxidized. It is shown that the as-grown Fe-SWCNHs includes metallic Fe, as indicated by the peak at 44.5° . It should be noticed that Fe is tuned to be Fe_3O_4 , which can be indicated by the peak at 35.3° , from an early oxidation time at 1 h. As a result, Fe_3O_4 -SWCNHs is obtained. In the present conditions, perfect conversion of Fe to Fe_3O_4 is not achieved, and Fe remains partially. It is remarkable that no paramagnetic Fe_2O_3 is formed. It should be noted that the oxidation treatment in air around 400°C commonly known to open small pores on SWCNHs causes the conversion from Fe to paramagnetic Fe_2O_3 even though the oxidation duration is extremely short [10]. In contrast, the heat treatment on Fe-SWCNHs in $\text{CO}_2\text{-N}_2$ mixture at 1000°C can exhibit selective conversion of Fe to ferrimagnetic Fe_3O_4 without generation of paramagnetic Fe_2O_3 , and this selectivity can be explained from thermodynamic viewpoint [10]. Ozone oxidation proposed here can realize the environment which is similar to the oxidation condition in $\text{CO}_2\text{-N}_2$ at 1000°C . It is remarkable that the present method can be performed at room temperature. Further study to find a condition to realize the complete conversion of Fe to Fe_3O_4 should be carried out in future.

Pore characterization was performed using an automatic BET N_2 adsorption analyzer at liquid

nitrogen temperature (Bel Japan, Belsorp-mini). The specific surface area based on unit mass of specimen including carbon, Fe and Fe₃O₄ are shown in Table 1 related with the ozone oxidation duration. In this table, pore volumes in the mesopore range (radii 1.0 - 20 nm) estimated by the method proposed by Dollimore and Heal [12] and the micropore evaluated by *t*-plot method [13] also are tabulated here. One can see that these small pores increase with ozone oxidation time, and thus the specific surface area can reach 576 m²/g. It should be recognized that the rate to increase the specific surface area is larger in early oxidation time range, but the specific surface area did not change significantly from 3 to 5 h. This tendency suggests that ozone oxidation in the present condition can preserve the main frame of carbonaceous horn structures though opening small pores is allowed. The specific surface area on the basis of carbon mass is supposed to reach 1034 m²/g provided that Fe is completely oxidized to Fe₃O₄, using the values of 16 wt% Fe content in Fe-SWCNHs estimated by thermal gravimetry analysis (Shimadzu, TGA-50) driven in air at 900°C for 60 min to remove carbon and 50 % of burn-off percentage of carbon stably sustained in mild oxidation conditions [10].

The Raman spectrum obtained from Fe-SWCNHs treated by a thorough ozone oxidation treatment by approximately 9 h is shown in Fig. 3. For this analysis, a Raman spectrometer (Ramda Vision) equipped with a 532 nm laser was used. In this figure, this spectrum can be compared with that obtained from as-grown Fe-SWCNHs without the ozone oxidation treatment. In the both spectra, the intensity of the graphite peak (G-peak) seen around 1600 cm⁻¹ is comparable to the disorder peak (D-peak) seen around 1350 cm⁻¹, and no significant change can be observed in this feature between the as-grown and the post-treated Fe-SWCNHs. The ozone oxidation treatment may eliminate weak

disordered carbons, contributing to the increase of the intensity ratio of G-peak to D-peak (G/D ratio), but this treatment simultaneously can add new pores on rolled graphene in Fe-SWCNHs, inversely contributing to the decrease of G/D ratio. As a result, Raman spectroscopy analysis could not resolve the structure change in the present products.

AC magnetic susceptibility of the specimen at room temperature was also measured by a magnetometer (Magqu Co., XacQuan-II). By this measurement, real and imaginary numbers of complex number of AC magnetic susceptibility can be obtained at varied frequency in AC magnetic field (15 mG). An example of the result by this AC magnetic susceptibility analysis is shown in Fig. 4a. It should be noted that DC magnetic susceptibility, which can be estimated by the real number of the AC magnetic susceptibility at 0 Hz, should be the determinant factor to drive Fe₃O₄-SWCNHs by a permanent magnet.

This magnetic susceptibility is obtained by extrapolation, and plotted against the ozone oxidation duration in Fig. 4b. This magnetic susceptibility apparently rises with the oxidation duration in early time range. This is because the weight of the specimen decreases by partial oxidation of carbonaceous part of Fe₃O₄-SWCNHs. In early time range, the weak part of SWCNHs (i.e. tips of horns in SWCNHs) are consumed by ozone oxidation, but the main part of the carbonaceous horn consisting of seamlessly rolled graphene can be stable against the ozone oxidation in the present condition. Thus, the increase of the 0 Hz magnetic susceptibility has stopped after 5 h. As a result, this magnetic susceptibility can increase from the as-grown Fe-SWNHs by approximately 20% using the ozone oxidation in the present conditions.

Ozone can be removed from water very easily [14, 15], and dissociation of ozone afterward can be processed without any significant energy input. For example, ozone can be adsorbed by activated carbons and one can wait for appropriate time until ozone naturally disappears by changing to oxygen. One may wonder why Fe-SWCNHs was oxidized in water in the proposed method, but not in gas phase. It should be cautioned that fine carbon powders in oxidative gas environment can be highly flammable. So, the oxidation of Fe-SWCNHs in ozone-contained gas is extremely dangerous, and such experiment must not be conducted. It should be recognized that the present method to oxidize Fe-SWCNHs dispersed in water is extremely safe and recommendable to prepare ferrimagnetic Fe_3O_4 -SWCNHs possessing enhanced porous properties.

4. Conclusions

Fe-SWCNHs were synthesized by GI-AIW method, and they were mildly oxidized by the treatment in water with ozone bubbling. An analysis by XRD Fe revealed that Fe in Fe-SWCNHs was converted to ferrimagnetic Fe_3O_4 without producing paramagnetic Fe_2O_3 . A BET analysis using N_2 adsorption suggested that the specific surface area on the basis of the specimen mass were doubled by this treatment. Their AC magnetic susceptibility being a determinant factor to magnetically handle the products in fluid was analyzed, resulting that their magnetic susceptibility can increase by this ozone oxidation in water. It can be expected that Fe-SWCNHs whose porous and magnetic properties are enhanced can be preferable materials for catalyst support or adsorption media which can be handled by applying magnetic field. It should be emphasized that the method proposed in this study

using ozone in water is extremely safe and environmentally benign.

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Table 1. Porous properties of Fe-SWCNHs and Fe₃O₄-SWCNHs prepared by varied oxidation duration.

oxidation duration (h)	specific surface area (m ² /g)	micropore volume (cm ³ /g)	mesopore volume (cm ³ /g)
0 (as-grown)	255	0.08	0.93
1	401	0.12	1.07
3	562	0.13	1.32
5	576	0.18	1.68

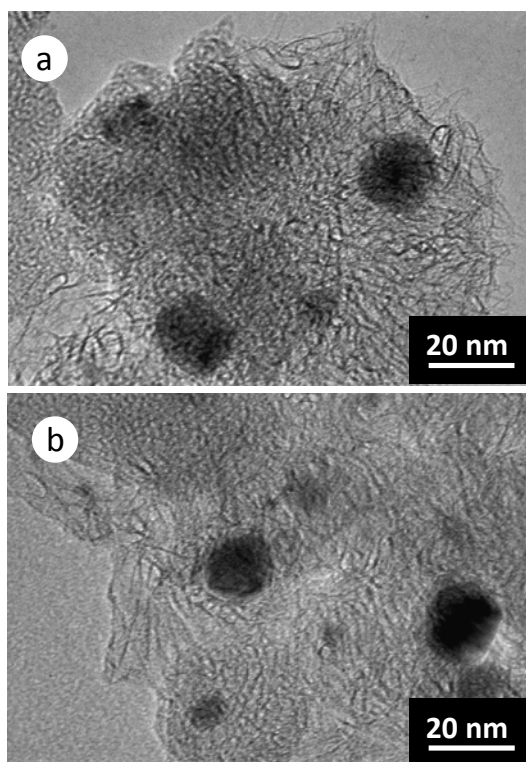


Fig. 1. TEM images of (a) as-grown Fe-SWCNHs and (b) Fe₃O₄-SWCNHs prepared by ozone oxidation with 5 h duration.

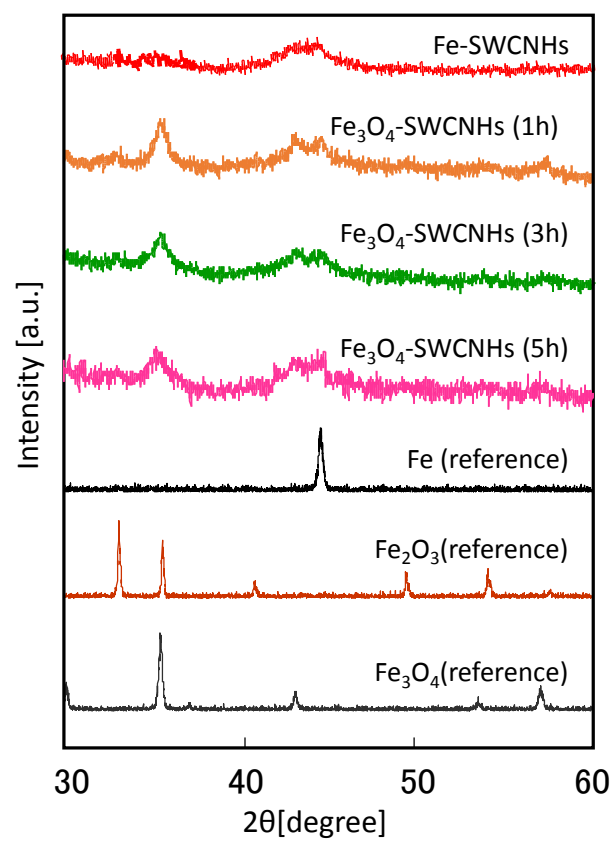


Fig. 2. XRD patterns of Fe-SWCNHs and Fe_3O_4 -SWCNHs prepared by varied ozone oxidation duration, 1, 3, and 5h together with XRD patterns of Fe, Fe_2O_3 and Fe_3O_4 for reference.

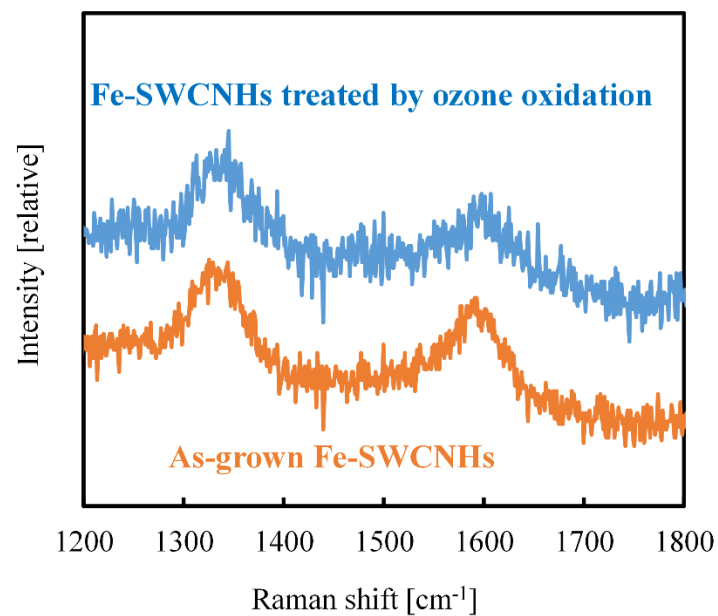


Fig. 3. Raman spectra of Fe-SWCNHs which are subject to an ozone oxidation treatment by approximately 9 h and as-grown Fe-SWCNHs.

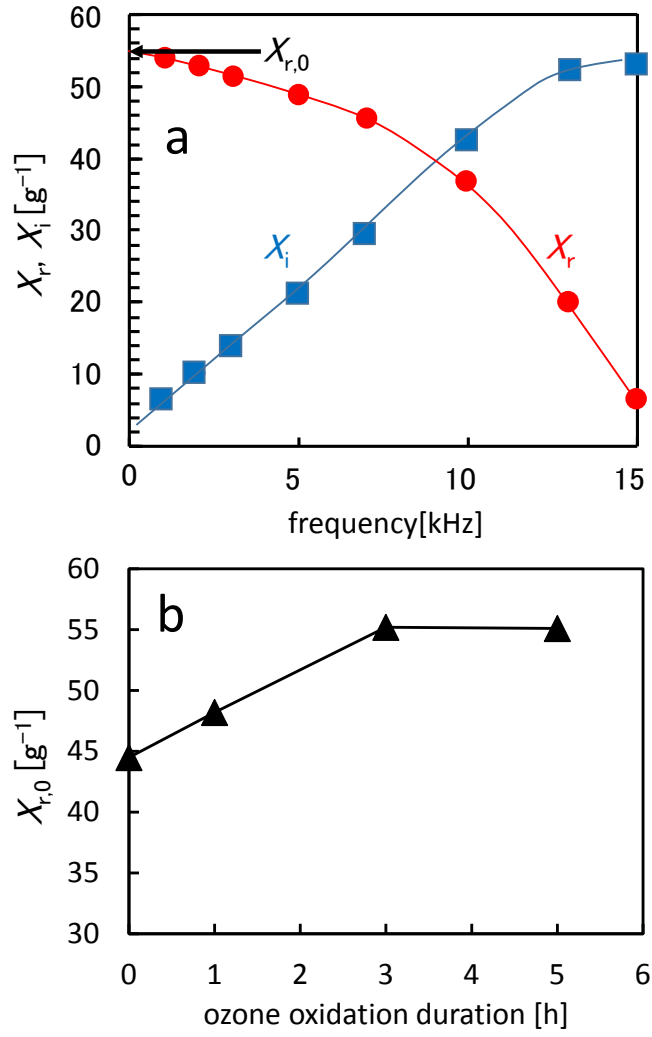


Fig. 4. (a) AC magnetic susceptibility of Fe_3O_4 -SWCNHs prepared with ozone oxidation duration of 5 h as function of frequency, and (b) 0 Hz magnetic susceptibility as function of oxidation duration. X_r and X_i are real and imaginary numbers of complex number of AC magnetic susceptibility. $X_{r,0}$ is the value of X_r at 0 Hz frequency estimated by extrapolation of the curves of X_r .