



# Simultaneous enhancement in porosity and magnetic property of Fe-dispersing single-walled carbon nanohorns by oxidation using CO<sub>2</sub>



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## HIGHLIGHTS

- Carbon nanohorns dispersed with Fe nanoparticles can be synthesized by one-step.
- Magnetic susceptibility can be preserved by activation in CO<sub>2</sub>-N<sub>2</sub> mixed gas.
- Activation in air cannot preserve the magnetic susceptibility.
- Porosity can be doubled by activation in CO<sub>2</sub>-N<sub>2</sub> mixed gas.

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## ABSTRACT

It was discovered that the specific surface area and magnetic susceptibility of Fe-dispersing single-walled carbon nanohorns (Fe-CNHS) were significantly increased without obvious destruction of CNH structures by oxidation in CO<sub>2</sub> (10%) diluted with N<sub>2</sub> at 1000 °C. As-grown Fe-CNHS synthesized by a submerged arc discharge method had a specific surface area of 184 m<sup>2</sup>/g, and this surface area was raised to 500 m<sup>2</sup>/g by opening of pores upon this oxidation treatment. Under this condition, the carbon-based specific surface area are enhanced from 211 m<sup>2</sup>/g to 863 m<sup>2</sup>/g. Fe nanoparticles dispersing in Fe-CNHS were transformed into ferrimagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles without obvious change in their particle sizes and frames of CNHS. The magnetic susceptibility of the Fe-CNHS was increased by this oxidation, suggesting that their magnetic mobility could be improved. The structure of Fe-CNHS was stable against the extended oxidation duration in the CO<sub>2</sub>-N<sub>2</sub>. In contrast to the oxidation in CO<sub>2</sub>-N<sub>2</sub>, the oxidation in air resulted in the transformation of Fe nanoparticles into paramagnetic Fe<sub>2</sub>O<sub>3</sub>, and the excessive oxidation led to destructive loss of CNHS.

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## 1. Introduction

Carbon-nanotube (CNT) family materials have been widely studied, and their superior performances can be found in a broad range of applications including micro-sized electric circuit [1,2], chemical and physical sensors [3,4], catalysts [5,6], gas energy storage [7,8], and so forth. Among those novel functional materials that have been explored, single-walled carbon nanohorns (CNHS) [9] are considered to be the materials that can exhibit useful chemical and physical properties. The structures of CNHS are regarded as the aggregated forms of single-walled closed horns, and it is widely known that a well-controlled oxidation in air can enlarge their specific surface area [10,11] and produce suitable structures for drug delivery applications by opening their pores [12]. Mass production of CNHS can be achieved by evaporation of graphite using

high-power laser [13,14] or arc discharge [15–18]. In addition to the oxidation, which serves as a post-treatment procedure [10,19], admixing metallic components in the fabrication step can improve the performance of CNHS, and CNHS dispersed with metallic nanoparticles can be obtained in this way [20,21]. Given the well-ground research basis, one may expect the novel functional materials to be fabricated by combining all these techniques together.

Aiming at investigating the diverse post-treatment conditions for developing new functional materials, this study focused on the mild oxidation of Fe-dispersing CNHS (Fe-CNHS) in CO<sub>2</sub>-N<sub>2</sub> mixture instead of the conventional oxidation in air. As one of potential applications of the materials developed in this study, it can be considered that they can be useful to create new catalyst support for many reactions because porous and magnetic Fe-CNHS can supply amphiphilic surfaces by hybridizing hydrophobic carbon and hydrophilic Fe. In addition, when Fe in Fe-CNHS is oxidized to form magnetite Fe<sub>3</sub>O<sub>4</sub>, it could be used for

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application to produce biodiesels [5]. Furthermore, it was expected that the magnetic property of Fe could contribute to the magnetically driven micro- and nano-systems using synthesized Fe-CNHS, and by enhancing the porosity, their applications can also be expanded to potential new research topics.

## 2. Experimental

CNHs were synthesized by a gas-injected arc-in-water (GI-AIW) method, and a detailed description of this method is reported elsewhere [18,19]. In brief, a graphite rod with a co-axially drilled hole was submerged in water acting as a cathode, and another piece of narrow graphite rod is used as an anode, where arc discharge is generated between these two electrodes. At the cathode,  $N_2$  was injected to realize a rapid quenching of vaporized carbon in  $N_2$  enriched atmosphere. The as-grown CNHs can be then collected in powder form floating on the water surface.

A modified GI-AIW method was used to synthesize Fe-CNHS [20,21] and the dimensions of the electrodes are summarized in Fig. 1. In our study, a 60 mm deep hole with 1 mm diameter was co-axially drilled into the anode with a diameter of 3 mm. Three pieces of Fe wires with diameter of 0.3 mm and length of 60 mm were inserted into the hole when the arc discharge was generated at discharge current of 80 A and DC voltage of 40 V. The anode was then shifted at a constant speed of  $2.2 \text{ mm s}^{-1}$  to sustain the arc discharge, while Fe and carbon were simultaneously evaporated by the arc discharge, and Fe-CNHS can be synthesized by their co-condensation.

The oxidations of as-grown Fe-CNHS in both  $CO_2-N_2$  and air were carried out using a cylindrical furnace that allows the formation of pores in the structures. The inner diameter of the quartz cylinder used in the furnace was 38 mm, and the length was 650 mm. For the Fe-CNHS oxidized in  $CO_2-N_2$ , the concentration of  $CO_2$  was controlled in which  $CO_2:N_2$  molar ratio was 1:9 and the total flow rate was adjusted to  $300 \text{ cm}^3/\text{min}$ . The as-grown Fe-CNHS were placed in the furnace before the temperature was raised to  $1000 \text{ }^\circ\text{C}$  at a steady rate of  $7 \text{ }^\circ\text{C min}^{-1}$ , and the temperature was kept constant for a varied duration up to 120 min. In the case of the Fe-CNHS oxidized in air, the quartz cylinder was open at its both ends. The furnace temperature was increased from  $350 \text{ }^\circ\text{C}$  to  $450 \text{ }^\circ\text{C}$  in accordance to the targeted burn-off percentage of the specimen, and the duration of the oxidation was 30 min for all the oxidations.

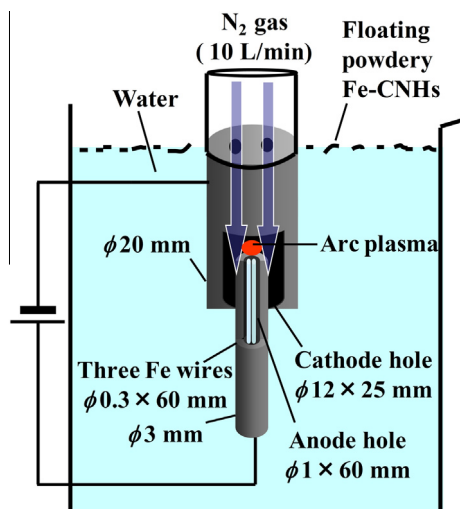


Fig. 1. Structures and dimensions of electrodes in GI-AIW method to synthesize Fe-CNHS.

The porosity of the Fe-CNHS was analyzed by a volumetric adsorption analyzer (Bel Japan, Belsorp-mini) using  $N_2$  adsorption at 77 K. A transmission electron microscope (TEM) (JEOL, JEM1010) was used to investigate the structural formation of Fe-CNHS. In addition, the crystal structures of the dispersing nanoparticles in Fe-CNHS were characterized by an X-ray diffractometer (Rigaku, RINT2100) with  $CuK\alpha$  radiation at the power of 40 kV and 40 mA. Furthermore, AC magnetic susceptibility was measured at room temperature by a magnetometer (Magqu Co., XacQuan-II), with maximum magnetic flux of 15 mG and varied frequencies.

## 3. Results and discussion

### 3.1. Microscope observation

The structure of Fe-CNHS was observed by TEM to investigate the influence of the oxidation treatments. TEM images obtained from the Fe-CNHS before oxidation are shown in Fig. 2a and b. It is shown here that Fe nanoparticles are dispersed in Fe-CNHS. Fe-CNHS oxidized in  $CO_2-N_2$  environment are shown in Fig. 2c. One can notice that the nanoparticles with diameters ranging from 3 to 15 nm were dispersed in CNH matrix, and these particles are identified to be ferrimagnetic  $Fe_3O_4$  as explained later. In comparison, the TEM images obtained from the non-oxidized Fe-CNHS seemed similar to those from the Fe-CNHS oxidized in  $CO_2-N_2$  environment. The Fe-CNHS structures oxidized in  $CO_2-N_2$  and the size of  $Fe_3O_4$  nanoparticles seemed irrelevant to the oxidation duration, which was extended up to 120 min. It is suggested that the frames of CNHS were not influenced by the oxidation in  $CO_2-N_2$  under the present oxidizing conditions.

In contrast to the  $CO_2-N_2$  oxidation, the oxidation in air had a significant influence on the Fe-CNHS structures. The TEM image in Fig. 2d shows an example that carbonaceous CNHS were removed when undergoing an excessive oxidation treatment. During the oxidation in air, the nanoparticles dispersing in the Fe-CNHS were transformed into paramagnetic  $Fe_2O_3$  that tended to be merging with each other, and this will be discussed in details in the subsequent sections.

To evaluate the influence of the oxidation, a burn-off percentage is defined by Eq. (1) as follows.

$$B = (W_0 - W_1)/W_0 \times 100 \quad (1)$$

where  $B$  [%],  $W_0$  [g], and  $W_1$  [g] are the burn-off percentage, weight of as-grown Fe-CNHS before the oxidation, and weight of Fe-CNHS

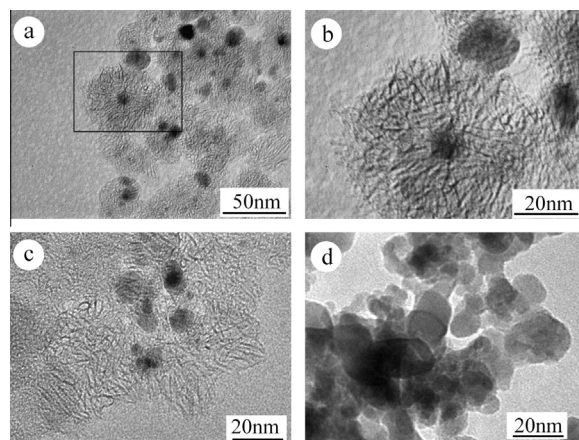


Fig. 2. TEM images of the Fe-CNHS (a) before oxidation in low magnification, (b) in high magnification, (c) after oxidation in  $CO_2-N_2$  at  $1000 \text{ }^\circ\text{C}$  for 60 min, and (d) in air at  $425 \text{ }^\circ\text{C}$  for 30 min.

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