Effect of Aqueous Ion Species on Carbon Nanoparticles Synthesis using Arc Discharge in Water Method

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ABSTRACT

Carbon nanoparticles (CNPs) synthesis has increasingly been investigated because of its versatile applications in various fields ranging from novel electronic to biomedical products. Recently, arc discharge in water technique have been accepted as one of the most economical methods to product CNPs because it does not require any highly invested vacuum system, high pressure, and other expensive equipments. Moreover, arc in water technique is adaptable for mass production process. Therefore many attempts to investigate the operating parameters affecting the yield of CNPs synthesis using this method have been conducted. Among those parameters, however, the effects of ion species dissolved in the water on the synthesis of CNPs have not been clearly understood. Therefore, this investigation will be conducted to study the effect of aqueous ions added into the water with discharge current in the range of 30-100 A. The aqueous species investigated are Sodium carbonate representing ionic compound and ethanol representing organic species. As the preliminary results of our investigation using SEM and TEM analysis it is found that synthesized CNPs consisted of multi-walled carbon nanotubes, polyhedral particles and crystalline products. The concentration of aqueous species has significant effect on the structure of the synthesized CNPs. For the salt solutions, ion provided an influence on the types of CNPs formed meanwhile the existence of hydrocarbons also gave rise to similar influence.

KEYWORDS
carbon nanoparticles, arc discharge in water, ion, TEM&SEM analysis

INTRODUCTION

According to versatile applications in various fields ranging from novel electronic to biomedical products, carbon nanoparticles (CNPs) synthesis has increasingly been developed. In 1991 Carbon Nanotube (CNT) was serendipitously discovered by S. Iijima while nano-onions was also successfully synthesized by D. Ugarte in the following year. So far many various methodologies, i.e. laser ablation, arc discharge in vacuum environment, thermal pyrolysis of organic gaseous compound, plasma-enhanced chemical vapor deposition and so on has been proposed and developed for producing such CNPs. Nevertheless, it is well known that those conventional methods have short-coming of high investment and running costs for mass production. Meanwhile state-of-the-art catalysts of which price and strong dependence on their supplier might be taken into account.

So far, there have been some efforts on developing a novel process to fabricate carbon nanoparticles by using arc discharge submerged in de-ionized water which is more possibly economical. Sano et al. have successfully unveiled that types of synthesized carbon nanoparticle rely on the quenching conditions of the submerged arc discharge. Such simple method could fabricate high-quality nanoparticles including spherical carbon onions and elongated fullerene-like nanoparticles similar to nanotubes without
the use of vacuum equipment. From their investigation, it is also known that temperature gradient in the arcing zone is one of important operating parameters playing an important role in selective synthesis of CNPs. More recently they have also investigated the effect of water pressure and convective flow field on the formation of carbon nanoparticles fabricated in submerged arc discharge. Under condition of lower pressure or the optimized flow rate of the convective jet, the highest production yield, largest hydrodynamic diameter of the products with significantly lower defect could be obtained from the arc discharge.

Aqueous ion species including other carbon sources in the medium where the arc discharge is conducted is considered to play a crucial role in formation of CNPs. An investigation of arc discharge in aromatic hydrocarbon reveals that more nano-onions could be obtained. Therefore investigation on production of CNPs with incorporation of other aqueous ion species will provide other new information of the submerged arc discharge which is considered as an alternative way for economically producing CNPs. The objective of this work is to investigate the effect of aqueous species (Na₂CO₃ representing ionic compounds and C₂H₅OH representing organic compounds) on the formation of CNPs by arc discharge method. Some essential analyses of field emission scanning electron microscopy, transmission electron microscopy, dynamic light scattering and Raman spectroscopy were conducted for determining as-produced CNPs characteristics both qualitatively and quantitatively.

**EXPERIMENTAL**

Schematic experimental set-up for synthesize carbon nanoparticles (CNPs) using submerged arc discharge is available elsewhere. De-ionized water added with aqueous additives of which concentration was carefully controlled was employed as medium for arc discharge. Pure carbon electrodes (99.999%, Toyo Tanso) with diameter of 6 mm. were employed as anode and cathode. The stable arc with current of 60 A and voltage of ca. 20-25 V could be maintained after being initiated by approaching the anode to the stationary cathode and then steadily feeding the anode to keep an optimum gap between the electrodes at ca. 1 mm.

The synthesized solid products were characterized and analyzed by field emission scanning electron microscopy (FESEM; HITACHI, S-900), transmission electron microscopy (TEM; JEOL2010), dynamic light scattering (DLS; MALVERN, ZETASIZER300HSA) and Raman spectroscopy (JASCO, NR1100). TEM specimens were subjected to ultrasonic treatment in toluene with sufficient time for ensuring its uniform dispersion and then transferred to a Cu grid coated with a porous carbon film. For Raman spectroscopic analysis, as-grown substrate of solid deposit was filled into the hole of specimen holder and then was bombarded by an Ar ion laser (514.5 nm) at room temperature.

**RESULTS AND DISCUSSION**

**Effect of addition of Na₂CO₃ into de-ionized water**

Field emission scanning electron microscopy (FESEM) was employed for qualitative characterization of the obtained product. It could be seen from Fig. 1 (a) that the synthesized products are mixtures of carbon nanoparticles with different morphology similar to those of previous investigations. These CNPs are mainly composed of entangling multi-walled carbon nanotubes (MW-CNTs) and polyhedral crystalline carbon shells as well as some of amorphous carbon fine particles. It is reasonable that these different nanoparticles could be synthesized by the different conditions co-existing in the reaction zone and then mixed up by agitation due to bubbles emerging at vicinity of the electrodes.
Similarly, consistent images obtained from Transmission Electron Microscopic Analysis in Fig. 1(b) shows the clear appearance of CNP mixture obtained from the aqueous solution of 0.1 M Na$_2$CO$_3$. This higher magnification image of TEM shows that the MW-CNTs have diameter of ca. 30 nm with length of ca. 700 nm while the nearly spherical polyhedral particles have the size range of 20-120 nm. From our previous experience, we could observe that the walls of CNPs synthesized in aqueous solution was comparatively composed of some defects different from that of pure de-ionized water. There were some amorphous carbon nanoparticles with irregular morphology existing in the synthesized products. However, their size distribution is much broader than that of crystalline polyhedral particles. From this result, it could be implied that existence of ions in arc discharge zone would play a role as catalyst to enhance formation of elongated MW-CNTs. Nevertheless, no metal or metallic compounds encapsulated in the obtained CNPs could be observed from TEM images of analyzed specimens.

![FESEM image](image1.png) ![TEM image](image2.png)

**Figure 1. Microscopic analyses of CNPs obtained from arc discharge in 0.1 M Na$_2$CO$_3$ solution**

For quantitative analysis, Dynamic Light Scattering analysis shown in Fig. 2 had been employed for statistically determining size distribution of specimens obtained from the arc discharge in 0.1 M Na$_2$CO$_3$ solution. It should be remarked that since DLS analysis is based on the measuring of dispersion of light scattered by particles moving in the liquid solvent the value of particle size will be considered as hydrodynamic equivalent diameter not the actual diameter of some particles with complicated morphologies like MW-CNT or even irregular-shaped particles. Fig. 2 shows that addition of 0.1 M Na$_2$CO$_3$ into de-ionized water gave rise to longer hydrodynamic diameter of ca. 105 nm compared with that of pure de-ionized water (ca. 85 nm.). This is consistent with the microscopic evidence shown in Fig. 1.

**Effect of addition of Ethyl alcohol into de-ionized water**

It is clearly seen from TEM images shown in Fig. 3 that CNPs mixture could also be obtained from arc discharge in 0.3 M ethanol solution. The synthesized products are mixtures of CNPs with different morphology similar to that of sodium carbonate solution. However, more polyhedral crystalline carbon shells could be clearly observed from the specimens obtained from arc discharge in the solution of ethanol. The polyhedral carbon nanoparticles exhibiting cohesiveness could be found to attached to the outer surface of MW-CNTs. Sano et al. recently reported that arc discharge in liquid benzene would
provide more fractions of polyhedral carbon nano-onions. Even though well graphitized structure could be thoroughly found from both MW-CNTs and polyhedral nanoparticles, some defects could also be observed. This could be implied that addition of extra carbon atoms from alkyl group might lead to more complicated formation of these nanoparticles.

Figure 2. Particle Size Distribution of synthesized CNPs synthesized in De-ionized water and 0.1 M Na₂CO₃ solution

Figure 3. TEM images of CNPs synthesized by using 0.3 M ethanol solution

Similarly, DLS analysis shown in Fig.4 had been conducted for quantitatively determining size distribution of CNPs obtained from the arc discharge in the 0.3 M ethanol solution. However, Fig. 4 reveals that addition of 0.3 M ethanol into de-ionized water gave rise to shorter hydrodynamic diameter of ca. 50 nm compared with that of Fig. 2. This result gave us a hint that existence of alkyl group would induce a faster formation of polyhedral nanoparticles or on the other hand it would hinder the formation of high aspect-ratio particles like CNTs.
From TEM and DLS analyses, it gave us a suspicion whether the existence of ionic species will affect the crystalline of generated product. Therefore we had carried out its crystalline analysis by using Raman spectroscopy. It is well know that a G-band peak with Raman shift of 1580 cm⁻¹ and a D-band peak at 1353 cm⁻¹ respectively represent well-ordered and defective graphitized crystalline of the carbonaceous materials. Fig. 5 shows that carbon nanoparticles synthesized from 0.3 M ethanol solution have both peaks with clearly different intensity. The intensity ratio of G-band to D-band (G/D ratio) in the spectrum of the as-produced CNPs indicates that the obtained CNPs have well graphitized structure. This could be implied that CNPs could be produced with few defects by arc discharge submerged in ethanol solution.

**CONCLUSION**

From the experimental results, it could be concluded that addition of ions into arc discharge zone could give rise to formation of CNPs which consisted of MW-CNTs and polyhedral nanoparticles of which hydrodynamic diameters is longer than that of pure de-ionized water. This could be implied that
the existence of some ions would play a catalytic role to promote formation of MW-CNTs. However, based on the recent results, there have not been any metal encapsulated nanoparticles observed in the specimens of the arc discharge in \( \text{Na}_2\text{CO}_3 \) solution. On the other hand, addition of ethanol into de-ionized water could provide CNP mixture with shorter hydrodynamic diameter. From microscopic analysis it could be clearly seen that there were more polyhedral nanoparticles produced from arc discharge in the 0.3 M ethanol solution. Raman analysis also revealed that well graphitized nanoparticles could be obtained when ethanol solution was employed.

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