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Hydrophilic Carbon Materials Synthesis by Discharge Plasma at Pressurized Argon/Aqueous Solution Interface

高圧アルゴン／水溶液界面プラズマを利用した水溶液中における親水性カーボン材料の生成

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Carbon materials synthesis from organic compound in water and hydrophilization of carbon were conducted in one step by using pulsed arc discharge plasma at pressurized argon/aqueous solution interface. Products were carbon nanoparticles whose diameters were about 50 nm when we used aqueous solution containing glycine. Carbon nanoparticles doped nitrogen and modified with carboxylic acid. These materials could be produced only at high pressure condition. Smaller nanoparticles were formed by discharge at higher pressure condition due to generation of high condensation plasma.

1. Introduction

The arc discharge method has been widely used for preparation of carbon materials such as graphene and carbon nanotube [1-3]. In most cases, carbon materials synthesis by arc discharge is performed at low pressure condition [4,5].

Carbon nanomaterials have potential application in various fields because of their extraordinary properties. However, it is generally difficult to disperse carbon products in water without chemical modification. To extend the application of carbon nanomaterials especially in medical field, water dispersible carbon is desired. If these materials want to be dispersed in water, carbon surfaces have to be modified with hydrophilic group. In conventional methods, surface modification of carbon materials are treated by chemical agents or physical treatment after carbon materials synthesis by arc discharge [6,7].

In this work, pulsed arc discharge plasma was generated from metal electrode in pressurized argon. This method enabled carbon nanoparticles synthesis and chemical modification of carbon in one step. Discharge at these conditions can induce different plasma properties from discharge at low pressure condition [8] and expect to synthesize new carbon materials with new value.

2. Experiment

Fig. 1 shows diagram of inside reactor. The cylindrical copper electrode is set at 3 mm over aqueous solution surface which contained organic material. A voltage was applied to the copper electrode charged by DC power supply. Pulsed arc discharge plasma was generated from electrode in gas phase to liquid cathode. Experiments were conducted at high pressure argon over atmospheric pressure. Products were observed by field emission scanning electron microscope (FE-SEM) and analyzed by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

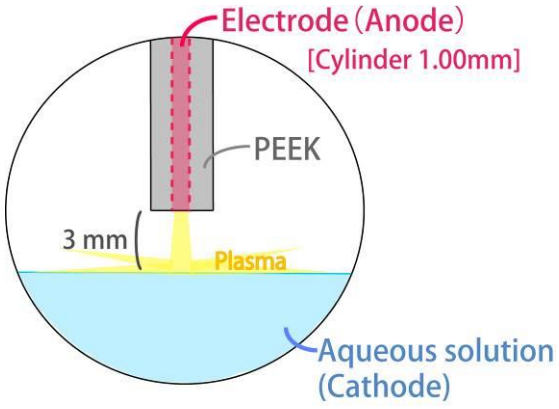

Fig.1. Diagram of inside of the reactor

3. Results and Discussion

Hydrophilic carbon nanoparticles were synthesized when plasma was discharged for aqueous solution surface containing 100 g/L glycine ($CH_2(NH_2)COOH$) under pressurized argon. Carbon materials were formed gradually by

repeating DC pulsed discharge. Carbon sources of products were glycine in aqueous solution. Fig.2 shows picture and SEM image of products after 10,000 of pulsed discharge under 4.0 MPa argon. After discharge at high pressure condition, color of solution turned black from colorless liquid. Products were spherical particles whose diameters were 50 nm or less.

D peak and G peak which were characterized carbon materials were observed by Raman spectra. The D/G band intensity ratio (I_D/I_G) was 1.15. In addition, carbon products by this method kept the dispersion in water. It implied that carbon nanoparticles formed by discharge at high pressure were modified with hydrophilic group.

To identify surface condition of particles, carbon products after dialysis were analyzed by ATR-FTIR and XPS. Products surfaces modified carboxylic acid (-COOH) as the functional group which caused to keep hydrophilic property. Moreover, nitrogen was doped in carbon nanoparticles.

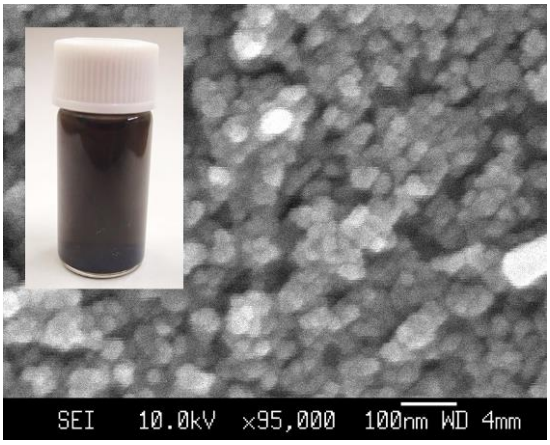

Fig.2. Picture and SEM image of products by discharge under 4.0 MPa argon

Pressure dependence of liquid products after 10,000 of pulsed discharge is shown in Fig.3. Carbon nanoparticles were produced by discharge only high pressure condition over 1.5 MPa argon. Discharge under atmospheric and 1.0 MPa argon atmosphere couldn't produce these carbon materials. With increasing pressure, generation of carbon was fast and small nanoparticles were produced. Nanoparticles growth was easily induced by high condensation plasma which has high temperature, high pressure and high density [9]. In this work, electron density of plasma under 4.0 MPa argon was about 45 times as much as ambient pressure. Therefore, discharge under pressurized argon could produce carbon nanoparticles.

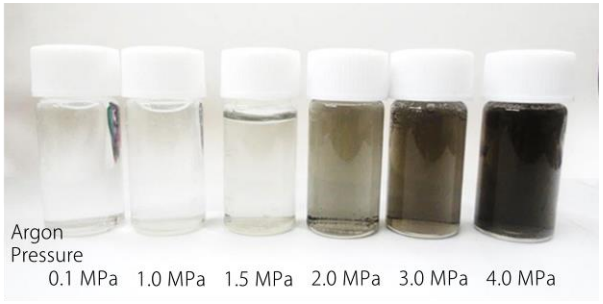

Fig.3. Pressure dependence of products

4. Conclusion

Water dispersible carbon nanoparticles were produced by pulsed discharge over glycine solution under pressurized argon. Carbon particles doped nitrogen and particles surfaces were modified carboxylic acid as hydrophilic group. Carbon materials could be formed only over 1.5 MPa argon because discharge at high pressure condition generated high condensation plasma. Smaller nanoparticles were produced with increasing pressure.

Acknowledgments

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