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Synthesis of hydrophilic carbon nanoparticles from amino acids by pulsed arc discharge over aqueous solution in argon under near-critical pressure

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ABSTRACT

Hydrophilic carbon nanoparticles (CNPs) were synthesized from amino acids using a pulsed arc discharge over an aqueous solution surface under pressurized argon at 4 MPa. The CNPs produced using this method were highly dispersible in water because their surfaces were modified by hydrophilic groups derived from the amino acids. The number of carbons in the straight chain of the source amino acids affected the generation of the CNPs, leading to different particle sizes, crystallinities, and nitrogen compositions. The oxygen content in the CNPs was independent of the source amino acid, but the nitrogen content was affected by the atomic ratio of nitrogen in the source amino acid.

1. Introduction

Hydrophilic carbon-based materials have the potential to be used in medical and environmental applications because such applications often utilize materials in aqueous media [1–4]. In general, carbon-based materials are hydrophobic and do not disperse in water. In order to make them dispersible in water, the surface must be modified by hydrophilic groups such as hydroxyl (–OH) or amino groups ($–NH_3$). In nearly all the existing surface modification methods, the carbon surface is modified by chemical agents [5,6] or physical treatments [7–9] after synthesis of the carbon materials. We have been developing reaction process induced by gas-liquid interface plasma [10–12]. Here, we propose a simple technique for the synthesis of hydrophilic carbon materials from amino acids by using a pulsed arc discharge under pressurized conditions. Amino acids are organic compounds containing two hydrophilic groups: amino ($–NH_2$) and carboxyl groups (–COOH). Synthesized carbon materials may exhibit dispersibility in water if these groups are present on the surface of the carbon products. There are various kinds of amino acids with different characteristics. Accordingly, the structure and composition of the resultant carbon products can be controlled by utilizing different amino acids as the carbon source.

An arc discharge in liquid media is one of the simplest techniques for the synthesis of carbon materials. For example, carbon nanotubes or amorphous carbon have been produced from organic compounds using this method [13–15]. In general, these syntheses are conducted at atmospheric pressure. However, a discharge plasma under high pressure creates a particular reaction field [16,17], which a few researchers have confirmed to produce materials [18–21] that could not be synthesized by a discharge at low pressure or atmospheric conditions.

In this study, pulsed arc discharges were generated under a pressurized argon atmosphere, and used for a one-step synthesis of carbon nanoparticles (CNPs) from amino acids. The pulsed discharge was applied at a pressurized gas/aqueous solution interface, which has the potential to produce unique materials with high affinity for water. We examined the effects of the amino acid on the CNPs by using several amino acids as carbon precursors.

2. Experimental

A pulsed arc discharge was generated repeatedly from a cylindrical electrode in pressurized argon at an aqueous solution surface in a stainless steel batch reactor (AKICO Co. Ltd.), as shown in Fig. 1. A 7.0 mL aqueous solution containing an amino acid at 50 g/L was filled into the reactor. In the present work, we used five different amino acids (purity >99.0%): glycine, D,L-alanine, L-threonine, L(+)-ornithine monohydrochloride, and L(+)-lysine monohydrochloride as carbon precursors. The atmosphere in the reactor was replaced

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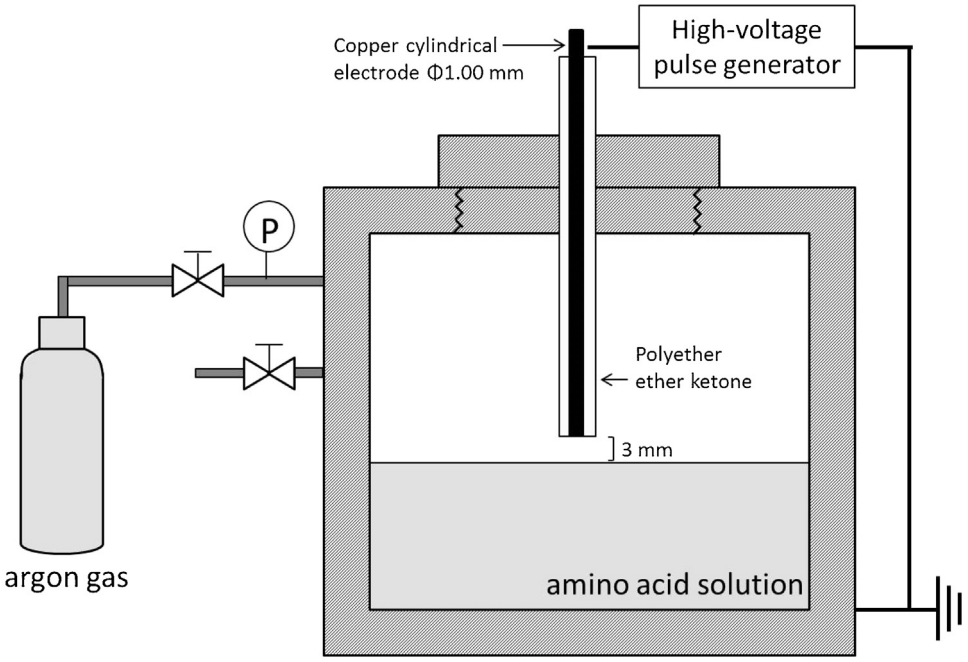

Fig. 1. Schematic diagram of experimental setup.

and pressurized with argon gas at a pressure of 4.0 MPa. The temperature of the experiment was around 298 K. The critical point of argon is 150.7 K and 4.86 MPa. Thus, the argon phase was in a subcritical condition where the pressure was slightly lower than the critical pressure. A copper cylindrical electrode of 1.00-mm diameter was set at a distance of 3 mm from the solution surface. The outside of the electrode except for the end surface was covered with polyether ether ketone (PEEK), which has good insulation. A pulsed voltage of 18.6 kV was applied to the electrode repeatedly by a high-voltage pulse generator (MPC2000S, Suematsu Electronics Co., Ltd.). The reactor was grounded such that the power was applied between the upper electrode and the grounded reactor body. After the reaction, the produced solid carbon materials were recovered in the following manner. In order to remove unreacted amino acids remaining in the solution, the solution was dialyzed with a dialysis membrane (Spectra/Por3, Spectrum Laboratories Inc.) whose pore size was about 5 nm. The characteristics of the carbon products were determined by field emission scanning electron microscopy (FE-SEM, JSM-6330, JEOL, Ltd.), Raman spectroscopy (NRS-1000, JASCO), and X-ray photoelectron spectroscopy (XPS, ESCA-3000, Shimadzu Co.).

3. Results and discussion

Pulsed arc discharges were generated over an amino acid solution surface and carbon materials were synthesized. Fig. 2 shows photographs of the products after the discharge of 20000 and 40000 pulses with the corresponding molecular structures of the amino acid carbon sources. CNPs were assumed to be produced from every amino acid judging from the color of the liquid products. When the same experiments were carried out at atmospheric pressure, the color of the solution did not change, indicating that carbon solid materials were not produced. Although the reason why the CNPs was produced only under high pressure is not clear yet, there may be two reasons to support the influence of the pressure. One is that the energy given to the system by the discharge is higher at higher pressure. When we calculate the energy from the current and voltage waves of the pulsed power, charged energy at higher pressure was higher. Moreover, intensity of emission of discharge was higher at higher pressure condition. Thus, larger amount of active species are given to the solution at higher pressure condition. Another reason is solubility of argon in aqueous phase. Solubility (mole fraction) of argon at 298 K is 9.28×10^{-4} at 4 MPa whereas it is 0.252×10^{-4} at 0.1 MPa [22,23]. Thus, larger amount of argon and related activate species may be dissolved in aqueous phase due to the higher solubility of argon in aqueous solution at higher pressure.

All CNPs produced by the present method were dispersed in water without sedimentation, implying that the surface of the CNPs was modified by either one or both of the carboxylic and amino groups in the original amino acids. FTIR analysis and XPS analysis indicated that the surfaces contained carboxylic groups (-COOH). The 20000 pulses of arc discharge turned the solutions containing glycine, alanine, and threonine black, as shown in Fig. 2, implying the production of the CNPs. In contrast, carbon materials could not be visually confirmed when the 20000 pulses were applied to solutions containing ornithine and lysine. However, the formation of carbon materials from ornithine and lysine were confirmed upon increasing the pulse number to 40000 pulses, as shown in Fig. 2. Comparing ornithine and lysine in Fig. 2, carbon materials were more easily formed when ornithine was utilized as the carbon source. Thus, it was more difficult to produce the CNPs from amino acids with longer carbon straight chains compared to those with shorter carbon chains. During the synthesis of the CNPs from amino acids, the amino acids should react with each other and create C—C, C—N, or C—O bonds. In the case of the CNPs synthesized from amino acids consisting of long, straight carbon chains such as ornithine and lysine, this reaction may be more difficult because of the steric hindrance of the larger molecules. This in turn leads to slower generation of the CNPs from longer chain amino acids.

The structure of the materials was observed by FE-SEM. Fig. 3 shows the SEM images of the solid materials produced from amino acids by the 20000 pulses of arc discharge. Nanoparticles were formed by the discharge. Every sample had the same spherical shape, but particle sizes of the materials were different depending on the carbon sources. Fig. 4 shows the number-average particle diameters of the CNPs as a function of carbon chain number of the source amino acids. When the CNPs were produced from amino

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