

**One-step Synthesis of Water-Dispersible Carbon Nanocapsules by Pulsed Arc
Discharge over Aqueous Solution under Pressurized Argon**

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Abstract

Water-dispersible carbon nanocapsules were synthesized in one-step process by a pulsed arc discharge over glycine solution under pressurized argon. Pulsed arc discharge from copper electrode was introduced to the glycine solution surface to generate carbon materials. The experiments were conducted at room temperature under argon atmospheric pressure to 4.0 MPa. The carbon products seemed to have high dispersibility in water. They composed of carbon nanocapsules with few graphitic layers doped with nitrogen. The generated carbon nanocapsules looked to react with carboxylic active compounds. The carbon nanocapsules were produced only under high pressures, over 1.5 MPa. The pressure affected on the synthetic rate of carbon nanocapsules and nitrogen doped levels, conversely, it has a small influence on the amount of oxygen atoms in the carbon products.

Keywords: Pulsed arc discharge, Plasma, Carbon nanocapsules, Glycine.

1. Introduction

Arc discharge in a liquid medium is one of the simplest techniques for the synthesis of carbon materials. Two different approaches can be applied within this technique. The first method involves using two graphite electrodes; carbon vapors produced by arc discharge from these electrodes are rapidly quenched in a liquid, leading to the formation of carbon materials. Previous studies have reported the synthesis of carbon nanotubes (CNTs) [1,2], carbon onion particles [3,4], and porous carbon [5] based on this method. The other approach is arc discharge in organic solvents. In this case, the carbon precursor is not supplied by the electrodes, but by organic materials in a liquid phase. This approach was previously applied to synthesize CNTs or amorphous carbon [6,7]. In the present work, we utilized organic compounds in aqueous solution as the carbon precursor. As the discharge with an organic solvent or with an aqueous solution containing organic compounds allows to supply a different source of carbon, these approaches can be used to control the doping density of specific elements in the carbon material. Consequently, the unique properties can be achieved by doping various atoms in carbon. For example, nitrogen doping leads to enhance catalytic activity of carbon materials [8], and boron doping may alter their electrical characteristics [9]. By achieving full control over the doping density of specific elements into the carbon materials, the target several desirable features of carbon materials could be achieved.

Generally, carbon materials do not disperse in water. Their surface must be modified by hydrophilic groups in order to achieve dispersibility in aqueous media. Water-dispersible carbon is widely applied in medical and environmental applications [10,11] that involve an aqueous medium. In conventional methods to prepare water-dispersible carbon,

the carbon surface is modified by chemical agents [12,13] or by a physical treatment [14] after synthesis of carbon materials. Jiang et al. [15] and Shirafuji et al. [16] reported that arc discharge in a liquid also induced modification of the carbon surface. Here, we demonstrated a method involving synthesis of carbon nanocapsules and surface modification in one-step process, by arc discharge over an aqueous solution containing organic compounds, under a pressurized argon gas. It was known that carbon nanocapsules had positive effects on cell cultivation [17,18], and moreover they had low toxicity for cells [19]. When carbon nanocapsules were applied for biomedical applications, they were required to disperse in water due to the cell cultivation generally was conducted in water mediums. It was expected that carbon nanocapsules generated by this method has high dispersibility in water, due to the organic compounds as carbon precursors certainly have hydrophilic groups. Thus, the present method can simplify the synthesis of water-dispersible carbon.

Glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) dissolved in deionized water might be converted into carbon nanocapsules by pulsed arc discharge over a liquid surface under pressurized argon gas. It has two hydrophilic groups: an amino ($-\text{NH}_2$) and carboxyl groups ($-\text{COOH}$). The existence of these groups on the surface of carbon materials after synthesis process led to the carbon products having high dispersibility in water. Moreover, glycine is one of the amino acid, namely it is harmless and not affect to the cells. If glycine stays in products even after separation of carbon nanocapsules, it has no effect on the biomedical applications. Therefore, in this work glycine dissolved in deionized water was subjected as starting material to generate carbon nanocapsules by using pulsed arc discharge.

2. Experimental

2.1 Materials

Glycine (purity >99.0%, Wako Pure Chemical, Osaka, Japan) was used as a starting material. It was dissolved in deionized water (Wako Pure Chemical, Osaka, Japan). A cylindrical copper with 1 mm diameter, purchased from Nilaco Co., Japan, was employed as an electrode. Argon gas (purity >99.999%) as a gas environment was supplied by Taiyo Nissan, Kanagawa, Japan.

2.2 Experimental setup and methods

Pulsed arc discharge was generated at a gas/liquid interface from a cylindrical copper electrode placed in gas phase as shown in Fig. 1. Glycine was dissolved in deionized water to a concentration of 100 g/L, and 7.0 mL of the solution were filled into a reactor. An electrode of 1.00 mm-diameter, whose side was covered with insulator (polyether ether ketone), was set at a distance of 3 mm from the water surface. The reactor, made of stainless steel, was grounded. Argon gas was filled in the reactor at a pressure ranging from atmospheric (0.1 MPa) to 4.0 MPa. A DC pulsed voltage of 18.6 kV which supplied by DC pulsed power (MPC2000S, Suematsu Electronics, Kumamoto, Japan) was repetitively introduced into aqueous solution via copper electrode at room temperature. After discharge, the products in liquid state were dialyzed by dialysis membrane (Spectra/Por3, Spectrum labs, CA, USA) in order to remove the raw material (glycine) before the analysis. Structure and properties of carbon products were characterized by high-resolution transmission electron microscopy (HRTEM, JEM2010, JEOL, Japan) and Raman spectroscopy (NRS-1000, JASCO, Japan). The functional groups on the carbon surface were characterized by X-ray photoelectron spectroscopy (XPS, ESCA-3300, Shimadzu, Japan) and Fourier

Transform Infrared Spectroscopy (FTIR, Spectrum two, Perkin Elmer, England). In order to examine reaction mechanism, optical emission spectra of the discharge were observed by using a high-resolution spectrometer (HR4000, Ocean Optics, USA).

3. Results and Discussion

3.1 Synthesis of carbon materials

Pulsed arc discharges were repeatedly introduced over an aqueous solution containing 100 g/L glycine under argon gas at pressures between 0.1 and 4.0 MPa. Fig. 2 shows a photograph of the liquid products after 10000 discharge pulses at several different pressures. Clearly, the carbon materials were generated from glycine by pulsed arc discharge in deionized water only at high argon pressures (Fig. 2c, 2d, 2e, and 2f; over than 1.0 MPa). At these conditions, the pulsed arc discharge seems easily to generate carbon materials from glycine solution. However, no carbon materials were generated from glycine solution by the pulsed arc discharge at atmospheric pressure or under pressurized argon 1.0 MPa. It has been reported that the operating pressure had high influence on the structure of multi-walled CNTs prepared by pulsed arc discharge in water with graphite electrodes. The operating pressure allowed to enhance the quenching rate of the carbon vapor bubbles and the thermal conductivity of the arc plasma [20]. In these experiments, although the synthesized mechanism of carbon materials was not clear, it can be informed that the operating pressures may change the thermal conductivity of pulsed arc discharge which affected on the production of carbon materials from the aqueous glycine solution. In addition, the carbon materials produced by the present method exhibited dispersibility in water which implies the existence of hydrophilic groups on their surface.

3.2 Structure and functional groups of carbon products

The structure of carbon products after 10000 discharge pulses at 4.0 MPa was characterized by HRTEM. Fig. 3 showed the highlight of multi-walled carbon nanocapsules with walls comprising two to six graphene layers. The distance between atomic layers were around 0.34 ± 0.02 nm which corresponded to the lattice spacing of graphene. This was similar to the carbon nanocapsules that synthesized by elevating temperature with and without vacuum pressure [21,22] or by an acetylene flame method [23]. It was reported that an instantaneous temperature increase led to the formation of carbon nanocapsules. Pulsed arc discharge at a gas/liquid interface was also found ~~could to~~ induce an increase in the temperature at the solution surface in a moment [24], leading to the production of carbon nanocapsules. As shown in Fig. 3b, the atomic layers of the carbon nanocapsules are not well defined due to the existence of nitrogen and oxygen doping. These elements came from glycine which used as a carbon source. At these conditions, nitrogen and oxygen elements had high reactivity. As a result, they could react and enter easily into the graphene layer during the formation of carbon nanocapsules.

Fig. 4 ~~showed~~ shows Raman spectrum of the carbon nanocapsules which generated from glycine solution with 10000 pulsed arc discharge at 4 MPa. The bands at 1340, 1582, and 2670 cm^{-1} were assigned to the D, G, and 2D peaks, respectively. The G band denotes the growth of the graphene layer, while the D band is associated to structural defection, doping, and surface modification of generated carbon. The intensity ratio between D and G bands was 1.32. However, the defection, doping, and surface modification ratio of carbon could not be determined easily, because the curve of carbon nanoparticles also detected the

D band [25]. Clearly, the peak at 2920 cm^{-1} which assigned to the OH group was also detected [26]. It can thus be inferred that COOH groups might react and modify the external surface of the generated carbon nanocapsules, imparting hydrophilic properties to the carbon nanocapsules products.

In order to identify the functional groups which existed on the generated carbon nanocapsules surface, the generated carbon nanocapsules products in liquid state were analyzed by FTIR. Fig. 5 shows the FTIR spectra of pure glycine and the generated carbon nanocapsules when the experiment was performed at 4.0 MPa argon pressure with 10000 pulsed arc discharge. A broad band at 3375 cm^{-1} corresponds to the carboxylic OH groups was found at each FTIR spectra. The amine groups were observed at 3150 cm^{-1} band, and it was partially overlapping with the weak-intensity signal of the C-H vibration at $\sim 3000\text{ cm}^{-1}$ band. The four peaks between 1300 and 1650 cm^{-1} bands are characteristic of amino acids [27,28]. In particular, the peaks at 1608 and 1325 cm^{-1} regions were assigned to the C=O stretch, and the peak at 1510 cm^{-1} band to the C-N-H vibration. The C-H vibration is associated to the peak at 1408 cm^{-1} region.

In Fig. 5b, the OH and C=O peaks were observed at 3375 and 1633 cm^{-1} regions respectively. The shift of the C=O band from 1608 to 1633 cm^{-1} band occurred due to the consuming of C-N and C-H groups during carbon nanocapsules formation [29]. The peak intensity of the C-H decreased due to the formation of the graphene layer. The disappearance of the NH_3^+ and C-N-H peaks indicated that only a small amount of amine groups were existed on the carbon surfaces. On the contrary, the carboxylic (-COOH) groups were found on the generated carbon nanocapsules surface as the main functional

groups. Due to the properties of carboxylic groups, the generated carbon nanocapsules enable to disperse well in water.

The XPS analysis was performed to determine the doping density in the graphene layers. ~~Fig. 6 shows the XPS spectra of the carbon nanocapsules produced by pulsed discharge at 4.0 MPa.~~ To determine the density of elements doping in the generated graphene layers, the generated carbon nanocapsules were characterized by using XPS. Fig. 6 shows the XPS spectra of the generated carbon nanocapsules produced by 10000 pulsed arc discharge at 4.0 MPa argon pressure. The peak at 284.8 eV ~~corresponds~~ corresponding to the C-C bonding was found clearly in the C1s spectrum. Other peaks with higher binding energy were also found this spectra. They are 285.6 eV, 286.5 eV, and 288.8 eV assigned to C-N bonding, C-O bonding, and O-C=O bonding, respectively [27]. The existence of C-O and O-C=O bonds are mostly associated with the surface modification of generated carbon nanocapsules by carboxylic groups. The C-N peak related to nitrogen doping in the graphene layer was also found in this spectra. The existence of nitrogen in the generated carbon nanocapsules was also confirmed by the N1s spectrum. Therefore, it could be said that the generated carbon nanocapsules products obtained by pulsed arc discharge from glycine solution were composed of graphene layers with and without nitrogen doped, and their surface ~~have been~~ is modified by carboxylic groups.

3.3 Pressure effects on the synthesized carbon nanocapsules

Table 1 ~~showed~~ shows the effects of pressure on the generated carbon nanocapsules produced by pulsed arc discharge that analyzed by comparing the Raman and XPS data at 2.0, 3.0, and 4.0 MPa argon pressure. The intensity ratio between the D and G bands (I_D/I_G)

in the Raman spectra may provide information on the density of defects in the generated graphene layers and their modification ratio. The generated carbon nanocapsules produced by the pulsed arc discharge under higher argon pressure had a high I_D/I_G ratio, showing that defects density or modification ratio in the generated carbon nanocapsules increased with increasing pressure.

Based on the ratio between nitrogen and carbon that determined by XPS, the higher nitrogen contents were found in the generated carbon nanocapsules at higher pressure leading to higher I_D/I_G . Fig. 7 shows the optical emission spectra of pulsed arc discharge over glycine solution at 0.1 to 4.0 MPa argon pressures. The emissions observed not only argon and hydrogen elements but also CN molecule at 359 nm derived from glycine in water. It might be occurred due to synthesis of carbon nanocapsules. As shown above (see Fig. 2), the rate of generation of carbon nanocapsules by pulsed arc discharge increased with increasing pressure which indicated by the color changes of the solution products. The intensity of CN molecule in Fig. 7 became strong at higher pressure condition. The CN molecules might ~~come~~ be originated from glycine degradation during the formation of carbon nanocapsules by pulsed arc discharge. This also affected the nitrogen doping levels in carbon products. Nevertheless, the amount of oxygen in the generated carbon nanocapsules ~~seemed~~ is hardly ~~affected~~ by the argon pressure.

The intensity ratio of 2D and G bands (I_{2D}/I_G) in the Raman spectra denotes a higher I_{2D}/I_G for carbon products which produced by the pulsed arc discharge at higher pressures. In the case of nitrogen doped in graphene layers, it was reported that I_{2D}/I_G tends to decrease, while I_D/I_G increases [30]. The large amounts of nitrogen doped in graphene layers also ~~affects~~ affected on the reduction of 2D band intensity [31]. In this work,

although higher amounts of nitrogen atoms were doped in the graphene layers upon the high-pressure treatment, the I_{2D}/I_G ratio of the generated carbon nanocapsules increased with increasing pressures. Moreover, the intensity of the 2D band diminishes relative to that of the G band when the number of graphene multi-layers increases [32]. The same phenomenon was also shown by carbon onions which composed of carbon nanoparticles with graphene layers [33]. Based on the pressure effect on the I_{2D}/I_G ratio, it seemed that the number of graphene layers in the generated carbon nanocapsules will decrease at higher pressure conditions. Therefore, it could be said that the I_{2D}/I_G ratio in the generated carbon nanocapsules was probably affected by the number of graphene layers.

4. Conclusions

Water-dispersible carbon materials have been produced from glycine solution by generating a pulsed arc discharge on the surface of glycine solution under pressurized argon. Carbon materials were generated only at high pressure conditions, over 1.5 MPa. The products had a capsule structure consisting of several graphene layers. The graphene layers of the generated carbon nanocapsules were doped with nitrogen atoms, and their surfaces were modified by carboxylic groups. The CN molecules related to the formation of generated carbon nanocapsules produced from glycine during process. Due to the production of CN molecules promoted by the pulsed arc discharge with increasing argon pressure, the pulsed arc discharge under higher pressures could result carbon nanocapsules rapidly with high nitrogen doped levels. However, the amount of oxygen atoms in the carbon products was not affected by the operating pressures.

Acknowledgments

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Table captions

Table 1. Pressure effects on carbon products obtained by pulsed discharge under pressurized argon.

Figure captions

- Fig. 1.** Schematic of experimental apparatus.
- Fig. 2.** Liquid products after treatment by pulsed arc discharge under argon at a pressure of (a) 0.1, (b) 1.0, (c) 1.5, (d) 2.0, (e) 3.0, and (f) 4.0 MPa, respectively.
- Fig. 3.** TEM images of carbon products generated by pulsed arc discharge at 4.0 MPa: (a) an aggregate of carbon nanocapsules; (b) enlargement of a carbon nanocapsules.
- Fig. 4.** Raman spectrum of carbon nanocapsules produced by pulsed arc discharge at 4.0 MPa argon pressure.
- Fig. 5.** FTIR spectra of (a) pure glycine and (b) carbon products obtained by pulsed discharge at 4.0 MPa.
- Fig. 6.** XPS spectra of carbon nanocapsules produced by pulsed discharge under 4.0 MPa argon pressure: (a) C1s and (b) N1s spectra.
- Fig. 7.** Optical emission spectra of pulsed discharge over glycine solution at 0.1 to 4.0 MPa argon.

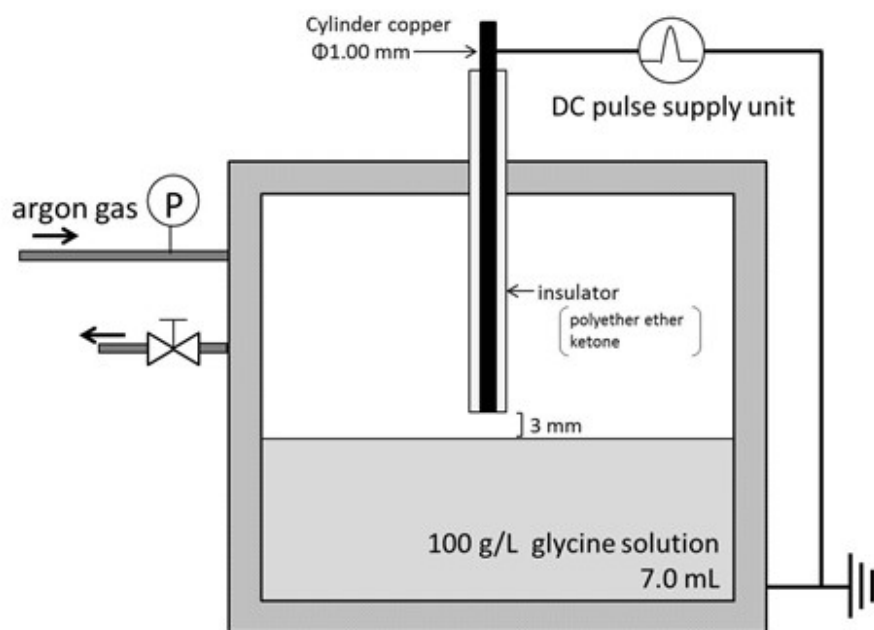


Figure 1

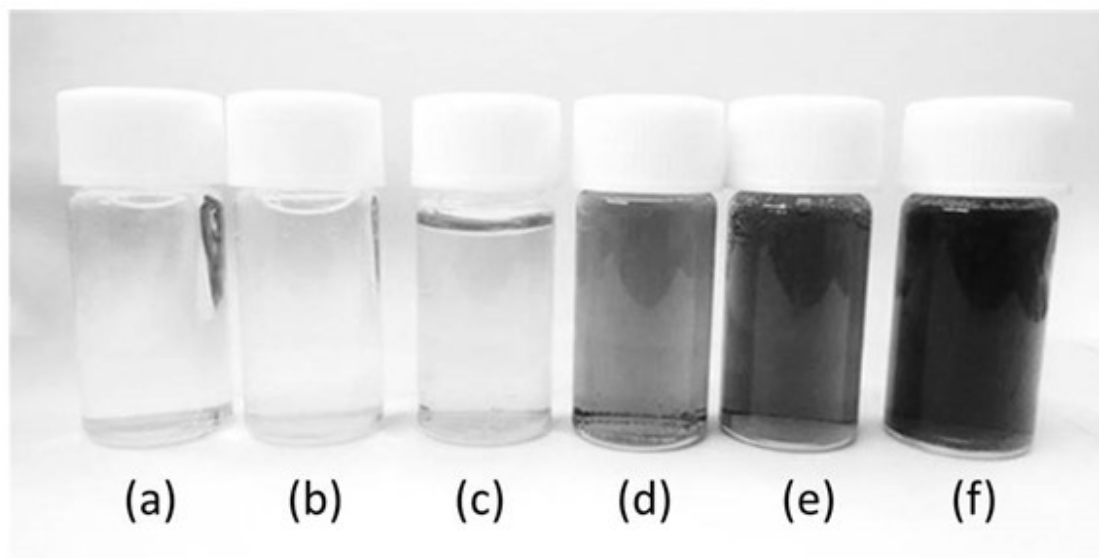


Figure 2

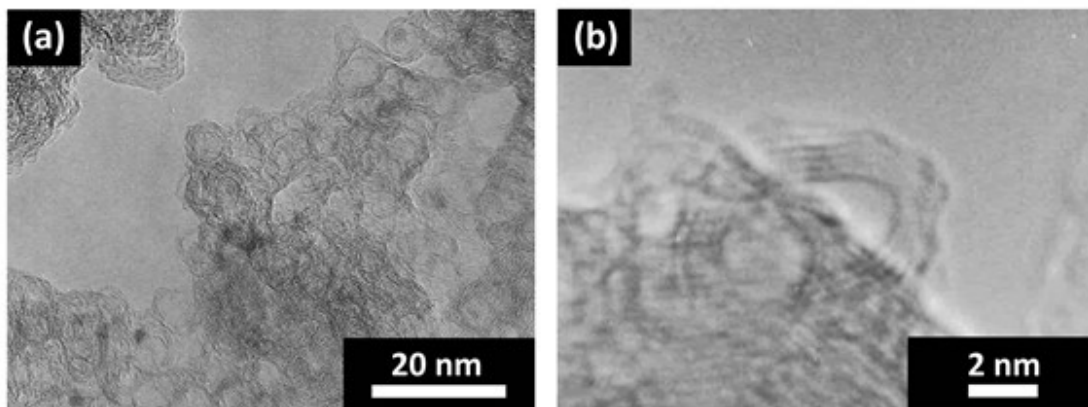


Figure 3

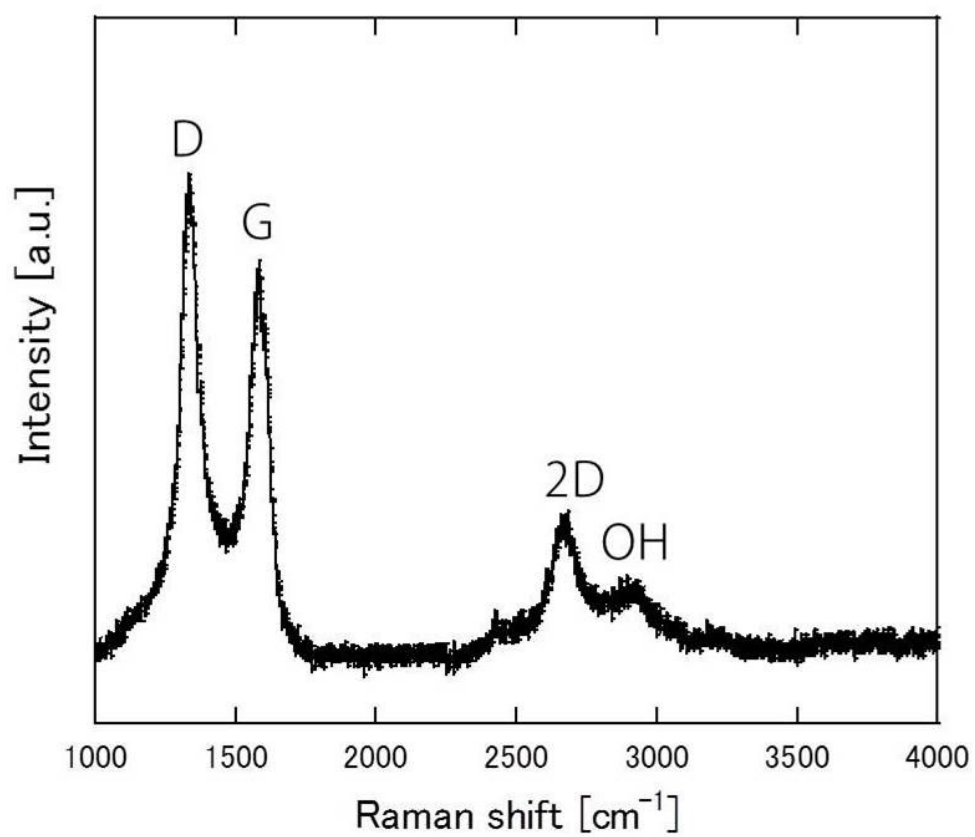


Figure 4

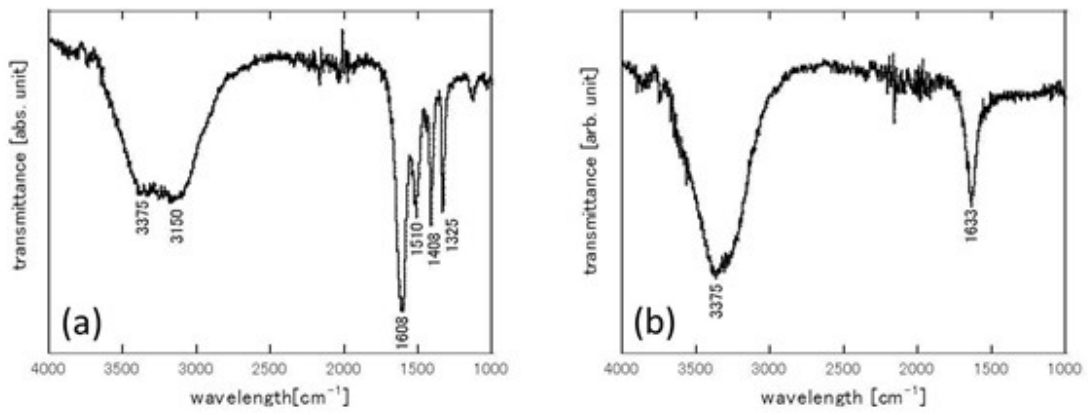


Figure 5

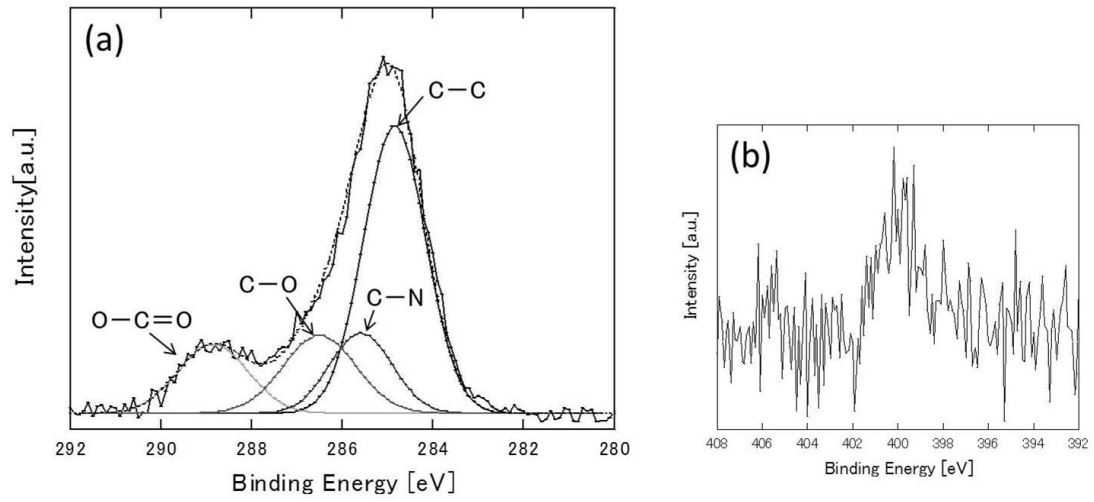


Figure 6

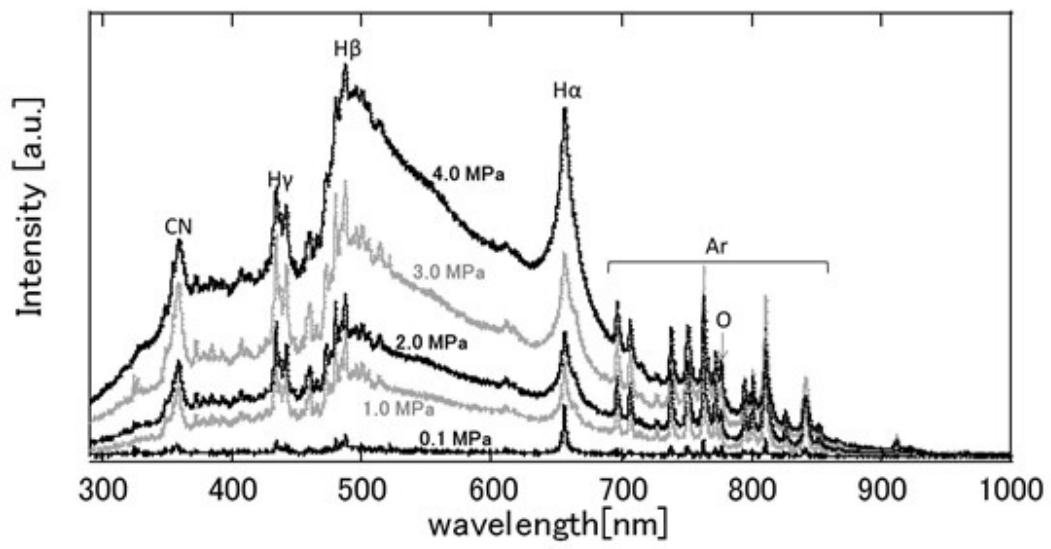


Figure 7

Table 1. Pressure effects on carbon products obtained by pulsed discharge under pressurized argon.

Pressure [MPa]	Raman		XPS	
	I _D /I _G	I _{2D} /I _G	N/C	O/C
2.0	1.22	0.30	0.04	0.37
3.0	1.25	0.43	0.10	0.37
4.0	1.32	0.48	0.15	0.38