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Electrochemical properties of modified highly ordered pyrolytic graphite by using ambient plasma

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ABSTRACT

Surface of highly ordered pyrolytic graphite (HOPG) is reformed by using ambient plasma. The HOPG film shows various pore structures after the plasma treatment, indicating improved electrochemical properties for supercapacitor applications because of the increase of the surface area. We also compare water effect on the film during the plasma treatment. Water might protect HOPG surface from the plasma and provide oxygen functional groups onto it, resulting in lower infected pores and higher impedance compared with them of HOPG film without water. Ambient plasma, therefore, could be considered as an economic and effective method for sample reformations.

1. Introduction

Graphene has much attention recently due to its unique and excellent properties in various applications [1–3]. However, graphene also needs to be reformed its surface or structure for enhanced performance in bio sensors, gas sensors, supercapacitors and so on because of inert and inactive surface of graphene in the applications [4–6]. For example, supercapacitor consists of two electrodes (anode and cathode), a separator and electrolyte between the electrodes [7]. Its performance (capacitance) is proportional to not only the surface area and conductivity of electrodes, but also wettability of it with electrolyte ions [7–9]. Therefore it is necessary to reform or functionalize the electrodes for better performance. Carbon allotropes, which have large specific surface area, have been used as electrodes typically [7–10].

There are chemical and physical approaches for the surface reformation. Graphene oxide and many graphene composites would be examples obtained from the chemical methods [11–13], and physical methods applying voltage, current, plasma, and heat onto samples are used [14–16]. Here we applied ambient plasma, generated by our home-made generator, onto highly ordered pyrolytic graphite (HOPG) to see the change of electrochemical properties.

HOPG is a graphite material which has oriented crystalline structure following the vertical direction of substrate. It can be obtained by annealing at high temperatures approximately 3400–3600 °C under compression [17]. It has a uniform plane and a flat surface to the atomic levels, so it is used mainly in the elemental analysis of a scanning probe microscope which requires a clean and parallel substrate [18,19].

Plasma is one of the fourth state of matter [20], the others being solid, liquid, and gas. When apply a high energy to gas state, the gas is separated into electrons and ions. Therefore, plasma is consists of electrons, ions, neutral gas, and radicals, and it also has a high electrical conductivity due to free electrons. It is widely used in many applications such as etching, cleaning, deposition, and synthesis [21–23].

In this report, we applied DC discharge plasma onto HOPG to change of its surface properties for supercapacitor application. The HOPG film shows various pore structures after the plasma treatment, indicating improved electrochemical properties for supercapacitor applications because of the increase of the surface area. We also compare water effect on the film during the plasma treatment. It has been known that water molecules could stack onto graphene oxide and make ripples on the surface as the humidity increased [24]. We, therefore, expect particular morphology with water on HOPG surface and water might distribute plasma to the surface uniformly.

2. Experimental

HOPG films are taken off from bulk HOPG (Advance Ceramics, STM-1 grade, mosaic spread of 0.8 ± 0.2, 12 mm × 12 mm × 2 mm) by using a double-side copper tape, whose one side attached onto a thin glass substrate, and then polyimide tape of an 1 cm diameter hole was on top of HOPG film as shown in Figure 1a. The DC plasma, generated at 10 kV, was then applied to HOPG film for

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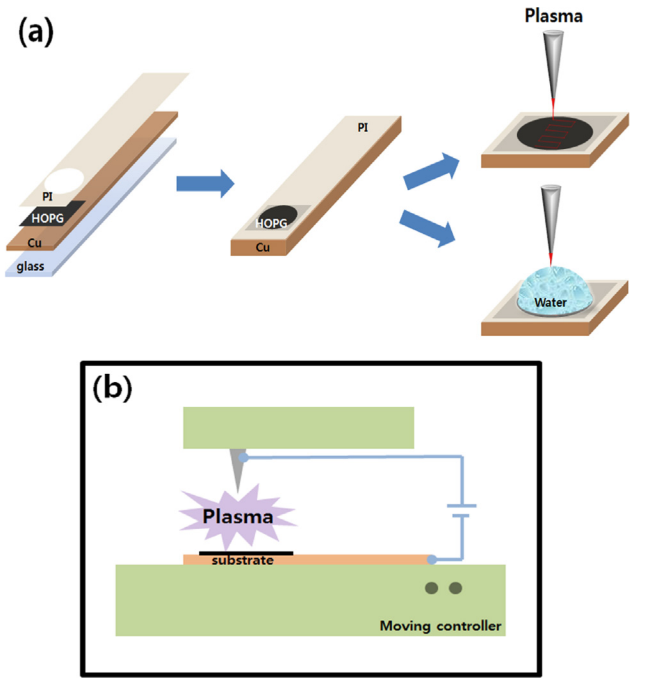

Figure 1. The schematics of (a) sample preparations and (b) an experimental setup for the plasma treatment.

5, 15, and 30 min, respectively, and each sample was named as P5_HOPG, P15_HOPG, P30_HOPG, respectively, depending on the plasma treatment time. Speed of the scan was 48 mm/s, and the area applied by the plasma was 4 mm × 5 mm. In order to see water effect on HOPG film deionized (DI) water was dropped onto HOPG film and then plasma was applied for 5, 15, and 30 min. Each sample was referred as WP5_HOPG, WP15_HOPG, and WP30_HOPG, respectively, and the number refers the plasma applying time on HOPG film covered with DI water. Figure 1b shows the schematic of our plasma equipment.

Electrochemical properties were measured using a three-electrode cell in 0.5 M H_2SO_4 solution. The reference electrode and counter electrode are Ag/AgCl and platinum electrode, respectively, and the HOPG films prepared above were used as the working electrodes (Figure 1a). Cyclic voltammetry (CV, BioLogic, SP-200) and electrochemical impedance spectroscopy (EIS, BioLogic, SP-200) were measured under the same area for electrochemical properties. Morphology was investigated by using scanning electron microscopy (SEM, HITACHI S-4300), and composition analysis was performed by using energy dispersive X-ray spectroscopy (EDX, HITACHI S-4300).

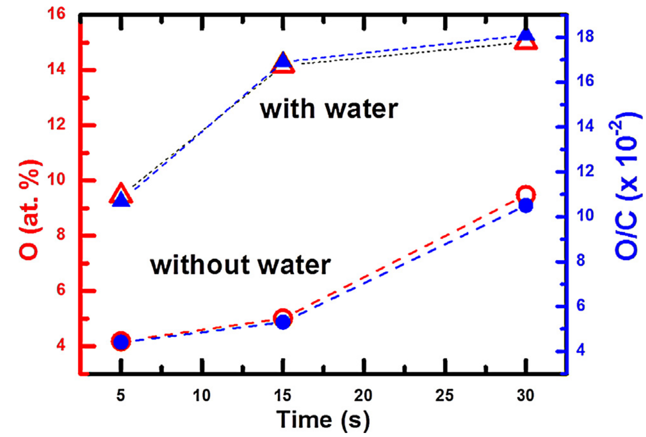

Figure 3. Oxygen atomic percentage (left) and oxygen to carbon atomic ratio (right) of the samples after the plasma treatment with and without water.

3. Results and discussion

Morphology of HOPG film applied by plasma for different time (5, 15, and 30 min) was shown in Figure 2. The first and second row present the sample covered without and with water. More severe pores are generated and the surface becomes rougher as the plasma time increases in the first raw, indicating three dimensional pore structures are generated, as shown in Figure 2a–c. This might be positive effect on the supercapacitor performance because of the enhancement of the surface area consequentially. The morphology of HOPG film covered with water, however, is different after the plasma treatment as shown in Figure 2d–f. Wrinkles appeared on the surface of HOPG film and become fine and small as the plasma time goes. Water seems to help stripping away a few top layers of HOPG film.

The oxygen atomic percent and oxygen to carbon atomic ratio are shown in Figure 3. Oxygen atomic percent of HOPG with and without water increases as the plasma treatment time increases, indicating that water and atmosphere provided oxygen source. Especially HOPG covered with water has more than twice of oxygen content than that of HOPG in atmospheric state. The oxygen to

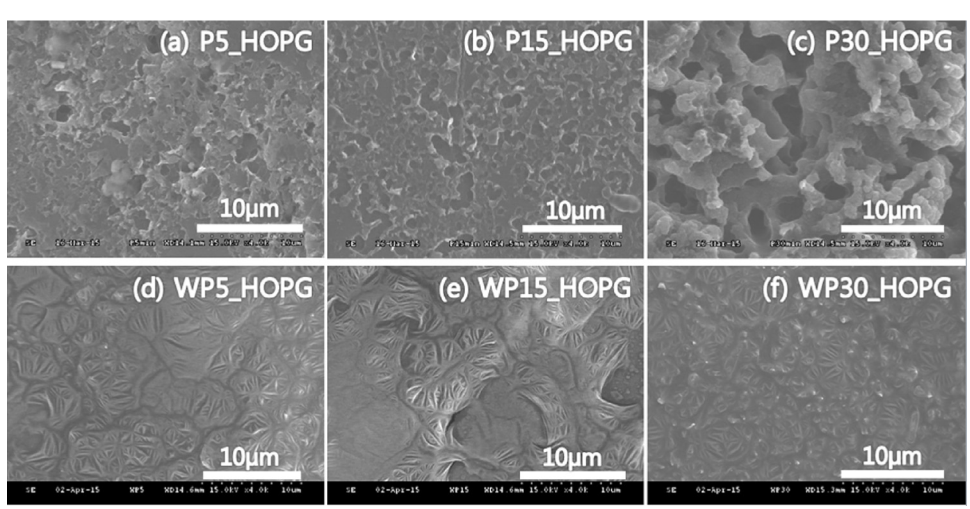

Figure 2. SEM images of HOPG samples without water after the plasma treatment for (a) 5, (b) 15 and (c) 30 min, and with water for (d) 5, (e) 15, and (f) 30 min.