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Influence of Bulk Graphite Density on Electrical Conductivity

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Abstract

Electrical conductivity of bulk graphite was investigated as a function of its volume density and temperature. The bulk graphite was prepared from pressing natural graphite powders obtained from two different conditions: i) without any treatment and ii) with 24 hr of ultrasonic treatment. Powders from each condition were consolidated using an isobaric press of different pressures, including 5, 10, 20, 30, 40 and 50 MPa. Ultrasonic treatment helped to exfoliate graphene from its parent graphite which enhanced the electrical conductivity of the compressed bulk graphite. Scanning electron microscopy (SEM) and UV-Vis spectroscopy confirmed that multilayer graphenes and nanographite were obtained after the sonication. Raman spectroscopy was also used to investigate the graphitic characteristics of sonicated graphite. The bulk graphite of 50 MPa consolidation from the sonicated powders offered the highest electrical conductivity which was due to its highest density as well as a combination of multilayer graphene. Effect of temperature on the electrical conductivity was discussed. The conductivity increases when increasing the temperature.

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Keywords: Electrical Conductivity; Graphite; Volume density; Temperature

1. Introduction

Carbon has been known as an important element for century. In our atmosphere, one carbon atom attached to two oxygen atoms in a gas called carbon dioxide. Carbon can be represented in many forms. The most well-known forms of carbon include diamond, graphite, and charcoal [1]. In the past decade,
carbon nanotube, graphite, and graphene have shown a profound effect on various applications due to their unique properties, including mechanical, optical, and electrical characteristics [2]. In this report, graphite and graphene were studied. Graphene was claimed to be the thinnest 2D material, whose structure is about one-atom thick of sp²-bonded carbon atoms packing in a honeycomb structure [3]. Graphite flake normally consists of several graphene sheets stacked together. Both graphite and graphene have been investigated for various applications, such as composite material [4], conductive ink [5], electrode [6], coating [7] etc. However, most of the graphite-graphene-based reports are focusing on their application relied on nano-microscale characteristics, but few of them reported on their behavior on macroscopic behavior. One of an important phenomenon is to study effect of electrical conductivity on bulk graphite under different compression pressures. Sánchez-González et al. reported that the conductivity of carbon black increases when increasing a compression pressure [2]. In general, increasing the compression pressure mechanically reduces the gaps between carbon particles, directly enhancing the electrical contact. The information may be related to the contact theory from Mrozowski and Holm [8, 9] proposing that the electrical conductivity of a carbon black depends on the separation distance between each particle [10] and the average size [11].

In this work, effect of the volume density of the compressed graphite on its electrical conductivity was investigated. The compressed graphite was obtained from natural graphite powder of two different conditions: with and without ultrasonic treatment. The conductivity of the samples was measured by two probe technique. Effect of the sample temperature on its conductivity was also reported as the temperature could affect the bulk density and its electrical conductivity. The optical property of the graphite suspension was characterized using UV-Vis spectroscopy. Morphology of the graphite was investigated by scanning electron microscopy (SEM).

2. Experiments

2.1 Preparation and characterization of graphite powder

Two types of graphite powders were prepared: i) non-sonicated graphite (CC) powders and sonicated graphite (SC) powders. The UV-Vis spectrometer (Jasco V570) was used for investigating graphitic characterization of the sonicated graphite suspension. The samples were scanned in a 1-cm path length cuvette with a spectral range of 200-700 nm. Raman spectroscopy (Renishaw inVia) with an excitation wavelength of 514 nm was used for investigating the graphitic characteristics of sonicated graphite and determining the amorphous carbon contents. Prior to Raman measurement, the samples were prepared by drop-dried deposition technique. The suspension was dropped on silicon surface and kept dry using a hotplate at a temperature of 60 °C. The topography of the compressed graphite was investigated by scanning electron microscopy (SEM: JEOL, JSM-6510) at 10 kV.

Fig. 1(a) shows absorption spectra of raw graphite (non-sonicated) and sonicated graphite. The peaks between 180-280 nm normally correspond to the π → π* transition of C=C. The non-sonicated sample shows a strong peak at 224 nm, whereas that of the sonicated sample is barely observed. The sonicated sample shows a dominant peak at 268 nm which does not found in the non-sonicated sample. The peak may be resulted from the nano-graphite, graphene, or even amorphous carbon [12]. This assumption is correlated with the Raman spectra of the samples as shown in Fig. 1(b) and (c). G-band is generally originated from the graphitic characteristics of graphite and its sp² structure [13]. The G-band positions of the non-sonicated and sonicated samples are at 1571 and 1574 cm⁻¹, respectively. The slight difference in the G-band position may be due to a little change in the vibrational energy of the graphite after sonication. D-band is normally related to the sp³ nature of the carbon-related material. It could be used for an investigation of amorphous carbon species as shown in Fig. 1(c). In addition, there also have some evidences that the D-band may be influenced by the electronic nature of its surrounding [14]. For example, functionalization may cause a change in native electron delocalization, i.e. in the hybridization
of carbon atoms [15]. In this experiment, the D-band positions of the non-sonicated and sonicated samples are at 1351 and 1346 cm⁻¹, respectively. The intensity of the D-band from sonicated samples is very strong comparable to that of the G-band. This means that 24 hr of sonication affected exfoliation of graphene and it might generate plenty of amorphous carbon. However, it should be noted the amorphous carbon may come from the raw graphite directly and sonication just allowed these hidden amorphous carbons to come out. To have better understanding on this phenomenon, further experiment may be required.

2.2 Preparation of bulk graphite

Two types of graphite powders (with and without sonication treatment) were compressed into bulk graphites of different pressures: 10, 20, 30, 40 and 50 MPa as shown in Fig. 2. The terms ‘CC’ and ‘SC’ were used as symbols of the samples from non-sonicated graphite and sonicated graphite, respectively. The number after the short terms refers to the pressure of consolidation, i.e. CC10 means the bulk graphite obtained from non-sonicated graphite which was compress at 10 MPa and SC10 means the bulk graphite obtained from sonicated graphite which was compress at 10 MPa. Fig. 3(a) and (b) show the topography of the bulk graphites which were compressed at 10 and 50 MPa, respectively. The structure of the graphite flakes on the surface of the bulks is clearly different. It is very rough from 10 MPa.

The volume density of the bulk graphites from each condition was obtained from directly measuring a thickness and a diameter of the sample using a digital micrometer. Then, the density is calculated from

$$D = \frac{m}{V}$$

where \(D\) is a volume density (kg·m⁻³), \(V\) is a volume of the sample (m³) and \(m\) is a mass (kg). To do electrical measurement, the top and the bottom parts of the samples were attached to wire electrodes. They were connected to the Digital Reference Multimeter 8.5 digit (Fluke 8508A). The measurements were repeated for 5 times.

![Graph of the samples prepared from different conditions](image-url)
2.3 Preparation of temperature-dependent conductivity study

The temperature-dependent conductivity was carried out as shown in Fig. 4. The samples were kept inside a tubular furnace, where the temperature was precisely controlled up to 300 K. The measurements were repeated for 3 times.

![Fig. 4. Schematic diagram of experimental setup for a temperature-dependent conductivity study. (a) Digital Reference Multimeter, (b) Digital temperature controller and indicator, (c) Safety connecting box, (d) tubular furnace and (f) sample](image)

3. Results and discussion

3.1 Electrical conductivity at room temperature

Table 1. Electrical conductivity of raw graphite (non-sonicated) at 298 K (25 °C)

<table>
<thead>
<tr>
<th>No.</th>
<th>samples</th>
<th>Density (kg/m³)</th>
<th>Room temperature conductivity (S·m⁻¹)</th>
<th>Room temperature resistivity (Ω·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CC10</td>
<td>1921.990</td>
<td>8.567 ± 0.254</td>
<td>0.117 ± 0.005</td>
</tr>
<tr>
<td>2.</td>
<td>CC20</td>
<td>2033.353</td>
<td>9.043 ± 0.244</td>
<td>0.099 ± 0.005</td>
</tr>
<tr>
<td>3.</td>
<td>CC30</td>
<td>2077.702</td>
<td>13.038 ± 0.239</td>
<td>0.077 ± 0.005</td>
</tr>
<tr>
<td>4.</td>
<td>CC40</td>
<td>2161.955</td>
<td>15.954 ± 0.515</td>
<td>0.063 ± 0.012</td>
</tr>
<tr>
<td>5.</td>
<td>CC50</td>
<td>2251.187</td>
<td>17.662 ± 0.165</td>
<td>0.057 ± 0.004</td>
</tr>
</tbody>
</table>

The electrical conductivity is given by [16]

\[
R = \rho \frac{\ell}{A} \tag{2}
\]

\[
\rho = R \frac{A}{\ell} \tag{3}
\]

\[
\sigma = \frac{1}{\rho} \tag{4}
\]
where R is a resistance (Ω), A is a surface area of the sample (m²), ρ is a resistivity (Ω·m), ℓ is height of the sample (m) and σ is an electrical conductivity (S·m⁻¹).

The ohmic conductivities at room temperature of the non-sonicated graphite (CC) at different compressed pressures were different. The conductivity of the CC10, CC20, CC30, CC40 and CC50 were 8.567 ± 0.254, 9.043 ± 0.244, 13.038 ± 0.239, 15.954 ± 0.515 and 17.662 ± 0.165 S·m⁻¹, respectively, as shown in Table 1. Similarly, the conductivities at room temperature for the sonicated graphite (SC) increase when increasing the compressed pressure. The conductivity of the SC10, SC20, SC30, SC40 and SC50 were 12.435 ± 0.021, 13.403 ± 0.007, 15.165 ± 0.006, 16.646 ± 0.025 and 21.601 ± 0.012 S·m⁻¹, respectively, as shown in Table 2. Under compression, individual particles in the bulk material will break, refold, and become denser as shown in Fig. 5. The particles become closer in contact with other adjacent particles. Therefore, the electrical conductivity of the bulk material increases [17]. Thus, the electrical conductivity of the sample is assumed to be controlled by compression pressure as shown in Table 2.

<table>
<thead>
<tr>
<th>No.</th>
<th>samples</th>
<th>Density (kg·m⁻³)</th>
<th>Room temperature conductivity (S·m⁻¹)</th>
<th>Room temperature resistivity (Ω·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SC10</td>
<td>1950.959</td>
<td>12.435 ± 0.021</td>
<td>0.080 ± 0.014</td>
</tr>
<tr>
<td>2.</td>
<td>SC20</td>
<td>2026.087</td>
<td>13.403 ± 0.007</td>
<td>0.075 ± 0.001</td>
</tr>
<tr>
<td>3.</td>
<td>SC30</td>
<td>2098.146</td>
<td>15.165 ± 0.006</td>
<td>0.066 ± 0.004</td>
</tr>
<tr>
<td>4.</td>
<td>SC40</td>
<td>2768.071</td>
<td>16.646 ± 0.025</td>
<td>0.060 ± 0.002</td>
</tr>
<tr>
<td>5.</td>
<td>SC50</td>
<td>3243.066</td>
<td>21.601 ± 0.012</td>
<td>0.046 ± 0.001</td>
</tr>
</tbody>
</table>

According Fig. 5, when graphite flakes have been compressed under a high pressure, each of them will come closer and, consequently, the density of bulk graphite becomes higher. Higher density of bulk graphite leads to higher electrical conductivity because there is more chance for the electrons to move across them. In contrast, a lower density of the bulk graphite owns plenty of the gaps (the space between the adjacent graphites), which strongly reduces electron mobility, thus, resulting in a lower electrical conductivity of the bulk graphite [17].

Fig. 5. Model describing effect of compression pressure on the space of the particles inside a bulk material (a) low density and (b) high density. The inside particles stay much denser for higher compression pressure.
3. 2 Effect of temperature on the electrical conductivity

In the previous section, effect of the density of the bulk graphite on its electrical conductivity was discussed. However, all of the results were carried out at room temperature. Here, effect of the temperature of the sample on its electrical conductivity was investigated. The conductivities of the samples of different temperatures, ranging from 298-573 K, were measured. Fig. 5(a) shows the conductivity of the bulk graphites obtained from non-sonicated graphites (CC). The dark-filled circles and the hollow circles refer to the results from the non-sonicated graphites of 10 MPa compression (CC10 MPa) and the non-sonicated graphites of 50 MPa compression (CC 50 MPa), respectively. The results show that at all temperatures the electrical conductivity of the CC50MPa is much higher than that of the CC10MPa. For the CC50MPa, the conductivity of the sample 298 K was about 26 S·m⁻¹ and it was up to 46 S·m⁻¹ for 573 K. Fig. 5(b) represents the conductivity of the bulk graphites obtained from sonicated graphites (SC). Similar to Fig. 5(a), the dark-filled circles and the hollow circles refer to the results from the sonicated graphites of 10 MPa compression (SC10 MPa) and the non-sonicated graphites of 50 MPa compression (SC 50 MPa), respectively. The results were also similar to those of non-sonicated graphites (CC). Both compression pressure and temperature significantly affected the electrical conductivity of the samples. For example, the conductivity of the SC50MPa at 298 K was about 42 S·m⁻¹ and it was raised up to 54 S·m⁻¹ for 573 K. Fig. 5(c) presents the results obtained from both Fig. 5(a) and (c). It is obvious that the electrical conductivity of the samples depends on compression pressure,
temperature of the sample and sonication treatment. High temperature could increase the vibrational energy of the molecules overall the sample. If the thermal energy of the material is higher than their energy gap, there would have more chance to gain many free carriers on the material. Thus, increase in the free carriers leads to an increase in the electrical conductivity of the sample [17, 18]. The much higher conductivity of the sonicated graphite (SC) comparable to that of the non-sonicated graphite may be due to graphenes and nano graphites exfoliated from the parent graphite during sonication treatment.

4. Conclusion

In summary, we have successfully demonstrated that electrical conductivity of the bulk graphite depends upon the compression pressure, sonication treatment, and the temperature of the sample. Under a high compression pressure, individual graphite flakes in the bulk graphite may be broken, refolded, and become denser which consequently increases the volume density. Therefore, the electrical conductivity of the bulk graphite increases. Sonication treatment has shown strong effect on exfoliation of either graphene or nano-graphite as confirmed by UV-Vis and Raman analysis. Moreover, the temperature of the sample also affects the electrical conductivity of the sample. The conductivity increases when higher temperature is applied. Increase in electrical conductivity may be due to the thermal energy triggering the appearance of the free carriers on the sample. The results from this experiment may be very useful for many carbon-based applications such as pressure and temperature sensor.

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