



Preparation of high-crystallinity synthetic graphite from hard carbon-based carbon black

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Abstract

Hard carbon is difficult to prepare as high-crystallinity synthetic graphite even with graphitization (over 2400 °C), so only soft carbon has been used as a raw material for the preparation of synthetic graphite. Therefore, the selection of raw materials for synthetic graphite preparation is limited. In this study, synthetic graphite was prepared from hard carbon-based carbon black (HCCB) to overcome the issue of the limited selection of synthetic graphite raw materials. Synthetic graphite was prepared by a 3-step heat treatment from a mixture of HCCB and Si. SiC was synthesized from HCCB by a first heat treatment, and unreacted HCCB was removed through a second heat treatment. In a third heat treatment, synthetic graphite was prepared by removing Si from SiC. The prepared synthetic graphite had a high-crystallinity and few defects, and the powder electrical conductivity was approximately 22.7 times higher than that of graphitized HCCB. The introduced new method is expected to induce diversification of raw materials for the preparation of synthetic graphite, thereby solving the problems of the traditional preparation method.

Keywords Hard carbon · Synthetic graphite · Silicon carbide · Hard carbon-based carbon black · Electrical conductivity

1 Introduction

Synthetic graphite has a high electrical conductivity, thermal stability, and chemical stability and has been applied to electrode materials and sensor materials [1–4]. Since the

electrical performance of synthetic graphite is affected by its crystallinity, it must have a high-crystallinity to improve its electrical properties. In general, synthetic graphite is prepared by graphitization of soft carbon at temperatures higher than 2400 °C. To improve the crystallinity of synthetic graphite, a catalyst, such as AlCl₃ or BF₃, is required. Therefore, the traditional method for synthetic graphite preparation suffers from various problems, such as limited raw material selection. It requires a separate process to remove the metal used as the catalyst and corrosion of the reactor due to halogen compounds generated from the catalyst [5–8].

The graphite layer of hard carbon has a short length and a complicated orientation, so hard carbon is difficult to prepare as high-crystallinity synthetic graphite even with graphitization (over 2400 °C) [9–12]. If high-crystallinity synthetic graphite could be prepared from hard carbon, it would be possible to solve the issue of the limited raw material selection of the existing synthetic graphite, which can only use soft carbon. To prepare synthetic graphite from hard carbon, it is necessary to change the crystal structure of hard carbon to a soft carbon structure.

SiC was prepared by reaction with carbon materials (such as HCCB, carbon fiber, char, graphite) and Si precursors

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(such as silica, silicon, and silicon oil) at over 1500 °C [13–15]. During the SiC preparation process, the crystal properties of the carbon materials disappear and change to a β -SiC or α -SiC crystal structure depending on the treatment temperature. Therefore, the SiC preparation process is a method that can completely change the crystal structure of hard carbon. T. Seyller et al. [16] and M. Shi et al. [17] reported that it was possible to prepare synthetic graphite from SiC. Si is removed by sublimation at over 2200 °C, and the remaining carbon recombines to form a graphene layer. Therefore, if SiC is treated at temperatures higher than 2200 °C, synthetic graphite with high purity and excellent crystallinity is expected to be easily prepared. In this study, high-crystallinity synthetic graphite was prepared from HCCB to diversify synthetic graphite raw materials. The heat treatment contained three steps, and the properties of the samples are discussed according to these heat treatment steps. The introduced new method was expected to induce diversification of raw materials to obtain synthetic graphite, thereby solving the problems of the traditional method in synthetic graphite preparation.

2 Experimental

2.1 Raw materials and preparation method

HCCB (Ketjenblack EC-600 JD, dibutyl phthalate (DBP) absorption: 495 cm³/100 g (15 g method), specific surface area: 1270 m²/g (BET), pH: 9.0, ash content: 0.1%, Akzo-Nobel) and silicon powder (Si, ~44 μ m, 99% pure, Sigma Aldrich) were used as raw materials. HCCB and Si were mixed in a ratio of 1:0.1 ~ 1:1 molar ratio. Six grams of HCCB were stirred in 100 ml of isopropyl alcohol (IPA, 99.9%, Samchun Chemicals Co.) for 10 min, and then Si was added according to the molar ratio and ultrasonicated for 60 min. IPA was removed by drying at 90 °C for 12 h. The mixture was subjected to a 3-step heat treatment to prepare graphite. The first heat treatment was carried out by heating the mixture at 1500 °C for 1 h in a nitrogen atmosphere. The second heat treatment removed the unreacted HCCB of the first heat treatment and was performed at 600 °C for 3 h in an air atmosphere. Finally, the third heat treatment was carried out at 2700 °C for 1 h in an Ar atmosphere. The prepared samples were named according to each heat treatment step; samples named according to the first heat treatment were designated CB and SiC-x. Here, CB denotes first heat-treated HCCB, SiC-x denotes a sample containing Si, where x is the molar ratio of added Si. For example, SiC-0.1 refers to a sample obtained by the first heat treatment of a HCCB and Si mixture with a 1:0.1 molar ratio. The samples of the second heat treatment are named O_SiC-x. Since HCCB is removed in the second heat treatment, CB is excluded

from the sample name. O_SiC-x is a sample obtained by the second heat treatment of SiC-x. Samples of the third heat treatment are named G_CB and GO_SiC-x. G_CB and GO_SiC-x are samples obtained by third heat treatment of CB and O_SiC-x, respectively.

2.2 Properties analysis

The samples were analyzed at each heat treatment step. The crystal structure of the samples was measured by X-ray diffraction (XRD). XRD patterns of all the samples were analyzed with CuK α radiation (0.1541 nm) in the range of 10°–80° at a scanning rate of 3°/min. Field emission scanning electron microscope (FE-SEM) was used to analyse the morphology of the samples. Raman spectra (argon-ion laser at 514.5 nm) were used to analyse the defects of the graphitized samples. Additionally, the formation of the graphene layer was analyzed by Transmission electron microscopy (TEM). TEM analysis was performed by mixing the prepared sample and ethanol at a concentration of 0.1 mg/ml and then ultrasonication for 3 min. The pore structure of the prepared samples was analyzed by nitrogen adsorption isotherms, and the specific surface area was calculated from the nitrogen adsorption isotherm. The electrical properties of graphitized samples were evaluated using IEC TS 62,607–6–1 (Graphene-based material-volume resistivity: four-probe method).

3 Results and discussion

3.1 The crystal structure and defects of the samples after the heat treatment steps

XRD analysis was performed to evaluate the crystal structure after the heat treatment steps, as shown in Fig. 1. Figure 1(a) shows the XRD results of the sample after the first heat treatment (1500 °C for 1 h in N₂ atmosphere). β -SiC, α -SiC, and Si peaks appeared in the pattern of SiC-x. As the molar ratio of added Si increased, the Si peak intensity increased, and the α -SiC peak decreased. CB showed a broadened peak at approximately 26.4°. The patterns of SiC-0.1, SiC-0.3, and SiC-0.5 contained peaks related to CB, whereas SiC-1.0 did not. HCCB and Si react to form SiC in a 1:1 molar ratio. In SiC-1.0, since the molar ratio of HCCB and Si was 1:1, most of the HCCB reacted with Si, so the CB peak did not appear.

The XRD results of the second heat-treated samples at 600 °C in an air atmosphere are shown in Fig. 1(b). The CB peak did not appear in the patterns of O_SiC-0.1, O_SiC-0.3, and O_SiC-0.5. The β -SiC, α -SiC, and Si peaks were not changed. From Fig. 1(a) and (b), it was confirmed that HCCB and Si formed SiC during the first

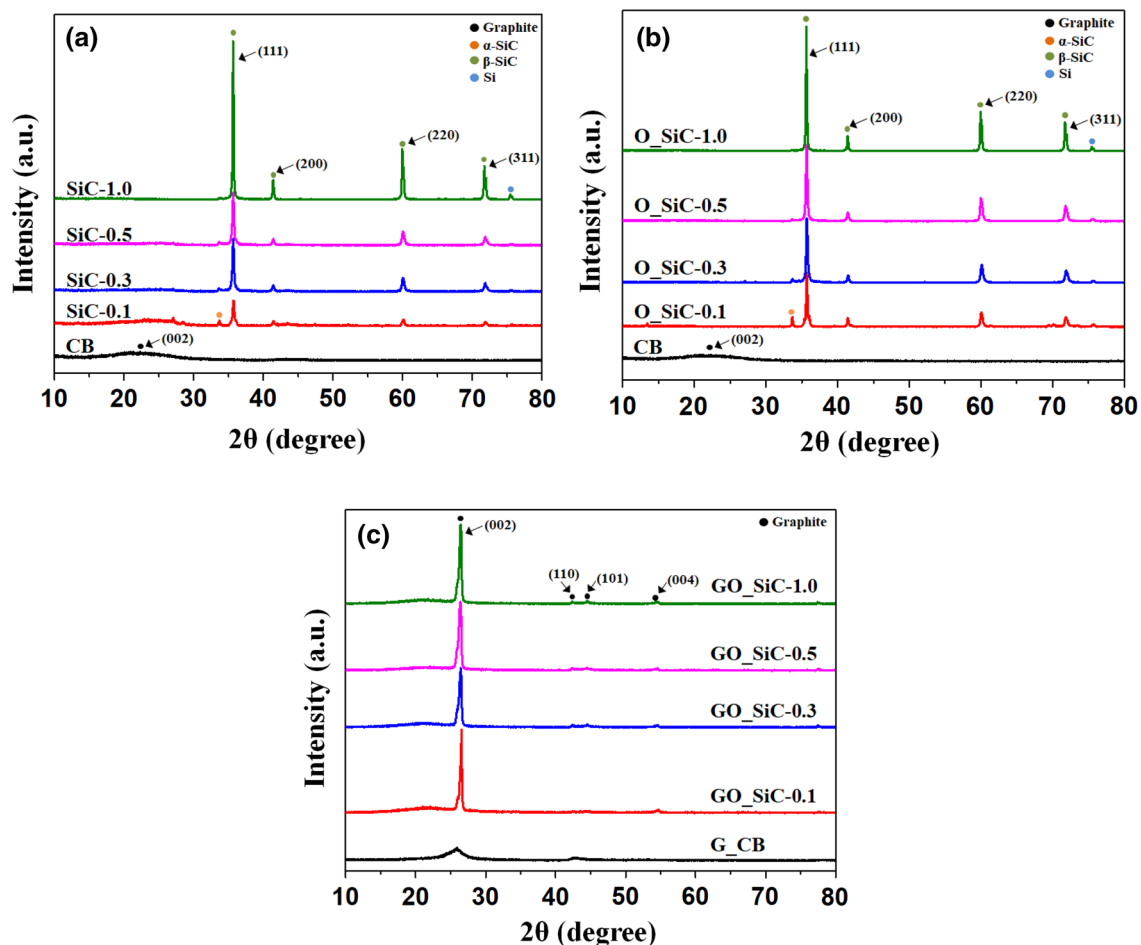


Fig. 1 XRD results of the samples according to the heat treatment step: **a** first heat treatment, **b** second heat treatment, and **c** third heat treatment

heat treatment, and unreacted HCCB was removed during the second heat treatment. Additionally, in Fig. 1(b), a new peak related to SiO_2 did not appear because the SiC (formed during the first heat treatment) was not oxidized during the second heat treatment.

Figure 1(c) shows the XRD results of the sample subjected to the third heat treatment (2700°C). The pattern of G_CB showed a low-intensity and broad peak at approximately 26.4° . This peak indicated that G_CB did not form a graphite structure and was amorphous carbon. In general, the hard carbon did not form a graphite crystal structure even when graphitized at high temperatures because the graphite layer in the hard carbon was thin, and the orientation was complicated [9–12]. In this study, the raw material was HCCB, so G_CB showed an amorphous carbon crystal structure after heat treatment at 2700°C . For GO_SiC- x , all of the SiC and Si peaks disappeared, and peaks representing graphite appeared. A sharp peak with high intensity appeared near 26.4° , indicating the highly crystalline structure of graphite. It was determined that SiC was removed by sublimation of Si during the third

heat treatment, and the remaining C recombined to form a graphene layer [18, 19]. These graphene layers are laminated to form a graphite crystal structure.

From the results shown in Fig. 1(c), the interlayer distance (d_{002}) and c -axis growth length (L_c) of graphite were calculated and are shown in Table 1. The d_{002} of GO_SiC-0.1 was 0.33545 nm, which is very close to the theoretical graphite interlayer distance of 0.3354 nm. As the molar ratio of Si increased, the interlayer distance of graphite increased, and GO_SiC-1.0 increased to 0.33720 nm. G_CB showed

Table 1 Structural parameters extracted from the XRD results

Sample name	2θ ($^\circ$)	D_{002} (nm)	L_c (nm)	The number of graphene layers
G_CB	25.92	0.34334	3.3	9
GO_SiC-0.1	26.54	0.33545	29.7	88
GO_SiC-0.3	26.42	0.33695	19.2	57
GO_SiC-0.5	26.40	0.33720	18.9	55
GO_SiC-1.0	26.40	0.33720	17.6	52

the greatest graphite interlayer distance of 0.34334 nm. The Lc of GO_SiC-0.1 was the highest and that of G_CB was the lowest. The number of graphene layers of the samples prepared from d002 and Lc was calculated. GO_SiC-0.1 contained approximately 88 graphene layers, and as the molar ratio of Si increased, the number of graphene layers decreased; GO_SiC-1.0 contained 52 graphene layers. Figure 1(a) and (b) confirmed that β -SiC and α -SiC were mixed in the generated SiC. The energy required for the sublimation of Si that occurs above 2200 °C depends on the crystal structure of SiC [18]. Therefore, Si in β -SiC with low sublimation energy was first sublimated, and Si in α -SiC was sublimated at high temperature to form a graphene layer step-by-step. In the case of mixed β -SiC and α -SiC, β -SiC and α -SiC sequentially formed a graphene layer according to the Si sublimation energy in SiC. The stepwise formation of the graphene layer induces stacking of the graphene layer; GO_SiC-0.1, the sample with the highest degree of β -SiC and α -SiC mixing, contained the largest number of graphene layers.

To evaluate the defects of the prepared samples, Raman analysis was performed, and the results are shown in Fig. 2. The defects of the samples were evaluated from the D band (1360 cm^{-1}), G band (1560 cm^{-1}), and 2D band (2710 cm^{-1}) [20]. The D band and G band represent the sp^3 bond and sp^2 bond of carbon, respectively. Since the graphene layer constituting graphite consists only of sp^2 bonds, the increase in sp^3 bonds indicated that the graphene layer contained many defects [21]. To compare, the defects of each sample were calculated the intensity ratio of Raman bands (I_d/I_g) from the Raman results, and the results are shown in Table 2. When comparing I_d/I_g , G_CB showed the highest value of 0.410, and GO_SiC-0.1 showed the lowest value of 0.034. Additionally, as the molar ratio of Si increased, I_d/I_g increased. This result suggested that GO_SiC-0.1 contained least defects or highest crystallinity [20, 21].

The 2D band indicates a defect in the graphite layered structure [20, 22]. In graphene, the 2D band showed a higher

Table 2 Spectroscopic function values and a-axis growth length of graphite for the third heat-treated sample

Sample name	I_d	I_g	I_d/I_g	L_a (nm)
G_CB	47.0	114.7	0.410	10.7
GO_SiC-0.1	7.1	210.7	0.034	130.0
GO_SiC-0.3	7.6	198.9	0.038	114.9
GO_SiC-0.5	8.5	158.2	0.054	81.5
GO_SiC-1.0	9.3	160.2	0.058	75.6

intensity than the G band [22–24]. However, in this study, the 2D band of all prepared samples showed lower intensity than the G band, which implied that the prepared samples formed a graphite structure. The a-axis growth length (L_a) was calculated from the Raman result by Kinight and White summarized equation, as shown in Table 2 [25]. L_a was higher as the I_d/I_g value decreased, and GO_SiC-0.1 showed the highest value of 130.0 nm.

3.2 Morphology of samples after the heat treatment steps

The morphologies of the samples after the heat treatment steps were analyzed by FE-SEM, and the results are shown in Fig. 3. In the CB, approximately 20 nm particles were aggregated to form a bundle structure. SiC-0.1 showed a morphology similar to that of CB. On the other hand, SiC-0.3 and SiC-0.5 contained large particles (over 100 nm) and small particles. In SiC-1.0, small particles were not observed, and the particles were agglomerated to form one large cluster. In O-SiC-x, small particles (appearing in SiC-x) were not observed, and only a large cluster remained. From Fig. 1(a) and (b), it was confirmed that the second heat treatment removed most of the unreacted HCCB. Therefore, the small particles in SiC-x were considered to be HCCB particles, and the large particles and the cluster were considered to be SiC particles. G_CB was not different from CB, whereas O_SiC-x completely changed in terms of morphology and particle size during the third heat treatment. SiC sintering occurs at a temperature of over 2000 °C, and SiC powders agglomerate with each other to form a large cluster [26, 27]. Therefore, SiC formed a cluster, and since Si was sublimated and removed afterward, the morphology and size of the particles completely changed.

The TEM images of the samples are shown in Fig. 4. For TEM image analysis, pretreatment was carried out; the samples were immersed in ethanol at a concentration of 0.1 mg/ml and then ultrasonicated for 3 min for dispersion purposes (ultrasonic power: 100 W). G_CB showed a TEM image similar to a typical carbon black TEM image [28, 29]. On the other hand, GO_SiC-x showed a TEM image similar to that of graphene [30, 31]. However, from the Raman results

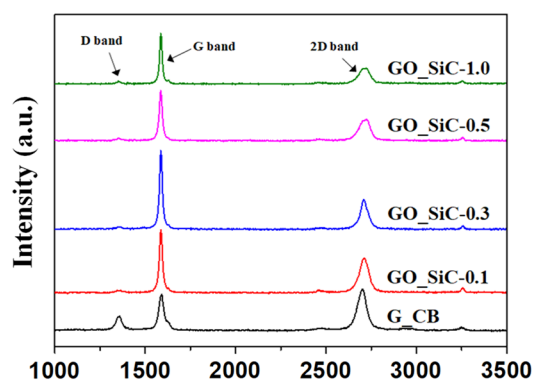


Fig. 2 The Raman spectrum of third heat-treated sample

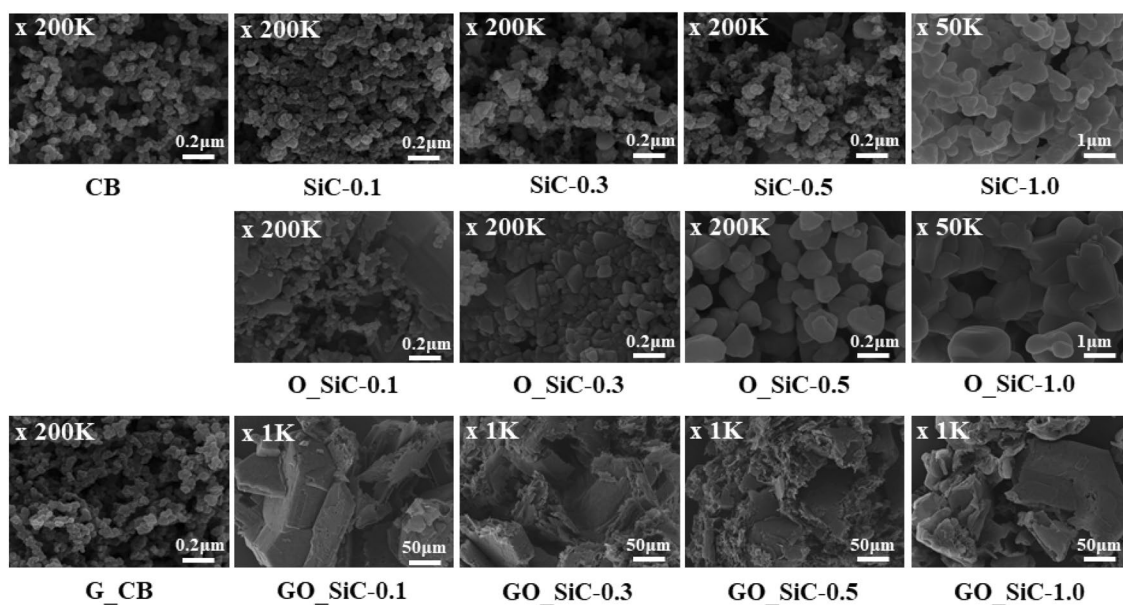


Fig. 3 The FE-SEM image of the samples after the heat treatment steps

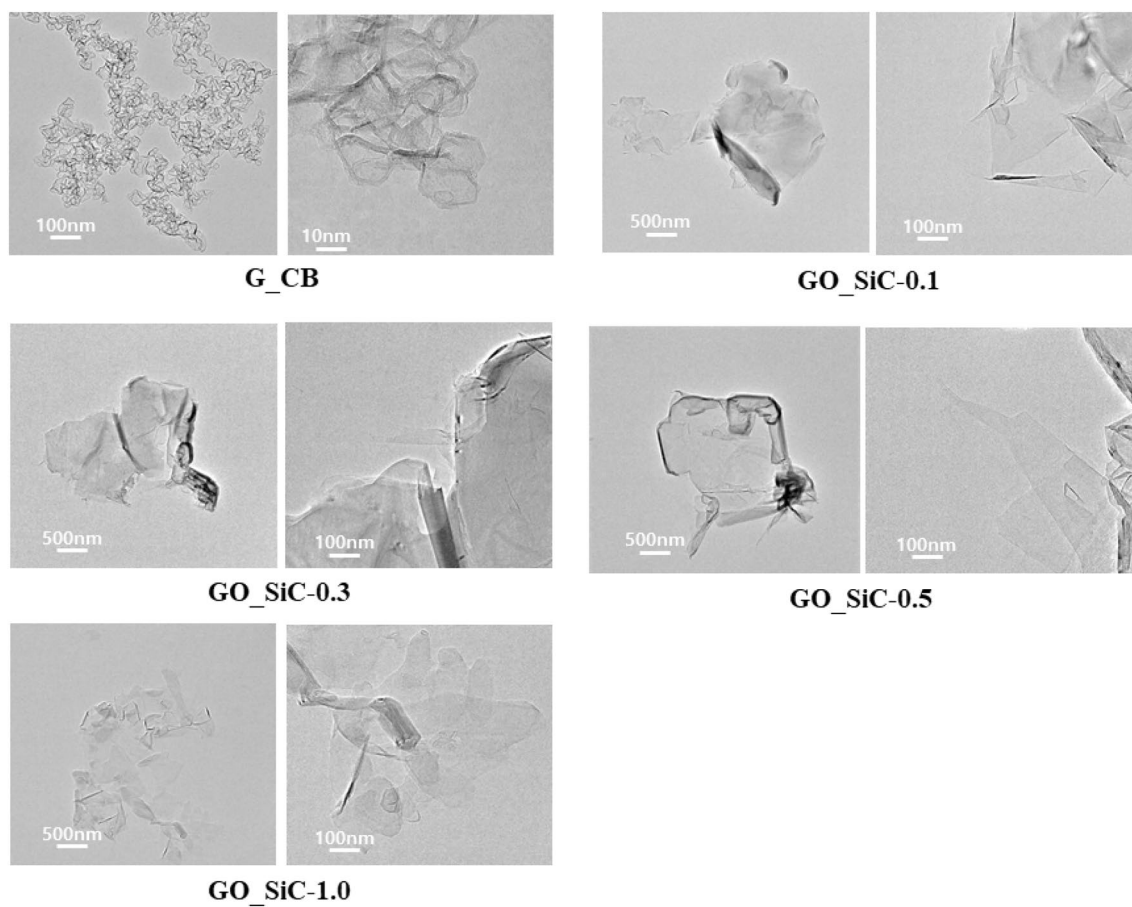


Fig. 4 TEM images of the third heat-treated samples

in Fig. 2, it was confirmed that the prepared sample was graphite. Therefore, the prepared graphite could be easily exfoliated by ultrasonic treatment.

3.3 Specific surface area of the samples

In this study, the HCCB used was Ketjen black EC600JD, which has a very high specific surface area of m^2/g . The specific surface area of the samples was calculated from the nitrogen adsorption isotherms. The nitrogen adsorption isotherms and the specific surface areas are shown in Fig. 5. The specific surface area of G_CB was $186.6 \text{ m}^2/\text{g}$, which was approximately 6.8 times lower than that of HCCB without heat treatment. The porosity of carbon materials decreases after high temperature heat treatment. G_CB had a decreased specific surface area due to the decrease in porosity. Except for G_CB, the samples had a very low specific surface area of $10.2 \pm 2 \text{ m}^2/\text{g}$. In general, graphene had a

high specific surface area of over $100 \text{ m}^2/\text{g}$. The specific surface area of all prepared samples was $10 \text{ m}^2/\text{g}$, closer to synthetic graphite ($\sim 3 \text{ m}^2/\text{g}$) than graphene [32]. This result indicated that the prepared sample was graphite, as shown by the 2D peak in the Raman spectra.

3.4 Mechanism of graphite preparation from hard carbon-based carbon black

From the XRD, Raman, FE-SEM, and nitrogen adsorption isotherm results, a mechanism for the graphite preparation from HCCB was defined, which is shown in Fig. 6. The mixture of HCCB and Si was prepared as SiC during step I, and unreacted HCCB remained. During step I, silicon (melting point of 1414°C) melts, and molten Si permeates into the HCCB pores by a capillary phenomenon. The molten Si reacts with HCCB to form SiC, and larger particles than HCCB are formed via mutual aggregation. The unreacted HCCB did not change the morphology and was mixed with the prepared SiC (Fig. 3). Step II was the process of removing unreacted HCCB, and it was confirmed from the XRD results that most of the unreacted HCCB was removed and that SiC was not oxidized. Step III and step IV were performed in the same reactor. During Step III, SiC powders were sintered to increase the particle size [26, 27]. It can be easily predicted that the aggregated SiC particles will have a rough surface because the SiC powders agglomerated with each other. During step IV, a graphene layer was formed by the sublimation of Si [18, 19]. From the Raman and nitrogen adsorption isotherms, it was confirmed that the prepared sample was graphite, not graphene. At a temperature of over 2300°C , the graphene layer is grown from the edge site of SiC; when the edge site growth is completed, it is followed by growth into a large area. When the graphene layers grown in different locations come in contact, they are not united into a single graphene layer but stacked onto

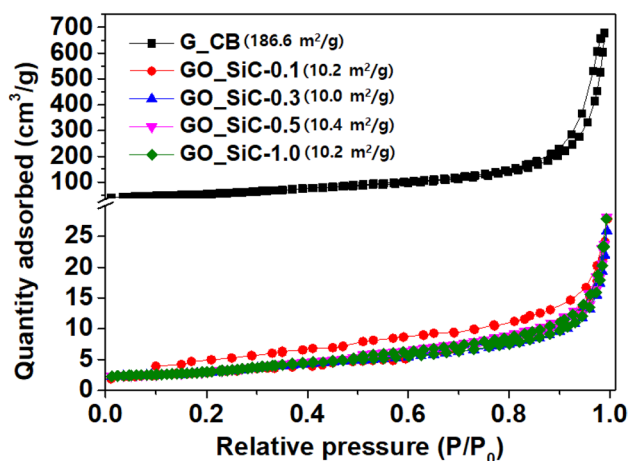


Fig. 5 The nitrogen adsorption isotherms of the third heat-treated samples

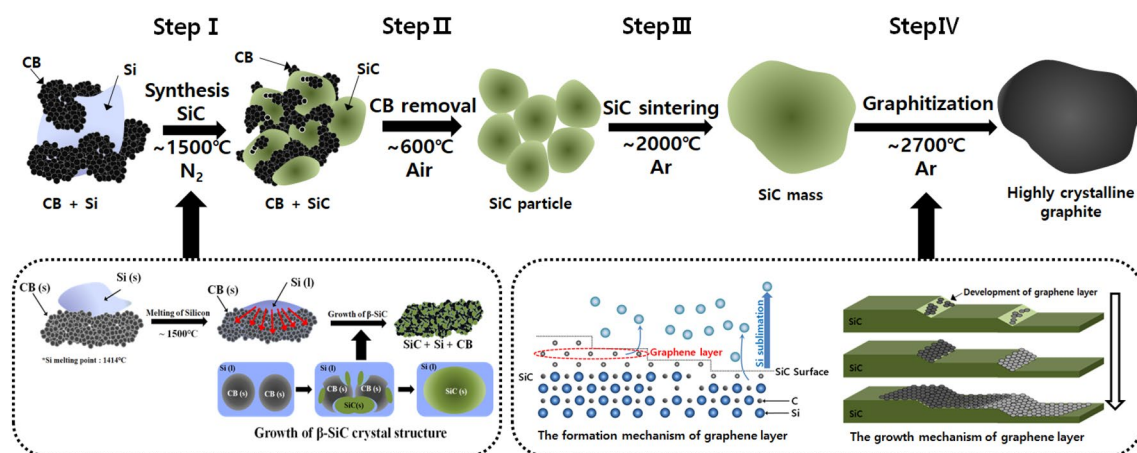


Fig. 6 The suggested mechanism of graphite preparation from hard carbon-based carbon black

each other [18]. During Step III, the sintered SiC has many rough surfaces, so the number of the generated graphene layers increases. Therefore, grown graphene layers laminate to form a graphite structure.

3.5 Electrical conductivity of the prepared samples

The densities and electrical conductivities of the prepared samples were measured as a function of pressure by IEC TS 62,607–6-1 (Graphene-based material-volume resistivity: four-probe method), which is shown in Fig. 7. The electrical conductivity as a function of pressure is shown in Fig. 7(a). GO_SiC-x had a similar electrical conductivity and showed a high conductivity of over 5×10^4 S/m. On the other hand, the conductivity of G_CB showed a maximum of 2.2×10^3 S/m at a pressure of 196.2 MPa (200 kgf/cm²), which was approximately 22.7 times lower than that of GO_SiC-x. According to the pressure, the density of the sample is shown in Fig. 7(b). The density of the sample was higher in GO_SiC-x than in G_CB. From the nitrogen adsorption isotherm analysis, the specific surface area of G_CB (186.6 m²/g) was much higher than that of GO_SiC-x (10.2 ± 2 m²/g), indicating that C-CB was the most

porous. Therefore, G_CB showed the lowest density due to the contained pores. To more objectively compare the electrical conductivity, it is shown as a function of density in Fig. 7(c). At a density of 0.72 g/cm³, the electrical conductivity of G_CB (2.1×10^3 S/m) was 6.9 times lower than that of GO_SiC-x (1.4×10^4 S/m). The electrical conductivity of carbon materials is greatly influenced by their crystallinity and defects. The XRD and Raman results confirmed that all of GO_SiC-x had a higher crystallinity and fewer defects than G_CB. For this reason, the electrical conductivity of GO_SiC-x was higher than that of G_CB. Additionally, among the GO_SiC-x samples, GO_SiC-0.1, which had the highest crystallinity and the lowest number of defects, had the highest electrical conductivity.

4 Conclusions

To overcome the limitation of using only soft carbon as raw material in the preparation of synthetic graphite, it was prepared from HCCB. To prepare synthetic graphite, HCCB and Si were mixed and then subjected to a 3-step heat treatment. The first heat treatment was carried out at 1500 °C

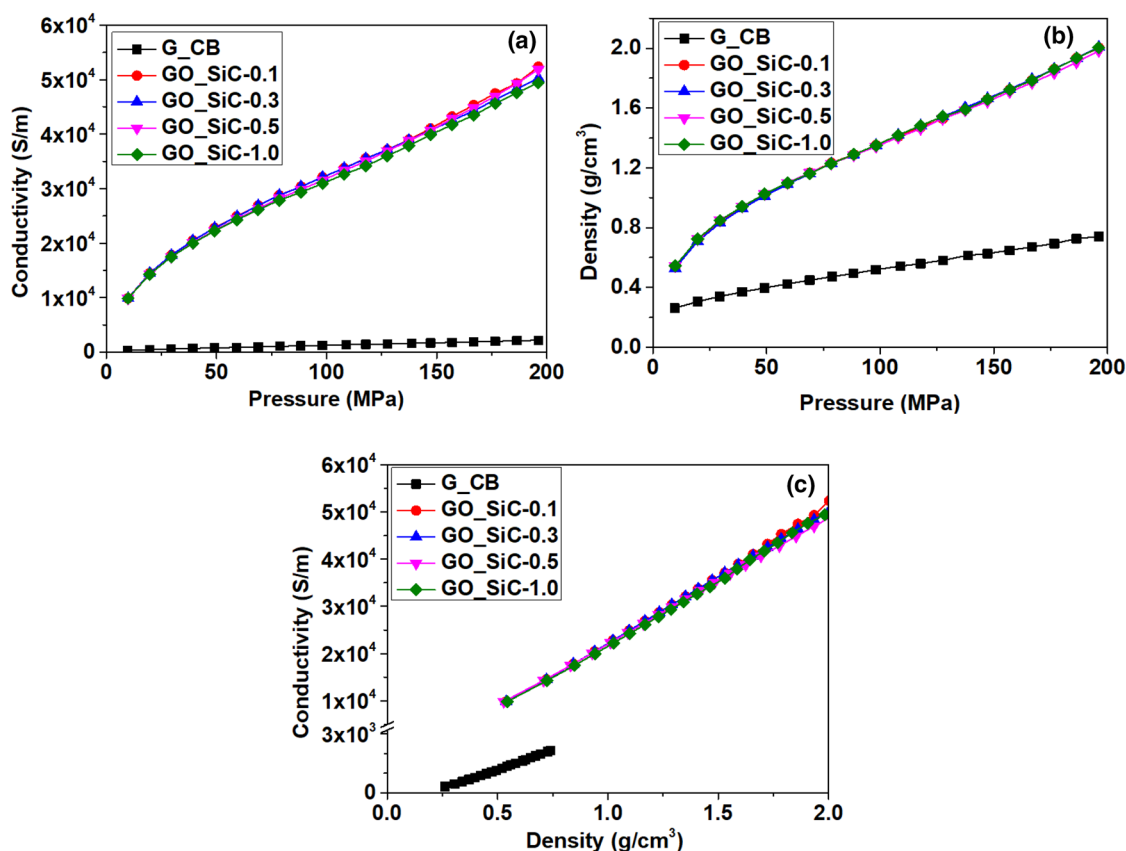


Fig. 7 The electrical conductivity of third heat-treated samples; **a** electrical conductivity as a function of the applied pressure, **b** density as a function of the applied pressure, and **c** electrical conductivity as a function of density

in a N_2 gas atmosphere, and HCCB and Si reacted to form SiC. The second heat treatment was carried out at 600 °C in air, and unreacted HCCB was removed by oxidation. The third heat treatment was carried out at 2700 °C in an Ar gas atmosphere, and a graphite structure was formed by Si sublimating in SiC. The prepared synthetic graphite from HCCB and Si (GO_SiC-0.1) showed the relatively high-crystallinity than synthetic graphite from HCCB (G-CB). La (29.7 nm) and Lc (130.0 nm) of GO_SiC-0.1 were relatively much higher than that (La: 3.3 nm, Lc: 10.7 nm) of G-CB. The interlayer distance of GO_SiC-0.1 was 0.33545 nm, which was very close to the theoretical graphite interlayer distance of 0.3354 nm. Additionally, the Id/Ig was 0.034, indicating that there were very few defects. The GO_SiC-0.1 showed a higher electrical conductivity of approximately 22.7 times than G-CB because of its relatively high-crystallinity and few defects. The newly introduced method for synthetic graphite preparation is expected to solve the problem of limited raw materials in the traditional method for synthetic graphite preparation.

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