Study on Structural Evolution of Synthetic Graphite Derived from Lignite Prepared by High Temperature–High Pressure Method

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Abstract: Abundant and cheap lignite is regarded as inferior fuel due to its disadvantages such as low heat and high moisture. In order to realize the high value and clean, non-fuel utilization of lignite, we used lignite as precursor to prepare high-quality synthetic graphite through graphitization treatment using the high temperature–high pressure (HTHP) method, and afterwards characterized the samples by XRD, Raman, FTIR, SEM-EDS, and HRTEM, and systematically analyzed the effect of P-T conditions on the structure evolution of lignite. Our results demonstrated that temperature dominates the graphitization of lignite, and high pressure accelerates the graphitization process of lignite. Under HTHP treatment, the aromatic layer of lignite accelerates directional rearrangement; the ordered domain increases rapidly, and the ductility and stacking degree of the carbon sheets of the lignite sample are greatly enhanced. Compared with the traditional high-temperature graphitization method, the HTHP method greatly reduces the graphitization temperature and shortens the graphitization time. Remarkably, the as-prepared graphite with a graphitization degree of 91.87% superior to graphite fabricated by the conventional high-temperature processing were rapidly prepared from lignite at 6 GPa and 1300 °C in 20 min. This study demonstrates that the HTHP method is a feasible and effective method to realize the green, efficient, and high value utilization of lignite.

Keywords: lignite; graphite; high graphitization; HTHP method

1. Introduction

Graphite material, increasingly being leveraged as a strategic resource, is widely used in advanced carbon material preparation, aerospace, energy storage batteries, lubricating abrasives, environmental protection, and so on, due to various merits in terms of lubrication, conductivity, heat conduction, high temperature resistance, corrosion resistance, and high plasticity [1–3]. In general, graphite can be categorized into natural graphite and synthetic graphite. As a mineral resource, natural graphite has limited reserves and is positioned as a strategic resource in Europe and America [4]. Natural graphite has uneven purity, a complex purification process, and high cost [5]. Compared with natural graphite, synthetic graphite has the advantages of high purity, wide carbon source, and strong controllability of the synthesis process. At present, petroleum coke is the main carbon source of synthetic graphite [6]. Coal is an organic compound composed of heterogeneous aromatic compounds. It is one of the most widely distributed and abundant carbonaceous materials on earth. The available reserves of coal exceed five times that of oil, and the price is one quarter of that of petroleum coke [7]. Therefore, coal is a reliable and low-cost ideal carbon source for the production of synthetic graphite.

Anthracite, as the highest metamorphic degree of coal, contains more than 90% carbon, in which most of the carbon exists in the form of aromatic carbon. Anthracite is typically characterized by the high aromaticity, relatively neat molecular structure, and strong graphitization ability, which renders it as the main coal type for the preparation
of synthetic graphite [8–10]. High temperature graphitization and catalytic graphitization are the two main means of coal transformed to graphite materials. Previous studies have shown that anthracite will form graphite materials with ordered structure at high temperatures $\geq 2500 \, ^\circ C$ [11–13], and the catalyst can reduce the graphitization temperature of carbon materials. Zhong et al. [14] successfully converted anthracite and semi-coke into open-shell hollow multilayer graphene spheres with the aid of a NiAc2 catalyst by calcination at 1500 $^\circ C$ for 6 h. Islam et al. [15] fabricated metal-supported few-layer graphene from bituminous coal over Fe catalysts at 1300 $^\circ C$ in virtue of a microwave-assisted catalytic graphitization process. Shi et al. [16] prepared synthetic graphite with special spherical structure derived from semi-coke using silicon as a catalyzer at 2300 $^\circ C$. However, these methods still encounter various drawbacks, such as the need for ultra-high temperatures, a protective atmosphere, and an additional catalyst that inevitably increases the experimental costs and deteriorates the quality of the final graphite product, restricting their application in large-scale industrial production.

Compared with the commonly studied anthracite, lignite suffers from low coalification degree, low heat, high volatile components, high moisture, and ease of spontaneous combustion, resulting in it being regarded as an inferior fuel [17]. Besides, the graphitization of lignite is difficult even at high temperatures up to 3000 $^\circ C$ [18,19]. Despite the significantly low carbon content in lignite compared with that of bituminous and anthracite, as well as its difficult graphitization, lignite reserves are huge and the price is lower than anthracite [20]. Furthermore, the conventional technologies for achieving the grading effective conversion and utilization of low-rank coal resources include square-retort pyrolysis technology, upgraded square-retort pyrolysis technology, solid-heat-carrier pyrolysis technology, and rotary-kiln pyrolysis technology, which sustain the main problems in the development of pyrolysis processes, namely, the dust separation of coal tar, wastewater treatment, and incomplete pyrolysis reaction mechanisms [21–23]. Therefore, developing a facile, clean, and efficient approach for the experimental realization of high-quality lignite-coal-derived synthetic graphite materials in large quantities is highly desirable for the goal of achieving the grading effective conversion and steady utilization of lignite, but remains a great challenge. Numerous reports have emphasized that pressure plays a significant role in promoting the graphitization process of coal [24,25], and pressure can even directly cause changes to the chemical structure of the coal, inducing graphitization [26]. Wilks et al. [27] suggested that shear strain was the dominant factor responsible for the natural transformation of anthracite to graphite at temperatures of 900 $^\circ C$. Zhao et al. [28] investigated the structural evolution from activated carbon to graphite by high-pressure sintering. The aforementioned works proved that the HTHP method was particularly suitable for the graphitization of carbonaceous material. However, research on the preparation of synthetic graphite from lignite using the high temperature–high pressure approach has not been reported.

In this study, we demonstrate a scalable preparation technology for the production of high-quality synthetic graphite from lignite using the HTHP method. By varying the temperature and pressure, graphite samples with controllable graphitization extent and the degree of stacking order can be synthesized. The structure and chemical component of lignite prepared by the HTHP method is investigated by XRD, Raman spectroscopy, HRTEM, and FTIR to trace their structural evolution during graphitization. Impressively, the graphite material with a graphitization degree of 91.87% was rapidly prepared from lignite at 6 GPa and 1300 $^\circ C$.

2. Experimental Section

2.1. Sample Preparation by Different Temperature and Pressure Experiments

The lignite used in the experiment was obtained from Puhe Coal Mine, Shenbei Mining area, Liaoning Province, China. The coal samples were wrapped in plastic wrap and sent to the laboratory; its industrial analysis is shown in Table S1. The raw coal was crushed and screened with a 200-mesh (75 µm) screen. The screened coal samples (5 g) were put into a
planetary ball mill (ball material ratio 20:1) and crushed for 2 h to produce ultrafine coal powder. The pulverized coal powder was dried under vacuum for reserve. The experiment was carried out in a cubic anvil-type high-pressure facility (YT-II6, Fushun, China). The pulverized coal material (0.2 g) was put into a magnesium oxide cylinder wrapped with a graphite tube heater. Then, the sample was placed into a pyrophyllite cube used for generating a fine quasi-hydrostatic environment, and the assembled sample was placed in the cubic anvil-type high-pressure facility. The experimental process was carried out at 2–6 GPa and 20–1300 °C for about 20 min, in which the rate of loading pressure was about 1 GPa/min, and the heating rate was about 100 °C/min, keeping the temperature and pressure for 10 min under the preset temperature and pressure conditions. The final samples were obtained by a quench from high temperature before releasing the pressure at a rate of about 0.5 GPa/min. The samples are denoted by n-m, where n is denoted as the exerted high-pressure value and m is expressed as the sintering temperature. For example, 2-20 indicates that the sample was prepared at 2 GPa and 20 °C.

2.2. Sample Characterization

The XRD patterns of the samples were obtained by SmartLab X-ray diffractometer (X’Pert3 diffractometer with a Cu-Kα target). The Raman spectra of the samples were measured using a Raman spectrometer (HR Evolution, JY Horiba) with an excitation wavelength of 532 nm, and the functional groups of the samples were analyzed using an Equinox 55 infrared spectrometer (Bruker, Germany). The morphology and nanostructure of the series samples of were characterized by FE-SEM (Carl Zeiss Ultra 55) and TEM (JEOL-2100Plus).

3. Result Analysis

3.1. XRD Analysis

The graphitization process of lignite under high pressure and high temperature can be characterized by X-ray diffraction patterns, as shown in Figure 1. There are metal oxide impurity peaks formed by the sintering of lignite at the high-temperature and high-pressure stage. According to the characteristic peak evolution, the graphitization process under the set pressure conditions can be distinctly viewed as having three regions: the non-graphitization region, the near-graphitization region, and the graphitization region, corresponding to the processing temperatures at 20 °C, 700 °C, and 1300 °C, respectively. In the non-graphitization region, the XRD spectra of samples 2-20, 4-20, and 6-20 are similar to that of raw material, as shown in Figure 1a–c and Figure S1 (in supplementary materials), and all have a relatively weak (002) peak because there is a large amount of disordered structures and amorphous carbons in lignite [29,30], and the elevated pressure seems to have no effect on the structure of the amorphous carbon. In the near-graphitization region, wide diffraction peaks appear in samples 2-700, 4-700, and 6-700 near 25° and 44°, corresponding to (002) band and (10) band of graphite-like, respectively, showing that lignite treated at 700 °C under different high pressures has an aromatic structure stacking growth phenomenon; a cross-lattice structure intermediate in type between the amorphous carbon and the graphite carbon appears, which is referred to as turbostratic carbon [31,32]. It is noted that in the graphitization region, the (002) peak of samples 2-1300, 4-1300, and 6-1300 become high and sharp, and the (10) band splits into (100) and (101) peaks, and (004) and (110) peaks appear, these characteristics indicate that the lignite crystallizes under high temperature–high pressure, and the three-dimensional structure of graphite mainly appears based on the 2H phase [10,13]. XRD patterns of samples 2-1300, 4-1300, and 6-1300 were indexed to be the hexagonal structure with the space group of P63/mmc (No. 194). The calculation of the three samples’ unit lattice parameters was performed by Rietveld refinement, which was 2.4673–2.4641 Å, the c was 6.7662–6.7363 Å, and the lattice volume was 35.67–35.42 Å³ (Table 1).
Generally, the (002) diffraction peak is reflected comprehensively by the carbon crystal peak (002 band), which is arranged regularly, and the carbon peak of the amorphous structure (γ band) [33,34]. The (002) band reflects the stacking height of the aromatic layer, and it corresponds to the crystallite formed by the polycondensation of the aromatic nucleus, namely, aromatic crystallite. The γ band located at $2\theta = 21^\circ$ is related to nonaromatic structures, such as aliphatic structures; in other words, it is caused by aliphatic side chains, functional groups, and aliphatic hydrocarbons attached to an aromatic nucleus [30,35]. Therefore, in order to investigate the coal pyrolysis process under HTHP, we made curve fitting aiming at the (002) diffraction peak, and the curve fitting of (002) diffraction peaks for these coal samples are shown in Figure S2. Under the high pressure of 2 GPa, the peak intensity of the γ band is higher than that of the (002) band, which is the result of the high oxygen functional groups in lignite [36]. As with the temperature up to 700 °C, the (002) peak becomes more pronounced than the γ peak in the pressure range from 2 to 6 GPa. More aliphatic components are thermally cracked, resulting in the reduction of oxygen functional groups in the products. Meanwhile, an amorphous aromatic layer is formed. When the pyrolysis temperature further increases to 1300 °C, the γ peak becomes imperceptible and the (002) peak becomes the dominant diffraction peak. The complex decomposition is extracted from the fracture of the branched chain in the carbon macromolecular skeleton. At the same time, the aromatic fragments undergo cross-linking and preferential re-arrangement [37]. The samples treated at 4 and 6 GPa undergo a similar transformation process.

In order to deeply understand the changes to the lignite microcrystalline structure, the crystallite lattice parameters (interlayer spacing ($d_{002}$), stack height ($L_c$), stack width ($L_a$), the average number of aromatic layer per crystallite ($N_{ave}$), aromaticity ($fa$), and $L_a/L_c$) were calculated using the Bragg’s equations and empirical equations derived from the Scherrer formula, and $L_a/L_c$ reflected the morphological characteristics of aromatic structures (Equations (S1)–(S5)) [12,35,36,38]. The Mering–Maire formula was used to calculate the degree of graphitization ($G$) of sample (Equation (S6)) [11]. As seen in Table 2 and Figure 2, the crystallite lattice parameters show obvious stage evolution characteristics with the change of temperature. At 6 GPa, $d_{002}$ decreases continuously from 0.3519 to 0.3361 nm with an increasing sintering temperature from 20 to 1300 °C, which indicates that the high temperature can effectively reduce the layer spacing of aromatic layers. It is noteworthy

![Figure 1. XRD patterns of lignite samples treated at (a) 2 GPa in the temperature range from 20 to 1300 °C, (b) 4 GPa in the temperature range from 20 to 1300 °C, and (c) 6 GPa in the temperature range from 20 to 1300 °C.](image-url)

| Sample  | Space Group       | $a$ (Å) | $c$ (Å) | $V$ (Å³) | $\rho$ (g/cm³) | $Z$ |
|---------|-------------------|---------|---------|----------|----------------|-----|
| 2-1300  | $P6_3/mmc$ (No. 194) | 2.4673  | 6.7662  | 35.67    | 2.2364         | 4   |
| 4-1300  | $P6_3/mmc$ (No. 194) | 2.4659  | 6.7491  | 35.54    | 2.2445         | 4   |
| 6-1300  | $P6_3/mmc$ (No. 194) | 2.4641  | 6.7363  | 35.42    | 2.2522         | 4   |
that the \(d_{002}\) of the lignite sample acquired at 6 GPa and 1300 °C approaches that of pure graphite (0.336–0.337 nm), superior to that of pyrolysis graphite (0.3508–0.3615 nm) [29,39], which indicates that the high pressure can induce high-quality graphite from low-level coal. The \(d_{002}\) shows a similar trend at different pressures: \(d_{002}\) decreases from 0.3517 to 0.3368 nm at 2 GPa, and varies from 0.3519 to 0.3381 nm at 4 GPa. According to the International Committee for Coal and Organic Petrology (ICCP) classification for anthracite, meta-anthracite, semi-graphite, and graphite [40], the anthracite has \(d_{002} > 0.340\) nm. The meta-anthracite is classified by \(d_{002}\) within the range of 0.338–0.340 nm, and semi-graphite is defined by \(d_{002}\) within the range of 0.337–0.338 nm. The \(d_{002}\) of 0.3354–0.337 nm represents the graphite zone. The \(d_{002}\) of samples 2-700, 4-700, and 6-700 is 0.3400, 0.3452, and 0.3382 nm, indicating that samples 2-700 and 6-700 are within the meta-anthracite range, while sample 4-700 belongs to the anthracite zone. As the temperature rises to 1300 °C, sample 4-1300 just falls into the meta-anthracite area, but samples 2-1300 and 6-1300 both belong to the graphite category. For the graphite samples, in order to evaluate the degree of ordering of the crystalline structure, the asymmetry index (AI) of (002) reflection is proposed based on the concept for the asymmetry index of (001) reflection of illite used for evaluating its degree of crystallinity [34]. Figure S3 shows that the AI of (002) reflection of samples 2-1300, 4-1300, and 6-1300 is calculated using left FWHM divided by right FWHM, due to the asymmetric nature of (002) reflection caused by the turbostratic structure and structure defect in the crystalline structure. In general, the high AI value can be used to reflect a more symmetric (002) reflection of coal-derived natural graphite, which indicates a high degree of ordering of the crystalline structure. Surprisingly, sample 4-1300 has the highest AI value compared with samples 2-1300 and 6-1300, while the \(d_{002}\) of sample 4-1300 is higher than that of samples 2-1300 and 6-1300, which is probably caused by the residual aliphatic side chains between the aromatic rings in highly ordered sample 4-1300. It is noteworthy that the range of AI > 0.63 can be used to assess highly ordered coal-derived natural graphite: samples 2-1300 and 6-1300 can rival most natural graphite in terms of structural order, and sample 4-1300 possesses a higher degree of ordering of graphite lamellae in a lateral direction than that of most natural graphite, as shown in Table S2. From the above analysis, we can conclude that the high pressure is in favor of eliminating dislocation in the stacking and in-plane defects of flat aromatic layers, further resulting in highly ordered graphite.

| Sample   | \(2\theta_{002}\) (deg) | \(2\theta_{100}\) (deg) | \(\beta_{002}\) (deg) | \(\beta_{100}\) (deg) | \(d_{002}\) (nm) | \(L_a\) (nm) | \(L_c\) (nm) | \(N_{ave}\) (-) | \(G\) (%) | \(f_a\) (-) | \(L_a/L_c\) (-) |
|----------|--------------------------|--------------------------|-----------------------|-----------------------|----------------|-------------|-------------|----------------|----------|-----------|----------------|
| 2-20     | 25.30                    | n.d.                     | 4.16                  | n.d.                  | 0.3517         | n.d.        | 1.9571      | 5.56           | n.d.     | 0.5260    | n.d.                   |
| 2-700    | 26.19                    | 44.17                    | 4.94                  | 2.86                  | 0.3400         | 6.1284      | 1.6511      | 4.85           | 46.51    | 0.8418    | 3.7117                  |
| 2-1300   | 26.44                    | 42.49                    | 0.47                  | 0.35                  | 0.3368         | 49.7871     | 17.3624     | 51.55          | 83.72    | 0.8619    | 2.8675                  |
| 4-20     | 25.29                    | n.d.                     | 4.47                  | n.d.                  | 0.3519         | n.d.        | 1.8214      | 5.17           | n.d.     | 0.5789    | n.d.                   |
| 4-700    | 25.79                    | 43.70                    | 4.71                  | 3.99                  | 0.3452         | 4.3855      | 1.7303      | 5.01           | n.d.     | 0.8574    | 2.5345                  |
| 4-1300   | 26.34                    | 42.43                    | 0.57                  | 0.33                  | 0.3381         | 52.7938     | 14.3135     | 42.33          | 68.61    | 0.9358    | 3.6884                  |
| 6-20     | 25.29                    | n.d.                     | 4.47                  | n.d.                  | 0.3519         | n.d.        | 1.8214      | 5.18           | n.d.     | 0.5789    | n.d.                   |
| 6-700    | 26.33                    | 43.37                    | 4.51                  | 4.53                  | 0.3382         | 3.8583      | 1.8090      | 5.35           | 67.44    | 0.7507    | 2.1328                  |
| 6-1300   | 26.50                    | 42.46                    | 0.44                  | 0.32                  | 0.3361         | 54.4491     | 18.5485     | 55.19          | 91.87    | 0.8896    | 2.9355                  |

n.d. denotes not determined.

In addition to lattice spacing, it is important to study the size of crystallites in the longitudinal (\(L_c\)) and transverse (\(L_a\)) direction. With the increasing high-pressure sintering temperature at 2, 4, and 6 GPa, the parameter \(L_c\) almost remains unchanged from 20 to 700 °C, while there is a drastic increase of \(L_c\) in the range of 700 to 1300 °C (a nearly tenfold increase). As for \(L_a\), the values are hard to be determined for cold-pressed samples prepared at 2, 4, and 6 GPa because of poor crystal quality, while all \(L_a\) increases rapidly from 700 to 1300 °C. \(N_{ave}\) is related to \(L_c\) and \(d_{002}\), and its trend is similar to that of \(L_c\). Moreover, \(f_a\) ranges from 0.5260 to 0.9358, and it increases rapidly from 20 to 700 °C, then becomes...
gradually more stable from 700 to 1300 °C. The $N_{ave}$ values are 51.55, 42.33, and 55.19 for samples 2-1300, 4-1300, and 6-1300, respectively, showing a remarkable increase from 4.85, 5.00, and 5.35 coming from samples 2-700, 4-700, and 6-700. It has been reported [38] that the $N_{ave}$ value exhibits little change from 2.09 to 4.55 for coal chars pyrolyzed at temperatures of 850 and 1600 °C. We can assert that the high pressure accelerates the graphitization. Besides, the graphitization degree of sample 6-1300 reaches 91.87%, superior to other preparation methods [9].

![Figure 2. Variation diagram of XRD microcrystalline structure parameters.](image)

The XRD quantitative analysis reveals the overall change of lignite during HTHP treatment, similar to other studies regarding the structure evolution of coal-derived natural graphite [29,34,35]. However, according to the evolution characteristics of the crystallite lattice parameters for the selected samples, the high pressure accelerates the condensation degree of aromatic rings and improves the order of the aromatic layers, which has never been explicitly emphasized before.

3.2. Raman Analysis

Coal has a polycrystalline structure between short-range order and long-range disorder. Since the Raman signal is sensitive to short range disorder, it is effectively utilized to inspect the effect of the pressure and temperature conditions over the extent of the formation of ordered and disordered structures in the final products during graphitization [38]. In the Raman first order region of samples, five distinct Raman frequency vibration bands were fitted, namely, Lorentzian-shaped bands $G(\sim 1580$ cm$^{-1}$), $D_1(\sim 1350$ cm$^{-1}$), $D_2(\sim 1620$ cm$^{-1}$), and $D_3(\sim 1200$ cm$^{-1}$), and the Gaussian-shaped band $D_3(\sim 1500$ cm$^{-1}$) [41]. The Raman parameters, such as band center, FWHM, and percentage of area obtained from the peak fitting are listed in Table S3. The $D_1$ band corresponds to the stretching vibration of the double carbon atom bond in the molecular structure, with the G band corresponding to the C–C vibration between the aromatic rings [42,43]. The weak $D_2$ band, as a shoulder on the high wavelength side (\sim 1620$ cm$^{-1}$) of the G band, stems from the $sp^2$ bond stretching mode of graphitic carbon in a hexagonal lattice. The $D_1$ and $D_2$ bands are attributed to the structural defect of graphitic carbon [41]. Furthermore, the $D_3$ and $D_4$ peaks located near 1500 and 1200 cm$^{-1}$ have been considered to be associated with amorphous carbon with $sp^2$–$sp^3$ mixed bond forms, and ionic impurities or $sp^3$-rich structures at the periphery
of crystallites \([43,44]\), respectively. The impact of treatment temperature on the crystallite structure at the pressure of 2, 4, and 6 GPa is similar, as shown in Figure 3. When increasing the pyrolysis temperature from 20 to 1300 °C, several major types of defect gradually decrease: the \(D_1\) and \(D_3\) bands are clearly visible in samples 2-20, 4-20, and 6-20, and disappear in samples 2-1300, 4-1300, and 6-1300. Meanwhile, the \(G\) band becomes sharper, and the \(D_1\) band becomes weaker, except for sample 4-1300. The temperature is beneficial for the reduction of crystal defects and the enhancement of the graphite characteristics. It has been reported that the higher pressure can promote the graphitization process of activated carbon \([28]\). However, when considering the coal pyrolysis in the HTHP process, the relation of the high pressure and the degree of the graphitization process is more complicated. The pressure may inhibit the pyrolysis of coal and result in the residual un-volatile matter, further reducing the degree of graphitization in the pressure range from 2 to 4 GPa. On the other hand, from 4 to 6 GPa, the high pressure can efficaciously reduce the interlayer spacing of the crystalline structure, which contributes to the extraction of residual matter.

In the second-order region, the Raman bands attributed to the overtone and combination of disorder-induced bands provide better information about the three-dimensional order of carbonaceous materials \([34,45]\). The prominent feature in the second order region is the \(~2700\) \(\text{cm}^{-1}\) band (Figure S4), which corresponds to the overtone of the \(D_1\) band \([46]\). The weak intense band at \(~2900\) \(\text{cm}^{-1}\) assigned to the \(D_1 + G\) bands exists in the Raman spectrum of sample 4-1300, but disappears in the Raman spectra of samples 2-1300 and 6-1300. Additionally, the \(~2700\) \(\text{cm}^{-1}\) band is a single sharp band for samples 4-1300, and splits for samples 2-1300 and 6-1300, as shown in Figure S5. The splitting of the 2700 \(\text{cm}^{-1}\) band and thorough disappearance of the 2900 \(\text{cm}^{-1}\) band manifest the formation of an or-

![Figure 3. Assignments of curve-fitted bands for first-order Raman spectra in case of samples (a) 2-20, (b) 2-700, (c) 2-1300, (d) 4-20, (e) 4-700, (f) 4-1300, (g) 6-20, (h) 6-700, and (i) 6-1300.](image-url)
dered three-dimensional crystalline structure in samples 2-1300 and 6-1300 [47,48], agreeing with the XRD analysis.

The degree of graphitization of the carbon structures was analyzed by the full width at half maximum (FWHM) of the D1 and G bands [49,50], as shown in Table S3. The 6-1300 sample shows the narrowest FWHM value for both D1 and G bands than the other samples, which could be a result of the relatively high crystallinity compared to the other samples. In addition, ID1/IG represents the degree of growth of the aromatic ring to a certain extent, and the decrease of the ID1/IG ratio represents the growth of the aromatic rings, namely, the structure of the sample is closer to the structure of graphite [30,50]. The rise of ID1/IG at 700 °C is due to the graphite microcrystals formed by the basic structural units of lignite through cross-linking, which have a turbostratic nature; at the same time, the broken free radicals generated by the removal of volatile substances at high temperatures embedded into the microcrystalline layers to inhibit the coupling between adjacent layers and further increase the defects [51]. For samples under treatment at 1300 °C, ID1/IG of lignite treated at 6.0 GPa possesses the smallest value compared with the other samples, which indicates that the degree of crystallinity in the lignite samples can be enhanced on account of the synergistic effect of the high temperature and the high pressure. In summary, the Raman data confirm the structural order evaluation of synthetic graphite prepared from lignite using the HTHP method, where the highest temperature and pressure offered a more ordered carbon structure.

3.3. Infrared Spectroscopy Analysis

Fourier transform infrared spectroscopy (FTIR) is one of the most versatile techniques to study the structure characteristic of materials, and it can provide important information about the variation of chemical structure, especially functional groups, under HTHP treatment [29]. The FTIR spectra of these samples are shown in Figure 4, where the functional group absorption peaks have been assigned in these coals. The FTIR spectra characteristic peaks of samples 2-20, 4-20, and 6-20 are similar in the position distributions and the intensity, indicating that the high pressure has no effect on the surface functional groups of coal at low temperatures. The 3600–3200 cm⁻¹ band is due to the hydroxyl group (–OH) stretching vibration. The –OH indicates the presence of phenol and alcohol in the coal sample [30]. The shape of this absorption peak is broad and belongs to a strong absorption peak. The absorption peak between 3000 and 2800 cm⁻¹ is attributed to the aliphatic structure [52]. The weak intensity peaks near 2925 cm⁻¹ and 2850 cm⁻¹ belong to the –CH₂ and –CH₃ groups, respectively. Moreover, the peak intensity at 2925 cm⁻¹ is greater than that at 2850 cm⁻¹, indicating the presence of long aliphatic chains in the coal [30,33]. In addition, a strong absorption peak was found in the 1600 cm⁻¹ region, corresponding to the aromatic –C=C– groups in the benzene ring [53,54]. The bands located near 1442 cm⁻¹ and 1377 cm⁻¹ can be attributed to the asymmetric deformation of –CH₂ and the symmetric deformation of the –CH₂– group. The peak intensity at 1442 cm⁻¹ is higher than that at 1373 cm⁻¹, showing the presence of long aliphatic pendants or methylene bridges between the aromatic rings in the coal [30]. The strong absorption band within the range of 1300–1000 cm⁻¹ is attributed to the phenolic deformation of C–O–C, indicating that a large amount of phenol, alcohol, ether, ester, and the like are contained [54,55]. The low-intensity absorption band between 900 and 700 cm⁻¹ is caused by the deformation vibration of the –CH outside the aromatic ring [33,37]. Furthermore, peaks within 700–400 cm⁻¹ in the IR spectrum of samples 2-20, 4-20, and 6-20 were caused by mineral matters [55].
As the pyrolysis temperature increases, the peak of the hydroxyl group (–OH) shifts toward the high frequency region, and the absorption peak intensity gradually decreases for the samples under the pressure of 2 and 4 GPa, while the absorption peak intensity ultimately vanishes for samples under the pressure of 6 GPa. The ejection of –OH can be effectively implemented by the temperature and further accelerated under high pressure. With regard to –C=C–, the peak intensity shows a decreasing trend due to depolymerization reactions [37], while the peaks between 1300 and 1000 cm\(^{-1}\) dominated by aliphatic ether C–O–C and alcohol C–O show varying degrees of enhancement when the temperature reaches 700 °C. This implies that oxygen-containing functional groups engage in the process of aromatic ring condensation. At higher pyrolysis temperatures (i.e., 1300 °C), most functional groups were lost during the graphitization process. It is noted that the peaks located at 2925 cm\(^{-1}\) and 2850 cm\(^{-1}\) corresponding to the –CH\(_2\) and –CH\(_3\) groups have always existed at the high pressure of 4 GPa, and even the pyrolysis temperature increases to 1300 °C. This indicates that benzene decorated with methyl and methylene is the main reason for the maximal \(d_{002}\) of sample 4-1300 compared with samples 2-1300 and 6-1300. In summary, we can assert that some stable aliphatics and oxygen-containing functional groups of lignite can be preserved under high temperature–high pressure, but a higher pressure reduces the activation energy of reaction and promotes the further decomposition of aliphatics and oxygen-containing functional groups of lignite with the assistance of high temperatures.

3.4. Morphological Evolution by SEM and HRTEM

The morphology and surface area analysis of lignite from HTHP pyrolysis were investigated by SEM. As can be seen from these micrographs (Figure 5a–c), the SEM analysis of samples 2-20, 4-20, and 6-20 showed that the particles had a rough surface just like the raw lignite (Figure 5a). It can be seen that with the temperature increasing up to 700 °C under high pressure (Figure 5d–f), samples 2-700, 4-700, and 6-700 had a relatively flat and compact structure. However, when the lignite sample was only pyrolyzed at 700 °C, the lignite surface was unconsolidated and covered with some lamellar fragments, as shown in Figure 5b. From the change of surface morphology, it can be inferred that the volatile release can be hindered under the action of high pressure, while the high pressure accelerates the contraction and densification of the carbon skeleton during the stage of coal plasticity. For lignite samples prepared at 1300 °C under high pressure, the organic matter of coal underwent further decomposition, so the release of volatile matter resulted in the formation of macropores (Figure 5g–i). As the pressure increases, the pores tend to collapse and turn into sheet-like structures, thus accelerating the graphitization of lignite. Table 3 is the EDS element table of the samples. According to the literature, at high temperatures, the carbon net structure increases and possesses a higher degree of structural order [28,33,56]. Therefore, it can be seen from Table 3 that the content of the C element in the sample increases and the content of volatile elements N and O decreases with the increase in temperature. These results could be related to the fact that the graphitization process of
lignite is characterized by carbon enrichment and the removal of volatile elements such as oxygen in the FTIR data. Basically speaking, the content of the C element in the sample increases with pressure, and the enrichment of the C element in 6-1300 is the most abundant, reaching 87.19%.

Figure 5. SEM images of samples (a) 2-20, (b) 4-20, (c) 6-20, (d) 2-700, (e) 4-700, (f) 6-700, (g) 2-1300, (h) 4-1300, and (i) 6-1300.

Table 3. EDS of lignite samples prepared at HTHP.

| Sample | C    | N    | O    | Si  |
|--------|------|------|------|-----|
| 2-700  | 74.19| 11.89| 13.66| 0.26|
| 2-1300 | 84.47| 6.27 | 4.95 | 1.31|
| 4-700  | 83.41| 9.44 | 6.70 | 0.46|
| 4-1300 | 87.01| 7.64 | 4.46 | 0.89|
| 6-700  | 79.72| 8.78 | 9.69 | 1.80|
| 6-1300 | 87.19| 7.27 | 5.04 | 0.49|

In order to further observe the nanostructure evolution of lignite at the nanoscale during high temperature–high pressure graphitization, the lignite samples prepared at 2 GPa were analyzed by TEM and HRTEM, as shown in Figure 6. It is observed that sample 2-20 exhibits abundant amorphous carbon from the observation of distorted layers [38]. Furthermore, sample 2-700 transforms into a translucent aggregate with folds, and a small
graphite transparent area appears at the edge. The formation of a strong system of cross-linking uniting between neighboring crystallites leads to the crystallite lattice of carbon displaying a high degree of turbostratic arrangements [19], and the microtexture in sample 2-700 is composed of several aromatic layers that have short in-plane dimensions and orient in a wavy pattern [34,39]. The monitored interplanar spacing of the (002) plane was measured to 0.342 nm, which is close to the 0.3400 nm value obtained by XRD. The TEM image (Figure 6c) shows that the cross-linking structure of sample 2-1300 is destroyed, there are a large number of transparent thin-layer graphite nanosheets, and the carbon crystallite is found to stack in groups of several short graphene layers with orientation and arrangement. The (002) \(d\)-spacing value for 2-1300 is about 0.331 nm, in agreement with the value obtained by XRD. As the temperature increases, the polymerization process links the adjacent aromatic layers to form a long-range ordered graphite structure [34,50]. Therefore, the structural evolution of amorphous carbon phase transformed to ordered graphite was detected.

Figure 6. TEM and HRTEM micrographs of lignite samples at different temperatures of 2 GPa: (a,d) 20 °C, (b,e) 700 °C, and (c,f) 1300 °C.

4. Conclusions

In this study, the structure characteristics of synthetic graphite transformed from lignite subjected to HTHP treatment were investigated by XRD, Raman, FTIR, SEM-EDS, and HRTEM. The structural evolution of the synthetic graphite derived from lignite during the graphitization process is analogous to the transformation process of graphite formed by high-temperature pyrolysis. As the temperature increases, the amorphous carbon skeleton gradually transforms into the wrinkled aromatic layers; further, the turbostratic structure gradually disappears and forms a highly ordered graphite structure. Furthermore, we demonstrated the strong synergistic effect of high temperature and high pressure on the graphitization process of lignite. The high temperature is certainly beneficial in terms of realizing the decomposition of the organic matter in lignite and the directional rearrangement of the aromatic layer, and the high pressure is crucial to achieve the enrichment of the carbon concentration and smaller interlayer spacing \((d_{002})\), thus significantly reducing...
the graphitization temperature of lignite. Finally, the highly ordered graphite material with a graphitization degree of 91.87% was rapidly prepared from lignite at 6 GPa up to 1300 °C. This proves that the utilization of lignite as a precursor is feasible to rapidly prepare synthetic graphite using the HTHP method.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12040464/s1. Table S1. Proximate analysis and ultimate analysis of coal samples. Table S2. Comparison of AI values of samples 2-1300, 4-1300, and 6-1300 with other natural graphite. Table S3. Raman parameters obtained from the peak fitting of Raman spectrum per sample. Figure S1. XRD pattern of raw lignite without further treatment. Figure S2. Curve fitting of XRD spectra of samples (a) 2-20, (b) 2-700, (c) 2-1300, (d) 4-20, (e) 4-700, (f) 4-1300, (g) 6-20, (h) 6-700, and (i) 6-1300 for (002) peak. Figure S3. The calculated asymmetry index (AI) of samples (a) 2-1300, (b) 4-1300, and (c) 6-1300 using the FWHM of (002) reflection. Figure S4. Second-order Raman spectra of lignite samples prepared at high pressure of (a) 2 GPa, (b) 4 GPa, and (c) 6 GPa. Figure S5. Peak fitting of second-order Raman spectrum of samples (a) 2-1300, (b) 4-1300, and (c) 6-1300. Figure S6. SEM images of (a) raw lignite and (b) lignite sample pyrolyzed at 700 °C in a horizontal tube furnace.

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