Fabricating Graphene and Nanodiamonds from Lignin by Femtosecond Laser Irradiation

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ABSTRACT: This study demonstrates a new transformation path from lignin to graphene and nanodiamonds (NDs) by femtosecond laser writing in air at ambient temperature and pressure. Graphene nanoribbon rolls were generated at lower laser power. When the laser power was high, NDs could be obtained apart from graphene and onion-like carbon intermediates. These structures were confirmed by scanning electron microscopy, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy. The effects of laser power and laser writing speed on the structure of laser-induced patterns were investigated. The results show that the laser power was more important than the writing speed for the synthesis of carbon nanoparticles, and high laser power contributed to enhanced electrically conductive performance. Therefore, the direct laser irradiation technique leads a simple, low-cost, and sustainable way to synthesize graphene and NDs and is promising for the fabrication of sensors and electric devices.

1. INTRODUCTION

Diamond and graphene are two allotropes of carbon attracting considerable attention for their different optical, electrical, and mechanical properties. Materials based on nanodiamonds (NDs) or graphene have been widely studied for their promising applications in various fields, such as sensors, energy storage, catalysis, pollutant treatment, and biomedical applications.1−3 According to the carbon phase diagram, diamonds are thermodynamically less stable than graphene at normal pressure and temperature.4 Therefore, the formation of diamonds usually requires extremely high pressure and temperature.

NDs are generally synthesized via several methods including detonation,5 chemical vapor deposition (CVD),6 and high-energy techniques, such as high-energy ball milling,7 high-energy arc plasma,8 and shock compression.9 Recent studies focused on the development and improvement of methods under a milder temperature−pressure, such as pulsed laser ablation.10 Although some high-purity hydrocarbon gas has been employed in the ND fabrication by the above techniques,11,12 these methods are still mainly limited to the use of expensive and unsustainable carbon allotropes such as graphite13 and carbon nanotubes.14 Therefore, it is attractive to explore the production of NDs from much abundant and renewable carbon sources. To date, very few studies were reported on the synthesis of NDs from biomass, although diamond structures could be found among pyrolytic graphite layers and onion-like particles after wood charcoal was carbonized at 700 °C.15 Our previous work has demonstrated the conversion from nanolignin/cellulose nanofibril (LCNF) composite films to NDs by laser direct writing and indicated that the lignin content played a major role in the generation of NDs.16 However, no more detailed studies have yet been reported on the carbonization mechanism of pure lignin nanoparticles for ND synthesis in laser irradiation.

Lignin, the second-most abundant natural polymer material next to cellulose on earth, is often considered as a byproduct and waste in biomass utilization, especially in the pulp and paper industry. It is difficult to degrade owing to its complex cross-linked phenolic structure. Now, the utilization of lignin is mostly limited to burning for energy even though numerous efforts have been made to prepare lignin-based chemicals and materials in lab.17,18 Since lignin contains over 60% carbon, it can be a renewable alternative source for the production of value-added nanocarbon materials such as graphene.19,20 In recent years, laser irradiation technology has been rapidly
developed in synthesizing graphene from lignin-containing natural carbon precursors, such as wood, paper, and leaves.6,22 These carbon precursors were graphitized for energy storage, electrocatalysts, and sensors. Meanwhile, some lignin-based composites have also been reported to be converted into porous graphene for solid-state supercapacitors.13–25 Niu et al. reported the conversion of sodium lignosulfonate to carbon composite with a few graphite and mostly disordered and amorphous structure using a CO₂ laser.26 However, the laser-induced carbonization of pure lignin still needs more studies, and it is also challenging to convert the lignin into graphene and NDs.

The catalytic graphitization of lignin for graphene-based materials has been extensively studied on the effects of catalysts,28 temperature, material properties,29 and ambient gas phase.23 Many studies conducted the graphitization of lignin with a pretreatment process to reduce the particle size of the material to the micron or nanometer level, and it was regarded that the lignin particle size should be a major factor affecting the degree of graphitization.20,28,30 Because thermal treatment often consumes lots of energy and expensive gases, it is of great importance to develop a facile method for converting lignin to graphene and even NDs. Previously, Hu et al. carbonized commercial lignin using a femtosecond laser and they obtained tetrahedral amorphous carbon without graphitic carbon as a result.31 Considering the significant effect of particle size on the graphitization of lignin, we report an easy and facile method for preparing thin solid films and NDs.3,33 Usually, it is regarded that pulsed laser can create high temperature and high pressure. However, limited information about the effect of laser parameters on the formation of NDs from lignin can be found in the literature. Laser power largely determines the instantaneous temperature and pressure around the laser spot. The effect of laser power on the structure of laser-induced patterns was investigated, and the results are shown in Figure 3. Only bubbles were formed on the surface of the lased pattern at 450 mW. These bubbles had a morphology similar to that of the vesicle on the char surface from the pyrolysis of lignin at low temperature.34 Also, the structural change was due to surface tension.14,30,34 As the laser power increased, lignin kept melting and aggregating as the temperature increased, and the shrunken carbon spheres formed after laser irradiation.37 Meanwhile, the polar bonds in nanolignin such as O=C=O, C=O, and O–H bonds broke and generated gases such as CO₂, CO, and H₂, resulting in a porous structure as shown in Figure 3c,d. However, the release of gases could take off some carbon particles causing the product loss. A dark smoke can be observed along the laser process (as seen in Figure 1c). Thus,

2. RESULTS AND DISCUSSION

2.1. Preparation of Nanolignin and Laser-Induced Patterns. It has been reported that the micro-to-nanoparticle size of precursors could be beneficial for a higher degree of graphitization in catalytic carbonization.30 Considering the outstanding properties of graphene and NDs, lignin nanoparticles were prepared from commercial lignin by mechanical grinding and irradiated by a femtosecond laser to explore the carbon transformation process (Figure 1). The transmission electron microscopy (TEM) image in Figure 2 presents its micromorphology as spherical nanoparticles, and their average size was around 100 nm. Then, the nanolignin powder was pressed to form tablets, which were scribed using a femtosecond pulsed laser (Figure 1c). Figure 1d displays the optical image of the laser-induced pattern on the nanolignin tablet. The rectangular part exhibited a darker coloration, demonstrating the carbonization on the surface induced by laser irradiation. Currently, various pattern structures have been tailored from lignin composites by direct laser writing, and they were investigated for the applications of supercapacitors, sensors, and power generators.24,25,32 It is impressive that we have fabricated circuit patterns from nanolignin/cellulose nanofibril composites, showing promising applications as flexible electrics and sensors.6 Since the patterns in this study contained graphene and ND microstructures and showed varying degrees of resistances in the following discussion, it was reasonable that these patterns can be applied for fabricating electric devices.

2.2 Formation of Carbon Nanoparticles. 2.2.1 Effect of Laser Power. Pulsed laser ablation has been an important method for preparing thin solid films and NDs.3,33 Usually, it is regarded that pulsed laser can create high temperature and high pressure. However, limited information about the effect of laser parameters on the formation of NDs from lignin can be found in the literature. Laser power largely determines the instantaneous temperature and pressure around the laser spot. The effect of laser power on the structure of laser-induced patterns was investigated, and the results are shown in Figure 3. Only bubbles were formed on the surface of the lased pattern at 450 mW. These bubbles had a morphology similar to that of the vesicle on the char surface from the pyrolysis of lignin at low temperature.34 Also, the structural change was due to surface tension.14,30,34 As the laser power increased, lignin kept melting and aggregating as the temperature increased, and the shrunken carbon spheres formed after laser irradiation.37 Meanwhile, the polar bonds in nanolignin such as O=C=O, C=O, and O–H bonds broke and generated gases such as CO₂, CO, and H₂, resulting in a porous structure as shown in Figure 3c,d. However, the release of gases could take off some carbon particles causing the product loss. A dark smoke can be observed along the laser process (as seen in Figure 1c). Thus,
it can be seen that the laser power clearly affected the generation process of carbon spheres from nanolignin. These figures show the formation process of carbon nanoparticles on lased patterns by different laser powers from 450 to 900 mW. A large number of carbon spheres were generated at 900 mW, as shown in Figure 3d, which were similar to the results of the preparation of NDs from the LCNF composite by femto-second laser irradiation in our previous study. However, owing to the more active aliphatic carbon, LCNFs degraded much faster and easier than nanolignin. The obvious bubble formation in Figure 3a was not found in the conversion from LCNFs to NDs. The LCNF composite carbonized to form apparent carbon spheres at 300 mW, while the conversion from nanolignin consumed at least 750 mW. Thanks to the large amount of reductive gas generated from cellulose decomposition, the LCNF composite converted to NDs at 600 mW. Without an additive pressure from these gases, the carbonization products of nanolignin should be much complex.

2.2.2 Effect of Laser Writing Speed. The laser irradiation speed on the precursor can affect the heat absorbed by the precursor. The effect of laser writing speed on the structure of laser-induced patterns was studied, and the results are shown in Figure 4. As for the patterns in the 600 mW group (Figure 4a–c), a slower writing speed was used in the study. Too lower writing speed (1 mm/s) leads to long-time laser irradiation and carbonization at the same place. Rare individual carbon particles are found in Figure 4a, and just bubbles were obtained at a high writing speed. When 900 mW laser power was employed in the study (Figure 4d–f), much higher writing speed was employed in the case of ablation and over-carbonization. As the speed increased, less individual carbon spheres formed. Thus, the suitable laser writing speed was 2.5 mm/s. The result indicates that high speed is unfavorable for the formation of carbon nanoparticles and laser power is more important than the laser speed for the synthesis of NDs.

2.3 Raman Spectroscopy. In order to investigate the structure of the carbon atoms, nanolignin tablet and laser-induced patterns were characterized by Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) in Figure 5. Due to the disordered structure of lignin, nanolignin’s Raman features were not obtained. The images in Figure 5a show typical D and G bands in the laser-induced patterns, which were centered at about 1380 and 1580 cm$^{-1}$, respectively. This indicates that both graphene and defects were formed during the laser irradiation. As the laser power increased, the $I_D/I_G$ ratio tended to decrease first and then increased, as shown in Figure 5b. The lowest $I_D/I_G$ ratio indicated that a 750 mW laser power induced the maximum crystallite size of graphene and the lowest degree of graphene defects. Also, the $I_D/I_G$ ratio at 900 mW was higher than that at 750 mW, which may be caused by the generation of NDs. Unfortunately, the characteristic Raman peak of bulk diamond at 1332 cm$^{-1}$ was not observed in Figure 5a. This may be mainly caused by the low content of NDs in the sample. The presence of disordered sp$^3$ carbon and other nanocarbons may also conceal the signals of NDs in Raman spectra. Purification of the sample will be carried out in our future plan to obtain the Raman spectra of NDs.

2.4 XRD Analysis. In the XRD image, both nanolignin and laser-induced patterns show very broad peaks below $2\theta = 30^\circ$ in Figure 5c. As for the NL900 sample, a weak peak at 44° can be observed, corresponding to the (100) plane of the graphitic structure. This result is in accordance with the Raman results in Figure 5a, while almost no graphitic peak was found in the NL750 sample by XRD detection. These different results in XRD and Raman spectra can be due to their detection methods. XRD measurements usually are performed on a bulk sample, while Raman spectra are measured one by one at a single point. The Raman spectra detected at a single point do not represent the structure of the entire material. In our study,
the Raman spectra were detected on four points and they exhibited similar results; thus, the image in Figure 5a can demonstrate the presence of graphitic carbon in the patterns. However, in the XRD images, it seemed that the signal of the abundant amorphous carbon was so high that it concealed that of the graphitic structures in NL750.

2.5 XPS Analysis. XPS was performed on the laser-induced products. As seen in Figure 5d, the C 1s XPS spectra were deconvoluted to five peaks centered at 284.4, 284.8, 285.9, 287.4, and 288.6 eV. Also, they revealed five different carbon structures, which are sp$^2$-hybridized C–C (namely, C≡C), sp$^3$-hybridized C–C, C–O, C≡O, and O≡C–O, respectively.$^{39,40}$ In the pristine nanolignin, the oxygen-containing groups such as C–O and O≡C–O should be due to the ether and carboxylic acid groups. Apparently, carboxylic acid groups were reduced or converted to CO$_2$ after laser irradiation, and thus, they were not detected in NL750 and NL900 patterns. One can note the significant C≡C features in the NL900 sample, and it was ascribed to the existence of large amounts of graphitic structures in the product. The peak area of sp$^1$-hybridized C–C in NL900 seemed bigger than that in NL750, and it was considered to be due to the presence of NDs and amorphous carbon in the NL900 sample. In addition, the oxygen-containing groups accounted for a large proportion in both laser-induced patterns. This may be because the femtosecond laser irradiation was performed in air.

2.6 TEM Analysis. Figure 6a–e shows the high-resolution TEM (HRTEM) images of the samples after laser writing. It is obvious that spherical carbon nanoparticles were generated at 750 mW (Figure 6a), and the average diameter of the carbon nanoparticles was around 30 nm, while the spherical structures in Figure 6c seemed to suffer damage, which would be caused by the higher laser power at 900 mW. Impressively, many graphene nanoribbon rolls with a lattice fringe space of 0.344 nm were produced in both patterns, as seen in Figure 6b,d. These graphene nanoribbon rolls displayed various sizes between 3 nm and 20 nm, and they contained 5–12 parallel-stacked carbon layers. Moreover, an onion-like carbon structure was found in the NL900 pattern. This onion-like carbon had about six layers and is circled in red in Figure 6d. Furthermore, there are some spherical particles in the size of 2–5 nm in the NL900 pattern in Figure 6g. Also, the interlayer spaces of these fringes were 0.269 and 0.316 nm, which correspond to the (200) and (111) planes of NDs.
respectively. Thus, these results demonstrated that the femtosecond laser irradiation transformed nanolignin into graphene at a low laser power, and the higher laser power can even convert it into NDs and onion-like carbon. This transformation phenomenon was also observed in our previous research on the formation of NDs from LCNFs. The generation of NDs from nanolignin was found at 900 mW in this study, much higher than that from LCNFs at 600 mW. This confirmed our inference about the positive role of cellulose nanofibrils in the biomass–ND conversion. In addition, it was previously reported that femtosecond laser-induced carbonization of lignin resulted in uniform tetrahedral amorphous carbon.

Figure 6. HRTEM images of the laser-induced patterns from nanolignin: (a,b) NL750 and (c–g) NL900. (h) Fast Fourier transform pattern of the crystal with a d-spacing of 0.269 nm in (g).

Figure 7. Possible formation mechanism of graphene and NDs from nanolignin.
structures.\textsuperscript{31} The different results indicate that the particle size of the precursor is a crucial factor for the formation of carbon nanoparticles in laser irradiation. Also, it is in accordance with the fact that the microparticle size of lignin played a significant role in improving the degree of graphitization in catalytic thermal treatment.\textsuperscript{28}

2.7 Formation Mechanism of Laser-Induced Graphene and NDs. As discussed above, nanolignin can be transformed to graphene and NDs after direct laser writing. The possible formation mechanism for this conversion can be explained in Figure 7. Lignin is composed of large numbers of aromatic moieties, which endow the resistance to thermal degradation. Therefore, more active aliphatic branches decompose easily in the laser irradiation. The resulting aromatic ring structure with free radicals is favorable to condense spontaneously due to electron and space effects. After the three-dimensional ordering, the graphitic structure is generated. The generation of graphene by laser writing has been reported from various lignin-containing precursors by many researchers,\textsuperscript{23,24,41} although the detailed transformation process has not been reported. Under higher laser irradiation, the C–C bonds broke and the graphene nanoribbon roll structure collapsed to form many carbon clusters with different sizes. Also, under the high temperature and pressure caused by laser pulses, these carbon clusters were inclined to bend and the carbon layers gradually close to form the onion-like carbon structure (Figure 6d,e). It is reported that the self-compression of carbon onions will take place at high temperature and the onion structure finally transforms to diamond crystals.\textsuperscript{52} Wei et al. accomplished the transition from carbon nanotubes to diamond via the carbon onion structure during laser irradiation.\textsuperscript{43} Xiao et al. reported a phase transformation of the intermediate in the laser irradiation process. The characterization of lased patterns using SEM, XRD, XPS, HRTEM, and Raman observation that the NL750 pattern contained large amounts of graphene nanoribbon rolls. Since the NL900 pattern contained some NDs and onion-like carbon, the corresponding resistance was inferior to that of NL750, while both patterns showed good conductivity performance and possessed the potential for electric applications.

As discussed above, NDs are generally synthesized by detonation,\textsuperscript{5} CVD,\textsuperscript{6} and some high-energy methods.\textsuperscript{7–9} However, these methods usually require either extreme temperature–pressure or expensive/hazardous unsustainable carbon precursors. Catalytic graphitization is effective for the production of graphitized products from chemical or renewable precursors. However, the high energy consumption and expensive high-purity gases are always major problems. Laser radiation is a kind of laser-based 3D printing technology, which can effectively solve the problems encountered in the preparation of diamond and graphene. In this study, graphene and NDs were easily prepared from nanolignin by femtosecond laser irradiation under ambient conditions, and they can be programed in various patterns with great conductivity. Impressively, lignin, a component in the cell walls of vascular plants and algae, is the second-most abundant biopolymer on earth and can act as a perfect carbon precursor. Therefore, this technique provides a good insight for the simple, low-cost, and renewable production of graphene and NDs in sensors and energy storage applications.

3. CONCLUSIONS

In summary, renewable lignin was converted into graphene and NDs using a pulsed femtosecond laser under ambient conditions. The onion-like carbon was found to be an intermediate in the laser irradiation process. The characterization of lased patterns using SEM, XRD, XPS, HRTEM, and Raman spectra demonstrated the formation of intermediates and products and confirmed the transition process. To facilitate the laser writing process, different laser powers and laser writing speeds on the pattern structure were investigated. Laser power exhibited a much greater effect on the ND formation than the writing speed. Moreover, high laser power was more favorable for the conversion to onion-like carbon and NDs. Thus, this technique developed a simple and economic method for the production of graphene and NDs from cheap and sustainable biomass. Besides, the laser-induced patterns exhibited low sheet resistance, showing the potential for sensors and energy storage devices.

4. MATERIALS AND METHODS

4.1 General. Softwood kraft lignin (Indulin AT) was purchased from MeadWestVaco (Virginia, US). It was washed with distilled water three times before use.

4.2 Production of Nanolignin Tablets. The production of nanolignin was conducted with a mechanical fibrillation method, which is similar to the preparation of lignin-coated cellulose nanofibrils reported in our previous publications.\textsuperscript{44,45} In brief, lignin was made into a slurry in water with about 1 wt % solid content. Then, it was milled with a Super MassColloider (MKCA6–5JR, Disk model: MKGA46, MASUKO SANGYO Co., Ltd., Japan) at a speed of 1500 rpm for 19 grinding passes. After being dried in air, nanolignin powders were pressed into tablets of 12.95 mm in diameter at 10 MPa.

Figure 8. Square resistance of laser-induced patterns.
4.3 Femtosecond Laser Irradiation. The laser irradiation tests were performed by a pulse femtosecond laser (fs laser, Model: Cazadero, Calmar Laser Inc.) with a wavelength of 1030 nm, a pulse duration of 150 fs, and a repetition frequency of 120 kHz. The laser power was adjusted from 0 to 1000 mW by an adjustable attenuator. The laser beam, focused with a 20 × 0.40 N.A. microscope objective lens, was set just upright above the nanolignin tablet on a monitored XYZ-working stage, and the process was conducted to give a controlled program design by moving the precursors in air at room temperature. In this study, the distance between two adjacent laser writing lines was set at 100 μm.

The effect of laser power (450—900 mW) on the structure and properties of the carbonized products was investigated. The laser-scribed nanolignin sample at 2.5 mm/s with different laser powers was labeled as NL450, NL600, NL750, and NL900. In order to evaluate the effect of the laser writing speed, patterns were prepared using writing speeds between 1 and 4 mm/s at a constant laser power.

4.4 Characterization. The morphology of the laser-induced samples was investigated with SEM (Zeiss Auriga, Germany) at 200 kV. The laser-irradiated carbonized samples were scraped from the laser-irradiated nanolignin and laser-induced samples was examined using TEM (Zeiss Libra 200MC, Germany) at 200 kV. The laser-carbonized samples were scraped from the laser-irradiated patterns and sonicated in ethanol before measurements. An X-ray diffractometer ( Rigaku, Japan) was used to measure the XRD patterns of the carbonized samples. XPS was carried out using an AXIS UltraDLD instrument ( Shimadzu, Japan). The Raman spectra were observed on a Raman microscope (DXR2xi, Thermo Scientific, USA) at 532 nm. The sheet resistance was measured with an M-6 handheld four-point probe tester (Xi’an, China).

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Notes
The authors declare no competing financial interest.

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