Shock-wave synthesis of multilayer graphene and nitrogen-doped graphene materials from carbonate

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A method for transforming carbonate into graphene using shock-wave loading is presented in this paper. Multilayer graphene was synthesized by impacting mixtures of calcium carbonate and magnesium using a detonation-driven flyer. Furthermore, by adding ammonium nitrate to the reaction system, nitrogen-doped graphene material was formed in a one-step shock-wave treatment. The recovered samples were characterized using various techniques such as transmission electron microscopy, Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The shock synthesis of graphene materials requires a balance between the growth rate of graphene materials and the formation rate of carbon atoms. The pressure and temperature are two important factors affecting the synthesis of graphene materials. Shock-synthesized nitrogen-doped graphene material was demonstrated to act as a metal-free electrode with an efficient electrocatalytic activity and long-term operation stability for the oxygen reduction reaction via two- and four-electron pathways in alkaline fuel cells.

1. Introduction

Graphene is a two-dimensional structure of carbon atoms packed into a honeycomb lattice, known to be the thinnest material thus far. Graphene can be used as a basic building block to build other carbon materials, which can be (1) folded into fullerenes, (2) rolled up into nanotubes, or (3) stacked into graphite\cite{1}. Since the discovery of stable graphene sheets by Novoselov et al. in 2004 \cite{2}, this one-atom-thick carbon material has attracted great interest due to its unique physical and chemical properties, and it can be used in batteries \cite{3}, electronic devices \cite{4}, and energy storage materials \cite{5}.

The most effective electrocatalyst for the oxygen reduction reaction (ORR) in the cathodes of commercial fuel cells is Pt or its alloys \cite{6}. However, the high cost, low selectivity, and poor durability of Pt hinder the large-scale application of fuel cells. Therefore, the search for Pt-free and metal-free catalysts with high activity and practical durability for the ORR has become one of the most active fields of research \cite{7,8}. Doping graphene with other elements can effectively tune its intrinsic properties, including its electronic properties and chemical activities \cite{9,10}. Nitrogen (N) has a comparable atomic size and five valence electrons for bonding with carbon atoms, and it has been widely used for doping carbon materials \cite{11}. For instance, N-doped graphene (NG) material exhibits a high metal-free electrocatalytic activity for the ORR in alkaline solution \cite{12–14} and better long-term operation stability than Pt-based electrodes.

Recently, a few approaches have been devised to synthesize graphene materials/NG, including chemical vapor deposition \cite{15}, arc discharge \cite{16}, plasma treatment \cite{17}, high-temperature pyrolysis \cite{18}, and solvothermal treatment \cite{19}. The shock-wave action of high temperature, high pressure, and a high strain rate lasting for a very short duration (\textasciitilde 10^{-6} s) can induce various chemical reactions and phase transitions in materials \cite{20}. Shock waves have been successfully used to produce various carbon-based materials. The shock synthesis of diamond has long been studied. Polycrystalline diamonds were successfully obtained by shock treatment of graphite-containing powder mixtures through shock-induced martensitic phase transformation \cite{21}. Nano-diamonds were synthesized by the detonation of pure and composite CHNO explosives with a negative oxygen balance \cite{22}. The formation of onion carbon has been observed during solid–solid transformation of highly pure graphite under high pressure (18 GPa) and high temperature (1800 K) \cite{23}. In the presence of catalysts, carbon nanotubes (CNTs) can efficiently grow in the environment generated by the rapid decomposition of normal explosives. Controlling the reaction parameters of a mixture of picric...
acid (PA) with cobalt acetate and paraffin can lead to a well-defined morphology of CNTs [24]. In this study, we present a new approach to synthesize graphene materials and NG using the shock-wave method.

2. Experiment

In this study, calcium carbonate, magnesium, and ammonium nitrate were used as the carbon source, reductant, and nitrogen-doping source, respectively, in the synthesis of multilayer graphene nanosheets and NG. A mixture of calcium carbonate and magnesium was used to synthesize graphene materials, and a mixture of calcium carbonate, magnesium, and ammonium nitrate was used to synthesize NG.

A scheme of the shock-loading apparatus is illustrated in Fig. 1. By detonating the main charge of nitromethane (CH₃NO₂) initiated by a booster charge of 8701 explosive, a steel flyer was propelled to a high velocity ranging from 1 to 3 km/s depending on the flyer thickness and mass main charge. The steel flyer impacted the sample container to generate shock-wave compression. Using the method proposed by McQueen et al. [25], the shock Hugoniot parameters of the porous powder were calculated. The shock pressure in the samples was calculated using the shock impedance-matching method [26]. The shock temperature was estimated using the Hugoniot data of the mixtures of CaCO₃ and Mg. For the synthesis of NG by shock-treating a mixture of CaCO₃, Mg, and ammonium nitrate, the shock pressure and temperature were estimated by considering the mixture of CaCO₃ and Mg and neglecting ammonium nitrate due to its low content. The experimental conditions are presented in Table 1. The calculation procedure is described in the Supporting Information.

After the test, the recovered container was cut open to remove the sample. To remove the impurities, nitric acid was used under heating conditions. Then, the sample was filtered and washed with deionized water until the pH of the filtrate was neutral. Finally, the sample was separated using a freeze dryer to remove all of the water for further characterization. A transmission electron microscope (TEM) (Tecnai 20) was used to observe the microstructure of the recovered samples at an accelerating voltage of 200 kV. Raman spectra were recorded on a Lab RAM Aramis Raman spectrometer with a He–Ne laser at an excitation wavelength of 633 nm. The phase composition of the products was determined using an X-ray diffractometer (XRD) (Rigaku D/MAX–2500) with Cu Kα radiation (λ = 0.15406 nm) at a work voltage of 40 kV and a work current of 200 mA. The minimum step size, ω₀, of the XRD machine is 0.001. Nitrogen doping was analyzed by X-ray photoelectron spectrometry (XPS) (Thermo ESCA LAB 250).

Electrochemical measurements were performed using a computer-controlled potentiostat (CHI 660D) in a standard three-electrode cell. A drop of Nafion solution (5 μl, 1%) was cast on ~20-μg NG. After drying in air, the resultant samples were attached to a glassy carbon electrode (GC, 3 mm in diameter) to fully cover the electroactive circle. A Pt wire (0.5 mm in diameter) and Ag/AgCl were used as counter and reference electrodes, respectively. For comparison, hydrothermally prepared graphene with a similar amount of commercial Pt/C catalyst (20 wt% platinum on carbon black) was also studied using the same electrode configuration. Measurements on the rotating ring-disk electrode (RRDE, ca. 0.25 cm² for disk with a diameter of ca. 5.6 mm and ca. 0.19 cm² for ring with a diameter of ca. 8 mm) and/or the rotating disk electrode (RDE, 5 mm in diameter) were carried out on a MSRX electrode rotator (Pine Instrument) and a CHI 660D potentiostat at a scan rate of 10 mV/s. For all electrochemical measurements, an aqueous solution of 0.1 M KOH was used as the electrolyte. N₂ or O₂ was used to purge the solution to obtain an O₂-free or O₂-saturated electrolyte solution. The voltammetric stability test of NG was performed in O₂-saturated 0.1 M KOH with the potential ranging from ~0.8 to 0.2 V at a scan rate of 50 mV/s for 2 days.

3. Results and discussion

The formation of carbon phases was largely affected by the shock-loading conditions. No carbon phase was formed for the No. 1 test at an impact velocity of 2.83 km/s with a shock pressure of 22.3 GPa and a shock temperature of 2628 K. An increase of pressure and temperature was observed to be favorable for the synthesis of carbon phases. Upon increasing the shock temperature from 2628 to 5215 K while keeping the pressure stable, multilayer graphene, CNTs, and graphite were produced in the No. 2 samples when the impact velocity was increased to 3.37 km/s and the initial density was decreased to 1.35 g/cm³ (see Fig. S2 in the Supporting Information). However, with the further increase in pressure and decrease in temperature, the CNTs and graphite

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**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Samples</th>
<th>Packing density, ρ₀₀ (g/cm³)</th>
<th>ρ₀₀/ρ₀⁴</th>
<th>Impact velocity (km/s)</th>
<th>Shock pressure (GPa)</th>
<th>Shock temperature (K)</th>
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<tr>
<td>1 A</td>
<td>1.72</td>
<td>0.72</td>
<td>2.83</td>
<td>22.3</td>
<td>2628</td>
<td></td>
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<tr>
<td>2 A</td>
<td>1.35</td>
<td>0.57</td>
<td>3.37</td>
<td>22.1</td>
<td>5215</td>
<td></td>
</tr>
<tr>
<td>3 A</td>
<td>1.73</td>
<td>0.73</td>
<td>3.07</td>
<td>25.4</td>
<td>2968</td>
<td></td>
</tr>
<tr>
<td>4 A</td>
<td>2.10</td>
<td>0.88</td>
<td>3.21</td>
<td>32.0</td>
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</tr>
<tr>
<td>5 B</td>
<td>2.18</td>
<td>0.91</td>
<td>2.83</td>
<td>29.7</td>
<td>1438</td>
<td></td>
</tr>
</tbody>
</table>

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a Sample A: CaCO₃ (2 g) + Mg (1 g). Sample B: CaCO₃ (2 g) + Mg (1 g) + NH₄NO₃ (0.2 g).
b ρ₀ is the theoretical density of materials.
disappeared, only multilayer graphene could be observed, and the number of graphitic layers in multilayer graphene decreased. In addition, monolayer graphene was observed under the optimized shock conditions of 32 GPa and 1956 K (No. 4 test). By adding ammonium nitrate as a doping agent, NG was formed in one step under similar loading conditions.

Typical TEM images of No. 4 sample are presented in Fig. 2. The result reveals the presence of very thin extended films, which are curved and loose (Fig. 2a). Depending on the number of graphitic layers, the graphene materials can be distinguished as monolayer, double-layer, or multilayer (less than about 10) graphene. High-resolution TEM images of the samples (Fig. 2b–d) clearly demonstrate the presence of monolayer, double-layer, and multi-layer graphene (three to six) with an interlayer distance of approximately 0.3–0.4 nm. Unlike most graphene films of symmetric hexagonal diffraction patterns [27], the electron diffraction patterns (selected area electron diffraction, SAED) of films (inset of Fig. 2a) show a ring-like diffraction pattern with dispersed bright spots. The difference observed here indicates the possible existence of rotational stacking faults in the matrix graphene sheets, which is in accordance with the results observed in few-layer graphene [28]. The four spots in each segment of the diffraction circle in Fig. S2(a) can be attributed to each of the four graphene sheets parallel to each other and rotated through 4–20° in succession about the c axis.

Typical TEM images of shock-synthesized NG in the No. 5 samples are presented in Fig. 3. As observed in Fig. 3a, the transparent membrane exhibits a morphology resembling large crumpled paper, demonstrating that the membrane is flexible. The monolayer, double layer, and multilayer (three to four) can also be observed in Fig. 3b–d. The SAED reveals that the shock-synthesized NG exhibits a typical hexagonal crystalline structure, allowing us to label the peaks with Miller–Bravais indices [27]. For multilayer graphene with AB stacking, the intensity ratio of the {100} and {110} diffraction spots is <1 [26]. The {110} spots appear to be more intense than the {100} spots (see Fig. S3 in the Supporting Information). Almost all objects in most images are identified as multilayer with a ratio of \( I_{100} / I_{110} < 1 \).

The Raman spectra of the shock-synthesized samples are presented in Fig. 4. All of the Raman spectra contain three obvious peaks at 1335, 1585, and 2665 cm\(^{-1}\), corresponding to the D, G, and 2D bands of the sp\(^2\) carbon phase. The G band originates from the stretching vibrations in the basal plane of the carbon sp\(^2\) atoms. The D band arises from the vibration of the defects, disorder, and doping in the hexagonal basal planes of the graphitic layers [29]. The 2D band is the most prominent feature in the Raman spectra of graphene. Its shape and the \( I_{2D} / I_G \) intensity ratio are sensitive to the number of graphene layers [30]. The \( I_{2D} / I_G \) intensity ratio gradually changes with the number of layers. \( I_{2D} / I_G \) and the full width at half maximum for the 2D band (2D-FWHM) obtained from the Raman spectra of the shock-synthesized samples are listed in Table 2. The \( I_{2D} / I_G \) intensity ratio of all of the samples is larger than 1, and the full width at half maximum is lower than 60 cm\(^{-1}\), which is consistent with those of few-layer graphene obtained using conventional methods [31]. The 2D band is a sharp single peak in the case of monolayer graphene, whereas splitting is...
generated from either the phonon branches or the electronic bands in the case of double- or multilayer graphenes [32]. The experimental data (Fig. 5) show that the 2D band can be decomposed into four peaks (2L), providing strong evidence in favor of multilayer graphene as the major product.

Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>$I_D/I_G$</th>
<th>$I_{2D}/I_G$</th>
<th>2D-FWHM (cm(^{-1}))</th>
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<tbody>
<tr>
<td>2</td>
<td>0.6</td>
<td>1.43</td>
<td>41</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>1.14</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>1</td>
<td>51</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
<td>1.39</td>
<td>45</td>
</tr>
</tbody>
</table>

Fig. 3. TEM images of the No. 5 samples. TEM images of (a) typical films. The inset of (a) shows SEAD pattern. HRTEM images of (b) monolayer, (c) double layer, and (d) three to four layers.

Fig. 4. Raman spectra of shock-synthesized samples.

Fig. 5. Deconvolution of 2D bands of Raman spectra, in which the green lines denote the four Lorentzian peaks used to fit the data, and the red lines are the fitted results of recovered samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
The $I_{D}/I_{G}$ intensity ratio is widely used to assess the density of defects in graphite materials [30]. The D band of the No. 5 sample is rather uniform and close to the noise level, indicating that the NG retains its high crystalline quality. It is noted that the $I_{D}/I_{G}$ for all samples in this work is much larger than that for chemical vapor deposition (CVD)-grown graphene [15]. In addition, a weak disorder-induced feature at 1620 cm$^{-1}$ can also be observed in the Raman spectra of the shock-synthesized samples. Based on these results, we can conclude that shock loading cannot produce pristine graphene materials, but graphene materials with many defects are formed due to their extreme loading process. The shock-wave action generates high temperature, high pressure, and high strain rate. This extremely nonequilibrium process may induce considerable defects in shock-synthesized products. This has also been verified in shock-synthesized diamond and graphite [33].

The XRD patterns of the shock-synthesized samples are presented in Fig. 6. The (002) peak in XRD is the typical characteristic of synthesized samples, although the peak location may shift slightly [34]. Compared with the (002) peak at 26.2°–26.4° for shock-synthesized graphene materials, the (002) peak of shock-synthesized NG shifts slightly to 26.5°. Based on the position of the (002) diffraction peak, the d-spacing for the graphene materials and NG were calculated to be 0.337–0.339 and 0.336 nm, respectively. In fact, similar to the (100) peak, another peak also appeared in the region of 40°–45° (2θ), although it is too weak to see clearly in the presented patterns.

The elemental compositions of the shock-synthesized samples were analyzed using XPS. As observed in Fig. 7a, the XPS spectra of both graphene materials and NG contain a sharp graphitic C 1s peak at 284.8 eV, along with an O 1s peak at 532.4 eV possibly due to the adsorption of some oxygen [9]. The N 1s peak was observed in the NG sample, whereas the N 1s peak was absent in the nitrogen-free sample. The N/C atomic ratio of the NG sample was calculated to be 3.84% from the peak areas of C 1s and N 1s and their atomic sensitivity factor. By fitting the high-resolution N 1s spectrum of NG (Fig. 7b), both pyridinic-like (398.7-eV) and pyrrolic-like (400.4-eV) N atoms can be distinguished [13].

In the literature, N-doped carbon materials such as N-doped CNTs [35] and NG [12] have been shown to be promising metal-free electrocatalysts, replacing the commercially available Pt-based catalysts for the ORR. Shock-synthesized NG is also expected to possess electrocatalytic ability for the ORR. Fig. 8a presents the cyclic voltammograms (CVs) for O$_2$ reduction on the NG. Similar to commercial Pt/C (Fig. 8b), a well-defined cathodic peak is clearly observed in the O$_2$-saturated but not N$_2$-saturated KOH solution. The onset potential of the ORR is approximately −0.15 V with a reduction peak at approximately −0.25 V, which is comparable to CVD-synthesized NG [12], indicating the great catalytic ability of NG in ORR. To examine the selectivity of NG and Pt/C catalysts for the ORR, the methanol crossover test was performed in the current–time measurement. The shock-synthesized NG electrode exhibits a stable ORR without any electroactivity specific to methanol in the methanol-containing electrolyte, suggesting a remarkable tolerance to a possible crossover effect. However, the Pt/C catalyst exhibits a substantially large current for the oxidation of methanol, reflecting its low tolerance to the fuel crossover effect. The higher methanol tolerance of NG compared with that of Pt/C indicates that NG may function as a methanol-tolerant cathode in fuel cells. As a control, ORR tests on nitrogen-free graphene materials were performed in O$_2$-saturated KOH solution, which shows no obvious ORR electrocatalytic activity. Therefore, the observed electrocatalytic activity for NG could be exclusively attributed to the N-doping effect.

The linear sweep voltammetry (LSV) curves of the ORR for the NG in an O$_2$-saturated 0.1 M KOH solution measured on a rotating disk electrode are presented in Fig. 8c for different electrode rotation rates. The measured current density represents the typical increase with increasing rotation rate due to the enhanced diffusion of electrolys [36]. Based on the Koutecky–Levich equation [37], the number (n) of electrons transferred during the ORR is calculated to be 2.8–3.4 at potentials ranging from −0.4 to −0.6 V (see Fig. S4 in Supporting Information). These results indicate that oxygen reduction follows the two- to four-electron pathway mainly [38].

The durability of the catalysts and the long-term stability of the electrocatalytic activity for ORR are of prominent concern in fuel cells. As observed in Fig. 8d, no obvious decrease in the current was observed after continuous cycling for 2 days, indicating no loss of catalytic activity for the NG electrode. Its excellent catalytic stability for the ORR demonstrates that shock-synthesized NG could be used as a promising catalyst in the long term.

The decomposition of CaCO$_3$ under shock–wave loading can be divided into three stages [39,40]. CaCO$_3$ is stable during the shock-loading process (stage 1). The decomposition of CaCO$_3$ only occurs when the shock pressure is released (stage 2). CO$_2$ can easily recombine with CaO to form CaCO$_3$ when the temperature decreases (stage 3). The formation mechanisms of graphene under shock conditions are difficult to investigate due to the extremely rapid and nonequilibrium process. We speculate that the formation of graphene materials under shock loading experience a gas-phase condensation process, and this process can be illustrated in Fig. 9. A steel flyer is propelled to a high velocity by detonating an explosive, and the flyer impacts the sample container to generate shock waves in the samples, resulting in a high-pressure and high-temperature environment. Under the high pressure and high temperature, CaCO$_3$ decomposes into CO$_2$ and CaO, with a simultaneous reaction between CO$_2$ and Mg, leading to the formation of carbon atoms and MgO. The back reaction of CO$_2$ with CaO is also inhibited due to the presence of MgO [41]. The carbon atoms are deposited on the surface of metal oxides, followed by the nucleation and growth of graphene materials. With respect to the shock synthesis of NG, ammonium nitrate was broken to form active nitrogen during the shock loading. During the formation of graphene materials, the nitrogen atoms form a chemical bond with the carbon atoms, and nitrogen doping occurs. The equation for the chemical reaction can be written as follows:

\[2CaCO_3(s) + MgO(s) \rightarrow 2CaO(s) + CO_2(g) + Mg(CN)_2(s)\]

\[2CaCO_3(s) + MgO(s) \rightarrow 2CaO(s) + CO_2(g) + Mg(CN)_2(s)\]

The shock pressure and temperature are important factors affecting the synthesis of graphene materials. When the shock pressure and temperature are very low (No. 1 test, impact velocity 2.83 km/s), the shock waves cannot generate sufficient energy to
induce the decomposition of CaCO₃ and the corresponding reaction between CO₂ and Mg. Graphene materials and other carbon phases can only be formed under sufficiently high pressures and temperatures. The shock synthesis of graphene materials requires a balance between the growth rate of graphene materials and the formation rate of carbon atoms. A high shock temperature can increase the formation rate of carbon atoms, with a resulting increase in aggregation and stacking of carbon atoms, which favors the formation of graphite. In addition, the formed graphene may also roll up to form a CNT at high temperatures. In the No. 2 test with a high impact velocity of 3.37 km/s and a high shock temperature of 5215 K, graphite and nanotubes were formed in addition to multilayer graphene. By contrast, high pressure will reduce the formation rate of carbon atoms and the carbon deposition efficiency. In the No. 3 test with a high pressure of 32 GPa and a relatively low shock temperature of 2968 K, only multilayer graphene.

Fig. 7. XPS spectra of as-synthesized graphene and NG.

Fig. 8. CVs of (a) NG and (b) commercial Pt/C on a glassy carbon electrode in N₂- and O₂-saturated 0.1 M KOH. (c) RDE curves of the NG in O₂-saturated 0.1 M KOH for different speeds. (d) Electrochemical stability of the NG using continuous cyclic voltammetry in O₂-saturated 0.1 M KOH.
Fig. 9. Schematic illustration of shock synthesis of graphene materials.

was formed without the other carbon phases. Appropriate high shock pressures and low shock temperatures are favorable for the synthesis of fewer-layer graphene.

4. Conclusion

In this work, a facile shock-wave treatment was developed to synthesize multilayer graphene and NG, which provides a simple and novel synthesis route. The shock pressure and temperature are two important factors in the synthesis of graphene materials by affecting the formation rate of carbon. When the shock pressure and temperature are too low, the shock waves cannot generate sufficient energy to produce the carbon phase. An increase in pressure and temperature was observed to be favorable for the synthesis of carbon phases. Appropriate high pressure and low temperature are favorable for the synthesis of fewer-layer graphene. Shock-synthesized NG was observed to act as a metal-free electrocatalyst for oxygen reduction reaction, J. Power Sources 251 (2014) 363–369.

was formed without the other carbon phases. Appropriate high shock pressures and low shock temperatures are favorable for the synthesis of fewer-layer graphene.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2015.07.078.

References


