

Shock induced conversion of carbon dioxide to few layer graphene



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ABSTRACT

Using solid CO₂ (dry ice) as the carbon source, few layer graphene sheets were synthesized by reduction of CO₂ with calcium hydride under shock wave loading. In addition, by adding ammonium nitrate to the reaction system, nitrogen-doped graphene material was formed in this one-step shock treatment. The recovered samples were characterized using various techniques such as transmission electron microscopy, scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy, and therein the nitrogen-doped graphene was demonstrated to act as a metal-free electrode with an efficient electrocatalytic activity toward oxygen reduction reaction in alkaline solution. This work provides an innovative route for producing one of the most promising carbon nanostructures by employing CO₂ as a raw material which is popularly known as the greenhouse gas.

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1. Introduction

The rising demand for fossil fuels from increasing energy consumption results in emissions of vast quantities of carbon dioxide (CO₂) in the atmosphere. This rapid increase in the level of anthropogenic CO₂ is a matter of great concern associated with global warming and climate change [1]. Therefore, recent years have seen a significant growing international interest in both developing CO₂ capture/sequestration technologies and conversion of CO₂ into useful products to solve the global challenge [2,3]. As a readily available, low-cost, and sustainable molecule, CO₂ has been considered as a source of elemental carbon and several techniques have been proposed for carbon oxides conversion and processing, such as catalytic hydrogenation [4], electrochemical and photochemical reduction [5,6], combustion synthesis [7] and CVD [8]. However, efficient chemical conversion of CO₂ remains to be a difficult synthetic problem, since CO₂ molecules are extremely stable, which demand enormous energy and require the application of powerful catalysts capable of inducing its selective conversion into targeted products.

Among the chemical transformations of CO₂, attractive options

include reducing CO₂ to diamonds [9], C₆₀ [10] and nanotubes [11], while either through direct CO₂ splitting or via reaction with alkali and alkaline-earth metals subject to pressure higher than 700 atm for over 10 h. Considering the extreme energy consumption and reaction time, researchers have found that burning Mg or lithium in a solid CO₂ could result in MgO, Li₂O and carbon powder [12]. Recently, sodium borohydride and ammonia borane were used as CO₂ fixation agents at moderate conditions to fix carbon with consequent graphenization of the composite to form graphene oxide and boron oxide nanocomposites [13]. Most of those listed methods are, however, inefficient with low production rates due to the excessive gaseous CO₂ consumption and relatively high stability of carbon oxides molecules during the conversion process. Herein, we provide an innovative shock wave loading methodology that can instantaneously transform CO₂ into larger quantity of high crystalline few layer graphene and nitrogen doped graphene.

Shock wave action of high temperature, high pressure and high strain rate lasting for very short time ($\sim 10^{-6}$ s) will cause a series of catastrophic changes of chemical and physical properties of materials [14], and up to now, there has been considerable research activity in materials development using this process to realize synthesis and modification [15–19]. This unique process can not only induce chemical reactions between the different elements, but also generate high pressure which may form a supercritical reaction environment in the order of microseconds. Shock wave synthesis combining shock-induced decomposition and chemical

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reaction may be a new method for the utilization of CO₂ via converting dry ice to useful carbon nanostructures. In an earlier study, we have reported the shock-induced synthesis of multilayer graphene and nitrogen-doped graphene from carbonate [20], which confirms that shock wave loading could act as a high-effective method for the synthesis and modification of carbon nano-materials. Accordingly, it is expected that graphene material might be obtained by employing CO₂ as a raw material under shock wave action.

2. Experiment

In this study, solid form CO₂ (dry ice), calcium hydride (CaH₂) and ammonium nitrate (NH₄NO₃) were used as the carbon source, reductant and nitrogen doping source, respectively. A mixture of CO₂ and CaH₂ with a molar ratio of 1:1 was used in the synthesis of few layer graphene nanosheets and 10 mol% NH₄NO₃ was added in the mixture for the synthesis of nitrogen doped graphene.

A scheme of shock synthesis of graphene material from CO₂ is illustrated in Fig. 1. By detonating the plane-wave lens initiated by an electronic detonator, a planar detonation wave propagates through the main charge RDX (C₃H₆N₆O₆). Then the steel flyer attached to the explosives is propelled to a high velocity in a range of 1–3 km s⁻¹ using various masses of explosive. The high velocity flyer impacted the sample container to generate shock-wave compression, resulting in a high-pressure and high-temperature environment in the samples. There occurs an instantaneous reaction between CO₂ and CaH₂, leading to the formation of graphene and CaO materials in a very short time. The calculation of the shock pressures and temperatures can be found in details in our previous work [20]. The shock temperature was estimated using the Hugoniot data [21] of the mixtures of CO₂ and CaH₂, and the shock pressure was estimated using the impedance-matching methods [22]. Herein, flyer velocities of 1.75 and 1.67 km s⁻¹ are selected and the experimental conditions are shown in Table 1.

After the shock loading, the recovered container was cut open to remove the sample. To remove the impurities in the sample, diluted hydrochloric 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) (JEM-2010) was used to examine the microstructure of the recovered samples at an accelerating voltage of 200 kV. Field emission scanning electron microscope (SEM) observations were performed on Hitachi S-4800 at an accelerating voltage of 15 kV. Raman spectra were recorded on a LabRAM Aramis Raman spectrometer with a He–Ne laser at an excitation wavelength of 633 nm. Nitrogen adsorption experiments were conducted at 77 K using a Quantachrome Autosorb-IQ-MP apparatus. Before adsorption measurements, the samples were degassed in vacuum at 473 K for 10 h. The pore size distribution and

the specific surface area (SSA) of the samples were obtained by Brunauer Emmett Teller (BET) analyses of their adsorption isotherms. Elemental analysis (EA) were carried out using Vario EL III (Elementar, Germany). Nitrogen doping was analyzed by an X-ray photoelectron spectrometry (XPS) (Thermo ESCA LAB 250).

Electrochemical measurements were conducted through oxygen reduction reaction (ORR) test using cyclic voltammetry (CV) and linear-sweep voltammetry (LSV) measurements in a three-electrode system. 4 mg N-Graphene was first ultrasonically dispersed in 1 ml ethanol with 50 μl of Nafion solution (5%), then the mixed suspensions (~10 μl) were attached onto a glass carbon (GC) electrode (ca. 0.25 cm²) as working electrode with the mass loading of 0.16 mg cm². Measurements on a rotating ring-disk electrode (RRDE) was carried out on a MSR electrode rotator (Pine Instrument) and the CHI 760D potentiostat. 0.1 M KOH was used as the electrolyte. A Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The commercial Pt/C catalyst (20 wt% platinum on carbon black) with the similar amount (~40 μg) was also studied for comparison. N₂ or O₂ was used to give the O₂-free or O₂-saturated electrolyte solution.

3. Results and discussion

The morphological and microstructural structures are investigated by SEM and TEM measurements. SEM observation of graphene sheets (Fig. 2a) reveals the existence of very thin extended films which is curved, loose and of micron scale, and the higher-magnification view (Fig. 2b) further confirms the presence of transparent graphene with wrinkles and folds. Typical TEM images of shock-synthesized graphene sheets and N-graphene are shown in Fig. 2c–g. The results reveal the presence of transparent membrane, which are curved and flexible (Fig. 2c,f). The rumpling may come from the growth process and the post-treatment process, which can also be observed in the graphene produced from carbonate under shock wave action [20]. High resolution TEM image reveal the thickness and detailed crystalline structure of the as-synthesized graphene sheets. As observed from Fig. 2d, e and g, the cross-sectional view of the suspended edge of the graphene sheets and N-graphene show only a few layers (typically, 1–4 layers) of graphene sheets. Adjacent interlayer distances in the graphene sheets are measured to be 0.3–0.4 nm, close to the d-spacing of (002) crystal plane (0.335 nm) of bulk graphite with slight distortion [23]. Meanwhile, the HRTEM images show highly crystalline interior, indicating a high degree of restructuring had occurred during the shock induced CO₂-CaH₂ reactions accompanied with high temperature and high pressure. The corresponding selected area electron diffraction (SAED) patterns further support the high crystallinity of shock-synthesized graphene sheets and N-graphene (inset of Fig. 2c and f). Like most graphene diffraction pattern of symmetric hexagonal diffraction patterns [24,25], electron diffraction of the shock recovered graphene sheets (inset of Fig. 2c) displays a typical hexagonal crystalline structure. However, the SAED pattern of N-graphene given in Fig. 2f shows a ring-like diffraction pattern with dispersed bright spots. The above observed difference indicates that the synthesized crystalline graphene sheets became partially disorientated in the N-graphene mainly due to the structural distortion caused by the interposition of nitrogen atoms into its graphitic planes, as also seen in N-doped carbon nanotubes [26].

Raman spectroscopy provides a quick and facile structural and quality characterization of carbon materials. As the Raman spectra shown in Fig. 3a, the synthesized graphene sample contain three obvious peaks at 1335, 1585, and 2663 cm⁻¹, corresponding to the D, G, and 2D bands of the sp² carbon phase. The D band arises from the vibration of the defects, disorder, and doping in the hexagonal

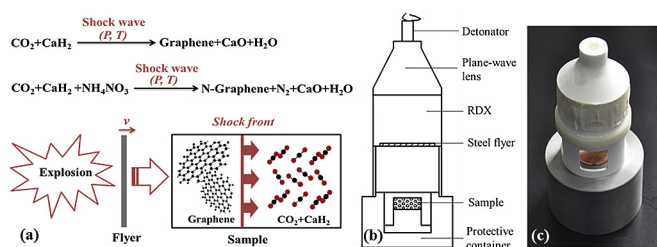


Fig. 1. Schematic representations: (a) Shock wave process for the synthesis of graphene material from dry ice. (b) Diagram of shock-loading apparatus. (c) Photo of real experimental setups. (A colour version of this figure can be viewed online.)

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