Laser induced self-propagating reduction and exfoliation of graphite oxide as an electrode material for supercapacitors

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ABSTRACT

Focused laser beam induced self-propagating reaction has been developed for fabrication of graphene rapidly and efficiently through simultaneous reduction and exfoliation of graphite oxide (GO) process. This chemical-free approach can realize the reduction and exfoliation at room temperature without assistance of any high temperature/vacuum environment. We found that the small sized spot can trigger an ultrafast and highly thermal transferred process by self-propagating reaction at ambient conditions. Benefiting from its high surface area and unique structure, the laser induced self-propagating reaction reduced graphene (LIG) shows excellent capacitive performance. Considering that the cost-effective and feasible process, this facile technique presented here will not only provide a promising method for production of graphene on an industrial scale, but also put forward the application graphene materials in energy storage and conversion.

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1. Introduction

Graphene, a two-dimensional sheet of sp^2 hybridized carbon with its exceptional physiochemical properties and promising applications, has aroused considerable interest in a wide range of fields since it was first synthesized by Andre Geim and Konstantin Novoselov through a facile micromechanical cleavage approach [1]. Until now, several different strategies including cleavage of graphite [2], epitaxial growth [3], chemical vapor deposition [4], organic synthesis [5], unzipping of carbon nanotubes [6], solution exfoliation of graphite powder [7], solution-based chemical oxidation-reduction [8], and arc discharge of graphite [9] have been put forward for the synthesis of graphene to fully exploit its fantastic properties. Among these reported techniques, solution-based chemical oxidation-reduction is one of the most attractive ways for large quantities production of graphene with respect to cost, procedure, layers and size issues [10–12]. Typically, graphene sheets with tunable structures can be produced in the presence of various reducing agents such as hydrazine hydrate [13], Fe powders [14], sodium borohydride [15], hydrohalic acid [16,17], and so on. The extra reducing agents, however, inevitably introduce a string of environmental and cost problems that are the major obstacles for

the development of this route [18]. Besides, graphene sheets usually suffer from irreversible agglomeration and restacking due to strong π-π interactions and van der Waals forces between neighboring sheets during solvent removal and chemical reduction process, resulting in a severely decreased surface area and therefore unsatisfactory performance of the fabricated devices [19].

In recent years, thermal exfoliation of graphite oxide (GO) has emerged as a promising approach for mass production of graphene on account of its fast speed within a few seconds to minutes and most importantly, avoiding uncontrollable aggregation in solvents [20–22]. The key points of this route are providing an ultrafast heating rate, meanwhile sufficient temperature and/or low pressure (<1 Pa) [20,23,24]. Nonetheless, the thermal treatment at high temperature and/or extremely low pressure with the rapid heating rate involves huge energy consumption and expensive to scale up for widespread commercialization. More recently, considerable attention has been paid to explore new method to produce graphene by further understanding the thermal behavior of GO. Laser, which is well-known with its monochromatic wavelength, small divergence and extremely high power density at the spot, has been gaining tremendous momentum as a powerful tools for fabrication of patterned graphene films [25]. The adsorbed energy converted onto local heat rapidly leads to intense heating, which effectively remove the oxygen-containing groups by thermal deoxygenating reactions [19–24]. There is no doubt that the use of lasers for GO reduction can eliminate the need for a reducing agent, which is

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a facile, chemical-free, room temperature process that made the scalable process for graphene synthesis feasible [25,26]. The Loh group employed a focused laser beam technique to construct an extended area of micropatterned GO and reduced GO multilayers on quartz substrates in a fast and controlled manner [27]. Xiao and co-workers also successfully developed a novel femtosecond laser nanowriting method to fabricate any desired micrometre sized graphene circuits on GO films [28]. Mukherjee et al. employed the laser writing process to produce free-standing graphene paper as high-rate capable anodes for lithium-ion batteries [29]. Elegantly, Kaner and colleagues developed light scribe DVD optical drive to do the direct laser reduction of GO films to graphene for electrochemical capacitors applications [30]. Several other groups also successfully applied laser to produce graphene by either irradiation of GO in solution or pattern GO films [31–33]. These encouraging results demonstrated exciting potential of the laser irradiation would be an ideal way to produce high quality graphene at fast manner. However, laser spot is quite small, it will inevitably take a long time to make every part of GO film to be exposed to laser beam to deoxygenation of GO [25–33]. Otherwise only patterned films are obtained. It would be highly desired if the energy from a small spot can transfer into the entire GO film effectively to deoxygenation and exfoliation of GO simultaneously. Furthermore, laser reduced GO mainly restricted in the form of thin films (typically in several GO layers) due to poor penetration depth, resulting in low productivity. In this regards, a dense GO flake should be used as precursor to realize laser reduction process for potential large scale production of graphene. To address these challenges, we developed a novel laser induced self-propagating reduction and exfoliation of GO to graphene in a facile manner. Instead of irradiation of the whole GO flake, the small size spot can trigger an ultrafast and highly thermal transferred process by self-propagating reaction. To the best of our knowledge, this is the first example of successful exfoliation and deoxygenation of GO simultaneously under ambient conditions without vacuum environment or any special atmosphere, which sheds new light for the bulk production of graphene. The laser induced self-propagating reaction reduced graphene (LIG) materials are of high specific surface area up to 520.086 $m^2\,g^{-1}$ based on BET analyses of N_2 adsorption–desorption method. Significantly, the as-prepared LIG exhibits outstanding capacitive behavior in terms of highly specific capacitance, good rate capability, and excellent cyclability as electrode materials for supercapacitors.

2. Experimental

2.1. Synthesis of LIG

All the chemicals were of analytical grade and were without further purification. GO was first synthesized through oxidation and exfoliation of graphite powder using an improved Hummers method as described previously [34]. The dialyzed GO suspension was freeze-drying, finally, GO foam was formed (Fig.S1). Afterward, a piece of GO foam was pressed at 0.2~0.5 MPa to form a relatively dense GO flake for the laser reduction experiment (Fig.S2).

The laser used in this work is a continuous wave semiconductor laser with wavelength of 808 nm and the output power can be adjusted between 0 and 2 W (Class IV laser product, **Cautions**: avoid eye/skin exposure to director scattered radiation!). The laser beam size is around 1.0 mm^2 after focusing. The laser beam is directed towards the quartz tube and using a focusing lens to obtain a small irradiation area. The distance between the focusing lens and the quartz tube is 3.5 cm. In a typical laser reduction experiment, the laser power was 1 W (the corresponding power density is about 127 $W\,cm^{-2}$, which is typically two orders larger than the previous reports), a GO flake was put onto the quartz tube directly at

ambient conditions, and the whole reaction process was very fast within 1 s upon laser irradiation. The reaction process can be seen from Video S1 (in supplementary data).

2.2. Characterization methods

The crystallographic structures of the pristine graphite, GO and graphene sheets were determined by a powder XRD system (XRD, TTR-III) equipped with Cu Ka radiation (λ = 0.15406 nm). Scanning electron microcopy (SEM) studies were carried on FEI, Quanta 200. The as-prepared graphene powder was directly attached to the aluminum holder by conductive tape for SEM characterization without gold/platinum coating. Note that for graphene oxide, a thin gold layer is sputtered onto the surface of the sample owing to its poor electric conductivity. The graphene sheets were also observed with a transmission electron microscope (TEM, JEOL JEM-1200EX) with an accelerating voltage of 100 kV. Graphene sheets samples were prepared by first dispersing the sample powder in ethanol by ultrasonic treatment, and then the dispersion was dropped onto a carbon coated copper grid, and dried in air for observation. X–ray photoelectron spectroscopy (XPS, X–ray monochromatisation, Thermon Scientific) was carried out with Al-Kα as the radiation source; the binding energies obtained in the XPS analysis were calibrated against the C 1s peak that was locked at 284.8 eV. The Curve fitting and quantitative analysis was performed with CASAXPS software after Shirley background subtraction. The peak areas were normalized with the theoretical cross-sections to obtain the relative surface elemental compositions. Raman spectra were obtained on an ALMEGA-TM Raman spectrometer (Therm Nicolet, USA) with 532 nm wavelength incident laser light. The N_2 adsorption–desorption isotherms of the samples were measured at 77 K in an ASAP 2020 (Micromeritics, USA) analyzer in order to determine the specific surface area. The sample was degassed at 100 °C for 10 h before measurement was performed. The specific surface area was calculated from the Brunauer–Emmett–Teller (BET) plot of nitrogen adsorption isotherm and pore size distribution of the samples was calculated from adsorption branch isotherms by Barrett–Joyner–Halenda (BJH) method. Thermogravimetric analysis (TG) study was performed on a Netzsch STA–409 PG/PC thermogravimetric analyzer (Germany). The TG curves were recorded in a dynamic N_2 atmosphere at a heating rate of 10 °C min^{-1} in the temperature range of 24–850 °C.

2.3. Preparation of electrodes and electrochemical measurement

The fabrication of working electrodes was carried out as follows: briefly, the as-prepared materials, acetylene black, and poly(tetrafluoroethylene) binder were mixed in a mass ratio of 80:10:10 and dispersed in ethanol with the assistance of ultrasonication for 15 min. Then the resulting slurry was rolled into a film with thickness approximately 60–80 μm and punched into 14 mm diameter electrodes. After dried at 80 °C for 10 h, the electrodes were weighted and pressed on to circular titanium mesh substrate. Then two electrodes with identical or very close masses were separated by a porous glass fiber film and were sandwiched in a CR2032-type coin cell. Before the cell was pressed to seal for electrochemical measurement, the working electrodes were soaked in 6 M KOH solution for 3 h under vacuum environment. Finally, the cell was aged for 12 h to further ensure good soakage of the electroactive material by the electrolyte [35]. For comparison, a commercially available, high surface area, activated carbon (AC, S_{BET} = 1800 $m^2\,g^{-1}$) based supercapacitor device was also assembled under same conditions.

Cyclic voltammetry (CV) tests were done between 0 and 1 V at the scan rate between 5 and 100 mV s^{-1}. The long-term