Laser-Induced Nitrogen-doped Graphene for High-Performance Flexible Supercapacitors

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***Abstract*—In recent years, with development of electronic devices in the direction of miniaturization, portability and multifunctionality, higher requirements are put forward for supercapacitors, including ultra-thinness, flexibility, high electrochemical performance, scale-up capability, and low cost. Among various electrode materials developed for supercapacitors, laser-induced graphene (LIG) is a promising material because of its simple operation, no mask, high efficiency and scalability. However, the electrochemical performance of LIG needs to be further improved. Here, a one-step method has reported for fabricating laser-induced nitrogen-doped graphene (LING) by using a laser direct writing technology. A three-dimensional (3D) structure of LING was obtained by engraving the surface of urea-containing polyimide (PI) film with a pulsed laser. Considering the synergistic effect of high concentration nitrogen doping and 3D porous structure, LING-based thin-film supercapacitor showed an ultra-high volumetric capacitance over 1260 mF/cm^3, much higher than that of LIG, and no significant attenuation was observed after 100,000 cycles. Moreover, this method could prepare conductive lines and patterns on a flexible substrate with high efficiency and is expected to become an alternative method for preparing existing circuits or energy storage devices.**

Keywords—laser-induced nitrogen-doped graphene, ultra-thin supercapacitor, flexible

I. Introduction

The rapid development of microelectronic devices towards miniaturization, portability, flexibility, and light-weight, requires flexible power devices to drive electronic units and microsensors [1]. Although the battery is a mature energy-storage device, it still has some limitations such as safety risks, moderate cycling life, and long charging times when used in a wearable device. Instead, flexible planar supercapacitors attracted more attention for wearable devices due to their advantages of small size, high energy density, fast charge/discharge capability, long cycle life, and size compatibility compared with rechargeable batteries [2].

In recent years, a large variety of electrode materials have been developed for planar supercapacitors, such as carbon materials [3], metal oxides [4], and conductive polymers [5]. Among them, graphene is the most promising material for its good electrical conductivity, excellent electrochemical performance, and mechanical flexibility. There are several methods for preparing graphene, such as mechanical exfoliation [6], chemical vapor deposition [7], and thermal reduction [8]. However, the aforementioned methods all involve multi-step processes for micro-supercapacitor fabrications, which undoubtedly increases the manufacture difficulty and fabrication cost of graphene-based planar supercapacitors. In recent years, the emergence of laser-induced graphene (LIG) has attracted widespread attention for its simple one-step process to fabricate electrode and active material. LIG featured with simple operation, no mask, high resolution, high efficiency, and low contaminations. It is highly suitable for the mass production of planar supercapacitors. There are lots of works that have been reported for performance enhancement of graphene-based planar supercapacitors [9, 10]. Among them, the introduction of heteroatoms was proven to be an effective method. Specifically, nitrogen atom doping can significantly influence the wettability on graphene surface, which can promote ion transfer between the nitrogen groups and the electrolytes [11].

In this work, a high-performance laser-induced nitrogen-doped graphene (LING) with three-dimensional (3D) porous structure was obtained following the laser direct writing process. The LING-SC showed a volumetric capacitance as high as 1260 mF/cm^3 at the condition of 10 mV/s, which is 1.8 times that of LIG. In addition, the effect of laser scanning speed on the performance of LING was further investigated. At a low laser scanning speed, LING will be excessively ablated; when at a high laser scanning speed, polyimide (PI) cannot be sufficiently induced to form graphite. The LING obtained under the most suitable processing conditions exhibits good flexibility and scalability and high volumetric capacitance. The high electrochemical performance LING manufactured using the one-step method can achieve large-scale production through roll-to-roll technology, which is promising for the application in wearable electronics.

II. Experimental

A. Fabrication of PI/Urea Films

Urea (99%, Shanghai Yuanye Bio-Technology Co., Ltd.) was added to the polyamic acid (PAA) solution (14 wt%) and then the uniform precursor solution was obtained by stirring for 24 h. The weight ratio of PAA to urea is 9:1. The mixture solution was cast onto glass and the coated film was dried at 80°C for 3 h. Next, the PAA/urea solid film was dehydrated at 150°C for 2 h to form the PI/urea film.

B. *Preparation and Packaging of LING based Supercapacitors*

Firstly, the conversion of PI/urea film to LING was achieved by using the laser direct writing method under different laser scanning speeds. In this work, the as-fabricated LING with a size of 10×10 mm^2, and the width and spacing of the integrated electrode were 300 μm and 200 μm, respectively. In addition, the control sample LIG was also prepared in the same way as LING. Next, sloid gel electrolyte was obtained by adding 1 g poly(vinyl alcohol) (PVA) and 2 g H_3PO_4 into 10 mL of deionized water and continuously stirring the mixture at 85 ºC for 2 h. Finally, the LING-SC was prepared by dropping PVA/H_3PO_4 gel electrolyte on the surface of LING and placed at room temperature overnight for removing excess water and using Kapton tape to protect LING-SC.

C. *Characterization and Measurements*

In order to investigate the morphology of LING, Scanning electron microscopy (SEM) was carried out by using an S4800 (HITACHI). The types and contents of elements in LING were obtained through X-ray photoelectron spectroscopy (XPS) tests, and the equipment used was ESCALABSB 250Xi. Furthermore, using the equipment LabRAM HR800 to study the defect information in LING through Raman spectroscopy. As for the electrochemical behavior of LING, the measurements including Cyclic voltammetry (CV) as well as galvanostatic charging/discharging (GCD) were carried out by using an electrochemical station (VMP3, Bio-Logic).

III. Results and Discussion

It can be clearly seen that each processing step of LING-SC fabrication from Fig. 1a. Firstly, the preparation process of the PI/urea film includes a drop-casting process, drying process, and imidization reaction. Secondly, as shown in Fig. 2b, the interdigitated electrode with 6 mm length was prepared through laser direct writing technology. Moreover, the width of the electrode is 300 μm and the electrode spacing is 200 μm (Fig. 2c). Finally, the LING-SCs were prepared by dropping the PVA/H_3PO_4 gel electrolyte on active areas as well as using Kapton tape as a protective layer. Large-scale preparation of planar supercapacitors has strict requirements on production efficiency and product performance. To this end, the electrochemical performances of samples under different laser scanning speeds were investigated, including 25 mm/s, 35 mm/s, 45 mm/s, 55 mm/s, and these samples were recorded as LING-25, LING-35, LING-45, and LING-55, respectively.

During the laser direct writing process, surface temperature of PI/urea film increased rapidly and local temperature was as high as 2,000 °C due to the photothermal effect, which resulted in the dissociation and carbonization of polymer molecules. Specifically, the atoms became excited at high temperature and then recombined as gases, including O_2, CO, CO_2, H_2, N_2 [12]. Finally, the remaining product is LING. Fig. 2a represents the typical morphology of LING after laser direct writing. The surface of LING is rough and uneven, and there are large lamellar structures. Fig. 2b is an SEM image of LING at high magnification. It can be seen that LING has numerous thin sheet structures and holes, which shows that NLIG has a 3D porous structure. This structure is conducive to the full contact of LING and the electrolyte, to achieve rapid ion transportation, and then give full play to the material properties of LING.

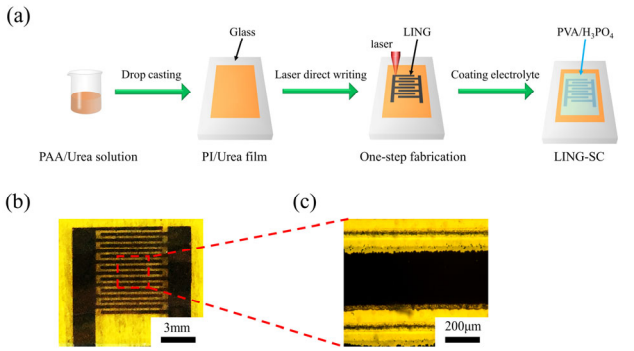

Fig. 1. (a) Fabrication process of LING. Optical photograph of LING-SC at low (b) and high (c) magnification.

Raman spectroscopy results can be seen in Fig. 2c, the peaks at 1326 cm^{-1} and 1580 cm^{-1} represent the D and G bands of LING [13]. By comparing the intensity values of the D-band and G-band peaks, the degree of defects in LING can be determined. The I_D/I_G values of LIG and LING are 1.36 and 1.60, respectively. This indicates that the degree of lattice defects and ion adsorption sites in LIG are increased by nitrogen doping, which helps to improve the electrolyte's wettability on the surface of LIG. XPS results (Fig. 2d) demonstrate that there are N1s peaks in both PI/urea film and LING, indicating the successful doping of nitrogen atoms. However, the N1s peak in LIG is negligible [13]. We also extracted the atomic percentage from the XPS data, in which the atomic percentage of N in PI/urea film is 5%, and 3.4% in LING. The N atomic percentage in LING was reduced because, during the laser direct writing process, part of the nitrogen atoms was converted into nitrogen and released into the air.

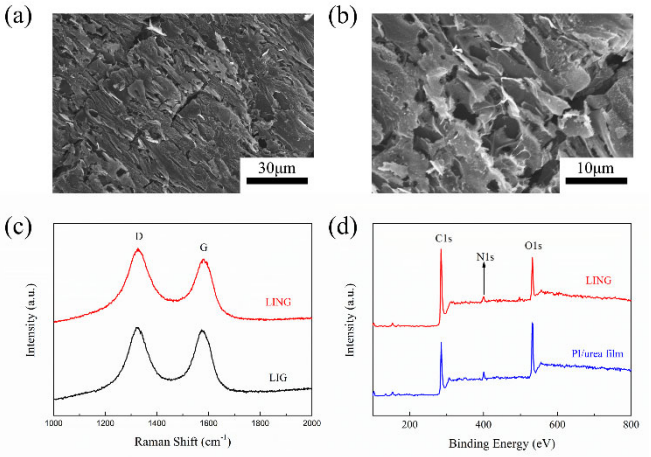

Fig. 2. SEM image of LING after laser direct writing at low (a) and high (b) magnification. (c) Raman spectrums of LING and LIG. (d) XPS spectra of LING.

After the preparation of LING was completed by one-step laser direct writing, PVA/H_3PO_4 gel electrolyte was added to the surface of LING and encapsulated with Kapton tape. The electrochemical test results of LING-SCs are in Fig. 3. More specifically, Fig. 3a demonstrates CV results of the symmetric supercapacitor NLIG-SC from 10 mV/s to 100 mV/s under the condition of -0.5 ~ 0.5V. And CV curves maintained a relatively rectangular shape at different scan rates, indicating the excellent charge/discharge performance of LING-SC. The volumetric capacitance of LING-25 and LIG calculated by the

CV curve were 1260 mF/cm^3 and 700 mF/cm^3 of each under the condition of 10 mV/s. Therefore, nitrogen doping can significantly improve the electrochemical performance of LIG. The GCD curves of LING-SC from 0.1 mA/cm^2 to 0.5 mA/cm^2 are shown in Fig. 3b and the ideal triangular shape of GCD curves illustrate the ideal capacitive behavior. Fig. 3c shows the curves of the volumetric capacitance of LING-SC with the scanning speed under different laser scanning speeds. Obviously, the volumetric capacitance of LING is higher than that of LIG. Also, the volumetric capacitance of LING increases first and then decreases when increasing laser scanning speed. This is because when at a low laser scanning speed, LING will be excessively ablated; when increasing laser scanning speed further, PI cannot be sufficiently induced to form graphene. As a result, the optimal laser scanning speed is 35 mm/s for LING to reach maximum performance. What's more, LING-SC exhibits excellent cycling stability, its capacitance retention rate as high as 92.1% after 100,000 cycles under 2,000 mV/s. As a conclusion, the electrochemical test results prove that LING has excellent performance, indicating that our one-step method can significantly improve the performance of LIG and it has a potential application for roll-to-roll mass production.

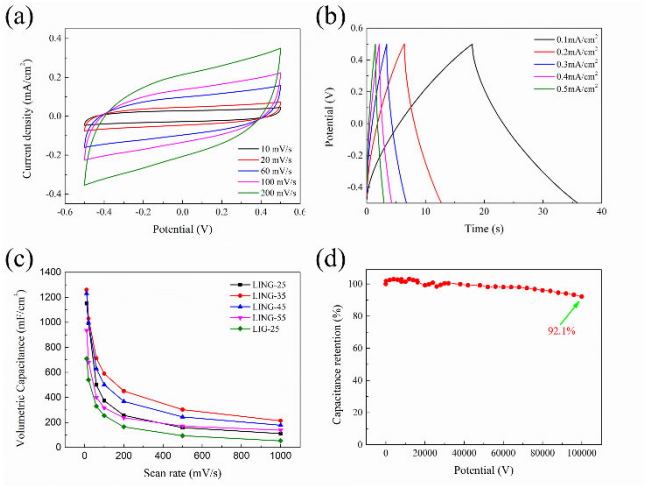

Fig. 3. CV (a) and GCD (b) results of LING-35 at different conditions. (c) The volumetric capacitance of LING-25, LING-35, LING-45, LING-55, LING-25 at different scan rates. (d) Cycling stability of LING-35.

IV. Conclusion

In a conclusion, we have reported an easy, one-step method for synthesizing LING and used for fabricating high-performance LING-SC. The LING-SC achieved a high volumetric capacitance of 1260 mF/cm^3 as well as excellent cycle stability that its capacitance retention rate reached 92.1% after 100,000 cycles, which is superior to traditional LIG-SC in term of cyclability. The reasons for the excellent performance of LING can be classified into the following two parts. On the one hand, the doping nitrogen atom can increase the number of defects in LIG, that is, add more ion adsorption sites, which promotes the ion transfer between LING and electrolyte. On the other hand, a 3D porous structure provides more specific areas and improves the contact area between LIG and electrolyte. Moreover, combining the one-step method and roll-to-roll fabrication, we look forward to achieving mass production for LING based devices. In the future, we believe that the high-performance LING featured with simple fabrication has a great potential application in energy-storage device for wearable electronics.

Acknowledgment

The authors thank the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01N111), Shenzhen Geim Graphene Center, Guangdong Province Science and Technology Department (Project No. 2015A030306010), and Shenzhen Government (Project Nos. JCYJ20170412171430026 & JSGG20170414143635496) for financial supports. This study is also partially supported by AME Individual Research Grant (Grant number: A1983c0026), Agency for Science, Technology, and Research (A*STAR) is appreciated.

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