Flexible ultrathin micro-supercapacitors based on laser-reduced graphene with superior electrochemical performance and aesthetic property

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***Abstract*—Supercapacitors with an outstanding electrochemical performance have emerged as a rapidly rising star on the horizon of energy storage devices and consumer electronics applications. With the rapid development of miniaturized and portable electronic technology, flexible ultrathin micro-supercapacitors have become more important than ever. The 2D network structure of graphene oxide (GO) with excellent mechanical and electrochemical performances has been reduced into reduced graphene oxide (rGO) by a pulse laser, which is a competitive candidate for the preparation of micro-planar supercapacitors. Micro-supercapacitors based on laser-reduced graphene with an ultrathin thickness of 20 μm exhibit a very high area capacitance up to 4.8 mF/cm^2 at a current density of 0.3 mA/cm^2 in LiCl-PVA gel electrolyte. Additionally, the energy storage device can possess a fantastic aesthetic property by virtue of the laser technology, which not only reveals the aesthetic art side of supercapacitors, but also provides a palette for the state-of-the-art micro-supercapacitors.**

Keywords—micro-supercapacitors; graphene; laser; aesthetic property

I. INTRODUCTION

Supercapacitors as a new type of energy storage device gradually play an indispensable role in industry owing to many intriguing characteristics, such as high power density, fast charge and discharge rate and long cycle life.[1-5] In order to adapt the trend of miniaturized and portable electronic components, more people have payed attentions to the planar micro-supercapacitors, which are advantageous in highly integrated electronic systems due to flexibility, lightweight, and small size.[6, 7] Additionally, a planar micro-supercapacitors whose diffusion length only depends on the electrode thickness can allow more active material loaded per unit area while maintaining excellent rate performance and capacitance, as compared with a sandwich structure of conventional supercapacitors.[8] What's more, the planar layout can lessen the total thickness of supercapacitor because of the elimination of separator, which exhibit great potential in microelectronic applications.

To date, graphene as a typical two-dimensional carbon material has been continuously compelling on account of the remarkable physical properties and promising applications in electrode materials for supercapacitor.[9] In addition, graphene with an ultrathin thickness showing relatively large surface areas and porous structure turns out to be an ideal active material for planar micro-supercapacitors. In the last few years, several approaches, such as micromechanical exfoliation of graphite[10], chemical vapor deposition[11, 12], thermal reduction[13, 14] and chemical reduction of GO to graphene (rGO)[15-19], have been developed. Recently, laser technology featured with extremely high directivity, high efficiency and concentrated energy distribution has been used to reduce GO into graphene, which is significant in miniaturized device fabrication. Owing to the rapid development of laser technology, we can realize laser patterning in various consumer electronics, showing not only excellent electrochemical performance, but also flexibility and shape versatility, which greatly highlights the aesthetic property of supercapacitors.[20-22]

Here, laser-reduced graphene based flexible ultrathin micro-supercapacitors (LRG-MS) with excellent electro-chemical performance and aesthetic characteristic are reported by a simple and scalable fabrication technology. Using electrostatic spraying technology, a GO layer was deposited on the current collector which a thin layer of nickel sputtered on a piece of poly(ethylene terephthalate) (PET) film. Via tuning the output power of laser, we can reduce GO thin layer into the laser-reduced graphene (LRG) and pattern various aesthetic geometries. In terms of packing process, the conventional stencil printing and the polyurethane (PU) based hot melt glue are employed to construct a cofferdam, a protective PET cover layer is applied for encapsulation. After that, LRG-MS with an ultrathin thickness of 20 μm exhibit a very high area capacitance up to 4.8 mF/cm^2 at a current density of 0.3 mA/cm^2 in LiCl-PVA gel electrolyte, which has a great potential for the production of state-of-the-art micro-supercapacitors with high electrochemical performance.

II. EXPERIMENTAL

A. Synthesis of GO and fabrication of nickel film

Graphene oxide (GO) powders were initially synthesized by a modified Hummers method[23], and then sonicated in deionized water for 2 h.

The nickel layer (thickness ~500 nm) was chosen as the current collector, which was sputtered on PET (6 μm thick) by magnetron sputtering at ambient temperature.

B. Fabrication of GO film

Using electrostatic spraying technology, GO solution and ethanol with a volume ratio of 1:1 as the precursor solution deposited on the current collector under 16 kV operating voltage with a injection speed of 0.5 mm/min at 50 ℃. Furthermore, in this process, we can obtain a uniform GO film with a certain thickness.

C. Fabrication of LRG-MS

A facile and scalable method was used in the fabrication of LRG-MS within two steps by laser technology (Han's Laser EP-15-DW, 355 nm, 20 μm). Briefly, the GO film was firstly reduced to LRG via laser scanning. And then the laser beam with more power was used to remove the LRG and nickel layer to form planar electrode arrays. In this work, the area of a single LRG-MS was 20 mm^2 which the width of integrated electrode and interspace were 80 μm and 100 μm, respectively, and these configurations can be easily modulated.

D. Materials characterizations and electrochemical measurements.

The morphologies of LRG and LRG-MS were characterized by scanning electron microscopy (SEM, ZEISS SUPRA 55, 5 kV, Germany). Fourier transformation infrared spectroscopy (FTIR, Nicolet iS50R, U.S.) and Raman spectroscopy (LabRAM HR800, HORIBA Jobin Yvon, Japan) were used to study the structural information of the samples.

Electrochemical tests were performed on an electrochemical station (VMP3, Bio-Logic, France) with a two-electrode configuration. Cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS) of the as-prepared samples were investigated, respectively. The applied potential window of CV and GCD was in the range from 0 V to 0.9 V with LiCl-PVA gel electrolyte. The EIS study was conducted in the frequency range between 100 KHz and 0.01 Hz with an amplitude of 5 mV at an open-circuit potential. The areal capacitance (CS), volumetric capacitance (CV), and the energy and power density (E and P) of micro-supercapacitor were calculated by the equations as follows:

$$C_S = \frac{I \cdot \Delta t}{\Delta U \cdot S} \quad (1)$$

$$C_V = \frac{I \cdot \Delta t}{\Delta U \cdot V} \quad (2)$$

$$E = \frac{C_V \cdot (\Delta U)^2}{2 \cdot 3600} \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

Where I is the applied current, Δt is the discharging time, ΔU is the operating voltage window, S and V are the total area and volume of LRG-MS respectively.

III. RESULTS AND DISCUSSION

The uniform GO film was loaded in a conductive substrate (PET film sputtered with Ni layer) via electrostatic spraying technology.[24] Subsequently, LRG-MS was fabricated within two steps by laser scanning technique, which rendered the reduction of GO to LRG and the etching of LRG and nickel layer, respectively. By adjusting the laser power, a series of planar electrode arrays with various patterns were fabricated effectively, which not only revealed superior electrochemical performance, but also emerged a fantastic aesthetic property of supercapacitors.

The formation of LRG was confirmed by FTIR and Raman characterizations, as shown in Fig. 1. The FTIR spectrum of GO shows a broad peak at around 3300 cm^{-1}, which is associated with the hydroxyl groups. The strong peak at approximately 1570 cm^{-1} is attributed to the stretching vibrations from carbonyl and carboxylic groups. And the peaks at 1370 cm^{-1} and 1050 cm^{-1} correspond to O-H bending in tertiary alcohol groups and C-O stretching vibration. After the laser reduction, the intensity of the characteristic peaks related to oxygen-containing functional groups were significantly reduced, especially the broad band at about 3300 cm^{-1}, which indicated that GO has been reduced into LRG effectively. Besides, the intensity ratio of I_D/I_G increased from 1.01 to 1.07 after the laser reduction showed in Raman spectra (Fig. 1a), demonstrating the randomness and conjugated domains of graphene have increased due to the high reduction degree of the laser processing.

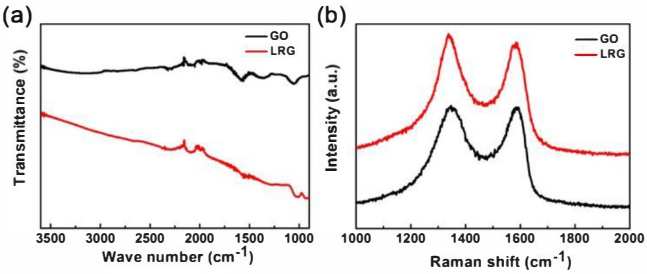

Fig.1 (a) FTIR spectrum of GO and LRG; (b) Raman spectrum of GO and LRG.

During the laser reduction, it involves not only photo-thermal reduction pathway but also photochemical pathway contributed to form an exfoliated and porous structure, as shown in Fig. 2a. Additionally, the as-prepared LRG possessed a vertical morphology with a thickness of approximately 5 μm, which enabled the ions easier to access the internal LRG network and provided fast transport channels for ions, as displayed in the cross-view SEM image (Fig. 2b). Based on laser processing technique, LRG electrode arrays were fabricated on a large scale and the planar electrode configurations could be easily modulated by altering the width and interspace of the electrode (Fig. 2c). As shown in Fig. 2d (dark: LRG electrodes, bright: ablated

bare PET surface), the sample changed from gray to black after laser reduction and the area of a single LRG-MS was 20 mm^2.

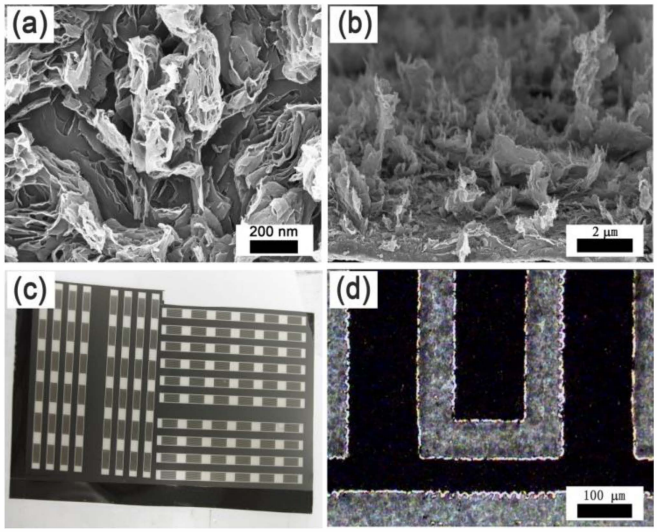

Fig.2 (a) High magnification SEM image of LRG. (b) Cross-view SEM image of LRG. (c) Photographic image of LRG-MS arrays. (d) Optical microscopic image of the electrode arrays.

After laser processing, the as-prepared LRG electrode arrays employed the conventional stencil printing combining with hot-melt binder (polyurethane) for encapsulation. To evaluate the electrochemical performance of LRG-MS, CV, GCD and EIS analyses were used. As shown in Fig. 3, The LRG-MS with LiCl-PVA gel electrolyte showed superior capacitive characteristic and rate performance. A series of CV curves under different scan rate ranging from 100 mV/s to 2000 mV/s are displayed in Fig. 3a. The shape of the CV curves exhibited nearly a symmetric rectangle at different scan rates, indicating excellent typical double layer capacitive characteristic and ultrahigh rate performance. It may be attributed to the vertical morphology and well-expanded and exfoliated structure of LRG, which can promote the ion transport efficiently. The GCD curves at different current densities exhibited nearly an ideal triangle shape, as shown in Fig. 3b. The IR drop calculated from the GCD curve under 0.3 mA/cm^2 was only 0.004 V, suggesting a low equivalent series resistance. The areal capacitance was up to 4.8 mF/cm^2 at a current density of 0.3 mA/cm^2, which was much higher than any other reported micro-supercapacitors. hat's more, the capacitance retention of LRG-MS still remained 80.4% after 20,000 cycles at 1000 mV/s scan rate, indicating excellent cycling stability. In Fig. 3d, the Nyquist plot of the sample was employed to evaluate the ionic mobility (Inset: magnified plot of the high-frequency region). The charge transfer resistance (R_{ct}) which caused by Faradic reactions and the double-layer capacitance on the grain surface was extremely low, indicating the good contact between nickel substrate and successful reduction of LRG. Moreover, the curve in low frequency which showed a more vertical curve in Nyquist plot represented faster ion mobility and a well capacitive behavior. Compared to some recently-reported planar supercapacitors,[25, 26] LRG-MS reveals a very high volumetric energy density up to 1.08 mWh/cm^3 at the power density of 272 mW/cm^3 in LiCl-PVA gel electrolyte. The superior electrochemical performances above can be ascribed to two aspects: 1) LRG-MS without the separator extremely minimizes the ion diffusion paths so that to improve the rate performance. 2) The vertical morphology and greatly expanded and exfoliated structure of LRG provide more surface area and promote the ion transport greatly.

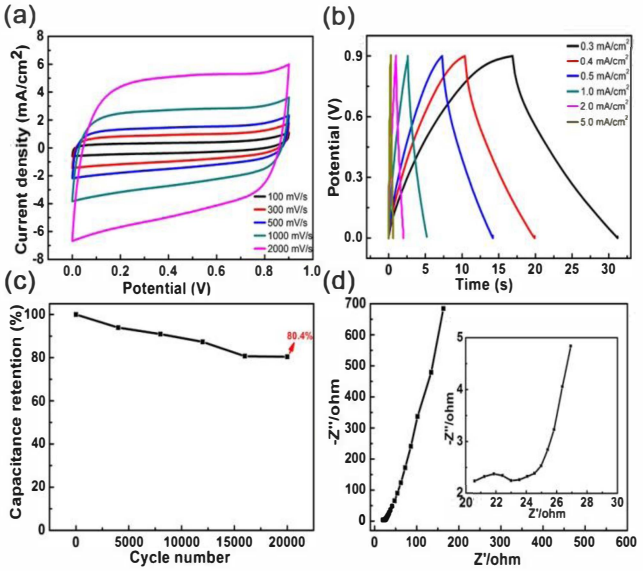

Fig.3 (a) CV curves of LRG-MS at different scan rates. (b) GCD curves of LRG-MS at different current densities. (c) Cycling stability of LRG-MS. (d) Nyquist plot of the EIS for LRG-MS. (Inset: magnified plot of the high-frequency region)

Based on laser processing technology, the energy storage device with a controllable shape or size can emerge a fantastic aesthetic property, as shown in Fig. 4 (light black substrate: GO film; bright black: LRG). Interestingly, the flexible electrodes can be designed as various words or letters, patterns and planar arrays, which can be encapsulated into supercapacitor with a sandwich structure or a planar layout to realize a magically visual and aesthetic property. Furthermore, it provides a versatile tool to design and fabricate the supercapacitor with a certain shape through a simple process and almost all electrode materials are available, which afford a great satisfaction for the applications of wearable, portable and flexible electronic devices. Hence, the flexible supercapacitors by virtue of the laser technology reveal not only superior electrochemical performance but also aesthetic property for a new era to meet the specific demand of the consumer electronics.[27]

Fig.4 photographic images of various designable electrode designs. (a) Words and letters. (b) Different kinds of patterns. (c) Planar electrode arrays.

IV. CONCLUSION

In summary, we successfully fabricated laser-reduced graphene based flexible ultrathin micro-supercapacitors (LRG-MS) by combining electrostatic spraying technology and laser processing technology. LRG-MS with an ultrathin thickness of 20 μm exhibit a very high area capacitance up to 4.8 mF/cm^2 at a current density of 0.3 mA/cm^2 in LiCl-PVA gel electrolyte. In addition, LRG-MS behaves an admirable cycling stability which remained 80.4% after 20,000 cycles at 1000 mV/s scan rate, and it reveals a very high volumetric energy density up to 1.08 mWh/cm^3 at the power density of 272 mW/cm^3. The outstanding electrochemical performances of LRG-MS is ascribed to the elimination of the separator and the unique open structure of LRG, which not only help to improve the rate performance, but also provide more surface area and benefit to a high mobility of the ions. Additionally, the energy storage device can exhibit a fantastic aesthetic property by virtue of the laser technology, which provides a versatile tool to design and fabricate the supercapacitor with a certain shape through a simple process and almost all electrode materials are available. Therefore, it may be a new trend for the consumer electronics both with superior electrochemical performance and aesthetic property, which may meet the specific demand for the wearable, portable and miniaturized devices.

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