Scalable Fabrication of All-Solid-State Supercapacitor Using Laser-Scribed Graphene

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ABSTRACT

Nowadays, Graphene is under intensive study for energy storage devices, such as battery and supercapacitors, due to its superior physical and electrochemical proprieties. The commercial methods to produce graphene are mechanical peeling, oxidation and reduction (ROX) and chemical vapor deposition (CVD), and so forth, but there is still a big challenge for mass production of graphene, and the restacking of graphene sheet impedes the application in preparing supercapacitors. In this paper we report a novelty method to fabricate all-solid-state supercapacitors using laser-scribed Graphene (LSG). Laser-scribed Graphene, which is directly reduced from graphene oxide (GO), seems to be a promising material for manufacturing solid-state, flexible transparent supercapacitors in large scale. In our work, PVA/LiCl-H_2O system is used for solid-state electrolyte, the supercapacitor reaches an area capacity ~2.1mF/cm^2 at 0.8mA/cm^2 with a good reversible ability and cycling performance.

Keywords: Supercapacitor, Laser-Scribed Graphene, Solid-State

1 INTRODUCTION

With the rapid growth of energy needs and depletion fossil fuels, more concerns have been given to energy storage for renewable wind, wave and solar power, and so forth [1]. The development of reliable and cost-effective energy storage devices has greatly satisfied raising energy demands for diverse applications, ranging from electrical vehicles to micro-chips, of which supercapacitors (SCs) have emerged as potential high-performance energy storage devices for long operation lifetimes, high power densities and environment-friendly operations [2-3]. Recently, flexible all-solid-state supercapacitors, in which solid or gel electrolytes have been used, are attracting more attentions due to their excellent performances in electrochemistry and mechanics, suitable for wearable and miniaturized electronic devices.[4] Flexible solid-state supercapacitors generally consist of flexible electrons, solid or gel-like electrolytes. Graphene is an ultra-thin graph-based material, serving as one of promising candidates of making flexible electrons of supercapacitors, benefiting from its outstanding properties, including large theoretic specific surface area (2630m^2/g), extraordinary conductivity (10^{6}s/cm), great flexibility and transparency [5-7]. An attractive approach for fabricating flexible electrons is coating or growing graphene on flexible, porous and light-weight substrates, another promising approach is to directly prepare free-standing graphene films and transfer on substrates. [4] However, there is a big challenge for both preparation methods in term of economy, efficiency and scalability, especially in planar and on-chip application. As such, we developed the method of using laser engraver to directly write graphene electrons onto Cu foil coated with a film of graphene oxide (GO), which can be reduced to graphene during the process[8]. In this scenario, the graphene reduced from graphene oxide (GO) via laser writing is called laser-scribed graphene (LSG), acting as electron and collector in the supercapacitor. Where as, hydrated graphene oxide (GO) is reported to be a good ionic conductor and an electronic insulator simultaneously, playing the roles of both separator and electrolyte in planar on-chip device. For sandwich-like devices, PVA/LiCl-H_2O system is used for solid-state electrolyte, owing to properties of low-cost, non-toxic, high ionic conductivity at ambient temperature, and excellent cycling stability [9]. The large problem of graphene electrons in supercapacitors (SCs) is restacking of graphene sheet, leading to serious degradation of their electrochemical performance. In our work, laser-scribed graphene (LSG) can effectively tackle the problems, with large specific surface area (1524m^2/g), high conductivity (1738s/cm) [10-11].

2 EXPERIMENTAL

Figure 1 shows the schematic of solid supercapacitor. Anode and cathode are made from same material, indicating it is symmetrical supercapacitor. Polymer gel electrolyte is used as separator between two electrons. Double-electric-lays is formed in the interface of electron and gel electrolyte to store electrons.

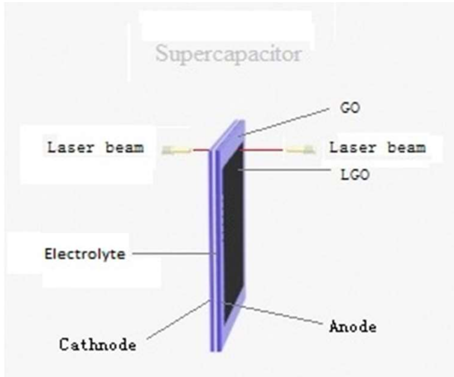

Figure 1: Schematics of fabrication of supercapacitor using laser-scribed graphene (LSG) and gel electrolyte

Figure 2: Preparation of Graphene electrodes for supercapacitors by laser

Fabrication of electrons for supercapacitor. Graphene Oxide (GO) was synthesized using a modified Hummer's method, dispersed in aqueous solution with the concentration (2.0 mg/ml). A piece of Cu foil (2cm x2cm) was glued to the surface of glass as substrate. An appropriate volume of graphene oxide (GO) solution was drop cast on Cu foil and allowed to dry overnight at room condition. As shown in Figure 2, a commercial laser engraver with a laser head (wavelength: 405nm and power energy: 200mw) was employed to pattern electrons on Cu foil coated with Graphene Oxide (GO) film. This laser scribing process converts golden-brown insulting GO into black conductive laser-scribed Graphene [12]. This scenario was repeated for several time, ensuring proper thickness of LGO on electrons.

Preparation of LiCl/PVA gel electrolyte. The LiCl/PVA-H_2O system was synthesized according to procedure report in previous literature [13]. A mount of 1g of polyvinyl alcohol (PVA) powder was dissolved in 20 ml of distilled water at 85℃ with vigorous stirring. After it became transparent, 1g of LiCl was added into the solution, and it was kept stirring until LiCl powder was completely dissolved. The solution was cooled at room temperature, forming a homogeneous and sticky gel.

Assembly of supercapacitor device. The gel electrolyte solution was dropped onto the laser-scribed graphene electrons formerly prepared, and dried under ambient condition. After being totally dried, two pieces of electrodes were assembled together in parallel, with solid electrolyte membrane in the middle. The sandwich-like supercapacitor device was further dried at 40℃ in an electric oven for 24h. Finally, the device was sealed in insulating foil, preventing its gel electrolyte from absorbing moisture.

Electrochemical Characterization. The electrochemical performance of as-fabricated supercapacitors were measured in a two electrodes system by Cyclic voltammograms CV and galvanostatic CD at an electrochemical workstation (CHI 760E). Electrochemical impedance measurements was performed in the same configuration. The cycling stability of the graphene supercapacitor was performed at room temperature with a sweep charge and discharge rate.

3 RESULTS

We fabricated a symmetrical all-solid-state supercapacitor based on graphene reduced form GO. Three Electrochemical testing were performed to evaluate its performance.

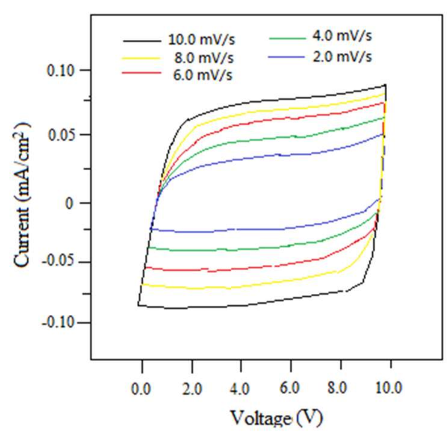

Figure 3: Cyclic voltammograms (CV) curves of the device at different scan rate

In Figure 3, CV profiles at different scan rate exhibit ideal symmetry, and near square in shape, indicating high reversibility on the surface of electrode, also verifying its good double electrical layer supercapacitor behavior. With the increasing of scan rate, the area enclosed between positive and reverse scan curves increases.

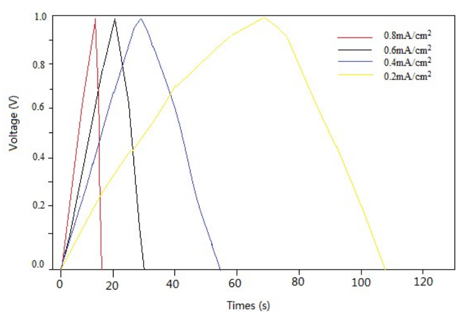

Figure 4：Galvanostatic charge-discharge (CD) curves of the supercapacitor at different current density.

PLA/LiCl-H_2O system is used as a gel electrolyte for supercapacitor. Mostly, for aqueous system, voltage window is under 1.0V. We observed voltage window of our devices was 0.0-0.8V. Galvanostatic DC curves at a collection of current density are showed in Figure 4. The symmetry of charge-discharge peaks provide evidence of reversible ability of the device.

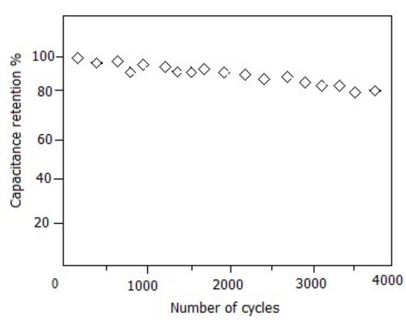

Figure 5: Performance durability test at a current density (0.8mA/cm^2)

Theoretically, a solid-state supercapacitor with gel electrolyte has better cycling performance than supercapacitor with liquid electrolyte, as there is less opportunity for electrode dissolved in electrolyte during charging and discharging cycle. Proven in Figure 5, capacitance remains 80% after 4000 cycles.

4 DISCUSSION

In our preliminary work, graphene is synthesized form graphene oxide by laser reduction. The laser-scribed graphene (LSG) have better mechanical prosperities than graphene flake from other source. The unreduced graphene oxide (GO) inserting between LSG flakes successfully prevent the restacking of graphene sheets, which leading to significant degradation of its performance. Additionally, gel electrolyte can stabilize LSG on electrode, increasing its cycling stability. Moreover, the laser beam can directly “print” electrode on graphene oxide (GO) film in any shape as designed. In planar system, graphene oxide (GO) between electrodes works as separator and electrolyte, both sandwich-like and planar devices can be fabricated in this scenario.

5 CONCLUSION

In conclusion, supercapacitors made with laser-scribed graphene electrode and gel electrolyte have acceptable performance in term of area capacity, voltage range, and cycling properties. Take advantage of their “green”, no leakage, flexibility, ease in manufacturing, we anticipate they will be next generation supercapacitors for wearable and miniaturized electronic devices.

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