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Original Research article

Preparation of Graphene/Graphene Oxide Microsupercapacitor by Using Laser-Scribed Method

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ABSTRACT

Graphene is a flat layer of carbon atom, and is a layer of graphite with a thickness of a few tenths of a nanometer that, due to its porous structure and high ionic transfer rate, has been considered in electronic applications, such as cloud storage capacitors with high energy. In this research work, laser-scribed technique has been regarded to synthesize graphene on the surface of a DVD with simples laser equipment and manufacture graphene and graphene composite supercapacitors for the first time without masking. For this purpose, first, by Hummer's method, graphite was converted to graphene oxide (GO) in an acidic environment containing sodium nitrate, potassium permanganate and sulfuric acid. Centrifuges and ultrasonic devices were utilized for the homogenization of graphene oxide solution. GO homogeneous solution was applied on the surface of specific DVDs and the set was dried at room temperature. For GO reduction and its transformation into graphene, a suitable laser, with programming of supercapacitor particular pattern was used. By applying energy with the amount of resonance frequency of graphene and oxygen bond, the laser broke the connection and the reduction in action and reaching to graphene was done. Thus, the optimal wavelength of laser was determined to reduce the GO. In this study, the process of graphene synthesis and applying the supercapacitor specific pattern were carried out in single step that is the biggest advantage of laser-scribed graphene (LSG) method. In present study, TEM was utilized to examine the mono layered structure of GO, SEM was used for microstructural studies of prepared arrays, two tests of cyclic voltammetry (CV) and galvanostatic charge/discharge (CC) were applied to study the performance and power of energy storage in supercapacitors (10 F/g) that six order higher than normal G supercapacitors with repeatability 95% in 10000 cycles, the XPS was used to investigate elements present in the layer applied on DVD, and the Raman spectroscopy was applied to investigate the quality of prepared graphene through studying G and D peaks.

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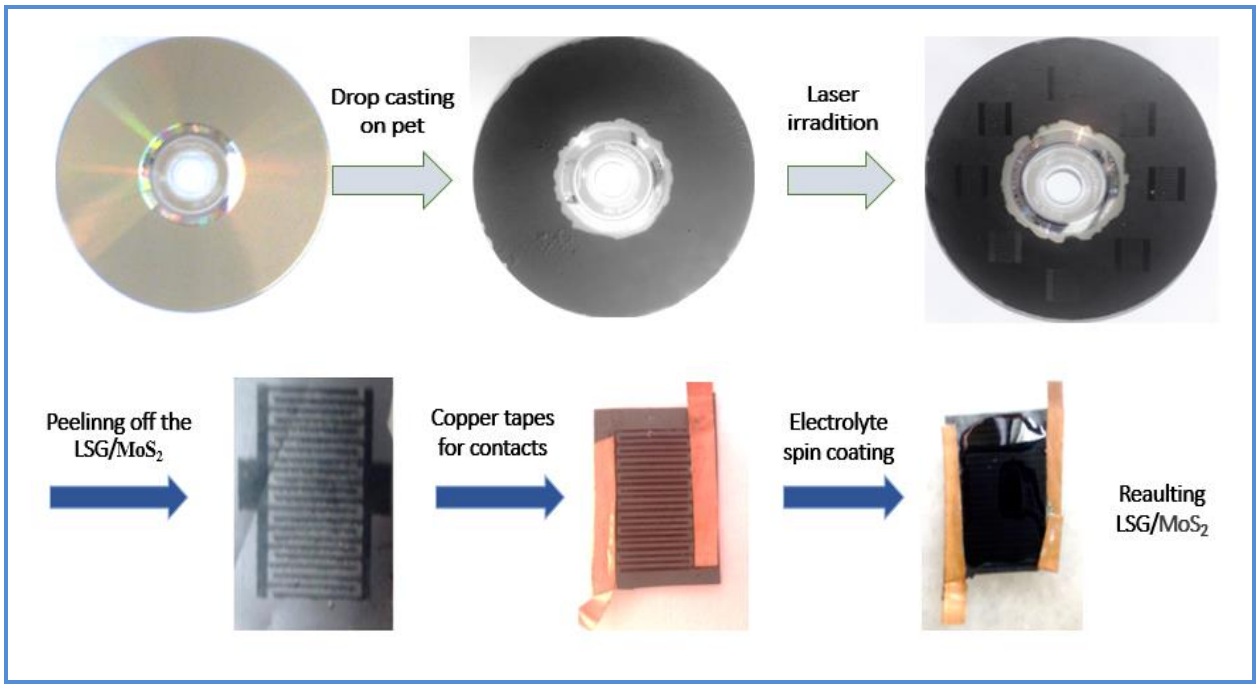
Graphical Abstract



Introduction

Nowadays, an increasing use of portable electronic devices can be seen in industrial and experimental applications, medical equipment and even daily used cell phones and laptops in which the power storage and power durability is a must have specification of all these devices [1, 2]. Miniaturized power storage devices are applied in these devices, where batteries and supercapacitors are the most used ones. Fast charge and discharge beside long cycle life and high power density are the three properties to make supercapacitors attract more attention than batteries [3, 4]. Carbon based materials play important role in manufacturing supercapacitor electrodes and have been heavily investigated [5]. Graphene, a 2D allotrope of carbon, possesses unique electrical and mechanical properties such as outstanding electrical conductivity, very high theoretical surface area of 2630 m^2/g, promising flexibility and tensile strength of 130 GPa. Thus, graphene nano-flakes are believed to be suitably applicable in supercapacitor and other energy storage devices [6-9]. The drawback of using graphene, however, is its restacking tendency after exposure to electrolyte [10].

It has been observed that production of graphene derivatives such as graphene oxide (GO) are more convenient than graphene sheets [12]. GO can be chemically [13], or thermally [14], reduced to form graphene. The reduced graphene oxide will contain numerous defect sites, which are favorable for electrochemical applications [15]. A recently invented method of reducing graphene

oxide by Kady et al., shows promising advantages over conventional techniques for energy storage applications. They use commercially available light-scribe DVD burner drivers to convert graphene oxide (GO) into reduced graphene oxide (rGO). The IR laser diode of the optical driver irradiates laser beam with a wavelength of 780 nm, which forces oxygen atoms to leave the graphene oxide structure. The resultant reduced graphene oxide called LSG (light-scribe graphene) is highly defective so that it possesses excellent performance as a supercapacitor [16].

By controlling the laser beam it is possible to pattern desired features on the graphene oxide [17, 18]. Kady et al., used this technique to fabricate interdigitated electrodes showing them as plausible candidates for flexible energy storage devices [19]. On the other hand, Tianet et al., facilitated LSG to build planar transistors, photodetector, load speakers and pressure and strain sensors concluding that wafer scale direct printing of graphene based devices can be achieved by light-scribe optical drives [20-23]. Electrochemical properties of LSG have been investigated by Griffiths et al. They take the advantage of highly effective surfaces of LSG's to fabricate working electrode with fastest heterogeneous electron transfer rate even in comparison with commercial ready edge plane pyrolytic graphite (EPPG) and basal plane pyrolytic graphite (BPPG), and illustrate that the LSG's fabrication method is inexpensive, scalable and compatible with disposable biosensor format [24].

Experimental

GO was prepared by the modified Hummers' method as reported elsewhere [10-25]. Briefly, 2 g graphite powders were added to a mixture of 1 g $NaNO_3$ and 46 mL H_2SO_4% and the mixture was cooled to 10 °C using an ice bath. In the next step, 6 g $KMnO_4$ was gradually added to the above solution and the reaction temperature was maintained below 20 °C. The mixture was then stirred at 35 °C for 2 h. The resulting solution was diluted by adding 92 mL of water until a dark brown suspension was obtained. Then, the solution was treated by adding 340 mL H_2O_2 solution. The resulting graphite oxide suspension was washed several times by 10% HCl aqueous solution and then by distilled water. Finally, a uniform suspension of GO nanosheets was obtained by adding water to the resulting precipitate and 12 h sonicating. The obtained slurry was centrifuged at 1,500 rpm for 45 min, and the top 1/2 supernatant was collected. The collected supernatant was further centrifuged at 3,000 rpm for another 45 min.

To produce a GO/DMF solution, GO was directly added to DMF at an initial concentration of 0.2 mg mL^{-1}, and then subjected to gentle sonication at 100 W for 60 min. The obtained GO/DMF solution was brilliant yellow, and could stand for weeks without obvious precipitates

The resulting suspension was uniformly drop cast on the laser-scribing DVD disk and then dried under air ambient. The GO coated DVD disk was placed in a simple light-scribe DVD drive with a wavelength of 780 nm and a spot size of 20 μm. To produce supercapacitor arrays without lithography process. The arrays irradiated by laser according to defined order that programed in matlab R 2016 a. The reduced composite was separated from DVD disk and was glued to the PET substrate. As prepared electrodes were wired out by copper wire using silver paste and the exposed areas of silver paste to electrolyte were passivated.

The electrochemical properties of GO/rGO supercapacitor working electrodes were evaluated in a three electrode system with platinum rod as counter electrode, a standard Ag/AgCl electrode as reference electrode and 0.5M KCL solution as electrolyte.

Cyclic voltammetry (CV) at different scan rates and galvanostatic charge-discharge at various current densities were carried out on a potentio/galvanostat system. The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 0.1 Hz to 100 kHz with 5 mV ac amplitude at open circuit potential. Furthermore, the laser-scribing process was utilized to pattern GO/rGO composite onto interdigitated electrodes for the fabrication of flexible micro supercapacitors. Copper tapes were glued to the patterned electrodes. The gel electrolyte for microsupercapacitor was composed of KCl and PAAK polymer. 2 g PAAK was added to 2 mL 0.5 M KCl solution under vigorous stirring, until a clear solution was obtained. A proper amount of gel electrolyte was dropped on the sample and then spin coated at 2000 rpm for 30 sec to create a uniform gel electrolyte surface. CV curves and galvanostatic charge and discharge profiles of GO/rGO based micro supercapacitor were taken between cut-off voltages of 0 and 1 V using the two electrode systems. Figure 1. illustrates the schematic representation of fabrication process for the flexible microsupercapacitor .

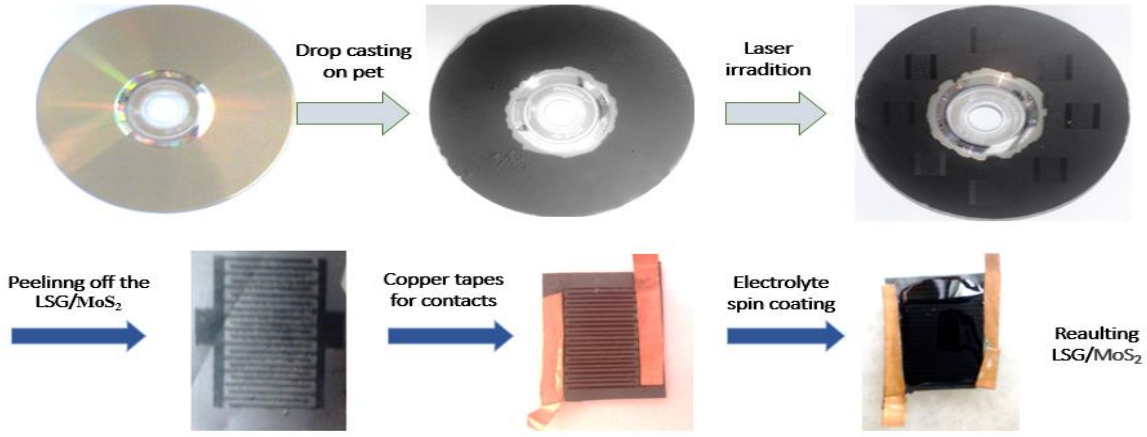


Figure 1. Schematic representation of flexible microsupercapacitor (LSG) fabrication

Result and Discussion

The Raman spectra of the GO and the LSG are shown in Figures 2a and 2b. As can be seen in the Figure 2, both the graphene oxide and the laser-scribed graphene exhibit typical disorder D bands at around 1350 cm^{-1}. Although, graphitic G bands and amorphous 2D bands existing at 1585 cm^{-1} and 2360 cm^{-1} can be found in both the GO and the LSG. Our LSG has a lower structural sp^3 defects as there is a slight decrease in relative intensity of ID/IG after laser scribing. This figure although presents the fact that few layers of graphene were generated after laser irradiation as can be deduced from the increase in relative intensity of 2D band [27].

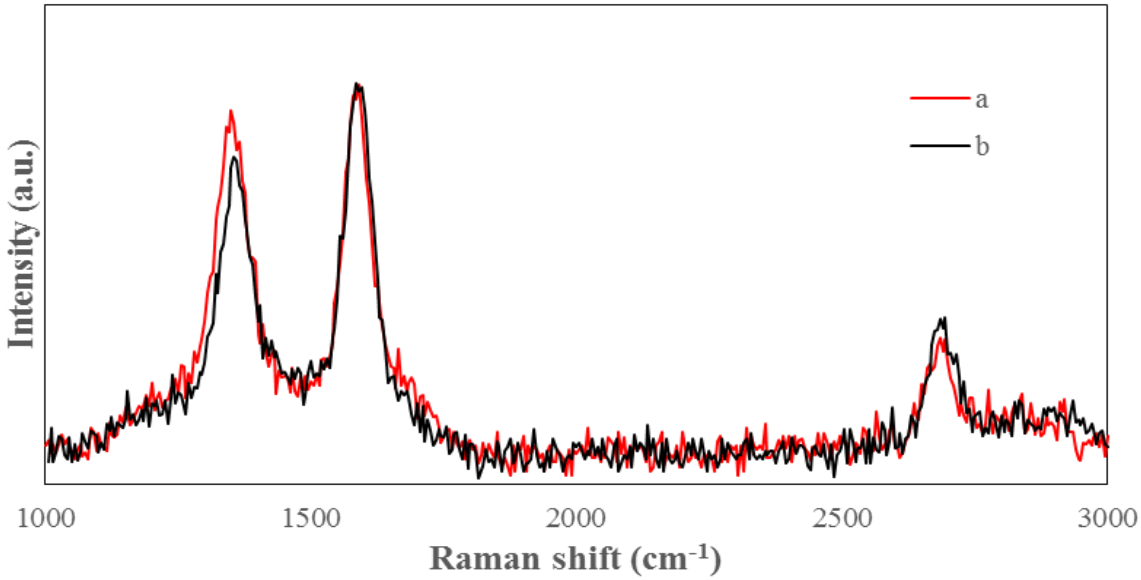


Figure 2. Raman spectra of graphene nanosheets, before (a) and after (b) laser irradiation

The comparison of bonding configuration of carbon and oxygen before and after the laser treatment of GO is presented through the following XPS study. Figure 3. shows XPS results of graphene oxide and laser-scribed graphene. Laser irradiation causing disappearance of the intense peak around 287 eV, which is attributed to sp3-type carbons, indicates that majority of carbonyl and hydroxyl groups were removed by laser irradiation [23, 24]. Another peak removed after laser irradiation was again around 287 eV, causing noticeable decrement in ratio of oxygen to carbon which indicates reduction of GO to rGO, followed by turning into rGO sheets.

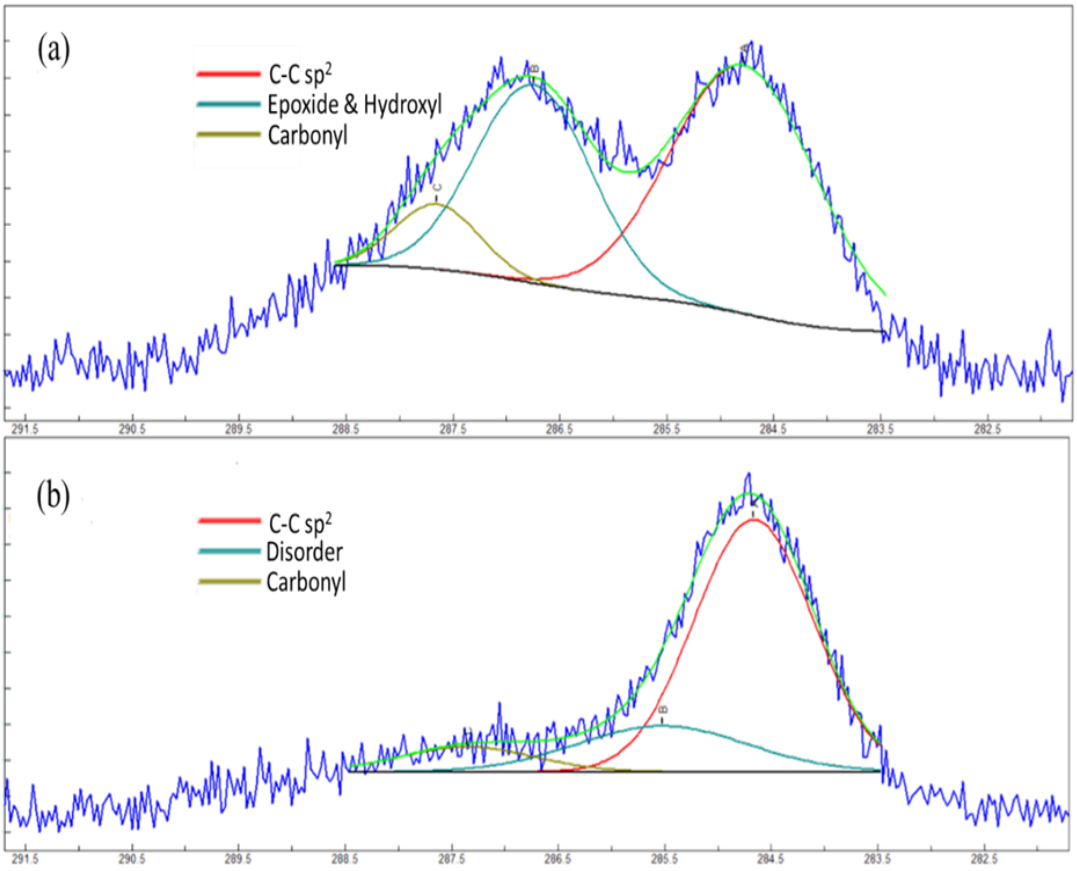


Figure 3. XPS results of graphene nanosheets, before (a) and after (b) laser irradiation

Figure 4. illustrates FESEM images of GO/rGO. The reduction of GO is clearly seen in (Figure 4) part (a). The size and density of rGO nano sheets are increased with increasing the laser's counts. The three dimensional shape of the GO/rGO multilayer has high useful surface.

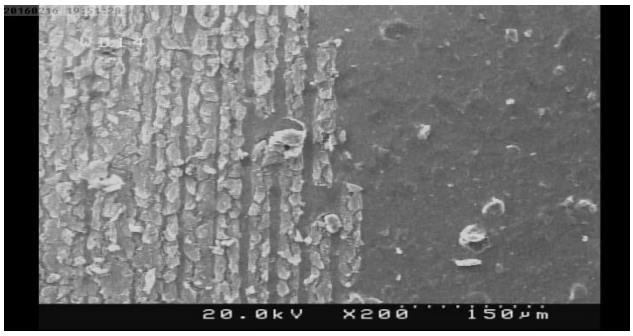


Figure 4. FESEM images of GO/rGO composites

To investigate the supercapacitance operation of GO/rGO composites with different mass ratios, their electrochemical properties have been investigated. For this aim, the CV curves of GO/rGO composites were taken between cut-off voltages of 0 and 1 V versus Ag/AgCl as a reference

electrode at different scan rates from 10 (mV/s) to 200 (mV/s) in electrochemical cell. These curves are gathered in Figure 5. as seen, the CV curves maintain nearly the rectangular shape, which refers to ideal capacitive behavior of EDLCs over the different scan rates from 10 (mV/s) to 200 (mV/s). It can be observed from this figure that the total currents increase with increasing the scan rates.

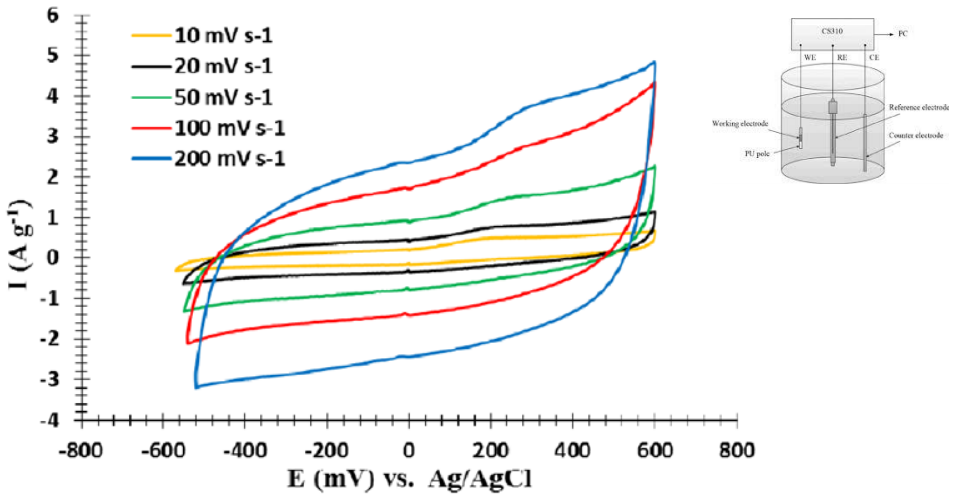


Figure 5. CV curves of GO/rGO composites at scan rate of 10, 20, 50, 100 and 200 mV/sec in a voltage range of 0 and 1000 mV in a three electrode system

For further investigations of proposed electrodes, the galvanostatic charge-discharge characteristic of five samples at different current densities are illustrated in Figure 6.

As shown in Figure 6, longer time is needed for discharging multilayer.

The specific capacitance of different electrodes can be calculated based on the following equation [27]:

$$Cm = (I \times \Delta t)/\Delta V \qquad \text{(eq.1)}$$

Where I refers to the discharge current density (A/cm^2), Δt is the discharge time, and ΔV is the discharge potential range (V).

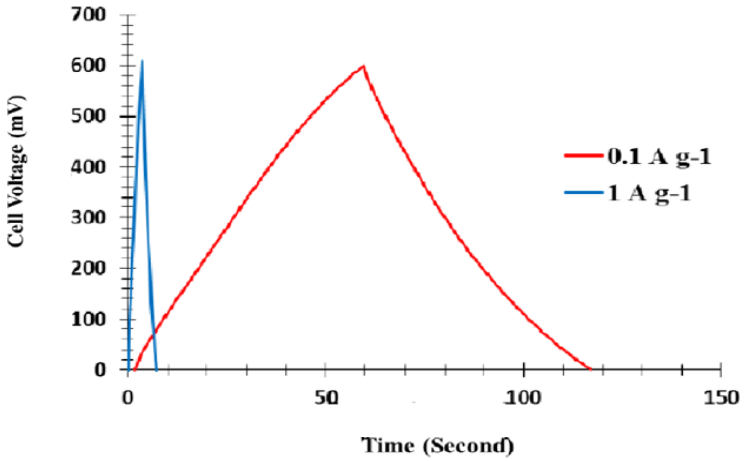


Figure 6. Charge discharge curves of GO/rGO composites at current density of 0.1, and 1 mA/cm2 in a voltage range of 0–1000 mV in a three electrode system

The long-term charge discharge stability of the GO/rGO composites were also investigated over 1000 cycles at a current density of 0.5 mA/cm^2 between cut-off voltages of 0 and 1 V versus Ag/AgCl reference electrode and are illustrated in Figure 7. It can be observed that the GO/rGO consequences in larger specific capacitance of the electrode, at the price of deterioration in capacity retention. However, even at the end of 1000th cycle, the specific capacitance of GO/rGo composite is about 10 F/g.

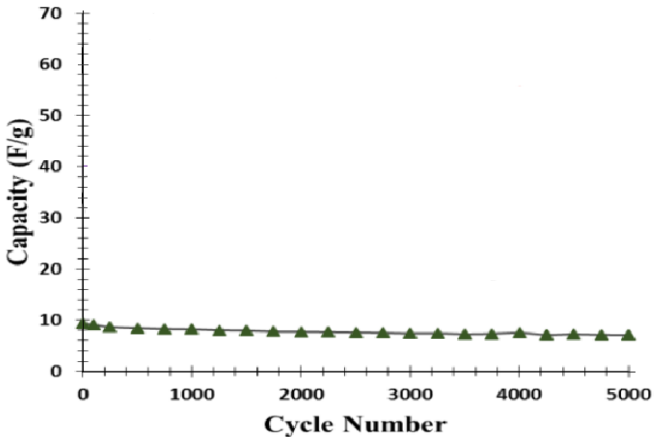


Figure 7. long-term charge discharge stability of GO/rGO composites at current density of 0.5 mA/cm2 in a voltage range of 0 and 1000 mV in a three electrode system

For this case, fabrication of laser-scribed micro supercapacitor electrode was accomplished which is illustrated in Figure 8. This micro supercapacitor is composed of 20 interdigitated electrodes of GO/rGO, separated by insulating spacers of GO/rGO.

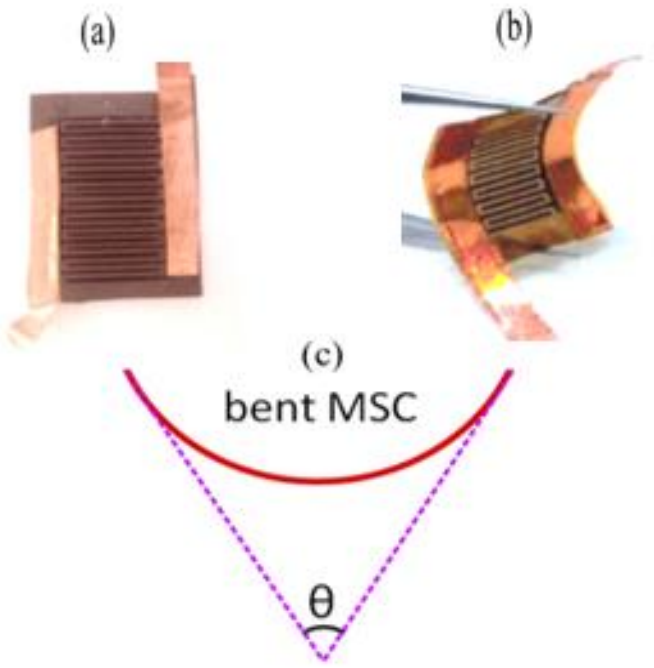


Figure 8. Optical image of GO/rGO electrode (a). An optical photograph showing the flexibility of the MSC electrode (b) and the bending angle representation for MSC electrode(c)

A comparison of the specific capacitance of LSG supercapacitors has been provided in Table 1. The cross section image of the LSG exposes a thickness of about 7 μm. The volumetric capacity of LSG multilayers was computed based on the areal capacitance and the cross section image. Our calculations offer that LSG micro supercapacitor has superior electrochemical properties rather than two previous works.

Table 1. Comparison of the specific capacitance of LSG supercapacitors produced by various methods

Electrode material	Specific capacitance (F/cm^3)	Reference
LSG	~2-3	[19]
LSG	~6	[26]
LSG	~10	This work

Conclusion

In summary, LSG multilayer was successfully obtained by laser irradiation of LSG on the DVD disk. Raman and XPS consequences confirm that the laser irradiation properly reduces GO to graphene sheets. Galvanostatic charge-discharge experiments, CV and EIS measurements were employed to characterize LSG composite as promising candidates for supercapacitor bulk electrodes and microsupercapacitors. The results prove that LSG flexible microsupercapacitors offer higher

specific capacity (10 F/g) and better capacity retention (95% in 10000 cycles) at both high and low current densities (0.1-1 A/g) than the reported graphene electrodes. In addition, the performance of these microsupercapacitors is still appropriate at different bending angles.

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