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RESEARCH PAPER

Fabrication of Graphene/MoS_2 Nanocomposite for Flexible Energy Storage

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ABSTRACT

In the present work, MoS_2 decorated graphene nano composite powders were synthesized by laser scribing method. The obtained flexible light-scribed graphene/MoS_2 composites are very suitable as micro-super capacitors and thus their performance was evaluated at different concentrations. The effect of laser scribing process to reduce graphene oxide (GO) was investigated. The GO/MoS_2 composite was synthesized using a chemical mixing of GO solution withMoS_2/Dim ethyl formamide (DMF) solution. The mixtures with various concentrations of MoS_2 were then coated on a Light Scribe DVD disk and laser scribed to reduce GO and create aMoS_2/laser-scribed graphene (LSG) composite. Four different concentrations of MoS_2/LSG composites (pristine rGO, 1:100, 1:75 and 1:50 MoS_2/LSG) were utilized as supercapacitor electrode and the electrode with the best performance was selected for flexible micro-supercapacitor applications. The present findings demonstrate that MoS_2/LSG micro-supercapacitor has high specific capacitance per area. The sample with MoS_2/LSG volume ratio of 1:50 shows the highest specific capacitance (~ 8 Fcm^{-3}) and its cyclic stability is favorable over 1000 cycles.

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INTRODUCTION

Supercapacitors are a category of electrochemical energy storage devices that to some extent have advantages of both batteries and capacitors. Nowadays, an increasing use of portable electronic devices can be seen in industrial and experimental applications, medical equipments and even daily used cell phones and laptops in which the power storage and power durability are the must-have specifications of all these devices [1-4]. Miniaturized power storage devices are used in these applications, among which batteries and supercapacitors are the most important. Fast charge and discharge beside long cycle life and high power density are three properties to which give the supercapacitors a great potential to complement or replace batteries [5-6]. Carbon based materials play serious role in manufacturing supercapacitor electrodes [7-8]. 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. Therefore, graphene nano-flakes are availed to be suitably applicable in supercapacitor and other energy storage devices [9-11].

It is known that the 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 (rGO) contains numerous defect sites, which are favorable for electrochemical applications [15]. Chen et al. reported that the specific capacitance per weight of graphene nano sheets could reach

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30.72 F g^{-1} at current density of 2 mA cm^{-2} [16]. In return graphene composites can significantly improve electrical conductivities, chemical stability and have large surface areas [17]. A Specific capacitance of 135.36 F g^{-1} at current density of 1 F g^{-1} has been reached for C60/ Graphene Composite supercapacitor by Ma et al [18]. Although an effort for a low-cost, high-performance supercapacitor for energy storage was carried out by yang, resulting in poly (safranine T)/reduced graphene oxide nanocomposite supercapacitor with a capacitance of 293.2 F g^{-1} at 20 mV s^{-1} [19]. A recently-invented method for reducing graphene oxide by El-Kady et al. [20] shows promising advantages over conventional techniques for energy storage applications. They used commercially available Light-scribe DVD burner drivers to convert GO into 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 laser-scribed graphene (LSG), is highly defective so that it possesses excellent performance as a supercapacitor [20].

By controlling the laser beam, it is possible to pattern desired features on the graphene oxide [21, 22]. El-Kady and Kaner [23] used this technique to fabricate inter digited electrodes, showing them as plausible candidates for flexible energy storage devices. On the other hand, Ian et al. [24-27] facilitated LSG to build planar transistors, photo detectors, 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. Electrochemical properties of LSG have been investigated by Griffiths et al.[28]. They took the advantage of highly-defective surfaces of LSG to fabricate a working electrode with the fastest heterogeneous electron transfer rate even in comparison with commercial edge plane pyrolytic graphite (EPPG) and basal plane pyrolytic graphite (BPPG), and illustrated that the LSG's fabrication method is inexpensive, scalable and compatible with disposable biosensor format[28]. CNT-graphene oxide mixture was laser treated by Wen et al. [29] to fabricate LSG/CNTs hybrid micro-supercapacitors. They studied the obtained devices based on the diameters of CNTs, reporting that LSG/CNT composite with smaller CNT dimension exhibited better energy storage performance.

Considering previous works in this field, we investigate the LSG-MoS_2 nanocomposite as a supercapacitor electrode with different concentrations of MoS_2 and compare their performance with each other. In this paper, the effect of laser scribing process for reduction of GO has been investigated. A mixture of MoS_2+LSG with different volume ratios (pristine rGO, 1:100, 1:75 and 1:50), as bulk electrode for super-capacitors has been used and the electrochemical properties of electrodes have been evaluated in a three electrode system.

MATERIALS AND METHODS

GO was prepared by the modified Hummers' method as reported elsewhere [10]. Briefly, 2g graphite powder was added to a mixture of 1g $NaNO_3$ and 46ml $H_2SO_4$and the mixture was cooled to 10 °C using an ice bath. In the next step, 6g $KMnO_4$ was gradually added to the 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 deionized water until a dark brown suspension was obtained. Then, the solution was treated by adding 340ml H_2O_2 solution. The resulting graphite oxide suspension was washed several times by 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 12h of sonication.

The exfoliated MoS_2 powderpurchased from Sigma-Aldrich was added toDi methyl formamide (DMF) at an initial concentration of 10 mg mL^{-1}, by centrifuging at 11,500 rpm for 60 min, and then subjected to sonication at 300 W for 60 min. The solution 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. The precipitated solid was collected and re-dispersed in DMF by sonication, yielding a dark green MoS_2/ DMFsolution (0.2 mg $mL^{-1)}$ containing relatively large MoS_2 nanosheets.

To produce a GO/DMF/MoS_2 solution, GO was directly added to DMF/$MoS_{2,}$ and then subjected to a gentle sonication at 100 W for 60 min. The obtained GO/DMF/MoS_2 solution was brilliant yellow in colour and could stand for weeks without any obvious precipitation.

The resulting suspensions were uniformly drop casted on a Light Scribe DVD disk and then dried under the air at an ambient temperature. The GO coated DVD disk was placed in a Light Scribe DVD drive with a wavelength of 780nm and a spot size of 20µm. The reduced composite was peeled off from the DVD disk and was glued to the polyethylene terephthalate (PET) substrate. The prepared electrodes were attached to copper wire using silver paste and the exposed areas of silver paste to electrolyte were passivated. Fig. 1 illustrates the schematic representation of fabrication process for the flexible micro-supercapacitor.

A R129348 Bruker Equinox 55 Fra 106/s spectrometer was used for Raman spectroscopy. The surface of electrodes was observed by FESEM (HITACHI S-4160). Cyclic voltammetry (CV) and galvanostatic charge/discharge (CC) techniques were employed to characterize the performance of LSG/MoS_2 composite with different mass ratios as a promising candidate for electrode materials for micro-supercapacitors. The electrochemical properties of MoS_2/rGO supercapacitor working electrodes were evaluated using a three-electrode system with platinum rod as a counter electrode, a standard Ag/AgCl electrode as a reference electrode and 0.5M KCl solution as an electrolyte. The CV at different scan rates and galvanostatic charge-discharge at various current densities were carried out on a potentio/galvanostat system (RNF 1224). The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 0.1 Hz to 100 kHz with 5mV ac amplitude at open circuit potential.

The laser scribing process was utilized to pattern MoS_2/rGO composite onto inter digitated electrodes for the fabrication of flexible micro-supercapacitors. Copper tapes were glued to the patterned electrodes. The gel electrolyte for micro-supercapacitor was composed of KCl and polyether ether ketone (PEEK) polymer. 2g PEEK was added to 2mL 0.5M 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 30sec to create a uniform gel electrolyte surface. The CV curves and CC profiles of MoS_2/rGO-based micro-supercapacitor were taken between cut-off voltages of 0 and 1 V, by using a two electrode system.

RESULTS AND DISCUSSION

Fig. 2 illustrates laser-scribed surface of graphene oxide, indicating how the laser scribe

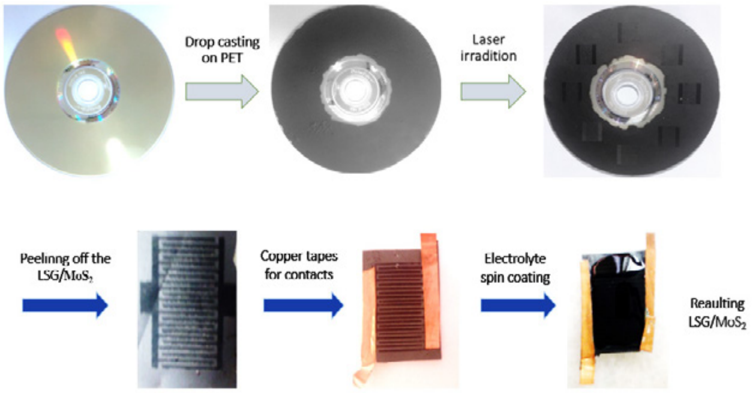

Fig. 1. Schematic representation of flexible micro-supercapacitor (LSG/MoS_2) fabrication.

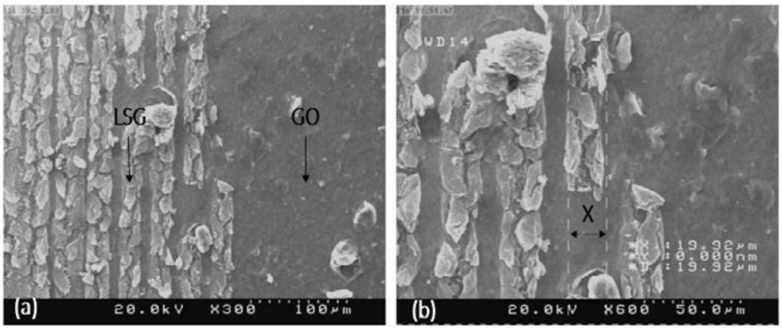

Fig. 2. SEM images of the laser scribed surface of graphene oxide at a low (a) and a high (b) magnification.

method works. Graphene synthesize and giving the supercapacitor pattern would occur simultaneously, which is considered the principal advantage of this method. Laser beam diameter is measured to be approximately 19.9 µm and the distance between adjacent scratches is about 4.6 µm.

Raman spectroscopy and XPS were used to evaluate the GO reduction during the laser-scribing method. The Raman spectra of GO and LSG are shown in Fig. 3. Both GO and LSG exhibit typical disorder D band at around 1350 cm^{-1}. Graphitic G band and amorphous 2D band existing at 1585 cm^{-1} and 2630 cm^{-1} can also be found in both GO and LSG. The present LSG has however a lower structural sp^3 defects as there is a slight increase in relative intensity of ID/IG after laser scribing[30,31].

The comparison of bonding configuration of carbon and oxygen before and after the laser treatment of GO is assessed through XPS, as shown in Fig. 4. The laser irradiation causing

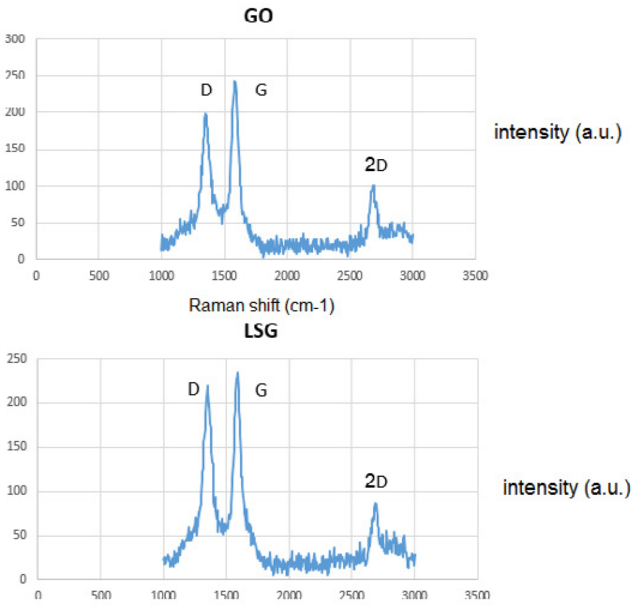

Fig. 3. Raman spectra of graphene oxide, GO and LSG.

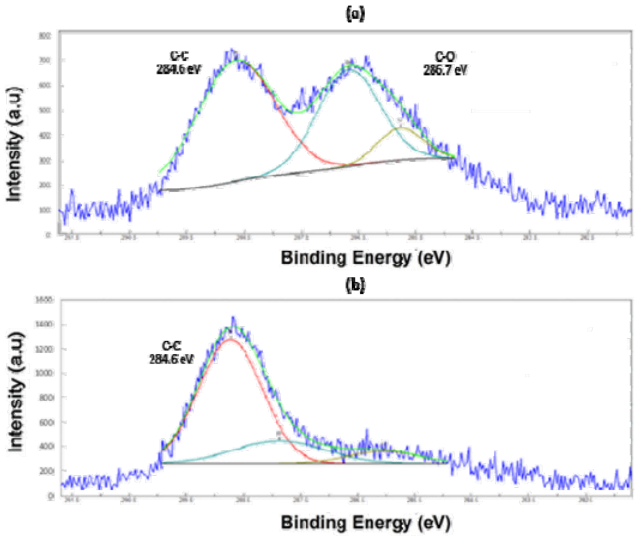

Fig. 4. XPS results of GO, before (a) and after (b) laser irradiation.

disappearance of the intense peak around 287eV, which is attributed to sp^3-type carbons, indicates that majority of carbonyl and hydroxyl groups were removed by laser irradiation [27, 28]. It causes noticeable decrement in the ratio of oxygen to carbon indicating the reduction of GO to rGO.

Fig. 5 illustrates FESEM images of rGO and MoS_2/rGO composites with three different volume ratios of MoS_2 to rGO (1:100, 1:75 and 1:50). The reduction of GO is clearly seen in Fig. 5 (a). In Fig. 5(b) through (d) the MoS_2 nano particles can be easily observed on the rGO sheets. The size and density of MoS_2 nano particles are increased with increasing the volume ratio of MoS_2 to rGO. Higher volume ratio of MoS_2 to rGO avoids the restacking of flakes more effectively, so it brings in easier ion transformation besides increasing the surface area of sheets. Thus, it is expected that the composite with the highest MoS_2 to rGO volume ratio have better electrical performance as a supercapacitor. The CV and CC analyses prove higher energy efficiency of MoS_2/rGO composites compared with the monolithic rGO. Similar results were obtained by HRTEM images. The EDX results shown that samples with Mo, S, and carbon components.

To investigate the supercapacitance characteristics of MoS_2/rGO composites with different volume ratios, their electrochemical properties have been investigated. For this purpose, the CV curves were taken between cut-off voltages of 0 and 1 V vs. Ag/AgCl reference electrode at different scan rates ranged from 10 to 200 mV s^{-1}. These curves are shown in Figs. 6 (a-d). Along with extension of current range, the

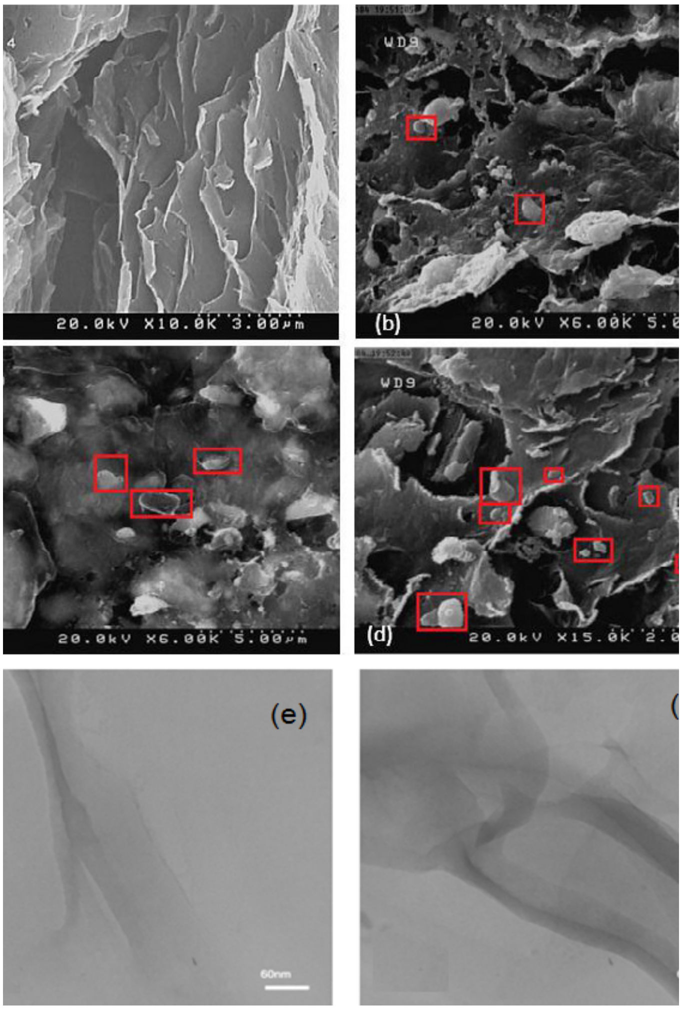

Fig. 5. FESEM images of pristine rGO (a) and MoS_2/rGO composites with MoS2 to rGO volume ratios of 1:100 (b), 1:75 (c) 1:50 (d) HRTEM image of rGO (e) and HRTEM image and EDX graph of MoS_2/rGO composites with MoS_2 to rGO volume ratios of 1:100respectively (f)

area of the curve increases which refers to the ideal capacitive behavior of electric double-layer capacitors)EDLCs(over the applied scan rates. It can be observed that the total currents increase with increasing the scan rates.

The specific capacitance (F g^{-1}) of different electrodes can be calculated based on the following equation [32]:

$$C_m = \frac{I \times \Delta t}{\Delta V} \qquad (1)$$

Where I refers to the discharge current density (A g^{-2}), Δt is the discharge time (s), and ΔV is the discharge potential range (V).

The galvanostatic CC curves of four samples at different current densities are illustrated in Fig. 7. It is clear that longer times are needed for discharging MoS_2/rGO composites with higher volume ratio of MoS_2 to rGO.

The long-term charge-discharge stability of the MoS_2/rGO composites with various volume ratios of MoS_2 to rGO are also investigated over 1000 cycles at a current density of 0.5 A g^{-1} between cut-off voltages of 0 and 1V vs. Ag/AgCl reference

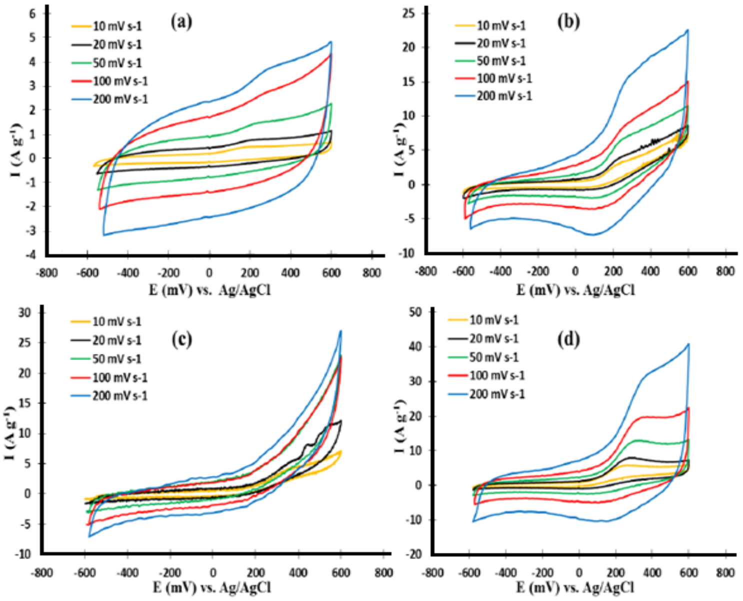

Fig. 6. The CV curves of pristine rGO (a) and MoS_2/rGO composites with MoS2 to rGO volume ratios of 1:100 (b), 1:75 (c) and 1:50 (d) at scan rate of 10, 20, 50, 100 and 200 mV s^{-1} in a voltage range of 600 and 600-mV in a three electrode system.

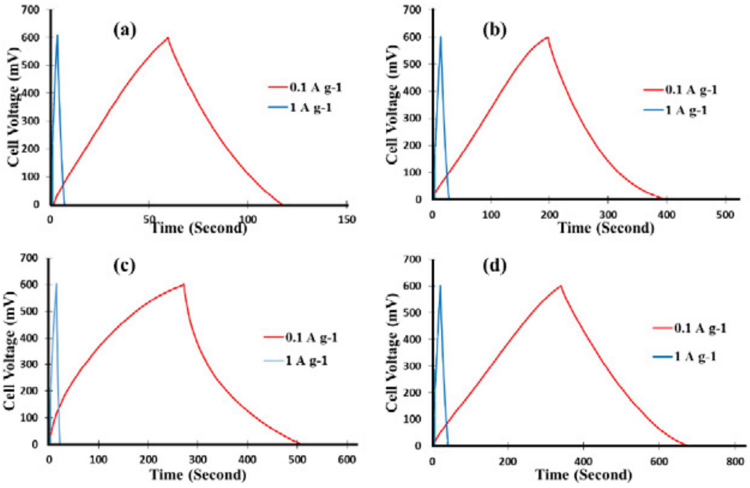

Fig. 7. Charge-discharge curves of pristine rGO (a) and MoS_2/rGO composites with MoS_2 to rGO volume ratios of 1:100 (b), 1:75 (c) and 1:50 (d) at current densities of 0.1and 1 A g^{-1} in a voltage range of 0 –600mV in a three electrode system.

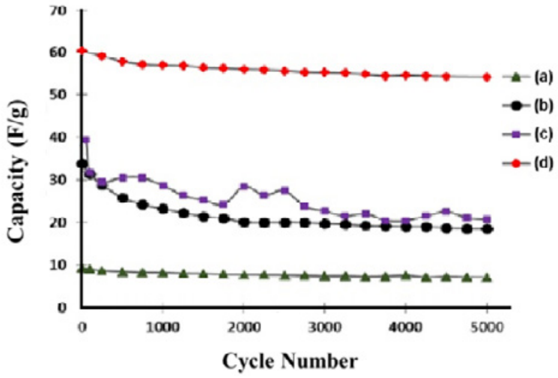

Fig. 8. The long-term charge-discharge stability of pristine rGO (a) and MoS$_2$/rGO composites with MoS$_2$ to rGO volume ratios of 1:100 (b), 1:75 (c) and 1:50 (d)at current density of 0.5 A g^{-1} in a voltage range of 0 and 1000mV in a three electrode system.

Fig. 9. (a) Optical image of MoS$_2$/rGO micro-supercapacitor electrode, (b) an optical photograph showing the flexibility of the MSC electrode.

Table 1. Comparison of the specific capacitance of LSG supercapacitors produced by various methods with the fabricated MSC in this work

Electrode material	Specific capacitance (Fcm^{-3})	Reference
LSG	~2-3	[19]
LSG/CNT	~6	[25]
LSG/MoS$_2$	~8	present work

electrode. The results are illustrated in Fig. 8. The addition of MoS$_2$ to rGO results in an increase in the specific capacitance of the electrode, at the price of a slight deterioration in capacity retention. However, even at the end of 1000th cycle, the specific capacitance of MoS$_2$/rGO composite with the 1:50volume ratio is about 6 times higher than pristine rGO.

In the sample with the highest MoS$_2$/rGO volume ratio of 1:50, the highest specific capacitance was obtained. Thus, the fabrication of laser-scribed micro-supercapacitor electrode was accomplished by using this composite. The fabricated MoS$_2$/rGO micro-supercapacitor electrode (Fig. 9) is composed of 20 inter digitated electrodes of MoS$_2$/rGO, which are separated from each other by insulating spacers of GO.

A comparison of the volumetric specific capacitance of the fabricated MoS$_2$/rGO MSC with 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/MoS$_2$ composite was computed based on the areal capacitance and the cross section image. Table.1 suggests that LSG/MoS$_2$ micro-supercapacitor has superior electrochemical properties in comparison to the pristine LSG and LSG/CNT composite.

CONCLUSIONS

In summary, LSG/MoS$_2$ composites were successfully processed by laser irradiation of graphene oxide and MoS$_2$ mixture on the DVD disks. Raman and XPS results confirm that the laser irradiation properly reduces GO to graphene sheets. As the sharp peak of 2D band in Raman spectrum presents, fabricated sheets have few layers. The performance of LSG/MoS$_2$ composite as promising candidates for supercapacitor bulk electrodes and micro-supercapacitors were confirmed by galvanostatic CC and CV experiments. Deduced from the long-term charge-discharge stability diagram, considering the 50 F g^{-3} increment in current density, the 5% decrease in current density after 1000 cycles for LSG/MoS_2 composite can be ignored since MoS_2 nanoparticles decrease the number of graphene layers, ion transformations will therefore be easier, surface area of sheets will increase and thus higher electrical quality will be achieved in this type of composite. The present results prove that LSG/MoS_2 flexible micro-supercapacitors offer higher specific capacity (8 Fcm^{-3})at both high and low current densities than pristine graphene electrodes (2-3 Fcm^{-3}).

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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