Electrochemical behaviour of ternary MoS$_2$/rGO heterostructure and PPyNTs nanocomposites for supercapacitor electrode

D Sarmah and A Kumar*

Material Research Laboratory, Department of Physics, Tezpur University, Napaam, Tezpur, Assam, India – 784028

*Email: ask@tezu.ernet.in

Abstract: Reduced graphene oxide (rGO) and molybdenum disulphide (MoS$_2$) are two dimensional materials used as charge storage electrode materials. MoS$_2$-rGO heterostructures have been synthesized by self-assembly of positively charged MoS$_2$ nanosheets with negatively charged graphene oxide (GO) nanosheets in varying ratios. GO was reduced by hydrothermal route without using any reducing agent. MoS$_2$-rGO heterostructures were synthesized in 3 different ratios of 1:2, 1:1, and 2:1. MoS$_2$-rGO/PPyNTs nanocomposite was prepared by adding 40 wt% of MoS$_2$-GO nanocomposite in pre-synthesized PPyNTs followed by hydrothermal reduction of GO. Structure and morphology of the nanocomposites were characterized by SEM, TEM, XRD, FTIR and TGA. Further, electrochemical properties of the nanocomposites were evaluated with cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). Capacitive response is found to be highest for the 1:1 MoS$_2$-rGO/PPyNTs/ITO electrode. 1:1 MoS$_2$-rGO/PPyNTs/ITO ternary electrode delivers enhanced specific capacitance of 1561 F g$^{-1}$ at 1 A g$^{-1}$ current density and specific capacitance of 786 F g$^{-1}$ (50% of capacitive retention) at 15 A g$^{-1}$ exhibiting an excellent rate performance. 1:1 MoS$_2$-rGO/PPyNTs/ITO ternary electrode exhibits 76% of cycling stability after 5,000 charge-discharge cycles at 10-fold of current density.

1. Introduction

Supercapacitors have been extensively studied for the last two decades owing to instant power delivery beyond rechargeable batteries and millions of fast sustainable charge-discharge cycles at higher current densities in order to store energy and minimize various environmental problems [1, 2]. The electrochemical supercapacitors consist of two current collectors with active material cathode and anode, separated by an electrolyte. The electrolyte can be either solid or liquid which separate the positive electrode from the negative one. Electrochemical supercapacitors are categorized in three different groups based on their charge storage mechanisms: (i) Electric double layer (EDL) capacitors, where capacitances are generated by the charges accumulated in the electrode/electrolyte interfaces, (ii) pseudocapacitors, corresponding to fast reversible redox reactions, and (iii) hybrid supercapacitors. In hybrid supercapacitors, both the physical and chemical charge transfer processes are responsible for charge storage. The charge storage capacity and cycle life of electrochemical supercapacitors (ES) depend on the properties of electrode materials. RuO$_2$ supercapacitors in H$_2$SO$_4$ aqueous electrolyte almost show the ideal capacitive responses with appreciable cycling stability [3]. Carbon materials are
famous as an EDLC source for ES electrodes, where charges are accumulated at the interface between the electrode and electrolyte. Activated carbon [4], carbon nanotubes [5], carbon aerogel [6], carbon nanofibre [7], graphene [8] are some of examples of the famous carbon materials used in supercapacitor electrodes. Graphene is the single layer of graphite and the most versatile carbon based electrode material for supercapacitors where the carbon atoms are sp² hybridized. It is famous for lightweight, tunable surface area (up to 2675 m² g⁻¹), excellent electrical conductivity, strong mechanical strength (~1 TPa) and chemical stability [9]. The theoretical specific capacitance of graphene is ~ 21 μF cm⁻² and experimentally ~ 550 F g⁻¹ while utilizes the total available surface area [10]. Graphene can be used as a conductive network with transition metal oxides, conducting polymer to assist the redox reactions and these hybrid composites exhibit enhanced electrochemical performances due to the synergetic effects of metal oxides/conducting polymers. Conducting polymers are a well-established source of pseudocapacitance and a deserving candidate for supercapacitor electrode material because of its high storage capacity, high conductivity when doped, high potential window, high energy density, environment-friendly, low cost and easy synthesis [11]. Among them, polypyrrole (PPy) is famous for energy storage application owing to its high flexibility and easy synthesis [12]. PPy minimizes the capacitive response of the polymer in thick coating electrodes due to the limited access of the electrolyte ions ascribed to high density. Suematsu et al. [13] stated that capacitance per unit volume of PPy is 100-200 F cm⁻³ but a typical PPy layer exhibited capacitance of about 400-500 F cm⁻³.

MoS₂ is a 2D transition metal dichalcogenides composed of one layer of molybdenum sandwiched between two layers of sulphur. MoS₂ is gaining attention due to higher intrinsic fast ionic conductivity than that of metal oxides and higher theoretical capacitance than that of graphite [14]. Chao et al., [15] have synthesized ternary nanocomposite of MoS₂/polyaniline/reduced graphene oxide and investigated the electrochemical performances in 1M aqueous H₂SO₄ solution. The ternary electrode exhibited specific capacitance of 520 F g⁻¹, rate capability of 44.9% in 30 A g⁻¹ current density and cyclic stability of 89.1% after 40,000 cycles. Another group Chuhan Sha et al. [16] have reported ternary nanocomposite of MoS₂/PANI/rGO aerogel and obtained specific capacitance of 618 F g⁻¹ at 1 A g⁻¹ current density and capacitive retention of 96% at 20 A g⁻¹ current density.

In this work, we have synthesized MoS₂-rGO heterostructures by varying the weight ratio of positively charged MoS₂ nanosheets to negatively charged graphene oxide nanosheets as 1:1, 1:2 and 2:1. Finally, the 1:1, 1:2 and 2:1 MoS₂-rGO/PPyNTs nanocomposites were obtained after hydrothermal reduction of GO supercapacitor electrodes. The electrodes were prepared with 1:1, 1:2 and 2:1 MoS₂-rGO/PPyNTs ternary nanocomposites and the electrochemical properties were investigated.

2. Experimental

2.1. Materials
Molybdenum disulphide powders, graphite powder, iron chloride, pyrrole monomer were purchased from Sigma-Aldrich. Cetyl trimethyl ammonium bromide (CTAB, Hi-media), methyl orange (SRL), sulfuric acid (avantor), potassium permanganate (Merck Emplura) and phosphoric acid (avantor) were also used in different steps of the synthesis process.

2.2. Preparation of MoS₂-GO nanocomposite
Bulk MoS₂ was exfoliated to nanosheets by adding 330 mg of raw MoS₂ powder in 30 ml of 1% CTAB containing double distilled (DD) water in water-bath sonicator (36 W) for 11 h. MoS₂ nanosheets were obtained after differential centrifugation performed at 4000 and 8000 rpm followed by vacuum drying at desiccator. Graphene oxides were prepared from improved hummer’s method [17] and exfoliated in DD water maintaining 1 mg ml⁻¹ of concentration by using ultrasound.

MoS₂-rGO heterostructures were synthesized in 3 different ratios (1:2, 1:1, 2:1). In 1:2 ratio 60 ml (1mg ml⁻¹) of MoS₂ was mixed with 120 ml (1mg ml⁻¹) of graphene oxide. In 1:1 ratio 60 ml of MoS₂ was mixed with 60 ml of graphene oxide. In 1:2 ratio 60 ml of MoS₂ was mixed with 30 ml of graphene oxide. The mixing of MoS₂ and GO was carried out at ice bath with constant stirring for 1 hour. Then
the precipitates were centrifuged at 4000 rpm and washed with DD water. The precipitates were spread in petri-dish and kept in the desiccator at room temperature for 3 days.

2.3. Synthesis of MoS$_2$-rGO/PPyNTs composite

Polypyrrole nanotubes were prepared using methyl orange as soft template and ferric chlorite as oxidant [18]. The MoS$_2$-GO nanocomposites were dispersed in N-methyl-2-pyrrolidinone using ultrasound for 20 minutes and addition of PPyNTs (40 wt. %). The solution is poured in teflon coated autoclave and put in oven at 150°C for 24 h. The obtained nanocomposites were washed with distilled water and ethanol for 3 times at 5000 rpm followed by oven heating for 12h at 65°C.

2.4. General characterization

X-ray diffraction (XRD) of the powder samples were carried out in D8 focus X-ray diffractometer, Bruker AXS, Germany at the scan rate of 1°/min. Fourier transform infrared (FTIR) spectroscopy was evaluated with Perkin Elmer Spectrum 1000 with KBr pellets in the range of 400-4000 cm$^{-1}$. Surface morphology was studied with scanning electron microscope (SEM) of JEOL, JAPAN, JSM 6390LV at the accelerating voltage 20 kV. Transmission electron microscopy (TEM) images were recorded by JEM-2100 at 60–200 KV. TGA was performed with thermogravimetry-differential thermal analyzer (Perkin Elmer STA-6000) at the heating rate of 20°C/min in nitrogen environment.

2.5. Electrochemical measurements

The electrochemical measurements were carried out in three electrode configuration (AUTOLAB 302N Modular, Potentiostat Galvanostat, FRA32M Module, Netherlands). Saturated KCl containing Ag/AgCl was used as reference electrode, platinum as counter electrode and active material deposited ITO was used as working electrode while doing the measurements. The working electrodes were fabricated by depositing the slurry of the active material mixed with carbon black and nafion on ITO coated glass slide having dimension of 1x0.5 cm$^2$ followed by vacuum drying at desiccator. The mass of active material deposited on ITO was nearly 1 mg while preparing the electrodes. 1 M KCl solution was employed as electrolyte for electrochemical measurements. Cyclic voltammetry (CV), charge-discharge (CD) and electrochemical impedance spectroscopy (EIS) were carried out to study the specific capacitance, coulombic efficiency, energy density, power density, cycling stability and electrode resistance.

3. Results and discussion

3.1. Morphology and Structure

3.1.1. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The morphology of MoS$_2$, rGO, MoS$_2$-rGO heterostructures and the ternary MoS$_2$-rGO/PPyNTs were studied with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images of MoS$_2$-rGO nanostructures synthesized by varying the MoS$_2$ and rGO ratios are displayed in figures 1(a-c), where the layer-by-layer structures are observed. The layered structures are more prominent in 1:1 MoS$_2$-rGO nanostructures. The SEM images of the ternary MoS$_2$-rGO/PPyNTs are depicted in figures 1(d-g) and the PPyNTs have been covered the layered nanosheets. The TEM image of single layer of MoS$_2$ nanosheet, displayed in figure 1(h), suggests the successful exfoliation of MoS$_2$ in presence of cationic surfactant CTAB. The paper like nanosheet of rGO is observed from figure 1(i). TEM images of MoS$_2$-rGO heterostructures are depicted in figure 1(j). In the ternary MoS$_2$-rGO/PPyNTs nanocomposites, the nanosheets are observed along with the nanotubes which forms a matrix like structure, as shown in the figures 1(k, l).
3.1.2. X-ray diffraction (XRD) analysis. XRD patterns of bulk MoS$_2$, exfoliated MoS$_2$, GO and rGO are depicted in figure 2 (a). For exfoliated MoS$_2$, small and broad peak corresponding to (002) plane appears and disappearance of the other peaks of bulk MoS$_2$ suggests the successful exfoliation of MoS$_2$. The characteristic peak of rGO at around 25° has shifted to 19° in the 1:1 MoS$_2$-rGO heterostructures due to the intercalation of MoS$_2$ nanosheets in between the rGO nanosheets. MoS$_2$ peaks at 49.9° and 58.3° have shifted to 39.4° and 49.6° and the rGO peak at 40° has shifted to 32.4° after the formation of heterostructure. For the ternary MoS$_2$-rGO/PPyNTs nanocomposites, a broad hump appears from 26° = 16° to 30° due to the overlapping of the characteristic peaks of PPyNTs at 25° and rGO peak at 19°.
3.1.3. Fourier transforms infrared (FTIR) spectroscopy. The different functional groups present in the nanocomposites have been investigated with FTIR analysis and depicted in figure 3. The vibrational bands at 904 cm\(^{-1}\), 926 cm\(^{-1}\), 1701 cm\(^{-1}\) and 549 cm\(^{-1}\) in the MoS\(_2\) FTIR spectrum correspond to S=S, M=O, M-O and S\(_2^2\) vibrations of MoS\(_2\). The broad absorption peak at 3411 cm\(^{-1}\) for all the FTIR patterns corresponds to hydroxyl group vibration is less intense in the rGO FTIR pattern due to the removal of oxygenated groups (Figure 3 b). The vibrational bands appeared at 1544 cm\(^{-1}\) and 2924 cm\(^{-1}\) for PPyNTs, 1:1, 1:2, and 2:1 MoS\(_2\)-rGO/PPyNTs ternary nanocomposites are due to the vibration of pyrrole ring and asymmetric stretching vibration of –CH bond, respectively [19]. The presence of the vibrational bands of PPyNTs, MoS\(_2\) and rGO in the ternary nanocomposites suggests the successful formation of the nanocomposites.

3.1.4. Thermo-gravimetric analysis (TGA). The thermal stability of the three ternary nanocomposites has been evaluated with thermo-gravimetric analysis upto 700°C at the constant heating rate of 20°/min under nitrogen environment. The first degradation appeared due to the dehydrtation of sample arround
110°C. The weight loss at the temperature of 280°C is corresponding to the degradation of polypyrrole chain. The major degradation occurs at around 425°-535° due to the phase change of MoS$_2$ to MoO$_3$ upon oxidation of MoS$_2$ for 1:1, 1:2 and 2:1 MoS$_2$-rGO/PPyNTs nanocomposites [20]. Continuous weight loss around 600°C for the three ternary MoS$_2$-rGO/PPyNTs nanocomposite is related to the degradation of graphene skeleton [21]. The 1:1 MoS$_2$-rGO/PPyNTs nanocomposites is found to be more thermostable than that of 1:2 and 2:1 MoS$_2$-rGO/PPyNTs nanocomposites with 56% of thermal stability at 700°C.

![Figure 4. TGA curves of 1:1, 1:2, 2:1 MoS$_2$-rGO/PPyNTs.](image)

3.2. Electrochemical characterization

Electrochemical measurements of the ternary 1:1, 1:2 and 2:1 MoS$_2$-rGO/PPyNTs/ITO electrodes were evaluated with cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) measurements in a potential window of -0.3 to 1 V (vs. Ag/AgCl) and electrochemical impedance spectroscopy (EIS) in 1M KCl electrolyte.

3.2.1. Cyclic Voltammetry (CV) studies. CV curves of 1:1, 1:2 and 2:1 ternary MoS$_2$-rGO/PPyNTs electrodes are displayed in figure 5 (a) at the scan rate of 30 mV s$^{-1}$ in 1 M KCl electrolyte. The CV curves of the three electrodes are exhibiting a quasi-rectangular geometry suggesting the contribution from both EDLC and pseudocapacitance. Here, MoS$_2$ and rGO are the sources of EDLC whereas, PPYNTs contributes pseudocapacitance. Highest capacitive response is observed for 1:1 MoS$_2$-rGO/PPyNTs ternary electrodes, which may be attributed to the proper utilization of electrode surface area and minimum agglomeration of rGO nanosheets as well as less restacking of MoS$_2$ nanosheets. Moreover, the 1:1 MoS$_2$-rGO heterostructures are more homogeneous as compared to 1:2 and 2:1 MoS$_2$-rGO nanocomposites, as observed from SEM images causing the enhanced capacitive response in 1:1 MoS$_2$-rGO/PPyNTs ternary electrodes. Figure 5 (b) shows the CV patterns of 1:1 MoS$_2$-rGO/PPyNTs ternary electrode with increasing scan rates from 10 mV s$^{-1}$ to 100 mV s$^{-1}$. It is observed that with increasing scan rate the current-voltage response also increases, suggesting a good rate ability of the ternary electrode [22].
3.2.2. Galvanostatic charge-discharge (GCD) measurements. Figure 6 (a) represents the galvanostatic charge-discharge curves of 1:1, 1:2 and 2:1 ternary MoS$_2$-rGO/PPyNTs electrodes in the potential window of -0.3 V to 1 V (versus Ag/AgCl) in three electrode configurations at 1 A g$^{-1}$ current density in 1 M KCl electrolyte. Specific capacitance ($C_{sp}$) and coulombic efficiency ($\eta$) are calculated using the following equations:

$$C_{sp} = \frac{I \times \Delta T_D}{m \times \Delta \theta}$$  \hspace{1cm} (1)$$

$$\eta = \frac{\Delta T_D}{\Delta T_C} \times 100$$  \hspace{1cm} (2)$$

where $I$, $\Delta T_D$, $\Delta T_C$, $m$, and $\Delta \theta$ are discharge current, discharge period, charging time, mass of the active material deposited and potential window during discharge. The GCD curves possess a non-linear pattern suggesting the contribution from EDLC and pseudocapacitance. The 1:1 MoS$_2$-rGO/PPyNTs ternary electrodes exhibit highest discharge duration which supports the CV results. 1561 F g$^{-1}$, 862 F g$^{-1}$ and 578 F g$^{-1}$ are the calculated specific capacitance for 1:1, 1:2 and 2:1 MoS$_2$-rGO/PPyNTs ternary electrodes at 1 A g$^{-1}$ current density in 1 M KCl electrolyte.
ternary electrodes, respectively. Figure 6 (b) displays the GCD curves of 1:1 MoS$_2$-rGO/PPyNTs ternary electrodes at 1, 4, 8, 12 and A g$^{-1}$ current densities. Almost 99% of coulombic efficiency reveals the excellent reversibility of the ternary electrodes.

Energy densities and power densities of the ternary electrodes are calculated according to the equations (3) and (4) and Ragone plot is displayed in figure 7 (a).

Energy density, $E = \frac{1}{2} C_{sp} (\Delta V)^2$  

(3)

Power density, $P = \frac{E \times 3600}{T_{dis}}$  

(4)

where, $C_{sp}$, $\Delta V$ and $T_{dis}$ are the specific capacitance calculated from electrochemical measurements, potential drop during discharge and discharge period, respectively.

Figure 7. (a) Ragone plot and (b) Cycling stability with cycle numbers

The calculated values of specific capacitance, coulombic efficiency, energy density and power density are displayed in table 1. The rate capability plot of specific capacitance vs. current density is depicted in figure 7 (b). The 1:1 MoS$_2$-rGO/PPyNTs ternary electrode possesses specific capacitance of 1230 F g$^{-1}$ (4 A g$^{-1}$), 1090 F g$^{-1}$ (8 A g$^{-1}$), 907 F g$^{-1}$ (12 A g$^{-1}$) and 784 F g$^{-1}$ (15 A g$^{-1}$) at different current densities and exhibits 50% of capacitive retention at 15 A g$^{-1}$ current density, suggesting a good rate capability of the electrode.

3.2.3. Cycling Stability analysis. Cycling stability analysis of supercapacitor electrodes is important for their potential practical applications. EDLC materials store charge without any chemical reactions and hence deliver excellent cycle life (~ 10$^5$) at the cost of specific capacitance. Cycling stability of the three ternary 1:1, 1:2, and 2:1 MoS$_2$-rGO/PPyNTs electrodes have been evaluated upto 5000 cycles in 1 M KCl electrolyte at 10 A g$^{-1}$ current density. 1:1 ternary MoS$_2$-rGO/PPyNTs electrode exhibits cycling stability of 76% after 5000 cycles. But 2:1 MoS$_2$-rGO/PPyNTs electrode shows cycling stability of 78% after 5000 cycles, attributed to the excellent cycle life of MoS$_2$ following EDLC charge storage mechanism [23]. The 1:2 MoS$_2$-rGO/PPyNTs electrode possesses cycling stability of 67% and may be due to the presence of more amount of rGO which agglomerates during repeated cycling processes.
Table 1: Specific Capacitance ($C_{sp}$), Coulombic efficiency ($\eta$), Energy density (E), Power density (P) and cycling stability of 1:1, 1:2 and 2:1 MoS$_2$–rGO/PPyNTs electrodes calculated from galvanostatic charge-discharge (GCD) measurements.

| Electrode   | Specific Capacitance (F/g) | Coulombic Efficiency (%) | Energy Density (Wh/kg) | Power Density (W/kg) | Cycling stability after 5000 cycles(%) |
|-------------|----------------------------|--------------------------|------------------------|----------------------|----------------------------------------|
| 1:1 MoS$_2$–rGO/PPyNTs | 1561                       | 99.98                    | 138.76                 | 2400.29              | 76                                     |
| 2:1 MoS$_2$–rGO/PPyNTs  | 862                        | 99.89                    | 68.56                  | 2400.19              | 78                                     |
| 1:2 MoS$_2$–rGO/PPyNTs  | 578                        | 99                       | 85.56                  | 2400.09              | 67                                     |

Figure 8. Cycling stability of (a) 1:1 MoS$_2$–rGO/PPyNTs nanocomposite, (b) 1:2 MoS$_2$–rGO/PPyNTs nanocomposite and (c) 2:1 MoS$_2$–rGO/PPyNTs nanocomposite at current density of 10 A g$^{-1}$ up to 5000 cycles at 1M KCl electrolyte.

3.2.4. Electrochemical Impedance Spectroscopy (EIS) studies. EIS is performed to understand the electrode kinetics in terms of faradic and diffusion reactions in the frequency range of 10 µHz - 10$^5$ Hz. The Nyquist plots of the ternary 1:1, 1:2, and 2:1 MoS$_2$–rGO/PPyNTs electrodes are depicted in Figure 9. EIS spectra are showing a straight line in lower frequency side and a semicircle in high-frequency side. The intercept of semicircle at X-axis is the equivalent series resistance (R$_s$), implies the intrinsic electrode resistance and electrolyte’s ionic resistance, and diameter of the semicircle gives charge transfer resistance (R$_ct$) of the electrochemical cell. It is observed that the values of R$_s$ for 1:1, 1:2, and 2:1 MoS$_2$–rGO/PPyNTs electrodes are 1.84 Ω, 1.02 Ω and 2.3 Ω, respectively. The lower ESR of 1:2 MoS$_2$–rGO/PPyNTs electrodes are attributed to the presence of rGO in more amounts which keep reducing the intrinsic series resistance of the electrode. The lowest value of R$_ct$ is observed to be 7.52 Ω.
for 1:1 MoS$_2$-rGO/PPyNTs electrode, which is due to the presence of well arranged alternate layers of MoS$_2$ and rGO providing more number of interfaces. This indicates easier charge transfer across the interface between the electrode and the electrolyte.

Figure 9. Nyquist plot of 1:1, 1:2, and 2:1 MoS$_2$-rGO/PPyNTs/ITO ternary electrodes (inset shows the equivalent circuit)

4. Conclusion
Layer-by-layer structures of MoS$_2$-rGO were synthesized by self-assembly of MoS$_2$ and rGO in the ratios of 1:1, 1:2 and 2:1. Ternary nanocomposites of MoS$_2$-rGO/PPyNTs were synthesized by mixing 40 wt% of PPyNTs followed by hydrothermal reduction of GO at 150°C. Layer-by-layer structures of MoS$_2$-rGO nanocomposite have been observed from SEM micrographs, which is more homogeneous in 1:1 MoS$_2$-rGO nanocomposite than that of other two nanocomposites. The 1:1 MoS$_2$-rGO/PPyNTs nanocomposite is found to be more thermostable with 44% of degradation at 700°C. 1:1 MoS$_2$-rGO/PPyNTs ternary nanocomposite delivers enhanced specific capacitance of 1561 F g$^{-1}$ at 1 A g$^{-1}$ current density and specific capacitance of 786 F g$^{-1}$ (50% of capacitive retention) at 15A g$^{-1}$ exhibiting an excellent rate performance. 1:1 MoS$_2$-rGO/PPyNTs/ITO ternary electrode exhibits 76% of cycling stability after 5000 galvanometric charge-discharge cycles at 10-fold current density. The ternary MoS$_2$-rGO/PPyNTs/ITO electrodes exhibit enhanced capacitive response due to the synergetic effects of MoS$_2$ and rGO as well as the nanotube morphology of PPy which provide a conductive network in the supercapacitor electrodes.

Acknowledgement
The authors gratefully acknowledge Science and Engineering Research Board (SERB), Department of Science and Technology, Government of India for their financial support (Project No: EMR/2015/000428) to carry out this research work. The author sincerely thanks DST-INSPIRE for support by providing INSPIRE fellowship.

References
[1] Purkait T, Singh G, Kumar D, Singh M and Dey R S 2018 Sci. Rep. 8 (1) 640
[2] Chiam S L, Lim H N, Hafiz S M, Pandikumar A and Huang N M 2018 Sci. Rep. 8 (1) 3093
[3] Juodkazis K, Juodkazytė J, Šukienė V, Grigucevičienė A and Selskis A 2008 J. Solid State Electrochem. 12 (11) 1399
[4] Farzana R, Rajarao R, Bhat B R and Sahajwalla V 2018 J. Ind. Eng. Chem. 65 387
[5] Wu G, Tan P, Wang D, Li Z, Peng L, Hu Y, Wang C, Zhu W, Chen S and Chen W 2017 Sci. Rep. 7 43676
[6] Fischer U, Saliger R, Bock V, Petricevic R and Fricke J1997 J. Porous Mater. 4 (4) 281
[7] Daraghmeh A, Hussain S, Saadeddin I, Servera L, Xuriguera E, Cornet A and Cirera A 2017 Nanoscale Res. Lett. 12 (1) 639
[8] Yang H, Kannappan S, Pandian A S, Jang J H, Lee Y S and Lu W 2017 Nanotechnology 28 (44) 445401
[9] Lee C, Wei X, Kysar J W and Hone J 2008 Science 321 (5887) 385
[10] Xia J, Chen F, Li J and Tao N 2009 Nat. Nanotechnol. 4 (8) 505
[11] Green R A, Lovell N H, Wallace G G and Poole-Warren L A 2008 Biomaterials 29 (24-25) 3393
[12] Li X, and Zhitomirsky I 2013 J. Power Sources 221 49
[13] Suematsu S, Oura Y, Tsujimoto H, Kanno H and Naoi K 2000 Electrochim. Acta 45 (22-23) 3813
[14] Ma G, Peng H, Mu J, Huang H, Zhou X and Lei Z 2013 J. Power Sources 229 72
[15] Chao J, Yang L, Liu J, Hu R and Zhu M 2018 Electrochim. Acta 270 387
[16] Sha C, Lu B, Mao H, Cheng J, Pan X, Lu J and Ye Z Carbon 2016 99 26
[17] Marcano D C, Kosynkin D V, Berlin J M, Sinitskii A, Sun Z, Slesarev A, Alemany L B, Lu W and Tour J M 2010 ACS Nano 4 (8) 4806
[18] Upadhyay J and Kumar A Mater. Sci. Eng. B 2013 178 (15) 982
[19] Sarmah D and Kumar A 2018 Synth. Met. 243 5
[20] Cho M H, Ju J, Kim S J and Jang H Wear 2006 260 (7-8) 855
[21] Alam S N, Sharma N and Kumar L Graphene 2017 6 (01) 1
[22] Ma G, Peng H, Mu J, Huang H, Zhou X and Lei Z J. 2013 Power Sources 229 72
[23] Wang Y X, Chou S L, Wexler D, Liu H K and Dou S X 2014 Chem. Commun. 50 10730