HIGH PERFORMANCE SUPERCAPACITOR ELECTRODE MATERIAL BASED ON FLOWER LIKE MoS$_2$/REDUCED GRAPHENE OXIDE NANOCOMPOSITE

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Abstract- A simple and cost effective hydrothermal method has been done for the synthesis of MoS$_2$ and MoS$_2$/rGO nanocomposites. The prepared MoS$_2$/rGO composite was characterized by XRD, FESEM and TEM which revealed the formation and as well as the morphological scenario of MoS$_2$/rGO nanocomposite. Pure MoS$_2$ and MoS$_2$/rGO nanocomposite show 3D hierarchical flowery architecture where rGO nanosheets were intercalated into the MoS$_2$ nanosheets. For the electrochemical performance, cyclic voltammetry and galvanostatic charge discharge measurements were carried out. The composite exhibits maximum specific capacitance of 253 F/g at a current density of 1 A/g with good cycling stability.

Keywords – MoS$_2$, reduced Graphene Oxide, Pseudocapcitance, Supercapacitor.

I. INTRODUCTION

Climate change and the availability of decreasing fossil fuels are the main reason behind the need for searching for a sustainable, renewable energy resource. In a parallel way, the new inventions like electronic gadgets such as smart phones, tablets, digital camera have made our life easier but the energy consumption per person has been increased frequently and it is also aided the reason why the researchers are going for a cheaper energy source. Therefore, the energy storage systems like electrochemical capacitors are needed. Electrochemical capacitors; also called supercapacitors have attracted a great deal of attention in recent years due to their interesting features such as high power density, fast charging/discharging process, long cycle life and small environmental impact, etc. [1].

Nanostructured materials have fascinated great interest in recent years because of their remarkable mechanical, electrical and optical properties. As a unique carbon nanomaterial, graphene has attracted more importance by virtue of its promising applications in supercapacitor electrodes materials because of its excellent conductivity, superior mechanical properties, exceptionally large specific surface area and chemical stability [2-4]. Recently, for electrochemical energy storage application, metal sulfides-based graphene composites such as In$_2$S$_3$/graphene [5], CoS$_2$/graphene [6] and NiS/graphene [7] have been studied.

MoS$_2$ is a typical family member of transition-metal dichalcogenides. The structure of MoS$_2$ facilitates itself to act as an excellent functional material. Here the metal Mo layer is stacked by two S layers held together by weak Van der Waals interactions [8]. The electron-electron correlations of Mo atoms would aid in enhancing planar electric transportation properties. The composites of MoS$_2$ with conductive carbonaceous materials such as graphene/MoS$_2$ [9], CNTs/MoS$_2$ [10], or mesoporous carbon/MoS$_2$ [11] have been highly explored for anode materials of lithium ion batteries (LIBs), hydrogen production and sensing like many other application field [12, 13].

Herein, we demonstrate an environment friendly, one pot hydrothermal synthesis of molybdenum sulfide/reduced graphene oxide (MoS$_2$/rGO) nanocomposite with the use of ammonium heptamolybdate and thiourea as sulphur source. As an electrode material for supercapacitors, MoS$_2$/rGO nanocomposite exhibits high specific capacitance of 253 F/g at a current density of 1 A/g with good cycling stability.

II. MATERIALS AND METHOD

IIA Materials used

All materials were used prior to the further purification. Ammonium heptamolybdate was purchased from Merck specialities privet Ltd., Mumbai. Thiourea was purchased from RFCL Ltd., New Delhi. Graphite fine powder, orthophosphoric acid (H$_3$PO$_4$), sulfuric acid (H$_2$SO$_4$) and hydrochloric acid (HCl) were supplied by Loba Chemie Pvt. Ltd. Mumbai (India). Nafion was purchased from Sigma Aldrich, Germany.

IIB Preparation of graphene oxide (GO)

Graphene oxide was prepared from natural graphite fine powder (extra pure) by modified Hummers method [14]. Briefly, a 9:1 mixture of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (360:40 mL) was taken with 3.0 gm graphite fine powder. Then 18.0 gm KMnO$_4$ was added pinch by pinch to the mixture solution because enormous heat is produced due to exothermic reaction. After stirring for 12 h the mixture solution was...
cooled to room temperature and poured onto ice (400 mL) with 3 ml 30% H₂O₂. The solution was stirred for another 4 h and centrifuged at 4000 rpm. The solid material was then washed in succession with water, 20% HCl, and ethanol. The solid material was dried for overnight at 60 °C temperature.

II C Synthesis of MoS₂/rGO nanocomposite

The preparation of layered MoS₂ was conducted by a simple hydrothermal method. Briefly, 20 ml 0.1 M ammonium heptamolybdate and 20 ml 0.1 M thiourea aqueous solution were taken with 50 mg graphene oxide and mixture solution was ultrasonicated for 30 min. Then the mixture solution was transferred into a stainless steel autoclave and kept in a furnace at 220 °C for 12 h. The black precipitate was washed by water and ethanol, and dried at 65 °C for 12 h. The pure MoS₂ was prepared by the same procedure without adding GO.

III. MATERIALS CHARACTERIZATION

The as-prepared products were characterized with X-ray diffractometer (XRD, Rigaku diffractometer with a Cu Kα radiation (λ= 1.54056 Å), field emission scanning electron microscopy (FESEM, Carl Zeiss-SUPRATM 40) and transmission electron microscopy (TEM, TECNAI G2-20S-TWIN).

III A Electrochemical measurements

For the electrochemical measurements we used a three electrode system, where active materials fabricated on glassy carbon (GC) electrode. Pt electrode and saturated calomel electrode (SCE) were chosen as working, counter and reference electrode, respectively. For preparation of working electrode, 0.1 mg of the sample was taken in 1% nafion solution (10 μl nafion in 1 ml ethanol) and ultrasonicated for 10 min. The prepared solution was cast onto the glassy carbon electrode (diameter-3 mm) and allowed to dry fully under air. The electrochemical tests, cyclic voltammetry (CV) and galvanostatic charge-discharge technique were performed by using Biologic SP-150 instrument in an aqueous Na₂SO₄ electrolyte (1.0 M).

IV. RESULTS AND DISCUSSION

IVA X-ray diffraction analysis

The XRD patterns of the products are shown in Fig. 1. For Graphene Oxide, the characteristic diffraction peak at about 10° indicating successful oxidation of the graphite and formation of GO [15]. For pure MoS₂, the diffraction peaks are well matched with the JCPDS Card No. 37-1492. The peaks appear at 14.2, 33.5, 39.8, 43.1, 49.1 and 59.3° corresponding to (002), (100), (103), (006), (105) and (110) planes, respectively. For MoS₂/rGO nanocomposite, all of the characteristic peaks of pure MoS₂ are present there but there is no obvious peak for the GO component. Only the broad peak observed at 2θ = 24–30° indicates the presence of RGO sheets [16].
MoS$_2$ + Na$^+$ + e$^-$ ⇌ MoS-SNa$^+$

Fig. 3 shows the TEM images of as synthesized MoS$_2$ and MoS$_2$/rGO nanocomposite, supporting the layered nanosheets obtained from FESEM images. The structural and morphological compatibility between rGO and single-layer MoS$_2$ sheets give a better integration to achieve the anticipated benefits of such integration. This tighter integration between MoS$_2$ and rGO could synergize their interaction to significantly improve the electrochemical performance of the MoS$_2$/rGO nanocomposite as materials for supercapacitor.

IVC Electrochemical Study

IVC1 Cyclic voltammetry

The electrochemical properties of the products were studied by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) techniques. Fig. 4 shows the cyclic voltammetry analysis at various scan rates in the potential range of (-)0.1 – 0.5 V. From the Fig. 4, it is observed that MoS$_2$/rGO nanocomposite has largest area surrounded by CV curve, indicating higher specific capacitance and the synergistic effect of MoS$_2$ and rGO. Additionally, it was found that quasi-rectangular shapes for all CV curves at various scan rates, indicating all materials shows good capacitive behavior. The large area at a high scan rate for a CV curve does not mean a higher capacitance because the effective interaction between the electrolyte ions and the electrode is greatly reduced with the increasing of scan rate. The possible mechanism is based on the pseudo-capacitive behavior due to the faradaic charge transfer process. During the redox process, there occurs intercalation of alkali metal Na$^+$ in the MoS$_2$ interlayers upon reduction, followed by deintercalation upon oxidation [17].

The specific capacitance ($C_{sp}$ in F/g) of the composites from the CV measurement can be calculated by using the following equation

$$C_{sp} = \frac{\int_{V1}^{V2} i(V) dV}{(V2-V1) V m}$$

where, $i$ (A) is the instantaneous current in cyclic voltammogram, $v$ is the potential scan rate (mV/s). $V1$ and $V2$ are the switching potential, $m$ is the mass of the electrode and $\int_{V1}^{V2} i(V) dV$ determines the area of the I-V curve. The variations of specific capacitance with scan rate for the pure MoS$_2$ and MoS$_2$/rGO nanocomposites are shown in Table 1. From the CV measurements, it is clear that at a scan rate of 2 mV/s, the highest specific capacitance exhibited by MoS$_2$/rGO composites is 275 F/g, whereas the pure MoS$_2$ shows a lower specific capacitance of 210 F/g at the same scan rate. Fig. 4(c) is the plot of the specific capacitance of pure MoS$_2$ and MoS$_2$/rGO composite as a function of the scan rates based on the CV curves.

**TABLE -1 THE VARIATIONS OF SPECIFIC CAPACITANCE WITH SCAN RATE FOR THE PURE MOS$_2$ AND MOS$_2$/rGO NANOCOMPOSITES.**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific capacitance (F/g) at different scan rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 mV/s</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>210</td>
</tr>
<tr>
<td>MoS$_2$/rGO</td>
<td>275</td>
</tr>
</tbody>
</table>
ICVC2 Galvanostatic Charge-discharge measurements

Fig. 5 Galvanostatic charge-discharge curves of MoS$_2$ (a) and MoS$_2$/rGO nanocomposites (b) at different current density of 1 and 5 A/g, respectively.

Fig. 5 shows the galvanostatic charge-discharge curves of MoS$_2$ and MoS$_2$/rGO nanocomposites at different current densities (1 and 5 A/g). The semi-symmetric GCD curves for both the materials reveal their pseudocapacitive behavior. The specific capacitance ($C_{sp}$) was calculated from the equation below:

$$ C_{sp} = \frac{i \times \Delta t}{m \times \Delta V} $$

where, $i$, $m$, $\Delta t$ and $\Delta V$ is the applied current (A), mass (g) of the active material, discharge time and potential window, respectively. The variations of specific capacitance with current density for the pure MoS$_2$ and MoS$_2$/rGO composites are shown in Table 2.

TABLE 2: THE VARIATIONS OF SPECIFIC CAPACITANCE WITH CURRENT DENSITY FOR THE PURE MOS$_2$ AND MOS$_2$/rGO NANOCOMPOSITES

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific capacitance (F/g) at different current density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 A/g</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>194</td>
</tr>
<tr>
<td>MoS$_2$/rGO</td>
<td>253</td>
</tr>
</tbody>
</table>

Fig. 6(a) shows the variation of the specific capacitance (F/g) with the current density (A/g) of MoS$_2$ and MoS$_2$/rGO nanocomposites. The specific capacitances of the MoS$_2$/rGO electrode at 1 and 5 A/g are 253 F/g and 192 F/g, respectively. The results indicate that the MoS$_2$/rGO composites have high specific capacitance value as one of the most important electrochemical properties for the electrode materials in the supercapacitor application field.

The advantages of MoS$_2$/rGO composites electrode over the MoS$_2$ electrodes are mainly intercalation of rGO nanosheets into the 3D flowery MoS$_2$ which improves the diffusion rate of ions within the bulk of the materials and also rGO behaves as a highly conductive current collector as its conjugative structure. This is why MoS$_2$/rGO composite shows better electrochemical performance.

Energy density and power density of the materials were calculated by the following equations:

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

$$ \text{Power density (P)} = \frac{E}{T} $$

TABLE 3: CALCULATED POWER DENSITY (W/kg) AND ENERGY DENSITY (Wh/kg) FROM CHARGE-DISCHARGE MEASUREMENT

<table>
<thead>
<tr>
<th>Electrode Materials</th>
<th>Power density (W/kg) at different current density (A/g)</th>
<th>Energy density (Wh/kg) at different current density (A/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 A/g</td>
<td>5 A/g</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>MoS$_2$/rGO</td>
<td>300</td>
<td>1500</td>
</tr>
</tbody>
</table>

Fig. 6(b) shows the energy density versus power density curve in terms of Ragone plot. It can be seen from the Ragone plot, as the power density increases from 300 W/kg to 1500 W/kg, the energy density of MoS$_2$ decreases from 9.6 Wh/kg to 3.2 Wh/kg and the energy density of MoS$_2$/rGO nanocomposite decreases from 12.65 Wh/kg to 9.7 Wh/kg, respectively.

The cycle stability of MoS$_2$ and MoS$_2$/rGO nanocomposites were evaluated by repeating the constant current charge-discharge test between (-0.1 and 0.5 V (vs. SCE) at a current density of 1.0 A/g for 1000 cycles. The retention of specific capacitance of MoS$_2$ and MoS$_2$/rGO nanocomposites are 85% and 90.3% of the initial capacitance, respectively. From the Fig. 6(c), apart from the initial increase of specific capacitance up to 100 cycles a linear decay can be seen. The initial increase is a consequence of wetting effect.

V. CONCLUSIONS

Layered MoS$_2$ and MoS$_2$/rGO nanocomposite with 3D hierarchical flowery architecture were synthesized by a
simple and cost effective one pot hydrothermal process. The maximum specific capacitance for MoS$_2$/rGO is 253 F/g at a current density 1 A/g compared to 194 F/g for MoS$_2$. The integration of graphene into the composites provides relatively large areas to loading MoS$_2$ sheets, leading to three-dimensional nanostructures. Thus MoS$_2$/rGO composites enable an easy access for both charge-transfer and ion transport throughout the electrode. Furthermore, the capacitance retention is still over 90.3% of initial capacitance after 1000 cycles. These results suggest that the MoS$_2$/rGO nanocomposites are quite a suitable and promising electrode material for high-performance supercapacitor.

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REFERENCES