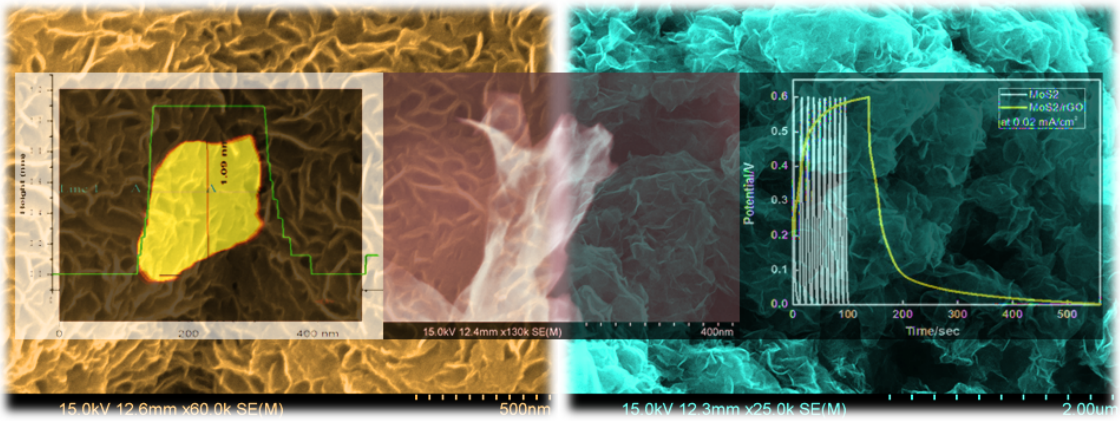
Chapter 7

MoS_2 Nanosheets/rGO Hybrid: An Electrode Material for High Performance Thin Film Supercapacitor



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7.1. Introduction

The growing demand for portable electronic has greatly promoted the development of thin film energy storage devices. It has been already reported that Graphene based supercapacitor obtained high volumetric capacitances of 300 F $cm^{-}3$.[1,2] Now a day this high values micro capacitors plays a crucial role for the development of the portable electronic technology. Atomic layer thickness and flat morphology of graphene analogues 2-D materials, such as transition metal dichalcogenides (MoS_2, $MoSe_2$, VS_2, and VSe_2 etc.) makes them promising candidates for thin film supercapacitor application. Unique structural (S-Mo-S) and electronic properties of MoS_2 nanosheets provide high specific surface area as well as due to the van der Waals forces between their layers, shows excellent intercalation of ions in layered MoS_2, which are the basic requirements for the high performance supercapacitor. [6-12] Several oxidation states from +2 to +6 of Mo centre in MoS_2 makes it a suitable candidate for pseudocapacitance. Graphene/MoS_2 [13] and polyaniline/MoS_2[14] hybrid electrodes have been already investigated as a supercapacitor.

We reported large scale production of MoS_2 and MoS_2/rGO hybrid by simple hydrothermal route followed by liquid phase exfoliation to get the nanosheets of the prepared sample.Electrochemical properties of hybrid electrode have been investigated systematically in 1M H_2SO_4 aqueous electrolyte using three electrode systems.

7.2. Experimental

7.2.1. Synthesis of MoS_2 and MoS_2/rGO

Bulk MoS_2 was prepared by simple hydrothermal route. 20 mmol MoO_3, 50 mmol potassium thiocyanate and 128 mg SDS (sodium dodecyl sulfate) were dispersed in 60 ml DI water using tip sonicator for 30 minutes and kept in 100 ml teflon coated autoclave at 220ºC for 24 hours. After cooling naturally the product was washed by centrifuging at 2000 rpm for 25 minutes with DI water and ethanol several times after that resulting sample was then collected and kept in vacuum drying oven at 60ºC for 24 hours.

To synthesis the MoS_2/rGO hybrid appropriate weight percentage of Graphene oxide (GO) was added to the above mixture and same process was done. In this method production yield of these materials is high and we can easily scale up the production of MoS_2 and rGo-MoS_2 hybrid materials by changing the amount of precursor in appropriate ratio.

7.2.2. MoS_2 and MoS_2/rGO thin film Preparation

To prepare thin film of MoS_2 and MoS_2/rGO hybrid, we have exfoliated as-prepared hydrothermal products in NMP followed by vacuum filtration on the cellulose membrane. After that the films were transferred on the Au-coated PET for further use as a working electrode. Careful measurement of film weight gives the area density of 23.23 μg /cm^2 for MoS_2/rGO hybrid film and 6.97μg/cm^2 for MoS_2 film.

7.3. Characterization:

Crystallinity and phase of the synthesized MoS_2 were characterized by X-ray diffraction, using Cu-Ka radiation (λ=1.541 A^0) on a D8 Advanced Bruker diffractometer. Surface morphology of prepared MoS_2 and MoS_2/rGO hybrid was investigated using FESEM, HITACHI S-4800.The morphology of the as prepared MoS_2 also analyzed by atomic force microscopy (AFM), Transmission electron microscopy (TEM) images were taken using JEOL-2010 transmission electron microscope instrument.

All electrochemical studies were carried out in a three electrode cell system using MoS_2 and hybrid film as a working electrode, platinum wire as a counter electrode, and an Ag/AgCl as a reference electrode with 1M H_2SO_4 aqueous solution as the electrolyte. All the electrochemical analysis including cyclic voltammetry (CV), galvanometric charging–discharging (CD), was carried out on CHI 660E electrochemical workstation.

7.4. Result & Discussion

7.4.1. Structural & morphological analysis:

An XRD pattern of the hydrothermally prepared MoS_2 is represented in the fig.7.1. All the diffraction peaks at 2θ value of 14.32º (002), 33.42 º (100), 39.37 º (103), 58.89 º (110) in this pattern can be well-indexed to the hexagonal phase of MoS_2 (JCPDS card: 37-1492). The sharp peaks also indicate that the synthesized MoS_2 is well crystallized. The most intense peak at 2θ=14.32º (002) provides the interplanar spacing between the nanosheets (6.18A^o), which indicates the formation of well-stacked layered structure of the MoS_2 nanosheets. Other d values corresponding to 2θ equal to 33.42º, 39.37º, and 58.89 º are 2.67A^o, 2.28A^o, and 1.57A^o respectively.

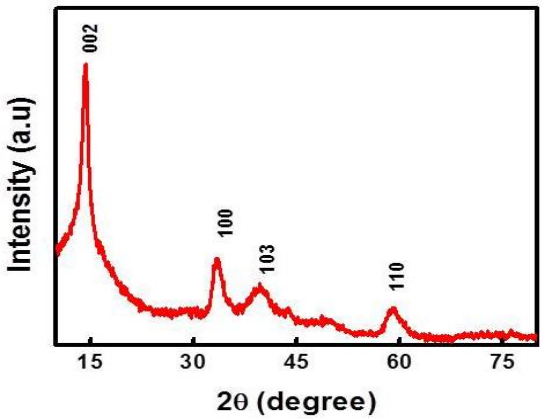

Figure7.1. X-ray diffraction patterns of MoS_2.

Transmission electron microscope (TEM) image of the MoS_2 is taken on a holy carbon coated grid as shown in the figure 7.2(a)which shows sheet like structure of MoS_2 with lateral dimension of <500 nm long. Atomic force microscope image of the MoS_2 shown in the figure 7.2(b), indicates the thickness of MoS_2 nanosheets is 1.09 nm. TEM and AFM samples were prepared after bath sonication of MoS_2 in NMP.

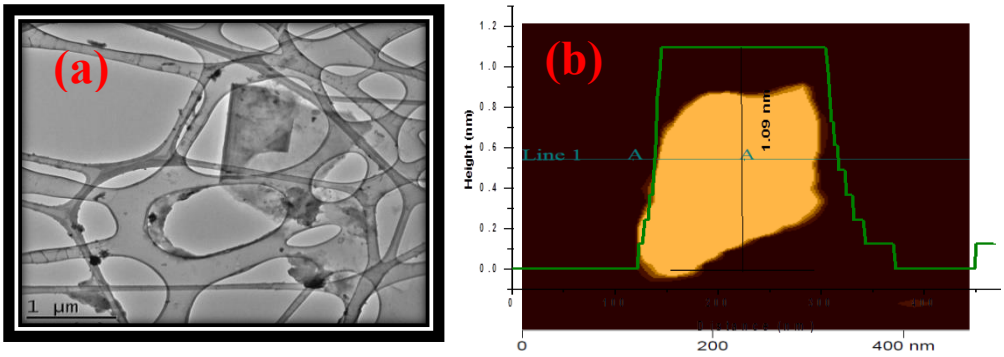

Figure.7.2. TEM image of MoS_2, and (d) AFM image of MoS_2 nanosheets**.**

Figure 7.3(a) and 7.3(b) shows the FESEM images of MoS_2 and MoS_2/rGO hybrid respectively. FESEM image of bare MoS_2 figure 7.3(a) shows the Graphene like morphology, whereas the inset of figure 7.3(b) shows the presence of rGO clearly in the hybrid sample.

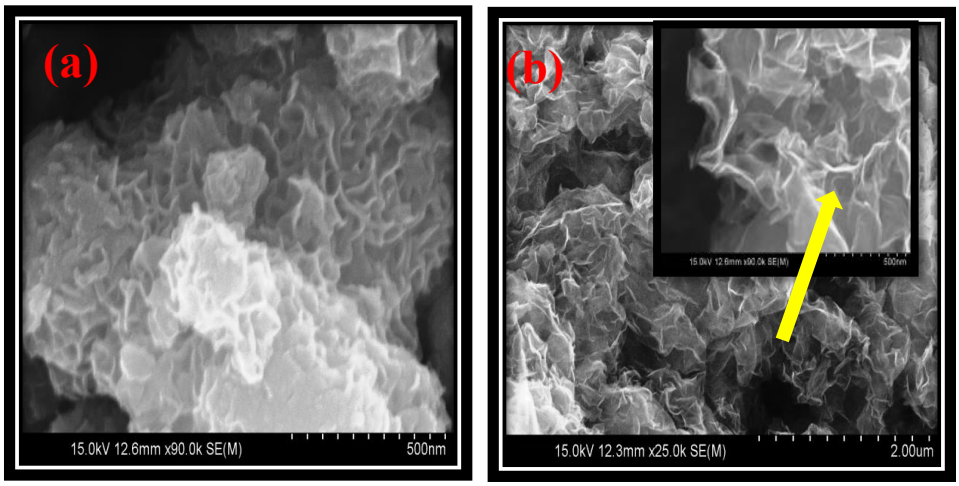

Figure.7.3. (a) FESEM images of MoS_2, (b) MoS_2/rGO.

7.4.2. Electrochemical Study:

The electrochemical performance of the electrode materials have been investigated measuring the cyclic voltammetry using three electrode system at different scan rates from 5 mV/s to100 mV/s with 1M H_2SO_4 aqueous solution as the electrolyte as shown in the figure 7.4(a). The areal capacitances of the hybrid electrode materials calculated from the CV curves to be 14.09mF/cm^2, 8.73 mF/cm^2, 4.025 mF/cm^2, 2.373mF/cm^2, and 1.493mF/cm^2 at 5, 10, 25, 50 and 100 mV/sec scan rates respectively. However the value of areal capacitance for MoS_2 electrode at 5 mV/s scan rate is 0.79mF/cm^2.The specific capacitance values are also calculated for both hybrid and MoS_2 electrodes. The corresponding obtained specific capacitance values are 607 F/g, 376 F/g, 173 F/g, 102 F/g, and 64 F/g at scan rates 5 mV/s, 10mV/s, 20mV/s, 50mV/s, 100mV/s respectively, whereas the specific capacitance value for the MoS_2 electrode is 113 F/g at 5mV/s. Firmiano, et al. [13] reported specific capacitance value of medium concentration MoS_2 and rGO was 265 F/g at 10 mV/sec scan rate whereas specific capacitance value of our sample at the same scan rate is 376 F/g. This might be due to high degree of exfoliation of materials in NMP which gives well dispersed ultrathin nanosheets of MoS_2 and rGO. Figure7.4 (b) represents the CV graphs of MoS_2 and MoS_2/rGO hybrid electrode at 5 mV/s scan rate. Changes of areal capacitance value of the hybrid electrode material with scan rate are shown in the figure 7.4(c). A plot of areal

capacitance vs cycle numbers is shown in the figure 7.4(d), which shows almost 95% retention in the areal capacitance value over 1000 cycles.

Galvanostatic charge–discharge was also investigated at 0.02mA/cm^2 current density in the voltage range between 0 and 0.6 V for the both MoS_2 and MoS_2/rGO hybrid as shown in figure 7.5(a).The areal capacitance values obtained from GCD are 0.170mF/cm^2 and 11.75mF/cm^2 respectively. The hybrid material exhibits a high energy density of 5.71 mWh/cm^2 and a power density of 54.1 mW/cm^2.

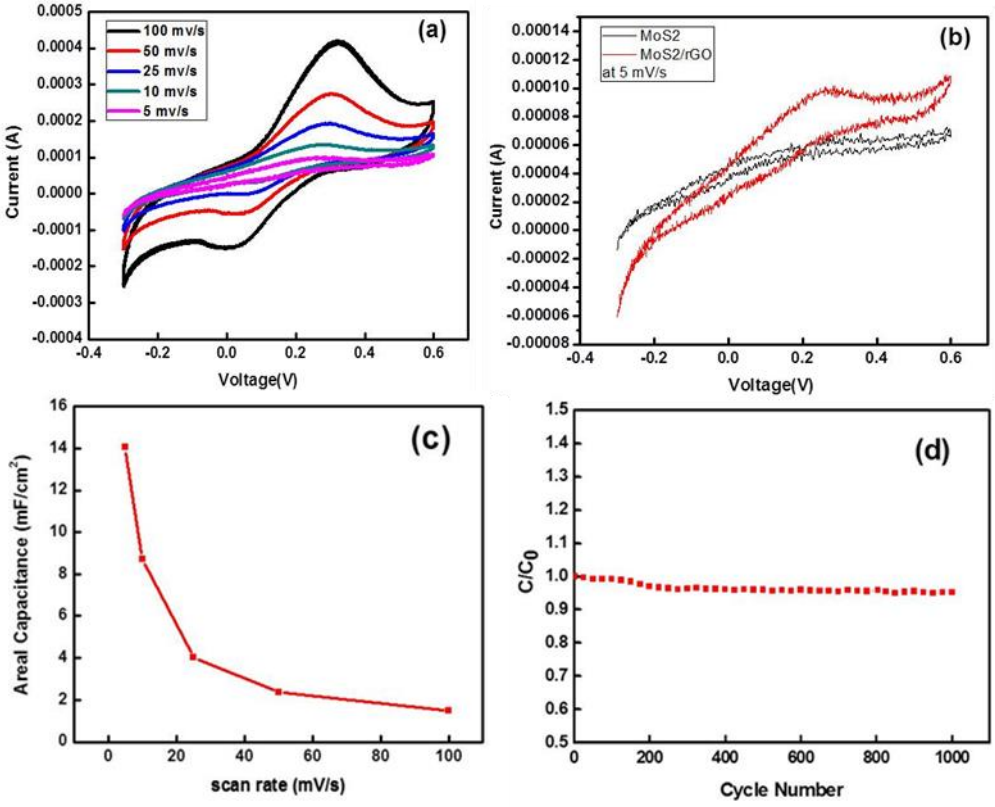

Figure.7.4. (a) CV graph of Hybrid materials at different scan rates,(b) CV graph of Hybrid materials and MoS_2 at 5 mV/s scan rate,(c)Areal capacitance vs scan rate graph of Hybrid material,(d) areal capacitance vs cycle number graph of hybrid material at 100mV/s.

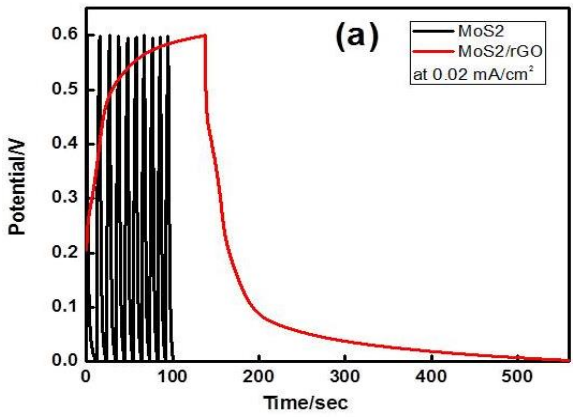

***Figure.*7. 5.** GCD graph of MoS_2 and MoS_2/rGO at constant current density at 0.02mA/cm^3

7.5.Summary

In summary, we have successfully synthesized MoS_2 nano sheets and MoS_2/rGO hybrid by hydrothermal route. Further, we have prepared thin film of hybrid electrodes on an Au coated PET to study the electrochemical nature of MoS_2 nanosheets and hybrid nanostructures of 2D - MoS_2/rGO nanosheets. The specific capacitance of hybrid electrodes was up to 14.09mF/cm^2 at 5mV/s, much higher than that of only MoS_2 electrodes 0.79mF/cm^2 at the same scan rate. Hybrid electrode exhibits high energy density of 5.71mWh/cm^2 and a power density of 54.1mW/cm^2. The composite electrode exhibits an excellent stability after 1000 cycles; almost 95% retention in the areal capacitance value over 250 cycles was seen for hybrid type electrode.Therefore MoS_2/rGO hybrids is a good choice as an electrode for supercapacitor application.

7.6. References

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