Chapter VI
SUPERCAPACITORS BASED ON 2D MoS$_2$, MoSe$_2$, WS$_2$ AND THEIR RGO COMPOSITES

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7.1. Introduction

Rapid invention and development of new technologies, such as portable consumer electronics, and hybrid electric vehicles, has generated a demand for capacitors that provides both high energy density and high power capability. Capacitors that stores energy within the electrochemical double layer at the electrode/electrolyte interface. These capacitors are known by various names such as double layer capacitors, supercapacitors, ultracapacitors, power capacitors, gold capacitors or power cache. Electrical double-layer capacitor is a name that describes the fundamental charge storage principle of such capacitor. However, due to the fact that there are additional contributions to the capacitance other than double layer effects; we will call these capacitors as supercapacitors throughout this chapter.

Electrochemical supercapacitors are passive and static electrical energy storage devices utilised for applications requiring high power density such as energy back-up systems, consumer portable devices and electrical/hybrid automobiles [1, 2]. In a supercapacitor, electrical energy is stored by means of the charge held in the interfacial double layer at a porous carbon material perfuse with an aqueous electrolyte as shown in Figure 6.1(A). In 1989, a program was commenced for the development of ultracapacitor in which short term and long term goals were defined for 1998-2003 and after 2003, respectively [3].

The hybrid vehicles required a power for the acceleration and recover the brake energy. The supercapacitor was supposed to boost the battery or the fuel cell in such hybrid electric vehicles to provide the essential power for acceleration and retrieval of brake energy. In electric vehicles, the applications visualized are primarily boost the components supporting to the batteries or replacing batteries. Supercapacitors constitute a bridge to fill the lacuna between batteries and conventional capacitors such as electrolytic capacitors or metalized film capacitors (Figures 6.1 (B) and (C)). Typically, low temperature fuel cells and batteries are low power devices whereas conventional
Figure 6.1: (A) Schematic diagram of electrostatic capacitors, electrolytic capacitors and electrochemical supercapacitors. (B) and (C) Sketch of Ragone plot for various energy storage and conversion devices. The indicated areas are rough guide lines.
Capacitors may have extremely higher power density (>10^6 watts/dm^3) at very low energy density. Thus, supercapacitors may improve battery performance in terms of power density or capacitor performance in terms of energy density when combined with the respective device. Furthermore, supercapacitors are expected to have much longer cycle life than batteries due to no or negligibly small chemical charge transfer reactions are involved. Figure 6.2 shows the differences between supercapacitors and batteries.

Figure 6.2: Differences between a battery and a supercapacitor: top panel shows the charge and discharge cycles of the two storage systems and table outlines the primary differences.
In electrochemical double layer capacitors (EDLCs), the electric charge is accumulated in double layer mainly due to the electrostatic forces without phase transformation in the electrode materials. The stored electrical energy is based on the separation of charged species in an electrical double layer across the electrode/electrolyte interface [4]. The maximal charge density is accumulated at the distance of the outer Helmholtz Layer formed at a solid/electrolyte interface. The electrochemical capacitor comprises positive electrode with electron deficiency and negative electrode with electron excess, build with same materials [2]. The amount of electrical energy (W) accumulated in such capacitor is proportional to capacitance C and the voltage V and can be expressed as:

\[ W = \frac{1}{2} CV^2 \]  

…….. (6.1)

The electrode materials should be electrochemically inert at all working voltage of the capacitor. The stability of electrolytic medium must be considered, especially in the aqueous solutions for which the maximum voltage is restricted to 1 V owing to the thermodynamic electrochemical window (1.23 V). The operating voltage of the capacitor is determined by the decomposition voltage of the electrolyte [2]. Hence, the electrical energy accumulated in an electrochemical capacitor can be significantly enhanced by the selection of an appropriate medium where the decomposition potential of the electrolyte varies from 3 V to 5 V. however, the possibility of reaching 3 V or more is still very attractive and multitude of research is being performed, particularly for applications with a low specific power. Finally, the selection of the electrolyte depends on the specific power and energy values demanded.

Presently the development of electrochemical capacitors is mainly connected with searching for optimal electrode materials capable of a high, efficient accumulation of electrical energy with long durability. An electrochemical capacitor is formed by two polarizable electrodes, a separator and an electrolyte (Figure 6.1). The specific capacitance C is determined by the series equivalent circuit, containing anode capacitance \( C_a \) and cathode capacitance \( C_c \) according to the equation:

\[ \frac{1}{C} = \frac{1}{C_a} + \frac{1}{C_c} \]  

…….. (6.2)
For electrochemical double layer capacitor, the amount of electrical charge accumulated by electrostatic forces depends on the surface of the electrode/electrolyte interface and on the ease of access of the charge carriers to this interface. The capacitance is proportional to surface area S of the material, relative permittivity of the solution ε, and reciprocally depends on thickness of double layer:

$$ C = \frac{S \varepsilon}{d} $$

The charge separation is of the order of a few Å in concentrated electrolyte solution. Theoretically, for higher value of the capacitance, the higher surface area and concentration of electrolyte is imperative. For example, in carbon, the double layer capacitance is appended with the electrode/solution interface and has a value of 15-50 µF/cm². For carbon, considering an average value of 25µF/cm² and specific area 1000 m²/g, the ideal attainable capacitance would be 250 F/g. But practically attained values are of few tens of F/g in electrochemical capacitors because the accessibility of carbon surface to the electrolyte. The developed surface area of carbon should consist of micropores (< 2 nm) often hardly accessible or not accessible to ions [5-7]. In order to achieve a higher capacitance the electrode surface area is additionally increased by using porous electrodes with an extremely large internal effective surface. Combination of two such electrodes gives an electrochemical capacitor of rather high capacitance. Figure 8.1 (A) shows a schematic diagram of an electrochemical supercapacitor consisting of two high surface-area electrodes separated by a porous separator. The electrodes along with the separator are soaked with a suitable electrolyte.

Supercapacitors have also been built using a different principle, wherein there is electron transfer between the electrode and the electrolyte, so called pseudocapacitance. Pseudocapacitance is another way to enhance the capacitance values which depends on the surface functionality of the carbon and/or on the presence of electroactive species. Pseudocapacitance arises when, for thermodynamic reasons, there is some continuous dependence of charge q, passed Faradiacally in oxidation or reduction, upon the electrode potential. Solid oxide redox systems like RuO₂ can also exhibit pseudocapacitance.

Poros carbon materials such as activated carbon [7, 8], xerogels [9], carbon nanotubes [10, 11], mesoporous carbon [12] and carbide-derived carbons [13] have been investigated for use as electrodes in EDLCs. In the last few years, there has been great
interest in graphene, TMDC and their composites which constitutes an entirely new class. Electrical characterization of single-layer graphene has been reported [14, 15]. We investigated the use of graphene as electrode material in electrochemical supercapacitors. For this purpose, we employed graphene prepared by hummer’s method and its supercapacitor behaviour was carried out with aq. Na$_2$SO$_4$ as electrolyte.

In this chapter, attempts have been made to study the supercapacitor behaviour of transition metal dichalcogenides and their hybrids grown by a facile hydrothermal process. Particularly influence of scan rate on the C-V curves and changes in the specific capacitance with scan rate are the primary interest of present chapter. The supercapacitor behaviour was carried out with 1M Na$_2$SO$_4$ as electrolyte for all samples. A typical comparative study of the above particular characteristics changes with different layered materials and their graphene composites are critically furnished in the following section.

6.2. Experimental details

The graphene oxide (GO) were synthesized by modified Hummer’s method using graphite powders as the starting material as discussed in section 3.2.1(a). The MoS$_2$, WS$_2$, MoSe$_2$ and their graphene composites were prepared by a facile one step hydrothermal process as described earlier (section 3.2). For MoS$_2$, appropriate amount of ammonium molybdate and thiourea were mixed in 40 ml deionized water. The mixture transferred in stainless steel autoclave of 60 ml volume and maintained at 220°C for 24h. The MoS$_2$/RGO composites were prepared by CTAB (Cetyltrimethyl Ammonium Bromide) assisted hydrothermal route. Further, 0.02M CTAB was dissolve in 25ml de-ionized water under stirring, as prepared GO (50 mg) was added into the solution under stirring. The same process was followed mention for MoS$_2$ sheets for the preparation of MoS$_2$/RGO. For MoSe$_2$, the sodium molybdate and selenium powder was dissolved in 30 ml ethylene glycol and mixed with 20 ml hydrazine hydrate. The mixture then transferred into 100 ml autoclave and heated at 200°C for 24h. Further, 10 ml of 5mg/ml GO solution was added to mixture of sodium molybdate and selenium. The same process of MoSe$_2$ followed for the preparation of MoSe$_2$/RGO. For WS$_2$, the tungsten hexachloride and thiourea were dissolved in 40 ml deionized water. Then the solution poured in 60 ml stainless steel autoclave and maintained at 265°C for 24h. Further, 8ml of 5mg/ml GO solution was added to mixture of tungsten hexachloride and thiourea and total volume was maintained at 40 ml. The same process was followed mention for WS$_2$ sheets for the
preparation of WS₂/RGO. Extremely fine quality nanosheets were obtained with optimized parameters and employed for electrochemical supercapacitor studies.

6.3. Fabrication of supercapacitor

Supercapacitors were fabricated using a swage-lok type electrode cell. The cyclic voltammetry experiments in a three-electrode electrochemical cell were carried out to know about the supercapacitor behavior. The cycling voltammetry measurements in the two electrode configuration were was carried out with the help of Autolab, AUT83984 potentiostat/galvanostat (Metrohm Ltd., Netherland). The samples loaded on glassy carbon as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode. The glassy carbon electrodes (GCE, working electrode) of 3.0 mm in diameter and were polished with finer emery paper and 0.3 µm Al₂O₃ powder and were cleaned in an ultrasonic bath, dried in a vacuum. In actual process, the RGO, TMDCs and TMDC/RGO materials were dispersed in ethanol to get a homogenous solution and drop coated on working electrode. The materials dried in vacuum followed by drop coating of 10 µL of Nafion solution. Mass of the samples used was measured using a microbalance. Electrochemical experiments at slow scan rates were carried out in 1 M aqueous Na₂SO₄ solution as the electrolyte and the potential window for cycling was optimized for each materials.

6.3.1. Evaluation of electrochemical properties

The electrochemical measurements of supercapacitors based on TMDC and TMDC/RGO hybrid were carried out with three-electrode electrochemical cell. The specific capacitance for the supercapacitors was enumerated from the cyclic voltammogram measurements using the following equation

\[ C_s' = \frac{\int I(V)dV}{2m(s(V_a - V_b))} \]  

where \( \int I(V)dV \) is the area under the CV curve, \( m \) is the mass of sample, \( s \) is the scan rate, and \( (V_a - V_b) \) is the working window. The specific capacitance of the material also calculated from the charge/discharge curves, was calculated using the following equation;

\[ C_s'' = \frac{\Delta t}{m\Delta V} \]
where $I$ be the current density, $\Delta t$ be the discharging time, $m$ be the mass of the sample loaded, $\Delta V$ be the potential window. The energy density ($E_d$) and power density ($P_d$) were calculate with following equations

\[
\text{Energy density (E)} = \frac{1}{2} C (\Delta V)^2 \\
\text{Power density (P)} = \frac{E}{\Delta t}
\]  

\[\text{……….. (6.6)}\]

\[\text{……….. (6.7)}\]

where $C$, $\Delta V$, $E$, $P$ and $\Delta t$ are the specific capacitance, applied potential, energy density, power density and discharge time respectively.

6.4. Results and discussion

6.4.1. Reduced graphene oxide (RGO)

The reduced graphene oxide has a potential to improve the electrochemical performance as supercapacitor electrode due to the unique microstructure and high surface area. Such improvement in the performance of supercapacitor attributed to the intercalation of Na$^+$ ions into the van der Waals gap of the RGO layers.

The electrochemical performance of the as-grown RGO sheets was carried out using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and impedance spectroscopy in a 1M Na$_2$SO$_4$ electrolyte solution. Figure 6.3(a) depicts the typical cyclic voltammetry (CV) curves recorded at different scan rates ranging from 2 to 130mV/s. The CV curves of RGO electrode exhibits quasi-rectangular shapes at different scan rates indicating their electrochemical behaviour. No peak is observed at different scan rates in the CV curves. The absence of any peak in the CV curves indicates that the electrode is charged and discharged at a pseudo-constant rate over the complete voltammetric cycle. Figure 6.3(b) shows the specific capacitances evaluated from the cyclic voltammetry curves as a function of different scan rates. The decrease in capacitance at higher scan rates is because of lower diffusion of charged ions. Similar phenomena have been observed in literature for supercapacitors based on carbon based materials [16, 17]. The specific capacitances evaluated from the CV curves were 117, 61, 40, 23, 19, 18, 17, and 15 Fg$^{-1}$ at scan rate of 2, 5, 10, 30, 50, 70, 100, and 130mV/s respectively. From experimental analysis, it is revealed that the specific capacitance of RGO nanosheets decreased abruptly up to 10mV/s and thereafter decreases with slower kinetics. Figure 6.3(c) shows the galvanostatic charging discharging curves of the RGO nanosheets.
electrodes measured at 0.3, 0.5 and 1 A g\(^{-1}\) current density in 1M Na\(_2\)SO\(_4\) electrolyte. During the charging and discharging process, the charge curve is symmetric with discharge curve which indicates the contribution of electrical double layer capacitance along with pseudocapacitance. The specific capacitance of RGO electrode could be enumerated with the equation (6.5). The calculated specific capacitance values for as prepared RGO electrode were 5.2, 4.6 and 3.33 F g\(^{-1}\) at current density 0.3, 0.5 and 1 A g\(^{-1}\) respectively. Figure 6.3(d) shows specific capacitance as a function of current density. The specific capacitance of RGO electrode decreased as the current density increased. This decrease in specific capacitance might be due to the insufficient time available for diffusion of the electrolyte ions into the inner electrode surface [18, 19]. Figure 6.3(e) exhibits the energy density as a function of power density for RGO.

6.4.2. Molybdenum disulphide (MoS\(_2\))

MoS\(_2\) is a layered-structured material analogous to graphene, characterized by a nanosheet-like morphology. In MoS\(_2\), the Mo metal layer is sandwiched between two S layers. The triple layers are stacked and held together by weak van der Waals interactions [20-23]. MoS\(_2\) continues to attract a lot of attention, particularly in supercapacitors because of its higher intrinsic fast ionic conductivity (than oxides) and higher theoretical capacity (than graphite) [20, 24]. Soon and Loh [25] have evinced the use of MoS\(_2\) as an electrode material for supercapacitors.

The cyclic voltammetric (CV) evolutions of the individual MoS\(_2\) nanosheets obtained from the 3-electrode configuration in 1M Na\(_2\)SO\(_4\) at different scan rate are as visualized in Figure 6.4 (a). From figure it is observed that, the cyclic voltammetry (CV) curves of the MoS\(_2\) materials shows quasi-rectangular shapes, which is a strong deviation from the ideal rectangular shape that was expected from the EDLC. The nearly rectangular shapes at different scan rates are indicate their potential as supercapacitors. Figure 6.4(b) shows the variation of specific capacitance as a function of the scan rate. The capacitance values of MoS\(_2\) based electrode decrease with increasing scan rates. The highest specific capacitance calculated from CV loop of MoS\(_2\) was found to be 127 F/g. The specific capacitance decreased rapidly up to the scan rate 10mV/s and then gradually decays with higher scan rates. The decrease in the capacitance at higher scan rate is due the fact that the lower diffusion of charged ions at higher scan rates. Figure 6.4(c) shows
Figure 6.3: (a) Cyclic voltammogram at different scan rates, (b) variation of specific capacitance with scan rate, (c) Galvanostatic charge/discharge curve, (d) variation of specific capacitance with current density (e) Ragone plot for RGO nanosheets.
the galvanostatic charging discharging curves of as-prepared MoS\(_2\) nanosheets electrodes measured at 0.3, 0.5 and 1 A g\(^{-1}\) current density in 1M Na\(_2\)SO\(_4\) electrolyte. The charging and discharging curves shows a triangular shape with slight distortion from linearity. It reveals that the material exhibits electrochemical charge storage behavior via EDLC and pseudocapacitance reactions. The specific capacitance of as-prepared MoS\(_2\) electrode could be calculated and can be found to be 6.25, 2.91 and 2.08 F g\(^{-1}\) at current density 0.3, 0.5 and 1 A g\(^{-1}\) respectively. Figure 6.4(d) shows specific capacitance as a function of current density. The specific capacitance of RGO electrode decreased as the current density increased. The decrease in specific capacitance might be due to the insufficient time available for diffusion of the electrolyte ions into the inner electrode surface [18, 19]. Figure 6.4(e) exhibits the energy density as a function of power density for MoS\(_2\).

6.4.3. Molybdenum disulphide/RGO

The energy storage devices with high efficiency are one of the greatest scientific and engineering challenges. These instill the need to initiate the research on innovative energy storage devices [26]. The development in modern technology will be supplemented by the energy storage solutions which are more compact, integrated and functional for power [27]. Supercapacitors are appealing energy storage that provides both high energy and power density [28]. The performance of supercapacitor extremely depends on the specific surface area of electrode and the properties of electrolytes [29]. Thus, modifying the surface properties is crucial in energy storage devices to achieve high power and energy density [30, 31]. In MoS\(_2\)/RGO hybrids, the large surface area and the nanoscale size of MoS\(_2\) and RGO significantly reduce the diffusion length over which both ions and electrons must transfer during the charge-discharge process. RGO helps to enhance the conductivity of the hybrids because of uniform coverage of MoS\(_2\) on RGO. This facilitates fast transportation of the electrons throughout the hybrid electrode material. The I–V characteristics of MoS\(_2\) and MoS\(_2\)/RGO films confirm the enhancement in conductivity of the MoS\(_2\)/RGO hybrids as compared to bare MoS\(_2\) nanosheets. The electrochemical properties of the MoS\(_2\)/RGO hybrids were carried out in 1M Na\(_2\)SO\(_4\) electrolyte by using cyclic voltammetry (CV) cycling process.

The cyclic-voltammetric (CV) observations of the MoS\(_2\)/RGO hybrid nanosheets obtained from the 3-electrode configuration in 1M Na\(_2\)SO\(_4\) at different scan rate are as
Figure 6.4: (a) Cyclic voltammogram at different scan rates, (b) variation of specific capacitance with scan rate, (c) Galvanostatic charge/discharge curve, (d) variation of specific capacitance with current density (e) Ragone plot for MoS$_2$ nanosheets.
visualized in Figure 6.5(a). These curves are symmetric, indicating that the hybrid composite has a good electrochemical capacitive characteristic. The cyclic voltammetry (CV) curves of the MoS$_2$/RGO material shows quasi-rectangular shapes at different scan rates indicating their potential as supercapacitors. Figure 6.5(b) shows the specific capacitance as a function of the different scan rates. The specific capacitances were determined from CV curves. The highest specific capacitance of MoS$_2$/RGO hybrid is 351 F/g at scan rate 2mV/s. The capacitance values of MoS$_2$/RGO based electrode decrease with increasing scan rates. Similar to the MoS$_2$ nanosheets, MoS$_2$/RGO also exhibits the phenomenon of decrease in capacitance with higher scan rates. The decrease in the capacitance of MoS$_2$/RGO electrode is due to the lower diffusion of charged ions at higher scan rates. Figure 6.5(c) shows the galvonostatic charging discharging curves of as-prepared MoS$_2$/RGO nanosheets electrodes measured at 0.3, 0.5 and 1A g$^{-1}$ current density in 1M Na$_2$SO$_4$ electrolyte. The charging and discharging curves shows a triangular shape with slight distortion from linearity. It reveals that the hybrid material exhibits better electrochemical charge storage behavior via EDLC and pseudocapacitance reactions. The specific capacitance of as-prepared MoS$_2$/RGO electrode could be calculated and were found to be 35.5, 25.83 and 17.08 Fg$^{-1}$ at current density 0.3, 0.5 and 1 Ag$^{-1}$ respectively. Figure 6.5(d) shows specific capacitance as a function of current density. The specific capacitance of MoS$_2$/RGO electrode decreased as the current density increased. The decrease in specific capacitance might be due to the insufficient time available for diffusion of electrolyte ions into the inner electrode surface [18, 19]. Figure 6.5(e) exhibits the energy density as a function of power density for MoS$_2$/RGO.

6.4.4. Molybdenum diselenide (MoSe$_2$)

The MoSe$_2$ is another member of the TMDC family and has a structure analogous to graphene. Molecular layers of MoSe$_2$ are formed by strong covalent bonding between Mo atoms and Se atoms. The individual layers are further stacked together via weak van der Waals interactions [32, 33]. MoSe$_2$ has a larger space between adjacent layers and a smaller bandgap compared to MoS$_2$. This leads to a better coulombic efficiency and higher electronic conductivity than MoS$_2$ [34, 35].

The typical cyclic voltammetry (CV) curves of MoSe$_2$ nanosheets drop coated on working electrode at different scan rates are depicted in Figure 6.6(a). The quasi-
Figure 6.5: (a) Cyclic voltammogram at different scan rates, (b) variation of specific capacitance with scan rate, (c) Galvanostatic charge/discharge curve, (d) variation of specific capacitance with current density (e) Ragone plot for MoS$_2$/RGO.
rectangular shape retain by all CV curves which confirms the ideal supercapacitor behaviour of the material with remarkable reversibility. The relationship between the specific capacitance of the MoSe₂ nanosheets at various scan rates is displayed in Figure 6.6(b). The specific capacitance of MoSe₂ calculated from the CV curves applying the equation (6.4). The highest specific capacitance of 113 F/g was achieved from MoSe₂ nanosheets electrode. From figure it is revealed that, the specific capacitance drop abruptly with increasing the scan rate up to 30 mV/s. Beyond 30 mV/s scan rate, the specific capacitances gradually decrease with increase in scan rate up to 130mV/s. This is because, at higher scan rates, the mass-transport limitation of Na⁺ ions between the electrolyte and the electrode limits the electrochemical performance, which leads to a lower capacitance [45-48]. Figure 6.6(c) shows the galvanostatic charging discharging curves of as-prepared MoSe₂ nanosheets electrodes measured at 0.3, 0.5 and 1A g⁻¹ current density in 1M Na₂SO₄ electrolyte. The charging and discharging curves shows nearly triangular shape with slight distortion from linearity. It reveals that the material exhibits electrochemical charge storage behavior via EDLC and pseudocapacitance reactions. The specific capacitances of as-prepared MoSe₂ electrode could be calculated and were found to be 4, 2.96, and 2.22 Fg⁻¹ at current density 0.3, 0.5 and 1 Ag⁻¹ respectively. Figure 6.6(d) shows specific capacitance as a function of current density. The specific capacitance of MoSe₂ electrode decreased as the current density increased. The decrease in specific capacitance might be due to the insufficient time available for diffusion of the electrolyte ions into the inner electrode surface [18, 19]. Figure 6.6(e) exhibits the energy density as a function of power density for MoSe₂.

6.4.5. Molybdenum diselenide/RGO

Molybdenum diselenide (MoSe₂), a member of TMDC family that has a layered structure (Se–Mo–Se), might be a good choice for energy storage devices [36, 37]. In addition, the interlayer spacing of MoSe₂ (0.646 nm) is larger than that of graphite (0.335 nm) and MoS₂ (0.615 nm) [38] and hence considered as promising electrode material for lithium-ion batteries, sodium-ion batteries, and supercapacitors. Besides, little bit attention paid towards MoSe₂ as an electrode for supercapacitor. It might be due to the poor electrical conductivity that obstructs its electrochemical performance and practical implementation. The enhancement in the electrochemical performance of MoSe₂ involves the design of a hybrid nanostructure with a carbon matrix. Graphene is most beneficial
Figure 6.6: (a) Cyclic voltammogram at different scan rates, (b) variation of specific capacitance with scan rate, (c) Galvanostatic charge/discharge curve, (d) variation of specific capacitance with current density, (e) Ragone plot for MoSe$_2$ nanosheets.
compared with other carbon materials to support host materials due to its large surface area, superior electrical conductivity, good chemical stability, and excellent mechanical flexibility [39, 40].

The typical cyclic voltammetry (CV) curves of MoSe$_2$/RGO nanosheets drop coated on working electrode at different scan rates are depicted in Figure 6.7(a). The quasi-rectangular shape retain by all CV curves which confirms the ideal supercapacitor behaviour of the material with remarkable reversibility. The relationship between the specific capacitance of the MoSe$_2$ nanosheets at various scan rates is display in Figure 6.7(b). The highest specific capacitance of 333 F/g obtained from MoSe$_2$/RGO hybrid at scan rate 2mV/s. From figure it is revealed that, the specific capacitance drop abruptly with increasing the scan rate up to 30 mV/s. Beyond 30 mV/s scan rate, the specific capacitance gradually decrease with increase in scan rate up to 130 mV/s. This is due to the fact that, the mass-transport limitation of Na$^+$ ions between the electrolyte and the MoSe$_2$/RGO nanosheets electrode limits the electrochemical performance, which leads to a lower capacitance at higher scan rates [41-44]. Figure 6.7(c) shows the galvonostatic charging discharging curves of as-prepared MoS$_2$ nanosheets electrodes measured at 0.3, 0.5 and 1A g$^{-1}$ current density in 1M Na$_2$SO$_4$ electrolyte. The charging and discharging curves shows nearly triangular shape with slight distortion from linearity. It reveals that the material exhibits electrochemical charge storage behavior via EDLC and pseudocapacitance reactions. The specific capacitance of as-prepared MoSe$_2$/RGO electrode could be calculated and were found to be 28, 21 and 13 Fg$^{-1}$ at current density 0.3, 0.5 and 1 Ag$^{-1}$ respectively. Figure 6.7(d) shows specific capacitance as a function of current density. The specific capacitance of MoSe$_2$/RGO electrode decreased as the current density increased. The decrease in specific capacitance might be due to the insufficient time available for diffusion of the electrolyte ions into the inner electrode surface [18, 19]. Figure 6.7(e) exhibits the energy density as a function of power density for MoSe$_2$/RGO.

6.4.6. Tungsten disulphide (WS$_2$)

WS$_2$ formed by 2D covalently bonded S–W–S layers separated by a van der Waals gap. These layers are stacked together by weak van der Waals force. WS$_2$ possesses hexagonal crystal structure with space group P63/mmc and each WS$_2$ monolayer contains an individual layer of W atoms with 6-fold coordination symmetry,
Figure 6.7: (a) Cyclic voltammogram at different scan rates, (b) variation of specific capacitance with scan rate, (c) Galvanostatic charge/discharge curve, (d) variation of specific capacitance with current density (e) Ragone plot for MoSe$_2$/RGO nanosheets.
which are then hexagonally packed between two trigonal atomic layers of S atoms [45]. The WS$_2$ material has attracted attention for diverse applications in future nanoelectronic devices because of its 2D layered structure and direct-band gap [45].

The typical cyclic voltammetry (CV) curves of the WS$_2$ electrode at different scan rates are as shown in Figure 6.8(a). The CVs show quasi-rectangular shapes at different scan rates indicating their potential as supercapacitors with considerable reversibility. Figure 6.8(b) shows the specific capacitance values obtained for the WS$_2$ at different scan rates. The highest specific capacitance value of 140 F/g obtained for WS$_2$ nanosheets electrode form CV curve at scan rate of 2mV/s. These CV curves are symmetric, indicating that the hybrid composite has a good electrochemical capacitive characteristic and superior reversible redox reaction. The capacitance values of WS$_2$ based cell decrease with increasing scan rates. Rapid decrement in the capacitance observed upto 30 mV/s scan rate, thereafter it decrease with slower kinetics. The decrease in the capacitance of WS$_2$ cell is mainly due to the lower diffusion of charged ions at higher scan rates. Figure 6.8(c) shows the galvonostatic charging discharging curves of as-prepared WS$_2$ nanosheets electrodes measured at 0.3, 0.5 and 1A g$^{-1}$ current density in 1M Na$_2$SO$_4$ electrolyte. The charging and discharging curves shows nearly triangular shape with slight distortion from linearity. It reveals that the material exhibits electrochemical charge storage behavior via EDLC and pseudocapacitance reactions. The specific capacitance of as-prepared WS$_2$ electrode could be calculated and were found to be 4, 2.67 and 1.67 Fg$^{-1}$ at current density 0.3, 0.5 and 1 Ag$^{-1}$ respectively. Figure 6.8(d) shows specific capacitance as a function of current density. The specific capacitance of WS$_2$ electrode decreased as the current density increased. The decrease in specific capacitance might be due to the insufficient time available for diffusion of the electrolyte ions into the inner electrode surface [18, 19]. Figure 6.8(e) exhibits the energy density as a function of power density for WS$_2$.

### 6.4.7. Tungsten disulphide/RGO

More scalable and cost effective development of TMDC and its hybrid materials for energy storage and energy conversion devices is extremely imperative. Among the energy storage devices, supercapacitors are an important power source. The supercapacitors are considered as one of the most promising energy-storage devices due to high power density, very long cycle life faster charge/discharge processes, and
Figure 6.8: (a) Cyclic voltammogram at different scan rates, (b) variation of specific capacitance with scan rate, (c) Galvanostatic charge/discharge curve, (d) variation of specific capacitance with current density (e) Ragone plot for WS$_2$ nanosheets.
relatively low cost [46-48]. Due to the high surface area and large in-plane conductivity, the 2D layered materials including graphene [46, 47] reduced graphene oxide, [49] metal oxides, [50-52] metal chalcogenides, [53-57] and their composites have shown efficient and promising materials for high performance supercapacitor electrodes. Thus, a homogeneous or heterogeneous nanostructured material for supercapacitor application strongly depends on the following factors: utilization of suitable methods to prepare desired nanostructure; selection of a proper composition of distinct materials; optimization of the heterogeneous nanostructure [58, 59]. Here, we employed WS₂/RGO hybrid material to investigate its electrochemical properties. The electrochemical properties of the WS₂/RGO hybrids investigated in 1 M Na₂SO₄ electrolyte with cyclic voltammetry.

To obtained information about the electrochemical properties of hydrothermally grown WS₂/RGO hybrid in three electrode system with Na₂SO₄ (1M) as electrolyte solution. Figure 6.9(a) shows the representative cyclic voltammetric (CV) curves recorded at different scan rate ranging from 2 to 130mV/s. The CVs curves show quasi-rectangular shapes at different scan rates indicating their potential as supercapacitors. These CV curves are symmetric, indicating that the hybrid composite has a good electrochemical capacitive characteristic and superior reversible redox reaction. The specific capacitance values evaluated from CV curves applying equation 6.4. Figure 6.9(b) shows the plot of specific capacitance values as a function of scan rate obtained for the WS₂/RGO. The highest specific capacitance of 356 F/g for WS₂/RGO was obtained at 2mV/s scan rate. Initially the capacitance values of WS₂/RGO based cell decrease rapidly at higher scan rates. The decrease in the capacitance of WS₂/RGO cell is mainly due to the lower diffusion of charged ions at higher scan rates. Hence WS₂/RGO hybrids emerge as one of the promising supercapacitor electrode material because of their high specific capacitance, energy density. Figure 6.9(c) shows the galvonostatic charging discharging curves of as-prepared WS₂/RGO nanosheets electrodes measured at 0.3, 0.5 and 1A g⁻¹ current density in 1M Na₂SO₄ electrolyte. The charging and discharging curves shows nearly triangular shape with slight distortion from linearity. It reveals that the material exhibits electrochemical charge storage behavior via EDLC and pseudocapacitance reactions. The specific capacitance of as-prepared WS₂ electrode could be calculated and available for diffusion of the electrolyte ions into the inner electrode surface [18, 19]. Figure 6.9(e) exhibits the energy density as a function of power density for WS₂/RGO.
Figure 6.9: (a) Cyclic voltammogram at different scan rates, (b) variation of specific capacitance with scan rate, (c) Galvanostatic charge/discharge curve, (d) variation of specific capacitance with current density (e) Ragone plot for WS$_2$/RGO nanosheets.
6.5. Conclusion

- The 2D semiconductor materials such as, MoS$_2$, MoSe$_2$, WS$_2$, and their RGO hybrids were synthesized by facile hydrothermal process.
- The supercapacitor structures were formed and behaviour of these was examined with a special significance.
- For all samples, the specific capacitance decreased significantly with increased in scan rates. With the addition of reduced graphene oxide, the specific capacitance increases significantly compare to pristine materials.
- The specific capacitance, energy density and power density of WS$_2$/RGO electrode was found to be higher than other.

Table 6.1: The performance parameters of supercapacitor based on 2D MoS$_2$, MoSe$_2$, WS$_2$ and their RGO composites photosensors.

<table>
<thead>
<tr>
<th>2D Semiconductor</th>
<th>Specific capacitance</th>
<th>Energy density (Wh/Kg)</th>
<th>Power density (W/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From CV (Fg$^{-1}$)</td>
<td>From C/D (Fg$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>RGO</td>
<td>117</td>
<td>5.2</td>
<td>2.6</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>127</td>
<td>6.3</td>
<td>2.0</td>
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<tr>
<td>MoS$_2$/RGO</td>
<td>351</td>
<td>35.5</td>
<td>22.7</td>
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<tr>
<td>MoSe$_2$</td>
<td>113</td>
<td>4.0</td>
<td>1.57</td>
</tr>
<tr>
<td>MoSe$_2$/RGO</td>
<td>333</td>
<td>28.0</td>
<td>11.3</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>140</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>WS$_2$/RGO</td>
<td>356</td>
<td>37.3</td>
<td>11.9</td>
</tr>
</tbody>
</table>
References


