QATAR UNIVERSITY

COLLEGE OF ARTS AND SCIENCES

PREPARATION AND CHARACTERIZATION OF FLEXIBLE ALL SOLID STATE CNTS/MNO2 SUPERCAPACITORS

BY

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ABSTRACT

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Title: Preparation and characterization of flexible all solid state CNT/MnO₂ Supercapacitors

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In this work, CNTs/MnO₂ hybrid supercapacitors were prepared using RF magnetron sputtering as deposition technique. The as-prepared composite materials were characterized by different morphology and spectroscopy techniques, CNTs/MnO₂ composites were then tested as electrode materials in symmetric supercapacitors in solution and in solid state.

The surface morphology, structural and mechanical properties of the CNTs and CNTs/MnO₂ electrodes were characterized by Raman spectroscopy, scanning electron microscope-energy dispersive spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). XRD, Raman spectroscopy and XPS measurements confirmed the formation of MnO₂ films. While SEM images demonstrated, the uniform distribution of MnO₂ layers. Furthermore, tensile tests demonstrated the flexibility of the prepared CNTs/MnO₂ composite electrodes.

The electrochemical behavior of three CNTs/MnO₂ composites with 350, 700, and 1000 nm thick MnO₂ was investigated in 1 M Na₂SO₄ aqueous solution via cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD). The CV and GCD tests showed that all electrodes with different MnO₂ thicknesses exhibit excellent pseudocapacitive behavior as compared with CNTs sheet in the potential window of 0 - 1.0 V for CV and 0 - 0.8 V for GCD.
At small scan rates (5 mV/s), the electrode of 1000 nm MnO₂ thickness displayed specific capacitance of CV (1676 F/g), which is much higher than that of the other electrodes (609, and 441 F/g) for the electrodes with 700 nm and 350 nm, respectively. The specific capacitance measured using charge/discharge process showed similar thickness dependence as in CV measurements, where the specific capacitance increases with increasing the MnO₂ thickness.

Additionally, the electrode with 1000 nm MnO₂ thickness exhibited a cyclic stability with capacitance retention of 85.8% of its peak value after 400 cycles meanwhile, the other electrodes exhibited almost the same cyclic stability with capacitance retention of 59% after 400 cycles.

The all solid-state flexible supercapacitors consisting of two-electrode system with a PVA/H₂PO₄/CNTs/MnO₂ symmetric capacitor with 1000 nm MnO₂ thickness showed the highest specific capacitance in comparison with the other devices with 350 and 700 nm thick MnO₂. The device with 700 nm thick MnO₂ exhibited the best cyclic stability with capacitance retention of 67% of its initial capacitance after 400 cycles compared with the other devices.
DEDICATION

This thesis is dedicated to my family who have always been a constant source of support and encouragement during the challenges of my whole life. Also to my friends who were the source of support, and power all through the journey towards achieving the best I can do.
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CHAPTER 1: INTRODUCTION

With the massive revolution of the global economy and the increase in the energy consumption, the demand for more energy sources, energy conversion and storage with high efficiency, environment-friendly, and sustainable becomes significant. Currently, the production of energy storage systems such as solar panels batteries and electrochemical supercapacitors (ES) is moved to more productive solutions to reach the highest sufficiency. Even though batteries dominate the energy storage market, they have low power density, low rate and a small number of charge-discharge cycles. These obstacles can be overcome using supercapacitors. Supercapacitors or known as ultracapacitors have attracted great attention for advanced energy storage due to their high power and energy densities\(^1\), high capability, long lifecycle and high charge-discharge rates.\(^2\)

There are two categories of supercapacitors depending on their charge storage mechanisms, electrical double-layer capacitors (EDLCs) and pseudocapacitors. In EDLCs the capacitance results from the charge separation at the electrolyte and electrode interface. In pseudocapacitors capacitance results from the reversible Faradaic reaction at the electrode surface. This indicates the importance of the electrode material in determining the efficiency and the capacitance of supercapacitors. In EDLCs carbon allotropes are the most commonly used electrode material; activated carbon (AC)\(^3,4\), graphene\(^5-7\), carbon nanofibers\(^8,9\), and carbon nanotubes (CNTs)\(^10,11\). Transition metal oxides and conducting polymers are used as pseudocapacitor electrode materials.\(^12\)
1.1 Types of Supercapacitors

There are three classifications of supercapacitors based on the charge storing mechanism such as electrochemical, electrostatic and hybrid as shown in Figure 1.

![Diagram showing the classification of supercapacitors]

*Figure 1: The classification of Supercapacitors*

1.1.1 Electrostatic capacitors (EDLC)

In general, the electrostatic capacitor is referred as EDLC which derived from the principle of storing the electrostatic charges in the electric double layer of supercapacitor
at the electrode-electrolyte interface.\textsuperscript{13,14} EDLC consists of three main parts electrode, electrolyte, and the separator. The distance of separation between the electrodes in conventional capacitors (in micrometer scale) is relatively bigger than the thickness of the double layer (in angstrom scale). The charges then stored in the interface between the electrolyte and the conductive carbon particles. The capacitance of EDLC can be measured by the equation\textsuperscript{15}:

\[
C_{dl} = \frac{(1\varepsilon)(2\varepsilon)A}{d}
\]

(1)

Where \(C_{dl}\) is the capacitance of EDLC, \(1\varepsilon\) is the relative dielectric constant, \(2\varepsilon\) is the permittivity of free space, \(A\) is the surface area of the electrode in the double layer and \(d\) is the thickness of the double layer.

Carbon or its derivatives like carbon aerogel, carbon nanotube (CNTs) and graphene are the most used as electrode materials for EDLC. It’s worth mentioning that the porous nature of carbon material delivers large surface area and reveal high conductivity. Carbon nanotubes (CNTs) have attracted much attention from different corners because of their useful thermal\textsuperscript{16}, mechanical\textsuperscript{17}, and electrical\textsuperscript{18} properties. In 1991, carbon nanotubes (CNTs) was discovered for its first time by Iijama\textsuperscript{19}. The researchers investigated CNTs in their work mainly in synthesizing the electrodes of supercapacitors because of its properties like high surface area, excellent cycling stability, low specific capacitance, superior rate capability and low energy density\textsuperscript{11} which in turn enhances the excellence of supercapacitors by improving the chemical stability, mechanical strength, and electrical properties.\textsuperscript{20} To improve the properties of CNTs based supercapacitors, conductive polymers or metallic oxides are added to CNTs electrodes.
The electrolyte is used to define the operating potential as well as to offer for ion conduction. Selection of the electrolyte is based on the type of electrode material, cost, the pore size and other parameters. The separator works as a barrier to avoid any electron or electrical contact between the supercapacitor electrode. Nonetheless, the ions can pass through the separator.

The mechanism of electrostatic supercapacitor is based on forming an electrical double layer at the surface which is produced from the particles of electrode material at the interface between the metal oxide particles for example (RuO, MnO₂ or ZnO) and electrolyte, where the overabundant electric charges are stored on the surfaces of the electrode, and also with the electrolyte ions with counterbalancing charge are built from the electrolyte side for to reach the electroneutrality. Through charging process, the electrons move from cathode (negative electrode) to the anode (positive electrode) over an external load. On the other hand, anions travel to the positive electrode through the electrolyte, while cations go from the positive electrode toward the negative electrode. However, the reverse process occurs in the discharge process. In electrostatic supercapacitor, there is no transfer of the charge across the electrode/electrolyte interface, besides no net ion exchanges, take place between the electrode and the electrolyte. This indicates that the concentration of electrolyte stays constant through the charging/discharging processes and the energy is stored in the double-layer interface. Figure 2 displays the structure and mechanism of EDLC.
1.1.2 Pseudocapacitors

On the contrary, pseudocapacitors can store electrical energy on the surface of the electrode by oxidation and reduction reactions.\textsuperscript{2,21,22} The energy density enhanced by the faradaic process that supports the energy stored in a pseudocapacitor, however, the efficiency of power density and cycle life faded compared to EDLCs.\textsuperscript{21} Pseudocapacitors electrode is mainly transition metal oxides (e.g. Co$_3$O$_4$,\textsuperscript{23,24} MnO$_2$,\textsuperscript{25,26} and RuO$_2$\textsuperscript{27–29} etc.) and conducting polymers,\textsuperscript{30–33} they are receiving particular attention owing to their high

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure2.png}
\caption{Structure of supercapacitor (EDLC)}
\end{figure}
theoretical capacitance and natural abundance.\textsuperscript{34} Furthermore, a high surface area with micro-pores supports the ion access to the electrode material.\textsuperscript{35} The capacitance of pseudo-capacitance can be found by the equation \textsuperscript{36}:

\[ C = \frac{Q}{V} \]  

(2)

Where C is the capacitance of pseudocapacitance, Q is the total charge of the electrode and V is the voltage change for a charge or discharge. Pseudo-capacitors showed a capacitance range from 10 to 100 times higher than that of a carbon double layer capacitor.\textsuperscript{36} Figure 3 presents the Faradaic charge-transfer by display the double-layer adsorbed ions that transfer their charges to the electrode.
Figure 3. A simplified view of a double-layer with specifically adsorbed ions which have transferred their charge to the electrode to explain the faradaic charge-transfer of the pseudocapacitance.

Among the several pseudocapacitive transition metal oxides materials, manganese dioxide (MnO₂) has displayed many interesting properties for its natural abundance, excellent electrochemical capacitive properties, environmental friendliness, wide potential
range, low cost,$^{37,38}$ and high theoretical specific capacitance 1370 F/g.$^{39}$ The pseudocapacitive reaction of MnO$_2$ considers as a surface dominant reaction, only the surface of the electrode or a very thin surface layer of the oxide can participate in this pseudocapacitive reaction. Despite, MnO$_2$ suffers from poor ionic and electrical conductivity ($10^{-5}–10^{-6}$ S/cm) which limits achieving the high theoretical capacitance for supercapacitors.$^{40}$ The microstructure and surface area of MnO$_2$ compounds play a major role in its electrochemical behavior. So, the enhanced fabrication methods should provide well-constructed nano-sized particles with higher active materials area.

1.1.3 Hybrid Supercapacitors

To reach higher improvements; advanced methods were used to enhance the EDLS capacitance and pseudocapacitors conductivity, by hybridizing both of the electrode material Faradaic and non-Faradaic supercapacitors.$^{41,42}$ Hybrid supercapacitors are categorized into three types composites, redox asymmetric and batteries-like as shown in figure 4. Hybrid supercapacitors are expected to increase the merits and reduce the demerits that exist in both EDLCs and pseudocapacitors. It has been proven that hybrid double-layer supercapacitors can reach greater energy density, better cyclic stability in addition to higher specific capacitance compared to EDLS and pseudocapacitors.$^{41}$ A composite film of graphene oxide maintained by needle-like MnO$_2$ nanocrystals presented excellent electrochemical performance compared to that of only using MnO$_2$.$^{43}$ A rational design of ternary nanocomposite composed of CNTs, MnO$_2$, with conducting polymer revealed great electrochemical performance as a result of the effective employment of all the desired functions of each component.$^{44}$
Various synthesis methods have been used to coat a thin film of MnO₂ on the surface of CNTs nanostructures substrates, for instance, co-precipitation³⁹, sol-gel⁴⁵, chemical redox deposition⁴⁶ and electrodeposition⁴⁷ techniques have been studied widely. Although chemical techniques used to fabricate metal oxide nanostructured exhibit toxic solvents and reagents. Also, the usage of binders and additive during these techniques leads
to combining them with the active materials which reduce the supercapacitor capacitance. The physical approach shows an environment-friendly way to produce contamination free metal oxide nanostructured materials. Physical vapor deposition (PVD) approach especially sputtering presents a successful method to synthesize high quality, binder free and eco-friendly nanostructures supercapacitor electrodes.

In this work, we introduce a strategy to produce flexible CNT/MnO$_2$ hybrid film. For the first time, RF magnetron sputtering technique used to grow a thin film of MnO$_2$ on CNT sheet at three different thicknesses (350 nm, 700 nm, and 1µm). The obtained sheet is utilized as a working electrode to improve the performance of supercapacitors. The electrode synthesis is done in two steps, CNTs sheet produced via floating catalyst chemical vapor deposition (CVD). Followed by deposition of MnO$_2$ on CNTs sheet by RF magnetron sputtering. The significant aspect of sputtered MnO$_2$ material is that it binds directly to CNTs current collector without any binder’s requirement. In this case, the specific capacitance is increased with great stability over long cycling. The effect of MnO$_2$ thickness on the electrochemical and mechanical properties of CNTs/MnO$_2$ hybrid material is evaluated. In addition, all solid state symmetric CNT/MnO$_2$ supercapacitors are fabricated using polyvinyl alcohol PVA-H$_3$PO$_4$ gel as the electrolyte.

**Objectives**

- To deposit MnO$_2$ layer on CNTs sheet using RF magnetron sputtering technique.
- To study the effects of MnO$_2$ thickness on supercapacitor application.
- To Study the performance and stability of the composites for supercapacitor application.
• To produce full supercapacitor device and study the performance.
CHAPTER 2: LITERATURE REVIEW

Electrochemical supercapacitors achieved the novel applications in different energy storage devices, for instance, electric and hybrid vehicles and aircraft.\textsuperscript{51,52} Finding the highest specific capacitance as well as energy density in the electrodes with high active mass loading is the main goal for the researchers to go with further discoveries by using various active materials like carbons derivatives and transition metal oxides. It has been demonstrated that MnO\textsubscript{2} is one of the most encouraging materials for charge storage due to its high theoretical specific capacitance of 1400 F.g\textsuperscript{-1} in a comparatively large voltage window.\textsuperscript{53} Though, due to poor electrolyte access to the material surface and the low electronic conductivity of MnO\textsubscript{2}, the specific capacitance reduced drastically with increasing the load of the active mass, chiefly at high charge-discharge rates.\textsuperscript{54–56} Researchers successfully combined CNT and pure MnO\textsubscript{2} into a composite of MnO\textsubscript{2}/CNT.\textsuperscript{57–63} In this chapter, the results and issues of available works in the literature on using CNTs coated with MnO\textsubscript{2} electrode materials for supercapacitors are presented.

Chemical redox deposition

Generally, to achieve redox deposition of metal oxides, a strong-oxidant precursor such as FeO\textsubscript{4}\textsuperscript{2–}, MnO\textsubscript{4}\textsuperscript{–} or RuO\textsubscript{4} are used and reacting at the surface of carbon (performing as reductant), which features of scalability, cost, and manufacturability.\textsuperscript{55} Lee, T., and co-authors (2018) improved the stability of asymmetric supercapacitors and studied the high energy and power densities via producing nanodot MoO\textsubscript{3}/CNT and mesoporous MnO\textsubscript{2}/CNT free-standing films. Asymmetric supercapacitors synthesized by two different electrode materials were both displayed pseudocapacitance type with great voltage window
of 2 V. Hence, the specific surface area enhanced to 343 m$^2$/g and 68 m$^2$/g for MoO$_3$/CNT. Moreover, the conductivity improved to 2.27 for MoO$_3$/CNT and 10.82 F/cm for MnO$_2$/CNT. Furthermore, asymmetric supercapacitors prepared with Na$_2$SO$_4$ as the electrolyte revealed a great energy density of 27.8 Wh/kg and power density 9.8 Wh/kg at a high power density of 10,000 W/kg. Additionally, the ASC demonstrated superb cycle stability with a capacitance loss of 3.2% after 10,000 cycles at 5 A/g.$^{64}$

Patil, B. et al. (2018) studied the lightweight, stackable all-solid-state supercapacitors based on MnO$_2$ material combined with highly conductive 3D-networked CNT web paper. By using the chemical technique to deposit a layer of MnO$_2$ on CNT-web paper and depicted a specific areal capacitance at 5 mV/s reached to 135 mF.cm$^{-2}$ with a capacitance fading of only 5% after 10,000 cycles. Thereafter, asymmetric solid-state supercapacitor synthesized by two electrodes of web paper of MnO$_2$/CNT that exhibited a high areal capacitance of 57 mF/cm$^2$ with an energy density of 0.018 mWh/cm$^2$ and a capacitance loss of 14% after 10,000 cycles.$^{65}$

Jin E. et al. (2017)$^{46}$ synthesized composites of CNT/MnO$_2$ by using chemical redox deposition to enhance the electrochemical pseudocapacitor properties and to improve the electrical conductivity, the composites were wrapped in functionalized graphene nanosheets (fGNSs) as shown in Figure 5. Furthermore, this method led to the reduction of MnO$_2$ loss during the charge-discharge process. After studying the electrochemical properties using a three-electrode system, they found that the CNT/MnO$_2$ electrode deposited for one hour presented the highest specific capacitance around 180 F/g, with only 10% loss of a discharge capacity. While the results presented in Figure 6 of the composite fGNS-CNT/MnO$_2$ electrode deposited at the same time (1 h) showed 202 F/g and a great
cycling stability of 95%. In addition, using the two-electrode system for producing an asymmetric capacitor with an activated carbon//fGNS-CNT/MnO$_2$ asymmetric capacitor, they found that the initial capacitance was reduced by only 5% after 1000 cycles, and the corresponding energy densities and power were calculated at 8 mA cm$^{-2}$ to be 46 W h kg$^{-1}$ and 720 W kg$^{-1}$ respectively.

Figure 5. Schematic illustration of CNTs-MnO$_2$ and graphene-wrapped fGNS-CNTs-MnO$_2$ nanocomposites.$^{46}$
Qi, W. et al. (2017) MnO₂ nanosheets were deposited on top of the CNTs paper by using a self-controlled redox method in KMnO₄ solution. Then the composite was fabricated as supercapacitor electrodes without using conductive agents or any binder. The composite film presented area specific capacitance of 1980 F/m² with great capacitance retention of 87% after 3000 cycles at 10 A/m². On the other hand, the symmetric supercapacitor maintained an energy density of 177 Wh/m² at a power density of 250 W/m². Chodankar, N., Ji, S. and Kim, D. (2017) studied the asymmetric solid-state supercapacitors via establishing of MnO₂/MWCNTs nanocomposite loaded on a stainless-
steel mesh substrate. A chemical method; potentiodynamic electrodeposition was used to enhance the capacitive properties of MnO₂ based electrodes. The prepared MnO₂/MWCNTs nanocomposite revealed a high specific capacitance of 614 F/g and a high specific energy of 85.3 Wh/kg. After assembling the MnO₂/MWCNTs nanocomposite electrode for asymmetric solid-state supercapacitor and using polyvinyl alcohol (PVA)/Na₂SO₄ gel electrolyte, the cell successfully obtained a great specific capacitance of 204 F/g with an energy density of 28.33 Wh/kg. Furthermore, the capacitance decreased by only 0.96%. Gueon, D. and Moon, J. (2017) introduced high-performance supercapacitors using MnO₂ nanoflake/CNT core-shell particles. MnO₂/CNT core–shell particles were prepared with different thicknesses of MnO₂ layers and are used to study the electrochemical performance and successfully reached a specific capacitance of 370 F/g at 0.5 A/g current density with only 85% of MnO₂/CNT core–shell particles upon their supercapacitor electrode application. Besides that, an asymmetric capacitor based on the CNT/MnO₂ particle is assembled and exhibited a high power density of 225 W/kg and an energy density of 27 Wh/kg. Zhao, Y. co-authors (2017) reported the compressible graphene/CNT/MnO₂ aerogel as the electrodes of SCs. They found the specific capacitance of 106 F/g. However, after measuring the compressive strains of the aerogel, it was found that recoverable compressive strains are an excessively low strain (50%) which resulted by the week attachment of MnO₂ particles on graphene/CNT scaffold. Huang, H. et al. (2015) used direct redox route to synthesize nanostructured MnO₂ on carbon nanotubes (CNTs). Moreover, the reaction time was changed to monitor the growth density of MnO₂ beside the structural integrity of CNTs. As a consequence, the prepared MnO₂/CNT electrodes displayed an excellent specific capacitance of 247.9 F/g, with
excellent cycling stability of 92.8% retention after 5000 cycles, suggesting for this electrode to be a potential modest contender in the application of supercapacitor.\textsuperscript{70} Likewise, in 2011, Wang, H. et al. combined MnO\textsubscript{2}/CNT via a facile direct redox reaction. After 2000 cycles, the composite with content 44.4\% of MnO\textsubscript{2} displayed a specific capacitance of 119.3 F/g and 90\% of its specific capacitance was remaining.\textsuperscript{71} Wang, H. et al. (2013) designed carbon-coated carbon nanotubes (C@CNT) and employed them as a conductive electrode to synthesis MnO\textsubscript{2}/C@CNT composite. The use of C@CNT with self-sacrificial carbon sheet as a preservation enables loading higher amount of MnO\textsubscript{2}. They were able to produce a MnO\textsubscript{2}/C@CNT composite with 78 wt\% MnO\textsubscript{2}. At a current density of 0.2 A/g, the electrochemical behavior of MnO\textsubscript{2}/C@CNT composite showed a high specific capacitance of 227 F/g. In addition, after 1000 CV scans, the stability was high with only 6\% decay of its maximal specific capacitance. Figure 7 shows the curves of cyclic voltammetry and galvanostatic charge/discharge of MnO\textsubscript{2}/C@CNT.\textsuperscript{38}
Hu, L. et al. (2011) reported the electrodeposition of MnO$_2$ nanoflowers on CNT enabled conductive textile fibers. The composite with a large mass loading of 8.3 mg/cm$^2$, showed an areal capacitance of 2.8 F/cm$^2$ and high specific capacitance of 410 F/g at 0.05 mV/s. In 2007, Jin, X. et al. prepared nanocrystalline MnO$_2$ to cultivate in the cavity of CNTs and on the surface. Moreover, it has been found that the CNT/MnO$_2$ offered a specific capacitance of 144 F/g with the amount of 65 wt % MnO$_2$ sample. Lee, S. et al. (2010) investigated MWNTs/MnO$_2$ nanocomposite ultrathin film using redox deposition of MnO$_2$ on layer-by-layer (LbL) accumulated MWNTs films. The electrodes LbL-
MWNT/MnO$_2$ revealed a high volumetric capacitance with great capacity retention reaching 246 F/cm$^3$ up to 1000 mV/s. This was due to rapid transport of ions and electrons within the electrodes.$^{74}$ Chou et al. (2008) CNT sheet was coated with MnO$_2$ nanowires via a cyclic voltammetric method. This composite showed a specific capacitance of 107.9 F/g. In conclusion, 19.8% of MnO$_2$ was deposited on the electrode and it was less than 12% of the initial capacitance after 3000 cycles.$^{75}$

**In-situ process**

In situ process in electrochemistry depends on performing electrochemical experiments under operating states of the electrochemical cell such as under specific potential control. Potential control maintains the electrochemical environment to preserve the double layer structure as well as the electron transfer reactions occurring at that certain potential in the electrode/electrolyte interfacial region.$^{76,77}$ Akbulut, S. et al. (2017) presented the production of 3D nanostructured supercapacitor micro-electrode arrays by utilizing MnO$_2$/CNTs composite on graphite foil substrate. Also for integrating a solid-state supercapacitor cell, PVA/H$_3$PO$_4$ solid polymer electrolyte used. The current conductor, which is the 3D CNT microelectrode arrays was synthesized by hot filament chemical vapor deposition (HFCVD) method. While an electrochemical technique; in-situ reduction of KMnO$_4$ was used to achieve the thin-film MnO$_2$ deposition on the CNTs. For the electrochemical characterization, KCL aqueous electrolyte used and exhibited a specific capacitance of 858 F·g$^{-1}$ at a scan rate of 1 mV·s$^{-1}$. Asymmetric solid-state supercapacitor cell assembled and obtained a specific capacitance round 830 F·g$^{-1}$ at 1mV·s$^{-1}$. The high specific energy of 115.2 Wh·kg$^{-1}$ and specific power of 73.9 kW·kg$^{-1}$ were achieved. Also,
it showed excellent cycling stability of 89% with a capacitance retention after 3000 cycles. Figure 8 illustrates the schematic diagram of the assembly method of the solid-state supercapacitor. In addition, the electrochemical characterization results of the flexible solid-state supercapacitor cell are shown in Figure 9.

**Figure 8.** A schematic diagram presenting the fabrication method used to produce the solid-state supercapacitor in a sandwich and symmetric configuration.
Figure 9. Electrochemical characterization shows (a) CV curves at different scan rates, (b) EIS, (c) charge/discharge at different current densities and (d) the cyclic stability of the flexible solid-state supercapacitor cell.

Liu, W. et al. (2016) prepared ternary coaxial hierarchical nanofibers using the in-situ technique to synthesize the polyaniline (PANI) MWCNT. Then, MnO$_2$ deposited on PANI/MWCNT nanofibers to form ternary hierarchical nanofibers MnO$_2$/PANI/MWCNT.
The results presented that the specific capacitance of MnO₂/PANI/MWCNT composites reveals high capacitance of 348.5 F g⁻¹ at 1 Ag⁻¹ and 88.2% of which can still be maintained after 2000 cycles. Chen, J., and co-workers (2015) fabricated the 3D graphene/CNTs/MnO₂ (GCM) nanocomposites electrode via a facile two-step method. The 3D forest-like rGO@CNTs (GC) functions as both ideal electron pathway and the backbone for MnO₂. The nanocomposites displayed a specific capacitance of 245 F g⁻¹ at 0.5 Ag⁻¹, outstanding cycling stability with capacitance retention of 91.4% after 2000 cycles at a current density of 1 A g⁻¹. Xie X. and co-authors (2007) fabricated MnO₂/MWCNT composite via in situ coating technique. Results demonstrated that a nanosized ε-MnO₂ uniform layer coated onto MWCNTs and the original structure of the pristine MWCNT was conserved through the coating process. The specific capacitance of the electrode exhibited around 250 F/g.

**Hydrothermal method**

Hydrothermal method states to any heterogeneous reaction in the existence of mineralizers or aqueous solvents under high pressure and high temperature (HPHT) conditions to dissolve and recrystallize the materials that are comparatively insoluble under ordinary conditions. A ternary composite electrodes have been fabricated by Cheng, T., and co-authors (2017), which is nitrogen-doped graphene foam/carbon nanotube/manganese dioxide (NGF/CNT/MnO₂), by chemical vapor deposition (CVD) with facile hydrothermal method. They proved the effect of MnO₂ mass loading in the production process and the nanoflake thickness in the electrochemical performance by loading 70% of MnO₂ which revealed a great areal capacitance and a high specific capacitance of 3.03 F/cm² and 284 F/g at the scan rate of 2 mV/s respectively. These results
showed that the reasonable proportion and the ultrathin flake-like structures of the MnO$_2$ are able to accomplish high specific areas, fast transport rate, and low aggregation resistance, which results in, high electrochemical performance. After the further tests, they found that the capacitance of the NGF/CNT/MnO$_2$ composite electrodes exhibited around 50% increase after 15,000 cycles.$^{84}$

Recently, Shinde, P. et al. (2017) presented various nanostructured morphologies of MnO$_2$ coated onto carbon via hydrothermal method at altered deposition temperatures. The high specific capacitance of 595 F/g, with a specific surface area of 109 m$^2$/g, the areal capacitance of 4.16 F cm$^{-2}$ at 5 mV/s was achieved at a temperature of 453 K Furthermore, over 2000 CV cycles, the MnO$_2$ weirds showed better cycling stability with capacity retention of 87 %. It has been demonstrated that the direct growth of highly porous MnO$_2$ weirds on carbon cloth enhanced the electrochemical performance.$^{85}$ Luo, X. and co-authors (2017) produced macroporous carbon material using mollusk shell material and deposit a thin layer of MnO$_2$ nanosheets via hydrothermal reaction to improve the performance of the electrode materials and supercapacitors. The electrode showed a high specific capacitance of 386 F/g at a current density of 1 A/g with an outstanding rate performance of 278.7 F/g at 10 A/g and a capacitance retention of 83% after 5000 cycles at 20 A/g.$^{86}$

**Sol-gel method**

The sol-gel technique is used to produce highly controlled inorganic materials that are characterized by homogeneous morphology.$^{87-90}$ Remarkably, because of the great potential that can be achieved from sol-gel processes and the mild reaction parameters that can be used, both of hydrolytic and non-hydrolytic processes have been massively studied.
for the synthesis of organic as well as inorganic materials.\textsuperscript{91} Both of Reddy, R. and Reddy, R. (2004) reported the synthesis of amorphous MnO\textsubscript{2} via sol-gel method that occurred by reduction the NaMnO\textsubscript{4} with solid fumaric acid. The composition exhibited a maximum capacitance of 110 F/g at 5 mV/s in 2 M NaCl solution.\textsuperscript{92}

**Electrophoretic Deposition**

Darari, A. et al. (2016) studied CNT-MnO\textsubscript{2} thin film designed by using electrophoretic deposition. They measured the capacitance of about 7.86 F. Figure 10 depicts the schematic of electrophoretic deposition method of CNT-MnO\textsubscript{2} deposited on the top of stainless steel foil.\textsuperscript{93}

![Electrophoretic Deposition Method Visualization](image)

*Figure 10. Electrophoretic Deposition Method Visualization.*\textsuperscript{93}
Dipping and drying

Successfully, Guo, G. et al. (2015) established a 3D porous CNT/MnO$_2$ composite electrode via a simple “dipping and drying” method. After that, a potentiostat deposition technology used supercapacitor applications. By preparing a symmetrical supercapacitor using the novel electrodes, the composite electrode displayed a high specific capacitance of 160.5 F/g at 1 A/g and revealed an energy density of 22.3 Wh/kg at the power density of 500 W/kg, the electrochemical behavior of CNT/MnO$_2$ supercapacitor is shown in Figure 11.
**Figure 11.** The electrochemical properties of CNTs/MnO₂ supercapacitor: A and B) CVs scanned at various scan rates, (C) GCD curves of CNT/MnO₂ supercapacitor at various current densities (D); the Nyquist plot of CNT/MnO₂ supercapacitor at open circuit potential. ⁹⁵

**One-pot reaction process**

Li, L., and co-workers (2014) produced MnO₂/CNTs composites by changed one-pot reaction method. In this method, the CNTs are coated homogeneously via cross-linked
MnO$_2$ flakes. The thickness of MnO$_2$ layers found about 50 nm with loading equal to 84% of MnO$_2$ on the CNTs surface. Additionally, the supercapacitive performance indicates that the composite exhibits an excellent specific capacitance of 201 F.g$^{-1}$ at 2 A.g$^{-1}$ in addition to excellent cycle stability at 1 A.g$^{-1}$ after 10 000 cycles since there was no capacitance decay. The as-assembled capacitor exhibited an elevated energy density of 13.3 Wh.kg$^{-1}$ at a power density of 600 W.kg$^{-1}$ in a voltage from 0 to 1.5 V.$^{96}$

**Simple vacuum filtration**

Simple vacuum filtration deposition is widely used in supercapacitor applications.$^{97-100}$ Wu, P. et al. (2016) presented flexible films operated as pseudocapacitor electrodes by using a simple vacuum-filtration process to load δ-MnO$_2$ at CNTs layer. At 0.2 A/g which is the low discharge current density, the composite films revealed an excellent areal capacitance of 0.293 F/cm$^2$ and specific capacitance of 149 F/g with a mass of 1.97 mg/cm$^2$ and thickness of 16.5 μm. Furthermore, the films displayed a great rate capability with capacitance loss of 15% after increasing the discharge current from 0.2 up to 5 A/g$^{-1}$. After 5,000 cycles, the remaining cycling stability reached 90% of the initial capacitance.$^{101}$ Figure 12 presents the electrochemical behavior of MnO$_2$@CNTs/CNTs supercapacitor.
Figure 12. Electrochemical behavior curves of MnO$_2$@CNTs/CNTs film electrodes (a) CV at various scan rates; (b) GCD at different current densities.$^{101}$

Particle extraction through a liquid-liquid interface (PELLI)

PELLI process supports the movement of the particles directly from an aqueous synthesis medium to an organic phase, therefore there no need for drying step and no agglomeration occurs for the particles.$^{102}$ In 2017, Chen, R. et al. fabricated CNT/MnO$_2$ composite by using PELLI method to synthesize non-agglomerated MnO$_2$ particles which gave advantages to produce a composite electrode through good dispersion of CNTs. The amount of mass loadings found in the range from 21 up to 50 mg.cm$^{-2}$. The analysis of capacitance data showed that the highest specific capacitance of 7.52 F.cm$^{-2}$ was accomplished at 2 mV s$^{-1}$ with the active mass loading of 47 mg cm$^{-2}$.$^{103}$
**Pulsed laser deposition**

The preparation of less binder of electrode materials will help the energy storage devices to enhance the conductivity and/or facile process.$^{104,105}$ Ataherian, F. et al. presented a method to improve the capability of MnO$_2$ electrode using pulsed laser deposition under vacuum with varying the oxygen partial pressures. They found that the electrode made at a slow potential scan rate of 1 mV/s, with MnOx prepared under vacuum and 10 mTorr of O$_2$ provided specific capacitance as high as 738 and 653 F/g, respectively.$^{106}$

In general, the chemical techniques used to deposit MnO$_2$ films on CNTs exhibit toxic solvents and reagents. In addition, the usage of binders and additive in these chemical processes leads to combining them with the active materials which reduce the supercapacitor capacitance. On the other hand, the Physical vapor deposition techniques such as sputtering are an environment-friendly and they produce contamination free metal oxide nanostructured materials. So, sputtering presents a successful method to synthesize high quality, binder free and eco-friendly nanostructures supercapacitor electrodes.

To the best of our knowledge, there is no report on using processes RF magnetron sputtering deposition technique to deposit a thin film of MnO$_2$ on CNTs sheet in order to produce flexible all solid supercapacitor.
CHAPTER 3: EXPERIMENTAL WORK

3.1 Materials

- Carbon nanotubes (CNTs) material
- Ethanol
- Ferrocene
- Sulfur
- Manganese dioxide, MnO$_2$ (99.9%, size F59.8 × 4 mm) target used for RF sputtering was purchased from Plasma Technology Limited (PTL).
- Sodium sulfate Na$_2$SO$_4$ (142.04 g/mol) were purchased from BDH laboratory supplies.
- Sulfuric acid, H$_2$SO$_4$ (98%) were purchased from BDH laboratory supplies.
- Ortho-phosphoric acid H$_3$PO$_4$ (85%) from Fluka.
- Polyvinyl alcohol (PVA) (MW 60000 Da) was obtained from Merck.

3.2 Experimental Work

3.2.1 Material Preparation

**Working electrode synthesis**

Carbon nanotubes are manufactured via floating catalyst chemical vapor deposition (CVD) method. The ethanol is used as the main carbon source. Iron catalyst particles used after dissolving the ferrocene in the fuel, which avails as the source for the catalyst. Sulfur is used as the catalyst conditioner. The fuel mixture is inoculated into the furnace in the existence of hydrogen. After that, the vaporized fuel mixture is collected through controlled thermal gradients to create a tight distribution of the appropriate size catalyst particles and
to remove the ethanol to produce a carbon source to utilize it in the nanotubes. The growth of nanotubes is endured through the furnace and then combined onto a moving drum until the desired dimensions are achieved. Lastly, CNTs sheet is removed from the furnace and used in the work.\textsuperscript{107} CNTs were cut into the small sheet. To remove impurities, CNTs sheet was thermally annealed at 400 °C for 6 hours under Ar gas (MTI corporation, GSL 1500X-OTF). MnO\textsubscript{2} thin film was deposited on CNTs fabric using RF magnetron sputtering technique (JCP-350M2).

The sputtering chamber was at first evacuated to a base pressure of $8 \times 10^{-3}$ Pa. Thereafter, the sputter deposition was achieved at a pressure of 0.4 Pa under a constant flow of Ar of 6 sccm. The deposition was carried out for one hour, two hours and three hours applying constant RF power of 150W at room temperature. During the sputtering process, the substrate was rotated to confirm a uniform distribution of MnO\textsubscript{2}. The mass of MnO\textsubscript{2} deposited on CNTs fabric was determined by mass difference before and after sputtering using microbalance (Mettler Toledo™ Excellence Plus, XPE Series).

3.2.2 Fabrication of symmetric all-solid CNTs/MnO\textsubscript{2} supercapacitor

The symmetric all solid supercapacitor was prepared by assembling two identical CNTs/MnO\textsubscript{2} fabrics separated with PVA-H\textsubscript{3}PO\textsubscript{4} gel. The PVA-H\textsubscript{3}PO\textsubscript{4} gel was prepared by mixing 8 g of H\textsubscript{3}PO\textsubscript{4} and 10 g PVA powder in 100 mL of deionized water. The mixture was heated to 90°C under vigorous stirring until a transparent gel was obtained as shown in Figure 13. The MnO\textsubscript{2} face of each CNTs/MnO\textsubscript{2} electrode was coated with PVA-H\textsubscript{3}PO\textsubscript{4} gel, dried at room temperature overnight, and then MnO\textsubscript{2} face-to-MnO\textsubscript{2} face assembled.
The electrical connection was assured by connecting CNTs face of each CNTs/MnO$_2$ electrode with copper foils as shown in Figure 14.

*Figure 13. PVA-$\text{H}_3\text{PO}_4$ gel preparation*
Figure 14. Assembled CNTs/MnO$_2$ electrodes with copper foils
3.2.3 Characterizations

3.2.3.1 RF sputtering technique

Sputtering technique is a physical vapor deposition technique. It is used to produce thin films of metals, alloys, nitrides, carbides or oxides materials. The sputtering process starts by creating a gaseous plasma. This is achieved by application of power (DC or RF). These gas ions have high energy and are attracted to the target. The bombardment of the gas ions with the target leads to the ejection of target atoms. In magnetron sputtering, very strong magnets are used to produce magnetic fields that confine the electrons in the plasma at or near the surface of the target. The ejected atoms will have enough kinetic energy to reach the surface of the substrate creating the desired thin film as shown in Figure 15.
Figure 15. Illustrative drawing of a magnetron sputtering technique.

The magnetron sputtering technique offers great advantages compared with other techniques such as uniform, homogeneous and great adhesion deposition over the comparatively large area, ability to choose the substrate material and target material with very high melting points and high deposition rate.\textsuperscript{110} Figure 16 illustrates the main factors used to tune the thickness of the synthesized films in sputtering technique. These factors are the integrated pulse energy, deposition time,\textsuperscript{111} chamber pressure, plasma gas, angle of target and the substrate, and substrate temperature which is important to reduce the dopant redistribution and defect formation related to high-temperature processing.\textsuperscript{112} Figure 17 shows the RF magnetron sputtering machine used in this work.
Figure 16. Main factors to tune the thickness of the synthesized films in sputtering technique
Sample’s morphology is characterized by using scanning electron microscope (SEM). It works by scanning the surface of the sample with a focused beam of electrons to create an image. Then the electron beam interacts with sample generating different signals as shown in Figure 18. Secondary electrons detector is used for detecting the secondary electrons released from the sample. These electrons are attracted to a high voltage of about...
10kV are amplified, modified into a signal and then transferred to the display unit producing SEM image of the sample\textsuperscript{113}. Different output signals can be measured for instance secondary electrons, forward-scattered and back-scattered electrons, and X-rays. The results were conducted by Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (SEM, Nova Nano SEM 450) with a voltage of 500 V to 30 KV. The distance between the electron beam and the sample was 10 mm to obtain good images.

\textit{Figure 18.} Mechanism of scanning electron microscopy
3.2.3.3 *Energy Dispersive Spectroscopy (EDS)*

Energy Dispersive Spectroscopy (EDS) or (EDX) technique is an analytical technique used to analyze the elements of samples. EDS depends on bombarding the sample with a focused beam of electrons that producing X-ray spectrum to generate a chemical analysis and identify the elemental compositions. Moreover, there are two analysis types in EDS; qualitative analysis contains the identification of the X-ray lines in the spectrum and quantitative analysis that determines the concentrations of each element by measuring line intensities.

3.2.3.4 *Raman Spectroscopy*

Materials are interacting with the light causing an incident light absorbed, scattered, reflected, or pass through the material. Raman spectroscopy is a technique applied to measure the wavelength and intensities of inelastically scattered light by measuring the change in rotational, electronic energy or vibrational of a molecule. The Raman scattering works when a photon is an incident on a molecule then it combines with the electric dipole of that molecule and undergoes a frequency shift (gain or loss of energy). This frequency shift of the scattered photons results from exciting the vibrational state of molecules in the material. In Raman spectroscopy, two types of scattering lines present; Stokes lines exist when the lines of frequency shorter than the exciting lines and the others anti-Stokes lines as shown in Figure 19.\textsuperscript{114,115} The results of Raman spectra are performed via Thermo Fisher Scientific (DXR™2 Smart) at a laser wavelength of 532 nm.
Figure 19. Raman scattering diagram presenting the energy level for; (a) Stokes scattering, (b) anti-Stokes scattering.

3.2.3.5 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a nondestructive technique used to analyze a crystal structure of materials and depends on the diffraction of an incident X-ray beam. Bragg’s law relates the x-rays wavelength, the lattice spacing of the crystal and the diffraction angle; so at Bragg conditions when x-rays scattered through the crystalline material, they interfere out of certain crystalline planes in a certain direction which is the diffraction angle (angle between the incident x-rays and the. The following relation is describing the Bragg’s law:
\[ n\lambda = 2d \sin \theta \]  

(3)

where \( n \) is an integer number (the order of diffraction), \( \lambda \) is the wavelength of the incident wave, \( d \) is the spacing between consecutive parallel planes, and \( \theta \) is the incident angle. Hence from Bragg’s equation, the lattice spacing can be calculated. Figure 20 presents the schematic-representation-of-the-Bragg-equation.

XRD measurements were accomplished via PANalytical diffractometer and Bragg-Brentano configuration. The X-ray source is generated in the tube using Copper anode which is the most common target material due to its coverage range and its Cu-K\( \alpha \) radiation wavelength is 1.5405\( \text{Å} \). The scans were operated using high voltage of 45 kV for the tube, current equal to 20 mA at a scan rate of 2°/min with a diffraction angle \( 2\theta \) between 10° and 80°.
3.2.3.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is an important method for the semi-quantitative analysis of surface composition that can investigate a sample to a depth of 2 to 5 nanometers (nm). Because of its features in estimating the chemical state and compositions, therefore, XPS used to study metallurgy, microelectronics, heterogeneous catalysis, corrosion science and polymer technology.\textsuperscript{116} In addition, XPS detects the surface’s chemical elements in addition to the chemical bond natures that occurs between these elements. It can reveal all the elements except helium and hydrogen. Figure 21
demonstrates the main components of an XPS mechanism which are a light source, an electron detector and an electron energy analyzer. XPS measurements were conducted via X-ray photoelectron spectroscopy (XPS; AXIS Ultra DLD (XPS)). The X-ray source is equipped with a monochromated Al-\(\text{k}\alpha\) and a spherical mirror analyzer with the ability to map the surface with a spatial resolution below 3 µm.

![Diagram of XPS experiment](image)

*Figure 21. Basic elements of XPS experiment*
3.2.3.7 Mechanical test

Mechanical properties are a great concern in detecting the material's behavior, especially in engineering applications. It’s used to study the characteristics of the material such as hardness, strength, and toughness. The tensile test is considered as a basic and a worldwide engineering test, where it is used to investigate the material parameters. Some important parameters such as Young’s modulus, yield strength, ductility, toughness and strain rate can be obtained using the test. These parameters are useful for engineers to select the suitable materials for specific applications. The particular material usually displays the relationship between the stress and strain which is presented in the stress-strain curve. Each material has a unique curve representing its properties and is found by measuring the amount of deformation known as strain at distinguished intervals of tensile stress or compressive loading stress. Figure 20 reveals the stress-strain curve demonstrating the properties of a material. The tensile test performed for several reasons such as in material specifications to maintain the quality.
3.2.3.8 Cyclic voltammetry (CV)

An electrochemical characterization technique used widely in research field because of its effectiveness and ability to measure the current over a wide potential range. CV technique records the potential of the working electrode (varied among minimum and a predetermined maximum potential) as it is cycled over time and measuring the resulting current. Repetitively, the electrode potential of CV test sweeps between two peak values specify the number of cycles. A pair of sweeps in opposite directions (forward and reverse
scan) is called a cycle. Moreover, the change of potential with time named with scan rate (v), measured from the slope with unit mV/s. As the scan rate increases, the voltammogram curve turns into tilted and the ohmic resistance is highly prominent, which lead to affect the forming of the double layer in the capacitors and store the charge in the electrode.\(^{119}\) Besides that, the potential of the working electrode is measured against a reference electrode (have a constant potential). Also, the potential range is affected by the type of the electrolyte, for example, in an aqueous solution, the maximum potential will be held around 1V to avoid the electrolys is of water (1.23V). While the non-aqueous solution potential range can be extended to approximately 3V in theory.\(^{119}\)

### 3.2.3.9 Electrochemical Impedance Spectroscopy (EIS)

The measurement of the capability of a circuit to resist the flow of electrical current is called impedance. To study the resistance, Ohm’s law state it in terms of the ratio between potential, \(E\ [V]\), and current, \(I\ [A]\):

\[
R = \frac{E}{I} \quad (4)
\]

which valid only for ideal resistors, and independent of phase, frequency, and follows the relationship of the previous equation for any current and voltage. However, Ohm’s law cannot explain the performance of more complex circuits. So, electrochemical impedance spectroscopy (EIS) describes the system response after applying a small periodic AC signal to the electrochemical cell with several frequencies are ranged from tens of mHz to MHz. Then it measures the emerging current passing through the cell. Studying EIS system offers important information about the EDLC interface and its chemical reactions. Furthermore,
since the excitation signal is very small, a linear or pseudo-linear response can be predictable. While the current response to a sinusoidal potential will be a sinusoid with an equal frequency but phase-shifted as illustrated in Figure 23.119

Figure 23. Sinusoidal Current Response in a Linear System
3.2.3.10 Galvanic charge/discharge (GCD)

GCD technique records the potential of the working electrode as it is cycled over time. The curve then gives an exemplary excitation signal and the triangular shape. The following formula is used to determine the specific capacitance from the charge-discharge curves in two electrodes symmetric cell configuration:\(^{120}\)

\[
SC=2\left(\frac{I\Delta t}{m\Delta V}\right)
\]  

(5)

where \(I\) represent the charge or discharge current, \(\Delta t\) is the charge or discharging time, \(m\) is the active mass of one electrode, and \(\Delta V\) is the voltage drop upon discharging. Moreover, to determine the specific capacitance from the charge-discharge curves in three electrode configuration from the equation:\(^{120}\)

\[
SC = \frac{I\Delta t}{m\Delta V}
\]  

(6)

where \(I\) exemplify the charge or discharging current, \(t\) is the charge or discharge time, \(\Delta V\) is the potential drop during discharge, and \(m\) is the mass of active material in the working electrode. This is the most common test on a cell to determine its capacity besides, the life cycle of a cell. Also, the test examines the performance of the cell after the charge transfer over a number of charge/discharge cycles. The supercapacitor will also exhibit self-discharge over time that can be measured for a long time period.\(^{121}\)

3.2.4 Performance Testing

Figure 24 shows the CorrTest electrochemical workstation instrument (CorrTest instruments, Chine) which was used to perform all electrochemical measurements. The measurements were achieved at room temperature 20±1 °C using a glass beaker with 1M
H$_2$SO$_4$ acidic solution for studying raw CNTs and 1M Na$_2$SO$_4$ aqueous solution as an electrolyte for studying CNTs/MnO$_2$ composites and three-electrode configuration. A circular shape of CNTs and CNTs/MnO$_2$ electrode with a surface area of 0.5 cm$^2$ applied as working electrodes, a saturated calomel electrode (SCE) served as the reference electrode and graphite bar availed as the counter electrode. CV measurements were taken at various scan rates (5, 10, 50, 100, and 200) mV/s within the potential range of 0 to 1 V for five cycles. EIS was achieved in the 10$^5$ to 0.0001 Hz range with voltage Amplitude 100 mV and 20 steps/decade. At last, GCD applied at various scan rates (0.5, 1, 2, 5, and 10) mA/mg by maintaining a potential range between 0 to 1 V vs reference electrode. The specific and facial capacitance of MnO$_2$ is calculated from both CV and GCD.
Figure 24. CorrTest electrochemical workstation instrument
CHAPTER 4: RESULTS AND DISCUSSIONS

In this work, three different thicknesses of MnO$_2$ 350 nm, 700 nm, and 1000 nm have been prepared on CNTs surface using RF magnetron sputtering technique to produce flexible CNT/MnO$_2$ hybrid film. The obtained sheet is utilized as a working electrode to improve the performance of supercapacitors. The electrode synthesis is done in two steps, CNTs sheet produced via floating catalyst chemical vapor deposition (CVD). Followed by deposition of MnO$_2$ on CNTs sheet by RF magnetron sputtering. The effect of MnO$_2$ thickness on the electrochemical and mechanical properties of CNTs/MnO$_2$ hybrid material is evaluated. In this chapter; results and discussion are divided into the following sections:

- Preparation of CNTs/MnO$_2$ composites.
- Characterization of CNTs/MnO$_2$ composites using Raman, XRD, SEM and Tensile test.
- Electrochemical performance of CNTs/MnO$_2$ composites using CV, EIS, and GCD.
4.1 Materials Characterization

CNTs sheet and CNTs/MnO$_2$ composite were examined using Raman spectra, XRD spectra, and SEM. As displayed in Figure 25a, the CNTs revealed three distinctive Raman bands, D, G and G’ bands, at 1366, 1583 and 2724 cm$^{-1}$ respectively.$^{122}$ D band represents defects originating from disordered carbon. G and G’ bands represent graphitic planes.

The D-band to G-band intensity ratio is 0.42 presenting the crystallinity of the pristine CNTs,$^{123}$ the intensity ratio of the D to the G band (I$_D$/I$_G$) offers a sensitive measure of the crystallite size and the qualitative change of defect content in CNTs layers.$^{124}$ Raman spectrum of CNTs/MnO$_2$ with different thicknesses were studied. Figures 25b-d show that the all CNTs/MnO$_2$ with different thicknesses exhibit a band at 645 cm$^{-1}$ related to birnessite-type manganese dioxides ($\delta$-MnO$_2$), in agreement with one major vibrational features of the birnessite-type MnO$_2$ compounds previously reported at 625 to 650 cm$^{-1}$.$^{125,101}$

Furthermore, the spectra of both samples with 350 nm and 700 nm thick MnO$_2$ exhibit D, G, G’ band peaks with identical D to G ratios of 0.98. The sample with 1000 nm thick MnO$_2$ does not exhibit any peak related to CNTs because of the thick MnO$_2$ layer.
Figure 25. Raman spectra of a) CNTs and CNTs/MnO$_2$ with different MnO$_2$ thickness
b) 350 nm, c) 700 nm and d) 1000 nm.
The XRD patterns of CNTs sheet and CNTs/MnO$_2$ composite are presented in Figure 26. It can be noticed that CNTs exhibited a sharp peak at 26° which corresponds to (002) planes with an interplanar spacing of 3.36 Å and another weak peak at 44.47° corresponds to (100) planes with an interplanar spacing of 2.04 Å. These peaks are characteristic of the graphite structure and can be distinguished from the others of the CNTs/MnO$_2$ on the XRD pattern.$^{34,127}$ The peaks of CNTs/MnO$_2$ composites at 18°, 35.8° and 38° correspond to the crystal planes of (001)$^{128}$, (201̅), and (003) planes in MnO$_2$ layered birnessite respectively.$^{101}$ The (002) peak of CNTs is clearly seen in the XRD pattern of CNTs/MnO$_2$ indicating that the deposition of MnO$_2$ to CNTs did not affect their phase structure.$^{101}$
Figure 26. XRD patterns of CNTs (black) and CNTs/MnO$_2$ of different MnO$_2$ thickness (red:350 nm, green: 700 nm, blue: 1000 nm).
In order to reveal the chemical state analysis and further detail of the elemental composition of the sputtered film, XPS measurements were conducted.

The acquired XPS full spectrum (Figure 27a), displays signals from Mn, O, N and C elements, indicating the existence of MnO$_2$ on the surface of CNTs. The high-resolution XPS spectrum of Mn 2p (Figure 27b) exhibits two peaks at 640.1 eV and 651.9 eV (11.8 eV energy separation) corresponding to Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, respectively. This confirms an oxidation state of +4 (Mn$^{4+}$) for Mn in the sputtered film, which is in agreement with MnO$_2$ formula. While the spectrum in Figure 27c shows the high-resolution Mn 3s core level. The energy separation is equal to 5 eV corresponding to MnO$_2$.$^{13,14,15}$
Figure 27. XPS of 1000 nm MnO$_2$ thickness of the CNTs/MnO$_2$ sample (a) full spectrum, (b) Mn 2p and (c) Mn 3s.
The morphology of the fabric obtained after MnO$_2$ sputtering was examined by Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX).

Figure 28 shows SEM images of CNTs at the scale of 3 µm (Figure 28a) and CNT/MnO$_2$ fabric with different MnO$_2$ thicknesses at the scale of 4 µm (Figure 28b-d.) Figure 28b shows that the surfaces of CNTs nanowires are totally covered by MnO$_2$ producing a shape of worms after one-hour deposition which results in 350 nm thick MnO$_2$ with clear interparticle boundaries. As the sputtered time increased to 2-hours (700 nm), almost the whole surfaces of CNTs nanowires are covered (Figure 28c.). Further increase in sputter time (3 hours) results in a uniformly distributed MnO$_2$ on the surface of CNTs nanowires with a complete coverage of the CNTs network (Figure 28d). The cross-sectional SEM image (Figure 28e) of the sample with 3-hour deposition time, reveals a 1000 nm thick MnO$_2$ film homogenously deposited on the surface of CNTs fabric.

In order to confirm the elemental composition of the film, the SEM and corresponding EDS mapping images are shown in (Figure 29 a-d) which presents the presence of C, Mn and O$_2$ are well distributed in the structure fabrics.
Figure 28. SEM images of (a) raw CNTs, (b) CNTs/MnO$_2$ composite with 350nm thick of MnO$_2$ (c) with 700nm thick of MnO$_2$ (d) with 1µm thick of MnO$_2$. 
Figure 29. SEM images for (a) cross section of CNTs/MnO$_2$, SEM mapping of (b) CNTs/MnO$_2$, (c) Mn and (d) O$_2$. 
The suitability and compatibility of the as-prepared CNTs/MnO₂ composite material (with 1000 nm thickness) was evaluated by tensile test to be applied as an electrode material in flexible and wearable supercapacitors. From the load applied versus elongation, the stress-strain curve can be obtained and the flexibility can be measured. Moreover, various mechanical properties such as elastic modulus, ultimate tensile stress and ductility may be calculated. Figure 30a presents stress-strain curves of CNTs and CNTs/MnO₂ composite with 1000 nm thick MnO₂. The elastic region could be measured from the linear part of the curve, in this region, the atomic bonds of the material are stretched. Young’s modulus (the slope of the elastic region) increased from 10 MPa for the CNTs fabric and to 15 MPa for CNTs/MnO₂ composite material. This result indicates that the elasticity of the CNTs fabric is enhanced after the deposition of 1000 nm MnO₂ thin film by RF magnetron sputtering. The ultimate tensile strength is 23.8 MPa for CNTs fabric, and 34.7 MPa for CNTs/MnO₂ composite material. Furthermore, the plastic region is wider in CNTs/MnO₂ composite material (23% strain) compared to that of CNTs fabric (16% strain), which indicates that the failure strain is greater for CNTs/MnO₂ composite material. Additionally, due to high conductivity and high porosity of CNTs, the flexibility of one-unit film bent to numerous angles of 0°, 45°, 90°, and bent at 180° which also did not effect after sputtering MnO₂. (seen in Figure 30b, the corresponding schematic optical images of CNTs/MnO₂ films). These results are favorable for the improvement of flexible and wearable devices profiting from the excellent mechanical properties of CNTs/MnO₂ composite material.
Figure 30. Mechanical characterization of CNTs and CNTs/MnO$_2$ sample with 1000 nm MnO$_2$ thickness (a) Tensile test (b) photographs of CNTs/MnO$_2$ sample at various angles
4.2 Electrochemical Performance

The electrochemical performance of the CNTs/MnO$_2$ composite as a capacitive energy storage is studied via CV, EIS, and GCD. The composite was examined with 1M Na$_2$SO$_4$ electrolyte in the three-electrode cell using SCE as a reference electrode and graphite as a counter electrode at room temperature. Figure 31 illustrates the CV curves of CNTs/MnO$_2$ samples with different MnO$_2$ thicknesses. Figures 31a-c, present the effect of the scan rate 5, 10, 50, 100 and 200 mV/s in the potential range between 0 and 1 V/SCE. At small scan rates (5 and 10 mV/s), CV curves of all CNTs/MnO$_2$ composites display a quasi-rectangle shape without a redox peak, demonstrating pseudocapacitive behavior with fast and reversible surface reactions indicating good capacitive characteristics. Under large scan rate (200 mV/s), CV curves are still symmetrical representing excellent capacitor behaviors for all MnO$_2$ thicknesses. Additionally, it can be noticed that at 5 mV/s the area of the CV loop of blank CNTs is much smaller than that of CNTs/MnO$_2$ composite films (Figure 31d) indicating that the specific capacitance is smaller than that of CNTs/MnO$_2$ composite films. Commonly, at the same scanning rate, the integral area of CV curves is commensurate with specific capacitance. The specific capacitances ($C_s$) of the CNTs and CNTs/MnO$_2$ electrodes were measured from their CV curves at various scan rates using the following equation:

$$C_s = \frac{1}{m \times v \times (V_2 - V_1)} \int_{V_1}^{V_2} I(V) dV \quad (7)$$

where $C_s$ (F/g) is the specific capacitance; $m$ (mg) is the mass of MnO$_2$; $v$ (V/s) is the scan rate; $I$ (A) is the discharge current; $V_2$ and $V_1$ (V) are high and low potential limit of the
CV tests, and \( \int_{V_1}^{V_2} I(V) dV \) is the integral area under the CV curve. Using Equation 7, the specific capacitance for CNTs electrode at 5 mV/s was calculated to be 200 F/g which is similar to values previously reported.\(^{134}\) While, the specific capacitance for the samples with 350, 700 and 1000 nm MnO\(_2\) thickness at same scan rates are 564, 609, and 1676 F/g respectively. Among these, the sample with a MnO\(_2\) thickness of 1000 nm showed the highest capacitance value followed by 700 nm and 350 nm. Hence, it can be speculated that increasing the distance of ionic motion from the electrolyte to the inner MnO\(_2\) in the electrode is necessary. The overall specific capacitances for the sample with 350 nm thick MnO\(_2\) are 564, 463, 230, 160 and 110 F/g at 5, 10, 50, 100 and 200 mV/s, respectively. While, the specific capacitances for the sample with 700 nm thick MnO\(_2\) are 608, 510, 239, 166 and 110 F/g and for the sample with 1000 nm thick MnO\(_2\) are 1676, 1267, 474, 295 and 177 F/g for same scan rates. The higher capacitance than the theoretical value (1370 F/g) (especially for low scan rates) is linked to pseudocapacitance due to reversible redox reactions and not limited to only Mn\(^{4+}/\)Mn\(^{3+}\) accompanied by the insertion/deinsertion of alkali Na\(^+\) cation or H\(^+\) protons from the electrolyte.\(^{135}\) Even so, there is no doubt that the as-prepared CNTs/MnO\(_2\) composites films have a good pseudocapacitive behavior.

Figure 31e shows the specific capacitance as a function of the MnO\(_2\) thickness and the scan rate. The specific capacitance decreases with increasing the scan rate because some alkali cations with high scan rates don’t have the time to be absorbed on the CNTs/MnO\(_2\) surface.\(^{136}\)
Figure 31. CV curves of CNTs/MnO$_2$ at different scan rates for samples with (a) 350 nm, (b) 700 nm, (c) 1000 nm MnO$_2$, (d) CNTs and CNTs/MnO$_2$ at scan rate of 5 mV/s in 1 M Na$_2$SO$_4$ and (e) The dependence of the specific capacitance on electrode film thickness, for various scan rates.
To more understand of the electrochemical behaviors of the electrodes with different MnO$_2$ thicknesses, EIS measurements were carried out on CNTs and CNTs/MnO$_2$ films based supercapacitors over a frequency range of $10^5$ to 0.0001 Hz with voltage amplitude 100 mV and 20 steps/decade vs SCE reference electrode. Figure 32a presents the Nyquist plots of the CNTs and three different thicknesses of MnO$_2$ electrodes. It can be seen that a semicircle pattern is observed in all of the electrodes at a mid-high frequency which represents the charge transfer resistance ($R_{ct}$) processes existing at the electrode/electrolyte interface, and the double layer capacitance.$^{137}$ A linear Warburg-type line is detected at a low-frequency range, which is related to the ion diffusion from the electrolyte to the electrode surface.$^{138}$ EIS can be fitted by an equivalent circuit shown in the Figure 32c. CNTs film shows small semicircle compared to that of CNTs/MnO$_2$ films, indicating a higher interfacial charge-transfer resistance for CNTs/MnO$_2$ films due to the poor electrical conductivity of the MnO$_2$ material. However, the diameter of the semicircle of the electrode with a thickness of 1000 nm is much lower than that of the electrodes 700 and 350 nm, due to the $R_{ct}$ of the electrode is much larger than that of the other electrodes. This is why a larger pseudocapacitance was obtained for the electrode with 1000 nm MnO$_2$ thickness at the same scan rates. Besides that, a sharper Warburg impedance for the CNTs/MnO$_2$ films depicted, indicating that the device has good capacitive behavior with fast ion diffusion. These results demonstrate that the composite has the capability to improve the electrolyte interaction with the active materials and assist the penetration of electrolyte into the MnO$_2$ surface, presenting a better capacitive performance and pathway for ion diffusion.
Figure 32. EIS spectra of (a) CNTs and CNTs/MnO$_2$ electrodes at fresh electrodes (inset the EIS spectra of CNTs), (b) CNTs/MnO$_2$ electrode with 1000 nm MnO$_2$ at different current densities and (c) the equivalent circuit.
The GCD curves of the composite films at different current densities 0.5, 1, 2, 5 and 10 A/g are shown in Figure 33a-c. The curves almost symmetric with linear shapes, indicating high specific capacitance and electrochemical activity and matching with the results of CV tests. The specific capacitances \((C_s)\) of the CNTs and CNTs/MnO\(_2\) electrodes in three electrode configuration were derived from their galvanostatic charge/discharge curves at various current densities using the following equation:\(^{120}\)

\[
C = \frac{I \cdot \Delta t}{m \cdot \Delta V}
\]  

(8)

where \(I\) represents the discharging or charging current, \(t\) is the discharge or charging time, \(\Delta V\) is equal to 1.0 V is the potential window of cycling, and \(m\) is the mass of MnO\(_2\). Using Equation 8, the specific capacitance for CNTs electrode at 0.5 A/g was calculated to be 191 F/g. While, according to MnO\(_2\) weight calculation, the specific capacitances of CNTs/MnO\(_2\) for 350 nm was 1600 F/g, for 700 nm was 3200 F/g and for 1000 nm was 6364 F/g at a small current density of 0.5 A/g. Figure 33d shows that as MnO\(_2\) loading on the surface of CNTs increases, the specific capacitance increased.

Furthermore, the specific capacitance with charging−discharging cycle numbers at 2 A/g from 0 to 1 V for 400 cycles in 1 M Na\(_2\)SO\(_4\) aqueous solution is shown in Figure 34a. It is clear that the pristine CNTs demonstrates better cyclic stability than the composites CNTs/MnO\(_2\) with only 16% degradation. Although, the specific capacitance of the composites is much higher than that of the CNTs. Figure 34b, CNTs/MnO\(_2\) electrode with 1000 nm thickness exhibits highest specific capacitance and cyclic stability with capacitance retention of 85.8% of its peak value after 400 cycles. While after the same
cycles the composite of 700 nm exposed 40% decay from the initial capacitance followed by 41% fading for the capacitance of 350 nm thickness as shown in Figure 35. The reason for the huge decay goes back to the dissolution of MnO$_2$ active material assigned to the disproportionate reaction, which mainly leads to fast performance declining during cycling.$^{139,140}$
Figure 33. GCD curves of charge/discharge at different current densities for a) 350 nm, b) 700 nm, c) 1000 nm MnO$_2$ thickness, d) specific capacitance vs MnO$_2$ thickness for three electrodes.
Figure 34. GCD test presenting a) charge/discharge and b) Cycling performance of CNTs and CNTs/MnO$_2$ at 2 A/g in 1 M Na$_2$SO$_4$ after 400 cycles.
Figure 35. The bar chart shows the change of specific capacitance before and after 400 cycles.
The electrochemical properties of the electrodes with one individual electrode were demonstrated in Figure 36. The symmetric all solid state flexible supercapacitor was prepared by assembling two identical CNTs/MnO$_2$ fabrics separated with PVA-H$_3$PO$_4$ gel and connected with copper foils to assure the electric collection. Re-calling Formula 5 that was used to determine the specific capacitance from the charge-discharge curves in two electrodes symmetric cell configuration:

$$SC = 2\left(\frac{I\Delta t}{m\Delta V}\right)$$

where I represents the constant discharge or discharge current, Δt is the discharging or charging time, m is the mass of MnO$_2$, and ΔV is equal to 0.8 V is the potential window of cycling. The discharge-specific capacitance values and charge-discharge efficiency for the three symmetric all solid supercapacitor at 2 A/g are presented in Figure 36a-c. The discharge-specific capacitance of the CNTs/MnO$_2$ electrode with 1000 nm thickness is larger than the other two composite electrodes started with 140 F/g. While the CNTs/MnO$_2$ electrode with 700 nm exhibits a specific capacitance of 120 F/g and the SC value for the electrode CNTs/MnO$_2$ electrode with 350 nm thickness is less than 90 F/g. The obtained results show that CNTs/MnO$_2$ considerably increases the specific capacitance. The difference between the electrodes 350 nm, 700 nm and 1000 nm in the capacitance behavior is associated with the thickness of the MnO$_2$ film. However, the stability of the electrodes studied after 400 cycles and found the specific capacitance of CNTs/MnO$_2$ electrode with 1000 nm thickness decreased by 40% decay of its initial capacitance, while the electrode with 700 nm thickness exhibited 33% decay of its initial capacitance.
Figure 36. The discharge specific capacitance values and charge-discharge efficiency for CNTs/MnO$_2$ at (a) 350 nm, (b) 700 nm and (c) 1000 nm symmetric all solid state supercapacitors at 2 A/g.
Figure 37. Cycling performance of CNTs and three different thicknesses of flexible all solid CNTs/MnO$_2$ symmetric supercapacitor at current density 2 A/g.
CHAPTER 5: CONCLUSION

CNTs/MnO$_2$ composites were successfully fabricated using RF magnetron sputtering deposition of MnO$_2$ for the first time. CNTs/MnO$_2$ composite electrodes with three different MnO$_2$ thicknesses (300, 700, 1000 nm) were prepared, characterized and compared with pure CNTs sheet. Different characterization techniques were conducted to study their properties. Surface morphology studied by SEM images that demonstrated, a uniform and homogenous MnO$_2$ layers structural. XPS, XRD, and Raman spectroscopy measurements confirmed the existence of MnO$_2$ films on the CNTs surface. In addition, stress-strain curves displayed the mechanical properties and the flexibility of the prepared CNTs/MnO$_2$ composite electrodes with 1000 nm MnO$_2$ thick compared with CNTs sheet.

The electrochemical behavior of the CNTs/MnO$_2$ composites was investigated in three electrodes starting with the thin electrode with 350 nm, medium electrode with 700 nm and a thick electrode with 1000 nm MnO$_2$ thickness in 1M of Na$_2$SO$_4$ via cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD). The CV curves and GCD test displayed that all electrodes with different MnO$_2$ thicknesses showed excellent pseudocapacitive behavior as compared with CNTs sheet with high specific capacitance reached to 1676 F/g under small scan rates of 1000 nm MnO$_2$ thickness followed with 700 nm and 350 nm MnO$_2$ thickness.

Furthermore, the electrode with 1000 nm MnO$_2$ thickness displayed a good cyclic stability with capacitance retention of 85.8% of its peak value after 400 cycles and approximately 41% degradation of the capacitance for the other two electrodes.

In a two-electrode system producing all solid-state flexible supercapacitor with a PVA/H$_3$PO$_4$/CNTs/MnO$_2$ symmetric capacitor, the specific capacitance of the electrodes
with 1000 nm MnO$_2$ thickness showed the highest capacitance among the other electrodes. Among all the thickness, the electrode with 700 nm thickness of MnO$_2$ exhibited the highest cyclic stability with 33% decay of its initial capacitance after 400 cycles.

All the results of CNTs/MnO$_2$ proved that this technique could be used with further enhancements for applications in an electrochemical supercapacitor and it is evidenced as the thickness increases, the specific capacitance increases, indicating that the utilization of MnO$_2$ became more efficient in the electrodes and present great pseudocapacitive behavior.

Our calculation of the active material is based on the weight of MnO$_2$ only. In the literature review, the reported values of the capacitance are based on the weight of CNTs and MnO$_2$. This will not allow for us to make a fair comparison between our findings and the literature review.
FUTURE WORK

Supercapacitors are attracting a lot of interest. These units, designed to store energy, with their ability to create rapid charging discharging as well as their large power density. In future work, we may change the sputtering conditions to improve the surface morphology and structure of the MnO$_2$ films deposited on CNTs. It would be interesting to anneal MnO$_2$/CNTs at different temperatures and study their effect on the performance of the device. Finally, it is important to test the all solid-state supercapacitor stability for longer life cycles.
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