

Nanostructure Enabled Memristor and Supercapacitor

by

Yongzan Zhou

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Mechanical and Mechatronics Engineering (Nanotechnology)

Waterloo, Ontario, Canada, 2022

© Yongzan Zhou 2022

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The composition of conventional circuits is based on four basic elements: resistors, capacitors, inductors, and memristors. Among them, resistors and inductors have been widely studied. Memristor has a desirable application prospect in information storage, artificial synapse, neural network, and artificial intelligence. Capacitors, specifically supercapacitors, have shown better performance, higher capacitance, and efficiency than traditional batteries and capacitors. With the development of technology, more and more electronic products have come into people's lives, and the application of the Internet of Things (IoT) has become more and more widespread. Supercapacitors as energy storage devices and memristors as data storage & computing device play crucial roles in the development of IoT.

The memristor is usually considered a non-linear resistor with a memory function. The more widely accepted mechanism is the formation of a conductive filament, which transforms the resistor from a linear resistive state to a resistive-capacitive coupled state and then to a pure memory state. However, there is still a lack of theoretical knowledge on the mechanism of memristors. Is it starting as a linear resistance? This is a problem worth exploring in the development of memristive devices.

In this thesis, a silver (Ag)/Prussian blue (PB)/In-doped Tin Oxide (ITO) structure shows a unique glucose-controlled transition from a linear resistive state to a capacitance-coupled storage effect and finally to a pure memristive storage effect. Unlike other methods of controlling circuit elements, glucose, as a new factor, is a very effective and direct method of controlling circuit elements. Ion transport recombination and redox reactions under bias in lead layers are controlled by glucose to form conductive filaments in the switching layer PB. This device further explores the mechanism of

conduction filament and provides a promising application in complex integrated sensor and artificial intelligence applications.

Supercapacitors have been extensively studied for their excellent rate performance and cycling stability. The electrode material is the main factor that determines the performance of the capacitor. Studies have shown that electrode materials' structure, surface area, and morphology are essential factors in determining electrochemical performance. However, constructing supercapacitors with high energy density, long cycle life, and high capacitance remains challenging. Therefore, to solve the current problems, it is crucial to research the electrode material with better performance.

In this thesis, magnetron sputtering techniques were first introduced to construct MnO_2 and V_2O_5 decorated carbon-based electrodes. First, spin coating the carbon nanofibers on the carbon cloth substrate and then sputter the MnO_2 and V_2O_5 multilayer. The addition of carbon nanofibers increases the electrical conductivity of carbon cloth and improves the electron transfer rate, while the double carbon core-shell structure improves the reaction site for metal oxide deposition. Electrodes with CC/CNFs/ MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 (MVMVMVM) structure show the best electrochemical performance. At a scan rate of 5 mV/s, the capacitance is increased by a factor of nearly 10 compared to the carbon cloth electrode based on CNFs, with a capacitance of 90 mF/cm³. As for the cell stability, after 2000 cycles of CV loops, the capacitance extension remains stable at 120%. Due to the nanostructured multilayer MnO_2 / V_2O_5 , the redox ion reaction can pass through the surface to the interlayer, exhibiting partial to full activation. This study constructs the supercapacitor electric double-layer pseudocapacitive electrode interface from the atomic scale, which provides an essential reference and impetus for the development of supercapacitors.

Acknowledgements

First, I would like to thank my supervisor, Professor Yimin Wu.

I would like to thank him for accepting me to the University of Waterloo for my master's degree. His encouragement and guidance have helped me to improve and grow. He is a great teacher who guided me in my life, a true friend who gave me comfort and encouragement when I failed, and a close family member who gave me a sense of belonging in a foreign country with a cozy research group.

I would also like to thank Dr. Youchao Teng, who helped me to understand and appreciate supercapacitors, generously offered many valuable suggestions and comments in my subsequent research, and provided great help in revising my thesis.

I would also like to thank Dr. Bai Sun, who introduced me to memristors and constantly guided me and encouraged me to explore them.

Finally, I would also like to thank my family and friends for their unconditional belief and support.

Table of Contents

Author's Declaration	ii
Abstract	iii
Acknowledgements	v
List of Figures	viii
List of Tables	xi
Chapter 1 Introduction.....	1
1.1 Background	1
1.2 Motivations and challenges	3
1.3 Thesis structure.....	6
Chapter 2 Literature Review	7
2.1 Memristor	7
2.1.1 Redox Mechanism	7
2.1.2 Switching Layer Transformation Mechanism	8
2.2 Supercapacitor	10
2.2.1 Double Layer Supercapacitor	11
2.2.2 Pseudocapacitance Supercapacitor	12
2.2.3 Electrode Fabrication Method	14
Chapter 3 Resistance state: An original state of the memristive effect	16
3.1 Overview	16
3.2 Introduction	16
3.3 Device Fabrication and its Characterization.....	19
3.4 Result and Discussion.....	20
3.5 Summary	28

Chapter 4 Interface Engineering on Multi-nanoscale MnO ₂ and V ₂ O ₅ Modified Carbon Cloth for Flexible Supercapacitor	29
4.1 Overview	29
4.2 Introduction	30
4.2.1 Materials	32
4.2.2 Electrolyte Configuration:	33
4.2.3 Preparation of CNFs Thin Film	33
4.2.4 Preparation of MnO ₂ and V ₂ O ₅ Thin Films	34
4.2.5 Device Fabrication.....	34
4.2.6 Characterizations	37
4.2.7 Calculation.....	38
4.3 Result and Discussion.....	39
4.3.1 Result.....	39
4.3.2 Discussion	56
4.4 Summary	57
Chapter 5 Conclusions and Future Work	59
5.1 Conclusions	59
5.2 Future Work	60
References	62

List of Figures

Figure 1.1. The four fundamental two-terminal circuit elements are resistor, inductor, capacitor, and memristor.	1
Figure 1.2 Smart home concept diagram [5]. Copyright 2017 Journal of Cleaner Production.	3
Figure 1.3 IoT system built with supercapacitors and memristor-based glucose sensors.	5
Figure 2.1. (a) The structure of a typical memristor. (b-d) TEM image of dendritic CF/C growth and break process in Ag/SiO ₂ /Pt structure. Reproduced with permission [32]. Copyright 2012 Nature Communications. (e-h) The growth of CF/C process in Pt/ZnO/Pt structure. Reproduced with permission [34]. Copyright 2013 Nano Letters.	10
Figure 2.2. Mechanisms for (a) EDLC and (b) redox pseudocapacitance, and (c) ion intercalation pseudocapacitance. (a–c) reproduced with permission [46]. Copyright 2018 Chemical Reviews.	11
Figure 2.3. Transistor structure diagram.	15
Figure 3.1. Three states of Memristor: (a) pure resistance, (b) capacitive-coupled (c) pure memristive.	18
Figure 3.2. (a) The powder of PB (b) PB's precursor solution. (c) Use the spin coating method to prepare PB film on FTO. (d) Schematic diagram of the molecular structure of PB (e) Schematic diagram of the design of a memristive device with the Ag/PB/ITO structure.	22
Figure 3.3. I-V curves under different percent of glucose, indicating a glucose-controlled transformation from resistor to capacitive-coupled memristive effect and then pure memristive effect.	23
Figure 3.4. Logarithmic I-V curves under different percent of glucose. It indicates a glucose-controlled transformation from resistor to capacitive-coupled memristive effect and then pure memristive effect.	24
Figure 3.5. The HRS and LRS two current states under a bias voltage of 1 V.	25
Figure 3.6. Plausible resistive switching mechanism during (a) 0%, (b) 15%, (c) 30%, and (d) 75% concentration of glucose solution.	26

Figure 3.7. Schematic diagram of the process of SET and RESET for the device under voltage of 16V, presenting the filament changes during the RS behavior.	27
Figure 4.1. SEM image of the cross-section electrode, scale bar: 500 μ m.....	33
Figure 4.2. The process of fabrication. (a) Spin coating CNFs. (b) RF magnetron sputtering for the MnO ₂ and V ₂ O ₅ thin films using Mn and V ₂ O ₅ targets, respectively. (c) Electrode's 3D diagram. (d) The schematic graph of the two-electrode AQSC.	35
Figure 4.3. FESEM and Mapping images of CC substrate with CNFs spun on (a) Scale bars: 500 μ m. (b) Scale bars: 200 μ m. (c) Scale bars: 100 μ m. (d) EDS elemental mapping analysis at 10 μ m scale bars. The green color represents carbon (C).....	40
Figure 4.4. FESEM and Mapping images. A represents the control group MVM, B represents the control group MVMVM, and C represents the control group MVMVMVM. (a) FESEM images with scale bars from 20 μ m to 500nm. (b-c) EDS elemental mapping analysis at 10 μ m scale bars. The green, red, and blue color represents vanadium (V), manganese (Mn), and oxygen (O), respectively.....	41
Figure 4.5. FESEM and Mapping images. A represents the control group VMV, B represents the control group VMVMV, and C represents the control group VMVMVMV. (a) FESEM images with scale bars from 20 μ m to 500nm. (b-c) EDS elemental mapping analysis at 10 μ m scale bars. The green, red, and blue color represents vanadium (V), manganese (Mn), and oxygen (O), respectively.....	42
Figure 4.6. FESEM and electrode images. (a) and (b) are the FESEM images of the control group MVMVMVM and VMVMVMV, respectively. (c) and (d) correspond to their electrode picture.	43
Figure 4.7. (a) FTIR spectrum of control group MV electrodes. (b) UV–visible spectra of control group MV electrodes.	44
Figure 4.8. XRD pattern of the MVMVMVM electrode before reaction (a) and after (b) reaction.	46
Figure 4.9. Load-extension behavior for electrodes' tensile strength. (a) Fracture diagram of a dumbbell-shaped electrode. (b) Local diagram of material fracture. (c) Group VM electrodes' Load-extension curve. (d) Group MV electrodes' Load-Extension curve.....	47

Figure 4.10. The tensile strength of electrodes.....	47
Figure 4.11. Electrochemical performance of seven groups electrode. CV curves at 5 mV/s for (a) MVM, (b) MVMVM, (c) MVMVMVM, (d) VMV, (e) VMVMV, and (f) VMVMVMV at potential window 0-0.6 V.	49
Figure 4.12. Electrochemical performance of seven groups electrode. Ten cycles' CV curves from 5 mV/s to 100 mV/s for (a) CNFs, (c) MVM, (e) MVMVM, (g) MVMVMVM at potential window 0-0.6 V. Capacitance calculated from the cure area for (b) CNFs, (d) MVM, (f) MVMVM, (h) MVMVMVM.	51
Figure 4.13. Electrochemical performance of seven groups electrode. Ten cycles' CV curves from 5 mV/s to 100 mV/s for (a) CNFs, (c) VMV, (e) VMVMV, (g) VMVMVMV at potential window 0-0.6 V. Capacitance calculated from the cure area for (b) CNFs, (d) VMV, (f) VMVMV, (h) VMVMVMV.	52
Figure 4.14. Electrochemical performance of seven groups electrode. Nyquist plots for two pairs of control groups (a) MV (b) MV. Capacitance retention for two control groups (c) MV, (d) VM.....	55
Figure 4.15. Important electrochemical performance of MVMVMVM electrode. (a) CV curves at scan rate 100 mV/s for control group MV. (b) Capacitance for control group MV.	57

List of Tables

Table 1. Comparison of the characteristics of memristor devices with different structures based on the conductive filament mechanism.	9
Table 2. Electrochemical performance of electrodes based on MnO_2 and V_2O_5	14

Chapter 1

Introduction

1.1 Background

In modern life, circuits have been widely used, it is an irreplaceable element in all electronic devices. The fundamental passive two-terminal circuit variables are resistor, inductor, memristor and capacitor [1,2]. The relationship between the four elements is shown in Figure 1.1.

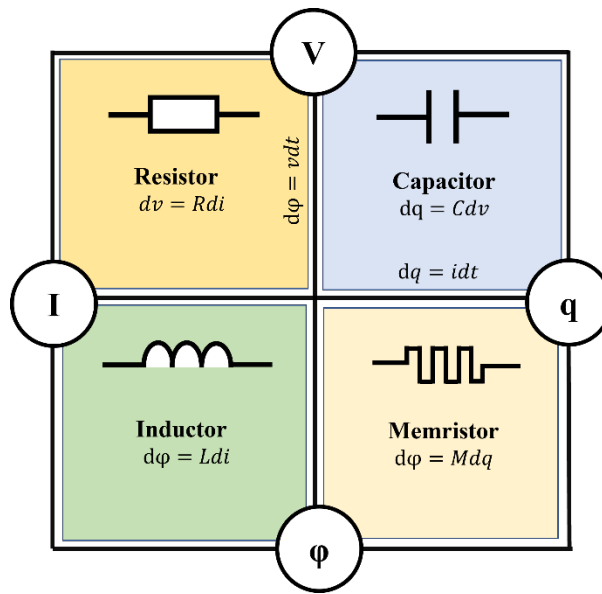


Figure 1.1. The four fundamental two-terminal circuit elements are resistor, inductor, capacitor, and memristor.

In circuits, resistors are passive, two-terminal resistive elements that are used primarily to reduce current, adjust signal levels, divide voltages, and activate bias components. Also, inductors are often

used in circuits. It controls any change in current by balancing the charge. Unlike these two, the memristors and capacitors drive demand attention and have been widely studied due to their essential behaviors and various applications.

First, memristor is an electrical component known as a nonlinear resistor because it limits or regulates the current flow in a circuit. However, unlike a resistor, it remembers the amount of charge that has previously flowed and keeps the memory even in the absence of a power supply, a phenomenon known as non-volatile storage. Thus, memristors could be used as memory storage device, and it has incredible applications, such as mimicking human synapses and neurocomputing. It drives the development of next-generation robotics and artificial intelligence technologies [3].

Capacitors as the vital energy storage components of the circuit. In the electric field under the action of electrostatic storage charge. It can also be used for noise reduction or circuit protection, as it allows AC to pass through and blocks DC. The advantages of capacitors for energy storage have also been studied in depth by scientists. Supercapacitors, between batteries and capacitors, have a higher energy density and can be charged and discharged quickly [4]. Thus, supercapacitors have attracted significant interest.

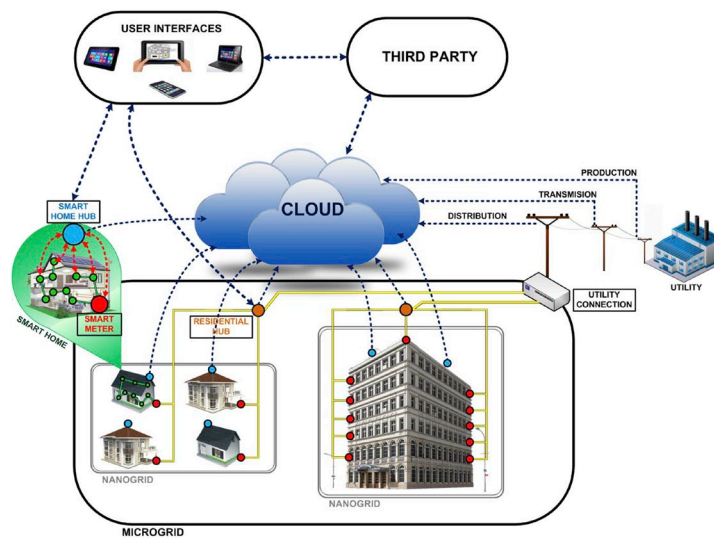


Figure 1.2 Smart home concept diagram [5]. Copyright 2017 Journal of Cleaner Production.

The Internet of Things (IoT) is the connection of objects to a network and their control through the network. For example, in smart home, switches, temperature, lights, humidity, etc. can be controlled by the IoT system. Meanwhile, in medical devices, IoT technology can realize real-time health monitoring, real-time blood sugar monitoring, etc. IoT system can also be used in smart city. The IoT devices placed in these physical objects fall into two main categories: switches (used to send commands to other objects) and sensors (used to collect data and send it out).

1.2 Motivations and challenges

Memristor:

As the fourth element of the two-terminal circuit, the memristor drives a revolution in electronics. It has several promising applications, such as resistive random-access memory (RRAM) [6], mimicking biological synapses [7,8], and neurocomputing [9]. To adjust to the necessities of different conditions and various sorts of uses, individuals require numerous methods for controlling the properties of devices. Scientists have created explicit strategies by controlling the material of the functional layer, the moisture, the concentration of ionic fluids, the temperature level, and the light power [10–15]. The working mechanism of the memristor could be simply explained in state change from resistive to resistive-capacitive coupled and then fully memristive. However, there is still some lack of knowledge about the theory. What is the original state of the memristor? How does the coupled phenomenon influence?

Therefore, the fundamental mechanism should be studied and explained through specific details to help create a more promising memristor in the future.

Supercapacitor:

The battery is an indispensable product in daily life. The chemical reaction between the electrode and the electrolyte indicates its energy transfer mechanism. The movement of the charge creates a current that can then be used through an external circuit. Due to their high energy density, batteries are often used in applications that draw current for long periods of time. However, batteries also have many problems, such as heat accumulation, which can lead to thermal runaway or even explosion under certain circumstances. At the same time, the service life will decrease with the increase of time, which is the main problem facing the electric vehicle industry [16].

In contrast, supercapacitors have higher capacitance and efficiency. A supercapacitor is unique in that it has a double layer of stored charge. It is not the same as a conventional capacitor, where the charge is stored electrostatically in this double layer. Compared to a battery, pseudocapacitance supercapacitors provide power almost immediately and have a longer cycle life.

However, creating long cycle life and high-capacitance supercapacitors is still challenging [17].

Carbon-based materials and metal oxides material can be used as supercapacitor electrodes. Carbon-based materials are widely used as base materials for electrodes because of their huge surface area. Metal oxides, e.g., manganese dioxide (MnO_2), are widely sought after because of their exceptionally high theoretical capacitance of about 1400 F/g. Also, the advantages of low cost, high quantity, and good environmental compatibility make them potential for designing excellent electrode materials for high-energy supercapacitors [18–21]. Meanwhile, the physicochemical properties of the materials themselves determine the performance of supercapacitors. For example, pseudocapacitance

supercapacitors based on redox or ion migration prefer materials like vanadium oxide (V_2O_5), which has multiple valence states itself [22]. However, the capacitance of supercapacitors still cannot reach the ideal capacitance value of the electrode material. The specific capacitance of electrode materials can be improved by various methods, such as controlling the granularity of nanoparticles [23] and arranging them in a highly ordered manner, coating carbon [24] to increase the surface area of the material, doping with metals[25] and introducing conductive components[26]. It has also been shown that the grain size, surface area and morphology of electrode materials are significant factors in determining their electrochemical properties [27].

Magnetron sputtering is a mature technology for depositing metal or metal oxide thin films. It can do the deposition by changing internal factors, such as temperature or gas flow. Besides, sputtered thin films usually have several advantages, such as uniform, controllable thickness, and morphology [28]. It has been widely used for semiconductor devices, such as transistors [29]. Meanwhile, it is an easy and efficient way to create supercapacitors' electrodes.

Thus, we chose MnO_2 , V_2O_5 , and carbon nanofibers to synthesize the carbon-based multilayer electrodes. And the main method is magnetron sputtering.

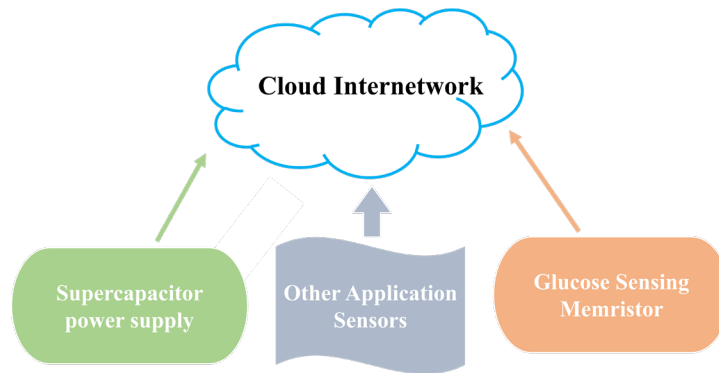


Figure 1.3 IoT system built with supercapacitors and memristor-based glucose sensors.

With the development of technology, the IoT has come into our modern life. Meanwhile, Supercapacitors and memristors device play crucial roles in the development of IoT. The supercapacitor could be used as energy storage devices and memristors as data storage & computing or other application sensor. As shown in Figure 1.3, these two components can form a complete IoT system.

1.3 Thesis structure

This thesis is divided into two main parts: the memristor and the supercapacitor. The structure of this thesis is arranged as follows.

Chapter 1 showed the background of the memristor, supercapacitor and IoT

Chapter 2 reviewed the working mechanism of memristors. In addition, the different types of supercapacitors' charge stored mechanisms and the method of AJA magnetron sputtering are briefly reviewed.

Chapter 3 studied the primary mechanism of memristors. Unlike the traditional voltage control method, it has new abilities in which glucose elements control behavior.

Chapter 4 developed a pseudocapacitive supercapacitor with MnO_2 and V_2O_5 decorated carbon-based electrodes electrode. It introduces the AJA sputtering method into the electrode fabrication process. The supercapacitor exhibit excellent electrochemical performance.

Chapter 6 summarized this thesis and indicates future research directions.

Chapter 2

Literature Review

2.1 Memristor

In 1971, the memristor was first proposed by Leon Chua, who pointed out that there should be a new element for the electric circuit (adding to the original resistor, inductor, and capacitor) [3]. With the development of technology, in 2008, Strukov *et al.* explained the hysteretic current-voltage resistive switching (RS) behavior [2]. Their contribution was an important milestone for the foundation of the memristor. The memristor structure is usually like a sandwich (top electrode-switching layer-bottom electrode), as shown in Figure 2.1(a). Several mechanisms of memristor have been proposed, such as the Schottky barrier [30], ferroelectric polarization [31], conductive filament/channel (CF/C), and so on. Meanwhile, the conductive filaments/channel is the most widely reported mechanism, which will be mainly discussed through examples in this section. The CF/C can be divided into two types: metal and nonmetal. In metal-based CF/C, the active metal ions are the leading actor. For nonmetal-based CF/C, switching layer transformation formed the filaments.

2.1.1 Redox Mechanism

The metal electrode controls the redox mechanism, which requests that the top electrode be active (usually Ag) and the bottom inert (Au, Pt). Yang *et al.* first observed the CF/C growth by TEM. Figure 2.1(b) shows a device through sputtering deposition with a simple structure (Ag-SiO₂-Pt) [31]. Under positive voltage, the active metal Ag oxidized to Ag cations and accumulated on the Pt/SiO₂ negative charged interface to form the Ag CF/C (reduction), as shown in Figure 2.1(c) [31]. The memristor is ON-state, changing from high resistance state to low resistance state. However, when the voltage

applied on the top electrode is negative, the Ag CF/C breaks at the interface of Pt/SiO₂ (oxidation) transfer to Ag⁺, as shown in Figure 2.1(d). The memristor changes from a low resistance state to a high resistance state [32]. Notably, the position where the CF/C forms depend on active metal cations' mobility.

2.1.2 Switching Layer Transformation Mechanism

There are two types of transformation in switching layers (SL) about this mechanism. One is valence change, and the other is phase change. For the valence change, the structure preferred (inert top electrode/metal oxide/inert bottom electrode). Moreover, for the phase change, the switching layers should be phase change material, such as s Ge₂Sb₂Te₅ [33].

Chen *et al.* sputtered ZnO thin film as the switching layer, and Pt is the electrodes, built a memristor (Pt/ZnO/Pt) [33]. Metal oxides naturally contain oxygen defects and oxygen vacancies. When an increasing voltage bias is applied to the electrode, oxygen ions move toward the anode electrode, which causes more oxygen vacancies to accumulate at the anode electrode [33]. The ZnO switching layer transforms from oxygen vacancy doped style to crystalline Zn-dominated ZnO_{1-x} due to the Zn atom's position/structure change [33]. Moreover, that transforms create the CF/C, which turns the memristor ON (low resistance state). As the voltage rises, the thermochemical reaction heating increases, the CF breaks, and the device changes to an OFF state (high resistance state) [34]. The formation of CF/C is shown in Figure 2.1 (e-h).

Scientists have created explicit strategies by controlling the material of the functional layer, the moisture, the concentration of ionic fluids, the temperature level, and the light power [10–15]. Table 1. compares the characteristics of memristor devices with different structures based on the conductive filament mechanism.

Table 1. Comparison of the characteristics of memristor devices with different structures based on the conductive filament mechanism.

Structure	SL fabrication method	Mechanism	SET voltage (V)	Operation current (A)	Ref
Ag/SiO ₂ /Pt	Sputtering	Oxide	10	1×10^{-9}	[32]
Ag/MoS ₂ -PVA/Ag	Liquid exfoliation	Oxide	3	6×10^{-8}	[35]
Ag/Ag-doped-LGB/FTO	Spin coating	Oxide, Ag ⁺ dope controlled	1.9	8×10^{-4}	[36]
Ag/Lotus Root/Cu	Spin coating	Oxide, pH value controlled	4	8×10^{-7}	[37]
Ag/ C ₁₅ H ₁₁ O ₆ /FTO	Spin coating	Oxide	4	1.5×10^{-4}	[38]
Ag/FLOBCZ/ITO	Spin coating	Oxide	1	1×10^{-2}	[39]
Al/MnO ₂ /stainless-steel	Hydrothermal	Oxide	1	1.5×10^{-6}	[40]
Pt/ZnO/Pt	Sputtering	Valence change	3.25	1.2×10^{-4}	[34]
TiN/Al-doped-HfO ₂ /Pt	Atom layer deposition	Valence change	2	1×10^{-3}	[41]
Ag/TiO ₂ /Cu	Sputtering	Valence change	0.7	1×10^{-2}	[42]
Pt/LaMnO ₃ /SrTiO ₃	Sputtering	Valence change	2	1×10^{-3}	[43]

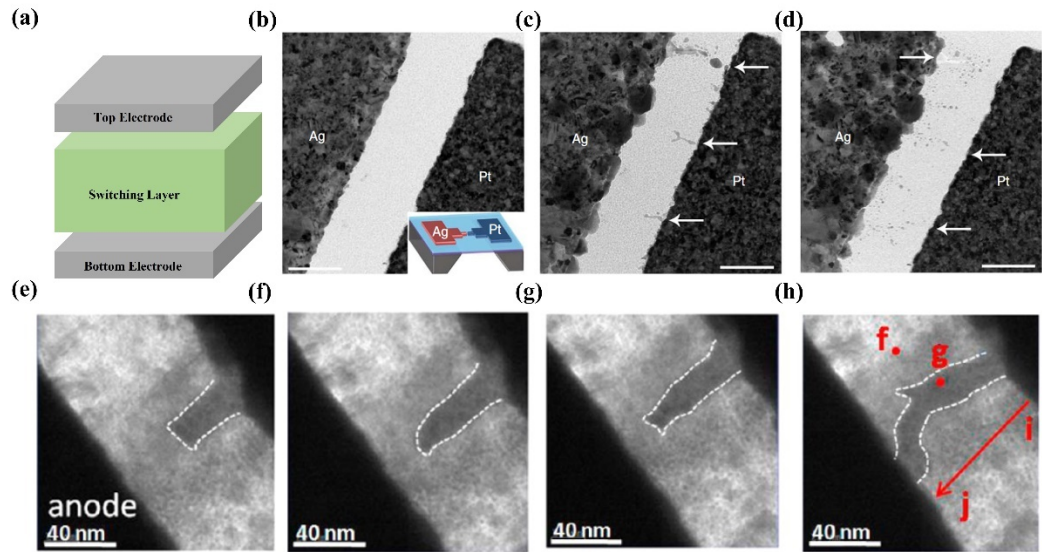


Figure 2.1. (a) The structure of a typical memristor. (b-d) TEM image of dendritic CF/C growth and break process in Ag/SiO₂/Pt structure. Reproduced with permission [32]. Copyright 2012 Nature Communications. (e-h) The growth of CF/C process in Pt/ZnO/Pt structure. Reproduced with permission [34]. Copyright 2013 Nano Letters.

2.2 Supercapacitor

In 1957, the first electrochemical supercapacitor was created by Howard Becker from General Electric. He suggested a capacitor with porous carbon electrodes and H₂SO₄ electrolyte solution, which was the pioneer of the electrochemical double-layer supercapacitor (EDLC) [44]. After two decades of development, the classification of supercapacitors has been more refined. In 1970, Conway introduced the concept of a pseudocapacitance supercapacitor [45]. These types of supercapacitors have been extensively studied in the following years. The diagram of different kinds of supercapacitors is shown in Figure 2.2(a-c). In this section, the three types of supercapacitors will be explained in detail to study their mechanism, and the influence of metal oxide electrodes will also be included.

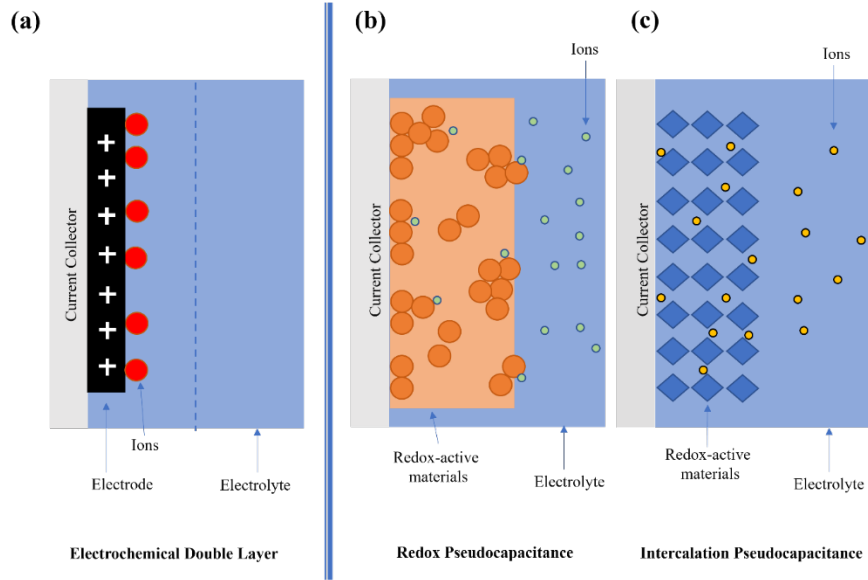


Figure 2.2. Mechanisms for (a) EDLC and (b) redox pseudocapacitance, and (c) ion intercalation pseudocapacitance. (a–c) reproduced with permission [46]. Copyright 2018 Chemical Reviews.

2.2.1 Double Layer Supercapacitor

Figure 2.2(a) shows that the charge storage mechanism of EDLC is based on the absorption of ions. When a conductive electrode is in an ion-conductive electrolyte, the charges are spontaneously absorbed on the electrode-electrolyte interface. There is no Faradaic process because the electrode and electrolyte interface has no charge transfer; the charge is physically electrostatically stored here. The equation of EDLC electrode capacitance is shown below [47].

$$C = \frac{\epsilon_r \epsilon_0}{d} A \quad (2.1)$$

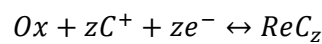
Where ϵ_r is the electrolyte's relative permittivity, ϵ_0 is the permittivity under vacuum. The distance and surface area is the d and A , respectively.

EDLCs have an excellent energy density and fast charge/discharge reaction. Electrodes with large surface areas and nanoscale charge distances have been widely studied. The large surface area of carbon-based material ($\sim 3000\text{m}^2/\text{g}$) can create an ideal capacitance of about 550 F/g [47], such as activated carbons (ACs) [48], carbon nanofiber [49], graphene [50,51], and carbon nanotubes [52]. Hu *et al.* reported that a carbon nanotube-enhanced electrode, which electrodeposit coated MnO_2 , has achieved a large surface area ($2.8\text{F}/\text{cm}^2$) [52]. It shows a nanostructure of the flow-like MnO_2 and porous carbon nanotube. The pseudocapacitor shows a high specific capacitance of 410F/g [53]. Chen *et al.* synthesized a graphene oxide-based needle-like MnO_2 nanostructure electrode through soft chemical reaction [25]. It acquired large surface, and the supercapacitor capacitance achieves 192.7 F/g [26].

2.2.2 Pseudocapacitance Supercapacitor

However, in pseudocapacitance supercapacitors, the charge storage mechanism differs from EDLC. As shown in Figure 2.2(b)(c), there are two types of pseudocapacitance supercapacitors, redox pseudocapacitance and intercalation pseudocapacitance, respectively. The pseudocapacitor electrode materials store charge through the Faradaic process. Simply, the ions oxide-reduction reaction with the electrode material. The difference between these two types is mainly dependent on the reaction place. Redox one is near or at the surface, and intercalation one is inside the electrode materials. Thus, electrode materials with several valence states and high theoretical capacitance are preferred.

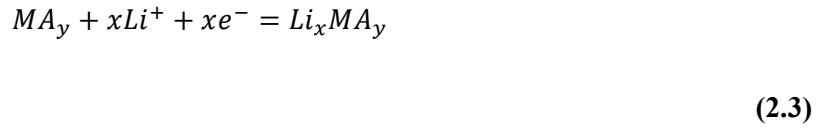
For the redox pseudocapacitance supercapacitor, the reaction is fast and reversible. Cations are absorbed on the oxidized species surface between the electrolyte and electrode. The equation is shown below.



(2.2)

Where Ox (oxide) and Re (reduce) mean the oxidized and reduced substances, respectively and the C^+ means the electrolyte ions (e.g., H^+ , Li^+ , Na^+ ...) , z indicates the number of transferred electrons. Most redox pseudocapacitors uses transition metal oxides, such as RuO_2 and MnO_2 [54]. Manganese dioxide is a popular material for use because of its abundance on the earth and low cost of use, as well as its high theoretical capacitance (about 1400 F/g) and good environmental compatibility [55].

As to the intercalation pseudocapacitance supercapacitor, the ions fast reversibly insert into the host material without a phase change, and the metal valance changes to balance the electric neutrality.



Where MA_y is the insert host material and x is the number of electrons. Typically, pseudocapacitive intercalation materials are not dependent on particle size and morphologies. Only if the scale is down to nano size, it may be because the ion diffusion distance is reduced. Materials such as MoO_3 , V_2O_5 , and $LiCoO_2$ are being widely used. Saravanakumar *et al.* used a capping-agent-assisted precipitation method to fabricate V_2O_5 nonporous structure electrodes [55]. Its unique structure made facile nanochannels for ion diffusion. The device shows a significant capacitance of 316 F/g and long cycle life [56]. The redox pseudocapacitive and intercalation appear simultaneously or alone. Zaeshad *et al.* recently developed an ultra-thin K^+ doped MnO_2 nanosheet electrode with high capacitance (366F/g) [56]. The mechanism combines redox and intercalation, MnO_2 fast redox, and K^+ intercalation/deintercalation in the Na_2SO_4 electrolyte. The device shows good electrochemical performance [56]. The energy density is 56Wh/kg, and the capacitance retention matins 98% after 10000 cycles [57]. Table 2. summarizes the electrochemical performance of the electrodes based on MnO_2 and V_2O_5 .

Table 2. Electrochemical performance of electrodes based on MnO₂ and V₂O₅.

Material	Method	electrolyte	Mechanism	Specific capacitance	Retention (cycles)	Ref.
MnO ₂ /CNTs-60	Electrodeposition	6 M Gel PVA/LiCl	Intercalation pseudocapacitance	3.54 F/cm ² (1mV/s)	98% (1000)	[58]
MnO ₂ /CNT	Redox reaction	0.5 M Na ₂ SO ₄	Intercalation Pseudocapacitance	162.2 mF/cm ²	90% (2000)	[24]
Ordered MnO ₂ /Graphene	Electrodeposition	1 M Na ₂ SO ₄	Intercalation pseudocapacitance	546.9 F/g (2 mV/s)	93.3% (5000)	[59]
MnO ₂ /graphene	Electrodeposition	1 M Na ₂ SO ₄	Intercalation pseudocapacitance	310 F/g (2 mV/s)	88% (15000)	[60]
MnO ₂ /graphene	Electrodeposition	1 M KCl	Redox/intercalation pseudocapacitance	328 F/g (10 mV/s)	99% (1300)	[61]
K _x MnO ₂ /CC	Hydrothermal	1 M Na ₂ SO ₄	Redox/intercalation pseudocapacitance	260 F/g	88% (5000)	[62]
K-MnO ₂ /AC	Hydrothermal	1 M Na ₂ SO ₄	Redox/intercalation pseudocapacitance	366 F/g	98% (10000)	[57]
MnO ₂ /MnO ₂ nanowire	Electrodeposition	1 M LiClO ₄	Intercalation pseudocapacitance	298 F/g (10 mV/s)	85.2% (1000)	[63]
Au/MnO ₂ /Au	Sputtering/ Electrodeposited	1 M Na ₂ SO ₄	Intercalation pseudocapacitance	11.9 F/cm ²	81.0% (1000)	[64]
Spinel/MnO ₂	Hydrolyzing	0.5 M K ₂ SO ₄	Intercalation pseudocapacitance	241 F/g (5 mV/s)	115% (500)	[65]
V ₂ O ₅ /CNT	Electrodeposition	1 M Na ₂ SO ₄	Redox/intercalation pseudocapacitance	440 F/g	90% (100)	[23]
V ₂ O ₅ nanoporous	Chemical reaction	0.5 M K ₂ SO ₄	Intercalation pseudocapacitance	316 F/g	76% (600)	[56]
V ₅ O ₁₂ /VO ₂ /graphene	Electrodeposition	5 M LiCl	Redox/intercalation pseudocapacitance	5.03 F/cm ²	84% (10000)	[66]

2.2.3 Electrode Fabrication Method

Magnetron Sputtering Deposition

Magnetron sputtering deposition has been widely used for depositing variable materials. Due to the low cost, high efficiency, and time-saving advantages, it became one of the most favored methods in nanofabrication. In this section, the method will be introduced through a primary transistor device.

Figure 1.4 shows the structure diagram of a typical transistor.

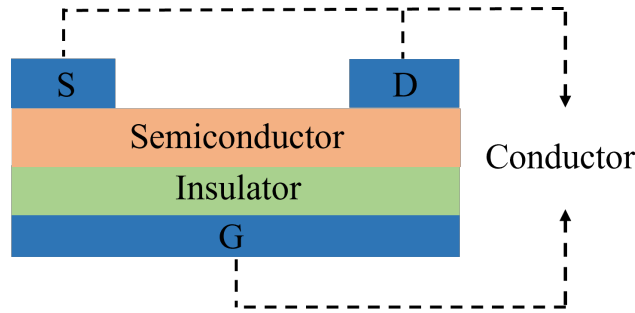


Figure 2.3. Transistor structure diagram.

As shown in Figure 2.3, the transistor builds up with three kinds of material, conductor, insulator, and semiconductor. All these thin film depositions can be produced by magnetron sputtering. Magnetron sputtering deposition depends on plasma. Accelerated ion plasma flows toward the target to sputter the atoms out, and then atoms move toward the substrate to grow a thin film. Usually, the sputtering gas should have a high molecular weight, such as Ar. However, for reaction deposition, the gas can be changed to oxygen or nitrogen [28]. Meanwhile, the thin film thickness and grain structure can be controlled by changing the base pressure and gas flow rate [67].

Reaction sputtering deposition usually happens with oxygen plasma or applied heating while depositing. Shijeesh *et al.* used copper-target through radio frequency sputtering to deposit a copper oxide thin film at room temperature [67]. The gas flow parameter he used is $\text{Ar}/\text{O}_2=20/1.3$ (sccm) [67]. In his study, the thin film transistor was fabricated all by sputtering, the electrode is gold, and the insulator is silicon oxide, copper oxide used as the semiconductor material. He mentioned that the oxygen flow rate could influence the phase of metal oxides [68].

Several studies have proved that sputtering deposition is one of the essential techniques in nanofabrication, such as memristor and transistor [40–44].

Chapter 3

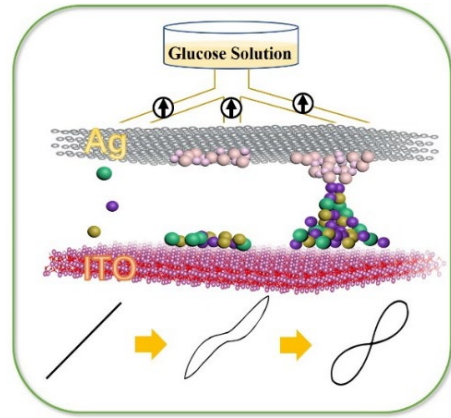
Resistance state: An original state of the memristive effect

3.1 Overview

As a new fourth fundamental circuit element, Memristor has a desirable application prospect in information storage, artificial synapse, neural network, and artificial intelligence.

The Memristor is usually considered as a non-linear resistor with a memory function. Is it starting as a linear resistance?

This is a problem worth exploring in the development of memristive devices. In this study, a storage device with a



silver (Ag)/Prussian blue (PB)/In-doped Tin Oxide (ITO) structure shows a unique glucose-controlled transition from a linear resistive state to a capacitance-coupled storage effect and finally to a pure memristive storage effect. Unlike other methods of controlling circuit elements, glucose, as a new factor, is a very effective and direct method of controlling circuit elements. Ion transport recombination and redox reactions under bias in lead layers are controlled by glucose from a linear resistive state to capacitive coupling memristive effect and finally to pure memristive effect. This device provides a promising application in complex integrated sensor and artificial intelligence applications.

3.2 Introduction

With the development of science and technology, emerging multifunctional electronic devices are being widely developed in environment protection, bio-medical monitoring, and factory production updates [74–77]. To adjust to the necessities of different conditions and various applications, individuals require

numerous methods for controlling the properties of instruments. Scientists have created explicit strategies by controlling the material of the functional layer, the moisture, the concentration of ionic fluids, temperature level and light power [10–15]. Memristive devices are getting well known because of their two-terminal structure, non-linear charge-magnetic flux, passivity, and memory properties. These characteristics play essential roles in high-performance resistive memories, biosensors, mimicking classical conditions, three-dimensional (3D) artificial synapse networks and chaotic circuits [78].

The emergence of memristors is expected to develop higher performance non-volatile resistance random-access memory (RRAM). Among numerous studies of the memory device, RRAM is widely researched for its simple geometrical structure and high integration density [79,80]. In general, the memristor is a circuit element that displays the relationship between magnetic flux and electrical charge. Its resistance value is variable and is determined by the charge flowing through the current [81]. Memristor is a non-linear resistor with a memory function, and its resistance value can be switched by controlling the pulse of the applied voltage or current. With the emergence of environmental issues, using non-toxic, green and non-polluting, degradable, sustainable electronic devices has become one of the current research hotspots [82]. Natural biomaterials and polymers-based memristors have proven to be promising for their applications due to their sustainable, non-toxic, environmentally friendly, degradable, and biocompatible properties. Also, biomaterials have many advantages, such as abundant sources and simple extraction processes, which make it broadly explored as a functional layer for switching in memristor applications [83–85].

As one of the basic passive circuit components, the resistor and capacitor are two crucial parts of electronic devices and semiconductor integrated circuits [86]. However, “what is the memristor’s original state?” is a fundamental question for applications. Memristors are often believed to evolve step

by step from the physical reconfiguration of ions or/and electrons in switching functional materials [87]. The I-V curve is widely used to reflect the state of the device. The pure resistance state should be a flat linear pattern, as shown in Figure 3.1(a). Images in the capacitive-coupled memristive effect state are usually non-zero-crossing (type II memristor) hysteresis loop, as shown in Figure 3.1(b). In contrast, pure memristor images are generally demonstrated as zero-crossing (type I memristor) hysteresis loop, as shown in Figure 3.1(c). Positive and negative ions accumulate at the interface between the electrodes and the functional layer, thus creating a capacitive effect. By applying an external factor, the concentration of positive and negative ions increases, thus creating a conductive filament between the top and bottom electrodes and the device is short-circuited. As a result, the capacitive effect disappears, and the device shows only a memory effect with a zero-crossing I-V hysteresis curve [78,88–91].

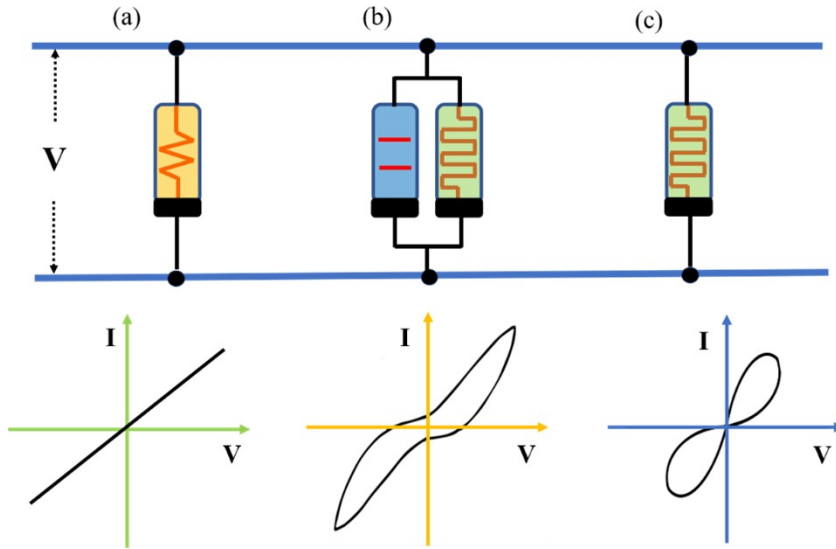


Figure 3.1. Three states of Memristor: (a) pure resistance, (b) capacitive-coupled (c) pure memristive.

In this work, we used Prussian blue (PB) to prepare a memristive device for glucose sensing. It was observed that a glucose-controlled transformation from resistance state to capacitive-coupled memristive effect, finally to pure memristive effect, as shown in Figure 1. Glucose, as a monosaccharide, is widely distributed in animals and plants and has a very important position. In the human body, glucose is the main source of energy, and a relatively stable level of glucose metabolism is extremely important in the human body. Plants produce oxygen by photosynthesis through light and also produce carbohydrates, and glucose is stored in storage organs. This makes it easy to extract glucose from nature, and using it simultaneously is an environmentally friendly, inexpensive way [92,93]. Glucose, as a new factor, is a very effective and direct way to control circuit elements with broad application prospects in complex integrated sensors and artificial intelligence.

3.3 Device Fabrication and its Characterization

In this experiment, all the chemical reagents used were purchased from Sigma. The detailed experimental process is as follows:

The solution preparation: Mixed Prussian blue (PB) with Polyvinylidene Fluoride (PVDF) in a ratio of 1:2 and dissolved in the electrolyte using magnetic stirring apparatus to get the PB solution. Mixed deionized water with glucose powder in a ratio of 0, 0.15, 0.30, 0.45, 0.60, 0.75 mol% to get different glucose solutions.

Device preparation process: The ultrasonic method was used to clean the indium tin oxide (ITO) substrate in deionized water for 20 mins and ultrasonically clean the ITO substrate in ethanol for 20 mins. Then, the ITO substrate was taken out to dry the substrate's surface and impurities was removed with a nitrogen spray gun. Before spin coating, the tape was wrapped around one end of the substrate.

Then, we spin-coated PB solution on the top side of the ITO substrate; once the film was fabricated on the substrate, it was placed in an oven and heated to 120 °C for 10 mins to dry the surface. After the coating was finished, the adhesive tape was removed to have a side without film, which was the bottom electrode. The last step was to utilize silver glue to deposit the silver top electrode.

Characterization: Keysight B2985A source-meter was used to present I-V characteristics; the silver electrode was contacted as the top electrode by positive terminal of power source, while the bottom electrode was connected with the ground. The tests went through the voltages of 4 V by adding 0, 15%, 30%, 45%, 60%, 75% percent glucose solutions to silver electrode. Each turn sample was tested for 200 points and it was repeated 100 turns for each voltage to reduce the error.

For time and other reasons, physical characterization such as SEM, AFM, XRD, UV-Vis, FTIR was not performed for the device materials in this paper.

3.4 Result and Discussion

PB is a hexacyanoferrate(II) compound of iron(III) with a cubic face-centred structure, as shown in Figure 3.2(d). The powder of PB shows in Figure 3.2(a). The coordination of Fe^{3+} ion with a nitrogen atom and Fe^{2+} ion with carbon atom forms the bond chain of $\text{Fe}^{+3}-\text{N}\equiv\text{C}-\text{Fe}^{+2}-\text{C}\equiv\text{N}-\text{Fe}^{+3}$ [77]. When other metals, such as Co or Mn, are substituted for iron ions, a family called Prussian blue analogue is created [94]. When a potential V is applied to the silver electrode, the Ag^+ cation flows through from the Ag, leading to the oxidation of PB, while the electrons flow through the external circuit. This will result in the removal of the holes in the PB main chain, thereby reducing its electron conductivity while ensuring the electrode's electrical neutrality [95]. In the process of redox of PB, the positive ions Ag^+ enter and leave the lattice of PB film to maintain charge balance: $\text{Fe}_4^{+3}[\text{Fe}(\text{CN})_6^{4-}]_3 + 4\text{Ag}^+ + 4\text{e}^- \rightarrow$

$\text{Ag}_4\text{Fe}^{4+}_2[\text{Fe}(\text{CN})_6^{4-}]_3$ [96]. The electrolyte also acts as a barrier to the transfer of electron charges, while the flow of the ions keeps the current flow. Figure 3.2(b) and Figure 3.2(c) present the process of preparation and fabrication for the devices. The PB precursor solution appears as a blue, viscous liquid. Due to the advantages of constant speed of spin coating, a uniform PB film can be coated on the ITO substrate [97]. ITO is a substrate with outstanding electrical performance, which can provide excellent electrical conductivity for memristor devices [98–102]. After the silver glue was interspersed on the PB membrane, the memristor electronic device was obtained as shown in Figure 3.2(e). In the order of top to bottom, here are the upper electrode Ag, the PB layer and the top surface of the ITO substrate in Figure 3.2(e).

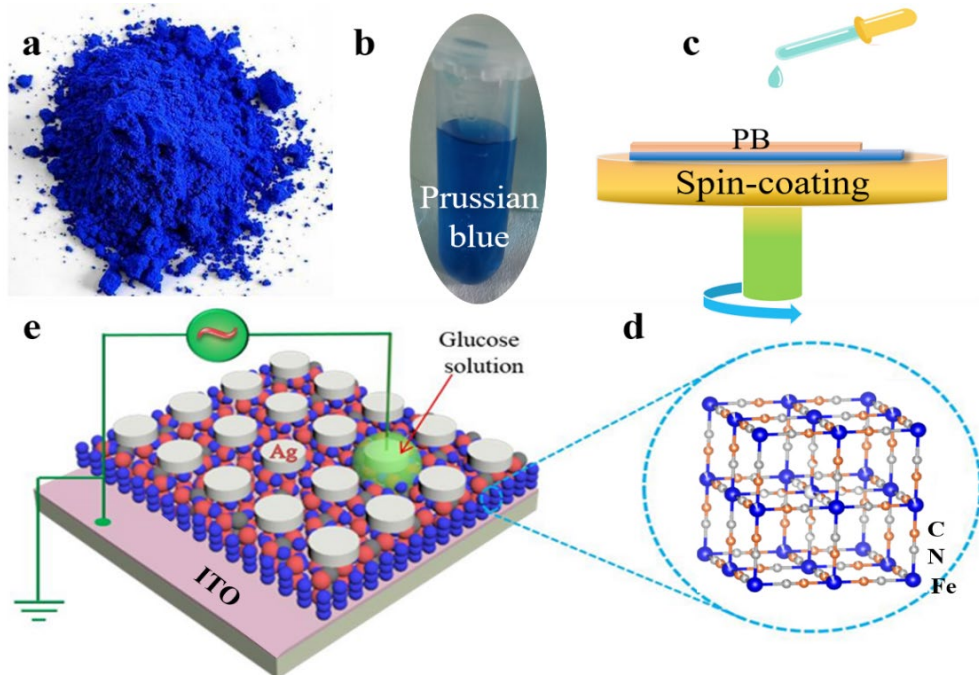


Figure 3.2. (a) The powder of PB (b) PB's precursor solution. (c) Use the spin coating method to prepare PB film on FTO. (d) Schematic diagram of the molecular structure of PB (e) Schematic diagram of the design of a memristive device with the Ag/PB/ITO structure.

The glucose-controlled memristor transformation from pure resistor effect to capacitive-coupled memristive effect and then pure memristive effect is shown in Figure 3.3. In the performance test of the memristor, Ag and ITO were used as the device's upper and lower electrode of the device, respectively. All the control groups were added with different concentrations of glucose solution under the condition of 4.0 V voltage and analyzed by comparing I/V curves. When 0% glucose solution was added, the I/V curve is linear, and the device is in a pure resistance state. When the concentration of glucose solution is increased to 15%, a hysteresis loop occurs, and the two curves are approximately parallel near the origin. This non-zero-crossing (type II memristor) is called capacitive memristor coupling. The non-zero-crossing I–V hysteresis behaviors have been studied extensively in different environments, temperatures and solution concentration, light intensity and other factors [10,103–105]. With the increase of glucose concentration, the I/V curve shows zero-crossing (type I Memristor) when it was greater than 30%, the I–V hysteresis curve changes from non-zero-crossing to zero-crossing and the device shows pure memristor effect at this time [79]. Bai Sun *et al.* proved that transformation between capacitive-coupled memristive and pure memristive behavior can occur through appropriate external stimulation [106]. In our work, higher concentration of glucose solution provided more ionized atoms in the functional layer, so the behavior of the memristor could be converted. At the concentration of 75%, a significant breakdown can be seen in the curve. It is due to the generation of conduction pathways between the PB layer.

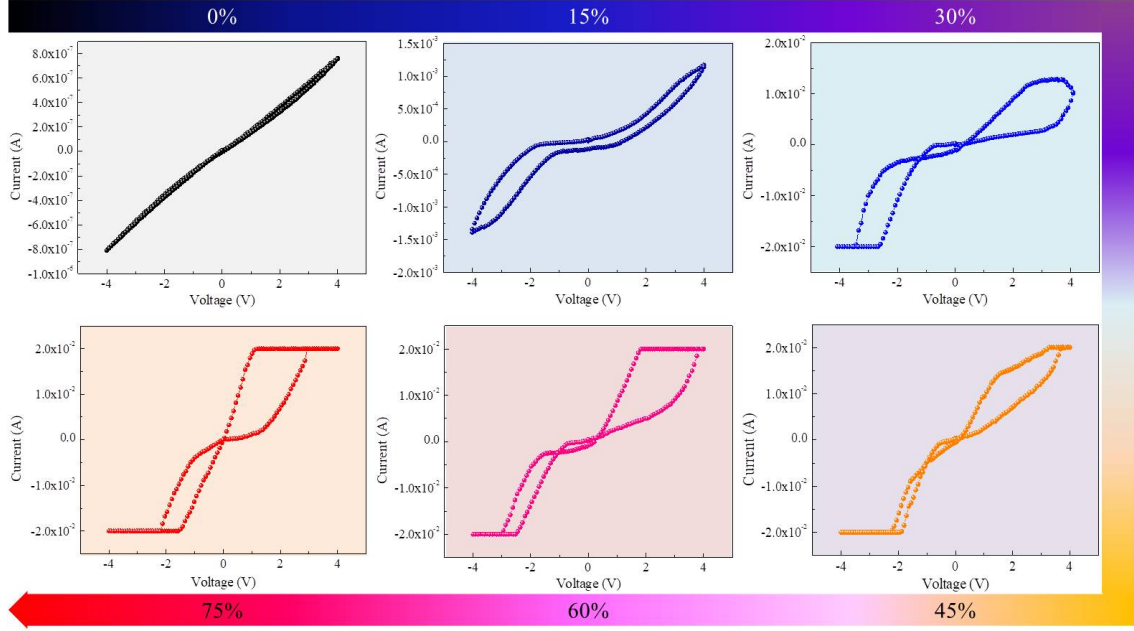


Figure 3.3. I-V curves under different percent of glucose, indicating a glucose-controlled transformation from resistor to capacitive-coupled memristive effect and then pure memristive effect.

The glucose-controlled transformation from resistor to capacitive-coupled memristive effect and then pure memristive effect's logarithmic I-V curves are shown in Figure 3.4. Resistive switching (RS) is a typical characteristic of the logarithmic I-V curve [11]. Initially, all devices are in the high resistance state (HRS) with negative voltage bias, the current increases slightly with voltage, and the memristor turn OFF. When the voltage is above the positive threshold bias, the current increases sharply. The memristor transitions from the high resistance state to the low resistance state (LRS) in quadrant 1, and the memristor turns ON. This process is the SET process for the device. When the applied voltage is equal to the negative threshold bias, the device switches from LRS to HRS and this process is the RESET for the device [107,108], as shown in Figure 3.5. In such logarithmic diagrams, the inflection point of the device switching between SET and RESET and the I-V state of pure memristive effect can

be seen more intuitively. The two lowest points correspond to the points where the current changes from positive to negative. The most important things are the distance between the two lowest points, whether they are zero or not. Since the RS is the special behavior for memristor, the two lowest points would get to zero if the installation transformed from capacitive coupled memristive effect to pure memristive effect. In our work, with 0% glucose solution, the distance is 0, and the device was in a pure resistance state. With the growth of glucose concentration, the distance became larger when it is below 15%. At this time, the device is a capacitive-coupled Memristor. When the concentration of glucose solution was increased to 75%, the distance kept decreasing to 0; the device transformed from capacitive coupled memristive effect to pure memristive effect.

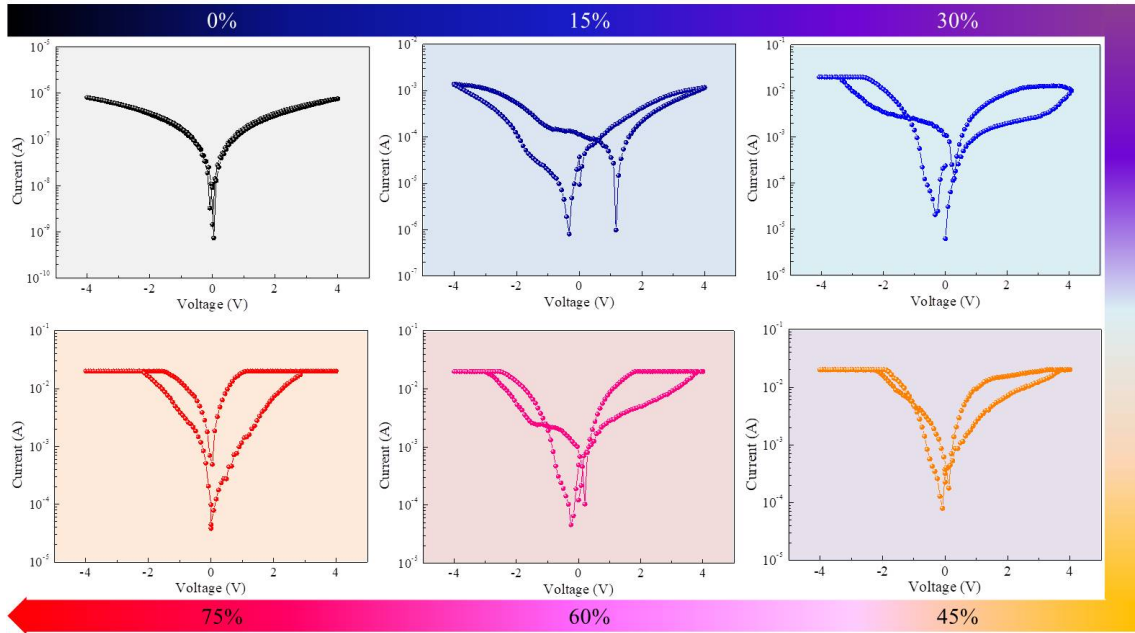


Figure 3.4. Logarithmic I-V curves under different percent of glucose. It indicates a glucose-controlled transformation from resistor to capacitive-coupled memristive effect and then pure memristive effect.

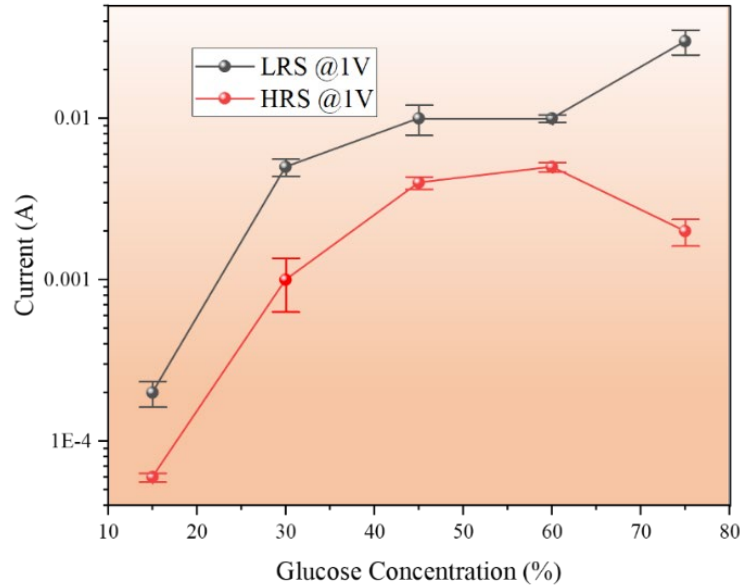


Figure 3.5. The HRS and LRS two current states under a bias voltage of 1 V.

According to the electrical and model fitting results, Ag/PB/ITO memristive devices' resistive switching mechanism is shown in Figure 3.6. In this study, Ag was used as the upper electrode, PB was used as the active layer, and ITO was used as the active switch layer. When the glucose content is 0%, under the voltage of 4V, the Ag electrode undergoes a redox reaction ($\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$) and produces Ag ions. Simultaneously, the Ag ions undergo a redox reaction with the PB active layer, causing the production of iron ions, as shown in Figure 3.6(a). Voltage stimulates oxygen ionization into oxygen ions ($\text{O} + 2\text{e}^- \rightarrow \text{O}_2$) [109]. During the drift process, few positive and negative ions can be neutralized, and a small amount of them are distributed between the two poles. Simultaneously, the active layer's effective dielectric thickness (DET) increases, resulting in a decrease in the current through the devices shown in Figure 3.6(b). During this period is a pure resistance state. When a 15% concentration of glucose solution was applied, the glucose and PB active layer was oxidized, and the number of ions in the active layer increases, triggering changes in ions. Ag ions, Fe ions and oxygen vacancies were

inserted along the applied electric field's direction toward the ITO electrode. While moving, the negatively charged electrons and oxygen ions move toward the cations. When glucose was increased (Figure 3.6c), more oxygen vacancies, Ag ions, Fe ions, electrons and oxygen ions were generated. During the migration process, the movement of the two ions resumes under critical conditions. Therefore, when the glucose concentration increases from 15% to 60%, the device characteristics were basically the same with the capacitive coupling effect. At a higher glucose concentration (75%), oxygen vacancies, iron ions, silver ions, electrons and oxygen ions were produced in substantial quantities. More Fe and Ag are deposited when the cations combine with electrons and were converted. Conductive filaments were formed in the active layer of PB, as shown in Figure 3.6(d), pure memristive effect.

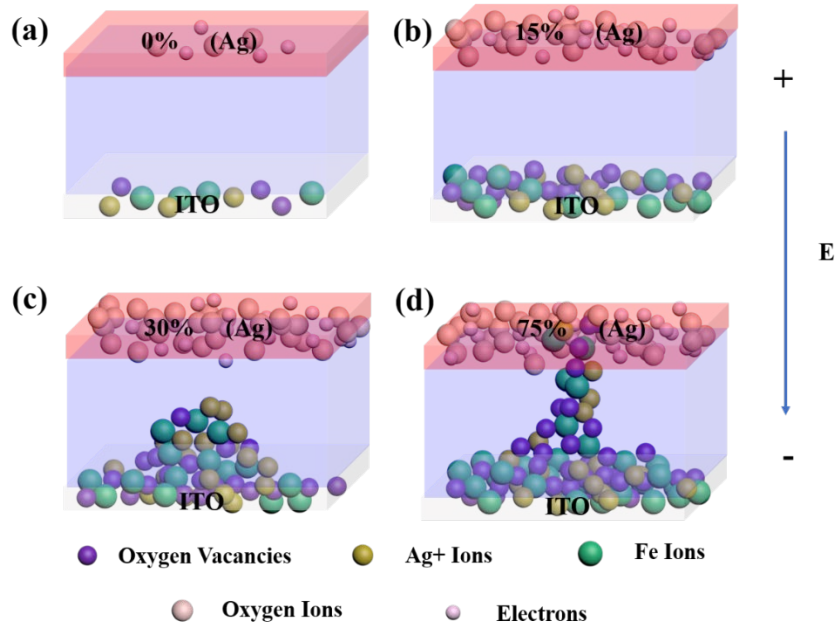


Figure 3.6. Plausible resistive switching mechanism during (a) 0%, (b) 15%, (c) 30%, and (d) 75% concentration of glucose solution.

When the concentration of the glucose solution was 75%, conductive filaments and current tunnels appeared, at the same time, the HRS state and LRS state were switched [87,110]. Figure 3.7 shows the RS states behavior. The cations and anions were moving under the drive of voltage, iron ions, silver ions, and oxygen vacancies combined with electrons and oxygen ions. Due to the fast electron migration rate, electrons were quickly combined with the cations through the migration process and formed conductive filaments, representing a pyramid shape at the ITO electrode, as shown in Figure 3.7(a). At this time, the device was in the LRS state. Under the voltage of opposite polarity, the Ag plate electrons combine with the cations faster. The conductive filament is broken and shows the shape of an inverted pyramid, as shown in Figure 3.7(b), which was in the HRS state. Therefore, the migration of ions promoted the resistance-switching behavior of Ag/PB/ITO devices.

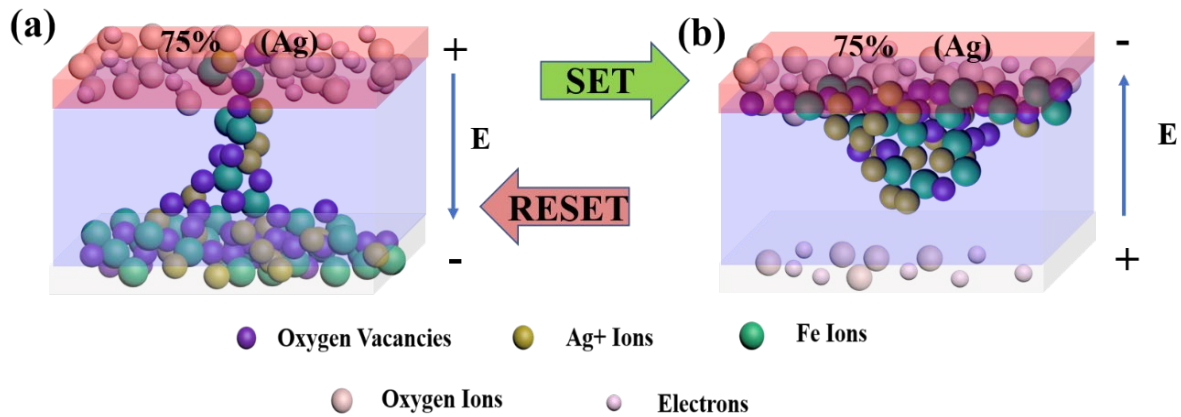


Figure 3.7. Schematic diagram of the process of SET and RESET for the device under voltage of 16V, presenting the filament changes during the RS behavior.

3.5 Summary

In this work, we fabricate an Ag/Prussian blue (PB)/In-doped Tin Oxide (ITO) memristor. By controlling glucose concentration, we used the PB layer and glucose's redox reaction under constant bias voltage to promote the transport and recombination of charge carriers in the device. The results show that the device transfers from linear resistance state to capacitive-coupled memory effect and finally to pure memristive effect. Unlike other methods, glucose as a new factor is a very effective and direct way to control circuit elements with broad application prospects in complex integrated sensors and artificial intelligence, as shown in Figure 3.8. It also provides a good mechanistic explanation for glucose sensing and has a positive impact on the development of glucose sensors.

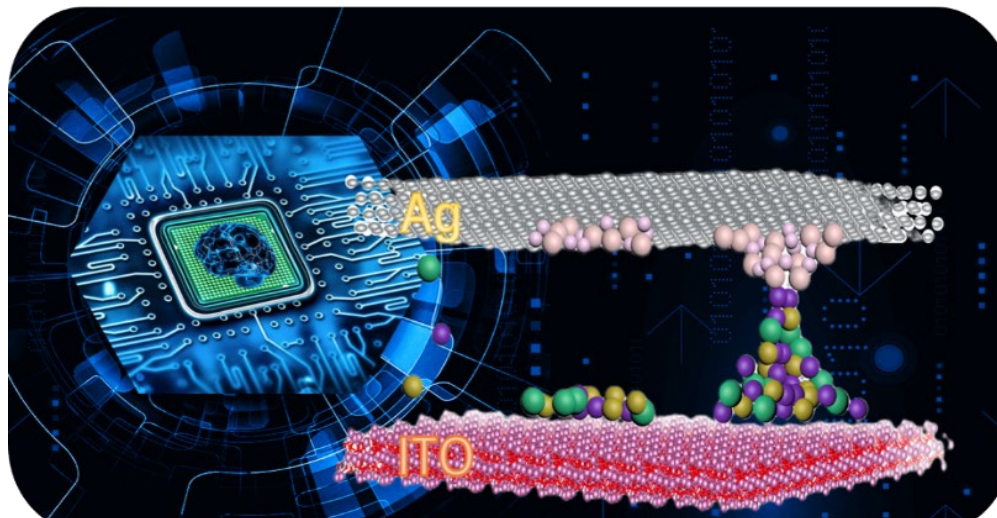


Figure 3.8. Schematic of the future neuromorphic computing system.

Chapter 4

Interface Engineering on Multi-nanoscale MnO₂ and V₂O₅ Modified Carbon Cloth for Flexible Supercapacitor

4.1 Overview

Supercapacitors have been extensively studied for their excellent rate performance and cycling stability. However, tuning the active material and current collector interface from the atomic scale to achieve high energy density supercapacitors is still challenging. We used spin coating and magnetron sputtering to construct a multilayer symmetric supercapacitor. We first used spin coating to deposit the carbon nanofibers on the carbon cloth substrate and then sputtered the MnO₂ and V₂O₅ multilayer. The purpose of adding carbon nanofibers is as follows: (i) to increase the conductivity of carbon cloth and increase the electron transmission rate; (ii) The double carbon core-shell structure can improve the reaction site of deposited metal oxide. After comparing with seven control groups, the CC/CNFs/MnO₂/V₂O₅/MnO₂/V₂O₅/MnO₂/V₂O₅/MnO₂ (MVMVMVM) fabricated sample shows the best electrochemical properties. At a scan rate of 5 mV/s, the capacitance is increased by a factor of nearly 10 compared to the carbon cloth electrode based on CNFs, with a capacitance of 90 mF/cm³. Due to the nanostructured multilayer MnO₂/V₂O₅, the redox ion reaction can pass through the surface to the interlayer, exhibiting partial to full activation. Therefore, the supercapacitor has excellent stability performance, and the capacitance expansion is stable at 120% after 2000 cycles of CV cycling. It is due to the fact that the reaction is initially concentrated on the electrode surface, and as the reaction material

is shed, the reaction gradually spreads throughout the electrode. This study demonstrated the supercapacitor electric double-layer pseudocapacitive electrode interface from the atomic scale, which provides an essential reference and impetus for the development of supercapacitors.

4.2 Introduction

The growing demand for fossil fuels such as oil, coal and natural gas is causing problems such as global warming and air pollution. Therefore, it is necessary to develop clean and green energy sources. Batteries and capacitors are low-cost and eco-friendly energy storage components [95–97]. Batteries have a high energy density but limited power output. On the contrary, capacitors possess a higher power output [114]. Supercapacitors, which contain higher energy density than conventional capacitors and more extended power density than batteries, have attracted considerable attention due to their potential applications in power tools, electric vehicles, electrical circuits, and backup power systems [115]. Its performance depends mainly on the physical and chemical properties of the electrode materials.

There are two types of supercapacitors, double-layer supercapacitors (DLCs) and pseudo supercapacitors. Simply, the mechanism of these two is the non-Faradaic process and the Faradaic process, respectively. Furthermore, the reaction mainly occurs near or at the surface of electrode material [116,117]. However, the current energy density of supercapacitors is still low and needs further improvement to meet the requirement of next-generation electronic devices [57,118]. The critical point is to solve this problem by developing pseudocapacitive hybrid electrode materials with uniform and stable structures.

Carbon materials such as carbon nanotubes, carbon nanofiber, and graphene have been widely used for electrodes due to their large surface area, electrical conductivity and high chemical stability [61]. MnO_2 is also one of the favorite materials for electrode. Because it is naturally abundant, low cost,

environmentally friendly, and has a high theoretical specific capacitance of 1370 F g^{-1} [16,115]. However, metal oxide usually has a low electrical conductivity [119]. So, combining MnO_2 with carbon-based material to synthesize a hybrid electrode is popular to achieve a higher specific capacitance supercapacitor. Besides, several techniques have been introduced for synthesizing these electrodes, such as hydrothermal deposition, electrospinning, and electrodeposition. Yan *et al.* prepared a carbon-based MnO_2 electrode by a redox reaction between carbon and potassium permanganate [59]. It takes him 3 steps and about 14 hours to get the hybrid electrode. And the MnO_2 growth is not uniform, and it prefers to grow at the edges of the graphene layer [60]. Saha *et al.* used the electrospinning method to fabricate a graphene-based MnO_2 electrode [58]. The MnO_2 solution was obtained from $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$ treatment [58]. The electrospinning mixture preparation time is 13 hours [59]. Meanwhile, the electrode, which has uniform and ordered electro-spun fibers, achieved a high specific capacitance of 928.8 F/g [59]. The higher-ordered MnO_2 provides better charge mobility, thus, better electrochemical performance. Duay *et al.* indicated an electrodeposition method to create a hierarchical structure MnO_2 nanowire [62]. During electrochemical reduction, the hierarchical structure MnO_2 grew uniformly [62]. The MnO_2 rod/ MnO_2 (hierarchical structure) electrodes achieved pure DLC behavior with a specific capacitance of 298 F/g [63]. Among these studies, the synthetic method above usually takes more time, and the thickness and concentration of MnO_2 are also hard to control.

Magnetron sputtering has advantages, such as time-saving, thin film thickness and morphology control, uniformity, clean deposition, and material properties. Accelerated ion plasma flows toward the target to sputter the atoms out, and then atoms move toward the substrate to grow a thin film [120]. It is capable of depositing metal and metal oxide. Therefore, this method can be used in supercapacitor electrode fabrication.

In this work, different from other traditional manufacturing methods, we introduce magnetron sputtering technology in the fabrication of supercapacitor. The fabrication processes include two steps. The first step is spin-coating carbon nanofibers solution, and the second step is sputtering deposition. We used magnetron sputtering to engineer the interface and create the multilayer $\text{MnO}_2/\text{V}_2\text{O}_5$ electrodes on the carbon cloth flexible substrate. This method provides excellent electronic/ionic conductivity while enhancing the pseudo-capacitive behavior of nanocrystalline $\text{V}_2\text{O}_5/\text{MnO}_2$. The electric double-layer pseudocapacitor achieved excellent electrochemical performance. The capacitance ($90\text{mF}/\text{cm}^3$) improved nearly 10 times compared with CNFs based-carbon cloth electrode. Moreover, the CV curves retain a rectangular, which shows good high-rate performance. Besides, the capacitance retention rate is stable at about 120% after 2000 cycles of CV measurement. Due to the nanostructured multilayer $\text{MnO}_2/\text{V}_2\text{O}_5$, the redox ion reaction can pass through the surface to the interlayer, exhibiting partial to full activation.

4.2.1 Materials

For the present study, material details are described in the following.

The Carbon cloth (CC) was purchased from the Fuel Cell Store. The manganese (Mn) and vanadium oxide (V_2O_5) targets were purchased from Angstrom Sciences company. The chemicals such as sulfuric acid (H_2SO_4), Carbon nanofibers (CNFs), and ultra-pure (UP) water were purchased from Sigma-Aldrich chemical company.

CC is a woven carbon cloth without a microporous layer (MPL). It has an average thickness of about $400\text{ }\mu\text{m}$, as shown in Figure 4.1.

CNFs solution was prepared by mixing 10mg CNFs ($D \times L$ 100 nm $\times$ 20-200 μm) and 10ml UP water under ultrasonic stirring at room temperature.

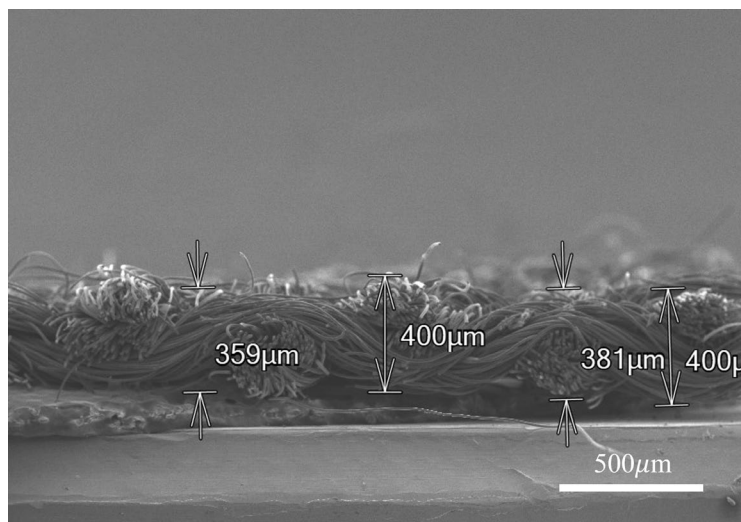


Figure 4.1. SEM image of the cross-section electrode, scale bar: 500 μm .

4.2.2 Electrolyte Configuration:

1 M of electrolyte is obtained by mixing approximately 10 ml of H_2SO_4 98% liquid in 100 ml of UP water and stirring continuously.

4.2.3 Preparation of CNFs Thin Film

The spin coating method is mainly used for the preparation of CNFs film. Before spinning, the CC was tapped flat on a 3-inch clean silicon wafer.

Spin coating CNFs have three steps. First, the speed is accelerated to 500rpm in 1 sec and it was spun for 5s. Then it was sped up to 3500rpm in 3 sec, and held for 35s. The last step was reducing the

speed to 500rpm and held for 5 sec. Spin coating 5 times to get the CC fully covered with CNFs and followed by hard bake at 110 °C for 600 sec. Finally, a nitrogen gun was used to blow away any unevenness or excess CNFs from the CC.

4.2.4 Preparation of MnO₂ and V₂O₅ Thin Films

The MnO₂ and V₂O₅ films were deposited by RF magnetron sputtering at room temperature. The specific process is as followed. A 3-inch diameter Mn (99.9%) target was used for MnO₂ thin film deposition. The distance between the target and the substrate was fixed at 45 mm, and the power was applied at 100 W at a base pressure of 7×10^{-7} Torr in the test chamber. Subsequently, a mixture of argon and oxygen at a pressure of 5 mTorr with a flow rate ratio of 12/11 sccm (standard cubic centimeters per minute) was introduced. The total deposition time was 20 mins.

A 3-inch diameter V₂O₅ (99.9%) target was used for V₂O₅ thin film deposition. The distance between the target and the substrate was fixed at 45 mm, and the power was applied at 100 W at a base pressure of 7×10^{-7} Torr in the test chamber. Subsequently, a mixture of argon and oxygen at a pressure of 5 mTorr with a flow rate ratio of 12/1 sccm (standard cubic centimeters per minute) was introduced. The total deposition time was 20 mins.

4.2.5 Device Fabrication

Electrode Material Fabrication Processes

We built a multilayer electrodes symmetric supercapacitor consisting of CNFs, V₂O₅, and MnO₂ materials. This study has seven control groups with the same fabrication parameters but different sequences or components. The fabrication process is shown in Figure 4.2(a-c). The electrodes coated with CNFs were rotated only as a blank control group. In the sputtering section, the order and number of depositions comprised the control groups 2 to 7. And it is divided into two pairs of control groups,

MV and VM. The deposition order to determine which of V_2O_5 and MnO_2 plays a major role in the reaction and affects the performance of the supercapacitor.

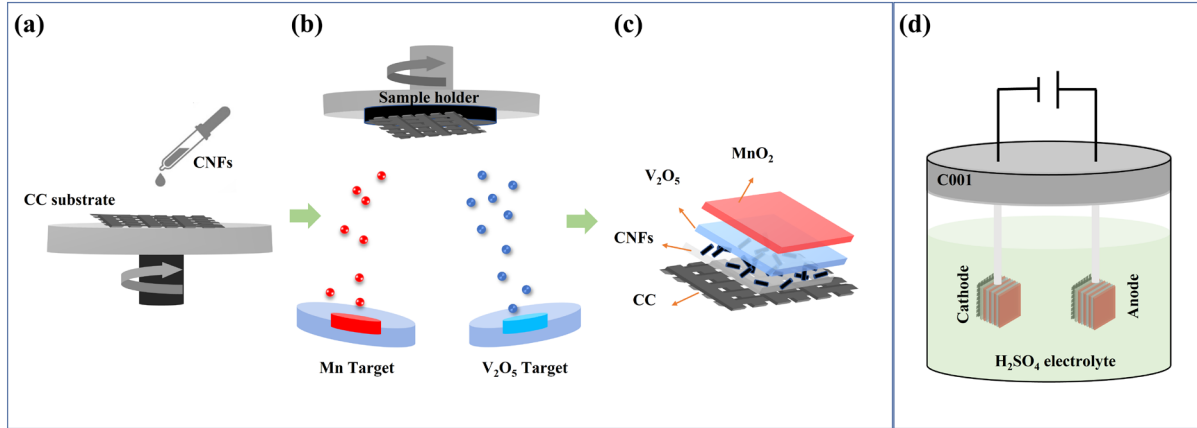


Figure 4.2. The process of fabrication. (a) Spin coating CNFs. (b) RF magnetron sputtering for the MnO_2 and V_2O_5 thin films using Mn and V_2O_5 targets, respectively. (c) Electrode's 3D diagram. (d) The schematic graph of the two-electrode AQSC.

Control Group 1: CC/CNFs (CNFs)

CC was wash by ultra-sonication in acetone solution for 5 minutes, then CC was sonicated in DI water for another 5 minutes, followed by 110 °C hard bake for 600 sec. CNFs thin film was spun on the treated CC.

MV

Control Group 2: CC/CNFs/ MnO_2 / V_2O_5 / MnO_2 (MVM)

CC was washed by ultra-sonication the in acetone solution for 5 minutes, then CC was sonicated in DI water for another 5 minutes, followed by 110 °C hard bake for 600 sec. CNFs thin film was spun on

the treated CC. Then magnetron sputtering was used to deposit MnO_2 , V_2O_5 and MnO_2 thin film in sequence.

Control Group 3: CC/CNFs/ MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 (MVMVM)

CC was washed by ultra-sonication in acetone solution for 5 minutes, then CC was sonicated in UP water for another 5 minutes, followed by 110 °C hard bake for 600 sec. CNFs thin film was spun on the treated CC. Then magnetron sputtering was used to deposit MnO_2 , V_2O_5 , MnO_2 , V_2O_5 , and MnO_2 thin film in sequence.

Control Group 4: CC/CNFs/ MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 (MVMVMVM)

CC was washed by ultra-sonication in acetone solution for 5 minutes, then CC was sonicated in DI water for another 5 minutes, followed by 110 °C hard bake for 600 sec. CNFs thin film was spun on the treated CC. Then magnetron sputtering was used to deposit MnO_2 , V_2O_5 , MnO_2 , V_2O_5 , MnO_2 , V_2O_5 and MnO_2 thin film in sequence.

VM

Control Group 5: CC/CNFs/ V_2O_5 / MnO_2 / V_2O_5 (VMV)

CC was washed by ultra-sonication in acetone solution for 5 minutes, then CC was sonicated in DI water for another 5 minutes, followed by 110 °C hard bake for 600 sec. CNFs thin film was spun on the treated CC. Then, magnetron sputtering was used to deposit V_2O_5 , MnO_2 , and V_2O_5 , thin film in sequence.

Control Group 6: CC/CNFs/ V_2O_5 / MnO_2 / V_2O_5 / MnO_2 / V_2O_5 (VMVMV)

CC was washed by ultra-sonication in acetone solution for 5 minutes, then CC was sonicated in DI water for another 5 minutes, followed by 110 °C hard bake for 600 sec. CNFs thin film was spun on

the treated CC. Then magnetron sputtering was used to deposit V_2O_5 , MnO_2 , V_2O_5 , MnO_2 , and V_2O_5 thin film in sequence.

Control Group 7: CC/CNFs/ V_2O_5 / MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 / V_2O_5 (VMVMVMV)

CC was washed by ultra-sonication in acetone solution for 5 minutes, then CC was sonicated in DI water for another 5 minutes, followed by 110 °C hard bake for 600 sec. CNFs thin film was spun on the treated CC. Then magnetron sputtering was used to deposit V_2O_5 , MnO_2 , V_2O_5 , MnO_2 , V_2O_5 , MnO_2 and V_2O_5 thin film in sequence.

Assembly of the two-electrode aqueous supercapacitor (AQSC)

Figure 4.2(d) shows the schematic diagram of the two-electrode AQSC. Firstly, two samples of MnO_2/V_2O_5 hybrid film with both length and width of 1 cm were cut out and clamped onto two Pt electrodes as cathode and anode electrodes, respectively. Then, the cathode and anode electrodes were immersed in the C001 electrolytic cell filled with 1M H_2SO_4 electrolyte.

4.2.6 Characterizations

The morphology of the samples and the presence of compounds were examined by Field Emission Scanning Electron Microscope (FESEM) (Hitachi SU5000 FESEM microscope) and Energy Dispersive Spectroscopy (EDS) (Oxford Instruments UltimMax 100 EDS), respectively. X-ray Powder Diffraction (XRD) (PANalytical X'pert Pro MPD Powder XRD) was used to identify the crystal structure and crystalline phases. The optical properties of the samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) (Bruker Tensor 27 FTIR) and Ultraviolet-visible

Spectroscopy (UV-Vis) (Perkin Elmer PE Lambda 35 & 1050). The Tensile Strength (Instron, Model 3367) was measured to characterize the mechanical behavior of the electrodes.

All electrochemical characterizations were measured using Gamry Interface 1010e. In this study, we built a symmetric supercapacitor with 1*1cm² cathodes and anodes. The electrode's average cross-sectional thickness was measured by SEM, as shown in Figure 4.1.

4.2.7 Calculation

The tensile strength (σ , Mpa) was calculated from the force-extension curve.

$$\sigma = \frac{P_{max}}{A_0} \quad (4.1)$$

Where P_{max} is the maximum load (N), A_0 represents the original cross section area (mm²). Besides, the samples' cross-section thickness is 400 μ m and the width is 5mm.

The areal capacitance (C_A , mF/cm²) and volumetric capacitance (C_V , mF/cm³) of the electrode were calculated from the cyclic voltammetry (CV) curves, according to the following equations:

$$C_A = \frac{(\int |I| dU)}{v \times \Delta U \times A} \quad (4.2)$$

$$C_V = \frac{(\int |I| dU)}{v \times \Delta U \times V} \quad (4.3)$$

Where I is the current density (A), U is the potential (V), v represents the scan rate (mV/s), and ΔU (V) is the voltage window. A (cm²) is the area of a single electrode and V (cm³) is the volume of a single electrode.

The cycle stability (C_s , %) of the supercapacitor is calculated from the 2000 cycles CV curves, according to the equation:

$$C_s = \frac{C_x}{C_0} = \frac{\int |I_x| dU}{\int |I_0| dU} \times 100\% \quad (4.4)$$

Where C_0 and C_x stand for the specific capacitance for cycle 1 or the rest cycle. I is the current density (A), U is the potential (V), “ x ” means the CV cycle number, which is larger than “1”, and “0” represents the start cycle “1”.

4.3 Result and Discussion

4.3.1 Result

We discussed seven control groups separately in this section by showing their characterization and electrochemical data. Moreover, compare the results at the end.

Physical characterization

1. FESEM and EDS

We first systematically studied the structure and morphology of thin films with FESEM and EDS mapping technology. In the meantime, spin coating and sputtering deposition methods were also evaluated. CNFs control group was mainly used to discuss the spin coating method, and the other six groups were all used for the sputtering deposition method.

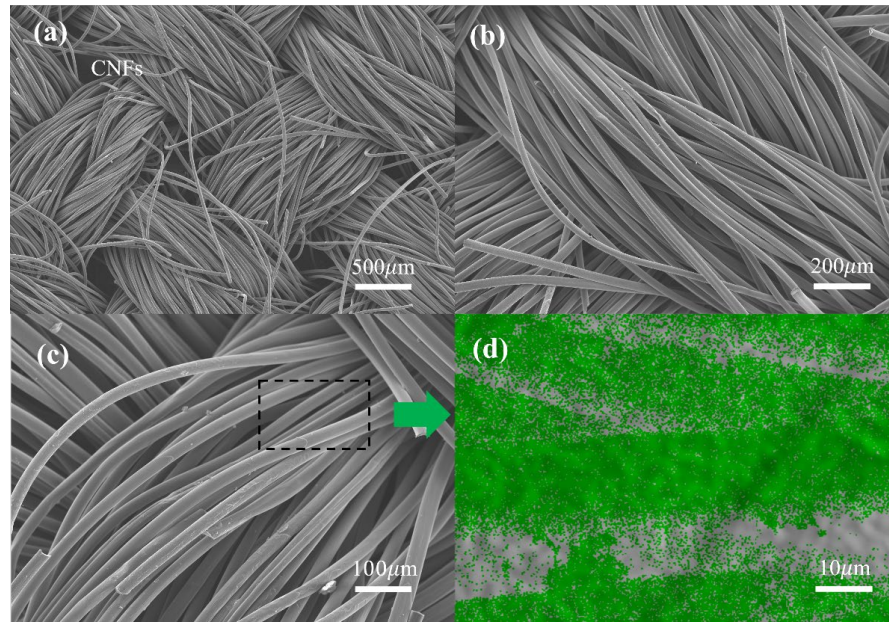


Figure 4.3. FESEM and Mapping images of CC substrate with CNFs spun on (a) Scale bars: 500 μm. (b) Scale bars: 200 μm. (c) Scale bars: 100 μm. (d) EDS elemental mapping analysis at 10 μm scale bars. The green color represents carbon (C).

Figure 4.3 shows that the CC has an interwoven structure. From the EDS element mapping (Figure. 4.3 d), we observed that CNFs are evenly distributed on the surface of the carbon fiber. However, the space between CC fibers was not covered, mainly due to the relationship between the spin coating process and the CNFs solution. From the method we mentioned above, the CNFs nanopowder was

dissolved in DI water as the spin coating solution. It may cause bad adhesion to the CC substrate. However, the surface structure of carbon cloth is interweaved and rough so that the fibers can catch the solutions.

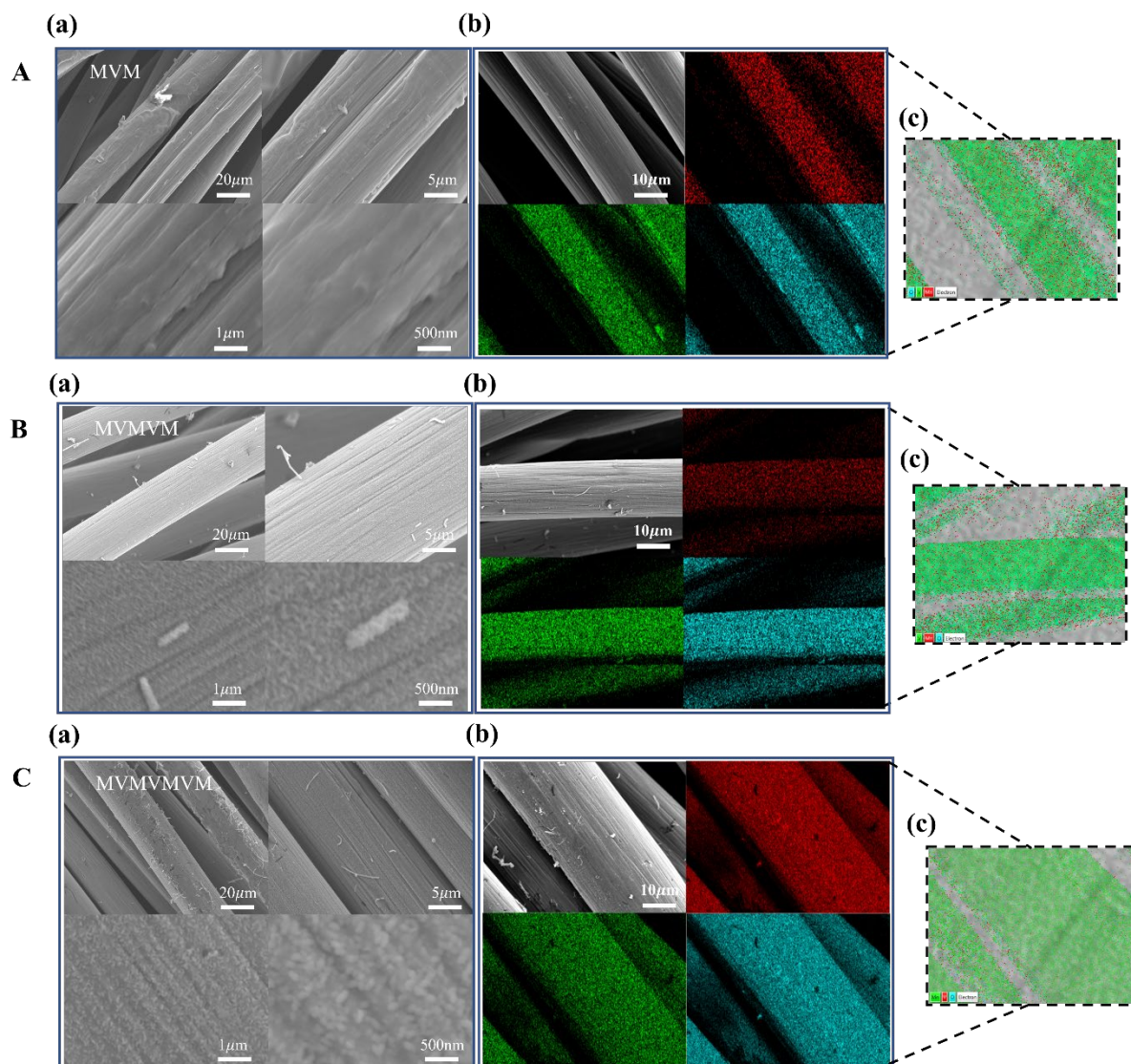


Figure 4.4. FESEM and Mapping images. A represents the control group MVM, B represents the control group MVMVM, and C represents the control group MVMVMVM. (a) FESEM images with

scale bars from 20 μ m to 500nm. (b-c) EDS elemental mapping analysis at 10 μ m scale bars. The green, red, and blue color represents vanadium (V), manganese (Mn), and oxygen (O), respectively.

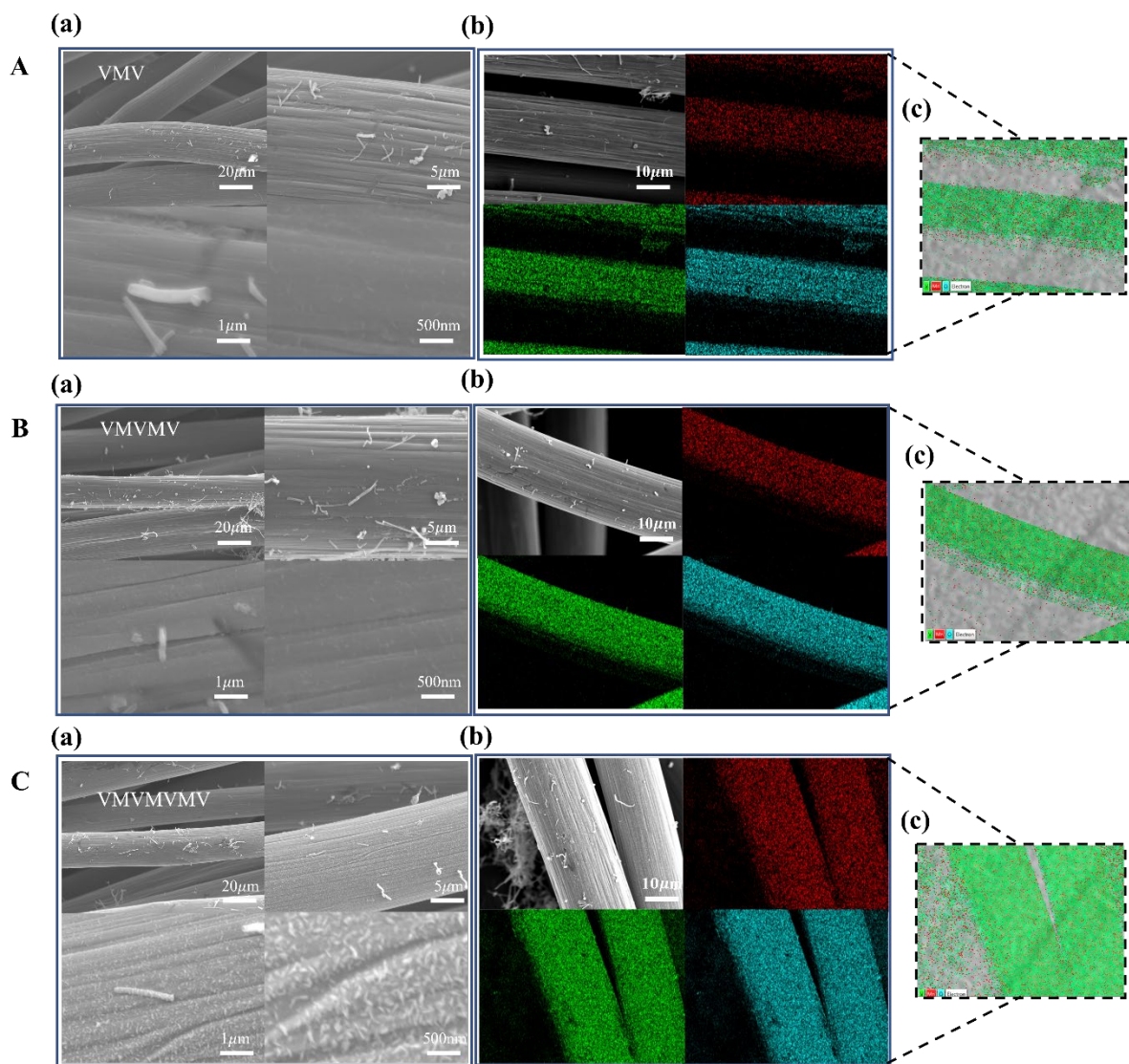


Figure 4.5. FESEM and Mapping images. A represents the control group VMV, B represents the control group VMVMV, and C represents the control group VMVMVMV. (a) FESEM images with

scale bars from 20 μm to 500nm. (b-c) EDS elemental mapping analysis at 10 μm scale bars. The green, red, and blue color represents vanadium (V), manganese (Mn), and oxygen (O), respectively.

Figures 4.4(a) and 4.5(a) sections are surface structures from the FESEM; it shows that the AJA RF magnetron sputtering deposition method creates uniform thin films on the CC substrate. The deposited times increased from Figures 4.4 and 4.5, A to C. Figure 4.4(b) and Figure 4.5(b) EDS mapping results prove that with the deposition time rise, the compound gathered more and more on the CC's surface, corresponding with the Mn, V and O elements' color becomes darker.

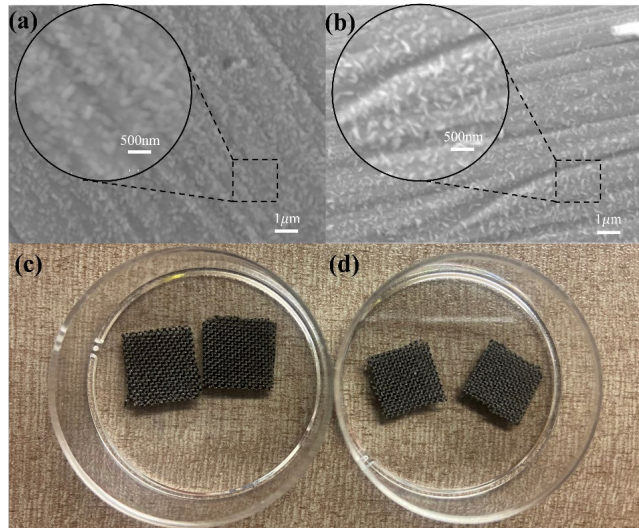


Figure 4.6. FESEM and electrode images. (a) and (b) are the FESEM images of the control group MVMVMVM and VMVMVMV, respectively. (c) and (d) correspond to their electrode picture.

Above the seven control groups, we further compared the MVMVMVM and VMVMVMV two groups. As Figure 4.6 (a) shows, the surface morphology of MVMVMVM is dense-packed spherical

MnO₂. The sputtered MnO₂-coated CNFs increased the electrode material's surface area and electrical conductivity [121]. The surface morphology of VMVMVMV, as shown in Figure 4.6 (b), forms small rods. Both rough structures may provide an excellent interface for ion intercalation and deintercalation and redox reaction [22]. Figure 4.6 (c), (d) is the digital image of the electrodes. It shows the surface-coated MnO₂ material has a darker color.

2. FTIR and UV-Vis

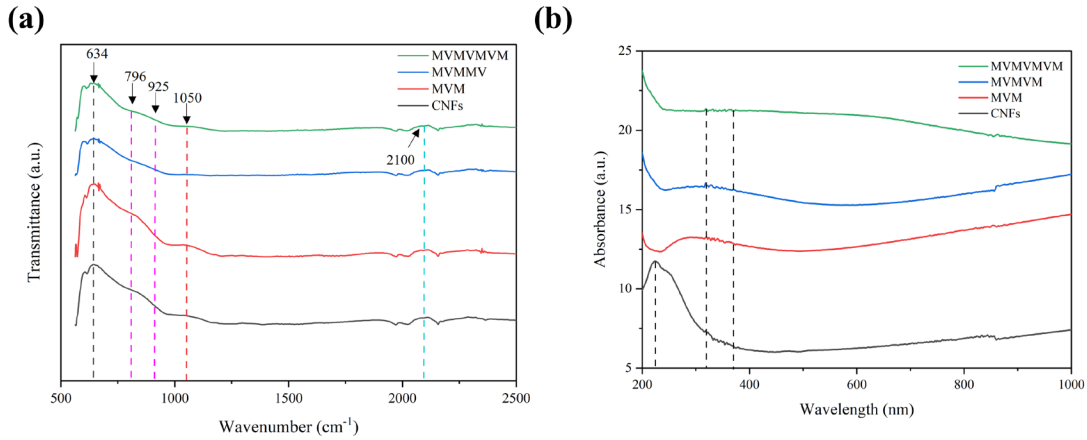


Figure 4.7. (a) FTIR spectrum of control group MV electrodes. (b) UV–visible spectra of control group MV electrodes.

Figure 4.7(a) shows the FTIR graphics of MV control groups. The MnO₂ peak is more pronounced, at 634 cm⁻¹, due to the fact that MnO₂ is on the surface of the film and its mode is the Mn-O vibration. The V₂O₅ shoulder peak is in the region of 796 to 925 cm⁻¹. The peak is less pronounced because V₂O₅ is in the interlayer film, and its mode is vanadium-based stretching (δ V-O) and V=O peak. The weak peak at 1050 cm⁻¹ corresponds to the bending vibration of the Mn atom with O-H. Meanwhile, hydrogen

bonding of hydroxyl groups with water molecules stretching vibrations causes a weak peak between 1076 cm^{-1} and 2430 cm^{-1} at around 2100 cm^{-1} . Experimental errors are mainly caused by flexible CC substrates, which may produce vibrational modes without dipole moment changes, vibrational modes in energy-degraded states, and vibrational modes that cannot be discerned by instrumental resolution [122].

For the UV-Vis, as shown in Figure 4.7(b), there are no clear peaks except for the apparent carbon peaks, which corresponds to the band at around 226nm is due to the $\pi-\pi^*$ transition of the aromatic C-C bond. The inconspicuous peak around 322-372 nm in the UV-Vis diagram corresponds to the absorption peak of MnO_2 , which is related to the d-d conversion of Mn ions in MnO_2 nanocrystals [123].

3. XRD

From the method mentioned above, we used Mn and V_2O_5 two targets to sputtering deposit MnO_2 and V_2O_5 thin films, respectively. It is necessary to clarify the crystal phase of the material that we got. Figure 4.8 shows the XRD patterns of the MVMVMVM electrode before (a) and after (b) the reaction.

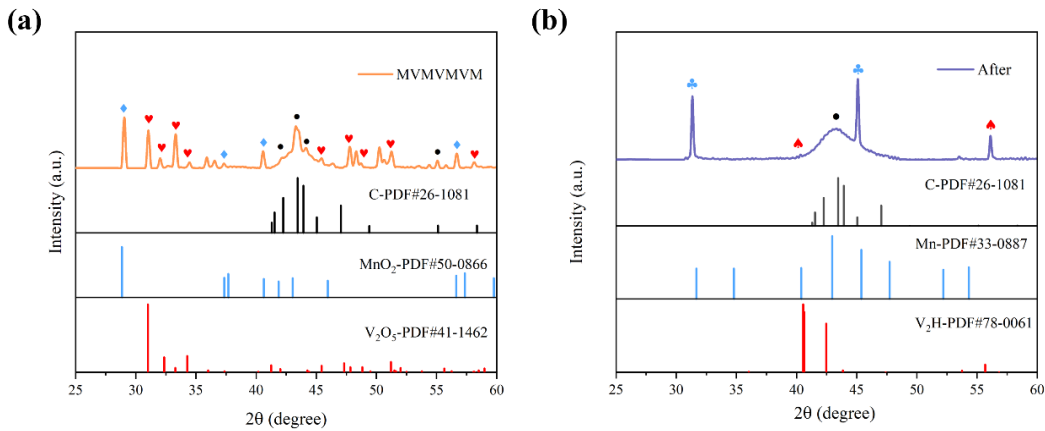


Figure 4.8. XRD pattern of the MVMVMVM electrode before reaction (a) and after (b) reaction.

It can be seen that the CNFs peak at around 43° (1 0 3) is the strongest (Figure 4.8 a), which is characteristic of hexagonal carbon (PDF#-26-1068).

For V_2O_5 , the most prominent peak appears at $2\theta = 31^\circ$ (3 0 1), which corresponds to orthorhombic V_2O_5 (PDF#-41-4162). In addition, other peaks at 2θ values of 32.36, 33.29, 34.28, 45.45, 47.32, 48.82, 51.20, and 58.99° correspond to the (0 1 1), (1 1 1), (3 1 0), (4 1 1), (6 0 0), (0 1 2), (0 2 0), and (4 1 2) planes of V_2O_5 .

For MnO_2 , the most prominent peak appears at $2\theta = 28.85^\circ$ (1 1 0), which corresponds to the orthorhombic MnO_2 (PDF#-50-0866). In addition, other peaks appearing at 2θ values of 37.68, 41.86, and 56.62° correspond to the (0 1 1), (0 2 0), and (2 1 1) planes of MnO_2 .

There are two main reasons for the weak or wide XRD peaks: (i) the formation of an ordered intercalation compound, which leads to the expulsion of intercalated water molecules from the nanostructure; (ii) the compound is amorphous [50,51]. The amorphous compound allows for easier insertion and extraction movement of the electrolyte, thus increasing the contact area between the electrolyte and the electrode and increasing the specific capacitance of the supercapacitor [52].

4. Mechanical Strength

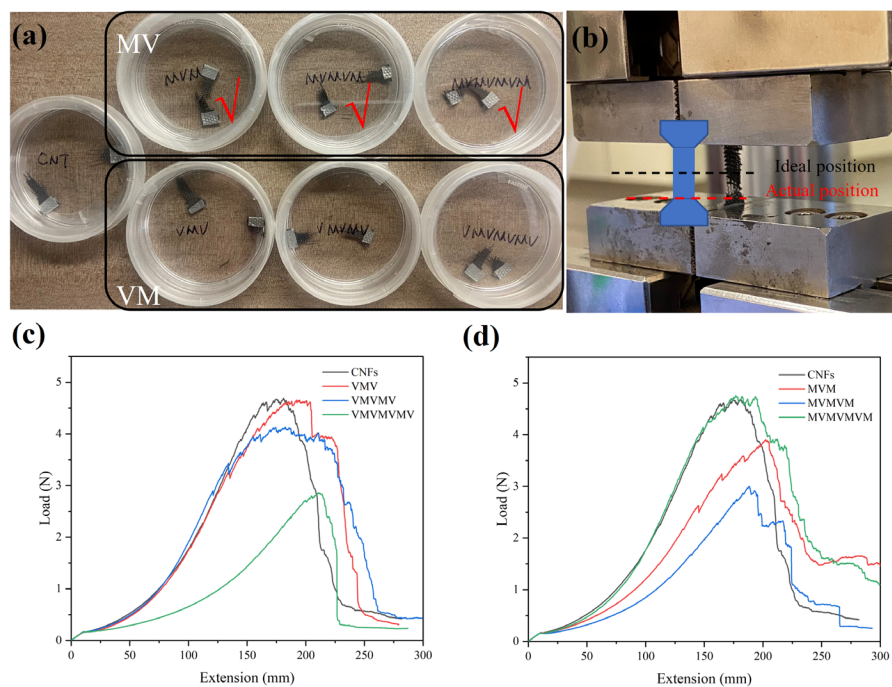


Figure 4.9. Load-extension behavior for electrodes' tensile strength. (a) Fracture diagram of a dumbbell-shaped electrode. (b) Local diagram of material fracture. (c) Group VM electrodes' Load-extension curve. (d) Group MV electrodes' Load-Extension curve.

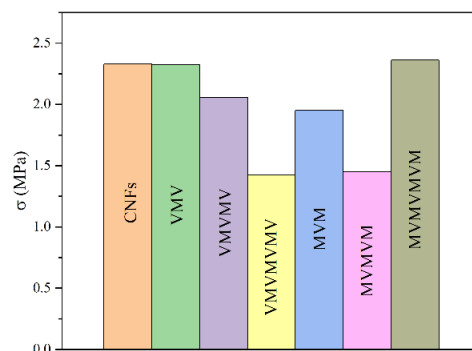


Figure 4.10. The tensile strength of electrodes.

Here is the sample preparation method for tensile strength test. The electrodes were cut in the dumbbell shape, providing clear results about tensile strength. Besides, the dumbbell sample was wrapped with 3M tape at both ends, which was designed to increase friction and prevent the sample from slipping off during stretching, improving the accuracy of the test. Further explained in Figure 4.9(b), the ideal crack position should be in the center of the bar. However, as shown Figure 4.9(a), the actual crack position among all electrodes was not the same; only the MV group has the ideal behavior. In Figure 4.9(c, d), all the electrodes showed good tensile properties, stretching from the original 1cm, more than doubled. It is mainly due to the ability of CC, the interwoven structure, which provides significant potential for further developing solid flexible devices. From Figure 4.10, the average tensile strength for all carbon cloth based electrodes is about 2 Mpa.

Electrochemical properties

1. CV

We first fabricated MVM electrodes and then optimized the parameter for better performance by increasing the deposition times for MnO_2 and V_2O_5 (MVMVM, MVMVMVM). We try to see the multilayer electrodes' influence. The deposition order was then changed as a pair of comparison groups (VMV, VMVMV, VMVMV) as a way to determine which of V_2O_5 and MnO_2 plays a major role in the reaction and affects the performance of the supercapacitor. First, the CV curve for these seven groups of electrodes was tested with 0-0.6V potential windows at a scan rate of 5 mV/s.

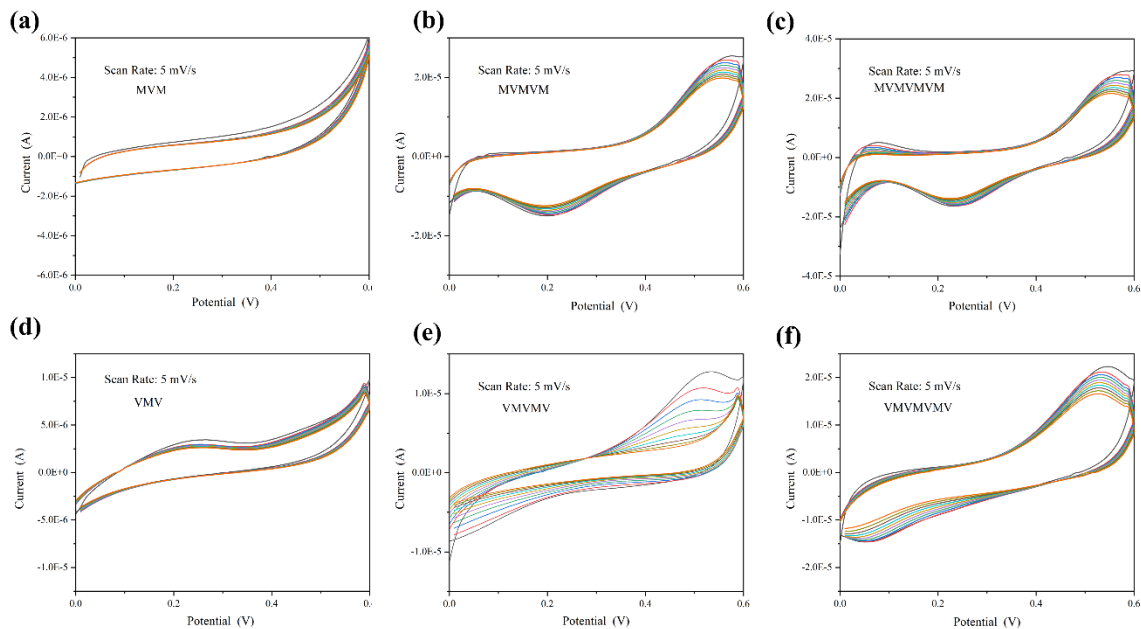


Figure 4.11. Electrochemical performance of seven groups electrode. CV curves at 5 mV/s for (a) MVM, (b) MVMVM, (c) MVMVMVM, (d) VMV, (e) VMVMV, and (f) VMVMVMV at potential window 0-0.6 V.

Figure 4.11(a-f) shows the shape of the curves like rectangular. When increasing the deposition times (MVM, MVMVM, MVMVMVM), as shown in Figure 4.10(a), (b), and (c), it comes with an oxidation peak at around 0-0.1V and a reduction peak at around 0.2-0.3 V., representing the typical CV characteristic of MnO_2 -based pseudocapacitor [24,125,126]. Based on the conventional charge storage mechanism of MnO_2 , a distinct peak appears at a low potential window of 0.2-0.3 V as a redox peak due to the insertion and removal of ions [62]. The first pair of control groups MV (MVM, MVMVM, MVMVMVM) (Figure 4.11a-c) shows better stability compared with the second pair of control groups VM (VMV, VMVMV, VMVMVMV) (Figure 4.11d-f). Moreover, the curve area raises when deposition times increase. The MVMVMVM electrodes, as shown in Figure 4.11 (c), exhibited the best

curve area, and the peak current achieved at about 3×10^{-5} (A), which is nearly an order of magnitude larger than the electrodes MVM (6×10^{-6}), as shown in Figure 4.11 (a). However, as for the other control group VM, the peak current for the VMVMVMV electrodes is shown in Figure 4.11 (f); compared with the VMV electrodes, as shown in Figure 4.11 (d), it offers a small raise, only improved 1×10^{-6} (A). The 5 mV/s CV curves show that the MVMVMVM electrode exhibit the most straightforward charge storage mechanism, the best stability, and the biggest curve area. It reached the maximum current at 3×10^{-5} A. Moreover, the shapes of all ten curves remain rectangular and a clear redox peak can be seen in the graph.

Above all, the MV groups shows better stability compared with the VM groups. Besides, the MVMVMVM electrode exhibit the most straightforward pseudocapacitor charge storage mechanism. It also has the best stability, and the biggest curve area. Furthermore, to indicate the convincing result, we applied several scan rates (100 mV/s, 90 mV/s, 80 mV/s, 70 mV/s, 60 mV/s, 50mV/s, 40 mV/s, 30 mV/s, 20 mV/s, 10 mV/s, 5 mV/s) and using the equation mentioned above, as shown in Equation (4.1,4.2), calculate the areal capacitance (C_A , mF/cm²) and volumetric capacitance (C_V , mF/cm³). In this study, the C_A (mF/cm²) and C_V (mF/cm³) are the same because the length and width of the electrode are the same, both 1 cm. The rest of the result will be provided by the C_V (mF/cm³) as the specific capacitance of the capacitor.

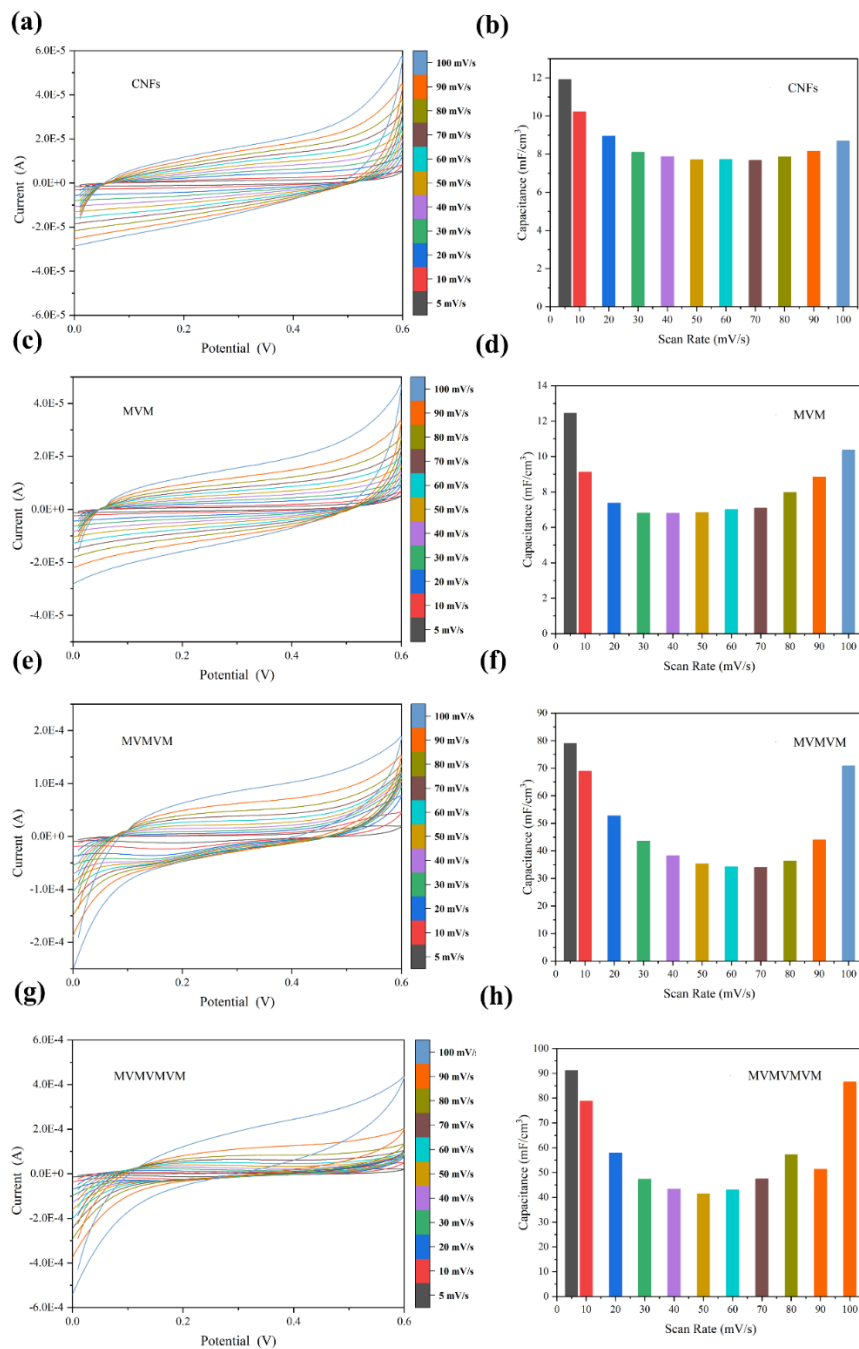


Figure 4.12. Electrochemical performance of seven groups electrode. Ten cycles' CV curves from 5 mV/s to 100 mV/s for (a) CNFs, (c) MVM, (e) MVMVM, (g) MVMVMVM at potential window 0-0.6 V. Capacitance calculated from the cure area for (b) CNFs, (d) MVM, (f) MVMVM, (h) MVMVMVM.

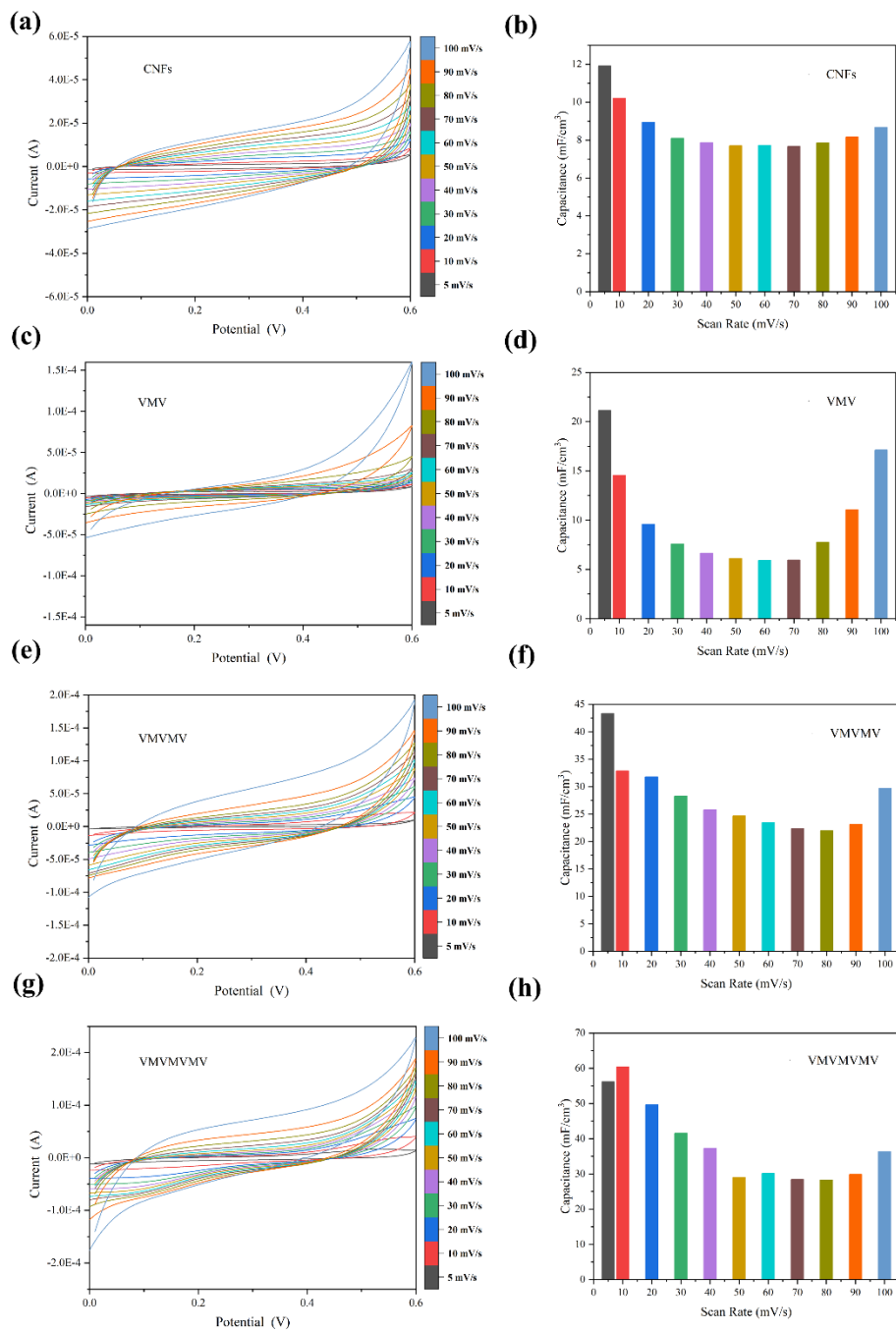


Figure 4.13. Electrochemical performance of seven groups electrode. Ten cycles' CV curves from 5 mV/s to 100 mV/s for (a) CNFs, (c) VMV, (e) VMVMV, (g) VMVMVMV at potential window 0-0.6 V. Capacitance calculated from the cure area for (b) CNFs, (d) VMV, (f) VMVMV, (h) VMVMVMV.

Figure 4.12 and Figure 4.13 are the CV curves at different scan rates from 100 mV/s to 5 mV/s, and their specific capacitance, corresponding to MV and VM, these two pairs of control groups, as shown in Figure 4.12 and Figure 4.13, respectively. In Figures 4.12(a-b) and 4.13(a-b), the CNFs capacitor is used as the blank control group. These two pairs of control groups have the same trend. The current becomes bigger when the scan rate increases, as shown in Figure 4.12(a, c, e, g) and Figure 4.13(a, c, e, g), respectively, and the CV curves retain a rectangular, which shows good high-rate performance.

However, in Figures 4.12(b, d, f, h) and 4.13(b, d, f, h) the capacitance shows a reduction from 5 mV/s to 70 mV/s followed by a rise from 80 mV/s to 100 mV/s. The VMVMVMV electrodes, as shown in Figure 4.13(h), at scan rate of 10 mV/s achieves the highest capacitance, reaching a value of 60 mF/cm³. Compared with the VMV electrodes (20 mF/cm³), which have the lowest capacitance, as shown in Figure 4.13(d), the capacitance value is 300% larger. The MVMVMVM electrodes, as shown in Figure 4.12(h), at lower scan rate (5 mV/s) achieves the highest capacitance, reaching a value of 90 mF/cm³. Compared with the electrodes CNFs and MVM (about 12 mF/cm³), which have the lowest capacitance, as shown in Figure 4.12(b)(d), the capacitance value is 750% larger.

Due to the reaction between electrolyte and electrode, the capacitance decreased with increasing the scan rate from 5 mV/s to 70 mV/s. At lower scan rates, the electrolyte ions H⁺ have sufficient time to penetrate the material's pores, while at higher scan rates, only it accumulates on the outer surface. Mishra *et al.* proved that the capacitance is linearly related to the scan rate and that a lower scan rate allows the electrolyte to fully penetrate the pores and increases the contact area between the electrolyte and the electrode material, resulting in a larger capacitance value [127]. After the 70 mV/s scan rate, the capacitance increased mainly because of the porous metal/CNFs/CC structure. As the scan rate increases, the reaction time becomes shorter and the reaction is concentrated on the surface until the

fully reacted material falls off, (also called a decrease in electrode weight) and new material continues to participate in the reaction so the capacitance increases. Besides, the MnO_2 and V_2O_5 grown by the magnetron sputtering method partially enter within the surface of the highly conductive CNF and CC. This gives it the characteristic that electrons and ions can enter and exit easily and efficiently, so the electrode material can provide fast redox reactions at high scan rates. Similar results were obtained by Lang *et al.* when creating a MnO_2 /gold nanostructured electrode. He used RF sputtering technique to deposit gold used to decorate MnO_2 , so the capacitance of this electrode increased with increasing scan rate [25]. Magnetron sputtering temperature as well as the reaction gas and pressure are the main factors that affect the surface morphology, composition and other physicochemical properties of MnO_2 and V_2O_5 films. Both Jamkhane *et al.* and Chandra *et al.* used sputtering to deposit cuprous oxide films and they demonstrated that this is a possible effect of this technique [72,128].

Most importantly, the MV-ordered control showed better electrochemical performance in terms of stability and capacitance compared to the VM-ordered control. Due to its large theoretical capacitance value, MnO_2 is the key material affecting the performance of supercapacitors when it is located on the surface of the electrode material compared to V_2O_5 . After further studying the rest electrodes in this group (MVM, MVMVM, MVMVMVM) by changing the deposition times, the MVMVMVM electrode shows the best performance among all electrodes. This is due to the increase in the thickness of MnO_2 and V_2O_5 resulting in an increase in the components involved in the reaction.

2. Nyquist plots and Capacitance Retention

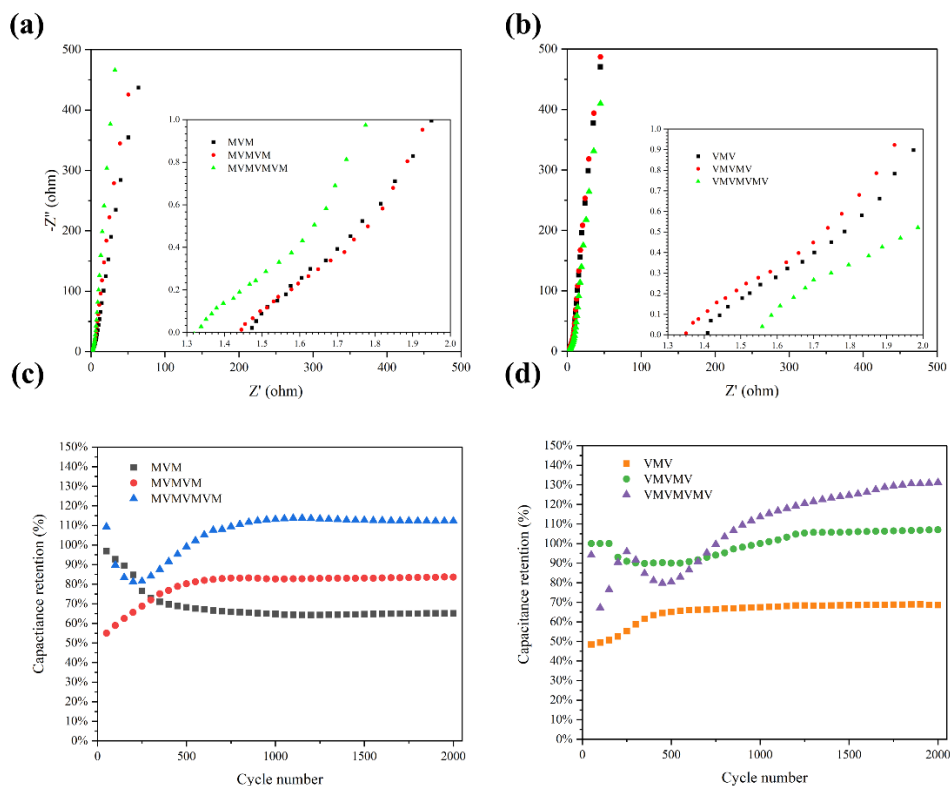


Figure 4.14. Electrochemical performance of seven groups electrode. Nyquist plots for two pairs of control groups (a) MV (b) MV. Capacitance retention for two control groups (c) MV, (d) VM.

Figure 4.14(a, b) shows the electrochemical impedance spectra of the electrode materials. In the local plot, all AC impedance spectra are composed of straight lines at both ends, where the initial straight line is the high-frequency region, and the line with a higher slope afterward is the low-frequency region. Different from the conventional supercapacitor, this study shows a pseudo supercapacitor behavior. The high-frequency region reflects electrolyte and bulk particle resistance [24,129]. In general, the high-frequency region belongs to charge transfer, while the low-frequency region belongs to the diffusion of ions.

The bulk particle resistance decreases with the increase of deposition times (about 0.7, 0.6, 0.43, 0.6, 0.45, 0.4 Ω for MVM, MVMVM, MVMVMVM, VMV, VMVMV and VMVMVM, respectively). For the low-frequency region, the straight-line slope also increases with the deposition times. All these further confirmed that the excessive $\text{MnO}_2/\text{V}_2\text{O}_5$ indeed causes the decrease of resistance. This is mainly due to the fact that, as the thickness of the film increases, the number of oxygen vacancies or low-valent vanadium cations (V^{4+} and V^{3+}) increases, thus promoting charge transfer and redox reactions [20].

As shown in Figure 4.14(c) and (d), after 2000 cycles CV at a scan rate of 100 mV/s measurements, we calculated the capacitance retention from the curve area. All the curves show that the capacitance retention rate rises as the deposition times increase. The retention is not stable for the first 750 cycles because of the nanostructure multilayers of MnO_2 and V_2O_5 electrodes. There may be some defects in the films, and the thick multilayers may lead to redox reactions not occurring completely at the electrodes. In the meantime, electrolyte ions are inserted into the electrode to balance the overall charge, which imposes mechanical stress on the physical structure of the electrode material. Therefore, when the redox reaction occurs completely and is ideally reversed, we can see that the retention gradually becomes stable after 750 cycles. In Figure 4.14(c) and (d), the two best-performing electrodes, MVMVMVM and VMVMVMV, achieve retention rates of about 120% and 124%, respectively. Moreover, the capacitive stability of MVMVMVM is better than that of VMVMVMV electrode.

4.3.2 Discussion

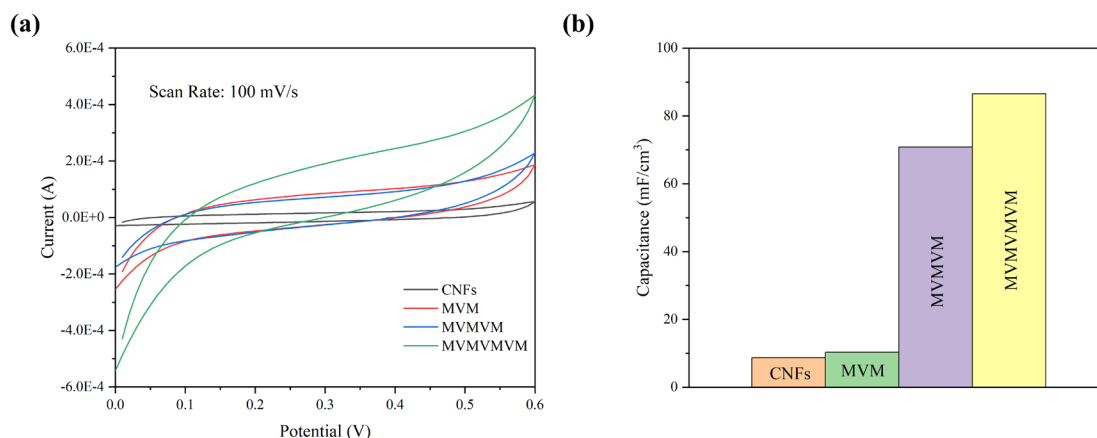


Figure 4.15. Important electrochemical performance of MVMVMVM electrode. (a) CV curves at scan rate 100 mV/s for control group MV. (b) Capacitance for control group MV.

Among all electrodes, the MVMVMVM electrode exhibits the best electrochemical performance. The capacitance improved by nearly 750%, and the CV curves retained a rectangular, showing good high-rate performance. Besides, the capacitance retention rate was stable at about 120% during the 2000 cycles CV measurement.

4.4 Summary

This present study, CNFs/V₂O₅/MnO₂ multilayer film electrodes were developed by combining spin coating and magnetron sputtering techniques. We performed seven comparisons by controlling the number of deposited metal oxide layers. This method provided good electronic/ionic conductivity while enhancing the pseudo-capacitive behavior of nanocrystalline V₂O₅/MnO₂. The electrode with MVMVMVM parameters shows the best performance. It has a very high specific capacitance and good cycling stability, making it one of the best electrode materials for high-performance supercapacitors.

In this study, magnetron sputtering technology was introduced, and the electrode interface of supercapacitor electric double-layer pseudo-electrode was constructed by controlling the metal oxide morphology and nanostructure, which provides a necessary reference and impetus for the development of supercapacitors.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

Circuits are an essential component of electronics. Among its four constituent parts memristor and capacitor are of great research significance, and they have been widely studied by scholars in the fields of artificial intelligence and energy storage, respectively, and good progress has been made. In this paper, we further investigate the memristors and supercapacitors.

For the memristor, the research on its mechanism is still imperfect and there is still a lack of knowledge. Therefore, we construct a silver (Ag)/Prussian blue (PB)/In-doped Tin Oxide (ITO) structure memristor. Unlike other methods of controlling circuit elements, glucose, as a new factor, is a very effective and direct method of controlling circuit elements. Ion transport recombination and redox reactions under bias in lead layers are controlled by glucose from a linear resistive state to capacitive coupling memristive effect and finally to pure memristive effect. This device further explores the mechanism of conduction filament and provides a promising application in complex integrated sensor and artificial intelligence applications.

For supercapacitors, how to increase capacitance and extend lifetime is a current issue facing the field. Studies point to electrode materials with large surface area and nanostructures as an important ending method. Therefore, we introduced the first magnetron sputtering deposition technique to fabricated MnO_2 and V_2O_5 decorated carbon-based electrodes. And carbon nanofibers were spin-coated on the carbon cloth substrate. The addition of carbon nanofibers increased the electrical conductivity of carbon cloth and improved the electron transfer rate, while the double carbon core-shell structure improved the reaction site for metal oxide deposition. Electrodes with CC/CNFs/ MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 / V_2O_5 / MnO_2 (MVMVMVM) structure showed the best

electrochemical performance. The capacitance value was increased nearly 10 times (90 mF/cm^3) compared to the control group that was spin-coated with carbon nanofibers only. As for the stability of the cell, the capacitance extension remained stable at 120% after 2000 cycles of CV cycling. This study constructs a supercapacitor electric double-layer pseudocapacitor electrode interface from the atomic scale, which provides a necessary reference and impetus for the development of supercapacitors.

5.2 Future Work

For future work, the details are as follows:

1. Optimization fabrication technique in the research of memristor.

The method of fabrication of the switching layer, PB, is spin coating, which may cause defects in the film. Electrochemical deposition is an excellent choice to make the film denser and uniform with controlled thickness. Also, the electrodes are deposited by the sputtering method through a shadow mask. The mask size is in μm range, which creates a larger electrode and thus affects the formation of conductive filaments. So, reducing the electrode size is also an essential plan.

2. Develop the application of the glucose-controlled memristor.

Unlike the introduction memristor, the device shows glucose-controlled behavior. So, it is a new factor that could connect with human health. It is possible to create a glucose testing or reporting application.

3. Optimization of the physical characterization of flexible supercapacitor

The UV-Vis and FTIR data do not meet the desired expectations. Therefore, further characterization of the carbon-based electrode materials decorated with MnO_2 and V_2O_5 is still needed to determine its functional groups and optical behavior.

4. Develop a solid device for the flexible supercapacitor

The aqueous solution supercapacitor exhibited good electrochemical properties. Also, the electrode material exhibits good ductility and tensile strength. Therefore, it is necessary to assemble a solid supercapacitor to explore this electrode's performance in more depth.

References

- [Vogt, C. 1999. Creating Long Documents using Microsoft Word. Published on the Web at the University of Waterloo.]
- [1] L. Chua, Memristor-The missing circuit element, *IEEE Trans. Circuit Theory*. 18 (1971) 507–519.
- [3] B. Sun, S. Wen, S. Wang, T. Huang, Y. Chen, P. Li, Quantized synchronization of memristive neural networks with time-varying delays via super-twisting algorithm, *Neurocomputing*. 380 (2020) 133–140.
- [4] X. Yu, H. Xiang, Y. Long, N. Zhao, X. Zhang, J. Xu, Preparation of porous polyacrylonitrile fibers by electrospinning a ternary system of PAN/DMF/H₂O, *Materials Letters*. 64 (2010) 2407–2409.
- [5] B.L. Risteska Stojkoska, K.V. Trivodaliev, A review of Internet of Things for smart home: Challenges and solutions, *Journal of Cleaner Production*. 140 (2017) 1454–1464.
- [6] P. Yao, H. Wu, B. Gao, J. Tang, Q. Zhang, W. Zhang, J.J. Yang, H. Qian, Fully hardware-implemented memristor convolutional neural network, *Nature*. 577 (2020) 641–646.
- [7] F. Alibart, S. Pieutin, D. Guérin, C. Novembre, S. Lenfant, K. Lmimouni, C. Gamrat, D. Vuillaume, An organic nanoparticle transistor behaving as a biological spiking synapse, *Advanced Functional Materials*. 20 (2010) 330–337.
- [8] L. Fang, S. Dai, Y. Zhao, D. Liu, J. Huang, Light-Stimulated Artificial Synapses Based on 2D Organic Field-Effect Transistors, *Advanced Electronic Materials*. 6 (2020) 1–8.

- [9] Z. Ballard, C. Brown, A.M. Madni, A. Ozcan, Machine learning and computation-enabled intelligent sensor design, *Nature Machine Intelligence*. 3 (2021) 556–565.
- [10] F. Messerschmitt, M. Kubicek, J.L.M. Rupp, How Does Moisture Affect the Physical Property of Memristance for Anionic-Electronic Resistive Switching Memories?, *Advanced Functional Materials*. 25 (2015) 5117–5125.
- [11] M.M. Rehman, G.U. Siddiqui, J.Z. Gul, S.-W. Kim, J.H. Lim, K.H. Choi, Resistive Switching in All-Printed, Flexible and Hybrid MoS₂-PVA Nanocomposite based Memristive Device Fabricated by Reverse Offset, *Scientific Reports*. 6 (2016) 36195.
- [12] H.A. Yildiz, New Area Efficient Memristor Realizations, *Microelectronics Journal*. (2021) 105037.
- [13] Y. Yu, C. Wang, C. Jiang, L. Wang, Z. Wang, Z. Du, J. Sun, I. Abrahams, X. Huang, Nitrogen-doped titanium dioxide nanorod array memristors with synaptic features and tunable memory lifetime for neuromorphic computing, *Journal of Alloys and Compounds*. 868 (2021) 159194.
- [14] Y.L. Zhu, K.H. Xue, X.M. Cheng, C. Qiao, J.H. Yuan, L.H. Li, X.S. Miao, Uniform and robust TiN/HfO₂/Pt memristor through interfacial Al-doping engineering, *Applied Surface Science*. 550 (2021) 149274.
- [15] C. Jiang, Q. Li, N. Sun, J. Huang, R. Ji, S. Bi, Q. Guo, J. Song, A high-performance bionic pressure memory device based on piezo-OLED and piezo-memristor as luminescence-fish neuromorphic tactile system, *Nano Energy*. 77 (2020) 105120.

- [16] D. Wu, X. Xie, Y. Zhang, D. Zhang, W. Du, X. Zhang, B. Wang, MnO₂/Carbon Composites for Supercapacitor: Synthesis and Electrochemical Performance, *Frontiers in Materials*. 7 (2020).
- [17] D. Majumdar, Review on Current Progress of MnO₂-Based Ternary Nanocomposites for Supercapacitor Applications, *ChemElectroChem*. 8 (2021) 291–336.
- [18] E. Moazzen, E.V. Timofeeva, C.U. Segre, Controlled synthesis of MnO₂ nanoparticles for aqueous battery cathodes: polymorphism–capacity correlation, *J Mater Sci*. 52 (2017) 8107–8118.
- [19] N. Kumagai, S. Tanifuji, K. Tanno, Electrochemical characteristics of MnO₂/V₂O₅ composites serving as positive material for secondary lithium batteries, (n.d.) 10.
- [20] X. Wu, Y. Tao, L. Dong, J. Hong, Synthesis and characterization of self-assembling (NH₄)_{0.5}V₂O₅ nanowires, *J. Mater. Chem*. 14 (2004) 901.
- [21] A. Yuan, X. Wang, Y. Wang, J. Hu, Textural and capacitive characteristics of MnO₂ nanocrystals derived from a novel solid-reaction route, *Electrochimica Acta*. 54 (2009) 1021–1026.
- [22] B. Pandit, D.P. Dubal, P. Gómez-Romero, B.B. Kale, B.R. Sankapal, V₂O₅ encapsulated MWCNTs in 2D surface architecture: Complete solid-state bendable highly stabilized energy efficient supercapacitor device, *Sci Rep*. 7 (2017) 43430.
- [23] Z. Chen, Y. Qin, D. Weng, Q. Xiao, Y. Peng, X. Wang, H. Li, F. Wei, Y. Lu, Design and Synthesis of Hierarchical Nanowire Composites for Electrochemical Energy Storage, *Adv. Funct. Mater*. 19 (2009) 3420–3426.

- [24] H. Wang, C. Peng, F. Peng, H. Yu, J. Yang, Facile synthesis of MnO₂/CNT nanocomposite and its electrochemical performance for supercapacitors, *Materials Science and Engineering: B*. 176 (2011) 1073–1078.
- [25] X. Lang, A. Hirata, T. Fujita, M. Chen, Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors, *Nature Nanotech.* 6 (2011) 232–236.
- [26] S. Chen, J. Zhu, X. Wu, Q. Han, X. Wang, Graphene Oxide–MnO₂ Nanocomposites for Supercapacitors, *ACS Nano*. 4 (2010) 2822–2830.
- [27] A. Kumar, A. Sanger, A. Kumar, Y. Kumar, R. Chandra, Sputtered Synthesis of MnO₂ Nanorods as Binder Free Electrode for High Performance Symmetric Supercapacitors, *Electrochimica Acta*. 222 (2016) 1761–1769.
- [28] M. Braun, Magnetron Sputtering Technique, in: A.Y.C. Nee (Ed.), *Handbook of Manufacturing Engineering and Technology*, Springer, London, 2015: pp. 2929–2957.
- [29] S.-Y. Sung, S.-Y. Kim, K.-M. Jo, J.-H. Lee, J.-J. Kim, S.-G. Kim, K.-H. Chai, S.J. Pearton, D.P. Norton, Y.-W. Heo, Fabrication of p-channel thin-film transistors using CuO active layers deposited at low temperature, *Appl. Phys. Lett.* 97 (2010) 222109.
- [30] R. Waser, R. Dittmann, G. Staikov, K. Szot, Redox-Based Resistive Switching Memories – Nanoionic Mechanisms, Prospects, and Challenges, *Advanced Materials*. 21 (2009) 2632–2663.
- [31] R. Guo, W. Lin, X. Yan, T. Venkatesan, J. Chen, Ferroic tunnel junctions and their application in neuromorphic networks, *Applied Physics Reviews*. 7 (2020) 011304.
- [32] Y. Yang, P. Gao, S. Gaba, T. Chang, X. Pan, W. Lu, Observation of conducting filament growth in nanoscale resistive memories, *Nat Commun*. 3 (2012) 732.

- [33] S. Raoux, Phase Change Materials, *Annu. Rev. Mater. Res.* 39 (2009) 25–48.
- [34] J.-Y. Chen, C.-L. Hsin, C.-W. Huang, C.-H. Chiu, Y.-T. Huang, S.-J. Lin, W.-W. Wu, L.-J. Chen, Dynamic Evolution of Conducting Nanofilament in Resistive Switching Memories, *Nano Lett.* 13 (2013) 3671–3677.
- [35] M.M. Rehman, G.U. Siddiqui, J.Z. Gul, S.-W. Kim, J.H. Lim, K.H. Choi, Resistive Switching in All-Printed, Flexible and Hybrid MoS₂-PVA Nanocomposite based Memristive Device Fabricated by Reverse Offset, *Sci Rep.* 6 (2016) 36195.
- [36] Y. Xu, L. Tan, B. Sun, M. Lei, Y. Zhao, T. Li, L. Zheng, S. Zhu, Y. Zhang, Y. Zhao, Memristive effect with non-zero-crossing current-voltage hysteresis behavior based on Ag doped *Lophatherum gracile* Brongn, *Current Applied Physics.* 20 (2020) 545–549.
- [37] T. Li, Y. Xu, M. Lei, Y. Zhao, B. Sun, H. Elshekh, L. Zheng, X. Zhang, W. Hou, Y. Zhao, The pH-controlled memristive effect in a sustainable bioelectronic device prepared using lotus root, *Materials Today Sustainability.* 7–8 (2020) 100029.
- [38] B. Sun, Y. Chen, M. Xiao, G. Zhou, S. Ranjan, W. Hou, X. Zhu, Y. Zhao, S.A.T. Redfern, Y.N. Zhou, A Unified Capacitive-Coupled Memristive Model for the Nonpinched Current–Voltage Hysteresis Loop, *Nano Lett.* 19 (2019) 6461–6465.
- [39] J.-Q. Yang, L.-Y. Ting, R. Wang, J.-Y. Mao, Y. Ren, C.-L. Chang, C.-M. Yeh, H.-H. Chou, Y. Zhou, S.-T. Han, Fluorenone/carbazole based bipolar small molecules for non-volatile memory devices, *Organic Electronics.* 78 (2020) 105584.
- [40] G.U. Kamble, A.V. Takaloo, A.M. Teli, Y.J. Kim, P. Sonar, T.D. Dongale, D. Kim, T.W. Kim, Highly-stable memristive devices with synaptic characteristics based on

hydrothermally synthesized MnO₂ active layers, *Journal of Alloys and Compounds*. 872 (2021) Article number: 159653.

- [41] Y.-L. Zhu, K.-H. Xue, X.-M. Cheng, C. Qiao, J.-H. Yuan, L.-H. Li, X.-S. Miao, Uniform and robust TiN/HfO₂/Pt memristor through interfacial Al-doping engineering, *Applied Surface Science*. 550 (2021) 149274.
- [42] N. Duraisamy, N.M. Muhammad, H.-C. Kim, J.-D. Jo, K.-H. Choi, Fabrication of TiO₂ thin film memristor device using electrohydrodynamic inkjet printing, *Thin Solid Films*. 520 (2012) 5070–5074.
- [43] Z. Xu, K. Jin, L. Gu, Y. Jin, C. Ge, C. Wang, H. Guo, H. Lu, R. Zhao, G. Yang, Evidence for a Crucial Role Played by Oxygen Vacancies in LaMnO₃ Resistive Switching Memories, *Small*. 8 (2012) 1279–1284.
- [44] H.J. Becker, V. Ferry, Low voltage electrolytic capacitor, (n.d.) 3.
- [45] C. Brian E, *Electrochemistry Encyclopedia -- Electrochemical capacitors*, (n.d.).
- [46] Y. Shao, M.F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R.B. Kaner, Design and Mechanisms of Asymmetric Supercapacitors, *Chem. Rev.* 118 (2018) 9233–9280.
- [47] L.L. Zhang, X.S. Zhao, Carbon-based materials as supercapacitor electrodes, *Chem. Soc. Rev.* 38 (2009) 2520–2531.
- [48] M. Shao, F. Ning, Y. Zhao, J. Zhao, M. Wei, D.G. Evans, X. Duan, Core–Shell Layered Double Hydroxide Microspheres with Tunable Interior Architecture for Supercapacitors, *Chem. Mater.* 24 (2012) 1192–1197.

- [49] A.G. Pandolfo, A.F. Hollenkamp, Carbon properties and their role in supercapacitors, *Journal of Power Sources*. 157 (2006) 11–27.
- [50] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, The chemistry of graphene oxide, *Chemical Society Reviews*. 39 (2010) 228–240.
- [51] M. Moniruzzaman Sk, C. Yoon Yue, Layer-by-layer (LBL) assembly of graphene with p -phenylenediamine (PPD) spacer for high performance supercapacitor applications, *RSC Advances*. 4 (2014) 19908–19915.
- [52] C. Kim, Y.-O. Choi, W.-J. Lee, K.-S. Yang, Supercapacitor performances of activated carbon fiber webs prepared by electrospinning of PMDA-ODA poly(amic acid) solutions, *Electrochimica Acta*. 50 (2004) 883–887.
- [53] L. Hu, W. Chen, X. Xie, N. Liu, Y. Yang, H. Wu, Y. Yao, M. Pasta, H.N. Alshareef, Y. Cui, Symmetrical MnO₂–Carbon Nanotube–Textile Nanostructures for Wearable Pseudocapacitors with High Mass Loading, *ACS Nano*. 5 (2011) 8904–8913.
- [54] M. Kandasamy, S. Sahoo, S. Kumar Nayak, B. Chakraborty, C. Sekhar Rout, Recent advances in engineered metal oxide nanostructures for supercapacitor applications: experimental and theoretical aspects, *Journal of Materials Chemistry A*. 9 (2021) 17643–17700.
- [55] M. Toupin, T. Brousse, D. Bélanger, Charge Storage Mechanism of MnO₂ Electrode Used in Aqueous Electrochemical Capacitor, *Chem. Mater.* 16 (2004) 3184–3190.
- [56] B. Saravanakumar, K.K. Purushothaman, G. Muralidharan, Interconnected V₂O₅ Nanoporous Network for High-Performance Supercapacitors, *ACS Appl. Mater. Interfaces*. 4 (2012) 4484–4490.

- [57] N. Zarshad, A.U. Rahman, J. Wu, A. Ali, F. Raziq, L. Han, P. Wang, G. Li, H. Ni, Enhanced energy density and wide potential window for K incorporated MnO₂@carbon cloth supercapacitor, *Chemical Engineering Journal*. 415 (2021) 128967.
- [58] J.-H. Jeong, J.W. Park, D.W. Lee, R.H. Baughman, S.J. Kim, Electrodeposition of α -MnO₂/ γ -MnO₂ on Carbon Nanotube for Yarn Supercapacitor, *Sci Rep*. 9 (2019) 11271.
- [59] S. Saha, P. Maji, D.A. Pethsangave, A. Roy, A. Ray, S. Some, S. Das, Effect of morphological ordering on the electrochemical performance of MnO₂-Graphene oxide composite, *Electrochimica Acta*. 317 (2019) 199–210.
- [60] J. Yan, Z. Fan, T. Wei, W. Qian, M. Zhang, F. Wei, Fast and reversible surface redox reaction of graphene–MnO₂ composites as supercapacitor electrodes, *Carbon*. 48 (2010) 3825–3833.
- [61] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya, L.-C. Qin, Graphene and nanostructured MnO₂ composite electrodes for supercapacitors, *Carbon*. 49 (2011) 2917–2925.
- [62] N. Jabeen, Q. Xia, S.V. Savilov, S.M. Aldoshin, Y. Yu, H. Xia, Enhanced Pseudocapacitive Performance of α -MnO₂ by Cation Preinsertion, *ACS Appl. Mater. Interfaces*. 8 (2016) 33732–33740.
- [63] J. Duay, S.A. Sherrill, Z. Gui, E. Gillette, S.B. Lee, Self-Limiting Electrodeposition of Hierarchical MnO₂ and M(OH)₂/MnO₂ Nanofibril/Nanowires: Mechanism and Supercapacitor Properties, *ACS Nano*. 7 (2013) 1200–1214.
- [64] H. Hu, Z. Pei, H. Fan, C. Ye, 3D Interdigital Au/MnO₂/Au Stacked Hybrid Electrodes for On-Chip Microsupercapacitors, *Small*. 12 (2016) 3059–3069.

- [65] O. Ghodbane, J.-L. Pascal, F. Favier, Microstructural Effects on Charge-Storage Properties in MnO₂-Based Electrochemical Supercapacitors, *ACS Appl. Mater. Interfaces*. 1 (2009) 1130–1139.
- [66] R. Dong, Y. Song, D. Yang, H.-Y. Shi, Z. Qin, M. Zhang, D. Guo, X. Sun, X.-X. Liu, Electrochemical *in situ* construction of vanadium oxide heterostructures with boosted pseudocapacitive charge storage, *J. Mater. Chem. A*. 8 (2020) 1176–1183.
- [67] T.G. Nyawo, N.P. Chonco, C. Thethwayo, A.P. Sefage, O.M. Ndwandwe, Synthesis and characterization of magnetron sputter deposited Ge-nanowires., (n.d.) 5.
- [68] M.R. Shijeesh, M.K. Jayaraj, Low temperature fabrication of Cu_xO thin-film transistors and investigation on the origin of low field effect mobility, *Journal of Applied Physics*. 123 (2018) 161538.
- [69] H. Klauk, Organic thin-film transistors, *Chem. Soc. Rev.* 39 (2010) 2643.
- [70] S. Ghosh, L. Rajan, Zinc Oxide Thin-Film Transistor with Catalytic Electrodes for Hydrogen Sensing at Room Temperature, *IEEE Transactions on Nanotechnology*. 20 (2021) 303–310.
- [71] S.K. Suresh Babu, D. Jackuline Moni, D. Gracia, A.G. Adigo, Investigation on V₂O₅ Thin Films for Field Effect Transistor Applications, *Advances in Materials Science and Engineering*. 2021 (2021) e2414589.
- [72] R. Chandra, A.K. Chawla, P. Ayyub, Optical and Structural Properties of Sputter-Deposited Nanocrystalline Cu₂O Films: Effect of Sputtering Gas, *J. Nanosci. Nanotech.* 6 (2006) 1119–1123.

- [73] A. Kumar, A. Sanger, A. Kumar, Y. Kumar, R. Chandra, Sputtered Synthesis of MnO₂ Nanorods as Binder Free Electrode for High Performance Symmetric Supercapacitors, *Electrochimica Acta*. 222 (2016) 1761–1769.
- [74] H. Dinis, P.M. Mendes, A comprehensive review of powering methods used in state-of-the-art miniaturized implantable electronic devices, *Biosensors and Bioelectronics*. 172 (2021) 112781.
- [75] W. Wang, W. Zhao, H. Xu, S. Liu, W. Huang, Q. Zhao, Fabrication of ultra-thin 2D covalent organic framework nanosheets and their application in functional electronic devices, *Coordination Chemistry Reviews Journal*. 429 (2021) 213616.
- [76] Z. He, Y. Yan, Z. Zhang, Thermal management and temperature uniformity enhancement of electronic devices by micro heat sinks: A review, *Energy*. 216 (2021) 119223.
- [77] X. Liu, W. Xiao, T. Tao, J. Yang, H. Li, Q. Chen, L. Huang, Y. Ni, L. Chen, X. Ouyang, X. Zhu, J. Li, Transparent, smooth, and sustainable cellulose-derived conductive film applied for the flexible electronic device, *Carbohydrate Polymers*. 260 (2021) 117820.
- [78] G.U. Kamble, A. V. Takaloo, A.M. Teli, Y.J. Kim, P. Sonar, T.D. Dongale, D. Kim, T. Whan Kim, Highly-stable memristive devices with synaptic characteristics based on hydrothermally synthesized MnO₂ active layers, *Journal of Hazardous Materials*. (2020) 124562.

- [79] B. Sun, M. Xiao, G. Zhou, Z. Ren, Y.N. Zhou, Y.A. Wu, Non-zero-crossing current-voltage hysteresis behavior in memristive system, *Materials Today Advances*. 6 (2020) 100056.
- [80] J.Q. Yang, L.Y. Ting, R. Wang, J.Y. Mao, Y. Ren, C.L. Chang, C.M. Yeh, H.H. Chou, Y. Zhou, S.T. Han, Fluorenone/carbazole based bipolar small molecules for non-volatile memory devices, *Organic Electronics*. 78 (2020) 105584.
- [81] B. Sun, S. Wen, S. Wang, T. Huang, Y. Chen, P. Li, Quantized synchronization of memristive neural networks with time-varying delays via super-twisting algorithm, *Neurocomputing*. 380 (2020) 133–140.
- [82] T. Li, Y. Xu, M. Lei, Y. Zhao, B. Sun, H. Elshekh, L. Zheng, X. Zhang, W. Hou, Y. Zhao, The pH-controlled memristive effect in a sustainable bioelectronic device prepared using lotus root, *Materials Today Sustainability*. 7–8 (2020) 100029.
- [83] B. Sun, G. Zhou, T. Guo, Y.N. Zhou, Y.A. Wu, Biomemristors as the next generation bioelectronics, *Nano Energy*. 75 (2020) 104938.
- [84] Y. Xu, L. Tan, B. Sun, M. Lei, Y. Zhao, T. Li, L. Zheng, S. Zhu, Y. Zhang, Y. Zhao, Memristive effect with non-zero-crossing current-voltage hysteresis behavior based on Ag doped *Lophatherum gracile* Brongn, *Current Applied Physics*. 20 (2020) 545–549.
- [85] N.S. Mohamad Hadis, A. Abd Manaf, S.H. Ngalim, S.H. Herman, Fabrication and characterisation of fluidic based memristor sensor for liquid with hydroxyl group, *Sensing and Bio-Sensing Research*. 14 (2017) 21–29.
- [86] J.R. Miller, Engineering electrochemical capacitor applications, *Journal of Power Sources*. 326 (2016) 726–735.

- [87] G. Zhou, J. Wu, L. Wang, B. Sun, Z. Ren, X. Cunyun, Y. Yao, L. Liao, G. Wang, S. Zheng, P. Mazumder, S. Duan, Q. Song, Evolution map of the memristor: from capacitive state to resistive switching state, *Nanoscale*. 11 (2019) 17222–17229.
- [88] S. Zhu, G. Zhou, W. Yuan, S. Mao, F. Yang, G. Fu, B. Sun, Non-zero-crossing current-voltage hysteresis behavior induced by capacitive effects in bio-memristor, *Journal of Colloid and Interface Science*. 560 (2020) 565–571.
- [89] S. Goswami, D. Thompson, R.S. Williams, S. Goswami, T. Venkatesan, Colossal current and voltage tunability in an organic memristor via electrode engineering, *Applied Materials Today*. 19 (2020) 100626.
- [90] N.A. Ahir, A.V. Takaloo, K.A. Nirmal, S.S. Kundale, M.Y. Chougale, J. Bae, D. kee Kim, T.D. Dongale, Capacitive coupled non-zero I–V and type-II memristive properties of the NiFe₂O₄–TiO₂ nanocomposite, *Materials Science in Semiconductor Processing*. 125 (2021) 105646.
- [91] B.O. Oresanya, G. Si, Z. Guo, X. Xu, Y. Bie, Mathematical analysis and emulation of the fractional-order cubic flux-controlled memristor, *Alexandria Engineering Journal*. 60 (2021) 4315–4324.
- [92] H. Mouadili, S. Majid, O. Kamal, E.L.H. ElAtmani, K. Touaj, L. Lebrun, M. Hlaïbi, New grafted polymer membrane for extraction, separation and recovery processes of sucrose, glucose and fructose from the sugar industry discharges, *Separation and Purification Technology*. 200 (2018) 230–241.
- [93] A. Safwan Alikasturi, S. Shaharuddin, M. Razealy Anuar, A. Radzuan Mohamad Radzi, A. Syafiq Fauzan Mohd Asnawi, A. Nadiah Husin, N. Asikin Aswandi, A. Izzat

Mustapha, Extraction of Glucose by Using Alkaline Hydrolysis from *Musa Sapientum* Peels, *Ananas Comosus* and *Mangifera Indica* Linn, *Materials Today: Proceedings*. 5 (2018) 22148–22153.

- [94] Z. Yang, J. Li, T. Peng, Study and application of prussian blue in the preparation of chemical sensors, *PTCA (PART B:CHEMICAL ANALYSIS)*. 83 (2002) 97–101.
- [95] Y. Van De Burgt, E. Lubberman, E.J. Fuller, S.T. Keene, G.C. Faria, S. Agarwal, M.J. Marinella, A. Alec Talin, A. Salleo, A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing, *Nature Materials*. 16 (2017) 414–418.
- [96] L.B. Avila, C.K. Müller, D. Hildebrand, F.L. Fata, B.F. Baggio, C.C. Plácido, A.A. Pasa, Resistive switching in electrodeposited Prussian blue layers, *Materials*. 13 (2020) 1–11.
- [97] J.Y. Na, B. Kang, D.H. Sin, K. Cho, Y.D. Park, Understanding solidification of polythiophene thin films during spin-coating: Effects of spin-coating time and processing additives, *Scientific Reports*. 5 (2015) 13288.
- [98] D. Zhu, Z. Jin, W. Li, Q. Wang, R. Wu, Y. Cui, Preparation and performance of Pb/ITO-PET flexible electrochromic films, *The Chinese Journal Process Engineering*. 221005 (2021) 1009-606.
- [99] J.-L. Chiang, S.-W. Li, B.K. Yadlapalli, D.-S. Wu, Deposition of high-transmittance ITO thin films on polycarbonate substrates for capacitive-touch applications, *Vacuum*. 186 (2021) 110046.

- [100] M. Ahmed, A. Bakry, A. Qasem, H. Dalir, The main role of thermal annealing in controlling the structural and optical properties of ITO thin film layer, *Optical Materials*. 113 (2021) 110866.
- [101] Y. Dai, T. Yan, R. Hong, C. Tao, H. Lin, Q. Wang, D. Zhang, Graphene oxide induced the enhancement of nonlinear optical response of ITO films, *Optical Materials*. 113 (2021) 110841.
- [102] S.J. Lee, S.H. Lee, H.W. Kang, S. Nahm, B.H. Kim, H. Kim, S.H. Han, Flexible electrochromic and thermochromic hybrid smart window based on a highly durable ITO/graphene transparent electrode, *Chemical Engineering Journal*. 416 (2021) 1385–8947.
- [103] B. Sun, T. Guo, G. Zhou, J. Wu, Y. Chen, Y.N. Zhou, Y.A. Wu, A Battery-Like Self-Selecting Biomemristor from Earth-Abundant Natural Biomaterials, *ACS Applied Bio Materials*. 4 (2021) 1976–1985.
- [104] Q. Li, I. Salaoru, A. Khiat, H. Xu, T. Prodromakis, Correlated resistive/capacitive state variability in solid TiO₂ based memory devices, *Applied Physics A: Materials Science and Processing*. 123 (2017) 1–5.
- [105] K. Macvittie, E. Katz, Electrochemical system with memimpedance properties, *Journal of Physical Chemistry C*. 117 (2013) 24943–24947.
- [106] B. Sun, Y. Chen, M. Xiao, G. Zhou, S. Ranjan, W. Hou, X. Zhu, Y. Zhao, S.A.T. Redfern, Y. Norman Zhou, A Unified Capacitive-Coupled Memristive Model for the Nonpinched Current-Voltage Hysteresis Loop, *Nano Letters*. 19 (2019) 6461–6465.

- [107] M. Zaheer, Y. Cai, A.B. Waqas, S.F. Abbasi, G. Zhu, C. Cong, Z.J. Qiu, R. Liu, Y. Qin, L. Zheng, L. Hu, Liquid-Metal-Induced Memristor Behavior in Polymer Insulators, *Physica Status Solidi - Rapid Research Letters*. 14 (2020) 1862–6270.
- [108] L. Chua, Five non-volatile memristor enigmas solved, Springer Berlin Heidelberg, 2018.
- [109] Z.T. Xu, K.J. Jin, L. Gu, Y.L. Jin, C. Ge, C. Wang, H.Z. Guo, H. Bin Lu, R.Q. Zhao, G.Z. Yang, Evidence for a crucial role played by oxygen vacancies in LaMnO_3 resistive switching memories, *Small*. 8 (2012) 1279–1284.
- [110] G. Zhou, Z. Ren, B. Sun, J. Wu, Z. Zou, S. Zheng, L. Wang, S. Duan, Q. Song, Capacitive effect: An original of the resistive switching memory, *Nano Energy*. 68 (2020) 104386.
- [111] S. Najib, E. Erdem, Current progress achieved in novel materials for supercapacitor electrodes: mini review, *Nanoscale Adv.* 1 (2019) 2817–2827.
- [112] M.F. El-Kady, M. Ihns, M. Li, J.Y. Hwang, M.F. Mousavi, L. Chaney, A.T. Lech, R.B. Kaner, Engineering three-dimensional hybrid supercapacitors and microsupercapacitors for high-performance integrated energy storage, *Proc. Natl. Acad. Sci. U.S.A.* 112 (2015) 4233–4238.
- [113] T. Brousse, P.-L. Taberna, O. Crosnier, R. Dugas, P. Guillemet, Y. Scudeller, Y. Zhou, F. Favier, D. Bélanger, P. Simon, Long-term cycling behavior of asymmetric activated carbon/ MnO_2 aqueous electrochemical supercapacitor, *Journal of Power Sources*. 173 (2007) 633–641.

- [114] M. Toupin, T. Brousse, D. Bélanger, Charge Storage Mechanism of MnO_2 Electrode Used in Aqueous Electrochemical Capacitor, *Chem. Mater.* 16 (2004) 3184–3190.
- [115] Y. Liu, Y. Qiao, W. Zhang, H. Xu, Z. Li, Y. Shen, L. Yuan, X. Hu, X. Dai, Y. Huang, High-performance aqueous sodium-ion batteries with $\text{K}_{0.27}\text{MnO}_2$ cathode and their sodium storage mechanism, *Nano Energy*. 5 (2014) 97–104.
- [116] S.-C. Pang, M.A. Anderson, T.W. Chapman, Novel Electrode Materials for Thin-Film Ultracapacitors: Comparison of Electrochemical Properties of Sol-Gel-Derived and Electrodeposited Manganese Dioxide, *J. Electrochem. Soc.* 147 (2000) 444.
- [117] Y. Yuan, A. Nie, G.M. Odegard, R. Xu, D. Zhou, S. Santhanagopalan, K. He, H. Asayesh-Ardakani, D.D. Meng, R.F. Klie, C. Johnson, J. Lu, R. Shahbazian-Yassar, Asynchronous Crystal Cell Expansion during Lithiation of K^+ -Stabilized $\alpha\text{-MnO}_2$, *Nano Lett.* 15 (2015) 2998–3007.
- [118] G. Wang, H. Wang, X. Lu, Y. Ling, M. Yu, T. Zhai, Y. Tong, Y. Li, Solid-State Supercapacitor Based on Activated Carbon Cloths Exhibits Excellent Rate Capability, *Advanced Materials*. 26 (2014) 2676–2682.
- [119] M. Toupin, T. Brousse, D. Bélanger, Influence of Microstructure on the Charge Storage Properties of Chemically Synthesized Manganese Dioxide, *Chem. Mater.* 14 (2002) 3946–3952.
- [120] K. Seshan, *Handbook of Thin Film Deposition Techniques Principles, Methods, Equipment and Applications*, Second Editon, CRC Press, Boca Raton, 2014.
- [121] Q.-Z. Zhang, D. Zhang, Z.-C. Miao, X.-L. Zhang, S.-L. Chou, Research Progress in MnO_2 -Carbon Based Supercapacitor Electrode Materials, *Small*. 14 (2018) 1702883.

- [122] M.V. Ananth, S. Pethkar, K. Dakshinamurthi, Distortion of MnO₆ octahedra and electrochemical activity of Nsutite-based MnO₂ polymorphs for alkaline electrolytes—an FTIR study, *Journal of Power Sources*. 75 (1998) 278–282.
- [123] M. Ramezani, M. Fathi, F. Mahboubi, Facile synthesis of ternary MnO₂/graphene nanosheets/carbon nanotubes composites with high rate capability for supercapacitor applications, *Electrochimica Acta*. 174 (2015) 345–355.
- [124] S.-I. Pyun, J.-S. Bae, Electrochemical lithium intercalation into vanadium pentoxide xerogel film electrode, *Journal of Power Sources*. 68 (1997) 669–673.
- [125] J. Kang, A. Hirata, L. Kang, X. Zhang, Y. Hou, L. Chen, C. Li, T. Fujita, K. Akagi, M. Chen, Enhanced Supercapacitor Performance of MnO₂ by Atomic Doping, *Angewandte Chemie International Edition*. 52 (2013) 1664–1667.
- [126] A. Khan, H. Wang, Y. Liu, A. Jawad, J. Ifthikar, Z. Liao, T. Wang, Z. Chen, Highly efficient α -Mn₂O₃@ α -MnO₂-500 nanocomposite for peroxymonosulfate activation: comprehensive investigation of manganese oxides, *J. Mater. Chem. A*. 6 (2018) 1590–1600.
- [127] N. Mishra, S. Shinde, R. Vishwakarma, S. Kadam, M. Sharon, M. Sharon, MWCNTs synthesized from waste polypropylene plastics and its application in super-capacitors, in: Mumbai, India, 2013: pp. 228–236.
- [128] P.G. Jamkhande, N.W. Ghule, A.H. Bamer, M.G. Kalaskar, Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications, *Journal of Drug Delivery Science and Technology*. 53 (2019) 101174.

- [129] K. Latha, S. Anbuselvi, P. Periasamy, R. Sudha, D. Velmurugan, Structural and electrochemical investigation of novel hybridized MnO₂/V₂O₅ nanocomposites prepared by one-step microwave-assisted method for electrochemical supercapacitor application, *J Mater Sci: Mater Electron*. 32 (2021) 23293–23308.