Structural-chemistry of molybdenum oxide and its derivatives and their application in supercapacitors

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**Structural-chemistry of Molybdenum oxide and its Derivatives and
their Application in Supercapacitors**

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School of Materials Science and Engineering

2015

Structural-chemistry of Molybdenum oxide and its Derivatives and their Application in Supercapacitors

School of Materials Science and Engineering

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Abstract

Electrochemical capacitors or supercapacitors are the alternative energy-storage (electrical as well as electrochemical) devices, which can deliver high power in a short period of time (ms-s). Supercapacitor devices are known to have high power density (1-10 kW/kg), but they have limited energy density (5-20 Wh/kg). The enhancement in the energy density without sacrificing the power density will be advantageous for various applications, such as portable electronic devices, industrial heavy vehicles, and energy back-up and so on.

This dissertation mainly focuses on the structural-chemistry of molybdenum oxides and their derivatives to improve the pseudocapacitive performance of transition metal oxide based electrode materials. In this dissertation, several strategies are proposed in order to enhance the electrochemical performance of molybdenum oxide based supercapacitor devices. The corresponding strategies are as follows; firstly, three dimensional or open-structure of molybdenum trioxide (MoO_3), i.e., hexagonal- MoO_3 (h- MoO_3) provides facile paths as well as additional intercalation sites for the electrolyte ions, which in response improves the specific capacitance. Secondly, incorporation of the metal or transition metal elements into the lattice of molybdenum oxide (metal or transition-molybdate) not only tunes the crystallographic structure but also improves the electrochemical properties, resulting in the high capacity and excellent energy density of supercapacitor device.

Moreover, evaluation of the localized electrochemical activity of the electrode material is of great interest to provide the insight into the mechanism of charge transfer across the interface. Scanning electrochemical microscopy (SECM) is employed for the local analyses at the surface of electrode materials. Besides studying the charge transfer kinetics, SECM is also used to study the growth of the diffusion layer or propagation of the electronic or ionic charges.

The work described herein contributes to the synthetic strategies to synthesize and to tune the crystal-chemistry of molybdenum oxide based nanomaterials for electrochemical energy-storage applications. Also, the work presented here has shed some light on the fundamental understanding and advancement to optimize the pseudocapacitive

performance of the electrode materials, in order to realize an excellent supercapacitor device.

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C. Nguyen, P. S. Lee, *Chem. Mater.* **2014**, 26, 5333”. Copyright (2014) American Chemical Society.^[43]

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Figure 9.2 Schematic illustration of the charge storage mechanism in a supercapacitor with redox additive polymer gel electrolyte.

Symbols with the same meaning in all chapters

C_{sp}	Specific capacitance	F/g
I	Current density	A/g
m	Mass of active material	mg
Δt	Discharge time	s
ΔV	Potential window of supercapacitor	V
E	Energy density	Wh/kg
P	Power density	W/kg
A	Area of the electrode	cm ²
k_{eff}	Effective heterogenous charge transfer constant	cm/s
D	Diffusion coefficient	cm/s ²
c	Concentration of the redox mediator	moles
F	Faraday constant	C/mole
r_T	Radius of microelectrode	μm
I_T	Microelectrode current	nA
d	Distance between microelectrode and substrate	μm
Z'	Real impedance	Ω
$-Z''$	Imaginary impedance	Ω
f	Frequency of AC signals	Hz
v	Scan rate of cyclic voltammetry	mV/s

Chapter 1: Introduction

The concern of providing the electrical energy for our growing civilization has far exceeded the challenge to harvest cleaner and greener energy. This commitment has facilitated the introduction of distributed energy generation technologies, primarily renewable energy sources. This chapter presents a brief overview of the global energy sources and their depletion with the time as well as need of the renewable energy sources. The importance of the emerging energy storage technology, and objectives as well as approaches for achieving enhanced pseudocapacitive performance is discussed. Lastly, the main contributions of the thesis are highlighted.

1.1 Problem statement and Hypothesis

With the rapid increase in the human population and development in the modern society has triggered diversification in the methods of energy consumption. The earth's energy sources are undoubtedly sufficient to meet growing demand for at least the next three decades. Global energy demand was projected to increase 1.7% every year from 2000 to 2030, and reaching an annual level of 15.3 billion tonnes of oil equivalent.^[1] Fossil fuels will remain the primary source of energy to meet more than 83% of the increase in demand, as shown in Figure 1.1 (a). Besides the challenge of depletion of fossil fuels, the consumption of fossil fuels causes significant anthropogenic climate change due to increase emission of greenhouse gases, in particular carbon dioxide (CO₂). As depicted in Figure 1.1 (b), the biggest increase in CO₂ emission comes from power generation followed by transpiration. Therefore, it is urgent to move towards the renewable and sustainable alternative energy sources.

Figure 1.1 (a) Fuel type and (b) carbon emissions, the two pi-charts depict the relationship between fuel type and carbon emission for U. S. Energy consumption. Data source: U. S. Energy Information Administration.

Renewable energy or non-fossil energy is generally defined as the energy that comes from the sources which are naturally replenished, i.e., wind, rain, sun-light, etc.^[2] As can be seen in Figure 1.1 (a), renewable energy or non-fossil energy contributes about 17% to our total energy consumption. The development of renewable energy sources will benefit energy security, climate change mitigation, etc.^[2] Wind power, hydropower, solar energy, biomass and geothermal energy are the example of renewable clean energy sources. When it comes to the energy conversion, one question is still unanswered that where will this renewable energy come from when the sun does not shine or wind does not blow? Also, during off-peak hours the generation of efficient electricity is a crucial task,^[3] but the aforementioned concerns can be addressed using energy storage devices, such as flywheel, battery, supercapacitor, etc. Among them, supercapacitors are of immense interest due to their overwhelming advantages, such as high power density, ultrafast charging and discharging rate, ultra-long cycling and calendar life, which make them very convenient for electric vehicle, portable electronics and so on.^[4]

Supercapacitors are the cutting edge technology of storing electric energy in the form of electrochemical or electrical energy.^[4] Attributed to the high power density and moderate energy density, supercpacitors work as bridge between batteries and conventional capacitors.^[5] In general, supercapacitors are of two types based on their charge storage mechanism, i.e., electrical double layer capacitor (EDLC) and pseudocapacitor.^[6] In

electrical double layer capacitors (EDLCs), charges store due to reversible adsorption of electrolyte ions (non-faradic) near the surface of high surface area electrode materials, such as carbonaceous materials. EDLCs are known to store purely electrical energy (~95% of the total energy).^[4] On the other hand, in pseudocapacitors during reversible redox reactions transfer of electric charge takes place across the interface (faradic) via several electrochemical processes, such as electrosorption (under potential deposition), intercalation redox reaction or surface or near surface redox reaction.^[4] Transition metal oxides, hydroxides, nitrides or sulphides and conducting polymers are the main stream candidates to represent pseudocapacitors.^[7] Due to significant difference in the charge storage mechanism, pseudocapacitors show the high energy density as well as high specific capacitance than that of the EDLC, while due to excellent reversibility of redox reactions in EDLC, high power density and ultra-long cycling stability can be achieved. Therefore, development of the high energy density as well as high power density pseudocapacitor electrode material is critical, but essential.

Minimizing the dimensions or in other words increasing the aspect ratio of nanostructures is the most prevalent approach adopted by most of the researchers in the past several years.^[8] Besides increasing the aspect ratio of nanostructures, nanostructuring of the binary or multi-components transition metal oxides in various crystallographic structures have also been considered promising and feasible approach to enhance the electrochemical performance of the electrode materials.^[9] To date, layered transition metal oxides have been studied hitherto due to their layered crystallographic structure, which provides facile paths for the conduction of electrolyte ions in two dimensions (2D).^[10] Binary transition metal oxides in open crystallographic structures could be one of the main streams to enhance the electrochemical performance, because they have the potential to increase the degree of freedom for electrolyte ions insertion. Moreover, integration of multi-components to form ternary transition metal oxides has also been introduced to further improve specific capacitance of electrode materials.^[11] Further, investigation of the local electro-activity of the electrode materials is essential to provide insight on the mechanism of charge storage and transfer across the electrode/electrolyte interface.

1.2 Research Objectives and scope

Recent years have witnessed to the efforts in developing the high performance pseudocapacitive electrode materials. Numerous efforts have been made to produce, to exemplify and to understand the mechanism of charge storage in pseudocapacitive electrode materials, but still there are many challenges; a material with high energy density without compromising the power density, excellent rate capability as well as long term cycling stability. The main objectives of this dissertation are to explore subsequent aspects of the electrode materials:

- To synthesize molybdenum trioxide nanostructures in hexagonal crystallographic structure (hexagonal-MoO₃).
- Heterostructured nanocomposites of MoO₃ for improved electrochemical performance.
- To prepare metal and transition metal molybdates and to investigate their electrochemical performance.
- To investigate the local electro-activity of pseudocapacitive electrode materials to provide insight on the mechanism of charge transport.

Currently, research on electrochemical capacitors is mainly focusing on redox-active electrode materials, such as functionalized carbon electrodes, transition metal oxides, conducting polymers and so no. In order to realize an improved electrochemical performance, electrode materials with the following features are obligatory; abundant redox-centre sites to facilitate the redox-process, sufficiently conducting, electronic as well as ionic conduction to promote the flow of charges, adequate lattice spacing to hold electrolyte ions, and last but not least availability of the heterovalent redox-centres to further push the operating potential window. To satisfy the aforementioned prerequisites, several strategies are proposed in this research work.

Primarily, molybdenum trioxide (MoO₃) is a well know redox-active system attributed to its versatile electrochemistry that originates from the various oxidation states (Mo²⁺, Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺).^[12] Fundamentally, MoO₃ is a very attractive material system due to existence of its various stable as well as metastable polymorphs. Polymorphs of MoO₃ can be crystallized (even in hydrated forms) in various crystallographic phases.^[13]

Nanostructures of MoO_3 in hexagonal phase are proposed to provide abundant redox-centre sites, which are available at different intercalation sites due to its three dimensional open-structure. Under this hypothesis one dimensional (1D) and two dimensional (2D) nanostructures are synthesized via soft chemistry or “chimie douce” route and characterized carefully.

Second, composite material of h-MoO_3 with conductive polymer, such as polyaniline in a novel physical structure is proposed to mitigate the electrode resistance in order to provide a facile conduction path within the electrode matrix. Attributed to the combinatorial effect between the kinetics of two redox-active materials, i.e., h-MoO_3 – diffusion controlled and polyaniline – surface controlled, an improved electrochemical performance of the composite material is achieved. The contributions of the charges stored by the surface as well as diffusion process are also distinguished.

The mixing of metal or transition metal elements into the lattice of molybdenum oxide leads to an interesting category of materials known as “metal or transition metal molybdates”. Metal or transition metal molybdates are highly electro-active due to their unique crystallographic structure and mixed conductivity character, i.e., electronic as well as ionic. Metal molybdate, i.e., silver molybdate in triclinic structure is proposed as a promising pseudocapacitive electrode material due to ordered structure of silver and molybdate ions. Due to ordered structure of metal and molybdate ions, co-existence of dual charge storage kinetics is observed, which in response improves the electrochemical performance of the electrode material.

Fourth, mixing of transition metal elements into molybdates forms rutile related transition metal molybdates. Here, electrochemistry of niobium molybdates in hydrated and dehydrated forms is explored. Dehydrated niobium molybdates showed spectacular electrochemical performances. Due to large inter layer spacing and availability of cage protons, dehydrated form of niobium molybdate could store enormous charges and delivered an excellent energy density and power density in two-electrode configuration.

Last but not least, evaluation of the local electro-activity of electrode materials is vital to understand the kinetics of the charge transport. A uniform electrode material prepared with novel 2D MoO_3 -II is selected to examine the local electro-activity of the material. The ultimate goal of this piece of work is to explore the kinetics of charge transfer at the

electrolyte/electrode interface in equilibrium (steady-state, open circuit) as well as non-equilibrium (non-steady state, substrate biasing) conditions.

1.3 Organization of Thesis

The research work described herein presents syntheses and characterizations of molybdenum oxides and their derivatives in various crystallographic phases to enhance the pseudocapacitive performance of molybdenum based electrode materials. In the end, the importance of local electro-activity of electrode materials is discussed.

Chapter 1 presents a brief overview of the global energy sources and their depletion with the time as well as need of the renewable energy sources. The importance of the emerging energy storage technology, and objectives as well as approaches for achieving enhanced pseudocapacitive performance is discussed.

Chapter 2 reviews a historic background of the supercapacitors technology, fundamental description of supercapacitors based on electrode materials or charge storage mechanism. A detailed background related to MoO_3 and transition metal molybdates based pseudocapacitive electrode materials is discussed. Lastly, the details of localized electrochemistry investigation using scanning electrochemical microscopy are presented.

Chapter 3 gives the details about the experimental procedure for the synthesis of the proposed electrode materials, and background information about the instruments that are used to characterize the electrode materials. Preparation of the electrode materials and their electrochemical testing is also presented in this chapter.

Chapter 4 introduces preparation and characterization of h- MoO_3 nanostructures using hexamethylenetetramine as the source of ammonium ions. In this chapter, I discussed the essential role of ammonium ions on achieving metastable phase of MoO_3 , i.e., h- MoO_3 phase in various morphologies. The pyramidal nanorods-like morphology of h- MoO_3 enables good electrochemical performance than that of the prismatic nanorods- and hexagonal nanoplates-like morphology of h- MoO_3 .

Chapter 5 demonstrates the formation of h- MoO_3 hollow nanorods taking cation exchange assisted Kirkendall effect into account using Fe^{3+} ions. Fe^{3+} ions play a twofold role; to form the hollow nanorods structure and to initiate the polymerization of aniline monomers. In this chapter, analysis of cyclic voltammograms is performed to decouple

the contributions of the components (polyaniline and h-MoO₃) in polyaniline-h-MoO₃ hollow nanorods (shell-core) using peak current vs. scan rate analysis into consideration. A thin polyaniline shell is found critical to improve the electrochemical performance, including cycling stability of the nanocomposites.

Chapter 6 introduces the preparation of silver molybdates, i.e., Ag₆Mo₁₀O₃₃ in triclinic crystal structure. Ag₆Mo₁₀O₃₃ in triclinic structure is achieved after air annealing of Ag₂Mo₃O₁₀ · H₂O. Ag₆Mo₁₀O₃₃ encompasses linear array of Ag⁺ ions enclosed by MoO₆ octahedra, which in response produces character of mixed conductivity, i.e., electronic as well as ionic. Ag₆Mo₁₀O₃₃ nanostructures deliver good energy density without sacrificing the power density.

Chapter 7 presents the synthesis and characterization of hydrated and dehydrated HNbMoO₆ nanoflakes. The formation of 2D HNbMoO₆ nanoflakes involves removal of the interlayer water molecules from 2D HNbMoO₆ · H₂O nanoflakes. Attributed to the layered structure (wide interlayer spacing) and availability of the cage protons, pseudocapacitive performance of 2D HNbMoO₆ nanoflakes is found superior to the 2D HNbMoO₆ · H₂O nanoflakes.

Chapter 8 introduces scanning electrochemical microscopy (SECM) for the localized electrochemistry investigation at the surface of 2D MoO₃-II in particular to extract the heterogeneous effective charge transfer constant in using feedback mode and competitive mode of SECM.

Chapter 9 summarizes concluding remarks of the above chapters, and makes recommendations for future work based on the above findings.

1.4 Main contributions of the Thesis

The major contributions of the work presented in this thesis are summarized as follows:

- Introducing a novel route to prepare two dimensional (2D) molybdenum oxide nanosheets and elucidation of the local electrochemistry.
- Transition metal molybdates for the high energy as well power density applications.

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Chapter 2: Literature Review

Supercapacitors are one of the promising classes of energy storage technology. Due to its intermediate energy and power characteristics, it bridges the gap between conventional capacitor and Li-ion batteries. In this chapter, I presented a historical background of supercapacitors technology, and the classification of supercapacitors based on the electrode materials. Merits and demerits of existed electrode materials are discussed in brief with the prospective electrode materials. I also emphasized on the need of using localize electrochemical testing tool. At the end, summary of the chapter is presented.

2.1 Overview of supercapacitors: Journey from a concept to commercial device

Storing an electric charge on the surface of materials originated from the phenomenon associated with rubbing of amber in prehistoric time. Certainly, the concept of “static-electricity” was not known at that time. In the early 1950s, it was Becker who demonstrated the concept of storing electrical energy in the pores of highly porous carbon material,^[1] but unfortunately he was not aware of the concept of storing electrical charges in a thin electric-double-layer. Even though in 1970, the first electrochemical capacitor demonstrated using activated carbon electrode was presented as “electrolytic capacitor” by Boos *et al.*^[2] The term supercapacitor was first coined by the NEC (Nippon Electric Company), after development of the first commercialized electric double-layer capacitor under the licence of SOHIO in 1978.^[3] On the other hand, in the same year Panasonic manufactured its first electric double-layer capacitor.^[4] The major differences between two products were that NEC used pasted electrodes with bipolar cell construction in an aqueous electrolyte, while Panasonic used non-pasted electrodes cell construction in a non-aqueous electrolyte. The first supercapacitor named “Goldcap” was commercialized by NEC in 1978.^[3] In the early 1980s, B. E. Convey carried out an extensive work in electrochemical capacitors and utilized a different approach called “pseudocapacitance” to explain the anomalous increment in the capacitance of RuO_2 .^[5] Presently, several

companies, e.g., Cap-xx, Nesscap, Ncc, etc. are out there putting significant amount of interest in the research and development of supercapacitors.^[6–8]

At the early stage, supercapacitors were used for low power and low energy applications, such as memory back-up,^[9] due to their limited energy as well as power density performance. But in the recent years, significant efforts have been devoted to improve their energy and power density, as a result; now supercapacitors are open for various applications.^[10]

Nowadays, the largest part of supercapacitors market is in the electronic products, specifically consumer electronic products, such as micro-computers, clocks and system boards.^[9] Supercapacitors can also be used in power quality systems, such as wind power applications to provide uninterrupted power distribution at the time of wind gusts or deep wind fluctuations.^[11] Probably, the second largest part of supercapacitors market comes under automotive applications.^[12] Undoubtedly, the batteries are the promising energy sources for electric vehicles due to their high energy density, but do not meet the high power requirements (while accelerating and climbing) due to their low power density.^[10] On the other hand, supercapacitors possess high power density and they can be charged quickly, therefore regenerative braking is possible. It is found that by combining supercapacitors with the batteries, effective life time of batteries can be improved as well as consumption of fuel can be reduced about 15%.^[13]

2.2 Principle of Supercapacitors

In general, an electrochemical capacitor or supercapacitor device consists of two electrodes namely, positive electrode and negative electrode separated by a conventional separator film (e.g., filter paper) and immerse into an electrolyte solution, as shown in Figure 2.1 (a).^[14–16] The electrochemical capacitance (electric-double-layer capacitor) is associated with the potential dependent accumulation of the charges (deficit or excess of conduction band electrons) at the electrode surface, and to establish the charge neutrality electrolyte ions with counterbalancing charge built up on the electrolyte side. During charging process, electrons travel from negative electrode to positive electrode due to external load, while cations in the electrolyte move towards negative electrode and anions move towards positive electrode. Thus, develops an inner Helmholtz plane or electric double layers capacitor (EDLC) configuration, and stores energy in the form of electric

charges, the profile of electric potential develops across the layer is shown in Figure 2.1 (b).^[14,16] However, the formation of outer Helmholtz plane as well as diffuse layer also takes place, but barely partakes to store charges. It has to be noted that there is no net charge (electronic or ionic) transfer across the electrode/electrolyte interface. This entails that the concentration of electrolyte ions remain fixed during the charging and discharging process.^[14] The maximum current density of supercapacitors is limited by the “equivalent series resistance” which consists of electronic as well as ionic resistance contributions.

Figure 2.1 (a) Schematic illustration of a single cell double-layer electrochemical capacitor and (b) illustration of the potential profile at the interface of electrode/electrolyte.

The ionic resistance depends on various factors, such as ionic conductivity of electrolyte, porosity of electrode surface, size of electrolyte ions, porosity of separator and thickness of electrode material.^[15] The size of electrolyte ions and requirements of porosity changes from aqueous electrolyte to organic electrolyte.^[17] Usually, requirement of the size of pores for organic electrolytes (1.5 nm – 2 nm) is slightly higher than that of the aqueous electrolytes (0.5 nm – 1 nm).

An electrochemical capacitor which stores electric energy via redox reactions comes under a new category known as “pseudocapacitor”.^[5] The origin of the generation of pseudocapacitance is entirely different than that of the double-layer capacitors. It is faradic in nature, involves passage of charges across the double-layer. Pseudocapacitance arises due to thermodynamic reasons between the acceptance of charge (Δq) and change in the electrode potential (ΔV) so that a derivative can exist, which is equivalent to a capacitance. In order to realize generation of pseudocapacitance, three types of redox process are accountable, as presented in Figure 2.2.

Figure 2.2 (a) Schematic illustration of a pseudocapacitor device consists of redox-active nanomaterials, i.e., porous host, layered host and conductive host.

First, reversible adsorption of ions (electrosorption valency) on the surface of the electrode, for example, adsorption of H^+ ions on the surface of gold or platinum.^[18] Second, reversible redox reaction at the surface of transition metal oxides (e.g., RuO_2),^[19,20] and reversible intercalation redox reaction, as happens in layered transition metal oxides (e.g., N_2O_5 and MoO_3).^[21,22] Moreover, reversible electrochemical doping-dedoping of electrolyte ions into the chains of conducting polymers also comes under pseudocapacitors.^[23] The mechanism of the energy stored in pseudocapacitors is different from that of the double-layer capacitor. Since the electrochemical processes take place at

the surface or near surface region or bulk of the electrode materials, pseudocapacitors exhibit much higher capacitance and energy density than the double-layer capacitor.^[24] The process of charging and discharging of pseudocapacitors can be expressed according to equation 2.1 and equation 2.2, respectively.^[15]

P, N, C⁺ and A⁻ are representing positive electrode, negative electrode, cation and anion, respectively. It is worth to mention that during charging the redox reactions which are taking place at the positive (P) or negative (N) electrode of supercapacitor will cause development of potential difference. More precisely, the positive electrode reactions increase the electrode potential with respect to open circuit potential, while, negative electrode reactions will reduce the potential of electrode with respect to open circuit potential. However, converse is true for discharging.^[15] Therefore, one has to bear in mind that both positive and negative electrode of supercapacitor should have electrochemical reactions in their respective potential window.

There are two main attributes of supercapacitors, i.e., energy density and power density.^[25] The power density describes how fast the energy can be delivered, while, energy density signifies the amount of energy that can be stored. The energy density and power density can be calculated according to equation 2.3 and equation 2.4, respectively.^[25]

$$\text{Energy density (E)} = 0.5 \times C_{sp} \times \Delta V^2 \quad (\text{eq. 2.3})$$

$$\text{Power density (P)} = E/\Delta t \quad (\text{eq. 2.4})$$

Where E is the energy density in Wh/kg and P is the power density in W/kg. C_{sp}, ΔV and Δt are the specific capacitance (F/g), potential window (V) and discharge time (sec), respectively. An ideal supercapacitor must have a high energy density, besides high power density, and based on the above expressions it should have high specific capacitance and wide potential window. The high specific capacitance can be achieved by finely controlling the electro-activity of the constituents in the material system. However, the operating potential window of the device not only depends on the overpotentials for oxygen or hydrogen evolution reactions, but also is dependent on the

configuration of the electrodes, i.e., symmetric (similar electrodes) or asymmetric (non-similar electrodes). Currently, the commercially available supercapacitors are based on the symmetric electrode configuration.^[6] In the recent years, the asymmetric device (or hybrid supercapacitor) configuration has been extensively studied in improving the operating voltage window of the cell, and so the energy density. It is worthy to mention that the overall specific capacitance of the device (asymmetric) is mainly dominated by the electrode of smaller specific capacitance ($C = C_1 C_2 / C_1 + C_2$).^[15] The aforementioned criterion directs us whether to fabricate a symmetric or asymmetric supercapacitor device. The Ragone plot represents the relationship between energy density and power density of energy storage devices. The supercapacitor bridges the gap between conventional solid-state capacitor and batteries, as can be seen in Figure 2.3. Despite the high power density of supercapacitors than that of the conventional capacitors, supercapacitors have yet to meet the energy densities of batteries.

Figure 2.3 Ragone plots of energy storage devices.

2.3 Electrode materials for supercapacitors

As discussed above, double-layer capacitors and pseudocapacitors employ different mechanism to store electrical energy in the form of electric charge and electrochemical charge, respectively. In general, the electrode materials for supercapacitors can be

categorized into three classes: first, carbon based materials with high active surface area. Second, transition metal oxides and hydroxides, and third, conducting polymers.^[26] In brief, classification of supercapacitors based on perspective electrode materials is presented in Table 2.1.

Table 2.1 Classification of the supercapacitors based on electrode materials,^[26]

Types	Materials	Mechanism	Merits	Shortcoming
Double layer capacitor	Carbonaceous materials	Separation of charges at electrode/electrolyte interface	High power density and excellent cycling life	Low energy density and low working potential window
Pseudocapacitor	Transition metal oxides and conducting polymers	Reversible redox reactions	High energy density and high specific capacitance	Poor cycling life and poor rate capability

2.3.1 Carbon based materials

Carbon based materials include activated carbon, porous carbon, carbon nanotubes, grapheme and other carbonaceous materials are considered prospective electrode materials for industrialization.^[27] The main advantages of carbonaceous materials comprise abundance, easy processing, low cost, high electrical conductivity, high chemical stability, and high surface area and so on. The specific capacitance of carbon based materials depends on specific surface area, pore size distribution, structure and size of pores, conductivity and surface functionality.^[26] Among the aforementioned factors, specific surface area and pore size distribution are the performance deciding factors. Regarding pore size distribution, a maximum double-layer capacitance can be achieved with the pore size very similar to the size of the electrolyte ions (based on ionic liquid electrolytes), and both smaller and larger pores yield a significant drop in the specific capacitance.^[28] In general, carbonaceous materials store charges in an electrochemical double-layer formed at the interface of electrode/electrolyte, and the action mechanism can be presented according to equation 2.5.^[15]

Commonly, high surface area carbon materials, such as activated carbon, ordered mesoporous carbon, functionalized carbon are used in electric double-layer capacitors. The performance of electric double-layer capacitor based materials is summarized in Table 2.2. The carbonaceous materials have the high power density and excellent chemical stability in aqueous as well as non-aqueous electrolyte systems. However, their specific capacitance and energy density are usually low.

Table 2.2 Summarization of electrochemical performance of carbonaceous materials based supercapacitors,^[27]

Materials	Aqueous electrolyte	Aqueous electrolyte	Organic electrolyte
	F/g	F/cm ³	F/g
Activated carbon	<200	<80	<100
Templated porous carbon	120-350	<200	60-140
Carbon Aerogels	100-150	<80	<80
Functionalized carbon	150-300	<180	100-150
Carbon Nanotubes	50-100	<60	<60
Carbon fibers	120-370	<150	80-200
carbon cloth	100-200	40-80	60-100

2.3.2 Oxide based materials

As mentioned above, carbonaceous materials have limited specific capacitance and energy density performance. In contrary, transition metal oxides based supercapacitors exhibit higher specific capacitance and energy density due to fast and reversible redox reactions. The fundamental requirements for oxide materials to be used as supercapacitor electrode or to exhibit pseudocapacitive property are examined by Dunn et al. and presented as follows; ^[24,29] the oxide material should be electronically conductive or moderately conductive. Second, metal or redox centres can exist in two or more than two oxidation states without bearing any phase change, and a facile conduction path for the electrolyte ions to intercalate into the inter-gallery region. The pseudocapacitive property of the materials was first attempted by Conway.^[5] In his description, whenever the inserted charge (Q) depends on the applied potential (V) the property of pseudocapacitance takes place. In other words, based on cyclic voltammetry analyses the overall capacity (C/g) of the electrode material must be constant throughout the whole

potential window. According to the recently published report “To be or not to be pseudocapacitive” by Long *et al.* the term pseudocapacitance can be used whenever the characteristics of the material approaches to the true capacitive behavior.^[30] For example, charging or discharging of pseudocapacitive electrode material during cyclic voltammetry (CV) must exhibit nearly identical capacity (C/g) or capacitance (F/g) in the various potential windows (e.g., 0 to 0.3 V, 0.3 to 0.5 V, etc.), as happens in case of a true capacitive material. The charge/discharge profile should be linear (a small hysteresis between the curves) and the discharge time should not exceed at the time scale of few minutes, and AC impedance profiles must possess vertical- or nearly vertical-line in the low frequency (<100 mHz) region.^[29] Pseudocapacitance is the property of the materials and it could be intrinsic as well as extrinsic.^[29] The electrode materials, including RuO₂·nH₂O, MnO₂, etc. exhibit intrinsic-pseudocapacitive property, and display the feature of capacitive-charge regardless their particle size or morphology. In contrary, the electrode materials with extrinsic-pseudocapacitive property display the pseudocapacitive response as a function of the particle size; these are the materials, including NiCo₂O₄, LiCoO₂, etc.^[29] In transition metal oxides based supercapacitors or pseudocapacitors, the specific capacitance can be acquired from the constant current charge/discharge analyses, as expressed in equation 2.6.^[29]

$$C_{sp} = I \Delta t / \Delta V \quad (\text{eq. 2.6})$$

Where I , Δt and ΔV are applied current density (A/g), discharging time (sec) and potential window (V), respectively.

The pseudocapacitive performance of routinely used electrode materials is summarized in Table 2.3. Attributed to the fast and reversible redox reactions, the theoretical specific capacitance and energy density of pseudocapacitors are much higher than those of the electric double-layer capacitors. An approximation about the theoretical specific capacitance of the transition metal oxides, for instance MoO₃ can be made taking the fundamental relationship into account, i.e., equation 2.7.

$$Q = nF = CV \quad (\text{eq. 2.7})$$

$$C_{sp} = nF / VM_e = 1 \times 96500 / 1.5 \times 144/6 \approx 2680 \text{ F/g}$$

Where n , F , V and M_e are the number of electrons transferred per molecules, faraday constant, operating potential window and equivalent mass, respectively.

The theoretical specific energy density (Wh/kg) can be determined using equation 2.3.

$$E = 0.5 \times C_{sp} \times (\Delta V)^2 = 0.5 \times 2680 \times (1.5)^2 \approx 3015 \text{ kJ/kg} \approx 830 \text{ Wh/kg}$$

Table 2.3 Summarization of electrochemical performance of transition metal oxide based supercapacitors

Materials	Theoretical C_{sp} (F/g)	Experimental C_{sp} (F/g)	Potential window (V)	Theoretical Energy density (Wh/kg)
RuO ₂	2000	700-1340	1.4	~967 ^[31]
MnO ₂	1370	399-600	0.8	530 ^[32,33]
V ₂ O ₅	–	400-1550	1.2	480 ^[33,34]
NiO	2573	124-1100	0.6	– ^[35]
MoO ₃	2680	25-350	1.5	830 ^[33,36]

Since the evaluation of the pseudocapacitive behaviour of RuO₂, it has been extensively studied as an emerging class of supercapacitive electrode materials. Attributed to high theoretical and experimental specific capacitance and energy density, RuO₂ nanostructures in hydrated and dehydrated forms in various morphologies have been investigated quite often.^[19,20] The capacitance of hydrated or dehydrated RuO₂ comes mainly from pseudocapacitance, which is due to reversible electro-adsorption of protons on the surface of RuO₂ nanostructures. However, high cost and toxicity of RuO₂ prevent it from being used in the commercialization of supercapacitors, because it has been indicated that almost 90% of the supercapacitor's cost comes from the electrode materials only.^[37] Therefore, in the attempt to mitigate the use of RuO₂, an extensive research has been conducted on the other cheaper metal oxides, such MnO₂. MnO₂ is one of the promising representatives of pseudocapacitive family with low cost, stable potential window, environmental friendly nature and high theoretical capacitance.^[38] Since the early attempt made by Lee and Goodenough,^[39] manganese oxides (MnO_x) have attracted significant attention due to its pseudocapacitive behaviour, which comes from fast and reversible surface redox reactions. However, the actual performance of manganese oxide is not satisfactory for high rate performance due to its poor electronic as well as ionic conductivity as well as low surface area and dissolution of particles during cycling.^[38] V₂O₅ bears similar electrochemical behaviour as MnO_x based electrodes exhibits, except

its intercalation property.^[40,41] Attributed to layered structure of V_2O_5 , the electrochemical performance comes from intercalation assisted redox reactions.^[42] Due to slow ionic diffusion into the inter-gallery region, the specific capacitance and energy density attained by V_2O_5 nanostructures is limited.^[43,44] NiO is also a promising electrode material for supercapacitors due to its fast surface assisted redox reactions. NiO is stable in basic electrolytes and the charge storage mechanism has been reported to be based on physical adsorption/desorption of OH^- ions.^[45] NiO based supercapacitors have relatively low specific capacitance value, and small operating potential window.^[45] The current-potential response of NiO based supercapacitors is potential dependent in contrast to the ideal supercapacitors response, which is potential independent.^[46,47]

Molybdenum oxide nanostructures have been synthesized in various crystallographic structures, and the study of literature indicates that the compounds of molybdenum oxides are important materials for numerous studies, including batteries, supercapacitors, etc.^[48] Molybdenum oxides and related materials are considered as promising electrode materials due to the fact that Mo can be existed in multiple oxidation states (Mo^{2+} , Mo^{4+} , Mo^{5+} and Mo^{6+}), besides their eco-friendly nature.^[48] Molybdenum oxides, exclusively MoO_3 and MoO_2 are very attractive electrode materials with the potential applications in electrochemical energy storage.^[49] Due to low electrical resistivity ($8.8 \times 10^{-5} \Omega \text{ cm}$) and high electrochemical stability, MoO_2 was proposed as the prospective electrode material (anode) for Li-ion batteries.^[50] Despite having satisfactory properties, relatively less attention has been paid to its capacitive performance. A couple of years ago, MoO_2 nanostructures, including nanorods,^[51] ordered mesoporous film,^[52] nanoparticles,^[53] etc. are used as an electrode in electrochemical capacitors. The specific capacitance of MoO_2 nanorods,^[51] and MoO_2 mesoporous film,^[52] as high as 140 F/g (at 1 mA/cm²) and 146 F/g (at 5 mV/s) was achieved in the three-electrode cell configuration. Despite knowing the fact that MoO_2 is fairly electrically conductive, the specific capacitance of MoO_2 is improved by introducing carbonaceous materials, for example, MoO_2/CNT could achieve 597 F/g at 10 mV/s,^[54] and 395 F/g at 2 mV/s is achieved by ordered mesoporous carbon/ MoO_2 .^[53] Thus, it is unclear in the literature that in which manner the electronic conductivity of MoO_2 contributes in the electrochemical reactions. Recently, Hercule *et al.* demonstrated that MoO_2 not only serves as an active component but also is capable to

function as a conductive support in case of $\text{MoO}_2/\text{Co}(\text{OH})_2$ nanohybrids.^[55] The specific capacitance of ~ 1697 F/g, ~ 2800 F/g and ~ 2000 F/g was achieved by $\text{MoO}_2/\text{Co}(\text{OH})_2$, MoO_2 and $\text{Co}(\text{OH})_2$, respectively, at an applied current density of 2 A/g.^[55] The results presented by Hercule *et al.* were not in commensurate with the documented performance of MoO_2 ,^[48] and the operating potential window was unexpectedly low (0.25 V). More importantly, the performance of MoO_2 nanostructured electrodes at the device level (two-electrode configuration) is rarely reported.^[55,56] The plausible reason could be its slow electrochemical kinetics,^[49] however, the factors that are tainting the performance of this potential material are not established at present.

On the other hand, MoO_3 nanostructures are studied widely as the prospective electrode in supercapacitors. Despite having the layered structure, the specific capacitance of MoO_3 is assumed to be the sum of both the surface- as well intercalation-redox reactions.^[22] However, the mechanism of charge storage in molybdenum oxide, e.g., MoO_3 is predominantly considered to be intercalation of electrolyte ions, i.e., M^+ (e.g., H^+ , Li^+ , Na^+ , etc.) into the inter-gallery region of MoO_3 , as expressed by equation 2.8.^[57]

Based on the fact that Mo complexes involve one electron/molecules transfer in a wide operating potential window of 1.5 V, the specific capacitance was calculated to be about 2680 F/g,^[36] however, the reported specific capacitance values are found to be varied from 50 F/g to 370 F/g.^[58–63] Specific capacitance of MoO_3 nanostructures is reported to be significantly affected by the route of preparation as well as physical aspects, such as morphology of the nanostructures, surface area, water content, etc.^[58,61–63] In general, MoO_3 based compounds can be stabilized in various crystallographic structures, such as stable layered α - MoO_3 phase,^[64] metastable 3D h- MoO_3 phase,^[65] metastable rutile related β - MoO_3 phase,^[64] metastable layered MoO_3 -II phase,^[66] etc. However, layered α - MoO_3 phase has been studied hitherto due to its layered structure that has potential to accommodate electrolyte ions.

2.3.3 Conducting polymers based materials

The conducting polymers are regarded as an alternative choice of supercapacitor electrode materials because of their high electronic conductivity.^[23,67] During redox reactions, conducting polymers involves both surface as well as bulk redox reactions,

thus, entire material contributes effectively.^[67] Due to effective utilization of the complete material, conducting polymer based supercapacitors can achieve high level of specific capacitance (~ 2300 F/g).^[67–70] The capacitive behaviour in conducting polymers comes from the pseudocapacitance, originated from doping (oxidation) and de-doping (reduction) of electrolyte ions during redox reactions.^[67] The electronic conducting polymers could be of p-type and n-type, but most of the conducting polymers used as supercapacitor electrode materials are p-type in nature, such as polyaniline, polypyrrole, polythiophene, etc.^[71] Benefiting from their high electronic conductivity, these materials usually have low equivalent series resistance, high power and good rate capability. However, mechanical stress during doping/de-doping reactions limits the cycling stability of these materials. The limitation of poor cycling stability has hampered the development of conducting polymer based supercapacitors.^[67]

In summary, pseudocapacitive electrode materials are of great interest for scientific research and development of the next generation high performance supercapacitors. However, several issues, such as low utilization of active materials, resistive contributions from the dead components, poor cycling life need to be addressed to elevate the supercapacitor performance to the next level.

2.4 Molybdenum trioxide (MoO_3) and related materials as supercapacitor electrode

There has been an immense interest in the compounds of molybdenum oxide due to ready reversible incorporation of protons or alkali ions into their inter-layer regions.^[57] The structure of molybdenum oxide predominantly consists of layers of MoO_6 octahedra, in a few cases it consists of layers of MoO_4 tetrahedra, and the layers of MoO_7 pentagonal bipyramids are rare.^[72] These octahedra usually share corner and edges to form infinite two-dimensional layered structure, infinite one-dimensional layered structure, and distorted layered as well as open structures. The crystallographic phase relationship between molybdenum-oxygen systems had been a subject of extensive investigations.^[72] The first phase analysis was performed by Hagg and Magneli by the means of X-ray diffraction, and identified the formation of several compounds, i.e., MoO_2 , MoO_3 , Mo_4O_{11} , Mo_8O_{23} and Mo_9O_{26} in the temperature range 650°C to 750°C ,^[72] as shown in the phase diagram, Figure 2.4; however, the stoichiometric formulas of these oxides or sub-oxides were developed by Magneli.^[72] Attributed to their slow transformation rates,

it was difficult to establish true stability range of various oxides, especially those occur below 600 °C, because there is a pronounced tendency for some of MoO_3 phases remain for long periods in metastable states. Several decades ago, the structural-chemistry of these oxides was thoroughly studied by Kihlberg in a series of papers.^[72–75]

Figure 2.4 Mo-O phase diagrams,^[76] reproduced from ref. 76 with permission of Springer Science + Business Media.

2.4.1 α - MoO_3 phase of MoO_3

The most commonly studied form of molybdenum oxide is molybdenum trioxide (MoO_3) in layered orthorhombic crystallographic structure, usually referred to as α - MoO_3 phase of MoO_3 . This phase of MoO_3 consists of double-layers of MoO_6 octahedra in contrast to the other layered transition metal oxides, e.g., V_2O_5 which possess single layer of octahedra.^[42] However, a single layer of MoO_6 octahedra is possible in case of hydrated MoO_3 .^[77] The MoO_6 octahedra in this layered configuration are thermally stable in a wide range of temperature. The crystallographic structure of this phase can be visualized as intra-chain corner sharing of MoO_6 octahedra, while these octahedra share inter-chain edges with other corner shared octahedral chains to construct layers of MoO_6 in ab -plane. The layers of MoO_6 octahedra in this phase stacked in an alternate manner along c -axis, and held together by weak van der Waal's forces, as shown in Figure 2.5. The structure

of this phase was first refined by Kihlberg, and found that MoO_6 octahedra in this phase are distorted and Mo-O bond length in each octahedral varies from 1.67 Å to 2.33 Å.^[42,73] In each MoO_6 octahedra, the shortest and strongest bond between Mo atom and apical O atom terminates at the unshared position and form a terminal $\text{Mo}=\text{O}$ bond along c-axis, whereas, in *ab*-plane, octahedra are connected via bridging Mo-O-Mo bonds.

Figure 2.5 Schematic illustrations of the MoO_6 octahedra arrangements in $\alpha\text{-MoO}_3$ phase along various crystallographic planes.

Due to anisotropy in the Mo-O bond length, MoO_3 structure can be visualized as consisting of infinite layers of MoO_6 octahedra in *ac*-plane and *bc*-plane, as shown in Figure 2.5.

As depicted in Figure 2.6, the crystal structure of $\alpha\text{-MoO}_3$ comprises double-layers of MoO_6 octahedra held together by weak van der Waal's forces, which facilitate intercalation of electrolyte ions into the inter-layer region (about 6.99 Å) of $\alpha\text{-MoO}_3$.^[57] The MoO_6 octahedra in MoO_3 are found to be highly distorted even higher than that of the other layered transition metal oxides, e.g., V_2O_5 .^[42] A more distorted MoO_6 octahedron was found to be more effective for the charge generation in electrochemical reactions due varied Mo-O bond lengths, which exert additional dipole moment.^[42] Attributed to its layered structure, $\alpha\text{-MoO}_3$ was first proposed as prospective cathode material in secondary Li-ion batteries, in early 1970s.^[78] In the past recently years, significant efforts have been exerted to utilize $\alpha\text{-MoO}_3$ as an anode material in batteries due to its multiple oxidation states and wide operating potential window.^[79]

Figure 2.6 Schematic illustration of the layered structure of α - MoO_3 showing available intercalation sites for electrolyte ions.

The reversible electrochemical behavior of α - MoO_3 was explained on the ground of topotactic redox reactions, because the lattice of α - MoO_3 was found unchanged during charge/discharge.^[57] In the topotactic redox reactions changes occur only in the electronic level of the material, i.e., uptake or loss of the electrons. The layered structure of MoO_3 and occurrence of topotactic redox reactions makes MoO_3 highly intriguing for the development of supercapacitor electrodes.

Most recently, the nanostructures of MoO_3 have gained enormous interest due to its high theoretical specific capacitance (2600 F/g),^[36] as well as high energy density (750 Wh/kg) performance.^[33] To achieve good pseudocapacitive behaviour from MoO_3 , nanostructure materials, such as nanoparticles, nanowires, nanobelts and nanoplates are developed to favor fast charging and discharging process.^[36,58,61–63,80] The mesoporous nanoparticles film of MoO_3 have been prepared via potentiostatic electrodeposition on conducting substrate, such as stainless steel.^[22] Nanowires-,^[61] nanobelts-^[63] and nanorods-like,^[58] morphology can be synthesized under hydrothermal conditions, whereas, nanoplates-like morphology was prepared using sol-gel chemistry.^[62]

Moreover, the nanocomposites of MoO_3 with other electrochemical active components are prepared in the recent years, including carbonaceous materials (carbon nanotubes, graphene, etc.),^[59,60] other binary metal oxides (ZnO , SnO_2 , etc.),^[81,82] and conducting polymers (polyaniline, polypyrrole, etc.).^[83,84] A highly uniform deposition of MoO_3 nanodots on carbon nanotubes with a weight ratio of 20:80 is prepared by a facile

sonochemical method.^[85] On the other hand, $\text{SnO}_2@\text{MoO}_3$ nanowires were prepared using a simple hydrothermal method followed by solvothermal reaction route, and the thickness of SnO_2 was controlled by controlling the loading amount of SnCl_2 in the reaction solution.^[82] Likewise, $\text{ZnO}@\text{MoO}_3$ core/shell nanostructures have also been prepared using electrodeposition route, in which the thickness of MoO_3 layer can be varied by changing the deposition time.^[81] Moreover, a thin layer of polypyrrole or polyaniline can be coated on MoO_3 nanostructures using an in-situ polymerization method.^[83,84]

When it comes to the electrochemical performance of MoO_3 , it is found that the electrochemical performance strongly depends on the morphology as well as synthesis route of MoO_3 nanostructures.^[36,58,61–63,80] In terms of electrochemical performance, it is identified that MoO_3 in nanobelts- and nanoplates-like morphology exhibit better performance among the rest of the morphologies. MoO_3 nanorods synthesized under hydrothermal conditions exhibit specific capacitance as high as 30 F/g at applied current density of 1 mA/cm².^[58] The redox peaks appeared in the CV analysis of MoO_3 nanorods in the potential window of -1 V to +1 V, were not symmetric. These peaks were corresponding to the reversible intercalation/de-intercalation of electrolyte ions. On the other hand, MoO_3 nanowires exhibit rectangular CV shape which indicates the mechanism of charge storage is governed by reversible ions adsorption at the electrode/electrolyte interface. The specific capacitance about 95 F/g was achieved at an applied current density of 200 mA/g.^[61] Shakir *et al.* prepared MoO_3 nanobelts/MWCNT nanocomposites to improve intrinsic conductivity of the electrode material, and achieved a specific capacitance as high as 210 F/g at a scan rate of 5 mV/s.^[59] Attributed to the synergistic effect between the components, an improved electrochemical performance was achieved. MoO_3 nanoplates have shown the highest specific capacitance (280 F/g at 1 mV/s),^[62] due to their two dimensional character which helps to provide a facile diffusion path to the electrolyte ions. Most recently, Jiang *et al.* reported highest achievable specific capacitance (369 F/g at 0.1 A/g) in MoO_3 nanobelts which is even higher than that of MoO_3 nanoplates.^[63] The authors assumed that the improved performance of MoO_3 nanobelts is due to its preparation route which involves H^+ and Na^+ ions, and it's well defined crystallographic structure (layered structure).

The nanocomposites of MoO_3 with conducting polymers are attractive and exhibit better electrochemical performances (specific capacitance, rate capability and cycling stability) than that of the pure MoO_3 nanostructures or nanocomposites with carbonaceous materials. Recently, Zhang *et al.* investigated the electrochemical performance of polypyrrole decorated MoO_3 nanorods, and observed an improvement in the specific capacitance (130 F/g at a scan rate of 5 mV/s) as well as their capacitive behaviour (nearly rectangular CV curves) when compared to the pristine MoO_3 nanorods (CV curve possessed a set of redox peaks).^[84]

Most recently, Jiang *et al.* studied the electrochemical properties of polyaniline decorated MoO_3 nanobelts which show extremely high specific capacitance of 632 F/g at an applied current density of 1 A/g.^[83] The as-prepared nanocomposites could retain 77% of the initial capacitance after 3000 cycles. This improvement in the performance was credited to the coaxial geometry of the nanocomposites. In addition, the coating of conductive components on the surface of MoO_3 nanostructures effectively utilizes MoO_3 nanostructures during cycling. Moreover, to get an overview about the supercapacitive response of α - MoO_3 nanostructures and their nanocomposites, a brief summary of the electrochemical performance of α - MoO_3 based electrode is presented in Table 2.4.

Table 2.4 Electrochemical performance of α - MoO_3 based electrode materials.

Materials and morphology	Specific capacitance	Current density or scan rate	Cycles/degradation	Voltage window
α - MoO_3 Nanorods	31	1 mA/cm ²	100/17%	2 V ^[58]
α - MoO_3 Nanowires	95	200 mA/cm ²	600/15%	0.5 V ^[61]
α - MoO_3 /MWCNT	210	5 mV/s	2000/4%	2 V ^[59]
α - MoO_3 Nanoplates	280	1 mV/s	400/1%	0.9 V ^[62]
ZnO@ α - MoO_3	236	5 mV/s	1000/10%	1.5 V ^[81]
α - MoO_3 decorated graphene	86.3	100 mA/g	100/3%	1 V ^[60]
Heterostructured α - MoO_3 NRs	135	1.3 A/g	1000/19%	1 V ^[86]
SnO_2 @ α - MoO_3 NRs	295	5 mV/s	1000/3%	1 V ^[82]
α - MoO_3 NPs in carbon matrix	179	50 mA/g	1000/20%	1 V ^[87]
Sputtered α -	70	10 mV/s	1000/18%	2 V ^[88]

MoO ₃ /CNT				
α -MoO ₃ Nanobelts	280	0.1 A/g	500/10%	1.25 V ^[89]
α -MoO ₃ Nanobelts	369	0.1 A/g	500/5%	1.3 V ^[63]
Hydrogenated α -MoO ₃ NB's	168	0.5 A/g	3000/3%	1 V ^[90]
Branch-like α -MoO ₃ - polypyrrole	124	5 mV/s	200/10%	1 V ^[84]
Coaxial α -MoO ₃ - polyaniline	632	1 A/g	3000/24%	1 V ^[83]

2.4.2 h-MoO₃ phase of MoO₃

In addition to the layered phase (α -MoO₃ phase) of MoO₃, another phase of MoO₃, i.e., hexagonal MoO₃ has been reported by several research groups around the world.^[65,91] Sometimes, the hexagonal phase was considered as a matter of confusion because the elemental composition in hexagonal phase resembles the hydrated phase of MoO₃.^[92] MoO₃ in hexagonal phase consists of similar zigzag chains of MoO₆ octahedra as those found in layered orthorhombic structure; however, different connectivity (inter-link through the *cis* position) gives rise to the hexagonal symmetry. For the first time, this phase was refined for potassium molybdate (KM₅O₁₅OH. H₂O), and the plausible structure was proposed as depicted in Figure 2.7.^[93]

Figure 2.7 Crystallographic structure of KM₅O₁₅OH. H₂O.

In the hexagonal framework, the molybdenum vacancies are assumed to be charge compensated by the structure stabilizing ions, i.e., K⁺ ions poised in the channels and the

hydrogen ions which are presumed to be attached with the oxygen ions.^[94] The formation of hexagonal phase of MoO_3 is at the paramount interest due to its unique crystallographic structure, which makes a 3D framework structure with various intercalation sites, for example, hexagonal tunnel, trigonal cavity and hexagonal square window, as presented in Figure 2.8.

Figure 2.8 Projection of oxygen packing in hexagonal MoO_3 along $[001]$.

Attributed to its tunnel structures, h- MoO_3 exhibits superior photo-electrochemical and photo-physical properties compared to its layered counterpart, i.e., $\alpha\text{-MoO}_3$.^[95,96] It is demonstrated that the tunnel structure expedite the rate of electron-hole separation under illumination conditions, which in response improves the catalytic as well as allochroic properties.^[95,96] In spite of possessing promising properties for potential applications, the development of h- MoO_3 phase remained a challenge due to its metastable nature. The metastability arises in h- MoO_3 phase was thought to be due to the absence of Mo cations which leads to form 1D tunnel structure.^[94] Commonly, H^+ , Na^+ , K^+ , NH_4^+ ions are introduce into the tunnel of h- MoO_3 phase to partially stabilize the crystal structure. Therefore, there is an urgent need to develop a synthetic strategy to prepare h- MoO_3 nanostructures.

From supercapacitors perspective, $\alpha\text{-MoO}_3$ phase of MoO_3 has widely been explored, whereas, h- MoO_3 phase is untapped yet. As discussed above, $\alpha\text{-MoO}_3$ phase is layered in which ions are accessible along one direction only, while, h- MoO_3 has open-structure in

which ions can move freely in any direction. The metastable h-MoO₃ phase can be considered as a promising electrode material in supercapacitors due to availability of the various intercalation sites, namely, hexagonal window, trigonal cavity and four-coordinated square window.

2.4.3 MoO₃-II phase of MoO₃

In the early 1990s, α -MoO₃ phase was considered the only layered polymorphs of MoO₃, but it was Mc-Carron III who revolutionized the crystal-chemistry of MoO₃ and introduced a new phase of MoO₃, i.e., MoO₃-II phase.^[66] He hypothesized that the combination of high temperature and pressure might be responsible to collapse the layers of α -MoO₃ to form a highly condense phase of MoO₃. The basic layered structure of the two polymorphs was found to be similar, but they differ significantly in terms of crystallographic structures, physical properties, and lattice constants, arrangement of the layers and stability of the phases.^[66] The stacking sequence from ABA for ambient pressure phase α -MoO₃ changed to AAA for the high pressure phase of MoO₃, i.e., MoO₃-II, as depicted in Figure 2.9. As noted, the lattice parameters a and b remain unchanged even after application of high pressure, however, the parameter c was found to be about 50% of α -MoO₃.

Figure 2.9 Transformation from ambient pressure α -MoO₃ phase to high pressure MoO₃-II phase of MoO₃.

After a couple of years, Baker *et al.* attempted to synthesize this high pressure phase using soft chemistry route.^[97] It was identified that monohydrated MoO₃ (MoO₃ H₂O) or hemihydrated MoO₃ (MoO₃ 0.5 H₂O) goes under topotactic phase transformation upon

dehydration. In their study, they showed that the phase transformation must involve a displace motion of molybdenum atoms along a -axis, because transition barrier from orthorhombic crystal symmetry (α -MoO₃ phase) to monoclinic symmetry (MoO₃-II phase) is substantial. This layered phase of MoO₃ is pretty much untapped due to its metastable nature and difficulty to synthesize.

Thus, having the almost similar electrochemical characteristics, as α -MoO₃ does have, except improved packing density and distorted MoO₆ octahedra configuration, the metastable layered phase of MoO₃, i.e., MoO₃-II can be considered as a potential candidate for the high performance energy storage devices.

2.5 Metal and Transition metal molybdates

Metal molybdates or transition metal molybdates are interesting host materials for ion insertion applications due to their mixed electronic and ionic conductivity. The introduction of metal or transition metal ions into the matrix of binary metal oxide or the combination of two metal ions in oxide-matrix produces a material with interesting functionalities and chemical or electrochemical properties compared to that of the binary metal oxide.^[98] In regards of transition metal molybdates, there are two salient features which make the structural-chemistry of molybdates so rich: molybdenum can appear in either MoO₆ octahedra or MoO₄ tetrahedra coordination in various structures, and second, polymolybdates can be formed with high MoO₃/AO ratio, where A is the transition metal ions.^[80] In general, ternary metal oxides form diverse crystallographic structures or phases or motifs, and these motifs can be span from simple structure to complex structures depending on the compositions and synthetic conditions.^[98] For example, polymolybdates prepared using solid-state synthetic routes consist of chains of Mo-O polyhedra, while solution synthesis tend to generate complexes of Mo-O and A-O polyhedra.^[77,99] In generally, transition metal molybdates share a common formula unit, i.e., AMoO₄, where A is Mg, Ni, Zn, Cu, Mn, Co and Fe, however, arrangement of octahedra or tetrahedra varies within the phase.^[100] For instance, in the crystallographic structure of MnMoO₄, Mn atoms favour octahedra coordination, while Mo atoms arrange in tetrahedra coordination and stabilizes in monoclinic crystal structure.^[101] On the other hand, in the lattice of CoMoO₄ or isostructural NiMoO₄, Co or Ni atoms with the Mo

atoms favour to arrange in highly distorted octahedra configuration and form a lattice of monoclinic structure.^[102,103]

AMoO₄ (A = Ni, Co, Mn, Bi, etc.) nanostructures have been prepared in various morphologies, e.g., nanowires,^[104] nanorods,^[105] nanoplates,^[106] etc. under diverse reaction routes. Most recently, Peng *et al.* reported hydrothermal synthesis of NiMoO₄ nanoplates and nanorods on various conducting substrates (Ni foam, Ti foil, Stainless steel and graphite paper).^[106] Importantly, the physical structure of NiMoO₄ nanostructures can be tuned easily from nanoplates to nanorods by changing the reaction solvent, i.e., ethanol to DI water. The nanocomposites of NiMoO₄ with graphene, MnO₂, Co(OH)₂ and Co₃O₄ have also been prepared using a facile hydrothermal synthesis route.^[107–110] Most likely in all the hydrothermal synthesis routes, Ni(NO₃)₂ · H₂O and Na₂MoO₄ precursor system was adopted often due to their simple reaction chemistry to achieve nearly perfect stoichiometry of the final product. Senthilkumar *et al.* synthesized MnMoO₄, NiMoO₄, and nanocomposites of NiMoO₄-CoMoO₄ · H₂O using a facile solution combustion route,^[111–113] in which urea was utilized as a fuel. In general, combustion synthesis technique is used to prepare nano-sized porous metal oxides due to its short reaction time and high reaction temperature. Recently, Mai *et al.* synthesized MnMoO₄/CoMoO₄ heterostructured nanowires using a simple micro-emulsion method under mild conditions.^[114] The growth mechanism of complex MnMoO₄/CoMoO₄ heterostructured nanowires was proposed as “self-assembly” and “oriented attachment”. Hierarchical Bi₂MoO₆ nanowires and nanoplates have been prepared using electrodeposition and solution combustion technique, respectively.^[115] The phase of the as-prepared nanostructures was found extremely sensitive to the annealing temperature. Recently, transition metal molybdate (AMoO₄, A = Ni, Co, Mn, Bi, etc.) based electrode materials have gained significant interest in supercapacitors due to their chemically stable crystal structure and redox behaviour of metal ions (A) in aqueous alkali electrolytes.^[98] With the purpose of enhancing the electrochemical performance of ternary metal molybdates, Mai *et al.* proposed hierarchical structure of MnMoO₄/CoMoO₄ heterostructured nanowires which exhibit specific capacitance as high as 210 F/g at an applied current density of 0.5 A/g and excellent cycling stability. The specific capacitance exhibited by MnMoO₄/CoMoO₄ heterostructured nanowires was much

higher than that of MnMoO_4 (9.7 F/g) and CoMoO_4 (62.8 F/g).^[114] Generally, hierarchical structure offers a synergistic integration of two length scales. Specifically, the smaller dimension shortens the diffusion path and increases the electrochemically active surface area, while the larger length could confer efficient electronic transport and reduce the internal resistance. Likewise, $\text{CoMoO}_4\text{-NiMoO}_4 \cdot \text{H}_2\text{O}$ nano-bundles could deliver a specific capacitance of 1039 F/g at an applied current density of 2.5 mA/cm^2 .^[116] The weight ratio of Co:Ni found a vital factor to affect the electrochemical performance of the nano-bundles, a ratio of 0.6:1.4 was found optimum to achieve a stable electrochemical performance. In the same year, Senthilkumar *et al.* attempted to synthesize the same materials ($\text{CoMoO}_4\text{-NiMoO}_4$) system in nanoparticles-like morphology and could achieve specific capacitance of 1472 F/g at an applied current density of 5 mA/cm^2 .^[112] The authors credited this improvement in the performance to the route of synthesis, synergistic effect of Ni and Co, and high weight fraction of Ni. In their study, they found that the weight ratio of 0.33:1 is the optimum amount of Co to Ni. The nanocomposites of NiMoO_4 , CoMoO_4 , MnMoO_4 , etc., with other binary metal oxides, such as MnO_2 ,^[108] Co_3O_4 ,^[109] Co(OH)_2 ,^[110] etc., and carbonaceous materials are also the promising electrode materials for high performance supercapacitors. Cai *et al.* prepared 3D $\text{Co}_3\text{O}_4\text{@NiMoO}_4$ nanowires array on Ni foam using two steps hydrothermal reactions route.^[109] The as-prepared hybrid electrode could exhibit a high specific capacitance of 1094 F/g at an applied current density of 30 mA/cm^2 . Most recently, Ren *et al.* synthesized $\text{NiMoO}_4\text{@Co(OH)}_2$ nanowires array using hydrothermal synthesis of NiMoO_4 on Ni foam followed by electrochemical deposition of Co(OH)_2 nanoflakes on the as-prepared NiMoO_4 nanowires.^[110] The as-designed hybrid electrode delivered a high specific capacitance of 2122.7 F/g at 4.5 A/g due to its unique 3D structure which facilitates transport of ions, superior electron collection efficiency and high electrochemically active surface area. Recently, Ma *et al.* synthesized 3D nanocomposites of $\text{Co}_3\text{O}_4\text{@AMoO}_4$ (A = Ni, Co) under two steps low temperature hydrothermal conditions, and showed that the as-prepared nanocomposites of $\text{Co}_3\text{O}_4\text{@NiMoO}_4$ and $\text{Co}_3\text{O}_4\text{@CoMoO}_4$ could achieve significantly high specific capacitance of 2041 F/g and 857 F/g at an applied current density of 0.5 A/g, respectively.^[117] The as-fabricated asymmetric supercapacitors, taking activated carbon

as negative electrode materials, could deliver a high energy density of 41.9 Wh/kg (@298 W/kg) and 38 Wh/kg (@275 W/kg) for AC//Co₃O₄@NiMoO₄ and AC//Co₃O₄@CoMoO₄, respectively.^[117] The other molybdate systems are also investigated in the recent years, including AC//NiMoO₄ H₂O (34.4 Wh/kg @ 165 W/kg),^[105] rGO//CoMoO₄ (8.17 Wh/kg @ 187.5 W/kg),^[118] FeMoO₄/NiMoO₄ (29 Wh/kg @ 190 W/kg),^[119] etc. More recently, Yu *et al.* constructed nanohoneycomb-like strongly coupled CoMoO₄-3D graphene hybrid electrode on Ni foam followed by etching of Ni foam in 3 M HCl solution, for symmetric (Co₃MoO₄//Co₃MoO₄) as well as asymmetric (AC//Co₃MoO₄) supercapacitors in coin cell configuration.^[120] The asymmetric and symmetric devices could deliver the energy density as high as 21.1 Wh/kg (@300 W/kg) and 37.25 Wh/kg (@900 W/kg) at an applied current density of 0.33 A/g. The as-prepared symmetric device was considered to become a choice of next generation supercapacitors due to its ultra-long (100000 cycles) cycling stability at a very high level of current density, i.e., 400 A/g.

Thus, based on the literatures survey, it is noteworthy that the transition metal molybdates are the potential candidates for the high energy applications, but at the same time they are sacrificing the power density, which could hamper their use in practical applications. Therefore, it is essential for the future applications to develop an electrode system which could deliver high energy density without compromising the power density.

2.6 Localized electrochemical activity of electrode materials

As discussed in the previous sections, miniaturising the particle size of the electrode materials in various physical structures is at utmost importance to enhance the electrochemical properties. During the electrochemical processes, only a few (~10 nm) particles at the interface of the electrode/electrolyte respond to the redox reactions; therefore, the interface is a bottleneck for the physicochemical processes in the electrode materials. The physical aspects of electrode materials, such as porosity and thickness may exert change in electrochemical processes due to distribution of the electric potential, current density and local concentration of electrolyte ions.^[121,122] The aforementioned concerns become critical particularly at high rate of charge or discharge applications. The conventional or macroscopic electrochemical techniques are not capable to deconvolute the kinetics of electrochemical events that take place at the interface. Therefore, the real time visualization of the electrochemical activity of the electrode materials remains a

challenge due to lack of effective analytical tools, not least because of the surface roughness of the electrode materials but show variation in the electrochemical activity at the nanoscale.^[123] Due to the variation in local electrochemical activity of the electrode materials, electrochemical responses are actually apparent not intrinsic, which sometimes undervalue the performance of the electrode materials.

So far, the understanding about the electrochemical processes at micro- or nano-scale has been fully relied on a few analytical tools. For example, microparticle-electrode technique,^[124] that be used to evaluate the electrochemical processes at a single active site for a microparticle at a time; this technique has been used to study local electrochemical activity of several electrode materials, for example, Ni(OH)₂, Zn, Mn, carbon, etc.^[124] But the ability to evaluate the state of charge (at a resolution of micron level) of the target materials strictly rely on spectroscopic tools, i.e., *in situ* optical or Raman microscopy. The other local microscopy technique, such as electrochemical strain microscopy (ESM) is capable to provide useful information about the dynamics of electrolyte ions into the host materials.^[125] This analytical tool basically relies on the strain response of the electrode materials, which may be intricate to interpret in multi-component system or a system with low strain response. Scanning ion conductance microscopy (SICM) has proven powerful principally for high resolution mapping applications.^[126] In contrast, scanning electrochemical microscopy (SECM) is known for its multi-functionality.^[127] SECM can be used not only to evaluate the topographical information of the electrode surfaces but also capable to capture valuable information about its electrochemical activity at a level or micro- or nano-meter.

2.6.1 Scanning electrochemical microscopy (SECM)

Scanning electrochemical microscopy (SECM) is one of the special types of scanning probe microscopy (SPM). SECM is suitable for studying localize electrochemical processes not only in bulk-electrochemistry,^[128] but also in biology, for example, membrane transport.^[129] The analytical methods of SECM are based on solid theoretical foundation with various demonstrated applications that have been developed in last three decades. SECM offers the possibility to track heterogeneous reaction rates,^[130] and locally modifying the surface of electrode materials by electro-generating the redox species.^[131] Furthermore, the kinetic aspects of the electrode materials in various energy

storage devices, such as battery,^[128] solar cell,^[132] fuel cell,^[133] etc., can also be studied using SECM.

2.6.1.1 Principle of SECM

SECM takes measurement of the currents through the microelectrode into account when it is held or moved in the vicinity of the electrode/electrolyte interface.^[134] Specifically, near to the substrate (which could be solid, such as glass, metal plate, biological material or polymer or liquid, for example, liquid or immiscible oils),^[135] which perturbs the electrochemical response of the microelectrode, and this perturbation gives information about the nature and properties of the surface.

A typical SECM setup consists of four electrodes, i.e., microelectrode, reference electrode, counter electrode and electrode surface, as displayed in a simplified schematic of SECM experimental cell, as shown in Figure 2.10 (a). The microelectrode is assumed as the essential part of this technique and the resolution of this technique directly depends on the radius of the microelectrode.^[131] A typical ultra-microelectrode or microelectrode consists of a Pt wire (diameter $<50\ \mu\text{m}$) encapsulated by insulating sheath.

Figure 2.10 (a) Schematic of SECM experimental cell and (b) typical voltammogram for the microelectrode.

Assuming the solution contains oxidized form of redox species, O, at a known concentration, c , and commonly holds supporting electrolyte to lessen the solution resistance, and ensures a facile transport of redox species to the target surface predominantly by diffusion. The electrochemical micro-cell also contains an auxiliary or counter electrode and reference electrode to complete the electric circuit, as shown in Figure 2.10 (a). As the potential applied to the tip using a bipotentiostat, reduction of

oxidized species ($O + ne^- \rightarrow R$) takes place at the tip of microelectrode, as a result current starts to flow, as shown in Figure 2.10 (b), the S-shaped curve. Simultaneously, a counter reaction ($R \rightarrow ne^- + O$) takes place at the counter electrode, but the products of this reaction do not reach to the microelectrode.

The S-shaped curve arises due to decrease in the concentration of electrochemical reactions from bulk solution to the electrode surface, which is completely controlled by the rate of mass transfer, and so the diffusion of oxidized species. The steady-state-diffusion-controlled current for a disk shaped microelectrode can be given by equation 2.9.^[131]

$$i_{T,\infty} = g n F D c_0 r_T \text{ (eq. 2.9)}$$

Where $i_{T,\infty}$ is the steady-state diffusion limited current, g is the geometry dependent factor, the value of 4 is assumed for disk shaped microelectrode embedded in an insulating sheath, n is the number of electrons/molecules transferred, F is the faraday constant, D is the diffusion coefficient of the mediator species, c_0 is the bulk concentration of mediator and r_T is the radius of microelectrode.

It is worth to mention that the tip current is relatively independent of the size of the insulating sheath, r_g , commonly expressed in SECM literature as $RG = r_g/r_T$. Due to small radius of the microelectrode, the flux ($\sim Dc_0/r_T$) of oxidized species by diffusion is quite large, additionally; the current at microelectrode also reaches steady-state quickly ($\sim r_T^2/D$). These features make SECM as steady-state system. Attributed to small currents (order of nA or pA) involved in SECM, resistive ohmic drops in the solution are generally negligible. To evaluate the electrochemical activity of the underlying surface, SECM can be performed in several modes, such as feedback mode (amperometric and potentiometric), generation/collection mode, etc., among them feedback mode (amperometric) of SECM is considered promising.^[131]

2.6.1.2 Amperometric Feedback mode of SECM

Amperometric method of SECM involves measurements of electrode current as a function of tip-substrate distance and tip or substrate potential. In principle, there are two main steady-state mode of amperometric technique; feedback back mode, generation/collection mode, whereas, shielding or competitive mode is a feedback mode under special circumstances (potential applied to the tip as well as substrate). However,

the focus will be given to feedback mode that is more relevant to the work described herein.

In the feedback mode, under steady-state conditions, the relationship between normalized tip current ($I_T = i_T/i_{T,\infty}$ = tip current normalized by steady-state current) and normalized distance ($L = d/r_T$ = tip-substrate separation normalized by tip radius) is called the approach curve.^[131,135] Besides giving information about the nature of the substrate surface, the approach curve analysis is particularly useful to determine the effective heterogeneous electron transfer rate constant ($k_{\text{eff}} = kD/r_T$).^[131,135]

Figure 2.11 Basic operating principles of SECM, (a) the microelectrode is far from the surface (a few tip diameter), only steady-state current flows due to diffusion, $i_{T,\infty}$ (b) the microelectrode is near to a conductive surface (typically less than half of the tip diameter), feedback diffusion current flows, $i_T > i_{T,\infty}$ and (c) the microelectrode is near to an insulating surface, hindered diffusion current flows, $i_T < i_{T,\infty}$.

When a potential is applied to the tip to reduce or oxidize the redox-species and the tip is situated far away from the substrate surface, the steady-state current, $i_{T,\infty}$ can be achieved

due to hemispherical flux of the oxidized species, as shown in Figure 2.11 (a). When the microelectrode approaches towards a conductive surface, although, there is some blockage of the oxidized species by the substrate, but regeneration of the oxidized species also takes place in the vicinity of the conductive surface that can be diffused back to the tip, as a result an increase in the flux of oxidized species, and so the tip current, as shown in Figure 2.11 (b). Thus, for a conductive surface, $i_T > i_{T,\infty}$ and this situation is also known as the positive feedback response.

Now, when the microelectrode approaches towards an insulating surface, the blockage of some of the oxidized species happens at the substrate surface, as a result flux of oxidized species decreases which leads to decrease in the tip current compared to the steady-state current, as shown in Figure 2.11 (c), therefore, for an insulating surface, $i_T < i_{T,\infty}$ this behaviour is commonly known as the negative feedback mode of SECM.

As an analytical tool, evaluation of the electrode surface is of great interest. Several studies have been carried out to study localize electrochemical activity of the electrode materials in the feedback mode, however, demonstration of the normal feedback mode of SECM vs. shielding mode or competitive mode have not studied much. Therefore, studying the electrode material in both the feedback modes are of great value to investigate.

2.6 Summary

As discussed above, the high performance supercapacitor electrode materials are of immense interest, the selected electrode materials should be capable to deliver high specific capacitance, excellent cycling stability and remarkable rate capability. As examined above, the layered thermodynamically stable phase of MoO_3 , i.e., $\alpha\text{-MoO}_3$ having difficulties to achieve the above mentioned requirements. Theoretically, it is showed to have very high specific capacitance value, thus exploring the other crystallographic phases, i.e., h-MoO_3 is worthy to realize any improvement in the electrochemical performance. The h-MoO_3 phase of MoO_3 is metastable in nature and known to have 3D open structure with various intercalation sites that are available for the electrolyte ions to intercalate.

Introducing conductive agent or supports is considered a promising way to improve the electrochemical performance of α -MoO₃ nanostructures, as discussed above. However, the detail mechanism of this improvement has not been discussed in the literatures.

Moreover, electrochemical performance of molybdenum oxide is improved by producing its derivatives (i.e., molybdates) with other transition metal elements. The as-produced transition metal molybdates proved to be the excellent candidate for supercapacitors having high specific capacitance and high energy density.

Generally, electrochemical characterizations of the electrode materials are performed at microscopic scale, which does not provide insight into the kinetics of charge transfer across the thin interface. The proposed scanning electrochemical microscopy (SECM) in feedback mode is recommended as a promising tool to look into the localized electrochemical activity of the electrode materials to design or fabricate a high performance electrochemical energy storage device.

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Chapter 3: Experimental procedure and Instrumentations

As discussed in the previous chapter, the molybdenum based compounds in various crystallographic structures can be synthesized under chemical or solid-state reaction conditions. The main advantage of using chemical route is that the atomic mixing of the constituents yields the final products of almost perfect stoichiometry, besides its simplicity. This chapter introduces experimental procedures of the synthesis of electrode materials that are used in this dissertation followed by overview of the relevant characterization tools to explore their physical, chemical or electrochemical properties.

3.1 Synthesis of Electrode Materials

3.1.1 Synthesis of Hexagonal-MoO₃ (h-MoO₃ phase) Nanostructures

As discussed in the previous chapter, the hexagonal phase of MoO₃ can be stabilized using structure stabilizing ions which compensate shortfall in charges due to molybdenum vacancies. Here, h-MoO₃ phase of MoO₃ is synthesized via solvothermal reaction route using hexamethylenetetramine as a source of ammonium ions. The electrode materials studied in Chapter 4 were synthesized as explained below.

In this typical synthesis procedure, Mo powder (500 mg) was mixed into 30%-H₂O₂ (5 ml) solution to prepare poly-peroxomolybdic acid solution in a 20 ml glass vial. The solutions of hexamethylenetetramine (C₆H₁₂N₄) in DI water (10 ml) with various weight amounts (100 mg, 150 mg and 250 mg) were prepared separately, and slowly mixed into the poly-peroxomolybdic acid solution, and allowed to stir for few hours. The as-prepared solutions were transferred to a lab oven for solvothermal reactions at 100 °C for 18 hours. The precipitates were collected and washed with copious amount of DI water and ethanol, and dried in a fume hood at 80 °C to obtain the final products. The as-obtained products were used directly for characterizations.

3.1.2 Synthesis of Polyaniline-h-MoO₃ Hollow Nanorods

The nanocomposites of polyaniline-h-MoO₃-hollow nanorods studied in Chapter 5 were synthesized according to the experimental procedure, as described successively.

Prior to the preparation of polyaniline-h-MoO₃ hollow nanorods, h-MoO₃ nanorods were prepared as described in 3.1.1. In particular, hexamethylenetetramine (100 mg) was mixed into 10 ml of DI water, and the as-prepared solution was slowly added into the poly-peroxomolybdic acid solution (5 ml). The resultant solution was further stirred for several hours until a clear yellow solution achieved. The as-obtained solution was allowed for solvothermal reactions in a lab oven at 100 °C for 18 hours. The precipitate was collected by centrifugation, and washed with copious amount of ethanol and DI water and dried at 80 °C.

In order to prepare h-MoO₃ hollow nanorods, cation-exchange assisted Kirkendall effect was employed. In the preparation of h-MoO₃ hollow nanorods, the as-prepared h-MoO₃ nanorods (100 mg) were dispersed in FeCl₃ 6H₂O (0.36 M) solution, and allowed to stir for 20 min at ambient conditions. Thereafter, the as-prepared solution was aged for 24 hours at room temperature to form h-MoO₃ hollow nanorods.

In the preparation of polyaniline-h-MoO₃ hollow nanorods, h-MoO₃ nanorods (100 mg) were dispersed in FeCl₃ 6H₂O (0.36 M) solution under vigorous magnetic stirring at room temperature. The anilinium chloride (C₆H₅N⁺H₃Cl⁻) solution was prepared by mixing various amounts (100 µl, 150 µl and 200 µl) of aniline monomers (C₆H₅NH₂) into HCl (2.6 M) solution. The thickness and microstructure of decorate polyaniline was varied by varying the molar ratio of oxidant to monomer (FeCl₃ 6H₂O/aniline) from 1 to 1.7. The as-prepared anilinium salt solution was drop wise added into the nanorods solution and stirred at 60 °C for 3 hours. The reaction solution was changed from khaki to deep green while mixing of anilinium salt solution, indicative of the commencement of polymerization process. After an aging time of 24 hours, the as-obtained precipitates were washed with abundant amount of ethanol and DI water, and dried at 80 °C in a fume hood.

3.1.3 Synthesis of Silver Decamolybdate Nanorods

The electrode material studied in Chapter 6 was prepared as follows. In this typical synthesis procedure, ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄] (877 mg) was mixed in 20 ml of DI water. A solution of silver nitrate [AgNO₃] (425 mg) in 20 ml of DI water was prepared separately, and drop wise added into the above solution. A dilute solution of HNO₃ (1M) was used to adjust the pH (~2) of the resultant solution. The as-obtained

greenish-yellow solution was then transferred to 50 ml capacity Teflon lined autoclave for hydrothermal reactions at 140 °C for 12 hours. A yellowish precipitate was centrifuged and washed with copious amount of ethanol and deionized water (DI) water several times, and dried at 70 °C. To obtain $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods, the as obtained yellowish precipitate was air-annealed at 455 °C for 3 hours. The as-produced powder was used for structural and electrochemical characterizations.

3.1.4 Synthesis of Tri-rutile related Layered Hydrogen-Niobium Molybdate Nanosheets

The synthesis procedure of the electrode materials that were studied in Chapter 7 involves several steps. In the first step, LiNbMoO_6 powder was prepared according to the procedure reported in the literature.^[1] In the preparation of LiNbMoO_6 , the oxides of Mo (MoO_3 , 99.9% purity), Nb (Nb_2O_5 , 99.97%) and lithium carbonate (Li_2CO_3) were mixed together in equal stoichiometric ratio, and the solid-state reaction was performed at 580 °C for 24 hours with one intermediate grinding followed by quenching of the product in air atmosphere.

Second, the proton exchange of LiNbMoO_6 was carried out as reported in the literature with slight modification.^[1] In this procedure, LiNbMoO_6 (500 mg) was dissolved in 50 ml of HNO_3 (2 M) at room temperature and allowed to stir for 4 days. After protonation, the product was washed and dried at 70 °C. This step yields the formation of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ nanosheets.

In order to realize the formation of HNbMoO_6 nanosheets, the as-prepared $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ nanosheets powder was annealed at 230 °C for 3 hours in air atmosphere.

3.1.5 Preparation of MoO_3 -II Nanosheets

The electrode system studied in Chapter 8 was prepared according to the following procedure. MoO_3 -II phase of MoO_3 is synthesized through h- MoO_3 phase of MoO_3 . Specifically, MoO_3 -II phase was the topotactic phase transformation product of h- MoO_3 phase. Firstly, h- MoO_3 nanorods were synthesized under solvothermal conditions as described above. The as-obtained nanorods were air annealed at 530 °C for 3 hours to initiate the phase transformation process (from h- MoO_3 phase to MoO_3 -II phase). The as-formed product was mechanically exfoliated using Scotch tape (3M ScotchTM). This

procedure was repeated multiple times until a faint reflection was observed onto the scotch tape, and then transferred to a previously cleaned SiO₂/Si substrate.

3.2 Materials Characterizations

The nanomaterials prepared during the course of project were thoroughly characterized using various characterization tools, depending upon the specific requirement.

Field Emission Scanning Electron Microscopy (FESEM; JEOL, JSM-7600 F) operated at 5 kV or 10 kV was used to evaluate the morphologies of the as-prepared electrode materials. The as-prepared electrode materials can be directly imaged in the powder form. Pt or Au (~10 nm) coating was used to avoid charging issues related to insulating electrode materials.

Electron dispersive X-ray spectroscopy (EDX) was performed using FESEM; JEOL, JSM-7600 F operated at 15 kV for both qualitative as well as quantitative determination of the elements or elemental compositions.

X-ray diffractometer Shimadzu XRD-6000 (voltage 40 kV, current 40 mA) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was used to determine the crystal structure of the electrode materials. Identification of the phase or indexing of the as-obtained diffraction profiles was performed using “Match” with International Centre for Diffraction Data (ICDD). The crystallographic information files (CIF) were generated using “Findit” software. The atomic structures can be generated using software like “Atoms”.

Transmission Electron Microscopy (TEM; JEOL, JEM-2010 and JEM-2100F) operated at 200 kV was used to investigate the detailed morphology and structure analysis of the as-prepared electrode materials. The samples first dispersed in acetone and then drop casted on a TEM specialized copper grid (300 square meshes) with carbon membrane.

X-ray Photoelectron Spectroscopy (XPS) was utilized to analyze the surface elemental identification in qualitative as well as quantitative manners. The quantitative analysis was carried out by fitting (CASA, XPS software) the profiles and calculating the area under the curves. Monochromatized Al K α X-ray source (1486.6 eV) on Kratos Analytical AXIS HSi spectrometer, with constant dwell time of 100 ms and pass energy of 40 eV were used during the analysis. The as-prepared electrode materials were sprinkled on the conductive adhesive carbon tape and used for XPS analysis.

Thermal analyses were carried out using TGA/DSC/DTA, STA-449C, max. temperature 1500 °C and TGA, TA-Instruments Q500/Q290, by heating the materials from room temperature to 900 °C at a ramping rate of 10 °C /min. Herein, DSC and TGA were used to identify the phase change and to estimate the weight percentage of each component in composite materials, respectively.

Dynamic Mechanical Analyzer (TA-Instruments, DMA, Q800) was used to study the mechanical properties of free-standing electrodes. The measurements were performed under tension mode using fixed- and movable-clamp configuration at a strain rate of 0.05%/min with a preload of 0.001 N.

Raman spectroscopy (Witec, Model WiTech alpha 300 SR, $\lambda = 488$ nm) was performed to quantitatively analyze the quality of electrode materials. The peak positions of Raman spectra were used to determine the chemical bonds present in the electrode materials. The as-prepared electrode materials were dispersed in ethanol and drop casted on ITO glass or glass or silicon substrate and used for Raman spectroscopy.

Fourier Transformation Infrared Spectroscopy (FTIR, Perkin Elmer FTIR System) was performed to analyze the chemical bonding present in the functional groups in the electrode materials. The samples were prepared by grinding nanomaterials with desiccative optical pure KBr, and pressed in the form of a pellet to perform the FTIR analysis in ATR mode.

3.3 Electrochemical Characterizations

In most of the cases the as-prepared electrode materials were in the powder form. In the preparation of electrode materials for electrochemical testing, the as-synthesized electrode material was mixed into conductive additives, such as carbon black and binding host, such as poly(vinylidene fluoride) were mixed in a fixed weight percentage of 85:10:05, respectively. A few drops (~500 μ l) of N-methylpyrrolidinone (NMP) were added into the above mixture of the powders to form slurry. The slurry was well stirred for 10 hours and then coated on the half portion (1×1 cm²) of a previously polished graphite paper. The electrodes were dried at a fixed temperature (100 °C) for 10 hours in the air atmosphere.

In contrast, 2D MoO₃-II solution in DI water was directly drop casted on Indium Tin Oxide glass (ITO glass, ~200 nm ITO coating) and insulating glass and used for

electrochemical testing. Likewise, Ppy-VM NP free-standing electrodes were used directly for electrochemical testing without further modifications.

3.3.1 Macroscopic testing (Three electrodes or half-cell testing)

All the electrochemical tests were performed in a three electrode cell configuration, in which Ag/AgCl, platinum sheet, and electrode materials were used as reference electrode; counter electrode and working electrode, respectively. All three electrodes were electrically connected to the potentiostat with the help of copper wires, and immersed into a cell containing electrolyte solution. Electrochemical working station (AutoLab PGSTAT 30 potentiostat and Solartron 1470E electrochemical interface) was utilized to provide electric signals and electrochemical data.

During electrochemical characterizations electrodes were tested using four different classes of electrochemical test, i.e., cyclic voltammetry (CV), galvanic charge/discharge, and electrochemical impedance spectroscopy (EIS) and cycling test.

Cyclic voltammetry (CV) measurements were performed at various scan rates to study the electrochemical responses of the as-prepared electrode materials. CV test is particularly important to determine the potential window and to identify the reduction and oxidation potentials. Specific capacitance (C_{sp}) using CV test can be determined using equation 3.1 or 3.2.

$$C_{sp} = \int i \, dV / m \, v \, \Delta V \quad (\text{eq. 3.1})$$

$$Q_r = Q / m \, \Delta V \quad (\text{eq. 3.2})$$

Where i , m , v , Q and ΔV are the peak currents (A), loading mass (g), scan rate (mV/s), stored charge (C) and potential window (Volt), respectively. Therefore, C_{sp} has a unit of F/g. This is the integral analysis of the specific capacitance of the electrode materials.

CV analysis is also important to study kinetic aspects of the electrochemistry of the electrode materials. The relationship between peak current (cathodic or anodic) and scan rate or peak voltage and scan rate gives significant information about the redox process/es involved during the charge storage. Assuming that the peak current obeys a power law with the scan rate according to equation 3.3

$$I_p = a \, v^b \quad (\text{eq. 3.3})$$

Where a and b are the adjustable parameters, where b values can be determined from the slope of the plot $\log(i)$ vs $\log(v)$. According to the approximations, $b=1$ indicates surface

controlled current (surface redox reactions) and $b = 0.5$ is corresponding to the current controlled by the semi-infinite linear diffusion (intercalation redox reactions).

Charge/discharge (C/D) tests were performed to study charge storage capability of the electrode materials. C/D tests were carried out in Galvanostatic mode in which a constant current was applied to the electrode between two fixed potential limits. C/D curves render the information about the change in potential with respect to time during C/D. The specific capacitance can also be determined using C/D test according to equation 3.4.

$$C_{sp} = I/m \times (-\Delta V/\Delta t) \quad (\text{eq. 3.4})$$

Where I , m and $-\Delta V/\Delta t$ are the applied current, loading mass and slope of the discharge curve, respectively. This is the differential analysis of the specific capacitance of the electrode materials.

Electrochemical Impedance Spectroscopy (EIS) is one of the important tests to evaluate the electrochemical properties of electrode materials. EIS gives the information about the charge transfer resistance ionic diffusion behavior of the electrode materials. The relationship between two components of the impedance (imaginary and real) is known as Nyquist plot. This test was performed in potentiostatic mode in which a constant potential was applied within certain range of frequency (10 mHz to 100 kHz) at constant AC amplitude of 10 mV.

Cycling stability tests were carried out using CV test. This test is important to examine the electrochemical stability of the electrode materials particularly with first 1000 cycles.

3.3.2 Prototype supercapacitor device tests (Two electrodes or full cell test)

The prototypic supercapacitor devices were assembled into a Swagelok cell in symmetric as well as asymmetric electrode configurations. In asymmetric cell design, activated carbon electrode was used as anode and active materials as cathode with a filter paper as separator. The specific capacitance in case of Swagelok cell was determined using CV tests or C/D tests and C/D tests, respectively, as discussed in the previous section.

Moreover, C/D tests were also used to evaluate the energy density as well as power density of the prototypic devices. Energy density and power density are the two important parameters of a supercapacitors device. Energy density signifies the energy storage ability, while power density shows the ability to deliver energy per unit time. The relationship between energy density and power density is known as Ragone plot.

Therefore, the specific energy density and power density can be determined according to equation 3.5 and 3.6, respectively.

$$E = 0.1385 \times \Delta t \times \Delta V \times I \quad (\text{eq. 3.5})$$

$$P = E/\Delta t \quad (\text{eq. 3.6})$$

Where E and P are the specific energy density (Wh/kg) and specific power density (W/kg), respectively

3.3.3 Microscopic testing (Localize testing)

Local electrochemistry of the electrode surface was studied using Scanning Electrochemical Microscopy (SECM) in feedback mode. To facilitate a better understanding, the experimental procedure, besides a brief introduction about the technique will be discussed in the following sections.

3.3.3.1 Instrumentation of SECM

In a simplified projection, SECM consist of two components, i.e., mechanical and electrical, as shown in schematic diagram, Figure 3.1. A piezo-driver is used to control the positioning in any direction (X, Y, and Z) with a minimum translation speed of 1 $\mu\text{m/s}$, while a bipotentiostat controls the electric signals (up to the range of pA) at the working electrode as well as at the substrate (if needed). SECMx software couples both the electrical and mechanical components, and able to display real time measurement signals from microelectrode or substrate or both.^[2]

Microelectrodes are widely been used in electrochemistry,^[3] and perhaps it is the most essential part of SECM, because the development in the SECM is closely related to the advancement of the microelectrodes.^[3] A typical ultra-microelectrode or microelectrode consists of a Pt wire (diameter <50 μm) encapsulated by insulating sheath. The microelectrodes assisted electrochemistry was introduced to avoid planner diffusion layer (expands quickly into the electrolyte region), and to circumvent the unnecessary ohmic drops.^[4,5] In contrast to the planner electrodes, microelectrode bears radial diffusion due to its smaller dimensions.^[6] Due to larger flux of the electro-active species, diffusion region evolves quickly, as a result steady state can be achieved readily.

Figure 3.1 Schematic illustrations of SECM instrumentations.

3.3.3.2 Experimentation of SECM

SECM measurements were conducted in a four-electrode cell configuration, as shown in the schematics Figure 3.1. The effective heterogeneous charge transfer rate constants (k_{eff}) were evaluated using approach curve analysis of SECM in feedback mode.

SECM studies were carried out on a instrument, manufactured by Sensolytics and CH instruments, Inc., running with XYZ-positioning system and a bipotentiostat in a four electrode configuration with the ME as working electrode [Pt wire embedded in glass-WE1, $r_T = 12.5 \mu\text{m}$, $RG = r_{\text{glass}}/r_T = 7$, (r_{glass} is the radius of the glass sheath), 2D MoO_3 -II decorated ITO glass substrate [WE2], a Pt wire as an auxiliary electrode and Ag/AgCl reference electrode. All the electrodes were fixed into a Teflon cell containing 2-3 ml of redox-active species-solution (1 mM of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ or 1 mM of $[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 M KCl). SECM approach curves were performed at translation rate of $2 \mu\text{m/s}$ and recorded by SECMx software, k (determines the shape of the approach curve) was obtained by fitting the normalized approach curves to an analytical approximation made by Cornut and Lefrou for finite sample kinetics, as described in Appendix.^[7,8] The effect of surface bias on the regeneration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was studied on a commercial SECM (CHI 920C, CH Instrument, USA). The microelectrode was positioned close to the surface ($\sim 150 \%$

of bulk current), and it was kept at -400 mV vs. Ag/AgCl reference electrode. The potential of the surface was scanned from 0.5 V to -0.35 V at 1 mV/s, and the corresponding current response of the surface and microelectrode was measured.

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Chapter 4*: Synthesis and pseudocapacitive properties of h-MoO₃ nanostructures

The hexagonal phase of molybdenum trioxide is of immense interest due to its crystallographic structure, which consists of various intercalation sites, i.e., hexagonal window, trigonal cavity and four-coordinated square window. In this chapter, I present a novel synthesis route to prepare h-MoO₃ nanostructures in various morphologies. The role of ammonium ions is found to be critical in altering the morphology of the nanostructures. The electrochemical properties of the as-prepared electrode materials are studied in a three-electrode cell configuration. Lastly the key findings of the study are summarized.

4.1 Introduction and Motivation

The α -MoO₃ phase of MoO₃ has widely been explored and known to have layered structure in which ions are accessible along one direction only, while, h-MoO₃ has open-structure in which ions can move freely in any direction. The metastable h-MoO₃ phase can be considered as a promising electrode material in supercapacitors due to the availability of the various intercalation sites, namely, hexagonal window, trigonal cavity and four-coordinated square window. Inspired from the aforementioned features of h-MoO₃, I propose to exploit the merit of h-MoO₃ nanostructures in supercapacitors to enable facile conduction of the charge carriers and realize the improved electrochemical performance.

The metastable phase of MoO₃, i.e., h-MoO₃ has widely been reported in the literature, although it was indexed as cubic and originally labeled as “molybdic C-phase”.^[1,2] However, it was further refined and indexed correspondent to hexagonal crystal symmetry, and its composition was best represented as $\text{AMo}_{6-x}[\text{vac}]_x\text{H}_{6x-1}\text{O}_y$, where A is the structure stabilizing ion.^[3,4] The negatively charged vacancies in the framework of h-MoO₃ are compensated by positively charged ions A in the tunnels and protons attached to the anionic framework. The most unique feature of this metastable phase is the

*This chapter is published substantially as the first author with reference. ^[28]

existence of a wide one dimensional tunnel (~ 3.5 Å), which allows readily intercalation or movement of the ions.^[4,5] The formation of one dimensional tunnel involves sharing of equatorial oxygen via six MoO₆ octahedra rings along *c*-axis.^[6] While, the sharing of three MoO₆ octahedra rings along *c*-axis forms cavity region called as “trigonal cavity”. In contrast, sharing of four MoO₆ octahedra rings along *a*-axis is accountable for the formation of four-coordinated square window. The metastable phases often show unique or novel properties compared to their thermodynamically stable phase, but preparation of their nanostructured usually put barriers to their applications.

Various allotropic forms of MoO₃, particularly h-MoO₃ have been synthesized via soft chemical routes or “Chimie douce” synthesis.^[7,8] Soft chemical or “chimie douce” synthesis of MoO₃ allotropes or polymorphs is interesting particularly partake of topotactic reactions (preservation of structural elements of the product) and the ability to form metastable derivatives.^[9] The soft chemical route is an effective route for the fine synthesis of inorganic nanomaterials, in which the chemical composition and structure of the precursor system can be altered by the host-guest chemistry, for example, intercalation and ion-exchange reactions.

Since the introduction of “molybdic C-phase” also known as h-MoO₃ phase many efforts have been exerted to synthesize this phase of MoO₃. In the early 1970, most of the authors overlooked the already existed literatures,^[1,2] and claimed the formation of new phase based on virtually identical XRD. The reported overall composition of h-MoO₃ phase varied from MoO₃ · nH₂O to MoO₃ · mNH₃ to MoO₃ · nH₂O · mNH₃, it was Kiss *et al.* who first correctly identified h-MoO₃ phase of MoO₃.^[10] Kumagai *et al.* had attempted to prepare h-MoO₃ using ammonium paramolybdate (H₆₆Mo₇N₆O₂₄) and nitric acid (HNO₃) as the precursor system under chemical precipitation conditions, and the chemical compositions, i.e., [(0.075-0.085)(NH₄)₂O] MoO₃ [0.032-0.42(H₂O)] were assigned to the product.^[5] Despite the long (three days) synthesis procedure, inhomogeneous micro-rods of h-MoO₃ were obtained.

Komaba *et al.* prepared h-MoO₃ phase along with the other phases of MoO₃ using sodium molybdate (Na₂MoO₄) and hydrochloric acid (HCl) as raw material, under hydrothermal conditions.^[11] They found that the ratio of Na⁺/H⁺ ions plays an important role to determine the final phase of the product, for example, Na⁺/H⁺ > 1 gives h-MoO₃,

on the other hand $\text{Na}^+/\text{H}^+ < 1$ forms $\alpha\text{-MoO}_3$ phase. In spite of the better control on the phase, the particle size of the product remained in the micro-meter regime. Thereafter, other synthesis routes were also introduced to synthesize h-MoO₃, for example, Song *et al.* used molybdic acid ($\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$) solution with the ammonia water ($\text{NH}_3 \cdot \text{H}_2\text{O}$) and pH (2-3) of the solution was adjusted using hydrochloric acid (HCl) solution.^[12] They used chemical precipitation followed by hydrothermal route to prepare h-MoO₃ nanorods, but due to lack of structure stabilizing ions the as-prepared phase of h-MoO₃ resembles the hydrated phase, i.e., $\text{MoO}_3 \cdot n\text{H}_2\text{O}$ of MoO_3 . Ramana *et al.* synthesized h-MoO₃ nanorods using chemical precipitation route taking ammonium heptamolybdate hexahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ and nitric acid (HNO_3) as the precursor system,^[13] but the as-obtained nanorods were agglomerated due to quick precipitation of ammonium heptamolybdate. Chithambararaj *et al.* adopted the similar precipitation route to prepare h-MoO₃ nanostructures, but the final products were remained agglomerated.^[14–16]

Recently, Guo *et al.* synthesize h-MoO₃ phase using polyvinylpyrrolidone (PVP) assisted aqueous route using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ and HCl as raw materials.^[17] They assumed that the linear structure of PVP is accountable to initiate the crystallization of h-MoO₃ phase, besides the ratio of H^+/Mo plays a key role for the synthesis of h-MoO₃ phase. The as-prepared h-MoO₃ has homogeneous dispersion of particles, but the size of the particles remained in the micro-meter range.

It is worth to mention that in the aforementioned literatures ammonium heptamolybdate is often chosen as the source of Mo^{6+} ions, and nitric acid or hydrochloric acid is used to alter the pH, but surprisingly the role of ammonium ions contained by the source of Mo^{6+} ions has not been disclosed. Therefore, it is essential to exploit the function of ammonium ions during the formation of h-MoO₃ phase of MoO_3 .

The h-MoO₃ nanostructures have been chosen as the potential host material in Li-ion batteries due to open structure of the h-MoO₃ framework.^[5] Attributed to existence of one dimensional tunnel in h-MoO₃, it is recently been used to catalyze the photo-chemical reactions.^[14] It is assumed that the tunnel structure helps to dissociate the electron (e^-) and hole (h^+) pairs, thereby, increasing their life time. Also, the h-MoO₃ nanostructures are gaining significant attention as a photochromic material due to distortion in the h-MoO₃ framework imposed by the vacancies.^[15,16] Attributed to the multiple oxidation states

(Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺) and the high theoretical specific capacitance (2600 F/g),^[18] MoO₃ in its thermodynamically stable phase (α -MoO₃) has widely been used as an electrode material in supercapacitors,^[19–23] however, the literature is kept devoid of pseudocapacitive behavior of h-MoO₃ phase.

Recently, a kinetically favored intercalation mechanism is introduced to attain high level of specific charge storage (650 C/g) in α -MoO₃, benefiting from iso-oriented and mesoporous nano-crystalline domain of α -MoO₃.^[24] On the other hand, Tang *et al.* enhanced the specific capacitance (280 F/g at 1 mV/s) of α -MoO₃ by using nanoplates-like morphology which facilitates diffusion of electrolyte ions. Most recently, Jiang *et al.* reported the highest achievable specific capacitance (326 F/g) in α -MoO₃ nanobelts, but the loading mass tends to be low (0.50 mg).^[25] Chang *et al.* explored the electronic and electrochemical aspects of α -MoO₃ by introducing the work-function dependent working potential of an asymmetric device based on r-GO- α -MoO₃.^[26] Despite exerting significant efforts the improvement in the performance of α -MoO₃ remained a challenge. Thus, exploring the electrochemical aspects of other crystallographic phases of MoO₃ is of immense interest.

In this chapter, besides introducing a novel route for the synthesis of h-MoO₃ nanostructures, I studied the effect of ammonium ions on the crystallization and morphology of the h-MoO₃ nanostructures. Here, pure molybdenum (Mo) powder in hydrogen peroxide (H₂O₂) is used as the source of Mo⁶⁺ ions. Under solvothermal conditions (at 100 °C for 18 hours), the formation of the h-MoO₃ nanostructures is the result of condensation and de-condensation of poly-peroxo-molybdic acid in the presence of ammonium ions taking hexamethylenetetramine as the source of ammonium ions followed by their pseudocapacitive behaviors. As the loading amount of hexamethylenetetramine increases from 100 mg to 250 mg, the morphology of h-MoO₃ nanostructures changes from pyramidal nanorods- to prismatic nanorods- to hexagonal nanoplates-like morphology. The electrochemical properties of the as-prepared h-MoO₃ nanostructure are evaluated in a three-electrode cell configuration and found that pyramidal nanorods exhibit the highest specific capacitance of 230 F/g at an applied current density of 0.25 A/g than that of the prismatic nanorods (160 F/g) and hexagonal nanoplates (103 F/g). The h-MoO₃ in pyramidal nanorods-like morphology retains about

75% of the initial capacitance upon 3000 cycles. While comparing to its thermodynamically stable, i.e., α -MoO₃ phase, metastable h-MoO₃ shows enhanced electrochemical performance.

4.2 Structural characterization of the products

The crystallographic structure of the samples prepared using hexamethylenetetramine (HMTA) (100 mg, 150 mg and 250 mg) is identified using XRD, as shown in Figure 4.1 (a). The diffraction peaks in the spectra matched exclusively with the hexagonal crystal symmetry of MoO₃ (ICDD-15-5332) with the cell parameters $a=10.54 \text{ \AA}$, $c=3.72 \text{ \AA}$ and cell volume $V=359.37 \text{ \AA}^3$.^[27] At the high loading (250 mg) of HMTA, XRD spectra showed a few impurity peaks that could be due to complex ammonium hydroxides of Mo, i.e., $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{38}$.

TGA was used to examine the thermal stability and chemical purity of the as-prepared materials, as shown in Figure 4.1 (b). Two consecutive weight losses in the temperature range of 150 °C-450 °C are due to removal of water and ammonium molecules, respectively.^[8] The amounts of water and ammonium molecules are determined to be 3.4 %, 1.3 % in the sample prepared using 100 mg of HMTA, 4.5 %, 2.5 % in the sample of 150 mg of HMTA and 3.35 %, 4.95 % in the sample of 250 mg, respectively. Based on the thermal analyses, approximate formula units are derived $(\text{NH}_4)_{0.11}\text{MoO}_3(\text{H}_2\text{O})_{0.28}$ for the sample prepared using 100 mg of HMTA, $(\text{NH}_4)_{0.23}\text{MoO}_3(\text{H}_2\text{O})_{0.39}$ for 150 mg of HMTA and $(\text{NH}_4)_{0.44}\text{MoO}_3(\text{H}_2\text{O})_{0.30}$ for 250 mg of HMTA. The major weight loss for the sample prepared using 100 mg of HMTA is found about 760 °C, and for 150 mg is at about 698 °C and for 250 mg HMTA is at 670 °C. The weight losses at different temperatures suggest that the stability of MoO₆ octahedra in h-MoO₃ structure drops from the sample prepared using 100 mg of HMTA to 250 mg of HMTA.

Figure 4.1 (a) XRD spectra and (b) TGA response of the samples prepared using 100mg (1), 150 mg (2) and 250 mg (3) of HMTA, (c), (d) and (e) FESEM micrographs of the samples prepared using 100 mg, 150 mg and 250 mg of HMTA, respectively. Reproduced from V. Kumar, X. Wang, P. S. Lee, *Nanoscale*, **2015**, 7, 11777, with permission from The Royal Society of Chemistry.^[28]

The morphology of the as-prepared h-MoO₃ nanostructures is examined using FESEM. Figure 4.1 (c), (d) and (e), depict pyramidal-, prismatic- and hexagonal nanoplates-like morphology of the samples prepared using 100 mg, 150 mg and 250 mg of HMTA, respectively. The effect of the concentration of HMTA is found crucial in altering the morphology of h-MoO₃ nanostructures.

The microscopic morphology and features of the as-prepared h-MoO₃ nanostructures were inspected by TEM. Figure 4.2 (a), (b) and (c), unambiguously reveal the pyramidal-, prismatic- and hexagonal nanoplates-like morphology for the samples prepared using 100 mg, 150 mg and 250 mg of HMTA, respectively. The typical diameter of pyramidal-like nanorods is about 100 nm and 400 nm at the tip and base, respectively. Whereas, the diameter of prismatic-like nanorods is about 350 nm. The lateral dimension of hexagonal-

like nanoplates is about 1 μm , while the vertical dimension should be in the range of 50–100 nm. HRTEM micrographs of pyramidal-, prismatic and hexagonal-like nanoplates are shown in Figure 4.2 (d), (e) and (f), respectively. As can be seen in Figure 4.2 (d) and (e) that the spacing between two neighbor fringes is about 0.21 nm and 0.18 nm, correspondent to the d-spacing of (221) and (002) plane of h-MoO₃, respectively.

Figure 4.2 TEM micrographs (a), (b) and (c), HRTEM micrographs (d), (e) and (f) and SAED and FFT patterns (g), (h) and (i) of the samples prepared using 100 mg, 150 mg and 250 mg of HMTA, respectively. The red and yellow spots in SAED images show standard patterns of h-MoO₃. Reproduced from V. Kumar, X. Wang, P. S. Lee, *Nanoscale*, **2015**, 7, 11777, with permission from The Royal Society of Chemistry.^[28]

The inter-fringe spacing in hexagonal nanoplates is found to be related to (101) and (210) plane of h-MoO₃. Moreover, the SAED show diffraction spots along the [-110], [100] and [1-2-1] zone axis for the tip of pyramidal nanorods, prismatic nanorods and hexagonal nanoplates, respectively.

4.3 Growth mechanism of h-MoO₃ nanostructures

The loading amount of HMTA is found crucial to fine tune the physical structure of h-MoO₃ nanostructures. HMTA is a hetero-cyclic, non-ionic organic compound with the chemical composition of (CH₂)₆N₄. At ambient conditions, upon hydrolysis HMTA dissociates into NH₄⁺ and OH⁻ ions. The reaction chemistry of HMTA with the peroxo-molybdic acid is accountable to form the hexagonal lattice. The chemical reaction between hydrolyzed product of HMTA (NH₄⁺ and OH⁻) and peroxo-molybdic acid solution can be expressed according to equation 4.1.

Where the amount of x and y is found to be critical in changing the morphology of the final products.

The pyramidal-like morphology of the nanorods is identified at low loading amount of HMTA (100 mg). The observation of this morphology can be credited to the depletion of the NH₄⁺ ions during synthesis reaction. The interaction between the growth species is constantly altered by the NH₄⁺ ions, when NH₄⁺ ions depleted, the growth of low-surface energy crystal planes takes place at the tip of pyramidal in order to stabilize the physical structure. Any incremental change in the loading amount of HMTA (150 mg) leads to form perfect prismatic-like morphology. Further increase in the loading amount of HMTA (250 mg) produces hexagonal nanoplates-like morphology of the product. The origin of the formation of this morphology lies in the fact that HMTA acts as a reducing agent, which partially reduces Mo⁶⁺ to lower oxidation states Mo^{6-x}. Further growth of the structure is hindered by the dissolution of the product formed by MO^{6-x} species, resulting rough or fractured surface of hexagonal nanoplates is achieved, as revealed by TEM micrograph Figure 4.2 (c).

X-ray photoelectron spectroscopy was conducted to analyze the valence states of Mo and the chemical shift due to different loading amount of ammonium ions. Figure 4.3 (a), (b) and (c) show XPS spectra of Mo atoms presented in pyramidal nanorods, prismatic nanorods and hexagonal nanoplates, respectively. All the spectra, Figure 4.3 (a-c) consist of two well defined binding energy peaks correspond to spin-orbit doublets of Mo⁶⁺(3d_{5/2}) and Mo⁶⁺(3d_{3/2}).^[29] For the pyramidal nanorods, Mo⁶⁺(3d_{5/2}) and Mo⁶⁺(3d_{3/2}) peaks are centered at 235.4 eV and 238.5 eV. Whereas, for prismatic nanorods, Mo⁶⁺(3d_{5/2}) and Mo⁶⁺(3d_{3/2}) peaks are identified at 234.9 eV and 238.2 eV, while for hexagonal nanoplates, they observed at 234.2 3 eV and 238 eV. The as reported binding energies are well commensurate with the previous literatures.^[29,30] With regards of the binding energies of Mo atoms in pyramidal nanorods, a negative shift of about 0.5 eV and 0.7 eV is identified in prismatic nanorods and hexagonal nanoplates, respectively. The shift in the binding energies is suggestive of the lowering of the valence state of Mo from pyramidal nanorods to prismatic nanorods to hexagonal nanoplates.

Figure 4.3 XPS spectra (a), (b) and (c) of Mo atoms, and (d), (e) and (f) of N atoms presented in pyramidal nanorods, prismatic nanorods and hexagonal nanoplates, respectively. Reproduced

from V. Kumar, X. Wang, P. S. Lee, *Nanoscale*, **2015**, 7, 11777, with permission from The Royal Society of Chemistry.^[28]

Besides lowering in the valance state, the integrated intensities of the profiles decreases from pyramidal nanorods to hexagonal nanoplates, which indicate the pyramidal nanorods hold higher content of Mo⁶⁺ ions. As discussed in the growth mechanism of the nanostructures, this change in the binding energies of Mo atoms could be due to different loading amount of ammonium ions. To verify this assumption, XPS analyses of N1s atoms are also performed, as shown in Figure 4.3 (d), (e) and (f) for pyramidal nanorods, prismatic nanorods and hexagonal nanoplates, respectively. N1s centered at 401 eV for all three samples is due to NH₄⁺ ions.^[31] The integrated intensities of N1s peaks is found to be increased from pyramidal nanorods to hexagonal nanoplates, which indicate N content increases from pyramidal nanorods to hexagonal nanoplates.

A shake-up satellite peak is identified at 404 eV for all three samples that could be due to non-stoichiometry of NH₄⁺ ions generated by the N-O complexes, however, not much is known about this behavior.^[32] The trend in the content of ammonium ions in all three samples, as revealed by XPS corroborates with the TGA analyses, Figure 4.1 (b).

4.4 Electrochemical characterization of h-MoO₃ nanostructures

It is generally acknowledged that the electrochemical performance of the electrode materials can be altered by tuning the morphology and particle size of the materials.^[33–35] The electrochemical properties of h-MoO₃ in three different morphologies were studied in a three-electrode cell configuration using 1 M H₂SO₄ as electrolyte. Cyclic voltammograms (CVs) of pyramidal, prismatic and hexagonal nanoplates are carried out at a scan rate of 25 mV/s, as shown in Figure 4.4 (a). The observation of two sets of redox peaks, i.e., A/A' and B/B' in the CVs indicates pseudocapacitive response of h-MoO₃ nanostructures due to reversible reduction and oxidation of Mo⁶⁺/Mo⁴⁺ and Mo⁶⁺/Mo⁵⁺, respectively.^[36,37] A slight shift in the redox peak potentials could be due to the reaction potential which is very sensitive towards the microscopic features of the nanostructures.^[33] CVs of all three samples at higher scan rates are presented in Appendix, Figure 1. The reduction and oxidation of Mo centers in h-MoO₃ at various

intercalation sites, i.e., hexagonal window (HW), trigonal cavity (TC) and four-coordinated square window (SW), is accompanied by ingress and digress of H⁺ ions according to equation 4.2.

The ingress/digress of electrolyte ions into the various intercalation sites depends on the electrode potential, e.g., $0.1 \leq V \leq 0.3$ (SW), $0.3 \leq V \leq 0.6$ (TC) and $V \geq 0.7$ (HW).

I assume that due to anisotropic distribution of ammonium ions into the lattice of h-MoO₃, the ingress/digress of H⁺ into the various intercalation sites is facilitated by NH₄⁺ ions. It is commonly believe that the proton conduction in hydrated materials occur via the Grotthuss (H₂O, H₅O₂⁺, H₃O⁺, OH⁻, etc.),^[38] or Vehicle (H₂O, NH₄⁺, N₂H₅⁺, CH₃NH₃⁺, etc.),^[39] types mechanism facilitated by the water molecules or proton carriers. In our case, h-MoO₃ contains NH₄⁺ and H₂O molecules, therefore, the charge-conduction mechanism may favor the Vehicle mechanism. In solids, Vehicle mechanism is limited to the materials with layered and open lattice structures.^[40,41] Moreover, it is believed that the materials with the lower amount of water molecules (<2 H₂O) conducts protons via Vehicle mechanism.^[42] In the lattice of h-MoO₃, water molecules (<2H₂O) are coordinatively attached with MoO₆ octahedra, which do not favor the formation of Zundel cations, i.e., H₅O₂⁺ (vital for Grotthuss mechanism).^[43] Thus, the conduction of protons in h-MoO₃ is more likely facilitated via Vehicle mechanism.

In order to insight the redox process in h-MoO₃ nanostructures, scan rate dependent peak current analysis was performed, as shown in Figure 4.4 (b). The linear change in the peak current vs. scan rate analysis indicates that the redox process is controlled by diffusion controlled charge transfer process.^[44] The slope of the peak current vs. scan rate curve can be used to deduce the electrochemically active area of the electrode, on the basis of the Randle-Sevcik equation 4.3.^[44]

$$I_p = 2.69 \times 10^5 D^{1/2} n^{3/2} \nu^{1/2} c A \quad (\text{eq. 4.3})$$

Where I_p is the peak current (anodic or cathodic), D is the diffusion coefficient ($D=1.55 \times 10^{-10} \text{ cm}^2/\text{s}$),^[45] n is the number of the transferred electrons/molecules ($n=1$), ν is the scan rate (1 mV/s-100 mV/s), c is the concentration of the electrolyte (1 M) and A is the area of the electrodes (cm²). Thus, the slope of the curves for pyramidal nanorods is found to be 1.5 times and 2 times higher than that of the prismatic nanorods and hexagonal

nanoplates, respectively, which is directly proportional to the electrochemically active surface area of the electrodes.

Figure 4.4 (a) Cyclic voltammograms of pyramidal nanorods (1), prismatic nanorods (2) and hexagonal nanoplates (3), and (b) peak current response of the as-prepared electrodes with respect to the square root of the scan rate, the dotted lines in Figure (b) indicates fitting profiles according to equation $y = a + bx$. Reproduced from V. Kumar, X. Wang, P. S. Lee, *Nanoscale*, **2015**, 7, 11777, with permission from The Royal Society of Chemistry.^[28]

It is worth gaining attention that the BET surface area (Appendix, Figure 2) of pyramidal nanorods (2.2 m²/g) and prismatic nanorods (1.92 m²/g) commensurates with the electrochemically active surface area (with the similar pore size of 15 nm and 20 nm for pyramidal nanorods and prismatic nanorods samples, respectively). Whereas, the hexagonal nanoplates sample with a higher BET surface area (7.86 m²/g) and larger pore size (~40 nm) does not translate to electrochemically active surface area, likely due to the ineffective bonding of electrolyte ions at the pore walls with reduced electric field that leads to sluggish redox reactions.^[46] Therefore, it is evident from the peak current vs. scan rate analysis that the pyramidal nanorods exhibit more electrochemical active area which results in improved electrochemical performance

The specific capacitance of the as-prepared electrodes is calculated taking Galvanostatic charge/discharge analysis into account. Figure 4.5 (a) shows the Galvanostatic charge/discharge curves of pyramidal nanorods, prismatic nanorods and hexagonal nanoplates at an applied current density of 0.25 A/g. The non-linearity associated with

the charge/discharge curves further confirms the pseudocapacitive behavior of h-MoO₃ nanostructures.^[47] The specific capacitance from the charge/discharge curves is calculated using integral form of the capacitance, as presented by equation 4.4.^[48]

$$C_{sp} = 2I \int V dt / m \Delta V^2 \quad (\text{eq. 4.4})$$

Where C_{sp} is the specific capacitance, V is the potential, I is the applied current, m is the mass of active electrode and ΔV is the potential window. The specific capacitance of 230 F/g, 160 F/g and 103 F/g are calculated for pyramidal nanorods, prismatic nanorods and hexagonal nanoplates, respectively, at an applied current density of 0.25 A/g. The loading mass of the active material in all three electrodes was about 1 ± 0.2 mg. Attributed to the higher loading amount of Mo⁶⁺ or lower content of ammonium ions possessed by pyramidal nanorods which results in an improved specific capacitance. The specific capacitance exhibited by h-MoO₃ nanostructures is distinctly better than that of α -MoO₃ nanorods (30 F/g at 1 mV/s),^[19] α -MoO₃ nanowires (95 F/g at 0.2 A/g),^[49] α -MoO₃ nanoribbons (140 F/g at 1.3 A/g),^[47] and comparable to α -MoO₃ nanoplates (280 F/g at 1 mV/s),^[20] and lesser than that of α -MoO₃ nanobelts (369 F/g at 0.1 A/g) nanobelts.^[25]

I attribute the exposure of the desirable crystallographic planes to be of significance interest. The hexagonal framework of h-MoO₃ resembles the hexagonal framework of h-WO₃.^[50] The occupancies of stabilizing ions, i.e., ammonium ions affect the allocation of intercalation sites. The hexagonal framework of h-MoO₃ contains of three different types of intercalation sites, i.e., hexagonal window (HW), trigonal cavity (TC) and four-coordinated square window running along [001] direction, as shown in Figure 4.5 (b)-i.^[51] Among the various intercalation sites, most of the space of HW site is preoccupied by the ammonium ions to stabilize the framework. In contrary, TC and SW are positioned along [001] and [100] directions, respectively. It is believed that TC cavity site can accommodate large higher amount of electrolyte ions then that of the rest intercalation sites.^[51] In our case, pyramidal nanorods are constructed by (100) and (-110) planes (shadow region in Figure 4.5 (b)-ii and iii) representing the base and tip of pyramidal nanorods, respectively, whereas, prismatic nanorods hold (100) plane only (shadow region in Figure 4.5 (b)-ii). Besides (100) plane, existence of (-110) plane in pyramidal nanorods enables additional degree of freedom to electrolyte ions to intercalate into TC and SW sites.

Figure 4.5 Charge/discharge profiles of (1) pyramidal nanorods, (2) prismatic nanorods and (3) hexagonal nanoplates are performed at an applied current density of (a) 0.25 A/g, (b) Atomic representation of hexagonal framework in the various plane configurations, (c) Cycling test of pyramidal nanorods, prismatic nanorods and hexagonal nanoplates using cyclic voltammetry (CV) at a scan rate of 50 mV/s and (d) Nyquist plots of pyramidal nanorods (1), prismatic nanorods (2) and hexagonal nanoplates (3) in a frequency bandwidth of 100 mHz to 100 kHz at open circuit potential (OCP). The inset shows the response of the as-prepared electrodes (pyramidal and prismatic nanorods) in the high frequency region (100 kHz-10 mHz). In the inset of figure (d) (Randles circuit), R_s , Z_d , R_c and C_{dl} indicates solution resistance, diffusion resistance or Warburg resistance, charge transfer resistance and double layer capacitance, respectively. Reproduced from V. Kumar, X. Wang, P. S. Lee, *Nanoscale*, **2015**, 7, 11777, with permission from The Royal Society of Chemistry.^[28]

The observation of two distinct redox peaks in CV analysis of pyramidal nanorods correspond to intercalation into SW ($0.1 \leq V \leq 0.3$) and TC ($0.3 \leq V \leq 0.6$), a similar behavior of was also identified in structurally identical Na doped V₂O₅.^[52] The inferior charge storage response of hexagonal nanoplates is due to not only the higher loading amount of

ammonium ions or lower content of Mo⁶⁺ ions but also the crystal plane, i.e., (1-2-1) exposed by them. The (1-2-1) plane of hexagonal nanoplates predominantly exposes HW and TC sites, which are preoccupied by the ammonium ions, the shadow region in Figure 4.5 (b)-iv represents (1-2-1) plane of h-MoO₃. Thus, the availability of SW sites in hexagonal nanoplates gives rise to the redox peaks, as shown in CV analyses, Figure 4.4 (a).

The long term cycling stability is crucial in supercapacitors applications, cycling up to 1000 cycles is necessary to demonstrate the reliability of the material. However, in case of α -MoO₃ only up to 1000 or less cycles are reported.^[19,20,25,47,49] To demonstrate electrochemical stability of h-MoO₃ nanostructure during continuous cycles, cyclic voltammetry test was conducted at a scan rate of 50 mV/s for 3000 cycles, as shown in Figure 4.5 (c). A capacitance of 74%, 65% and 62% of initial capacitance is retained after 3000 cycles for pyramidal nanorods, prismatic nanorods and hexagonal nanoplates, respectively. Despite achieving the good cycling stability in pyramidal nanorods, early stage (~300 cycles) degradation (~12%) is observed. To address this issue, an electrode without addition of carbon black and PVDF bonder was prepared using pyramidal nanorods, and was subjected to first 300 cycles. FESEM micrographs (Appendix, Figure 3) reveal that the early stage degradation is probably due to breakage of pyramidal nanorods. The breaking mechanism of h-MoO₃ particles can be expressed as: pyramidal nanorods can hold relatively higher amount of electrolyte ions, resulting in partial reduction of Mo⁶⁺ ions into Mo⁵⁺ ions. The Mo⁵⁺ ions are known to be mobile, and come out from the framework, now the surplus negative charges due to removal of Mo⁵⁺ ions can be compensated by H⁺ ions, as a result the framework is subjected to cyclic stress condition. Eventually, the framework of the nanostructures breaks at the low energy sites, i.e., the tip of the nanorods, and isolate the tip and base of pyramidal nanorods.

The electrochemical impedance spectroscopy (EIS) is performed to evaluate the charge transfer resistance and kinetics of the electrodes materials. Nyquist plot in Figure 4.5 (d) shows the charge transfer characteristics of pyramidal nanorods, prismatic nanorods and hexagonal nanoplates in the high (100 Hz-100 kHz) as well as low (<100 Hz) frequency regions. A semicircle in the high frequency region indicates the charge transfer resistance associated with the faradic reactions.^[48] Randles circuit diagrams are used to evaluate EIS

parameters (R_s , C_{dl} , R_c and Z_d), as presented in the inset of Figure 4.5 (d). The values of the parameters are presented in Table 4.1. As can be seen from the Nyquist plot that pyramidal nanorods bears low intercept value ($\sim 5.03 \Omega$) on the real axis, which indicates its low internal resistance (solution resistance R_s and other ohmic components) comparing with prismatic nanorods ($\sim 5.79 \Omega$) and hexagonal nanoplates ($\sim 6.31 \Omega$). A slight kink in the high frequency region (prismatic and pyramidal nanorods) is identified which could be due to adsorption of electrolyte ions with the surface of the electrodes, formation of a new resistive element takes place.^[53] In the low frequency region, sloping lines are related to the diffusive resistance (Warburg resistance) abided by electrolyte ions while emerging into the interior of host material.

Table 4.1 Calculated values of EIS elements from the Randles circuit,^[28]

Sample	R_s/Ω	R_c/Ω	Z_d/Ω	C_{dl}/mF
1-Pyramidal nanorods	5.03	0.10	9.71	2.31
2-Prismatic nanorods	5.79	0.16	10.2	2.73
3-Hexagonal nanoplates	6.31	0.45	11.71	3.01

4.5 Summary

In this chapter, a novel solvothermal route to prepare nanostructures of metastable h-MoO₃ phase of MoO₃ in various morphologies is successfully demonstrated. The loading amount of hexamethylenetetramine is found accountable not only to stabilize the h-MoO₃ phase but also to tune the physical structure of h-MoO₃ nanostructures. The pyramidal nanorods-like morphology is formed due to depletion of ammonium ions, whereas, the hexagonal nanoplates-like morphology is obtained due to excess of ammonium ions. The approximate chemical formula units of (NH₄)_{0.11}(H₂O)_{0.28} MoO_{2.89}, (NH₄)_{0.23}(H₂O)_{0.39} MoO_{2.77} and (NH₄)_{0.44}(H₂O)_{0.30} MoO_{2.56} are derived for pyramidal nanorods, prismatic nanorods and hexagonal nanoplates, respectively, taking thermal analysis in account. The (100) plane of h-MoO₃ is found to be common between pyramidal and prismatic nanorods, which is accountable to construct base of the nanorods. TGA and XPS analyses reveal that pyramidal nanorods uphold higher content of Mo⁶⁺ ions due to lower loading of ammonium ions.

The electrochemical performance of pyramidal nanorods (210 F/g) is found distinctly better than that of the prismatic nanorods (160 F/g) and hexagonal nanoplates (103 F/g) at an applied current density of 0.25 A/g. Besides the higher content of Mo⁶⁺ in pyramidal nanorods, the co-existence of (100) and (-110) planes enable additional intercalation sites, i.e., TC and SW to intercalate electrolyte ions. Also, the existence of ammonium ions facilitates the mechanism of charge storage via Vehicle assisted proton transportation. This represents the first attempt of preparing h-MoO₃ phase in various morphologies for electrochemical capacitors, delivering possibilities in catalytic, sensing and solar applications.

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Chapter 5*: Redox-active polyaniline-hexagonal-MoO₃ hollow nanorods for improved pseudocapacitive performance

The combinatorial approach in preparing nanocomposites of transition metal oxides and conducting polymers has gained significant interest due to their outstanding pseudocapacitive response which comes from coupled kinetics of the redox reactions. In this chapter, firstly I demonstrate a facile approach to prepare nanocomposites of polyaniline-h-MoO₃ hollow nanorods. The introduction of ferric ions played dual role; to form h-MoO₃ hollow structure via cation-exchange assisted Kirkendall effect, and as an oxidant to initiate polymerization of aniline monomers. Thereafter, the electrochemical properties of the as-prepared nanocomposites are studied in a three-electrode cell configuration. Lastly, key findings of the study are summarized.

5.1 Introduction and Motivation

In chapter 4, synthesis of h-MoO₃ nanostructures in various morphologies was demonstrated. Among them, h-MoO₃ in pyramidal nanorods-like morphology showed distinctively better electrochemical performance. In that study, altering the crystallographic structure of MoO₃ was employed so as to enable additional intercalation sites to facilitate the intercalation of electrolyte ions. Apart from altering the crystallographic structure of MoO₃, the conduction of electrolyte ions can be further facilitated by decorating the materials with conductive reagent, such as conductive polymers. In order to achieve an improved electrochemical performance, I propose to fabricate nanocomposites of structurally modified h-MoO₃, i.e., h-MoO₃ hollow nanorods with polyaniline.

The nanocomposites of conducting polymers with transition metal oxides have been synthesized in various morphologies,^[1–3] among them core-shell structure is of immense interest due to its unique characteristics.^[4,5] Usually, the electrode materials that exhibit high electrochemical performance employ conducting polymer as shell to enable better

*This chapter is published substantially as the first author with reference. ^[35]

electrical contacts with the other nanostructures and current collector, while less conducting material or transition metal oxide as the core material.^[6,7] Thus, exploring core-shell aspect of h-MoO₃-polyaniline is expected to improve the pseudocapacitive performance.

An extensive research is in progress to improve the electrochemical performance of thermodynamically stable phase of MoO₃, i.e., α -MoO₃.^[8] In the recent years several strategies, including coating of conductive polymers,^[9,10] deposition of other transition metal oxides,^[11,12] or carbon based materials,^[13,14] etc. are adopted more often to enhance the pseudocapacitive performance of the nanocomposites. Among them, coating of conductive polymers is considered to be promising due to tunable physicochemical properties of the polymer additives during polymerization process. There are three routes documented to prepare such nanocomposites: intercalation of monomers into the host matrix followed by oxidation due to an external agent,^[15] second, redox nature of host matrix enables the intercalation as well as polymerization,^[16] and third, direct intercalation of polymer macromolecules into the host galleries.^[17] In the past recent years, Zheng *et al.* prepared nanocomposites of polyaniline- α -MoO₃ nanosheets and polyaniline- α -MoO₃ nanotubes taking second approach into account in which MoO₃ host initiates intercalation and concomitant polymerization of aniline monomers.^[18] In their approach, they used peroxo-molybdate as a host as well as an oxidant to polymerize aniline monomers, because the oxidation potential of peroxo-molybdate (~1.5 V) was sufficient to achieve polymerization of aniline (~0.5 V is required to initiate the polymerization). The maximum specific capacitance that could be achieved was 180 F/g and 200 F/g for polyaniline- α -MoO₃ nanotubes and polyaniline- α -MoO₃ nanosheets, respectively, which is lesser than that of the specific capacitance of pure 2D α -MoO₃ nanoplates (280 F/g).^[19]

Liu *et al.* prepared nanocomposites of polypyrrole- α -MoO₃ nanobelts using sodium dodecylbenzenesulfonate (NaDBS) and ferric chloride (FeCl₃) as surfactant and oxidant (oxidation potential ~1.2), respectively.^[20] In their study, surprisingly they found that the specific capacitance of polypyrrole decorated- α -MoO₃ nanobelts (110 F/g) is lesser than that of α -MoO₃ nanobelts (125 F/g), in the first cycle of charge/discharge, which is a bit unusual. However, the specific capacitance of α -MoO₃ nanobelts fades quickly after

several cycles, whereas, the as-prepared nanocomposites remain stable under prolonged cycles. Nevertheless achieving the stable performance, the fundamental aspects of the nanocomposites remained unanswered,^[21] which could be critical on deciding the actual performance of the electrode material.

Xia *et al.* fabricated polyaniline decorated MoO₃ nanoparticles under in situ polymerization using ammonium persulfate and Mo₃O₁₀ (C₆H₈N)₂ · 2H₂O as the oxidant and source of aniline and Mo, respectively.^[22] The highest specific capacitance that could be attained by the as-prepared nanocomposites was about 200 F/g. The low specific capacitance value of the as-prepared nanocomposites is reported to be due to agglomeration of MoO₃ nanoparticles, resulting in the formation of micro-particles assembly.

Zhang *et al.* presented branch-like MoO₃/polypyrrole hybrids to achieve enhanced electrochemical performance.^[10] In their preparation route ammonium persulfate [(NH₄)₂S₂O₈] was utilized as an oxidant (oxidation potential ~2.01 V) for the polymerization of pyrrole monomers. Here, the maximum achievable specific capacitance attained by the nanocomposites (123 F/g) was higher than that of pure branch-like MoO₃ (25 F/g). However, a degradation of about 20% in the initial capacitance is observed after just 200 cycles of charge/discharge.

Most recently, Jiang *et al.* fabricated coaxial polyaniline-MoO₃ nanobelts heterostructure assembly under hydrothermal conditions followed by in situ polymerization using ammonium persulfate.^[9] It was found that the as-prepared nanocomposites showed spectacularly high specific capacitance of 632 F/g at an applied current of 1 A/g, whereas, pristine MoO₃ nanobelts showed 275 F/g. From their investigation, it was identified that the rate behavior of pristine MoO₃ nanobelts (~76 %) is better than that of polyaniline-MoO₃ nanobelts (~60 %), which is not consistent with the previous investigations.^[20–22]

Therefore, to tackle with the shortcomings associated with these nanocomposites, I propose a combinatory approach to modify not only the surface of nanorods but also their physical structure (solid nanorods to hollow nanorods) to minimize the number of boundaries between electrode and electrolyte.

The physical structure of nanomaterials can be altered by numerous approaches, for example, Kirkendall effect,^[23] Galvanic replacement,^[24] cationic or anionic

replacement,^[25] Ostwald ripening,^[26] etc. These approaches are known to produce a hollow architecture with great control on the composition and pore structure, which are basically essential to promote electrochemical reactions. The hollow nanostructures offer several unique characteristics, such as higher active surface area, short diffusion path for electrolyte ions, effective utilization of active material and ability to accommodate volume change during ingress/digress of electrolyte ions.^[27] Recently, Chen *et al.* and Wang *et al.* have demonstrated the use of hollow nanocomposites of graphene/MnO₂ and graphene/Co₃O₄, respectively, to achieve an improved electrochemical performance.^[28,29] Likewise, Guan *et al.* illustrated that the gap between the interfaces is essential to grasp an improved electrochemical response.^[30] In their demonstration, they used NiO or CoO nanowalls enclosed by TiO₂ nanotubes, realizing a “wall in a box” configuration. Most recently, Hunag *et al.* presented hollow CuO/MnO₂ nanostructure to improve the cycling stability of the hybrid assembly up to 93% of the initial value upon 1000 cycles.^[31] In this chapter, I describe the formation of h-MoO₃ hollow nanorods using cation-exchange assisted Kirkendall effect. A facile oxidative chemical polymerization of aniline monomers is presented taking ferric chloride as an oxidant. The fast and efficient polymerization of aniline monomer is realized due to unique chemistry of h-MoO₃. Due to partake of surface controlled and diffusion controlled redox reactions, an improved specific capacitance of 270 F/g at an applied current density of 1 A/g is achieved for polyaniline-h-MoO₃ hollow nanorods (PANI@h-MoO₃ HNs), which is higher than that of h-MoO₃ hollow nanorods (h-MoO₃ HNs) (126 F/g) and polyaniline (PANI) (180 F/g). Also, the as-presented strategy is helpful to improve the cycling stability up to 76% upon 5000 cycles of charge/discharge.

5.2 Structural characterization

X-ray diffraction was used to identify the crystallographic structure of the as-prepared samples. The XRD patterns of the samples, as shown in Figure 5.1 (a) can be easily indexed to hexagonal phase of MoO₃ (ICDD-29-0115).^[32] An intense peak at $2\theta \sim 25.6$ depicts the character of hexagonal phase of MoO₃. On the other hand, a diffraction peak at $2\theta \sim 14.4$ in the spectra of PANI indicates formation of PANI in monoclinic structure, while the other peaks at $2\theta \sim 20.4$ and $2\theta \sim 25.2$ render information about the periodicity of partially oxidized and reduced chains of PANI.^[33] These peaks also represent the

distance between two adjacent benzene rings.^[34] The peaks position for individual component in the XRD pattern of PANI@h-MoO₃ HNs is found unchanged, which indicates the attachment of PANI chains does not induce any change in h-MoO₃. Thus, the analyses presented herein suggest that the polymerization of aniline strictly happens on the surface of h-MoO₃.

Figure 5.1 (a) XRD patterns, and (b) TGA characteristics of (1) PANI@h-MoO₃ HNs, (2) PANI, and (3) h-MoO₃ HNs. Adapted with permission from V. Kumar, P. S. Lee, *J. Phys. Chem. C*, **2015**, 119, 9041. Copyright (2015) American Chemical Society.^[35]

TGA is conducted to examine the chemical composition and purity of the as-prepared samples. The loading amount of PANI on the surface of h-MoO₃ hollow nanorods is determined to be about 15 wt. %, as shown in Figure 5.1 (b). In the weight loss (%) vs. temperature analysis, the first weight loss (<200 °C) corresponds to the removal of moisture or water content from the lattice of all three samples. A second weight loss from 200 °C to 400 °C is due to the removal of ammonium ions and dopant or impurity from h-MoO₃ and PANI or PANI @ h-MoO₃ HNs, respectively.^[32] While a third weight loss in PANI and PANI@h-MoO₃ HNs occurred in the range of 400 °C -500 °C is due to the structural decomposition of PANI chains.^[36] The gradual decomposition (after 500 °C) of PANI@h-MoO₃ HNs indicates good thermal stability of PANI chains at the surface of h-MoO₃ HNs when compared with PANI only.

Figure 5.2 IR spectra of (1) PANI@h-MoO₃ HNs, (2) PANI, and (3) h-MoO₃ HNs. Adapted with permission from V. Kumar, P. S. Lee, *J. Phys. Chem. C*, **2015**, 119, 9041. Copyright (2015) American Chemical Society.^[35]

The presence of PANI on the surface of h-MoO₃ hollow nanorods was further evaluated using IR spectroscopy in absorption mode, as shown in Figure 5.2. The absorption peaks located at 692 cm⁻¹, 868 cm⁻¹ and 966 cm⁻¹ are observed in the spectra of pristine h-MoO₃ HNs and PANI@h-MoO₃ HNs, which can be assigned to an in-plane vibration of MoO₄²⁻ units, stretching of O–O bond and stretching of terminal oxygen (M=O) atom, respectively.^[37] The absorption bands at 1428 cm⁻¹ and at 1609 cm⁻¹ are due to the stretching and deformation of NH₄⁺ and absorbed –OH groups on the surface of h-MoO₃, respectively.^[32] It is worth to gain attention that the intensity of the band at 868 cm⁻¹ decreased significantly after the polymerization of aniline on the surface of h-MoO₃ HNs. This is due to protonated nitrogen atoms of anilinium salt, which prefer to attach with the surface oxygen atoms, while the absence of the band at 1609 cm⁻¹ in case of PANI @ h-MoO₃ HNs suggests the consumption of –OH groups during the attachment process. An IR band at 1107 cm⁻¹ correspond to delocalization of electrons in PANI and stretching of N=Q=N (Q is quinoid ring).^[38] A couple of bands located at 1233 cm⁻¹ and 1291 cm⁻¹ can be assigned to the stretching of C–N bond.^[39] An IR band at 1441 cm⁻¹ indicates vibration of rings 1, 3, 4 in the chain of PANI. The IR bands observed at 1479 cm⁻¹ and 1564 cm⁻¹

are correspond to stretching vibration of quinoid and benzenoid ring,^[7] respectively, suggest the as-prepared PANI is in emeraldine state rather than leucoemeraldine or pernigraniline state. Therefore, IR spectroscopy confirms the existence of both the constituents, i.e., PANI and h-MoO₃ in the as-prepared nanocomposites of PANI@h-MoO₃ HNs. IR spectrums of PANI@h-MoO₃ HNs (prepared using higher molar ratio of oxidant to aniline, i.e., 1.7 and 1.2) depict as the molar ratio increases a blue shift in the IR band (corresponding to delocalization) is noticed, as shown in Appendix, Figure 4. This shift in the frequency may be ascribed to the over-oxidation of PANI chains due to relatively higher concentration of the oxidant ions.^[40]

Figure 5.3 FESEM micrographs of (a) h-MoO₃ HNs and (b) PANI@h-MoO₃ HNs and TEM micrographs of (c) h-MoO₃ HNs and (d) PANI@hMoO₃ HNs. Adapted with permission from V. Kumar, P. S. Lee, *J. Phys. Chem. C*, **2015**, 119, 9041. Copyright (2015) American Chemical Society.^[35]

The morphology and physical structure of h-MoO₃ HNs and PANI@h-MoO₃ HNs are examined using FESEM and TEM, as shown in Figure 5.3 (a-b) and (c-d), respectively. The pyramidal hollow nanorods-like morphology can be seen in Figure 5.3 (a), and Figure 5.3 (b) shows the morphology of h-MoO₃ hollow nanorods after polymerization of aniline. From TEM micrographs, it is evident that the as-polymerized nanorods form a core-shell structure, as can be seen in Figure 5.3 (d). Figure 5.3 (c) shows TEM micrograph of the pristine h-MoO₃ HNs. The thickness and morphology of the PANI shell on the surface of h-MoO₃ HNs can be controlled by tuning the molar ratio of oxidant to aniline, i.e., 1.2 and 1.7. With an increase in the molar ratio of oxidant to aniline, the PANI coating changes from fractal-like shell to a more uniform and smooth layer as evaluated by TEM analysis (shown in Appendix, Figure 5).

5.3 Formation of h-MoO₃ HNs and mechanism of polymerization

MoO₃ is an acidic transition metal oxide due to existence of unsaturated coordination of MoO₆ octahedra, which acts as Lewis acid sites, and pH value of h-MoO₃ solution in our case was found to be about 4.3, at ambient conditions. When a solution of ferric ions introduced into the solution of h-MoO₃ nanorods, the formation of h-MoO₃ hollow nanorods takes place, the mechanism of this behavior can be schematically illustrated on the basis of cation-exchange assisted Kirkendall effect, as shown in Scheme 5.1 (a).^[35]

Scheme 5.1 Schematic representations of the steps involved during (a) the formation of h-MoO₃ hollow nanorods via Kirkendall mechanism and (b) oxidative chemical polymerization of aniline using ferric ions.

Kirkendall assisted exchange of cations disembarks in the polar solvents, containing the solvated form of ionic salt and non-solvated form of ionic or polar compounds.^[25,41] Here, water was used as the polar solvent containing the solvated form of Fe³⁺ ions and non-solvated form of h-MoO₃ nanorods. The exchange of Mo⁶⁺ ions by Fe³⁺ ions can be elucidated as follows: (1) initially, a diffused layer of Fe³⁺ ions on the surface of h-MoO₃ nanorods forms via inward diffusion of Fe³⁺ ions near to the surface layer of h-MoO₃, then (2) exchange of Mo⁶⁺ ions with the Fe³⁺ ions, and (3) outward diffusion of Mo⁶⁺ ions through the pores of h-MoO₃, followed by dissolution of Mo⁶⁺ ions into the bulk solution. The inward diffusion of Fe³⁺ ions can be considered as the rate limiting step of this exchange. Thus, the bulk of h-MoO₃ nanorods dissolve into the ionic solution via removal of Mo⁶⁺ ions, and only the anionic structure intact with the parent framework, which is accountable for the formation of hollow structure. Thermodynamic aspects, such as surface free energy of the structure can also be taken into account for selective etching of the structure.

The mechanism of aniline polymerization on the surface of h-MoO₃ hollow nanorods can be schematically illustrated on the basis of the Scheme 5.1 (b). The pK_a value for the anilinium monomers (conjugated acid of aniline) is of the order of 4.6, with a positively charged nitrogen atom out of the ring.^[42] The polymerization of anilinium monomers occur near the surface due to diffused layer of Fe³⁺ ions, simultaneously, the polymerized chains attach with h-MoO₃ surface due to availability of –OH functional groups, as verified by IR spectroscopy, Figure 5.2.

5.4 Electrochemical characterization of PANI@h-MoO₃ HNs

The apparent advantages of using hollow nanostructure are that they increase the number of accessible active sites, shorten the diffusion path, and efficiently can accommodate a large volume change during ingress/digress of electrolyte ions.^[27] It is evident from the area enclosed by cyclic voltammograms, Figure 5.4 (a) that h-MoO₃ HNs have better charge storage capability than that of h-MoO₃ nanorods. The detailed electrochemical performances of PANI@h-MoO₃ HNs and h-MoO₃ HNs and PANI are investigated using cyclic voltammetry (CV) and Galvanic charge/discharge methods. As depicted in Figure 5.4 (b), the introduction of PANI shell further improves the charge storage capability of

h-MoO₃ HN. The obvious redox peaks in CVs for all three samples suggest that the redox process involves faradic redox reactions. At a slow scan rate of 1 mV/s, a pair of redox peaks appeared at 0.40 V/0.23 V and 0.49 V/0.44 V in case of h-MoO₃ HN due to intercalation of electrolyte ions into various intercalation sites of h-MoO₃. For PANI, a pair of redox peaks located at 0.22 V/0.12 V and 0.53 V/0.43 V is due to transition from semiconducting state (leucoemeraldine form) to conducting state (polaronic emeraldine form) and faradic transformation of emeraldine to pernigraniline state, respectively.^[43] It is noteworthy that the nanocomposites of PANI@h-MoO₃ HN exhibit the characteristic of both the constituents, i.e., PANI and h-MoO₃ HN.

Figure 5.4 Cyclic voltammograms of (a) h-MoO₃ nanorods and h-MoO₃ hollow nanorods, and Cyclic voltammograms of (1) PANI@h-MoO₃ HN, (2) PANI, and (3) h-MoO₃ HN at a scan rates of (a) 1 mV/s and (b) 100 mV/s, respectively. Adapted with permission from V. Kumar, P. S. Lee, *J. Phys. Chem. C*, **2015**, 119, 9041. Copyright (2015) American Chemical Society.^[35]

In contrary, when the scan rate increased to 100 mV/s only those ions immediately next to the interface respond to the external electric field, as a result an increased capacitive

behavior is identified in PANI@h-MoO₃ HNs and PANI, whereas, h-MoO₃ HNs showed poor electrochemical response due to lack of proper utilization of intercalation sites at relatively higher scan rate, as shown in Figure 5.4 (c). This response indicates that PANI plays a vital role to enhance the charge storage capability of the nanocomposites. CVs of all three samples are shown in Appendix, Figure 6. The electrochemical performance of the nanocomposites prepared using oxidant/aniline molar ratio ~1, are found better than that of the rest of the nanocomposites prepared using higher molar ratios, as presented in Appendix, Figure 7.

The specific capacitance of the as-prepared electrodes is determined using Galvanostatic charge/discharge method. Charge/discharge response of PANI@h-MoO₃ HNs, PANI and h-MoO₃ HNs at an applied current density of 1 A/g is presented in Figure 5.5 (a). The specific capacitance as high as 270 F/g, 180 F/g and 126 F/g is achieved at an applied current density of 1 A/g for PANI@h-MoO₃ HNs, PANI, h-MoO₃ HNs, respectively. The specific capacitance of PANI@h-MoO₃ HNs is found higher than that of PANI- α -MoO₃ nanoparticles (200 F/g),^[22] PANI- α -MoO₃ nanotubes and nanosheets (180 F/g and 200 F/g),^[18] and polypyrrole- α -MoO₃ nanorods (110 F/g and 129 F/g).^[10,20] A recent study on PANI- α -MoO₃ nanobelts demonstrated that the maximum achievable specific capacitance is 632 F/g, however, the rate capability of the as-prepared nanocomposites was even lesser than that of pure α -MoO₃ nanobelts,^[9] which is in contrast with the existed literatures. Also, the mechanism of this improved charge storage was not addressed. As shown in Figure 5.5 (b), the rate capability of h-MoO₃ hollow nanorods improved up to 65% after addition of polyaniline shell. The improved specific capacitance and rate capability suggest the merits of polyaniline in the nanocomposites by conferring a fast electronic conduction path. The charge/discharge curves for all three samples at higher current densities are presented in Appendix, Figure 8.

The impact of using polyaniline in the nanocomposites is also identified on the cycling stability of PANI@h-MoO₃ HNs, as shown in Figure 5.5 (c). PANI@h-MoO₃ HNs could able to retain 76% of the initial capacitance upon 5000 cycles of continuous charge/discharge when compared to h-MoO₃ HNs, which could retain about 55% of the initial capacitance.

Figure 5.5 (a) Galvanostatic charge/discharge curves at an applied current density of 1 A/g, (b) specific capacitance as a function of applied current density, the loading mass of the active material for all three samples was about 1 mg (c) cycling stability test of (1) PANI@h-MoO₃ HNs, (2) PANI, and (3) h-MoO₃ HNs, and (d) Nyquist plot of h-MoO₃ HNs and PANI@h-MoO₃ HNs. Adapted with permission from V. Kumar, P. S. Lee, *J. Phys. Chem. C*, **2015**, 119, 9041. Copyright (2015) American Chemical Society.^[35]

This significant enhancement in the stability can be ascribed to the polyaniline shell over h-MoO₃ HNs core which helps to preserve the rate of reversibility by conferring a facile conduction path to the charge carriers. An early stage degradation and improvement in the cycling stability of h-MoO₃ HNs and PANI is due to breakage of h-MoO₃ nanorods and activation of polymers chains, respectively.^[18] The electrochemical cyclic stability of the as-prepared nanocomposites is found better than that of the other reported literatures, including PANI/ α -MoO₃ nanobelts,^[9] polypyrrole/ α -MoO₃ nanorods,^[20] etc. Thus, the combinatory approach of making nanocomposites is found useful to improve the cycling stability.

The kinetics of electrode-electrolyte resistance and charge transfer resistance is studied using electrochemical impedance spectroscopy (EIS) in the frequency range of 10 mHz to 100 kHz. The Nyquist plot of PANI@h-MoO₃ HNs and h-MoO₃ HNs shows relationship between real and imaginary components of impedance exerted by the electrode/electrolyte interface, as shown in Figure 5.5 (d). In the high frequency regime, Nyquist plot of PANI@h-MoO₃ HNs bears less solution as well as charge transfer resistance when compared h-MoO₃ HNs. On the other hand, in the low frequency region, a quasi-capacitive and purely resistive response is obtained for PANI@h-MoO₃ HNs and h-MoO₃ HNs, respectively. The reduced charge transfer resistance of PANI@h-MoO₃ HNs results in better rate capability, because it acts as a limiting factor in faradic redox reactions.^[44]

The mechanism of the enhancement in the specific capacitance and rate capability of PANI@h-MoO₃ HNs can be expressed by decoupling the contribution of the individual component, taking current vs. sweep rate analysis (from CV curves) into consideration. Assuming, current obeys the power-law relationship with the scan rate according to equation 5.1.^[45]

$$I_p = av^b \quad (\text{eq. 5.1})$$

Where a is the adjustable parameter, and value of b decides the approach of redox reactions. For example, $b=1$ indicates a surface or near-surface redox reaction, while $b=0.5$ shows semi-infinite diffusion controlled redox reactions are responsible for charge transfer. Figure 5.6 (a) shows the relationship between $\log(I_p)$ and $\log(v)$ for all three samples. From the Figure 5.6 (a), the b values found to be 0.54 and 1.02, indicating solid-state diffusion- and surface-controlled charge transfer kinetics for h-MoO₃ HNs and PANI, respectively. However, a mixed behavior is identified for PANI@h-MoO₃ HNs.

For scan rates <5 mV/s, the characteristics of PANI@h-MoO₃ HNs is found similar to h-MoO₃ HNs (diffusion controlled redox reactions), whereas, for scan rates >5 mV/s, PANI@h-MoO₃ HNs follows the characteristics of PANI (surface controlled kinetics), as presented in Figure 5.6 (a). The scan rate dependent kinetics of redox reactions in terms of current can be expressed taking following assumptions into account: (1) at a slow scan rate, electrolyte ions diffuse through polyaniline shell and reach h-MoO₃ HNs surface due to sufficiently slow response of electrolyte ions under external polarization, and (2) due

to excessive doping of electrolyte ions the state of polyaniline might be affected (changing from emeraldine to reduced leucoemeraldine). Nearly identical response of conducting polymers is also noticed by Gohy *et al.* in case of LiFePO₄-PTMA.^[46] A region left to the dotted line in Figure 5.6 (a), represents the response of PANI@h-MoO₃ HN, which is driven by the diffusion controlled redox reactions, while, the region right to the dotted line shows the response of PANI@h-MoO₃ HN controlled by surface-controlled redox reactions. Thus, the scan rate dependent response of PANI@h-MoO₃ HN highlights the benefit of using combinatorial approach to prepare nanocomposites.

Figure 5.6 (a) Cathodic peak current as a function of scan rate, (b) cathodic peak voltage as a function of scan rates, (c) relationship between normalized specific capacitance and square root of $1/\text{scan rate}$, and (d) projection of the contributions of the surface- and diffusion-controlled charge transfer kinetics in h-MoO₃ HN and PANI@h-MoO₃ HN. Adapted with permission from V. Kumar, P. S. Lee, *J. Phys. Chem. C*, **2015**, 119, 9041. Copyright (2015) American Chemical Society.^[35]

Another important feature of the as-prepared nanocomposites is revealed by analyzing the relationship between the shift in peak voltage and scan rate (from CV curves), as shown in Figure 5.6 (b). At slow scan rates <5mV/s, the shift in the peak voltage (in the range of 0.4 V to 0.5 V) are small (<30 mV) when compared with the h-MoO₃ HN (~80 mV). This suggests the presence of polyaniline shell over h-MoO₃ HN core effectively circumvents the abuse of voltage, which is prone at the slow scan rates. The absence of a tail in the CV curve of PANI@h-MoO₃ HN, Figure 5.4 (b) reflects this behavior. At slow scan rates, a shift of more than 100 mV in the peak voltage is mainly associated with the phase change of the materials during ingress/digress of electrolyte ions, as identified in various battery electrodes, for example, LiCoO₂.^[47] Thus, it is conclusive that the presence of PANI shell of h-MoO₃ HN not only improves the electrochemical performance and cycling stability but also effectively extends the operating potential window. Due to the existence of dual charge storage kinetics in PANI@h-MoO₃ HN an overall improved electrochemical performance is obtained. The contributions of the individual component to the overall performance are determined using the method developed by Trasatti *et al.* This approach allows us to decouple the contributions of surface controlled charge (outer charge) and diffusion controlled charge (inner charge).^[48] Thus the total charge is the sum of inner as well as outer charge, according to equation 5.2.^[48]

$$Q_{\text{total}} = Q_{\text{inner}} + Q_{\text{outer}} \quad (\text{eq. 5.2})$$

The outer charge is the easily accessible charge and assumed to be not dependent on scan rates, whereas, inner charge is diffusion controlled. Thus, the equation 5.2 can be modified according to equation 5.3.

$$Q_{\text{total}} = k/v^{1/2} + Q_{\text{outer}} \quad (\text{eq. 5.3})$$

At the high scan rates, the charge stored instantly at the outer surface of the nanocomposites, that is Q_{outer} . In contrast, when the scan rate is sufficiently slow all the electrochemically active sites are fully accessible to the electrolyte ions, and Q_{total} includes both the components. To determine Q_{inner} , CVs at various scan rates from 1-100 mV/s are performed, as shown in Appendix, Figure 6 (a) and (b). The value of Q_{inner} can be determined from the extrapolated value of Q_{total} (normalized charge) vs $1/v^{1/2}$ (scan

rate) analysis, as shown in Figure 5.6 (c). The outer and inner charges in terms of their resultant specific capacitance are shown in Figure 5.6 (d). The contributions of outer charges (surface controlled redox) and inner charges (diffusion controlled redox) to the overall charge are determined to be ~64%, 36% and 38%, 62% for PANI@h-MoO₃ HNs and h-MoO₃ HNs, respectively. Thus it is evident from the above mentioned analyses that the enhancement in the electrochemical performance of PANI@h-MoO₃ HNs is due to improved contribution of surface controlled redox reactions, which solely come from PANI.

5.5 Summary

I have successfully prepared PANI@h-MoO₃ HNs nanocomposites using cation-exchange assisted Kirkendall effect followed by oxidative chemical polymerization of aniline under solvothermal conditions. Here, Fe³⁺ ions played a vital role not only to initialize the Kirkendall effect but also accountable to polymerize aniline monomers. In h-MoO₃ charges are stored via diffusion controlled redox reactions, while in PANI surface controlled redox reactions dominates. The as-prepared nanocomposites showed enhanced specific capacitance and cycling stability. Due to merits of PANI over h-MoO₃ HNs, the rate capability of the composite materials improved noticeably compared to h-MoO₃ HNs.

Cyclic voltammetry based current vs. scan rate and shift in voltage vs. scan rate analyses are chosen to decouple the contributions of inner charges (diffusion driven redox process) and outer charges (surface controlled redox process) to the overall charge. It is identified that in the slow scan regime (<5 mV/s) PANI@h-MoO₃ HNs nanocomposites show the characteristics of h-MoO₃. In contrast, in the regime where scan rates are >5 mV/s, the nanocomposites behave more likely pure PANI. Besides improving the specific capacitance, cycling stability and rate capability, the introduction of PANI increases the contribution of outer charges up to double (~64%) of h-MoO₃ outer charges (38%). Thus, I have explicitly shown that the controlled integration of diffusion controlled component with the surface controlled component is beneficial to realize an overall improvement in the electrochemical performance of the nanocomposites.

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Chapter 6: Silver decamolybdate as advanced pseudocapacitive electrode material

Mixed-metal molybdates are interesting host materials due to their versatile crystal-chemistry, which confers a highway for the conduction of electronic as well as ionic charges. Silver molybdate in triclinic crystal structure is of immense interest because it consists of layers of MoO_6 octahedra separated by an array of silver ions. In this chapter, first I introduce the background of various transition metal molybdates, and then demonstrate the synthesis and electrochemical performance of silver molybdate in three-electrode as well as two-electrode configurations. A brief summary of the findings is presented.

6.1 Introduction and Motivation

As demonstrated in chapter 4, the performance of MoO_3 can be improved by altering its crystallographic structure, i.e., h- MoO_3 . In that approach, ammonium ions were used to achieve h- MoO_3 phase of MoO_3 , but the electrochemical performance of the as-prepared nanostructures in their pristine forms were not satisfactory, as discussed in chapter 5. The crystallographic structure of MoO_3 can also be altered using metal ions. Here, I propose to synthesize silver decamolybdate in triclinic crystal-structure to facilitate the electronic as well as ionic conduction during electrochemical reactions.

Metal or transition metal molybdates are known for their versatile crystal-chemistry driven by unique arrangement of metal or transition metal ions with MoO_6 octahedra.^[1,2]

In recent years, ternary metal molybdates (AMoO_x) as electrode materials have gained significant attention in supercapacitors due to their chemically stable crystal structure and redox behavior of metal ions (A).^[3,4] With the purpose of enhancing the electrochemical performance of ternary metal molybdates, Mai *et al.* proposed hierarchical structure of $\text{MnMoO}_4/\text{CoMoO}_4$ heterostructured nanowires which exhibit specific capacitance as high as 210 F/g at an applied current density of 0.5 A/g and excellent cycling stability.^[5] The specific capacitance exhibited by $\text{MnMoO}_4/\text{CoMoO}_4$ heterostructured nanowires was much higher than that of MnMoO_4 (9.7 F/g) and CoMoO_4 (62.8 F/g).^[5] Generally,

hierarchical structure offers a synergistic integration of two length scales,^[5,6] particularly, the smaller dimension shortens the diffusion path and increases the electrochemically active surface area, while the larger length could confer efficient electronic transport and reduce the internal resistance. However, the electrochemical performance demonstrated by MnMoO₄/CoMoO₄ heterostructured nanowires could not improve the performance significantly when compared with binary metal oxides.^[7,8]

Likewise, Liu *et al.* synthesized CoMoO₄-NiMoO₄ H₂O nano-bundles which could deliver a specific capacitance of 1039 F/g at an applied current density of 2.5 mA/cm².^[9] The weight ratio of Co: Ni was found a vital factor to limit the electrochemical performance of the nano-bundles, a ratio of 0.6:1.4 was presented as an optimum to achieve a stable electrochemical performance. In the same year, Senthilkumar *et al.* attempted to synthesize the same materials (CoMoO₄-NiMoO₄) system in nanoparticles-like morphology and could achieve specific capacitance of 1472 F/g at an applied current density of 5 mA/cm².^[10] The authors credited this improvement in the performance to the route of synthesis, synergistic effect of Ni and Co, and high weight fraction of Ni. In their study, they found that the weight ratio of 0.33:1 is the optimum amount of Co to Ni. Thus, regarding optimization of Ni and Co content, there is a lack of consistent findings on the influence on the electrochemical performance.^[9–12]

The nanocomposites of NiMoO₄, CoMoO₄, MnMoO₄, etc., with other binary metal oxides, such as MnO₂,^[13] Co₃O₄,^[14–16] Co(OH)₂,^[17] etc., and carbonaceous,^[18,19] materials are also the promising electrode materials for high performance supercapacitors. Cai *et al.* prepared 3D Co₃O₄@NiMoO₄ nanowires array on Ni foam using two steps hydrothermal reactions route.^[20] The as-prepared hybrid electrode could exhibit a high specific capacitance of 1094 F/g at an applied current density of 30 mA/cm², but the cycling stability remained a challenge.

Most recently, Ren *et al.* synthesized NiMoO₄@Co(OH)₂ nanowires array using hydrothermal synthesis of NiMoO₄ on Ni foam followed by electrochemical deposition of Co(OH)₂ nanoflakes on the as-prepared NiMoO₄ nanowires.^[17] The as-designed hybrid electrode delivered a high specific capacitance of 2122.7 F/g at 4.5 A/g due to its unique 3D structure which facilitates transport of ions, superior electron collection efficiency and

high electrochemically active surface area. However, the rate capability of $\text{NiMoO}_4@\text{Co}(\text{OH})_2$ nanowires was found inferior to NiMoO_4 nanowires.

Recently, Ma *et al.* synthesized 3D nanocomposites of $\text{Co}_3\text{O}_4@\text{AMoO}_4$ ($\text{A} = \text{Ni}, \text{Co}$) using two steps low temperature hydrothermal conditions,^[14] and showed that the as-prepared nanocomposites of $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ and $\text{Co}_3\text{O}_4@\text{CoMoO}_4$ could achieve significantly high specific capacitance of 2041 F/g and 857 F/g at an applied current density of 0.5 A/g, respectively. The as-fabricated asymmetric supercapacitors, taking activated carbon as negative electrode materials, could deliver a high energy density of 41.9 Wh/kg at a power density of 298 W/kg, and 38 Wh/kg at 275 W/kg for AC// $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ and AC// $\text{Co}_3\text{O}_4@\text{CoMoO}_4$, respectively. Liu *et al.* fabricated AC// NiMoO_4 H₂O asymmetric supercapacitor device which could deliver energy density as high as 34.4 Wh/kg at a power density of 165 W/kg.^[21] On the other hand, AC// CoMoO_4 - NiMoO_4 device could reached a maximum energy density of 16 Wh/kg at a power density of 1600 W/kg.^[9]

Most recently, Yu *et al.* constructed nanohoneycomb-like strongly coupled CoMoO_4 -3D graphene hybrid electrode on Ni foam followed by etching of Ni foam in 3 M HCl solution, for symmetric as well as asymmetric supercapacitors in coin cell configuration.^[22] The AC// CoMoO_4 asymmetric and $\text{CoMoO}_4//\text{CoMoO}_4$ symmetric devices could deliver the energy density as high as 21.1 Wh/kg (@300 W/kg) and 37.25 Wh/kg (@900 W/kg) at an applied current density of 0.33 A/g, respectively. The as-prepared nanohoneycomb-like strongly coupled CoMoO_4 -3D graphene hybrid electrode could become a choice of next generation supercapacitors due to its ultra-long (100000 cycles) cycling stability at a very high level of current density, i.e., 400 A/g. Thus, based on the above mentioned literatures it is noteworthy that the transition metal molybdates are a potential candidate for the high energy applications, but at the same time the power density is sacrificed, which could hamper their use in practical applications. Therefore, it is essential to develop an electrode system which could deliver high energy density without compromising the power density.

In this chapter, I synthesize and demonstrate silver decamolybdate ($\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$) as a promising pseudocapacitive electrode material. Silver molybdate can be crystallized in various crystal structures, for example, cubic (Ag_2MoO_4),^[23] orthorhombic

($\text{Ag}_2\text{Mo}_3\text{O}_{10}$),^[24] monoclinic ($\text{Ag}_2\text{Mo}_2\text{O}_7$),^[25] and triclinic ($\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$).^[26] Most recently, ultra-long nanowires of silver molybdates in orthorhombic structure ($\text{Ag}_2\text{Mo}_3\text{O}_{10}$) has been employed in photocatalysis, surface enhanced Raman spectroscopy (SERS), UV-Vis and photoluminescence applications.^[27] Antimicrobial, photocatalytic and photoluminescence properties of Ag_2MoO_4 nanostructures have also been studied in the recent years.^[28] Silver molybdate in triclinic structure ($\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$) possesses a wide range of applications, such as a novel non-Pt electrocatalyst for oxygen reduction reactions (ORR), fast ion-conducting glass, electrode in battery applications, etc.^[29–31] Silver molybdate in triclinic structure consists of a unique arrangement of ions, in which a chain of Ag ions resides in-between MoO_6 octahedra or vice-versa.^[32] For simplicity, the structure can be broken down into two basic units, one of six octahedral sharing edges and other a square arrangement of four octahedra sharing edges. An infinite zigzag chain of octahedra running along the *a* axis is formed by the six identical octahedra sharing edges and a group of four octahedra lies in-between these chains voids, which are then filled with silver ions. The as-prepared $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods could store high level of specific charges at a scan rate of 1 mV/s. Besides the fundamental electrochemical properties of $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods, prototypic asymmetric device is fabricated taking $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods as anode and commercially available activated carbon as cathode. The device exhibits remarkable electrochemical performance in the interior of a potential window of 1.5 V. The device could deliver a high energy density of 22.1 Wh/kg at a power density of 1.51 kW/kg. $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods enable high energy density without sacrificing the power density while comparing with transition metal molybdates, such as NiMoO_4 , CoMoO_4 , etc. More importantly, the as-fabricated device shows high energy density at a very high level of power density.

6.2 Structural characterization

The crystallographic phase of the material was evaluated using X-ray powder diffraction (XRD). Figure 6.1(a) shows XRD pattern of the product annealed at 455 °C. The diffraction peaks of the product are well matched with the standard diffraction pattern of $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ (ICDD card # 13-7646, $a = 7.59 \text{ \AA}$, $b = 8.31 \text{ \AA}$, $c = 11.42 \text{ \AA}$ and $V = 671.8 \text{ \AA}^3$).^[26] XRD patterns of the as-synthesized and the as-annealed samples are shown in Appendix, Figure 9. The crystallographic structure of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ is shown in Figure

6.1 (b), in which layered arrangement of MoO_6 octahedra and Ag ions can be seen clearly, Ag ions in $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ are present between the layers of MoO_6 octahedra.

Figure 6.1 (a) XRD pattern of the sample annealed at 455 °C, (b) atomic arrangement of Ag, Mo and O atoms in triclinic phase of silver molybdate, (c) DSC/TGA characteristics of the as-synthesized hydrothermal product and (d) FESEM micrographs of $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods. Inset of (d) shows the magnified view of $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods.

DSC/TGA was carried out to provide insight on the thermal behavior of the product. A typical DSC/TGA curve of the as-synthesized product is shown in Figure 6.1 (c). The observation of three endothermic peaks (at 295 °C, 455 °C and 536 °C) in the DSC curve shows the change in the phase of the material. The mass loss in the TGA curve below 250 °C is attributed to the removal of the water molecules from the lattice of the material. The consecutive mass loss is due to decomposition of the material, and a further gain in the mass as well as the observation of an endothermic peak (at 455 °C) that indicates

oxidation of the material ($\text{Ag}_2\text{Mo}_3\text{O}_{10} + 2\text{O}_2 \rightarrow \text{Ag}_6\text{Mo}_{10}\text{O}_{33}$).^[27] An endothermic peak identified at 536 °C shows melting of the constituents. Thus, the as-synthesized product was air annealed at 455 °C to obtain pure triclinic phase of silver molybdate.

Field-emission scanning electron microscopy (FESEM) analysis, Figure 6.1 (d), revealed that the as-annealed (at 455 °C) product stabilizes in nanorods-like morphology; a magnified view of the nanorods can be seen in the inset of Figure 6.1 (d). The as-obtained nanorods were found to be 400 nm in diameter and 2-10 μm in length, respectively. FESEM micrographs of the as-prepared sample and the annealed (295 °C and 536 °C) sample are presented in Appendix, Figure 10.

IR analysis is advantageous to identify the change in atomic arrangement imposed by the foreign atoms (interaction) as the shift in the corresponding vibrational frequency. IR spectra of MoO_3 shows two absorption bands attributed to the bending ($\sim 820 \text{ cm}^{-1}$) and stretching ($\sim 981 \text{ cm}^{-1}$) of terminal oxygen ions associated with the MoO_6 octahedra,^[33] and taken as a reference, as shown in Figure 6.2. Shifts in the IR bands of the as-synthesized silver molybdate are indicating the perturbation in the layered structure of MoO_3 due to incorporation of Ag ions. A shoulder peak ($\sim 900 \text{ cm}^{-1}$) in the spectra of as-synthesized silver molybdate is indicative of the change in the atomic arrangement of the constituents (asymmetric vibration). A small band ($\sim 1420 \text{ cm}^{-1}$) is indicative of the water molecules in the as-synthesized product.^[34] When the as-synthesized silver molybdate was annealed at 295 °C, the IR bands in the spectra became broader, which indicate asymmetric stretching of MoO_6 octahedra in the evolution of triclinic phase, and a pure triclinic phase was obtained at 455 °C. Further annealing at higher temperatures affects the quality of the triclinic silver molybdate, a broader IR peak $\sim 520 \text{ cm}^{-1}$ indicates this behavior.

Figure 6.2 IR spectrums of the as-synthesized and the as-annealed (at various temperatures) silver molybdate nanostructures; MoO_3 is taken as the reference materials for the analyses

Surface chemical states of the as-prepared $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods were examined by X-ray photoelectron spectroscopy (XPS). Typical survey and the high-resolution XPS spectra of $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods are shown in Figure 6.3. The high-resolution XPS spectrums are fitted well with the nonlinear least-squares fitting program using Lorentzian-Gaussian peak shapes, as shown in Figure 6.3 (b-d). The survey spectra contains $\text{Mo}3d$, $\text{Ag}3d$, $\text{O}1s$, Ag MNV and MoMNV peaks, which confirm the presence of Mo, Ag and O in the sample, as depicted in Figure 6.3 (a).

Due to spin-orbit splitting, the high-resolution spectrum of Mo contains a pair of XPS peaks at the binding energy of 232.6 eV and 235.7 eV correspond to $\text{Mo}3d_{5/2}$ and $\text{Mo}3d_{3/2}$ state of Mo^{6+} , respectively, as can be seen in Figure 6.3 (b). The peak separation of about 3.1 eV between $\text{Mo}3d_{5/2}$ and $\text{Mo}3d_{3/2}$ signals is in excellent agreement with the previous literatures.^[35] The area under the doublets and FWHM of the doublet are in

good agreement with the fundamental analyses of Mo^{6+} doublets, i.e., 3:2 for $\text{Mo}3d_{5/2}:\text{Mo}3d_{3/2}$. As shown in Figure 6.3 (c), the XPS spectrum of silver ions also possesses a pair of spin-orbit doublets at the binding energy of 367.9 eV and 373.9 eV assigned to $\text{Ag}3d_{5/2}$ and $\text{Ag}3d_{3/2}$ doublets of Ag^+ , respectively.^[36] The difference of the binding energy (~ 6 eV) between two doublets and FWHM of Ag^+ matches well with the reported values.^[36] Thus, XPS analysis ensures that Mo species and Ag species present in $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods are in the Mo^{6+} and Ag^+ oxidation states, respectively.

Figure 6.3 XPS (a) survey spectrum and (b), (c) and (d) high-resolution spectra of Mo, Ag and O, respectively, present in $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods.

The high-resolution spectrum of O 1s is shown in Figure 6.3 (d), indicating two well defined peaks at 530.7 eV and 532.3 eV correspond to O^{2-} in Ag-O and Mo-O, respectively.^[36,37] In the s state, O ions does not split into doublets, as the ratio of the area under the curve of lower energy signal to the higher energy signal does not hold 3:2. The same Lorentzian-Gaussian values are used to resolve the individual O 1s peak. Therefore,

the presence of two split peaks (almost equal intensity) could be due to two different types of bonding environments originated from two different types of cations, i.e., Ag^+ and Mo^{6+} ions. The electronegativity difference of O (3.5 eV) and Mo (2.2 eV) favors the formation of polar covalent bonds, whereas, the difference between O (3.5 eV) and Ag (1.9 eV) have a tendency to form ionic bonds, as a result the formation of different oxygen species commence, which is in excellent agreement with the reported literature values for Mo-O and Ag-O species.^[36,37] Also, the peak position of O atoms in T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ closely matches with the peak position of O atoms in other molybdates, such as BiMoO_4 ,^[38] indicating bipolar bonding nature of O atoms in molybdates.

6.3 Electrochemical characterization

The electrochemical properties of transition metal molybdates are studied in alkaline electrolyte (e.g., KOH or NaOH) due to high electrochemical activity of transition metal ions that are distributed within the layers of MoO_6 octahedra.^[2,13] As shown in Figure 6.4 (a), cyclic voltammograms (CVs) of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods are carried out at various scan rates in a three-electrode cell configuration using 2 M KOH as electrolyte solution. The observation of obvious redox peaks in CVs is due to step wise oxidation and reduction of Ag ions located at various sites in the structure (Mo-O-Mo/Ag/Mo-O-Mo) indicates pseudocapacitive behavior of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$. The pseudocapacitive behavior in T- $\text{Ag}_3\text{Mo}_{10}\text{O}_{33}$ is originated from the reversible redox reaction of Ag^+ ions, as explained on the basis of the Pourbaix diagrams of Ag and Mo, Appendix, Figure 11.^[39] In the defined potential window and pH range, Ag ions can change reversible to $\text{Ag}(\text{OH})_2^-$, whereas, Mo ions exist in the form of MoO_4^{2-} ions which do not partake in the redox reactions.^[40] The inset of Figure 6.4 (a) shows CV of T- $\text{Ag}_3\text{Mo}_{10}\text{O}_{33}$ at a scan rate of 2 mV/s. There is a noticeable peak shift identified as the sweep rate increased from 1 mV/s to 100 mV/s. This shift in peak potential could be due to increase in resistance from several sources, i.e., internal resistance active material, solid-electrolyte interface resistance.^[41]

Cyclic voltammetric (CV) analysis is used to establish the relationship between peak current (cathodic as well as anodic) vs. scan rate to rationalize the mechanism of charge transfer. Figure 6.4 (b) and (c) show the relationship between $\log(i)$ vs $\log(v)$ in the

range of scan rate from 1 mV/s to 100 mV/s for both (1 and 2) cathodic and anodic peaks, respectively. Considering that the measured current, i follows a power law relationship with the scan rate, v , according to equation 6.1.^[41]

$$i = av^b \text{ (eq. 6.1)}$$

Figure 6.4 (a) Cyclic voltammograms (CVs) of the as prepared electrode at various scan rates, the inset shows CV at a slow scan rate of 2 mV/s, (b) and (c) linear fitting of the peak current vs. scan rate for the first and second set of redox peaks in CVs, respectively, (d) specific charge as a function of the scan rate, the loading mass of the active material was about 1.25 mg.

Though, a and b are the adjustable parameters, however, the value of b justifies the mode of redox charge transfer that can be determined from the slope of $\log(i)$ vs $\log(v)$ curve, as shown in Figure 6.4 (b) and (c). According to the approximation, $b=1$ indicates surface controlled redox reactions are the dominating component, while $b=0.5$ indicates the charge transfer is governed by diffusion controlled redox reactions.^[42] From Figure 6.4 (b), the slope of the lines is calculated to be ~ 1 (for the first pair of anodic/cathodic redox

peaks), which indicates the mechanism of charge transfer is controlled by surface controlled redox reactions.^[42] However, deviation in the slope is noticed for the second pair of anodic/cathodic redox peaks, as shown in Figure 6.4 (c). This change in the slope is due to descendent in the b values to 0.7, for both cathodic as well as anodic redox peaks.

T-Ag₆Mo₁₀O₃₃ nanorods based electrode could hold maximum specific charge about 398 C/g (specific capacitance ~320 F/g) at a slow scan rate of 1 mV/s, and it could maintain a specific charge of about 135 C/g (specific capacitance ~108 F/g) at a high scan rate of 100 mV/s, as depicted in Figure 6.4 (d).

Figure 6.5 (a) Normalized capacitance vs. $1/(\text{scan rate})^{1/2}$ allows for the separation of intercalation redox reactions contribution from the surface redox reactions induced capacitance. Region-1 and Region-2 emerge when scan rate varied from 1-100 mV/s, extrapolated diagonal dashed line in Region-1 helps to determine surface redox reaction induced capacitance, and (b) projection of the contribution of surface and intercalation redox reaction contribution at the various scan rates.

In order to decouple the contribution of surface controlled and diffusion controlled redox reactions to the overall performance, the approach developed by Trasatti et al., is used.^[42] In the relationship between normalized specific capacitance (C_{sp}) and square root of scan rate (v), the linear region in the curve suggests the charges are limited by semi-infinite linear diffusion, whereas, capacitive contribution does not influence by the scan rates.^[41,42] The capacitive contribution can be calculated from the extrapolated y-intercept in the plot of normalized C_{sp} vs $1/v^{1/2}$. Figure 6.5 (a) depicts the relationship between

normalized C_{sp} vs. $1/v^{1/2}$ for T-Ag₃Mo₁₀O₃₃ nanorods in the scan rate window of 1-100 mV/s. Similar to the behavior of the peak currents in Figure 6.4 (b) and Figure 6.4 (c), there are two distinct regions in Figure 6.5 (a). In region – 1 (scan rate 1-10 mV/s), normalized C_{sp} is found to be independent or mildly dependent on the scan rates. An extrapolated y-intercept estimated the capacitive or surface controlled contributions to the overall performance, which is determined to be approximately ~ 53 % (~47 % is attributed to the diffusion kinetics). Whereas, in region – 2 (scan rate >10 mV/s), normalized capacitance decreases rapidly as a function of the sweep rates. Attributed to partake of the diffusion controlled kinetics in the region – 1, a high normalized C_{sp} is realized. Therefore, at a scan rate of 1 mV/s, the contribution of diffusion kinetics is found maximum and decreases as the scan rate increases, and eventually becomes independent at a sweep rate >10 mV/s. The kinetics of diffusion process is strongly dependent on crystallite size as well as crystalline quality of the material.^[43] Figure 6.5 (b) presents the estimated contributions of the surface-controlled and diffusion controlled kinetics to the overall performance of T-Ag₃Mo₁₀O₃₃.

6.4 Electrochemical testing of asymmetric device

To exploit T-Ag₃Mo₁₀O₃₃ in practical applications, an asymmetric device is fabricated using activated carbon (AC) and T-Ag₃Mo₁₀O₃₃ as negative and positive electrodes, respectively. From the CV analyses of AC (Appendix, Figure 12) and T-Ag₃Mo₁₀O₃₃ (Figure 6.4 (a)) electrodes, it is evident that the charges can be stored in a potential window between -1.2 V and +0.85 V. Ideally, the as-fabricated device should have achieved a maximum potential window of 2.05 V, but due to activity of T-Ag₃Mo₁₀O₃₃ in negative potential regime, it reduces the effective potential window to 1.6 V. To achieve a maximum device performance, the charge-storage capacity of both the electrodes should be balanced and that was balanced by adjusting the mass of the electrodes.^[44] Figure 6.6 (a) shows CV curves of the as-prepared asymmetric device collected at different working potentials at a sweep rate of 50 mV/s. Attributed to the pseudocapacitive behavior of T-Ag₃Mo₁₀O₃₃, a set of well-defined redox peaks is observed in CV analysis of the device. Galvanostatic charge/discharge (CD) curves of the device at an applied current density of 5 A/g is carried out in various potentials windows,

as shown in Figure 6.6 (b). CD curves further confirm that the device is completely functional within the adjusted potential window.

Figure 6.6 (a) Cyclic voltammograms of asymmetric device collected at different voltage window at scan rate of 50 mV/s, and (b) Galvanostatic charge/discharge curves of asymmetric device collected at different voltage window at an applied current density of 5 A/g.

Figure 6.7 (a) depicts the CVs of the as-prepared asymmetric device at various scan rates (10-100 mV/s). The distorted rectangular CVs render the information about the pseudocapacitive contribution of T-Ag₆Mo₁₀O₃₃. Galvanostatic charge/discharge tests are carried in a potential window of 0-1.6 V at various current densities, as shown in Figure 6.7 (b). Figure 6.7 (b) further confirms that the device is fully functional and exhibits pseudocapacitive behavior, which is suggestive of a good charge-storage performance.^[45] The specific capacitance of the full cell at different current densities is calculated from Figure 6.7 (b), and is shown in Figure 6.7 (c). The specific capacitance is calculated according to equation 6.2.

$$C_{sp} = I/m (-\Delta V/\Delta t) \quad (\text{eq. 6.2})$$

Where I/m is the discharge current density, taking total mass of the device into account, and $-\Delta V/\Delta t$ is the slope of the discharge curve after IR drop correction. As shown in Figure 6.7 (c), the C_{sp} of the device could reach up to 65 F/g at a current density of 2 A/g, while it maintains 28 F/g at 20 A/g, which indicates good rate characteristic of the device. The long term cycling stability of a supercapacitor device is crucial, to demonstrate its

reliability in device applications. To show cycling stability of the asymmetric supercapacitor, continuous charge/discharge test is performed up to 2500 cycles at a scan rate of 50 mV/s, as shown Figure 6.7 (d). The capacity of asymmetric device fades about 17% of the initial capacity after the first 250 cycles and additional 15% upon 1000 cycles. After this initial stage degradation, the device maintains its stability and achieves about 68% of initial capacity after 2500 cycles. The possible reason of this initial stage degradation can be explained on the basis of the inset of Figure 5(d). The first stage degradation (17%) could be ascribed to the irreversibility of the redox reactions (descent in the peak current) and increase in the components resistance (shift in the peak position). However, second stage degradation (15%) could be due to evolution of oxygen (a small tail at ~1.5 V, the inset of Figure 6.7 (d) indicates this behavior). To better understand the mechanism of this degradation, electrochemical impedance spectroscopy (EIS) of the cell before and after 2500 cycles, is carried out. Figure 6.7 (e) shows the charge transfer resistance of device increased slightly after cycling, which could be accountable to degrade the capacity of the asymmetric device. However, to understand the exact mechanism of this degradation, further study should be carried out.

Figure 6.7 (a) Cyclic voltammograms of asymmetric device at the various scan rates scan rates (10-100 mV/s), (b) Galvanostatic charge/discharge curves of asymmetric device at the various current densities (2-20 A/g), the loading mass of the active components was about 2.1 mg (whole cell) (c) specific capacitance of the device as a function of applied current density, (d) cycling stability of asymmetric device under continuous charge/discharge at a scan rate of 50 mV/s, inset of Figure 6.7 (d) shows CVs before (1) and after 2500 cycles (2), (e) Nyquist plots of the device before and after cycling, inset of Figure 6.7 (e) shows cell response in the high frequency region, and (f) Ragone plot of the asymmetric device.

To assess the feasibility of using new electrode material for actual device performance, energy density and power density (Ragone plot) are the real device parameters.^[46] Ragone plot of our asymmetric device is derived from constant-current charge/discharge characteristics, as shown in Figure 6.7 (f). The asymmetric device made from activated carbon (AC)//T-Ag₆Mo₁₀O₃₃ delivers the energy density as high as 22.1 Wh/kg at a power density of 1.51 W/kg (at a discharge current of 2 A/g). Even at a high power

density of 15.1 kW/kg (corresponding to a discharge current of 20 A/g), the device could hold an energy density of 9.1 Wh/kg, an indication of its high performance ability. The energy and power density performance of AC//T-Ag₆Mo₁₀O₃₃ device is found better than that of the other transition metal molybdates, such as AC//NiMoO₄-CoMoO₄,^[9] AC//β-NiMoO₄-CoMoO₄,^[10] and AC//Mo-MnO₂,^[47] AC//Ni-Co oxide,^[48] etc., representing a significant improvement over the current state-of-the-art of molybdenum oxides based supercapacitors. Based on the results discussed in this study, the spectacular performance of T-Ag₆Mo₁₀O₃₃ can be ascribed to the followings: (a) mixed crystal-chemistry, i.e., electronic as well as ionic conduction of silver molybdates, (b) favorable arrangement of Ag and Mo atoms, i.e., chain of Ag⁺ ions between two MoO₆ octahedra in tetragonal silver molybdate and (c) co-existence of surface and intercalation redox reactions due to layered structure of T-Ag₆Mo₁₀O₃₃. Additionally, the performance of the as-prepared T-Ag₆Mo₁₀O₃₃ can be further improved by miniaturizing the particle size to less than 50 nm. I also anticipate that the performance of the as-fabricated asymmetric device can be further improved by configuring a fully sealed device.

6.4 Summary

In summary, I have successfully synthesized novel ternary oxides, i.e., silver molybdate under hydrothermal conditions. Silver molybdate in triclinic crystal structure, i.e., T-Ag₆Mo₁₀O₃₃ was achieved after annealing of the as-synthesized product in air atmosphere. IR analysis revealed that the formations of T-Ag₆Mo₁₀O₃₃ phase involve removal of water molecules from the lattice of the as-prepared silver molybdate. T-Ag₆Mo₁₀O₃₃ involves biphasic coordination of oxygen atoms with Mo⁶⁺ and Ag⁺ ions, in order to form an ordered structure of metal and molybdates ions.

In the half-cell configuration, a detailed CV analyses was carried out to provide insight on the mechanism of redox reactions. Attributed to partake of surface controlled redox reactions, an improved charge storage performance of the material was evaluated. Such fundamental understanding about the electrode material provides quantitative insight into the ration design of the high performance supercapacitor.

Further, a well optimized asymmetric device was successfully designed based on T-Ag₆Mo₁₀O₃₃ nanorods and commercially available activated carbon as positive and

negative electrode materials, respectively. The as-fabricated asymmetric supercapacitor shows enhanced energy density (221. Wh/kg) without compromising the power density (1.5 kW/kg) comparing with the other molybdate system. More importantly, the asymmetric device delivers a good energy density of 9.1 Wh/kg at a level of very high power density of 15.1 kW/kg. These features make this asymmetric supercapacitor promising for high energy as well high power applications.

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Chapter 7: High performance supercapacitor based on tri-rutile 2D layered hydrogen-niobium-molybdates

Electrode materials with new crystallographic structures, for example, perovskite, rutile or tri-rutile, etc. are of immense interest due to their electrochemically rich crystal-chemistry. Among them tri-rutile related structure materials are gaining significant interest in electrochemical applications due to their three-dimensional layered structures, which can accommodate large amount of the charges. In this chapter, I synthesize and evaluate the electrochemical properties of tri-rutile based layered HNbMoO_6 . The half-cell as well as full-cell supercapacitor device is fabricated using HNbMoO_6 as positive as well as negative electrode materials. At the end, key findings of the work are summarized.

7.1 Introduction and Motivation

The performance of molybdenum based ternary oxides system can be improved by positioning the metal ions in an ordered arrangement as demonstrated in Chapter 6. Despite significant improvement in the specific capacitance after introduction of metal ions, the increment in the energy density of the device was not remarkable that could be due to electro-activity of the single component, i.e., the silver ions. In order to harvest the electro-activity of both the components (transition metal ions and the molybdates), here I propose a novel transition metal molybdate, i.e., hydrogen-niobium-molybdate that utilizes the electro-activity of both molybdates as well as niobium ions.

In general, energy density and power density are the two known parameters to evaluate the performance of a supercapacitor that can be expressed according to equation 7.1 and 7.2, respectively.^[1,2]

$$E \text{ (Wh/kg)} = 0.5 \times 0.277 \times C \times (\Delta V)^2 \text{ (eq. 7.1)}$$

$$P \text{ (W/kg)} = E/\Delta t \text{ (eq. 7.2)}$$

Where E is the energy density and P is the power density; C, V and Δt are the specific capacitance, potential window and discharge time, respectively. A factor of 0.277 is introduced to convert the unit of energy density to Wh/kg. In order to improve the energy

density, it is obvious that one has to increase the specific capacitance and operating potential window of the supercapacitor. The specific capacitance can be improved through the selection of pseudocapacitive electrode material with internal-activity (low internal resistance, multiple redox-centers, availability of the fractional sites to adsorb or to intercalate, and the reversibility of electrochemical reactions),^[3] whereas, improvement in the potential window (within the electrolyte stability window) can be achieved through the configuration of electrodes (asymmetric or symmetric),^[4] optimization of mass balancing.^[5]

Metal oxide based pseudocapacitors has gained significant interest due to their high specific capacity (reversible faradic redox reactions). The charge-storage mechanism in metal oxide based pseudocapacitive electrode materials involves either adsorption of electrolyte ions on the electrode surface (so-called electrosorption valency),^[6] or surface redox reactions (in case of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$),^[7] or intercalation of electrolyte ions into the bulk of electrode material (in case of layered materials).^[8,9] It has been addressed that the pseudocapacitive charge-storage is very sensitive to the crystalline quality, crystal phase and microstructure of the electrode materials.^[10] Most recently, it is demonstrated in perovskite compound (i.e., LaMnO_3) that the pseudocapacitive charge-storage can even be realized through the movement of the lattice oxygen ions (anion charge-storage); however, nature of the intercalated oxygen ions is still not understood clearly.^[11] The perovskite and related family materials have widely been studied in electrocatalysis,^[12] ionic conductors and solid-oxide-fuel-cells (SOFCs),^[13] but have not exploited much as an electrode material in pseudocapacitors technology.

The transition metal oxides with spinel structure (AB_2O_4) have recently been emerged as one of the promising pseudocapacitive electrode materials due to partake of both the constituents in the charge storage process. Besides various spinel oxides, including Mn_3O_4 ,^[14] Fe_3O_4 ,^[15] Co_3O_4 ,^[16] etc., other mixed spinel oxides, such as MnFe_2O_4 has also been explore for electrochemical energy storage purpose.^[17] In MnFe_2O_4 system, the highest achievable specific capacitance was about ~115 F/g for ferrite component, excluding the contribution of carbon black. Another category of electrode materials possesses a general formula of ABO_4 , for example, NiMoO_4 ,^[18] CoMoO_4 ,^[19] MnMoO_4 ,^[20] etc., as discussed in chapter 6. An additional category of the electrode materials with the

general formula of $A_3B_2O_8$ ($M = \text{Co, Ni, etc.}$) have been introduced that exhibits improved specific capacitance due to relatively higher ratio of A/B (1.5:1) than that of AB_2O_4 (1:2) and ABO_4 (1:1), which in response attains stronger redoxomorphism.^[21] For example, Zhang *et al.* demonstrated the synthesis and pseudocapacitive performance of $\text{Co}_3\text{V}_2\text{O}_8$ nanoplates, which exhibit a high specific capacitance of 739 F/g at an applied current density of 0.5 A/g.^[22] Thus, a vast potential of the materials chemistry of these complex oxides ($A_xB_yO_z$) can be exploited as prospective electrode material in pseudocapacitors technology.

The transition metal oxides with tri-rutile structure of composition AB_2O_6 exist for various combination of monovalent, pentavalent and hexavalent ions, for example $A = \text{H}^+$, Li^+ , Na^+ , etc., and for $B = \text{Nb}^{5+}$, Mo^{6+} or W^{6+} , etc.^[23,24] The structure of tri-rutile related oxides can be expressed as a superlattice of a normal rutile structure unit-cell, in which B and O ions form a matrix of edge- and corner-shared BO_6 octahedra with an interpenetrating array of A ions, and form a layered framework along c axis and leaving a tunnel along b axis.^[24] The materials of composition AB_2O_6 , for example, $\text{H}(\text{NbMo})\text{O}_6$ are preferably synthesized using the high temperature solid-state reaction route (melt-diffusion conditions) to achieve a thermodynamically stable product with desired stoichiometry, which cannot be realized using solution synthesis. The catalytic properties of tri-rutile related oxides, such as $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and its anhydrous product HNbMoO_6 have recently been studied attributed to their strong inter-layer Bronsted acid functionality.^[25] Due to the ultra-large inter-spacing ($\sim 26 \text{ \AA}$) of the layers in $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$, polymerization of aniline monomers in the inter-gallery region has been demonstrated successfully.^[26,27] The solid-acid catalytic properties of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and the enriched protonated form of HNbMoO_6 has also been studied to catalyze the Friedel-Crafts alkylation of toluene, anisole, benzene with benzyl alcohol, etc.^[25,28] The transition metal oxides with the novel structure of composition AB_2O_6 could be advantageous to realize the advancement in the electrochemical charge-storage properties of pseudocapacitors. Therefore, the spectacular features, such as large inter-layer spacing, availability of the inter-layer protonic sites, the ability of aliovalently substitution, and intrinsic two dimensional characters, associated with $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 drive us to study electrochemical charge-storage properties of these oxides.

Inspired from the properties of tri-rutile related oxides, in this chapter I present electrochemical charge-storage properties of 2D layered $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 nanosheets. A synthetic solid-state reaction followed by proton-exchange route is adopted to prepare 2D layered $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$, while the layered HNbMoO_6 is collected as the anhydrous product of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$. 2D layered HNbMoO_6 showed much improved charge-storage ($\sim 600 \text{ F/g}$) characteristic than that of its hydrated counterpart ($\sim 250 \text{ F/g}$) in an aqueous electrolyte system. The electrochemical properties of 2D layered HNbMoO_6 are further studied in half cell (three electrode cell) as well as full cell (two electrode symmetric cell) configurations. This improvement can be ascribed to the novel structural chemistry of the electrode material which consists of large-inter layer spacing between the layers and availability of the cage protons.

7.2 Structural characterization

The materials are synthesized similar to the previously reported procedure with slight modifications (as explained in the experimental section, Chapter 3).^[23] In the parent material, i.e., LiNbMoO_6 the molar ratio of Nb/Mo was fixed at 1:1. The as obtained product was treated with 2M HNO_3 to facilitate the protonation of the product, and the as-protonated product was dehydrated at 230°C , as revealed by thermogravimetric analysis (TGA), Appendix, Figure 13. The crystallographic identification of the as-produced hydrated and dehydrated products is obtained by X-ray powder diffraction (XRD). XRD analysis confirms that both hydrated and dehydrated products belong to the body-centered tetragonal crystal structure of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 with cell parameters $a = 4.690 \text{ \AA}$, $c = 26.75 \text{ \AA}$ and $a = 4.694 \text{ \AA}$, $c = 21.34 \text{ \AA}$, respectively.^[23] As shown in Figure 7.1 (a), the position of diffraction peaks is almost identical in both the samples except a slight shift in (002) peak for dehydrated sample. A slight shift in the peak position indicates $\sim 20\%$ contraction of the inter-layer spacing in HNbMoO_6 due to removal of the water molecules from the lattice of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$, the atomic structures of the hydrated and dehydrated samples are depicted in Figure 7.1 (b) and Figure 7.1 (c), respectively. To examine the consequence of the removal of water molecules on the chemical bonding of Nb, Mo, O and OH, Fourier transformation infrared spectroscopy (FTIR) was performed. As shown in Figure 7.1 (d), the absence of a broad band in the range of $3300\text{--}3500 \text{ cm}^{-1}$ in HNbMoO_6 indicates removal of structural water molecules

from the inter-layers region, however, a small band at 1620 cm^{-1} reflects the existence of co-ordinatively attached $-\text{OH}$ molecules in HNbMoO_6 .^[29,30] The position of $\text{Nb}=\text{O}$ and $\text{Mo}=\text{O}$ stretching bands is found unchanged even after dehydration of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$, except a drop in the intensity.^[25] A significant fall in the intensity of the bands in case of dehydrated $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ reflects that the concentration of terminal oxygen ($\text{Mo}=\text{O}$ or $\text{Nb}=\text{O}$) is decreased due to decrease in the inter-layer spacing after removal of water molecules.

Figure 7.1 (a) XRD patterns of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ (1) and HNbMoO_6 (2), (b) and (c) schematic illustration of atomic structure of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 , respectively, and (d) IR spectroscopy of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ (1) and HNbMoO_6 (2).

The microstructures of both the samples were investigated using field-emission scanning electron microscopy (FESEM). The micrographs of both $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 showed nanosheets-like morphology, as shown in Figure 7.2 (a) and Figure 7.2 (b), respectively. The lateral dimensions of the nanosheets in both the samples span from

hundreds of nanometers to few micrometers. To examine the nanoscale morphology of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 nanosheets, transmission electron microscopy (TEM) was performed. As shown in Figure 7.2 (c) and Figure 7.2 (d), a corrugated nanoosheets-like morphology is revealed for $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$, while a uniform nanoosheets-like morphology is observed in case of HNbMoO_6 , respectively.

Figure 7.2 FESEM micrographs of (a) $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$, and (b) HNbMoO_6 , (c) and (d) TEM micrographs of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 , respectively.

To quantify the thickness and surface uniformity of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 nanosheets, atomic force microscopy (AFM) surface profiles and topography were conducted, as shown in Figure 7.3 (a-b) and Figure 7.3 (c-d), respectively.

Figure 7.3 (a-b) and (c-d) AFM topography and the height profile of HNbMoO₆ H₂O nanosheets and HNbMoO₆ nanosheets, respectively

Figure 7.3 (a) and Figure 7.3 (c) present the topography of the as-prepared HNbMoO₆ H₂O and HNbMoO₆ nanosheets, respectively. Whereas, Figure 7.3 (b) shows that the thickness of HNbMoO₆ H₂O nanosheets, which is about 8 nm (equivalent to 3 double layers of NbO₆/MoO₆), while the thickness of HNbMoO₆ nanosheets is about 13 nm (equivalent to 6 double layers of NbO₆/MoO₆), as depicted in Figure 7.3 (d). Although, the actual cause of increase in the thickness is not known, but I assume that the increase in the thickness of HNbMoO₆ nanosheets could be due to colligation of the nanosheets during removal of inter-layer water molecules. However, the surface uniformity of both the samples is found almost identical with the surface roughness of <2 nm, as can be seen in Figure 7 (c) and (d).

7.3 Electrochemical characterization

To demonstrate the high electrochemical activity of HNbMoO₆ nanosheets, the electrochemical testing of HNbMoO₆ H₂O and HNbMoO₆ electrodes were first carried

out in a three-electrode (half-cell) configuration using 1M H_2SO_4 as electrolyte. As depicted in Figure 7.4 (a), the area enclosed by the cyclic voltammogram (CV) of HNbMoO_6 nanosheets is much higher than that of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ nanosheets, which indicates the higher capacity of HNbMoO_6 to hold the charges in the given potential domain (-0.4-1.0 V). As shown in Figure 7.4 (a), both the CVs exhibit a pair of redox peaks, that can be assigned to the reduction/oxidation of $\text{Mo}^{6+}/\text{Mo}^{5+}$ or $\text{Nb}^{5+}/\text{Nb}^{4+}$ in the potential window of 0.2 V to -0.4 V.^[31,32] This improvement in HNbMoO_6 could be ascribed to the facile diffusion of H^+ ions into the inter-layer region via hopping between H_2O and OH^- sites due to existence of cage-protons. The detailed mechanism of proton conduction and storage is presented in the next section. In fact, the characteristics of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 resemble the hydrated form of RuO_2 .^[33] Early studies carried out on $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ show that the hydrous region, i.e., inter-particle or inter-layer region plays an important role in determining the specific capacitance.^[34] Attributed to the removal of disproportionate inter-layer water molecules, a facile diffusion of electrolyte ions is realized in HNbMoO_6 nanosheets. HNbMoO_6 nanosheets showed excellent pseudocapacitive response in a wide range of scan rates (5-100 mV/s), as shown in Figure 7.4 (b). Figure 7.4 (c) presents specific charge stored in $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 as a function of scan rate, indicating the maximum charge that can be stored in $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ is about 350 C/g, while HNbMoO_6 could store as high as 801 C/g at a scan rate of 5 mV/s. Thus, the as-produced HNbMoO_6 nanosheets could hold almost 150% higher charge than that of the charge of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$. The specific capacitance obtained for this class of material, i.e., 3D tri-rutile is fairly higher than that of the other classes of the materials, such as spinel,^[14,15] perovskite,^[35,36] layered,^[37] etc. It is evident from the EIS analysis that HNbMoO_6 nanosheets not only bear low internal impedance (solution resistance and material's intrinsic resistance) of about 2 Ω , but also a very low diffusion resistance in the low frequency region, as shown in Figure 7.4 (d).

Figure 7.4 (a) Cyclic voltammograms (CVs) of HNbMoO₆·H₂O and HNbMoO₆ nanosheets at scan rate of 10 mV/s, (b) CVs of HNbMoO₆ nanosheets at various scan rates, (c) specific charge stored in HNbMoO₆·H₂O and HNbMoO₆ nanosheets as a function of scan rate, the loading mass of the active material was about 1.2 mg, and (d) Nyquist plot of HNbMoO₆·H₂O and HNbMoO₆ nanosheets.

7.4 Mechanism of proton conduction and storage

The mechanism of proton transportation has been studied widely by several groups.^[38–40] The main well accepted mechanisms are; Grotthuss mechanism,^[41] and vehicular mechanism,^[42] but there are some divergence between two mechanisms. In the former, proton diffuses by the combination between molecular reorientation around the oxygen ions and jump of the proton from oxygen to nearest neighbor ions, this mechanism is found in solid-acid salts (CsH₂PO₄),^[43] perovskite (BaZrO₃) materials,^[44] etc. In the later, the vehicular mechanism, proton diffuses on a vehicle like, H₃O⁺, NH₄⁺, etc.,^[45] This mechanism can be found in several materials systems, for example, Nafion,^[42] SnO₂·nH₂O,^[46] WO₃·nH₂O,^[47] etc. The conduction of protons in vehicular mechanism

commences the formation of one bond followed by breaking of another bond, and the strong interaction with the lattice oxygen avoids the need of extra energy to break O-H bond.

Here, I assume that H^+ ions exist as OH^- centers in the lattice of $HNbMoO_6$, which acts as proton compensated sites. These proton compensated sites enhance the thermodynamic reactivity of $HNbMoO_6$ lattice by lowering the activation energy needed to shuttle the proton throughout the layered lattice of $HNbMoO_6$ taking vehicular proton mechanism into account. The mechanism of proton conduction is schematically illustrated in Figure 7.5. In the first step, electrolyte ions (H^+) interact with the OH^- centers of MoO_6 octahedra via cage protons. Besides interacting with the proton compensated sites, i.e., OH^- centers, electrolyte ions may directly hop through lattice cations, i.e., Mo^{6+} ions, however, this process requires higher activation energy.

Figure 7.5 Schematic illustrations of the steps that take place during charge conduction and storage in $HNbMoO_6$ nanosheets.

In the second step, protons make jump from OH^- site of one MoO_6 octahedra to O^{2-} site of other MoO_6 octahedra. In this step hopping of H^+ ions from O^{2-} sites to Mo^{6+} sites occurs (both are electron donating centers), this step is crucial to store the protons. Because the rate of hopping greatly dependent on the distance between O and Mo, and decreases with increasing the distance. I believe that the mechanism of proton conduction in $HNbMoO_6$ mimics the mechanism of charge transfer and storage in cation deficient systems, such as V_2O_5 ,^[48] Fe_2O_3 ,^[49] and MnO_2 .^[50,51]

7.5 Electrochemical testing of symmetric device

Considering the advantages of $HNbMoO_6$ nanosheets, I chose to fabricate a symmetric supercapacitor device. As demonstrated in the three electrode (half-cell) testing,

HNbMoO₆ nanosheets electrode can hold a high specific charge of ~801 C/g in a potential window of 1.4 Volt. In a two electrode cell configuration, the capacitance of the cell would be equal to the series capacitance of the components; therefore the total cell capacitance can be expressed according to equation 7.3.

$$C_{\text{total}} = C_1 \times C_2 / (C_1 + C_2) \quad (\text{eq. 7.3})$$

Where C_1 and C_2 are the specific capacitance of electrode 1 and 2, respectively (calculated on the basis of half-cell configuration).

The above expression shows that if the capacitance value of C_1 is much higher than that of C_2 , the capacitance of the cell will be decided by C_2 only. On the other hand, if $C_1 = C_2$, the total capacitance of the cell would be the half of the capacitance of C_2 . Therefore, to avoid any discrepancy between the cell components (mainly electrodes); I favored the fabrication of symmetric supercapacitor device.

A prototypic symmetric device was fabricated using HNbMoO₆ as positive as well as negative electrode. An advantec filter paper was soaked in 1 M H₂SO₄ solution before use and was applied as a separator. Based on the optimized potential window of the device, CVs and Galvanostatic charge/discharge tests were performed to evaluate the electrochemical performance of symmetric device. Figure 7.5 (a) presents CVs of symmetric device carried out at various scan rates ranging from 5-50 mV/s. As can be seen in Figure 7.5 (a), the CV curves show a pair of redox peaks, indicating well defined pseudocapacitive response of this device.

To examine the performance of the device, Galvanostatic charge/discharge tests were performed, as shown in Figure 7.5 (b). The charge/discharge curves at various applied current densities show typical symmetric non-triangular curves, indicating partake of redox reactions in charge storage. The specific capacitance of the device is calculated using charge/discharge analyses, according to equation 6.2.

As shown in Figure 7.5 (c), at an applied current density of 1 A/g, the device exhibits a specific capacitance as high as 165 F/g. The as obtained specific capacitance is much higher than that of the other transition metal molybdates supercapacitors, for example, AC//NiMoO₄·H₂O (96.7 F/g),^[52] AC//CoMoO₄-NiMoO₄ (98 F/g),^[53] rGO//CoMoO₄ (26.1 F/g),^[54] FeMoO₄//NiMoO₄ (81 F/g),^[55] AC//Co₃O₄@NiMoO₄ (128 F/g),^[56] AC//NiMoO₄ (150 F/g),^[57] and lower than that of NiMoO₄//NiMoO₄ (392 F/g).^[58]

Importantly, this device could retain about 55% of the initial capacitance at an applied current of 5 A/g, indicating good rate performance.

Figure 7.6 (a) CVs of HNbMoO₆/HNbMoO₆ symmetric device carried out at various scan rate, (b) Galvanostatic charge/discharge curves of the device, (c) specific capacitance of the device as a function of scan rate, the loading mass of the active material was about 2.3 mg (whole cell), and (d) cycling stability of the device at a scan rate of 50 mV/s.

The cycling stability is one of the most important requirements of supercapacitor. As can be observed in Figure 7.5 (d), HNbMoO₆/HNbMoO₆ symmetric device retains about 70% of the initial capacitance after 3000 consecutive CV cycles. The initial stage capacity fade in supercapacitors mainly occur due to either a loss of active material or increased overall cell resistance, the increased resistance imposes electrode polarization that lead to a reduced charge storage capacity over a fixed potential range. These issues may result from physical or electrochemical effects that commence during cycling test. In our case, the early stage (~1500 cycles) capacity degradation may arise from loss of the active material, after that device maintains a constant performance, and retains about 70% of the initial capacitance after 3000 consecutive CV cycles. The cycling stability of our device

is found better than AC//Co₃O₄@NiMoO₄ (68%),^[56] and comparable to the AC//NiMoO₄-CoMoO₄ (78%).^[53]

Figure 7.7 Ragone plot of HNbMoO₆/HNbMoO₆ symmetric device along with the various symmetric and asymmetric devices.

The energy density and power density are the two important parameters of supercapacitors, and are vital for practical applications. The relationship between energy density and power density is termed as the Ragone plot. The energy densities and the power densities are calculated according to equation 7.1 and 7.2, respectively. The Ragone plot of HNbMoO₆/HNbMoO₆ symmetric device is presented in Figure 7.7. A maximum energy density of 52.4 Wh/kg can be achieved at an average power density of 800 W/kg. Most importantly, device could maintain the energy density of 25.2 Wh/kg at a high power density of 3.81 kW/kg. The energy density and power density performance of the symmetric device is found superior to the other transition metal molybdate systems, including AC//NiMoO₄ H₂O (34.4 Wh/kg and 165 W/kg),^[52] AC// CoMoO₄-NiMoO₄ (16 Wh/kg and 1600 W/kg),^[53] rGO//CoMoO₄ (8.17 Wh/kg and 187 W/kg),^[54] FeMoO₄//NiMoO₄ (29 Wh/kg and 190 W/kg),^[55] AC//Co₃O₄@NiMoO₄ (41.9 Wh/kg and 298 W/kg),^[56] AC//β-NiMoO₄-CoMoO₄ (28 Wh/kg and 100 W/kg),^[59] NiMoO₄//NiMoO₄ (43.5 Wh/kg and 500 W/kg),^[58] CoMoO₄//CoMoO₄ (37.2 Wh/kg and 900 W/kg),^[60] and slightly lower than that of AC//NiMoO₄ (60.9 Wh/kg and 850 W/kg).^[57]

I credit the superior electrochemical performance of $\text{HNbMoO}_6/\text{HNbMoO}_6$ symmetric device to the following points; (1) ultra-large inter-layer spacing accommodates large number of electrolyte ions. In this case device shows high specific capacitance. (2) A facile conduction path is conferred by the cage-protons, this feature of the materials is critical to improve the rate capability of the device, and (3) the interfacial contact between electrode/electrolyte is greatly improved due to thin HNbMoO_6 nanosheets structures. Moreover, the performance of the device can be further improved by controlling the microstructure and amount of the cage-protons in HNbMoO_6 nanosheets. I also believe that the performance of the symmetric device can be further improved by fabricating a fully sealed device structure.

7.6 Summary

In summary, I have synthesized and demonstrated the electrochemical properties of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ and HNbMoO_6 nanosheets. HNbMoO_6 nanosheets were successfully synthesized under melt-diffusion conditions using LiCO_3 , Nb_2O_5 and MoO_3 in their stoichiometric ratios. The protonation step was essential to change the 2D rutile structure of LiNbMoO_6 to 3D tri-rutile structure of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$. HNbMoO_6 nanosheets were obtained after removal of the structure water molecules from the lattice of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$. The lateral size of the nanosheets was reduced after air annealing of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$. On the other hand, due to removal of water molecules, thickness of the nanosheets was increased which is a result of the collapse of the individual layer of $\text{MoO}_6/\text{NbO}_6$ octahedra.

The half-cell testing showed that HNbMoO_6 nanosheets were potent to stock up a high level of charges than that of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$ nanosheets. The superior charge storage ability of HNbMoO_6 nanosheets was originated from its intrinsic properties, i.e., wide interlayer spacing and the cage protons to facilitate the conduction of electrolyte ions. The actual potential of the material was executed in the full-cell testing taking HNbMoO_6 as positive as well as negative electrode material. The as-prepared symmetric device showed excellent charge storage performance. Due to relatively wide potential window and high level of charge storage, the energy density as high as 52.4 Wh/kg at a power density of 800 W/kg was obtained, which is superior to the other symmetric as well as asymmetric devices out there. Moreover, at high level of power density (3.8 kW/kg) our

device could maintain a high energy density of ~25.2 Wh/kg. Thus, the material system proposed here has distinctly better charge storage performance than that of the other molybdate systems. In other words, 3D tri-rutile related material systems bear intriguing chemical as well as electrochemical properties, which could be beneficial to enhance the supercapacitive performance.

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Chapter 8*: Localized electrochemical analyses of 2D MoO₃-II using Scanning electrochemical microscopy (SECM)

Scanning electrochemical microscopy (SECM) is a powerful method to investigate the local-electrochemical changes at the vicinity of the electrode surface during chemical or electrochemical reactions. In this chapter, I demonstrated a facile route to prepare 2D nanosheets of MoO₃-II, and studied the localized electrochemical activity of this novel electrode system, i.e., 2D MoO₃-II in the presence of cationic as well as anionic redox mediators. SECM is also used to gain insight on the growth of the diffusion layer. At the end, the effect of substrate potential on the local electrochemical activity of charge transfer is explored followed by concluding remarks of the work.

8.1 Introduction and motivation

The electrochemical properties of the electrode materials studied in the previous chapters are evaluated at the macroscopic scale, which measures the overall average non-localized effect across the interfaces. During the electrochemical processes, only sub-tens of nanometer layer from the interface of the electrode/electrolyte respond to the surface redox reactions; therefore, the interface is a critical region for the physicochemical processes in the electrode materials. The physical aspects of electrode materials, such as porosity and thickness may exert change in the electrochemical processes due to distribution of the electric potential, current density and local concentration of electrolyte ions. The aforementioned concerns become critical particularly at high rate of charge or discharge applications. The conventional or macroscopic electrochemical techniques are not capable to deconvolute the kinetics of electrochemical events that take place at the interface. Therefore, the real time visualization of the electrochemical activity of the electrode materials remains a challenge due to the lack of effective analytical tools, complications due to surface roughness of the electrode material that causes variation in the electrochemical activity at the nanoscale. Attributed to the variation in the local

*Part of the chapter is published substantially as the first author with reference. ^[43]

electrochemical activity of the electrode materials, the actual electrochemical activity sometimes undervalued.

Scanning electrochemical microscopy (SECM) is known for its multi-functionality in electrochemical analyses.^[1] SECM can be used not only to evaluate the topographical information of the electrode surfaces but also capable to capture valuable information about its electrochemical activity at microscopic scale.^[2] SECM is suitable for studying localized electrochemical processes not only in electrochemistry but also in biology, for example, membrane transport and DNA hybridization.^[3,4] The analytical methods of SECM are based on solid theoretical foundation with various demonstrated applications that have been developed in last three decades.^[5,6] SECM offers the possibility to track heterogeneous reaction rates and locally modifying the surface of electrode materials by electro-generating the redox species.^[7] Furthermore, the kinetic aspects of the electrode materials in various energy storage devices, such as battery,^[8–10] dye sensitized solar cell,^[11–13] fuel cell,^[14,15] etc., can also be studied using SECM.

In general, SECM is used in feedback mode to provide the insight into the reaction kinetics taking place across the interface, i.e., solid/liquid, liquid/liquid, liquid/gas, and beyond.^[16–18] In the past and the past recent years, this mode of SECM has been employed to investigate ingress/digress of cation or anion in various electrode systems, including CNT,^[19] polyaniline,^[20,21] WO₃,^[22] MnO₂,^[23] etc. For the measurement in feedback mode (FBM), a quasi-reversible redox couple in its oxidized (O) or reduced (R) form is added to the supporting electrolyte as a mediator. At the microelectrode (ME), a sufficient potential is applied to reduce or oxidize the mediator couple, according to equation 8.1.

Due to reversible reduction/oxidation of mediator, a steady-state faradaic current starts to flow according to equation 8.2.

$$i_{T,\infty} = g n F D c_0 r_T \text{ (eq. 8.2)}$$

Where $i_{T,\infty}$ is the steady-state diffusion limited current, g is the geometry dependent factor, the value of 4 is assumed for disk shaped microelectrode embedded in an insulating sheath, n is the number of electrons/molecules transferred, F is the faraday constant, D is the diffusion coefficient of the mediator species, c_0 is the bulk concentration of mediator

and r_T is the radius of microelectrode. In the steady-state current expression (equation 8.2), subscript ∞ indicates that the separation (d) between microelectrode and target surface should be at least five times larger ($d \geq 5r_T$) than the radius of the microelectrode. Taking oxidized form of redox mediator, when the ME approaches near to the conductive surface, re-oxidation or regeneration of reducing species take place at the surface due to electro-chemical conversion, resulting an improved steady-state current, this response is commonly known as “positive feedback mode”. In contrary, if the microelectrode approaches towards an insulating surface, due to hindrance of the reducing species towards the microelectrode, a decreased steady-state current is resulted, this behavior termed as “negative feedback mode”. The positive or negative feedback responses can be drawn on the measurement scale taking the change in i_T with respect to d (i.e., approach curve) into account.^[1]

The approach curve is the relationship between normalized tip current, i.e., $I_T = i_T/i_{T,\infty}$ and normalized distance, i.e., $L=d/r_T$. Generally speaking, the normalized curve does not depend on the mediator concentration (first-order rate law with respect to R), microelectrode radius, and diffusion coefficient; however, the achievable lateral resolution is directly dependent on the radius of microelectrode.^[2] It must be taken into account that the normalized tip current not only depends on the normalized distance but also on the thickness of the insulating sheath, which makes a thin cell with the electrode surface.^[24] Thus, the geometry of the microelectrode is vital and characterized by the RG value (ratio of the radius of insulating sheath to the radius of active electrode). It is identified that the factor g in the expression of steady-state current (equation 8.2) changes as the RG of the microelectrode change, for example, $g \sim 4$ for $RG=10$ and $g \sim 4.95$ for $RG=1.2$.^[24] It is noteworthy that the RG value is critical while approaching an insulating surface (negative feedback), while on positive feedback substrate it merely affects the normalized current response.^[24]

The tip current i_T can be obtained for a given r_T , RG (~ 10), and d value for a semi-infinite target electrode ($r_s \geq r_T + 1.5 d$),^[5] that is insulating or conducting by solving the diffusion equations with various numerical methods, as expressed in equation 8.3 and 8.4, respectively.^[24]

$$I_T^{\text{inu}}(L) = i_T/i_{T,\infty} = \frac{1}{0.4047 + \frac{1.6018}{L} + 0.5881 + \exp\left(-\frac{2.372}{L}\right)} \quad (\text{eq. 8.3})$$

$$I_T^{\text{cond}}(L) = i_T/i_{T,\infty} = 0.7262 + \frac{0.7765}{L} + 0.2601 \exp\left(-\frac{1.4132}{L}\right) \quad (\text{eq. 8.4})$$

The vertical positioning of the microelectrode becomes easier if the RG and reactivity of the samples are known. The local reactivity of the sample surface portrays a vital role to influence the tip current. Though, due to local reactivity, each finite reaction at the sample surface yields a new approach curve.^[5,25] An analytical approximation was developed to simplify this complexity, as expressed in equation 8.5 and 8.6.^[26]

$$I_T(L) = i_T/i_{T,\infty} + i_T^{\text{ins}}(L) + i_T^{\text{kin}}(L)(1 - I_T^{\text{inu}}(L)/I_T^{\text{cond}}(L)) \quad (\text{eq. 8.5})$$

$$I_T^{\text{kin}}(L) = 0.7837/L \left(1 + \frac{1}{kL}\right) + \frac{0.68 + 0.3315 \exp\left(-\frac{1.067}{L}\right)}{1 + \left(\frac{11}{kL}\right) + \frac{7.3}{110 - 40L}} \quad (\text{eq. 8.6})$$

In the equation 8.6, the parameter $k = k_{\text{eff}} r_T / D$, is a dimensionless parameter. Thus, the first-order heterogeneous charge transfer rate constant can be determined if the radius of microelectrode and diffusion coefficient of the mediator are known.

Turyan *et al.* employed SECM in feedback mode to study electron transfer at WO₃ thin film taking approach curve analysis into consideration.^[22] In their study, FeSO₄, *N,N*-dimethyl-4, 4'-bipyridinium dichloride (methyl viologen, MV²⁺) and dichloro-tris(phenanthroline) iron(II) [Fe(phen)₃Cl₂] were used as mediator couple, and found that the feedback response greatly changes with the substrate potential, mediator concentration and thickness of the film. At the neutral pH conditions, the heterogeneous rate constant at the surface of WO₃ was found to be about 4×10^{-3} cm/s using LiCl as the supporting electrolytes. Also, in their later work electrochemical patterning of WO₃ film using SECM in feedback mode was demonstrated taking MV²⁺ as the redox mediator.^[27]

Jensen *et al.* examined the activity of aluminum alloy (copper enrich) surface using SECM in feedback mode.^[28] Hydroquinone, hydroquinone sulfonate, anthraquinone-2,6-disulfonate, and anthraquinone-2-sulfonate were employed as redox mediator couple. It is found that the copper containing particles exhibit highest electron transfer activity for both the oxidation and reduction reactions.

In the recent years, electrochemical properties of two-dimensional (2D) nanomaterials, such as graphene have garnered significant attention in various fields. Ritzert *et al.* employed SECM feedback mode to studied kinetics of interfacial electron transfer at

single layer of graphene electrode using various redox mediators.^[29] At sufficient overpotential, a transition from negative feedback response to positive feedback response was identified for FeEDTA, [Fe(CN)₆]³⁻, [Fe(CN)₆]⁴⁻, [Ru(CN)₆]⁴⁻ and [Mo(CN)₈]⁴⁻ due to quasi-reversible nature of redox mediators. On the other hand, only positive feedback response was observed for FcMeOH and CoSep, although the kinetics was quasi-reversible. In contrary, [Ru(NH₃)₆]³⁺, MV²⁺ and [Ru(bpy)₃]²⁺ exhibited reversible kinetics of redox mediators. In the same year, Tan *et al.* studied the defect induced reactivity of monolayer graphene, and found that the electrochemical reactivity at site with higher defect density was approximately one order of magnitude higher than that of the pristine graphene surface.^[30]

Sumboja *et al.* demonstrated the correlation between heterogeneous charge transfer rate constant and effectiveness of the electrode material (i.e., MnO₂) for supercapacitor applications, and found that the charge storage ability is directly proportional to the heterogeneous rate constant.^[23] Most recently, Sumboja *et al.* showed the correlation between microscopic electro-kinetics of polyaniline film determined by SECM and macroscopic supercapacitor electrode characteristics, which enable the rational guidelines to optimize microstructural and physical properties to realize improved supercapacitive characteristics.^[21] Thus, SECM in feedback mode has proven its viability to be used to explore the kinetics of interfacial charge transfer.

Among the various layered transition metal oxides, molybdenum trioxide is of particular interest due to its electrochemically- and structurally-rich properties.^[31–34] α -MoO₃ is widely studied and known to be a layered material, but α -MoO₃ is not the only layered phase of MoO₃. A layered structure can also be obtained in its metastable polymorph, i.e., MoO₃-II. This metastable phase of MoO₃ in a layered framework was first evaluated from the thermodynamically stable phase of MoO₃ under high temperature and pressure, in which α -MoO₃ decreased in lattice parameters and increased in density, resulting in a high packing efficiency of MoO₃-II.^[35] The topotactic dehydration of monohydrated MoO₃ (MoO₃ · H₂O) and hemihydrated MoO₃ (MoO₃ · 0.5H₂O) could also lead to the formation of a MoO₃-II phase, earlier identified as the high-pressure phase of α -MoO₃.^[36] A reaction is said to be topotactic if the lattice of the as-formed product possesses one or a few crystallographically equivalent and definite orientations with respect to the lattice

of the parent crystal. Therefore, it was believed that the amount of water molecules and mode of sharing of the MoO₆ octahedron chains (edge- and corner- sharing) inside the framework plays a vital role in achieving the MoO₃-II phase.^[35,36] Furthermore, transformation of α -MoO₃ into MoO₃-II must involve breakage of the Mo–O bond followed by rotation and translation by a $\frac{1}{2}$ unit cell along *b* axis. The Mo–O₁ bond of α -MoO₃ can be broken by the application of high pressure only, as demonstrated recently. Less is known about this phase of MoO₃ than the other polymorphs because it is an intermediary metastable phase in the evolution to the thermodynamically stable phase, i.e., α -MoO₃. Therefore, it has been considered to be difficult to achieve.

MoO₃ in its oxidized state appears colorless or transparent insulator ($\sim M\Omega$), whereas, it can be changed to colored state (light blue to deep blue to red to green) or reduced state or quasi-conducting state by chemical or electrochemical treatment.^[37] The reduction of α -MoO₃ is accompanied by the incorporation of ions such as H⁺, Li⁺, K⁺, etc., and the state of coloration depends on the amount of incorporated ions.^[37] The electrical properties of α -MoO₃ vary dramatically on the incorporation of ions, for example, H⁺ ions due to the formation of molybdenum hydrogen bronze, i.e., H_xMoO₃, where *x* shows the degree of incorporation (Type-I, Type-II, Type-III and Type-IV) and varies in the interval $0 < x \leq 2$. For $x \leq 2$ (Type-IV) it appears green with excellent electrical conductivity, but poor environmental stability, while for $1 < x < 1.6$ (Type-III) it shows the red color with decent electrical conductivity, if $0.8 < x < 1$ (Type-II) it appears deep blue in color and changes in light blue for $0.2 < x < 0.4$ (Type-I).^[38,39] An extensive research has been conducted on electrochemical, electrical and physical properties of α -MoO₃, but I am not aware of the research carried out about the electrochemical properties of MoO₃-II. MoO₃-II is analogous to α -MoO₃ except for the order of the stacking of the layers (AAA) rather than (ABA).

In the present chapter, I demonstrate the preparation of new metastable polymorphs of MoO₃, i.e., MoO₃-II, and subsequently a facile route to prepare 2D MoO₃-II. Also, I employed two different redox-active species in aqueous solution to investigate the kinetics of interfacial charge transfer at the surface of 2D MoO₃-II using Scanning Electrochemical Microscopy (SECM). By locally electrogenerating reducing species, i.e., [Ru(NH₃)₆]²⁺ on the microelectrode, I was able to locally reduce MoO₃-II. Due to good

electronic conductivity of reduced MoO₃-II, the regeneration of the oxidizing species takes place at the surface of locally reduced MoO₃-II. The charges contributing to enhance the steady state current of the ME predominantly flow lateral to the interface of 2D MoO₃-II\electrolyte rather than vertically to the substrate.

8.2 Structural characterizations

MoO₆ octahedra are the basic building blocks used to construct MoO₃ in various phases. The arrangement of the MoO₆ octahedra (formation of any phase) depends on the external conditions, e.g., temperature, pressure and impurities.^[40,41] At the high temperature, MoO₆ octahedra favorably arrange in the α -MoO₃ phase (sharing corners and edges to form layers of the MoO₆ octahedra in an *ABA* arrangement).^[40] Meanwhile, the h-MoO₃ phase (shares corners and edges to form pillars of MoO₆ octahedra) dominates in the presence of cations, such as H⁺, Na⁺, K⁺ or NH₄⁺.^[42] Here, I introduce a novel route to produce the MoO₃-II phase (sharing corners and edges to form layers of MoO₆ octahedra in an *AAA* arrangement), and then prepare MoO₃-II nanosheets, using a two-step procedure, as depicted in Scheme 8.1. The MoO₃ pillar-like structure involves the corner- as well as edge-sharing of the octahedra via O₁ and O₃ atoms along *a* axis (of the other chains) and *c* axis (of the same chain), respectively. In the first step, the dehydration and deammonization of h-MoO₃ (a phase of (NH₄)_{0.21} MoO₃ (H₂O)_{0.26}) nanorods was carried out to produce MoO₃-II microsheets. This step involves the rearrangement of the octahedron chains. The new octahedra share corners and edges with the adjacent octahedra in the horizontal and vertical planes, respectively, and form a layered framework of MoO₃-II. The as-prepared MoO₃-II microsheets were then mechanically exfoliated (due to the layered structure of MoO₃-II) to obtain MoO₃-II nanosheets.

Scheme 8.1 Schematic illustrations of the steps involved in the preparation of MoO₃-II nanosheets. Adapted with permission from “V. Kumar, A. Sumboja, J. Wang, V. Bhavanasi, V. C. Nguyen, P. S. Lee, *Chem. Mater.* **2014**, 26, 5333”. Copyright (2014) American Chemical Society.^[43]

X-ray diffraction patterns of the h-MoO₃ nanorods and as-prepared MoO₃-II microsheets are represented in Figure 8.1 (a). The diffraction patterns are readily indexed to the hexagonal and monoclinic phases of MoO₃ with the space groups P6₃/m and P2₁/m, respectively (ICDD # 29-0115 and 47-1320). From the XRD analysis, the cell parameters $a = 10.54 \text{ \AA}$, $c = 3.72 \text{ \AA}$ and $a = 3.95 \text{ \AA}$, $b = 3.68 \text{ \AA}$, $c = 7.09 \text{ \AA}$ and the cell volumes $V = 359.37 \text{ \AA}^3$ and $V = 100.47 \text{ \AA}^3$ are determined for h-MoO₃ and MoO₃-II, respectively.^[35,44] The hexagonal phase is represented by (M)_x MoO₃ (H₂O)_y, where M is the framework-stabilizing ion (Na⁺, K⁺, NH₄⁺, etc.) and x and y are the variables ($0 < x < 1$, $0 < y < 1$).^[42] XRD analysis shows that a definite crystallographic relationship exists between the lattice parameters of the two phases, i.e., $b_{\text{MoO}_3\text{-II}} \sim c_{\text{h-MoO}_3}$ and $(b + c)_{\text{MoO}_3\text{-II}} \sim a_{\text{h-MoO}_3}$, which indicates that the two phases, i.e., h-MoO₃ and MoO₃-II are crystallographically correlated with each other. The structure of MoO₃-II consists of layers of MoO₆ octahedra, connected along a axis (100) and growing along c axis (001) to form a layered framework structure, which resembles the structure of α -MoO₃ (growing along b axis (010) and connecting along c axis (001)). A single unit cell of MoO₃-II consists of two layers of MoO₆ octahedra or a single double-layer with a fundamental thickness of 0.709 nm including the respective van der Waals gaps,^[35] as represented in the inset of Figure 8.1 (a). The fundamental thickness of a single double-layer of MoO₃-II was found to be

~57% that corresponding to α -MoO₃ (~1.3 nm), indicating the high packing efficiency in MoO₃-II.^[35]

Figure 8.1 (a) Comparison of the XRD patterns of MoO₃ powder before (h-MoO₃) and after (MoO₃-II) annealing at 530 °C, showing distinct phase formation. Inset: the crystal structure of MoO₃-II, illustrating the layered framework structure of MoO₃-II. A minute fraction of the parent phase (h-MoO₃) was found in the diffraction (♦) spectra of MoO₃-II. (b) DSC/TGA results for h-MoO₃ nanorod powder, showing the dehydration and deammonization of hexagonal nanorods, which leads to the formation of a new phase of MoO₃. Adapter with permission from “V. Kumar, A. Sumboja, J. Wang, V. Bhavanasi, V. C. Nguyen, P. S. Lee, *Chem. Mater.* **2014**, 26, 5333”. Copyright (2014) American Chemical Society.^[43]

The transformation of monohydrated and hemihydrated MoO₃ into MoO₃-II has been reported previously,^[36] but the transformation of h-MoO₃ (a phase of (NH₄)_{0.21} MoO₃ (H₂O)_{0.26}) into MoO₃-II has not been realized before. This transformation is dependent on the impurity content, e.g., the content of water molecules within MoO₃ H₂O and MoO₃ 0.5H₂O. The transformation of h-MoO₃ nanorods into MoO₃-II microsheets began at 450 °C (the exothermic peak indicates the beginning of solid-state reactions or crystallization; Figure 8.1 (b) indicates partial phase formation) and was completed at 530 °C (presence of an endothermic peak in Figure 8.1 (b), signifies the phase formation of MoO₃-II). This is corroborated by the XRD patterns of the samples, which were recorded before and after annealing at 530 °C, as seen in Figure 8.1 (a). Subsequent annealing at 650 °C results in the α -MoO₃ phase (the thermodynamically stable phase of

MoO₃). The appearance of a broad endothermic peak at 650 °C indicates that a large amount of energy is required, to realize the formation of α -MoO₃. A strong endothermic peak at ~ 780 °C designates the melting or sublimation of the material. XRD patterns of the samples annealed at 450 °C, 530 °C and 650 °C are shown in the, Figure 8.1 (b). It should be noted that no polymorphic phase was identified throughout the transformation temperature interval ($\Delta T \sim 100$ °C), as seen in the DSC analysis in Figure 8.1 (b).

The morphology of the nanorods before and after annealing at 530 °C was evaluated using FESEM, as presented in Figure 8.2 (a) and (b), respectively. It is believed that the microsheets are the result of the decomposition and recrystallization of the nanorods (as shown in DSC analysis, Figure 8.1 (b)). The inset of Figure 8.2 (a) shows a magnified view of the h-MoO₃ nanorods. FESEM micrographs of h-MoO₃ nanorods annealed at 450 °C and 650 °C are shown in the Appendix, Figure 14.

Figure 8.2 FESEM micrographs of h-MoO₃ nanorods (a) before and (b) after annealing at 530 °C. Figure (b) clearly shows the rectangular shape of the microsheets with a lateral size of 5 µm x 10 µm and thickness of 1.5 µm, which corresponds to ~ 2138 stacks of double-layers (red arrows in the image). The inset of figure 8.2 (a) shows magnified views of the h-MoO₃ nanorods (scale bar ~100 nm). Adapter with permission from “V. Kumar, A. Sumboja, J. Wang, V. Bhavanasi, V. C. Nguyen, P. S. Lee, *Chem. Mater.* **2014**, 26, 5333”. Copyright (2014) American Chemical Society.^[43]

To evaluate the crystallographic relationship between two polymorphs of MoO₃, transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were used, and the results are shown in Figure 8.3 (a) and (b),

respectively. From the HRTEM analysis, I found that the inter-spacing between two fringes are 0.22 nm and 0.33 nm, corresponding to the (-103) and (011) plane of MoO₃-II, respectively. The apparent fringes in the HRTEM micrograph reveal the good crystalline quality of the as-obtained nanosheets. The crystallographic relationship can also be established, based on the inter-planar spacing relationship, i.e., $d_{(-103) \text{ MoO}_3\text{-II}} \sim d_{(221) \text{ h-MoO}_3}$ and $d_{(011) \text{ MoO}_3\text{-II}} \sim d_{(210) \text{ h-MoO}_3}$. The crystallographic relationship between the h-MoO₃ phase and the MoO₃-II phase proves that the two phases are topotactically correlated. Figure 8.3 (c) and (d) show the fast fourier transformation (FFT) of the HRTEM image exposing the (-31-1) plane of MoO₃-II and the atomic representation of MoO₃-II in the (-31-1) plane, respectively.

Figure 8.3 (a) Transmission electron microscopy (TEM) image, (b) high-resolution TEM (HRTEM) image, (c) FFT pattern along [-31-1] zone axis and (d) unit cell of MoO₃-II exposing the (-31-1) plane. Red and green balls depict Mo and O atoms, respectively. The inset of figure (d) shows a magnified HRTEM image with the corresponding Mo and O atom positions. Adapter

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8.3 Macroscopic electrochemical characterizations

In the present study, I chose [Ru(NH₃)₆]Cl₃ ($E^0 \sim -260$ mV vs. Ag/AgCl) and K₃[Fe(CN)₆] ($E^0 \sim 180$ mV vs. Ag/AgCl) due to their redox potential which lies within the redox-active range of MoO₃-II (-500 mV to 500 mV). Prior to SECM experiments, basic electrochemistry of 2D MoO₃-II was studied using routine electrochemical techniques. Cyclic voltammograms (CVs) of the as-prepared samples (2D MoO₃-II/ITO glass, optical micrographs are shown in Appendix, Figure 15 (a) and (b)), are shown in Figure 8.4. CVs are carried out using 1 mM of anionic and cationic redox-active species, i.e., [Fe(CN)₆]³⁻ and [Ru(NH₃)₆]³⁺ in 0.1 M KCl (as supporting electrolyte) in the potential window of 0 V-0.5 V and -0.5 V-0 V, respectively. CVs in Figure 8.4 (a) and (b) show that an enhance response (reaction of redox-active species in terms of current-Faraday’s first law) can be acquired using [Ru(NH₃)₆]³⁺ redox species (due to faradic contributions) when compared to [Fe(CN)₆]³⁻ redox species (only polarization or charging current). It is evident from the CV analysis that 2D MoO₃-II went under an irreversible reduction due to mild-reducing tendency of the electrogenerated species, i.e., Ru[(NH₃)₆]²⁺.

Figure 8.4 Cyclic voltammograms (CVs) of 2D MoO₃-II/ITO glass and ITO glass in (a) 1 mM K₃[Fe(CN)₆]³⁻ + 0.1 M KCl (1) and (2), respectively, and 2D MoO₃-II/ITO glass and ITO glass in (b) 1 mM Ru[(NH₃)₆]³⁺ + 0.1 M KCl (1) and (2), respectively. Number-3 in (a) and (b) indicates

CV of 2D MoO₃-II/ITO glass in 0.1 M KCl solution (background electrolyte). All the CVs were carried out at a scan rate of 25 mV/s.

On the other hand, the electrogenerated product of [Fe(CN)₆]³⁻ redox species, i.e., [Fe(CN)₆]⁴⁻ may also reduce MoO₃-II surface, however, no such behavior is identified (Figure 8.4 (a)). Therefore, the kinetics of charge transfer (CT) at a localized state will be advantageous to examine the real electrochemical activity at the surface of 2D MoO₃-II.

8.4 Microscopic electrochemical characterizations

In the feedback mode of SECM, with the ME tip immerse in a solution containing redox active species. When a sufficient positive or negative potential was applied to the ME, electrochemical reduction of mediator ([Ru(NH₃)₆]³⁺ or [Fe(CN)₆]³⁻) occurs, according to equation 8.7 and 8.8, respectively.

The rate of this reaction is governed by the diffusion of [Ru(NH₃)₆]³⁺ or [Fe(CN)₆]³⁻ to the ME. If ME is positioned far away ($\geq 5 \times$ radius of the tip of the ME) from the surface of the substrate, then the steady state current $i_{T,\infty}$ can be expressed according to equation 8.2.

Figure 8.5 (a) shows the ME CVs, which were carried out in [Fe(CN)₆]³⁻ redox-active species at a scan rate of 5 mV s⁻¹, at a distance far away from the surface ($\sim 200 \mu\text{m} > 5 r_T$) and near to the surface ($\sim 2 \mu\text{m} < 1/2 r_T$) of 2D MoO₃-II, respectively. The CVs obtained using the ME differ remarkably from those obtained by conventional electrochemical techniques (as shown in Figure 8.4 (a)) due to differences in the mass transfer within the diffusion layer. The tip voltammetry recorded at 200 μm away (from the surface) was purely due to the diffusion of redox species in the bulk solution (diffusion-controlled regime). The redox process was considered as one electron transfer process due to single oxidation and reduction wave in CV. When the ME was positioned within or less than the diameter of the tip away from the surface of the substrate, the ME current was decreased. To get the insights into the kinetics of interfacial redox reactions, feedback (FB) mode approach curves were measured.

Figure 8.5 (a) ME tip cyclic voltammetry in $[\text{Fe}(\text{CN})_6]^{3-}$ redox-active species recorded at away ($\sim 200 \mu\text{m} > 5 r_T$) (1) and near to the surface of 2D MoO₃-II ($\sim 2 \mu\text{m} < 1/2 r_T$) (2), (b) and (c) show SECM approach curves in the FB mode for ITO glass and 2D MoO₃-II (open spheres), and solid lines show conductor (1) and insulator (2) and fitting curves, respectively.

Figure 8.5 (b) and (c) show the SECM approach curves carried out on pristine ITO glass and 2D MoO₃-II in a solution containing $[\text{Fe}(\text{CN})_6]^{3-}$ redox species, respectively. In both the cases the tip was fixed at a constant potential of 200 mV vs. Ag/AgCl to ensure complete reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ according to equation 8.8. As the ME approaches near to the surface (stopped at $\sim 2 \mu\text{m}$ away from the surface), the steady state current decreases gradually due to hindrance in the diffusion of $[\text{Fe}(\text{CN})_6]^{3-}$ redox species to the ME (as shown in Figure 8.5 (c)). This situation mimics the negative or nearly negative feedback response. The underlying mechanism of this characteristic will be discussed in the next section.

Figure 8.5 (b) and (c) depict the normalized coordinates I_T vs. L measured on various substrates. I_T is normalized i_T by the steady state current $i_{T,\infty}$, L is normalized d by the radius r_T of the tip of the ME. The current-distance curve can be fitted well to the analytical approximation model by Cornut and Lefrou (as presented in Appendix),^[45,46] for the finite sample kinetics by changing the normalized heterogeneous rate constant k . The effective heterogeneous charge transfer rate constant was calculated according to $k = k_{\text{eff}} r_T/D$, taking diffusion coefficient $D = 6.6 \times 10^{-6} \text{ cm}^2/\text{s}$, and $r_T = 12.5 \mu\text{m}$, the k_{eff} values were calculated to be $0.049 \times 10^{-2} \text{ cm/s}$ and $1.18 \times 10^{-2} \text{ cm/s}$ at the surface of 2D MoO₃-II and ITO glass, respectively. These results indicate that the kinetics of

heterogeneous electron transfer at the interface (2D MoO₃-II/redox-active species-solution) is approximately one order of magnitude lower at the surface of 2D MoO₃-II than that of the ITO glass, when [Fe(CN)₆]³⁻ redox-active species are being employed.

An interesting feature of 2D MoO₃-II was revealed when SECM experiments were conducted in a solution containing [Ru(NH₃)₆]³⁺ redox-active species. Figure 8.6 (a) shows the ME CVs at a distance away from and near to the surface of the substrates.

Figure 8.6 (a) ME tip cyclic voltammetry in Ru[(NH₃)₆]³⁺ redox-active species recorded at away ($\sim 200 \mu\text{m} > 5 r_T$) (1) and near to the surface of 2D MoO₃-II ($\sim 2 \mu\text{m} < \frac{1}{2} r_T$) (2), (b) and (c) show SECM approach curves in the FB mode for ITO glass and 2D MoO₃-II (open spheres), and solid lines show conductor (1) and insulator (2) and fitting curves, respectively.

The ME CVs show that the current recorded at $200 \mu\text{m}$ away was purely steady-state current due to diffusion of redox species. However, CV near to the surface, as represented in Figure 8.6 (a), shows an incremental change in the ME current.

The kinetics of this improved steady state current was further explored by analyzing the ME approach curves at the surface of bare ITO glass and 2D MoO₃-II in the presence of [Ru(NH₃)₆]³⁺ redox-active species as presented in Figure 8.6 (b) and (c), respectively. The ME tip was fixed at $-400 \text{ mV vs. Ag/AgCl}$, to ensure complete reduction of the redox-couple, and moved towards the surface at a translation rate of $2 \mu\text{m/s}$ and stopped at $\sim 2 \mu\text{m}$ away from the surface of the substrate. As the ME approaches close to the ITO glass surface, a positive feedback behavior was identified.

The approach curves recorded at the surface of 2D MoO₃-II and ITO glass showed positive feedback and the charge transfer rate constant at the surface of 2D MoO₃-II and ITO glass was found to be $\sim 2.99 \times 10^{-2} \text{ cm/s}$ and $\sim 4.21 \times 10^{-2} \text{ cm/s}$, respectively. The

effective heterogeneous rate constant was found distinctly better than that of other oxide systems, including WO₃,^[22] and MnO₂.^[23] Moreover, the kinetics of charge transfer was found almost three order of magnitude higher than that of HOPG ($k_{\text{eff}} = 9 \times 10^{-4}$ cm/s).^[47,48] One might consider the possibility that the diffusion of the charged redox-active species to the ITO support through the spacing between 2D MoO₃-II, and induce possible distortion in the approach curve once the penetration depth of the ions is comparable to the radius of the tip of ME. However, this is not possible in our case due to sufficiently thick 2D MoO₃-II film (~90 μm) on ITO glass substrate. Moreover, all the approach curves were fitted well according to the analytical approximations made by Cornut and Lefrou. This issue was further verified by 2D MoO₃-II film coated on an insulating glass substrate that also showed positive feedback current indicating that the positive feedback response solely comes from 2D MoO₃-II (Appendix, Figure 16)

8.5 Mechanism of the positive and negative feedback responses

The electrochemical potential of electrolytes and semiconductors is defines by their redox potentials and Fermi level, respectively. For a reversible redox system with the concentration of C_O and C_R for oxidizing and reducing species, respectively, the redox potential can be defined using Nernst equation, equation 8.9.

$$E_{\text{redox}} = E_{\text{redox}}^0 + \frac{0.059}{nF} \log (C_O/C_R) \quad (\text{eq. 8.9})$$

Where E_{redox}^0 is the standard redox potential of electrolyte system, n is the number of electrons/molecules transferred and F is the faraday constant. At the absolute energy scale, the energy of redox couple can be given by equation 8.10.

$$E'_{\text{redox}} = E_{\text{ref}} - eE_{\text{redox}} \quad (\text{eq. 8.10})$$

Where E_{ref} is the energy of the reference electrode with respect to the vacuum level and E_{redox} is the redox potential of redox mediators, respectively. The relationship between solid-state energy scale and electrochemical energy scale is presented in Figure 8.7, taking -4.5 eV as the reference potential with respect to NHE (Normal Hydrogen Electrode).

Figure 8.7 Schematic illustration of the relationship between the energy in solid-state system and electrochemical potential of electrolyte.

The surface reactions and charge transfer processes evaluated by SECM are based on its abilities to perturb the local equilibrium and measure the resulting flux of the species across the phase boundary.^[17] To explore the mechanism of charge transfer across the interface (2D MoO₃-II/redox species solution). In the positive or negative feedback regime, the regeneration of oxidizing species only takes place at the surface of 2D MoO₃-II and diffuses back or block to the tip of the ME. It is assumed that the current measured at the tip of the ME is the sum of the currents contributed by the diffusion of redox-active species in bulk solution I_{Diff} , interfacial electron transfer I_{Et} (across the interface of 2D MoO₃-II/redox-active species solution), charge transfer within 2D MoO₃-II I_{Ns} , charge transfer across 2D MoO₃-II $I_{\text{Ns'}}$ and the charge transfer at the interface of 2D MoO₃-II and substrate I_{Ne} . Therefore, the overall rate of the reactions (taking place at different sites) can be written according to equation 8.11.

$$1/v = \sum 1/v_i \quad (\text{eq. 8.11})$$

Where, v is the overall rate and v_i is the rate of all the consecutive reactions, and it proportionally depends on current ($I = nFv$). Therefore, equation 8.11 can be rewritten as equation 8.12.

$$1/I = \sum 1/I_i$$

$$1/I = 1/I_{\text{Diff}} + 1/I_{\text{Et}} + (1/I_{\text{Ns}} + 1/I_{\text{Ns'}}) + 1/I_{\text{Ne}} \quad (\text{eq. 8.12})$$

The kinetics of charge transfer will be determined by the charge transfer across the interface (2D MoO₃-II/redox species solution) and charge transfer within and across 2D MoO₃-II, because the rate of charge transfers across ITO glass and 2D MoO₃-II will be relatively higher. It is noticeable that the contribution of I_{Diff} in both the cases is nearly equal; though, it is I_{Et} , I_{Ns} and $I_{\text{Ns'}}$ which make the difference. The contribution of I_{Ns} and $I_{\text{Ns'}}$ depends on the lateral and vertical conductivity (second rank tensor) of 2D MoO₃-II.

Figure 8.8 Schematic illustration of the (a) negative or nearly negative feedback response and (b) positive feedback response in the surrounding of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+}$, respectively.

As revealed by SECM approach curves analyses that 2D MoO₃-II exhibits nearly negative and positive feedback behavior in the surround of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+}$, respectively. Considering the relationship between the energy of two phases, Figure 8.7, $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple is unable to inject electrons to the conduction band of MoO₃ (empty 4d bands), because the conduction band edge of MoO₃ has less positive or more negative value than that of the formal potential of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple. A nearly negative feedback can be ascribed to the injection of the electrons to the mid-gap states of MoO₃. Due to lack of the complete reduction of MoO₃-II surface and so regeneration of the oxidizing species in the close proximity to the surface, as schematically illustrated in Figure 8.8 (a), the contribution of I_{Et} , I_{Ns} and $I_{\text{Ns'}}$ to the steady state current is hampered.

In contrary, when the ME approaches near to the surface and locally generate the mild reducing $[\text{Ru}(\text{NH}_3)_6]^{2+}$ species, the electrons donated by the reduced species were trapped

by some of Mo⁶⁺ centers to from Mo⁵⁺. The insertion of electrons into the bulk of MoO₃-II, is accompanied by concomitant incorporation of equal number of the protons, in order to maintain the charge neutrality of the system, according to equation 8.13.^[37]

Thus the formation of localize hydrogen-molybdenum bronzes takes place in the close proximity to the surface, as schematically illustrated in Figure 8.8 (b). The metallic or nearly metallic character in MoO₃ bronzes (actually responsible for regeneration) comes from partially filled 4d bands (pristine MoO₃ has empty 4d bands).^[38] The formation of molybdenum bronze (H_xMoO₃) and regeneration of oxidizing species take place concomitantly in the vicinity of the surface, and gives rise to the I_{Et}, I_{Ns} and I_{Ns'}, therefore an enhanced steady state current was achieved.

8.6 Analysis of the growth of the diffusion layer

Lateral diffusion of charges can be considered as an additional path for the conduction of the redox species into the domain that engaged with the ME. In the surrounding of mild reducing species, i.e., [Ru(NH₃)₆]²⁺, the absorption (or generation of Mo⁵⁺ or Mo⁴⁺) of electrons by the surface of MoO₃-II occurs in a spot (similar shape region as the ME), which perturbs the pre-established equilibrium at the surface of 2D MoO₃-II. The diameter of the colored spots (reduced MoO₃-II) grew as a function of time, as shown in Figure 8.9 (a), (b) and (c), and exceeded the size of microelectrode, unambiguously proves that the formation of reduced MoO₃-II (H_xMoO₃) must involve lateral electron transport within 2D MoO₃-II. The change in the local electronic density of MoO₃-II serves to drive protons laterally to the surface, which in turn forms reduced MoO₃-II (r-MoO₃-II, blue colored area) and gives rise to the local electronic conductivity of 2D MoO₃-II.

Figure 8.9 (a), (b) and (c) are showing the effect of the interaction of the ME with the surface of 2D MoO₃-II for 15 min., 30 min. and 60 min., and (d) shows dependence of the spot diameter and rate of spreading on the time of interaction.

Figure 8.9 (d) shows the diameter of the reduced part of MoO₃ or diffusion layer ($\text{diffusion layer}^2 = \text{time} \times \text{diffusion coefficient}$) as a function of the time, which indicates that the diffusion layer grows linearly with the time without depletion. The monotonic increase in the diffusion layer can be credited to the lateral flow of the charges within 2D MoO₃-II rather than vertically to the substrate. The velocity of the propagating or rate of spreading of charges within 2D MoO₃-II decreases (from 0.23 $\mu\text{m/s}$ to 0.058 $\mu\text{m/s}$) as a function of time (from 2 min. to 60 min). This could be due to poor connections and non uniformity among 2D MoO₃-II. The non-uniformity associated with the periphery of the colored spots can be ascribed to the sluggish and random diffusion of charges.

8.7 Substrate potential dependent localize electro-activity of 2D MoO₃-II

The interfacial potential difference (potential across the interface of the 2D MoO₃-II/electrolyte solution) plays a vital role in determining the kinetics of heterogeneous electron transfer across the boundary. In fact, it develops without excess charge on either phase. Therefore, it is essential to evaluate the effect of the substrate potential (E_{surf}) on the kinetics of charge transfer.

Figure 8.10 characteristics behavior of the current at the surface (i_{surf}) and at the tip of the ME (i_{tip}) as a function of the sweep potential applied to (a) ITO glass and (b) MoO₃-II/ITO glass substrate.

To demonstrate the effect of E_{surf} , a scanning potential was employed at the substrate in the presence of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ species, while the tip was held at a constant potential (-400 mV). Figure 8.10 (a) and (b) depict the effect of the sweeping potential (at the substrate) on the current recorded at the tip (i_{T}) as well as at the substrate (i_{surf}), at the surface of ITO glass and MoO₃-II/ITO glass, respectively. The i_{surf} at ITO glass remains constant in the positive potential domain (until -120 mV, first knee potential), whereas i_{surf} at MoO₃-II/ITO glass increases monotonically as a function of the sweep potential (full range of potential). An incremental change in the i_{surf} at MoO₃-II/ITO glass renders information about the electroactivity of MoO₃-II. After the first knee potential, the current at ITO surface increases sharply due to regeneration of the redox species at the substrate. However, in case of ITO glass, as the substrate potential becomes more negative (~ -350 mV, second knee potential) i_{surf} starts to decrease due to depletion of the redox species. On the other hand, tip currents (i_{T}) remain constant for both the samples until the knee potential (ITO_{knee} ~-120 mV and MoO₃-II_{knee} ~-100 mV). After the first knee potentials, i_{T} increases gradually at the surface of MoO₃-II, while decreases in case of ITO glass. This discrepancy is encountered due to difference between the reactivity of two surfaces.

In other words, as the sweep potential becomes more negative MoO₃-II starts to convert into H_xMoO₃; all the polymorphs of MoO₃ are known to make hydrogen molybdenum bronzes which are fairly conductive to transport the charges.^[38] In the beginning, reduction of the mediator species commences at the tip of the ME, but as the conductivity of the surface increases part of the redox species start to reduce at (substrate potential - 200 mV, is the second knee potential) the surface of the substrate. After the second knee potential, the current at the tip decreased sharply as a consequence of the conductive nature of the reduced MoO₃-II. The behavior in which regeneration of the redox species takes place at the surface instead of at the tip is known as the “shielding effect”. Therefore, it is evident from the substrate potential dependent analyses that the kinetics of charge transfer strongly dependent on the potential applied to the substrate.

8.8 Summary

In summary, I have demonstrated the topotactic phase transformation of h-MoO₃ nanorods into MoO₃-II microsheets, which involves the rearrangement of MoO₆ octahedra and a strategy to create MoO₃-II nanosheets. The MoO₃-II nanosheets produced using this synthetic approach exhibit high crystalline quality. As a result of their true 2D character and excellent crystalline quality, this class of nanomaterials offers a vast array of possibilities for the further development of next-generation light-weight and transparent optical or electrical devices with robust chemical and environmental stability. The strategy for the MoO₃-II nanosheets synthesis presented in this work paves a path to produce layered materials using the hydrothermal product as the starting material.

The charge transfer kinetics at the interface was examined using Scanning Electrochemical Microscopy (SECM) in feedback (FB) mode. The surface of 2D MoO₃-II showed a positive and nearly negative (or intermediate) feedback response in the ambience of [Ru(NH₃)₆]³⁺ and [Fe(CN)₆]³⁻ redox-mediator, respectively. The origin of the positive feedback on the surface of 2D MoO₃-II lies in the electro-active nature of MoO₃-II. Localized diffusion layer grows linearly with the time due to increase in local electronic conductivity of individual nanosheet. Moreover, at a more negative substrate potential “shielding effect” was observed due to effective reduction of redox-active species at the surface of 2D MoO₃-II than that of the ME. Therefore, the study presented

here contributes to the fundamental of electrochemistry and opens up the possibility to study the kinetics of charge transfer at the surface of 2D nanomaterials, which are essential for electrochemical device applications to realize improved performance.

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Chapter 9: Conclusion and Future Work

This chapter summarizes the concluding remarks of the work presented in this dissertation followed by the future recommendations.

9.1 Conclusion

In this dissertation, I have emphasized on the strategic steps to enhance the electrochemical performance of molybdenum oxide based supercapacitor electrode materials. The main hypothesis is to facilitate the electrochemical processes by minimizing the rate limiting factors, such as electronic as well as ionic barrier for the conduction of charge carriers. The corresponding strategies are as follows; (1) constructing new crystallographic structures, (2) hybridized nanomaterials of active component with the conducting polymers, (3) improving the electronic as well ionic contributions by creating new electrode materials with unique crystal-chemistry.

In chapter 4, h-MoO₃ nanostructures in various morphologies were proposed to realize an improved electrochemical performance. It was identified that the amount of HMTA or ammonium molecules is crucial not only to stabilize hexagonal framework but also to tune the morphology of the nanostructures. Benefiting from the various intercalation sites, i.e., HW, TC, SW available in h-MoO₃ framework, an improved specific capacitance was achieved. Moreover, h-MoO₃ nanostructures in pyramidal-like morphology was found distinctly better than that of the rest of the morphologies due to exposure of the favorable crystallographic plane present at the tip of the nanorods. The performance of the as-prepared h-MoO₃ nanostructures in pyramidal-like morphology was found better than that of α -MoO₃ nanostructures in various morphologies.

In chapter 5, nanocomposites of polyaniline-h-MoO₃ hollow nanorods were presented. The formation of hollow nanorods was the result of the cation exchange assisted Kirkendall effect. Fe³⁺ ions are not only accountable for the hollowing mechanism but also initiate the mechanism of oxidative polymerization of aniline monomers. The as-prepared nanocomposites showed improved specific capacitance as well as cycling stability. The improved performance was credited to the presence of thin polyaniline shell over h-MoO₃ core. The mechanism of this improvement was also investigated taking CV

analyses into account. It was identified that in the slow scan regime, nanocomposites follow the characteristics of pure h-MoO₃, while at higher scan rates it shows the behavior of pure polyaniline.

In chapter 6, an alternative high performance pseudocapacitive electrode material, namely, T-Ag₆Mo₁₀O₃₃ was synthesized under hydrothermal conditions. T-Ag₆Mo₁₀O₃₃ consists of layers of MoO₆ octahedra separated by the array of silver ions, situated at the (five-coordinated) voids sites between MoO₆ octahedra. T-Ag₆Mo₁₀O₃₃ nanorods could stock up a specific-charge as high as 398 C/g at a scan rate of 1 mV/s. The contributions of the surface and diffusion controlled redox reactions to the overall capacitance were also evaluated. A prototypical asymmetric supercapacitor device of activated carbon//T-Ag₆Mo₁₀O₃₃ exhibited gravimetric capacitance of 64 F/g (in a potential window of 1.6 V), which delivered energy density of 22.1 Wh/kg at a power density of 1.51 kW/kg (at an applied current density of 2 A/g), moreover, device could maintain the energy density of 9.1 Wh/kg at a high power density of 15.1 kW/kg (at 20 A/g). The improvement in the energy density without sacrificing the power density indicates that T-Ag₆Mo₁₀O₃₃ could be attractive for a wide range of applications.

In chapter 7, synthesis of a 3D tri-rutile related layered HNbMoO₆·H₂O and HNbMoO₆ nanosheets were demonstrated. Both HNbMoO₆·H₂O and HNbMoO₆ consist of well separated (~20 Å) layers of MoO₆/NbO₆ octahedra. The inter-layer spacing between the layers was pre-occupied by the water molecules and protons in case of HNbMoO₆·H₂O and HNbMoO₆, respectively. The electrochemical performance of HNbMoO₆ nanosheets was found superior than that of HNbMoO₆·H₂O nanosheets as well other transition metal oxides. A prototypical symmetric device of HNbMoO₆//HNbMoO₆ exhibited excellent gravimetric specific capacitance (potential window of 1.5 V) and delivered a high energy density of 52.4 Wh/kg at a power density of 800 W/kg. More importantly, this device was able to maintain a high energy density of 25.2 Wh/kg at a high power density of 3.81 kW/kg.

The work presented in this dissertation contributes significantly to the synthesis and design of the high performance supercapacitor electrode materials. Moreover, it sheds light on the fundamental understanding and advancement to optimize the electrode materials for an improved electrochemical performance of the device.

Figure 9.1 Ragone plot of supercapacitor (pseudocapacitor/double layer) along with the other energy sources.

In our study, $\text{HNbMoO}_6/\text{HNbMoO}_6$ symmetric supercapacitor showed superior electrochemical performance. As shown in Figure 9.1, the highest energy density that could be achieved by $\text{HNbMoO}_6/\text{HNbMoO}_6$ symmetric supercapacitor is 52.4 Wh/kg at a power density of 800 W/kg which is superior when comparing with other molybdate systems, including AC// $\text{NiMoO}_4 \cdot \text{H}_2\text{O}$ (34.4 Wh/kg and 165 W/kg)^[1], AC// $\text{CoMoO}_4\text{-NiMoO}_4$ (16 Wh/kg and 1600 W/kg)^[2], rGO// CoMoO_4 (8.17 Wh/kg and 187 W/kg)^[3], $\text{FeMoO}_4/\text{NiMoO}_4$ (29 Wh/kg and 190 W/kg)^[4], AC// $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ or CoMoO_4 (41.9 Wh/kg and 298 W/kg or 38 Wh/kg and 275 W/kg)^[5], AC// $\beta\text{-NiMoO}_4\text{-CoMoO}_4$ (28 Wh/kg and 100 W/kg)^[6], $\text{NiMoO}_4/\text{NiMoO}_4$ (43.5 Wh/kg and 500 W/kg)^[7], $\text{CoMoO}_4/\text{CoMoO}_4$ (37.2 Wh/kg and 900 W/kg)^[8] or AC// CoMoO_4 (21.1 Wh/kg and 300 W/kg)^[8] and slightly lower than that of AC// NiMoO_4 (60.9 Wh/kg and 850 W/kg)^[9].

On the other hand, AC//Ag₆Mo₁₀O₃₃ asymmetric supercapacitor exhibited an average energy density of 22.4 Wh/kg at a power density of 1.5 kW/kg, which is extremely higher than that of the other molybdate based electrode system. More importantly, this asymmetric device could maintain relatively good energy density (9.1 Wh/kg) at a very high level of power density (15.1 kW/kg). The superior power density at a good level of energy density allows the device to compete with the double layer electrochemical capacitors, as depicted in Figure 9.1.

In chapter 8, a novel route to prepare 2D MoO₃-II was introduced. Localize electrochemical activity of the as-prepared 2D MoO₃-II was explored using SECM in feedback mode. The electrochemical activity of 2D MoO₃-II was dependent on the nature of the redox mediator. SECM in feedback mode was found viable to study the growth of diffusion layer or propagation of the electronic as well as ionic charges. More importantly, competitive mode of SECM was proven to be useful to explore substrate potential dependent charge transfer kinetics across the interface. Moreover, SECM analyses has provided knowledge about the reactions kinetics, such as effective heterogeneous charge transfer rate constant, which has been considered a parameter to determine the effectiveness of the electrode materials.

9.2 Future recommendations

Based on the research work presented herein, the possible efforts to improve the performance of supercapacitor devices may consider following recommendations.

9.2.1 Redox-assisted hydrogels as solid-state electrolyte for the high performance supercapacitors

Apart from achieving the high level of charge storage in the supercapacitor device, another important aspect is to achieve long term stability of the device. Presently, most of the supercapacitor devices are using single phasic liquid electrolytes (aqueous or organic electrolyte). Though remarkable electrochemical performance has been demonstrated using liquid electrolytes, but their limitations, including leakage or evaporation, reduced flexibility, packing problems, toxicity, corrosion, etc., hamper to maintain the actual performance of the device without failure of any component. Solid-state or quasi solid-state electrolytes, such as polymer gel electrolytes have been recommended in order to replace liquid electrolytes and assurance long term stabile performance of the device. The

polymer content and the ionic conductivity in the gel electrolyte are very competitive to each other, thus assigning the polymer content is critical. According to the Flory-Huggins theory,^[10] the vapor pressure of polymeric solution is inversely proportional to the loading amount of polymer, which means a solution of low polymeric content (reasonable ionic conductivity) could not resolve completely the problem regarding leakage or long term stable performance. Also, polymer gel electrolyte based supercapacitors exhibit lower specific capacitance than that of the liquid electrolyte due to low ionic mobility, low ionic accessibility, etc. compared to the liquid electrolytes. Therefore, to overcome the aforementioned concerns introduction of redox additive into the polymer gel electrolyte is of great interest because redox additives are directly involve in the redox reactions via transferring of electrons to the surface of the electrode materials, as schematically illustrated in Figure 9.2.

Figure 9.2 Schematic illustration of the charge storage mechanism in a supercapacitor with redox additive polymer gel electrolyte.

The mechanism of enhanced charge storage with redox additives lies in the fact that the redox centers partake in the redox reactions via de-solvation and solvation of the species while entering or exiting near the electrode surface. Prior to the electron transfer reaction, redox species must reach to the transition state, as happens in the conventional electrolyte system, and then conversion from transition state to adsorbed state, which may not be present in the conventional electrolyte systems. In the adsorbed state, electron transfer causes conversion of the adsorbed species into the oxidized or reduced species. A very few redox assisted hydrogel systems are attempted.^[11] These types of electrolytes are

studied only on the carbon materials, exploring these electrolytes or other redox assisted polymer gel electrolyte for the oxides, for example, Chapter 4-8 will further strengthen the performance of the redox assisted polymer gel electrolytes based supercapacitors for the practical applications.

9.2.2 Microscopic visualization of the electrode/electrolyte electrochemistry during charging/discharging using SECM

To understand the influence of nanoscale heterogeneities at the electrode/electrolyte interface is paramount to the development and optimization in various fields of electrochemistry, including batteries, fuel-cell, supercapacitors, etc. Electrochemical imaging of these interfaces provides a means to insight the interfacial phenomena that are relevant to the aforementioned applications. Moreover, evaluation of the localized electrochemical activity of the interfaces is widely applicable in numerous applications, such as heterogeneous catalysis and biology (e.g., live cell analysis).

Scanning electrochemical microscopy (SECM) is an electrochemical imaging tool that allows *in situ* topography of the interfaces as well as microscopic visualization of the variation in the electrochemical reactivity of the electrode surfaces. The spatial resolution of SECM is limited by the size of the tip and the minimum current that can be measured accurately.

Hitherto, understanding the microscopic redox activity of supercapacitor electrode materials rely on the measurement of the heterogeneous charge transfer rate constant, as presented in Chapter 8. Determination of the charge transfer kinetics of the electrode materials does not enable the state of the electrode during charging or discharging. Also, it is intricate to analyze the distribution of the current activity or the potential across the electrode surface. To map the spatial nanoscopic heterogeneities in the electrochemistry of supercapacitive electrode materials and to correlate them to the surface chemistry and local topography of the electrode materials is of immense interest.

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Appendix

Analytical approximations made by Cornut and Lefrou for the evaluations of the electro-kinetics determined by SECM:

Cornut and Lefrou proposed a modified analytical expression in which the important parameters, such as L (normalized tip-substrate distance), k (dimensionless substrate kinetics parameter) and RG (ratio of the radius of glass sheath to the radius of platinum wire) can take variable values, which were limited in the previous models. Therefore, this analytical model is useful for various SECM experiments.

First and foremost, before making any new approximation the accuracy of the existed analytical expressions (for micro-disk shaped microelectrodes) needs to be examined precisely. For a given range of L ($0.1 \leq L \leq 1.5$) and a fixed RG of 10, the normalized tip current can be expressed as a function of k , equation 1.

$$I_T = \frac{1}{1.019} \left(\frac{0.7837}{L + \frac{1}{k}} + \frac{0.68 + 0.331 \exp\left(-\frac{1.0672}{L}\right)}{1 + \frac{7.3 + \frac{11}{Lk}}{110 - 40L}} \right) \left(1 - \frac{I_{T6c}^{ins}}{I_{T6c}^{cond}} \right) + \frac{I_{T6c}^{ins}}{1.019} \quad (\text{eq. 1})$$

Where I_T is the dimensionless normalized tip current, L is the normalized tip-substrate distance, k is the normalized heterogeneous charge transfer rate constant, c is the normalized concentration of the mediator species, I_T^{ins} and I_T^{cond} are the tip currents on the insulating (negative feedback) and conducting (positive feedback) substrates, respectively.

It was shown that the accuracy of equation 1 is not so good especially for the small values of k ($0.25 < k$) and this formula works well only with the RG value of 10. These limitations point out the necessity of the modified or new analytical approximations.

In case of the negative feedback, meaning small k values ($0.25 < k$), the analytical approximation for the variable RG and L (not only L , as before) presented by Cornut and Lefrou are as follows, equation 2.

$$I_T^{ins} = \left(\frac{2.08}{R_G^{0.358}} \left(L - \frac{0.145}{R_G} \right) + 1.585 \right) \left(\frac{2.08}{R_G^{0.358}} (L + 0.0023 R_G) + 1.57 + \frac{\ln R_G}{L} + \frac{2 \ln 1 + \pi R G 2 L \pi R G - 1}{1} \right) \quad (\text{eq. 2})$$

For the positive feedback, the analytical formulation can be presented as in equation 3.

$$I_T^{cond} = \alpha(R_G) + \frac{\pi}{\beta(R_G)4 \text{ Arc tan } L} + \frac{\left(1 - \alpha(R_G) - \frac{1}{2\beta(R_G)}\right)^2}{\pi} \text{Arc tan } L \quad (\text{eq. 3})$$

Where α and β can be expressed as in equation 4 and 5, respectively.

$$\alpha = \ln 2 + \ln 2 \left(1 - \frac{2}{\pi} \text{ArcCos} \frac{1}{R_G}\right) - \ln 2 \left(1 - \left(\frac{2}{\pi} \text{ArcCos} \frac{1}{R_G}\right)^2\right) \quad (\text{eq. 4})$$

$$\beta = 1 + 0.639 \left(1 - \frac{2}{\pi} \text{ArcCos} \frac{1}{R_G}\right) - 0.186 \left(1 - \left(\frac{2}{\pi} \text{ArcCos} \frac{1}{R_G}\right)^2\right) \quad (\text{eq. 5})$$

The overall analytical approximation can be derived using equation 2 and 3, and presented in equation 6.

$$I_T(L, R_G, k) = I_T^{cond} \left(L + \frac{R_G}{k}\right) + (I_T^{ins}(L, R_G) - 1)/(1 + 2.47R_G^{0.31}Lk)(1 + L0.006Rg + 0.113k - 0.023RG + 0.91) \quad (\text{eq. 6})$$

The aforementioned expression, equation 6 is valid for $L > 0.1$, $R_G < 20$ and any value of k , while the previous analytical approximations were valid for $R_G = 10$ and limited values of k .

Figure 1. Cyclic voltammograms (CVs) of (a) pyramidal nanorods, (b) prismatic nanorods and (c) hexagonal nanoplates of h-MoO₃ in 1 M H₂SO₄ solution in a three electrode cell configuration.

Figure 2. BET isotherm of (a) pyramidal nanorods, (b) prismatic nanorods and (c) hexagonal nanoplates, and (d) pore size distribution of pyramidal nanorods, prismatic nanorod and hexagonal nanoplates.

Figure 3. (a) FESEM micrograph of the pyramidal nanorods before cycling, (b) nanorods after 300 charge/discharge cycles of cyclic voltammetry (CV), dotted red circles indicate broken parts of the pyramidal nanorods.

Figure 4. IR spectra of all the as-prepared h-MoO₃ nanorods, h-MoO₃ hollow nanorods, PANI and PANI @ h-MoO₃ HNs at various molar ratio of oxidant to aniline monomers (1.7, 1.2 and 1)

Figure 5. TEM micrographs of the as-prepared PANI @ h-MoO₃ HNs using various molar ratio of oxidant to aniline (a) ~1.7 (b) ~1.2 and (c) ~1

Figure 6. Cyclic voltammograms of (a) PANI @ h-MoO₃ HNs, (b) h-MoO₃ HNs and (c) PANI at various scan rates, carried out in a three electrode cell configuration.

Figure 7. Cyclic voltammograms of PANI@h-MoO₃ HNs prepared using various oxidant/monomer molar ratios, i.e., (1) ~1, (2) ~1.2 and (3) ~1.7.

Figure 8. Charge-discharge profiles of (a) PANI @ h-MoO₃ HNs (b) h-MoO₃ HNs and (c) PANI at various applied current densities.

Figure 9. XRD patterns of the as-synthesized and the as-annealed (at various temperatures) silver molybdate nanostructures.

Figure 10. FESEM micrographs of (a) the as-synthesized silver molybdate, (b) annealed at 295 °C, and (c) annealed at 536 °C.

Figure 11. Pourbaix diagrams of (a) Ag and (b) Mo.

Figure 12. (a) CV analyses of activated carbon electrode at various sweep rates and (b) Galvanostatic charge/discharge analysis of activated carbon electrode at various applied current densities.

Figure 13. Thermogravimetric analysis of $\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$, shaded region in the curve indicates the temperature at which annealing is performed.

Figure 14. SEM images of (a) nanorods annealed at 450 °C and (b) nanorods annealed at 650 °C.

Figure 15. Optical micrograph of (a) top and (b) cross sectional view of 2D MoO₃-II/ITO glass, optical micrographs are clearly revealing the rough surface of the nanosheets with a thickness of the nanosheets film about ~ 90μm

Figure 16. Feedback mode approach curves recorded over 2D MoO₃-II on insulating glass substrate in the surrounding of [Ru(NH₃)₆]³⁺ redox-active species