Chapter

Review on Transition Metal Oxides and Their Composites for Energy Storage Application

Nithya S. George, Lolly Maria Jose and Arun Aravind

Abstract

Supercapacitors evolved as a breakthrough to the existing shortages in energy resources because of its enhanced capacitive performance, long-term stability, and high power density. Transition metal oxides (TMOs), a redox active material in energy storage applications, showing high specific capacitance (100–2000 F/g) than the electrical double-layer capacitor (EDLC) material has been reviewed a lot. Among various TMOs, nickel oxide (NiO), tin oxide (SnO2), manganese dioxide (MnO2), tungsten oxide (WO3), vanadium pentoxide (V2O5) are widely used by researchers due to their high theoretical capacitance, low cost, and long cycle life. The limitations of TMO-based electrode material includes low electrical conductivity, ion mobility, and low energy density. It is thus important to develop proper combination of TMO with other transition metals, TMOs, transition metal dichalcogenides (TMDs), conducting polymers (CPs) and carbon-based materials (graphene oxide (GO), activated carbon (AC) and reduced GO (rGO)). This chapter focuses on ongoing development in six TMO-based electrode material (NiO, ZnO, MnO2, SnO2, WO3, V2O5) fabrication for the enhancement of electrochemical performance, their synthesis method and then review about the recent progress in studying the supercapacitor performance of the material. The limitations of each TMOs listed separately, providing new insights for future energy storage applications.

Keywords: transition metal oxides, nanocomposites, transition metal dichalcogenides, supercapacitor

1. Introduction

It is a matter of great concern that the conventional energy sources on our planet are getting exhausted day by day. As the energy consumption demand is constantly increasing, new alternative energy sources are being developed across the world[1–5]. The highly threatening increase in pollution level and global warming invites our attention to the necessity of developing a clean energy portfolio. Special focus should be given in the development of alternative energy sources as well as its storage [6]. The most well-known energy production and storage technologies are batteries, fuel cells, and supercapacitors. In contrast to fuel cells and batteries, supercapacitors use a different energy generating technique. Even though these three systems have distinct energy storage and conversion processes, there exists some electrochemical similarities between them. Common characteristics include the separation of electron and ion transport and the fact that the energy-producing activities occur at the electrode/electrolyte interface's phase boundary. Also, the basic structure of these three systems consists of two electrodes in contact with an electrolyte solution [7].

Coming to the differences, in fuel cells and batteries, energy production occurs from chemical reaction via redox reaction, whereas in supercapacitors, energy is liberated through the diffusion of ions at the interface between the electrolyte and the inner side of the capacitor electrode plates forming electrostatic double layers. Supercapacitors are also called ultracapacitors. They act as a bridge between conventional capacitors and batteries. Conventional capacitors deliver high power density with low energy density and the batteries possess high energy density with low power density. Supercapacitors are generally preferred over batteries because they enable quick charging and can deliver energy at a pace that is comparably faster. Also, they are acceptable in terms of durability, stability, and life span [8]. Comparatively lower energy density of this system can be enhanced by wisely choosing the electrolyte and electrode material. **Figure 1** demonstrates the Ragone plot representing various energy storage systems.

Devices fabricated with TMOs are sophisticatedly important since they exhibit excellent performance in energy storage, wastewater treatment, gas sensing, photovoltaics, etc. In chemical industries, TMOs find application in dye degradation and for the conversion of various hydrocarbons. In energy storage devices, TMO acts as an efficient electrode material especially in supercapacitors and solar cell application. The incomplete d shell corresponding to TMOs resulted in these properties

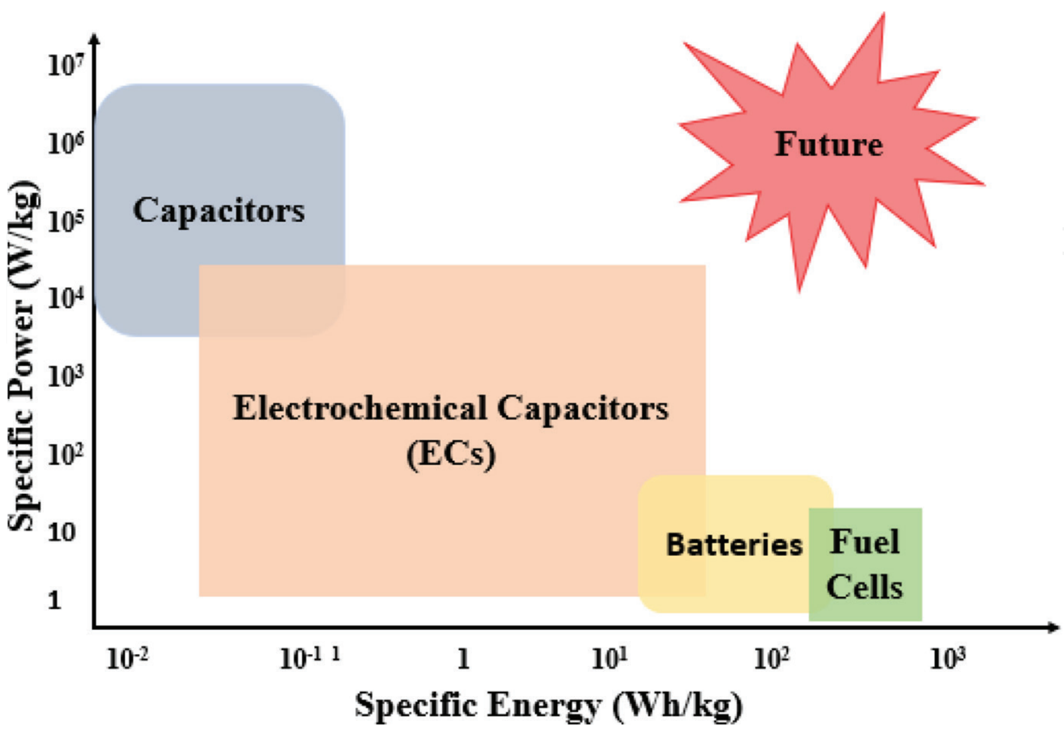

Figure 1.
Ragone plot representing various energy storage systems.

including wide band gap, enhanced chemical reactivity, electrical conductivity, stability, and anti-corrosiveness [9]. To enhance the efficiency of materials, researchers are working on combining TMOs with other transition metals, metal oxides, carbon-based materials, etc. This can modify the surface area, pore characteristics, ion intercalation/deintercalation, conductivity, etc. Many works extending from ZnO/activated carbon to ternary composites such as ZnO/rGO/RuO_2 are still under research study [5].

Graphene, the wonder material with single-atom thickness is one of the most well-liked carbon-based materials because of its high surface area (around 2630 m**2**/g), high conductivity, and chemical stability. The existence of Vander Waals force in graphene results in sudden agglomeration and causes a reduction in surface area and capacity [10]. Carbon-based materials including carbon nanotube (CNT), graphene oxide (GO), activated carbon, etc., are much attracted due to the highly porous structure and enhanced surface area. A combination of TMO with these materials can thus make better electrochemical performance. The size and shape of the nanoparticles can able to tune even the band gap energy of the material; thus, it can control various properties of the nanomaterial including the surface reactivity [11]. These characteristic features of nanostructures can be controlled by various synthesis methods and thus can control the band gap, pore features, etc.

In this chapter, we are focused on the synthesis of some selected TMOs and their composites and discuss the effect of synthesis procedure on the structural and optical characteristics of the material. Also, the article incorporates the device application of the proposed materials.

2. Mechanism of supercapacitors

The reason behind the overview of SCs energy storage system is that SCs weigh less than that of battery with same energy storage capacity, fast access to stored energy, charging very fast than battery, charge/discharge cycle is 106 times, storage capacity is independent of number of charging discharging cycles, negligible environmental concerns, and energy density of SC is 10–100 times larger than that of traditional capacitors [12]. SCs can store substantially more energy than conventional capacitors because the charge separation takes place across a very small distance in the electrical double layer that constitutes the interface between an electrode and the adjacent electrolyte and an increased amount of charge can be stored on the highly extended surface area electrode materials. Electrochemical capacitors also known as supercapacitors exhibit high specific capacitance, high specific power, long cycle life, and fast charge/discharge rate. Theoretical capacitance values of some TMOs are represented in a bar diagram (**Figure 2**).

Supercapacitors are classified according to the energy storage mechanism as electrical double-layer capacitors (EDLCs), pseudocapacitors (PCs), and hybrid capacitors. In EDLCs, charge storage is based on reversible adsorption desorption mechanism at the electrode-electrolyte interface and not involving any faradaic reaction. Electric double layers are formed with the accumulation of charge over the opposite electrodes. Here, the electrode's exposed surface area to the electrolyte determines the capacitance. In other words, pore size of the electrode material should match with the ion size of the electrolyte to avoid capacitance drop. On the other hand, in pseudocapacitors or redox capacitors, charge storage is based on rapid

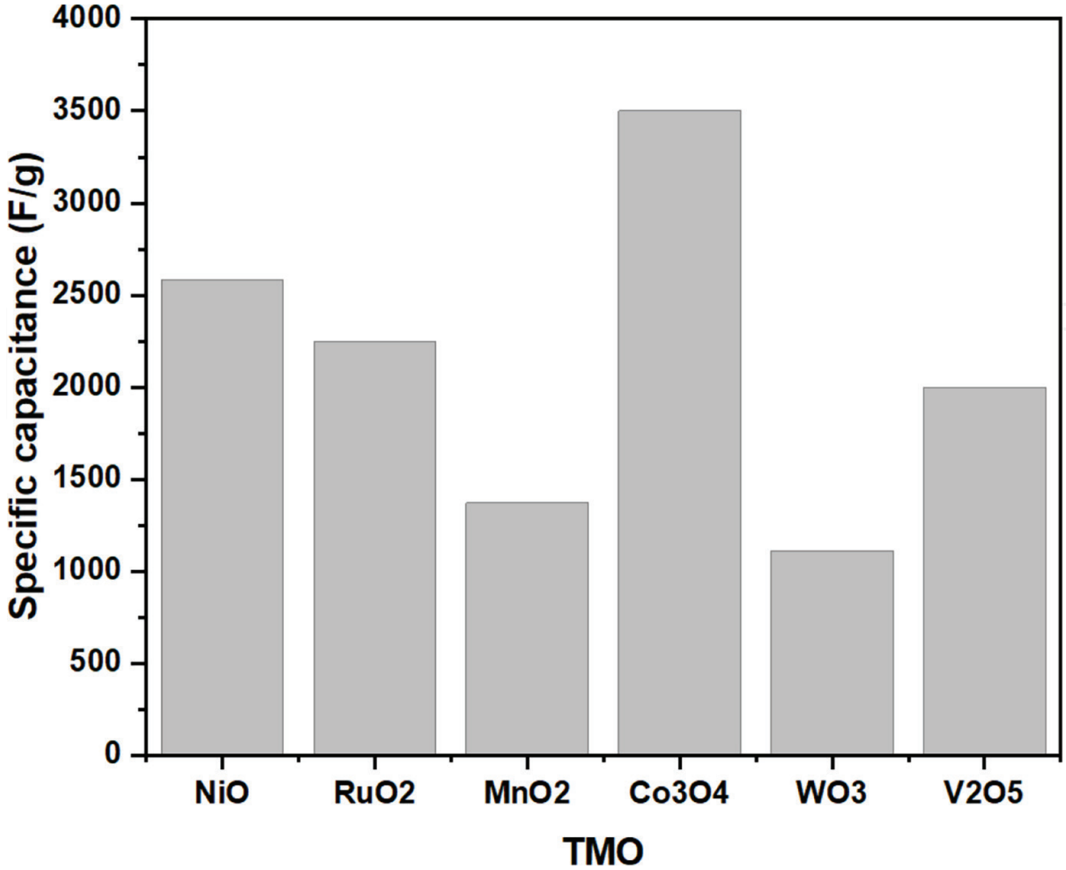

Figure 2.
Theoretical specific capacitance of some TMOs.

faradaic reaction at the surface of electrode material. Generally, pseudocapacitors provide capacitance value higher than EDLCs. In hybrid systems, materials for EDLCs (capacitor-like power sources) and pseudocapacitors (energy sources that resemble batteries) are combined on a single electrode substrate [13].

Electrode is the key factor that determines the performance of any supercapacitor. Depending on the anode and cathode materials in SC device fabrication, it is classified into symmetric, asymmetric, and hybrid device. If two electrodes of the SC are of same material, it is called symmetric device and includes EDLC, pseudocapacitive, and hybrid-type material electrodes. If cathode and anode electrodes are of different types, then the combination is called asymmetric devices. Another classification is based upon the electrolyte. Water-based electrolyte refers as aqueous electrolyte devices, and solvent-based electrolytes come under organic electrolyte-based devices [14].

The electrode material of a supercapacitor is chosen such that it should possess some unique characteristics such as high conductivity, better resistance toward temperature change, large specific surface area, and environmental compatibility. Performance of a supercapacitor relies upon the ability of electrode material for the smooth conduct of faradaic charge transfer [15]. Porosity of the electrode material should be well tuned according to the application where it is used. Small pores yield better surface area, which in turn enhances the specific capacitance and energy density. The better surface area of a porous material enables much more reactive sites and promotes the transfer of electrons and ions. However, this small pore increases the equivalent series resistance (ESR) and hence reduces the specific

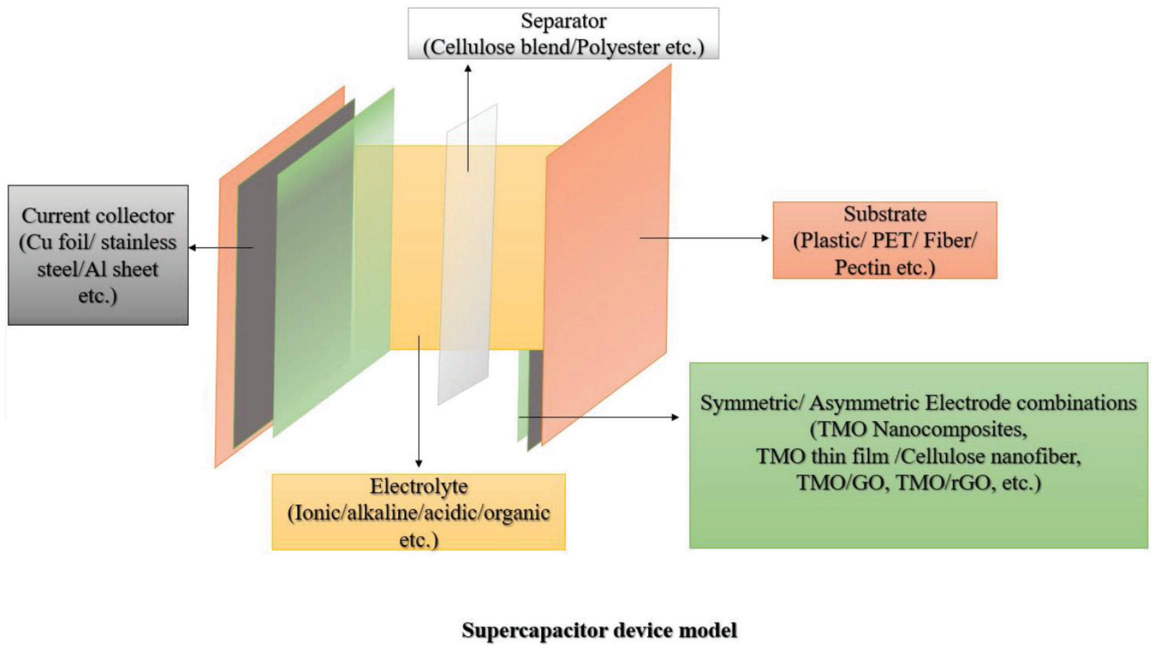

Figure 3.
Schematic representation of supercapacitor device model.

power. Therefore, less porous materials are preferred for applications where high peak current is demanded [16]. Schematic representation of supercapacitor device model is shown in **Figure 3**.

3. Overview of different electrode materials

3.1 Transition metal oxide–based electrode materials

Transition metal oxides (TMOs) are well studied by researchers in the energy storage field. Pseudocapacitive nature of these materials is due to the fast and reversible redox reactions at the surface of electrode material [17]. Theoretical specific capacitance of some TMOs is shown in **Figure 2**.

3.1.1 Manganese dioxide (MnO_2)

Manganese dioxide is well noticed because of high theoretical capacitance (1370 F/g), low cost, and natural abundance. The charge storage mechanism of MnO_2 can be as follows [12]:

$$MnO_2 + \mathrm{M} + +\mathrm{e}^- \leftrightarrow \mathrm{MnOOM} \quad (1)$$

Where M corresponds to electrolyte cations such as K^+, Li^+, Na +, etc. The multiple oxidation states exhibited by MnO_2 result in transition from Mn^{2+} to Mn^{6+} within the potential window. The crystal structure variation by MnO_2 with various polymorphs such as β, α, δ, γ, λ results in variation in electrochemical performance of the material. Other than various advantages, the low conductivity of MnO_2 limits its application as SC electrode material [18].

3.1.2 Vanadium oxide (V_2O_5)

Vanadium pentoxide is an intercalation compound with monovalent cation residing the oxide structure without changing the original structure of the material [14]. The charge storage mechanism is shown as below:

$$V_2O_5 + 2\,M^+ + 2e^- \leftrightarrow M_2V_2O_5 \tag{2}$$

Layered vanadium oxide structures show better potential for intercalation of diverse ions. Thus, they can be effectively used in LIBs and electrochemical capacitors [19].

3.1.3 Zinc oxide (ZnO)

ZnO is considered as an ideal capacitive material with high energy density of 650 A/g. ZnO is regarded as one of the most suitable materials for pseudocapacitor applications because of its higher electrochemical activity and lower cost. Electric double-layer capacitor (EDLC) nature exhibited by bulk ZnO is replaced by pseudocapacitive behavior by inherently defective nanoscale ZnO. The intrinsic point defects play an important role in device performance as well as energy storage [20]. In this regard, inherently defective ZnO suits well for the pseudocapacitive applications.

3.1.4 Tungsten oxide (WO_3)

Tungsten oxides with WO_6 as the basic octahedra units arranged via sharing corners, edges, or planes, varied with respect to the position of W atoms in the octahedral structure in which the hexagonal phase is reported as one showing best performance.

The charge storage mechanism in WO_3 as follows:

$$WO_3 + M^+ + e^- \leftrightarrow HWO_3 \tag{3}$$

By different synthesis methods, WO_3 with different size and shape can be synthesized, which includes nanorod, nanopillars, nanosphere, nanoplate, etc. [21]. By controlling the synthesis temperature and reaction time, the morphology as well as the performance of the material can be altered.

3.1.5 Tin oxide (SnO_2)

SnO_2 nanostructures find potential application in the much-needed fields such as energy storage and conversion. This n-type semiconductor holds high electrical conductivity (21.1Ωcm), better theoretical capacity (~782 mAh g^{-1}), low charge-discharge plateau, superior electron mobility (100–200 cm^2/Vs), low synthesis cost, making them a worthy choice for supercapacitor application [22]. Shin et al. [23] obtained a specific capacitance of 40.5 $\mu F/cm^2$ from hierarchical SnO_2 nano branches. They reported a loss of only 8.9% of specific capacitance after 1000 cycles. The large volume change (200, 300%) reported during the charge/discharge process for supercapacitor and Li-ion application leads to pulverization and loss of electrical contact between particles, resulting in low device performance.

3.1.6 Nickel oxide (NiO)

NiO, a p-type semiconductor, has emerged as an efficient electrode material for its higher theoretical capacitance, low toxicity, and environmental impact. Pseudo capacitance property of NiO is greatly affected by its morphology, crystallinity, and conductivity. In general, the pseudo capacitive performance test of NiO is carried out using three-electrode system with nickel foam loaded with active NiO material as the working electrode, platinum sheet and saturated calomel electrode as counter electrode and reference electrode, respectively. A suitable alkaline solution will be selected as the electrolyte. NiO exhibits CV curves like battery materials. Observed redox peaks result from the mutual transformation between Ni (II) and Ni (III). The OH− ions diffused on or inside the electrode participates in the charging and discharging process. The electrochemical reaction can be expressed as [24].

$$NiO + zOH^{-} \leftrightarrow \mathrm{zNiOOH} + (1-\mathrm{z})\,NiO + ze^{-} \tag{4}$$

Observations from various studies record the excellent supercapacitive performance of NiO electrode materials with lower ESR and charge transfer resistance (R_{ct}) [6]. Similarly, in most of the cases, the residual capacitance of NiO electrode materials is more than 90% of initial capacitance even after thousands of charge-discharge cycles.

3.2 TMO/TMO composite

The idea of preparing a composite structure is always encouraged because it imposes a positive result on the overall electrochemical properties of the material. Under the combined effect of various materials/ions, many of the limitations of the transition metal oxides can be surmount [25]. Zheng et al. [26] fabricated a nanostructured electrode material by combining ZnO and NiO. Here ZnO acted as the electrode modifier, and hence, the specific capacitance was improved. Materials capable of exhibiting multiple oxidation states are of particular interest when it comes to electrode fabrication. NiO is one such candidate, whose multiple valence states favor the fast redox reaction, which in turn enhances the specific capacitance. Varshney *et al* investigated the electrochemical properties of nanocomposite of SnO_2 and NiO synthesized by modified sol-gel route. They exhibited a maximum specific capacitance of 464 F/g at a scan rate of 5 mV/s and appreciable capacitance retention of 87.24% after 1000 cycles signifying the fitness of this nanocomposite for high-energy-density supercapacitor electrode material [27].

Multicomponent nanomaterial combination with TMO-TMO heterostructure results in combining both the advantages of individual nanostructures. Tan et al. demonstrated such combination of MnO_2 and V_2O_5 core-shell nanotube by aqueous-based method. It results in a high specific capacitance of 694 F/g at 1 A/g current density with excellent stability [28]. Yu et al. reported the synthesis of $ZnCo_2O_4$ at MnO_2 core-shell nanosheet for asymmetric supercapacitor device fabrication using hydrothermal method. It shows a high specific capacitance of about 2170 F/g at 3 mA/cm^2 in KOH electrolyte. Device fabrication was carried out with TMO heterostructure as the positive electrode and activated carbon as the negative electrode showing an energy density of 29.41 Wh/g with 95.3% retention after 3000 cycles [29].

3.3 TMO/carbon-based composite

Carbon-based materials are generally selected for various applications including supercapacitors, thanks to their high abundance and easy preparation and cost-effectiveness. The porous nature and excellent conductivity make carbon-based materials—graphene, carbon nanotubes, activated carbon, and various other carbon derivatives, a widely accepted electrode materials for supercapacitor applications [30]. As the synthesis techniques are approaching new heights, carbon-based electrodes are generated in various morphologies including nanofibers, nanoflowers, nanorods, nanotubes, etc. MnO_2, V_2O_5, ZnO, and RuO_2 are some of the promising electrode materials.

The performance and structure of electrode material play crucial role in determining the effective capacity of the SC. The limitations of using MnO_2 as electrode material in SC including the poor conductivity can be alleviated by combining with conductive materials such as carbon to make hybrid electrode material. Carbon-based materials such as activated carbon, carbon nanotube, graphene, etc., are attracted due to their pore structure, volume, specific surface area, and presence of functional groups [18]. Cai W et al. proposed an effective method to synthesis of N-doped Carbon@MnO_2 3D core-shell composite, which shows excellent electrochemical performance. The composite shows high specific capacitance with excellent cyclic stability and high retention [31]. Carbon nanotube finds application as electrical double-layer capacitor with high specific surface area and conductivity. But the low specific capacitance limits its usage, thus combined with TMOs. Lei et al. demonstrated a facile method to synthesis MnO_2 nanosheets at graphenated CNTs by hydrothermal method. It shows a high specific capacitance of 575.4 F/g at 0.5 mA/cm^2 and considerably large energy density of about 51.2 Wh/kg [32]. Long et al. reported flexible SC electrode with delta MnO_2 nanosheets anchored on activated carbon cloth. It exhibits a high specific capacitance of 360.5 F/g with capacitive retention of 89.5% after 10,000 cycles [33]. Guo et al. proposed a 3D vertically aligned ZnO nanorods sandwiched between rGO films by chemical vapor deposition. Specific capacitance of 51.6 F/g is achieved at 10 mV/s for supercapacitor performance [34]. Poor electrical conductivity of V_2O_5 can be balanced by the proper combination with conducting materials as that proposed by Perera et al. CNT/V_2O_5 nanowire nanocomposite thus exhibits an ideal capacitive behavior with specific capacity of 48.5 F/g and power density of 5.26 kW/kg [35].

Compared with all other carbon-based materials, graphene has attracted tremendous attention in high-performance energy storage systems because of its intriguing properties including large surface area, excellent conductivity, commendable thermal, optical, and mechanical properties. Basically, graphene is a single layer of atom constructed by sp2-bonded carbon atoms arranged in a poly aromatic honey comb crystal structure. Theoretical specific capacitance of graphene-based EDLC is 550 Fg^{-1}. In literature, one can see that supercapacitors based on graphene exhibited a specific capacitance of 75 Fg^{-1} with an energy density of 31.9 $Whkg^{-1}$ in ionic liquid electrolytes and 135 Fg^{-1} specific capacitance in aqueous electrolyte. On the other hand, it showed a specific capacitance of 99 Fg^{-1} in organic electrolytes [36]. But it is noted that the restacking of graphene sheets reduces its conductivity and results in poor specific capacitance. Restacking occurs due to the van der Waals interaction between the sheets, and it diminishes coulombic efficiency also. In order to improve the capacitive nature of graphene, they are usually made composites with other capacitive materials. Graphene-metal oxide composite seems to be a good combination since metal oxide hinders graphene from restacking. Metal oxides carry the role of a stabilizer, which prevents the accumulation of graphene sheets. Combination of graphene and metal oxide compliments each other by eliminating the complications faced by these materials individually. Development of composites with pseudocapacitive materials possesses an advantage of generating capacitance from redox charge transfer in addition to the double-layer capacitance. In metal oxide-graphene composite, graphene acts as a passage for charge transfer, whereas metal oxides provide pseudo capacitance. ZnO is a versatile material possessing 3.37 eV bandgap, with an exciton binding energy of 60 meV, which makes it suitable for a wide range of applications including supercapacitors. Regardless, the lower specific capacitance exhibited by ZnO compared with other metal oxides, ZnO superiors with low cost, high abundance, and less toxicity. Also, the electron donating nature of ZnO makes it a good partner for electron acceptor graphene to make efficient electrode materials. As reported by Dutta et al. [37], ZnO/rGO composite electrode can achieve a high specific capacitance of 1012 F/g at a current density of 1 A/g with an outstanding power density of 3534.6 W/kg. Sreejesh et al. [38] further prepared ZnO/rGO nanocomposite by microwave-assisted technique to achieve a high capacitance up to 631 F/g and a long life cycle tested up to 2000 cycles. Introduction of graphene can effectively transcend the poor electrical conductivity of NiO, another promising transition metal oxide candidate. The core-shell hybrid NiO/rGO electrode prepared by electrophoretic deposition method shows a capacitance of 940 F g^{-1} at a current density of 2 A g^{-1} [39]. Pore et al. reported the achievement of specific capacitance of 727.1 F g^{-1} at 1 mA cm^{-2} current density with good cyclic stability of about 80.4% over 9000 cycles for the hydrothermally prepared NiO/rGO electrodes [40].

3.4 TMO/TMD nanocomposite

In energy storage application, the limitations in 2D materials as potential electrodes for energy storage include the graphene-based electrodes having high electrical conductivity and mechanical strength, but it demonstrates only moderate capacity due to the charge storage on the surface only, thus decreasing its conductivity. Transition metal dichalcogenide (TMDs) shows high initial capacities, but undergoes a conversion reaction on the first discharge cycle leading to poor capacity retention. Some TMDs demonstrate relatively high electronic conductivity; many of the phases are semiconducting [41]. Transition metal oxides (TMOs) show high redox activity in intercalation reactions and relatively high working potentials making them especially attractive for use as electrodes [42]. However, low electronic conductivity of oxides imposes a requirement to mix them with a conductive additive to improve their performance. Electrochemical properties of MXenes strongly depend on the synthesis conditions and surface chemistry, and methods for control of their surface terminations need to be developed to minimize irreversible capacity. Thus, research studies point toward an active material development, construction of low cost, large scale, eco-friendly production of TMD/TMO heterostructure. To overcome the limitations of individual 2D materials such as irreversible capacity loss due to consumption of large amounts of electrolyte in the solid-electrolyte interface, electrolyte decomposition due to large no of active sites for ions intercalation, it can be combined with high redox activity of TMO. The heterostructure can create an abundance of structural defects and multiple accessible electrochemically active sites for ion/electron migrations, which would largely enhance the redox reaction activities toward electrochemical energy storages [43]. A rough schematic diagram involving fabrication of TMO/TMD heterostructure is shown in **Figure 4**.

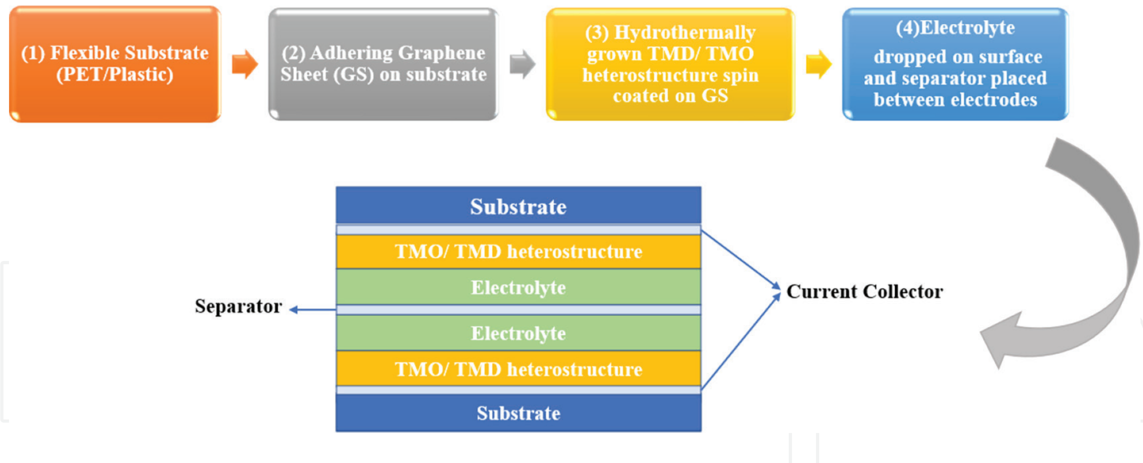

Figure 4.
The fabrication process in TMO/TMD heterostructure-based supercapacitor.

Kai Wang and coworkers [44] focused on general solution-processed formation of porous transition-metal oxides on exfoliated molybdenum disulfides for high-performance asymmetric supercapacitors. They prepared few-layered MoS_2 (f- MoS_2) with a series of TMOs (Ni, Co, and Fe-based oxides) via a chemical bath deposition method at ambient conditions. Each combination of MoS_2 with the abovementioned TMO is synthesized and compared its electrochemical performances. They assembled asymmetric supercapacitor electrode device with a MoS_2-NiO//MoS_2-Fe_2O_3 configuration, and the device shows a maximum energy density and good cycling performance. K. Chanda and coworkers [45] prepared 3D hierarchical nanoform based on TiO_2 sphere and MoS_2 flake by low-temperature hydrothermal synthesis protocols. Surface area increased due to the wrapping of MoS_2 flakes over TiO_2 sphere. Hydrothermal treatment of these spheres creates a drastic change in their morphology. The electrochemical performance of the hybrid is compared with pristine TiO_2 and found the improvement in capacitance values.

3.5 TMO/conducting polymer for SC

Conducting polymers are pseudocapacitive materials, which store charge under fast redox reaction at the surface and bulk part of electrode material. CPs having good intrinsic conductivity show poor cyclic stability due to the variation observed in polymer chain during the doping-dedoping process. It is a low-cost material with excellent charge density. It includes polyaniline (PANI), polypyrrole (PPy), and poly (3,4- ethylenedioxythiophene) (PEDOT) having theoretical capacitance of about 100 F/g. The specific capacitance shown by CPs is two times greater than that of EDLCs. On the other hand, TMOs having low conductivity limit its applicability to achieve the high theoretical capacitance. By combining the advantages of both, the performance might be enhanced with high specific capacitance and good electrical conductivity compared with pure ones [46] without any loss in the pseudocapacitance of the material.

4. Summary

Supercapacitors are currently a new class of energy storage devices that have applications in many different industries. The development of novel, effective electrode materials is a global priority. Transition metal oxides are a desirable material for supercapacitors due to their ideal capacitive performance and much lower cost and environmental compatibility. They store charge in a pseudocapacitive manner. The primary properties of TMO are its significant inherent stability and its challenging valence, which allow for the intercalation of electrons and ions into the lattice of metallic compounds. For high-performance supercapacitors that can give high capacitance, higher cyclic stability, and exceptional rate, transition metal oxides, carbonaceous electrode materials, and their composites considered in this chapter look promising.

Author details

Nithya S. George, Lolly Maria Jose and Arun Aravind*
Center for Advanced Functional Materials, Department of Physics, Bishop Moore College, Mavelikara, India

*Address all correspondence to: arun@bishopmoorecollege.org

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