ISSN: 3064-6758 www.aristonpubs.com/sciengg-advances https://doi.org/10.69626/sea.2025.0001

REVIEW ARTICLE

Mn_3O_4 Nanomaterials in Supercapacitor Applications: A Review

Tanaji S. Patil [1], Raviraj S. Kamble [2], Satish A. Gangawane [3,*]

ABSTRACT: Supercapacitors, bridging the gap between conventional capacitors and batteries, have gained significant attention due to their high power density, moderate energy density, and long cycle life. Central to their performance is the development of effective electrode materials with high surface area, optimal porosity, and abundant active sites for efficient charge storage. This review explores the fundamentals of supercapacitors, specifically focusing on pseudocapacitive charge storage mechanisms, performance evaluation metrics, and the essential characteristics of advanced electrode materials. Manganese-based oxides, particularly Mn_3O_4, have emerged as promising candidates due to their high theoretical capacitance (up to ~1370 F/g) and unique structural characteristics. However, limitations such as low electrical conductivity hinder their application as effective supercapacitor materials. This review further examines recent advancements in the enhancement of Mn_3O_4-based nanomaterials for supercapacitor electrodes, emphasizing methods to improve conductivity and capacitance through heteroatom doping, structural modifications, and composite formation. Integration with materials like graphene has shown potential to mitigate conductivity issues, though improvements in energy density at lower charge-discharge rates remain challenging. Additionally, layered manganese compounds intercalated with alkali metal ions are investigated for their ability to improve ion diffusion within the electrode material, effectively boosting electrochemical performance. The promising outcomes of these approaches underscore the need for continuous research to fully harness the potential of Mn_3O_4 in energy storage applications. This review thus aims to provide researchers with a comprehensive overview on the role Mn_3O_4 nanomaterials in supercapacitor technology, paving the way for innovative applications in future energy storage devices.

Keywords: Supercapacitors, Mn_3O_4 Nanomaterials, Pseudocapacitance, Electrode Nanomaterials.

Received: 23 July 2024; Revised: 15 September 2024; Accepted: 13 November 2024; Available Online: 03 December 2024

1. INTRODUCTION

Due to the global problems such as pollution and global warming, the world has focused on the development of alternative energy sources. Renewable energy sources are continually reloaded automatically by the earth, wind, water, plants, and sun. They have additional advantages such as clean, eco-friendly, sustainable, and security with some limitations such as expensive, less efficient. The interruption of energy supply due to unavailability of renewable sources can be accomplished with stored electrical energy by the devices such as batteries and supercapacitors. The existing devices does not store large energy and delivers it rapidly as required. Therefore, it becomes essential to improve the existing design, method and materials which can fulfill the requirements of the desired energy storage. Also, these devices should be efficient, less expensive, eco-friendly, and non-hazardous. Supercapacitors are the useful devices which have many merits such as high-power density, moderate energy density, largely reproducible, and converts energy directly [1]. Supercapacitors have wide applications such as electric vehicles, military, electronics, and power grids, telecommunication devices, in which high power and higher

[1] Department of Physics, Bhogawati Mahavidyalaya Kurukali, Shivaji University Kolhapur 4160012, India.
[2] Department of Chemistry, Bhogawati Mahavidyalaya Kurukali, Shivaji University Kolhapur 416001, India.
[3] Department of Physics, Doodhsakhar Mahavidyalaya Bidri, Shivaji University Kolhapur 416001, India.

*Author to whom correspondence should be addressed:
gangawane.satish98@gmail.com (S. A. Gangawane)
tanajipatil11@gmail.com (T. S. Patil)

© Ariston Publications 2025. All rights reserved.

energy storage are necessary for their operation. Still lot of work is needed to improve the performance of the supercapacitors. There is a need to improve the energy density by designing innovative electrode materials, electrolytes and devices [2].

The electrode nanomaterial deposited on two conducting electrodes in the supercapacitor device plays vital role for the charge storage. The electrode nanomaterial must be of low cost and has eco-friendly synthesis, enormous electrochemical active states. These two electrodes are immersed in electrolyte and separated by a separator to fabricate the supercapacitor device. The electrode nanomaterials derived from the transition metal oxides have shown excellent supercapacitive properties than any other types of nanomaterials such as polymers, carboneous materials. The examples transition metal oxides such as RuO_2, NiO, Co_3O_4, V_2O_5, MnO_2, Mn_3O_4, IrO_2have shown the exceptional electrochemical properties due to high surface area and porosity [3].

Due to its high theoretical capacitance of approximately 1370 F/g, manganese-based oxides have emerged as the most promising electrode materials for supercapacitors. In particular, the stacking of [MnO_6] octahedra in MnO_2 forms 1D tunnel structures and layers of varying sizes. Electrodes made from MnO_2 with larger tunnels tend to be more effective at storing alkaline cations, such as Na+, K+, and Li+, and show improved capacitance. Some studies have highlighted the charge storage mechanisms of Mn oxides and their dependence on structural configurations [4]. However, the structural complexity of Mn (IV) oxides often leads to conflicting findings regarding the relationship between their microstructures and electrochemical performance. Meanwhile, mixed-valence manganese oxides also exhibit high specific capacitance, making them promising candidates for electrode materials in supercapacitors. In particular, mixed-valence spinel Mn_3O_4 has garnered significant attention due to its potential applications in areas such as catalysis, rechargeable lithium-ion batteries, molecular adsorption, and gas sensing. The tunable capacitive behavior of Mn_3O_4 nanostructures, particularly in terms of size and shape, has been studied extensively. However, the inherently poor electrical conductivity of Mn_3O_4 materials significantly limits their capacity. A common approach to improve the performance of low-conductivity electrode materials is the fabrication of graphene-metal oxide hybrid nanostructures. While this method enhances the rate performance, it has not resulted in a substantial increase in capacity at low charge-discharge current densities. To further boost the electrochemical performance of supercapacitors, manganese oxides with higher capacities are still required. One promising approach has been the synthesis of alkali metal ion-intercalated layered manganese compounds, which improves the diffusion of electrolyte ions within the electrode's solid phase, leading to enhanced electrochemical activity and an effective pre-intercalation effect [5].

Doping with transition metal ions is a widely used technique to alter the properties of functional materials. In Mn-based nanostructures, doping can introduce novel phenomena that are not observed in bulk materials, due to the confinement of electronic states and the tendency of dopants to occupy specific sites in the crystal structure [6]. For example, 3d transition metal cation doping has been applied to stabilize the spinel structure of $LiNi_{0.5}Mn_{1.5}O_4$ and eliminate impurity phases. Additionally, doping is an effective strategy to enhance the intrinsic conductivity of manganese oxides, thereby improving the capacitive performance of Mn oxide electrodes via morphological modification as shown in Figure 1.

2. BASICS OF SUPERCAPACITORS

Supercapacitors or ultracapacitors have high power density with greater life than batteries and high energy density with greater specific capacitance than conventional capacitors. Both capacitors work on similar principle but in the supercapacitors, a thin film electrode made up of nanomaterial possessing highly porosity and surface area with small separation, suitable pore size, high electrical conductivity, and stability are employed. The electrochemical performance of supercapacitors also strongly depends on type of nanomaterial and electrolyte. Therefore, it is essential to develop new device structure, nanomaterial, and active surface of the nanomaterial. Also, ecofriendly nature, cost, stability, efficiency are the parameters which are also important to study. Different studies were elaborated that the tabular, irregular and spherical shaped nanomaterials have high surface area and are useful for the applications such as catalyst, sensor, energy storage devices [7]. Quantum confinement and reduced particle size increases the surface to volume ratio/larger number of atoms on the surface than inside the bulk. It causes to change physical, chemical, mechanical and optical properties of the nanomaterial. Depending on charge storage mechanisms, supercapacitors are categorised into three types

(i) Electric Double-Layer Capacitors (EDLC's)
(ii) Pseudocapacitors and (iii) Hybrid capacitors.

2.1. Electric double-layer capacitors (EDLCs)

Electric double-layer capacitors (EDLCs) are a key type of supercapacitor where energy is stored electrostatically, unlike in batteries, which use chemical reactions for energy storage. In EDLCs, charge storage happens through the formation of a double layer at the boundary between the electrode and the electrolyte. When a potential is applied, ions from the electrolyte move toward the electrode's surface, creating two parallel layers of opposite charges without any actual electron transfer across the interface. This charge separation results in an electric field that allows the capacitor to store energy.

Carbon-based nanomaterials are the primary materials used in EDLCs due to their high surface area, which enhances charge storage by providing ample sites for ion

 © Ariston Publications 2025. All rights reserved.

adsorption [8]. Materials like activated carbon, graphene, carbon nanotubes, and carbon aerogels are popular choices, offering a combination of high electrical conductivity, chemical stability, and mechanical strength. Carbon nanomaterials essentially act as a "sponge" for ions: they adsorb ions from the electrolyte during charging and release them during discharging. However, one of the challenges with EDLCs is their limited energy density compared to other energy storage devices, as they rely purely on electrostatic charge rather than faradaic reactions, resulting in lower specific capacitance and energy storage capacity (Figure 2).

2.2. Pseudocapacitors

In contrast to EDLCs, pseudocapacitors store energy through faradaic charge transfer, which involves redox reactions at the electrode-electrolyte interface. This faradaic process enables pseudocapacitors to achieve a higher energy density and specific capacitance than EDLCs. Materials like transition metal oxides (e.g., RuO_2, MnO_2) and conducting polymers (e.g., polyaniline, polypyrrole) are commonly used in pseudocapacitors due to their ability to undergo rapid and reversible redox reactions. These materials offer a wide potential window and a larger surface area, which enhances their charge storage capability. However, pseudocapacitors typically have a lower power density than EDLCs because the faradaic reactions, while providing greater capacitance, occur more slowly compared to the purely electrostatic processes in EDLCs [9].

2.3. Hybrid capacitors

Hybrid capacitors combine the strengths of both EDLCs and pseudocapacitors to achieve higher energy densities and rapid charging and discharging within a single cell. By merging the stable, high-power performance of EDLCs with the high energy density and specific capacitance of pseudocapacitors, hybrid capacitors can address the limitations of each individual type. They leverage the large potential window of organic electrolytes and the high-capacity electrode materials commonly found in battery-like electrodes. Hybrid capacitors are generally classified into three types based on electrode configuration: (a) composite, which uses a single material that combines EDLC and pseudocapacitive properties, (b) asymmetric, which pairs one EDLC-type electrode with one pseudocapacitive electrode, and (c) battery-type, where one electrode behaves similarly to a battery anode, providing additional capacity [10].

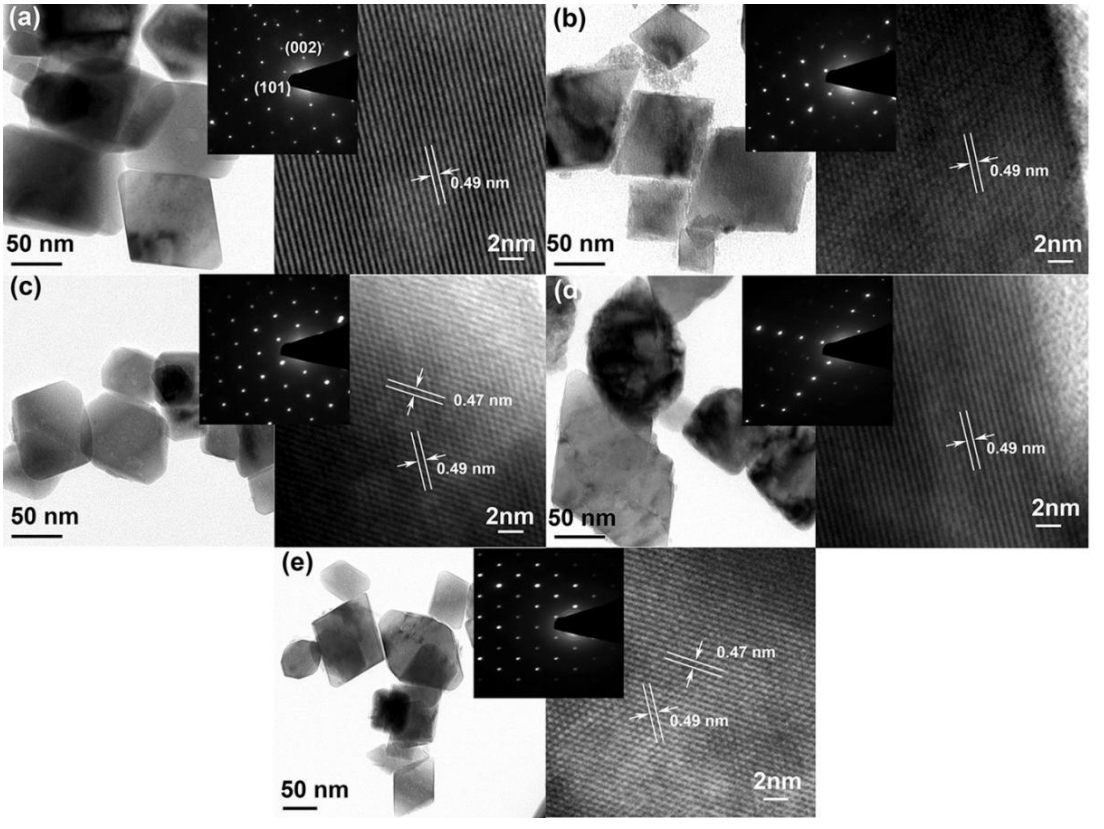

Fig. 1. TEM and HRTEM images of pristine (a), Cr-doped (b), Co-doped (c), Ni-doped (d), and Cu-doped (e) Mn_3O_4 nanocrystals. The insets show the SAED patterns. Reprinted with permission from ref. [6], Dong, R., Ye, Q., Kuang, L., Lu, X., Zhang, Y., Zhang, X., Tan, G., Wen, Y. and Wang, F., 2013. Enhanced supercapacitor performance of Mn_3O_4 nanocrystals by doping transition-metal ions. *ACS Applied Materials & Interfaces*, *5*(19), pp.9508-9516. Copyright © American Chemical Society.

© Ariston Publications 2025. All rights reserved.

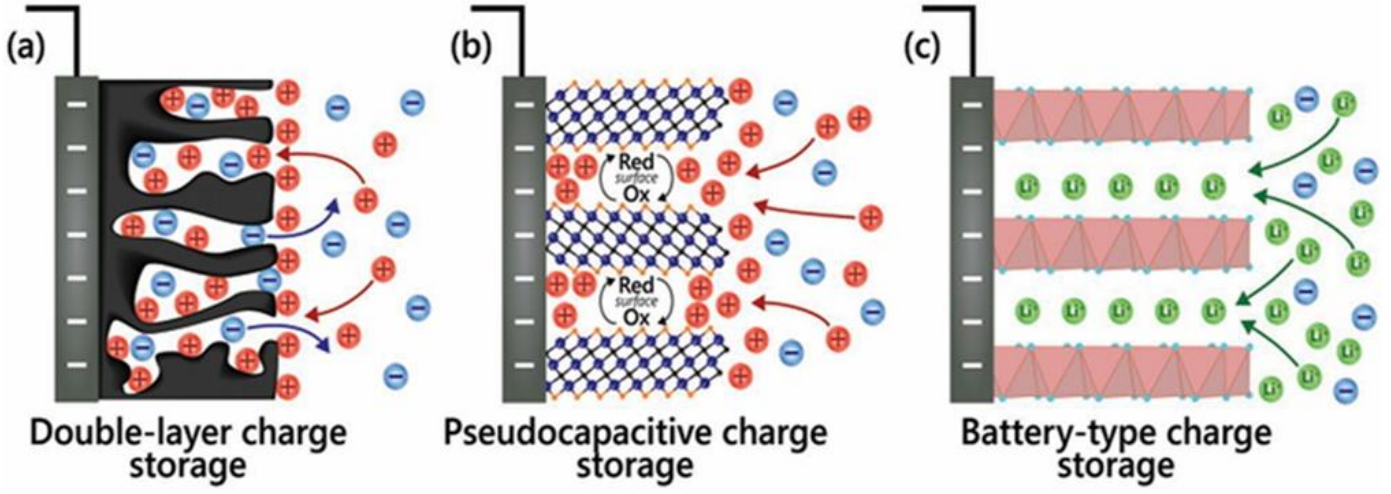

Fig. 2. Electrochemical processes occurring in (a) EDLCs, (b) Pseudocapacitors, and (c) battery. Reprinted with permission from ref. [11], Mathis, T.S., Kurra, N., Wang, X., Pinto, D., Simon, P. and Gogotsi, Y., 2019. Energy storage data reporting in perspective—guidelines for interpreting the performance of electrochemical energy storage systems. *Advanced Energy Materials*, *9*(39), p.1902007. Copyright © American Chemical Society.

2.4. Electrochemical Identification of Capacitor Types

Electrochemical techniques such as cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) are vital tools for identifying the characteristics of supercapacitors. EDLC materials display a rectangular CV curve due to the linear, capacitive current response, and a symmetrical, triangular shape in GCD curves reflecting the pure electrostatic charge and discharge. In contrast, pseudocapacitive materials exhibit non-rectangular CV curves and asymmetric triangular GCD curves due to faradaic redox reactions. Hybrid capacitors show mixed behavior in both CV and GCD profiles, with non-rectangular CV and non-triangular GCD shapes, indicating the coexistence of both capacitive and faradaic charge storage mechanisms. These characteristics make hybrid capacitors versatile for applications requiring both high power and high energy density.

3. CHARGE STORAGE MECHANISM IN PSEUDOCAPACITORS

The charge storage mechanism in pseudocapacitors relies on three primary faradaic processes, each allowing energy storage through distinct electrochemical reactions at the electrode surface or within the bulk of the material. These processes enable pseudocapacitors to achieve higher energy densities compared to electric double-layer capacitors (EDLCs), while maintaining high charge/discharge rates. The three pseudocapacitive mechanisms are as follows:

Underpotential Deposition (UPD): In underpotential deposition, a monolayer of metallic ions is deposited onto a different metallic surface at potentials below the element's standard reduction potential. This monolayer formation occurs through electrostatic attraction between ions and the electrode surface without creating bulk deposits, making it a reversible process. Underpotential deposition is advantageous for high-performance charge storage, as it enhances the electrode's capacitance while maintaining stability over multiple cycles.

Redox Pseudocapacitance: In this mechanism, electrolytic ions are adsorbed on the electrode's surface, participating in reversible redox reactions that allow charge storage. When charged, ions transfer electrons to the electrode material, causing it to change its oxidation state; during discharge, the opposite reaction occurs, and ions are released. Redox pseudocapacitive materials, such as transition metal oxides and conducting polymers, undergo faradaic reactions confined to the electrode surface or near-surface regions, resulting in rapid charge and discharge cycles. This mechanism provides greater specific capacitance than EDLCs, but its reliance on surface reactions may limit the power density compared to intercalation processes.

Intercalation Pseudocapacitance: Unlike redox pseudocapacitance, intercalation pseudocapacitance involves ions entering the electrode's inner structure, typically in channels or tunnels, without altering the material's phase. The ions reversibly intercalate or insert themselves into the host material, exchanging charges with the electrode without causing structural changes. This mechanism can store significant amounts of charge in a stable manner, as the lack of phase transition minimizes stress and enhances longevity. Intercalation pseudocapacitance is commonly seen in materials with layered or porous structures, like transition metal dichalcogenides.

Cyclic Voltammetry (CV) and Analysis of Charge Storage Mechanisms: Cyclic voltammetry (CV) is instrumental in

 © Ariston Publications 2025. All rights reserved.

distinguishing between diffusion-controlled and surface-controlled (capacitive) charge storage mechanisms. For pseudocapacitive materials, current response in CV varies depending on the charge storage mechanism. For diffusion-controlled mechanisms, current varies with the square root of the scan rate $(\upsilon)^{1/2}$, while capacitive processes vary linearly with the scan rate (υ). This behavior is summarized by the relationship:

$$i(V) = k_1\upsilon^{1/2} + k_2\upsilon$$

$$i(V) = i_{diffusion} + i_{capacitive} = a\,\upsilon^b$$

where i(V) represents the total current, k_1 the diffusion-controlled component, and k_2 the capacitive component. Simplifying further, $i(V) = av^b$, where a and b are adjustable parameters. By taking the logarithm of this expression, a plot of log (*i*) vs. log (*v*) yields a straight line with slope b. A *b* value around 0.5 indicates a diffusion-controlled mechanism, similar to battery-like behavior, while values between 0.5 and 1 suggest a capacitive, surface-dominated charge storage. The parameters k_1 and k_2 can be further isolated by analyzing CV data, allowing quantification of diffusion-controlled and capacitive contributions. This approach helps researchers understand the relative importance of each mechanism in a given pseudocapacitive material [11]. Figure 3 shows graph of 'b' values against MnMo thin films.

AC Impedance and Pseudocapacitive Nature: AC impedance spectroscopy, especially the Nyquist plot, provides additional insights into pseudocapacitive properties. In an ideal capacitor, the Nyquist plot shows a vertical line with a phase angle of 90°, indicating pure capacitive behavior. For pseudocapacitive materials, however, the plot's vertical line inclines at a phase angle smaller than 90°, which reflects the presence of faradaic reactions contributing to the impedance. This inclination reveals a combination of capacitive and resistive (diffusion-related) components in the material, allowing differentiation between ideal capacitors and pseudocapacitors. The Nyquist plot and CV analysis, therefore, are complementary tools that help elucidate the charge storage mechanisms in pseudocapacitive materials, guiding material design for optimal energy storage and performance in supercapacitor applications [12, 13].

4. KEY PARAMETERS FOR PERFORMANCE EVALUATION OF SUPERCAPACITORS

Evaluating the performance of supercapacitors involves several critical parameters associated with the characteristics of the electrode nanomaterials used. Ideal electrode materials must possess specific properties to achieve optimal supercapacitor performance. These include: (1) a high specific surface area, which significantly impacts specific capacitance; (2) a highly porous structure, which enhances both specific capacitance and rate capability by providing ample paths for electrolyte ions; (3) high electronic conductivity, which directly influences power density and rate capability; (4) a sufficient number of active sites for charge storage; (5) high thermal and chemical stability to ensure long-term stability and durability of the device; and (6) low manufacturing cost for scalability and practical use.

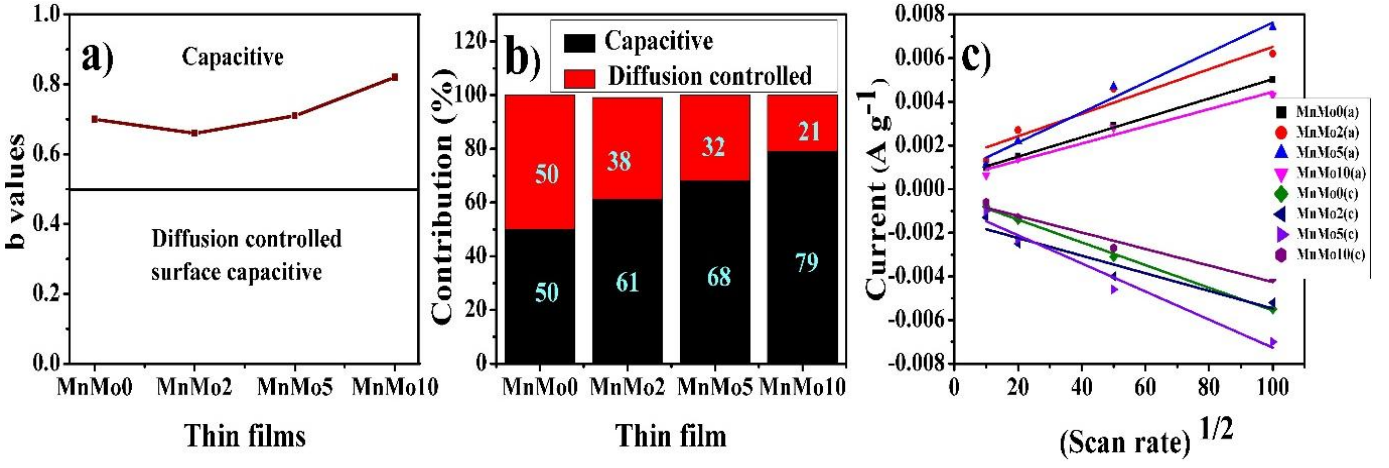

Fig. 3: (a) Graph of b values against thin films, (b) Column graph showing contribution percentage of diffusion-controlled surface intercalation and pure capacitive mechanisms at different scan rates, and (c) the plot of anodic and cathodic currents against the square root of scan rate ($v^{1/2}$) for $MnMo_0$, $MnMo_2$, $MnMo_5$, and $MnMo_{10}$ thin films. Reprinted with permission from ref. [13], Patil, T.S., Kamble, R.S., Patil, R.B., Takale, M.V. and Gangawane, S.A., 2024. Enhanced supercapacitive performance of electrophoretically deposited nanostructured molybdenum-doped Mn_3O_4 thin films. *International Journal of Materials Research*, *115*(1), pp.47-58. Copyright © Walter de Gruyter GmbH.

© Ariston Publications 2025. All rights reserved.

Nanostructured materials, spanning dimensions from zero to three, bring unique advantages to supercapacitors, each morphology contributing distinct electrochemical characteristics:

Zero-dimensional (0D) nanostructures like activated carbon have a large surface area ideal for charge storage. These materials can accommodate significant ion adsorption, boosting specific capacitance. However, their lack of structure limits charge transport efficiency, which can impact the rate capability and overall power performance.

One-dimensional (1D) nanostructures, such as nanowires and nanotubes, offer more effective charge transport pathways. Their elongated, organized structure improves electron mobility, enhances rate capability, and supports cyclic stability. The unique 1D structure allows for faster ion movement, making these materials suitable for applications requiring quick charge-discharge cycles.

Two-dimensional (2D) nanostructures provide even greater advantages due to their combination of high surface area and enhanced electrical conductivity. Materials like graphene and transition metal dichalcogenides (e.g., MXene) demonstrate excellent electrochemical performance as supercapacitor electrodes. MXene, in particular, has shown promising results, with enhanced charge storage due to its layered structure and high surface reactivity. A primary limitation of traditional 2D materials has been their relatively low energy density; however, composites of metal oxides, polymers, and carbon materials address this issue by improving specific capacitance and energy density through increased active surface areas and synergistic effects.

In recent years, three-dimensional (3D) porous nanostructures have gained attention for their high surface area and hierarchical pore structures, which support improved ion transport and electrolyte diffusion. Pseudocapacitive materials, particularly metal oxides and conductive polymers, are often used in 3D configurations, as they can incorporate the necessary pore size distributions for optimal charge storage. There are three main categories of pore sizes in these materials: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). Among these, mesoporous structures are particularly effective, balancing surface area and electrolyte accessibility to enhance electrochemical performance [14].

3D nanomaterials, including foam-like composites, have been shown to further improve supercapacitor performance. Foam structures, due to their open-cell design, enhance ion diffusion and improve conductivity, providing ample access to electrolyte ions. Their interconnected frameworks facilitate rapid charge-discharge cycles, while the combination of different material properties in composite foams enables better electronic conductivity and mechanical stability [15]. These attributes make foam-like composites promising candidates for next-generation supercapacitor electrodes.

Hybrid or composite materials bring the advantages of different nanostructures together to maximize specific capacitance, rate capability, and energy density. For instance, 2D composites made from graphene combined with metal oxides or polymers can mitigate limitations related to conductivity and charge storage. Such composites integrate the high conductivity of carbon-based materials with the redox-active sites of metal oxides or polymers, resulting in improved performance metrics.

Similarly, the development of 3D nanomaterials has opened new avenues for designing advanced supercapacitors. By combining various nanomaterials into structured composites, researchers aim to achieve the ideal balance of porosity, conductivity, and stability, enabling high performance even in demanding applications. Thus, these composites can fulfill the key parameters needed to enhance the supercapacitance and overall energy storage capability of future supercapacitor devices.

The morphology and composition of electrode nanomaterials play pivotal roles in determining supercapacitor performance. From 0D to 3D structures, each dimensional framework offers unique advantages, and combining these into composite or hybrid structures addresses specific performance limitations. With ongoing research into advanced materials and composite structures, the development of efficient, stable, and cost-effective supercapacitors is within reach, enabling their broader use in energy storage applications.

5. PSEUDOCAPACITIVE ELECTRODE NANOMATERIALS

Pseudocapacitive electrode nanomaterials, particularly those based on transition metal oxides, have garnered significant interest in recent years due to their promising electrochemical properties for supercapacitors. Pseudocapacitance arises from faradaic reactions that occur at the electrode surface and interstitial sites, where redox reactions involving ions from the electrolyte take place. These reactions are facilitated by functional groups on the material surface, as well as defects and grain boundaries, which serve as active sites for redox processes. Although transition metal oxide-based materials have demonstrated superior charge storage capabilities over carbon-based electrodes, they also come with limitations that hinder their standalone effectiveness as supercapacitor electrode materials.

The key drawbacks associated with transition metal oxide-based nanomaterials include: High resistivity: These materials generally exhibit higher resistivity compared to carbon-based alternatives. This high resistivity results in increased charge transfer resistance, which in turn raises the electrode resistance. Elevated resistance reduces the power density of the supercapacitor, limiting its efficiency in high-power applications where rapid charging and discharging cycles are essential. Structural instability**:** During continuous charge and discharge cycles, the metal oxide electrodes are prone to cracking, particularly due to volume changes

 © Ariston Publications 2025. All rights reserved.

associated with ion intercalation and deintercalation. This structural degradation negatively affects the long-term stability and cycle life of the electrode, making it unsuitable for applications demanding sustained performance over many cycles. Limited control over surface properties**:** Transition metal oxides typically lack tunability in terms of surface area, porosity, and pore size. This limitation restricts the material's ability to maximize ion accessibility and optimize charge storage. The inability to tailor the porosity and surface area of these materials is a significant drawback, as these parameters are crucial for enhancing the material's capacitance and overall performance.

To overcome these limitations, researchers have focused on heteroatom doping and creating composite materials. Heteroatom doping involves introducing other metal ions into the metal oxide structure to improve its electronic conductivity. Doping can enhance the material's electron mobility, which, in turn, boosts its charge storage capability and rate performance. By modifying the electronic structure of the metal oxide, heteroatom doping effectively lowers resistivity and increases the number of active sites for redox reactions, resulting in improved electrochemical performance [16].

In addition to doping, forming composites of transition metal oxides with other nanomaterials—such as carbon-based materials or conductive polymers—has shown promise in addressing the inherent weaknesses of metal oxides. Carbon materials like graphene, carbon nanotubes, and activated carbon have excellent conductivity and mechanical stability, making them ideal candidates for composites. When combined with transition metal oxides, these materials provide a conductive network that supports better charge transport, while the oxide component contributes high capacitance through faradaic reactions. This synergy enables higher energy and power densities and improves the structural stability of the electrode [17].

One of the most studied transition metal oxides for pseudocapacitor applications is manganese oxide (Mn_3O_4). Mn_3O_4 is valued for its high theoretical capacitance (~1500 F g^{-1}), ease of preparation, and inherent chemical and thermal stability. Additionally, it is eco-friendly and cost-effective. However, the lower conductivity of Mn_3O_4 limits its effectiveness as a standalone material in supercapacitor electrodes. Researchers have employed various strategies to mitigate these drawbacks, such as doping Mn_3O_4 with conductive elements or combining it with carbon-based nanomaterials to improve charge transport and structural integrity. Through these modifications, Mn_3O_4-based nanocomposites can achieve enhanced performance metrics, making them viable candidates for next-generation supercapacitors.

While transition metal oxide nanomaterials demonstrate excellent pseudocapacitive properties, their application in supercapacitors requires addressing key limitations. Through advancements in doping and composite formation, these materials can be engineered to provide higher conductivity, greater stability, and optimized charge storage, paving the way for more efficient energy storage solutions.

6. SELECTED METHODS TO SYNTHESIZE MN_3O_4 NANOMATERIALS

Synthesis techniques for Mn_3O_4-based nanomaterials have been explored extensively to enhance their properties for supercapacitor applications. These techniques aim to improve the electrochemical performance of Mn_3O_4, particularly its conductivity, surface area, and overall stability. By creating composites with other materials such as reduced graphene oxide (rGO) or introducing other metal oxides, researchers can overcome limitations of Mn_3O_4, such as low conductivity and structural instability. Below are some synthesis techniques that have been effectively utilized to prepare Mn_3O_4-based nanomaterials.

One notable method for synthesizing Mn_3O_4 nanocomposites involves the combination of a manganese-based metal-organic framework (MOF) and reduced graphene oxide (rGO) to create an rGO/Mn_3O_4 composite. This synthesis process begins with the Mn(II) − 1,3,5-benzenetricarboxylate (Mn-BTC) MOF, which provides a framework for the manganese ions, combined with a hydrothermally prepared rGO aerogel. The two components are initially mixed using a ball milling technique, which aids in the formation of a homogeneous mixture. This technique not only ensures uniform dispersion of rGO within the Mn-BTC framework but also reduces the particle size, increasing the surface area for redox reactions. After milling, the mixture is subjected to calcination, which transforms the Mn-BTC MOF into Mn_3O_4, while maintaining a tight integration with the rGO network. This final rGO/Mn_3O_4 composite exhibits improved conductivity and specific capacitance, making it suitable for high-performance supercapacitors [18].

The SILAR technique is another method for synthesizing Mn_3O_4-based composites, specifically in the form of thin films. This method involves alternating layers of manganese ions and graphene oxide (GO) on a substrate. Starting with manganese and GO precursors, the materials are deposited in successive layers through controlled immersion in precursor solutions. By varying the deposition time, the thickness and surface morphology of the GO/Mn_3O_4 thin films can be fine-tuned to optimize electrochemical properties. The layered architecture created by the SILAR method promotes ion diffusion and allows for rapid redox reactions across the surface. This is advantageous for supercapacitor electrodes, as it enables high energy storage and efficient charge-discharge cycles [19].

Microwave-assisted synthesis has gained attention as a rapid, energy-efficient method for creating nanocomposites with high dispersion and uniform particle size. This approach has been used to synthesize a binary metal oxide composite, specifically Mn_3O_4-Fe_3O_4, anchored onto rGO nanosheets. In this method, the rGO, Mn_3O_4, and Fe_3O_4 components are combined under microwave irradiation, which accelerates the reaction and reduces synthesis time compared to conventional heating. The microwave-assisted approach not only produces nanoscale particles with uniform size distribution but also allows for better integration of the metal oxides with the rGO matrix. The rGO/Mn_3O_4-Fe_3O_4

© Ariston Publications 2025. All rights reserved.

composite exhibits improved electrochemical properties due to the synergy between Mn_3O_4 and Fe_3O_4, which provides higher specific capacitance, and rGO, which enhances conductivity. This composite structure also promotes ion transport and stability during charge-discharge cycles, which is crucial for supercapacitor applications [20].

To address the performance limitations of Mn_3O_4-based electrodes, several advanced synthesis techniques and modifications have been developed. These approaches, outlined in Table 1, focus on achieving improved specific capacitance, enhanced conductivity, and greater structural stability. Techniques such as doping with conductive elements, creating multi-dimensional composite structures, and integrating Mn_3O_4 with polymers or other carbon-based materials have demonstrated considerable success in enhancing the overall performance of Mn_3O_4-based supercapacitors. Each approach aims to mitigate specific limitations of Mn_3O_4, whether by increasing surface area, facilitating ion transport, or enhancing mechanical stability during cycling.

Table 1. Recent approaches employed to improve the supercapacitive performance of Mn_3O_4 based supercapacitor electrode nanomaterials.

S. No.	Electrode material	Method	Morphology	Specific / Volumetric capacitance	Capacitance retention	Ref.
1.	1.5 at % Cu doped Mn_3O_4	Hydrothermal and subsequent calcination	Hollow bud-like	257.6 F g^{-1} at current density 1 A g^{-1}	90.6% after 6000 cycles	[21]
2.	3 wt % Cr-doped Mn_3O_4	SILAR	Nano-needle like structure	181 F g^{-1}	--	[22]
3.	Mn_3O_4/ rGO	Air oxidation	Nanoparticles wrapped in RGO sheets	52.2 F cm^{-3} at 0.2 A cm^{-3}	115% after 60 000 cycles.	[23]
4.	NiO/ $ZnMn_2O_4$	Hydrothermal	Sheet-like	886 F g^{-1} at current density 1 A g^{-1}	100 % after 1000 cycles.	[24]
5.	Mn_3O_4/rGO	Sol–gel based in situ reduction method	Nanosheets and nano particles	427 F g^{-1} at current density 1 A g^{-1}	100 % after 3000 cycles.	[25]
6.	Ag - MnO_2/GO	SILAR	Flower-like	877 F g^{-1} at scan rate 5 mV s^{-1}	94.57 % after 5000 cycles.	[26]
7.	$ZnMn_2O_4$/ Mn_2O_3	Ultrasonication and microwave irradiation assisted hydrothermal method	Petals flower-like	380 Fg^{-1} at current density 0.5 A g^{-1}	92 % after 2000 cycles	[27]
8.	Cu- Mn_3O_4@ Mn- CuO@ CC	Simple solution process	Mixture of spherical and rod-shaped Nanostructures	997.2 F g^{-1} at scan rate 5 mV s^{-1}	95.3 % after 5000 cycles	[28]
9.	Mn_3O_4@ Mixed biomass-AC	Carbonization, activation, Hydrothermal	Porous and nanowires	716.49 Fg^{-1} at 0.75 A g^{-1}	98.7 % after 5000 cycles	[29]
10.	Mn_3O_4@ N, P-doped carbon (NPC)	Chemical method	Flower-like	370.8 F g^{-1}	92.7 % after 10000 cycles	[30]
11.	Graphene/	ball milling-	Nanoparticles	219 F g^{-1} at current	91.4 % retention at 10	[31]

© Ariston Publications 2025. All rights reserved.

	carbon/ Mn_3O_4	thermal annealing process		density 0.5 A g^{-1}	A g^{-1} after 5000 cycles	
12.	Mn_3O_4/$NiMoO_4$ @NiCo layered double hydroxide	Electrodeposition / hydrothermal	Sheet-like	815 F g^{-1} at current density 1 A g^{-1}.	77 % after 15000 cycles	[32]
13.	Mn_3O_4/MnS	Solvothermal Synthesis	Nanoparticles	176.9 F g^{-1} at current density 0.2 A g^{-1}	80 % after 10000 cycles	[33]
14.	(3D) g-C_3N_4 /Mn_3O_4	Freeze-drying process and thermal polymerization	Honeycomb	753.9 F g^{-1} at current density 1 A g^{-1}	84 % after 5000 cycles	[34]
15.	Mn_3O_4/ graphene	Deposition-solvothermal process	Nanoparticles	490 F g^{-1} at current density 0.25 A g^{-1}	0 % after 1000 cycles	[35]
16.	MnO@ Mn_3O_4	Calcination treatment.	Junction	331.2 F g^{-1} at current density 1 A g^{-1}	----------	[36]
17.	Ppy@ FeOOH/ /Mn_3O_4	Electrochemical deposition	Micro-nano structures	107.3 mF cm^{-2} at 0.2 mA cm^{-2}	85% after 5000 cycles	[37]
18.	Mn_3O_4–NPCS/CF	Pyrolysis	porous	519 F g^{-1}	96% after 5000 cycles	[38]
19.	S/Mn_3O_4	Electro deposition	Crispy flake-like Sulphur decorated elongated cub Octahedron	1595 F g^{-1} at scan rate 5 mV s^{-1}.	---------	[39]
20.	ITO@Mn_3O_4	SILAR/Electro-spinning technique	Nanoplates over ITO nanofibers	823 Fg^{-1} at 1 mA/cm^2	----------	[40]
21	NiO@ Mn_3O_4/rGO	Hydrothermal	Catkins structure	533.9 F g^{-1} at current density 1 A g^{-1}	75 % after 2000 cycles	[41]
22.	Mn_3O_4-Fe_3O_4@C	Electro spinning technique	Oolite-like particles	178 F g^{-1} at current density 1 A g^{-1}.	95% after 1000 cycles at 3 A g^{-1}	[42]
23.	GO/Mn_3O_4	SILAR	Nanosheets of GO with Mn_3O_4 nanograins (deposited at 40 cycles)	532.54 Fg^{-1}at scan rate 5 mVs^{-1}	----------	[19]
24.	(35%) MnO_2–(65%) Mn_3O_4	Facile reduction-induced exfoliation	MnO_2 nanowires and Mn_3O_4 Nanoparticles	278.2 F g^{-1} at current density 20 Ag^{-1}	99.3% after 5000 cycles	[43]
25.	Mn_3O_4-CeO_2/holey-graphene	Bio-template hydrothermal reaction	Mn_3O_4 and CeO_2 nanoparticles sprinkled over the wrinkle and surface of porous graphene	310 F·g^{-1} at current density 2 A·g^{-1}	92.4%% after 1000 cycles	[44]

© Ariston Publications 2025. All rights reserved.

26.	Mn_3O_4/ N-rGO	Hydrothermal	Mn_3O_4 nanoparticle anchored on the surface of N-rGO nanosheets	141 F g^{-1} at current density 0.2 A g^{-1}	90.3% after 5000 cycles	[45]
27.	rGO/Mn_3O_4	A ball-milling method/ hydrothermal	porous rods comprising nanoparticles	420 Fg^{-1} at current density 0.5 Ag^{-1}	----------	[18]
28.	Mn_3O_4@ C nanocages	Plasma evaporation and thermal oxidation	Core-shell structure	422 Fg^{-1}	95% after 1000 cycles	[46]
29.	IrO_2@ Mn_3O_4	Electrospinning technique/SILAR	2-D Mn_3O_4 nanoflakes grown over 1-D IrO_2 nanofiber	1027 Fg^{-1} at 1 mA/cm^2	88 % after 10000 cycles	[47]
30.	Mn_3O_4 -lignin derived laser scribed graphene (L-LSG)	Sol-gel hydrothermal	Nanosheets of L-LSG with Mn_3O_4 nano octahedrons	136.19 $mFcm^{-2}$ at 0.08 $mAcm^{-2}$.	93.4 % after 5000 cycles at 0.5 $mAcm^{-2}$	[48]
31.	Ag/Mn_3O_4	Sol-gel assisted green synthesis route *(Withania somnifera* leaf extract)	Nanorods	254 Fg^{-1} at a scan rate 5 mVs^{-1}	92.3 % after 2000 cycles	[49]
32.	Zn-doped Mn_3O_4	Electro Deposition	Nano crystals	21.34 mF cm^{-2} at the scan rate of 5 mVs^{-1}	80 % after 2000 cycles	[50]
33.	Mn_3O_4-Fe_2O_3/Fe_3O_4@ rGO	Simple microwave-assisted approach	Mn_3O_4-Fe_2O_3/Fe_3O_4 nano particles with size of <100 nm effectively anchored on the surfaces of rGO nanosheets	590.7 Fg^{-1} at scan rate of 5 mVs^{-1}	64.5% after 1000 cycles at scan rate of 50 mV/s.	[20]
34.	Mn_3O_4 /G	Modified Hummers' method followed by a heat treatment	Mn_3O_4 nanoparticle anchored on the surface of graphene nanosheets	58 F g^{-1} at a scan rate of 1 mVs^{-1}.	97% over 2000 cycles	[51]
35.	Mn_3O_4/rGO/ polycaprolactone (PCL)	Electro spinning technique	Nanofibres of average diameter 100 to 200 nm	690 F g^{-1} at a current density of 1 A g^{-1}.	----------	[52]
36.	Ni/Mn_3O_4	Electrophoretic deposition	Nanoflakes of thickness 30 to 50 nm	690 F g^{-1} at current density of 0.3 A g^{-1}.	93% over 2000 cycles	[53]
37.	Mo/Mn_3O_4	Electrophoretic deposition	Porous and non-uniform nano structure	497 F g^{-1} at current density of 1.6Ag^{-1}.	190% over 2000 cycles	[13]

© Ariston Publications 2025. All rights reserved.

38	Pure Mn_3O_4	Two step hydrothermal	20–30 nm nanoparticles anchored on 500–600 nm nanorods.	233.41 F g^{-1} at a current density of 0.5Ag^{-1}	108.4 % over 10000 cycles	[54]
39.	Mn_3O_4/rGO	Solution-phase method	Nanoparticles on graphene layers	313.7 F g 1 at a current density of 0.2 A g 1	90.3 % over 10000 cycles	[55]

The synthesis of Mn_3O_4-based nanomaterials for supercapacitor electrodes has seen remarkable progress, with techniques such as ball milling, SILAR, and microwave-assisted synthesis contributing to the development of high-performance materials. These methods allow for fine control over particle size, morphology, and composite structure, all of which play a crucial role in optimizing electrochemical properties. By continuing to explore new synthesis techniques and composite formulations, researchers can further enhance the potential of Mn_3O_4-based nanomaterials, paving the way for next-generation supercapacitor electrodes with higher energy storage capabilities and improved durability.

7. CONCLUSION

This review highlights the critical role of Mn_3O_4 nanomaterials as promising candidates for supercapacitor electrodes, underscoring their favorable pseudocapacitive properties, high specific capacitance, and eco-friendliness. As discussed, the performance of supercapacitors relies heavily on the morphological and electrochemical characteristics of the electrode materials, with parameters such as surface area, porosity, and conductivity playing pivotal roles. Among various nanomaterials, manganese-based oxides, especially Mn_3O_4, have shown considerable promise due to their moderate cost and availability, as well as their electrochemical stability. However, relatively low electrical conductivity of Mn_3O_4 has limited its practical application, necessitating the exploration of methods to improve its overall performance. Several strategies have been developed to enhance the conductive and capacitive properties of Mn_3O_4. For instance, doping with transition metal ions such as Ni, Co, and Cr, has proven effective in modifying the structural properties, reducing resistivity, and increasing its active surface area of Mn_3O_4. Such dopants can create lattice distortions, facilitating faster ion transport and improving charge-discharge characteristics. Similarly, the formation of composites with conductive materials, particularly graphene and other carbon-based nanostructures, provides a conductive matrix that aids electron mobility while maintaining the pseudocapacitive behavior of Mn_3O_4. These composites have shown improved rate capability, though challenges remain in achieving substantial capacitance at lower current densities. Additionally, recent studies have highlighted the benefits of intercalating alkali metal ions into Mn_3O_4's layered structures. This approach facilitates the movement of electrolyte ions within the electrode material, enhancing ionic diffusion and increasing overall capacitance. The versatility of Mn_3O_4, combined with its potential for structural modification, positions it as a highly adaptable material for next-generation supercapacitors. Despite these advances, further efforts are required to overcome the conductivity challenges and stability issues associated with Mn_3O_4 nanostructures under high operational demands. Future research should focus on innovative synthetic approaches and the integration of Mn_3O_4 with novel materials that promote synergistic effects, potentially leading to supercapacitors with higher energy and power densities. As energy storage demands continue to rise, Mn_3O_4-based supercapacitors could play an essential role in creating efficient, sustainable solutions for modern energy challenges.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

Funding

Not applicable

Availability of data and material

All of the data obtained or analyzed during this study is included in the report that was submitted.

Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

© Ariston Publications 2025. All rights reserved.

All authors contributed equally in the preparation of this manuscript.

ACKNOWLEDGEMENTS

Authors are grateful to Shivaji University, Kolhapur for financial support through the Diamond Jubilee Research Initiation Scheme 2022-23.

REFERENCES

[1] Jampani, P.H., Manivannan, A. and Kumta, P.N., **2010.** Advancing the supercapacitor materials and technology frontier for improving power quality. *The Electrochemical Society Interface*, *19*(3), p.57.

[2] Navale, S.T., Mali, V.V., Pawar, S.A., Mane, R.S., Naushad, M., Stadler, F.J. and Patil, V.B., **2015.** Electrochemical supercapacitor development based on electrodeposited nickel oxide film. *RSC advances*, *5*(64), pp.51961-51965.

[3] Kamble, T. P., Shingte, S. R., Chavan, V. D., Kim, D. K., Chougale, A.D. and Patil, P. B. **2024.** MOF Derived $CoFe_2O_4$@Carbon Nanofibers for Supercapacitor Application. *ChemSci Advances* 1(1), pp. 34-40.

[4] Ghodbane, O., Ataherian, F., Wu, N.L. and Favier, F., **2012.** In situ crystallographic investigations of charge storage mechanisms in MnO_2-based electrochemical capacitors. *Journal of Power Sources*, *206*, pp.454-462.

[5] Beknalkar, S.A., Teli, A.M., Bhat, T.S., Pawar, K.K., Patil, S.S., Harale, N.S., Shin, J.C. and Patil, P.S., **2022.** Mn_3O_4 based materials for electrochemical supercapacitors: Basic principles, charge storage mechanism, progress, and perspectives. *Journal of Materials Science & Technology*, *130*, pp.227-248.

[6] Dong, R., Ye, Q., Kuang, L., Lu, X., Zhang, Y., Zhang, X., Tan, G., Wen, Y. and Wang, F., **2013.** Enhanced supercapacitor performance of Mn_3O_4 nanocrystals by doping transition-metal ions. *ACS Applied Materials & Interfaces*, *5*(19), pp.9508-9516.

[7] Sajanlal, P.R., Sreeprasad, T.S., Samal, A.K. and Pradeep, T., **2011.** Anisotropic nanomaterials: structure, growth, assembly, and functions. *Nano reviews*, *2*(1), p.5883.

[8] Li, F., Jiang, X., Zhao, J. and Zhang, S., **2015.** Graphene oxide: A promising nanomaterial for energy and environmental applications. *Nano energy*, *16*, pp.488-515.

[9] Chen, K., Yang, Y., Li, K., Ma, Z., Zhou, Y. and Xue, D., **2014.** $CoCl_2$ designed as excellent pseudocapacitor electrode materials. *ACS Sustainable Chemistry & Engineering*, *2*(3), pp.440-444.

[10] Ramachandran, R., Saranya, M., Kollu, P., Raghupathy, B.P., Jeong, S.K. and Grace, A.N., **2015**. Solvothermal synthesis of Zinc sulfide decorated Graphene (ZnS/G) nanocomposites for novel Supercapacitor electrodes. *Electrochimica Acta*, *178*, pp.647-657.

[11] Mathis, T.S., Kurra, N., Wang, X., Pinto, D., Simon, P. and Gogotsi, Y., **2019.** Energy storage data reporting in perspective—guidelines for interpreting the performance of electrochemical energy storage systems. *Advanced Energy Materials*, *9*(39), p.1902007.

[12] Augustyn, V., Simon, P. and Dunn, B., **2014.** Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy & Environmental Science*, *7*(5), pp.1597-1614.

[13] Patil, T.S., Kamble, R.S., Patil, R.B., Takale, M.V. and Gangawane, S.A., **2024.** Enhanced supercapacitive performance of electrophoretically deposited nanostructured molybdenum-doped Mn_3O_4 thin films. *International Journal of Materials Research*, *115*(1), pp.47-58.

[14] Parveen, N. and Ansari, S. A. **2024.** Fabrication and Characterization of High-Capacity Manganese Oxide Based Supercapacitor Electrode, *ChemSci Advances* 1(1), pp. 41-46.

[15] Yu, Z., Tetard, L., Zhai, L. and Thomas, J., **2015**. Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. *Energy & Environmental Science*, *8*(3), pp.702-730.

[16] Hepel, M., **2023.** Advances in micro-supercapacitors (MSCs) with high energy density and fast charge-discharge capabilities for flexible bioelectronic devices—A review. *Electrochemical Science Advances*, *3*(3), p.e2100222.Mm

[17] Yadav, M.S., **2020.** Metal oxides nanostructure-based electrode materials for supercapacitor application. *Journal of Nanoparticle Research*, *22*(12), p.367.

[18] Li, W., Xu, A., Zhang, Y., Yu, Y., Liu, Z. and Qin, Y., **2022.** Metal-organic framework-derived Mn_3O_4 nanostructure on reduced graphene oxide as high-performance supercapacitor electrodes. *Journal of Alloys and Compounds*, *897*, p.162640.

[19] Nwankwo, M.C., Ezealigo, B., Nwanya, A.C., Nkele, A.C., Agbogu, A., Chime, U., Asogwa, P.U., Ezekoye, B.A., Ekwealor, A.B.C., Osuji, R.U. and Ejikeme, P.M., **2020.** Syntheses and characterizations of GO/Mn_3O_4 nanocomposite film electrode materials for supercapacitor applications. *Inorganic Chemistry Communications*, *119*, p.107983.

[20] Kumar, R., Youssry, S.M., Ya, K.Z., Tan, W.K., Kawamura, G. and Matsuda, A., **2020.** Microwave-assisted synthesis of Mn_3O_4-Fe_2O_3/Fe_3O_4 @ rGO ternary hybrids and electrochemical performance for supercapacitor electrode. *Diamond and Related Materials*, *101*, p.107622.

[21] Chen, X., Chen, C., Xu, T., Xu, Y., Liu, W., Yang, W. and Yang, P., **2018.** Performance enhancement of asymmetric supercapacitors with bud-like Cu-doped Mn_3O_4 hollow and porous structures on nickel foam as

 © Ariston Publications 2025. All rights reserved.

positive electrodes. *RSC Advances*, *8*(63), pp.35878-35887.

[22] Immanuel, P., Senguttuvan, G., Chang, J.H., Mohanraj, K. and Kumar, N.S., **2021.** Effect of Cr doping on Mn_3O_4 thin films for high-performance supercapacitors. *Journal of Materials Science: Materials in Electronics*, *32*, pp.3732-3742.

[23] Xiong, T., Lee, W.S.V., Huang, X. and Xue, J.M., **2017**. Mn_3O_4 /reduced graphene oxide based supercapacitor with ultra-long cycling performance. *Journal of Materials Chemistry A*, *5*(25), pp.12762-12768.

[24] Pearline, C.L., Abel, M.J., Pramothkumar, A., Senthilkumar, N., Anbalagan, P. and Prince, J.J., **2021.** Investigation on structural, optical and electrochemical behavior of NiO/$ZnMn_2O_4$ ternary nanocomposites via two-step synthesis approach for supercapacitor application. *Chemical Papers*, *75*, pp.641-651.

[25] Mohamed Ismail, M., Hemaanandhan, S., Mani, D., Arivanandhan, M., Anbalagan, G. and Jayavel, R., **2020.** Facile preparation of Mn_3O_4/rGO hybrid nanocomposite by sol–gel in situ reduction method with enhanced energy storage performance for supercapacitor applications. *Journal of Sol-Gel Science and Technology*, *93*, pp.703-713.

[26] Mane, V.J., Kale, S.B., Ubale, S.B., Lokhande, V.C. and Lokhande, C.D., 2021. Enhanced specific energy of silver-doped MnO_2/graphene oxide electrodes as facile fabrication symmetric supercapacitor device. *Materials Today Chemistry*, *20*, p.100473.

[27] Sannasi, V. and Subbian, K., **2021.** A facile synthesis of $ZnMn_2O_4/Mn_2O_3$ composite nanostructures for supercapacitor applications. *Ceramics International*, *47*(9), pp.12300-12309.

[28] Barai, H.R., Lopa, N.S., Ahmed, F., Khan, N.A., Ansari, S.A., Joo, S.W. and Rahman, M.M., **2020.** Synthesis of Cu-doped Mn_3O_4@ Mn-doped CuO nanostructured electrode materials by a solution process for high-performance electrochemical pseudocapacitors. *ACS omega*, *5*(35), pp.22356-22366.

[29] Mohammed, A.A., Das, J.K., Hota, A., Sahoo, S., Ayinla, K.I. and Tripathy, B.C., **2024.** Mixed biomass-derived multi-heteroatom doped carbon-decorated Mn_3O_4 for a high-performance asymmetric all solid-state supercapacitor. *Materials Research Bulletin*, *177*, p.112849.

[30] Ding, Y., Dai, L., Wang, R., Wang, H., Zhang, H., Jiang, W., Tang, J. and Zang, S.Q., **2021.** Bio-inspired Mn_3O_4@ N, P-doped carbon cathode for 2.6 V flexible aqueous asymmetric supercapacitors. *Chemical Engineering Journal*, *407*, p.126874.

[31] Li, L., Jiang, Y., Guo, C., Han, K., Cui, X., He, C., Chen, Y. and Yang, Y., **2024.** Mechanochemical production of graphene/amorphous carbon/Mn_3O_4 nanocomposites for asymmetric supercapacitor. *Applied Surface Science*, *653*, p.159388.

[32] Liang, R., Liu, S., Lin, J., Dai, J., Peng, J., Huang, P., Chen, J. and Xiao, P., **2023.** A high mass loading flexible electrode with a sheet-like Mn_3O_4/$NiMoO_4$@ NiCo LDH on a carbon cloth for supercapacitors. *RSC Advances*, *13*(47), pp.33463-33470.

[33] Yang, M., Ning, H., Xiao, L., Cui, F. and Zhang, F., **2022.** Mn_3O_4/MnS heterostructure for electrode and asymmetric supercapacitor under high charge/discharge current. *Electrochimica Acta*, *424*, p.140630.

[34] Wang, Y., Wang, B., Shi, R., Chen, L., Che, Q., Wang, J. and Yang, P., **2022.** 3D g-C_3N_4/Mn_3O_4 heterostructures towards high energy density supercapacitor. *Journal of Electroanalytical Chemistry*, *926*, p.116928.

[35] Mohamed, M.M., Khairy, M., Amer, A.A. and Mousa, M.A., **2022.** Nonconventional synthesis of polyhedral Mn_3O_4 nanoarchitectures incorporated reduced graphene oxide: superior supercapacitor capabilities. *journal of materials research and technology*, *21*, pp.2555-2570.

[36] Wang, S., Zhao, R., Yao, S., Wang, X., Wang, J., Gao, X., Hou, Z., Liu, X., Fu, Z., Wang, D. and Xie, J., **2023.** Spatially expanded built-in electric field via engineering graded junction enables fast charge transfer in bulk MnO@ Mn_3O_4 for Na+ supercapacitors. *Nano Energy*, *115*, p.108725.

[37] Lv, X., Zhang, Y., Li, X., Fan, Z., Liu, G., Zhang, W., Zhou, J., Xie, E. and Zhang, Z., **2022.** High-performance magnesium ion asymmetric Ppy@ FeOOH//Mn_3O_4 micro-supercapacitor. *Journal of Energy Chemistry*, *72*, pp.352-360.

[38] Sun, L., Fu, Q. and Pan, C., **2020**. Mn_3O_4 embedded 3D multi-heteroatom codoped carbon sheets/carbon foams composites for high-performance flexible supercapacitors. *Journal of Alloys and Compounds*, *849*, p.156666.

[39] Purushothaman, S., Jeyasubramanian, K. and Hikku, G.S., **2021.** In-situ fabrication of sulphur decorated elongated cuboctahedron shaped Mn_3O_4 as high-performance active charge storage material for supercapacitor application. *Surface and Coatings Technology*, *426*, p.127782.

[40] Beknalkar, S.A., Teli, A.M., Harale, N.S., Pawar, K.K., Patil, D.S., Shin, J.C. and Patil, P.S., **2021**. Hierarchical ITO nanofibers coated Mn_3O_4 nanoplates core-shell nanocomposites for high performance all-solid-state symmetric supercapacitor device. *Ceramics International*, *47*(21), pp.29771-29785.

[41] He, X., Cheng, Y., Qi, H. and Zhang, Y., **2021.** One-step hydrothermal synthesis of bimetallic oxides (NiO@ Mn_3O_4) supported on rGO: a highly efficient electrode material for supercapacitors. *Electrochimica Acta*, *388*, p.138609.

[42] Hu, B., Wang, Y., Shang, X., Xu, K., Yang, J., Huang, M. and Liu, J., **2021.** Structure-tunable Mn_3O_4-Fe_3O_4@ C hybrids for high-performance supercapacitor. *Journal of Colloid and Interface Science*, *581*, pp.66-75.

[43] Kang, L., Huang, C., Zhang, J., Zhang, M., Zhang, N., He, Y., Luo, C., Wang, C., Zhou, X. and Wu, X., **2019.** A new strategy for synthesis of hierarchical MnO_2–

© Ariston Publications 2025. All rights reserved.

Mn_3O_4 nanocomposite via reduction-induced exfoliation of MnO2 nanowires and its application in high-performance asymmetric supercapacitor. *Composites Part B: Engineering*, *178*, p.107501.

[44] Qian, J., Wang, Y., Chen, Z., Liu, C., Zhou, Y., Yang, Y., Song, Y. and Kong, B., **2019.** Three dimensional Mn_3O_4-CeO_2/holey-graphene hierarchical architectures from stem for high-performance asymmetric supercapacitors. *Inorganic Chemistry Communications*, *104*, pp.8-13.

[45] Zhou, X., Meng, T., Yi, F., Shu, D., Li, Z., Zeng, Q., Gao, A. and Zhu, Z., **2021.** Supramolecular assisted fabrication of Mn3O4 anchored nitrogen-doped reduced graphene oxide and its distinctive electrochemical activation process during supercapacitive study. *Electrochimica Acta*, *370*, p.137739.

[46] Camacho, R.P., Wu, A.M., Gao, S., Jin, X.Z., Cao, G.Z. and Huang, H., **2019**. Mn_3O_4 nanoparticles encapsulated in carbon cages as the electrode of dual-mechanism supercapacitors. *Materials Today Chemistry*, *12*, pp.361-372.

[47] Beknalkar, S.A., Teli, A.M., Harale, N.S., Shin, J.C. and Patil, P.S., **2021.** Construction of IrO_2@Mn_3O_4 core-shell heterostructured nanocomposites for high performance symmetric supercapacitor device. *Journal of Alloys and Compounds*, *887*, p.161328.

[48] Remesh, S., Loganathan, N.N., Perumal, V., Ovinis, M., Karuppanan, S., Edison, T.N.J.I., Raja, P.B., Ibrahim, M.N.M., Arumugam, N. and Kumar, R.S., **2024.** A high performance selectively grown nano-octahedral Mn_3O_4 on lignin derived laser scribed graphene for microsupercapacitor applications. *Journal of Energy Storage*, *77*, p.109920.

[49] Sun, Y.A., Chen, L.T., Hsu, S.Y., Hu, C.C. and Tsai, D.H., **2019.** Silver nanoparticles-decorating manganese oxide hybrid nanostructures for supercapacitor applications. *Langmuir*, *35*(44), pp.14203-14212.

[50] Animasahun, L.O., Owoeye, V.A., Olumurewa, K.O., Buremoh, W., Busari, H.K., Ajayeoba, Y.A., Popoola, M.M., Adeleke, J.T. and Adewinbi, S.A., **2023.** Enhanced optoelectronic and supercapacitive performance of electrodeposited Mn_3O_4 thin film prepared from two-electrode: an effect of Zn-ion incorporation. *Results in Surfaces and Interfaces*, *11*, p.100123.

[51] Das, S.K., Kamila, S., Satpati, B., Kandasamy, M., Chakraborty, B., Basu, S. and Jena, B.K., **2020.** Hollow Mn_3O_4 nanospheres on graphene matrix for oxygen reduction reaction and supercapacitance applications: Experimental and theoretical insight. *Journal of Power Sources*, *471*, p.228465.

[52] Chanu, S.N., Devi, P.S. and Swain, B.P., **2024.** Structural and electrochemical properties of manganese oxide/rGO/PCL nanofiber for supercapacitor electrode material. *Journal of Materials Science: Materials in Electronics*, *35*(9), p.646.

[53] Patil, T.S., Kothavale, V.P., Malekar, V.P., Kamble, R.S., Patil, R.B., Gurav, K.V., Takale, M.V. and Gangawane, S.A., **2024.** Effect of Nickel (Ni) Ion Doping on the Morphology and Supercapacitive Performance of Mn_3O_4 Thin Films. *Journal of Electronic Materials*, *53*(1), pp.394-407.

[54] Wang, Z., Fang, J., Hao, Y., Chen, C. and Zhang, D., **2021.** High-performance Mn_3O_4 nanomaterials synthesized via a new two-step hydrothermal method in asymmetric supercapacitors. *Materials Science in Semiconductor Processing*, *130*, p.105823.

[55] Gao, M., Wu, X., Qiu, H., Zhang, Q., Huang, K., Feng, S., Yang, Y., Wang, T., Zhao, B. and Liu, Z., **2018.** Reduced graphene oxide-mediated synthesis of Mn_3O_4 nanomaterials for an asymmetric supercapacitor cell. *RSC Advances*, *8*(37), pp.20661-20668.

 © Ariston Publications 2025. All rights reserved.

ABOUT THE AUTHORS



Dr. S.A. Gangawane is an Associate Professor at Doodhsakhar Mahavidyalaya, Bidri, affiliated with Shivaji University. He earned his Ph.D. from Shivaji University, Kolhapur, where his research focused on "Studies on Surface Deformation of Materials by Holographic Interferometry Technique." Dr. Gangawane currently supervises three Ph.D. students and has completed a minor research project. With over 30 research articles published in reputed refereed journals, his contributions add significant value to the field of materials science and holographic interferometry. His ongoing research emphasizes innovative applications of interferometry in material deformation studies, reflecting his commitment to advancing academic research and mentorship in this specialized area.



Dr. Tanaji S. Patil serves as an Assistant Professor of Physics at Bhogawati Mahavidyalaya, Kurukali, affiliated with Shivaji University, Kolhapur. With 14 years of teaching experience at the undergraduate level, Dr. Patil brings extensive expertise to his field. His doctoral research focused on doped thin films of metal oxides for supercapacitor applications, contributing valuable insights into energy storage technologies. Currently, he is working on a minor research project funded by Shivaji University. His academic pursuits and hands-on projects in advanced material applications highlight his dedication to both teaching and research, specifically within the areas of thin-film physics and sustainable energy solutions.



Dr. Raviraj Kamble is an Associate Professor of Chemistry at Bhogawati College, Kurukali, under Shivaji University, Kolhapur. With 17 years of undergraduate teaching experience, Dr. Kamble completed his Ph.D. at H.N.B. Garhwal University, Uttarakhand, focusing on solid acid catalysts and their role in light alkane conversions. His research interests include solid acid catalysis applications within petrochemicals and innovations in chemistry pedagogy for higher education. Dr. Kamble has successfully concluded a minor research project funded by the UGC, underscoring his commitment to both scientific and educational development. His work bridges the gap between academic research and practical applications, advancing knowledge in catalysis and educational strategies

© Ariston Publications 2025. All rights reserved.