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Review Article

A Review: Recent Advancement in Graphene Based Titanium Oxide, Manganese Oxide and Zinc Oxide Nanocomposites as Electrode Material For Supercapacitor

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Abstract — Modern times have seen an increase in the use of non-renewable fossil fuels for energy, raising grave concerns for the survival of humankind worldwide. Building an environmentally friendly, reasonably priced, reliable, and renewable energy storage system is therefore essential. Supercapacitors are a promising energy technology because of their superior cycle stability, better power density, and quick charge and discharge times. Supercapacitors have been identified as one of the most promising energy storage technologies among other systems. The materials used for the electrodes are crucial in enhancing the supercapacitor's accuracy in terms of capacitance, power, and energy density. The composition of the electrode materials and the kinds of electrolyte in particular control the capacitors' electrical and thermal characteristics. In this mini reviews paper, we overview on graphene based titanium oxide, manganese oxide and zinc oxide nanocomposites as an electrode material for supercapacitors.

Keywords — Supercapacitors, Graphene, titanium oxide, manganese oxide and zinc oxide and nanocomposites.

1. Introduction

Supercapacitors have much higher capacitance values than traditional capacitors. Supercapacitors have lower voltage limits, which can even eliminate the performance difference between rechargeable batteries and conventional electrolytic capacitors. [1] Issues related to modern society's dependence on fossil fuels include rising fuel prices, pollution, global warming, and geopolitical concerns. Mitigating these problems is an increasingly important goal that can be achieved through the development of alternative energy sources and storage technologies. As a result, interest in high-performance, high-energy-density energy storage systems has recently increased.

[2] The slow charge-discharge rate, short life cycle, and high battery weight limit its application in wearable and wearable devices. Currently, supercapacitors are receiving countless considerations due to their important properties such as high energy density, high power density, light weight, fast charge-discharge rate, and long life. [3] The performance of inexpensive and environmentally friendly energy storage and conversion components, mainly required by electrical energy storage systems, such as batteries and capacitors, depends on the properties physics and chemistry of electrode materials.[4] In this study, metal oxides such as MnO2, ZnO, TiO2 along with graphene were effectively studied.

Specifically, we specifically discussed the latest materials for supercapacitor applications and their future developments.

[5] The combination of carbon materials with polymers/metal oxides or both has been found to have higher specific capacitance due to the combination of redox reaction of the metal oxide and surface area/ Graphene has a higher electrical conductivity than its individual form due to its positive synergistic effect. [6] Recently, transition metal oxides such as TiO2, ZnO, MnO2, etc. can improve the electrochemical performance of carbon-based supercapacitors, as they can contribute pseudocapacitance to the total capacitance, in addition to the double-layer capacitance provided by the carbon material. However, most of them are uncommon and expensive. Therefore, there is a need to explore more desirable materials for applications in the CE field [7].

2. Classification of Supercapacitor

The electrochemical device capable of storing charge greater than normal capacitors and supplying it at a higher rate than a battery is called as supercapacitor. The main characteristics of supercapacitor are that it can charge and discharge rapidly, high power density, high rate capability and can passage the slit between conventional capacitors and batteries. The supercapacitors are also called ultracapacitors or electrochemical capacitors, which use large-area electrode materials and thin dielectrics to achieve higher capacitance than conventional capacitors. The energy storage of supercapacitors is based on charge accumulation or reversible redox reactions and therefore, supercapacitors are classified into three main types based on storage criteria, which are: EDLC and pseudo Capacitors and their combinations are called hybrid supercapacitors.

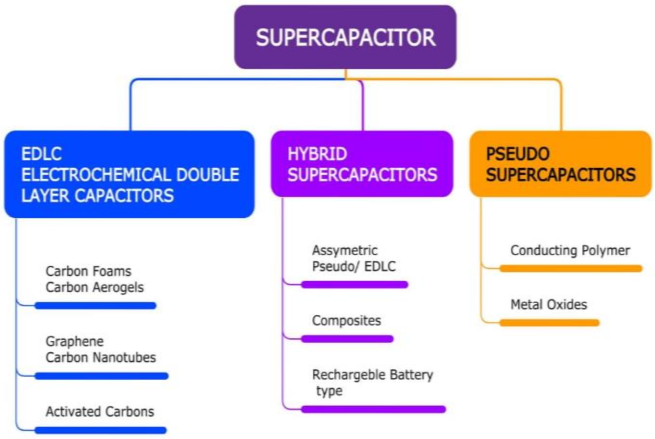

Fig. 1 Classification and Types of Supercapacitor

2.1 Electrochemical Double Layer Capacitors (EDLCs)

EDLC consists of an electrolyte, two carbon-based materials, an electrode, and a separator. EDLCs can store charge electrostatically or through non-Faradaic processes that do not require charge transfer between the electrolyte and electrodes. Electrochemical double layer is an energy storage concept used in EDLC. When a voltage is applied, no charge is accumulated on the surface of the electrode. This is because the potential difference at the electrode surface creates an attraction of opposite charges, causing electrolyte ions to diffuse across the separator and in the oppositely charged electrode pores. A double layer of charge was created to prevent ion recombination within the electrode. EDLC allows the bilayer to achieve high energy densities with increased specific surface area and reduced distance between electrodes. Moreover, the storage mechanism of EDLC enables rapid energy acquisition, distribution, and superior power supply. There are some differences between batteries and EDLCs due to the non-faradaic phase, which is not a chemical reaction. This is because batteries can withstand up to thousands of cycles, whereas EDLC can withstand millions of cycles. Additionally, no electrolyte solvent is required for charging. When a high potential cathode or graphite anode is used in a lithium-ion battery. It leads to a solid electrolyte interface.

2.2 Pseudo Supercapacitor

Pseudocapacitors can store charge through electrophoresis, redox reactions, or intercalation, resulting in higher capacitance and energy density than EDLC. Note that pseudocapacitors do not have the same properties as conventional batteries because they undergo redox reactions on the surface, unlike batteries, where redox reactions occur on most of the electrode material. If the pseudocapacitor is used repeatedly to charge and discharge, it will wear out faster than the EDLC. Spurious capacitance can be generated on the electrode surface and throughout the electrode. This allows for higher capacity and energy density compared to EDLC. For the same electrode surface, the capacitance of the pseudocapacitor is 10 to 100 times the capacitance of the electric double layer. Pseudocapacitors, commonly classified as metal oxides and conductive polymers, have high resistivity, leading to inefficient electron transport in electrochemical processes and low energy density.

2.3 Hybrid Capacitor

Hybrid supercapacitors combining EDLC and pseudocapacitors exhibit better characteristics than the combined components. In EDLC, energy storage is based on the intrinsic surface area of the shell and the atomic charge separation length. In contrast, energy storage is achieved through a rapid and reproducible redox reaction between the electroactive part on the active electrode material and the electrolyte solution in the pseudocapacitor. The combination of these two storage mechanisms forms the energy storage mechanism of hybrid supercapacitors. Half of the hybrid supercapacitor acts as an EDLC and the other half acts as a pseudocapacitor. In comparison, hybrid supercapacitors have higher energy and power density than EDLCs and conventional pseudocapacitors.

3. Parameters for Supercapacitor

Capacitance C is defined as the ratio of the stored (positive) charge Q to the applied voltage V:

$$C = Q / V \tag{1}$$

For a conventional capacitor, C is proportional to the area surface A of each electrode and inversely proportional to the distance D between the electrodes:

$$C = \varepsilon 0\ \varepsilon r\ A/D \text{ or } C/A = \varepsilon 0\ \varepsilon r/D \tag{2}$$

Where ε0 = dielectric constant of free space and εr = dielectric constant of the insulating material between the electrodes.

The energy E stored in a capacitor is proportional to its capacitance

$$E = ½\ CV2 \tag{3}$$

The voltage during discharge is determined by these resistors.

When measured at the appropriate impedance (R = ESR), the maximum capacity P max of the capacitor is given by

$$P = V2/4 \times ESR \tag{4}$$

(Cs) (F/g) at the single electrode of the device is calculated by:

$$Cs = \frac{1}{mV(Vc-Va)} \int_{Va}^{Vc} I(v)dV \tag{5}$$

where m is the mass (g cm−1) deposited, I(v) is the response current response (mA) of the electrode material per unit area, V is the scan rate, Vc-Va is the operating potential window in (V), anode current Va and cathode current Vc.

The energy density E (Wh kg−1) and power density P (W kg−1) of a supercapacitor are calculated using the following relationships:

$$E = \frac{0.5\ X\ Cs}{3.6}\left(V_{max}^2 - V_{min}^2\right) \qquad (6)$$

$$P = \frac{E}{tD} \qquad (7)$$

where Cs is the specific power (Fg−1), Vmax and Vmin are the maximum and minimum voltages obtained during charging and discharging, respectively, in volts (V) and tD is(s) Discharge time in one cycle of the supercapacitor.

The specific capacitance retention is calculated using the relationship

$$\eta = t^D / t^C \qquad (8)$$

where t^C and t^D are the charging and discharging times during one cycle of the supercapacitor, respectively.

4. Recent Advances in Graphene based metal oxides (ZnO, TiO_2 and MnO_2) Supercapacitor

Graphene, GO, and rGO are extensively studied materials for a inclusive range of applications. Graphene, in the form of rGO and GO, has extraordinary surface area, high mechanical electrical conductivity, and tensile strength, and light weight, which is essential for improved device performance. However, inherent defects such as vacancies, lines, carbon, and edge dislocations affect efficiency. Due to the inherent properties of graphene, the use of graphene alone as an electrode material results in poor electrochemical performance. Transition metal oxides (TMOs) have been intensively studied in recent decades due to their promising charge transfer and accumulation mechanisms. Several active substances are featured in this review article. During enrichment, it was observed that these metal oxides achieve synergistic effects when combined with graphene or graphene derivatives. The contribution of these metal oxides limits the formation of dendrites, intercalations, and solid interfaces between the electrolyte and electrodes, ensuring safe operation.

4.1 Recent advances in graphene based zinc oxide (ZnO) supercapacitor

Recently, Rai et al [8] reported that electrochemical studies of reduced ZnO/graphene oxide were carried out using an electrolyte (0.5 M H2SO4). The observed value of the specific capacitance of nanohybrid is 345 Fg-1, almost double that of rGO, which has a value of only 190.5 Fg-1 at the same scan rate. The nanohybrid also demonstrated excellent capacity retention after 1000 cycles. Milon and co-workers [9] reported the fabrication of reduced graphene oxide (rGO) composite decorated with ZnO nanoparticles and its electrochemical performance for supercapacitor applications.

The specific capacitance of the composite material was studied using a two-electrode configuration and from the charge-discharge diagram, the specific capacitance obtained was 949 Fg-1 to 1 Ag-1 with high cycling stability and it maintains a high capacitance value of 91 even after 10,000 cycles, demonstrating good long-term stability. Swati et al [10] studied the electrochemical properties by measuring the specific capacitance using cyclic voltammetry (CV) and charge discharge technique in 3 M KOH solution.

These CV studies have clarify that the positive synergistic effect of rGO and ZnO nanorods shows exceptional deployability. The best results were obtained from a 1: 2 ratio of rGO: ZnO, verifying a specific capacitance of 472 F/g, an energy density of 2. 62 Wh/kg, and a power density of 32.

24 W/kg. Morteza and co-workers [11] demonstrated that flexible micro-supercapacitors fabricated by spin-coating a gel electrolyte, showed a high stacking capacitance of 9 F/cm3 at a current density of 150 mA/cm2. This micro-supercapacitor provides a power density of 70 mW/cm3 and an energy density of 1.2 mWh/cm3. Furthermore, the performance of the device is studied under different curvature angles. P. Geetha et al [12] demonstrated that FLG/ZnO NCs displayed a maximum specific capacitance of 389 Fg-1 related to other compositions at a scan rate of 50 mV/s. Using EIS, the equivalent series resistance of the nanocomposite was obtained in the range of 6–8 ohms. This shows the excellent electrical conductivity of the graphene sheets in ZnO nanoparticles, allowing easy access to charges through the electrode and electrolyte, leading to good specific capacitance values. The results of this study show that FLG/ZnO NCs are suitable as electrode materials for supercapacitors. K. Subhramani and co-workers [13] reported the facile and scalable synthesis of hexagonal crystalline nanoflowers of ZnO/RGO nanocomposite (ZnO-NF/RGO NC) via direct chemical decomposition. of zinc hexacyanoferrate (ZnHCF) on reduced graphene oxide (RGO) nanosheets. Hierarchical ZnO nanoflowers, consisting of 2D nanosheets coated with RGO nanosheets, were identified from FE-SEM and HR-TEM images. The blended ZnO-NF/RGO showed high specific capacitance of 203 F g-1 at a current density of 1 A g-1 and also reveal excellent electrochemical stability 98 %. for 10,000 cycles at a high current density of 20 A g-1.

Edmund et al [14] reported that the non-vacuum ESD technique was used for the synthesis of a binder-free ZnO/graphene composite electrode material. The improved ZnO/graphene composite electrode, ZG-2, exhibits a specific capacitance of 89 mF.cm -2 at a current density of 1 mA.cm -2. Additionally, after being charged/discharged for 1,000 cycles, the symmetric cell retains 90% of its original capacity. v. Rajeshwari et al [15] reported that graphene-ZnO composite electrode material was successfully synthesized by hydrothermal method for supercapacitor applications. In terms of electrochemical performance, the composite electrode material yielded high capacitance value and was found to be 719.2 F/g at a scan rate of 5 mV/s. The improved supercapacitor performance of this electroactive material can be attributed to the increased conductivity of ZnO and better consumption of graphene sheets.

Rajesh et al [16] demonstrated one-step and scalable synthesis of zinc oxide nanoparticles (ZnO NPs) supported on very thin reduced graphene oxide (rGO) nanocomposites/

transparent (ZnO@rGO) by direct microwave irradiation by decomposing zinc acetate dihydrate (Zn(CH3CO2)2·2H2O) which has graphite oxide reducing properties.The synthesized ZnO@rGO nanocomposite has a specific capacitance of 102. 4 F/g at a scan rate of 30 mV/s and exhibits good cycling stability of 82.5% over 3000 cycles at a high scan rate of 100mV /S. Sudha et al [17] reported that hexagonal zinc oxide was combined with reduced graphene oxide (rGO) composites and interestingly, the composites had 1:.2 wt% rGO vs. ZnO and exhibits an excellent specific capacitance of 251.16 F/g at 2 mV. Time-potential analysis demonstrated good charge and discharge properties of the mixture, while electrochemical impedance spectroscopy showed good charge transfer properties. Zhen et al [18] reported that a simple one-pot green electrode deposition process was presented to synthesize ZnO/graphene nanosheet composites. The electrochemical performance of the resulting composite used as a supercapacitor electrode was investigated by cyclic photocurrent, charge/discharge, and electrochemical impedance tests.

At a current density of 3 Ag-1, the resulting ZnO/GNS composite has an increased specific capacitance of 291 Fg-1, much higher than that of pure ZnO (118. 8 Fg-1).

Table.1 Graphene-Zno nanocomposites based supercapacitors

Sr.	**Materials**	**Method of Synthesis**	**Electrolytes**	**Specific Capacitance**	**Year**
1	ZnO/rGO	Reduction-based process	0.5M H2SO4	345 f/g	2021
2	ZnO nanosphere/ rGO	Ex-situ wet chemical	3 M KOH	949 f/g	2020
3	rGO/ZnO nanorod	Thermal reaction	3 M KOH	472 f/g	2019
4	LSG/ZnO	Laser scribing	0.5 M KCL	9 F/cm3	2016
5	FLG/ZnO	Modified Hummer's method	6 M KOH	398 f/g	2019
6	ZnO-NFs/RGO	Chemical decomposition	3.5 M KOH	203 f/g	2018
7	ZnO/graphene	Electro spraying	1 M Na2SO4	89 mF·cm -2	2018
8	graphene-ZnO	Hydrothermal method	-	719.2 F/g	2017
9	ZnO@rGO	Microwave irradiation	0.1 M KOH	102.4 F/g	2020
10	ZnO-rGO	Centrifugation process.	1 M KCl	251.16 F/g	2020

4.2 Recent advances in graphene based titanium oxide (TiO_2) supercapacitor

Alif et al. [18] reported that multiwalled carbon nanotubes (MWCNT), reduced graphene oxide (rGO), and titanium dioxide (TiO2) were tested in an in situ hydrothermal process. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tested in a two-electrode system showed that MWCNT-rGO-TiO2 has a specific capacitance of 308F g-1 and an energy and work density of Capacity is 15 Wh kg. This result is higher for other electrodes due to the distal and non-distant processes in the electrode.

Golnaush et al. [19] demonstrated a simple hydrothermal technique to synthesize three-dimensional three-dimensional graphene-tin-titanium dioxide (3DG-SnO2-TiO2) nanocomposites. The ternary nanocomposite electrode in 6 M KOH was found to have a maximum specific capacitance of 232.7 C g-1 at 1 A g-1. The UPS achieves a maximum energy density of 28.6 Wh kg-1 and a power density of 367. 7 W kg-1.

Additionally, the device achieved excellent cycling stability of approximately 97 over 5000 cycles, demonstrating its promise as a commercial ASC electrode.

Farrar et al. [20] reported the use of atomic layer deposition to fabricate TiO2 nanofilms (NM) with precisely controlled thickness. Then, TiO2 NMs were used as electrodes in high-performance pseudocapacitors. Experimental results show that TiO2 NM material with 100 ALD cycles has the highest capacity of 2332 F/g at a rate of 1 A/g and an energy density of 81 Wh/kg. The improved performance can be attributed to the large surface area and connectivity in the case of ultrathin and flexible NM.

Shashank et al. [21] reported the supercapacitor performance of a rGO/TiO2 nanosheet composite electrode (prepared by a simple one-step hydrothermal reaction) combined with a redox-doped electrolyte in 1M Na2SO4. The synergistic effect of the porous rGO/TiO2 nanosheet electrodes and the optimized redox electrolyte allowed us to achieve an extremely high specific capacitance of 1565 F/g at a current density of 3 A/ g (operating potential window from 0.1 V to 0.5 V).

This specific capacity value is much higher than what can be achieved using simple aqueous electrolytes (e.g. 1 M Na2SO4). Furthermore, by using rGO/TiO2 nanosheet electrodes to fabricate symmetric supercapacitor devices, it achieved an excellent specific capacitance value of 204.5 F/g at current density is 1.5 A/g. In addition to long-term stability, the device also achieves promising values for energy density (15.5 Wh/kg) and energy density (1.1 kW/kg), cycling stability (~87%), even after 1000 consecutive charges -discharge cycle.

Shilpa et al. [22] presented another strategy to improve the capacitive electrochemical properties of electrodes using a simple multi-step green electrode positioning and brush coating technique of PEDOTTiO2/GO composites. /PEDOT-TiO2 has been developed. The synthesized composite exhibits both EDLC and pseudocapacitive behavior, with an excellent specific capacitance of 501 Fg-1 in the 1 Ag-1 sandwich structure.

The results show that the synthesized composite material has a better ion transport mechanism, leading to fast charge-discharge cycles and very high power density (500 kW/kg), suitable for supercapacitor applications electricity. The material shows excellent electrochemical stability and retains 94% of its capacity after 2,000 cycles.

Dengzhou et al. [23] detailed that PPy-wrapped graphene/TiO2 composite hydrogels display a synergistic impact of interconnected three-dimensional nanostructures, the pseudocapacitance of PPy and TiO2, and the electric twofold layer capacitance of graphene. The impact appeared that the electrochemical capacity was progressed. The bond-free composite hydrogel has an great particular capacity of 300 F g-1 at a current thickness of 0.5 A g-1. Moreover, the composite hydrogel shows steady capacity amid long-term cycling, with a particular capacity maintenance of more than 90ter 3000 charge-discharge cycles.

Murat et al. [24] performed electrochemical tests utilizing galvanostatic charge/discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) to decide the Csp 431.23 F/ of [rGO] detailed that the most noteworthy particular capacity of g was uncovered. o/[Py]o 1/1, 10 mV/s. The ternary rGO/TiO2/PPy nanocomposite has Csp 122.12 F/g at 10 mV/s for rGO/PPy, Csp 93.17 F/g at 4 mV/s for rGO, Csp 45, 16 F/ g and higher Csp values. at 4mV/sec. s is GO. A tall vitality thickness of E 2.03 Wh/kg and control thickness of P 18.3 kW/kg at 1000 mV/s was gotten for the rGO/TiO2/PPy nanocomposite. The rGO/TiO2/PPy nanocomposite had moderately tall coulombic productivity and held more than 100% of its unique capacity for [rGO]o/[Py]o 1/1 after 1000 cycles.

Elmira et al. [25] detailed that a novel ternary nanocomposite conductive polymer of decreased graphene oxide/poly(1,5-dihydroxynaphthalene)/TiO2 (RGO/PDHN/TiO2) was effectively connected to gold terminals for supercapacitor applications. We detailed over that it can be synthesized electrochemically. The RGO/PDHN/TiO2 nanocomposite polymer film within the three-electrode framework features a huge vitality thickness of 556 F g-1 compared to those created with RGO/PDHN (432 F g-1) and PDHN (223 F g-1). Demonstrates particular capacity. Gotten at a current thickness of 2.4 A g-1. The RGO/PDHN/TiO2 nanocomposite shows longer self-stability than other polymers after 1700 cycles, holding around 74% of its unique capacity esteem. Crucial et al. [26] detailed titanium dioxide (TiO2)/graphene nanocomposites with synchronous N-doping (N-TiO2/NG) synthesized by one-pot aqueous union for vitality capacity applications. The N-TiO2/NG cathode displayed a particular capacity of 205.1 F g -1 at 1 mV s -1 and great cycling soundness of 78.8ter 5000 continuous charge-discharge cycles at 1 A g -1. I did. Here, TiO2/rGO incorporates a maintenance rate of 67%, appearing potential for vitality capacity applications.

Nagaraju et al. [27] detailed that the nanocomposites utilized as the supercapacitor anode in three cathode framework shown higher particular capacitance esteem of 585 Fg−1 at a current thickness of 1 Ag−1 in 1 M H2SO4 as related to graphene oxide (174 Fg−1) and TiO2 anode (66 Fg−1). The upgraded capacitive execution is due to the intercalation of TiO2 nanoparticles on the graphene sheet.

Table 2 Graphene-TiO2 nanocomposites based supercapacitors

Sr.	**Materials**	**Method of Synthesis**	**Electrolytes**	**Specific Capacitance**	**Year**
1	MWCNT-rGO-TiO2 30 %	In-situ hydrothermal	1 M H2SO4	168 f/g	2022
2	3DG−SnO2 −TiO2	Facile hydrothermal	6 M KOH	232.7 C g−1	2022
3	TiO2 NMs	Atomic layer deposition	1 M KOH	2332 F/g	2019
4	rGO/TiO2	Hydrothermal	1 M Na2SO4	204.5 f/g	2019
5	pedot-TiO2/GO/PEDOT-TiO2	Facile electrodeposition brush coating	1.0 M H2SO4	501 f/g	2023
6	PPy-graphene/TiO2	One-pot hydrothermal	1.0 M Na2SO4	300 f/g	2019
7	rGO/TiO2/PPy	Chemical oxidation polymerization	1 M H2SO4	431.23 F/g	2018
8	RGO/PDHN/TiO2	Electrochemical	1.0 M HClO4	556 F/g	2018
9	N-TiO2/NG	One-pot hydrothermal	1 M Na2SO4	205.1 F/g	2018
10	TiO2/graphene	Facile in-situ microwave	1 M H2SO4	f 585 Fg−1	2018

4.3 Recent advances in graphene based manganese oxide (MnO_2) supercapacitor

Bhaskar et al. [28] showed that symmetric SCs fabricated with ternary MWCNT/MnO2/rGO nanocomposites exhibited significantly higher capacitive performance than SCs using binary nanocomposites (MnO2/rGO and MnO2/MWCNT).

The synergistic effect of simultaneous growth of graphene and MnO2 on MWCNTs under ultrasonic irradiation leads to the formation of a porous tertiary structure with effective ion diffusion channels and a large electrochemically active surface area. The SC is symmetrical with a commercially available bulk charging electrode (about 12 mg cm-2) providing high specific capacitance (314.6 F g-1) and energy density (21.1 W h kg -1 to 150 W kg-1). The overall operating voltage is 1.5 V. In addition, SC has excellent longevity and does not lose capacity after 5,000 charge/discharge cycles.

Kuan et al. [29] showed that the LP-MnO2/CCMC(R1/5) based electrode has a 1000 times higher specific capacitance of 74.2 F/g (at a current density of 0.1 A/g) and Good performance during discharge cycles. It has been shown to be electrically durable. At the same time, the sandwich supercapacitor consisting of LP-MnO2/CCMC(R1/5) electrodes has a maximum specific capacitance of 49.7 F/g at a current density of 0.1 A/g. In addition, the power system based on LP-MnO2/CCMC(R1/5) is used for LED lighting, opening up the great potential of supercapacitors based on LP-MnO2/CCMC(R1/5) for Electrical appliances.

Raphael et al. [30] reported that MnO2@GO, NiO@GO, and MnO2@NiO@GO electrodes were hydrothermally prepared for use in supercapacitor energy storage devices.
The maximum specific capacitance was measured by cyclic voltammetry (CV) at a scan rate of 10 mV/s and GCD at a current density of 1.0 A/g for MnO2@GO, NiO@GO and MnO2@ NiO@GO are 652 and 652. , respectively 425, 985 and 773, 487, 1141 F/g for MnO2@GO, NiO@GO and

MnO2@NiO@GO. The performance of different electrodes shows that the mixture of two transition metal oxides/GO has higher performance than a single transition metal oxide/GO and the addition of graphene oxide increases the supercapacitor performance electrode electricity.

Xiang et al. [31] combined chemical vapor deposition and hydrothermal methods for in situ synthesis of 3D graphene/MnO2 foam composites to fabricate high-performance graphene/metal oxide hybrid supercapacitors. In supercapacitors, 3D graphene/MnO2 composite electrodes exhibit high specific capacitance (333.4 F g-1 at 0.2 A g-1) with excellent cycling stability under ambient conditions.
VJ Mane et al. [32] demonstrated that silver (Ag)-doped manganese oxide (MnO2)/graphene oxide (GO) composite thin films were deposited by an ionic layer sequential adsorption reaction method and without a binder (SILAR).
Its MnO2eAg3/GO electrode tested in 1 M sodium sulfate (Na2SO4) electrolyte gave a maximum specific capacitance (Cs) of 877 F g-1 at a scan rate of 5 mV s-1, with the ability to maintain Maintain capacitance is 94.57 is Stability after 5000 cycles.

Ming et al.
[33] reported that MnO2 and MnO2 reduced graphene oxide nanocomposites were prepared by a simple binder-free electrochemical deposition method under an argon atmosphere. The short-time deposited MnO2/RGO composite electrode (50 s) has excellent electrochemical performance and the specific capacitance can be maintained at 175 F/g.

Yufei et al. [34] demonstrated a new strategy to solve this problem by fabricating a highly interconnected and weakly crystalline MnO2/Graphene oxide (rGO) nanosheet composite. During the charge/discharge process, the resulting composite electrode has a specific capacitance of up to 234.8 F g-1 at 0.1 A g-1 and maintains capacitance after 20,000 cycles at 10 A g - 1 under neutral conditions is 100%.
Na2SO4 on electrolyte.

Linxin et al. [35] reported that the addition of graphene improved the specific capacitance of the MnO2/Co3O4 electrode material, reaching 502.3 F/g at a current density of 1 A/g. After 1000 discharge cycles, the capacitance of all materials synthesized in this study remained above 94.

7% at a current density of 10 A/g.
Bal et al. [36] demonstrated a simple one-step synthesis of reduced graphene oxide-manganese oxide (rGO-MnO2) nanocomposite using graphene oxide (GO) and its KMnO4 in the presence of sulfuric acid. The rGO-MnO2 nanocomposite exhibits maximum capacity, energy, and specific power density of 290 F g-1, 25.7 Wh kg-1, and 8008. 7 W kg-1, respectively, in 1 M Na2SO4 electrolyte and high retention capacity (87.5) % capacity after 5000 cycles.

Jun et al. [37] reported that a nanocomposite consisting of mesoporous MnO2 nanotubes anchored with reduced graphene oxide (MG) was synthesized by a simple and inexpensive reflux reaction. The specific capacitance of MG as an electrode is 466.7 F g-1 at a current density of 1 A g-1, which is 3.33 times that of pure MnO2 (140 F g-1) and 3.19 times compared to MnO2. of graphene (146 Fg−1). The current is 10 A g-1 and the specific power is 454.8 F g-1.
Capacity retention is 92% over 2000 cycles at 1 A g-1.

Table 3 Graphene-MnO2 nanocomposites based supercapacitors

Sr.	**Materials**	**Method of Synthesis**	**Electrolytes**	**Specific Capacitance**	**Year**
1	MWCNT/ MnO2/rGO	Facile ultrasound-assisted	1 M Na2SO4	314.6 F/g	2022
2	LP-MnO2/CCMC	Laser direct writing	1 M ZnSO4	74.2 F/g	2023
3	MnO2@NiO@GO	Hydrothermal	1.0 M Na2SO4	1141 F/g	2022
4	3D-graphene/MnO2	In –situ synthesis	1 M Na2SO4	333.4 F/g	2020
5	MnO2eAg3/GO	SILAR method	1 M Na2SO4	877 F g	2021
6	MnO2/RGO	Electrochemical deposition	1 M Na2SO4	175F/g	2020
7	MnO2 / rGO	Redox reaction	1 M Na2SO4	234.8 F/g	2018
8	G/MnO2/Co3O4	Ultrasonification	1 M KOH	502.3F/g	2017
9	rGO-MnO2	Hydrothermal	1 M Na2SO4	290F/g	2017
10	MnO2 Nanosphere /G	Reflux Reaction	1 M Na2SO4	466.7 F g	2017

5. Conclusion and Future Scope

A comprehensive study of graphene based metal oxide nanocomposites with unique structures and properties, as described here, provides an excellent opportunity to address energy conversion and storage challenges. Recently, graphene-based nanocomposites of zinc oxide, titanium oxide, and manganese oxide have attracted much attention as electrode materials for supercapacitors. These hybrid materials have excellent properties such as good mechanical and electrical properties, large specific surface area, and long-term stability. Supercapacitors are gaining popularity to meet the growing demand for flexible energy storage. A variety of materials have been developed using new strategies for supercapacitors. Among them, graphene metal oxide (ZnO, TiO2, MnO2) nanocomposites are considered to be very valuable and productive for this purpose. Therefore, it is fascinating to study graphene to open up new opportunities to fabricate graphene-based nanocomposites and gain a deeper understanding of its properties and related phenomena.

Conflict of Interest
The author declares no conflict of interest.

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Author's contribution

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