Recent Developments in Nanostructured Materials for Supercapacitor Electrodes

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Abstract: This review focuses on nanostructures-based systems and aims to provide a comprehensive overview of recent advancements in energy storage technologies and modified energy storage materials. The transition towards a sustainable and carbon-free energy system hinges on the progress of efficient and safe energy storage technologies. Supercapacitors have garnered significant interest in diverse energy storage applications due to their rapid charge/discharge rates, high power density, and extended cycle life. Nanostructures have conclusively demonstrated their capability to significantly enhance supercapacitor electrodes' performance. MXene, an innovative category of 2D materials, has emerged as a promising candidate for energy storage applications due to its substantial surface area, exceptional electrical conductivity, and versatile characteristics. Supercapacitors, nanostructures, and MXene are the main topics of the research articles and reviews in this special issue, highlighting recent developments in the design, synthesis, and characterization of advanced energy storage materials and devices. Additionally, this study presents an in-depth investigation of various carbon-based nanomaterials, their synthesis techniques, and their performance in supercapacitors. It also emphasizes the potential of recycling waste materials for developing high-performance nanomaterials for energy storage applications. Finally, this review encourages further research and development of advanced energy storage technologies by giving readers a thorough overview of the current state-of-the-art and future directions in this rapidly expanding sector.

Keywords: Supercapacitor, MXene, nanostructures, energy storage systems.

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1. INTRODUCTION

In recent years, the global population growth rate has surged, paralleled by a corresponding expansion in the size of industries. As these industries proliferate and extend their reach across broader geographical regions, the demand for energy experiences a steep and substantial rise. Due to reasons such as global warming and the limited availability of fossil fuels, the significance of equipment necessary for efficient energy storage, transmission, and alternative fuels becomes increasingly prominent. The storage of energy derived from renewable resources and its efficient conversion into power necessitate a more sophisticated infrastructure. This requirement fosters equipment production, such as new battery types and supercapacitors, driven by advancements in materials science (1–3).

Enhancing energy efficiency through the development of capacitors and batteries is a focal point of research driven by the need to address various drawbacks. These drawbacks include limited energy storage capacity, a short operational lifespan characterized by a small number of cycles, as well as restricted charge and discharge rates. While certain studies focus on refining existing devices, a significant portion of research strives to create energy storage and transmission devices using innovative techniques and novel materials. Consequently, the goal is to fabricate equipment characterized by remarkable attributes such as high energy storage capacity, rapid charging/discharging capabilities, lightweight design, resistance to corrosion and external influences, cost-effectiveness, and ease of production. One of the foremost concerns is the realization of equipment boasting elevated charge/discharge speeds, commonly referred to as high energy density, while preserving their initial stability over numerous charging/discharging cycles. In the contemporary landscape, there is a prevalent shift towards adopting wireless, portable, and compact devices that demand substantial energy due to their technological functionalities. This contrasts with the traditional use of stationary devices tethered to networks via cables. Consequently, the imperative to harness novel materials and technologies to advance sophisticated batteries and capacitors becomes exceedingly significant. These developments cater to devices designed for everyday and specialized applications, including biomedical devices (4–6).

In this context, a multitude of novel products have emerged as a direct outcome of conscientious research endeavors focused on ecologically friendly and sustainable advancements in capacitors and batteries. Among this array of products, several stand out prominently owing to their diverse advantages.

Solid-state battery: Solid-state battery manufacturing is an intriguing study area for enhanced energy storage materials (7). Due to the solid electrolytes used instead of liquid ones, these batteries' cycle life, safety, and energy density can all be improved. Solid-state batteries. They are a desirable alternative for electric car applications because they can produce better energy densities than lithium-ion batteries. These battery systems replace conventional liquid electrolytes, enhancing security, power density, and cycle stability.

Redox flow battery: Redox flow batteries are another cutting-edge energy storage method that is gaining popularity since they are simple to scale up and down (8). The energy reservoir in these batteries is derived from the liquid electrolyte, which can be physically isolated from the electrodes. With enhanced adaptability and customization, energy storage technologies are more suitable for large-scale energy applications. As a result, storage technology options are becoming increasingly scalable and flexible.

Lithium-ion battery: One of the most widely acclaimed intricate energy storage devices is the lithium-ion battery. Lithium batteries have emerged as the best choice for many applications, including stationary energy storage, portable devices, and electric vehicles. Lithium-ion batteries are an excellent solution for several applications due to their high energy capacity and prolonged cycle stability. They rely on the electrochemical properties of electrolytes to produce and store electricity. Furthermore, due to their size, weight, and suboptimal performance, conventional lithium-ion batteries (LiB), characterized by an energy density of less than 500 watt-hours per kilogram, are not advisable for application in portable or wearable electronic devices (9–11).

Supercapacitors: A supercapacitor, also known as an energy storage device or an electrochemical capacitor, is a high-tech energy storage device that generates electricity by separating negative and positive charges on opposite sides of a membrane. Unlike batteries, which store energy through chemical reactions, supercapacitors do so through electrostatic interactions. They are perfect for applications demanding a high power density because of their quick charging and discharging characteristics. Due to their ability to quickly charge (i.e., short discharge times of 1–10 seconds compared to 10–60 minutes for Li–ion batteries) and maintain performance over an extended period (over 30,000 hours compared to 500 hours for batteries), supercapacitors have grown in popularity (12).

Compared to traditional batteries, supercapacitors have several benefits. Because they have a higher power density, they can deliver more power in less time. They may also be charged and discharged more often than batteries before their performance starts to decline. Supercapacitors can be more dependable in challenging circumstances since they are more resistant to temperature changes than batteries. Advanced energy storage materials play a crucial role in facilitating the transition to a future dominated by renewable and sustainable energy sources, as they have the capability to enhance the efficiency, dependability, and availability of energy storage systems.

Supercapacitors can be categorized into several types based on how they store their charge. These types include pseudocapacitors, hybrid supercapacitors, and electric double-layer capacitors (EDLCs). Among these, pseudocapacitors utilize redox reactions occurring at the electrode surface to store energy. At the same time, EDLCs achieve energy storage by forming an electric double layer at the interface between the electrolyte and electrode surface. Combining the EDLC and pseudocapacitive mechanisms to enhance charge storage, hybrid supercapacitors demonstrate significantly higher energy and power densities than EDLCs or pseudocapacitive mechanisms used separately. EDLCs are a specific type of supercapacitor that stores electrical charge by creating an electric double layer at the interface between the electrode and the electrolyte. This double layer enables EDLCs to have high capacitance, allowing for storing large amounts of energy through electrostatic means. Carbon-based materials such as carbon nanowires, carbon nanotubes, activated carbon, graphene, and graphene oxide are commonly used as electrodes in EDLCs due to their extensive surface area, facilitating efficient charge storage.

On the other hand, pseudocapacitors store charge by utilizing electrochemical Faradaic redox reactions that take place at the electrode surface. This mechanism allows pseudocapacitors to store more energy than EDLCs, giving them a higher power density. Pseudocapacitive materials, including metal oxides like ruthenium oxide and manganese oxide, as well as conducting polymers like polyaniline (PANI) and polypyrrole (PPy), are commonly employed as electrodes in pseudocapacitors. It is worth noting that while pseudocapacitors offer higher energy storage capabilities, the long-term stability of these devices can be limited by changes in the electrolyte and modifications to the electrode surface over time. These factors can lead to performance degradation in pseudocapacitors, highlighting the need to consider the materials and design used in their construction carefully.

2. CLASSIFICATIONS OF SUPERCAPACITORS

Supercapacitors can be divided into three categories: thin film, flexible, and planar. Thin film supercapacitors, frequently used in small electronic devices, comprise thin layers of materials like metal oxides and carbon. Flexible supercapacitors, on the other hand, are more common and can continue to perform even when bent, twisted, or stretched. Because of their great power density, planar supercapacitors, which have a rectangular, level architecture, are frequently utilized in bigger electronic equipment. Depending on the special needs of the device, each of these three types of supercapacitors offers a different set of advantages and can be applied to various applications. Supercapacitors can be categorized based on their construction, which includes electrochemical capacitors, pseudocapacitors, and hybrid capacitors. Electrochemical capacitors are composed of two conductive plates separated by an electrolyte, having a high capacitance but lower energy density compared to other supercapacitor types. On the other hand, pseudocapacitors employ electrode materials such as metal oxides or conducting polymers, leading to higher energy density but lower capacitance.

By striking a balance between high energy density and high capacitance, hybrid capacitors amalgamate the benefits of electrochemical and pseudocapacitors. High power density, energy density, low internal resistance, and quick charge-discharge periods are just a few of the characteristics of supercapacitors. High energy density refers to storing a significant quantity of energy in a compact device, whereas high power density allows for great power delivery in a short time. Effective energy transfer between the powered device and the supercapacitor is facilitated by low internal resistance, thus enhancing overall performance. Quick charge-discharge times are essential for applications requiring an immediate power boost, like electric automobiles or regenerative braking systems. Due to their categorization and physical characteristics, supercapacitors present an intriguing solution for a wide range of applications requiring high power and rapid energy transfer.

The materials utilized for the electrodes in supercapacitors are classified due to their charge storage mechanism. Additionally, electric double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors are the three main varieties (13,14). Activated carbon serves as the electrode material in EDLCs, also known as electrostatic capacitors, which exploit the electric double layer they produce at the electrode-electrolyte interface to store energy. In a non-Faradaic process, where the concentration of electrons at the electrode is electrostatic, EDLCs use the electrical double-layer between the electrode and electrolyte to store energy. This procedure has no chemical mechanism or charge transfer between the electrode and electrolyte. Because no chemical connections are formed or broken, charges are therefore dispersed evenly across surfaces by physical processes, leading to great reversibility and cycle stability. Moreover, electrode polarization can distort the solvation shell around ions, potentially leading to partial desolvation. EDLCs feature a rapid energy storage system that enables swift charging, discharging, and high-power output.

3. SUPERCAPACITORS: HIGH-POWER ENERGY STORAGE DEVICES

Supercapacitors are divided into three according to the material class they are made from, apart from these classifications. All of them are nano-sized, but chemically and morphologically, they can be formed from classical nanomaterials, structures occurring with innovative MXenes, and various carbon-based structures. Material-based classification of supercapacitors is given in Figure 1.

3.1. Nanostructure-Enhanced Supercapacitor Electrodes

The electrodes of supercapacitors can benefit specifically from nanostructures. Nanostructures have significantly improved the functionality of supercapacitor electrodes thanks to their enormous surface area, better electrical conductivity, and adjustable properties. Nanostructured materials have improved charge transfer kinetics, better electrochemical stability, and energy storage capabilities. This section thoroughly analyzes several nanostructures used in supercapacitor electrode design, emphasizing the synthesis methods used and the resulting performance gains.

Metal oxide-based nanostructures have gained significant popularity in various energy applications due to their exceptional characteristics, such as a high surface area-to-volume ratio and small particle sizes. These qualities make them highly desirable for energy-related applications, including energy storage, catalysis, and sensors. The large surface area facilitates enhanced interactions with reactants and electrolytes, promoting efficient charge transfer and overall performance improvement. Furthermore, the smaller particle sizes allow for greater accessibility to active sites, improving functionality and responsiveness. Utilizing metal oxide-based nanostructures holds great promise in advancing energy technologies by enhancing their effectiveness and performance. In line with this approach, Haldorai et al. conducted a study focused on synthesizing a novel composite material (15). The study involved decorating reduced graphene oxide (rGO) with zinc oxide nanoparticles (ZnO NPs) using a one-pot method in a supercritical carbon dioxide medium. The primary objective of this study was to enhance the performance of supercapacitors by leveraging ZnO NPs as nanostructures, thereby achieving improved energy storage capabilities. In another study, Sivakumar et al. presented a study on the synthesis of novel copper-doped zinc oxide nanoparticles (Cu-doped ZnO NPs) with an average crystallite size ranging from 25 to 22 nm (16). These nanoparticles demonstrated remarkable electrochemical performance, exhibiting an outstanding specific capacitance of 539.87 F/g at a scan rate of 10 mV/s. The primary objective of this research was to enhance both the photocatalytic activities and electrochemical performance of the Cu-doped ZnO NPs, with potential applications in wastewater treatment and supercapacitors. Integrating nanostructures, particularly metal oxide-based nanomaterials, holds immense potential for advancing energy storage technologies. Research findings suggest that thorough exploration and optimization of ZnO nanostructured materials can significantly enhance the efficiency and performance of supercapacitors. This progress contributes to developing more efficient and sustainable energy storage techniques. To further improve energy storage technologies, it is crucial to fully unlock the potential of nanostructures and continuously evaluate the benefits derived from their utilization. By doing so, we can drive innovation, foster continuous improvement, and achieve remarkable advancements in the field of energy storage. In 2023, Kambale et al. used spray pyrolysis to produce copper oxide (CuO) nanorods (17). The obtained CuO electrode was extremely appropriate for supercapacitor applications since it had a maximum specific energy of 108.18 Wh/kg and had outstanding cycling stability by maintaining 87.78% of its capacitance after 5000 cycles. For the advancement of energy storage systems, the incorporation of nanostructures, in particular metal oxide-based nanomaterials, offers great promise. Exploring and utilizing the potential of metal oxide nanostructured materials has improved supercapacitor performance and efficiency, opening the door for more efficient and long-lasting energy storage options. Enhancing energy storage systems requires employing nanostructures to their maximum capacity and continually assessing the benefits received from doing so. These continual research and development efforts are crucial for stimulating innovation and attaining more improvements in the sector.

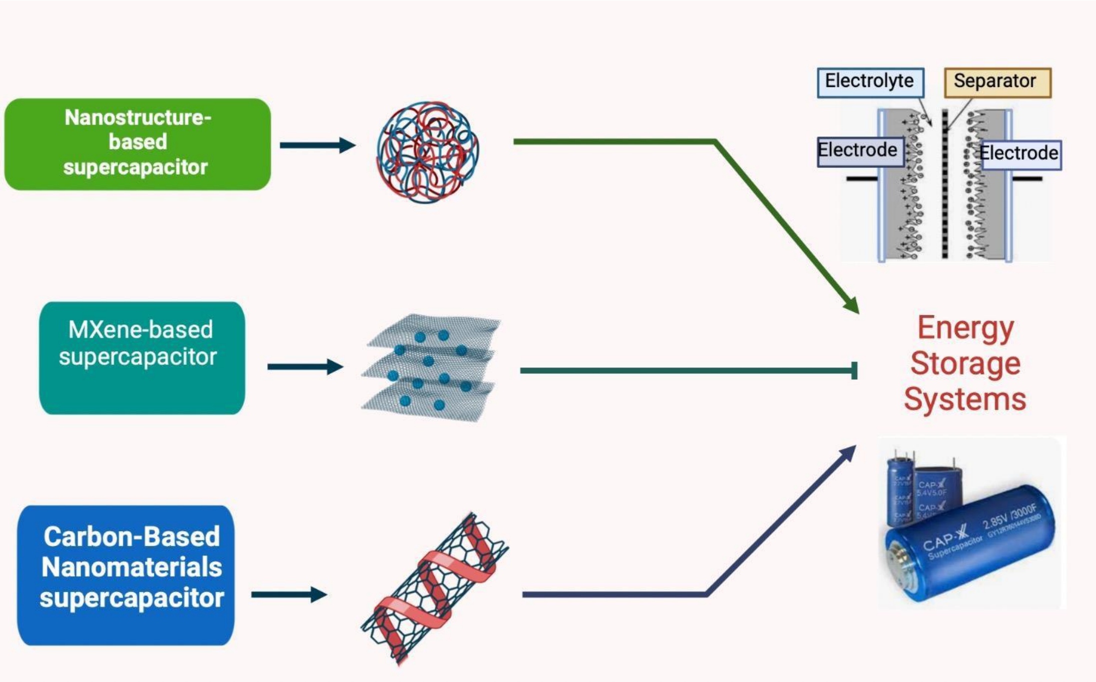

Figure 1: Material-based classification of supercapacitors.

Metal-organic frameworks (MOFs) consist of porous, crystalline compounds formed by metal ions or clusters bonded to organic ligands. Their properties can be highlighted for various purposes based on the utilized metal, the valency of metal ions in the structure, and the type of organic molecule. Concerning supercapacitors, MOFs with a smooth crystal structure, substantial surface area, and easy adjustability are preferred for producing high-capacity electrodes. One significant drawback of these materials lies in their inherent low electrical conductivity and weak stability in their pristine state, especially when compared to their diverse composite structures. Nevertheless, MOFs remain extensively employed in this field due to their adaptability to alternative structures and compatibility with additives. Discovered by Yaghi et al. in 1995, MOFs have continued to undergo development and customization since then (18). In the realm of energy, MOFs and their derivatives find application in various areas, including hydrogen production and storage, fuel cells, lithium-ion batteries, superconductors, and solar cells. Three alternatives exist for employing MOFs in superconductor fabrication: a) Pristine MOFs can be utilized due to electrolyte ions adsorbed on their inner surfaces or due to reversible redox reactions occurring at their metallic centers. b) Metal oxides obtained by the transformation of MOFs are employed, with charge transfer between the electrolyte and the electrode safeguarding electrons. c) The MOFs are subjected to pyrolysis, resulting in a porous carbonaceous structure that enhances conductivity and capacitance (19).

The notable advantages of MOFs over traditional supercapacitors include their expansive design possibilities and the capability to fine-tune composition, adjust porosity, and control surface area width. Furthermore, their distinctive structures enable a harmonious fusion of organic molecule flexibility with the inherent rigidity of inorganic molecules. Nonetheless, challenges such as low conductivity, potential particle aggregation, and structural degradation during cycling must be addressed. Consequently, research on MOFs has reached advanced stages, with the integration of newly discovered materials into these frameworks being actively explored. MOF-derived composites harness the favorable attributes of MOFs and other materials. The metallic content within MOFs furnishes redox sites that exhibit Faraday pseudocapacitive behavior, while the organic components contribute a conjugated π electron cloud and a porous structure that elicits EDLC behavior. The resultant structure can exhibit hybrid capacitive behavior when both behaviors are sufficiently developed. The high stability of the structures can reach extraordinary degrees when compared to batteries. Ni-MOF sample structures produced by electrophoretic deposition, $Ni_3(HAB)_2$ showed 81% stability after 50.000 cycles (20), $Ni_3(HITP)_2$ showed 84% capacitance stability after 100.000 cycles (21). It has been shown that crystallization in the desired direction can be achieved by adjusting the concentrations of organic ligands in Ni(Tdc)(Bpy) based 3D MOF nanocrystals (22). Considering this, it has been asserted that a diverse range of shapes can be synthesized, including nanorods, nanosheets, and 3D structures.

Using Co as the metal is a common practice. The widespread utilization of Co-MOFs can be attributed to factors such as low cost, straightforward synthesis, excellent structural stability, and environmentally friendly attributes. An exemplary illustration is the Co(II)-TMU-63 MOF structure, wherein both μ4-tpa2 and μ-dapz ligands are simultaneously employed. This structure showcases the incorporation of multiple organic compounds and has demonstrated remarkable performance concerning capacitance, energy density, and cyclic life (23). The investigation of polymetallic MOFs featuring multiple metallic constituents has also garnered attention. Comparative to structures comprising solely Ni or Co, Ni/Co-MOF nanoflakes exhibited heightened efficiency (24). While the solvothermal method was employed in this study for material fabrication, an alternative investigation utilizing ultrasound treatment yielded greater capacitance due to the creation of more electroactive sites (25). Furthermore, the advancement of solvothermal synthesis, achieved via metal ion exchange, has increased capacitance. This is attributed to the facilitated diffusion of the electrolyte, achieved by augmenting the gap between layers within the multilayer structure alongside the augmentation of the count of electroactive sites (26). In conjunction with Ni and Co, the incorporation of Mn into the MOF structure has also demonstrated an elevation in capacitance (27). Mn-based MOFs offer electrochemical advantages such as a hierarchical configuration and shortened ion diffusion pathways (28). The profound impact of morphologies on capacitive behavior has been explored from various vantage points. For instance, the amorphous form of UiO-66 MOF outperformed its crystalline counterpart (29). Ni-MOF and Cu-MOF stand as instances where different MOFs have been combined to augment dimensions (30).

Additionally, introducing diverse compounds into the structure is recommended to bolster capacity (31). Employing MOFs as composite constituents represents a strategy for enhancing their electrochemical or physical attributes. For instance, incorporating Cu-MOF onto δ-MnO_2 resulted in nanosheets that amplified the original structure's capacitance and extended its cyclic lifespan (32). While integrating metal oxides into the materials leads to composite formation, an additional boost in capacitance can be achieved by grafting them with metallic compounds (33).

Certain polymers, recognized for their remarkable electrical conductivity, are often favored in supercapacitor fabrication. Due to their adaptable attributes, diverse functional groups, isomeric variety, flexibility, ease of production, and cost-effectiveness, polymers emerge as preferred choices in this field and various other domains. The presence of conjugated bonds between monomers imparts these exceptional characteristics to conducting polymers. Moreover, non-inherently conductive polymers can acquire conductive attributes by incorporating dopants during monomer bonding. These dopants may also confer additional functional properties. Neutral (Br_2, I_2), ionic ($FeClO_4$, $LiClO_4$), organic (CH_3COOH, CF_3SO_3Na), polymeric (PVA, PVS), metal oxide (SnO_2, TiO_2) dopants can be selected based on the material and the desired trait (34). Polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and their derivatives rank among the most frequently utilized conductive polymers. The rate of dopant incorporation hinges on the proximity of positive charges along the polymeric chain. For instance, while this ratio stands at 0.5 for polyaniline, it is 0.33 for the polymers listed above (35).

The initial high capacitance observed in stand-alone conductive polymers typically experiences a significant reduction after a short cyclic life (36). Naturally, exceptional cases exist, and performance varies based on factors such as synthesis method, dopant, nanostructure morphology, and more. For instance, the practical performance of PANI was found to lag its theoretical potential (37,38). In investigations where PPy and PTh were utilized in their pure forms, incorporating a surfactant (39) or dopant (40,41) substantially elevated capacitance and cyclic stability. However, the advantageous attributes of polymeric materials, even if not exhibiting exceedingly high performance on their own, find utility when integrated into composite structures within supercapacitors. For instance, carbon materials exhibit relatively low capacitance despite their notable electrical conductivity, physical resilience, and adaptable surface properties. Numerous studies have been undertaken to surmount this limitation by employing polymers. Graphite (42), graphene (43), graphene oxide (44), and carbon nanoparticles of diverse configurations (45–49) have been combined with conductive polymers, yielding performance surpassing that of pure constituents. Moreover, the range of synthesis methods employed is considerably extensive (50–54). A recent study presents specific capacitance values for various polymers and polymeric composites alongside their respective synthesis methods (55). For example, producing a PPy/graphene composite featuring a uniform nanosheet morphology, in contrast to a cauliflower-like structure, bolstered electrochemical properties by creating ion diffusion pathways (56). In examining a PANI/graphene composite, an increase in the graphene ratio led to a more orderly placement of PANI monomers and heightened conductivity due to robust structural bonding (57). Alongside the research conducted by scholars who established a similar correlation within the PPy/MWCNT blend (54), another study revealed that the performance of the composite material exhibited enhancement up to a 15% MWCNT ratio, after which it declined at higher proportions (58). The utilization of PANI with graphene oxide yielded a more than twofold increase in capacitance, accompanied by elevated material conductivity (59). When subjected to a current density of 0.3 A/g, among PANI, PEDOT, and PPy combined with reduced graphene oxide, PEDOT displayed the highest stability (88%) after 1000 cycles despite possessing the lowest specific capacitance (108 F/g). PANI, boasting a higher specific capacitance (361 F/g) compared to PPy (248 F/g), also exhibited superior stability (82% vs. 81%) (60). Furthermore, when coated onto a pencil graphite electrode, PTh exhibited the lowest specific capacitance but demonstrated the greatest stability when compared to poly(3-methylthiophene) and PEDOT (61).

As elucidated in the preceding section, metal oxides are frequently employed in conjunction with polymers due to their inherent low conductivity and susceptibility to instability in acidic environments, notwithstanding their notable high capacity (62). Especially the wide band gaps of the oxides of the transition metals are the main reason for their low conductivity. However, for example, n-octadecyl-trimethyl-ammonium-intercalated MnO_2 used with PANI both maintained its high conductivity and increased the specific capacity of PANI from 187 F/g to 220 F/g at a current density of 1 A/g (63). There are many other studies in which the same binary mixture is used in different morphologies (27,64,65). The PANI/CuO composite performed better than PEDOT/CuO and PPy/CuO (51). On the other hand, PPy has still been evaluated in producing supercapacitors by using it with many metal oxides. CoO (66), WO_3 (67), MnO_2 (68), and V_2O_5 (69) are some metal oxides whose electrochemical properties are strengthened thanks to their synergistic effects with PPy. In addition to carbonaceous materials and metal oxides, compounds can also be incorporated to create composites with polymers for application in supercapacitors. PANI, for instance, facilitates the crystal growth of $Ni(OH)_2$, resulting in enhanced electrochemical performance (52). It also bolsters the conductivity of hydroquinone, rendering it suitable for utilization in supercapacitors (70). Moreover, PANI contributes to the capacitance and stability of MoS_2 (71).

Table 1 comprehensively compares recent breakthroughs in nanomaterials tailored for supercapacitor applications. The table outlines specific capacitance, energy, power densities, cycling stability, and rate capability, highlighting the significant impact of nano-based materials on elevating supercapacitor electrodes' design and operational prowess, ultimately leading to enhanced efficiency and effectiveness.

3.2. An Innovative Class of 2D Materials for Energy Storage: MXene

MXene has emerged as a promising contender among the most recent developments in energy storage materials. MXene is a name for a class of two-dimensional materials made of carbides, nitrides, or carbonitrides of transition metals. These substances have outstanding qualities such a high conductivity, a sizable surface area, and customizable surface chemistry. MXene is an appealing option for energy storage applications, such as supercapacitors, due to its distinctive qualities. The synthesis, characterization, and performance of MXene-based energy storage materials are covered in detail in this section, along with information on their potential to play a significant role in developing new energy storage technologies. The improved MXene-based composites outperform traditional materials regarding cycle lifetime and energy density while dramatically lowering the MXene stacking phenomenon and enhancing oxidation resistance. They work well with a variety of materials, including small molecules, polymers, and oxides. The complex relationship between their structural properties and electrochemical performance has been revealed through extensive investigation. This includes the way in which the characteristics are organized, the microstructure, the steric arrangement, and the makeup of the material, all of which influence the charge storage processes, ion transport, conductivity, and stability. Thanks to their systematic analysis of these interactions, researchers have made it possible to construct MXene-based electrodes with knowledge, resulting in more effective and efficient energy storage systems. These composite materials predominantly comprise conductive polymers, metal oxides, and carbon nanostructures. Approximately 40% of MXene-based composite publications focus on metal oxides, conducting polymers, and carbon nanomaterials. In the literature, Vigneshwaran made a significant contribution by successfully developing a novel three-dimensional (3D) nickel cobalt tungstate-MXene nanocomposite specifically designed for coin cell supercapacitors (83). The nanocomposite demonstrated remarkable capacitance, achieving an impressive value of 587 F/g at a current density of 1 A/g in a three-electrode cell configuration. These outstanding results highlight the exceptional performance of this nanocomposite and its tremendous potential for high-performance supercapacitor applications. In 2023, MXene-bacterial cellulose (MXene-BC) composite sheets, a novel substance that Weng et al. reported, have enormous potential for the creation of self-charging supercapacitors. These composite films have exceptional qualities that allow it possible to store and discharge electrical energy effectively. This research's ability to achieve a charging voltage of 0.6 V for the self-chargeable supercapacitor is one of its notable accomplishments. This substantial voltage milestone was reached using synthetic sweat as the electrolyte, further boosting the supercapacitor's efficiency and usefulness. The MXene-BC composite films are formed by combining MXene, a two-dimensional nanomaterial with high surface area and outstanding electrical conductivity, with bacterial cellulose, a biocompatible and durable material. This effective combination creates a material with effective charge storage and great mechanical characteristics (84). Tin-cobalt-sulfide (Sn-Co-S) coated on 2D MXene sheets was the ground-breaking cathode material for high-performance asymmetric supercapacitors developed by Kim et al. in a recent work (85). A high specific capacity value of 305.71 mAh/gm at 1 A/g is one of the innovative 0D/2D Sn-Co-S/MXene hybrid material's impressive features. The Sn-Co-S/MXene hybrid material's remarkable electrochemical performance is due to its highly electroactive and conductive design. This study produces outstanding efficiency qualities by enabling effective charge storage and transfer. Hence, the deliberate integration of precisely engineered binary sulfide nanoparticles in conjunction with 2D scaffold-like MXene sheets presents exciting prospects for developing energy storage systems with outstanding performance and long-term stability.

Table 1: Comparative overview of nanomaterials for supercapacitors.

Nanomaterials	Results	Reference
Graphene	The specific capacitance: 523 F/g at 1.0 A/g, good rate capability and cycling stability.	(72)
Silver (Ag)-doped reduced graphene oxide (rGO)/PANI composite	The specific capacitance: 0.5–30 A/g, the highest capacitance value:379 F/g	(73)
N-doped crumpled carbon nano-tubes (CNTs)	The high capacitance: 336 F/g, cycling stability: 96.1% capacitance retention after 10,000 cycles, and good rate capability.	(74)
$SmNiO_3$/Multi walled carbon nanotube (SWCNT)//CNT	Capacitance retention: 79.34% and coulombic efficiency: 97.52% (20,000 cycles)	(75)
Multi-walled carbon nanotube (MWCNTs)/$MgMn_2O_4$ composite	The specific capacitance: 1208 F/g at 1 A/g, high energy density of 54.39 W h/kg, and power density of 775.46 W/kg at 1 A/g.	(76)
Zn-Co metal-organic frameworks (MOFs) nanospheres/rGO	The specific capacitance: 2925 F/g at 0.5 A/g, and good rate capability of 45.4% capacitance at a high current density of 50 A/g.	(77)
MOF-derived NiS_2@carbon micro-spheres wrapped with CNTs	The specific capacitance: 1572 F/g at 0.5 A/g, energy density: 21.6 Wh/kg and 94.8% cycling stability after 10,000 cycles.	(78)
MOF derived $NiCo_2O_4$ nanosheets	Energy density: 84.26 Wh/kg, power density: 1185 W/kg with 83.23% capacitance retention after 10,000 cycles.	(79)
3D MXene@graphene hydrogel	The maximum area capacitance: 4.33 F/cm^2 at 10 mA/cm^2 and a high area capacitance: 1.76 F/cm^2 at 1000 mA/cm^2, the high capacitance retention: 40.6%, a high cyclic stability of 8.37% decrease after 100,000 cycles.	(80)
PANI-MXene composite	The specific capacitance: 222 F/g. The capacitance retention of 98.5% after 10,000 charges.	(81)
$CuMn_2O_4/Ti_3C_2$ MXene composite	The specific capacitance: 496 mF/cm^2 at 6 mA/cm^2 with cyclic stability of 80% for up to 10,000 cycles, and a power density: 1.5 m/cm^2 at a higher energy density of 0.073 mWh/cm^2	(82)

3.3. Carbon-Based Nanomaterials: Synthesis Techniques and Performance in Supercapacitors

Due to their superior electrochemical qualities, carbon-based nanomaterials have attracted a lot of interest in the field of energy storage. This section examines several carbon-based nanomaterials and their synthesis processes, including carbon nanotubes, graphene, and carbon nanofibers. Additionally, it looks at how well they work as electrode materials in supercapacitors, concentrating on elements like pore structure, surface chemistry, and morphology that affect how much energy they can store. The promise of these materials for upcoming energy storage applications is also highlighted in this section, along with current developments in modifying carbon-based nanoparticles to enhance their electrochemical performance. The performance of carbon-based nanomaterials in supercapacitors can vary depending on various factors such as material structure, surface area, pore size, and electrode configuration. The green method for Carbon Dots (CDs), hydrothermal synthesis of Graphene Quantum Dots, Chemical Vapor Deposition (CVD) for Graphene and Reduced Graphene Oxide, electrochemical exfoliation for Reduced Graphene Oxide and Carbon Nanotubes (CNTs), and the template method for Mesoporous Carbon/nanoparticles have all been investigated for carbon-based nanomaterials in supercapacitor applications.

In fabricating electrodes especially designed for supercapacitors, various deposition processes, including physical vapor deposition, chemical vapor deposition, and electrodeposition, are employed (86–88). These techniques offer various ways to create electrode materials with specific characteristics and enable fine control over the thickness of the deposited films. The electrodes produced because of this customized process are guaranteed to have the best properties, such as increased surface area, electrical conductivity, and charge storage capacity, all of which are essential for the greater performance of supercapacitor devices. Additionally, the ability to precisely control the film thickness helps optimize the supercapacitor's energy and power density, allowing it to transmit and store electrical energy effectively in various applications. These techniques yield materials with a wide range of performance characteristics, including affordability, straightforward growth, high stability, excellent rate capability, high specific capacitance, long cycle life, low resistance, and good electrical conductivity, enabling researchers to choose materials based on specific application requirements. The Table 2 provides a general overview of their performance characteristics.

Table 2: A general overview of the performance characteristics of nanomaterial in supercapacitor applications.

Synthesis Method	Nanostructure	Performance	Characterization Results	Reference
Green Method	Carbon Dots (CDs)	Low specific capacitance, cost-effectiveness, simple growth, and high stability	10-20 nm	(89)
Hydrothermal Method	Graphene quantum dots	Low specific capacitance, cost-effectiveness, simple growth, and high stability	Lateral dimensions: 10–20 nm	(90)
Chemical Vapor Deposition (CVD)	Graphene	Excellent rate capability, high specific capacitance, long cycle life, and low resistance	Spherical nanoparticles diameter: 80±8 nm and the lateral size 500 nm (PPY grown on dopamine-coated graphene)	(91)
Chemical Vapor Deposition (CVD)	Reduced graphene oxide	Excellent rate capability, high specific capacitance, long cycle life, and low resistance	the average crystallite size of GO and thermally reduced graphene oxide (TRGO)/Ni-Foam (NF) 35.43 and 1.61 nm	(92)
Electro-chemical Exfoliation	Carbon nanotubes	Excellent electrical conductivity, high specific capacitance, and rapid charge/discharge rates	The high specific surface area: 219 - 210 m^2/g	(93)
Electro-chemical Exfoliation	Carbon nanofibers	Long cycle life, good electrical conductivity, and moderate specific capacitance	Diameter: 10–40 nm	(94)
One-pot synthesis technique	Mesoporous carbon/nanoparticles	Excellent ion accessibility, high specific capacitance, and good stability	The high specific surface area: 686 m^2/g	(95)
Solvothermal Method	Heterostructure hollow spheres	Low cost, good stability, moderate specific capacitance, and simple scalability	Size: 1140 and 1520 nm.	(96)
Pyrolysis	Porous carbon	Large surface area, low cost, strong stability, and moderate specific capacitance	Pores with width between 10 nm and 50 nm	(97)
Sonication	Nb_2C MXenes composites	Good cycling stability, electrical conductivity, and high specific capacitance	100 nm for single layer	(98)
Sonication	$MnFe_2O_4$/MXene/NF nanosized composite	Good cycling stability, electrical conductivity, and high specific capacitance	quasi-2D MXene sheets	(99)

4. CHALLENGES AND FUTURE OPPORTUNITIES

In the realm of energy storage, the pursuit of innovative solutions remains paramount to meet the escalating demand for environmentally sustainable and carbon-neutral power sources. This review, focused on nanostructure-based systems, endeavors to provide a comprehensive panorama of recent advancements in energy storage technologies and refined energy storage materials. Facilitating the transition to a sustainable energy landscape necessitates the development of efficient and secure energy storage techniques. Supercapacitors have emerged as a central focus across a diverse array of energy storage applications, driven by their swift charge/discharge kinetics, high power density, and extended cycle life. The integration of nanostructures has incontrovertibly demonstrated their potential to significantly amplify supercapacitor electrodes' effectiveness. Running parallel to this, the evolution of MXene, an inventive class of two-dimensional materials, holds great promise as a formidable contender in the energy storage arena. MXene's expansive surface area, remarkable electrical conductivity, and adaptable properties render it an appealing candidate for diverse energy storage applications.

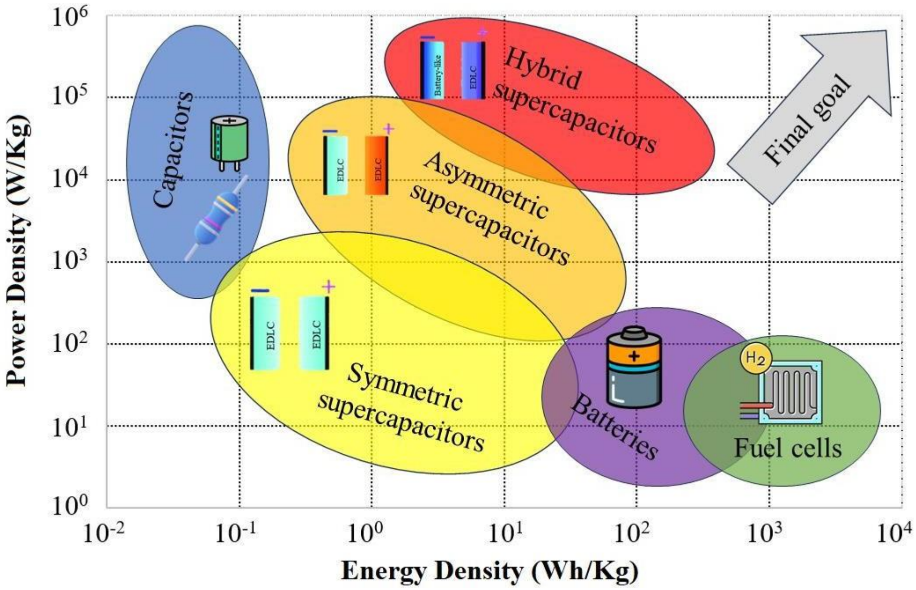

Figure 2: Energy density vs power density of capacitors, batteries, fuel cells, and supercapacitors.

The Ragone plot (Fig. 2), a graph that juxtaposes electricity storage and transmission devices along the energy density (Wh/kg) -power density (W/kg) axes, offers valuable insights. As data points populate this graph, batteries, characterized by their high storage capacities and low transmission forces, populate the high energy density-low power density quadrant. In contrast, classical capacitors occupy a different region. Fuel cells notably exhibit higher energy density compared to batteries. Devices closest to the ideal region align with mechanical components like engines and turbines. Supercapacitors, positioned along the graph's axial line, showcase their structure and composition diversity. This expansive variety positions supercapacitors, spanning a wide spectrum, to deliver superior densities. To encapsulate, the journey from EDLC to asymmetric and hybrid structures progressively enhances energy density.

Biological materials are used too, besides polymeric and other chemical materials in the separators that are expected to prevent unwanted ions' transition and be stable throughout the working life. Materials can present negative features along with some superior features. For example, PVA, which is preferred in terms of properties such as permeability, biodegradability, can withstand low voltages (100). In addition to organic structures, it is seen that ceramic-like inorganic structures are also developed. Eggshell is one of the biologically based separators (101). In general, in addition to the stability of the separators, flexibility is another desired feature. Conductive liquids used as electrolytes can also be supplemented with other solutions that can give ions. For example, adding a solution that will make the pH move away from neutral but will not adversely affect other components will increase the power density (102). Materials such as anodic aluminum oxide, polystyrene colloidal particles, and sugar cubes are some of the auxiliary materials that can be used to increase the surface area of the electrodes. The smaller size of the ions also increases the performance, providing a faster transfer. While carbon itself, as active material, shows a weak capacitance, its derivatives with various morphological properties can improve performance. Although metal oxides, which are frequently used for this purpose, have different energy levels that facilitate charge transfer, they can be disadvantageous regarding environmental pollution, cyclic life, and charging efficiency (103). Conductive polymers, which are environmentally friendly, easily produced, and provide high power density, are another material class used as active material. Polypyrrole, polyaniline, polythiophene, polyphenylenevinylene, and polyacetylene are the most widely used conductive polymers. They can also be easily used in composite production with other materials and increase the adjustability of properties (104). The diffusion rate of immobilized ions into the electrolyte is a parameter that affects the energy density. Materials with very different contents and structures have been designed to develop this speed in a controlled way. Hierarchical nanoarrays offer an advantageous approach when the one-pot strategy of hierarchical structures is used for dimension increase. Asymmetric fiber structures create folds and twists on the surface, creating a 3D morphology, which increases capacitance and power density. The properties of some supercapacitors, such as transparency, flexibility, lightness, small size, and biodegradability, increase the possibility of using these materials in biomedical engineering. This is a very important development in the field of medical electronics. It is possible to use supercapacitors in wearable electronics, electric vehicles, solar cells, etc (105).

In contrast to lithium-ion batteries, supercapacitors boast safer and more straightforward electrolytes. Moreover, the realm of biodegradable supercapacitors introduces an added advantage in this domain. Their distinctive structural makeup ensures an extended cyclic life and elevated power density. As illustrated in the examples, many of these supercapacitors exhibit substantial performance retention even after enduring thousands or even up to 100 thousand cycles. While their relatively lower energy densities may be perceived as a drawback; this aspect often pales compared to their many advantages. Furthermore, the emergence of novel materials and techniques holds the promise of surmounting this limitation. Various production methods, including lithography, electrospinning, printing, laser scribing, deposition (electrophoretic, electrolytic, physical/chemical vapor), and sputtering, form the backbone of supercapacitor fabrication from diverse materials. Within this comprehensive review, the exploration spans diverse nanomaterials, their synthesis processes, and their functional performance within supercapacitor frameworks. Reported studies also spotlight the untapped potential inherent in waste recycling, underscoring the capacity to craft high-performance nanomaterials tailored exclusively for energy storage applications. Ultimately, the overarching objective is to establish a robust foundation for advancing energy storage technologies, thereby catalyzing a surge of research and development endeavors.

5. CONCLUSION

Recent developments in energy storage technology have focused on nanostructures for modifying energy storage materials. Creating effective and secure energy storage systems is necessary to transition to a carbon-free and sustainable energy system. As a result of their high power density, quick charge/discharge rates, and long cycle life, supercapacitors have attracted a lot of attention. Supercapacitor electrode performance has been demonstrated to be improved by the incorporation of nanostructures. MXene, a 2D material renowned for its sizable surface area, superior electrical conductivity, and varied features, is one promising substance in this domain. With a focus on supercapacitors, nanostructures, and MXene, this special issue includes various research articles and reviews highlighting the most recent advancements in advanced energy storage materials and systems. While highlighting the possibility of recycling waste materials to produce high-performance nanomaterials for energy storage applications, the paper also examines the synthesis methods of carbon-based nanomaterials and their performance in supercapacitors. Overall, regarding the current state-of-the-art and future directions in this quickly developing sector, this study seeks to encourage more research and development in energy storage technologies.

6. CONFLICT OF INTEREST

The authors have no conflicts of interest to declare.

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