



Review

Emerging Trends of Miniaturized Carbon Nanomaterial Based Energy Storage Microdevices

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Received: 13 May 2024; **Revised:** 6 June 2024; **Accepted:** 6 June 2024

Abstract: Off lately, an increasing reliance on energy-consuming equipment has resulted from the tremendous growth of industry. Owing to the rapid increase in energy use, coupled with the environmental impact of traditional energy supplies, a quest of energy storage device development has begun. Hence, supercapacitors with strategic designs have been developed extensively in last couple of years. This review aims to concise a brief account of the emerging trends in designing of supercapacitors. A snapshot of various materials being used for the development of energy storage device is discussed. New materials such as graphene, carbon nanotubes, perovskites, MXenes, and other nanostructures that can enhance the performance of supercapacitor are being analysed. This review focus primarily on carbon nanomaterial based supercapacitors explored in last couple of years. Electrodes mainly control capacitance, power density, and energy storage, therefore, carbon based electrodes have proven to be significant in this aspect. Various carbon materials give high performance and these have been tabulated in this review for a better understanding. In further, state-of-the-art approaches adapted for fabrication of supercapacitors are also discussed here. Overall, this review gives information about carbon based emerging supercapacitors for the researchers to understand their working, research gap and future prospects.

Keywords: miniaturized; supercapacitor; carbon material; microelectrode; energy storage

1. Introduction

Producing new and improved, renewable energy is of utmost importance as global energy needs have been increasing at an unprecedented rate because of the global economic expansion. Detailed studies are being carried out world over on producing efficient energy storage (Example: supercapacitors and batteries) and energy conversion (Example: solar cells, fuel cells) devices to accommodate this energy surge. In this context, Nanotechnology has brought in a revolution and to large extent carbon nanomaterials has been a boon for creating high performance energy conversion and energy storage devices [1].

Carbon with an atomic number six is one of the most common and abundant elements on earth which can form bonds in different hybridisations (SP, SP², SP³) not only with itself but also with non-metallic elements to form extensive range of structures and molecules. Diamond and Graphite are one of the oldest and abundantly available allotropes compared to the recently discovered carbon Nano allotropes such as fullerenes and carbon nanotubes (CNT). Carbon Nano allotropes can be further classified into broadly three categories based on there morphology. Figure1 shows the flow chart for the classification.

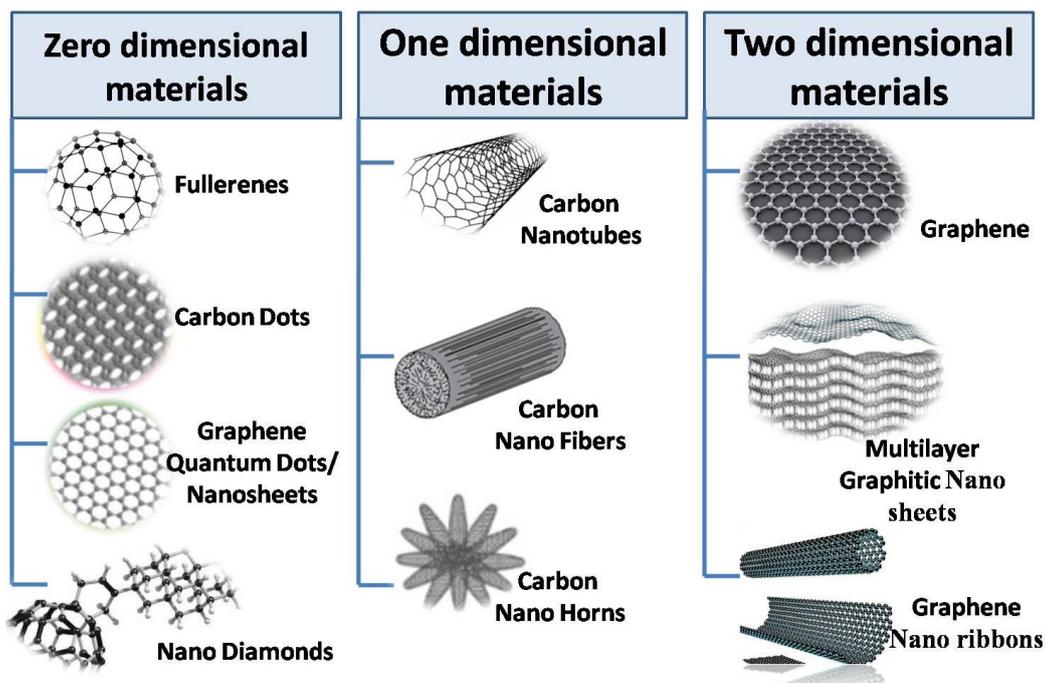


Figure 1. Flow chart for morphological classification for Carbon nanomaterials

In recent times, there has been an extensive research to deploy carbon based materials in energy storage. Owing to the fact that carbon materials are cost effective in comparison to other forms of materials, gives high output, and are simpler to fabricate in large scale, there is a huge demand of these in energy devices. Therefore, last couple of years has seen tremendous growth in carbon based supercapacitors. This review focuses to give a brief snapshot about recent development strategies of supercapacitor fabrication using various carbon materials as these are most readily available materials. Herein, prime focus is to highlight the key findings, in terms of applications of these carbon material devices in real time. Comparison of power densities and out put has been shown for better understanding. Detailed classification of carbon materials is also shown for the readers to understand the morphological and structural parameters of the materials that plays a key role in improving performance. Discussion about fabrication approaches is also done for simplifying the understanding of the readers to reproduce them. Overall, this review adds up to the literature and could be beneficial for researchers to understand and identify the research gap which could lead to future prospects.

2. Classification of Carbon Based Materials

2.1 Zero dimensional materials

2.1.1 Fullerenes

The discovery of Fullerene by Kroto et al. in 1985 [2] has had a domino effect and led to the discovery of many new allotropes of carbon. Among them are carbon nanotubes, first discovered in the year 1991 by Iijima [3]. Fullerenes are hollow spheres with a pentagonal and hexagonal network of carbon atoms and are ≤ 1 nm in diameter[4] there are several kinds of fullerenes with similar structures but with higher or lower number of carbon atoms (example: C_{20} , C_{32} , C_{60} , C_{70} , C_{76} , C_{82} , C_{84} , C_{540}). The most commonly studied and generously available fullerene is C_{60} . C_{60} is a truncated icosahedron containing 12 pentagons and 20 hexagons with a diameter of 0.71nm.

Fullerenes have been characterized by various spectroscopic and spectrometric techniques such as NMR, FTIR, UV -Vis, Raman and mass Spectroscopy. The ^{13}C NMR spectrum of C_{60} contains only a single resonance at 143.2ppm as its carbon nuclei are equivalent. The Fourier Transform infrared FTIR spectrum of C_{60} contains characteristic bands at 1428, 1183, 577 and 527 cm^{-1} . The UV Visible absorption spectrum of C_{60} contains intense bands at 213, 257 and 329 nm and a weak band 500 and 700 nm, while that of C_{70} has several intense peaks at 214, 236, 360, 378 and 468 nm.) [5].

2.1.2 Carbon dots or C- dots

Carbon dots mostly contain a mixture of SP^3 and SP^2 hybridised carbon atoms in various ratios. These are a new class of carbon nanomaterials with sizes below 10 nm. The carbon dots are first discovered and identified during the purification of single-walled carbon nanotubes by gel electrophoresis in 2004 [6] and also by laser ablation of graphite powder and cement in 2006[7]. Significant research has been conducted in the synthesis, properties and applications of carbon-based dots, as reviewed by Baker *et al.*, [8] Lee *et al.*, [9] and Zhu *et al.* [10].

The C-dots are obtained by a chemical oxidation method followed by thermal reduction, and introducing RuO_2 to obtain the composites. the hybrid shows exceptional cycling stability with 96.9% capacity retention over 5000 cycles at $5 A g^{-1}$ [11]. C-Dots are known to have more advanced properties in photoluminescence when compared to traditional semiconductor quantum dots and organic dyes. The superior electronic properties of carbon-based quantum dots as electron donors and acceptors, causing chemiluminescence and electrochemical luminescence, resulting in a wide application with areas such as optronics, catalysis and sensors. C-dots based hybrids act as an excellent electrode material for supercapacitors which was reported recently [12]. The UV–Vis spectrum of these C-dots contains two bands with maxima at 360 and 240 nm.

2.1.3 Graphene Quantum Dots (GQD)

GQD also known as graphene nano sheets are produced by cutting a graphene monolayer into small disks of diameter ranging from 2-20nm. GDQ consists of SP^2 hybridised carbon and are crystalline. GQD have photoluminescence, electronic and optoelectronic properties because of their band gaps which can be calibrated by changing the size, shape, geometry of the graphene. The UV–vis absorption spectra of GQDs feature a broad band that starts at around 600 nm and rises smoothly [13].

2.1.4 Nanodiamonds

Nanodiamonds consist primarily of tetrahedral SP^3 carbon atoms and have diameters that are greater than 1–2 nm but less than 20 nm. They are prepared by top-down methods such as jet milling or abrasion of microdiamonds [14]. The surfaces of nanodiamonds are usually decorated with several organic functional groups, including carboxyl groups, hydroxyl groups, lactones, and ketones. These groups provide a larger platform for incorporating various other organic molecules thus opening up numerous applications in diverse fields. The presence of functional groups can be proved by FTIR spectroscopy: OH species adsorbed on or covalently bonded to the surface generate characteristic bands at $3200\text{--}3600$ and $1630\text{--}1640\text{ cm}^{-1}$, C=O groups give bands at $1700\text{--}1800\text{ cm}^{-1}$, and CH_2 or CH_3 groups produce bands at $2850\text{--}3000\text{ cm}^{-1}$. The Raman spectra of nanodiamonds contain a broad peak near $1320\text{--}1330\text{ cm}^{-1}$ representing the first-order diamond line [15]. Nanodiamonds exhibit quite a few properties similar to that of a diamond. Like diamond, nanodiamond is a wide-band semiconductor with the largest optical band gap (5.4–5.6 eV at room temperature) of all known materials [16]. They are known to have high Young's modulus, high refractive index, electrical resistivity, and thermal conductivity. It also undergoes little thermal expansion, exhibits optical transparency from the deep-ultraviolet to the infrared region of the electromagnetic spectrum, and has a high breakdown voltage and carrier mobility. Nanodiamonds exhibit bright luminescence due to the presence of non-carbon atoms (usually an impurity such as nitrogen) with adjacent vacant sites[17–19].

2.2 One Dimensional Materials

2.2.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are SP^2 hybridized and its structure consists of rolled-up graphene sheet which gives it the shape of a tube. CNT have unique properties apart from similar properties to that of graphene. There are several kinds of carbon nano tubes based on the number of concentric layers of rolled graphene sheets [20].

(I) Single walled nano tubes (SWCNT), which is again sub divided into a) chiral, b) arm chair and c) zig zag based on their chirality. The outer diameter of CNTs is around 0.8 to 2 nm for SWCNTs.

(II) Multi walled nanotubes (MWCNTs). The outer diameter of CNTs is around 5–20 nm for MWCNTs.

(III) Double walled nanotubes (DWCNT) which are precisely engineered structure.

CNT tensile strength and thermal conductivity is much more than steel and diamond respectively. Depending on their chirality, CNTs can be either semiconductors or metals. CNT are almost chemically inert unless they are brought into contact with high temperature and oxygen simultaneously. Graphene nanoplatelets and CNTs are the

strongest known materials possessing high flexibility. SWNTs have a high threshold of endurance considering the capability to elongate 280% longer and 15% thinner before disintegrating which indicates 'Superplasticity'. This is due to the high strength covalent C=C bonds between SP² carbon atoms [21]. As a result of their extraordinary properties, CNT has a wide range of not only industrial application but also scientific research. To mention a few, it includes application in electronic devices such as transistors, electron-field emitters, chemical/electrochemical sensors, biosensors, lithium-ion batteries, hydrogen storage cells, supercapacitors, and electrical shielding devices [22].

Due to their large surface area, high mesoporosity and electrolyte accessibility, and good electrical properties, carbon nanomaterials, especially graphene and carbon nanotubes, are very promising candidates to replace activated carbons as the electrode materials in high-performance supercapacitors.

2.2.2 Carbon Nanofibers

Carbon nanofibers were identified and studied extensively before the discovery of Carbon nanotubes. Carbon nanofibers are described as SP² based linear filaments ranging between 50–200 nm in diameter and their aspect ratio exceeds 100. The techniques to synthesize Carbon nanofibers are identical to those producing Carbon nanotubes [23–25]. The two methods that allow a controlled synthesis of Carbon nanofibers are Catalytic Chemical Vapour deposition (C-CVD) and enhanced Chemical Vapor deposition (C-PECVD). These methods in particular allow us to control the Alignment, shape, location and size of each individual Carbon nanofiber [23]. Depending on the way, the Graphene sheets are arranged, Carbon nanofibers have been recognized into various categories. Figure 2 gives the overview.

A) Platelet Carbon Nanofibers	B) Ribbon Carbon Nanofibers	C) Herring Bone Carbon Nanofibers	D) stacked up & conestacked carbon nanofibers	E) Cone-Helix Carbon nanofibers
In these carbon nanofibers the graphene layers are perpendicular to the fibre axis	Also known as tubular carbon nano fibers In these carbon nanofibers the graphene layers form a stacked pack parallel to the fiber axis	Also known as fishbone carbon nano fibers. In these carbon nano fibers the graphene sheets are tilted to the fibre axis	These carbon nanofibers consists of truncated cones arranged to form a hollow core	In these carbon nanofibers the graphite layers form a continuous helix - spiral with an internal hollow core

Figure 2. Overview of the various carbon nanofibers

2.2.3 Carbon Nano Horns

A new type of carbon particle named as Carbon Nanohorns are discovered by Iijima in 1999 while studying CNT formation [26]. Nanohorns are tubule-like/cone like structures and an individual particle is made up of numerous horn shaped sheaths of single walled graphene sheets and are around 80–100 nm in diameter which looks like Dahlia flowers. Individual Nanohorns have diameters of 1–2 nm at the tips and 4–5 nm at the base of the cone [27]. These can also be produced by CO₂ laser ablation of a graphite target at room temperature without a metal catalyst [28,29] or by the arc-discharge technique [30]. The Raman spectra of these single walled nano horns exhibit a broad graphitic band around 1550–1600 cm⁻¹ (the G band) that shows vibrations in the SP² - bonded carbon network. There is also another broad peak of same height at around 1320–1345 cm⁻¹ (the D band), which shows single-bonded SP³ carbon atoms that are present within the SWNH aggregates [31]. These shows semiconductor properties [32,33].

2.3 Two Dimensional Materials

2.3.1 Graphene

Graphene is quite an abundant material and theoretically, it can be considered a foundational stone for natural graphite. A Graphene sheet takes the form of a robust honeycomb lattice (HCB) by virtue of the covalent bond

shared by a Carbon atom with other 3 carbon atoms. This makes it the strongest known material presently and is discovered in the year 2004 by Novoselov et. al. [34]. Microchemical cleavage of bulk graphite is the optimal way for obtaining high quality graphene crystallites of up to 100 μm in size [34]. In principle, Graphene can be resized to create various forms like 0D fullerene, 1D CNT or even a multilayered carbon nanosheet by the way it is folded or cut [35]. A structure of a Graphene can be conceptualized to create a Nanohorn by elaborating it in a more sophisticated way. Its aromatic character is due to the interaction of the unhybridized p orbitals of the carbon atoms with perpendicular orientation to the other carbon atoms in the sheet that forms a half-full π band. The Young's modulus of graphene was observed to have ~ 1.0 TPa.

2.3.2 Multilayer Graphitic Nanosheets

Multilayer Graphitic Nanosheets (MGNs) containing 2 to 10 Graphene monolayers are created using the Ultrasonic liquid exfoliation of graphite in various solvents. The chemical vapour deposition (CVD) technique results in the same outcome of MGNs [36]. Due to this, MGNs have similar properties as Graphene and are considered a byproduct of Graphene production. There are multiple ways to produce MGNs. The Ultrasonic method is at a disadvantage considering a low yield. Air pyrolysis of Organic molecules such as Betaine is considered an alternate method to produce MGNs. This method has a better yield compared to Ultrasonic method and delivers MGNs of the size less than 10 nm. The low ID/IG ratio of MGNs exhibit long-range graphitization with low number of structural defects. Raman spectra of MGNs can be used to depict a corrupt Graphitic structure. This can be inferred by the presence of both G (1600 cm^{-1}) and D (1385 cm^{-1}) bands. Alternatively, MGNs can be produced using hydrothermal carbonization of glucose at the air-liquid interface using sodium dodecyl sulphate as a template [37], or by the solvothermal treatment of carbon tetrachloride [38].

2.3.3 Graphene Nanoribbons

Oxidizing conditions trigger the Graphitic layers of MWNTs to unfold releasing Graphene Nanoribbons (GNRs). These are decorated with groups at the edge and surface which are rich in Oxygen containing groups such as Carbonyl, Carboxyl and Hydroxy. These oxidizing conditions are created with the chemical treatment of MWNTs with Sulfuric acid and Potassium Permanganate [39]. Due to the finite dimension and defined edges, Graphene Nanoribbons are defined as One dimensional sp^2 -hybridized carbon strip at which the carbon atoms are of non-3-coordinated characteristic. Depending on their edge termination [40], GNRs are classified into three types namely (i) Armchair (ii) Zigzag and (iii) Chiral. The Armchair GNR is depicted as the number of dimer C-C lines (N_a) across a Nanoribbon. In the case of a GNR with jagged edges, the width is given by the number of 'Zigzag' chains (N_z) across the nanoribbon. The Raman spectra of graphene nanoribbons obtained from MWNTs contain a stronger D band than the starting materials due to the greater numbers of defect sites and higher edge-to-surface ratios of the nanoribbons [41].

3. Energy Storage Devices

Global industry has advanced tremendously in the last few decades. In parallel, the world's energy needs and consumption have increased due to population growth. The extensive usage of petroleum and other non-renewable fossil fuel-based resources to date has put a strain on the current energy infrastructure and raised concerns for the future. Global warming, geopolitics, increased fuel costs, and environmental risks are a few dangers associated with long-term reliance on these fuels [42]. There is an intense need for alternative renewable energy sources in this situation. To address the energy difficulties, a great deal of research and development has been done at the academic and industry levels to create more efficient technology. Recently, a number of energy harvesting and storage devices, such as supercapacitors and batteries, have been realized. Compared to batteries, supercapacitors—also known as electrochemical capacitors—show higher power and higher density energy storage. Moreover, supercapacitors have garnered a lot of attention since, in comparison to batteries, they have a lower internal resistance, a higher capacity, and are easier to store and distribute energy due to their energy storage method, which involves a charge separation at the electrode-electrolyte interface [42]. Researchers working on fuel cells in 1957 initially noticed the phenomenon of energy storage in carbon porous materials. This effect is later rediscovered in 1966. In order to provide computers with a backup power source, NEC finally created supercapacitors in 1978 based on these observations [43]. Typically, a separator and an electrolyte are used to keep two electrodes electrically apart in a supercapacitor. Supercapacitors are an improved energy storage technology due to their benefits such as less maintenance, light weight, portable packing, high power, wider temperature range, and longer life. In spite of these benefits, there are several drawbacks to using them on a large

and commercial scale, including as more self-discharge, less cost-effectiveness, poorer energy density, and less voltage per cell. To close these research gaps and preserve stability, high power and energy density, and a faster charge/discharge cycle, much study is being done. The introduction of innovative electrode materials is one strategy. The electrode's substance is crucial in producing high capacitance and density [44]. Supercapacitor development uses a variety of materials, including metal oxides, polymers, nanomaterials, carbons, redox mediators, and others. However, because of their large surface areas, materials based on carbon are frequently used. The electrolyte interface, where electron exchange occurs, is the fundamental idea behind the operation of a supercapacitor and energy storage. Supercapacitors can be roughly classified into three types based on how energy is stored: (a) hybrid supercapacitors, (b) pseudocapacitors, and (c) electrochemical double-layer capacitors (EDLC). Furthermore, the electrode materials used in each variety varies [45]. Figure3 is the pictorial representation of three types of supercapacitors.

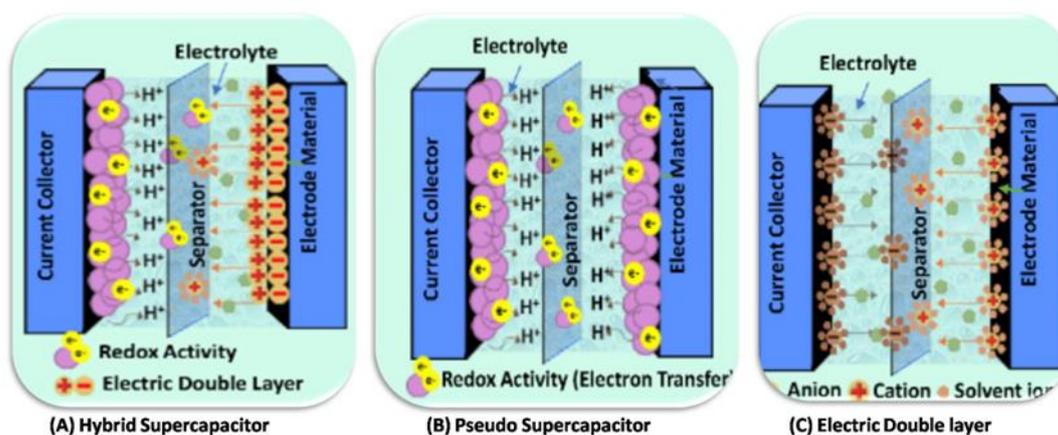


Figure 3. Pictorial representation of the Experimental set up of three types of supercapacitors

Irrespective of the type of supercapacitor, the major working principle is the electrode-electrolyte interface. Hence, the electrode fabrication plays a major role in supercapacitor based energy storage device.

4. Electrode Fabrication/Modification

There are several materials which are used for modification of electrode surface to prepare a working electrode. However, carbon based materials are more cost effective and high through put. Hence, materials like carbon nano tubes, graphene, nano fibers, nano ribbons etc. are used. These materials are deposited over base electrodes via different methods. Figure4 gives a pictorial representation of different approaches for deposition of various materials.

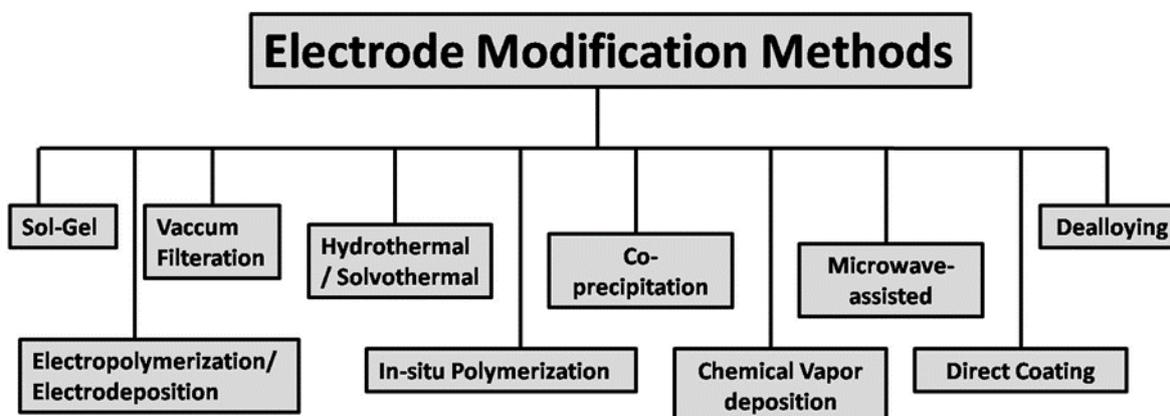


Figure 4. A pictorial representation of different approaches for deposition of various materials on electrode surface

The current method entails miniaturizing these supercapacitor electrodes. To prepare tiny, micro, and nanoelectrodes, some recent breakthroughs in this domain include lithography, 3D printing, screen printing, laminating, and embossing techniques. Figure 5 gives an over view of these approaches [45].

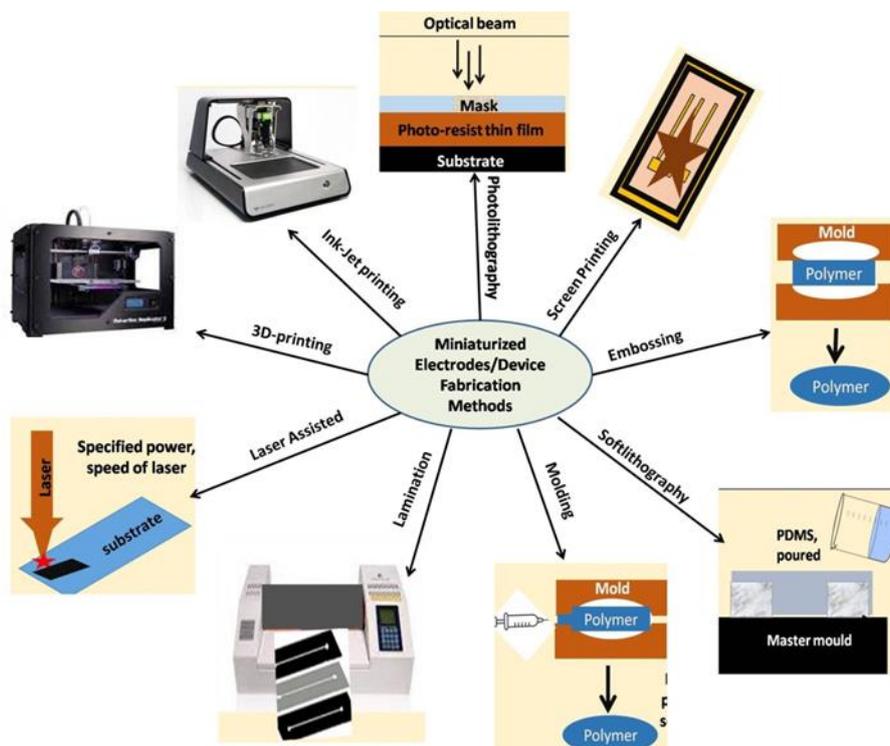


Figure 5. State-of-the-art approaches for fabrication of miniaturized devices

5. Miniaturized Energy Storage Devices

Miniaturized energy storage devices are becoming more and more necessary due to the proliferation of the growing need for wearable and portable electronics. A flexible, safe, highly power-dense, and long-lasting micro- and nanosupercapacitors—those that can withstand more than 100,000 charge/discharge cycles—are the ideal option. There have been reports that the base of a tiny supercapacitor can be made of fibers, textiles, papers, flexible substrates, etc. For instance, a solid state microsupercapacitor made of polyethylene terephthalate (PET) substrate is created by Si et al. Here, photolithography is utilized to create 24 interdigitated fingers that served as the anode and cathode. Additionally, electrode materials and electrical connections are deposited using the electron beam evaporation process. Multiple 50 nm-thick layers of MnOx (manganese oxide)/Au are formed on the electrodes. The energy density and power density of their apparatus is $1.75 \text{ mW h cm}^{-3}$ and 3.44 W cm^{-3} , respectively. Additionally, it demonstrated an amazing cycling stability of over 15000 times, which is 74.1% greater than that of conventional bulk systems [46]. Similar to this, Kim et al. used a five-beam interference lithography technique to report a three-dimensional porous carbon pattern doped with boron. The proposed electrodes are carbonized in an argon atmosphere at high temperatures ($700\text{--}1000^\circ\text{C}$). The planned pattern is dipped into a boric acid solution to induce boron doping. An interdigitated electrodes mask is then used to deposit gold over the electrode pattern. An Au layer 50 nm thick is deposited. The experiment is conducted using a gel electrolyte. The apparatus displayed a power density of 66 W/cm^3 , an energy density of 7.1 mWh cm^{-3} , and a capacitance of 7.15 mF/cm^2 [47]. Wang et al. created a micro-supercapacitor based on a reduced graphene oxide/TiO₂ composite. On top of the PET substrate, the composite is applied in thin layers. UV light is used to create interdigitated electrodes across these films using a photomask. In addition, a 45 nm coating of gold is deposited. Lastly, an electrolyte made of polymer gel is applied to the surface and allowed to dry. Their apparatus demonstrated an impressive 312 W cm^{-3} , 7.7 mW h cm^{-3} , and capacitance of 233.0 F cm^{-3} [48].

Similarly, Wang et al. used ink jet printing to create $\delta\text{-MnO}_2$ nanosheets in order to produce a solid-state micro-supercapacitor. $\delta\text{-MnO}_2$ ink is printed in five layers on substrates made of polyimide and glass. Two more layers of PEDOT polymer are printed on top of this. After printing, annealing at high temperatures is done to

allow the print to dry. The printed films served as electrodes in conjunction with a modified polyvinyl alcohol polymer gel electrolyte. After 3600 charge-discharge cycles, the device demonstrated good cycling stability and capacitance retention. The apparatus displayed a capacitance of 2.4 F cm^{-3} , a power density of 0.018 W cm^{-3} , and an energy density of $1.8 \cdot 10^{-4} \text{ Wh cm}^{-3}$ [49]. Choi et al. used ink-jet printing to create a tiny supercapacitor made of paper. Here, an A4-sized piece of paper is printed with a suspension of carbon nanofibers (CNF) serving as the base electrode. In addition, a typical technique is followed to generate a viscous conductive ink containing a composite of single walled carbon nanotube-activated carbon and silver nanowires, which is then ink-jet printed over CNF patterns. Here, the medium is an ionic liquid-polymer gel electrolyte. The apparatus demonstrated notable functionality [50]. Li et al. used ink-jet printing to create tiny supercapacitors based on graphene. Electrochemical exfoliation is used to remove graphene from graphite foil. The resulting graphene is divided into a viscous suspension for printable ink by dispersing it in DMF solvent. This is put into an inkjet printer and printed in an interdigitated array format on a variety of substrates, including glass and silicon wafer. Additionally, ink is printed and dried for the electrolyte polymer gel (poly(4-styrenesulfonic acid) [51]. CNT based microsupercapacitors are designed by Yu et al. via 3D printing. The authors followed normal approach to manufacture CNT ink with solvent in this work. Feeding pressures for the 3D printer micronozzle ranged from 10 KPa to 30 KPa. As base substrates, glass plates are used and heated to remove the solvent. Annealing is done afterwards. The microsupercapacitor is finished by printing and drying the polyvinyl alcohol gel electrolyte [52]. Large-scale manufacture of tiny supercapacitors based on graphene over flexible substrates is described by Kadyet al. Here, they used a light scribe DVD burner and direct laser writing to create over 100 tiny supercapacitors on graphite oxide layers. An areal capacitance of 2.32 mF cm^{-2} , a volumetric capacitance of 3.05 F cm^{-3} at 16.8 mA cm^{-3} , and a power density of 200 W cm^{-3} are obtained from the device [53]. Lambertiet al. devised a method of employing a CO_2 pulsed laser to fabricate graphene electrodes atop flexible polyimide sheets. They are put on top of a Polymer substrate. Moreover, Polymer layer and glass are thermally fused to prevent heat loss and establish an electrolyte reservoir. At last, the gel electrolyte is added to the chamber using a syringe. At 50 mV s^{-1} , the apparatus produced an areal capacitance of $650 \mu\text{F cm}^{-2}$ [54]. Ye et al. provided evidence of graphene film formation using CVD on copper substrates. There are several graphene layers deposited. These films are also transferred over substrates coated in gold. Laser scribing is used over these to create microelectrode patterns. The device demonstrated a good power density of 1860 W cm^{-3} and an energy density of 23 mW h cm^{-3} , respectively [55].

Using a CO_2 laser, Lin et al. created graphene-based electrodes over polyimide and other polymer sheets. The design of interdigitated electrodes produced an impressive 4 mF cm^{-2} specific capacitance and 9 mW cm^{-2} power density [56]. Zhang and colleagues created a 3D miniaturized supercapacitor on a chip. Here, lignin film served as the substrate on top of which a laser is utilized to scribe graphene. An digitized electrode pattern is created and put to the test for use in energy storage. Good areal capacitance of 25.1 mF cm^{-2} , energy density of 1 mW h cm^{-3} , and power density of 2 W cm^{-3} are obtained as a result [57]. Xiao et al. grew MnO_2 particles via electroless deposition using carbon fiber as the basis material. These are positioned over the PET substrate and utilized as two parallel electrodes. Moreover, an electrolyte consisting of PVA gel is applied and allowed to harden. This apparatus produced a $2.2 \times 10^{-4} \text{ Wh cm}^{-3}$ energy density and a volume capacitance of 2.5 F cm^{-3} . Up to 50 fibers can be used to create the same device in order to further improve performance [58]. Similarly, Sun et al. synthesized hybrids by combining reduced graphene oxide (rGO) fibers with transition metal nanoparticles. To create MSCs, these were constructed using PVA gel electrolyte. With this setup, the apparatus demonstrated a 1.5 F cm^{-3} volumetric capacitance [59]. Sun et al. used Mxene nanosheets and a carbon nanotube scaffold to create the MXene/CNT helical fiber structure. To create a solid-state, small supercapacitor, these electrodes are positioned atop a PET substrate and filled with PVA gel electrolyte. The apparatus displayed a power density of 45.9 mW cm^{-3} , an energy density of 2.55 mWh cm^{-3} , a volumetric capacitance of 22.7 F cm^{-3} , and a current density of 1.0 A cm^{-3} [60].

Using conductive polymer composite and multiwalled carbon nanotube (MWCNT) fibers, Cai et al. created microsupercapacitor wires. Here, MWCNT fibers are dipped into an acidic aniline solution to integrate the aniline into the fibers. To create polyaniline, the coated fibers underwent further electrochemical polymerization. After coating, a PVA gel electrolyte was dried. The device's gravimetric capacitance is 274 F g^{-1} [61]. Zhenget et al. described a novel technique in which they used a graphite rod to draw electrodes on printing paper. On paper, the electrodes are sketched, and a paper separator is stored. The capacitance of this device is 2.3 mF cm^{-2} [62]. Bin et al. created a device on a sheet of printing paper, and they drew the electrodes for the graphite layer with a pencil. Moreover, polyaniline nanowire is electrodeposited on top of these electrodes. A PVA gel electrolyte is used to assemble a solid state device. This apparatus demonstrated a power density of 0.054 W cm^{-3} and an energy density of $0.32 \text{ mW h cm}^{-3}$ [63]. To create a scalable method for producing MSCs, Zhe et. al. employed cellulose paper using a soak and dry technique together with graphene solution. The apparatus demonstrated a capacitance of 46

mF cm⁻² [64]. According to Kristy et al., carbon inks can be used for screen printing on cotton and polyester materials. Their apparatus displayed 210 mF cm⁻² of capacitance [65]. Jae et al. used weavable, knottable, braidable, and sewable yarns to show a redox supercapacitor. A CNT was added to these yarns. Volumetric capacitance measured by the instrument was 179 F cm⁻³ [66]. Overall, carbon based miniaturized energy storage supercapacitors are being extensively explored. Table 1 gives a comparison of these literature for better understanding.

Table 1. Comparison of various literatures

Material	Energy Density	Power Density	Capacitance	Ref
MnOx (manganese oxide)/Au	1.75 mW h cm ⁻³	3.44 W cm ⁻³	-	46
three-dimensional porous carbon pattern doped with boron.	7.1 mWh cm ⁻³	66 W/cm ³	7.15 mF/cm ²	47
reduced graphene oxide/TiO ₂ composite	7.7 mW h cm ⁻³	312 W cm ⁻³	233.0 F cm ⁻³	48
δ-MnO ₂ ink	1.8.10-4Wh cm ⁻³	0.018 W cm ⁻³	2.4 F cm ⁻³	49
graphite oxide layers	--	200 W cm ⁻³	2.32 mF cm ⁻²	53
graphene electrodes atop flexible polyimide sheets	--	--	650 μF cm ⁻²	54
Graphene over copper sheets	23 mW h cm ⁻³	1860 W cm ⁻³	--	55
graphene-based electrodes over polyimide	--	9 mW/cm ²	4 mF cm ⁻²	56
Lignin-Laser scribed graphene	1 mW h cm ⁻³	2 W cm ⁻³	25.1 mF cm ⁻² ,	57
MnO ₂ particles via electroless deposition using carbon fiber	2.2 × 10 ⁻⁴ Wh cm ⁻³	--	2.5 F cm ⁻³	58
reduced graphene oxide (rGO) fibers with transition metal nanoparticles	--	--	a 1.5 F cm ⁻³	59
Mxene nanosheets and a carbon nanotube scaffold	2.55 mWh cm ⁻³	45.9 mW cm ⁻³	22.7 F cm ⁻³	60
conductive polymer composite and multiwalled carbon nanotube	--	--	274 F g ⁻¹	61
graphite rod over paper substrate	--	--	2.3 mF cm ⁻²	62
Pencil/ polyaniline nanowire	0.32 mW h cm ⁻³	0.054 W cm ⁻³	--	63
cellulose paper using a soak and dry technique together with graphene solution	--	--	46 mF cm ⁻²	64
carbon inks	--	--	210 mF cm ⁻²	65
Yarns/Carbon nanotube	--	--	179 F cm ⁻³	66

6. Conclusion and Future Perspective

In this review, emerging trends and recent advances in fabrication of miniaturized supercapacitors using strategic carbon materials is discussed. In comparison to the existing review, this is particularly focussed on material and very recent advances in last couple of years. The previous once have been excluded to show the modern approaches. Furthermore, this review also helps the readers to understand the fabrication methods, electrode fabrications and applications. This is suitable for understanding of non-expert readers and is one stop reading material to understand the basics as well as the advances.

The development of miniaturized supercapacitors and its upcoming trends are covered in this review. A brief overview of the various types of supercapacitors, their operation, reported electrode preparation techniques, electro-active materials, and fabrication methods—such as ink-jet printing, screen printing, photolithography, laser scribing, and 3D printing—used to fabricate miniaturized supercapacitors are provided. Furthermore, there has been discussion on the latest developments in the production of microsupercapacitors employing flexible substrates such as fiber, paper, and cloth. Energy storage device shrinking has occurred despite the increased requirement to build smaller, wearable electronics for the future generation. Although in its early stages, the development of micro and nanosupercapacitors faces a number of obstacles. Stretchable, bendable, and portable, flexible substrate-based supercapacitors have experienced a notable surge in popularity recently. These can be applied to wireless smart sensors, RFID tags, biomedical implanted devices, and other MEMS devices that gather and exchange data on energy as stand-alone power sources. Considerable investigation has been conducted to improve the performance of these nanosupercapacitors, and multiple production techniques have been documented. The field of miniaturized supercapacitor is expanding, leading to the emergence of diverse new applications. Future research should focus on the limitations particularly with regard to performance, safety, increased power and energy density, and cost-effective large-scale manufacturing. Numerous innovative electro-active materials, substrates, and production techniques are being investigated for this purpose. Most of the electrolytes used in these are gel-based, dry types that are less conductive than liquid types. If liquid electrolytes are utilized, leakage and corrosion are problems. To get around this, stronger encapsulation techniques probably need to be created. Despite the fact that numerous flexible substrates for MSCs have been documented, their capacitance is not as good. Improvements in design and the use of additional conductivity-containing nanoparticles could be beneficial. There is still much work to be done to create solid electrolytes with better

qualities. Much work needs to be done in order to structurally develop materials that can be used for electrode changes in a large-scale, cost-effective manner. There is an immediate need to create quick and controlled fabrication processes for flexible mini supercapacitor assemblies. Despite ongoing development, nanosupercapacitors are still in their infancy but have enormous potential for the future.

Acknowledgments

The authors Dr. Khairunnisa Amreen and Beverly John thanks St. Anns College for Women-Mehdipatnam, for the support.

Conflict of interest

There is no conflict of interest for this study.

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