Research article

Current insights and future prospects of graphene aerogel-enhanced supercapacitors: A systematic review

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ABSTRACT

Supercapacitors present a compelling alternative to conventional batteries, offering rapid energy storage and high power density. Despite their advantages, they typically fall short in energy density compared to traditional batteries, primarily due to limitations in electrode materials. Graphene Aerogels (GA) have emerged as a promising solution to enhance supercapacitor performance because of their unique properties, such as high surface area and excellent conductivity. This systematic review provides a comprehensive analysis of recent advancements in GA technology, focusing on their synthesis methods and applications in supercapacitors. It highlights significant improvements that GA can bring to Electric Double-Layer Capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors. Additionally, the review explores GA's potential for enhancing electric generators and integrating into flexible, wearable technologies. Future research directions are emphasised, particularly regarding GA's potential applications in waste management and environmental protection. The review was conducted through a thorough literature search, prioritising peer-reviewed sources related to GA synthesis and supercapacitor applications. Methodological quality and potential biases of the included studies were assessed using principles similar to the Cochrane Risk of Bias tool. Thematic analysis was employed to synthesise findings and identify key trends and challenges. Limitations such as potential biases and methodological variations are discussed. Overall, this review highlights the technological prospects of GA and provides guidance for future research in supercapacitor development and applications.

1. Introduction

Energy storage technology is crucial for the development of modern applications such as electric vehicles, renewable energy systems, and portable electronics. The growing demand for efficient, high-performance energy storage solutions has led to significant advancements in supercapacitors. These devices bridge the gap between traditional capacitors and batteries, offering high power density, rapid charge-discharge rates, and long cycle life [1].

Supercapacitors store and release electrical energy quickly and reliably through mechanisms distinct from traditional batteries. Electric Double-Layer Capacitors (EDLCs) store energy electrostatically, while pseudocapacitors utilise faradaic processes involving

electron charge transfer. This rapid charge-discharge capability makes supercapacitors ideal for various industrial applications, such as regenerative braking systems in electric vehicles and power backup for data centres. Unlike chemical batteries, which undergo electrochemical reactions that degrade their performance over time, supercapacitors maintain their functionality without significant degradation. This resilience is due to the absence of such reactions, resulting in a typical lifespan exceeding one million charge-discharge cycles [2].

However, supercapacitors generally exhibit lower energy density compared to traditional batteries. For instance, while lithium-ion batteries can achieve energy densities up to 250 Wh/kg, supercapacitors typically range from 5 to 10 Wh/kg. This limitation is primarily due to the electrode materials used in supercapacitors, which, despite their high surface area and conductivity, cannot store as much energy. Researchers are actively exploring advanced materials, such as graphene aerogels and hybrid composites, to enhance the energy storage capabilities of supercapacitors, aiming to bridge the gap between power and energy density. These advancements could pave the way for more versatile and efficient energy storage solutions in the future [3].

Graphene Aerogels (GA) have emerged as a promising solution to enhance supercapacitor performance. GA features a complex structure with nano-sized pores formed by graphene layers of remarkable atomic thickness. This unique structure provides exceptional electro-mechanical properties, including high surface area and excellent conductivity. Among the various synthesis methods for GA, hydrothermal synthesis is particularly noteworthy. This method involves using a high-temperature, high-pressure aqueous solution to produce GA with controlled structural properties and high purity. Hydrothermal synthesis is valued for its scalability and ability to produce large quantities of GA with uniform quality, making it a popular choice for industrial applications [4].

In addition to hydrothermal synthesis, other methods such as chemical vapour deposition (CVD), sol-gel processes, and template-assisted techniques have been developed to produce GA. Each method offers distinct advantages in terms of material properties, scalability, and cost. Chemical vapour deposition allows for the precise control of graphene layer thickness, while sol-gel processes enable the incorporation of various functional groups into the GA structure. Template-assisted methods, on the other hand, provide a way to create GA with specific shapes and sizes by using templates that are later removed [5].

The versatility of GA has led to various material subsets, such as graphene nanosheets, graphene oxide (GO), and reduced graphene oxide (rGO). In supercapacitors, GA offers significant advantages, including a large surface area, high electrical conductivity, and mechanical strength. GA's lightweight and flexibility make it suitable for applications like bendable energy storage devices, wearable technology, and flexible electronics [6].

Despite its impressive attributes, GA has limitations, such as low mechanical strength and flexibility. Polymer composites are a notable approach to overcoming these challenges. By incorporating polymers, the mechanical properties of pure GA are improved, and multiple functionalities are added [7].

This systematic literature review (SLR) aims to provide a comprehensive analysis of recent advancements in GA technology, focusing on their synthesis methods and applications in supercapacitors. The review seeks to highlight significant improvements in Electric Double-Layer Capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors, while exploring GA's potential for enhancing electric generators and integrating into flexible, wearable technologies. Future research directions are emphasised, particularly regarding GA's potential applications in waste management and environmental protection. This review aims to synthesise findings, identify key trends and challenges, and guide future research in supercapacitor development and applications.

2. The fundamentals of supercapacitors

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, are energy storage devices that bridge the gap between conventional capacitors and batteries. They offer higher energy density than traditional capacitors and higher power density than batteries, making them suitable for various applications requiring quick charge and discharge cycles. Traditional capacitors store energy purely through the electrostatic separation of charges across a dielectric material [8]. They are characterised by their relatively
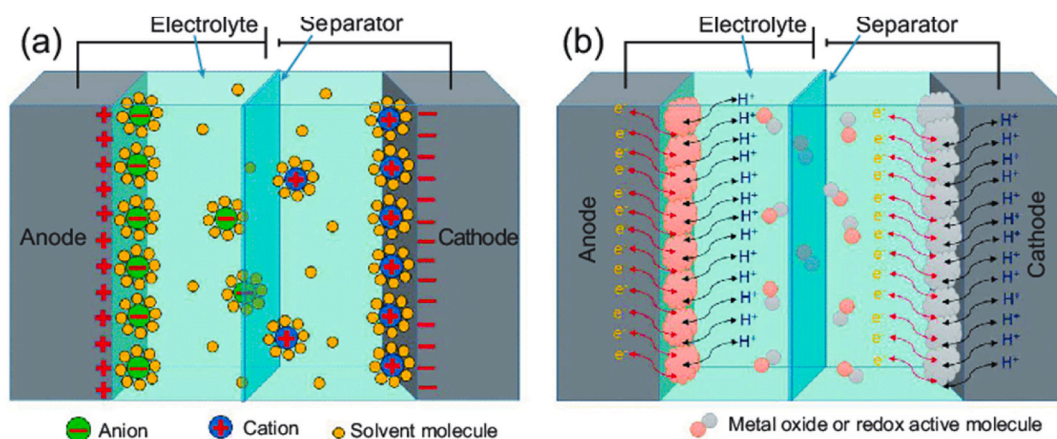

Fig. 1. The simplified diagram of (a) EDLCs and (b) pseudocapacitor [3].

low energy density but high power density and fast charge/discharge rates. Traditional capacitors typically use materials like ceramic, aluminium oxide, or tantalum for their dielectrics, with metal plates acting as the electrodes. Higher energy density and capacity in supercapacitors are exceptionally suitable for rapid energy release, often finding applications in areas where traditional capacitors fall short. While traditional capacitors are excellent for applications requiring very short bursts of energy, supercapacitors are better suited for applications demanding sustained energy delivery over longer periods, such as in backup power systems, regenerative braking in electric vehicles, and load levelling in renewable energy systems [9].

Supercapacitors store energy through two main mechanisms: electrostatic double-layer capacitance (EDLC) and pseudocapacitance. In EDLC, energy is stored by the separation of charge in an electrostatic field at the interface between the electrode material and the electrolyte. Typically, high surface area carbon materials like activated carbon, carbon nanotubes, or graphene are used. The capacitance in EDLC is directly proportional to the surface area of the electrode and the dielectric constant of the electrolyte. On the other hand, pseudocapacitance involves reversible redox reactions at the electrode surface, leading to faradaic charge transfer. Materials such as transition metal oxides (e.g., RuO_2, MnO_2) and conducting polymers (e.g., polyaniline, polypyrrole) are commonly used in pseudocapacitors, which offer higher capacitance than EDLC due to the contribution of faradaic processes [10].

In energy storage systems (ESS), supercapacitors are categorised as pseudocapacitors and EDLCs (see Fig. 1). EDLCs represent a class of supercapacitors renowned for their efficient and rapid energy storage capabilities. Functioning through a unique electrostatic phenomenon, EDLCs store electrical energy by forming an electric double-layer at the interface between the electrode and the electrolyte [3]. This process occurs when a voltage is applied, prompting ions from the electrolyte to accumulate at the surface of the electrode, creating layers of charges. The physical separation of charges, rather than involving chemical reactions, enables EDLCs to achieve fast charging and discharging rates. The capacitance of EDLCs is primarily influenced by the specific surface area of the electrode material, with higher surface area facilitating greater ion storage and, consequently, higher capacitance [11].

In contrast, pseudocapacitors operate on a different principle, utilising reversible faradaic redox reactions to store electrical energy. These electrochemical energy storage devices employ materials with intrinsic electrochemical activity, such as transition metal oxides or conducting polymers, as their active electrode materials. During the charging process, ions from the electrolyte participate in redox reactions with the active electrode material, resulting in the storage of charge [11]. Pseudocapacitors typically exhibit higher specific capacitance compared to EDLCs due to the additional contribution from faradaic reactions. However, this enhanced capacitance may be accompanied by slower charge-discharge kinetics due to the involvement of redox reactions [11].

The classifications are crucial in categorising supercapacitors into specific applications, understanding their charge storage mechanisms, and optimising their performance. Pseudocapacitors operate through oxidation-reduction (redox) reactions at the electrode-electrolyte interface, which offers superior energy storage capacities than EDLCs [12]. On the other hand, EDLCs store energy by generating electrostatic double-layers at the electrode-electrolyte boundary, enabling rapid and efficient electrical energy arrangements without faradaic reactions [4]. The specific characteristics of pseudocapacitors render them suitable for long-term or high-density energy storage devices. Conversely, supercapacitors are excellent 'on the go' energy-conveying devices. The devices store energy more rapidly, albeit at lower density, than pseudocapacitors.

Supercapacitors have several key parameters that define their performance, including capacitance, energy density, and power density. Capacitance measures a supercapacitor's ability to store charge, energy density refers to the amount of energy stored per unit mass or volume, and power density indicates the rate at which energy can be delivered. In contrast, traditional capacitors, such as ceramic, film, and electrolytic capacitors, store energy purely through electrostatic charge separation without any faradaic processes [13]. These capacitors use dielectric materials like ceramic, plastic film, or aluminium oxide to separate the conductive plates. The capacitance of traditional capacitors is determined by the surface area of the plates, the distance between them, and the dielectric constant of the material. Traditional capacitors have lower energy density than supercapacitors, typically in the range of 0.01–0.1 Wh/kg. They provide quick bursts of energy but are not suitable for sustained energy supply. However, traditional capacitors are capable of very high power output for extremely short durations. Supercapacitors, on the other hand, offer a balance of high power and moderate energy density, making them ideal for applications requiring frequent charge/discharge cycles [13].

Supercapacitors and traditional capacitors also differ in their charge/discharge cycles. Traditional capacitors have practically unlimited cycle life, with minimal degradation over time. Supercapacitors also have very high cycle life, typically more than 1 million cycles, but can experience slight degradation in capacity over time due to electrode and electrolyte wear. In terms of applications, traditional capacitors are used in filtering, buffering, and energy storage for electronic circuits, where quick charge and discharge are required. Supercapacitors are suitable for applications such as regenerative braking in electric vehicles, power backup systems, and grid energy storage, where both high power and reasonable energy storage are needed [13].

Supercapacitors provide a versatile energy storage solution, offering higher energy density than traditional capacitors and higher power density than batteries. Their ability to deliver quick bursts of energy, combined with their long cycle life, makes them ideal for various modern applications. While traditional capacitors still hold significance in electronic circuits for their simplicity and reliability, supercapacitors are increasingly being adopted for more demanding energy storage and power management applications [13].

2.1. Graphene and its importance in supercapacitors

Graphene, a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice, has garnered significant attention since its discovery due to its remarkable physical and chemical properties. It is celebrated for its exceptional electrical conductivity, high surface area, mechanical strength, and flexibility. These characteristics make graphene an attractive material for a wide range of applications, including electronics, energy storage, and materials science. One of the most notable properties of graphene is its exceptional properties that make it a valuable material for supercapacitors, offering high capacitance, superior conductivity, and

mechanical stability. Electrons can move through the graphene lattice with minimal resistance, making it one of the best conductors of electricity known. This property is particularly advantageous for applications requiring efficient charge transfer and minimal energy loss [14].

Graphene's high surface area, which can reach up to 2630 m^2/g, provides ample space for energy storage when used in supercapacitors. The large surface area allows for a greater number of electrochemical reactions to occur, increasing the overall capacitance of the device. Additionally, graphene's mechanical strength, which is 200 times stronger than steel, ensures the durability and stability of supercapacitors, even under extensive cycling and mechanical stress. The unique properties of graphene make it an ideal material for enhancing the performance of supercapacitors. In these energy storage devices, graphene can be utilised in various forms, such as graphene oxide (GO), reduced graphene oxide (rGO), or in combination with other materials to form composite electrodes. Here are several key advantages of using graphene in supercapacitors [15–17]:

● *High Capacitance*: Graphene's large surface area provides numerous active sites for charge storage, resulting in high specific capacitance. This is particularly important in supercapacitors, where maximising capacitance directly translates to increased energy storage capacity.
● *Superior Conductivity*: The excellent electrical conductivity of graphene facilitates rapid charge and discharge cycles in supercapacitors. This ensures efficient energy transfer and high power density, which is crucial for applications requiring quick bursts of energy.
● *Mechanical Stability*: Graphene's robustness enhances the mechanical stability of supercapacitor electrodes, enabling them to withstand repeated charge and discharge cycles without significant degradation. This contributes to the longevity and reliability of supercapacitors.
● *Versatility*: Graphene can be functionalized or combined with other materials to tailor its properties for specific applications. For instance, composite electrodes made from graphene and metal oxides or conducting polymers can synergistically enhance the performance of supercapacitors by combining the high capacitance of pseudocapacitive materials with the conductivity of graphene.
● *Environmental Impact*: Graphene-based materials are considered to be environmentally friendly, especially when derived from natural graphite or through sustainable synthesis methods. This aligns with the growing emphasis on developing eco-friendly energy storage solutions.

Despite these advantages, there are several challenges to the widespread adoption of graphene in supercapacitors. The high cost of high-quality graphene production and the difficulty in scaling up the synthesis processes are significant barriers. Additionally, achieving uniform dispersion and integration of graphene into composite electrodes without compromising its properties remains a technical challenge [3].

Nonetheless, ongoing research and development efforts are focused on addressing these issues. Innovations in graphene production techniques, such as hydrothermal reduction, chemical vapour deposition (CVD) and electrochemical exfoliation, are making high-quality graphene more accessible. Moreover, advancements in material engineering are improving the integration of graphene into supercapacitor electrodes, enhancing their performance and commercial viability.

2.2. EDLCs

EDLCs store energy through the electrostatic separation of charge at the interface between an electrode and an electrolyte. They typically use carbon-based materials such as activated carbon, carbon nanotubes (CNTs), or graphene for their electrodes due to these materials' high surface area, electrical conductivity, and chemical stability [18]. The high surface area of these carbon materials allows for a larger electric double layer, enhancing the overall capacitance of the device [19,20].

EDLCs offer excellent solutions for quick charging and releasing energy storage devices. The effectiveness of the device has been influenced by several complex factors, with each parameter contributing to the overall efficiency of supercapacitors. A primary factor is the specific surface area, which is commonly assessed with the Brunauer–Emmett–Teller (BET) equation (see Equation (1)). The equation quantifies accessible surfaces for charge storage and has been applied in numerous studies [4]. According to the equation, a higher specific surface area or more surface sites enhances the capacitance of an EDLC, thus increasing its energy storage capability.

$$\frac{C}{C_m} = \frac{P}{(1-P)}\left(\frac{C}{C_m} - 1\right)$$

(Eq. 1)

where C represents the amount of gas adsorbed at a given pressure, C_m is the amount of gas required to form a complete gas molecule monolayer onto the surface of a solid material where the energy is stored, and P denotes the pressure.

Another parameter that improves the efficiency of supercapacitors is their active electrode material design. Imbuing, wrapping, or chemically growing materials on electrodes could significantly affect the performance of the electrodes. Consequently, GA has gained prominence for its exceptional properties, including high surface area, electrical conductivity, and mechanical strength. Furthermore, altering the pore size and structure of GA electrodes via the synthesis method and template selection has increased ion transport in EDLCs. Electrolyte composition is also critical in influencing ionic conductivity, which directly affects the charge transfer kinetics in supercapacitors [4].

2.3. Pseudocapacitors

Pseudocapacitors store energy through fast, reversible redox reactions at the surface of the electrode materials. These capacitors often employ metal oxides (e.g., ruthenium oxide, manganese oxide) or conducting polymers (e.g., polyaniline, polypyrrole) as electrode materials. Pseudocapacitors offer higher capacitance and energy density compared to EDLCs due to the faradaic charge transfer processes. However, they may have lower cycle life due to the potential degradation of the electrode materials during repeated redox cycling.

Pseudocapacitors operate by storing electrical energy at their electrode-electrolyte interfaces through faradaic redox reactions. Compared to EDLCs that rely on physical charge separation mechanisms, pseudocapacitors utilise materials with inherent electrochemical activity, such as transition metal oxides or conducting polymers for their active electrode materials [4]. The capacitance in pseudocapacitors is derived from reversible redox reactions occurring at the electrode surfaces. This characteristic enables pseudocapacitors to achieve a broader range of energy storage compared to EDLCs [4]. Although pseudocapacitors demonstrate slower energy transport than EDLCs, they possess higher energy density storage capabilities. Surface area, conductivity, and redox activity are factors influencing the superior specific capacitance values of pseudocapacitors and considerably enhance their energy storage abilities. The quest for advanced pseudocapacitor materials and optimised electrode architectures drives researchers to obtain efficient energy storage solutions with enhanced power and energy densities [4].

2.4. Hybrid supercapacitors

Hybrid supercapacitors combine the mechanisms of both EDLCs and pseudocapacitors to achieve a balance between high energy density and power density. These devices use a combination of carbon-based materials and faradaic materials for the electrodes. For example, one electrode may consist of activated carbon (typical of EDLCs) while the other electrode is made of a metal oxide or conducting polymer (typical of pseudocapacitors). This configuration leverages the high power density of EDLCs and the high energy density of pseudocapacitors, resulting in enhanced overall performance [19]. Hybrid supercapacitors typically integrate EDLC-type electrodes with pseudocapacitor-type electrodes or combine different types of active materials within a single cell. This configuration allows hybrid capacitors to utilise the high surface area of EDLC materials for rapid charge and discharge processes while benefiting from the high energy density of pseudocapacitor materials through faradaic reactions. One of the primary advantages of hybrid supercapacitors is their ability to bridge the performance gap between traditional EDLCs and pseudocapacitors. They offer a more balanced performance profile, which includes [19]:

● Improved Energy Density: By incorporating pseudocapacitor materials, hybrid capacitors achieve higher energy storage capabilities compared to standard EDLCs.
● Enhanced Power Density: The EDLC components contribute to rapid charge and discharge rates, maintaining high power density.
● Extended Cycle Life: Hybrid capacitors benefit from the stability of EDLCs, often resulting in longer cycle life compared to pseudocapacitors alone.

Hybrid capacitors are employed in a range of applications where both high energy density and high power density are required. These applications include regenerative braking systems in electric vehicles, backup power systems, and other energy storage applications where rapid energy delivery and storage are crucial. Recent innovations in hybrid capacitor technology focus on optimising the electrode materials and improving the interfaces between different materials to enhance overall performance. Researchers are exploring advanced materials such as graphene-based composites and transition metal oxides to further improve the efficiency and applicability of hybrid capacitors [6,12,19].

2.5. Performance characteristics comparison

Performance characteristics are critical for evaluating the suitability of supercapacitors for various applications. These metrics include specific capacitance, energy density, and power density. Specific capacitance measures the capacitance per unit mass (F/g) or volume (F/cm^3), indicating how much charge the supercapacitor can store relative to its size or weight, which is crucial for applications where space or weight is limited. Energy density, measured in watt-hours per kilogram (Wh/kg), represents the amount of energy a supercapacitor can store per unit mass. High energy density is essential for applications requiring long-duration energy supply, such as electric vehicles or portable electronic devices. Power density, expressed in watts per gram (W/g), indicates how quickly a supercapacitor can deliver energy. This is vital for applications that need rapid bursts of energy, like power backup systems, regenerative braking, and load levelling. Understanding these metrics helps in selecting the right type of supercapacitor for specific use cases, balancing the needs for energy storage capacity, rapid energy delivery, and overall efficiency [2,21].

2.5.1. Working mechanics

EDLCs store energy electrostatically by accumulating charge at the electrode-electrolyte interface. This non-faradaic mechanism relies on the physical separation of charge without involving chemical reactions. The primary advantage of EDLCs is their ability to charge and discharge rapidly, providing high power density and long cycle life. However, the energy density of EDLCs is relatively low compared to other energy storage technologies. On the other hand, Pseudocapacitors store energy through faradaic reactions involving electron transfer between the electrode and electrolyte [3]. This mechanism allows for higher specific capacitance and energy density

compared to EDLCs, as it involves redox reactions, intercalation, and electrosorption processes. The trade-off is that pseudocapacitors may have shorter cycle life and slower charge/discharge rates due to the involvement of chemical reactions. In addition, the Hybrid supercapacitors combine the electrostatic storage of EDLCs and the faradaic reactions of pseudocapacitors [3]. This dual mechanism enhances both energy density and power density, offering a balanced performance profile. Hybrid supercapacitors aim to leverage the strengths of both EDLCs and pseudocapacitors, providing improved energy storage capacity while maintaining high power delivery. However, this comes with potential trade-offs in cycle life, cost, and complexity. Finally, the trusty Lithium-ion batteries store energy through the intercalation and deintercalation of lithium ions within the electrode materials. This faradaic mechanism provides high energy density and long-term storage capabilities. Lithium-ion batteries are known for their efficiency in storing large amounts of energy and their relatively long lifespan. However, they have lower power density compared to supercapacitors and longer charge times [12,17].

The performance characteristics of EDLCs, pseudocapacitors, hybrid supercapacitors, and lithium-ion batteries are crucial for understanding their potential applications and limitations. Table 1 provides a comparative analysis based on several key parameters, including specific capacitance, energy density, and power density.

EDLCs exhibit a specific capacitance ranging from 1 to 10 F g^{-1}, which, while adequate for high-power applications, results in a relatively low energy density of 1.5–3.9 Wh/kg. The primary advantage of EDLCs is their exceptionally high power density, which ranges from 10,000 to 15,000 W/kg. This high power density allows for rapid charging and discharging, making EDLCs ideal for applications that require quick energy delivery. However, the trade-off is their lower energy density, which limits their ability to store large amounts of energy. Pseudocapacitors, on the other hand, leverage faradaic reactions to achieve higher specific capacitance values, typically between 10 and 100 F g^{-1}. This results in an improved energy density of 4–9 Wh/kg compared to EDLCs. While pseudocapacitors offer better energy storage capabilities, their power density ranges from 1000 to 10,000 W/kg, which is lower than that of EDLCs. The involvement of chemical reactions also means that pseudocapacitors may have a shorter cycle life and slower charge/discharge rates. Hybrid supercapacitors aim to combine the best attributes of both EDLCs and pseudocapacitors. They offer specific capacitance values ranging from 20 to 200 F g^{-1} and energy density from 10 to 15 Wh/kg. The power density of hybrid supercapacitors is similar to that of EDLCs, ranging from 10,000 to 15,000 W/kg, making them versatile for various applications. However, the combination of electrostatic and faradaic mechanisms can lead to challenges in manufacturing complexity, cost, and potential trade-offs in cycle life. Lithium-ion batteries, known for their high energy density, range from 100 to 265 Wh/kg. This makes them suitable for applications that require long-term energy storage. However, their power density, which ranges from 100 to 1000 W/kg, is significantly lower than that of supercapacitors. Lithium-ion batteries also have longer charge times compared to supercapacitors but offer a relatively long lifespan and efficiency for energy storage [21,22].

Looking at the strength and weaknesses in energy storage and release, the EDLCs excel in delivering high power quickly due to their electrostatic storage mechanism. This makes them highly efficient for applications requiring rapid energy delivery and high power output. Their long cycle life and ability to charge and discharge rapidly are significant advantages. However, the lower energy density of EDLCs limits their use in applications that require substantial energy storage over longer periods. Pseudocapacitors provide better energy storage capabilities through faradaic reactions, resulting in higher energy density and specific capacitance. This makes them suitable for applications needing moderate energy storage. However, the chemical reactions involved can reduce their cycle life and slow down charge/discharge rates, making them less ideal for applications requiring rapid energy delivery. Hybrid supercapacitors, by combining the electrostatic storage of EDLCs and the faradaic reactions of pseudocapacitors, offer a balanced performance profile. They provide enhanced specific capacitance and energy density while maintaining high power density. This versatility makes them suitable for a wide range of applications. However, they may face challenges related to manufacturing complexity, cost, and potential trade-offs in cycle life. Lithium-ion batteries are known for their efficiency in storing large amounts of energy and their relatively long lifespan. They are ideal for applications requiring high energy density and long-term storage. However, their lower power density and longer charge times compared to supercapacitors limit their suitability for applications requiring rapid energy delivery. Each energy storage technology has its strengths and weaknesses, making them suitable for different applications based on their performance characteristics. EDLCs are ideal for high-power applications, pseudocapacitors for moderate energy storage with higher specific capacitance, hybrid supercapacitors for a balanced approach, and lithium-ion batteries for high energy density and long-term storage [23,24].

Specific capacitance is a key parameter for supercapacitors, indicating how much charge they can store relative to their size or weight. EDLCs have a specific capacitance ranging from 0.1 to 470 F, which is lower compared to pseudocapacitors and hybrid

Table 1
Performance comparisons between supercapacitors and lithium-ion battery [12,19,33].

Parameter	EDLC	Pseudocapacitor	Hybrid	Lithium-ion Battery
Temperature range, degrees Celsius (°C)	−40 – +70 °C	−20 – +70 °C	−20 – +70 °C	−20 – +60 °C
Maximum charge, volts (V)	1.2–3.3 V	2.2–3.3 V	2.2–3.8 V	2.5–4.2 V
Recharge cycles, thousands (k)	100 k – 1000 k	100 k – 1000 k	20 k – 100 k	0.5 k – 10 k
Capacitance, farads (F)	0.1–470 F	100–12,000 F	300–3300 F	–
Specific energy, watt-hours per kilogram (Wh/kg)	1.5–3.9 Wh/kg	4–9 Wh/kg	10–15 Wh/kg	100–265 Wh/kg
Specific power, watts per gram (W/g)	2–10 W/g	3–10 W/g	3–14 W/g	0.3–1.5 W/g
Self-discharge time at room temp.	medium (weeks)	medium (weeks)	long (month)	long (month)
Efficiency (%)	95 %	95 %	90 %	90 %
Working life at room temp., years (y)	5–10 y	5–10 y	5–10 y	3–5 y

supercapacitors, making them less suitable for applications requiring high charge storage. Pseudocapacitors offer a significantly higher specific capacitance, ranging from 100 to 12,000 F, making them ideal for applications needing substantial charge storage. Hybrid supercapacitors fall in between, with specific capacitance values ranging from 300 to 3300 F, providing a balance between charge storage capacity and other performance metrics [25].

Energy density is another critical performance characteristic, representing the amount of energy a supercapacitor can store per unit mass. Supercapacitors generally have lower energy density compared to lithium-ion batteries. EDLCs have an energy density of 1.5–3.9 Wh/kg, suitable for applications requiring moderate energy storage. Pseudocapacitors offer an improved energy density of 4–9 Wh/kg. Hybrid supercapacitors achieve the highest energy density among supercapacitors, ranging from 10 to 15 Wh/kg, making them competitive for applications needing both energy storage and rapid energy delivery. However, lithium-ion batteries still outperform supercapacitors with an energy density of 100–265 Wh/kg, making them suitable for applications requiring high energy storage over extended periods [26].

Power density indicates how quickly a supercapacitor can deliver energy, and supercapacitors excel in this area. EDLCs have a power density of 2–10 W/g, while pseudocapacitors offer a similar range of 3–10 W/g. Hybrid supercapacitors provide the highest power density, ranging from 3 to 14 W/g, making them suitable for applications like power backup systems and regenerative braking. In contrast, lithium-ion batteries have a lower power density of 0.3–1.5 W/g, which limits their suitability for applications needing rapid energy delivery [27].

Other considerations include self-discharge time, efficiency, and working life. Supercapacitors have a medium to long self-discharge time, with hybrids and lithium-ion batteries maintaining charge for longer periods. Both supercapacitors and lithium-ion batteries exhibit high efficiency, approximately 90–95 %. In terms of working life, supercapacitors generally have a longer working life at room temperature, ranging from 5 to 10 years, compared to lithium-ion batteries, which typically last 3–5 years. This makes supercapacitors more durable for long-term applications [28].

This comparison highlights the strengths and weaknesses of each technology, aiding in the selection of the appropriate type of supercapacitor based on specific application needs. By understanding the performance characteristics of EDLCs, pseudocapacitors, hybrid supercapacitors, and lithium-ion batteries, one can make informed decisions about their use in various energy storage and delivery scenarios.

2.6. General theoretical supercapacitor efficiency equations

The equation for determining supercapacitor performance involves current density, specific capacitance, and cycle retention. Current density (J) gauges the charge and discharge rate, revealing swift energy storage or delivery, which could be calculated according to Equation (2). Meanwhile, Equation (3) establishes specific capacitance (C), which quantifies the ability of a device to store electrical charge per unit voltage. Nevertheless, the specific capacitance (C_s) of a supercapacitor is often related to the parallel plate capacitor (see Equation (4)) [4].

$$J = \frac{\Delta Q}{\Delta t} \qquad \qquad \text{(Eq. 2)}$$

$$C = \frac{\Delta Q}{\Delta V}, \qquad \qquad \text{(Eq. 3)}$$

$$C_s = \frac{\varepsilon \cdot A}{d} \qquad \qquad \text{(Eq. 4)}$$

where ΔQ denotes the charge transferred, Δt is the time taken for storage processing and delivery, ΔV represents the change in voltage, ε denotes the permittivity of the material between the electrodes, A represents the surface area of the electrodes, and d is the separation between the electrodes [4].

Equations (3) and (4) are relevant in the supercapacitor context and commonly employed in studies. Nevertheless, Equation (3) is typically preferred for supercapacitors as it directly relates stored charge (ΔQ) to voltage (ΔV) alterations. Consequently, the equation quantifies the ability of a device to store electrical charge per unit voltage as the measure of its performance. On the other hand, Equation (4) is more significant and commonly used to explain the factors influencing capacitance in a parallel plate capacitor. The equation also provides insights into the structural factors influencing capacitance [4].

Supercapacitors are stacked to achieve improved capacity per unit weight or price. The arrangement could be in series, parallel, or a combination of both, depending on the specific requirements of the application. Supercapacitors arranged in series increase the total voltage rating of the assembly, while parallel arrangement enhances the total capacitance. The total capacitance (C_{cell}) and voltage (V_{total}) of capacitors arranged in series is determined according to Equation (5). Conversely, the C_{cell} of individual capacitances in parallel connected capacitors reflects the sum of the capacitance of the assembly (see Equation (6)) [2,4].

$$\frac{1}{C_{cell}} = \frac{1}{C_1} + \frac{1}{C_2} + \ldots + \frac{1}{C_n} \qquad \qquad \text{(Eq. 5)}$$

$$C_{cell} = C_1 + C_1 + \ldots + C_n \qquad \qquad \text{(Eq. 6)}$$

C_{cell} is the total capacitance of the supercapacitor cell, C_1 denotes the capacitance of the positive electrode, C_2 represents the

capacitance of the negative electrode, C_n is the capacitance of individual capacitors.

Supercapacitors are often arranged in specific configurations to achieve desired voltage and capacitance values tailored to particular applications. Based on Equations (5) and (6), the total voltage of supercapacitors in series is shared among the capacitors, while the total capacitance of parallel-arranged supercapacitors is the sum of the individual capacitances. Equation (7) directly links the total capacitance of a supercapacitor cell to its energy storage capacity (*E*).

$$E = \frac{1}{2}CV^2$$
(Eq. 7)

where *E* is the energy stored, *C* denotes the capacitance, and *V* represents the voltage across the capacitor.

Supercapacitor cells are composed of two electrodes: positive and negative. The total energy stored in the cell is the sum stored in each electrode, which could be determined with Equation (8). The equation suggests that higher total capacitance is associated with a more significant energy storage capacity for the supercapacitor cell, which is crucial for theoretical maximum energy storage determinations in supercapacitor efficiency applications [3].

$$E_{total} = \frac{1}{2}C_{cell}V^2$$
(Eq. 8)

where C_{cell} denotes the total capacitance of the supercapacitor cell and *V* represents the voltage across the cell.

2.7. Limitations of graphene aerogel-enhanced supercapacitors

Graphene aerogel (GA) is celebrated for its exceptional properties, including high surface area, electrical conductivity, and mechanical strength. However, there are several limitations to consider when using GA in supercapacitors [29–31]:
Cost and Scalability:

● High Production Costs: The synthesis of graphene aerogel often involves complex and costly processes, which can make GA-based supercapacitors expensive to produce. This limits their commercial viability for widespread applications.
● Scalability Issues: The production of large quantities of high-quality graphene aerogel poses significant challenges. Achieving consistent quality and performance in scaled-up production remains a major hurdle.

Performance Challenges.

● Limited Capacitance Enhancement: While GA provides a high specific surface area, the actual improvement in capacitance may be limited by factors such as poor electrode-electrolyte interactions or suboptimal material integration.
● Electrical Conductivity: Although GA is highly conductive, the performance of supercapacitors can still be affected by the conductivity of the overall electrode material and the interface between the graphene aerogel and other components.

Environmental and Mechanical Considerations.

● Environmental Impact: The environmental impact of synthesising and disposing of graphene aerogel materials needs to be carefully considered. The processes involved may have ecological consequences if not managed properly.
● Mechanical Stability: Graphene aerogel, while lightweight and porous, may suffer from mechanical stability issues, including fragility or degradation under certain conditions. This can affect the long-term durability and reliability of supercapacitors.

2.8. The physical supercapacitor architecture design for optimised energy transport

Physically, the specific capacitance of graphene supercapacitors could be influenced by graphene type (graphene, GO, or rGO), size and structure of the electrodes, and the electrolyte employed [32]. Typically, rGO is selected for supercapacitor applications due to its relatively remarkable conductivity and enhanced electrochemical properties. Similarly, electrode size, structure, electrolyte composition, and various other factors influence the specific capacitance of an assembly. Accordingly, theoretical calculations of specific capacitance equations are useful starting points [32].

Precautions should be considered when building supercapacitors to optimise their efficiency and performance. In any design, selecting the best materials, namely graphene, GO, and rGO, relies on the specific supercapacitor application requirements and depends on the researchers or manufacturers. Cyclic retention is also an imperative physical parameter in quantifying device longevity. The factor determines the ability of the supercapacitor to maintain performance across multiple charge and discharge cycles [32].

Several common factors affecting supercapacitor effectiveness are electrode materials, electrolyte composition, and device architecture physicality [33]. Electrode material selection encompassing carbon-based materials or metal oxides also influences the overall performance of supercapacitors [6]. On the other hand, electrolyte composition dictates ionic conductivity, thus crucially affecting charge transfer kinetics in the devices. Incorporating electrode arrangement and separator materials into supercapacitor cell designs also plays a pivotal role in optimising the device for specific applications [34]. The implications of GA synthesis and application in supercapacitors are discussed in the subsequent sections of this review.

3. GA preparation

Graphene Aerogels (GA) are categorised based on their pore sizes: micropores, mesopores, or macropores. Typically, micropores are of <2 nm diameter, mesopores are within the 2–50 nm range, while macropores are >50 nm. The classification provides a better understanding of the internal structure of aerogels and how they affect the performance of supercapacitors [5]. Balancing surface area and ion diffusion is crucial for versatility in energy storage and transfer applications, including supercapacitors [35].

Micropores offer high surface area due to their small size, thus rendering them suitable for applications requiring precise ion adsorption control and specific characteristics. The attribute also renders GA with micropores applicable in sensing or self-sensing devices. On the other hand, mesopores offer intermediate-sized pores with less surface area than micropores. Macropores have the largest pore size and could facilitate rapid mass and energy transport. The GA type is also commonly beneficial in bulk material properties and transport dynamics applications, such as catalyst support structures [36].

The GA stands out as the best candidate for improving the efficiency of supercapacitors in almost any application, owing to its extraordinary surface characteristics. The 3D nanopore network in GA, including micropores, mesopores, and macropores, results in an expansive internal surface area exceeding 99 % [37,38]. The complex porous arrangement is also crucial in enhancing supercapacitor performance.

The remarkable surface area offered by GA promotes increased electrode-electrolyte interface, improving capacitance from the numerous charge storage sites. Consequently, mesopores and micropores GA are ideal for energy storage. The material also enables rapid charge and discharge cycles by improving ion movements with a larger surface area, which supercapacitors are known for [39].

The readily available active sites within GA pores play a crucial role in efficient charge storage, thereby optimising the overall performance of supercapacitors. Furthermore, the internal surface area in the porous structures of GA is also critical in supercapacitors, as large pores maximise the sites available for charge storage and release. However, it's important to note that considerations of surface area in material supercapacitors differ from those in heat transfer or electrical conduction. In thermodynamics, surface area in contact is preferred for heat transfer within a medium [39].

Despite their remarkable attributes, graphene aerogel (GA)-enhanced supercapacitors face several significant limitations that impact their practical applications. One major challenge is the complexity and cost associated with their synthesis. Techniques such as hydrothermal synthesis, while beneficial for controlling material properties and ensuring scalability, often involve sophisticated equipment and precise reaction conditions. This complexity can lead to high production costs, limiting the economic feasibility of GA-based supercapacitors for widespread commercial use. Another critical issue is the mechanical stability and durability of GA structures. Due to their highly porous and lightweight nature, graphene aerogels can exhibit poor mechanical integrity. Over time, these materials may deform or collapse under stress, negatively affecting the performance and longevity of the supercapacitors. Ensuring long-term stability and durability remains a significant challenge in the development of GA-enhanced devices. Performance trade-offs are also a concern with GA-enhanced supercapacitors. While the high surface area provided by GA is advantageous, an excessive focus on increasing pore size or surface area can lead to reduced electrochemical stability and lower energy density. Achieving an optimal balance between pore size, surface area, and overall performance characteristics is crucial but difficult. Scalability issues further complicate the use of GA in industrial applications. Although hydrothermal synthesis produces high-quality GA, scaling this process to meet industrial demands presents challenges. Maintaining consistent reaction conditions and quality control in large-scale production is resource-intensive and problematic, impacting the commercial viability of GA-enhanced supercapacitors. Environmental impact is another consideration, as the production and disposal of graphene aerogels may involve hazardous by-products or require significant energy inputs. Developing more sustainable synthesis methods and addressing the life cycle environmental impacts are essential for minimising the ecological footprint of GA materials. Finally, integrating GA with other materials in supercapacitor designs can be challenging. Ensuring compatibility between GA and electrode materials, electrolytes, and other components is vital for optimal performance. Issues such as poor adhesion or mismatched properties can hinder the effectiveness of the supercapacitor, requiring careful consideration in material selection and design [39].

3.1. GA synthesis methods

GA are categorised based on their pore sizes into micropores, mesopores, and macropores. This classification is crucial as the internal structure of aerogels significantly affects the performance of supercapacitors. Balancing surface area and ion diffusion is essential for optimising energy storage and transfer applications. Micropores offer a high surface area, making them suitable for applications requiring precise ion adsorption and specific characteristics, such as sensing devices. Mesopores provide intermediate-sized pores with moderate surface areas, while macropores facilitate rapid mass and energy transport, making them beneficial in catalyst support structures. The 3D nanopore network in GA, including micropores, mesopores, and macropores, results in an expansive internal surface area exceeding 99 %. This complex porous arrangement enhances the performance of supercapacitors by promoting increased electrode-electrolyte interface and improving ion movements, thereby enabling rapid charge and discharge cycles. The synthesis methods for GA are critical in defining their structural, thermal, electrical, chemical, and mechanical properties. Below are detailed discussions on the most common synthesis methods and their contributions to supercapacitor performance [40].

3.2. The top-down and bottom-up GA synthesis methods

Top-down methods involve breaking down larger structures into smaller components. In the context of GA synthesis, this typically involves the exfoliation of graphite or other bulk materials into graphene sheets, followed by their assembly into aerogels. Mechanical

exfoliation involves physically breaking down graphite into graphene layers. This method can produce high-quality graphene sheets, but it is often limited in scalability. Mechanical exfoliation-derived GA has shown excellent electrical conductivity and mechanical strength, making it suitable for high-performance supercapacitors. Chemical exfoliation uses chemical reactions to separate graphite into graphene sheets. This method can produce large quantities of graphene, though the quality may vary. The resulting GA from chemical exfoliation can exhibit high surface area and good electrical properties, enhancing the capacitance of supercapacitors [41].

Bottom-up methods involve building up graphene structures from smaller precursor molecules. These methods allow for precise control over the composition and structure of the resulting GA. CVD is a widely used bottom-up method where graphene is synthesised on a substrate from gaseous precursors. The process allows for precise control over the graphene layer's thickness and quality. CVD-derived GA is known for its high purity and well-defined structure, contributing to superior electrical and thermal properties in supercapacitors. The sol-gel process is another bottom-up method that involves forming a colloidal suspension (sol) from precursor materials, which then forms a gel and eventually a 3D porous structure. This method offers control over the pore size and surface area of the GA, making it suitable for various supercapacitor applications [42].

Top-down methods generally provide high-quality graphene with excellent electrical and mechanical properties but may face scalability challenges. Bottom-up methods, on the other hand, offer greater control over the structure and composition of GA, making them suitable for large-scale production and applications requiring precise material properties. Fig. 2 shows schematic representation of most common methods of GA production, while Fig. 3 present a summary of the different graphene synthesis in the industry.

3.2.1. Bottom-up method: the sol-gel process

The sol-gel technique is one of the earliest GA preparation methods in the bottom-up synthesis method. The process involves synthesising sol, a colloidal suspension, from precursor materials, such as alkoxides or metal salts. Subsequently, a dried gel structure is formed through hydrolysis and condensation, procuring a 3D porous shell known as GA.

The sol-gel process allows arrangement, composition, and structure control, producing aerogels with well-defined pore structures and tailored chemical compositions. Nonetheless, pore definitions are commonly influenced by GO concentration, solvent type, pH levels, and drying conditions. The parameters affect the porosity, stability, and graphene structure size of the aerogel. The technique has been employed to manufacture GA-based energy storage devices, particularly supercapacitors, high-performance sensors, and efficient adsorbents in water treatments [44].

3.2.2. Bottom-up method: the template-based synthesis

The template-based synthesis utilises sacrificial templates made of polymers or ceramics to define the pores and structures of the resultant aerogels. Typically, the template is coated with graphene material, which is removed after obtaining the desired structure. Similar to the sol-gel method, the template-based approach offers precise regulation of morphology and pore size. Nevertheless, the
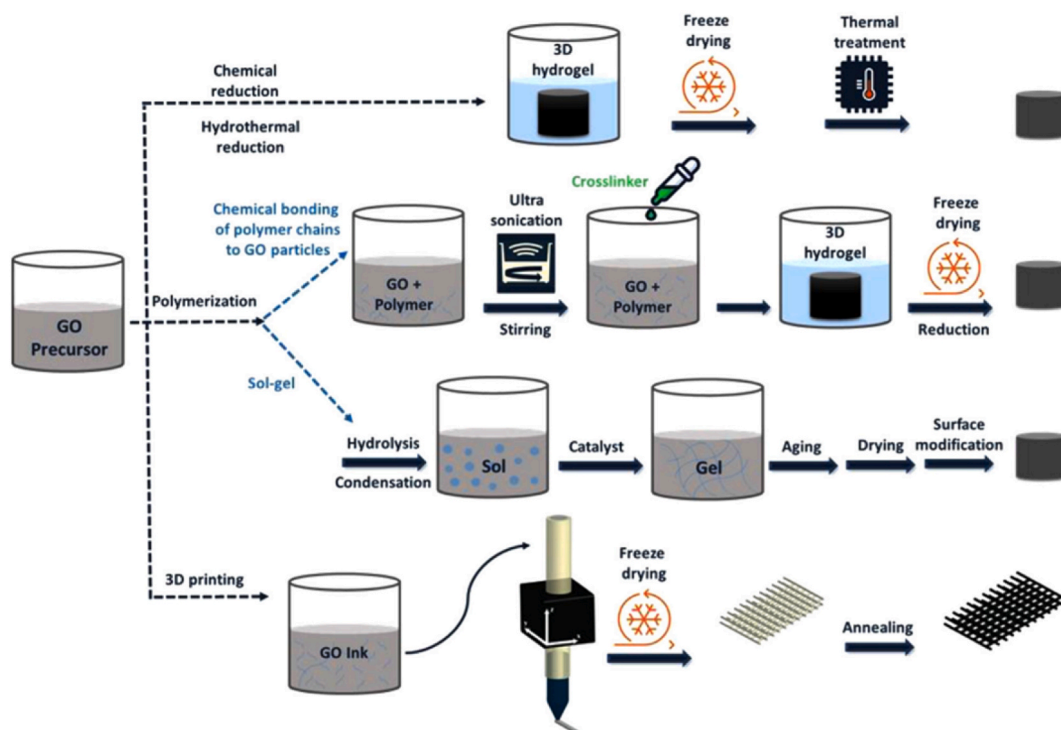

Fig. 2. A schematic representation of the most common methods of GA production [3].
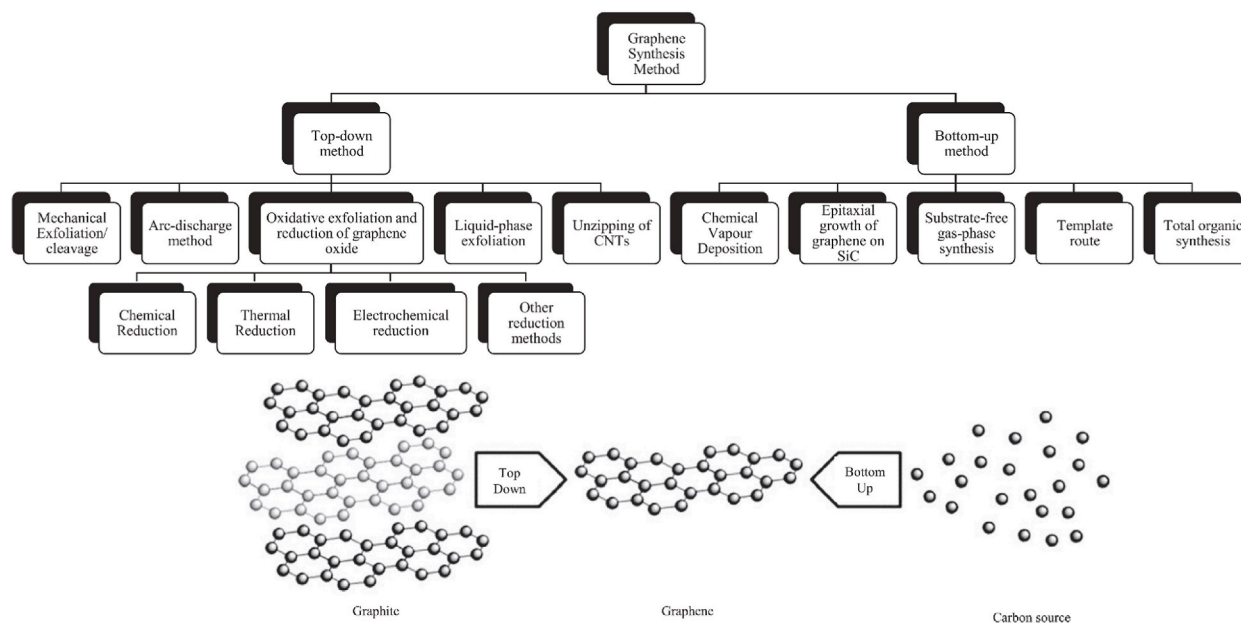
Fig. 3. Graphene synthesis methods in the industry [43].

template-based technique has the added advantage of creating aerogels with specific shapes and complex architectures. Sacrificial template utilisation leads to the final structure of the GA being influenced by parameters such as template type, coating method, and template removal process. The technique also results in supercapacitors customised for various applications and sizes, including serving as catalyst supports in different chemical processes [44].

3.2.3. Bottom-up method: the self-assembly approach

The self-assembly method employs unique non-covalent interactions, such as van der Waals forces or π-π stacking, to organise graphene sheets into a 3D construction and create the GA structure. Commonly, the resulting GA exhibits well-defined porous arrangements and considerable specific surface area. Consequently, the approach benefits manufacturing effective energy storage devices and sensors requiring defined porous structures. Furthermore, the self-assembly technique also enables flexible electronics with tailored properties production. Nevertheless, parameters, including assembly conditions, solvent choice, and graphene sheet concentration, critically determine the final GA structure [45].

3.2.4. Bottom-up method: freeze drying

Freeze drying or lyophilisation is a meticulous process involving freezing a GO solution, followed by sublimation to remove the frozen solvent. The resultant aerogels are characterised by low density and exceptional porosity. The technique is valuable for creating materials with unique properties well-suited for various applications [3]. A notable application of freeze-dried GO aerogels is thermal insulation. The excellent thermal insulating properties of the aerogels are attributable to their low density and porous structures. The characteristics also render the substance ideal for applications requiring minimal heat transfer, such as developing advanced insulation materials [3]. The versatile porous freeze-dried GO aerogels have also made them valuable components in sensor technologies. The porous nature of the material results in its efficient diffusion and interactions with external substances, thus rendering it suitable for sensor applications with considerable surface area and reactivity requirements [46].

Factors affecting the freeze-drying process include the freezing temperature, duration, and sublimation rate. The parameters are crucial in determining the overall structure and properties of the resulting aerogel. The factors impact the size and distribution of pores in aerogels, which, in turn, influence their mechanical, thermal, and sensing attributes. Consequently, optimising the parameters is essential in tailoring the properties of the aerogel to specific applications. The complexity of freeze drying, particularly when applied to GO solutions, presents possibilities for producing materials with exceptional characteristics. The ability to control freezing conditions and sublimation rates empowers researchers and engineers to fine-tune aerogel properties for diverse applications from thermal insulation to advanced sensor technologies [47].

3.2.5. Bottom-up method: supercritical drying

Supercritical drying, which utilises supercritical fluids (carbon dioxide), is emerging as a versatile method with employment beyond catalysis. The resultant GA is distinguished by its low density and well-preserved structure, which are advantageous in various domains. The low density and porosity of supercritical dried GA contribute to its superior heat-trapping capabilities, which are crucial in energy-related industries (aerospace) or applications, where effective thermal insulation holds significance [48].

The intricate structure of the aerogels, characterised by remarkable porosity and lightweight nature resulting from supercritical drying, provides a large surface area. This feature enhances their sensitivity and responsiveness, making them suitable for applications in sensor devices. Furthermore, supercritical drying is widely acknowledged for its role in catalyst production, extending its applicability to diverse areas. The involvement of the GA crafted through the precise and sophisticated approach in thermal insulation and sensor technologies demonstrates its adaptability and broad utility [48].

3.2.6. Bottom-up method: vacuum drying

Vacuum or thermal drying is a methodological advanced material synthesis technique. The approach efficiently removes solvents in a vacuum, offering scalability for large-scale manufacturing. Vacuum drying mitigates potential heat-related issues associated with conventional drying methods by reducing or eliminating moisture under controlled pressure. Furthermore, vacuum pressure, temperature, and drying duration play a decisive role in shaping the properties of GA, thus contributing to its specific characteristics in advanced material technologies. Consequently, the GA produced through vacuum-induced drying exhibits distinct properties suited for applications requiring energy efficiency on a significant production scale, including thermal insulation [49].

3.2.7. Top-down method: chemical synthesis

Chemical synthesis encompasses diverse methodologies, such as the Hummer, Staudenmaier, Tour, and Brodie methods. Each technique contributes nuanced features to sculpting rGO [50]. The Hummer's method employs a graphite, sodium nitrate, and sulphuric acid mixture. The technique is utilised in superconductor technology due to its ability to produce GA with specific electrical conductivity properties conducive to such applications. Similarly, the Staudenmaier's approach, which utilises nitric and sulphuric acids, produces tailored GA suitable for specific uses in energy storage systems. The versatility aligns with supercapacitor application demands, demonstrating adaptability. The two-step Tour's method involves controlled oxidation, contributing to the precisely tuned pore structures of the resultant GA. The fine-tuning results in materials ideal for applications in catalysis, a specific niche within the broad chemical synthesis spectrum. Another chemical synthesis approach is Brodie's technique, which employs chromium trioxide as the oxidising agent. The unique features of the Brodie approach produce GA applicable in thermal insulation, further illustrating the specificity and tailored outcomes achievable through distinct chemical synthesis pathways [44,51].

Chemical reduction is a prominent method used to convert graphene oxide (GO) into graphene. This technique involves reducing the oxidation state of GO by transferring electrons from a reducing agent. Unlike thermal reduction, which requires high temperatures, chemical reduction operates under milder conditions with various reducing agents such as Vitamin C, sodium ascorbate, ethylenediamine, hydrazine vapour, and sodium sulphide. The process generally unfolds in three stages: first, GO is reduced in an aqueous solution using these agents. Following reduction, the graphene sheets self-assemble into a hydrogel. Finally, this hydrogel is freeze-dried to yield a graphene aerogel. The properties of the resulting aerogels can vary depending on the reducing agent used. For example, using ethylenediamine results in aerogels with a specific surface area of 1099.43 m^2/g and substantial pores measuring 50 μm. The aerogel exhibits significant adsorption capabilities, with methyl orange adsorbed at 166.67 mg/g and methyl blue at 212.77 mg/g. Another method, involving L-Phenylalanine, produces aerogels that are remarkably lightweight, with a density of only 5 mg/cm^3, and possess excellent absorption properties. In addition to these methods, the use of L-Ascorbic acid combined with sodium bisulfite in the reduction process yields aerogels with a specific surface area of 135 m^2/g. These aerogels demonstrate a high specific capacitance of 165 F g^{-1} and strong cycling stability, retaining 91 % of their capacitance after 1000 cycles. The application of thermal annealing can further enhance the electrical conductivity and surface area of these aerogels, improving them by up to 15 %. Incorporating transition metal oxides such as Fe_2O_3 or MnO_2 into graphene aerogels can significantly enhance their performance. For instance, specific capacitances can reach up to 768 F g^{-1}. Additionally, palladium-functionalized aerogels and nitrogen-doped 3D graphene aerogels further improve electrochemical characteristics. The latter can achieve a capacitance of 345.8 F g^{-1} and maintain substantial stability over numerous cycles. Overall, chemical reduction methods offer considerable advantages in surface area, porosity, and electrochemical performance, making them well-suited for various applications in energy storage and advanced materials [44,52].

Both chemical reduction and hydrothermal synthesis are top-down methods used for preparing graphene-based materials, each with distinct advantages and limitations. Chemical reduction typically employs milder conditions and a range of reducing agents to convert GO into reduced graphene oxide (rGO), resulting in aerogels with high surface areas and good electrochemical properties. This method allows for precise control over the reduction process and can produce highly porous structures. In contrast, hydrothermal synthesis involves a high-pressure, high-temperature environment to facilitate the reduction of GO, often using complex cross-linkers and additives. While hydrothermal methods can also yield graphene aerogels with excellent properties, they generally require more stringent conditions and can be less flexible compared to chemical reduction. Hydrothermal synthesis may produce materials with different structural characteristics due to the high temperature and pressure conditions, which can lead to variations in porosity and surface area [53,54].

3.2.8. Top-down method: hydrothermal synthesis

Hydrothermal synthesis, a subset of the oxidative exfoliation and reduction of GO, relies on high-temperature and high-pressure water to facilitate the reduction of GO and the assembly of graphene sheets into a 3D porous structure. This method is particularly valued for its precision and scalability in large-scale production, offering precise control over the output properties of the resulting GA. During the hydrothermal process, a GO suspension is subjected to high temperature and pressure in an aqueous environment. This facilitates the reduction of GO and the self-assembly of graphene sheets into a 3D aerogel structure. Parameters such as temperature, pressure, reaction time, and GO concentration are crucial in determining the final properties of the GA. Hydrothermal synthesis is

preferred for mass-producing tailored GA due to its scalability and accuracy, crucial for customizations required in applications like supercapacitor technology [14].

Hydrothermal synthesis relies on high-temperature and high-pressure (HTHP) water, making it a primarily accepted advanced material synthesis technique, particularly in the supercapacitor category. In the process, GA forms in an HTHP-applied aqueous environment. This method is valued for its versatility and precision in large-scale production, offering precise control over output properties. Hydrothermal synthesis is preferred for mass-producing tailored GA due to its scalability and accuracy, crucial for customizations required in applications like supercapacitor technology. Several parameters, including temperature, pressure, reaction time, and GO concentration, affect the complexity of hydrothermal synthesis. The variables collectively determine the characteristics of the synthesised GA. Accordingly, researchers and manufacturers navigate the factors to achieve scalability and precision, ensuring the resultant GA meets the specific requirements of diverse applications. The subsequent sections provide details on hydrothermal synthesis, offering insights into its versatility and adaptability in advanced GA production [16,55].

The hydrothermal synthesis method typically involves the reduction of graphene oxide in an aqueous solution, where the resultant graphene hydrogel is transformed into aerogel via drying processes such as freezing or supercritical drying. The process leverages self-assembly of graphene sheets, driven by the reduction of graphene oxide, which promotes the formation of interconnected three-dimensional structures. Key parameters influencing the hydrothermal reduction include temperature and reaction duration. Optimal conditions for reduction are generally within a temperature range of 80–150 °C. For example, Li et al. demonstrated a method that involves hydrothermally reducing graphene oxide followed by the self-assembly of graphene sheets. Their process resulted in a graphene aerogel with an enhanced specific surface area of 1230 m^2/g and impressive mechanical strength. Similarly, Niu et al. reported the successful integration of various nanomaterials into the graphene aerogel matrix, achieving a high specific capacitance of 295 F g^{-1} and notable stability in supercapacitor applications. Graphene aerogels synthesis using hydrothermal methods exhibit high porosity, hydrophobicity, and mechanical resilience. These properties are particularly advantageous for applications such as oil spill cleanup. For instance, graphene aerogels reduced with vitamin C have shown a maximum oil absorption capacity of approximately 35 g/g. In contrast, those reduced with ammonia have demonstrated even higher adsorption capabilities, with a maximum capacity of 50 g/g. The choice of reducing agent significantly affects the aerogel's properties. L-ascorbic acid reduced aerogels, while offering high mechanical strength, exhibit a specific capacitance of 180 F g^{-1}. On the other hand, ammonia-reduced aerogels, while showing superior adsorption capacity, present a slightly lower specific capacitance of 170 F g^{-1} [56]. Ethylenediamine-reduced aerogels strike a balance with a specific capacitance of 195 F g^{-1} and an optimal adsorption capacity. Phosphoric acid has been utilised in the reduction process to enhance the specific capacitance of graphene aerogels. Aerogels treated with phosphoric acid achieved a specific capacitance of 204 F g^{-1} and demonstrated a high rate retention capability of 69 %. This treatment also resulted in reduced series resistance and time constant, improving charge storage and ion kinetics. Advanced hydrothermal synthesis methods have led to the development of hierarchical honeycomb graphene aerogels, incorporating functionalized carbon nanotubes. These aerogels exhibit a low density of 0.07 g/cm^3, high compressive strength of 0.5 MPa, and excellent electrical conductivity of 800 S/m. These properties make them suitable for flexible and wearable electronics, maintaining compressive strength and elasticity across a wide temperature range. Further advancements include the use of different reducing agents and synthesis conditions to optimise aerogel performance. For example, the incorporation of carbon quantum dots and manganese dioxide particles in hydrothermal treatment yielded aerogels with a specific capacitance of 315 F g^{-1} and an energy density of 17.5 Wh/kg. Nitrogen-doped graphene aerogels, activated with sulphuric acid, have demonstrated a specific surface area of 1100 m^2/g, enhanced wettability, and long-term cycling stability with a capacitance retention of 85 % over 10,000 cycles [57–60].

4. Planning the review

The present study reviewed reports on GA, synthesis methods, and specific applications by examining associated factors. A systematic literature review (SLR) is a detailed and transparent scientific approach. Consequently, the present study adopted SLR due to its distinct advantages over other review types. For instance, the approach yielded superior quality outcomes while mitigating biases. Moreover, SLR utilisation ensures methodological reproducibility with a comprehensive overview of the research domain under study [43]. Preceding review reports offered a one-dimensional GA synthesis view, while the GA applications reviewed were predominantly

Table 2
The search strategy workflow.

Search strategy flow
Stage 1: Comprehensive search strategy was developed to identify relevant academic papers, journal articles, conference proceedings, and other scholarly sources in the WoS database
Stage 2: Databases, including IEEE Xplore, Google Scholar, and academic library resources, were employed
Stage 3: The search terms in this study were defined as follows
Graphene based terms: Graphene aerogels, Graphene Oxide aerogels, 3D graphene structures, nanomaterial aerogels, carbon-based aerogels, and porous graphene materials
Supercapacitors terms: Supercapacitors, pseudo-capacitor, electrochemical capacitors, energy storage devices, ultracapacitors, double-layer capacitors, and electrochemical energy storage
Stage 4: Combine search terms: Boolean operators (AND, OR) were employed to refine searches. For example, "graphene aerogels AND supercapacitors", "graphene aerogel-enhanced supercapacitors", "nanomaterials in energy storage", "graphene materials for supercapacitor applications", "3D graphene aerogel in energy storage", and "electrochemical capacitors with graphene aerogel"

3D assembly-centred. The current study aimed to bridge the knowledge gap through a multifaceted perspective on the practical, versatile, and scalable hydrothermal approach [61].

4.1. The search string

In conducting a Systematic Literature Review (SLR), it's imperative to ensure a thorough and unbiased search process. This involves employing robust methods to evaluate a wide range of literature and identify the most relevant publications. The review typically begins by defining keywords and search criteria, which are then used to establish inclusion and exclusion parameters. In this case, two databases, namely Web of Science (WoS) and Scopus, were chosen after consulting with database experts. The search focused on quantitative articles from scholarly, peer-reviewed journals published between 2013 and 2023 [62]. Table 2 provides the detailed search approach workflow applied in this systematic literature review.
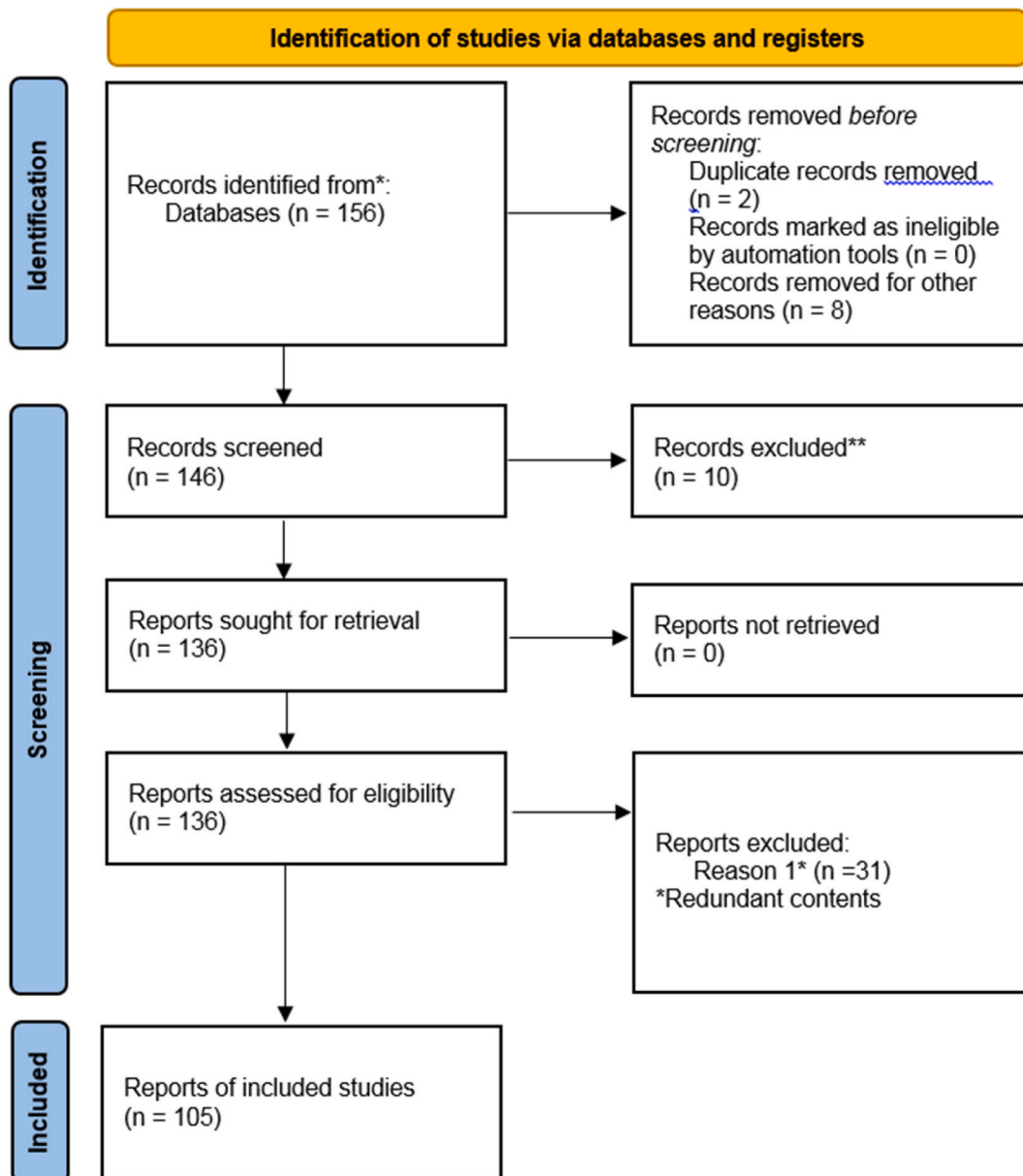

Fig. 4. The PRISMA flow diagram [61].

4.2. The PRISMA diagram

Fig. 4 demonstrates the PRISMA flow diagram employed during the design of this review. The development of PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) was the result of a concerted effort by key organisations and individuals dedicated to advancing evidence synthesis in research and healthcare [62]. Spearheaded by the Cochrane Collaboration, a global network of researchers and healthcare professionals committed to producing high-quality systematic reviews, PRISMA emerged as a standardised approach to reporting systematic reviews and meta-analyses [62].

Contributions from organisations like the Centre for Reviews and Dissemination (CRD) at the University of York in the United Kingdom were pivotal. The CRD, renowned for its expertise in evidence synthesis, played a crucial role in shaping the PRISMA guidelines, drawing from its extensive experience in conducting and disseminating systematic reviews [62]. Methodology experts and leaders in evidence-based medicine lent their insights and expertise to the development of PRISMA. Their contributions ensured that the guidelines were grounded in sound methodological principles, reflecting best practices in research synthesis [62]. Supported by funding agencies and academic institutions, the collaborative effort behind PRISMA exemplifies a commitment to enhancing the transparency and reliability of systematic reviews and meta-analyses. Today, PRISMA stands as a cornerstone of evidence synthesis, providing researchers and practitioners with a robust framework for conducting and reporting systematic reviews that inform evidence-based decision-making in healthcare and beyond [62].

The Cochrane Risk of Bias tool serves as a comprehensive framework used in appraising the methodological quality and potential biases of the included studies. Each study underwent meticulous scrutiny involving a thorough examination of various aspects such as the random assignment of participants, concealing of allocation, blinding procedures, handling of incomplete outcome data, potential biases stemming from selective reporting, and other factors contributing to any discrepancies or uncertainties encountered. It is notable that no investigations into possible causes of heterogeneity among the included literature results were conducted as part of this assessment. During the assessment, processes were carefully deliberated upon and resolved through rigorous analysis and discussion. Additionally, particular attention was given to the context and aspects of each article to ensure a thorough understanding of its methodological strengths and limitations. This review aimed to ensure the reliability, validity, and robustness of the included studies adhering to the principles outlined in the Cochrane Risk of Bias tool rigorously. Thereby enhancing the credibility and trustworthiness of the synthesised evidence for this systematic review [61,62].

Thematic analysis in methodological approach is used to synthesise the diverse findings across the included studies. Through systematic examinations of literature identification, thematic analysis enabled the identification of trends, key patterns, and recurring themes applicable to GA's synthesis methods and applications in supercapacitors. Such a rigorous analytical process helps us to extract meaningful insights, thus providing a comprehensive understanding of the current technological advancements in the field of supercapacitors. Thematic analysis provided a robust framework for identifying emerging trends and addressing the research questions posed in this systematic review by systematically categorising and interpreting the included studies [62].

This systematic review meticulously addressed the limitations inherent in the included studies to acknowledge the importance of transparency. The limitations of each included study along with the variations in methodologies across the selected literature are considered. These processes assess the potential biases that may affect the generalisability of findings on GA for supercapacitor applications. In a nutshell, this systematic review aims to enhance the credibility and trustworthiness of its findings, while also guiding the direction of this systematic review. It is to note that these data are sought primarily from the literature and none from any participants, interventions, and funding sources [62].

Table 3

List of journals and frequency.

Publisher	Journal	Journals related to GA
Multidisciplinary Digital Publishing Institute (MDPI) Journals	Polymers	5
	Molecules	2
Carbon Trends	Carbon Trends	2
Nanotechnology	Nanotechnology	4
Carbohydrate Polymers	Carbohydrate Polymers	7
Nanoscale Advances	Nanoscale Advances	4
Nanomaterials	Nanomaterials	3
Materials Research Express	Materials Research Express	3
American Chemical Society (ACS) Omega	ACS Omega	3
Journal of Colloid and Interface Science	Journal of Colloid and Interface Science	12
Nanoscale Research Letters	Nanoscale Research Letters	12
Nanoscale	Nanoscale	5
ACS Applied Materials and Interfaces	ACS Applied Materials and Interfaces	6
Frontiers in Chemistry	Frontiers in Chemistry	3
Chemistry - A European Journal	Chemistry - A European Journal	4
ACS Sustainable Chemistry and Engineering	ACS Sustainable Chemistry and Engineering	3
Journal of Energy Storage	Journal of Energy Storage	4
Nature Communications	Nature Communications	3
Heliyon	Heliyon	2
ACS Applied Materials and Interfaces	ACS Applied Materials and Interfaces	7
Frontiers in Materials	Frontiers in Materials	11

In this systematic review, publications focusing on GA-based electrodes in supercapacitors were reviewed initially without specific exclusion or inclusion criteria. The systematic search process identified 156 records from various databases and additional sources. After eliminating duplicates, 110 publications remained. The screening phase involved assessing the eligibility of 110 full-text articles according to predefined criteria. Subsequently, 20 records were excluded. Of the eligible publications, 31 were excluded with justifications. Ultimately, 105 reports met the inclusion criteria for qualitative synthesis and were included in the quantitative synthesis.

4.3. Descriptive results

A total of 105 articles were reviewed in the current study. These publications were selected based on various criteria, including their publication year, the journals they were published in, and their specific applications of GA within supercapacitors. This analysis aimed to identify emerging trends and potential future directions for the utilisation of GA in supercapacitor technology.

4.4. Publication year and journal database

The current trends in GA-based supercapacitors were reflected in articles published within the last decade. The databases sourced from WoS are outlined in Table 3, detailing the frequency of journals related to GA.

5. The scalability, versatility, and redox processes of hydrothermal synthesis-GA for supercapacitor applications

5.1. EDLCs

Hydrothermal synthesis is a fundamental technique in tailoring GA characteristics, specifically in EDLC production. Typically, the hydrothermal reaction employed for manufacturing applications specifically catered to EDLCs operates within 180–200 °C. The parameter precisely regulates GO reduction to rGO. The controlled process is also performed under pressure conditions spanning 15–20 atm to ensure the formation of a well-defined porous structure in GA. The microstructural development accentuates micropore significance, characterised by diameters under 2 nm. The pores expand the surface area critical for targeted ion adsorption, and precise surface interactions are pivotal for the swift and controlled charge and discharge cycles in EDLCs [63,64].

5.2. Pseudocapacitors

The hydrothermal synthesis methodology for pseudocapacitors involves adjusting various parameters to optimise redox reactions, particularly at the electrode-electrolyte interface. In this method, the synthesis operating temperatures are slightly higher than those of conventional methods, typically ranging between 190 °C and 220 °C. This tailored thermal environment facilitates the integration of metal compounds or conducting polymers into the GA structure, thereby promoting pseudocapacitive behaviours [65].

The hydrothermal synthesis method yields graphene aerogels (GA) with inherent mesopores, typically ranging from 2 to 50 nm in diameter. These mesopores provide an optimal balance of surface area and ion diffusion, facilitating rapid ion movement and thereby enhancing the overall energy density of the aerogel. Moreover, precise regulation of pressure conditions within the range of 20–30 bar during synthesis optimises the impregnation of active materials, further enhancing the pseudocapacitive behaviour of the aerogel.

A one-pot hydrothermal and freeze-drying method that utilises elongated TiO_2 nanotubes (eTNTs) and graphene produced a novel multifunctional aerogel material with dual applications in supercapacitors and organic pollutant adsorption. The term eTNT stands for elongated TiO_2 nanotubes. These are elongated nanotubes made of titanium dioxide, a material commonly used in various applications due to its unique properties. In the context of the paragraph provided, eTNTs are utilised in conjunction with graphene to create a novel multifunctional aerogel material with applications in supercapacitors and organic pollutant adsorption. The GA also exhibited a remarkable specific surface area of 343.2 m^2 g^{-1}. The 3D interconnected structure of the GA procured, which had uniform eTNTs integrated into its porous framework, facilitated efficient electrolyte ions and electron migrations, leading to excellent electrochemical performance in supercapacitors. Furthermore, the binder-free aerogel electrode demonstrated impressive specific capacitance (476.8 F g^{-1} at 5 mV s^{-1}) and cycle stability (92 % capacitance retention after 5000 cycles). The aerogel also recorded notable adsorption capacity for bisphenol A, an organic pollutant, reaching 523.5 mg/g. The dual functionalities, namely, remarkable electrochemical and adsorption capacities, positioned the aerogel as a promising material for energy storage and environmental remediation applications. Consequently, the material effectively addresses energy and environmental challenges [63].

The hydrothermal synthesis technique enables the manipulation of graphene aerogel (GA) transparency, thereby introducing a new category of transparent GA supercapacitors. These transparent GA materials hold promise for applications such as computer screens and wearables, offering potential advancements in future computing technologies. Additionally, vacuum-assisted low-temperature synthesis of reduced graphene oxide (rGO) combined with hydrothermal treatments yields thin-film electrodes suitable for high-performance transparent and flexible all-solid-state supercapacitors [22]. However, it is crucial to note that the optical transparency and electrochemical performance of these materials are influenced by factors such as graphene oxide (GO) concentrations and initial dispersion. For instance, the highest recorded capacitance (~650 μF cm^{-2}) was achieved at a relatively low optical transmittance of 24 %. These transparent and flexible supercapacitors have potential applications in various fields, including wearable electronics, transparent displays, and energy-efficient devices. Nonetheless, all-solid-state supercapacitors demonstrated excellent mechanical flexibility with over 90 % capacity retention under various bending angles and cycles [64,66].

The low volumetric energy density of rGO-based electrodes limits its application in commercial electrochemical energy storage

devices requiring high-performance energy storage capacities in small volumes. The volumetric energy density of rGO-based electrode materials is considerably low due to their low packing density [22]. Consequently, supercapacitors with enhanced packing density and remarkable volumetric energy density are fabricated utilising doped rGO scrolls (GFNSs) as electrodes. Restacking rGO sheets is successfully controlled by synthesising the doped scroll structures, increasing packing density. Furthermore, the fabricated cell exhibits an ultrahigh volumetric energy density (49.66 WhL^{-1}) and excellent cyclic stability (>10,000 cycles) [67].

5.3. Key steps and divergences

N-doping is a method of augmenting electronic graphene material characteristics by introducing nitrogen atoms into graphene lattices. The modification alters the original GA electronic structure, generating additional charge carriers and enhancing the electrical conductivity of the GA. N-doping refers to the process of introducing nitrogen atoms into the lattice structure of graphene, a method aimed at enhancing the electronic characteristics of graphene-based materials. The addition of nitrogen atoms modifies the electronic structure of graphene aerogel (GA), leading to the generation of additional charge carriers and improving the overall electrical conductivity of the material. Nitrogen doping is a well-established technique used to tailor the properties of graphene materials for various applications, including energy storage devices, sensors, and catalysis. By incorporating nitrogen atoms into the graphene lattice, researchers can fine-tune the electronic properties of GA to meet specific performance requirements, thus expanding the range of potential applications for these advanced materials [15,68].

A recently developed BC/PPy/N15-rGO paper electrode, or electrode in a flexible sheet of plastic casing synthesised with nitrogen-doped hydrothermal treatments, recorded a remarkable mass-specific capacitance (441.9 $F\,g^{-1}$) with prolonged cyclic capability (96 % retention after 3000 cycles) and exceptional rate performance. BC/PPy/N15-rGO paper electrode refers to a type of electrode used in energy storage devices, particularly in supercapacitors. This electrode typically consists of a composite material composed of bacterial cellulose (BC), polypyrrole (PPy), and reduced graphene oxide (rGO) that has been doped with nitrogen (N15). This combination of materials provides enhanced electrical conductivity, mechanical strength, and electrochemical performance, making it suitable for use in high-performance energy storage devices. The approach allows large-scale flexible supercapacitor fabrication due to the attributes of the paper electrodes. The final product is also reportedly safe, biodegradable, has low energy consumption, and requires mild preparation conditions [69,70].

A method called P-doping refers to the process of introducing electron-acceptor dopants into a material, typically graphene or other semiconductors. These dopants create "holes" in the electronic band structure of the material, leading to an increase in the concentration of positive charge carriers. This results in a net positive charge within the material and enhances its electrical conductivity. P-doping is commonly used to modify the electronic properties of materials for applications such as semiconductor devices, sensors, and energy storage systems. In p-doping, electron-acceptor dopants are incorporated into graphene structures. The method involves modifying its graphene aerogel (GA) electronic configuration by introducing electron-deficient elements or molecules, such as boron or nitrogen. These dopants create 'holes' in the electronic band structure of graphene, resulting in a net positive charge within the material. As a result, p-doping significantly improves the overall electrical conductivity of graphene-based materials by enhancing the mobility of charge carriers. This process allows for precise control over the concentration and distribution of charge carriers within the GA, ultimately optimising its electronic properties for various applications, including energy storage devices, sensors, and electronic components [71,72].

Growing ultrathin and highly crumpled CoP/rGO nanosheet arrays on nickel foams (NF) through a hydrothermal-phosphatization route demonstrates the significant potential of p-doping in supercapacitor energy transport. The CoP/rGO composite material comprises cobalt phosphide (CoP) nanoparticles deposited onto reduced graphene oxide (rGO) sheets. This combination offers synergistic effects, enhancing conductivity and electrochemical performance. CoP nanoparticles serve as active sites for electrochemical reactions, while rGO sheets provide a conductive framework and support structure [12,54,73].

Moreover, the CoP/rGO/NF//AC supercapacitor exhibits exceptional cyclic durability even after 10,000 cycles while retaining 89 % capacitance. The innovative approach of combining high-capacitive metal phosphides with conductive carbon could significantly impact the future of energy storage systems. The CoP/rGO/NF//AC notation denotes a specific configuration of the supercapacitor device. "CoP/rGO/NF" refers to the electrode material composed of CoP/rGO nanosheet arrays grown on nickel foams (NF). The NF substrate provides a three-dimensional conductive scaffold for the CoP/rGO nanosheets, facilitating efficient charge transfer and electrolyte penetration. "//" signifies the separator between electrodes, and "AC" stands for activated carbon, commonly used as the counter electrode or second electrode in supercapacitor devices. The CoP/rGO/NF//AC supercapacitor configuration highlights the integration of high-performance electrode materials in a comprehensive energy storage solution [12,74,75].

Hummers' method is a classic oxidative approach often employed in producing GO from graphite. The technique oxidises graphite flakes with concentrated acids and potassium permanganate, forming a GO applicable as a precursor for various graphene materials and applications. Hummers' method also provides a versatile and scalable route of obtaining GO. Consequently, the approach is considered as a foundational step in GA synthesis, which permits GA property tailoring for diverse applications. Numerous modifications to Hummer's method have been reported, which is also the primary reason for the wide adoption of the technique in various applications. For instance, the process was integrated with hydrothermal treatments to prepare a novel 3D porous GA with partially unzipped multi-walled carbon nanotubes inserted into the graphene nanosheets. The procured GA has demonstrated a 348.4 Fg^{-1} specific capacitance at 5 mVs^{-1} scan rate and maintained 89.7 % capacitance retention after 5000 cycles [76]. Fig. 5 illustrates the fabrication route employed by a study to enhance low-grade coals such as lignite [77]. By subjecting lignite to hydrothermal treatments, RGO is synthesised from abundant and inexpensive low-grade coal, hence producing supercapacitor electrodes with outstanding volumetric capacitance (30.6 $F\,cm^{-3}$), high energy density (4.2 mW h cm^{-3}), flexibility (79.5 % retention of initial

capacitance at 180° bending), and extended lifespan (112.3 % retention of initial capacitance after 20,000 cycles) [77].

Researchers are investigating ways to enhance lower-quality graphene suitability to produce GA applicable in supercapacitors. An innovative approach involves incorporating partially unzipped multi-walled carbon nanotubes (PU-MWCNTs) into GA via self-assembly. The process leverages the spontaneous PU-MWCNTs organisation in the graphene matrix, generating a synergistic composite. The partially unzipped carbon nanotubes offer additional active sites and facilitate efficient charge transfer, thus improving performance in supercapacitor applications [10,78].

In-situ deposition is another versatile technique that integrates additional materials, such as metal compounds or conducting polymers, into GA structures during synthesis, not unlike the doping process. Nonetheless, in-situ deposition facilitates the simultaneous formation and integration of desired components into the GA compared to doping. Consequently, precisely controlling the morphology and properties of the composite is easier. In-situ deposition could be applied to tailor specific GA for particular applications, including supercapacitors, with enhanced electrochemical performance and structural characteristics. A chemical in situ deposition of conducting polymer poly(3,4-ethylenedioxythiophene)(PEDOT) on rGO nanosheets has been reported. The innovation permits the integration of supercapacitors into clothing, which resembles the doping process and adds new features that ensure washability and excellent flexibility of the clothes. Furthermore, the product maintained 98 % of its initial capacitance after 3000 bending cycles [14].

Another interesting research involves the utilisation of hydrothermal synthesis in conjunction with silica etching through electrospinning. The technique applies a high voltage to a polymer solution containing graphene, forming nanofibers. Electrospinning produces GA or graphene material with a fibrous morphology. The fibrous attribute increases surface area and porosity, which improves the properties of the graphene, including mechanical strength and ion transport. Moreover, combining electrospinning and silica etching resulted in GA with enhanced structural integrity and a specific surface area suitable for energy storage and sensing
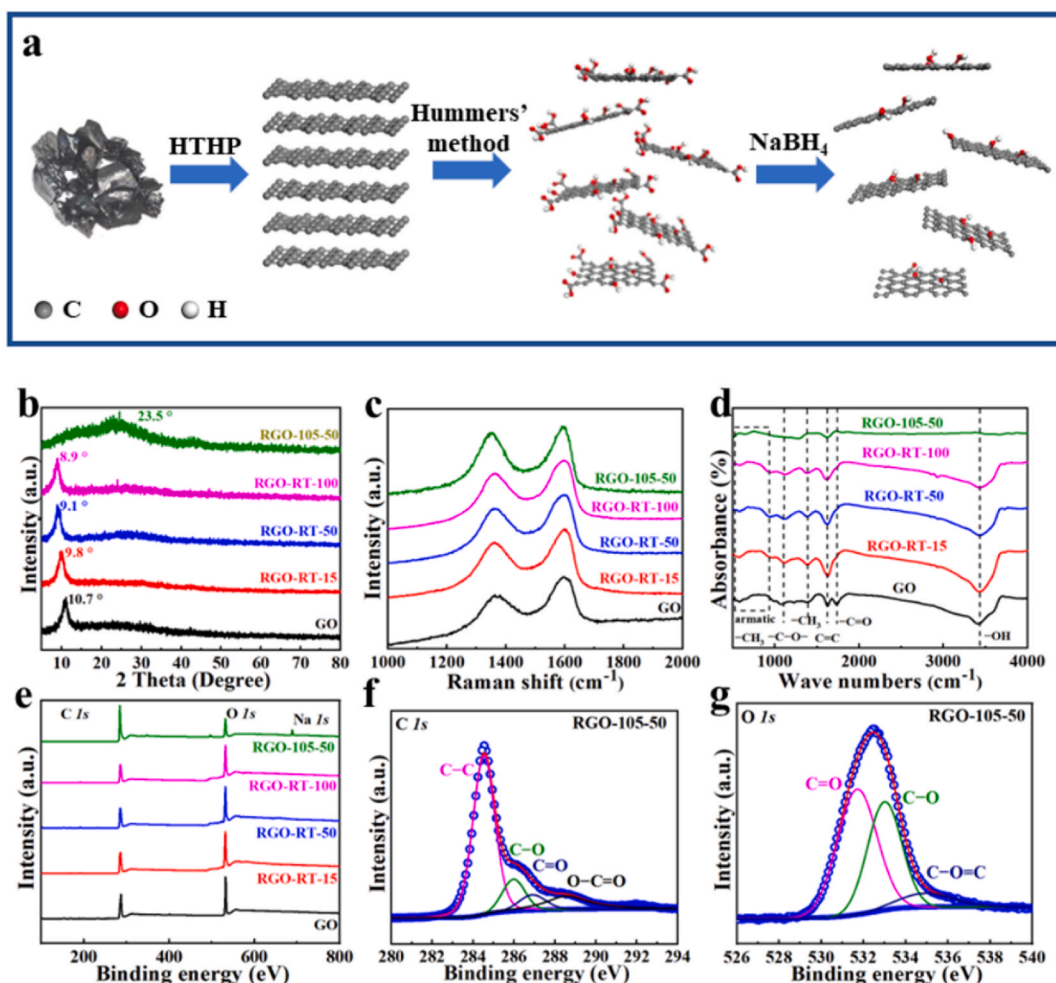

Fig. 5. The (a) schematic illustration of lignite-derived rGO fabrication process, (b) X-ray diffraction (XRD) patterns and (c) Raman, (d) Fourier transform infrared (FTIR), (e) X-ray Photoelectron Spectroscopy (XPS) survey spectra of GO and rGO at different $NaBH_4$ molar concentrations at room temperature and 50 mM $NaBH_4$ at 105 °C, and high-resolution (f) C 1s XPS and (g) O 1s XPS spectra of RGO-105-50 [77].

devices [26]. In the research, reduced graphene oxide (rGO)/thorn-like TiO2 nanofiber (TTF) aerogels, or GTTF aerogels, with different TTF weight ratios were successfully prepared by electrospinning, silica etching and hydrothermal combination method. The electrochemical performance of the GTTF aerogels was assessed using cyclic voltammetry and galvanostatic charge–discharge measurements in a 1 M aqueous Na2SO4 electrolyte. The TTF-to-rGO ratio of the aerogel material significantly affected the electrochemical performance of the aerogel electrodes, and the GTTF aerogels prepared with 20 wt% TTF (denoted GTTF-20) exhibited excellent electrochemical performance rGO/thorn-like TiO$_2$ nanofiber (TTF) GA exhibited excellent electrochemical performance, making them potential candidates for stable supercapacitors and pseudocapacitors [23].

Electro-polymerisation applies a straightforward synthesis of conducting polymers on GA surfaces through electrochemical processes. The technique also offers precise control over the deposition of conducting polymer layers, enhancing the overall conductivity and electrochemical properties of the GA. For instance, a study reported distinguished specific capacitance and retention rates under a carbon nanotube/graphene/polypyrrole ternary composite produced via electro-polymerisation under extensive charge and discharge cycles. The approach has also demonstrated significant potential in tailoring surface chemistry to improve GA compatibility with various applications, including sensors and energy storage devices [79].

Table 4
The materials and performance characteristics of supercapacitors with hydrothermal synthesis-GA.

Material	Fabrication method	Energy density	Specific capacitance	Cycle retention	Reference
Bc/Ppy/N15-rGO paper electrode	Nitrogen-doped and hydrothermal treatments	167.9 mWh cm^{-3}	441.9 Fg^{-1}	96 %	[64]
ZnCo$_2$O$_4$	Nanocomposites via hydrothermal treatments	92.63 Wh kg^{-1}	1693 F g^{-1}	96.7 %	[21,22,84, 85]
Low-grade coal lignite-derived rGO	Hydrothermal treatments	4.2 mWh cm^{-3}	30.6 F g^{-1}	112 %	[7,86]
Elongated TiO$_2$ nanotubes (Etnts) and graphene	Freeze drying and hydrothermal treatments	343.2 Wh kg^{-1}	476.8 F g^{-1}	92 %	[62,87]
CoFe$_2$O$_4$ hollow spheres	Hydrothermal treatments	65.8 Wh kg^{-1}	1032 F g^{-1}	96 %	[9]
3D interconnected porous partially unzipped Mwcnt/graphene composite	Hummer's method and hydrothermal treatments	348.4Fg^{-1}	348.4 F g^{-1}	90 %	[10]
Cop/Rgo/Nf//Ac	Hydrothermal-phosphidation doping	43.2 Wh Kg^{-1}	3595.0 F g^{-1}	90 %	[12]
Ni-Mof/Rgo (Homogeneous)	Facile hydrothermal treatments	17.13 Wh Kg^{-1}	954 F g^{-1}	82 %	[88]
Hierarchical doped gelatin-derived GA	N-doping and hydrothermal treatments	20.88 Wh Kg^{-1}	232 F g^{-1}	90 %	[88]
Pedot on rGO nanosheets	In-situ deposition and hydrothermal treatments	22 Wh Kg^{-1}	202.7 F g^{-1}	90 %	[15,89]
Rgo/Pedot nanocomposite	Doping and hydrothermal polymerisation treatments	12.95 Wh kg^{-1}	325 F g^{-1}	99 %	[15,89]
Graphene nanosheets	N-doping, P-doping, and time manipulation via hydrothermal treatments	Robust graphene nanosheet with N-doping. Able to manipulate pore generation (size, shapes, and average number).		90 %	[90]
G-NimoO$_4$ composite as the positive electrode and Fe$_2$O$_3$ quantum dot-decorated graphene (G-Fe$_2$O$_3$-Qds) as the negative electrode	Nimoo4 nanorods uniformly decorated on graphene nanosheets (G-Nimoo4) synthesised through a ` hydrothermal method	130 Wh·kg^{-1}	714C g^{-1}	113 %	[69,91]
Tin-doped indium oxide coated polyethylene terephthalate substrates	Facile hydrothermal treatments	2.9 W h kg^{-1}	650 μF cm^{-2}	>90 %	[28,92]
Flexible all-solid-state Sc on 3D Rgo/Polyaniline array hybrid composite bases	One-step self-assembled hydrothermal process	25 W h kg^{-1}	432 F g^{-1}	85 %	[93]
Flexible ZnCO$_2$O$_4$ nanowire arrays on GA	Hydrothermal reaction and thermal annealing	25 W h kg^{-1}	143 F g^{-1}	93.4 %	[94]
Three-Dimensional Hierarchically Mesoporous Znco2o4	Hydrothermal treatments	43.2 Wh Kg^{-1}	1116.6 F g^{-1}	93.4 %	[95]
Ternary ZnCO$_2$O$_4$/rGO/Nio (Zcgno) nanowire arrays	Hydrothermal treatments	62.8 Wh kg^{-1}	1256 Fg^{-1}	80 %	[96]
Low volumetric Energy density rGO (rGO-based electrode)	Hydrothermal treatments	49.66 Wh L^{-1}	200 Fg^{-1}	89 %	[96,97]
rGO/Thorn-Like TiO$_2$ nanofiber (Ttf)	Electrospinning, silica etching, and hydrothermal combination method	C 40.1 Wh kg^{-1}	178 Fg^{-1}	90 %	[98,99]
Monolithic 3D Fe$_2$O$_3$ graphene GA	Solvothermal-induced self-assembly	42.43 Wh kg^{-1}	922.6 mAh g^{-1}	90 %	[100,68]
Homogeneously distributed self-assembling hybrid 3D interconnected pores, employing three carbohydrates (glucose, B-cyclodextrin, and chitosan)	Hydrothermal treatments	42.43 W h kg^{-1}	305.5 F g^{-1}	98 %	[21,101]

In condensation reactions, GA is procured by subjecting GO or precursor materials to a polymerisation process through condensation. The process involves removing water or other small molecules, similar to vacuum drying, to obtain GA with 3D networks. Nevertheless, condensation reactions require thermal energy to condense water. Condensation reactions contribute to producing interconnected structures with desired properties for supercapacitor applications. The interconnected arrangement ensures optimal charge storage and efficient ion transport within aerogels. For example, modified polyhedral oligo silsesquioxane (POSS) has been utilised to enhance the electrochemical performance of rGO by introducing POSS spacers, resulting in considerable specific capacitance, power density, and durability after extensive cycling [80].

Electrochemical exfoliation involves the electrochemical delamination of graphite to produce dispersed graphene materials. Electrochemical reactions are employed to induce the separation of graphene layers from graphite. The separation leads to a dispersed graphene suspension, the GA. Electrochemical exfoliation demonstrated potential in large-scale production of GA with controlled properties for various applications, including energy storage devices, due to its direct synthesis method. Furthermore, optimised conditions reportedly produced mesoporous and macroporous GA with considerable specific surface areas, low densities, electrical properties, and electrochemical stability [81].

Hydrothermal synthesis is a versatile method for producing supercapacitors using GA materials, owing to its adaptability, scalability, and suitability for various environments, ranging from laboratory settings to manufacturing facilities. This synthesis technique involves controlling precursor material reactions under specific temperature and pressure conditions to regulate the morphology, porosity, and composition of the resulting GA. Additionally, hydrothermal synthesis has been optimised and combined with other synthesis methods, serving as a precursor process in some cases. It is also utilised as a final step in supercapacitor manufacturing for specific applications, leading to enhanced electrochemical performance, particularly in charge storage and transport [82].

The GA has emerged as a promising supercapacitor material following its remarkable storing and transporting energy properties. Moreover, GA with tailored properties obtained through various synthesis methods, including hydrothermal treatments, has led to supercapacitors with enhanced specific capacitance, improved cycling stability, and excellent rate capabilities. Nonetheless, GA multifunctionality extends beyond energy storage, including wastewater management and organic pollutant adsorption]. The material also demonstrated potential in smart wearables, screens, and flexible devices. Table 4 summarises the materials and performance characteristics of supercapacitors with GA synthesised via hydrothermal methods [83].

Procuring GA via hydrothermal approaches reveals a transformative avenue for developing advanced materials in energy storage and environmental remediation. The GA synthesis under controlled temperature and pressure conditions exhibit exceptional properties, such as high specific surface area, efficient charge storage, and excellent cyclic stability. The versatility of hydrothermal synthesis also enables tailored aerogel creations, which could revolutionise supercapacitors and other diverse fields, including environmental science, flexible electronics, and wearable technology [102].

6. Conclusion

Graphene has been rapidly industrialised in the past decade. The material has evolved into a versatile nanomaterial with diverse structures, types, mixtures, and composites, fueling numerous applications and procedures. Nevertheless, considerable attention has been directed towards developing and fabricating porous graphene structures, commonly known as aerogels. Aerogels boast outstanding properties, including high surface areas and expansive internal spacings. Hydrothermal synthesis, whether employed as a standalone method or combined with contemporary advancements in GA manufacture, has garnered significant interest. The fundamentals, recent developments, and manufacturing processes of GA tailored for supercapacitor applications were discussed in this comprehensive review. Various GA fabrication techniques were also highlighted.

Pristine, or combined with other materials, GA has emerged as a promising electrode material in high-energy-density supercapacitors. The present review discussed GA electrochemical performance enhancements through different strategies, such as elevating electrical conductivity, specific surface area, and porosity and doping/co-doping with various non-metals. Improving GA with metal compounds and conducting polymers was also scrutinised. The modifications aimed to bolster capacitor properties and overall performance. Preparing and implementing graphene aerogels GA in supercapacitors presents several technical and commercial challenges that need to be addressed to advance practical applications. One key challenge is ensuring enhanced accuracy and precision in tailoring the size of GA for specific end-use applications. Additionally, there is a need to develop GA in various shapes, incorporating unique functionalities and improved mechanical properties to meet diverse application requirements. This customisation of GA is particularly important in fields like future computing, where wearable computers and smart clothing are becoming increasingly significant. Another challenge involves the adoption of more accurate and cost-effective fabrication strategies to propel the field of GA into new frontiers in materials science.

Looking ahead, several key areas offer promising directions for future research in the synthesis of graphene aerogels. First, the development of advanced synthesis techniques is essential. Research should focus on exploring novel methods that provide better control over the structural and chemical properties of graphene aerogels. Alternative synthesis routes, such as electrochemical or sol-gel processes, could offer new advantages in terms of scalability, cost, and material properties, beyond the traditional hydrothermal methods [103].

Second, enhancing scalability and reproducibility is crucial for transitioning from laboratory-scale to industrial-scale production. Optimization of synthesis methods to ensure uniformity of GA properties across large batches and consistent quality throughout the production process is needed. Innovations in reactor design, automation, and process control could play a pivotal role in achieving these goals.

Third, tailoring porosity and functionalization of graphene aerogels is an important research avenue. Future studies should focus on

refining techniques to precisely control the porosity of GA, including enhancing microporosity, mesoporosity, or macroporosity based on specific application needs. Additionally, advancements in functionalization strategies are needed to introduce specific chemical groups or dopants that can customise GA properties for targeted applications, such as high-performance supercapacitors or advanced filtration systems.

Fourth, integrating hybrid materials with graphene aerogels offers the potential for enhanced or novel properties. Research should explore methods to effectively combine GA with other materials, such as metals, polymers, or nanoparticles, optimising the interactions between different components to achieve superior performance characteristics.

Fifth, addressing sustainability and environmental impact is increasingly important. Future research should focus on developing more sustainable synthesis routes that reduce the use of hazardous chemicals and minimise waste. Exploring green chemistry approaches and evaluating the lifecycle environmental impact of different synthesis methods can promote more sustainable practices in the field.

Lastly, gaining a deeper mechanistic understanding of GA synthesis is crucial for optimising material properties. Research should aim to elucidate the relationships between synthesis parameters, structural features, and performance characteristics. This knowledge will guide the development of new synthesis strategies and enhance the overall efficiency and effectiveness of graphene aerogels.

Other informations

In the course of conducting the systematic literature review, it is noted that no registration was pursued, hence a protocol was not developed. As such, no amendments were made to registration or protocol information. It is pertinent to mention that no external funding was secured for this review, and there are no conflicts of interest among the authors. Additionally, no supplementary materials, including data, code, or other resources, are available for public access as there are no extra materials in the production of this systematic review.

CRediT authorship contribution statement

Khaled Abdou Ahmed Abdou Elsehsah: Writing – review & editing, Writing – original draft. **Zulkarnain Ahmad Noorden:** Writing – review & editing, Supervision. **Norhafezaidi Mat Saman:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

References

[1] Z. Wang, et al., A review of graphene Materials/Polymer composite aerogels, Polymers 15 (8) (2023), https://doi.org/10.3390/polym15081888.

[2] G. Nassar, E. Daou, R. Najjar, M. Bassil, R. Habchi, A review on the current research on GA and their applications, Carbon Trends 4 (2021), https://doi.org/10.1016/j.cartre.2021.100065.

[3] X. Chen, R. Paul, L. Dai, Carbon-based supercapacitors for efficient energy storage, Natl. Sci. Rev. 4 (Apr. 2017) 1–37, https://doi.org/10.1093/nsr/nwx009.

[4] J.S. Shaikh, et al., The implementation of graphene aerogel in the field of supercapacitor, Nanotechnology 32 (36) (2021), https://doi.org/10.1088/1361-6528/ac0190.

[5] Q. Li, R. Tang, H. Zhou, X. Hu, S. Zhang, A high-performance and flexible electrode film based on bacterial cellulose/polypyrrole/nitrogen-doped graphene for supercapacitors, Carbohydr. Polym. 311 (2023), https://doi.org/10.1016/j.carbpol.2023.120754.

[6] R. Mohanty, Kaushik Parida, Kulamani Parida, Redox mediator-enhanced charge storage in dimensionally tailored nanostructures towards flexible hybrid solid-state supercapacitors, Nanoscale Adv. 5 (17) (2023), https://doi.org/10.1039/d3na00279a.

[7] Yi Ming Wang, Chun Hua Zhang, rGO derived from low-grade coal for high-performance flexible supercapacitors with ultrahigh cyclability, Nanomaterials 12 (17) (2022), https://doi.org/10.3390/nano12172989.

[8] Y. Zhang, et al., Prepared multifunctional aerogel for high-performance supercapacitors and effective adsorbents, Mater. Res. Express 5 (5) (2018), https://doi.org/10.1088/2053-1591/aac258.

[9] D. Gogoi, M.R. Das, N.N. Ghosh, CoFe2O4 hollow spheres-decorated three-dimensional rGO sponge for highly efficient electrochemical charge storage devices, ACS Omega 7 (13) (Mar. 2022) 11305–11319, https://doi.org/10.1021/acsomega.2c00374.

[10] J. Zhou, Y. Zheng, D. Chen, Three-dimensional interconnected porous partially unzipped MWCNT/Graphene composite aerogels as electrodes for high-performance supercapacitors, Nanomaterials 12 (4) (2022), https://doi.org/10.3390/nano12040620.

[11] Y. Zhong, et al., Homogeneous nickel metal-organic framework microspheres on rGO as novel electrode material for supercapacitors with outstanding performance, J. Colloid Interface Sci. 561 (2020), https://doi.org/10.1016/j.jcis.2019.10.023.

[12] H. Xing, et al., Ultrathin and highly Crumpled/Porous CoP nanosheet arrays anchored on graphene boosts the capacitance and their synergistic effect toward high-performance battery-type hybrid supercapacitors, ACS Appl. Mater. Interfaces 13 (22) (2021), https://doi.org/10.1021/acsami.1c04921.

[13] A. Kandasamy, et al., Hierarchical doped gelatin-derived carbon aerogels: three levels of porosity for advanced supercapacitors, Nanomaterials 10 (6) (2020), https://doi.org/10.3390/nano10061178.

[14] S. Li, et al., Modifying rGO by conducting polymer through a hydrothermal polymerization method and its application as energy storage electrodes, Nanoscale Res. Lett. 14 (1) (Dec. 2019) 226, https://doi.org/10.1186/s11671-019-3051-6.

[15] L. Peng, Q. Guo, Z. Ai, Y. Zhao, Y. Liu, D. Wei, Nitrogen-doped carbons derived from graphene aerogel templated triazine-based conjugated microporous polymers for high-performance supercapacitors, Front. Chem. 7 (APR) (2019), https://doi.org/10.3389/fchem.2019.00142.

[16] E. García-Bordejé, S. Víctor-Román, O. Sanahuja-Parejo, A.M. Benito, W.K. Maser, Control of the microstructure and surface chemistry of GA: via pH and time manipulation by a hydrothermal method, Nanoscale 10 (7) (2018), https://doi.org/10.1039/c7nr08732b.

[17] W. Teng, et al., Hierarchical Poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)/rGO/Polypyrrole hybrid electrode with excellent rate capability and cycling stability for fibre-shaped supercapacitor, J. Colloid Interface Sci. 636 (2023), https://doi.org/10.1016/j.jcis.2023.01.019. K.K.Liu, B. Jin, and L. Y. Meng, "Glucose/GA for gas adsorption and electric double layer capacitors," Polymers, vol. 11, no. 1, 2019. doi: https://doi.org/10.3390/polym11010040.

[18] S. Chen, L. Qiu, H.M. Cheng, Carbon-based fibers for advanced electrochemical energy storage devices, Chem. Rev. 120 (5) (2020) 1328–1338, https://doi.org/10.1021/acs.chemrev.9b00466.

[19] Y. Yang, Y. Xi, J. Li, G. Wei, N.I. Klyui, W. Han, Flexible supercapacitors based on polyaniline arrays coated graphene aerogel electrodes, Nanoscale Res. Lett. 12 (2017), https://doi.org/10.1186/s11671-017-2159-9.

[20] P. Simon, A. Burke, Nanostructured carbons: double-layer capacitance and more, Electrochem. Soc. Interface 17 (1) (2008), https://doi.org/10.1149/2.f05081if.

[21] I.K. Moon, S. Yoon, J. Oh, Three-dimensional hierarchically mesoporous ZnCo2O4 nanowires grown on Graphene/Sponge foam for high-performance, flexible, all-solid-state supercapacitors, Chem.–Eur. J. 23 (3) (2017), https://doi.org/10.1002/chem.201602447.

[22] S. Sahoo, J.J. Shim, Facile synthesis of three-dimensional ternary ZnCo2O4/rGO/NiO composite film on nickel foam for next generation supercapacitor electrodes, ACS Sustainable Chem. Eng. 5 (1) (2017), https://doi.org/10.1021/acssuschemeng.6b01367.

[23] T.W. Kim, S.J. Park, Synthesis of rGO/thorn-like titanium dioxide nanofiber aerogels with enhanced electrochemical performance for supercapacitor, J. Colloid Interface Sci. 486 (2017), https://doi.org/10.1016/j.jcis.2016.10.007.

[24] R. Wang, et al., Solvothermal-induced self-assembly of Fe2O3/GS aerogels for high li-storage and excellent stability, Small 10 (11) (2014), https://doi.org/10.1002/smll.201303371.

[25] Chen Chen Ji, et al., Self-assembly of three-dimensional interconnected GA and its application in supercapacitors, J. Colloid Interface Sci. 407 (2013), https://doi.org/10.1016/j.jcis.2013.06.054.

[26] T. Islam, Md Mahedi Hasan, S. Sarker, A.J. Saleh Ahammad, Intrinsic properties of GO/RGO bilayer electrodes dictate their inter-/intralayer intractability to modulate their capacitance performance, ACS Omega 8 (15) (2023), https://doi.org/10.1021/acsomega.3c00573.

[27] S. Ratha, C.S. Rout, J.N. Behera, 3D cuboidal vanadium diselenide embedded reduced graphene oxide hybrid structures with enhanced supercapacitor properties, Chem. Commun. 53 (2) (2017) 1140–1143, https://doi.org/10.1039/c6cc08035a.

[28] T. Aytug, et al., Vacuum-assisted low-temperature synthesis of rGO thin-film electrodes for high-performance transparent and flexible all-solid-state supercapacitors, ACS Appl. Mater. Interfaces 10 (13) (2018), https://doi.org/10.1021/acsami.8b01938.

[29] Z. Peng, C. Yu, W. Zhong, Facile preparation of a 3D porous aligned graphene wall network architecture by confined self-assembly with shape memory for artificial muscle, pressure sensor, and flexible supercapacitor, ACS Appl. Mater. Interfaces 14 (15) (2022), https://doi.org/10.1021/acsami.2c00987.

[30] X. Cui, et al., Comparative study of nanocarbon-based flexible multifunctional composite electrodes, ACS Omega 6 (4) (2021), https://doi.org/10.1021/acsomega.0c04313.

[31] S. Korkmaz, Afşin Kariper, Graphene and GO based aerogels: synthesis, characteristics and supercapacitor applications, J. Energy Storage 27 (2020), https://doi.org/10.1016/j.est.2019.101038.

[32] Włodzimierz Czepa, Samanta Witomska, A. Ciesielski, Paolo Samorì, rGO-silsesquioxane hybrid as a novel supercapacitor electrode, Nanoscale 12 (36) (2020), https://doi.org/10.1039/d0nr05226d.

[33] J.R. Rani, Ranjith Thangavel, S.I. Oh, Yun Sung Lee, Jae Hyung Jang, An ultra-high-energy density supercapacitor; fabrication based on thiol-functionalized GO scrolls, Nanomaterials 9 (2) (2019), https://doi.org/10.3390/nano9020148.

[34] S.R. Prasad, S. Srivastava, R. Nagar, N. Bhagat, Graphene-based supercapacitors and their future, J. Nanostructures 12 (2) (2022), https://doi.org/10.22052/JNS.2022.02.014.

[35] Y. Zhao, M.P. Li, S. Liu, M.F. Islam, Superelastic pseudocapacitors from freestanding MnO2-Decorated graphene-coated carbon nanotube aerogels, ACS Appl. Mater. Interfaces 9 (28) (2017), https://doi.org/10.1021/acsami.7b06210.

[36] G. Yilmaz, X. Lu, Ghim Wei Ho, Cross-linker mediated formation of sulfur-functionalized V2O5/GA and their enhanced pseudocapacitive performance, Nanoscale 9 (2) (2017), https://doi.org/10.1039/c6nr08233e.

[37] M. Kotal, J. Kim, J. Oh, Il Kwon Oh, Recent progress in multifunctional GA, Frontiers in Materials 3 (2016), https://doi.org/10.3389/fmats.2016.00029.

[38] Y. Gogotsi, et al., Nanoporous carbide-derived carbon with tunable pore size, Nat. Mater. 2 (9) (2003), https://doi.org/10.1038/nmat957.

[39] Sung Mi Jung, Daniela Lopes Mafra, Cheng Te Lin, Hyun Young Jung, J. Kong, Controlled porous structures of GA and their effect on supercapacitor performance, Nanoscale 7 (10) (2015), https://doi.org/10.1039/c4nr07564a.

[40] C.C. Ji, et al., Self-assembly of three-dimensional interconnected GA and its application in supercapacitors, J. Colloid Interface Sci. 407 (2013), https://doi.org/10.1016/j.jcis.2013.06.054.

[41] A.G. Pandolfo, A.F. Hollenkamp, Carbon properties and their role in supercapacitors, J. Power Sources 157 (1) (2006) 11–27, https://doi.org/10.1016/j.jpowsour.2006.02.065.

[42] X.J. Lee, B.Y.Z. Hiew, K.C. Lai, L.Y. Lee, S. Gan, S. Thangalazhy-Gopakumar, S. Rigby, Review on graphene and its derivatives: synthesis methods and potential industrial implementation, J. Taiwan Inst. Chem. Eng. 98 (2019) 163–180, https://doi.org/10.1016/j.jtice.2018.10.028.

[43] P. Sharma, T.S. Bhatti, A review on electrochemical double-layer capacitors, Energy Convers. Manag. 51 (6) (2010) 1328–1338, https://doi.org/10.1016/j.enconman.2010.06.031.

[44] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, Carbons and electrolytes for advanced supercapacitors, Adv. Mater. 26 (14) (2014) 2219–2251, https://doi.org/10.1002/adma.201304137.

[45] W. He, C. Wang, F. Zhuge, X. Deng, X. Xu, T. Zhai, Flexible and high energy density asymmetrical supercapacitors based on core/shell conducting polymer nanowires/manganese dioxide nanoflakes, Nano Energy 35 (2017) 199–207, https://doi.org/10.1016/j.nanoen.2017.03.045.

[46] C. Peng, J. Yu, S. Chen, L. Wang, High-performance supercapacitor based on ultralight and elastic three-dimensional carbon foam/reduced graphene/polyaniline nanocomposites, Chin. Chem. Lett. 30 (2) (2019) 387–392, https://doi.org/10.1016/j.cclet.2019.02.007.

[47] B. Liu, M. Yang, H. Chen, Y. Liu, D. Yang, H. Li, Graphene-like porous carbon nanosheets derived from salvia splendens for high-rate performance supercapacitors, J. Power Sources 398 (2018) 46–52, https://doi.org/10.1016/j.jpowsour.2018.06.100.

[48] G. Zhang, X. Xiao, B. Li, P. Gu, H. Xue, H. Pang, Transition metal oxides with one-dimensional/one-dimensional-analogue nanostructures for advanced supercapacitors, J. Mater. Chem. A 5 (4) (2017) 1787–1807, https://doi.org/10.1039/c7ta02454a.

[49] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos, A.A. Firsov, Two-dimensional gas of massless Dirac fermions in graphene, Nature 438 (7065) (2005) 197–200, https://doi.org/10.1038/nature04233.

[50] Z.S. Wu, W. Ren, L. Gao, J. Zhao, Z. Chen, B. Liu, D. Tang, B. Yu, C. Jiang, H.M. Cheng, Synthesis of graphene sheets with high electrical conductivity and good thermal stability by hydrogen arc discharge exfoliation, ACS Nano 3 (4) (2009) 911–917, https://doi.org/10.1021/nn900020u.

[51] C. Zheng, X. Zhou, H. Cao, G. Wang, Z. Liu, Synthesis of porous graphene/activated carbon composite with high packing density and large specific surface area for supercapacitor electrode material, J. Power Sources 251 (2014) 93–98, https://doi.org/10.1016/j.jpowsour.2014.01.056.

[52] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, Nat. Mater. 7 (11) (Nov. 2008) 845–854, https://doi.org/10.1038/nmat2297.

[53] Y. Beeran P.T., V. Bobnar, S. Gorgieva, Y. Grohens, M. Finsgar, S. Thomas, V. Kokol, Mechanically strong, flexible and thermally stable graphene oxide/nanocellulosic films with enhanced dielectric properties, RSC Adv. 6 (49) (2016) 49138–49149, https://doi.org/10.1039/C6RA06744A.

[54] M. Wu, C. Zhong, and Y. Zhang, "In situ synthesis of 3D graphene–reduced graphene oxide–polyaniline hybrid aerogels with enhanced electrochemical performance," RSC Adv., vol. 10, no. 2, pp.

[55] M.I.A. Abdel Maksoud, et al., Advanced materials and technologies for supercapacitors used in energy conversion and storage: a review, Environ. Chem. Lett. 19 (1) (2021), https://doi.org/10.1007/s10311-020-01075-w.

[56] S.W. Bokhari, et al., Advances in graphene-based supercapacitor electrodes, Energy Rep. 6 (2020), https://doi.org/10.1016/j.egyr.2020.10.001.

[57] Y. Qian, I.M. Ismail, A. Stein, Ultralight, high-surface-area, multifunctional graphene-based aerogels from self-assembly of graphene oxide and resol, Carbon N. Y. 66 (2014) 464–473, https://doi.org/10.1016/j.carbon.2013.10.082.

[58] D. Ponnamma, A. Erturk, H. Parangusan, K. Deshmukh, M.B. Ahamed, M. Al Ali Al-Maadeed, Stretchable quaternary phasic PVDF-HFP nanocomposite films containing graphene-titania-SrTiO3 for mechanical energy harvesting, Emergent Mater. 1 (2) (2018) 109–118, https://doi.org/10.1007/s42247-018-0007-z.

[59] Y.B. Pottathara, S. Thomas, N. Kalarikkal, T. Griesser, Y. Grohens, V. Bobnar, M. Finšgar, V. Kokol, R. Kargl, UV-Induced reduction of graphene oxide in cellulose nanofibril composites, New J. Chem. 43 (2) (2019) 681–688, https://doi.org/10.1039/C8NJ03563F.

[60] D. Moher, A. Liberati, J. Tetzlaff, D.G. Altman, The PRISMA Group, Preferred reporting Items for systematic reviews and meta-analyses: the PRISMA Statement, PLoS Med. 6 (7) (2009) e1000097, https://doi.org/10.1371/journal.pmed1000097.

[61] H.A. Mohamed Shaffril, S.F. Samsuddin, A. Abu Samah, The ABC of Systematic Literature Review: the basic methodological guidance for beginners, Qual. Quantity 55 (4) (2020) 1319–1346, https://doi.org/10.1007/s11135-020-01059-6.

[62] Z. Wu, N. Ambrožová, E. Eftekhari, N. Aravindakshan, W. Wang, Q. Wang, S. Zhang, K. Kočí, Q. Li, Photocatalytic H_2 generation from aqueous ammonia solution using TiO_2 nanowires-intercalated reduced graphene oxide composite membrane under low power UV light, Emergent Mater. 2 (1) (2019) 79–89, https://doi.org/10.1007/s42247-019-00029-5.

[63] J. Xu, K. Wang, S.Z. Zu, B.H. Han, Z. Wei, Hierarchical nanocomposites of polyaniline nanowire arrays on graphene oxide sheets with synergistic effect for energy storage, ACS Nano 4 (5) (2010) 3154–3160, https://doi.org/10.1021/nn1006539.

[64] L. Manjakkal, C.G. Núñez, W. Dang, R. Dahiya, Flexible self-charging supercapacitor based on graphene-Ag-3D graphene foam electrodes, Nano Energy 49 (2018) 83–92, https://doi.org/10.1016/j.nanoen.2018.06.072.

[65] M. Khalid, A.M.B. Honorato, Bendable tube-shaped supercapacitor based on reduced graphene oxide and Prussian blue coated carbon fiber yarns for energy storage, J. Energy Chem. 27 (4) (2018) 1065–1071, https://doi.org/10.1016/j.jechem.2017.06.011.

[66] Y. Wang, Y. Wang, Y. Wang, J. Liu, Facial preparation of covalent modified rGO/polyaniline composite and its stable-enhanced electrochemical performance, Heliyon 9 (1) (2023) e13002, https://doi.org/10.1016/j.heliyon.2023.e13002.

[67] Y. Shabangoli, M.S. Rahmanifar, M.F. El-Kady, A. Noori, M.F. Mousavi, R.B. Kaner, Thionine functionalized 3D graphene aerogel, combining simplicity and efficiency in fabrication of a metal-free redox supercapacitor, Adv. Energy Mater. 8 (7) (2018), https://doi.org/10.1002/aenm.201802869.

[68] J. Kim, J.H. Eum, J. Kang, O. Kwon, H. Kim, D.W. Kim, Tuning the hierarchical pore structure of graphene oxide through dual thermal activation for high-performance supercapacitor, Sci. Rep. 11 (1) (2021), https://doi.org/10.1038/s41598-021-81759-7.

[69] J. Yang, et al., Ultrahigh energy density battery-type asymmetric supercapacitors: NiMoO4 nanorod-decorated graphene and graphene/Fe2O3 quantum dots, Nano Res. 11 (9) (2018), https://doi.org/10.1007/s12274-018-2059-z.

[70] S. Sharma, P. Chand, Supercapacitor and electrochemical techniques: a brief review, Results Chem. 5 (2023), https://doi.org/10.1016/j.rechem.2023.100885.

[71] Q. Zhang, F. Zhang, S.P. Medarametla, H. Li, C. Zhou, D. Lin, 3D printing of graphene aerogels, Small 12 (45) (2016) 6168–6173, https://doi.org/10.1002/smll.201503524.

[72] R. Kumar Singh, S. Kumar Mishra, V.V. Mehtre, Supercapacitor construction, principle, operation, characteristics, advantages, disadvantages and applications, Int. J. Innov. Res. Electr. Electron. Instrum. Control Eng. 9 (2021).

[73] M. El-Kady, Graphene Supercapacitors: Charging up the Future, Ph.D. dissertation, Univ. of California, Los Angeles, 2013.

[74] S. Chen, A. Skordos, V.K. Thakur, Functional nanocomposites for energy storage: chemistry and new horizons, Mater. Today Chem. 17 (2020), https://doi.org/10.1016/j.mtchem.2020.100304.

[75] Y. Guan, K. Hu, N. Su, G. Zhang, Y. Han, M. An, Review of NiS-based electrode nanomaterials for supercapacitors, Nanomaterials 13 (6) (2023), https://doi.org/10.3390/nano13060979.

[76] M.E. Şahin, F. Blaabjerg, A. Sangwongwanich, A comprehensive review on supercapacitor applications and developments, Energies 15 (3) (2022), https://doi.org/10.3390/en15030674.

[77] N.I. Jalal, R.I. Ibrahim, M.K. Oudah, A review on supercapacitors: types and components, J. Phys. Conf. Ser. 1973 (1) (2021), https://doi.org/10.1088/1742-6596/1973/1/012015.

[78] D. Gao, Z. Luo, C. Liu, S. Fan, A survey of hybrid energy devices based on supercapacitors, Green Energy Environ. 8 (4) (2023), https://doi.org/10.1016/j.gee.2022.02.002.

[79] Y. Lu, Z. Gao, Q. Yang, C. Xiong, G.H. Hu, 3.6 V high-voltage symmetrical supercapacitor based on reduced graphene oxide/polythiophene aerogels with uniform dispersion, J. Energy Storage 72 (2023), https://doi.org/10.1016/j.est.2023.108224.

[80] M.A.A. Mohd Abdah, N.H.N. Azman, S. Kulandaivalu, Y. Sulaiman, Review of the use of transition-metal-oxide and conducting polymer-based fibres for high-performance supercapacitors, Mater. Des. 186 (2020), https://doi.org/10.1016/j.matdes.2019.108199.

[81] J.P. Jyothibasu, R.H. Wang, Y.C. Tien, C.C. Kuo, R.H. Lee, Lignin-derived Quinone redox moieties for bio-based supercapacitors, Polymers 14 (15) (2022), https://doi.org/10.3390/polym14153106.

[82] H. Lv, Y. Yuan, Q. Xu, H. Liu, Y.G. Wang, Y. Xia, Carbon quantum dots anchoring MnO2/graphene aerogel exhibits excellent performance as electrode materials for supercapacitor, J. Power Sources 398 (2018), https://doi.org/10.1016/j.jpowsour.2018.07.059.

[83] J. Zhang, et al., Unveiling of the energy storage mechanisms of multi-modified (Nb2O5@C)/rGO nanoarrays as anode for high voltage supercapacitors with formulated ionic liquid electrolytes, Electrochim. Acta 313 (2019), https://doi.org/10.1016/j.electacta.2019.04.160.

[84] C.F. Liu, Y.C. Liu, T.Y. Yi, C.C. Hu, Carbon materials for high-voltage supercapacitors, Carbon 145 (2019), https://doi.org/10.1016/j.carbon.2018.12.009.

[85] D. Sheberla, J.C. Bachman, J.S. Elias, C.J. Sun, Y. Shao-Horn, M. Dincă, Conductive MOF electrodes for stable supercapacitors with high areal capacitance, Nat. Mater. 16 (2) (2017), https://doi.org/10.1038/nmat4766.

[86] S. Kumar, G. Saeed, L. Zhu, K.N. Hui, N.H. Kim, J.H. Lee, 0D to 3D carbon-based networks combined with pseudocapacitive electrode material for high energy density supercapacitor: a review, Chem. Eng. J. 403 (2021), https://doi.org/10.1016/j.cej.2020.126352.

[87] S.S. Shah, Md A. Aziz, Properties of electrode materials and electrolytes in supercapacitor technology, J. Chem. Environ. 3 (1) (2024), https://doi.org/10.56946/jce.v3i1.309.

[88] Z. Song, Characters of different materials as supercapacitor electrodes, IOP Conf. Ser. Earth Environ. Sci. 813 (1) (2021), https://doi.org/10.1088/1755-1315/813/1/012009.

[89] M.F. El-Kady, Y. Shao, R.B. Kaner, Graphene for batteries, supercapacitors and beyond, Nat. Rev. Mater. 1 (7) (2016), https://doi.org/10.1038/natrevmats.2016.33.

[90] C. Yang, Review of graphene supercapacitors and different modified graphene electrodes, Smart Grid Renew. Energy 12 (1) (2021), https://doi.org/10.4236/sgre.2021.121001.

[91] A. Velasco, et al., Recent trends in graphene supercapacitors: from large area to microsupercapacitors, Sustain. Energy Fuels 5 (5) (2021), https://doi.org/10.1039/d0se01849j.

[92] J. Li, X. Li, D. Xiong, L. Wang, D. Li, Enhanced capacitance of boron-doped graphene aerogels for aqueous symmetric supercapacitors, Appl. Surf. Sci. 475 (2019), https://doi.org/10.1016/j.apsusc.2018.12.152.

[93] X. Wang, C. Lu, H. Peng, X. Zhang, Z. Wang, G. Wang, Efficiently dense hierarchical graphene based aerogel electrode for supercapacitors, J. Power Sources 324 (2016), https://doi.org/10.1016/j.jpowsour.2016.05.085.

[94] Y.B. Pottathara, H.R. Tiyyagura, Z. Ahmad, K.K. Sadasivuni, Graphene based aerogels: fundamentals and applications as supercapacitors, J. Energy Storage 30 (2020), https://doi.org/10.1016/j.est.2020.101549.

[95] P. Qi, H. Zhu, F. Borodich, Q. Peng, A review of the mechanical properties of graphene aerogel materials: experimental measurements and computer simulations, Materials 16 (5) (2023), https://doi.org/10.3390/ma16051800.

[96] J.A. Baimova, S.A. Shcherbinin, Strength and deformation behavior of graphene aerogel of different morphologies, Materials 16 (23) (2023), https://doi.org/10.3390/ma16237388.

[97] J. Mao, J. Iocozzia, J. Huang, K. Meng, Y. Lai, Z. Lin, Graphene aerogels for efficient energy storage and conversion, Energy Environ. Sci. 11 (4) (2018), https://doi.org/10.1039/c7ee03031b.

[98] V.B. Mbayachi, E. Ndayiragije, T. Sammani, S. Taj, E.R. Mbuta, A. Ullah Khan, Graphene synthesis, characterization and its applications: a review, Results Chem. 3 (2021), https://doi.org/10.1016/j.rechem.2021.100163.

[99] M. Saeed, Y. Alshammari, S.A. Majeed, E. Al-Nasrallah, Chemical vapor deposition of graphene—synthesis, characterization, and applications: a review, Molecules 25 (17) (2020), https://doi.org/10.3390/molecules25173856.

[100] D. Wei, et al., Fabrication, structure, performance, and application of graphene-based composite aerogel, Materials 15 (1) (2022), https://doi.org/10.3390/ma15010299.

[101] P. Russo, A. Hu, G. Compagnini, Synthesis, properties and potential applications of porous graphene: a review, Nano-Micro Lett. 5 (4) (2013) 260–273, https://doi.org/10.5101/nml.v5i4.p260-273.

[102] A. Thakur, Graphene aerogel based energy storage materials – a review, Mater. Today Proc. 65 (2022), https://doi.org/10.1016/j.matpr.2022.05.477.

[103] S.-C. Pang, M.A. Anderson, T.W. Chapman, Novel electrode materials for thin-film ultracapacitors: comparison of electrochemical properties of sol-gel-derived and electrodeposited manganese dioxide, J. Electrochem. Soc. 147 (2) (2000), https://doi.org/10.1149/1.1393216.