Advances in biomass-derived carbon composites as electrode materials for supercapacitors

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Abstract. As electrode materials (EMs) for supercapacitors (SCs), biomass-derived carbon composites (BDCC) are frequently used because of their plentiful supply, renewable properties, affordable manufacturing prices, large specific surface area (SSA), and porous structure with straightforward synthesis methods. The performance of SCs can be extremely boosted by BDCC, which has a wide range of potential applications. This paper outlines the advances in synthesis methods and application of BDCC as EMs for SCs and introduces the characteristics of these methods. Thereafter, the advances in biomass-derived carbon combined with carbon nanotubes (CNTs), graphene, and conductive polymers as EMs and the peculiarities and electrochemical properties (SSA, energy density, cycle stability, specific capacitance), as well as some research achievements over the past few years are reviewed. Finally, the future orientations, challenges, and prospects of BDCC as EMs for SCs are discussed.

Keywords: Biomass-derived Carbon, Supercapacitors, Electrode materials, Composites, Synthesis methods.

1. Introduction

Due to the rapid development of the economy and science, the demand for energy has increased significantly, and the problem of energy consumption has aroused great concern around the world. Traditional fossil fuels (oil, coal, natural gas) were the primary energy sources utilized in practically all industries in the past, including transportation, agriculture, and power, and they accounted for at least 80% of all energy used worldwide [1]. However, the unrestrained exploitation and use of fossil energy around the world have led to an increasingly scarce reserve of fossil energy, which will not be able to meet the needs of human use in the future. What's more, the extensive utilization of fossil fuels has resulted in significant environmental pollution, which has seriously harmed the environment where living things exist by producing copious amounts of the greenhouse gas CO_2 and hazardous smoke [2, 3]. The current solution to the issues raised is to develop and utilize renewable energy sources, which contain energy sources other than conventional ones, such as ocean energy, wind energy, solar energy, biomass energy and hydro-energy, etc. They have quickly developed since more academics are focusing on the exploitation and application of renewable energy sources [1]. Renewable energy is unstable and intermittent, and it's unevenly distributed in both time and space [4]. These energy sources fall short of this requirement when it comes to providing electricity continuously. Therefore, the aforementioned issues cannot be resolved simply by creating technologies for the exploitation and application of renewable energy. For renewable energy to gradually replace traditional fossil energy, effectively decrease the use of fossil energy, and alleviate the traditional fossil energy shortage, and in consequence, it's necessary to simultaneously develop new energy storage devices based on renewable energy as well as energy storage devices, such as lithium-ion batteries, Supercapacitors (SCs), fuel cells, and solar cells [5].

SCs, also referred to as electrochemical capacitors, have several advantages over lithium-ion batteries, incorporating high power density, dependable cycling stability, quick charging/discharging

speed, long service life, and wide operating temperature limit [6, 7]. Academics have paid a lot of attention to SCs in recent decades, and excitingly, some of SCs are now commercially available and function well. Although having an order of magnitude less energy density than batteries [8], their numerous advantages make them the most potential energy storage devices. Currently, SCs are employed in many different application, such as those for wearable devices, energy storage systems, power supplies for electric vehicles, and power backups [9]. SCs can be categorized as pseudocapacitors (PCs) and electrochemical double-layer capacitors (EDLCs) depending on how electrons are stored. The EDLCs store energy by electrostatic attraction between electrolyte ions and the porous electrode surface. The energy storage process is a physical process and does not involve chemical reactions, which realize fast charging/discharging [10]. PCs store energy through redox reactions involving transition metal oxides and conductive polymers, and the primary reaction is a reversible Faraday reaction [11]. Thus, although power density of PCs is lower than that of EDLCs, their energy density is higher than EDLCs' [12]. Moreover, since EDLCs and PCs each have advantages and limitations of their own, it's possible to combine them into the new SCs known as "asymmetric SCs" [13]. Asymmetric SCs electrode materials (EMs) differ from EMs of EDLCs and PCs. Asymmetric SCs can perform better by using composites as electrodes owing to the poor specific capacitance of rough carbon materials as the electrodes and the low conductivity of metal oxides and other materials [14]. The same unquestionably applies to PCs and EDLCs. So it can be considered that the EMs determine the performance of SCs. Carbon nanotubes (CNTs), graphene, activated carbon and numerous carbon composites have been explored in depth and used as EMs for SCs [15]. To augment the energy density of SCs, the porosity of the EMs has also been altered by doping with activators [16]. Nevertheless, the complexity of the synthesis process, the difficulty of experimental control and the high cost of the raw materials make it a challenge to obtain idealized EMs.

As a consequence, creating carbon composites that are more affordable and have long-term availability is very essential. Biomass-derived carbon composites (BDCC) are one of the finest possibilities for researching innovative carbon-based materials as EMs for SCs. Biomass raw materials are widely accessible, affordable, and plentiful, and they can be utilized in an eco-friendly method to prepare carbon composites and serve as EMs for SCs [17]. Following a straightforward preparation, biomass raw materials with high specific surface area (SSA), homogeneous pore distribution, and physicochemical stability are used as EMs for SCs. This provides convenient conditions for improving the power density and energy density of SCs. High SSA can make it easier to store more electrons and ions on the surface of electrodes of SCs, and homogeneous pore size distribution is beneficial for ion transport and charge storage [7]. Other components and elements in biomass can be doped as heteroatoms, providing more active sites without additional doping of activators [18, 19]. To expand the diversity of preparation of EMs, several academics have also suggested numerous straightforward and effective biomass-derived carbon synthesis methods, such as self-activation and self-template [20]. BDCC can be derived from a variety of nanostructures with different dimensions, covering 1 D nanofiber structures, 2 D nanosheet layer structures, and 3 D spatial nanostructures [17]. The performance of BDCC as EMs for SCs is further enhanced by using these structures, which have strong structural stability and ionic conductivity. Moreover, recycling biomass waste for the preparation of EMs greatly contributes to environmental protection by preventing environmental contamination brought on by the direct combustion of biomass waste. The use of BDCC as EMs for SCs has been the theme of extensive research in recent years, but there is still more to be done. More opportunities will probably arise from further research in this area. There haven't been as many reviews in this field. Hence, this paper reviews the synthesis methods used to prepare BDCC in recent years, and focuses on their advantages such as their superior high SSA, good electrical conductivity, and well-proportioned pore distribution. Furthermore, a review is done on the qualities and features of BDCC when mixed with CNTs, graphene, conductive polymers. Finally, the prospects of BDCC as EMs for SCs are suggested.

2. Synthesis methods of biomass-derived carbon materials

Biomass resources which include all plants, animals and microorganisms, as well as metabolized or excreted organic matter are renewable organic resources obtained through photosynthesis [21]. Biomass-derived carbon material is a carbon material prepared from biomass, which has the characteristics of general carbon materials, such as excellent chemical stability, outstanding electrical conductivity and low price [22]. The SSA, porosity, and electrochemical properties of biomass-derived carbon materials depend mainly on the activation temperature and heating rate of the biomass precursor, the ratio of precursor to the activator, the synthesis methods, and its properties [23, 24]. Among them, the synthesis methods are very significant and include pyrolysis, hydrothermal carbonization (HTC), template methods, ionothermal carbonization, molten salt carbonization, and physicochemical activation method. Only HTC and template methods are described in this review.

2.1. Hydrothermal carbonization

HTC is a feasible method to convert biomass into functional carbon materials in a closed water environment at low temperatures [25]. The key determinants of the biochar yield, nanostructure, morphology, and surface chemical state are the aqueous solution, temperature, pressure, and time that are applied [25]. The precursor undergoes complicated reactions such as dehydration, polymerization, and aromatization as the reaction proceeds, decomposing into smaller monomers [26]. Under 200 °C, the porosity of biochar rises as the operating temperature rises. As the biochar composition increased and the temperature continued to rise, the prepared porous carbon materials had high SSA and pore volume [27]. Although the standard HTC method can produce porous carbon materials, the SSA and material structural features are constrained, leading to mediocre electrochemical performance. A possible solution is adding additives to the HTC process which can greatly enhance their electrochemical characteristics and offer a solid choice for creating superior SCs. To put it in practical terms, Chen et al. [28] described the fabrication of porous carbon materials by adding citric acid (CA) to help the HTC of bamboo, which considerably boosted the SSA (3132 m^2 g^{-1}) and the specific capacitance (435.5 F g^{-1} at the current density of 0.5 A g^{-1}) of EMs. A similar method was utilized by Susanti et al. [29] to synthesis porous carbon materials. In certain studies, porous carbon materials are prepared utilizing chitosan and diluted acetic acid solutions as hydrothermal solvents [30]. The literature [31] contains a thorough report on the HTC approach.

2.2. Template Methods

In order to prepare porous carbon materials with more uniform porosity and higher SSA, template methods are introduced. With the help of the methods, morphology, structure, and other characteristics of porous carbon materials can be controlled to prepare more attractive carbon materials. Templates for the preparation of porous carbon materials including hard templates and soft templates have been regarded as effective methods for preparing porous carbon materials with controllable porosity and organized morphology [23]. Carbon precursors mixed with hard templates such as $KCl/ZnCl_2$, ZnO nanoparticles, and Na_2SiO_3 are carbonized, and removal of the template leads to porous carbon materials with good electrochemical performance. Xi et al. [32] generated biomass carbon porous materials using alginate as a precursor as well as in-situ generated $Fe(OH)_3$ as a hard template with outstanding electrochemical performance. Its specific capacitance as an EM was 302 F g^{-1} at 0.5 A g^{-1}, and the energy density of a symmetric SC that uses the materials as electrodes is 11.32 W h kg^{-1} at a power density of 250 W kg^{-1}. The capacitance retention after 10000 cycles was 88.39% at 5 A g^{-1}. Qin et al. [33] utilized ZnO nanoparticles as hard templates to synthesize alginate-derived porous carbon with the same excellent electrochemical properties (SSA: 2589 m^2 g^{-1}, specific capacitance: 316 F g^{-1} at 0.5 A g^{-1}, and capacitance retention of 94.4% at 5 A g^{-1} after 5000 cycles), demonstrating the enormous potential of the hard template methods for preparing of porous carbon materials. Moreover, soft templates are thought to provide excellent candidates for the production of ordered porous carbon [34]. Materials that use the soft templates have higher energy

density and more stable cycling than those that use the hard templates. The materials which use soft templates do not require further template removal and are more user-friendly and ecologically friendly. Moreover, they have high specific capacitance. Sun et al. [35] proposed an environmentally friendly and simple synthetic route to prepare 3 D honeycomb-like N/S-codoped hierarchically porous carbon materials from chitosan-protic salt ([Chit][HSO]) using a combination of dual soft templates and solvent-free self-assembly with the specific capacitance of 302 F g^{-1} in KOH electrolyte and the 99% capacity retention after 5000 cycles. The energy density of the SCs using the materials as electrodes is 17.6 Wh kg^{-1} at a power density of 250 W kg^{-1}. Consequently, in the future, soft-template methods will be crucial for preparing porous carbon materials from biomass carbon.

3. Biomass-derived carbon composites as electrode materials for supercapacitors

3.1. Biomass-derived Carbon/CNTs Composites

CNTs are hollow tubes formed by the convolution of single-layer graphene or multilayer graphene. Excellent mechanical qualities like elastic modulus and tensile strength are present in CNTs, along with outstanding thermal properties and a high theoretical current density [36]. Because of these exceptional performances and their unique characteristics, they have attracted a lot of research and application as EMs for SCs. By combining CNTs and biomass carbon, EMs with better SSA and conductivity may be prepared. These EMs for usage in SCs have higher specific capacitance as well as continuous conductive channels for charge transfer. This combination can improve performance. He et al. [37] synthetized a novel porous carbon composites (CGCM@GNS&CNT) using coffee grounds as a 3D carbon skeleton by combining one-dimensional CNTs and two-dimensional graphene sheets through a simple self-assembly synthesis method. The synthesis schematic is demonstrated in Figure 1. Besides, Figure 2 displays the structure diagram for SEM scanning. The SSA and electrical conductivity of the material were extremely enhanced by the CNTs and graphene. According to the findings, the composite has a SSA of 460 m^2 g^{-1}, is interconnected with conducting channels, and contains a lot of heteroatom doping. What's more, the energy density of CGCM@GNS&CNT-based symmetric SC in 1.5 M Na_2SO_4 was 31 μWh cm^{-2} at a power density of 800 μW cm^{-2}, showing that composites made of biomass carbon and CNTs may achieve higher energy densities and powers with promising future applications.

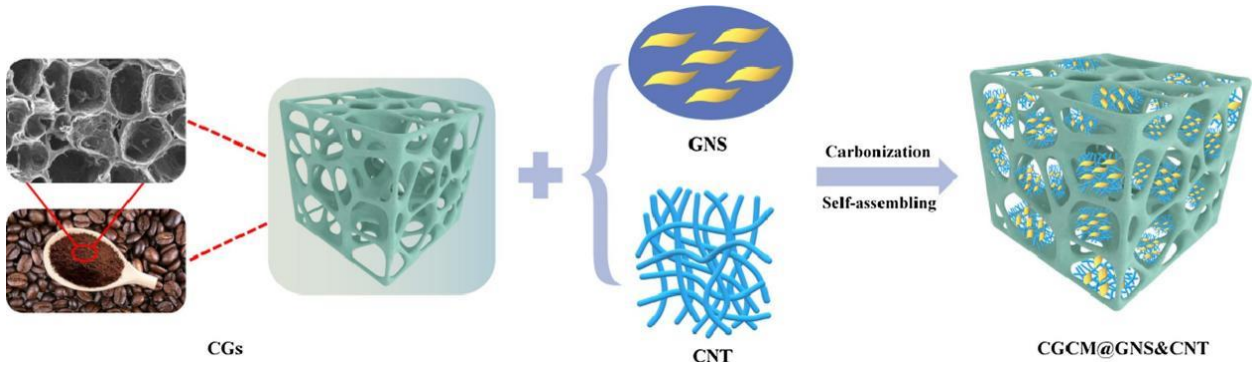

Figure 1. Illustration of the synthesis in a schematic form for CGCM@GNS&CNT. [37].

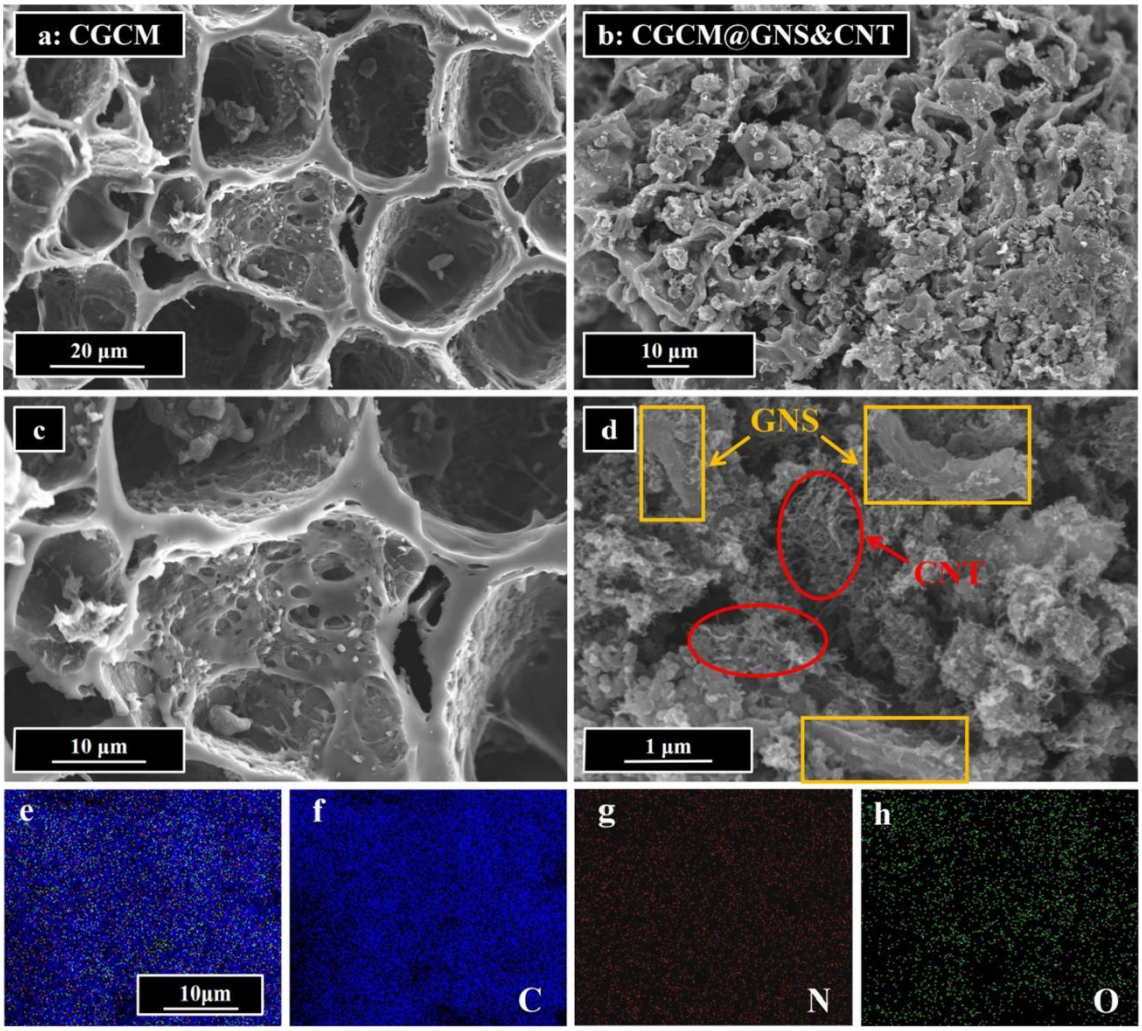

Figure 2. SEM pictures of the CGCM, CGCM@GNS&CNT and element mapping images of CGCM@GNS&CNT are demonstrated in (a, c), (b, d), and (e-h), respectively. [37].

In addition to having a large SSA and energy density, the biomass-derived carbon/CNTs composites as EMs exhibit outstanding cycling stability and rate capability. Vedhanarayanan et al. [38] carbonized a composite (rGO@-C-PANI/CNT-SS) consisting of CNTs, graphene oxide, and polyaniline (PANI) on a stainless steel plate and examined its electrochemical performances as a binder-free and independent electrode. The electrode at 550 °C demonstrated experimentally acquired initial capacitance retention of 78% (current density of 1 mA cm^{-2} to 8 mA cm^{-2}) and capacitance retention of 84% after 1000 charge/discharge cycles. Because of its superior rate capability and cycling stability, this EM can be employed in SCs. Excitingly, CNTs are flexible and have great potential for application as a flexible EM for SCs when combined with biomass-derived carbon. For instance, carboxymethylcellulose-PANI/carbon nanotube (CMC-PANI/CNT) [39] has excellent physical properties and malleability and can be utilized directly as EMs for SCs without binders and additives, and symmetric SC combined with CMC-PANI/CNT exhibits a high energy density (99.89 μW h cm^{-2} at a power density of 400.02 μW cm^{-2}), a high specific capacitance (3106.3 mF cm^{-2} at 5 mA cm^{-2}/348.8 F g^{-1} at 0.5 A g^{-1}) and an splendid cycling stability (capacitance retention of approaching 90% after 5000 cycles). Its specific capacitance, initial capacitance retention, and cycling performance are better than other electrodes, as demonstrated in Figure 3.

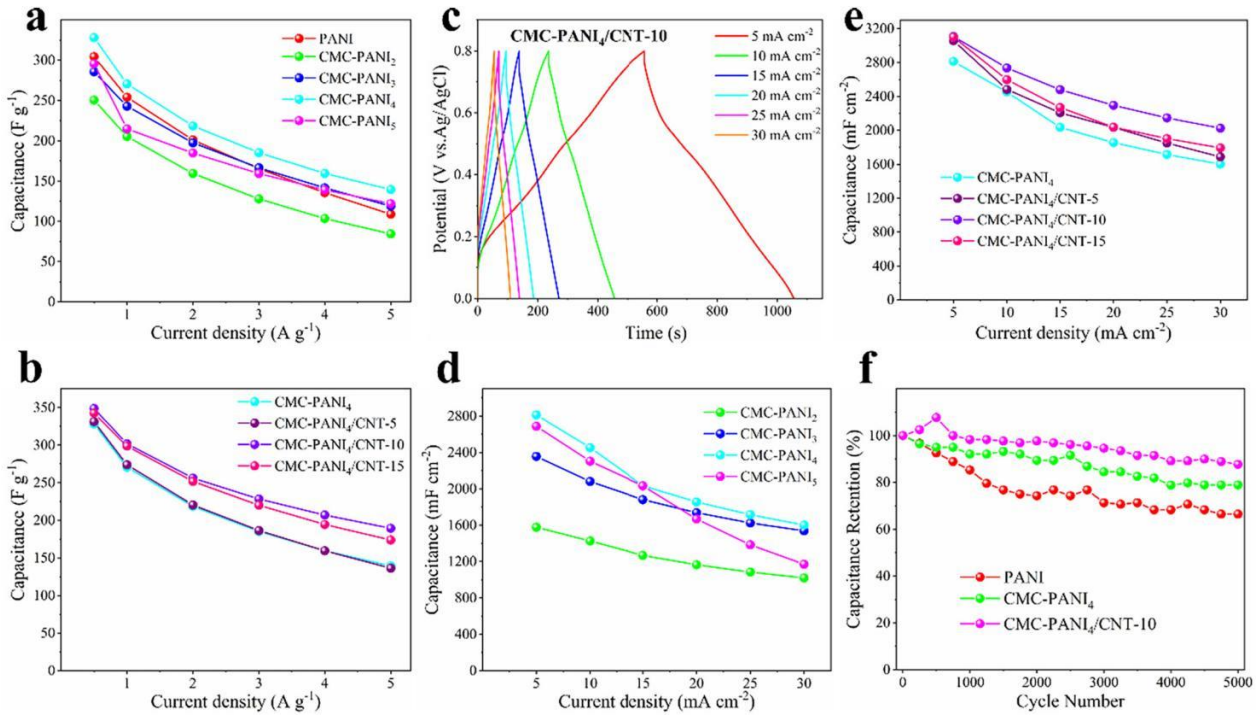

Figure 3. Gravimetric capacitances of the PANI, CMC-PANI, and CMC-PANI4/CNT electrodes are displayed in (a) and (b) based on various current densities. (c) GCD curves of the CMC-PANI4/CNT-10 electrode at various current densities; (d) and (e) estimated areal capacitances of the CMC-PANI and CMC-PANI4/CNT electrodes. (f) The PANI, CMC-PANI4, and CMC-PANI4/CNT-10 electrodes' cycling stability. [39].

The findings of the experiments prove the viability and superiority of composite electrodes consisting of biomass carbon and CNTs, and the flexible electrodes enable higher energy and power densities in smaller SCs. Moreover, the low cost of biomass-derived carbon combined with CNTs to obtain superb mechanical properties and flexibility is enough to be employed as flexible electrodes for SCs and achieve satisfactory performance. In addition to being employed as flexible electrodes for SCs, the material will play a significant role in future wearable electronic devices and other energy storage systems.

3.2. Biomass-derived Carbon\Graphene Composites

Graphene has a special 2D planar structure, which is composed of a hexagonal honeycomb lattice formed by the sp^2 hybridization of carbon atoms. Graphene has ultra-high intrinsic carrier mobility and thermal conductivity [40]. It also offers outstanding micro-strength and elasticity [41]. Moreover, graphene can be doped with heteroatoms to change the electrochemical properties. The doping of heteroatoms will cause graphene to produce pseudocapacitance, further increasing the specific capacitance of the material [42, 43]. Figure 4 depicts the basic synthesis process of graphene-doped nitrogen. Arkhipova et al. [44] prepared mesoporous nitrogen-doped sp^2-hybridized graphene nanoflakes (N-GNFs) by chemical vapor deposition (CVD) utilizing a mixture of acetonitrile and benzene as a precursor, and the nitrogen maximum content was 10.7%. The specific capacitance of N-GNFs as electrodes for EDLC in ionic liquid electrolyte reaches 167 F g^{-1} at a scan rate of 5 mV s^{-1} and the energy density reaches 46.3Wh kg^{-1}. The energy density is still high at 36.1 Wh kg^{-1} even when the power density is as high as 9.7 kW kg^{-1}. It's advantageous to modify its electrochemical performance and broaden its application in the fields of energy storage and energy conversion according to the different types and contents of heteroatoms.

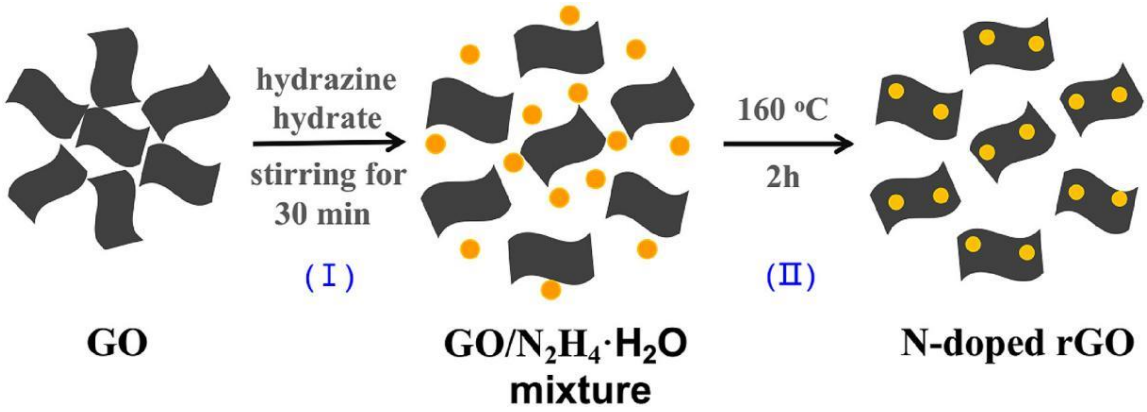

Figure 4. Schematic graph of preparing N-doped graphene material. [45].

3.3. Biomass-derived Carbon/Conductive Polymer Composites

Conductive polymers, commonly including polyethylene (PA), polypyrrole (PPy), PANI, and polythiophene (PTH), are widely used in EMs for SCs due to their excellent electrical conductivity, good flexibility, and low price. Although the materials are deficient in cycling stability, the cycling stability of the material can be improved by utilizing doping methods. In the meantime, charge transfer was facilitated by superior electrical conductivity of carbon, which improved the kinetics of the redox process of hybridization. Wang et al. [46] prepared nitrogen-doped porous carbons (NPC) and NPC/PANI composites using biomass from poplar sawdust. The SSA and specific capacitance of the NPC/PANI composite are as high as 2149 $m^2 \cdot g^{-1}$ and 312 $F \cdot g^{-1}$ at 5 $A \cdot g^{-1}$, respectively, and the energy density of materials measured in a two-electrode system utilizing 6 M KOH as the electrolyte is 15.45 $Wh \cdot kg^{-1}$. Due to the addition of the conductive polymer (PANI) to prepare the composites, these data outperform NPC (a specific capacitance: 252 $F \cdot g^{-1}$, an energy density: 5.66 $WH \cdot kg^{-1}$), demonstrating that biomass carbon doped PANI has promising research value and application potential. Celery was used as a carbon precursor by Du et al [47], who then synthesized nitrogen-doped activated carbon through carbonization, activation, and polymerization. They then created nitrogen-doped graded porous carbon materials utilizing the wet-chemical method for activated carbon/PANI polymerization (carbonization). Interestingly, the material exhibited a high specific capacitance of 402 F g^{-1} at 1 A g^{-1} in 1 M H_2SO_4 electrolyte as an electrode and excellent cycling stability (97% capacitance retention after 10000 CDG cycles). It was proved that biomass carbon combined with conductive polymers performed electrochemically better.

4. Conclusion and Prospects

The exploitation and use of renewable energy sources is an inevitable future trend since existing fossil fuel sources must be replaced to successfully handle the concerns of declining fossil fuel reserves and environmental degradation. Energy storage devices with excellent performance can also be utilized to hasten the advancement of renewable energy technologies while solving defects of renewable energy, such as intermittency, instability, and uneven distribution in space and time. Therefore, SCs stand out in this context, and their many advantages make them the most promising energy storage devices. High specific capacitance, high energy density, and high power density of SCs are primarily influenced by the attributes of the EMs (SSA, porosity, surface properties). To enhance performance and lower the cost of manufacturing SCs, raw materials must be readily available. Biomass-derived carbon, which is easily accessible, renewable, straightforward to synthesize, and has great performance, has been extensively explored in recent years as EMs for SCs to accelerate the development and application of energy storage devices. Using this as a foundation, this study covers the current progress in BDCC research as SCs, discusses the preparation methods for these composites as EMs for SCs, and then gives examples of their effectiveness and superiority. The review of BDCC containing CNTs, graphene, and conductive polymer is covered in the section

that follows, along with a description of their peculiarities and attributes, such as high SSA, symmetrical pore distribution, excellent electrical conductivity, satisfactory cycling stability, high power density, and high energy density. Lastly, a summary of the study on BDCC in SCs is given and the prospects of BDCC in SCs are as follows.

It's crucial to select biomass raw materials with high carbon content, stable element ratios, and ample energy storage to address the issue of unstable performance of EMs and accomplish large-scale manufacturing. Understanding how other elements of biomass affect biomass carbon and using specialized treatment methods to make the pore size distribution of biomass carbon more uniform and precise are the main development goals for the future. This will allow for a significant increase in the power and energy density for SCs with a solid understanding of the chemical and structural peculiarities of biomass, making it easier to synthesize high-performance and affordable BDCC. Although it has been demonstrated that biomass-derived carbon has a lot of potential as EMs for SCs, the way it's prepared is crucial. In the future, it will be necessary to create less complex preparation methods, utilize fewer chemicals, cut production costs, as well as reduce the creation of byproducts and improve the stability of the material. Another development destination is to blend biomass carbon with other materials and employ appropriate preparation methods to combine the benefits of each resource to prepare BDCC that performs better. Biomass raw materials have various heteroatoms, and it's a better choice to improve the electrochemical properties of their heteroatoms without adding additional heteroatomic functional groups, simplifying the preparation process and reducing the cost of production. BDCC utilized as flexible electrodes must be extremely flexible and mechanically robust to satisfy the requirements of actual applications. When twisted or folded, they also need to maintain their structural integrity. It's required to synthesize materials with high flexibility and mechanical strength, like biomass-derived carbon combined with CNTs, which have excellent flexibility and mechanical strength, to provide high performance, low cost, and EMs with high flexibility and mechanical strength. High-performance SCs are being created and manufactured to advance energy storage and renewable energy technologies. What's more, important is to expand the synthesis methods of BDCC to a high industrial level or commercial level, and to find more optimized processes to leapfrog the development of SCs.

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