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Review on Biomass-derived Carbon Materials for Energy Storage Applications

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Abstract: Green and sustainable source of energy is the demand of ever-increasing global crisis. Environmentally friendly carbon materials with special porous structure derived from naturally abundance biomass sources have attracted much interest. Due to unique porous structure, high surface area and conductivity, the biomass-derived carbon materials are demonstrated as promising electrode material for clean energy. Recently, there is huge interest in the development of heteroatoms doped carbon material derived from biomass sources that showed excellent electrochemical performance. In this review, we focused current development in the preparation of activated porous carbon materials from environmentally friendly and naturally abundance biomass and their characterization technique. In addition, how the activated porous carbon materials work as an electrode material in supercapacitor applications are the main focus of this review.

Keywords: biomass; carbon material; supercapacitor; electrode material; energy storage

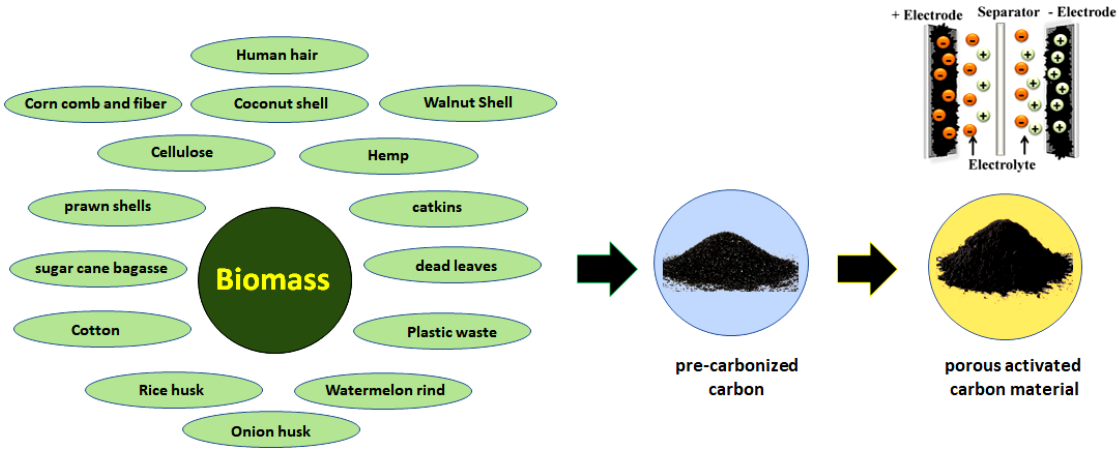
1. Introduction

In recent years, with the exhausting energy and polluting environment, energy is becoming an important factor to restrict development of economy.[1] However, irreplaceable fossil fuels are the most consumed one for filling the energy demands.[2] To fulfil the needs of the energy consumption, a green energy source that are clean and renewable energy sources (like wind, solar, and tide) are focused by researchers.[3] However, the drawback of that power acquisition is mainly intermittent need to be settled.[4] In addition to the increasing of portable and miniaturized electronic equipment, means efficient electrical energy storage materials and technology should be come out.[5] Electrochemical capacitors (ECs, also known as ultracapacitors or supercapacitors), are one of the most promising energy storage devices. In recent years, they have been drawing increasing attention because of their excellent cyclability, high power density, and high charge and discharge rate. Immense numbers of biomass derived electrode materials are developed for the energy storage application.[6]

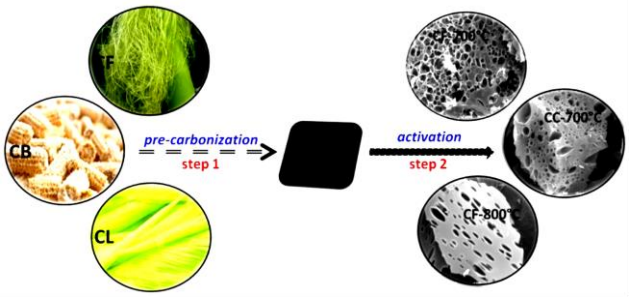
In this review, biomass derived activated carbons are explored as an effective electrode material for the energy storage applications. Part of this review focuses on the preparation method and the characterization techniques if the biomass derived activated carbon materials.

2. Biomass sources

The biomass-derived activated carbon possesses this interconnected, multi-channelled and porous structure, which is needed for designing better supercapacitors. So far, immense number of biomass sources is utilized for the preparation of porous carbon materials. A wide variety of raw materials including corncobs,[7] tea waste,[8] sugarcane bagasse,[9] rice husk,[10] peanut shell,[11] onion husk,[12] olive pits,[13] pinecones,[14] watermelon rind,[15] almond shell,[16] coconut shell,[17] banana peel,[18] Neem and Ashoka leaves,[19] walnut shell,[20] areca fibres,[21] algae,[22] catkins,[23] rice,[24] orange peel,[25] camellia pollen,[26] rice stem,[27] sunflower stalk,[28] tamarind seed coat,[29] almonds,[30] Jujun grass,[31] etc. are already used as precursors in the literature. Recently, human hair, hemp, cotton, dead leaves and so on are utilized for the preparation of heteroatoms (N, O and/or S) doped porous activated carbon materials. In fact, heteroatoms in the carbon matrix improve the wettability and electron transfer in electrolyte. Scheme 1 shows the preparation of biomass-derived activated porous carbon materials, in which the most widely used biomass sources are mentioned. Recently, there are several sea-food based sources are also considered to prepare the carbon materials with highly unique porous electrode materials.



Scheme 1. Biomass-derived activated porous carbon materials.



Scheme 2. Two-step preparation of three-dimensional cheese-like carbon nanoarchitecture with tremendous surface area and pore construction from corn comb, fibres and leaves porous carbon materials.[34]

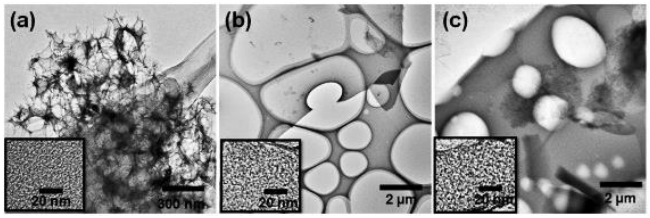


Fig. 1. HR-TEM images of (a) CF-700°C, (b) CL-800°C and (c) CC-700°C (inset: magnified HRTEM images show the surface pores).[34]

3. Carbon Materials from Biomass: Preparation and Characterization

The preparation of biomass-derived porous activated carbon involves two main steps. In the first step, pre-carbonization of biomass precursor is performed *via* any one technique i.e., either through pyrolysis or hydrothermal pre-carbonization.[32] Pre-carbonization or stabilization involves the decomposition of the organic materials at elevated temperatures (most often 300°C-500°C) under inter or air atmosphere at low heating rate. However, the hydrothermal carbonization involves the thermochemical treatment of the material at low temperature (120°C-250°C) in pressurized aqueous condition. The second step is the most important process involves the activation of the carbonaceous materials by increasing their high specific surface area and developing well defined hierarchical porous network. The second and the activation process involves both the chemical and physical activation and helps to achieve the carbonaceous materials with desired porous properties (micro, meso- and macropores and their uniform distribution).[33] Second step involves high temperature carbonization at elevated temperatures (700°C-1200°C). Alkali such as NaOH or KOH, and metal salts are often used for the activation of such carbonaceous materials. Recently, due to green and rapid activation process, several physicochemical and microwave induced processes have gained much attention as an alternative activation process.

Gopiraman et al,[34] prepared three-dimensional cheese-like carbon nanoarchitecture with tremendous surface area and pore construction from corn comb, fibres and leaves, and used it as superior electrode materials. The common two step (stabilization and carbonization) activation process by using NaOH was opted for achieving the three-dimensional cheese-like carbon nanoarchitecture. They noticed an interesting morphology of the carbon materials with an exciting 2D and 3D nanoarchitectures. The obtained carbon materials showed excellent physicochemical properties. They varied the activation temperature (700°C, 800°C and 900°C) to obtain the activated carbon materials. The materials activated at 900°C showed better electrochemical performance when compare to low temperature activation. Scheme 2 shows the two-step preparation of 3D cheese-like carbon nanoarchitecture -with tremendous surface area and pore construction from corn comb, fibres and leaves porous carbon materials. Well-developed 2D and 3D nanoarchitectures are confirmed by the HR-TEM images as shown in Fig. 1.

Qian et al.,[35] utilized heteroatom doped porous carbon flakes via carbonization of Chinese human hair fibers and employed for high-performance supercapacitor electrode materials. KOH was used as an activating agent, and the two-step preparation method was adopted for the preparation of the heteroatom doped porous carbon flakes. Similarly, Gopiraman et al.[36] prepared heteroatom-rich hierarchically porous carbon nanosheets derived from human hair for catalytic applications.

Mi et al.,[37] prepared porous carbons with a tunable micro/mesopore ratio by using coconut shells. A one-step thermal treatment, i.e., combined pyrolysis and steam activation process, was performed by heating 3 g of the raw coconut shells under N_2

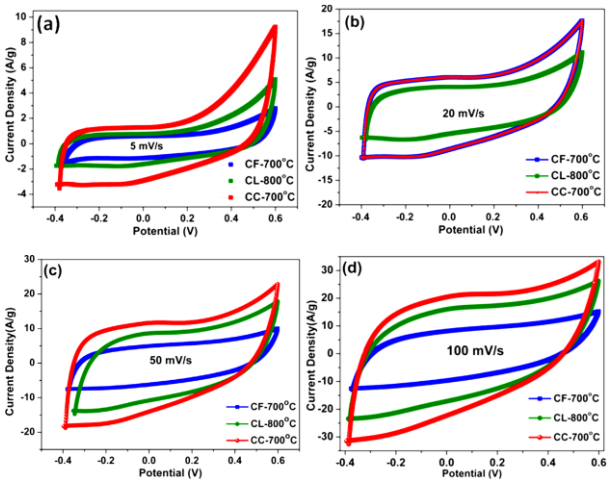


Fig. 2. Typical CV curves of CF-700◦C, CL-800◦C and CC-700◦C at different scan rates (5, 20, 50 and 100 mV/s).[34]

flow at a rate of 3°C min^{-1} up to 400°C, maintained for 1 h, heated at a rate of 5°C min^{-1} up to the set temperature (750, 800, or 850°C).

Peanut shells were used to prepare activated carbon by combining hydrothermal and chemical activation process. CO_2 and $ZnCl_2$ are used for activating the carbon. The process namely hydrothermal pre-treatment followed by activation is followed for the preparation of carbon.[38]

Interconnected carbon nanosheets were derived from hemp by a simple two-step process. After stabilization, the resultant biochar and KOH were thoroughly ground in an agate mortar in a 1:1 mass ratio, and then the mixture was heated at 700–800 °C (3°C min^{-1}) for 1 h under Air flow. After that, the activated samples were thoroughly washed with 10wt% HCl and distilled water and dried in an oven at 100°C for 12 h to obtain the interconnected carbon nanosheets.[39] Sponge-like hierarchical porous structure was prepared by Zhang and co-workers.[40] Lian et al.,[41] utilized banana peel for preparing carbon materials for supercapacitor applications.

4. Carbon Electrode Materials in Energy Storage

Activated porous carbon materials derived from biomass have attracted huge attention as an electrode material in energy storage applications. It is divided into three main categories depending upon the charge storage mechanism, (1) electric double layer capacitors that store the charge electrostatically by adsorption of ions at the surface of the electrode, (2) pseudocapacitor, which stores the energy electrochemically by rapid surface-controlled redox reactions, and (3) hybrid supercapacitor combines capacitive type nature with faradic type to achieve the higher energy density along with its power density.

The corn-comb derived exciting 2D and 3D carbon nanoarchitectures with excellent physicochemical properties were successfully derived from biowaste materials such as corn cob, corn leaves and corn fibers by Gopiraman et al. The carbon material showed specific capacitance of 220-575 F/g. The specific capacitance exhibited by corn comb (575 F/g) is the highest value by the biomass derived activated carbons in aqueous electrolytes to date. The carbon showed 375 F/g even after 20,000 cycles. Fig. 2 shows typical CV curves of CF-700◦C, CL-800°C and CC-700°C at different scan rates (5, 20, 50 and 100 mV/s). Fig. 3 shows the Nyquist plots, galvanostatic charge-discharge curves at different current densities, cycling stability of carbon materials after 3000 cycles, and cycling stability of and retention rate of the carbon after 20,000cycles, Galvanostatic charge-discharge curve and schematic illustration shows the penetration of ions into the pore.

The heteroatom doped porous carbon flakes synthesized via carbonization of human hair by Qian et al., exhibited high charge storage capacity with a specific capacitance of 340 F g^{-1} in 6 M KOH at a current density of 1 A g^{-1} and good stability over 20 000 cycles. They found that the high supercapacitor performance is mainly due to the presence of micro/microporosity combined with high effective surface area and heteroatom doping effects, combining double layer

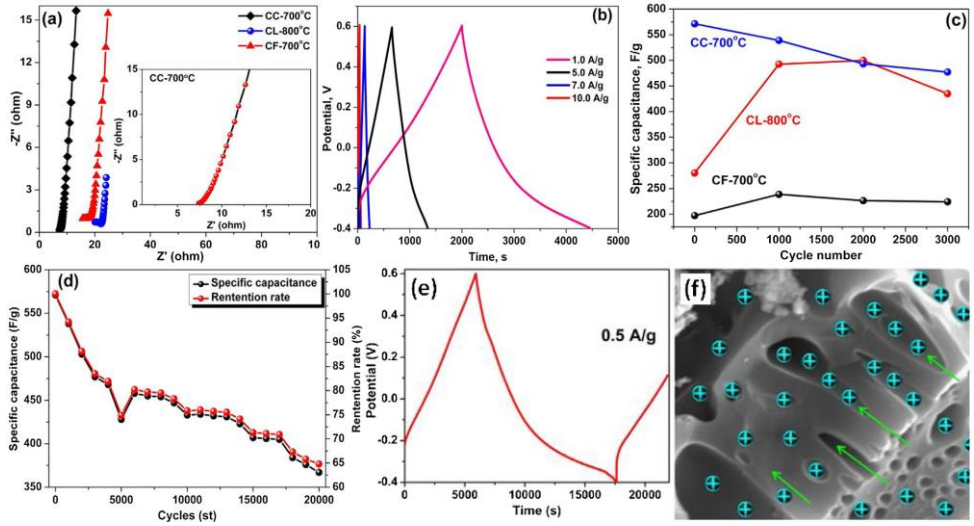


Fig. 3. (a) Nyquist plots of HPCNs, the inset shows the magnified view of the high-frequency region, (b) galvanostatic charge-discharge curves of HPCNs at different current densities (1–10 A g^{-1}), (c) cycling stability of CF-700°C, CL-800°C and CC-700°C after 3000 cycles, and (d) cycling stability of and retention rate of CC-700°C after 20,000 cycles, (e) Galvanostatic charge-discharge curve of CC-700°C at 0.5 A g^{-1}, and (f) schematic illustration shows the penetration of ions into the pore.[34]

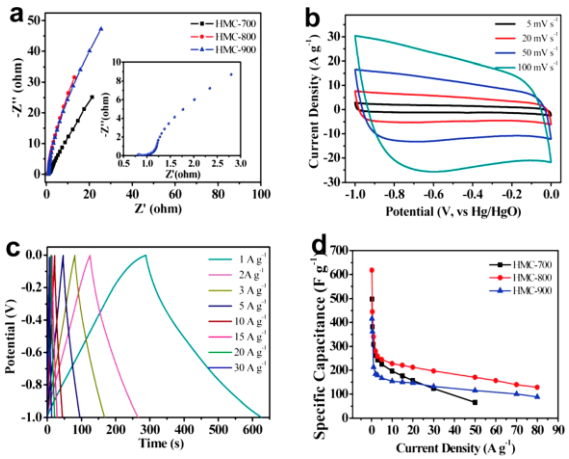


Fig. 4. Electrochemical performance characteristics measured in three-electrode system in the 6 M KOH electrolyte. (a) Electrochemical impedance spectra (inset: magnified 0.5–3 U region) under the influence of an AC voltage of 5 mV. (b) Cyclic voltammograms of HMC-800 at different scan rates. (c) Charge–discharge curves of HMC-800 at different current densities. (d) Specific capacitances of HMC-700, HMC-800, HMC-900 at different current densities.[35]

and Faradaic contributions. Fig. 4 shows the electrochemical performance characteristics measured in three-electrode system in the 6 M KOH electrolyte. (a) Electrochemical impedance spectra (inset: magnified 0.5–3 U region) under the influence of an AC voltage of 5 mV. (b) Cyclic voltammograms of HMC-800 at different scan rates. (c) Charge–discharge curves of HMC-800 at different current densities. (d) Specific capacitances of HMC-700, HMC-800, HMC-900 at different current densities.[35]

Ojha et al.,[42] used various natural sources like sugar, rice husk and jute to obtain graphene-like activated and non-activated carbon nanostructures. They found that the activated carbon nanostructures exhibit higher specific capacitance compared to that of non-activated carbons (non-Ac sugar). The activated carbon (Ac-jute) exhibits maximum specific capacitance of 476 F/g at an applied current density of 0.2 A/g which is much higher than that of graphene oxide (GO).

Ruan and co-workers[43] prepared a low-cost and high-performance carbon material for supercapacitors is fabricated via a simple yet versatile strategy using a renewable natural resource: bean dregs. They concluded that the carbon material has superior capacitive performance, including high specific capacitance, impressive rate performance, and excellent cycle stability.

5. Conclusions

In this review, we summarized the current developments in the preparation of activated porous carbon materials from environmentally friendly and naturally abundance biomass. The physicochemical properties of the carbon materials and their characterization techniques are also discussed. High surface area and the importance of heteroatoms present in the carbon matrix, and the function of interconnected porous structure are well discussed.

Conflicts of Interest

The authors declare no conflict of interest.

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