



Fish gill-derived activated carbon for supercapacitor application



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ABSTRACT

Fish gill-derived porous activated carbon (FGAC) has been successfully prepared by simultaneous carbonization and activation. The FGAC composed of cross-linked thin carbon nanosheets reveals large specific surface area, wide-range hierarchical porous structure and appropriate contents of oxygen and nitrogen functional groups. As a supercapacitor electrode material, the FGAC shows high specific capacitance of 334 F g⁻¹ at 2 A g⁻¹ in 6 M KOH, good electrochemical stability and excellent rate capability (only 7% capacitance fading when the current density is increased by 20 times). These attractive electrochemical performances are ascribed to the multiple synergistic effects of the structure and chemistry of the FGAC, which can not only facilitate ion diffusion, transport and adsorption, but also increase surface area for charge accumulation.

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1. Introduction

Supercapacitor, as a typical electrical energy storage device, has attracted tremendous attention due to the advantages of high power density, long cycle life, rapid charging-discharging rate and short charging period. Activated carbons (ACs) are the most widely adopted electrode materials because of their high specific surface area, good electronic conductivity and excellent chemical stability [1–3]. Traditionally, the precursors of ACs mainly involve the petroleum, coal and their derivatives, which are expensive and non-renewable. Considering the scalable and sustainable applications, the development of carbon materials from low-cost and renewable resources is highly desirable [4,5]. In recent years, a wide variety of biomass or bio-waste materials, such as willow catkins [6], bagasse [7], corncobs [8], hemp [9], bacteria [10], fungi [11], fish scale [12], animal's bone and feather [13,14], have been promoted as new potential precursors or templates to prepare carbonaceous materials for high-performance supercapacitor applications.

Gill, the primary site of aquatic respiration for the majority of fish species, has a high surface area enhancing gas exchange

between fish's blood and environment. In teleosts, gill is essentially composed of arch, filament and lamellae [15,16]. Gill filaments radiate off a gill arch, and leaflike lamellae are evenly distributed along the filament's length. These structure characteristics of the gill make it a promising but unexplored precursor to synthesize porous carbon. First, fish gill has a hierarchical structure with high surface area, which can be retained during carbonization and activation processes. Second, fish gill is an organic and mineral matrix [16]. The organic component can act as carbon precursor. Meanwhile, the mineral phase can act as natural template for the formation of a porous structure, which can be easily removed after the preparation process. In addition, fish gill, as a kind of food byproducts, is very cheap and environment friendly with abundant production. Converting fish gill into porous carbon as electrode materials will be an economical and environment friendly route.

In this work, fish gill was used as the precursor to prepare porous activated carbon (FGAC) by a process for the first time. Unlike conventional activation, typically performed with already carbonized carbons, this treatment, simultaneous carbonization and activation, to prepare 3D hierarchical porous carbons is facile, cost-effective and easy to apply in large-scale production [17]. The obtained FGAC has a large specific surface area with three-dimensional interconnected large pores in micrometer size and abundant micropores and mesopores, and contains high levels of oxygen and nitrogen functional groups. Such characteristics are expected to make the FGAC display remarkable electrochemical properties as an electrode material for supercapacitors.

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2. Experimental

2.1. Materials synthesis and characterization

The fish gill used in the experiment was collected from food market. First, the fish gill was washed with deionized water to remove adherent impurities and dried at 100 °C for 48 h. Then, the clean and dry fish gill was pre-carbonized at 300 °C for 3 h under air atmosphere. The pre-carbonized sample was ground and mixed with KOH at a mass ratio of 1:1, followed by carbonization and activation at 800 °C for 1 h under Ar atmosphere. Finally, the obtained product was washed with 5 M HCl solution and hot deionized water until the pH value of filtrate became about 7, and then dried in vacuum at 80 °C for 24 h.

The morphology and structure of the obtained FGAC were characterized by scanning electron microscopy (SEM, Hitachi SU8010), transmission electron microscopy (TEM, FEI Tecnai G2 F20), X-ray diffraction (XRD, Bruker D8 Advance with Cu K_α radiation) and Raman spectroscopy (HORIBA Jobin Yvon XploRA PLUS, λ = 532 nm). The surface area and porous texture were determined by nitrogen adsorption-desorption measurement (Quantachrome Quadrasorb SI). The specific surface area (S_{BET}) was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution (PSD) was analyzed using the density functional theory (DFT) method from the adsorption branch. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD with Al-K_α radiation.

2.2. Electrochemical measurement

All electrochemical experiments were conducted using a three-electrode system in 6 M KOH aqueous solution with FGAC electrode, Pt foil and Hg/HgO electrode as the working, counter and reference electrodes, respectively (illustrated in Fig. 1). The working electrode was prepared as reference [18]. The weight ratio of FGAC, acetylene black and polytetrafluoroethylene (PTFE) was 80:15:5. The mass loading density of each working electrode was about 5 mg cm⁻². The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on a CHI 660D electrochemical workstation. The galvanostatic charge-discharge tests (GCD) were performed on a LAND CT2001A instrument. Three replicate measurements were performed for each type of electrode.

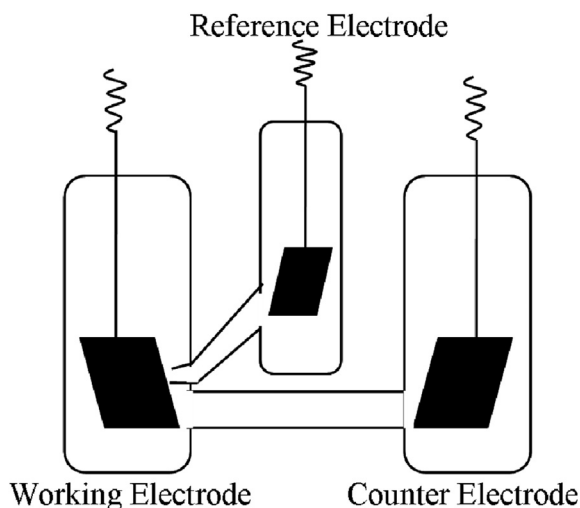


Fig. 1. Schematic illustration of the three-electrode system.

3. Results and discussion

The morphology and microstructure of the as-prepared FGAC were characterized by SEM and TEM. From the SEM image (Fig. 2a), it can be seen that the FGAC shows well-developed pore structure with three-dimensional interconnected micrometer-level large pores. A closer observation of the wall of the large pores reveals the secondary structure which is composed of cross-linked thin carbon nanosheets (Fig. 2b). The TEM image shown in Fig. 2c provides more information about the cross-linked sheet-like structure of the FGAC, in which nanosheets are intercalated with disorder. The thickness of each carbon nanosheet is in the range of 10–20 nm. The high resolution TEM (Fig. 2d) presents that the carbon sheets have abundant micropores. No evident lattice fringe can be observed. The weak and highly diffusive ring pattern of selected area electron diffraction (SAED) (inset in Fig. 2d) also confirms the amorphous feature of the FGAC. Moreover, the structure of the FGAC is further studied by XRD and Raman spectroscopy. In the XRD pattern (Fig. 3a), there are two broad diffraction peaks. The peak centered at 28° corresponds to the (002) diffraction of turbostratic carbon, indicating the amorphous nature and low graphitization degree. The other peak centered at 43° can be indexed as the (100) diffraction of a graphitic-type carbon with disordered or amorphous nature [6,19], which are well in accordance with the TEM analysis. In addition, it is worth noting that the intensity of the scattering peak increases at low angle, which suggests the existence of abundant micropores in the FGAC [7,20]. Fig. 3b shows the Raman spectroscopy of the FGAC. Two distinct peaks located at around 1334 and 1585 cm⁻¹ correspond to the disorder-introduced D-band and graphitic lattice vibrational G-band of carbon materials, respectively [9]. The intensity ratio of the two bands (I_D/I_G) can reflect the disordered or graphitization degree of carbon materials. The relatively high value of I_D/I_G (about 0.94) demonstrates the high disordered or low graphitization degree of the FGAC.

To investigate the porous structure, the N₂ adsorption-desorption isotherm of the FGAC was measured. As shown in Fig. 4a, the FGAC exhibits a combined type I/IV isotherm according to IUPAC classification, suggesting the existence of pores ranging from micropores to macropores. Specifically, the steep uptake at low relative pressure (P/P₀) demonstrates the formation of micropores in large quantities. The following slope and the hysteresis loop at P/P₀ from 0.4 to 1.0 indicate well-developed mesoporous structure and the existence of macroporosity. The BET specific surface area and total pore volume at P/P₀ = 0.989 are up to 2082 m² g⁻¹ and 1.63 cm³ g⁻¹, respectively. The pore size distribution analyzed using the DFT method is given in Fig. 4b. It can be seen that the FGAC has a hierarchical pore structure with detectable pore sizes from 1.2 to 10 nm. The micropores with two peaks at 1.5 and 1.8 nm are generated during KOH activation process [20,21]. KOH activation involves the main reaction between KOH and C (6KOH + 2C → 2K + 3H₂ + 2K₂CO₃), followed by decomposition of K₂CO₃ and/or reaction of K/K₂CO₃/CO₂ simultaneously, which can generate abundant pores for achieving high surface area carbons [14,17]. The mesopores with a maximum peak at about 2.3 nm might be formed by the removal of the apatite-based inorganic composition, which acts as the natural template. On the basis of the above results, it can be concluded that the FGAC has a three-dimensionally hierarchical pore structure with interconnected large pores in micrometer size and abundant micropores and mesopores. Such a porous structure is expected to improve electrochemical energy storage because the large pores and mesopores are helpful for ion diffusion, and the micropores are efficient to accumulate charge.

X-ray photoelectron spectrum (XPS) was used to confirm the

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