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Heteroatom doped porous carbon sheets derived from protein-rich wheat gluten for supercapacitors: The synergistic effect of pore properties and heteroatom on the electrochemical performance in different electrolytes

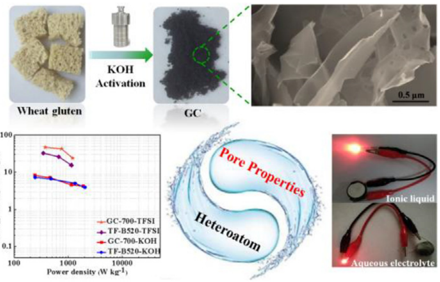
Shao-Wen Xu[a], Yong-Qing Zhao[a,*], Yi-Xuan Xu[a], Qing-Han Chen[a], Guo-Qing Zhang[b], Qian-Qian Xu[a], Dan-Dan Zhao[a], Xuan Zhang[c], Cai-Ling Xu[a]

[a] *State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Laboratory of Special Function Materials and Structure Design of the Ministry of Education, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China*
[b] *Chongqing Key Laboratory of Inorganic Special Functional Materials, Yangtze Normal University, Chongqing, 408100, China*
[c] *Department of Materials Engineering, KU Leuven, Leuven, 3001, Belgium*

HIGHLIGHTS

- GC possesses high SSA, porous sheet-like structure, and abundant O and N groups.
- GC exhibits high capacitance, excellent rate performance, and long-term stability.
- In aqueous and ionic liquid electrolytes ion sieving effect affects performance.
- Pore properties determine the performance of GC in ionic liquid electrolytes.
- Synergistic effect of pore properties and heteroatom exists in aqueous electrolyte.

GRAPHICAL ABSTRACT



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ABSTRACT

Developing high-performance biomass-derived carbons and understanding the relationship between their structures and performance are highly desired for carbon-based supercapacitors. Herein, a wheat gluten-derived carbon with porous sheet-like structure, high specific surface area, and oxygen- and nitrogen-based heteroatom groups is fabricated. Their pore properties and heteroatom doping amount are adjusted through controlling the activation temperature. In aqueous electrolyte there is a significant synergistic effect between pore properties and heteroatom amount on the electrochemical performance of the gluten-derived carbon; while their performance is mainly determined by their pore properties in ionic liquid electrolytes. Besides, whatever in the aqueous and ionic liquid electrolytes ion sieving effect also affects their capacitive performance. The gluten-derived carbon prepared at 700 °C with reasonable pore properties and heteroatom amount shows the highest specific capacitance of 350 $F\,g^{-1}$ at 0.5 $A\,g^{-1}$ in 6 $mol\,L^{-1}$ KOH. But the gluten-derived carbon prepared at 800 °C with the highest specific surface area of 2724 $m^2\,g^{-1}$ possesses a high specific capacitance of 197 $F\,g^{-1}$ at 0.25 $A\,g^{-1}$ in the ionic liquid electrolyte. This work can provide a guideline for optimizing the performance of biomass-derived carbons through matching their pore properties and heteroatom with different electrolytes.

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[*] Corresponding author.
E-mail address: yqzhao@lzu.edu.cn (Y.-Q. Zhao).

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1. Introduction

Owing to high power density, ultra-fast charge – discharge rate, and long cycle life, carbon-based supercapacitors have attracted significant attention in the field of energy storage [1–8]. According to charge storage mechanism, supercapacitors based on pure carbonaceous electrode materials are called electrochemical double-layer capacitors (EDLCs), which store energy through electrostatic charge accumulation at electrode/electrolyte interfaces [9]. Because of this characteristic, they have better rate capability and cycling performance than batteries. Nevertheless, the energy density of EDLCs is far lower than that of batteries, which seriously prevents them from satisfying the ever-growing energy demands in modern electronics, especially for portable devices and electric vehicles [4,10]. To date, tremendous research efforts have been dedicated to increasing the energy density and reducing the fabrication costs of EDLCs without sacrificing their power density and cycle life. In addition to increasing the operating voltage to elevate the energy density of EDLCs, an alternative and effective pathway is promoting the electrochemical performance of carbon materials [2–8,11]. As for the latter, various strategies have been successfully performed, such as increasing the specific surface area (SSA) and optimizing the pore size along with its distribution of carbon materials [4,8,12,13]; doping carbon materials with heteroatoms (including N, O, B, P, and S) [2,4,8,14]; developing new carbon materials with well-defined structures and functions [6,8]. Obviously, the pursuit of high-performance carbon materials is highly desirable.

In recent years, biomass-derived carbon has been paid considerable attention in the energy conversion and storage areas [15–17]. Due to tunable pore structures with high SSA and heteroatom doping effect, this specific carbon exhibits great potential as electrode material for high-performance carbon-based supercapacitors [16–46]. For example, Jin et al. used silk proteins as carbon source to fabricate microporous carbon nanoplates containing numerous heteroatoms (H-CMNs) [18]. Because of microporous structure with high SSA ($2557\,m^2\,g^{-1}$) and abundant N and O functional groups, the H-CMNs display a high specific capacitance of $264\,F\,g^{-1}$ at $0.1\,A\,g^{-1}$ in $1\,M\,H_2SO_4$ electrolyte. In particular, the energy density ($133\,Wh\,kg^{-1}$) of supercapacitor device based on the H-CMNs with $BMIMBF_4$/AN electrolyte is comparable to that of Li-ion battery, and the power density ($217\,kW\,kg^{-1}$) is several orders higher than that of Li-ion battery. Mitlin et al. prepared an egg white-derived porous carbon with hierarchical mesoporosity, high SSA, and a high N-content of 10%, which exhibits an exceptionally high specific capacitance of $390\,F\,g^{-1}$ at $0.25\,A\,g^{-1}$ in $1\,M\,H_2SO_4$ electrolyte and good cycle stability with less than 7% capacitance loss after 10000 cycles [19]. Besides, various biomass, such as human hair, wheat flour, pine needles, and bacterial-cellulose, etc., has also been selected as carbon precursors, and these biomass derived carbons also show an excellent electrochemical capacitive performance for supercapacitors [20–46]. On the other hand, compared with other carbon materials, such as carbon nanotubes, graphene, and carbon onions, etc., precursors with facile processability, easier accessibility, and renewability result in lower cost of biomass-derived carbon, which perfectly meets the need of a sustainable future for carbon materials and broad range of applications of supercapacitors [16,17]. Therefore, developing high-performance biomass-derived carbon is quite promising and highly urgent for carbon-based supercapacitors.

Wheat gluten is a complex mixture of hundreds of proteins found in wheat and related grains [47–49]. It can be readily obtained by washing wheat dough with running water to remove starch and water-soluble constituents [48]. Depending on the thoroughness of washing, the gluten comprises 75–85% protein and 5–10% lipids on a dry weight basis along with starch and other carbonhydrates being the major residue [49]. Wheat gluten prevails in food (such as breads, noodles, pasta, and cookies) and non-food industries including its use to produce cosmetics, detergent, and bioplastic, etc. [50–52]. Recently, protein-based biomass, such as silk protein [18], egg white [19], and human hair [20], has exhibited exciting performance in preparing superior carbon materials for supercapacitors. However, wheat gluten is not yet considered as carbon source to prepare biomass-derived carbon materials for supercapacitors application. More importantly, although the pore properties and heteroatom show a dominant influence on the electrochemical performance of biomass-derived carbon materials, the synergistic effect of the both is still needed to be further revealed, especially in the different electrolytes. This is a key issue for the design of the pore properties and heteroatom aims to match these factors with different electrolytes to optimize the electrochemical performance of biomass derived carbons. In this work, a novel wheat gluten-derived carbon (GC) has been fabricated through a hydrothermal carbonization and KOH activation strategy. The GC possesses porous sheet-like structure, high SSA, and numerous heteroatom (O and N) groups. Due to these beneficial properties, as supercapacitors electrode material the GC exhibits high capacitance, excellent rate performance, and outstanding long-term stability. For example, the specific capacitance (C_s) of GC-700 is as high as $350\,F\,g^{-1}$ at current density of $0.5\,A\,g^{-1}$ in $6\,mol\,L^{-1}$ KOH electrolyte, and can maintain at $270\,F\,g^{-1}$ even at $30\,A\,g^{-1}$. After 10000 charge – discharge cycles at $5\,A\,g^{-1}$, the C_s of GC-700 is not decayed. The energy density of the GC supercapacitor is as high as $47\,Wh\,kg^{-1}$ at $374\,W\,kg^{-1}$ in an ionic liquid (EMIMTFSI) electrolyte. Furthermore, the synergetic effect between the pore properties and heteroatom on the electrochemical performance of GC was investigated in aqueous and ionic liquid electrolytes.

2. Experimental

2.1. Materials

Wheat gluten was purchased from local market, which is usually fabricated by thoroughly washing wheat dough with running water, and then steamed by boiling water for half an hour to be edible. After freeze drying, the raw samples were used without further treatment. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI, 99%, J&K Scientific) and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$, 99%, J&K Scientific) were both used as purchased. For purpose of comparison, a commercial activated carbon (TF-B520) was purchased from Shanghai Carbosino Material Co., Ltd., China.

2.2. Preparation of wheat gluten-derived carbon (GC)

GC was prepared through hydrothermal carbonization and potassium hydroxide (KOH) activation strategy. In a typical procedure, 6 g wheat gluten and 60 ml distilled water were placed in a 100 ml Teflon lined stainless autoclave. The autoclave was heated up to 200 °C and held for 12 h, then naturally cooled to room temperature. The solid product (hydrochar) was obtained by filtration and washed with distilled water many times, and then dried at 120 °C overnight. Subsequently, the hydrochar was carefully mixed with KOH at a weight ratio of 1:3 (hydrochar/KOH) in an agate mortar. The mixture was placed in a horizontal furnace and heated to target temperature at a heating rate of $5\,°C\,min^{-1}$ in nitrogen gas flow, and the temperature was maintained for 1 h. The activated hydrochar was first thoroughly washed with $1\,mol\,L^{-1}$ HCl to remove inorganic salts and then with distilled water for neutralization. After dried at 120 °C overnight the GC was obtained. The GC prepared at different activation temperature were denoted as GC-600 (600 °C), GC-700 (700 °C) and GC-800 (800 °C), respectively.

2.3. Material characterization

Field-emission scanning electron microscopy (FESEM) images were obtained by a Hitachi S4800 microscope. Transmission electron microscopy (TEM) and Scanning transmission electron microscopy