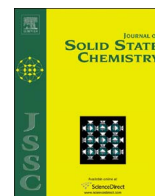




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Three-dimensional hierarchical and interconnected honeycomb-like porous carbon derived from pomelo peel for high performance supercapacitors

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ABSTRACT

The urgent need for sustainable development of human society has forced material scientists to explore novel materials starting from cheap natural precursors for next-generation energy storage devices by using environmentally friendly strategies. In this work, heteroatom-functionalized porous carbonaceous materials with 3D hierarchical and interconnected honeycomb-like structure have been successfully synthesized by using waste biomass pomelo peel as raw material through the combination of hydrothermal carbonization and followed KOH activation procedure. Benefiting from the unique honeycomb-like structure and high specific surface area, the as-obtained carbon material exhibits satisfactory capacitive behavior: 374 F/g at 0.1 A/g; excellent cycling stability of 92.5% capacitance retention over continuous 5000 cycles. More importantly, the as-assembled symmetric supercapacitors based on as-prepared electrode material can deliver high gravimetric and volumetric energy density of 20 W h/kg and 18.7 W h/L in 6 M KOH, respectively, as well as outstanding cycling stability. The obtained results demonstrate the possibility for taking full advantage of sustainable and large scale advanced carbon materials by choosing waste biomass, particularly the pomelo peel as a raw material.

1. Introduction

With the increasing depletion of fossil fuels and environmental pollution, the exploration of new energy and high energy utilization efficiency is one of the most important issues faced by national governments in the twenty-first century. Energy storage, which is an intermediate step to the efficient utilization of energy, has attracted large-scale concern and increasing research interest [1]. Supercapacitor is a new concept of environmentally friendly electrochemical energy storage systems. Combined with superior specific capacitance, exceptionally long cycle life and high power density, supercapacitors can bridge the energy/power gap between traditional batteries/fuel cells and capacitors [2–4]. An ideal supercapacitor, whose cycle life is typically measured in hundreds of thousands to millions of cycles, can deliver high power delivery > 10 kW/kg in few seconds. The electrochemical performances can be successfully increased by the excellent combination of the adopted electrode materials with a proper electrolyte [5,6]. In recent years, the main electrode materials — carbon materials have been deeply studied with the widening of the application areas of supercapaci-

tors, because of their high surface area, chemical stability and low cost [7,8].

As a kind of environmental friendly renewable resource, biomass, can be a qualified raw material for the synthesis of valuable carbon [9]. At present, hydrothermal carbonization (HTC) process has been turned into a powerful and efficient synthetic method for the production of functional carbonaceous materials from biomass [10,11]. This method could increase the dehydration, decomposition, condensation and polymerization of carbohydrate or cellulose [12]. Generally speaking, the prepared solid hydrochars possess stable physico-chemical properties and abundant oxygen-containing functional groups [13]. As a result, the hydrochar materials can be excellent precursors for synthesizing hierarchical three-dimensional and interconnected porous carbonaceous materials. Currently, 3D hierarchical and interconnected porous carbonaceous nanomaterials have attracted more and more attention due to 3D porous structures of active materials can provide large surface area, well-defined pathways to electrolyte access and mechanical stability for efficient supercapacitor electrodes. Therefore, tremendous effort has been made to synthesize nanoporous carbon materials via a variety of activation procedures. Wu et al. prepared 3D

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interconnected honeycomb-like porous carbon foam by carbonizing alkali-treated wheat flour under nitrogen atmosphere at 700 °C [14]. Long et al. had synthesized three-dimensional densely porous graphene-like carbon materials through hydrothermal treatment of fungus and subsequent carbonization/activation process under N₂ at 800 °C. The as-prepared material shows a high volumetric capacitance of 360 F/cm³ [15]. Moreover, Long et al. also prepared functionalized porous carbons with 3D interconnected pore structure through a facile thermal-treatment of KOH-soaked soybeans [16]. Therefore, the effective combination of HTC and heat-treatment/KOH activation may take full advantage of the unique structure of sustainable biomass and achieve high performance electrode materials. On account of the structural interconnectivities, 3D carbonaceous nanostructures not only possess hierarchical porous channels which provides continuous electron pathway, but also can allow the electrolyte to penetrate the electrode material and maintain better structural mechanical stability.

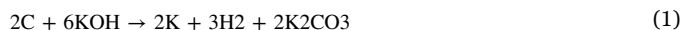
In this work we demonstrate a simple and economic strategy for the preparation of 3D hierarchical and interconnected honeycomb-like porous graphitic carbonaceous materials (HPGC) from waste biomass (pomelo peels). Cellulose, hemicellulose, polysaccharides and other organic components of pomelo peels could be transformed into hydrochars and carbon spheres by the HTC procedure. Hydrothermal carbonization can solve the problem that the carbonaceous material prepared from biomass contains certain impurities and high ash content. On the other hand, the hydrochar precursors with their networks of uniformly distributed oxygen within the structure can be efficiently turned into hierarchical and interconnected porous carbons with high specific surface area by subsequent simultaneous heat-treatment/KOH activation. Compared with previous work reported in the literature [17], the combination of HTC and heat-treatment/KOH activation can produce interconnected honeycomb-like porous carbon foam with satisfying electrochemical performances. Therefore, this facile route is beneficial for large-scale production of biomass-derived carbon materials for energy storage devices.

2. Results and discussion

The main process of preparing heteroatom-functionalized hierarchical porous carbon carbonaceous materials derived from pomelo peel is schematically illustrated in Scheme S1. The detailed fabrication processes are explained in detail in the Experimental Section (Supporting information). In the first HTC procedure, organic components (cellulose, hemicellulose, polysaccharides) in the pomelo peel are decomposed, dehydrated, condensed and polymerized to form thermodynamically stable hydrochar with high content of oxygen-containing functional groups. After freeze-drying and carbonization/activation process, HPGCs can be obtained. To further optimize the pore size distribution and prepare hierarchical porous structures, the obtained hydrochar precursors were mixed with different concentrations of KOH solution. The resulting mixture was then washed and dried, yielding hierarchical and interconnected honeycomb-like porous structure.

The field emission scanning electron microscopy (FESEM) images shown in Fig. 1(a)–(c) clearly exhibit the as-prepared HPGC-4 has a typical 3D hierarchical honeycomb-like structure. High resolution FESEM image (Fig. 1(c)) further demonstrates it consists of abundant highly interconnected macropores (labeled by yellow arrows) and mesoporous. It is worth noting that these mesopores are ben0065fit for the diffusion of electrolyte ion into the inner micro-pores. Fig. 1(d) presents the honeycomb-like carbon spheres synthesized via the hydrolysis of polysaccharides and post activation process. Compared with HPGC-4, other HPGC materials display rather dense micro structure without honeycomb-like structure or with decreasing levels of well-organized macroscopic “openness” in the same order (Fig. S1). It can be seen that the pore structure of the samples became more

obvious until destructive with the increase of concentration of KOH solution. A fraction of non-crystalline components of cellulose or hemicellulose are hydrolyzed and dissolved, which leading to the formation of porosity. The partially carbonized hydrochar precursor with high levels of oxygen-containing functional groups are responsive to the subsequent KOH treatment. Pores that formed during the hydrothermal process can serve as channels for the capillarity-driven infiltration of liquid KOH, further loosening the micro-fibril networks to create the carbon nanosheets [18]. Shown in Eq. (1) [19], KOH can etch the dense carbon framework or carbon nanosheets to generate the secondary mesoporous and micropores (Fig. S2):



In a general way, the reaction between carbon and KOH starts with solid–solid reactions. Then proceeds via solid–liquid reactions including the reduction of potassium (K) compound to form metallic K. The phase separation between water and hydrophobic carbon during the pyrolysis procedure also can generate the macropores and mesopores [20]. Finally, the as-prepared metallic K, which could efficiently intercalate/permeate into the lattices of the graphitic type layers during the activation, results in the expansion of the carbon lattices. After the rapid removal of the intercalated metallic K and other K compounds by diluted hydrochloric acid/distilled water washing, the expanded carbon lattices cannot convert back to their previous compact structure and thus the 3D hierarchical and high porosity honeycomb-like structure is created [21]. It is well-known that the carbonization temperature and hydrothermal solvent have deep influence on the morphology and electrochemical performances. SEM images of HPGC-4-600, HPGC-4-800 and WTC-4 are shown in Fig. S3. Obviously, the overall structure of material is destroyed with increasing carbonization temperature. Disordered pore structure of WTC-4 demonstrates the citric acid could co-carbonize with biomass during the hydrothermal process. TEM result (Fig. 1(e)) could further highlight the 3D honeycomb-like of HPGC-4 consists of highly interconnected carbon nanosheets. Fig. 1(f) shows a high resolution TEM micrograph that clearly confirms the partially graphitic ordered structure of HPGC-4. The obvious lattice fringes of the graphitic crystallites with mean lattice spacing of 0.36 nm are in consistent with the interlayer distance of graphite [22]. High graphitization degree of as-prepared HPGC-4 is beneficial to increase its electrical conductivity, which is vital to the rate capability of supercapacitors.

Fig. 2(a) clearly shows the HPGC-4 possesses a (002) reflection of graphitic-type lattice at 22.3°. A broad diffraction peak at around 43.7° accords with the formation of a higher degree of interlayer condensation of the (100) and (101) reflections of the graphitic-type lattice, i.e., (10) reflection, which could efficiently enhances the electrical conductivity [23]. Moreover, the average graphene interlayer distance can be calculated from the center position of (002) diffraction peaks [18]. The mean inter graphene layer spacing (d_{002}) of corresponding HPGC-4 material is 0.458 nm, which is larger than that of graphite (0.3354 nm). This dilated inter graphene spacing may result from the separation the potassium compounds that inserted in into the lattices of the graphitic type layers during the activation. What's more, the dilated inter graphene spacing could allow electrolyte ion for facile intercalation into the bulk of the electrode materials. An empirical parameter (R) put forward by Dahn et al. [24] is employed for further understanding the number of carbon sheets arranged as single layers in as-prepared HPGC materials. The calculation method of R is illustrated in inset of Fig. 2(a). It has been demonstrated that a larger R value indicates a lower percentage of single graphene sheets within carbon materials [25]. Obviously, the R value of HPGC-4 is 1.22, indicating the large concentrations of nonparallel single layers and turbostratic nature of graphited carbon for HPGC-4 [26]. Furthermore, the increase in the intensity at low diffraction angle demonstrates the presence of a high

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