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Potassium vapor assisted preparation of highly graphitized hierarchical porous carbon for high rate performance supercapacitors

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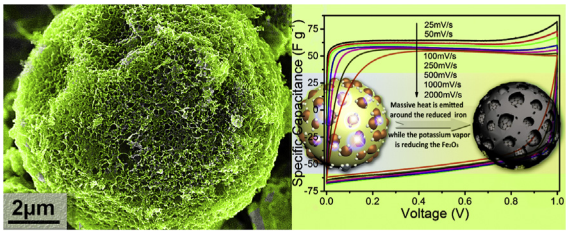
HIGHLIGHTS

- Highly graphitized hierarchical porous carbon microspheres are obtained.
- One-step KOH activation-carbonization method is adopted to assist graphitization.
- The mechanism of OACS improving graphitization degree is illustrated clearly.
- The obtained products used for supercapacitors deliver high power densities.

GRAPHICAL ABSTRACT



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ABSTRACT

Ultrahigh graphitized carbon microspheres with rich hierarchical pores (AGHPCM-1) have been successfully synthesized through the one-step activation-carbonization strategy (OACS) with porous sulfonated poly-divinylbenzene as the carbon precursor, iron as the hard template and catalyst, and potassium hydroxide (KOH) as activation agent. Through the XRD, TEM, Raman and BET analysis, AGHPCM-1 shows very high graphitization degree and rich micro-, meso- and macro-pores. More importantly, the mechanism for KOH to improve the graphitization degree of carbon materials in OACS has been illustrated by the thermodynamical theory. The tremendous heat releasing from the reaction between the catalyst precursor of Fe_2O_3 and potassium vapor plays a key role in the formation of graphitized carbon. It may provide a general direction to prepare highly graphitized porous carbon at a moderate temperature. Integrating the advantages of high graphitization degree and rich hierarchical porous structure, the AGHPCM-1 exhibits an excellent rate performance with a response to up to the high current density of 150 A g^{-1} and high scan rate of 2000 mV s^{-1}. No obvious capacitance decay can be observed after 10000 charge/discharge cycles even at the high current density of 20 A g^{-1}.

1. Introduction

Supercapacitors as fast energy storage devices have become an international research focus due to their long cycle life, high power density and specific capacity, as well as environment-friendliness

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[1–3]. Recently, with the expanding application fields of supercapacitors, specifically, in the field of high power applications (such as supercapacitor bus, emergency door, etc.), considerable research efforts [4,5] have been focused on enhancing their high rate performances. The electrode material is one of the two key factors that decide the rate performance of supercapacitors (electrode material and electrolyte). Up to now, porous carbon materials are mainly used as the active electrode materials in commercial electrochemical double layer capacitors (EDLCs) owing to their large surface areas, pore structure and excellent stability. Activated carbons (ACs), as a representative in conventional porous carbon materials, have attracted a wide attention due to its large specific surface area [6]. However, ACs offer narrow pore size distribution in the range of 0.5–1.5 nm and poor conductivity due to low degree of graphitization, which restricts the applications in the high power field [7]. Therefore, there is an urgent demand to develop novel and advanced carbon-based materials with enhanced characteristics (hierarchical pores, high specific surface area, high electrical conductivity, etc.) through a facile synthesis route for highly efficient energy storage devices.

Graphene (Gr)-based or carbon nanotubes (CNTs)-based materials seem to be promising candidates due to their unique nanostructures, larger theoretical specific surface area and excellent electrical conductivity [8,9]. However, Gr and CNTs generally have low effective specific surface area because of the characteristics that they are easy to conglomerate, wind (CNTs) or stack (Gr), resulting in unsatisfactory specific capacitances [10]. Hence, it is usually needed to construct three-dimensional (3D) porous structures through complicated processes [11,12],which is difficult to apply for large-scale production. To date, porous carbons with a high graphitization degree are successfully synthesized by some researchers [13,14]. However, unfortunately, these as-prepared graphitized porous carbons often possess relatively poor porosity or low specific surface area. At present, various precursors have been applied to the preparation of porous carbon materials, such as biomass or biomass derivatives [15,16], polyphenols [17] and polymers [18]. Among them, polymers as the ideal carbon precursors have the advantages of low cost, easy to produce at large scales, controllable morphology and porous structure. While, in general, polymer-based porous carbons have relatively low graphitization degree, leading to poor electrical conductivity.

To improve the graphitization degree of polymers-derived carbon materials, two primary routes (high temperature treatment and catalytic graphitization) are usually adopted. However, the high temperature treatment method is a high-energy consumption process with low yield and poor porosity, which is not suitable for commercialized production. Catalytic graphitization is an ideal method to achieve high graphitization degree at a moderate temperature. Nevertheless, the ordinary carbon precursors are difficult to increase the adsorption amount of catalysts, leading to relative low degree of graphitization. Functionalized polymer is considered to be one of the promising candidates for carbon precursor because its abundant functional groups can adsorb a large amount of catalysts and thus enhance the graphitization degree of the products. Some functionalized polymers such as sulfonated poly (styrene-co-methacrylic acid) spheres [19] can be used to improve the graphitization degree by adsorbing Fe ion, which can simultaneously increase the porosity of the obtained carbons. However, such a strategy cannot satisfy the adsorption of these catalytic ions inside the polymer microspheres due to their compact structure, which results in less development of both porosity and graphitization. Obviously, the carbon precursor with abundant porous structure before functionalization is required for adsorbing metal ions effectively.

Based on the concerns above, porous sulfonated poly-divinylbenzene microspheres (SPDVBs) have been chosen as the carbon precursor to prepare graphitized hierarchical porous carbon microspheres (GHPCMs), which possesses several advantages as follows: (1) It is easy to obtain abundant porous structure just by adding solvent porogens such as toluene or n-heptane in the polymerization process of poly-divinylbenzene microspheres (PDVBs) [20]. (2) The sulfonic acid functional groups throughout the SPDVB can promote the infiltration and absorption of the iron precursor Fe^{3+} ions and make them distribute evenly in the polymer microspheres so that they can effectively act not only as the catalyst to improve the graphitization degree, but also as a hard template to maintain the pore structure in the heat treatment process of SPDVB. (3) SPDVB has the advantages of excellent morphology-keeping ability and high carbon yield characters in pyrolysis process, which can keep the original porosity of SPDVB for the product after pyrolysis.

Subsequently, in order to further enhance the graphitization degree and porosities of the products, chemical activation has been adopted to prepare activated graphitized hierarchical porous carbon microspheres (AGHPCMs). KOH activation, a very traditional method is usually considered for making micropores, however, its unique effects on improving the graphitization degree of carbon materials in the one-step activation-carbonization strategy (OACS) are rarely concerned and the mechanism is still a puzzle. Herein, we have successfully used the OACS not only to efficiently increase the specific surface area, but also greatly improve the graphitization degree and the meso- & macro-pores ratio of the products. Moreover, we have clearly illustrated the mechanism of it by thermodynamical theory for the first time. The tremendous heat releasing from the reaction between the catalyst precursor of Fe_2O_3 and potassium vapor will greatly promote formation of graphitized carbon. It may provide a general direction to prepare highly graphitized porous carbon or graphene-like carbon at a moderate temperature. The hierarchical porous structure and high specific area of the OACS product (AGHPCM-1) are very beneficial to transfer ions and store the ions, while the high graphitization degree lead to excellent electrical conductivity. The synergistic effect of these advantages leads to a superior capacitance performance especially an excellent rate capability.

2. Experimental section

2.1. Materials

Divinylbenzene (DVB, mixtures of isomers, 55% grade) and 2, 2’-azo-bis-isobutyronitrile (AIBN, analytical grade) were purchased from Macklin Inc. (Shanghai, China), and used without any purification. Other chemical reagents were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

2.2. Synthesis of GHPCMs and AGHPCMs

2.2.1. Synthesis of PDVB

The porous poly-divinylbenzene microspheres (PDVBs) were synthesized by micro-suspension polymerization in a three-neck glass reactor. Firstly, 1.5 g polyvinyl pyrrolidone (PVP), 1.14 g hexadecyl trimethyl ammonium bromide (CTAB) and 600 ml deionized water were mixed into the glass reactor, and heated to 80 °C under argon atmosphere. Secondly, at the stirring speed of 400 rpm, the mixture of 12 mL divinylbenzene, 32 ml toluene and 16 mL n-heptane was added into the reactor. After that, 0.72 g AIBN was added as an initiator to start the polymerization process, and the polymerization was carried out for 6 h at 80 °C. After polymerization, the products were washed twice with hot distilled water,