



Ultra-facile fabrication of phosphorus doped egg-like hierarchic porous carbon with superior supercapacitance performance by microwave irradiation combining with self-activation strategy



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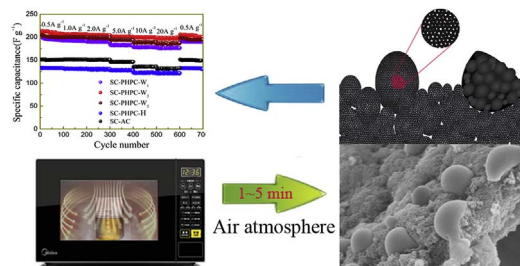
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HIGHLIGHTS

- An ultra-facile method was developed for fabricating phosphorus doped egg-like HPC.
- The reported method exhibits incomparable merits comparing with the traditional method.
- Carbonization and self-activation process finish in 3 min under air atmosphere.
- Capacitance retention rate reaches 96.2% as current density increasing to 20 A g⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report an ultra-facile fabrication method for a phosphorus doped egg-like hierarchic porous carbon by microwave irradiation combining with self-activation strategy under air atmosphere. Comparing with the traditional pyrolytic carbonization method, the reported method exhibits incomparable merits, such as high energy efficiency, ultra-fast and inert atmosphere protection absent fabrication process. Similar morphology and graphitization degree with the sample fabricated by the traditional pyrolytic carbonization method under inert atmosphere protection for 2 h can be easily achieved by the reported microwave irradiation method just for 3 min under ambient atmosphere. The samples fabricated by the reported method display a unique phosphorus doped egg-like hierarchic porous structure, high specific surface area (1642 m² g⁻¹) and large pore volume (2.04 cm³ g⁻¹). Specific capacitance of the samples fabricated by the reported method reaches up to 209 F g⁻¹, and over 96.2% of initial capacitance remains as current density increasing from 0.5 to 20 A g⁻¹, indicating the superior capacitance performance of the fabricated samples. The hierarchic porous structure, opened microporosity, additional pseudocapacitance, high electrolyte-accessible surface area and good conductivity make essential contribution to its superior capacitance performance.

1. Introduction

How to significantly reduce the cost of high-performance electrochemical energy storage (EES) devices is a key challenge for the

advancement of electrical vehicles and renewable energy [1,2]. The cost of the EES devices mainly depends on price of electrode materials [3], so it is extremely important to develop cost-efficient electrode materials without sacrificing high performance. Currently, various

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carbons are dominant electrode materials for EES devices, such as lithium-ion batteries (mainly for anode) and electrochemical supercapacitors, due to large specific surface area, good electrical conductivity, excellent physical and chemical stability, and environmental friendliness [4–6]. Many novel carbon materials, such as graphene, carbon nanotube, hollow carbon shell and ordered mesoporous carbon, exhibit excellent energy storage capability, and are suggested to use as electrode materials for high-performance EES devices [4], but the high cost of these materials obstructs their practical application. Alternatively, low-cost porous carbons (PCs), especially for activated carbon (AC), attracts constant attention of researchers and engineers, and have been extensively applied in commercial EES devices [5,7,8].

However, commercial high-quality porous carbons for energy storage application still have two main bottlenecks: a tedious and highly energy intensive fabrication process, and low energy density, which significantly limit their broad application [9]. The cost advantage of PCs comparing with other carbon materials mainly bases on the cheap and easily accessible raw materials [3]. Biomass and industrial wastes, such as egg white, seaweed, rice husk, honeysuckle, oily sludge, etc., can be readily utilized for fabricating porous carbons [10–14]. However, a carbonization process at high temperatures (600–1000 °C) for 1–4 h under a protection of inert atmosphere is necessary for fabricating porous carbons by using above raw materials, energy utilization efficiency in that process is intolerable low, and the necessary inert atmosphere protection makes fabrication condition rigorous. Furthermore, various activators, such as KOH, ZnCl₂ or phosphoric acid, are used to get high porosity and large surface area utilizing the chemical reaction between activators and carbon under high temperatures, which causes low convert ratio of raw materials and tedious post-treatment process [10,11]. Comparing with the traditional pyrolytic carbonization, microwave heating converses energy by dipole rotation and ionic conduction inside the substances which inducing temperatures of up to 1000 °C within just few minute [15], so microwave irradiation is regarded as a fascinating and promising tool for preparation of porous carbon material [15–21]. However, due to the poor microwave adsorption for most of carbonaceous material, in the first stage, the carbonaceous precursor, such as coconut shells or pineapple peel, is pyrolyzed under an inert atmosphere, and then the carbonized production is impregnated with an activation agent, e.g., KOH or K₂CO₃, followed by a microwave-induced chemical activation under an inert atmosphere [17–19]. Alternatively, porous carbons also can be facilely obtained by a simple one-step microwave treatment of the activation agent/microwave absorber impregnated precursor under or without the protection of inert atmosphere. For instance, Eder C. Lima et al. obtained an activated carbon with a specific surface area of up to 619 m² g⁻¹ by microwave irradiating a mixture of cocoa shell and inorganic components (lime + ZnCl₂ + FeCl₃) for about 10 min under nitrogen [20]. Ali U. Shaikh et al. reported a heteroatom doped mesoporous carbon with a specific surface area of 855 m² g⁻¹ synthesized by microwave irradiating tannin cross-linked melamine for 30 min using polyphosphoric acid as microwave absorber and activation agent under ambient atmosphere [15,21]. As far as our knowledge, there are rare studies on the one-step fabrication of porous carbons by microwave irradiation combining with self-activation under air atmosphere.

The relatively low energy density of porous carbons comparing with other carbon electrode materials is mainly due to poor electrolyte accessibility caused by the micropores dominant pore structure [22]. Fortunately, the research conducted by Y. Gogotsi et al. revealed that electrolyte accessibility of micropores can be efficiently improved by constructing short opened micropores [23], which provides an efficient strategy for enhancing the energy density of PCs. Thus, the hierarchical porous carbon with short opened micropores connected to mesopores and macropores is extensively exploited as high-performance electrode material for EES application [24,25]. For example, a hierarchical porous carbon microtube with a specific surface area of 1775.7 m² g⁻¹ derived from willow catkins exhibited a high capacitance of 292 F g⁻¹

at a current density of 1 A g⁻¹ in 6 M KOH aqueous solution, and a high energy density of 37.9 Wh kg⁻¹ at a power density of 700 W kg⁻¹ in 1 M LiPF₆ electrolyte [26]. Recently, Junke Ou et al. also reported a hierarchical porous carbon with opened micropores derived from honeysuckle, which reversible capacity reached up to 1215 mAh g⁻¹ at a current density of 100 mA g⁻¹ when used as an anode of lithium-ion batteries [12]. Furthermore, recent researches indicated that the heteroatoms doping, such as N, S and P doping, could be another efficient strategy for improving the electrolyte accessibility of micropore and small mesopore. The difference in electronegativity between the heteroatoms and host C atoms provides a more polarized surface, which consequentially promoting the wettability of the carbon surface and thus ensures a fast transfer rate of electrolytic ions in micropores and small mesopores, and finally improves their electrolyte accessibility [25,27,28]. The improved electrolyte accessibility enhances the utilization ratio of micropores and small mesopores, thus improves the energy storage/release capability of porous carbons. So a dramatic improvement for energy density of porous carbons by combining heteroatoms doping with hierarchical porous structure is reasonable to expect [15,25].

In this work, we report an ultra-facile fabrication method for a phosphorus doped egg-like hierarchic porous carbon by microwave irradiation combining with self-activation strategy under air atmosphere using phytic acid as precursor. Comparing with the traditional pyrolytic carbonization method, the reported method exhibits incomparable merits, such as high energy utilization efficiency, absence of inert atmosphere protection and ultra-fast fabrication process. The samples fabricated by the reported method with high specific surface area (up to 1642 m² g⁻¹) and developed opened microporosity exhibit a superior capacitance performance when used as an electrode material for symmetric supercapacitor cell, which specific capacitance reaches up to 209 F g⁻¹ at a current density of 0.5 A g⁻¹, and over 96.2% of initial capacitance remains as the current density increasing to 20 A g⁻¹.

2. Experiment

2.1. Fabrication of the phosphorus doped egg-like hierarchic porous carbons by a microwave irradiation combining with self-activation strategy

The phosphorus doped egg-like hierarchic porous carbon was facilely fabricated by a microwave irradiation combining with self-activation strategy using phytic acid as precursor under an air atmosphere. The general fabrication process is summarized and illustrated in Fig. 1. Briefly, 5 g of the phytic acid solution (50% w/w in H₂O, Sigma) was directly microwave irradiated in a household microwave oven (M1-231A, Midea, China) under a radiation power of 800 W for 1–5 min, followed by washing with deionized water and drying under a radiation power of 500 W in microwave oven for 2 min. The final product refers to as PHPC-W_x, where x denotes the microwave irradiation time.

2.2. Fabrication of the phosphorus doped egg-like hierarchic porous carbon by traditional pyrolytic carbonization

For demonstrating the advantages of the method presented above, a phosphorus doped egg-like hierarchic porous carbon was also fabricated by traditional pyrolytic carbonization. In brief, 5 g of the phytic acid solution (50% w/w in H₂O, Sigma) was directly carbonized in a tube furnace under 650 °C for 2 h with the protection of argon atmosphere, followed by washing with deionized water and drying at 105 °C for 12 h. The final product refers to as PHPC-H.

Furthermore, a commercial AC (yp-50F) with a specific surface area of 1687 m² g⁻¹ purchased from Kurary Co., Ltd.(Japan) was used to compare the capacitance performance with the reported phosphorus doped egg-like hierarchic porous carbon.

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