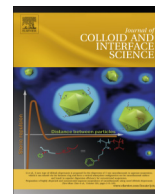




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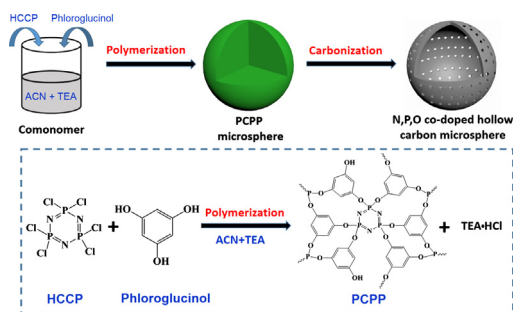
A self-template and self-activation co-coupling green strategy to synthesize high surface area ternary-doped hollow carbon microspheres for high performance supercapacitors

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GRAPHICAL ABSTRACT

A self-template and self-activation co-coupling strategy was developed to fabricate high surface area ternary-doped (nitrogen, phosphorus and oxygen) hollow carbon microspheres for high-performance supercapacitors.



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ABSTRACT

Development of facile and cost-effective routes to achieve hierarchical porous and heteroatoms-doped carbon architectures is urgently needed for high-performance supercapacitor application. In our study, ternary-doped (nitrogen, phosphorus and oxygen) hollow carbon microspheres (NPO-HCSs) are fabricated by one-step pyrolysis of single poly(cyclotriphosphazene-co-phloroglucinol) (PCPP) microsphere, which is generated through a facile polymerization between hexachlorocyclotriphosphazene and phloroglucinol at mild conditions. The whole preparation process is not used any additional template or activating agent. The obtained NPO-HCS-950 with average diameter of 580 nm and shell thickness of about 80 nm have a high specific surface area ($2390 \text{ m}^2 \text{ g}^{-1}$), a large pore volume ($1.35 \text{ cm}^3 \text{ g}^{-1}$), hierarchically interconnected pore texture, and uniform ternary heteroatom doping (O: 3.04 at%; N: 1.33 at% and P: 0.67 at%). As an electrode material for supercapacitors, the specific capacitance of the NPO-HCS-950 reaches 253 F g^{-1} of 1 A g^{-1} and 176 F g^{-1} at 20 A g^{-1} , revealing superior rate performance. The capacity retention after 10,000 consecutive charge-discharge cycles at 20 A g^{-1} is up to 98.9%, demonstrating excellent cycling stability. Moreover, the assembled symmetric supercapacitor using NPO-HCS-950 exhibits a relatively high energy density of 17.6 W h kg^{-1} at a power density of 800 W kg^{-1} . Thus, a promising electrode material for high-performance supercapacitors is obtained through a facile, green and scalable synthesis route.

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1. Introduction

A major issue on the development of energy storage systems for storing electricity from sustainable and renewable energy has emerged in the past decades, owing to the ever-increasing global energy demand and decreasing availability of fossil fuels [1–3]. Supercapacitor is recognized as a new class of energy-storage device due to their unique advantages on high power density, long cycling life, rapid charge-discharge process, and safety in use [4–8]. To date, activated carbon is the commonly used electrode material for commercial supercapacitors because of their large specific surface area ($>1000\text{ m}^2\text{ g}^{-1}$) and pore volume ($>0.5\text{ m}^3\text{ g}^{-1}$), moderate cost, chemical inertness and good electrical conductivity [9–12]. However, their energy storage performance is often unsatisfactory at high charge-discharge rates because a large quantity of micropores are not favorable for rapid transport of electrolyte ions. This fact results in a huge diffusion resistance, decreasing the rate performance of supercapacitors greatly [13–15].

In comparison with conventional activated carbons, hollow carbon microspheres with hierarchical porous structures have several advantages, such as regular morphology, high surface-to-volume ratio, controllable porosity and particle size, which could greatly decrease the ion diffusion resistance and lead to the enhancement of electrochemical performances [16–19]. Moreover, the inner cavity of hollow carbon microspheres could act as ion-buffer reservoirs, shortening the diffusion distance of electrolyte ions to the interior carbon surfaces [20]. Therefore, hollow carbon microspheres have been one of the most promising electrode materials for high-performance supercapacitors. In order to endow hierarchical porous texture and increase their accessible surface area for ionic adsorption, several strategies including hard templates or soft templates [17,21–23] as well as chemical activation treatments [24,25] are often utilized. Although the expected hollow carbon microspheres with multimodal porous features have been achieved, the complicated synthetic steps and harsh reaction conditions greatly hinder their large-scale industrial applications. Therefore, it is highly desirable to develop a facile, green and cost-effective method to prepare hollow carbon microspheres with reasonable pore architecture for high-performance supercapacitor.

On the other hand, the incorporation of heteroatoms into carbon materials could effectively modify and improve their electrochemical performances [26–30]. For instance, when the carbon materials were doped by N atom, the electrical conductivity, chemical reactivity and surface wettability of the carbon matrix can be modified greatly. These are necessary for the electrochemical energy storage [28]. Up to now, single-heteroatom-doped carbon materials using N, B, S, P or O as dopant has been studied widely to ameliorate their performance in energy-storage systems [26]. In the meantime, it is believed that co-doping could further enhance the electrochemical performances of single-heteroatom-doped carbon materials. The enhanced performances of co-doped carbon materials are generally assigned to the synergistic effect of multiple heteroatom doping [31–36]. However, to achieve the co-doping of two or more separate dopants, multi-step preparation processes, high cost or toxic precursors, or the precise control of synthesis conditions are commonly needed [37,38], which greatly limits the large-scale fabrication of co-doped carbon materials for practical applications.

Herein, we demonstrate, for the first time, the synthesis of ternary-doped (nitrogen, phosphorous and oxygen) hollow carbon microspheres (NPO-HCSs) with high specific surface area via one-step direct carbonization of cross-linked poly(cyclotriphosphazene-co-phloroglucinol) (denoted as PCPP) micro-

spheres. PCPP microspheres are selected as single precursor for NPO-HCSs owing to its easy synthesis, low cost, high C, N, P and O content, and excellent stability at relatively high temperature. It should be noted that the preparation process of NPO-HCSs with high specific surface area was not used any assistance of exterior template or additional chemical activation process. As a new class of advanced porous carbon materials, the developed NPO-HCS-950 exhibits very attractive capacitive properties when utilized as electrodes for aqueous electrolyte supercapacitors, including high specific capacitance of 253 F g^{-1} at 1 A g^{-1} , excellent rate capability (retention of 70% from 1 A g^{-1} to 20 A g^{-1}), and excellent cycling stability (98.9% initial capacitance retention after 10,000 cycles). Additionally, we found that for N, P, and O ternary-doped carbon electrode materials the contribution of N and P dopants is mainly to increase pseudocapacitance and that of O dopant is mainly to enhance the surface wettability of the carbon materials towards electrolyte solution, facilitating the ion transportation in the porous channels of NPO-HCSs. The initial result might provide a useful guidance to rationally design the multiple heteroatom doping carbon materials. Therefore, we think this study provides a facile low-cost and readily scalable strategy for the efficient fabrication of novel NPO-HCS materials for high-performance supercapacitors.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP), phloroglucinol, triethylamine (TEA) were obtained from Sinopharm Chemical Reagent Co., Ltd. Acetonitrile (ACK), ethanol, were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. and used directly.

2.2. Synthesis of PCPP microspheres

PCPP microspheres were prepared by a facile precipitation polymerization between HCCP and phloroglucinol according to the modified method developed by our group [39]. Briefly, 125 mg HCCP (0.36 mmol) and 90.6 mg phloroglucinol (0.72 mmol) were dissolved into 100 mL acetonitrile to form a clear solution. Then, 5 mL TEA was quickly added to the above solution and milky white solution could form at once. Subsequently, the polymerization was carried out under ultrasonic irradiation for 3 h at 40°C . The resulting particles were obtained by centrifuging and then washed three times with deionized water and ethanol, respectively. Finally, the obtained particles were dried in a vacuum oven at 60°C for 12 h to yield PCPP microspheres.

2.3. Preparation of NPO-HCSs

To obtain the NPO-HCSs, the above PCPP microspheres as single precursor were directly carbonized at a certain temperature for 2 h under a nitrogen atmosphere with a heating rate of 5°C min^{-1} . For convenience, the as-prepared carbon materials were named as NPO-HCS-850, NPO-HCS-950, and NPO-HCS-1050, respectively, wherein the NPO-HCS means N, P and O co-doped hollow carbon microsphere and 850, 950, and 1050 are the carbonization temperature used.

2.4. Characterization

The microscopic morphology was observed by scanning electron microscopy (SEM, JEOL JSM-7401F) with an acceleration voltage of 5.0 KV and transmission electron microscopy (TEM, JEOL

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