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Design and synthesis of three-dimensional hierarchical ordered porous carbons for supercapacitors

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ABSTRACT

Three-dimensional hierarchical ordered porous carbons (3D HOPCs) have been successfully prepared through templating method using silica sphere nano-array as a hard template, triblock copolymer P123 as a soft template and sucrose as a carbon source, and used as the electrode materials for supercapacitors. The structure, morphology and physicochemical properties of the as-prepared 3D HOPCs are characterized by nitrogen adsorption–desorption isotherm, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) tests, and cycle life measurements. The results show that the 3D HOPCs possess well-interconnected 3D hierarchical ordered porous structure. Especially, the 3D HOPC-80, of which the pore size is 4.01 nm, shows the specific surface area of 1182 $m^2 g^{-1}$ and a specific capacitance of 247 $F g^{-1}$ at the current density of 1 $A g^{-1}$. Besides, the supercapacitors based on 3D HOPCs exhibit excellent rate performance, high energy densities of 7.5 $W h kg^{-1}$ and 5.8 $W h kg^{-1}$ at the power densities of 500 $W kg^{-1}$ and 10000 $W kg^{-1}$, respectively. Moreover, the supercapacitors using 3D HOPCs as electrode materials hold high capacitance retentions over 91% even after 10000 cycles.

1. Introduction

There has been ever-increasing interest in exploring and developing more efficient energy storage devices for the past decades [1,2]. Supercapacitor, as a promising candidate for energy storage system, is attracting more and more attention owing to its advantages of high power density, long cycle life and fast charge–discharge rate [3,4]. Due to good conductivity, high specific surface area and low cost, the porous carbons have been widely used as electrode materials for supercapacitors, especially the electrical double layer capacitors (EDLCs) [5,6].

Recently, the porous carbons with three-dimensional (3D) interconnected ordered structure have been proposed as promising electrode materials for supercapacitors because of their distinctive structural features and good physicochemical properties [7,8]. The 3D interconnected ordered porous structure can improve the access of electrolytes to the inner of the electrode and promote the electrolyte transportation by providing shorter diffusion pathways [9–11]. For example, Su et al. prepared 3D interconnected ordered macroporous carbons by chemical vapor deposition of bezene with inverse silica opal as the template, and found that the 3D interconnected open pore structures can contribute to the enhancement of the electrochemical characteristics of the porous carbons [12]. However, although the 3D ordered porous carbons can facilitate the rapid ion transportation, the specific surface area is still relatively low due to the few micropores and mesopores, leading to a limited specific capacitance [13].

On the other hand, the porous carbon materials can usually be divided into three categories according to their pore sizes: micropores (<2 nm), mesopores (2–50 nm) and macropores (> 50 nm) [14]. The pore size will play an important role in the formation of the electrical double layer based on the energy storage mechanism of the EDLC [15]. In general, the micropores mainly contribute to the electrical double layer capacitance, while the mesopores and macropores facilitate the kinetics of electrical double layer formation and transportation of the electrolyte ions [16]. Thus, the carbons with hierarchical porous structure are of great potential in the EDLC, to which many efforts have been devoted [17–21]. Liu et al. found that the unique hierarchical

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structure of carbon materials can provide a favorable path for electrolyte penetration and transportation, which resulted in attractive capabilities in supercapacitors and fuel cells [22]. Xing et al. synthesized the hierarchical porous carbons through self-assembly of triblock copolymer, phloroglucinol and formaldehyde followed by KOH post-activation, which maintained the specific capacitance of 180 F g^{-1} at the frequency of 1 Hz [17]. Zhang et al. obtained the hierarchical porous carbons by KOH activation of coal liquefaction residue and coal, and the specific capacitance can be highly up to 186 F g^{-1} at the scan rate of 5 mV s^{-1} [20].

Apparently, it will be very necessary and significant to combine the advantages of 3D ordered structure and those of hierarchical porous structure in the carbon materials for the application of high performance supercapacitors. However, great success has been achieved in the porous carbons with hierarchical structure and/or 3D structure with/without ordered porous structure [10,12,13,17,18,20–22], the porous carbons combined the advantages of the hierarchical structure and 3D ordered porous structure have rarely been reported in the studies of supercapacitors. In addition, the currently reported methods are too complex to effectively control the pore structural parameters, or the pore size of the carbon material is not very suitable for the application of supercapacitors [23].

Herein, we put forward a strategy using the silica sphere nano-arrays self-assembled by monodisperse silica particles as a hard template and a short triblock copolymer $PEO_{20}PPO_{70}PEO_{20}$ (P123) as a soft template to synthesize 3D hierarchical ordered porous carbons and explored their application in supercapacitors for the first time. Moreover, the effects of size of silica particle templates on physicochemical properties and supercapacitive behaviors of the 3D HOPCs have also been investigated.

2. Experimental

2.1. Synthesis of silica sphere nano-arrays

Firstly, the three solutions containing monodisperse silica spheres with sizes of 80, 150, and 230 nm were prepared according to the reported method [24]. The prepared silica spheres were uniform in size with deviation of less than 5%. Next, the solutions were centrifuged, rinsed with water, and dried to be slurry colloids. Then, the silica colloids were deposited onto the surface of clean glasses according to Colvin [25]. Subsequently, the ordered silica sphere nano-arrays were left on glasses after the solutions evaporated. Finally, the nano-arrays were dried at 60 °C and sintered at 750 °C for 2 h.

2.2. Preparation of 3D HOPCs

The preparation strategy of 3D HOPCs is schematically shown in Fig. 1. The P123 and sucrose were introduced into the voids of the silica sphere nano-array. After carbonization, the soft template P123 was decomposed to leave some mesopores in the carbon/silica composite. The composite was further immersed in HF solution to resolve the silica, resulting in the porous carbons.

A typical procedure was as follows. The as-prepared silica sphere nano-arrays were put in a Büchner funnel attached to a vacuum of ca. 100 mTorr. Then, the aqueous solution with mass ratio of 10 sucrose:2.5 P123:1 sufuric acid was added into the voids of the silica sphere nano-arrays. After drying in oven at 60 °C, the above composite nano-arrays were heated at 150 °C for 6 h and carbonized at 700 °C for 3 h with a heating rate of 5 °C min^{-1} under Ar flow. The resulting silica/carbon composites were immersed in 20 wt% HF, washed until pH = 7, and dried at 100 °C. The prepared carbons were named as 3D HOPC-x, where "3D HOPC" denotes three-dimensional hierarchical ordered porous carbon, and x depends on the sizes of silica spheres.

2.3. Characterization and electrochemical measurements

Both scanning electron microscopy (JSM-6610LV, JEOL) and transmission electron microscopy (JEM-2100, JEOL) were used to study the microstructure of the prepared 3D HOPCs. N_2 adsorption–desorption isotherms were measured at 77 K (TriStar II 3020, Micromeritics) after being degassed in a vacuum at 200 °C for 3 h. The specific surface areas (S_{BET}) were evaluated by the

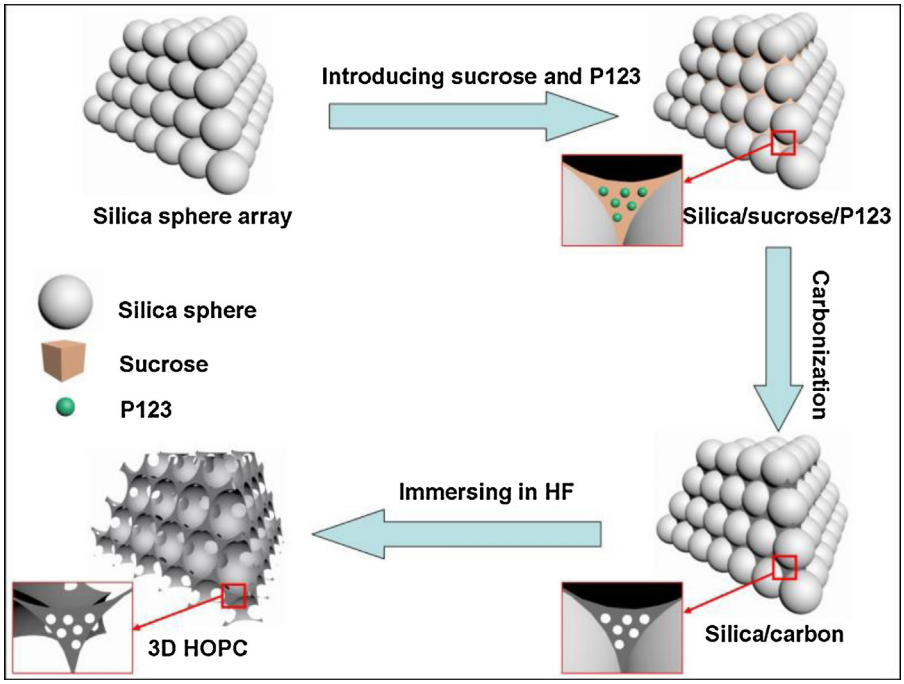

Fig. 1. Schematic illustration of preparation strategy of the 3D HOPCs.