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Size-controllable templates for the synthesis of porous carbon with tunable pore configurations

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ABSTRACT

Microporous carbon (MPC) and hierarchically porous carbon (HPC) were precisely designed by a colloidal process using the same carbon source and pore template. Tetraethyl orthosilicate (TEOS) hydrolysis and condensation reaction under acid condition yields the MPC featuring a highly microporous structure with BET surface area of $2068 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.99 \text{ cm}^3 \text{ g}^{-1}$ while the reaction under alkaline condition makes the resulting carbon with hierarchically porous structure (HPC), giving a surface area of $1051 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.8 \text{ cm}^3 \text{ g}^{-1}$. MPC is also proved to be a promising candidate for supercapacitors with a high capacitance of 287 F g^{-1} at 0.5 A g^{-1} and 152 F g^{-1} at 50 A g^{-1} .

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1. Introduction

Porous carbon materials are still the most preferable electrode materials for electrochemical double-layer capacitors (EDLCs) due to the large surface area, good electronic conductivity, chemical inertness and environmental friendliness [1]. Based on the EDLCs mechanism, namely, ion diffusion and adsorption at electrode-electrolyte interfaces inside nanopores, pore configuration (e.g. microporous carbon, mesoporous carbon and hierarchical porous carbon) poses great impacts on the capacitive performance of carbon materials. Of the concern to provide high capacitance, micropores perform better than mesopores [2] because the stored electrical energy will be theoretically proportional to the surface area of the electrode. Besides, mesoporous or hierarchical porous carbons have been suggested to provide high ion diffusion efficiency through large pores and lead to improved rate performance [3].

As known, nano-sized silica particles from tetraethyl orthosilicate (TEOS) hydrolysis and condensation process have been demonstrated effective as pore template for the synthesis of porous carbon materials [4,5]. Controlling the conditions of TEOS hydrolysis and condensation process, including catalyst, pH value and solvents could endow the resulting silica particles with various aggregation state and sizes [6]. Herein, microporous carbon (MPC) and hierarchically porous carbon (HPC) were precisely designed using the same carbon source (phenolic resin) and pore template (TEOS). By simply tuning the pH values of precursor solution

under acid and basic conditions, SiO_2 colloidal crystals with different sizes can be obtained and leave the carbon products with microporous structure and hierarchically porous structure after carbonization and washing. The as-synthesized MPC was also demonstrated to exhibit excellent supercapacitive performance with a high capacitance of 287 F g^{-1} at 0.5 A g^{-1} and still maintaining 152 F g^{-1} at high rate of 50 A g^{-1} .

2. Materials and methods

2.1. Sample preparation

As illustrated in Fig. 1, simply controlling the pH values of precursor solution results in the porous carbons with tunable pore structure. For the synthesis of microporous carbon (MPC), 0.61 g of phenol was firstly added to a round-bottom flask and was melted at $40 \text{ }^\circ\text{C}$. Afterwards, 10 mL deionized water, 10 mL formalin aqueous solution (37 wt%) and 1 mol L^{-1} NaOH solution were sequentially added for pH value to 9. The reaction mixture was stirred and refluxed at $80 \text{ }^\circ\text{C}$ for 1 h. Then, 10 mL ethanol and 0.1 mol L^{-1} HCl solution were added into above reaction system for pH value decreasing to 3. After cooling down, 2.1 g of TEOS was added with vigorous stirring for 30 min. Subsequent drying the solution gave the solid precursor which further experienced a carbonization ($8 \text{ }^\circ\text{C min}^{-1}$ to $900 \text{ }^\circ\text{C}$ under N_2 for 3 h) and washing process (10 wt% HF and water) to yield the MPC sample. The synthesis of hierarchically porous carbon (HPC) follows the same procedure as MPC except for keeping the pH value of precursor solution at 9.

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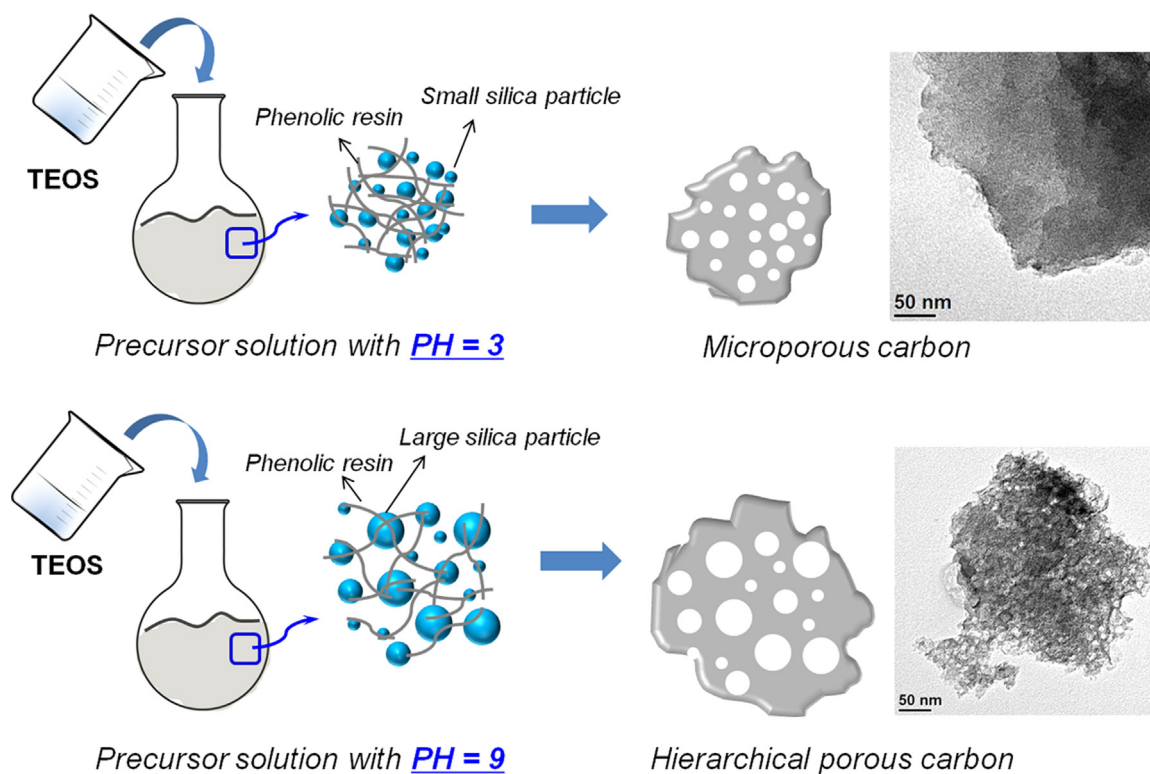


Fig. 1. Schematic illustration of the synthesis process of microporous carbon (MPC) and hierarchically porous carbon (HPC).

2.2. Characterization

The morphology and microstructure of prepared samples was analyzed using scanning electron microscopy (JSM-7401F) and transmission electron microscopy (TEM, JEOL-2010) with an acceleration voltage of 120 kV. The pore structure characteristics were determined by N_2 adsorption at -196°C using ASAP 2020 volumetric sorption analyzer. BET surface area was calculated from the isotherm using the Brunauer-Emmett-Teller equation. Pore size distribution was calculated based on nonlocal density functional theory (NLDFT) method on the basis of the adsorption branch. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5700 ESCA system using AlKa X-ray at 14 kV and 6 mA.

2.3. Preparation of electrode and electrochemical measurement

A three-electrode configuration, using 6 M KOH as the electrolyte, was constructed to evaluate the supercapacitive performance of the prepared samples. The working electrodes were prepared by mixing the active materials with conducting carbon black and binder poly-tetrafluoroethylene (PTFE) with the ratio of 8:1:1. Nickel-foam was used as current collector. The active material on each electrode was ~ 1.0 mg. Pt slice and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. Cyclic voltammetry curves and galvanostatic charge-discharge curves were tested on VMP3 Electrochemical Workstation (Bio-logic). Specific capacitances (C_s , F g^{-1}) of materials were calculated based on the following formula: $C_s = I\Delta t / (m\Delta V)$, where I is discharge current, Δt is discharge time, m is the mass of active material and ΔV represents voltage window (excluding the IR drop).

3. Results and discussion

The TEM images of obtained microporous carbon (MPC) and

hierarchically porous carbon (HPC) are presented in Fig. 1. Both MPC and HPC show amorphous structure with different scale nanopores embedding in the carbon framework. Specifically, MPC shows a smooth and compact surface morphology consisting of abundant internal micropores while HPC features a hierarchical porous structure containing some mesopores with diameter around 10 nm. The SEM images also reveal the small pores of MPC and large-dimension pores of HPC (Fig. S1).

N_2 adsorption-desorption isotherms further reveal the pore configuration and corresponding pore parameter of MPC and HPC, as illustrated in Fig. 2 and Table S1. When TEOS hydrolysis and condensation process take place in an acid condition ($\text{pH}=3$ in our work), the resultant MPC features a typical I type isotherms, suggesting the dominant microporous structure [7] which yields a BET surface area of $2068 \text{ m}^2 \text{ g}^{-1}$ and total pore volume of $0.99 \text{ cm}^3 \text{ g}^{-1}$. The pore size distribution was centered at ~ 1 nm and ~ 2 nm which are favorable for most electrolyte ions penetration (Fig. 2b). The microporous structure of MPC is derived from the relatively small silica particles which are attributed to the slow cross-link and growth rate of silica clusters in acid condition. In contrast, when TEOS adding into a basic condition ($\text{pH}=9$ in our work), in addition to the growth of small-sized silica colloids from the hydrolysis of TEOS by a Stöber growth process, the basic condition could promote the secondary nucleation of existing silica seeds which enables the resulting silica particles with relatively large sizes [8]. Accordingly, the resulting HPC sample exhibits a combined I/IV type isotherms with a small hysteresis loop within the relative pressure P/P_0 of 0.4–0.8 indicating the coexistence of micro- and meso-pores (Fig. 2a) [9]. Pore size distribution of HPC also suggests the hierarchical pore structure with enlarged and expanded pore sizes around 1.5 nm, 3 nm and 10 nm (Fig. 2b). X-ray photoelectron spectroscopy (XPS) measurements were conducted to elucidate the chemical composition in HPC and MPC (Fig S2 and Table S1). As expected, only C1s and O1s signals can be observed and the F contents of MPC and HPC from XPS analysis are only 0.04% and 0.06%, respectively, which demonstrate

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