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Post-treatment-free synthesis of highly mesoporous carbon for high-performance supercapacitor in aqueous electrolytes

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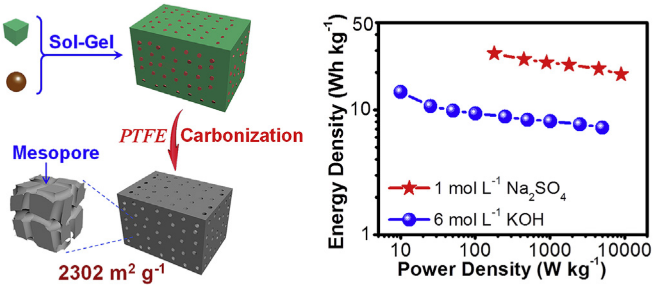
HIGHLIGHTS

- Highly mesoporous carbon was prepared by developing a post-treatment-free route.
- Carbonization and silica template removal were accomplished simultaneously.
- Energy density of 28.3 Wh kg^{-1} at power density of 180 W kg^{-1} was achieved.
- High capacitance retention was achieved in 1.8 V aqueous supercapacitor.

GRAPHICAL ABSTRACT



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ABSTRACT

Exploring well-defined pore structure with high porosity has been a long-pursued goal for the development of porous carbon as high-performance supercapacitor electrodes. The pursuit of high surface area while maintaining uniform pore size remains a formidable challenge because their current template-directed synthetic processes are quite complex and time consuming. Here, we report herein a facile and post-treatment-free approach for synthesis of carbon materials with simultaneously high surface area and uniform mesopore size. The key to this preparation strategy is utilization of polytetrafluoroethylene that can *in-situ* generate hydrofluoric acid to etch out the silica templates during carbonization process. This strategy not only reduces synthesis procedure by combining post-silica-removal and carbonization in a single step, but also eliminates the direct usage of hazardous hydrofluoric acid or corrosive sodium hydroxide. The as-synthesized disordered mesoporous carbon presents higher Langmuir surface area (3257 m^2 g^{-1}), Brunauer-Emmett-Teller surface area (2302 m^2 g^{-1}) and mesopore rate (99.6%) when compared to traditional mesoporous carbon. With combination of high surface area and uniform mesopore size, the mesoporous carbon exhibits attractive capacitive properties in aqueous electrolytes, including large capacitance of 201 F g^{-1}, high energy density of 28.3 Wh kg^{-1} and excellent cycling stability.

1. Introduction

Supercapacitor, an emerging class of energy storage device with high power density, long cycle life and short charging time, is highly attractive as power source for portable electronic devices [1–4]. Currently, the core technology of supercapacitors is

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employment of high-performance electrode materials. Up till now, porous carbons are recognized as one of the most promising electrode materials due to their large surface area, excellent physicochemical stability and good conductivity [5–7]. Those carbon materials with simultaneously high porosity and well-defined pore structure are particularly pursued. Main motivation behind this activity is that exploitation of such state-of-the-art porous carbon electrodes may open unprecedented opportunities for performance breakthroughs in the field of supercapacitor.

Many strategies have been developed to prepare porous carbons with high surface area (*e.g.*, above 1500 m^2 g^{-1}). Generally, activation is recognized as the most common and effective way [8–12] However, extensive creation of pores will undoubtedly cause the collapse of their nanostructures and then leads to ill-defined pore structures such as a wide pore size distribution. Moreover, in ordered to remove impurities derived from chemical activators, repeated and fuzzy post-purification treatments are often required after activation.

With the development of templating methods, porous carbons with precise pore structure can be easily produced [13–17]. Particularly, the employment of a minority of porous silica as hard templates is successful in preparing porous carbon with simultaneously high surface area and narrow uniform mesopore size. These mesoporous carbons exhibit enhanced electrochemical performance and thus offer great potential in supercapacitor, especially for applications for which high power output are required [15,18,19]. A typical mesoporous carbon electrode in aqueous supercapacitor shows specific capacitance and energy density in the range of 100–200 F g^{-1} and 10–50 Wh kg^{-1}, respectively [20–26]. Despite these developments, however, challenges still remain, considering that the hard-templating techniques are associated with some significant bottlenecks [27,28]. For example, removal of the sacrificial silica usually requires harsh chemical post-treatments, such as hazardous hydrofluoric acid or corrosive sodium hydroxide etching. Besides, these repeated post-treatments often use plenty of water to wash off the product, which inevitably generates a large amount of waste liquid and tremendous environmental pollution. Thus, the development of facile synthetic procedures is still an important challenge for synthesis and application of carbon materials with simultaneously high surface area and narrow pore size distribution.

We report herein a facile and post-treatment-free approach for synthesis of carbon materials with simultaneously high surface area and uniform mesopore size. The key to this preparation strategy is utilization of polytetrafluoroethylene (PTFE) that can *in-situ* generate hydrofluoric acid to etch out silica templates during carbonization process. As illustrated in Fig. 1, highly mesoporous carbons (HMPCs) with narrow pore size distribution are obtained by simply mixing the PTFE powder and sucrose-silica organic-inorganic hybrid, followed by direct carbonization. That is to say, the carbonization and silica removal are accomplished simultaneously, avoiding the fussy post-treatment and then decreasing synthetic steps when compared with normal hard-templating procedures. Meanwhile, the handling of toxic hydrofluoric acid or repeated sodium hydroxide washes for the post-removal of silica is eliminated. In addition to being much simpler procedures, this post-treatment-free approach affords HMPC with higher Langmuir surface area (3257 m^2 g^{-1}) and Brunauer-Emmett-Teller (BET) surface area (2302 m^2 g^{-1}) in comparison to the current methods to disordered mesoporous carbon (2674 and 1604 m^2 g^{-1}, respectively). Besides, the as-harvested HMPC exhibits an unusually ultrahigh mesopore rate of 99.6% and a uniform pore size distribution (4.9 nm). Tuning of such a well-defined pore structures of HMPCs could be accomplished by variation of carbonization conditions. Benefiting from the well-orchestrated porous structure, the obtained HMPCs show attractive electrochemical properties when utilized as aqueous supercapacitor electrodes, including large capacitance of 201 F g^{-1}, high energy density of 28.3 Wh kg^{-1} and excellent cycling stability.

2. Results and discussion

In general, the conventional silica-templated mesoporous carbon is prepared by standard two-step process involving carbonization of organic-inorganic hybrid materials, followed by post-etching of silica with hydrofluoric acid or sodium hydroxide [29–31], as shown in Fig. 1. In a significant deviation from this conventional two-step route, the hybrid material with silica content of 44 wt% is simply mixed with PTFE powder and carbonized in N_2 at 900 °C for 9 h, leading to formation of HMPC-1 sample. Representative transmission electron microscope (TEM) images of HMPC-1 at different magnifications are displayed in Fig. 2. It can be vividly found that HMPC-1 possesses interconnected porous network structure with wormholelike, disordered and uniform-sized pores (Fig. 2a). Magnified TEM image of Fig. 2b displays that the carbon framework of HMPC-1 demonstrates an amorphous carbonaceous structure with abundant nanopores. The disappeared silicon peak in the energy-dispersive X-ray spectroscopy (Fig. S1) confirms the complete removal of silica component, indicating the addition of an adequate amount of PTFE power can remove the silica template effectively during carbonization. For comparison, a control sample is prepared by a traditional two-step synthetic technique. TEM (Fig. S2) and scanning electron microscope (SEM) images (Fig. S3) show that HMPC-1 and control sample have very similar morphologies. Therefore, it is well demonstrated that similar to the traditional two-step process, the current one-step approach is also able to afford disorder porous carbon materials with uniform pore size.

N_2 adsorption method is used to quantitatively elucidate the porous structure. As shown in N_2 adsorption-desorption isotherm of Fig. 3a, the HMPC-1 sample exhibits a typical type-IV curve with an obvious hysteresis loop, implying that it is a type of mesoporous materials. The small hysteresis loop appears at relative pressures of 0.5–0.7, which is attributed from the disorder nanopores templated by silica frameworks. According to calculation results obtained by Barrett–Johner–Halendar (BJH) method, HMPC-1 exhibits a very narrow pore size distribution with a maximum at 4.9 nm (see the inset of Fig. 3a). Using the sorption data, the BET surface area (S_{BET}) and Langmuir surface area of HMPC-1 are as high as 2302 and 3257 m^2 g^{-1}, respectively. The mesopore volume and mesopore surface area (S_{mes}) are measured to be 2.23 m^3 g^{-1} and 2292 m^2 g^{-1}, respectively (Table S1). The ratio of mesopores to total pores for HMPC-1 is up to 99.6% (S_{mes}/S_{BET}). These values are significantly higher than those of control sample and many other mesoporous carbons [32–36], indicating that HMPC-1 is a highly mesoporous carbon material with a narrow pore size distribution.

In contrast, the control sample has smaller BET surface area of 1604 m^2 g^{-1} and mesopore volume of 0.94 m^3 g^{-1} (Fig. S4 and Table S1). Such a difference in porous structure is possibly due to the creation of additional pores by the removal of volatile non-carbon elements and carbon-containing compounds upon further pyrolysis. It is demonstrated that when a silica-containing hybrid is mixed with PTFE and heated in inert atmosphere, simultaneous carbonization and silica removal occurs within 650 °C [28]. That is to say, silica component of the sucrose-silica hybrid can be completely removed at the carbonization temperature of 650 °C, leading to formation of porous carbonaceous structure. When further increasing temperature until 900 °C and maintaining 900 °C for several hours, more mass loss occurs because the porous structure provides a quite more rooms for large quantities of