TEMPLATE-FREE FABRICATION OF PITCH-BASED CARBON NANOSHEETS WITH TUNABLE MESOPORES BY MILD MODIFICATION FOR ALL-SOLID-STATE SUPERCAPACITORS

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Introduction

All-solid-state supercapacitors are promising energy storage devices used in portable power tools and wearable electronics due not only to their high power ratings, long cycle life and good reversibility, but also their reliable safety[1]. Carbon nanosheets have been constructed and used as high-performance electrodes by virtue of their smooth short path and continuous conductive pathway for charge carriers[2]. Meanwhile, porous carbons rich in 2~5 nm mesopores with accessible pore volumes and acceptable surface areas are typically regarded as the most brilliant electrode materials[3]. Porous carbon nanosheets (PCNs) with tunable 2~5 nm mesopores are urgently needed although their preparation remains a challenge. Recently, we found that the β-resins extracted from CTP exhibited relatively homogeneous molecular structure with moderate molecular weight[4]. In this work, honeycomb PCNs (HPCNs) with tunable mesopores were synthesized from β-resins by a simple self-assembly method under mild conditions without using templates for the first. The as-obtained HPCNs exhibit the characteristics of a well-defined nanosheet and tailored porosity. Moreover, the honeycomb PCNs-based electrode exhibited superior electrochemical performance with outstanding specific capacitance, excellent rate capability and high cyclic stability.

Materials and Methods

Typically, 150 g β-resins were oxidized with 300 mL H_2O_2 solution, followed by incubation in an ultrasonic water bath for 30 min. The obtained mixture was then heated at 80°C with stirring for another 2 h. The oxidized β-resins (βO) was washed with distilled water and dried at 100°C in a vacuum oven. Subsequently, 100 g βO were reacted with different amounts of rosin (10, 20, 30, and 40 g) at a mild temperature of 300°C for 4 h in a 1-L autoclave with stirring. The obtained product was named βO-Rx, where x represents the amounts of rosin. To obtain HPCNs, βO-Rx and KOH were mixed and heated up to 750°C for 1 h under a nitrogen atmosphere. The products were repeatedly washed with deionized water and dried in an oven at 120°C for 12 h and designated as βO-R_xA.

Results and Discussion

The specific morphology of βO-R_{30}A is confirmed by the HRTEM image in **Figure 1**. Under low magnification, abundant bright holes are clearly observed, indicating the formation of a continuous three-dimensional pore network. The high magnification images of βO-R_{30}A display the relatively ordered graphitic layers of edges and corresponding lattice fringes, which is composed of a short-range ordered polycrystalline structure of nanosheet carbons. The polycrystalline structure is further confirmed by the annular selected area electron diffraction (SAED) pattern. The data reveals that βO-R_{30}A has a specific surface area of 3058 $m^2\ g^{-1}$ and well-developed micropores and mesopores compared with the other samples (**Table 1**). The βO-R_{30}A based electrode showed a high specific capacitance of 354 F g^{-1} at a current density of 0.5 A g^{-1} in 6 M KOH. Additionally, a symmetrical all-solid-state supercapacitor achieves a high energy density of 12.8 W h kg^{-1} at a power density of 249.5 W kg^{-1} (at the current density of 0.5 A g^{-1}). The acceptable performance of the βO-R_{30}A electrode might benefit from the nanosheet structure together with abundant narrow mesopores.

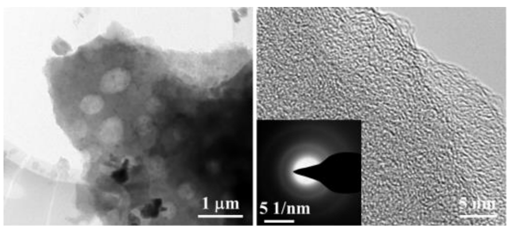

Figure 1. HRTEM images of the βO-R_{30}A

Table 1. The pore parameters and capacitance performance of βO-R_{30}A

pore parameters	S_{BET} ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)
	3058	1.58	0.97
capacitance performance	SC (F g^{-1})	ED (W h kg^{-1})	PD (W kg^{-1})
	354	12.8	249.5

Conclusions

We have demonstrated an effective and template-free strategy to fabricate βO-R_{30}A from modified β-resins using H_2O_2 and rosin. As-obtained βO-R_{30}A exhibits honeycomb mesoporous characteristic with a large specific surface area as well as outstanding capacitance performance. This work paves a path for high-value pitch-based products and provides a carbon nanosheet material with promising potential for application in flexible supercapacitor devices.

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