CONSTRUCTION OF HIERARCHICAL ARCHITECTURE IN WORMHOLELIKE NANOPOROUS CARBON FOR SUPERCAPACITORS

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Introduction

Recently, wormholelike nanoporous carbon (WNC) has been successfully prepared by templating technique, in which wormholelike mesopore (WMP) is obtained from silica gel. This type of carbon nanomaterials has been touted for their enormous potential use as electrodes of electrochemical energy devices for their high surface areas and great pore volumes. However, their WMPs are relatively small in diameter and uninterconnected [1-2]. Without doubt, it would impose serious problems relating to the resistance of ion diffusion within these small WMPs and thus severely reduces the rate performance, which is one of the most important decisive factors for supercapacitors. Therefore, a number of efforts have been devoted to construct proper amounts of secondary larger mesopores as mass transport pathway (MTP) in the WMP framework via using multiple templating techniques [1-3].

Though it has been shown that the introduction of MTP is able to improve ion diffusion performances to a certain [3], the nanostructure of these novel WNCs still shows an intrinsical limitation. That is the insufficient macropores, which can shorten diffusion distance from the external electrolyte to the interior surfaces as ion-buffering reservoirs during charging-discharging process [4], would undoubtedly hinder the further improvement. So much is known, there are few attempts to construct macropores, especially 3D ordered macropores, in the WNC with MTP.

In this work, a novel WNC with hierarchical architecture (HA) was successfully fabricated via a nanocasting route (Fig. 1). The 3D ordered macropores and MTP in the HA were constructed by using the templates of PMMA colloidal crystal and SiO_2 nanoparticle, respectively. Based upon this, their structure-electrochemical property relationship was investigated in detail.

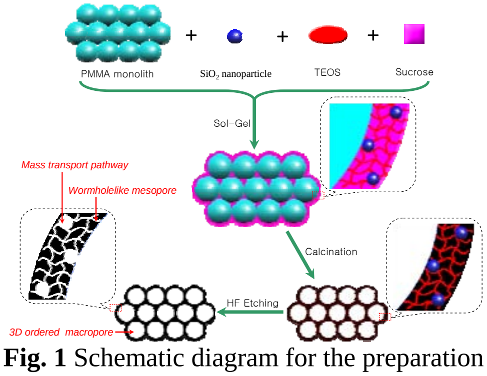

Fig. 1 Schematic diagram for the preparation procedure of WNC with HA.

Experimental

PMMA colloidal crystal was prepared by emulsifier-free emulsion polymerization of MMA, as described elsewhere [5]. For the preparation of WNC with HA, 2 g sucrose, 4 mL TEOS and 0.2 g SiO_2 nanoparticles (Aerosil-200, Degussa) were mixed in 2 mL of 0.5 mol/L H_2SO_4 aqueous solution under stirring until complete homogenization. After that, a proper amount of these mixtures were added to an open flask containing 2.8 g PMMA. Keep the solution level below the top of colloidal crystal until completely infiltrated. The obtained composite was aged at 40 ^oC for 24 h, followed by heating at 60 ^oC for a further 24 h and subsequently at 100 ^oC for another 24 h. The sample was heated to 800 ^oC with a heating rate of 5 ^oC/min, and kept at carbonization temperature for 3 h in N_2 flow. WNC with HA was obtained after the carbon/SiO_2 were washed using HF. The WNC without HA was prepared by exactly the same procedure as that of WNC with HA, except that the employment of SiO_2 and PMMA was bypassed.

Results and Discussion

As showed in Fig. 2A, the WNC without HA shows that erose carbon pieces aggregate and stack each other into a scrap paper-like carbon. Their structure is lack of macropores. In comparison, the WNC with HA shows a 3D ordered macroporous framework. Its average pore diameter is 150 nm estimating from SEM images (Fig. 2B). Meanwhile, pore windows are formed between these macropores and they are well-interconnected, which can be observed from the TEM image of Fig. 2C. It can also be seen from Fig. 2C that the WNC with HA has a unique hierarchical porous texture. The carbon skeleton, which circle round and bridge to form 3D ordered macropore, are nanoporous in themselves. Furthermore, these nanopores evenly distributed in 3D ordered skeletons include WMP (ca. 2~3 nm) and MTP (ca. 8~12 nm), which are obtained from silica gel and SiO_2 nanoparticles, respectively.

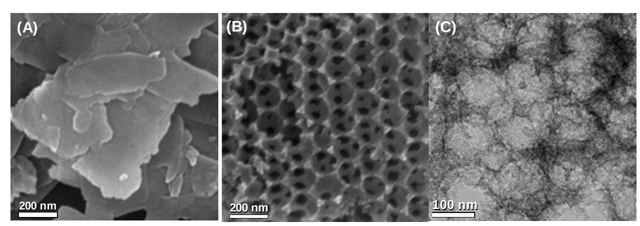

Fig. 2 SEM images of (A)WNC without HA; (B) WNC with HA, and (C) TEM image of WNC with HA.

The pore structures of the WNCs were evaluated in detail by N_2 adsorption-desorption properties. For WNC without HA, a small hysteresis loop is presented at a relative pressure of about 0.4, which results from the capillary condensation of N_2 within WMPs. The diameter of these WMPs is 2.7 nm calculated by DFT method (see the inset in Fig. 3). When SiO_2 nanoparticles and PMMA colloidal crystal were employed, the as-prepared WNC exhibits three hysteresis loops at relative pressures of ca. 0.4, 0.7 and 0.9 in its N_2 adsorption-desorption isotherm, demonstrating that the presence of a significant amount of pores with an increasing average pore diameter. The pore size distribution reveals that besides WMPs, a lot of MTPs with the maximum peak at 10 nm are generated. They probably originate from the SiO_2 nanoparticles. As a result of aftermentioned pore properties, this novel WNC with HA has a high BET surface area of 1695 m^2/g and a total pore volume of 1.3 cm^3/g. Such a gorgeous porosity could provide abundant active surface for the formation of electrical double layer, and the unique hierarchical pore system designed also may give a better ion diffusion performance.

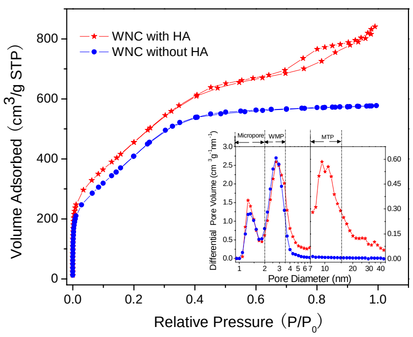

Fig. 3 N_2 adsorption-desorption isotherms of WNC with and without HA (the inset show their DFT pore size distribution).

The influence of HA construction on the capacitive behavior is evaluated by EIS and CV. Fig. 4A presents the Nyquist plots recorded in an alkaline electrolyte of 6 mol/L KOH. For the typical Nyquist plots of porous carbon material, a semicircle would occur in the high frequency region. Considering the fact that both the electrolyte and electrode-fabrication technique are the same, the diameter of the semicircle is only referred to the polarisation resistance (R_p) of active electrode materials. Such R_p is believed to reflect the penetration of the electrolyte into the pores of carbon samples [6]. The comparison of the semicircles shows that the R_p of WNC with HA (2.5 Ohm) is much smaller than that of WNC without HA (5.2 Ohm), suggesting a lower impedance on electrode/electrolyte interface and accelerated movement of ions inside the naopores in WNC with HA. On the other hand, the inclined line of WNC with HA is more close to the theoretical vertical line than that of WNC without HA, indicating a better pore accessibility for electrolyte in WNC with HA.

As a result, no matter at high or low sweep rates, the WNC with HA shows excellent improved mass specific capacitances compared to traditional WNC (Fig. 4B). For example, when operating at 5 mV/s, the former possesses a specific capacitance as high as 247 F/g, whereas the latter has only 176 F/g. It is noteworthy that both WNCs mentioned above are derived from the same carbon source and carbonization conditions, thus have identical conductivity and electrolyte wettability. Therefore, the superior ion diffusion behavior of WNC with HA must arise from the possession of a pore structure that is beneficial to ion diffusion properties. Considering the action of the pores in WNC with HA , it is believed that the 3D ordered macropores serve as ion-buffering reservoirs, which can shorten the diffusion distance from the external electrolyte to the interior surfaces, while the MTPs can minimize the ion transport resistance in WMP and micropores of carbon wall [4].

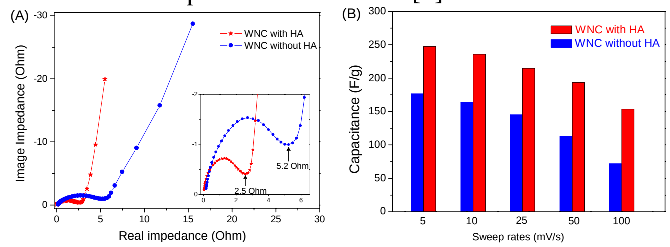

Fig. 4 Electrochemical properties of WNC with and without HA: (A) Nyquist plots in the range of 10 k to 10 mHz; (B) Specific mass capacitance calculated from CV measurement.

Conclusions

We have successfully constructed HA in wormholelike nanoporous structure by using PMMA colloidal crystal and SiO_2 nanoparticle as the templates of 3D ordered macropores and MTP, respectively. The electrochemical experiments showed that the introduction of HA within WMP network is very helpful in meliorating ion diffusion properties, thus resulting in a better capacitive performance. It is believed that the 3D ordered macropores served as ion-buffering reservoirs and the MTPs minimized ion transport resistance contribute synergistically to the improved performance.

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