

AN APPROACH TO MICROPORE-ENRICHED CARBON AEROGEL BY EMPLOYING NITROGEN AS AN ATOM LEVEL TEMPLATE

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Introduction

Carbon aerogels (CAs) show a great potential application in high power density supercapacitor because of their three-dimensional (3-D) continuous mesoporous structure and skeleton which are able to provide much faster ion transport and electron pathways, respectively. However, these CAs still exhibit a limited useable surface area for electric double-layer (EDL) formation, thereby resulting in a low energy density of the as-prepared supercapacitors. Usually, KOH activation is taken to increase the useable surface area for EDL formation [1, 2]. Nevertheless, this strategy may sometimes cause the skeleton collapse and accordingly narrow or even destroy the mesopore and also leads to a tedious procedure since the residual KOH must be removed by using a lot of acid and water [1, 2]. Here, we report a novel strategy for the production of micropore-enriched CA (MCA) by introducing ammonia (NH₃) as a pore generating reagent. NH₃ could react with the oxygen functional groups (OFG) of organic aerogels (OAs) and then hide into the carbon matrix during semi-carbonization. At the subsequent carbonization step, such latent nitrogen would escape as an atom-level soft template, remaining a large number of micropores without changing the skeleton and mesoporous structure of CA noticeably. In consequence, the as-prepared sample showed a more extraordinary supercapacitance behavior than the origin CA.

Experimental

The synthesis of OA was based on the previous report via a microemulsion-templated sol-gel polymerization method [3] with some modifications. In brief, resorcinol (R), formaldehyde (F), deionized water (W) and cetyltrimethylammonium bromide (CTAB) were mixed by a magnetic stirrer at room temperature and then transferred into a glass vial (R/F=1/2, R/CTAB=125). The vial was sealed and then put into a water bath (85 °C) to cure for 3 days. After curing, the as-prepared OA was directly dried in the air at room temperature for 1 day first, and finally dried in an oven at 100 °C under ambient pressure for over 8 h. Subsequently, approximately 1 g of OA was semi-carbonized at 500 °C under a flowing mixture gas of N₂ and NH₃ at a volume ratio of 7: 1 for 3 h, and then carbonized at different temperatures of 600-900 °C under N₂ atmosphere for 3h. The resulting semi-

carbonized and carbonized samples were denoted as CA-N-500 and MCA-N-500/*x*, respectively, where *x* represented the carbonization temperatures of the as-prepared samples. At the same time, another two semi-carbonized and carbonized CA samples were prepared under N₂ atmosphere without ammonia at 500 °C and 900 °C, which were denoted as CA-500 and CA-500/900, respectively.

Some powders of the CA-500/900 and MCA-N-500/900 samples were dispersed with ethanol onto a copper grid for microscopic examination. The structures of the CA and MCA samples were observed by a transmission electron microscope (TEM, JEOL JEM-2010). About 0.1 g samples were heated to 250 °C to remove all the adsorbed species. Nitrogen adsorption and desorption isotherms were then taken using an ASAP 2010 surface area and porosity analyzer (Micromeritics Instrument Corporation). XPS measurements were carried out with an ESCALAB250 instrument.

Electrochemical capacitance was measured in 1 M H₂SO₄ using a sandwich-type two-electrode testing cell. The electrodes were prepared by pressing a mixture of carbon samples, polytetrafluoroethylene and commercial carbon black in the ratio of 8.5:0.5:1 onto a stainless steel mesh current collector. The net weight of each electrode was between 6 and 8 mg. A sandwich-type supercapacitor consisting of two similar sample electrodes was assembled. And the electrodes and separators were soaked in 1 M H₂SO₄ electrolyte for over 8 h before each assembling. All electrochemical measurements were performed with the assembled two-electrode supercapacitors at ambient temperature. Galvanostatic charge-discharge tests were executed at different current densities between 0.1 A g⁻¹ and 2.5 A g⁻¹ using an ARBIN instrument.

Results and Discussion

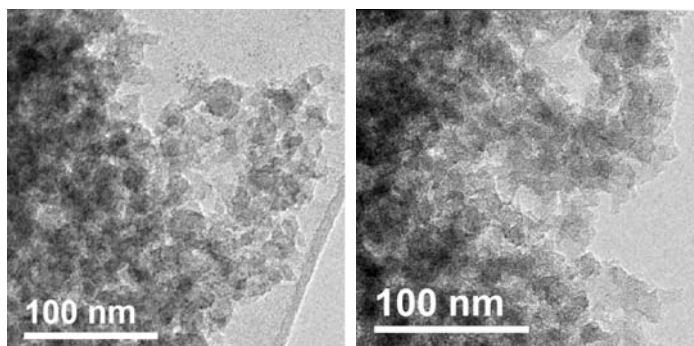


Figure 1. TEM images of CA-500/900 (left) and MCA-N-500/900 (right)

According to TEM observation and N₂ adsorption-desorption measurements, the as-prepared MCA samples represented comparable carbon skeleton and mesopore structure as well as a much higher micropore surface area (736 m² g⁻¹) compared to CA (353 m² g⁻¹). As a result, MCA has much higher BET surface area (1100 m² g⁻¹) than CA (620 m² g⁻¹). Interestingly, the two semi-carbonized samples with and

without NH_3 -assisted showed identity pore structures. Judging from this phenomenon, the formation of micropores should process by following 3 steps: (1) a large quality of OCF form on the OA arising from the oxygen-enriched raw material of R and F; (2) NH_3 reacts with such OCF and then the nitrogen atom hides into the carbon matrix during NH_3 -assisted semi-carbonization; (3) the latent nitrogen then escapes from the carbon matrix like a kind of atom-level soft template during the carbonization process, and thus a lot of micropores are created. Furthermore, XPS test also confirm that the decomposition of the latent nitrogen is one of the main factors of micropores formation.

Table 1 Pore parameters of the as-prepared samples

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{mic} ($\text{m}^2 \text{g}^{-1}$)	S_{mes} ($\text{m}^2 \text{g}^{-1}$)
CA-500/900	620	353	268
MCA-N-500/900	1100	736	359
CA-500	564	263	271
CA-N-500	530	248	281

Electrochemical measurements showed that the C_m and C_s for the MCA capacitors are much greater than ones obtained from CA, which is primarily attributable to the following two factors: (1) the more developed microporosity of MCA provides the more place where EDL forms, and (2) the N-6 and N-5 groups offer unnegligible pseudocapacitance considering from the higher C_s of MCA, which has been reported before. In the same time, MCA also shows a high capacitance retention ratio (about 85%) compared with CA when the current density increases from 0.1A to 2.5A (Figure 2) because that the 3-D continuous carbon skeleton and pore structure of MCA are kept well under nitrogen-assisted semi-carbonization. Therefore, such CA obtained by nitrogen-assisted semi-carbonization would be an attractive prospect with potential for both high energy density and high power density supercapacitors.

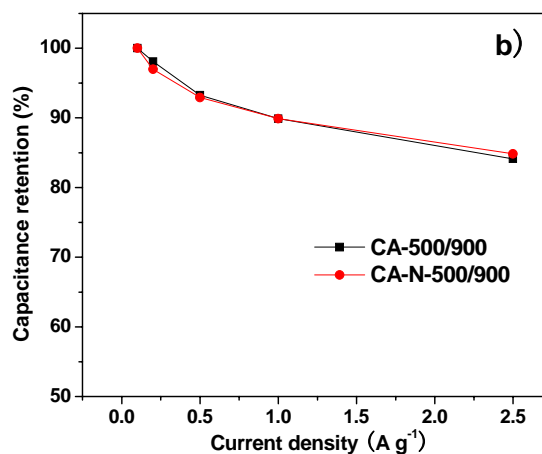
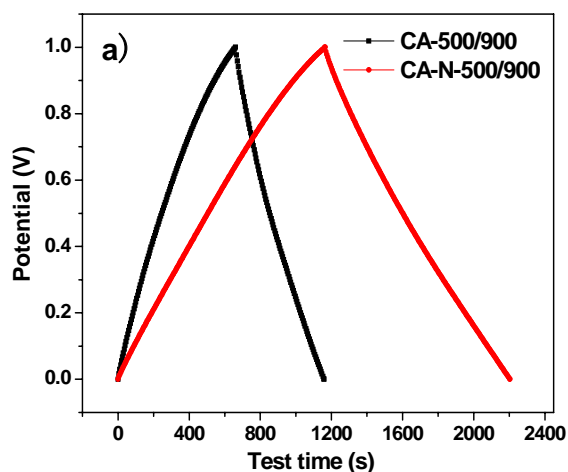


Figure 2 a) Galvanostatic charge-discharge curves at 0.1 A g^{-1} and b) specific capacitance retention at different current densities of CA-500/900 and MCA-N-500/900

Conclusions

An atom-level soft template of nitrogen was introduced into the matrix of CA by NH_3 -assisted semi-carbonization in order to introduce abundant micropores without damaging the pristine skeleton of carbon aerogels. Experimental results showed that a high S_{BET} of $1100 \text{ m}^2 \text{g}^{-1}$ can be reached, while the mesoporosity remained unchanged. Through the combination of the advantages of high microporosity and well-maintained mesopore structure, the resulting MCA shows much higher C_m (208 F g^{-1}) compared with the origin CA (99 F g^{-1}) as well as with a comparable capacitance retention (about 85%) when the current density increases by 25 times. The results presented here are of technological interest as this MCA is a promising candidate for electrode materials of supercapacitors with high energy density and high power density.

Acknowledgements

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