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Bilayer N-doped carbon derived from furfuryl alcohol-wrapped melamine sponge as high-performance supercapacitor

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ABSTRACT

Bilayer carbon is synthesized via carbonization of furfural alcohol-wrapped melamine sponge. Such materials combine the merits of carbonized furfuryl alcohol and melamine sponge: melamine sponge-derived three dimensional N-doped carbon serves as skeleton and support to avoid the agglomeration of furfuryl alcohol; while the furfuryl alcohol coating enhances the carbon yield, avoids the nitrogen loss of melamine sponge and introduces the second carbon layer. Carbonized furfuryl alcohol-wrapped melamine sponge shows the highest specific capacitance of 184 F g^{-1} at the scan rate of 5 mV s^{-1}, which is almost four times that of carbonized melamine sponge without furfuryl alcohol coating (47.3 F g^{-1} at 5 mV s^{-1}). Based on the electrochemical measurements, it suggests that the nitrogen content, especially the quaternary nitrogen content and the graphitization degree of carbon are two key dominant factors in enhancing the capacitive performance after furfuryl alcohol coating.

1. Introduction

Recently, three-dimensional (3D) carbon and carbon-based materials such as carbon aerogels, carbon nanotube sponges, carbon nanofiber foams and graphene foams have been extensively studied for use in supercapacitors [1–5]. However, the major problem of such 3D materials is the lack of macro- and mesopores; thus limiting ion diffusion rate in their internal structure [2,6–9]. To address the above-mentioned problems, the prepared 3D materials should have hierarchical pores with macro- and mesopores to facilitate the electrolyte and ion diffusion whereas the micropores increase the capacitance by increasing the ion-accessible surface area [10–13]. Besides the structure design, introducing heteroatoms in the carbon network is another way to enhance the supercapacitor performance [14–17]. These heteroatoms can enhance the wettability of the interface between the electrolyte and the electrode, improve the electronic conductivity and generate reversible pseudocapacitance [18,19].

Melamine sponge (MS) is an environmentally friendly material and has been widely used in kitchen and as building materials [20–22]. 3D N-doped carbon network with macro and mesopores can be formed after carbonization; thus making it an ideal materials to be used as electrode materials [23]. However, direct carbonization of MS usually gives very low carbon yield and great nitrogen loss occurs during carbonization, resulting in limited nitrogen doping; thus greatly restricting the further improvement of capacitive performance [24–26].

In this study, furfuryl alcohol (FA) was used to modify MS [20]. By coating a thin PFA layer onto MS, bi-layer carbon would be formed with the MS-derived N-doped carbon as core and skeleton and FA-derived porous carbon as outer layer. Compared to direct carbonization of MS, the introduction of FA on MS can enhance the carbon yield of MS, inhibit the loss of nitrogen and improve the conductivity of the MS-derived carbon. Furthermore, FA can produce micropores via the carbonization [27], and the 3D MS-derived carbon acts as the support to avoid agglomeration of FA. Therefore, due to the bi-layer structure, 3D pore structure and synthetic effects of FA and MS, high capacitive performance of such carbonized FA-MS is expected.

2. Experimental

Commercial MS (LD-1539F, 8 × 5 × 2.5 cm^3) was firstly cut into small blocks with a size of 1 × 0.5 × 0.5 cm^3 and then soaked into 100 mg/mL FA-ethanol solution overnight. After soaking, MS was taken out and dried at 200 °C to allow the polymerization of FA. The samples were then carbonized in nitrogen at 750–950 °C for 3 h with a heating

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rate of 10 °C/min to obtain porous N-doped carbon with two carbon layers. The samples were named as FA-MS-x whereas x indicates carbonization temperature. For comparison, pristine MS was carbonized at 900 °C and named as MS-900. Carbon yield for MS and FA-MS was measured by weighing the sample before and after carbonization. The morphology of the samples was examined by scanning electron microscopy (SEM, JSM-7600F, JEOL Ltd., Japan) and transmission electron microscope (TEM, Model 2100F, JEOL Ltd., Tokyo, Japan). Raman spectra were collected by a Themor DXR530 with an argon ion laser operating at 523 nm for excitation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Daojin AXIS UltraDLD spectrometer equipped with an Al-Ka X-ray source. The as-prepared carbon material (the active material) was mixed with poly (tetrafluoroethylene) (PTFE) and acetylene black in a weight ratio of 8:1:1 to make electrodes. Around 2 mg of the active material was infiltrated into commercial Ni foam with the help of ethanol. After being dried at 65 °C for 24 h, the Ni foam loaded with the active material was pressed under 10 MPa to act as the working electrode. A three-electrode system consisting of the above working electrode, Pt foil (the counter electrode) and Hg/HgO (the reference electrode) was used to test the electrochemical performance of the carbonized MS and FA-MS in 6 M KOH aqueous solution within a potential range from −1 to 0 V. The cyclic voltammetry (CV) and galvanostatic charge-discharge properties (GCD) tests were performed on an electrochemical working station (CHI 760e). A two-electrode system was also examined by using carbonized FA-MS as both positive and negative electrodes in 6 M KOH aqueous solution. The distance between two electrodes was ~1 cm. The CV and GCD tests were performed on the same electrochemical working station mentioned above and the energy density and power density of symmetrical supercapacitors were calculated based on CV and GCD tests.

3. Results and discussions

The optical views of MS, FA-wrapped MS (FA-MS) and carbonized FA-MS are shown in Fig. 1a–c. After MS being coated by FA and dried in oven, the color of MS changed from pure white to brownish (Fig. 1b), indicating the successful polymerization of FA wrapping around melamine wires. In our previous study, we proved that FA can react and bond with melamine sponge, and then form the second layer around melamine skeleton via the polymerization. After carbonization, FA-MS greatly shrank and formed into small black blocks (Fig. 1c). Compared to pristine MS, FA-MS had higher carbon yield after carbonization (the carbon yields of MS and FA-MS were approximately 6% and 25%, respectively).

SEM image of MS (Fig. 1d) shows that MS has an interconnected network with a smooth surface. After carbonization, the melamine wires were broken as shown in Fig. 1e (MS-900). However, after FA coating, FA-MS still maintained the original 3D skeleton structure. The surface of melamine wires became rougher with the second carbon layer wrapped at the outer side, especially at interlacing points where the thin flat carbon layers with a size of several microns was formed to “connect” the neighboring wires together (Fig. 1f and g). Through TEM image of FA-MS-900 (Fig. 1h), bilayer carbons were observed with the core formed by the carbonization of melamine wires and the shell formed by carbonization of polymerized furfuryl alcohol (PFA) as the second porous carbon layer.

In order to study the graphitization degree, Raman spectroscopy and XRD were performed and the results are shown in Figs. 2a and S1. From XRD patterns of MS-900 and FA-MS-900 (Fig. S1), both samples show an obvious peak at 26° ((002) facet of the graphite), which indicated the formation of graphitized carbon [28]. From Raman spectra, the peaks located at 1363 and 1603 cm^{-1} correspond to the D- and G-bands of carbon, respectively (Fig. 2a). The higher values of I_G/I_D indicates higher degree of graphitization in carbon materials [29]. The values of I_G/I_D for FA-MS-950, FA-MS-900, FA-MS-800, FA-MS-750, MS-900 and MS-950 were calculated to be about 1.24, 1.02, 0.95, 0.91, 0.97 and 1.03, respectively, indicating that higher carbonization temperature resulted in higher graphitization degree and at the same carbonization temperature, the introduction of FA on MS facilitated the carbon graphitization; thus higher conductivity is expected in FA-MS compared to MS.

The CV curves of carbonized FA-MS-900 and pristine MS at different scan rates from 5 to 200 mV s^{-1} are shown in Fig. 2b and c. All the curves have a quasi-rectangular shape with broad humps at −1–−0.4 V, indicating that both double-layer capacitance and pseudo-capacitance contributed to the total capacitance. The pseudo-capacitance can be attributed to the Faradic redox reactions of the surface nitrogen in the carbon network resulted from the carbonization of MS. Trasatti method was used to roughly estimate the contribution of pseudo-capacitance caused by N-doping to the total capacitance [30]. For FA-MS-900, the total capacitance, electrical double capacitance and the maximum pseudo-capacitance were calculated to be 204.08, 120.08 and 84.00 F g^{-1} and for MS-900, the total capacitance, electrical double layer capacitance and the maximum pseudo-capacitance were

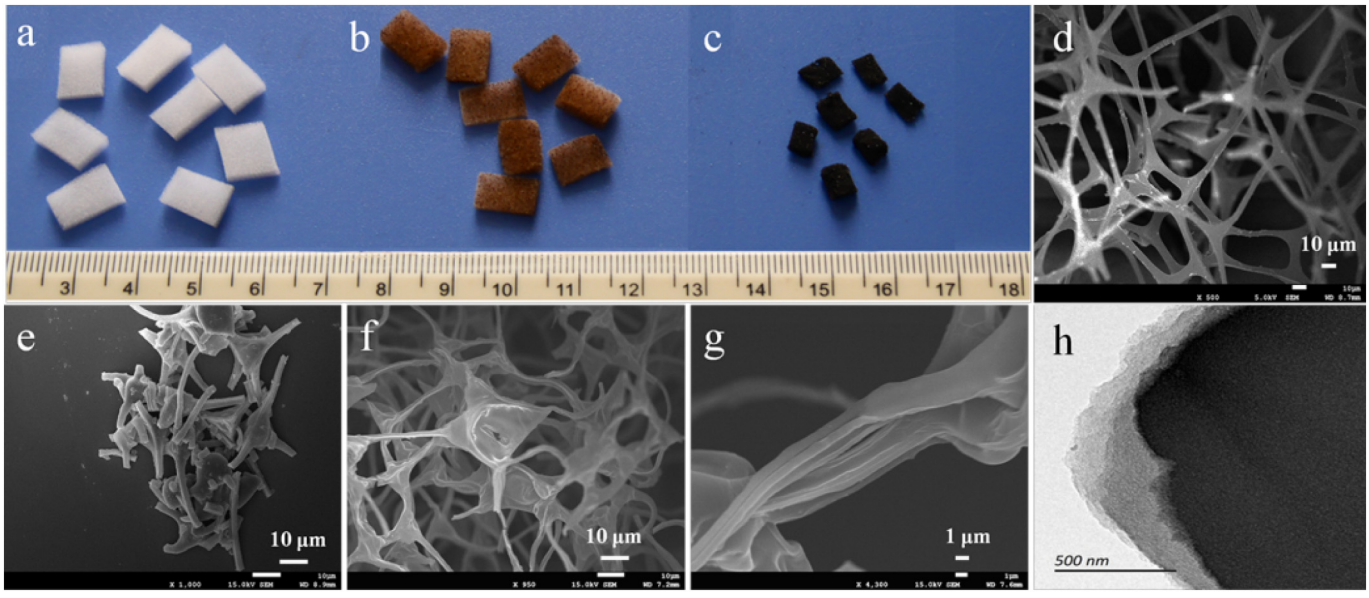

Fig. 1. Optical view of MS (a), FA-MS (b) and carbonized FA-MS at 900 °C (c), SEM images of MS (d), MS-900 (e) FA-MS-900 (f, g), and TEM image of FA-MS-900 (h).