Interconnected mesoporous carbon sheet for supercapacitors from low-cost resources

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1. Introduction

Supercapacitors have attracted much attention as the promising energy storage device. Porous carbons including microporous carbon, mesoporous carbon and macroporous carbon, are the main electrode materials for supercapacitors due to their high surface area and good conductivity [1,2]. Aqueous [2] and organic electrolytes [1] as well as ionic liquids [3] are the main electrolytes used in supercapacitors. Ionic liquids show potential applications due to their high decomposition voltage (V) because the energy density of supercapacitor (E) is based on $E=0.5CV^2$. Nevertheless, the energy density of supercapacitors fabricated from microporous carbons obviously decreases at higher current density because of the longer and narrower channels in microporous carbons for the bigger size of electrolyte ions [4,5]. As such, it is of great interest to synthesize mesoporous carbon sheets (MCSs) with shorter and wider channels by using templates or porogens coupled with KOH activation [6]. Nanostructured carbon materials, for example, graphene [7,8] and carbon nanotubes, are also used to prepare supercapacitors, however, they are suffering high costs. Therefore, it is highly desirable to prepare MCS electrode materials for supercapacitors from low-cost resources. In this work, we prepare interconnected MCS for supercapacitors by using low-cost materials as both carbon precursors and porogens. Coal tar pitch is used as carbon precursor for this aim because it is thermoplastic with high carbon yield and low ash content [5]. CaCO3 nanoparticles were selected as templates and porogens because they could be removed easily by diluted acidic solutions. Additionally, a surfactant, cetyltrimethyl ammonium bromide (CTAB) was also used in the synthesis of MCS to improve the dispersibility of CaCO3 nanoparticles and simultaneously functions as a co-porogen to generate additional micropores and mesopores in the carbonization step.

2. Experimental

A coal tar pitch with a softening point of 110 °C provided by Maanshan iron & steel Co., Ltd, was used as the carbon precursor [9]. First, coal tar pitch with a particle size below 100 μm, CaCO3 nanoparticles (ca. 50–100 nm in size from Ruicheng Xintai Nano-Materials Technology Co., Ltd), and CTAB (99.0%) were dispersed in tetrahydrofuran (THF, 99.0%) solution and ethanol solution, respectively. The mixed solution was dried in water bath at 90 °C, and then was transferred to a corundum crucible. The corundum crucible was heated at 5 °C min$^{-1}$ to 850 °C, then kept at 850 °C for 1 h in flowing nitrogen (99.999%). After cooling down to room temperature, the obtained sample was washed with 2 M HCl solution and distilled water thoroughly, then dried at 110 °C for 24 h. The as-made carbon is denoted as MCS-x:y:z, where the subscript x, y and z stand for the mass ratio of CaCO3, coal tar pitch and CTAB. The pore structure of MCS was analyzed by the nitrogen adsorption–desorption isotherms at $-196$ °C (Micrometrics, ASAP 2010)
The microstructures of MCSs and CaCO$_3$ were characterized by field emission scanning electron microscopy (FESEM, Nanosem430), transmission electron microscopy (TEM, JEOL-2100), and X-ray diffraction (XRD, Philips X, CuKα Radiation). The electrodes were prepared by mixing MCS, poly(tetrafluoroethylene) and carbon black in a mass ratio of 89:6:5, and pressed at 15.0 MPa for 10 s, then dried at 110 °C for 1 h under vacuum conditions. More details can be found elsewhere [9]. Button-type supercapacitors were assembled with two similar carbon electrodes separated by a separator in 1-butyl 3-methyl imidazole six fluoride phosphate (BMIMPF$_6$) electrolyte in an Ar-filled glove box. The galvanostatic charge/discharge performance of supercapacitors was evaluated on a land cell tester (CT-2001A) at room temperature.

### 3. Results and discussion

The nitrogen adsorption–desorption isotherms of the as-made MCSs are shown in Fig. 1(a), which indicate that all of the MCSs contain a number of mesopores and macropores as evidenced by the hysteresis loop [10]. Fig. 1(b) shows that MCS$_{2-1-1}$ possesses the continuous distribution pores, ranging from 25 to 150 nm. MCS$_{2-1-2}$ and MCS$_{1-1-1}$ also have wide distribution pores, respectively. Yet, the pores of MCS$_{2-1-0}$ center at 19–69 nm and 234–256 nm. The above results show that the pore size can be adjusted by the addition of CTAB to the reactants. Fig. 1(c) shows the XRD patterns of MCS samples. The diffraction peaks at ca. 25°–28° and 40–45° are (002) and (100) peaks of MCSs, respectively. The interlayer spacing (d$_{002}$), the average crystallite size along the c-axis ($L_c$) and the size of the layer planes ($L_d$) of MCSs were calculated using Bragg’s equation and the Scherrer equation, respectively [11]. The $L_c$ and $L_d$ of MCS$_{2-1-2}$ reaches 123 nm and 48 nm, which is the biggest among all the MCSs, respectively. Correspondingly, the d$_{002}$ of MCS$_{2-1-2}$ is 0.349 nm while that of the other three samples ranges from 0.350 nm to 0.358 nm, which are bigger than that of graphite (d$_{002}$=0.335 nm). The higher d$_{002}$ value means that the MCSs were disordered and proper graphitization had not taken place.

The pore structure parameters of MCSs are summarized in Table 1. Compared to MCS$_{2-1-1}$, the S$_{BET}$ and $V_t$ of the MCS drops with decreasing CaCO$_3$ content or increasing CTAB content in the mixture. The S$_{BET}$ of MCS$_{2-1-1}$ is 129 m$^2$ g$^{-1}$ with a $D_{ap}$ of 6.71 nm, a $V_t$ of 0.02 cm$^3$ g$^{-1}$ and a yield of 11.7%.

Fig. 2(a) and (c) shows the TEM images of the CaCO$_3$ nanoparticles and MCS$_{2-1-1}$. Fig. 2(a) shows that the diameters of the CaCO$_3$ templates are ca. 50–100 nm (circled by white circles). Fig. 2(b) shows that the pore sizes of MCS$_{2-1-1}$ are ca. 100 nm, which are formed due to the site-occupation of CaCO$_3$ particles in the precursor matrix. Fig. 2(c) proves that the thin sheets in MCS are interconnected, and a macropore can be seen after CaCO$_3$ particle is removed. Compared to the bigger pore sizes of MCS$_{2-1-0}$ in Fig. 2(d), Fig. 2(b) illustrates that the pore sizes of MCS$_{2-1-1}$ can be decreased by adding CTAB to the reactants, which is consistent with the variation of the D$_{ap}$ in Table 1.

Fig. 3(a) is the charge–discharge curves of MCS electrodes in BMIMPF$_6$ electrolyte at 0.05 A g$^{-1}$, which demonstrates that the MCS electrodes have the typical capacitive behavior. Fig. 3(b) shows the variation of the specific capacitance of MCS electrodes with the current density. The specific capacitance of MCS$_{2-1-1}$ electrode only drops from 117 to 63 F g$^{-1}$ with the current density increasing from 0.05 to 2.0 A g$^{-1}$ because the thin sheet significantly shortens the electrolyte ion diffusion length and the interconnected sheets offer effective electron transport pathways. The surface area-normalized capacitance of MCS$_{2-1-1}$ reaches 90.7 μF cm$^{-2}$ at 0.05 A g$^{-1}$, and 48.8 μF cm$^{-2}$ at 2 A g$^{-1}$ in BMIMPF$_6$ electrolyte, which is even larger than that of 3D hollow porous graphene ball electrode in 6 M KOH electrolyte [9]. The capacitance of MCS$_{2-1-1}$ is always higher than that of other three electrodes due to its continuous distribution pores. The variation of energy density of MCS capacitors with the average power density is shown in Fig. 3(c). The energy densities of MCS$_{2-1-1}$ capacitor are obviously higher than those of other electrodes. At an average power density of 115 W kg$^{-1}$, the energy density of MCS$_{2-1-1}$ capacitor is 64.18 Wh kg$^{-1}$, and remains 22.19 Wh kg$^{-1}$ at 4267 W kg$^{-1}$, being the highest among all the MCS capacitors and still obviously higher than that of Ru/mesoporous carbon composites in 6 M KOH electrolyte [12]. The variation of the specific capacitance with the cycle number at 0.1 A g$^{-1}$ current density is

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**Table 1** Pore structure parameters and yields of MCSs.

<table>
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<tr>
<th>MCSs</th>
<th>$D_{ap}$ (nm)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_t$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{mic}$ (cm$^3$ g$^{-1}$)</th>
<th>Yields (%)</th>
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<tr>
<td>MCS$_{2-1-0}$</td>
<td>6.71</td>
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<td>0.02</td>
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<td>43.9</td>
</tr>
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Fig. 1. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution of MCSs. (c) XRD patterns of MCSs.
shown in Fig. 3(d). After 90 cycles, the capacitance of all the MCS electrodes almost remain the same, and that of MCS$_{2-1-1}$ reaches 93.1% after 100 cycles, displaying excellent cycle stability. The results prove that the MCS made from coal tar pitch using CaCO$_3$ and CTAB as porogens is a low-cost and efficient approach for the production of high performance MCS electrode materials for supercapacitors.

4. Conclusions

Interconnected MCSs for supercapacitors were prepared from low-cost resources with coal tar pitch as carbon precursors by using CaCO$_3$ and CTAB as porogens. The MCS retains a capacitance of 87 F g$^{-1}$ at 0.1 A g$^{-1}$ after 100 cycles in ionic liquid electrolyte with 93.1% capacitance retention, exhibiting excellent cycle
stability. The supercapacitor fabricated from MCS$_{2.1-1}$ shows good rate performance and high surface area-normalized capacitance. This method suggests a low-cost route to synthesize MCS for energy storage materials.

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References