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Outstanding capacitive performance of ordered mesoporous carbon modified by anthraquinone

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ABSTRACT

Ordered mesoporous carbons (OMCs) is one of the most promising electrode material for supercapacitor. However, pure OMCs have low specific capacitance due to its simplex storage mechanism based on electric double layer. In this work, anthraquinone (AQ) is used as a modifier to boost the capacitance of OMCs. The modified materials (AQ/OMCs) can not only provide mesoporous channels facilitating rapid ion diffusion, but also generate extra pseudocapacitance improving specific capacitance greatly. As evidenced by electrochemical measurements, AQ/OMCs can exhibit specific capacitance as high as 346 F g^{-1} in 1 M H_2SO_4 electrolyte at the current density of 0.5 A g^{-1}. Besides, the AQ/OMCs also possess excellent rate performance with capacitance retention ratio of up to 84.3% even at a very high current density of 30 A g^{-1}. The outstanding capacitive performance of AQ/OMCs can be ascribed to the synergic effect between OMCs and AQ, in which ordered mesoporous channels facilitate rapid ion diffusion, and AQ generates large pseudocapacitance. In addition, asymmetric supercapacitor is assembled using AQ/OMCs and OMC as negative and positive electrode, respectively, which can deliver a very high energy density of 14.51 Wh kg^{-1} and excellent long-term cycle stability, retaining 96.3% of initial capacitance, after 10,000 cycles.

1. Introduction

In 21st century, people are looking for alternative energy to solve the crisis of fossil energy and reduce the environmental pollution due to fossil consumption. Supercapacitors, also called electrochemical capacitors or ultracapacitors, are new energy storage devices which store much more energy than traditional capacitors and exhibit higher power density than secondary batteries. Supercapacitors have been considered to be a good candidate for high-power sources to meet the demand for fast growth in power required by devices. Supercapacitors have a variety of merits such as fast charge-discharge rate, long cycle life and wide temperature applicability [1–4]. These features make supercapacitors applicable in electronic products, vehicle hybrid power, mobile communication, and other fields. For such applications, electrode materials play a crucial role in promoting the amount of energy that can be stored by supercapacitors [5,6]. Carbon materials are the most widely used electrode materials for supercapacitors, which have such merits as low cost, good physical and chemical stability, high specific surface area, good electrical conductivity and corrosion resistance [7,8]. However, pure carbon materials have low specific capacitance due to its simplex energy storage mechanism based on electric double layer (EDL). Therefore, many efforts have been made on the introduction of pseudocapacitance into carbon materials.

Organic matter is mostly composed of earth-abundant elements such as carbon, oxygen and hydrogen, which is widely distributed in the nature and can be manufactured in large scales at low price. Among naturally occurring organics, quinone-based structures are remarkable for their reversible electrochemical redox couples that could produce pseudocapacitance [9]. Therefore, quinones [10–12] such as hydroquinone (HQ), benzenequinone (BQ), anthraquinone (AQ), can be used in combination with carbon materials to prepare quinone/carbon composites for supercapacitors. Duan et al. introduced HQ into a three-dimensional graphene framework via π-π interaction to prepare functionalized graphene hydrogels (FGHs).

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The FGHs exhibited both good capacitive performances and excellent mechanical flexibility [13]. Unfortunately, HQ is hydrophilic and easily dissolved in aqueous electrolyte, which leads to the loss of HQ from the electrode and the deterioration of capacitive performance. Hu and coworkers [14] have introduced tert-butylhydroquinone (TBHQ) into graphene nanosheets (GNS), which resulted in the decrease of quinone solubility in aqueous electrolyte. As a result, the TBHQ-modified graphene nanosheets showed a maximum value of 302 F g^{-1} that is 51% higher than GNS in specific capacitance [14]. Gollas and coworkers introduced 2-nitro-1-naphthol into carbon black. The organic redox couple contributed a capacity of 35 $mAhg^{-1}$ to the overall charge storage capacity and the pseudocapacitance decreased by less than 20% after 1000 charge/discharge cycles [15]. Pickup et al. have introduced AQ into carbon fabric named Spectracarb 2225 [16]. The AQ-modified Spectracarb 2225 acting as negative electrode for supercapacitors can provide a 40% enhancement in capacitance and 56–86% rise in energy density than the unmodified counterpart. Compared with HQ and TBHQ, AQ is more hydrophobic and has an extended electron system which can increase the strength of its non-covalent attractions (e.g. through π-π stacking) with carbon surface.

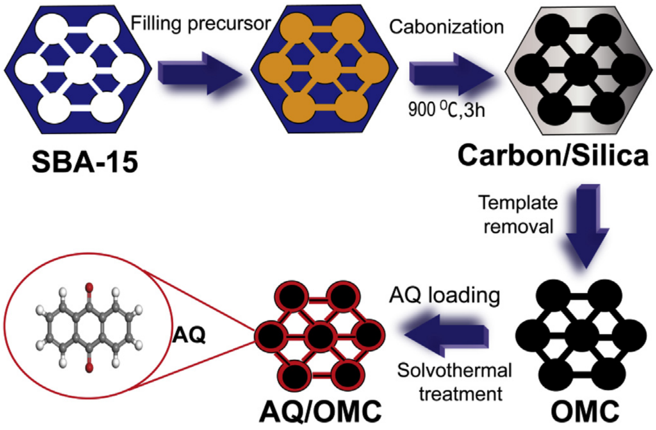
Bélanger and coworkers have introduced AQ into high specific surface active carbon (Black Pearls 2000) with different AQ loadings. They found that most ultramicropores (<0.8 nm) of the carbon were blocked when grafting a small amount of AQ molecules, and larger pores with diameter between 0.8 and 4 nm were also partially blocked at higher AQ loadings [17]. It can be deduced from the above researches that active carbons are not quite suitable for loading of AQ due to its small pore size. Compared with active carbon, ordered mesoporous carbons (OMCs) [18–21] has a variety of merits, such as large pore size, uniform and easily accessible pore channels, which make OMCs a better supporter for AQ, because mesoporous channel of OMCs could effectively avoid being blocked by AQ molecules. This will not only prevent the loss of EDL capacitances caused by pore-blocking, but also contribute pseudocapacitance by AQ molecules. Therefore, the AQ/OMC composites are supposed to be excellent electrode materials for supercapacitors.

Herein, we report for the first time the preparation of AQ-modified OMC (AQ/OMCs) through solvothermal loading. AQ molecules were introduced into the OMCs by π-π stacking [14] between the benzene rings of AQ molecules and carbon surface. This non-covalent combination will not disrupt the sp2 structure of the carbon surface of OMC and not deteriorate the electron transfer on the carbon surface. It was demonstrated that AQ/OMCs exhibit excellent capacitive performance as an electrode material for supercapacitor, which is ascribed to the synergistic effect between OMCs and AQ, in which ordered mesoporous channels facilitate rapid ion diffusion, and AQ generates large pseudocapacitance.

2. Experimental

2.1. Materials

A schematic representation for the preparation of AQ/OMCs is shown in Scheme 1. Mesoporous SBA-15 template was first filled with sucrose precursor. Subsequently, ordered OMC was prepared through the carbonization of sucrose/silica composite and subsequent silica removal. Finally, AQ molecules were adsorbed onto the OMC by solvothermal treatment. The detailed process was depicted as follows:



Scheme 1. Schematic diagram for the preparation of AQ/OMCs.

(1) **Synthesis of the SBA-15 template.** Mesoporous SBA-15 silica template was prepared according to the method reported by Ryoo et al. [22]. SBA-15 silica was synthesized using the tri-block copolymer, $EO_{20}PO_{70}EO_{20}$ (Pluronic P_{123}, MW = 5800, Aldrich) as the surfactant and tetraethyl orthosilicate (TEOS, 98%) as the silica source. In brief, 0.5 g of P123 was added to 19.0 mL of 1.6 M HCl at 35 °C. 1.1 g of TEOS was added to the mixture then stirred with magnetic stirring until TEOS was completely dissolved. The mixture was placed in an oven for 24 h at 35 °C, and subsequently further heated for 6 h at 100 °C. The obtained solid sample was filtered, dried without washing, followed by calcining in air at 550 °C to remove the P123 surfactant.

(2) **Synthesis of OMC material.** The OMC was synthesized using SBA-15 silica as the template and sucrose as the carbon source by a nano-replication method similar to Ryoo's report [22]. The precursor solution, consisted by sucrose (1.25 g), sulfuric acid (0.14 g, 98 wt %) and distilled water (5 g), were mixed with mesoporous silica template SBA-15 (1.0 g) at room temperature. The mixture was dried in an oven at 100 °C for 6 h, then further dried at 160 °C for another 6 h. The sample turned dark brown or black during the treatment in the oven. Additional 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 g of H_2O were added to the obtained dried composite material for second infiltration, and the mixture was dried repeatedly once more as described above. Next, the new composite was carbonized at 900 °C for 3 h in Ar atmosphere. The carbon-silica composite obtained after pyrolysis was washed with HF (5 wt %) solution to remove the silica framework. Finally, the OMC material with two-dimensional hexagonal structure was obtained after filtered, washed with ethanol, and dried at 100 °C.

(3) **Synthesis of AQ-modified OMC (AQ/OMC) Materials.** The AQ-modified OMC (AQ/OMC) materials were prepared by solvothermal treatment. Firstly, a certain amount of AQ was added to 40 ml of ethanol at 65 °C and stirred until AQ was completely dissolved. Then 0.05 g of OMC was added under magnetic stirring. The stirring was continued for 2 h to form a well dispersed solution. Finally, the dark homogeneous solution was dried in an oven at 60 °C for 1 h. The dried products were denoted as TAQX/OMC, where T denotes the solvothermal temperature (60 °C, 65 °C, 70 °C) and X indicates the mass percent of AQ to OMC ($X = m_{AQ}/mOMC \times 100$). For example, 65AQ40/OMC stands for the composite material that was prepared at solvothermal temperature of 65 °C with mass percent of AQ to OMC 40.