Cotton fabric derived hierarchically porous carbon and nitrogen doping for sustainable capacitor electrode

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ABSTRACT

Cotton fabric has been processed into hierarchically porous carbon with a two-step chemical-free method, *i.e.* carbonization in nitrogen and controlled thermal oxidation in air. By optimizing thermal oxidation temperature, large surface area of 777 m^2/g could be achieved in cotton fabric derived carbon. The processed carbon remained the micron-meter tubular structure (same as cotton fiber), while meso-/micro-pores were also generated on tube wall. This uniquely structured porous carbon was then doped with nitrogen via a thermal pyrolysis process by using melamine as nitrogen source. The nitrogen doping level was controlled by adjusting the mass ratio of melamine and porous carbon. The nitrogen content in the doped porous carbon could reach up to 9.0 atom% without sacrificing the porous structure and surface area. The nitrogen doping significantly improved the electrochemical capacitance up to 180 F/g at 0.5 A/g, which is 74% enhancement compared to the nitrogen-free carbon (104 F/g). Both origin carbon and nitrogen doped carbon show excellent cycling stability that 95% of the capacitance could be remained after 5000 charge-discharge cycles.

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1. Introduction

Carbon materials have been widely studied as energy storage materials due to their unique features of tunable pore size, high electrical conductivity and excellent chemical stability [1—4]. Previous research reveals that the electrochemical capacitance is proportional to the surface area of the electrode and inversely proportional to the charge separation distance [5]. To improve the capacitance, electrode materials with high surface area and low charge separation distance are demanded. To reduce the charge separation distance, electrical double layer capacitor (EDLC) has been developed in which the charged electrode surface is balanced by counter ions in the electrolyte to form a double layer. With such configuration, charge separation distance can be reduced significantly to angstrom level [6] and the capacitance can be enhanced significantly. Although extremely high EDLC capacitance could be expected in theory, the experimentally measured capacitance of most carbon materials is typically below 300 F/g [7]. To further increase electrochemical capacitance, redox reactions were involved in electrodes to generate pseudocapacitance. Until now,

two different approaches have been explored to incorporate pseudocapacitance in carbon electrode. One is to integrate pseudoactive components such as metal oxides [8—13] and conductive polymers [14—16] onto carbon substrate; the other is to dope heteroatoms into carbon framework. The former approach suffers from poor stability due to the volumetric expansion and shrinkage of the pseudoactive components during charge/discharge [6,17]. Moreover, the weak interfacial interaction between pseudoactive component and carbon substrate would accelerate the degradation of electrode in extended testing cycles [8]. The later approach has been proved to be effective in improving electrical conductivity [18], surface wettability [19] as well as capacitance by introducing pseudocapacitance [20]. Among the wide range of heteroatoms including nitrogen, boron, phosphor, sulfur et al. [21—25], nitrogen is the most extensively studied hetero-element in carbon modification. Depending on the nitrogen source and doping conditions, pyrrolic, pyridinic and graphitic nitrogen can be doped into carbon framework [26].

According to the preparation process, nitrogen doping can be divided into in-situ synthesis and post treatment. For in-situ synthesis, chemical vapor deposition technique has been used to synthesize nitrogen-doped carbon nanotubes [27] and graphene [28]. Typically, a nitrogen-containing precursor such as ammonia and pyridine, will be introduced into a gas flow that contains

carbon sources simultaneously. Direct carbonization of nitrogen-containing substances provides another way to in-situ synthesize nitrogen-doped carbon. Successful examples include but not limited to ionic liquid [29], biomass [30] and polymers [31]. Post-treatment usually involves a reaction process that carbon matrix is reacted with nitrogen-containing molecules, such as melamine [32], urea [33], ammonia [34], polyaniline [35], cyanamide [36] and etc., typically through thermal annealing [37], microwave-assisted heating, plasma [38], and arc-discharge [39].

To improve the overall electrochemical performance of carbon based electrode, both EDLC and pseudocapacitance need to be maximized. Therefore, nitrogen doping was mostly performed on high surface area carbons such as graphene [40], carbon nanotubes [41], activated carbon [42], templated porous carbon [43] and other porous carbon materials [44,45]. For example, Jeong et al. prepared nitrogen-doped graphene by a plasma process. The prepared material showed a specific capacitance of 280 F/g, which is about 4 times compared to that of pristine graphene [46]. Despite the good electrochemical performance, the high manufacturing cost and complicated fabrication process of graphene and carbon nanotubes greatly restrict their practical applications. Biomass seems promising carbon resource due to its low cost and wide availability. For example, Wang et al. doped nitrogen on raw cotton to produce nitrogen-doped aerogels, which showed a capacitance of 107.5 F/g at 2 mV/s [47]. Nitrogen-containing gelatin was carbonized and then activated, the resulting product showed a nitrogen content of 9.26 at% and a capacitance of 172 F/g at 0.05 A/g [48]. Although activation helps to improve capacitance through increasing surface area, the use of corrosive chemicals in the activation process poses great risks to environment.

In this work, a facile two-step process was used to fabricate hierarchically porous carbon directly from cotton fabrics without introducing chemicals. Large surface area carbon can be generated and served as a substrate for binding nitrogen element. The nitrogen doping process is achieved by simply carbonizing a mixture of porous carbon and melamine. The nitrogen content can be easily tuned by controlling the mass ratio between melamine and porous carbon. Electrochemical properties of these carbon materials with different nitrogen doping levels were investigated and compared with other reported work.

2. Experimental

2.1. Materials

Cotton fabrics were obtained from commercial T-shirt made with 100% cotton (Hanes). Melamine (>99%), polyvinylidene fluoride and N, N-dimethylformamide (>99.8%) were purchased from Sigma Aldrich. Potassium hydroxide was purchased from EMD Millipore. Acetylene carbon black was purchased from Stream Chemicals. Deionized water (Millipore) was used in all the experiment. All materials were used as received without further purification.

2.2. Synthesis of porous carbon from cotton fabrics

Cotton fabrics were firstly carbonized at 800 °C in nitrogen atmosphere with a heating rate of 5 °C/min to produce C-800. Then, C-800 was oxidized in air for 5 h at different temperatures of 320, 340, 350, 360 and 370 °C (note: C-800 would turn into ash when oxidized at higher temperature beyond 370 °C). These oxidized carbon materials were named as OC-T (T stands for the oxidation temperature). To improve the electrical conductivity, OC-T was carbonized at 800 °C for 2 h to obtain COC-T.

2.3. Synthesis of nitrogen-doped carbon

To fabricate nitrogen-doped carbon, OC-350 was grinded into powders and mixed with different amount of melamine. The mixture was further carbonized in nitrogen at 800 °C for 2 h. The mass ratio of melamine to OC-350 was controlled at 0, 0.5, 1, 3 and 5 and the resulting samples were named as COC-350, NOC-0.5, NOC-1, NOC-3 and NOC-5, respectively.

2.4. Characterization

The microstructure and elemental mapping of the materials were obtained by scanning electron microscopy (SEM, JEOL-7401) equipped with energy dispersive X-ray spectroscopy (EDS). Nitrogen adsorption-desorption analysis was performed at 77 K on a Micromeritics Tristar II 3020. Before nitrogen adsorption test, samples were degassed at 373 K for 12 h using a Micromeritics FlowPrep 060 degas system. Surface area was calculated by Brunauer-Emmet-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was performed using a PHI VersaProbe II Scanning XPS Microprobe with an Al K α line excitation source.

2.5. Electrochemical test

The electrochemical properties of the prepared materials were evaluated on a VersaSTAT 4 electrochemical workstation (Princeton Applied Research). After the carbonization-oxidation-carbonization process, COC-T samples still remain as a flexible fabric. These fabrics can be directly used as electrode without adding binder and electrically conductive additives. Two-electrode method was used to characterize the electrochemical properties of COC-T and three-electrode method was used to test the electrochemical properties of nitrogen doped carbons. As for the two-electrode method, two identical pieces of circular-shaped electrode materials (diameter = 9 mm, thickness = 0.22 mm) were cut from the fabrics and soaked with 6.0 M KOH electrolyte for 24 h. The electrode materials were then separated by an electrically insulating but ionic conducting porous media (Whatman filter paper), and assembled into a coin cell current collector (CR2430) with symmetric configuration. Cyclic voltammograms (CV) were recorded at scanning rates of 2, 5, 10, 20, and 50 mV/s in the potential range of 0−1 V, and galvanostatic charge−discharge (GCD) tests were conducted at different current densities of 0.5, 1, 2, and 5 and 10 A/g. For three-electrode method, the working electrode was prepared by mixing 80 wt% active materials, 10 wt% carbon black and 10 wt% of polyvinylidene fluoride. During mixing, a few drops of N, N-dimethylformamide were added into the mixture and ground into a slurry. The slurry was pasted onto the Ni foam (pre-cleaned by acid) and dried at 100 °C for 12 h in a vacuum oven to ensure the binding between active electrode materials and the Ni foam. In the three-electrode method, platinum wire was used as the counter electrode, saturated calomel electrode was used as reference, and 6.0 M KOH aqueous solution was used as electrolyte. CV was recorded in the potential range of −1 to 0 V, and GCD tests were conducted at different current densities of 0.5, 1, 2, and 5 and 10 A/g. Electrochemical impedance spectroscopy (EIS) was performed by applying a sinusoidal signal with amplitude of 10 mV over a frequency range of 1,000,000−0.01 Hz. Cycling retention was recorded for up to 5000 cycles at current density of 5.0 A/g for all samples. The specific capacitance C_{sp} (F/g) of COC-T measured with two-electrode method is calculated by Equation (1):