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Nitrogen-doped worm-like graphitized hierarchical porous carbon designed for enhancing area-normalized capacitance of electrical double layer supercapacitors

Zheng Liu [a], Kuikui Xiao [a], Hui Guo [a, c], Xiaohua Ning [a], Aiping Hu [a, b], Qunli Tang [a, b], Binbin Fan [a], Yanfei Zhu [a], Xiaohua Chen [a, b, *]

[a] College of Materials Science and Engineering, Hunan University, Changsha, 410082, China
[b] Hunan Province Key Laboratory for Spray Deposition Technology and Application, Changsha, 410082, China
[c] Hunan Key Laboratory for Super-microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha, 410083, Hunan, China

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ABSTRACT

Electrical double layer supercapacitors (EDLC) have an upper limit for their area-normalized capacitance (C_A) and lead to a bottleneck that impede the commercialization of high-energy-density supercapacitor devices. Quantum capacitance (C_Q) in series with electrical double layer capacitance (C_{EDL}) has been demonstrated to be a tremendous obstacle for enhancing the C_A of EDLC. Nitrogen doping can up-shift the Fermi-level and graphitization can improve the density of states (DOS), both of which can significantly mitigate the limiting influence of C_Q. Here, a facile approach is developed for synthesizing an ideal carbon-based EDLC electrode material by simply adding ferrous sulfate heptahydrate (FSH) into the polymer when colloid aggregation. The morphology, porous structure, graphitization degree, doped N content and the types of the doped N of the samples can be easily tuned through changing the FSH ratio. The optimized nitrogen doped worm-like hierarchical porous carbon with graphitized porous carbon embossment (NWHC-GE) exhibits an exceptionally high C_A (24.6 μF cm^{-2} at 1 A g^{-1} and 18.5 μF cm^{-2} at 100 A g^{-1}). This demonstrates a way to enhance the C_A and provides a potential strategy for breaking through the limiting specific capacitance of carbon-based materials.

1. Introduction

Electrical double layer supercapacitors (EDLC), which bridge the storage gap between the relatively high energy pseudo-capacitors and high power dielectric capacitors, have been considered as an important role in complementing or partially replacing batteries in various energy storage fields, such as hybrid vehicles, forklifts, and emergency doors [1–3]. Supercapacitors based on electrical double layer (EDL) energy storage mechanism possess obvious advantages, including high power densities, long service life, a wide thermal operating range, flexible packaging, and low maintenance [4–6].

Typically, activated carbon materials have been suggested as effective electrodes for most existing commercially manufactured EDLC due to their large specific surface area (SSA). Nevertheless, the existing structure of these active materials limits their supercapacitive performance especially the power density due to diffusion limitations related to inner-pore ion transport as well as the accessible specific surface area at high-rate [7,8]. The CNTs have a large ion-accessible surface area and excellent electronic conductivity that can provide outstanding rate performance, but the electrical double-layer capacitance is limited by its smaller SSA [9]. Graphene, consisting of a single layer or a few layers of graphitic carbon, is regarded as a potential candidate for EDLCs due to its large theoretical surface area, good electronic conductivity, and high electrochemical stability [10,11]. Unfortunately, the strong van der Waals forces among individual graphene nanosheets lead to a seriously depressed performance compared with theoretical data [12]. Though, various routes have been developed for preparing 3D graphene-based materials to prevent restacking, including freeze-drying [13,14], self-assembly [15] and chemically assisted assembly [16–18], the poor mechanical stability of 3D graphene and the

* Corresponding author. College of Materials Science and Engineering, Hunan University, Changsha, 410082, China.
E-mail address: xiaohuachen@hnu.edu.cn (X. Chen).

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time-consuming as well as environmentally harmful preparation processes from graphite to 3D graphene should not be neglected. Therefore, to develop novel carbon-based electrode materials with high performance for supercapacitors is still an urgent challenge.

Various strategies have been developed so far to optimize the supercapacitive performances of carbon-based electrode materials, and most of the efforts focus on increasing the SSA. Chemical activation such as KOH activation is recognized as a well-established method for generating highly porous structures with very large SSA (up to 3000 $m^2\ g^{-1}$) [7,18–20].However, it has been demonstrated that a plot of gravimetric specific capacitance (C_g, F g^{-1}) versus SSA exhibits a plateau for carbon materials at SSA above 1500 $m^2\ g^{-1}$ (BET SSA), which is probably ascribed to a space constriction for charge accommodation yielded incomplete charge screening and limited capacitance [2,8]. In other words, the areal capacitance normalized by specific surface area, i.e., the area-normalized capacitance ($C_A = C_g/S_{BET}$, μF cm^{-2}) gradually decreases and stabilizes at about 4–5 μF cm^{-2} when the SSA is larger than 1500 $m^2\ g^{-1}$ for porous carbon electrodes with no additional functionalities or dopants [21]. Therefore, despite the good supercapacitive performance of 3D hierarchical porous graphene-like (3D HPG) [7], 2D porous carbon nanosheets (PCNS) [19], their C_A are still at the general level of carbon materials, below 12 μF cm^{-2} at the current density of 1 A g^{-1} [21,22]. In some sense, to enlarge the SSA without destination have no use on enhancing the C_g but decreasing the C_A as well as increasing the cost. Since the C_g contributed by SSA has the upper limit, in order to develop novel carbon-based electrode materials for next generation energy storage devices, it's an urgent demand to enhance the C_A rather than the SSA of carbon materials.

There are two intrinsic bottlenecks that impede the enhancement of C_A: i) the ion-accessible surface area is typically only 50–70% of the theoretical surface area [23,24], and ii) the so-called small quantum capacitance (C_Q) exists at the interfaces of carbon layers, which in series with Helmholtz capacitance (C_H) and diffuse layer capacitance (C_D) in EDLC (measured capacitance $C_m=(C_{EDL}^{-1}+C_Q^{-1})^{-1}=(C_H^{-1}+ C_D^{-1}+C_Q^{-1})^{-1}$, when convert C_m to the gravimetric specific capacitance, $C_m=C_g$, F g^{-1}), resulting from their low density of states (DOS) at the Fermi level, overwhelms the high C_{EDL} further limiting the C_A [21,25–28]. To enhance the C_A, firstly, a hierarchical porous carbon framework with micro-, meso-, and macropores may be a good choice. The macropores can serve as a fast buffering reservoir which can minimize the diffusion distances of the electrolyte to the interior surfaces, while the meso- and micropores provide a large accessible surface area for ion transport and charge accommodation [18,29]. Moreover, the macropores enable the storage of substantial electrolyte volumes that would contribute through redox reactions to the energy density [30]. Secondly, doping carbon materials with substituent heteroatoms, especially nitrogen, can effectively modulate the electronic properties, surface characteristics, and local chemical features of them, thus greatly enhancing the functionality and performances [17,31]. Definitely, nitrogen doping can not only effectively improve wettability but also up-shift the Fermi-level of carbon materials which significantly boost the C_Q and thus enhance the C_A [22,32,33]. Last but not least, graphitization of carbon, a key but often overlooked feature of carbon materials especially porous carbon, is recognized commonly to enhance the conductivity but rarely C_Q [34]. The graphitization can be used as a tool to tailor the degree of electrochemical doping and a higher graphitization degree can enhance the DOS and yields a great increase in specific capacitance [27].

With the above consideration, herein, for the first time, a novel supercapacitor material based on nitrogen doped worm-like hierarchical porous carbon with graphitized porous carbon embossment (NWHC-GE) was synthesized by means of a facile polymerization-induced colloid aggregation method and a simple coordination–pyrolysis combination process successively, in which tetraethyl orthosilicate (TEOS), ferrous sulfate heptahydrate (FSH), and melamine-fomaldehyde (MF) resin were adopted as porogent agent, graphitic catalyst precursor, and carbon & nitrogen source, respectively. The prepared NWHC-GE owns several outstanding characteristics that an ideal carbon-based EDLC electrode material should feature [2,22,35]: 1) appropriate SSA to provide sufficient and accessible surface area for charge accommodation; 2) hierarchical pores especially the worm-like hollow structure works like a capillary through capillarity for facilitating the diffusion of electrolyte ions and enlarging the efficient surface area; 3) moderate N-doped content to provide a superior wettability with the electrolyte to optimize the ion-accessible surface area and up-shift the Fermi level to enhance the C_Q; 4) a high graphitization degree can not only ensure high rate capability and power density but also enhance the DOS and then improve the energy density. The NWHC-GE demonstrates ultrahigh C_A (24.6 μF cm^{-2} at 1 A g^{-1} and 18.5 μF cm^{-2} at 100 A g^{-1}), which are superior compared with those previously reported for carbon electrodes [7,19,22]. This strategy may open a new avenue for the design and construction of ideal carbon-based electrode materials for challenging energy and environmental issues.

2. Experimental section

2.1. Synthesis of sample

Typically, 9.45 g (75 mmol) melamine and 15.0 ml (196 mmol) formaldehyde solution (36 wt%) were firstly added into 37.5 ml deionized water and stirred at 85 °C for 30 min to obtain a clear solution (denominated as solution A). Tetraethyl orthosilicate (15 ml, purity≥99.9%), OP-10 (7.5 mL, 10 wt% aqueous solution) and 0.01 mol FSH were mixed in deionized water under magnetic stirring at 50 °C for 60 min to obtain a laurel-green emulsion (denominated as emulsion B). When the resulting precursor solution A was cooled down to 50 °C, it was poured slowly into emulsion B under stirring at 50 °C. After that, pH value of the mixtures was adjusted to 4.5 by using HCl solution (2.0 M) and the mixtures were kept continuous stirring for 2 h to obtain the MF/silica/Fe^{2+} composites. These composites were collected by filtration, washed with water and ethanol, and dried in air at 80 °C. In order to prepare the NWHC-GE, the MF/silica/Fe^{2+} composites were firstly cured at 200 ℃ for 24 h in air, then carbonized under argon and hydrogen up to 900 °C for 2 h to obtain the graphitic carbon/silica composites. Finally, 20 wt% HF and 5 wt% HCl compound solution was used to etch the silica template and Fe-based catalyst at room temperature to obtain the NWHC-GE materials. As a control experiment, other carbon materials obtained under various mass of FSH were synthesized in the same way. The resulted materials are denoted as N-doped hollow carbon sphere (NHCS, without adding FSH) and N-doped hollow carbon capsule (NHCC, 0.02 mol FSH was added).

2.2. Physicochemical characterization

Scanning electron microscope (SEM) images were obtained using an S-4800 field emission SEM (Hitachi, Japan) operating at 5 kV. Transmission electron microscope (TEM) images were obtained using a Titan G2 60–300 (FEI, America) operating at 200 kV. Raman spectra were measured using a Jobin-Yvon T6400 (Horiba Jobin-Yvon, France) micro-Raman system at room temperature with excitation by an argon-ion laser at 532 nm. Nitrogen sorption measurements were carried out with N_2 at 77 K after degassing the samples using a TriStar II 3020 (micromeritics, America). Surface