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Electric double layer capacitors employing nitrogen and sulfur co-doped, hierarchically porous graphene electrodes with synergistically enhanced performance

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HIGHLIGHTS

- Nitrogen and sulfur co-doped, hierarchically porous graphene is synthesized.
- EDLC with co-doped graphene exhibits high capacitance and good cycling stability.
- Good performance is attributed to co-doping and hierarchical porous structures.

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ABSTRACT

Hierarchically porous graphene nanosheets co-doped with nitrogen and sulfur are synthesized via a simple hydrothermal method, followed by a pore activation step. Pore architectures are controlled by varying the ratio of chemical activation agents to graphene, and its influence on the capacitive performance is evaluated. The electric double layer capacitor (EDLC) assembled with optimized dual-doped graphene delivers a high specific capacitance of 146.6 F g^{-1} at a current density of 0.8 A g^{-1}, which is higher than that of cells with un-doped and single-heteroatom doped graphene. The EDLC with dual-doped graphene electrodes exhibits stable cycling performance with a capacitance retention of 94.5% after 25,000 cycles at a current density of 3.2 A g^{-1}. Such a good performance can be attributed to synergistic effects due to co-doping of the graphene nanosheets and the presence of hierarchical porous structures.

1. Introduction

Electrical double layer capacitors (EDLCs) have attracted considerable attention as preferential energy storage devices for hybrid electric vehicles and load leveling applications due to their high power densities and long cycle life [1,2]. EDLCs store electrical energy via non-Faradaic reactions in the double layer formed at the electrode and electrolyte interface, where no charges are transported across the interface [2]. Such a reaction mechanism is dependent on the surface characteristics of the electrode materials. Various carbon-based electrode materials have been widely explored for EDLC applications [3]. In particular, hierarchically porous activated carbon with controlled pore architectures have been actively investigated with regard to EDLCs [4,5]. The capacitive performance of these carbon materials is highly dependent on the carbon source and the type of activation process used to create the pores [6,7]. Graphene nanosheets with two-dimensional and sp^2-hybridized carbon structures have received tremendous attention for EDLC applications due to their high surface area, high electrical conductivity, chemical inertness, thermal stability and mechanical robustness [8–10]. The capacitive performance of EDLCs assembled with graphene-based electrode materials is dependent on various characteristics such as the surface area, number of graphene layers, pore size distribution and the presence of surface functional groups, which are primarily determined by the synthetic methods to prepare the graphene nanosheets [11]. Additionally, the capacitive performance of graphene-based EDLCs could be greatly enhanced by a rational design of active materials, electrode architectures and capacitor assemblies [12,13]. Recently, Kim et al. synthesized micron-scale graphene nanomeshes with

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periodic nanoholes that exhibited superior capacitance performance [14]. In another instance, Liu et al. utilized the intrinsic surface capacitance of single-layer graphene by preparing curved graphene sheets to prevent their re-stacking during the synthetic process [15]. Apart from these strategies, heteroatom doping of graphene-based materials has been proved to be very effective in enhancing electronic conductivities and capacitive performance [16–19]. Several heteroatoms such as nitrogen, boron, sulfur, fluorine and phosphorus have been successfully doped into graphene nanosheets. Co-doping of graphene nanosheets with two or more heteroatoms has been shown to synergistically enhance performance through an increased asymmetry in charge and spin densities, in addition to the generation of induced structural distortions [20–22]. These characteristics result in enhanced electronic conductivity and easy adsorption of ions from the electrolyte to enhance the specific capacitance. In addition, the presence of doped heteroatoms improves the surface wettability of electrolyte, increases the number of active sites and facilitates electrostatic interactions with organic ions [23]. However, co-doping of graphene nanosheets along with engineered pore architectures has been rarely reported so far for EDLC applications [24–29].

In this study, hierarchically porous nitrogen and sulfur co-doped graphene nanosheets (m-NSG) with high surface area were synthesized using a simple hydrothermal method, followed by a pore activation step, as schematically illustrated in Fig. 1. Pore architectures were controlled by varying the amount of chemical activation agent in the second step, and its effect on the capacitive performance was investigated. EDLCs assembled with m-NSG electrodes exhibited high specific capacitance and stable cycling performance over 25,000 cycles in comparison to un-doped and single-heteroatom doped graphene electrodes.

2. Experimental

2.1. Synthesis of m-NSG

Graphite oxide was prepared from graphite powder (SP-1, 30 μm nominal particle size, Bay Carbon, USA) using a two-step modified Hummers' method. In the first step, graphite was pre-oxidized, as reported by Kovtyukhova et al. [30]. In subsequent step, further oxidation was carried out via Hummers' method [31]. The prepared graphite oxide was exfoliated using ultra-sonication to form graphene oxide (GO) nanosheets. The m-NSG preparation involved the synthesis of nitrogen and sulfur co-doped graphene nanosheets (NSG), followed by a pore activation step. NSG was prepared from GO and thiourea using a hydrothermal method as reported earlier [32], in which thiourea was used as a source for both dopants. In a typical synthesis procedure, GO (300 mg) was dispersed into 70 mL of DI water, followed by the addition of 900 mg of thiourea. The solution was stirred for 4 h prior to being transferred into a 100 mL Teflon-lined stainless steel autoclave, which was placed in a pre-heated oven at 180 °C. The autoclave was allowed to cool naturally, and the resulting NSGs were alternatively washed with DI water and ethanol, and were dried overnight in a vacuum oven at room temperature. NSG was activated using potassium hydroxide (KOH) as a chemical activation agent at 800 °C for 1 h in Ar atmosphere. NSG and KOH were mixed with different weight ratios (1:4, 1:5 and 1:6), and the resulting products were denoted as m-NSG(x), where x denotes the ratio of KOH to NSG. The powder was washed with a 10% hydrochloric acid solution to remove any metallic residues, followed by rinsing with excess DI water until the pH was neutralized. Finally, the obtained products were dried overnight in a vacuum oven at 120 °C. Single heteroatom (nitrogen or sulfur) doped (m-NG and m-SG) and un-doped (m-G) hierarchically porous graphene was also prepared using the same synthetic procedures used to obtain m-NSG with KOH/graphene ratio of 5 in the second step.

2.2. Electrode preparation and cell assembly

The electrodes were prepared by coating an ethanol-based slurry containing graphene-based active material, Ketjen black as a conductive carbon and Teflonized acetylene black binder (80:10:10 by weight) onto a stainless-steel mesh. The electrodes were dried in a vacuum oven at 160 °C for 4 h. To evaluate the cycling characteristics of the graphene-based electrodes, EDLCs were assembled by sandwiching a polypropylene separator (Celgard 3401) between two symmetrical graphene-based electrodes in a CR2032 cell. The cell was then injected with an electrolyte solution consisting of 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1 by volume, battery grade, PANAX ETEC Co. Ltd). This electrolyte was chosen because it exhibited large electrochemical stability, and when used in EDLCs allowed an operative voltage of 3.0 V [14,33–35]. For performance comparison, the cell was also assembled with conventional liquid electrolyte (1 M tetraethyl ammonium tetrafluoroborate in acetonitrile, 1 M $TEABF_4$ in AN). The cell using commercialized activated carbon powder (MSP-20, Kansai Coke) was also assembled and investigated. All cells were assembled in an argon-filled glove box containing less than 1 ppm H_2O and O_2.

2.3. Characterization and measurements

Morphologies of the synthesized samples were examined with a scanning electron microscope (SEM, JEOL JSM-6300) and transmission electron microscopy (TEM, JEOL, JEM 2100F). Energy dispersive X-ray spectroscopy (EDS) mapping images were obtained to examine the distributions of heteroatoms in the m-NSG

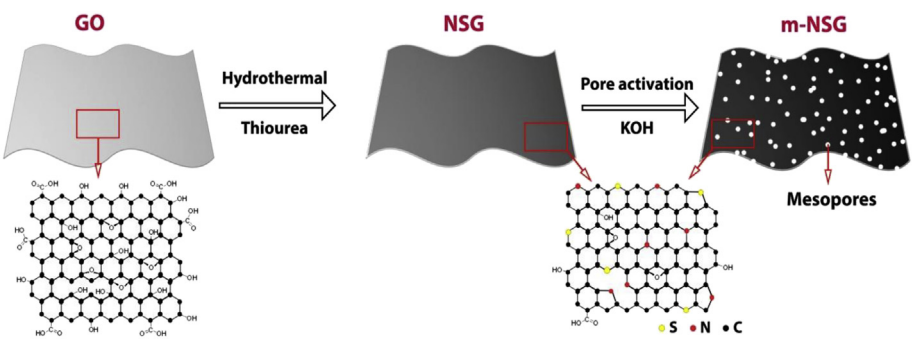

Fig. 1. Schematic illustration of the synthesis of m-NSG using a two-step method.