Preparation of three-dimensional nitrogen-doped graphene layers by gas foaming method and its electrochemical capactive behavior

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ABSTRACT

A porous graphene layers with a three-dimensional structure (3DG) was prepared via a gas foaming method based on a polymeric predecessor. This intimately interconnected 3DG structure not only significantly increases the specific surface area but also provides more channels to facilitate electron transport. In addition, 3D N-doped (3DNG) layers materials were synthesized using melamine as a nitrogen source. The nitrogen content in the 3DNG layers significantly influenced the electrochemical performance. The sample denoted as 3DNG-2 exhibited a specific capacitance of 335.2 $F\,g^{-1}$ at a current density of 1 $A\,g^{-1}$ in a three-electrode system. Additionally, 3DNG-2 exhibited excellent electrochemical performance in aqueous and organic electrolytes using a two-electrode symmetric cell. An energy density of 58.1 $Wh\,kg^{-1}$ at a power density of 2500 $W\,kg^{-1}$ was achieved, which is approximately 3 times that (19.6 $Wh\,kg^{-1}$) in an aqueous electrolyte in a two-electrode system. After 1000 cycles, the capacity retention in aqueous electrolyte was more than 99.0%, and this retention in organic electrolytes was more than 89.4%, which demonstrated its excellent cycle stability. This performance makes 3DNG-2 a promising candidate as an electrode material in high-power and high-energy supercapacitor applications.

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1. Introduction

In recent decades, considerable efforts have been devoted to the development of alternative energy storage/conversion devices with high power and energy densities due to the rapid depletion of fossil fuels [1,2]. Supercapacitors, which are also known as ultracapacitors or electrochemical capacitors, have recently attracted much attention due to their ability to provide a higher power density than batteries and a higher energy density than conventional electrostatic capacitors [3]. Supercapacitors can be classified into two main types based on their energy storage mechanism: pseudocapacitors and electrical double-layer capacitors (EDLCs) [4–6].

Graphene, which is a two-dimensional (2D) carbon sheet, has been used as a novel material for EDLCs [7,8]. Unfortunately, the unavoidable restacking and agglomeration due to the strong π-π stacking and van der Waals forces induces adhesion between the neighboring nanosheets in standard graphene products, which diminishes the accessible surface area [9,10]. In addition, the poor inter-sheet connections between isolated graphene nanosheet building blocks disrupt the continuous pathway for electron transport and severely suppress the intrinsically high conductivity and mechanical strength of individual graphene nanosheets [11]. Therefore, 2D graphene suffers from a lower specific capacity, and the following factors may provide feasible solutions to this problem. First, a foam structure with multilayer graphene could provide a three-dimensional (3D) interconnected network that exhibits high electrical conductivity and low weight for EDLCs material with improved rate capability and specific capacity [12,13]. These excellent properties of the graphene units can be translated into the resulting macroscopic devices with hierarchical structures to enhance the performance. Second, the introduction of heteroatoms (e.g., B, N, P, and S) into graphene materials is a facile method for enhancing their pseudocapacitance [14–16]. Specifically, in supercapacitor applications, nitrogen doping (N-doping) has been reported to generate pseudocapacitance by acting as an

electron donor to attract protons and/or strengthen redox reactions [17,18].

Alternatively, significant efforts have been dedicated to the design and development of methods for modulating the properties of graphene with different shapes. For example, wang and co-workers reported the preparation of freestanding multilayered graphene films by vacuum-assisted filtration [19]. Chen and co-workers synthesized graphene foam using porous Ni foam as a template for the chemical vapor deposition (CVD) growth of graphene [20]. Zhu et al. prepared porous graphene paper via microwave-assisted exfoliation of graphene oxide [21]. Yao et al. utilized a commercially available polyurethane sponge as a template and fabricated a 3D rGO-PU sponge based on a simple dip-coating method [22]. Niu et al. used a so-called "leavening" strategy, which is similar to the process of baking bread, to fabricate 3D porous rGO films [23]. In addition, 3D structure graphene was prepared by a modified Hummers method and a simple solvent treatment, as reported by Hu et al. [24]. These results suggest that it is possible to change the properties and shapes of graphene materials by controlling their preparation process.

In 2012, Li and co-workers firstly reported the versatile approach—calcination of glucose—to prepare monolayer-patched graphene [25]. Additionally, 3D strutted graphene was in the work reported by Wang et al. via a sugar (glucose)-blowing technique in 2013, in which the natural organic carbon source was proved again to produce graphene material [26]. In this technique the solid glucose was mixed directly with NH_4Cl crystals, and the mixture was heated to synthesize a 3D strutted graphene based on a polymeric predecessor. However, a simple and direct mixing of glucose and NH_4Cl crystals creates a 3D strutted graphene with a larger bubble diameter (0.168 mm). In addition, this 3D strutted graphene exhibits a low specific capacity via a single double layer capacitive mechanism. In our study, we report a gas foaming method for the preparation of porous 3D N-doped graphene layers (3DNG) based on Mailard browning process[24,25], this method is also similar to that in our previous work to prepare 3D structure graphene layers [27]. Glucose and NH_4Cl were distributed into an aqueous solution, and then, a recrystallization method using rotary evaporation was employed in this study to prepare the solid mixture consisting of glucose and NH_4Cl on the molecular level. Then, this mixture which likes a dough was used to, using NH_4Cl as

a foaming agent, synthesis porous 3D graphene (3DG) layers with smaller pore diameter by controlled the heating process. In this process, a molten viscous syrup was gradually polymerized, and chemically released gases from NH_4Cl blew the neighboring glucose-derived polymers, leaving a porous 3D structure with pores on the molecular level. In addition, N-doped materials were achieved via heat treatment in the presence of melamine (1,3,5-triazine-2,4,6-triamine) in the mixture, furthermore, melamine could be a foaming agent as well. The key aspect of the gas foaming method is the match between gas foaming and melamine decomposition, which is crucial for producing the highest quality 3DNG. The mismatched decomposition of nitrogen-containing compounds, such as dicyandiamide and urea, results in products with low nitrogen content.

In this study, 3DG and 3DNG layers with porous structures were prepared by a gas foaming approach. Due to the N-doping in these materials, the 3DNG electrodes exhibited better electrochemical properties than a 3DG electrode. In addition, the effect of the nitrogen content on the electrochemical properties of the 3DNG materials was investigated as well. The results from the electrochemical measurements indicate that 3DNG-2 layers exhibited good electrical capacitance performance in aqueous and organic electrolytes. In particular, in an organic electrolyte, this material exhibited a significant high energy density, which makes 3DNG-2 a promising candidate for use as an electrode material in high-power and high-energy supercapacitor applications.

2. Experimental

2.1. Preparation of 3DG and 3DNG materials

3DG layers was synthesized by a gas foaming method. In this synthesis, 1 g of glucose (Chemical Reagent Ltd.) was mixed with 0.25 g of NH_4Cl crystals (Chemical Reagent Ltd.), which were dissolved and then re-crystallized using a rotary evaporator (N-1200BV-WD). The re-crystallized mixture was heated from room temperature at a specific heating rate (i.e., $3\,°C\,min^{-1}$ is recommended) to $1100\,°C$ for 2 h under a N_2 atmosphere in a tube furnace (SK-G08123 K, 100 cm in length by 8 cm in diameter). Finally, a black foam-like product was collected, which is referred to as 3DG layers. The synthesis procedure for the 3DNG layers was similar to that of 3DG layers (Scheme 1). Typically, 2 g of glucose
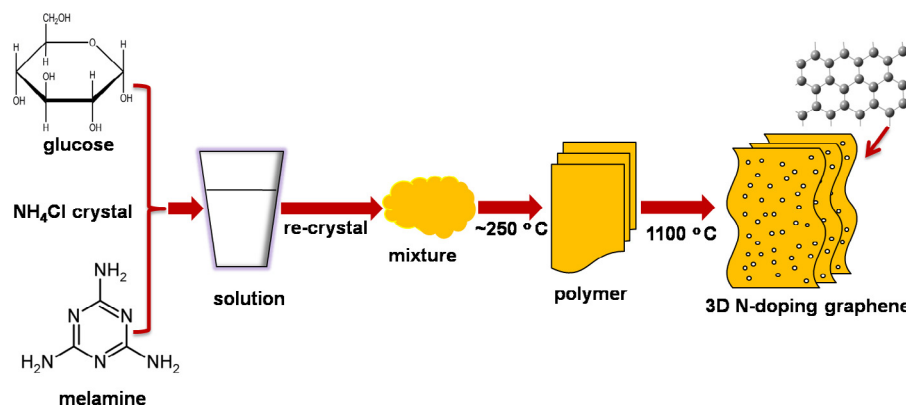
Scheme 1. A schematic illustration of the procedure for preparing 3D N-doped graphene honeycombs via a gas foaming method.