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# The fabrication of graphene/polydopamine/nickel foam composite material with excellent electrochemical performance as supercapacitor electrode

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## ABSTRACT

A three dimensional composite electrode consisted of reduced graphene oxide (rGO), polydopamine (PDA) and nickel foam (NF) (rGO/PDA/NF) was fabricated by immersing NF into PDA aqueous solution and then graphene oxide (GO) suspension solution respectively, and followed by annealing treatment. During the procedure, GO was coated on NF with assistance of cohesive effect of the PDA middle film, and the reduction of GO and nitrogen doping occurred simultaneously while annealing. Through XRD analyzing, the composites GO/PDA and rGO/PDA treated in experiment are amorphous. The resulted rGO/PDA/NF composite electrode was directly applied as a supercapacitor electrode and showed excellent electrochemical performance, with a high specific capacitance of 566.9 F $g^{-1}$ at 1 A $g^{-1}$, the maximum energy density of 172.7 W h $kg^{-1}$ and a power density of 27.2 kW $kg^{-1}$ in 1 mol $L^{-1}$ $Na_2SO_4$ electrolyte.

## 1. Introduction

As a new type of high efficient, environmental-friendly energy storage devices, supercapacitors have the advantages of high power density, ultra-fast charging and discharging rate, long cycle life, excellent stability and wide operating temperature range. Therefore, supercapacitors have attracted worldwide attentions and have broad application space and development prospects in the fields of transportation, aerospace, national defense, etc [1,2].

Electrode material, an important component of supercapacitor, plays a key role in determining its electrochemical performance. Until now, many materials, including metal oxides and hydroxides, conducting polymers, carbon-based nano-materials, etc., have been developed. Among them, carbon materials, such as activated carbon [3], carbon fiber [4], carbon aerogels [5], carbon nanotubes (CNTs) [6] and graphene [7] have been widely investigated because of their high specific surface area and easy accessibility. More importantly, graphene stands out due to its large surface area (theoretical surface area of 2630 $m^2$/g), superior conductivity (electrical conductivity up to $10^6$ S/m) and abundant sandwich construction [8–10]. Unfortunately, the self-aggregation and restacking of graphene sheets during the preparation process, leads to a low specific surface area of graphene less than 800 $m^2$ $g^{-1}$ and a low actual capacity which is far less than the theoretical value of 550 F $g^{-1}$[11]. Therefore, these mentioned drawbacks have limited the specific capacitance of graphene and it is very important to take effective measures to prevent the stacking of graphene [12–15].

Many attempts have been made to improve the actual specific capacitance of graphene. As demonstrated in a number of studies that assembling graphene sheets into three-dimensional (3D) microstructures, commonly named graphene hydrogels, has been considered as an effective approach to achieve high specific capacitance. For example, Li *et al.* prepared Nitrogen/sulfur co-doped and hierarchical porous graphene hydrogels (DHGHs) by facile self-assembly process [16]. The DHGHs prepared at basic condition (DHGH-12) delivers a specific capacitance of 251 F $g^{-1}$ (0.5 A $g^{-1}$). Nevertheless, the graphene hydrogels contain 99 wt% water, which results in poor graphene packing density. Another one strategy to modify graphene is doping nitrogen [17–20], such as N-graphene prepared by a solid microwave method in which EDA (enthylenediamine) was used as the nitrogen source (197 F $g^{-1}$). However, the methods of introducing N-containing functional groups are usually time-consuming (3 or 4 days or even longer). In this paper, with assistance of polydopamine (PDA) middle film, graphene oxide (GO) was uniformly coated on nickel foam surface and then reduced to reduced graphene oxide (rGO) via annealing. Benefiting from the method above, the stacking of graphene sheets were prevented effectively and the preparation process needs only 8 h, which was time-saving.

Nickel foam (NF) is a new functional material with 3D network

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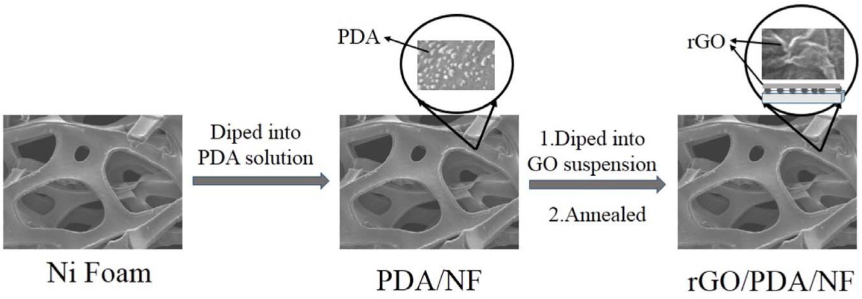

**Fig. 1.** Schematic diagram of the preparation procedure of the rGO/PDA/NF electrode.

structure, low density and high porosity whose void content can reach to 98%. It is usually applied to the fields of filtration, heat exchange or insulation, shock absorption, catalyst carrier, and so on. Also, at present, it can be used as the electrode substrate to carry active substances and act as the current collector [21]. The thickness of NF has a direct effect on the capacitance density of the electrode. The mass per unit area, the size and uniformity of the pore are connected with the amount and utilization of the active substance. One peculiar avenue to prevent the stacking of GO is to take advantage of the porosity of NF. Therefore, when GO was deposited on NF and then formed a 3D structural composite electrode, the aggregation and stacking of graphene is prevented to some extent and the specific surface area is enhanced [22].

PDA exhibits extraordinary surface activity due to the presence of surface functional groups (-OH, -$NH_2$), and it is almost the best adhesive polymer which could functionalize various chemical materials. Therefore, its unique modification function for surfaces is widely used in medical and energy equipment [23]. In addition, PDA is hydrophilic and oxidized easily for the reason of a large number of phenolic hydroxyl groups and nitrogen groups. Thus, PDA films have been widely used for surface modification of Au and Pt nanoparticles, carbon nanotubes and GO [24–26]. On the other hand, PDA contributes to conductivity. Liu *et al.* proved that carbon nanoparticles after PDA carbonization performed better conductivity [27] for the reason that the carbon atom of PDA in the ring was more easily converted to $sp^2$ hybridization. As the decrease of $sp^3$ hybridization and the doping of electrochemical-activity nitrogen, the impedance highly decreased. Therefore, as a special adhesive with reducibility, PDA is expected to improve the electrochemical performance and be applied to supercapacitors.

In this study, GO was deposited on the NF surface by using PDA as a middle layer via chemical immersion method. GO was reduced and turned to be rGO in the following annealing process, and the nitrogen element was doped into the composite meanwhile. The experiment procedure only needs 8 h and the stacking of graphene sheets could be prevented effectively. When tested in 1 mol $L^{-1}$ $Na_2SO_4$ electrolyte, the rGO/PDA/NF composite electrode exhibited remarkable electrochemical performance with high specific capacitance and favorable cycle stability.

## 2. Experimental section

### 2.1. Materials

Graphite, dopamine (DA), sodium hydroxide (NaOH) and mirabilite ($Na_2SO_4 \cdot 10H_2O$) were purchased from Beijing Fine Chemical Co. Ltd., China. All chemicals were of analytical grade and were used as received without any further purification. Doubly distilled water was used in all experiments.

### 2.2. Preparation of rGO/PDA/NF composite electrode

GO was synthesized from graphite according to a modified Hummers' method [28]. Typically, the NF sheets (2.0 cm × 1.0 cm × 0.025 cm) were ultrasonically cleaned with acetone, alcohol and doubly distilled water respectively, and then dried under vacuum for 24 h as reserve. The preparation of rGO/PDA/NF composite electrode consists of two steps, as illustrated in Fig. 1. The first step was to deposit PDA on NF substrate. The cleaned NF sheet was immersed into 20 mg $mL^{-1}$ PDA solution whose pH was about 8.5 for 1 h at room temperature. After washing with distilled water, the NF with PDA (PDA/NF) was obtained. The second step was to deposit GO onto the surface of PDA/NF composite uniformly. The as-synthesized GO was exfoliated into deionized water by ultra-sonication with the help of an ultrasonic cleaning bath for 4 h. The PDA/NF film was then placed into 0.5 mg $mL^{-1}$ GO suspension solution for 3 h at room temperature. Thus a GO/PDA/NF composite was obtained. Finally, the as-prepared GO/PDA/NF composite was annealed at 200 °C for 1 h. In this way, the final electrode material, rGO/PDA/NF composite electrode, was synthesized successfully. In addition, the sample named rGO/NF without PDA middle film was fabricated by the method similar to above.

The orthogonal test of four factors at three different levels were used to select the optimal conditions. The four factors and three levels are showed in Table 1. The detailed experimental operating conditions are showed in Table 2. The gravimetric specific capacitances of the nine

**Table 1**
Four factors at three different levels.

| | Reaction time in PDA (min) | Reaction time in GO (h) | Annealing temperature (°C) | Annealing time (h) |
|---|---|---|---|---|
| Level 1 | 40 | 2 | 100 | 1 |
| Level 2 | 60 | 3 | 150 | 2 |
| Level 3 | 80 | 4 | 200 | 3 |

**Table 2**
Detailed experimental operating conditions.

| Ordinal | Reaction time in PDA (min) | Reaction time in GO (h) | Annealing temperature (°C) | Annealing time (h) |
|---|---|---|---|---|
| 1 | 40 | 2 | 100 | 1 |
| 2 | 60 | 2 | 150 | 3 |
| 3 | 80 | 2 | 200 | 2 |
| 4 | 40 | 3 | 150 | 2 |
| 5 | 60 | 3 | 200 | 1 |
| 6 | 80 | 3 | 100 | 3 |
| 7 | 40 | 4 | 200 | 3 |
| 8 | 60 | 4 | 100 | 2 |
| 9 | 80 | 4 | 150 | 1 |