3D Nitrogen-enriched graphene porous graphene hydrogel for high-performance supercapacitor

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Abstract. 3D interconnected porous nitrogen-enriched graphene (NG) hydrogel was fabricated through ethanedianime as reducing and doping agent. The 3D porous structure of the NG enhances the accessibility to ion diffusion. Notably, when the NG material works as binder-free electrode, it achieves a high specific capacitance of 316.8 F g$^{-1}$ at 0.5 A g$^{-1}$. After the current density increased 40 folds, it still can reach 173.6 F g$^{-1}$. 54.8% of capacitance retention can be achieved after the current density increased by 40 folds. This study provides a scalable approach to prepare 3D porous NG hydrogel.

1. Introduction

Graphene has caught tremendous researchers’ eyes owing to its characteristic properties. The exceptional electronic properties make it using at supercapacitor [1-3]. In fact, the strong π-π interactions between graphene make that the capacitance of graphene-based material is below the theoretical capacitance (550 F g$^{-1}$), which decreases the space that required for the electrochemical reaction, leading to a low specific capacitance [4].

Recently, researchers transform 2D graphene to 3D structure to achieve specific surface area and better electrochemical property [5]. Moreover, Heteroatom doping can readily modify the electrochemical properties of graphene [6]. Particularly, replacement carbon atoms with nitrogen atoms can effectively regulate electronic characteristics of network, thereby immensely improving the functionality and performance [7,8]. The incorporation nitrogen atoms into graphene can gain the wettability of the contact surface and accessibility of the ions [9,10]. Thus, various approaches were employed to acquire nitrogen-contained graphene, including chemical route with sodium borohydride, electron beam and irradiation methods [11-13]. However, these methods required harsh terms and expensive cost, which hinders nitrogen-doped graphene materials large-scale applications. Thus, it is necessary to exploit a succinct way to prepare nitrogen-enriched graphene for supercapacitors.
Herein, a facile way was employed to synthesize 3D porous NG using ethanediamine (EDA) through a simple hydrothermal treatment. During the process, EDA serves as reducing and doping agent, resulting in that graphene oxide was functionalized and self-assembled into 3D porous structure. Benefiting from the unique porous structure, NG exhibits better specific capacitance and high rate capability. The 3D NG not only exhibit superior advantages but also simplify preparation process.

2. Experiments and results

Graphite oxide (GO) was synthesized by a reported approach [14]. The fabrication routes for NG is schematically displayed in Figure 1. EDA (1 mL) were added into a beaker with 34 mL 4 mg mL\(^{-1}\) GO dispersion, and the mixed solution was added into a sealed system at 180 °C for 12 h. After removing impurities and freeze-drying, NG was obtained. The rGO was synthesized in addition to adding EDA. The deoxygenation reduction process of GO is related to the diamine of EDA. There are two possible explanation for the interaction between ethylenediamine and GO to restore the sp\(^2\) structure of graphene: (1) ethylenediamine reacts with the functional group located at the same side of graphene oxide to form a ring, then the ring with tension is instability to proceed elimination reaction. (2) EDA as an open-loop reagent reacts with epoxy group to forms -Ar-NH-C- and continues to react with adjacent hydroxyl group to form hydroxylamine.

![Figure 1. The formation process of NGH.](image)

Phase information was obtained from X-ray diffractometer (XRD Holland). Defects of NG was checked by Via Raman microscope. Scanning (SEM, S-4800,) and transmission electron microscopy (TEM, JEM-2100F) were measured to characterize the morphologies. In addition, the working electrodes were obtained via pressing 4 mg of sample onto on nickel foam substrate (1.0 × 1.0 cm).

Figure 2a shows the XRD patterns. The curve of GO has a peak at 10.73° corresponding to (001) plane. The obtained rGO shows a broad peak at 28.5°, indicating that GO layers were effectively exfoliated into disordered graphene [15]. The pattern of rGO exhibits a broad peak, suggesting that the stacking of graphene present disordered. Compared with rGO, the curve of NG shows a broadening of the peak centered at 24.9° corresponding to (002) plane, which indicates that NG has greater interlayer space than that of rGO.

Raman analyses were performed to check defects in NG in Figure 2b. The peak at 1580 cm\(^{-1}\) was assigned to G band, which mainly derived from sp\(^2\) carbon structure. The peak at 1353.4 cm\(^{-1}\) is imputed to structural defects in the carbon material [15]. The introduced defects in NG samples have been predicted by the value of the I\(_D/I_G\) ratio. The I\(_D/I_G\) ratio for rGO was 1.39, which is increased to 1.67 for NG. The increment in defects of NG is imputed to the porous structure and hetero atom doping. Nitrogen doping augment the defects of NG via altering the bond properties and bond strength of the adjacent carbon atoms.
Figure 2. (a) XRD curves of the samples, (b) Raman spectra of rGO and NG.

The morphology of NG was also determined displayed in Figure 3. The SEM images of NG shows an interconnected network structure with abundant of pores in Figures 3a-b. Moreover, some wrinkles and curly edges can also be seen. The in-plane pores derived from the chemical reaction between EDA and graphene. The unique network structure was also observed in the Figure 3c and d, and the dark strips resulted from the overlapping edges of the graphene sheet.

Figure 3. SEM (a-b) and TEM (c-d) images of NG.

The electrochemical properties of the NG were exhibited in Figure 4. Figure 4a exhibits the contrastive CV curves at 50 mV s$^{-1}$. NG electrode has a more area than that of rGO electrode, suggesting an improved electrochemical performance. Figure 4b displays the contrastive CD curves at 1 A g$^{-1}$. The two curves show nearly perfect triangle shape, suggesting the materials possess observed double layer capacitance [16]. Moreover, the longer discharge time of NG compared with rGO means better capacitive property. The CV curves of NG at 10-200 mV s$^{-1}$ are presented in Figured 4c, the curves show rectangular shapes, which reveal the behavior of electronic double layer capacitance (EDLC). Fig. 4c presents the GCD curves of the NG measured at 0.5-20 A g$^{-1}$. Good symmetry can be seen, which also imply the characteristic of EDLC. Moreover, no voltage drop can be seen, meaning NG has a low resistance. Figure 4d plots capacitance of NG at 0.5-20 A g$^{-1}$. NG electrode reaches
316.8 F g\(^{-1}\) at 0.5 A g\(^{-1}\), and 54.8% of capacitance retention can be achieved after the current density increased to 40 folds. In addition, the electrochemical performance of NG is not only higher than that of rGO, but also far higher than other reports based on doped carbon materials, including N/S-Porous carbon (138.8 F g\(^{-1}\), 0.05 A g\(^{-1}\)) [17], NG (312 F g\(^{-1}\), 0.1 A g\(^{-1}\)) [1], N/S-Graphene (251 F g\(^{-1}\), 0.5 A g\(^{-1}\)) [18], N-doped carbon sphere (278 F g\(^{-1}\), 0.1 A g\(^{-1}\)) [19]. The good performance of the NG can be imputed to the two aspects: i. NG electrode exhibits interconnected porous structure that allows efficient accessibility of electrolyte ions and provides a path for charge transport; ii. Nitrogen doping can offer more active sites enhancing the capacitance performance. Moreover, Nyquist plot of NG electrode is near-vertical to the real axis at low frequency in Figure 4f, indicating a lower interfacial resistance [20].

![Figure 4](image_url)

**Figure 4.** (a) Contrastive CV curves at 50 mV s\(^{-1}\). (b) Contrastive GCD curves at 1 A g\(^{-1}\). (c) The CV curves of NG at 10-200 mV s\(^{-1}\). (d) GCD curves of NG at 0.5-20 A g\(^{-1}\). (e) The specific capacitance at 0.5-20 A g\(^{-1}\), and (f) Nyquist plot of NG.

### 3. Conclusion

3D interconnected porous nitrogen-doped graphene hydrogel was fabricated using ethanediamine as reducing and doping agent. The NG materials can work as binder-free electrode. Notably, the NG has a high specific capacitance of 316.8 F g\(^{-1}\) at 0.5 A g\(^{-1}\). 54.8% of capacitance retention can be achieved after the current density increased to 40 folds. Consequently, the prominent electrochemical performance of NG can be imputed by the interconnected porous pathways and nitrogen doping.

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