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Nickel skeleton three-dimensional nitrogen doped graphene nanosheets/nanoscrolls as promising supercapacitor electrodes

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A novel nickel skeleton 3D nitrogen doped graphene (N-GR/NF) superstructure with interconnected graphene nanosheets and nanoscrolls was synthesized using a facile two-step method. By varying the precursor concentration, the assembly of a graphene aerogel can be easily regulated, yielding different micro-structures and morphologies which accelerate the fast electron/ion transportation. The N-GR/NF composites demonstrate enhanced capacitance of 250 F g^{-1} at 5 A g⁻¹, good rate performance (237 F g⁻¹ at the current density of 12 A g⁻¹) and cycle stability (90.9% retention after 5000 cycles) in 1 M KOH electrolyte. This study provides a new strategy for the microporous engineering of graphene gel, promising for further exploitation in various other applications.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene, as an ideal supercapacitor electrode material [1–3], is receiving growing attention due to its excellent electronic conductivity, good electrochemical stability, high surface area and flexibility [4–11]. Assembling graphene sheets into three-dimensional interconnected porous micro-structures, namely, graphene aerogels has been considered the most effective approach to achieve a high specific capacitance [12–14]. To date, several graphene gelation principles have been developed, including self-assembly [15–20], template-assisted preparation [21–28] and direct deposition [29–32]. And the reduction of graphene oxide (GO) is promising in the preparation of supercapacitor electrodes [33]. The performances of rGO-based supercapacitor electrode materials strongly



Herein, we report a facile and effective method of inserting nickel foam into nitrogen doped three-dimensional graphene aerogels to form the N-doped graphene/Ni foam (N-GR/NF) composites electrode. Based on the introduction of ethylenediamine (EDA), GO can be controllably



Figure 1. Raman spectra of the as-prepared GO and graphene gel.

functionalized and self-assembled into nanosheets or nanoscrolls, at the same time the EDA also served as a reducing and doping agent. By varying the precursor concentration, the assembly of the graphene aerogel can be easily regulated, yielding different micro-structures and morphologies. Benefitting from the hierarchical porous structure, high conductivity, and large specific surface area the N-GR/NF exhibited better specific capacitance, long durability, and high rate capability. Moreover, its properties suggest potential applications as a highly stable electrode material.

2. Experimental section

2.1. Preparation of the Ni foam framework threedimensional N-GR

N-GR/NF was prepared according to the following procedure. Typically, EDA (120 μ L) was added into GOdispersion (3 mg mL⁻¹, 10 mL), then Ni foam sheets (15 × 15 × 1.6 mm) were immersed in the GO suspension. The system was sealed in a glass vessel and heated for 6 h at 95 °C. After purifying and freeze-drying for 48 h, the EDA incorporated GR aerogel was loaded into a quartz tube and heated at 900 °C for 1 h under high vacuum conditions; giving rise to the final nitrogen doped three-dimensional graphene aerosol.

2.2. Materials characterizations

The morphology information was determined by a FEI Sirion 200 scanning electron microscope (SEM). Surface composition of the sample was analyzed by x-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Kratos, Japan). Raman spectroscopy was recorded on Renishaw in Via-reflex system at room temperature. A laser wavelength of 532 nm was used as the excitation sources.

2.3. Electrochemical measurements

The electrochemical properties were performed using a PARSTAT 4000 workstation with a standard three-electrode system. Using the prepared samples as the working electrodes with a Pt clamper, Pt gauze as the counter electrode, and Ag/AgCl as a reference electrode (figure S1 is available online at stacks.iop.org/NANO/28/365402/mmedia). Cyclic voltammetry with scan rate of 0.05 mV s⁻¹ was conducted in 1 M KOH. The galvanostatic charge–discharge (GCD) measurements and cycle stability were performed on a LAND CT-2001A.

3. Results and discussion

A typical N-GR/NF composite electrode is prepared by immersing nickel foam in a suspension of GO and EDA. Then the composite film is subsequently heated at 95 °C for 1 h. During this process, GO sheets are functionalized and reduced to a graphene hydrogel. After lyophilization, the solvent was removed from the lyogel to produce a functionalized three-dimensional graphene aerogel, followed by heating at 900 °C for 1 h to make nitrogen doped N-GR/NF. Figure 1 shows a comparison of the Raman spectra to characterize extents of GO reduction. The Raman spectrum of GO and N-GR has two prominent bands around 1355 and 1600 cm⁻¹, and they are assigned to the D and G bands of carbon. The D band at around 1355 cm^{-1} is common for disordered sp² carbon, while the G band at around 1600 cm^{-1} is usually assigned to well-ordered graphite. After hydrothermal treatment at 95 °C for 1 h, the ratio of the intensities of the D and G bands (I_D/I_G) increases from 0.81 to 0.98. The change in the I_D/I_G ratio suggests a decrease in the average size of re-established G network (sp² carbon), confirming the reduction of GO.

To study the chemical constitution and the chemical bonding of constituent elements, high-resolution x-ray photoelectron spectra (XPS) of GO and N-GR/NF were carried out. The presence of C1s, N1s, and O1s peaks can be seen in figure 2(a). A signal deconvolution with Gaussian curve fitting points out the chemically different C species to further characterize the electrochemical reduction of the GO. As shown in figure 2(b), for the GO, two typical peaks are located at 284.6 and 286.7 eV, which are usually assigned to sp²-hybridized carbon from the GO, and the oxygen-containing carbonaceous bands (C-OH). The strong peak for C-OH bonds indicates the efficient oxygenation of graphite by a modified Hummer's method. For the N-GR, the spectrum is deconvoluted into four peaks, and the significant loss of oxygen-containing functional groups is observed in figure 2(c). The sharp peak for C-O (286.5 eV) almost vanishes, and the peaks for C=O (287.9 eV) and O=C-O (289.0 eV) still exist, but have much lower intensities than those in GO, which indicate the sufficient reduction of GO to GR after hydrothermal reduction treatment of EDA. It should be noticed that N-GR exhibits nitrogen content (4.39 at%),



Figure 2. XPS spectras of N-GR/NF and high resolution XPS spectra of N1s.

which confirms the EDA functionalization on the surfaces of GO, as clearly shown in the high resolution XPS spectra of N1s in figure 2(d). This exhibits the partial conversion of N atoms into the pyridinic N (398 eV), pyrrolic N (399 eV) and graphitic N (400.7 eV) during the nitrogen doping process. The EDA with high N content can react with oxygen-containing functional groups in GO, thus acting as the nitrogen source to form the N-doped structure. Due to the relatively high content percentage of pyridinic N and graphitic N in the N-GR, the prominent capacitive and cycling performance of this electrode material was anticipated for a supercapacitor.

To investigate the structural evolution of N-GR under various conditions involving the EDA and different concentrations of GO, N-GR-0.5, N-GR-1 and N-GR-2 were first fabricated at a GO content of 0.5, 1 and 2 ml with 60 μ L EDA. SEM images show that the samples with different concentrations of GO clearly exhibit different 3D hierarchical architecture (figure 3). Among them, the N-GR-0.5 interestingly shows a nanoscroll interconnecting three-dimensional porous structure. The nanoscrolls coated onto the Ni foam and the framework can be clearly observed (figures 3(a), (d)).

With the increasing content of GO to 1 ml, the 3D GR become thicker. Compared with N-GR-0.5, besides the nanoscrolls, more nanosheets are assembled in N-GR-1 (figures 3(b), (e)). The interpenetrating porous structure with pore sizes in the range of a sub-micrometer to several micrometers. The porosity could reach to 99% [35]. With increasing the content of GO to 2 ml, a greater number of nanosheets were enabled (figures 3(c), (f)), since it is obtained with a higher concentration of GO. Based on the observations described above, we predict that the ratio of EDA to GO plays a key role in the morphology formation of the nanoscroll/ nanosheet superstructures. Hence, we further investigate the variations in EDA effect on microstructure under same content of GO. A similar structural evolution was observed for the samples synthesized using 20, 60 and $120 \,\mu\text{L}$ EDA (figure 4). For the low ratio of EDA to GO sample, GR only formed dense nanosheets with a large diameter. By contrast, the GR nanoscrolls arise with the increasing concentration of EDA. As the EDA content increases to $120 \,\mu$ L, highly interconnected nanoscrolls formed on a three-dimensional Ni framework similar to the N-GR-0.5. Higher magnification

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Figure 3. SEM micrographs of the N-GR/NF composites with different GO concentrations, 0.5 ml for (a) and (d), 1 ml for (b) and (e), 2 ml for (c) and (f).



Figure 4. SEM micrographs of the N-GR/NF composites with different EDA concentration, 20 μ l for (a) and (d), 40 μ l for (b) and (e), 100 μ l for (c) and (f).

SEM images shows that the GR have a tubular hollow structure which is favorable to the transport of electrolyte ions (figure 5).

Based on these results, we propose an EDA induced, concentration dependent self-assembly mechanism for explaining the formation of 3D superstructures. In a GO dispersion, the EDA with a NH_2 group can react with the oxygen-containing functional groups on the surface of GO to form EDA-modified GO [36–38]. After the hydrothermal

process, GO was reduced by the restoration of a portion of sp^2 regions. For the low proportion EDA modified GR, small piece graphene sheets assemble into large films resulting in the graphene sheets stacking 3D network. As the concentration of EDA increased, more molecules were functionalized on the surface which may act as a cationic surfactant. Due to the high hydrophilicity and electrostatic repulsion of the NH₃⁺ group, graphene sheets spontaneously bend into nanoscrolls driven by the surface charge imbalance, which



Figure 5. (a), (b) SEM micrographs of the GR with a tubular hollow structure.



Graphene oxide

EDA-mediated GR

GR nanoscroll

Figure 6. Schematic illustration of mechanism of EDA-mediated functionalization and self-bending formed nanoscroll.



Figure 7. (a) CV profiles of as-prepared N-GR/NF composites with different GO concentrations. (b) CV profiles of as-prepared N-GR/NF composites with different EDA concentrations. The scan rate is 50 mV s^{-1} .

interconnect with each other resulting in superstructures (figure 6). The bonded EDA molecules on the surface may also cause steric hindrance and reduce the restacking of sheets to provide hydrogels with negligible volume shrinkage [38].

The unique hierarchical 3D N-GR/NF superstructure combining the nanosheets and nanoscrolls arising from the self-assembly of GR sheet with the controllable macropores makes it a highly promising material for high-performance supercapacitor. The performances of N-GR can be easily modulated by controlling the concentration of a GO and EDA precursor. Correspondingly, the cyclic voltammogram (CV) curves of the N-GR were recorded in 1 M KOH solutions by using Ag/AgCl as the reference electrode without any binders or conducting additives. Figure 7(a) shows the CV of the N-GR/NF with a different concentration of GO in the potential range -0.9 to -0.1 V at scan rates of 5 mV s^{-1} . The CV curves of the 3D N-GR/NF composites are nearly rectangular in shape, which characterizes the formation of an

electrical double layer to store energy. As the GO increased from 0.5 to 1 or 2 ml with a EDA content 60 μ l, a sufficient amount of GR was formed to fully fill the micropores of NF, leading to the increase of the GR mass per unit area in the Ni framework N-GR electrode. The specific capacitances of the N-GR are approximately proportional to the content of GO because of the linear increments of rGO in their electrodes.

The microstructure of N-GR can be tuned by varying EDA/GO ratio. The current density response of the N-GR/NF at the same scan rates slightly increased with a rise in the concentration of EDA from 30 to $60 \,\mu$ l with a GO content 2 ml, implying a slight increase of the gravimetric specific capacitance from 325 Fg^{-1} to 375 Fg^{-1} which were obtained from the CV measurements (figure 7(b)). The increase of the specific capacitance can be explained by the fact that the pores significantly increased, leading to the rise in efficiency of electrolyte ion diffusion. With a further increase of EDA concentration, the specific capacitance decreases to 262 Fg^{-1} , the shape of the CV profiles of N-GR/NF became more oblique, suggesting that the diffusion of electrolyte ions was less effective. Simultaneously, the increase of EDA creates more mesopores which provide a large, accessible surface area for ion transport/charge storage; the increase of EDA continuously decreases the specific surface area.

Figure 10(a) depicts the galvanostatic discharge curves of the N-GR/NF electrode prepared with 2 ml GO and 60 μ l EDA at different current densities. The shape of the curves are almost typically highly linear, indicating that the electrode material has ideal capacitive characteristic and excellent electrochemical reversibility. Furthermore, only a small voltage drop (0.15 V) was observed at the beginning of discharge (IR drop) even at a high current of 12 A g⁻¹, suggesting a low internal resistance which can be attributed to the high conductivity of N-doped graphene sheets and Ni framework [39–43]. Low internal resistance is of great importance in energy storing devices, because less energy is wasted producing unwanted heat during charge processes.

Figure 10(b) shows the CV curves of the N-GR/NF at different scan rates ranging from 5 to 200 mV s⁻¹. The current response demonstrated a corresponding increase with the scan rate increase. The CV profiles remained quasi-rectangular at a high scan rate of 200 mV s⁻¹, suggesting superior capacitance behavior, low equivalent series resistance (ESR), and fast diffusion of electrolyte ions throughout the N-GR/NF electrodes. The electrochemical impedance spectroscopy (EIS) was collected over a frequency range from 10 mHz to 100 kHz at an open circuit voltage, with 10 mV sinusoidal amplitude (figure 8). The Nyquist plot is almost perpendicular to the real axis at the low frequency region with a segment of the circle at high frequencies, showing the N-GR/NF has a good capacitive behavior [38], representative of easy ion diffusion to the surfaces in the electrode structure.

Correspondingly, the relationships between specific capacitance calculated from the discharge curves and the current densities are summarized in figure 9. Significantly, the specific capacity does not show a distinct reduction at high discharge rates. The specific capacity at 0.5 Ag^{-1} is 325 Fg^{-1} , which decreases to 270 Fg^{-1} at 1 Ag^{-1} . As the

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Figure 8. Nyquist plot of N-GR/NF.



Figure 9. Specific capacitance against different discharge current density with 1 M KOH solution as an electrolyte.

current density increases to 12 A g^{-1} , the capacitance still preserved a high value of 237 F g^{-1} . The high rate capability of our N-GR is better than those of previous reported bulk graphene gels with random network morphology (table S3). Long electrolyte diffusion pathways via random network morphology principally limits the rate performance of the bulk graphene gels. Moreover, due to the intrinsic fragility of a graphene random network, it is hard use it directly as a working electrode. By contrast, our 3D graphene foam with a nickel framework inside is inherently stable with micrometer scale thickness.

Cycling stability, a crucial property of supercapacitors for their practical applications, was evaluated using the GCD technique at a current density of 5 A g^{-1} . The capacitance retentions of the as-prepared N-GR were 90.9% of its initial capacitances, retained after 5000 charge/discharge cycles (figures 10(c), (d)). The obvious capacitance decay in the initial cycles could be ascribed to the removal of a few oxygen-containing groups on graphene sheets that contribute to pseudocapacitance and electrode/electrolyte interface wetting [44].



Figure 10. (a) GCD of as-prepared N-GR/NF composites at various current densities. (b) CV curves measured at different scan rates. (c) Cycling stability at a current density of 5 A g^{-1} . (d) GCD curve of the first 20 cycles.

On the basis of the above results, it can be concluded that the self-assembly created macropores between graphene nanosheets and nanoscrolls are a key factor in maintaining the high performance and stability, which afford fluent ion transport through an open porous structure. Simultaneously, these macropores, acting as ion buffering reservoirs, can minimize the diffusion distances to the interior surfaces. The improved capacitance, rate capability and stability of N-GR/NF can be ascribed to the unique Ni framework 3D porous architecture combining self-bending nanoscrolls, support nanosheets with a large surface area, and high electrical conductivity, which promoted ion transport and electron migration, as well as increased the mechanical strength of the structure.

4. Conclusion

In summary, we have developed a nickel framework nitrogen doped three-dimensional superstructure graphene aerogel via a two stage process through chemical reduction of the GO dispersion with EDA. The micropores and morphology can be facile engineered through the hierarchical, simultaneous selfassembly and self-bending of EDA-mediated GO sheets into interconnect nanoscrolls with a typical GO and EDA concentration dependent structural evolution process. The controllable micropores of N-GR are exposed to the electrolyte, for the access of ions to form electrochemical double-layers, and the nickel framework shortened the distances of charge transfer and ensured that the N-GR can be directly used in the capacitors electrode. Due to the synergistic effect of aforementioned features, it exhibited enhanced capacitance of 250 F g^{-1} at 5 A g^{-1} good rate performance $(237 \text{ Fg}^{-1} \text{ at the current density of})$ 12 Ag^{-1}) and cycle stability (90.9% retention after 5000 cycles) in 1 M KOH electrolyte. More importantly, the microporous and morphology engineering of graphene gel can be further exploited for various other applications, such as a current collector for a battery, an electrocatalytic electrode, sensors, electronics devices and so on.

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