

Facile Approach to Preparation of Nitrogen-doped Graphene and Its Supercapacitive Performance

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Abstract: Nitrogen-doped graphene nanosheets (N-GNSs) with good morphologies were successfully synthesized by a facile solvothermal method. The result of X-ray photoelectron spectroscopy (XPS) revealed that most oxygen containing functional groups on the surface of graphene oxide (GO) were removed during solvothermal reduction, and nitrogen atoms from dimethylformamide (DMF) were effectively doped into graphene structure in the form of pyrrolic-N and graphite-N. As an electro-active material, the N-GNSs exhibited superior capacitive behavior in 2 mol/L KOH electrolyte with a high specific capacitance of 181.3 F/g at the current density of 0.5 A/g. Also, it displayed good electrochemical stability with 92.5% of the initial capacitance over consecutive 2000 cycles. Therefore, the N-GNSs can be an attractive candidate as electrode materials for supercapacitors.

Key words: graphene; nitrogen-doped; solvothermal; supercapacitors

Graphene, a single layer of two-dimensional nano-structure sp² carbon material, due to its excellent mechanical, electrical, thermal and optical properties, has shown great promise for applications in fields such as electronics^[1-2], sensors^[3-4], catalysts^[5-6], field emission^[7], and energy storage^[8-9]. Graphene is also proposed as the next generation electrode material for supercapacitors owing to its chemical stability, excellent electrical conductivity and exceptionally large theoretical surface area (over 2600 m²/g)^[10-12].

Doping graphene with heteroatoms can effectively tune their intrinsic properties, including electronic characteristic, surface and local chemical features. The nitrogen atom, having a comparable atomic size and five valence electrons for bonding with carbon atoms, has been widely used for chemical doping of graphene^[13-14]. Recently, some works have showed that nitrogen doping is favorable to enhance the capacitance of graphene, because nitrogen atoms can modify the electron donor/acceptor properties of the graphene layer, and are consequently expected to affect the charging of the electrical double layer and to give pseudocapacitance faradaic reactions.

Up to now, various methods such as chemical vapor deposition (CVD)^[15], arc discharge^[16], and nitrogen plasma process^[13] have been successfully employed to

prepare nitrogen-doped graphene nanosheets (N-GNSs). However, these processes suffer from rigorous conditions and complicated equipments, accompanied by low-yields and high-cost. In our previous studies, we adopted one-step solvothermal method to prepare strongly fluorescent graphene quantum dots (GQDs)^[17], which obtained by a vacuum filtration. In the preparation process, the majority of the filter cake (more than 65%) is discarded, and very wasteful. Furthermore, the prepared GQDs have a high nitrogen content (9.75at%), which also prompted us to improve the process and study the application of the filter cake in terms of supercapacitors.

In this work, the morphology and composition of the filter cake were characterized. Electrochemical behaviors of the N-GNSs were investigated in three-electrode system in 2 mol/L KOH electrolyte.

1 Experimental

1.1 Preparation of N-doped graphene (N-GNSs)

The procedures for synthesis graphene oxide (GO) are shown in our previous report^[18]. Based on the preparation of graphene quantum dots (GQDs) by solvothermal method^[17], we improved the process to prepare N-GNSs. In a typical synthesis, GO powder was dissolved in 40 mL

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DMF with the concentration of 13.5 mg/mL. The GO/DMF suspension was under ultrasonication for 1 h at 500 W with ultrasonic cell crusher. The suspension was then transferred to a Teflon-lining autoclave (60 mL) and heated at 200°C for 8 h. After cooling to room temperature, the mixture was filtered using a 0.22 μm microporous membrane to obtain products. The black filter cake was collected (The brown transparent suspension was unpurified GQDs solution.). The filter cake was then washed with anhydrous ethanol and water rigorously, and the N-GNSs sample was obtained by freeze-drying (yield *ca.* 65%).

1.2 Characterizations

The morphology of the N-GNSs was investigated using field emission scanning electron microscope (FE-SEM, JSM-6701F), transmission electron microscope (TEM, FEI TECNAT G²) and atomic force microscope (AFM, Multimode 8), respectively. The surface chemical species of the N-GNSs was performed using X-ray photoelectron spectrometer (XPS, Thermo Scientific ESCALAB250xi).

1.3 Electrochemical measurements

Electrochemical measurements were performed on electrochemical workstation (CHI660D, Chenhua, Shanghai). The working electrodes were prepared by mixing the 80wt% as-prepared N-GNSs (8 mg), 7.5wt% of acetylene black (>99.9%), 7.5wt% of graphite powder and 5.0wt% of poly (tetrafluoroethylene) were mixed together in an agate mortar until a homogeneous black paste was obtained. The resulting paste was pressed onto a foam nickel plate at 10 MPa. The assembled electrode was dried at 60°C for 16 h in air. All electrochemical measurements were carried on three-electrode system in 2 mol/L KOH electrolyte: Ni foam coated with N-GNSs powders as the working electrode, platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. Capacitance values are calculated from the discharge process by the formula: $C = \frac{I \cdot \Delta t}{\Delta V \cdot m}$, where C , I ,

Δt , ΔV , m are the specific capacitance (F/g), the current loaded (A), the discharge time (s), the potential change during discharge process (V) and the mass of active material (g), respectively. Electrochemical impedance spectroscopy (EIS) measurement was tested in the frequency ranging from 100 kHz to 0.01 Hz at open circuit potential with alternate current amplitude of 5 mV. The cycling stability test was evaluated with a Land CT2001A battery program-control test system (LAND, Wuhan, China).

2 Results and discussion

As shown in FE-SEM and TEM (Fig. 1(a) and 1(b)),

these images demonstrate thin and wrinkled sheets transparent to electrons. Unlike ammonia-assisted hydrothermal method^[19] and hydrothermal reaction of graphene oxide and urea^[20], this method prepared N-GNSs has many tiny graphene sheets, which can be seen clearly from Fig. 1(b) (the red dotted circle). These tiny graphene sheets are about 10 nm, also known as graphene quantum dots, which is generated by solvothermal cutting process^[17]. Indeed, the typical AFM image and thickness analysis of the N-GNSs sample reveal that the thickness of N-GNSs is about 0.95 nm (Fig. 1(c) and 1(d)). This thickness is thicker than pristine graphene with 0.34 nm, which may be caused by the resultant defects during the preparation of GO^[21].

The typical XPS survey spectra of the as-synthesized GO and N-GNSs are displayed in Fig. 2(a). The N1s peak can be observed in the N-GNSs but not in GO, which indicates that N from DMF doped into GO during the solvothermal process. As shown in Fig. 2(b), the N1s peak in the N-GNSs sample could be well fitted into two components, pyrrolic-N (N1, 399.9 eV, 52.1at%) and graphitic N (N2, 400.8 eV, 47.9at%)^[19]. The existence of pyrrolic-N suggests that there are many defects in initial GO and nitrogen atoms preferring to form a pyrrole structure, while graphitic N is due to substitute carbon atoms to form a hexagonal graphite structure. Figure 2(c) shows the well-fitted C1s spectra of GO (up) and N-GNSs (down). The C1s spectra of GO can be divided into four different peaks, which corresponds to the signal of C–C (284.6 eV), C–O (285.5 eV), C=O (286.5 eV), and O–C=O (288.6 eV). Comparing with the C1s spectra of GO, N-GNSs appears a new peak at 285.2 eV attributing to C–N bonds^[14]. Moreover, as shown in Fig. 2(d) (Table 1), the oxygen content in GO reduce sharply from 23.65at% to 16.8at%, while the nitrogen content increase from 0.45at% to 1.98at%, further revealing that the solvothermal process can make GO reduced and doped nitrogen atoms simultaneously.

The electrochemical properties of the N-GNSs electrode were investigated under a three-electrode system in 2 mol/L KOH electrolyte. Figure 3(a) shows the CV curves of the N-GNSs electrode at different scan rates from 5 to 200 mV/s. It can be seen that CV curves of the N-GNSs electrode are close to the rectangular shape, which indicates that the electrochemical behavior based on N-GNSs is more like double layer capacitance (EDLC). However, a pair of reversible peaks appears in the CV profile which attributed to the redox reactions of N-GNSs, behaving as pseudocapacitance. Thus, the high specific capacitance of the N-GNSs electrode results from the simultaneous contributions of the EDLC and the pseudocapacitance. Figure 3(b) shows the charge/discharge curves

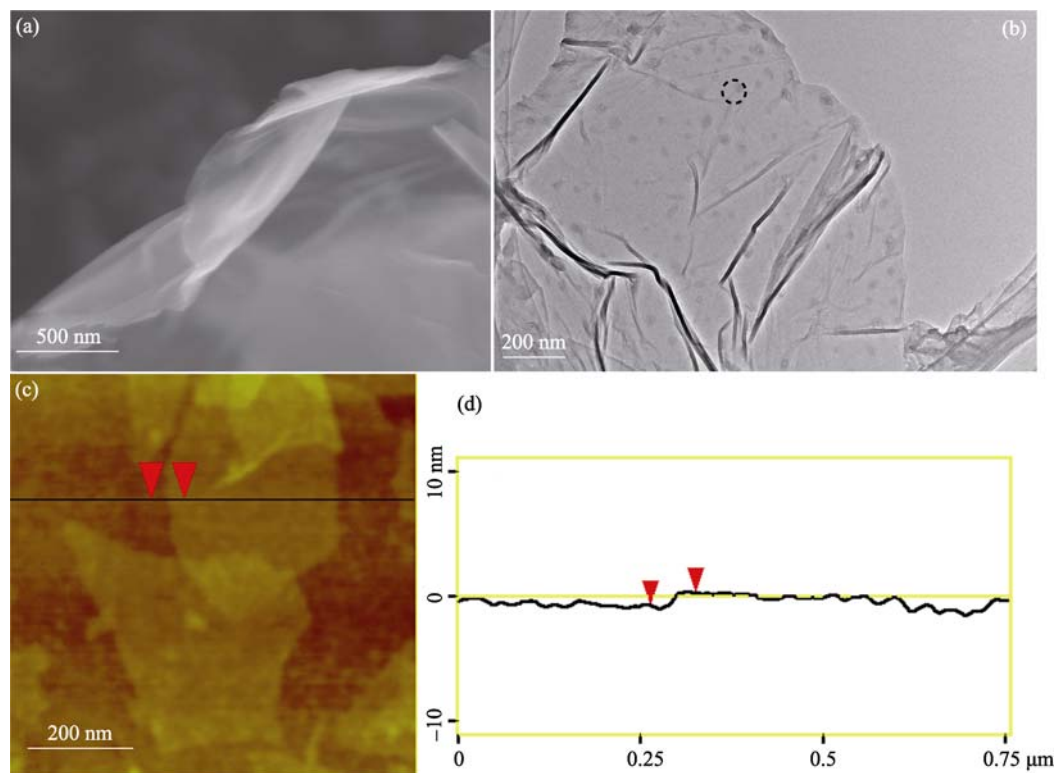


Fig. 1 Morphological characterization of as-synthesized N-GNSs

(a) FE-SEM image; (b) TEM image, the inset of red dotted circle represents the typical graphene quantum dot (GQDs); (c) AFM; (d) Corresponding height analysis taken around the line in (c), the thickness of sheets is 0.947 nm

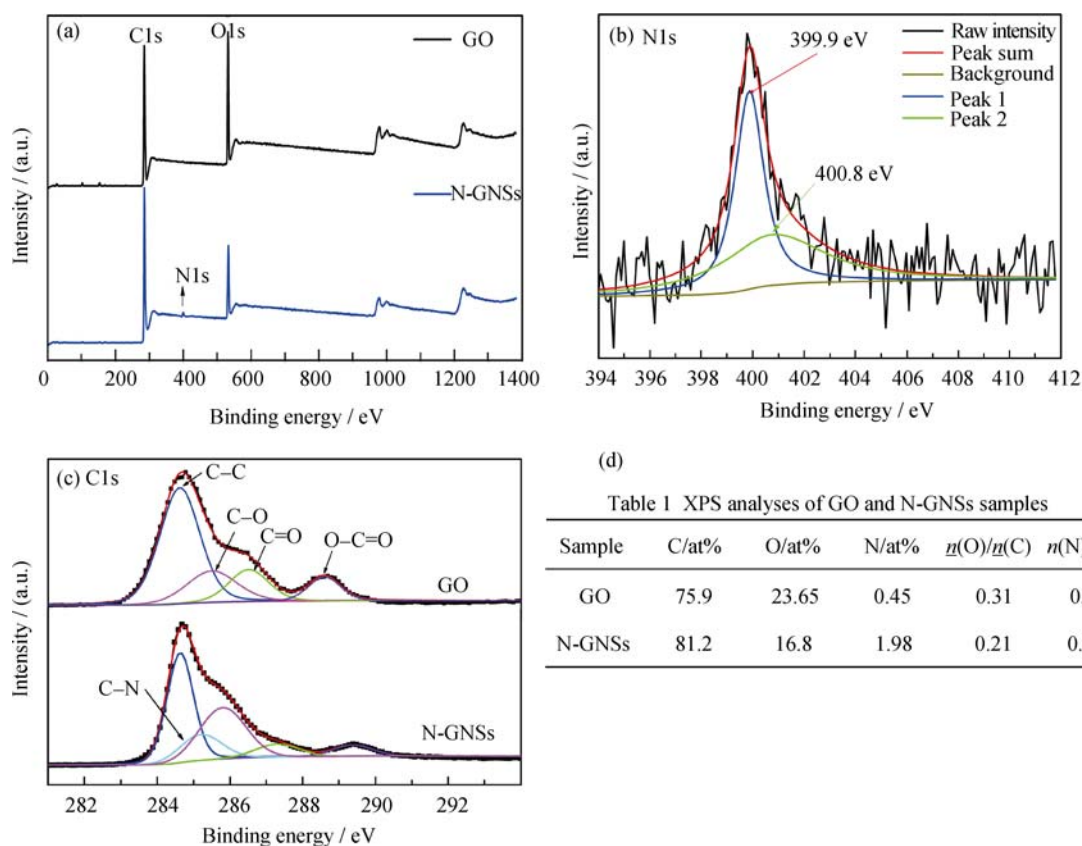


Fig. 2 (a) XPS survey spectra of as-synthesized GO (black) and N-GNSs (blue); (b) Well-fitted XPS N1s spectra of N-GNSs; (c) Well-fitted XPS C1s spectra of GO (up) and N-GNSs (down); (d) XPS analysis of GO and N-GNSs samples

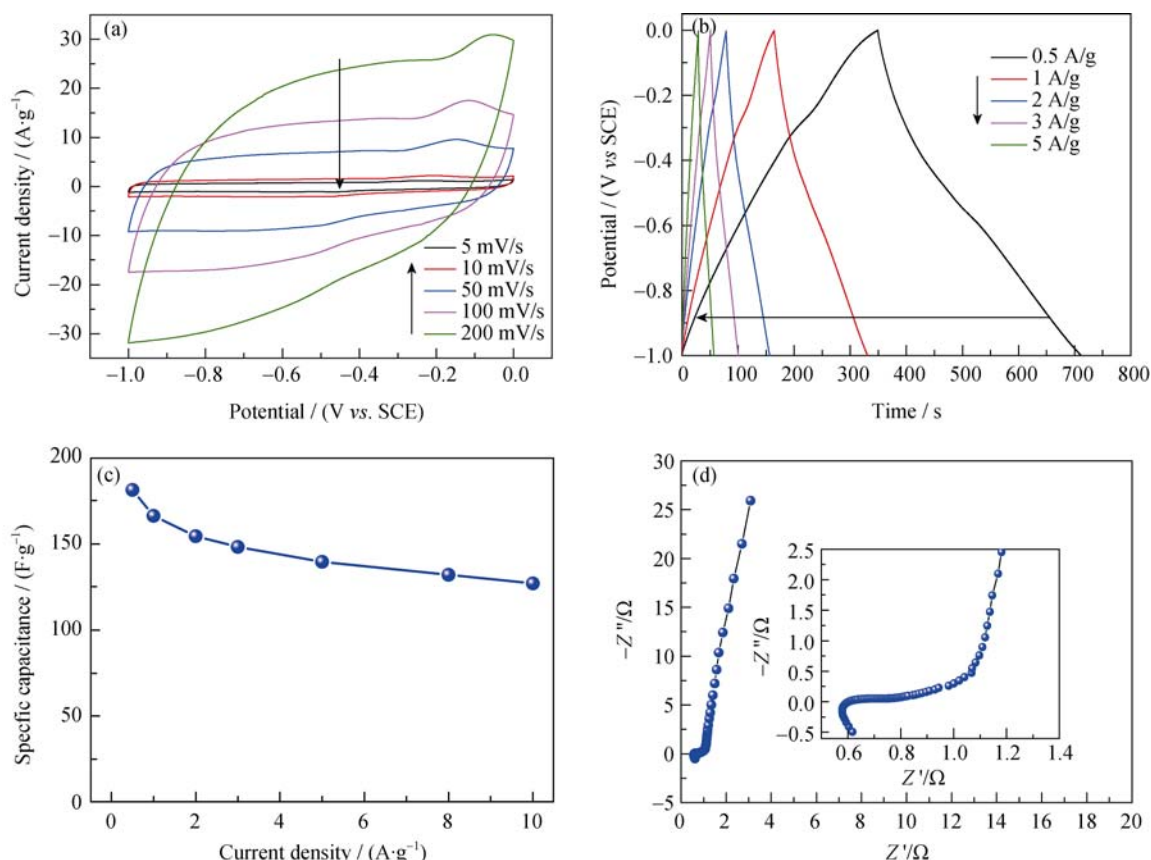


Fig. 3 Electrochemical performance of the N-GNSs electrode in 2 mol/L KOH electrolyte

(a) CV curves at different scan rates; (b) Charge/discharge curves at different current densities; (c) Specific capacitance as a function of discharge current density; (d) Nyquist plots of the N-GNSs. The inset shows the expanded high-frequency region of the plots

of the N-GNSs electrode at different current densities. It can be observed that the shape of all the charge-discharge curves of the electrode is closely linear and show a typical triangle symmetrical distribution, displaying a good capacitive property. The specific capacitance (C_g) of the electrode calculated from galvanostatic discharge is 181.3 F/g at a current density of 0.5 A/g, which is higher than some reported graphene^[22-23] and N-doped graphene^[19]. Figure 3(c) presents the relationship between specific capacitance and charge/discharge current densities. It is important to note that the C_g value of the N-GNSs is still as high as 127 F/g even at a high current density of 10 A/g. The superior performance of the N-GNSs can be attributed to dope graphene structure with nitrogen heteroatom and appropriate nitrogen species^[19], which can provide pseudocapacitance and lead to excellent electric conductivity. The facilitated ion-transport kinetics and electrode conductivity were further confirmed by EIS (Fig. 3(d)). To better understand the processes taking place at the electrode/electrolyte interface, the Nyquist plot is divided into two regions, the high-frequency region and the low-frequency region. In

the high-frequency region, the intercept of the semicircle with the real axis represents the equivalent series resistance (ESR), where the resistance of the electrolyte solution is usually predominant. As the plots shown, in the high-frequency region, the N-GNSs electrodes have small ESR and charge transfer resistance (Fig. 3(d) inset). Furthermore, in the low-frequency region, the slope of the plot for the N-GNSs shows a straight line, indicating that the N-GNSs shows characteristic of better capacitive behavior^[20].

The cycle life of the N-GNSs electrode was examined by galvanostatic charge-discharge measurement at a current density of 5 A/g. As shown in Fig. 4, the special capacitance of as-prepared N-GNSs still remains 92.5% of the initial specific capacitance after 2000 cycles. This indicates that, within the voltage window of -1~0 V, the repeating charge-discharge process does not seem to induce a significant structural breakage for the N-GNSs electrode. The long-term stability implies that our N-GNSs can be used as an excellent potential electrode material for supercapacitors.

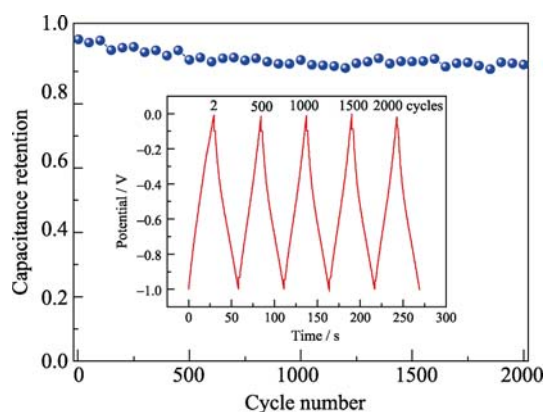


Fig. 4 Cycle life of the N-GNSs electrode at the current density of 5 A/g in KOH electrolyte. The inset shows the charge-discharge curves for N-GNSs electrode at the end of different cycles

3 Conclusions

In summary, a simple and effective solvothermal route has been employed to prepare N-GNSs with nitrogen level about 2%. The N-GNSs exhibit excellent electrochemical properties and the specific capacitance reaches 181.3 F/g in 2 mol/L KOH electrolyte. In addition, the N-GNSs sample shows excellent cycle stability after 2000 cycles (maintained at 92.5%). Thus, the N-GNSs could be used as a kind of promising electrode material for high-performance supercapacitors.

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氮掺杂石墨烯的简易制备及其超级电容性能

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摘 要: 采用简易溶剂热法成功制备出了氮掺杂石墨烯(N-GNSs), 结构表征显示其形貌良好。X 射线光电子能谱(XPS)结果表明在溶剂热过程中, 氧化石墨烯表面的大部分含氧功能团已被成功除去, 而且二甲基甲酰胺中的氮原子通过吡咯氮和石墨氮的形式成功掺杂到石墨烯结构中。作为电极活性材料, N-GNSs 展现出优异的电容特性, 在 2 mol/L KOH 电解液中电流密度为 0.5 A/g 时比电容可达 181.3 F/g。此外, N-GNSs 还展示出良好的循环稳定性, 2000 次连续循环后容量仍保持为初始数值的 92.5%。因此, 氮掺杂石墨烯是一种潜在的超级电容器电极材料。

关 键 词: 石墨烯; 氮掺杂; 溶剂热; 超级电容器

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