

Nitrogen-Doped Graphene Materials for Supercapacitor Applications

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Development of advanced functional materials for energy conversion and storage technologies play a key role in solving the problems of the rapid depletion of fossil fuels and increasingly worsened environmental pollution caused by vast fossil-fuel consumption. Supercapacitors (SCs), also known as ultracapacitors, which store energy based on either ion adsorption or fast/reversible faradaic reactions, are supposed to be a promising candidate for alternative energy storage devices due to their high rate capability, pulse power supply, long cycle life, simple principles, high dynamics of charge propagation, and low maintenance cost. The performance of supercapacitors highly depends on the properties of electrode materials. Nitrogen-doped graphene (NG)-based materials exhibit great potential for application in supercapacitors because of their unique structure and excellent intrinsic physical properties, such as large surface area with appropriate pore structure, controllable two- or three-dimensional morphology, and extraordinarily electrical conductivity. In this review, we provide a brief summary of recent research progress on NG-based electrode materials for SCs, including the various synthesis methods and the mechanisms of electrochemical performance enhancement.

Keywords: Graphene, Nitrogen-Doped, Supercapacitors.

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1. INTRODUCTION

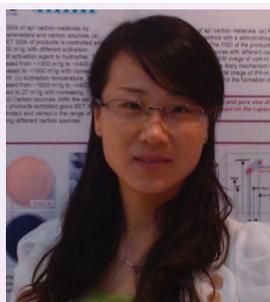
Given the rapid depletion of fossil fuels and increasingly worsened environmental pollution caused by vast fossil

fuel consumption, sustainable energy storage technologies are urgently needed in order to make efficient use of energy and to seek renewable and clean energy sources. Among the various alternative energy storage technologies, electrochemical energy storage shows advantages of high efficiency, versatility, and flexibility.¹ Supercapacitors (SCs), also called electrochemical capacitors or ultracapacitors, have been extensively explored and have become a promising technique to various emerging energy conversion and storage applications in high-power electronic devices, electric vehicles, or hybrid electric vehicles attributed to their simple principle—high dynamic of charge propagation, pulse power supply, and long cycle life (> 100,000 cycles), as well as the environmentally friendly, high safety, and low maintenance requirements.^{2–5} An SC has two electrodes immersed in an electrolyte with a separator between the electrodes. Depending on their charge storage mechanisms, SCs can be catalogued into electrochemical double-layer capacitors (EDLCs) and pseudo-capacitors (PCs).⁶ EDLCs store and release energy dependent on the electrostatic interactions between ions in

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the electrolyte and the active electrode materials (Fig. 1); thus, they can be charged/discharged within seconds and over 100,000 cycles.⁷ EDL, with around 1 nm thickness, consists of three parts, including a space charge layer in an electrode, a compact Helmholtz layer, and a diffusive layer in an electrolyte.¹ The electrochemical activity and kinetic feature of the electrode are crucial to the performance of EDLCs. On one hand, the electrode materials for EDLCs should have a high specific surface area, large pore volume and appropriate pore distribution, because the electric energy is stored in aggregated charges at the

surface of active electrode materials and is proportional to the electrode surface area. On the other hand, the power density of EDLCs is mainly determined by the kinetics of ion and electron transport in electrodes, and at the electrode/electrolyte interface. Hence, in order to obtain high performance EDLCs, electrode materials with proper pore structure and good electronic conductivity are highly desirable. Generally, porous carbon materials such as activated carbon (AC)^{8–13} carbon nanotubes (CNTs),^{14–19} xerogels,²⁰ mesoporous carbon²¹ and carbide-derived carbons²² have been widely used as electrode materials for EDLCs,



Yanhong Lu received her M.S. in 2006 at the Institute of Polymer Chemistry from Nankai University under the direction of Professor Yongsheng Chen. After six years of experience in the Department of Chemistry at Langfang Teacher's School, she took up a Ph.D. scholarship to work under the supervision of Professor Yongsheng Chen and Professor Mingjie Zhang. Her research is focused on the applications of carbon nanotubes and graphene-based materials in the fields of electrochemistry sensors, high-performance supercapacitors, and photoelectronic devices.



Yi Huang has been a full Professor of Chemistry at Nankai University since 2011. He is currently serving as an Assistant Dean in the College of Chemistry. He received his Ph.D. degree in Materialogy from Sichuan University in 2001. Following this he spent two years as a Postdoctoral Fellow at the Department of Chemical Engineering in Tsinghua University. In 2004, he joined Nankai University as an Associate Professor and was elected Full Professor in 2011. His research interests focus on controlled synthesis and application of carbon nanomaterials (graphene and carbon nanotubes), polymer-based intelligent materials, and devices. He has published over 80 peer-reviewed journal articles with more than 3,500 citations and a H-index of 27. He has 10 granted patents.



Mingjie Zhang received his Ph.D. at the College of Chemistry from Nankai University in 1988. He then spent two years as a Postdoctoral Fellow at the Department of Chemical at Peking University. After two years of experience at Morehead State University in America, he joined the Department of Chemistry of Tianjin University, as an Associate Professor, and in 1995 became a Professor. His main research interest focuses on selective organic synthesis catalyzed by metal and asymmetrical organic synthesis.



Yongsheng Chen graduated from the University of Victoria in 1997 with a Ph.D. degree in Chemistry, and then joined the University of Kentucky and the University of California at Los Angeles for postdoctoral studies from 1997 to 1999. From 2003, he has been a Chair Professor at Nankai University. His main research interests include: (1) carbon-based nanomaterials, including carbon nanotubes and graphene; (2) organic and polymeric functional materials, and (3) energy devices including organic photovoltaics and supercapacitors. He has published over 130 peer-reviewed papers with over 6,000 citations, and has over 20 patents.

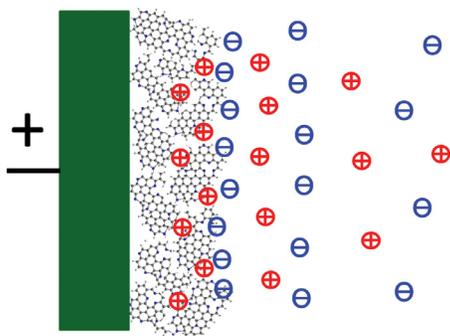


Figure 1. The electrochemical double layer structure of EDLC.

owing to their extra high specific surface area (SSA) and excellent electronic conductivity. PCs store energy by fast surface Faradaic redox reactions between electrode materials and electrolyte ions. There are two types of electro-active materials widely used in PCs. One kind is transition metal oxides or hydroxides with the typical candidate of ruthenium oxide,^{23,24} manganese oxide,^{25–27} and nickel hydroxide,^{28,29} etc. The other kind is conductive polymers, including polyaniline,^{30,31} polypyrrole,^{32,33} polythiophene,³⁴ poly(3,4-ethylenedioxythiophene),³⁵ and so on. The capacitance of PCs is commonly much higher than the EDLCs. However, the relatively low power density arising from the poor electrical conductivity and the weak cycling stability generated from the easily damaged structure of the materials during the redox process limits the practical applications of these electro-active materials for PCs. In order to overcome these problems and increase the performance of PCs, carbon-based materials with high electrical conductivity and large SSA are usually utilized for the backbone materials for PCs.^{36–40}

From what has been discussed above, it is clear that carbon materials with many excellent properties are considered as one of the most suitable electro-active materials for fabricating both EDLCs and PCs with high specific capacitance and energy density, while keeping their high power density unchanged.⁴¹ Although the AC and CNT materials have been widely investigated for the application of SCs, these materials-based SCs have not delivered the expected performance due to the uncontrollable pore size distribution, and surface functional groups for AC and the relative low SSA, high contact resistance between the electrode and the current collector, and adventitious chemical impurities for CNTs.⁴²

Graphene, a two-dimensional sheet of sp^2 -hybridized carbon that is widely used in self-healing materials,⁴³ actuators,^{44–47} electronic circuits^{48–50} and photoelectronic devices^{51–53} is viewed as one of the most promising materials, and has taken up the challenge for high performance SCs^{54–61} in recent years, since its discovery in 2004 by Geim and coworkers;⁶² mainly due to its fascinating properties such as large SSA, fast-charged carrier

mobility, low mass density, high mechanical strength, good chemical, environmental, and mechanical stability coupled with easy accessibility, good processing ability, and robust surface chemical environment.^{63–69} Great achievements of graphene-based SCs have been obtained, but for application, the pristine graphene-based SCs couldn't satisfy the high demand, including high specific capacitance, energy and power density, and excellent cycling stability. In order to improve the capacitance of graphene-based SCs many methods have been reported, including the introduction of fillers or dopants to graphene, such as transition metal oxides or hydroxide,^{70–72} conducting polymers^{73,74} and carbon nanotubes,^{75–78} etc. As known, chemical doping with foreign atoms is an effective way to enhance the intrinsic properties of host materials.^{79,80} Among various heteroatoms doping, nitrogen is a potential candidate because it is in a comparable size, and contains five valence electrons available to form strong valence bonds with carbon atoms.⁸¹ In addition, theoretical studies also predicted that doping graphene with nitrogen can tailor its electronic properties and chemical reactivity. Recently, nitrogen-doped carbon materials such as nitrogen-doped AC,^{82,83} and nitrogen-doped CNTs⁸⁴ have been widely investigated for the application of SCs. Additionally, experiments have shown that combining with the outstanding advantages of graphene, nitrogen-doped graphene sheets, (NG)-based SCs can significantly show extraordinary performance.⁸⁵ The study of NG-based SCs has attracted many scientists, so it is important for theory studies and realistic applications to summarize the NG materials in the SCs field. Some previous reviews on NG have reported, which focused on the chemical doping approaches or the characterization and applications in fuel cell, field-effect transistor and lithium ion batteries fields,⁸⁶ but the special application in SCs, especially the mechanism of enhancement of capacitors, is still no systematical study.

In this review, we will summarize the progress made so far in NG-based SCs. We will discuss NG synthesis methods, explore the mechanisms for electrochemical performance improvement, and summarize the already achieved high SCs performance.

2. SYNTHESIS OF NITROGEN-DOPED GRAPHENE

According to the report, the reliable and straightforward approaches to fabricated NG materials can be divided into five categories:

- (1) Chemical vapor deposition (CVD) method in the presence of nitrogen-containing precursors for the growth of doped films.
- (2) Arc discharge between carbon electrodes in the presence of the nitrogen-containing compounds.
- (3) N_2 or NH_3 plasma treatment.

- (4) High-temperature pyrolysis or annealing graphene oxide with nitrogen-containing precursor.
- (5) Hydrothermal and solvothermal method or reflux reaction.

2.1. CVD Method

In an energy storage device, the weak adherence between the electrode and the current collector hinder the electron transport, which leads to a poor capacitance and cycling stabilities. So it is important to directly fabricate graphene electron materials on current collector substrates by the CVD process. CVD is the common method for the synthesis of NG, which employs organic molecules as the carbon source and nitrogen-containing compound as the nitrogen source to synthesize NG via rearranging the carbon and nitrogen atoms on metal catalysts at high temperatures. The typical nitrogen-containing precursor for NG growth includes a gaseous and liquid compound. Using ammonia gas as a nitrogen source, Yu's group⁸⁷ synthesized the single-layer graphene doped with pure pyridinic-N by thermal chemical vapor deposition of hydrogen and ethylene on Cu foils. By adjusting the flow rate of ammonia, the atomic ratio of nitrogen and carbon can reach 16%. Liu's⁸⁸ and Dai's⁸⁹ groups also use ammonia as nitrogen precursor-prepared few-layer NG, respectively. Besides gaseous nitrogen-containing precursors, liquid ones have attracted intensive attention because the latter are easy to handle and transport and are low cost. Ajayan's group⁹⁰ reported a controlled growth of NG layers by liquid precursor (hexane and acetonitrile)-based CVD technique. The graphene electrode grown directly on a Cu current collector, with a large number of surface defects and a high percentage of pyridinic-N atoms, shows almost double reversible discharge capacity in a lithium battery, compared to the pristine ones. Consequently, Kang's group⁹¹ investigated the effect of acetonitrile feed rate on the growth of NG in detail. They revealed that there exists a critical feed rate, and then discussed the reason. Using liquid pyridine as the sole source of both carbon and nitrogen, Tour's group⁹² prepared the monolayer NG in centimeter-scale sheets by the CVD process. The preparation of large-area NG provides a viable route to modify the properties of monolayer graphene and promote its applications in electronic devices. CVD methods commonly proceeded at high temperature (about 1000 °C). However, the high temperature process will lead to some problems such as low nitrogen doping content, relatively more defects in lattice, and a polycrystalline nature, which would reduce the device performance. In order to solve this, Liu's group⁹³ fabricated highly nitrogen-doped tetragonal-shaped single crystal graphene arrays via a self-assembly of pyridine molecules on Cu surface by the CVD method at 300 °C, which is the lowest temperature reported to date for growing NG. NG is almost 100% single layer, and the nitrogen content reaches 16.7%, which is much higher than the

other's NG. Additionally, combined with the assistance of microwave hydrogen plasma, Zhang's group⁹⁴ developed a facile one-step technique to prepare NG from a solid carbon source (PDMS) and nitrogen gas. Saiki's group⁹⁵ also reported the synthesis of NG by a plasma-enhanced CVD method. In the above CVD routes, metal catalysts such as nickel and copper are used to form graphene frameworks, and thus metal catalysts may remain in the resultant NG product inserting into the graphene layers. The metal impurities may seriously weaken the NG's electrochemical performance. So it is imperative to develop the metal-free approaches to the synthesis of NG.

2.2. Arc Discharge Method

By the arc discharge method, NG is synthesized through disintegrating hydrocarbon and nitrogen gas using a high voltage. Rao's group⁹⁶ successfully prepared NG by performing the arc discharge of graphite electrodes in the presence of pyridine or NH₃ vapor. X-ray photoelectron spectroscopy (XPS) data shows there exists two types of nitrogen in NG, which are pyridinic-N and quaternary-N, and the nitrogen content is around 0.6–1.4 at.%. Moreover, an interesting transformation of nanodiamond was carried out in the presence of He and pyridine vapor at 1650 °C. Shi's group⁹⁷ described a possible route for the mass production of nitrogen-doped multi-layered graphene sheets by the arc discharge method using NH₃ as nitrogen source. The nitrogen-doped multi-layered graphene sheets are mainly of 2–6 layers, with the size of 100–200 nm, and the content of nitrogen is about 1%. The type of nitrogen in NG is still pyridinic-N and quaternary-N. By this method they can get about 9.6 g graphene sheets per hour, and this provides the possibility for industrialized production. Although its metal-free production is in the arc discharge process, special instruments or rigorous conditions are certainly required. Importantly, the nitrogen content is very low, which would limit this preparing method in the electrochemical devices.

2.3. Plasma Process

In the plasma process, the carbon six-ring structure was destroyed by the bombardment of nitrogen ions, and then nitrogen was introduced to fill the vacancies of carbons. Lin's group^{98,99} obtained NG by exposing graphene to nitrogen plasma. The nitrogen exists in the form of pyridinic-N, pyrrolic-N and quaternary-N, and the content is 1.35 at.%. Ramaprabhu's group¹⁰⁰ also obtained the NG by nitrogen plasma treatment. Choi's group¹⁰¹ successfully prepared NG using the nitrogen plasma method (Fig. 2). The bulk-scale XPS data indicate that nitrogen content for the NG are 1.68–2.51 wt% produced by 0.5–3 min plasma processes. Importantly, they construct SCs with the NG materials and show excellent electrochemical performance, which resulted from the nitrogen-doped sites at basal planes produced by the plasma process. Besides nitrogen,

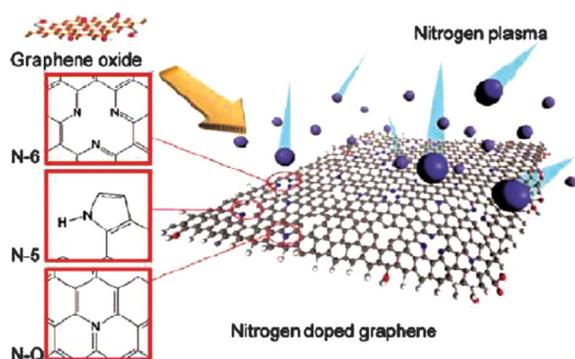


Figure 2. A schematic illustration of the plasma doping process. By the plasma process with physical momentum, nitrogen atoms replace the existing carbon atoms. Inset: possible nitrogen configurations by the doping treatment. Reprinted with permission from [101], H. M. Jeong, et al., *Nano Lett.* 11, 2472 (2011). © 2011, American Chemical Society.

ammonia plasma has also been used to prepare NG by Chiu's group.¹⁰² Different from other synthesis methods, the defects and oxygen-containing groups are introduced during the plasma exposure process. This may be caused by the reactive carbon atoms at the edge of defects that are created by the plasma treatment. This method usually requires protective atmosphere and high temperature, which may cause the doped nitrogen to escape easily as time persists.

2.4. High-Temperature Pyrolysis or Annealing Method

Pyrolysis, or annealing, refers to the method using high temperature to produce NG. Chen's group¹⁰³ developed an efficient and facile strategy of pyrolysis (900 °C) GO and cyanamide to fabricate highly crumpled NG with a large Brunauer–Emmett–Teller (BET) surface area of 465 m² g⁻¹ and a pore volume as high as 3.42 cm³ g⁻¹. The morphology of NG is highly crumpled and the nitrogen content reaches 9.96%. Müllen's group¹⁰⁴ also developed a cost-effective synthesis of NG by pyrolyzing GO and cyanamide. The NG with 12.0% nitrogen content shows outstanding catalytic ability to an oxygen reduction reaction (ORR) in an alkaline solution. Dai's group¹⁰⁵ successfully obtained three-dimensional (3D) NG foams (N-GFs), with the nitrogen content as high as 7.6%, by annealing the freeze-dried graphene oxide foams in ammonia. NG applying in the metal-free counter electrode materials of dye-sensitized solar cells showed a power conversion efficiency as high as 7.07%, which should, thanks to the high electron conductivity and good electrocatalytic activity, bring from the 3D foam structure with a large surface area, good surface hydrophilicity, and well-defined porosity for enhanced electrolyte/electrode interaction and electrolyte/reactant diffusion.

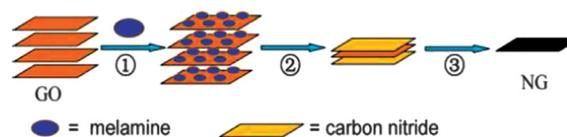


Figure 3. Illustration of the nitrogen doping process of melamine into GO layers. (1) Melamine adsorbed on the surfaces of GO when temperature is < 300 °C. (2) Melamine condensed and formed carbon nitride when temperature is < 600 °C. (3) Carbon nitride decomposed and doped into graphene layers when temperature is > 600 °C. Reprinted with permission from [106], Z. H. Sheng, et al., *ACS Nano* 5, 4350 (2011). © 2011, American Chemical Society.

Xia and Wang's group¹⁰⁶ report a facile and catalyst-free approach for the synthesis of NG by thermal annealing graphite oxide (GO) using low-cost industrial material melamine as a nitrogen source (Fig. 3). The nitrogen bonding configurations in their NG are composed mainly of pyridinic-N, and the content could reach up to 10.1 at.%. Their NG exhibits excellent electrocatalytic activity toward the ORR in alkaline electrolytes. Then they investigated the electrocatalytic activity of NGs with different nitrogen content toward the ORR process. As a result, it is not the nitrogen content but the nitrogen bonding configurations in NGs that could be the key factor for electrocatalytic performance toward ORR. NG, with highly wrinkled structures and a high N content of 7.86 at.%, was also obtained by pyrolyzing (800 °C) of GO with urea by Wong's group.¹⁰⁷ The NG materials have high catalytic activity toward the oxygen-reduction reaction, which is superior to Pt/C catalysis. Besides the ammonia, cyanamide, urea, and melamine as the nitrogen source, 5-aminotetrazole monohydrate¹⁰⁸ and polyaniline¹⁰⁹ also were used as the nitrogen precursors in the high temperature pyrolysis reaction. Different from the above high temperature treatment, the methods of chemical reduction prior to thermal annealing were proposed by Chung's¹¹⁰ and Kurungot's¹¹¹ groups, respectively. Through the method, Chung et al. obtained enhanced quaternary nitrogen content in NG, which could provide more efficient electrocatalytic activity. Kurungot et al. prepared NG with a large SSA of 528 m² g⁻¹ and a large number of mesopores with the pore size around 3–7 nm, which is of benefit to electrocatalyze the ORR. Although the high nitrogen content is obtained and it is low cost, scalable, and ecofriendly, the pyrolysis methods universally proceed in high-temperature conditions, which make the structural manipulation of the catalysts extremely difficult.

2.5. Hydrothermal/Solvothermal Method

The approaches to synthesize NG of CVD, arc discharge, nitrogen plasma process, and pyrolysis treatment must suffer from rigorous conditions and sophisticated equipment, and sometimes together with low product yield and high cost. Recently, it has been found that hydrothermal or solvothermal reaction has the merits of

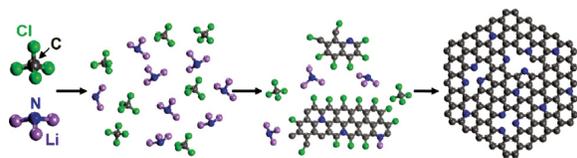


Figure 4. Scheme of a proposed mechanism for solvothermal synthesis of NG via the reaction of CCl_4 and Li_3N , where gray balls represent C atoms, blue for N, green for Cl, and purple for Li. Reprinted with permission from [112], D. H. Deng, et al., *Chem. Mater.* 23, 1188 (2011). © 2011, American Chemical Society.

mild conditions, scale-up synthesis, a high nitrogen-doped level, and has been a strong research focus, especially in producing the NG materials applied to SCs. Earlier, Bao and coworkers¹¹² synthesized NG with an exceptional nitrogen level of up to 16.4 wt% by a solvothermal reaction between tetrachloromethane and lithium nitride without GO as precursor (Fig. 4). The high yield with 1.2 g per batch can be scaled up for gram-scale production. And the first time the distinct electronic structure perturbation induced by the incorporation of nitrogen in the graphene network is observed by scanning tunneling microscopy (Fig. 5). The obtained NG exhibited an outstanding performance in the ORR of the fuel cell. According to the nitrogen-containing precursor, we demonstrate the development of hydrothermal/solvothermal methods in recent years in the following sections.

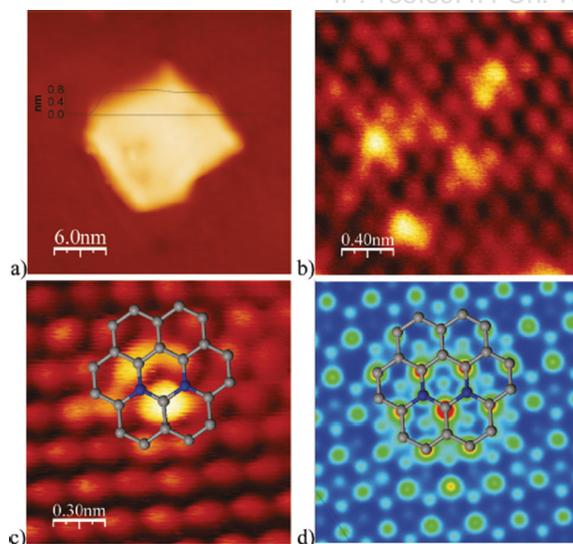


Figure 5. STM images of NG-2. (a) Isolated bilayer NG and the black curve on top showing the height measurement across this bilayer. (b), (c) High resolution images with defects arranged in different configurations, measured at a bias = 0.5 V, current $I = 53.4$ pA, and bias = 0.9 V, $I = 104$ pA, respectively. (d) Simulated STM image for (c). The inserted schematic structures represent nitrogen-doping graphene, with the hexagons in gray balls highlighting the atomic network of graphene, and deep blue balls labeling nitrogen atoms. Reprinted with permission from [112], D. H. Deng, et al., *Chem. Mater.* 23, 1188 (2011). © 2011, American Chemical Society.

2.5.1. Aqueous Ammonia

Yoon's group¹¹³ developed a novel hydrothermal reaction to prepare NG through a reduction of GO in the presence of hydrazine and ammonia. The nitrogen level of 5 wt% was achieved, and they found slightly wrinkled and folded features were obtained at the relative low temperature (≤ 120 °C), the nitrogen content decreased slightly, and more pyridinic-N incorporated into the graphene network with the increase of hydrothermal temperature. Sun and coworkers¹¹⁴ also developed a promising approach using aqueous ammonia as a nitrogen source to simultaneously dope and reduce GO by a hydrothermal process. They achieved three forms of NG, including stable dispersion, hydrogel, and aerogel, and also demonstrated that the pressure has a promoted effect on reduction and the nitrogen-doping of GO. Another ammonia-assisted hydrothermal method to prepare NG was reported by Fu's group.¹¹⁵ They also demonstrated that the nitrogen doping and reduction of GO were processed at the same time, and the doping level is 7.2 at.%.

2.5.2. Urea

Fu's group¹¹⁶ reported a one-step hydrothermal reaction using low-cost urea as a nitrogen precursor to synthesize NG with both a high nitrogen level (10.13 at.%) and a large SSA ($593 \text{ m}^2 \text{ g}^{-1}$) that exhibited excellent performance for SCs. With urea and GO as raw materials, NG also fabricated by Guo and coworkers¹⁰⁹ through a one-pot hydrothermal route. A nitrogen content of 6.61 at.% with pyrrolic-N as the main component of NG was obtained. Additionally, a large SSA of $> 1300 \text{ m}^2 \text{ g}^{-1}$ in the wet state and mesoporous structure were achieved, which strongly influenced the electrochemical properties.

2.5.3. Pyrrole

The hydrothermal process with pyrrole as precursor was reported by Qu and coworkers. With 5 vol% pyrrole and 0.35 mg ml^{-1} GO dispersion as reactors, they prepared 3D NG framework,¹¹⁷ which mainly consists of the network of only a few graphene layers, and has an ultra-low density of $2.1 \pm 0.3 \text{ mg cm}^{-3}$. Their NG materials have the excellent adsorption capacity or common pollution and organic solvents, high specific capacitance for SCs, and efficient electrocatalytic ability to ORR.

2.5.4. Aqueous Hydrazine

With aqueous hydrazine, Yu's group¹¹⁸ synthesized pyrrolic structure-enriched NG by a hydrothermal process. They discussed the influence of hydrothermal temperature on the morphology, structure, and composition of NG. They point out that the temperature not only influenced the nitrogen content, but also lead to the change of the percentage of nitrogen types in different products. The nitrogen content was 3.2, 2.7, 2.7 at.% for NG80, NG130, and NG180, respectively (prepared at

80, 130, and 180 °C, respectively). The percentages of the nitrogen components show the pyrrolic-N predominates in all samples. However, for NG130, the ratio of the pyrrolic-N to the overall nitrogen is the highest, which would be responsible for the high capacitance of SCs. Up to now, various nitrogen-containing compounds had been used the reactor of the hydrothermal process. Besides the above mentioned, other molecules such as ethylenediamine,¹¹⁹ hexamethylenetetramine,¹²⁰ dimethylformamide,¹²¹ *o*-phenylenediamine,¹²² *p*-phenylenediamine,¹²³ and pentachloropyridine¹²⁴ were reported.

3. APPLICATION FOR SCs AND THE MECHANISMS FOR ELECTROCHEMICAL PERFORMANCE IMPROVEMENT

Graphene with various microtextures and wide availabilities represent very attractive materials for SCs. Based on this, NG, with its unique structures and novel characteristics, are supposed to be a promising candidate for electron-active materials of SCs to achieve better capacitor performance, including remarkable specific capacitance, extraordinary energy and power density, and outstanding cycling stability. Table I gives a summary of the comparative analysis for structure and electrochemical performance of SCs with various synthesis methods. Detailed discussion on the mechanisms for performance improvements of

SCs is elaborated below. The NG shows different properties compared with the pristine graphene. The reasons are summarized as follows.

3.1. Opening Band Gap

The Fermi level shifts above the Dirac point, and the density of state near the Fermi level is suppressed after nitrogen doping, and so, the band gap between the conduction band and the valence band will be opened. Yu and coworkers¹¹⁸ demonstrated the energy band gap (E_g) of NG prepared at different hydrothermal temperatures using UV absorption data and Tauc's equation. NG130 showed the smallest energy band gap, suggesting it has the highest intrinsic conductivity and lower internal resistance. So NG130 exhibits superior SC performance. The band gap in NG makes it a candidate to be used in semiconductor devices.

3.2. Nitrogen Content and Configurations

Choi et al.¹⁰¹ revealed that the different nitrogen configurations have different contributions to the performance of SCs. The basal-plane pyridinic-N (N-6) was claimed to have a dominant role in the capacitance enhancement because of their larger binding energy, which would result in a larger number of ions in electrolytes to be accommodated on the electrode surface even for the given surface area of an electrode. They further pointed

Table I. Electrochemical performance of supercapacitors based on nitrogen-doped graphene.

No	Synthesis method	Nitrogen content	Nitrogen types	SSA m ² g ⁻¹	Pore size (nm)/ pore volume (m ³ g ⁻¹)	Specific capacitor (F g ⁻¹) Aqueous/organic	Energy density (Wh kg ⁻¹)/power density (W kg ⁻¹)	Cyclic stability (capacitance retention/%)	Ref.
1	Plasmer	1.68–2.51 wt.%	Basal-plane Pyridinic N	–	–	280/~220 at 1 A/g	~48/8 × 10 ⁵	10000 (99.8)	[101]
2	Hydrothermal	10.13 at.%	Pyridinic N Pyrrolic N	593	~3/-	326/- at 0.2 A/g	25.02/7980	2000 (~100)	[116]
3	Hydrothermal	42 at.%	Quaternary N Pyridinic N Pyridinic N	280	–	484/- at 1 A/g	–	–	[117]
4	Pyrolysis	8.2 at.%	–	465.0	6.3/3.42	-/245.9 at 1 A/g	–	5000 (96.1%)	[103]
5	Freezing	–	–	–	–	259/- at 1 A/g	–	5000 (93%)	[130]
6	Annealing	–	–	630.6	3–35/-	-/138.1 at 1 A/g	80.5/16680	2000 (94.3%)	[42]
7	Low temperature approach	13.52 at.%	Pyridinic N Pyrrolic N Quaternary N	–	–	170/- at 0.5 A/g	–	10000 (96.4%)	[129]
8	Hydrothermal	6.61 at.%	Pyridinic N Pyrrolic N (main) Quaternary N	300	3.81/0.27	308/- at 3 A/g	–	1200 (92%)	[81]
9	Hydrothennal	7.2%	Pyridine N, Quaternary N, Pyridine-N oxides	–	–	144.6/- at 0.2 A/g	–	500 (90%)	[115]
10	Hydrothennal	3.72–9.63%	Pyridinic N Pyrrolic N Quaternary N	–	–	190.1/- at 10 A/g	4.5/205	4000 (95.2%)	[119]
11	Hydrothermal	8.62 at.%	Pyridinic N Pyrrolic N Quaternary N	–	–	161/- at 0.5 A/g	–	5000 (98.1%)	[120]

out that the superior power densities of SCs based on NG could be ascribed to the significant graphite-like N (N-Q), which enhanced the conductivity of NG. According to the literature reported,^{125,126} the total capacitance (C_T) of an ionic liquid (IL)/grapheme-based electrode strongly depends on the relative contributions from both the double-layer capacitance (C_D) and electrode quantum capacitance (C_Q). The C_Q of graphene is proportional to the electronic density of states (DOS), which can be altered from chemical doping. Hwang and coworkers¹²⁷ studied the effects of nitrogen doping on both C_Q and C_D . They evaluated the interfacial capacitance of NG in [BMIM][PF₆] IL using the combined density functional theory (DFT) and classical molecular dynamics (MD) calculations. According to their calculations, the nitrogen configurations, including substitutional nitrogen (N₁) and trimerized pyridinetype nitrogen (N₃V) (Fig. 6), significantly tend to enhance the C_Q of graphene near the Fermi level, compared to the pristine one. Ruoff's group¹²⁸ also demonstrated that the Dirac Point shifts upwards with increasing nitrogen concentration in NG. Their study's results show that the increase of capacitance of EDLC is primarily attributed to the modification of the electronic structure of the graphene by the nitrogen dopant. It was further found that the C_Q is closely related to the nitrogen dopant concentration, and nitrogen doping provides an effective way to increase the density of the states. Liu et al.¹²⁹ proposed that pyridinic-N contributes the major part of the capacitance increment of NG among three nitrogen configurations. Fu et al.^{115,116} demonstrated that not only the nitrogen content but also the nitrogen type are very significant for the capacitive behaviors. They discussed that the pyridinic-N and pyrrolic-N mainly play roles for improving pseudo-capacitance by the redox reactions, and quaternary-N is contributed to enhance the conductivity of NG, which is favorable to the transport of electrons during the charge/discharge process. Qu¹¹⁷ and Guo⁸¹ also agreed that the higher capacitance of their NG-based electrodes could be ascribed to possible pseudo-capacitance contribution of heteroatom doping, also the

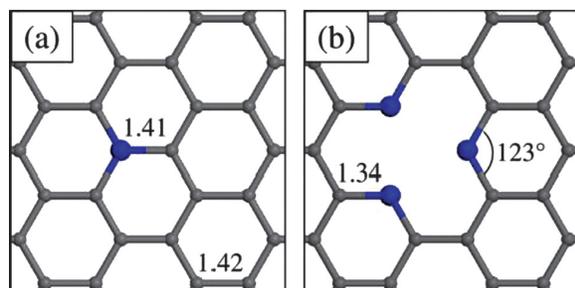


Figure 6. Schematic of (a) the substitutional nitrogen site (N₁) and (b) the trimerized pyridine-type nitrogen site (N₃V) considered in this work. Gray and blue balls are C and N atoms, respectively, and bond lengths are given in Å. Reprinted with permission from [127], E. Paek, et al., *J. Phys. Chem. C* 117, 5610 (2013). © 2013, American Chemical Society.

highly exposed graphene sheets with minimum stack. Furthermore, our group¹²³ obtained a new nitrogen type in NG, phenazinic-N, double nitrogen atoms existing in the same hexagon skeleton of a benzene ring at the edge of graphene, which cannot only enhance the cycling stability of SCs, but also improve the electronic conductivity of the materials because of the π - π conjugated system between graphene and the electron-rich nitrogen.

3.3. Pore Volume

The remarkable electrochemical performance of NG attributed to ultra-high pore volume was reported by Chen's group.¹⁰³ They obtained NG with pore volume as high as 3.42 cm³ g⁻¹ and a considerably large surface area of 465.0 m² g⁻¹. The high pore volume can provide rich sites for adsorbing ions and accelerating electron transfer or decreasing electric resistance loss. Additionally, they illustrated that the high nitrogen-doping content with a large number of crumpled structures also benefits the electrochemical performance. Fan's group¹³⁰ also illustrated that the high specific capacitance, excellent rate capability and cycling stability of NG-based SC are thanks to the large surface area and pore volume, which facilitate fast ionic transport within the electrode, while preserving excellent electrical conductivity.

3.4. Conductivity

Yang's group⁴² successfully achieved NG with dramatically enhanced electrical conductivity (1000–3000 S m⁻¹). The NG electrodes show an outstanding specific capacitance of 138.1 F g⁻¹ at a current density of 1 A g⁻¹ without any carbon additive, which could ascribe to the fast electron transport of NG.

4. CONCLUSION

NG materials with various microtextures and wide availabilities are very fascinating materials for SCs. Although most of the research has been performed, NG-based materials represent very attractive materials with great potential in the active field of SCs. Based on our journey, the key factors of NG materials for SC electrodes contain high SSA, controlled pore structure, and pore size suited for the electrolyte ions, large nitrogen content and designable nitrogen configuration, excellent electrical conductivity, good wettability toward the electrolyte, and electrochemical stability. It is extremely urgent and significant to further research the above issues. Additionally, NG materials-based SCs are relatively high cost. Scientists should develop mass production approaches as well as simplify the preparing process, because one-step synthesis without an additional activation process to obtain high-performance NG materials would be beneficial for the application of NG-based SCs. The design and synthesis of NG-based SCs with excellent performance will also be an important task in the future.

Acknowledgments: The authors gratefully acknowledge financial support from the Science and Technology Research Project of Higher Education of Hebei Province (Grant z2012064), Science Research Project of Langfang Teachers College (Grant LSZQ200908), MOST (Grants 2012CB933401 and 2011DFB50300), NSFC (Grants 50933003 and 51273093).

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Received: 28 July 2013. Accepted: 16 August 2013.

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IP: 155.69.4.4 On: Wed, 11 Jun 2014 11:23:50
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