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Nitrogen Doped Graphene as a high efficient electrode for next generation supercapacitors

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This study reports the preparation of nitrogen doped graphene (NG) by hydrothermal synthesis. The morphology, structure, and composition of the prepared NG were confirmed with SEM, XRD, XPS and Raman spectroscopy. The material was tested for supercapacitive behavior. Our emphasis here is focused on the method of synthesis as an energy saving process, compared to other methods utilizing high temperatures or plasma techniques. The results confirmed that 2.77% nitrogen was chemically doped to graphene. Furthermore, it was found that doping with nitrogen increased the supercapacitance of graphene by 45%, reaching 131 F/g. An equivalent two electrode cell fabricated from NG material could provide energy density as high as 4.55 Wh/kg and a stable average power density of 2.46 kW/kg.

Introduction

Supercapacitors are devices that can store greater amounts of energy than conventional capacitors, and they are able to deliver more power than batteries. Furthermore, they have relatively long cycle life and rapid charging and discharging at high power density (1, 2). There is a great interest for supercapacitors for a wide and growing range of applications, including electric vehicles, electric utilities, power backup and more (2-4). Various materials have been used as electrode materials for supercapacitors including, carbon materials (5-9), metal oxides (10-12) or conducting polymers (13). However, carbons are the most common electrode materials for supercapacitor applications aiming at high specific capacitance together with high power density. Graphene, the 2D carbon nanostructure, has attracted great interest for application in the field of energy storage and conversion (14-17). Its excellent and unique properties e.g. high chemical stability (18, 19), high electrical conductivity (20, 21) and large surface area (21, 22) qualify it for many potential applications (23, 24), including supercapacitors (16, 25).

Many attempts have been made to modify graphene properties by controlling its structure. Chemical doping with hetero atoms such as N are considered an effective method to intrinsically modify graphene (26-30). Due to its comparable atomic size and high electronegativity, nitrogen doping increases the functionality of graphene. There are two major means to chemically dope graphene. The first is by adsorption of either gas or

organic molecules to the graphene surface (31, 32). The second is the introduction of a heteroatom such as N or B into the carbon lattice of graphene. Nitrogen doped graphene (NG) can be synthesized by a CVD approach where the nitrogen containing precursors are introduced to graphene at high temperature with controlled atmosphere. Other methods include plasma treatment or arc-discharge approach.

In this paper we introduce an economical approach to produce nitrogen doped graphene using hydrothermal method in which reduction of graphene oxide and doping of graphene happen simultaneously and in one step. The structure of the NG was elucidated by SEM, XRD, Raman and XPS spectroscopy. The supercapacitive behavior of NG was studied by cyclic voltammetry (CV), and Charge/Discharge (CD).

Experimental

Synthesis of graphitic oxide. The graphite oxide was prepared following the modified Hummers' method in which graphite flakes are oxidized using a mixture of potassium permanganate, sulfuric acid and sodium nitrate (33). In a typical synthesis 2 g of graphite powder and 1 g of sodium nitrate were added to 46 mL conc. H_2SO_4 in a round bottom flask with stirring while keeping the temperature at 0^oC by ice bath. Then 6 g of $KMnO_4$ were added slowly then mixture is diluted by deionized water followed by adding 40 mL of 30% H_2O_2. Then the mixture is filtered, washed and dried.

Synthesis of NG. For preparation of NG a solution of graphitic oxide in deionized water was made with concentration of 2 mg/mL under sonication for an hour. Then the pH is adjusted to 10-11 using ammonia solution, 1.75 mL of aqueous hydrazine is added and the mixture is magnetically stirred for 10 minutes. The mixture is then transferred to a Teflon-lined autoclave and subjected to hydrothermal treatment at 180^oC for 3 hours. After cooling, the mixture is filtered, washed and dried in a vacuum oven. For the preparation of the regular graphene, $NaBH_4$ was used instead of ammonia and hydrazine and the rest of the reaction conditions were maintained the same as that of NG.

Electrochemical measurements. Electrochemical measurements were carried out using a CHI 760D electrochemical workstation (CH Instruments, USA) and a three electrode cell. Cyclic voltammetry (CV), charge discharge (CD), and electrochemical impedance spectroscopy (EIS) techniques were all carried out following a 25-cycle CV activation between −0.4 and 0.6 V versus SCE at a scan rate of 0.1 V/s in 1 M KCl electrolyte. CV was carried out between −0.4 and 0.6 V versus SCE at scan rates between 0.01 and 0.20 V/s. CD was carried out between −0.4 and 0.6 V versus SCE at current densities between 0.5 and 1.0 A/g. The capacitances of the supercapacitors were calculated based on the CV data and the mass of the graphene or NG.

Results and Discussion

Structure and morphology characterization.

Figure 1 elucidates the morphology and structure of the nitrogen doped graphene obtained by hydrothermal treatment of graphitic oxide. The SEM micrograph in Figure1a

shows an exfoliated and wrinkled nanoplatelet texture characteristic of graphene. Figure 1b confirms the structure of graphene by showing the (002) peak at about 24^{o} for both graphene and nitrogen doped graphene. Figure 1C of the Raman spectra shows the typical D, G and 2D band of both graphene and NG. The D band peak as well as the very weak 2D band is a typical characteristic of the chemically synthesized graphene (34-36). The G band is attributed to the first order scattering of the stretching vibration mode E_{2g} observed for sp_2 carbon domain. The D band is strongly associated with the disorder degree of graphene (37). A quantitative measure to estimate the degree of disorder in graphene is the ratio of the intensities between the D and G bands i.e. I_D/I_G (35, 36). As seen from Figure 1C the NG has higher ratio of I_D/I_G than the pristine graphene which is 1.34 to 1.29, respectively. This implies that the doped graphene is more disordered, or has more defects, than the pristine graphene. The percentage of doped nitrogen was estimated by XPS analysis to be 2.8%. Figure 1d shows the full XPS spectrum of the NG as well as high resolution, in the onset, showing the detailed configuration of the several types of nitrogen. The result is summarized in Table 1 which reveals the presence of nitrogen as well as oxygen and carbon. The high resolution XPS shows that nitrogen bonds to the graphene matrix in four different ways including pyridinic, pyrrolic, quaternary and pyrolidone, which are centered at 398.9, 400.3, 401.8 and 405.0 eV(38-40), respectively. The relative percentages of both pyrrolic and quaternary nitrogen are the highest.

Table 1: Summary of the result of the XPS for N-graphene

	Relative %			
Overall Nitrogen	Pyridinic	Pyrrolic	Quaternary	Pyrolidone
2.77	7.48	40.27	40.46	11.79

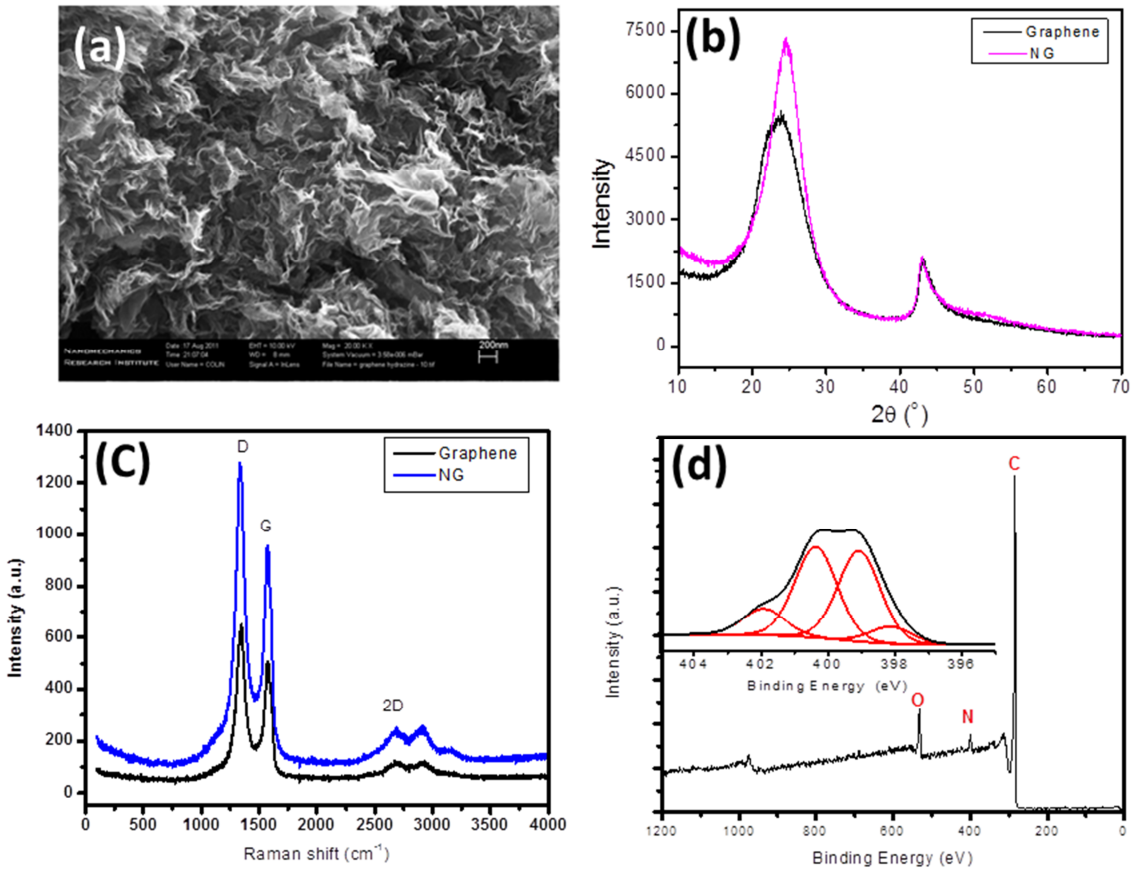

Figure 1. Elucidation of the morphology and structure of N-graphene, (a) SEM micrograph of NG prepared at 180°C, (b) XRD comparing both graphene and NG, (c) Raman spectroscopy, and (d) XPS spectroscopy.

Electrochemical measurements.

Figure 2 shows the cyclic voltammetry curves for graphene and NG with various scan rates in 1 M KCl. The CV curves for pristine graphene are virtually rectangular showing that an approach to ideal and reversible capacitive behavior is almost achieved (41). The CVs for NG deviate slightly from rectangular shape indicating little contribution from faradic pseudocapacitance. The specific capacitances of the electrode materials were determined based on the CVs according to the following equation:

$$C_s = \frac{\int idV}{2\ x\ m\ x\ \Delta V\ x\ S} \qquad (1)$$

where C is the specific capacitance in farads per gram, $\int idV$ is the integrated area under the CV curve, m is the mass of the electrode active materials in grams, ΔV is the scanned potential window in volts, and S is the scan rate in volts per seconds. The results of these calculations are listed in Table 2. The results show that by introducing nitrogen functionalities to graphene it clearly increases the capacitive behavior. The reason may be

attributed to the high electronegativity of nitrogen help creating dipoles on the surface of graphene which results in higher tendency to attract charged species to the surface.

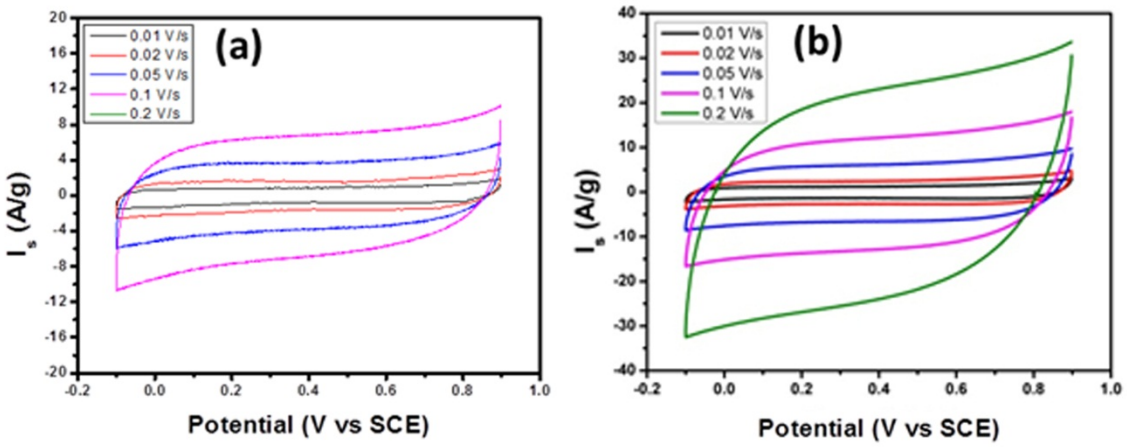

Figure 2. The cyclic voltammetric i-V curves for (a) graphene and (b) NG electrodes with different scan rates measured in 1 M KCl.

Table 2. Comparison of the specific capacitance of graphene and N-graphene

Scan Rate (V/s)	CV Specific Capacitance (F/g)	
	Graphene	N-Graphene
0.01	90.93	131.17
0.02	84.53	125.41
0.05	80.72	116.88
0.10	69.32	109.49
0.20	65.91	98.40

Figure 3 shows the galvanostatic charge discharge behavior of graphene and NG. The nearly ideal behavior as an EDLC (Electrical Double Layer Capacitor) is visibly seen throughout the highly linear charge/discharge slopes as well as the symmetry observed for the curves. The highest average specific capacitance of 99 F/g was observed at 0.5 A/g. The capacitance was calculated from the slopes of the discharge curves following the equation $\boldsymbol{C_s = I_s/(\Delta V|\Delta t)}$.

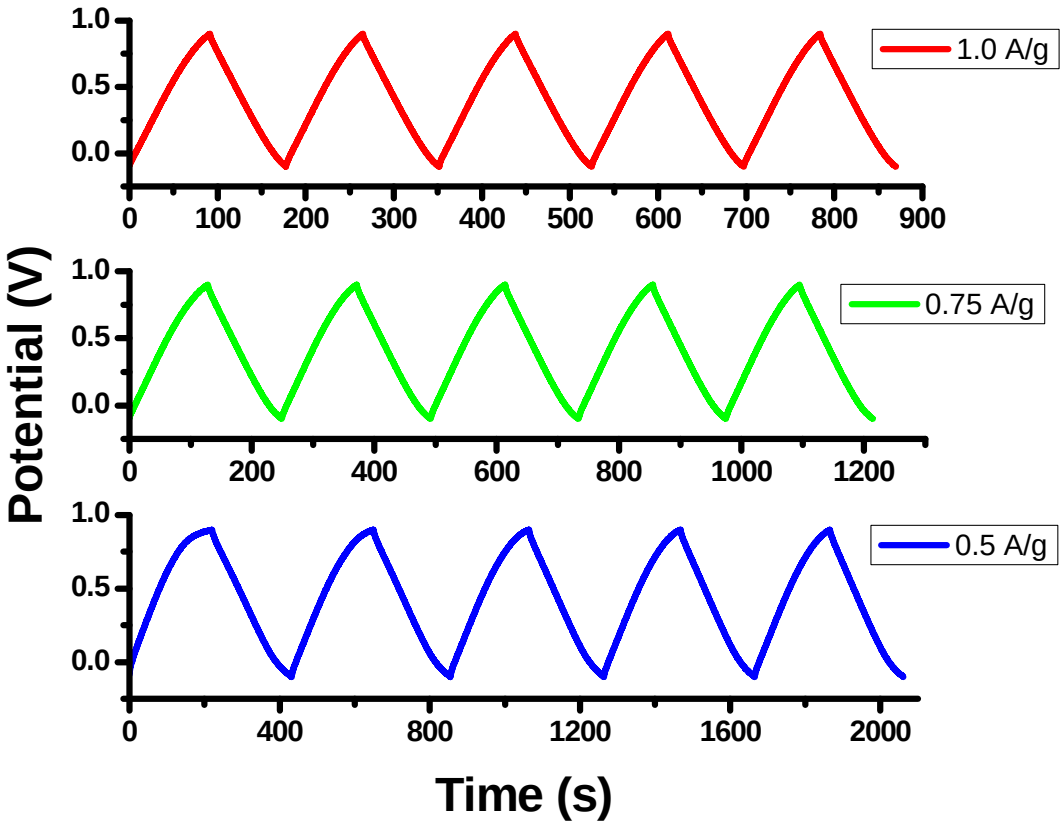

Figure 3. Galvanostatic Charge/Discharge curves for NG measured at different current.

For supercapacitors, energy and power densities for an equivalent two electrode cell are two important parameters. The energy densities of the equivalent cell was calculated using the following equation (42):

$$\boldsymbol{E} = \frac{(\boldsymbol{C_s}/4)\ \boldsymbol{x}\ (\Delta \boldsymbol{V})^2}{7.2} \qquad (2)$$

where $\boldsymbol{C_s}$ is the materials specific capacitance in farads per gram, $\Delta \boldsymbol{V}$ is the potential window for CV measurements in volts, and $\boldsymbol{E}$ is the energy density in W.h/kg. Utilizing the data from the cyclic voltammetry measurements, the energy densities (measured at a scan rate of 0.01 V/s) are 4.55 and 3.16 W.h/kg for the N-graphene and graphene, respectively. The corresponding highest average power densities of an equivalent two electrode cell was calculated from the discharge time *t*, from CV at 0.2 V/s, using the following equation (43):

$$\boldsymbol{P} = \frac{\boldsymbol{E}}{\boldsymbol{t}} \qquad (3)$$

The equivalent two electrode cell values for average power density were found to be 2.46 and 0.87 kW/kg for NG and graphene respectively.

Conclusion

Graphene and nitrogen doped graphene have been synthesized by hydrothermal technique from graphitic oxide. The morphology of the NG was confirmed by SEM and the structure was elucidated by XRD and Raman spectroscopy. XPS confirmed the percentage of doping to reach up to 2.77%. From the cyclic voltammetry measurements it was found that doping with nitrogen increased the supercapacitance of graphene by 45% to 131 F/g. Furthermore, a two electrode cell fabricated from N-graphene could be able to provide energy density as high as 4.55 Wh/kg and an average power density of 2.46 kW/kg.

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