Thermochemistry of Nitrogen Doped Reduced Graphene Oxides

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Abstract

The thermodynamic stability of a series of nitrogen - doped reduced graphene oxidesprepared by ammonolysis of graphene oxidehas been investigated by high temperature oxidation calorimetry. In terms of enthalpy and depending on the concentration of nitrogen, the nitrogen-doped reduced graphene oxides can be up to 73 $kJ \cdot mol^{-1}$ more stable than graphite plus nitrogen. There is a linear relationship between the nitrogen content and the formation enthalpy, which indicates a decrease in stability with increasing nitrogen content.

Keywords: N-doped graphene oxide, calorimetry, stability

1. Introduction

Among the various nanoscale allotropes of carbon, graphene has captured the imagination of scientists worldwide since thereport in 2004 by Geim and coworkers[1].The enormous interest in graphene stems from its unique and extraordinary physical and chemical properties including large surface area[2], high thermal and electrical conductivity[3], mechanical strength, transparency and structural flexibility[4].The versatility of the material, whose structure is readily modified by a variety of approaches, has paved the way toward the preparation of derivatives with improved performance that can potentially translate into next generation applications in wide ranging fields such as energy conversion and storage[5, 6], catalysis[7, 8] electronics[2, 9] and composite materials [10, 11].Embedding graphene within ceramic matrices is a promising approach for the large scale production of materials with enhanced mechanical properties[12].For instance, Simsek*et al.* reported improvements in the electrical conductivity andfast heat release of aluminum nitride, a dielectric material with potential applications such as microelectromechanical systems (MEMs) or light emitting diodes (LEDs), after using graphene nanoplatelets as filler[13]. In a more recent study, the authorstook advantage of the properties of both the filler and the ceramic structure to obtain YSZ-graphene composites with mixed-ionic and electronic conduction and enhanced stability [14].

Graphene oxide (GO)is a chemically functionalized variant of graphene containing oxygen in the form of hydroxyl and epoxide groups in the defect free regions and carboxyl, carbonyl, and phenol groups on the sheet edges[15].It is typically prepared by oxidation of graphite into graphitic oxide and subsequent exfoliation of the layered structure[15].Due to difficulties in the large scale production and processing of single layer graphene, itsoxidized form is considered a promising alternative. The functional groups on the surface of GO makes it

water dispersible[16]and attractive for catalytic[17]and biomedical applications[18]. GO properties can be modified by controlling morphology and size[19]. In addition,the reactivefunctional groups on the GO surface can be employed for the covalent attachment of selected (bio)molecules [20]and inorganic nanoparticles[21]or for chemical doping[22]. Chemical doping is an effective method to tune electronic, magnetic and thermal properties, thus broadening the range of applications[23, 24].

Substitutional replacement by heteroatoms such as nitrogen and boron is a popular chemical doping method for GO[25, 26].Nitrogen doping has attracted special interest due to the potential application of the resulting materials in a variety of fields including electrocatalysis[27, 28], energy storage and harvesting[29-31], and flame retardant additives[32-35].A wide range of methods have been developed to achieve varying nitrogen concentrations[36-38].The high temperature reaction of GO with NH_3gas can achieve doping levels as high as 13 wt. %[39-41].The oxygen content in GO and the reaction temperature playkey roles in the final nitrogen content.The presence of oxygen facilitates functionalization by other chemical groups, thus favoring the formation of C-N bonds[42].Different bonding environments for nitrogen have been identified in the graphene structure, the most commonly reported beingpyridinic, pyrrolicand graphitic groups[36].Their relative abundance is determinedby the synthetic method and the reaction parameters.GO processed under such reducing conditions has lower oxygen content and is called reduced graphene oxide (rGO)[43]. The reduction of oxygen content in rGO partially restores graphene-like properties[44].The electronic and structural changes caused by doping confer new interesting attributes[44].N-containing groupsallow tuning the band gap of the conjugated lattice[45] andenhance the thermal oxidation stability of reduced graphene oxide in air[39].

GO was first synthesized in 1859[46] and, despite extensive development of synthetic methods and study of properties in subsequent decades, the thermochemistry and stability of GO and its derivativesrelative to other forms of carbon are relatively unexplored. We have successfully investigated the thermodynamic stability of nanodiamonds[47] and carbon onions using high temperature direct oxidation calorimetry [48].Suslova*et al.*have determined the formation and combustion enthalpy of several N-containing carbon allotropes by bomb calorimetry[49]. In the present work, we have carried out high temperature oxidation calorimetry of a series of nitrogen doped rGO samples with varying contents of nitrogen (7.1 to 11.4 at. %) and report their formation enthalpies at room temperature. We conclude that, although nitrogen stabilizes the rGO phase energetically, such stabilization decreases with increasing nitrogen doping.

2. Materials and Methods

2.1. Synthesis of graphene oxide

Graphene oxide was prepared via a modified Hummer's method[41]. Briefly, 5 g of graphite powder (< 20 μm, Sigma-Aldrich) were treated with a mixture of concentrated H_2SO_4 (115 mL) and $NaNO_3$ (2.5 g). This reaction mixture was cooled to 0 ºC and left for 30 min. Next, $KMnO_4$ (15 g) was added slowly. After stirring for 30 min at about 35 ºC, distilled water (230 mL) was slowly added maintaining the reaction temperature at 98 °C for 2 h. Finally, additional water (1 L) and 30% H_2O_2(5 mL) were added and the reaction mixture was cooled down. The resulting material was purified by subsequent centrifugation and washing with distilled water until the pH of the solution was neutral.

2.2. Preparation of nitrogen doped reduced graphene oxide(N-doped rGO)

N-doped rGO was prepared following a previously reported protocol[41].100 mg of graphene oxide were spread in an alumina boat. The alumina boat containing the GO was then placed in the center ofa silica tube inside a horizontal furnace. The whole system was purged under nitrogen for 1 h to remove air from the system before introducing ammonia gas (CarburosMetálicos 99.99%) at a flow rate of 300 $mL \cdot min^{-1}$. Samples were heated for 1 h at temperatures between 500 and 800 ºC,to obtain simultaneous reduction and doping of graphene oxide.

*2.3.*Morphology of *N-doped rGO samples*

The morphology of N-doped rGO samples was determined by means of microscopic analyses. TEM and SAED patterns were obtained using a JEOL 1210 microscope, operating at 120 kV. HRTEM images were acquired using a FEI, Tecnai microscope operating at 200 kV. Samples were prepared by dispersing a small amount of powder in hexane using bath sonication. Afterwards, the dispersions were placed dropwise ontoa lacey carbon support grid.

2.4.Elemental composition of the samples

Elemental analyses (EA) wereperformed on a Thermo Scientific™ FLASH 2000 Series CHNS Analyzer using a Mettler Toledo MX5 microbalance.The atomiccomposition of the samples (C, N, O) and the distribution of oxygen and nitrogen in different bonding environments were obtained by X-ray photoelectron spectroscopy(XPS),usinga Kratos AXIS ultra DLD spectrometer with Al Kα radiation. All samples were introduced in the preparation chamber as received and placed on a copper substrate for analysis. A general survey scan performed on the samples confirmed the presence of C, N, and O as the only constituent elements. High resolution

spectra over the C 1s, O 1s and N 1s regions were registered and employed to determine the elemental composition of each of the samples.

2.5.High temperature oxidation calorimetry

The oxidation enthalpy of the samples was determined by high temperature oxidation calorimetry using an AlexSYSSetaramisoperibol Tian-Calvet twin microcalorimeter.Approximately 1 mg pellets were made using a pellet press, weighed on a microbalance and dropped from room temperature(25 °C) into a silica glass crucible containing a small piece of silica wool at its bottom in the calorimetermaintained at 800 °C. The samples were rapidly oxidized to CO_2 gas at thecalorimeter temperature by the reaction: C(s,25 °C) + O_2(g,800 °C) → CO_2(g,800 °C). Air was flushed through the area close tothe silica wool at 40 mL·min^{-1} and through the calorimeterassembly at 50 mL·min^{-1} to ensure complete oxidation of samplesto CO_2.Oxygen atmosphere caused the samples to flare during the drop and so air atmosphere was chosen for these experiments to ensure that oxidation of the samples occurs only in the calorimeter chamber. Measurementswere repeated8-12times to obtain statisticallyreliable enthalpy values. The calorimeter was calibrated againstthe heat content of platinum pieces. The procedure followed here is similar tothat established previously in the work on nanodiamonds and onion-like carbons by Costa *et al.*[47, 48].

3. Results and discussion

Four samples were prepared following a previously reported methodology using GO and NH_3 gas at different temperatures (500 °C, 600 °C, 700 °C and 800 °C)[41]. In agreement with previous observations[41], electron microscopy analyses of the prepared samples reveal the presence few-layered N-doped rGO. The wrinkled morphology of N-doped rGO is clearly visible in the TEM image of Figure 1a. The intensity profile along the diffraction spots of the

corresponding selected electron diffraction (SAED) pattern (Figure 1b)indicates the presence of a single layered specimen (the inner spots show about twice the intensity of the outer spots)[50].The elongated appearance of the spots might arise from lack of crystallinity due to structural defects.A HRTEM image of the sample prepared at 500 ºC is included in Figure 1c. The line profile across the edge of the flake indicates the presence of four layers with the expected separation of *ca.* 0.34 nm. Additional analyses are include in Figure S1 confirming that the prepared samples consists of few-layered N-doped rGO.

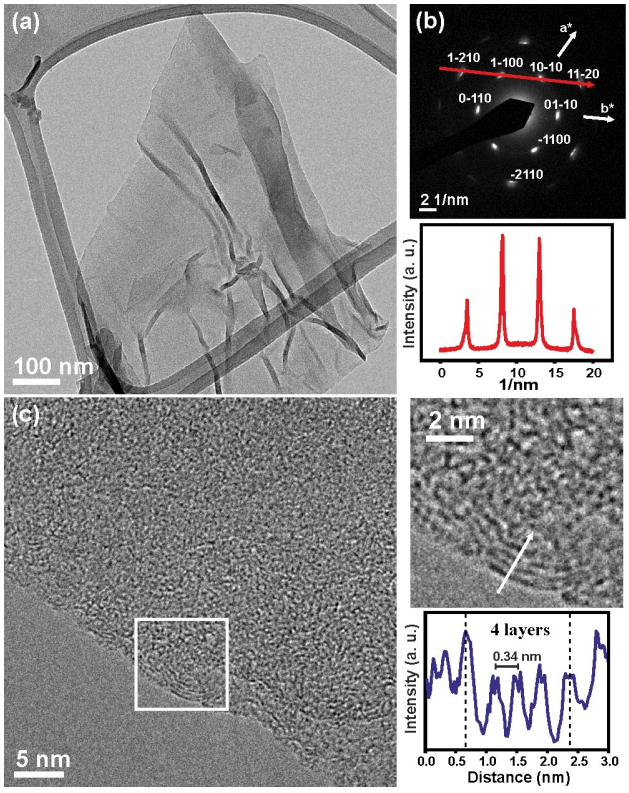

Figure 1. (a) Transmission electron microscopy image and (b) SAED pattern anddiffracted intensity profile taken along the 1–210 to 11–20 axis for a sample of N-doped rGO prepared at 700 °C. (c) HRTEM of N-doped rGOprepared at 500 °C; an image magnification of the area marked with a white square is included on the right panel along with theintensity profile across the edge.

The reduced graphene oxide samples doped with varying amounts of nitrogen were analyzed by calorimetry. The measured (800 °C) and calculated (25 °C) oxidation enthalpies of the resulting N- doped rGO samples along with their formation enthalpies from elements (25 °C) are listed in Table 1. The table also includes oxidation and formation enthalpies calculated with respect to the carbon content of each sample(atomic composition, at. %), as determined by X-ray photoelectron spectroscopy (XPS). The calculations are based on the thermodynamic cycle in Table 2.XPS has been widely employed to determine the atomic composition of N-containing graphene derivatives.[40, 51-53] Nevertheless, in order to confirm the composition of the synthesized samples, elemental analysis (wt. %) was also performed (Table S1).

Table 1. Atomic composition, measured oxidation enthalpies and calculated room temperature oxidation and formation enthalpies of nitrogen-doped rGO samples.

Sample #	Atomic Composition			ΔH_{ox}, 800 °C (kJ·mol^{-1})	ΔH_{ox}, 25 °C (kJ·mol^{-1})	ΔH_{ox}, 25 °C (kJ·g^{-1}·C-atom^{-1})	ΔH_f, 25 °C (kJ·mol^{-1})	ΔH_f, 25 °C (kJ·g^{-1}·C-atom^{-1})
	C	N	O					
1	90.6	7.1	2.3	-312.07±0.88	-324.42±1.07	-358.08±1.18	-38.40±0.93	-42.38±1.03
2	89.1	9.0	1.9	-314.33±2.25	-326.63±2.44	-366.59±2.74	-28.72±2.30	-32.23±2.58
3	87.5	10.4	2.1	-315.09±1.27	-327.27±1.46	-374.02±1.67	-17.85±1.31	-20.40±1.50
4	85.5	11.4	3.1	-310.38±2.18	-322.54±2.36	-377.24±2.76	-13.92±2.22	-16.28±2.60

Table 2. Thermodynamic cycle used to calculate the room temperature oxidation enthalpy and formation enthalpy for the nitrogen-doped rGO samples.

(1) $C_xN_yO_{z\,(s,25°C)} + (x\text{-}z/2)\ O_{2\,(g,800°C)} \rightarrow x\ CO_{2\,(g,800°C)} + y/2\ N_{2\,(g,800°C)}$	ΔH1 (Expt.)
(2) $O_{2(g,800°C)} \rightarrow O_{2(g,25°C)}$	ΔH2 = 25.26±0.10 kJ·mol^{-1}
(3) $CO_{2(g,800°C)} \rightarrow CO_{2(g,25°C)}$	ΔH3 = 37.41±0.10 kJ·mol^{-1}
(4) $N_{2(g,800°C)} \rightarrow N_{2(g,25°C)}$	ΔH4 = 24.20±0.24 kJ·mol^{-1}
(5) $C_{\,(graphite,25°C)} + O_{2(g,25°C)} \rightarrow CO_{2(g,25°C)}$	ΔH5 = -393.52±0.05 kJ·mol^{-1}
(6) $C_xN_yO_{z\,(s,25°C)} + (x\text{-}z/2)\ O_{2\,(g,25°C)} \rightarrow x\ CO_{2\,(g,25°C)} + y/2\ N_{2\,(g,25°C)}$	

$$\Delta H_{(ox,25°C)} = \Delta H1 + (x\text{-}z/2)\,\Delta H2 - \Delta H3 - (y/2)\,\Delta H4$$

(7) $xC_{(graphite,25°C)} + (y/2)N_{2\ (g,25°C)} + (z/2)O_{2\ (g,25°C)} \rightarrow C_xN_yO_{z(s,25°C)}$

$$\Delta H_{(f,25°C)} = x\,\Delta H5 - \Delta H_{(ox,25°C)}$$

While all N-doped rGOsamples exhibit highly exothermic oxidation enthalpies (in the range of -327to -322 kJ·mol^{-1}),these values are significantly lower in magnitude than the corresponding oxidation enthalpy for graphite(-393.5 kJ·mol^{-1}). For comparison, the oxidation enthalpies of major carbon allotropes are given in Table 3. Thus, N-doped rGOappearsto be more stable in enthalpy than graphite by 65-73 kJ·mol^{-1}.Unlike graphite, purely formed by C atoms,N-doped rGO samples containpartially oxidized surfaces, as in the case of the carboxylic functionalized nanodiamonds, as well as nitrogen in their structure. Therefore, less heat is released on their complete combustion to CO_2 and N_2(Table 2), compared to pure carbon allotropes. In fact, since the measured enthalpy refers to a material containing C, N, and O and not to pure carbon, strictly speaking, N-doped rGOs are not allotropes of carbon but different phases in a multicomponent system.

Table 3. Room temperature oxidation enthalpies and enthalpies relative to graphite (plus O_2 and N_2 as appropriate)of various carbon forms.

Allotrope		**$\Delta H_{ox,800°C}$(kJ·mol^{-1})**	**$\Delta H_{ox,25°C}$ (kJ·mol^{-1})**	**$\Delta H_{t,25°C}$(kJ·mol^{-1})**
Graphite			-393.52±0.05	0.0
Diamond			-395.42±0.50	1.9±0.50
Fullerene, C_{60}			-432.76±0.19	39.24±0.20
Nanodiamond(COOH)	4.5±0.4 nm	-329.25±0.67	-344.08±2.03	-49.44±2.03
	80.3±5.5 nm	-365.97±0.84	-379.45±1.82	-14.07±1.82
Carbon onion	UD90, 1800 °C	-396.04±0.67	-408.14±0.68	14.62±0.68
	UD50, 1300 °C	-382.67±0.78	-394.77±0.78	1.25±0.78
N-doped rGO	7.1% N	-312.07±0.88	-324.42±1.07	-69.10±1.07
	9.0% N	-314.33±2.25	-326.63±2.44	-66.89±2.44
	10.4% N	-315.09±1.27	-327.27±1.46	-66.25±1.46
	11.4% N	-310.38±2.18	-322.54±2.36	-70.98±2.36

To evaluate the effect of nitrogen on thermodynamic stability, care has been taken during the synthesis to ensure that the oxygen content (1.9-3.1 at. %) does not vary significantlybetween the four N-doped rGO samples. To identify trends in the relation between sample composition and heat effects, the calculated room temperature oxidation enthalpies in kJ·mol^{-1} and kJ·g^{-1}·C-atom^{-1}areplotted against the carbon content of the samples (Figure 2). While a clear trend cannot be established in theoxidation enthalpy(kJ·mol^{-1})*vs.* carbon content plot (Figure 2-(a)), the enthalpies calculated per gram atom of carbon (kJ·g^{-1}·C-atom^{-1}) indicate more favorable thermodynamic stability with increasing carbon content (Figure 2(b)). The stability decreases linearly at first with decreasing carbon content andthenevolves to a more gradual change,reaching the least stable value for the sample with 85.5 at. % C (11.4 at. % N). When the same data set is plottedagainst the nitrogen content of the samples (Figure 2), the plotsreveal similartrends. Although the enthalpies in kJ·mol^{-1}again show scatter (Figure 2(a)), the sample prepared at 500 ºC (11.4 at. % N) shows a higher energetic stability than the sample prepared at 800 ºC (7.1 at. % N) in agreement with the report of Sandoval *et al.*[39]. When the data are represented in kJ·g^{-1}·C-atom^{-1}a clear trend is observed (Figure 2(b)).

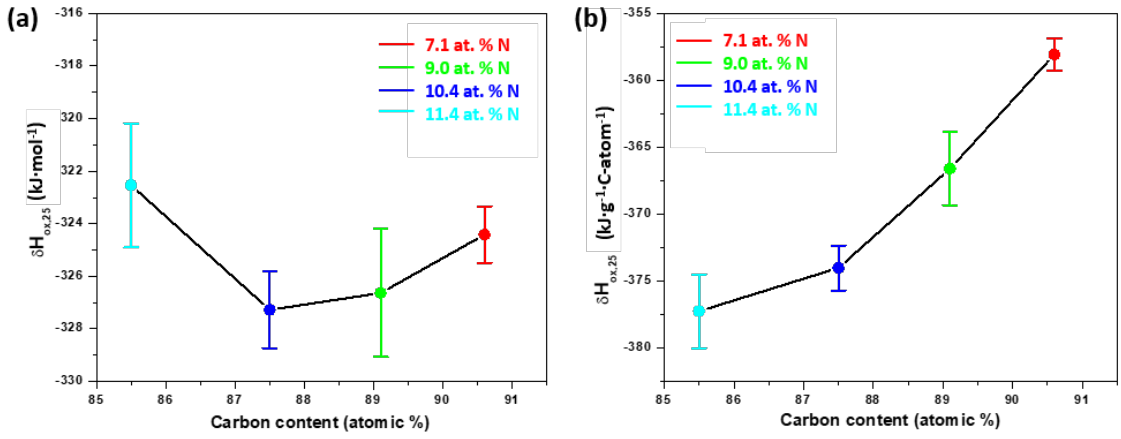

Figure 2. Room temperature oxidation enthalpies of N-rGO samples in (a) kJ·mol^{-1}and in (b) kJ·g^{-1}·C-atom^{-1}plotted against carbon content (atomic percent).

A linear relationship is seen between the nitrogen content and calculated enthalpies of oxidation, which become more exothermic with increasing nitrogen content, indicating diminishing energetic stability, as it can be observed in **Figure 3 (b).**

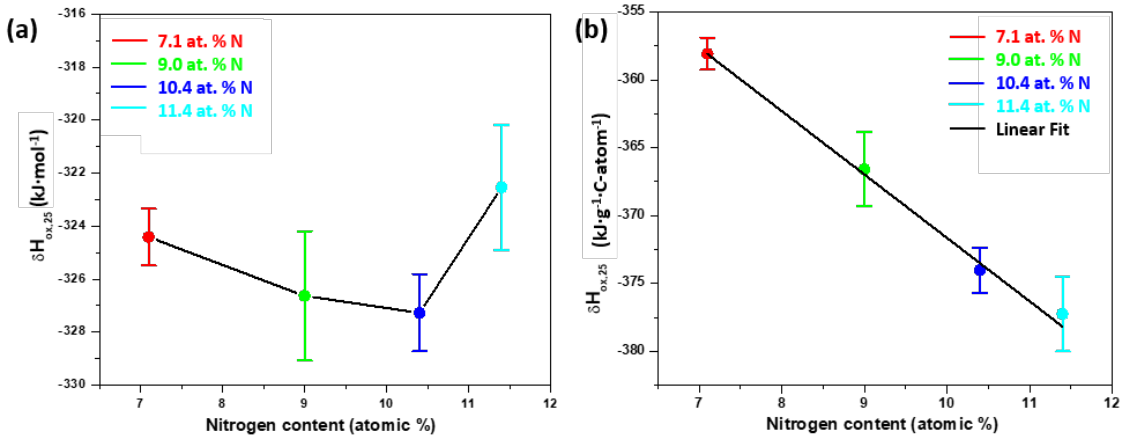

Figure 3. Room temperature oxidation enthalpies of N-rGO samples in (a) $kJ \cdot mol^{-1}$and in (b) $kJ \cdot g^{-1} \cdot C\text{-}atom^{-1}$plotted against atomic percent of nitrogen.

The formation enthalpies of these samples were calculated using equation 7 and are givenin Table 1. They are exothermic ranging between -12 and -39 $kJ \cdot mol^{-1}$and become more negative with increasing carbon content. The values become slightly more exothermic when calculated with respect to gram atom carbon (Figure 4). Both plots reveal similar trends confirming more favorable energetic stability with increasing carbon content.

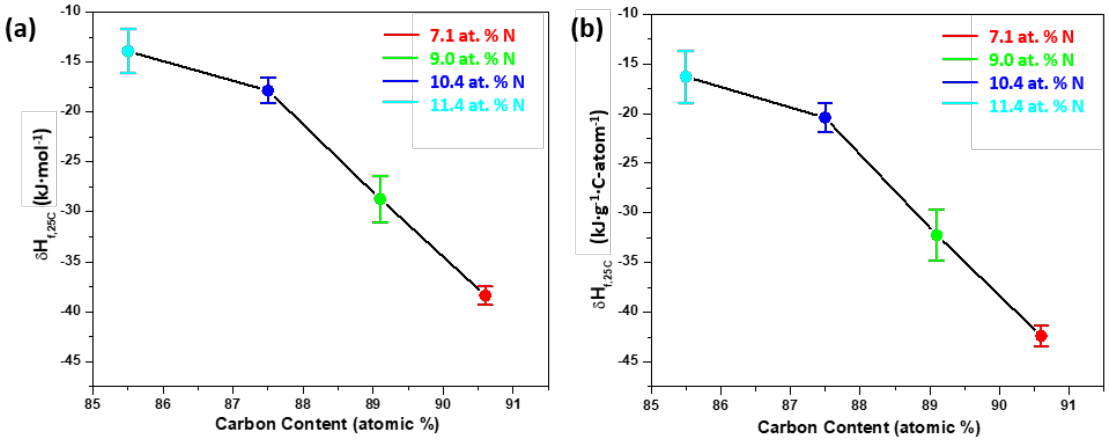

Figure 4. Formation enthalpies of N-rGO samples plotted against atomic percent of carbon in (a) kJ·mol^{-1}and (b)kJ·g^{-1}·C-atom^{-1}.

The formation enthalpies show a linear trend with nitrogen content (Figure 5), showing that the substitution of nitrogen is energetically destabilizing. This study clearly indicates that formation of a nitrogen-free sample with oxygen is more thermodynamically favorable than nitrogen incorporation.

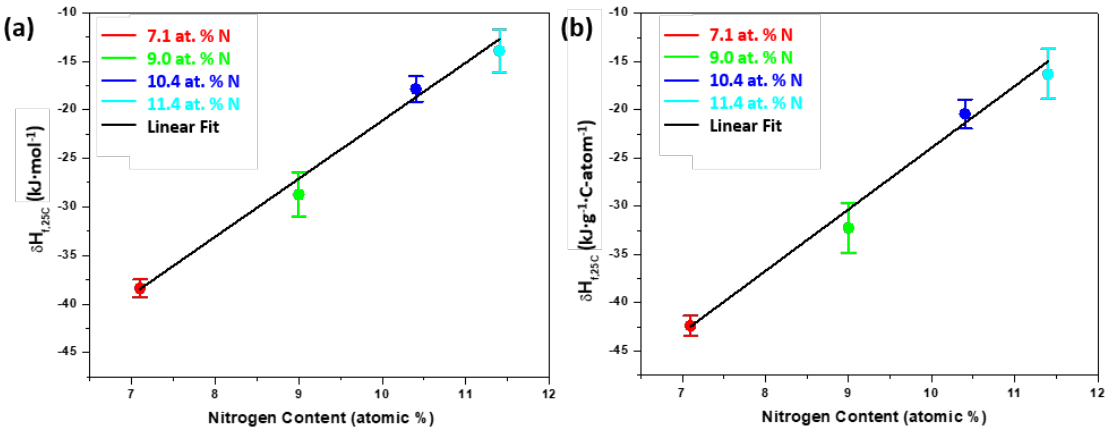

Figure 5. Formation enthalpies of N-rGO samples plotted against atomic percent of nitrogen in (a) kJ·mol^{-1}and (b) kJ·g^{-1}·C-atom^{-1}.

Sandoval *et al.* considered a simplified model of a graphene fragment and its variants containing each type of nitrogen (pyrrolic, pyridinic and graphitic N) and calculated the

combustion enthalpies of the fragments using mean bond enthalpies [39]. The calculated Gibbs energy (ΔG) associated with each of those reactions showed that the reaction of the undoped fragment would be more spontaneous. The calculations were performed for 500 ºC since this was the average onset combustion temperature of the analyzed samples as determined by thermogravimetric analysis. They suggested that variations in thermal stability (onset of oxidation reactions) were related to their calculated trends in thermodynamic stability. Because thermal stability reflects both thermodynamic and kinetic factors we consider these arguments to qualitatively support energetic stabilization by nitrogen substitution.

Table 4. N, C and O content in N-rGO samples determined by X-ray photoelectron spectroscopy

Sample	**Nitrogen (at. %)**			**Oxygen (at. %)**			**Carbon (at. %)**
	PyridinicN	**PyrrolicN**	**GraphiticN**	**O=C-O**	**O=C**	**O-C**	
	4.8	4.2	2.4	1.1	0.9	1.1	
11.4 % N	11.4			3.1			85.5
	4.1	3.7	2.6	0.7	0.7	0.7	
10.4 % N	10.4			2.1			87.50
	3.2	3.2	2.6	0.5	0.6	0.8	
9.0 % N	9.0			1.9			89.1
	2.8	2.3	2.0	0.6	0.8	0.9	
7.1 % N	7.1			2.3			90.6

A wide range of methods have been published for doping nitrogen into graphene and relatedstructures. The distribution of nitrogen environments in the structure has been observed to vary with different preparation methods[36]. In this work, rGO samples have been prepared by post treatment of graphene oxides with ammonia at high temperatures (500-800 °C). This method typically results in samples rich in pyridinic and pyrrolicnitrogen due to the ease of incorporation of nitrogen at the edges. A higher annealing temperature is required to promote the formation of graphitic nitrogen(for high resolution N1s and O1s XPS spectra see Figure S2 and Figure S3, respectively)[36].In the samples investigated here, the distribution of the nitrogen

atoms in the three different bonding configurations does not vary significantly at different nitrogen concentrations (Table 4). Therefore,it is not possible to deconvolutethe effect of different nitrogen centers on the resulting trends in thermodynamic properties.

4. Conclusions

We have experimentally determined the oxidation enthalpies of a series of N-doped rGO samples with N contents ranged between 7.1 and 11.7 at. % by high temperature (800°C) oxidation calorimetry studies. Our results confirm that the nitrogen doped reduced graphene oxide samples are significantly more stable in enthalpy than pure graphite and diamond. This reflects the incorporation of both oxygen and nitrogen and their resulting multicomponent nature. Formation enthalpies ($\Delta H_{f,25°C}$) indicate more favorable energetics of materials with highercarboncontents.As a consequence, the formation of a nitrogen-free sample (or one with low N content) ismore favored thermodynamically. A linear decrease in the energetic stability with increasing nitrogen content is observed within the studied range.Thus oxygen stabilizes the rGO phases while nitrogen destabilizes them.Thus,thermodynamic stabilization by nitrogen doping is not seen and therefore cannot be responsible for the enhanced thermal stability previously reported inN-doped rGO.samples, and kinetic factors must be considered. The present study contributes toward understanding the properties of emerging heteroatom-enriched graphene derivatives.

Acknowledgments

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Appendix A. Supplementary data

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