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Influence of External Heating Rate on the Structure and Porosity of Thermally Exfoliated Graphite Oxide

Yang Qiu, Samuel Moore, Robert Hurt, and Indrek Külaots¹

School of Engineering, Brown University, 182 Hope St., Providence, RI, USA, 02912

Abstract

Fast external heating rates in graphite oxide thermal exfoliation have been reported to be advantageous for generating high surface area graphene-based materials for a variety of applications. The study yields the surprising result that the surface area and porosity developed in reduced graphite oxide under some conditions are independent of instrument-set external heating rates. The true “total” heating rate experienced by the sample is shown to be the sum of the external rate and the local self-heating rate associated with the exothermicity of graphite oxide exfoliation, and under many conditions, the local self-heating contribution dominates. In these instances, increasing external heating rate does not increase the total rate, improve exfoliation degree or enhance surface area. These results are important for optimizing the conditions for fabrication of reduced graphene oxide with tailored properties.

Graphical abstract

1. Introduction

Porous graphene-based materials with high surface areas have great potential for a variety of applications in the fields of energy storage, catalysis, separation and biomedicine [1–6].

¹Corresponding author. Tel: 401 863-2674. Indrek_Kulaots@brown.edu (Indrek Külaots).

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Thermal reduction or disproportionation of graphite oxide (GO) is one of the most common ways to produce large-scale, porous, graphene-based materials, due to its ease of scale-up and avoidance of externally introduced heteroatom impurities [7–9]. The process is based on energetic thermal exfoliation of the lamellar structure of GO upon heating, which was first reported by the British chemist Brodie in 1859 [10]. Since then, the energetic behavior of GO has been observed by many other studies [9–12]. GO's energetic behavior during thermal exfoliation has also been described in numerous articles published during the 20th century that predate the era of intensive graphene research beginning in 2004 [9, 13–19]. Due to GOs unique chemical nature (low C/O ratio, abundant epoxide functionalities) explosive thermal exfoliation is initiated when the rates of heat and product gases generated exceeds the rates of heat and gas removed from the sample [8, 9, 20–25]. Today, explosive thermal exfoliation has been widely used by many research laboratories and industry manufacturers to generate porous exfoliated graphene-based materials for a variety of applications [7, 26–33]. In general, high temperature and/or vacuum are found to be beneficial to overcome the van der Waals forces between individual sheets in GO and promote explosive exfoliation, which in turn has supported the generation of porous structures in the reduced graphite oxide (rGO) product [8, 20, 31, 34–40]. Many factors can affect thermal exfoliation of GO and influence the morphology and surface area of the product rGO. For instance, various GO synthesis methods (Hummers, Staudenmaier, Hofmann, Tour or Brodie methods) lead to a GO products with varying C/O ratios and oxygen functionalities on graphene basal plane and edge sites and, therefore, to dissimilar thermal exfoliation reaction onset temperatures and product rGO surface areas [22, 23, 41]. Another key factor that affects the rGO product surface area is the externally imposed heating rate during GO thermal exfoliation [20, 31]. McAllister et al. proposed that fast heating to temperatures above 550°C at ambient pressure yields high rGO surface areas and few-layered solid products, which is achieved through the fast insertion of GO sample into a pre-heated tube furnace. Since then, the process of fast insertion of the GO sample into a pre-heated furnace has been adopted by many other research groups [20, 34–36]. More recently, Yang et al performed a study on the relationship between the thermal reduction parameters - including high vacuum, target decomposition temperature and instrument imposed external heating rate effects (up to 50 K/min) - on the product rGO surface area [24]. Generally, it is accepted that for the explosive mode thermal exfoliation to take place, the local GO sample heating rate must reach to a threshold heating rate for the particular GO investigated (Brodie, Hummers, Staudenmaier), at which point the violent GO disintegration takes place [21, 24, 28, 42, 43]. However, it remains unclear whether the rGO surface area could be further increased or what behavior is expected at high - or even very high - external heating rates (>100 K/min). Herein, we systematically explore low (here defined as <100 K/min) and high external heating rate (up to 1600 K/min) influence the rGO product surface area and morphology during Hummers GO thermal exfoliation.

2. Experimental

2.1. Materials

Graphite oxide (GO) was prepared by applying a modified Hummers method [21, 44]. The GO preparation process utilizes high purity graphite powder (SP-1 from Bay Carbon), which

is pre-oxidized with $K_2S_2O_8$ and P_2O_5 in concentrated H_2SO_4 and further oxidized with $KMnO_4$ in concentrated H_2SO_4 while continuously stirred. After the severe oxidation process, vigorous two-step washing with HCl and acetone is applied. The product GO is then dried under ambient condition in a dark environment. Raw GO product was stored as bulk solid, or so-called GO “cake”.

2.2. GO thermal exfoliation

GO thermal exfoliation studies at low and medium heating rates (<100 K/min) were performed in standard mode with the differential scanning calorimeter (DSC) and thermogravimetric apparatus (TGA), both manufactured by TA Instruments. The TGA was customized to allow exploring high external heating rates (100 to 1590 K/min) by moving the sample compartment into the pre-heated (500°C to 900°C) TGA furnace, while recording the sample temperature on a video clip with a camera. A plot of the sample temperature vs. time was then constructed, and the average slope, as an indication of heating rate, determined. Multiple test runs were performed to assure reproducibility of obtained external heating rates. The physical dimensions of the GO cake samples were kept approximately constant since they affect mass and heat transfer behaviors that in turn affect local sample heating [25].

2.3. GO characterization

GO and rGO chemical structures were studied with X-ray photoelectron spectroscopy (XPS) and JASCO FT/IR-4100 Fourier Transform Infrared Spectroscopy (FTIR) with the ATR accessory. Quantachrome Instruments Autosorb-1 instrument was applied to obtain N_2 isotherms at 77 K and CO_2 isotherms at 273 K, from which the surface areas based on the Brunauer–Emmett–Teller (BET) theory and pore size distributions (PSDs) based on the non-local density functional theory (NLDFT) slit pore model [45] were obtained. The morphologies and surface feature of GO and rGO samples were characterized with a LEO 1530 field emission scanning electron microscope (SEM).

3. Results and discussion

XPS analysis of our Hummers GO provided a C/O atomic ratio of 2.1. The ratio is normally calculated from the total content of C1s and O1s peaks. The potential GO impurities - such as S, Mn, K, Cl and P - were not detected with XPS.

Figure 1 exhibits TGA and DSC curves of GO thermal exfoliation at three external instrument imposed heating rates. The TGA curves of the decomposed GO cake shown in Figure 1A indicate that no explosion has occurred when GO is heated at relatively low external heating rates (<8 K/min). However, when the sample is heated at higher external heating rates (>8 K/min) for this particular GO sample and sample size, an abrupt micro-explosion event occurs with near instantaneous mass loss. As the external heating rate increases, the heat curve onset temperature is shifted to a higher temperature, as is expected for a kinetic process in a non-isothermal TGA [25]. Similar phenomenon is observed in DSC data (see Figure 1B).

The DSC curve at low heating rates is quite symmetric and smooth, with no signature of micro-explosion. As a consequence, it yields a relatively large heat of decomposition, at 1360 J/g, since the process is not truncated by explosive sample loss and the full heat of decomposition is entirely absorbed by the instrument sensor. In contrast, the explosive mode yields about one third of this heat effect (~500 J/g). The rGO product obtained is a fluffy, low-density powder (image in Figure 1A insert), as compared to GO cake precursor (image in Figure 1A insert).

The explosive mode thermal exfoliation significantly expands the cake, producing a fluffy powder with porous microstructures, as shown in SEM images in Figures 2A–2C and their higher magnification images on Figures 2A'–2C'. These microstructures of the fluffy rGO powder appear very similar across all the rGO products produced at all external heating rates above 8 K/min tested (within the explosive range). The SEM images shown in Figure 2 are representative of all rGO samples obtained from rGO powders after explosive thermal exfoliation at various external heating rates.

Figures 3A and 3B show the chemical structures of non-explosively and explosively exfoliated rGO samples obtained by FTIR and XPS spectrums analysis. Both FTIR and XPS analysis results indicate that there is no difference in chemical structure of rGO when thermally exfoliated at external heating rates from 3 to 1590 K/min. Therefore, it seems evident that all rGO-s C/O atomic ratio is independent of the heating rate applied in thermal exfoliation (see Figure 3C) and whether the thermal exfoliation is explosive or non-explosive.

As presented in Figure 4A, the N₂ adsorption isotherms of rGO powders obtained after GO explosive mode thermal exfoliation at four external heating rates (from 10 to 1590 K/min) are quite similar.

For all rGO product powders, the N₂ isotherms exhibit a large hysteresis loop in the mesopore region, which can be attributed to the capillary condensation in rGO powder mesopores. Figure 4B reveals the N₂ isotherm rGO powder pore size distributions (PSDs), which also are quite similar, with the inset showing the data about rGO average N₂ micro-, meso- and macroporosity. Most of the surface area that the N₂ adsorbate probe sees is on the outside of rGO multilayer flakes that are not perfectly stacked. The N₂ probe mesoporosity (4 to 23 nm) detected in all rGOs can be inversely correlated with the rGO platelet thickness as observed by microscopy [46]. Figure 4C shows that all the rGOs exfoliated at several external heating rates do include the microporosity (pore sizes below 2 nm), which were not detected with the N₂ probe. The CO₂ sensed microporosity seen in rGO samples ranges from 0.45 to 0.5 nm, from 0.55 to 0.65 nm and from 0.7 to 0.85 nm. Based on PSDs shown in Figure 4C, it is evident that there seems to be no clear trend in CO₂ sensed microporosity with the instrument imposed external heating rate set during GO thermal exfoliation. The CO₂ microporosity is likely associated with the stacked regions between aligned flakes, which are in close contact but where the atomic step edges, impurities and grain boundaries prevent perfect pi-pi platelet restacking. Therefore, the meso- and microporosity in these multilayer rGO platelets mostly originates from the irregular stacking of rGO flakes.

The N₂ BET surface area of the GO cake prior to thermal exfoliation is 12 m²/g, which is almost the same magnitude surface area as the N₂ BET surface area of 16 m²/g of non-explosively exfoliated rGO product (still intact in original monolithic cake form). The CO₂ BET area of non-explosive rGO is 38 m²/g, which is also a very low area. The explosive mode decomposition of GO generates a higher surface area rGO product; the rGO surface area is approximately 350 to 400 m²/g if measured with the N₂ probe. The CO₂ BET surface areas calculated for all of the rGOs tested range from 238 to 312 m²/g, which suggests that there is no significant contribution to the surface area from the micropores obtained from CO₂ vapor adsorption at 273K. The rGO surface area of 400 m²/g corresponds to approximately 7-layer rGO platelets, when the scaling law $N = 2600/A$ is applied [21]. The present data suggests that the rGO surface area and porosity generated is largely independent of the external heating rate set by the instrument when explosive GO exfoliation occurs (here at rates between 10 and 1590 K/min, see results in Figure 4).

An rGO surface area of 400 m²/g is not especially high relative to other graphene-based material surface areas reported in the literature. Most reduced GO N₂ BET surface areas reported range from 500 to 900 m²/g [8, 20, 31, 34–40], and one of the study even reports the surface area as high as 1500 m²/g [31]. Table 1 lists all the rGO surface areas reported by various studies as a function of GO synthesis method (Hummers, Brodie, Staudenmaier, Tour and Hofmann), reduction mode (thermal and chemical), target heating temperature and heating rate.

In general, the reported rGO surface areas above 500 m²/g were obtained by exfoliating Staudenmaier GO [20, 31, 48] except in the case of the Yankovsky, 2016 study [23], which reports very low, 25 m²/g rGO surface area produced from Staudenmaier GO. The rGO produced from Hofmann GO consistently tends to show the highest surface areas reported - areas from 758 to 925 m²/g [23, 38, 47]. In general, Hummers GOs rGO surface areas are consistent with our study (300 to 400 m²/g) ranging from 100 to 600 m²/g, except one study by Li et al, 2013 [35], which reports the Hummers rGO surface area to be as high as 809 m²/g. Since, the latter study applied vacuum, it could be that vacuum presence (one extra atmosphere of pressure) does support thermal exfoliation with higher surface area rGOs.

The independency of rGO surface areas and porosities from external heating rates observed in our work (see Figure 4) implies a similar exfoliation mechanism in all cases in which external heating rate is above the critical threshold. To investigate this matter further, we have looked more closely into experimental temperature and time DSC data for each test of GO thermal exfoliation. The temperatures recorded in a DSC cell versus time should ideally exhibit a straight line with a slope close to the externally-set heating rate. However, in these data sets we observe a small, transient increase in local temperature (a small “bump”) beyond the external heating rate right before the explosion takes place (see graphical Abstract for an example temperature versus time plot with a “bump”), which is an indication of local GO cake self-heating prior to explosion. All of the non-explosive mode temperature versus time data (DSC data sets with external heating rates <8 K/min) show no such “bump” or increase in local temperature. Although, the GO sample was self-heating (large exothermic heat release was observed), the self-heating rates of the GO are low enough not to be detected by the DSC temperature sensor. This is an interesting observation, which may

help to understand our constant surface area and porosity rGO results when GO is exfoliated at 10 K/min. When we use this data to estimate the average maximum rate of local temperature increase for all the explosion cases, we obtain roughly similar rate values of ~200 K/min (see results in Table 2).

It seems that the local sample heating rates in explosive mode GO cake thermal exfoliation are independent of the external heating rates for cases where external heating rates are 10 K/min. The heating rate recorded as a temperature increase in time ('bump') by the DSC is of course the total local heating rate perceived by the sample, which is the sum of the user programmed external heating rate and the local self-heating rate of GO, as shown in Equation 1.

$$\left(\frac{dT}{dt}\right)_{\text{total}} = \left(\frac{dT}{dt}\right)_{\text{external}} + \left(\frac{dT}{dt}\right)_{\text{local self-heating}} \quad (1)$$

Therefore, for our particular Hummers GO sample, when the external heating rate is set to 8 K/min and below, the total heating rate is dominated by the external term programmed by the user. Above the 8 K/min threshold, the opposite is true - the large self-heating rate dominates in Equation 1 and the total heating rate perceived by the sample prior to explosion is more-less constant (~200 K/min), even as external heating rate rises further. Previous analytical work has shown that self-heating rates can easily reach 200 K/min or more, depending on sample size and local heat transfer conditions [25], which supports the experimental values for the self-heating contribution extracted here from the local slopes of DSC traces. We believe this is a clear and fully sufficient explanation for the otherwise surprising observation that the rGO products obtained by explosive thermal exfoliation in the high heating rate regime (>8 K/min) all have similar surface areas and morphologies.

4. Conclusions

This work clarifies the role of externally imposed heating rate on the surface area and porosity of thermally rGO materials. Earlier studies report that high heating rate increases the surface area and degree of exfoliation, but the present study shows a more complex behavior. At low external heating rates, graphite oxide undergoes a smooth, non-explosive decomposition and yields products with low surface area and low degrees of exfoliation. Above a critical heating rate, the decomposition switches to the explosive mode and produces much higher internal porosity and surface area. Importantly, further increases in external heating rate beyond this threshold do not yield further increases in surface area, with all products ranging between 350 and 400 m²/g by N₂ vapor adsorption at 77K. No significant extra surface area and porosity is detected in these rGOs when tested with the CO₂ probe at 273K. We show that this heating-rate independence is the result of the local, sample self-heating phenomenon. At instrument-set external heating rates of 10 K/min and above, the exothermic reaction becomes fast enough to cause significant local deviation of the GO sample temperature from its environment and thus a higher overall heating rate as perceived by the sample. Once the thermal runaway reaction is triggered, the fast sample self-heating dominates the total heating rate (sum of external plus self-heating), and the

externally-applied heating rate is no longer important. Thus further increases in external heating rate do not change the total heating rate nor the reaction kinetics nor the area or exfoliation degree of the final products of graphite oxide thermal decomposition. We hope this insight will be useful for researchers trying to optimize the GO thermal treatment process to produce valuable graphene-based materials.

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Figure 1.

A) Thermal exfoliation of Hummers graphite oxide (GO) in standard TGA mode. Varying external heating rate, 8 K/min non-explosive mode GO decomposition, 37 K/min and 100 K/min explosive mode GO decompositions, B) Thermal exfoliation of GO in DSC, 8 K/min non-explosive mode GO decomposition, 37 K/min and 100 K/min explosive mode GO decompositions.

Figure 2.

A) and A') SEM images of rGO powder obtained in thermal exfoliation experiment with the external heating rate at 20 K/min, B) and B') SEM images of rGO powder obtained at external heating rate of 37 K/min. C) and C') SEM images of rGO powder obtained at external heating rate of 70 K/min. Most of the particles display a layered lamellar structure with the rGO particle size ranging from about 3 to 10 μm .

Figure 3.

A) FTIR spectrums of GO and rGOs. The C-OH and COOH groups are all gone from GO during thermal exfoliation at any heating rate tested. The C=C peak at 1600 cm^{-1} and C=O peak at 1750 cm^{-1} seem present in all rGOs tested. B) XPS results of rGOs tested at the same external heating rates. As evidenced, most oxygen functionalities are gone in rGO. C) Plot of the atomic C/O ratio versus external heating rate.

Figure 4.

A) N₂ adsorption isotherms of rGO powders obtained by thermal exfoliation of GO at external heating rates from 10 to 1590 K/min, B) the corresponding rGO powder N₂ pore size distributions (PSDs), where the insert shows the micro-, meso- and macroporosity values, C) an overlay of CO₂ PSDs for all heating rates tested, where the insert shows the CO₂ BET surface area range, D) N₂ BET surface area versus external heating rate in GO thermal exfoliation experiments.

Reported rGO surface areas in literature depending on GO preparation method, exfoliation method (thermal or chemical), target heating temperature and heating rates.

Table 1

GO prep. method	Exfoliation	Target Temp. [°C]	Heating rate, K/min	N ₂ BET area, m ² /g	Ref.
Hummers	Thermal	300 to 900	10 to 1590	350 to 400	Current study
Hummers	Thermal	700	5	390	[22]
		1000	5	300	[22]
		2000	5	140	[22]
Hummers	Thermal	1000	preheated furnace	533	[23]
Hummers	Thermal	900	preheated furnace, vacuum assisted	809	[35]
Hummers	Thermal	900	preheated furnace, vacuum assisted	763	[34]
Hummers	Thermal	200	vacuum assisted	368	[39]
		300	vacuum assisted	370	[39]
		400	vacuum assisted	382	[39]
Hummers	Thermal	300	10	300	[21]
Hummers	Thermal	800	5	466	[28]
Hummers	Thermal	1050	preheated furnace	351	[37]
Hummers	Thermal	200	1	30	[24]
Hummers	Thermal	200	5	144	[24]
Hummers	Thermal	200	50	580	[24]
Hummers	Thermal	135	vacuum assisted	350–490	[8]
Brodie	Thermal	700	5	660	[22]
		1000	5	570	[22]
		2000	5	140	[22]
Brodie	Thermal	1000	preheated furnace	626	[23]
Brodie	Thermal	350	2.5–10	550	[41]
Hofmann	Thermal	1000	preheated furnace	781	[23]
Hofmann	Thermal	1050		925	[47]
Hofmann	Thermal	135 to 145	vacuum assisted	758	[38]

GO prep. method	Exfoliation	Target Temp. [°C]	Heating rate, K/min	N ₂ BET area, m ² /g	Ref.
Staudenmaier	Thermal	1000	preheated furnace	25	[23]
Staudenmaier	Thermal	1050	preheated furnace	600 – 900	[20]
Staudenmaier	Thermal	1050	>2000	700 – 1500	[31]
Staudenmaier	Thermal	1000	preheated furnace	540	[48]
Tour	Thermal	1000	preheated furnace	579	[23]
Hummers	Chemical			520	[14]
Brodie	Chemical			13.7	[23]
Hofmann	Chemical			25	[23]
Hummers	Chemical			247	[23]
Staudenmaier	Chemical			5.5	[23]
Tour	Chemical			560	[23]

Table 2

External heating rate set by DSC versus total local heating rate recorded by DSC.

External heating rate set by DSC, K/min	8	10	37	50	100
Total heating rate recorded by DSC, K/min	8.03	218	194	187	224