

# Crumpled Nanopaper from Graphene Oxide

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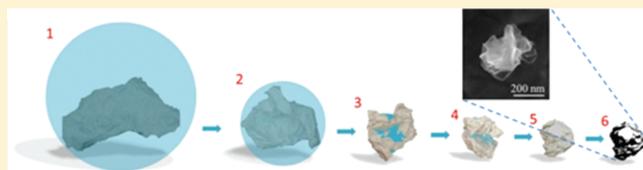
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**S** Supporting Information

**ABSTRACT:** Graphene oxide (GO) in aqueous solution was aerosolized and rapidly dried to produce crumpled nanopaper-like sheets. Online size selection and aerosol mass analysis was used to determine the fractal dimension ( $D$ ) of crumpled GO nanosheets as  $2.54 \pm 0.04$ . That is identical to macroscale materials, such as crumpled balls of paper and foil. Thermal reduction of crumpled GO nanosheets did not change  $D$ , even after loss of nearly 25% of the nanosheets mass. We demonstrate that  $D$  is able to be tuned by altering solvent conditions. A 10% acetone mixture increased  $D$  to  $2.68 \pm 0.02$ . Calculations of the confinement force show that crumpling of GO nanosheets is driven by the capillary force associated with rapid solvent loss.

**KEYWORDS:** Graphene, graphene oxide, crumpling, fractal dimension, aerosol, ion mobility



The crumpling of materials is observed in objects as small as biological membranes, in objects such as paper, and in systems as large as the Earth's crust. The processes and the models used to understand these phenomena have shown that the bending and folding of a sheet into a crumpled conformation where the thickness is small relative to the sheet area, a so-called two-dimensional material, are similar over more than 12 orders of magnitude.<sup>1–3</sup> A confining force applied to a two-dimensional sheet initially form ridges which grow until the ridges stress and fold into a three-dimensional conformation observed in familiar objects like crumpled paper.<sup>1,3</sup> The most ideal and simple case for studying the crumpling of a sheet is found where the material does not interact with itself (self-avoiding). Models and observations show that when noninteracting materials, such as papers and foils, are crumpled into balls they obey a scaling law<sup>2</sup>

$$M \propto R_M^D \quad (1)$$

where  $M$  is the sheet mass,  $R_M$  is the particle diameter, and  $D$  is the fractal dimension of the crumpled sheet.  $D$  varies as  $2 \leq D \leq 3$ , where  $D = 2$  is a flat sheet and a  $D = 3$  is a sphere, and in noninteracting sheets  $D = 2.5$ . Efforts to prepare and measure  $D$  of nanoscale materials have concentrated on model sheetlike materials such as graphene oxide (GO), a water-soluble material comprised of a mixture of aromatic and C–O containing groups that can be prepared with sheet lengths  $>1 \mu\text{m}$ .<sup>4–6</sup> Light scattering experiments of GO in aqueous solution have shown that  $D = 2.15$ , consistent with a nearly planar material.<sup>6</sup> Others have used this planarity and layer-by-layer growth to construct pliable GO papers on the macroscale.<sup>7</sup> To date, the observation of crumpling at the nanoscale has been difficult to control, most likely due the complexity of preparing materials that are noninteracting at the nanoscale. In this study,

we measure the fractal dimension,  $D$ , for GO nanosheets for a case where solvent evaporation drives the crumpling process in a GO containing aerosol droplet. The resulting dried and crumpled GO sheet is characterized in the aerosol state using a combined mass–mobility diameter measurement.

GO was prepared using a modified version of the Hummer's synthetic scheme as described previously.<sup>8</sup> Dried GO powder was added to water at  $\sim 2 \text{ mg/L}$  and formed into an aerosol using an aerosol generator. Formation of crumpled GO nanosheets was similar to recent work forming aerosolized GO, however particles created here were quickly dried using a diffusion drier after which the aerosol was passed through a temperature controlled tube furnace and a second diffusion drier.<sup>9</sup> The aerosol was sorted using a diffusion mobility analyzer (DMA) and its mass was measured using an aerosol particle mass analyzer (APM). More details of the operating principles of the instruments can be found in prior publications.<sup>10–12</sup> This method formed particles from 100 to 400 nm, or particles comprised of sheets spanning from  $4.4 \times 10^{-13}$  to  $1.5 \times 10^{-11} \text{ m}^2$  with around 3000 particles/ $\text{cm}^3$  at a 150 nm mobility diameter and 100 particles/ $\text{cm}^3$  at a 400 nm mobility diameter. APM measurements of the size selected GO particles were made using  $\approx 1 \times 10^{-19} \text{ kg}$  mass steps for each mobility diameter and processing temperature (see Supporting Information Figure S1). The reported particle mass was determined by fitting the data to a Gaussian line shape to a particle count versus mass plot at each mobility diameter. Transmission electron microscopy images were collected on grids after size selection and prior to the mass measurement. Dynamic light scattering of the GO solution used to prepare

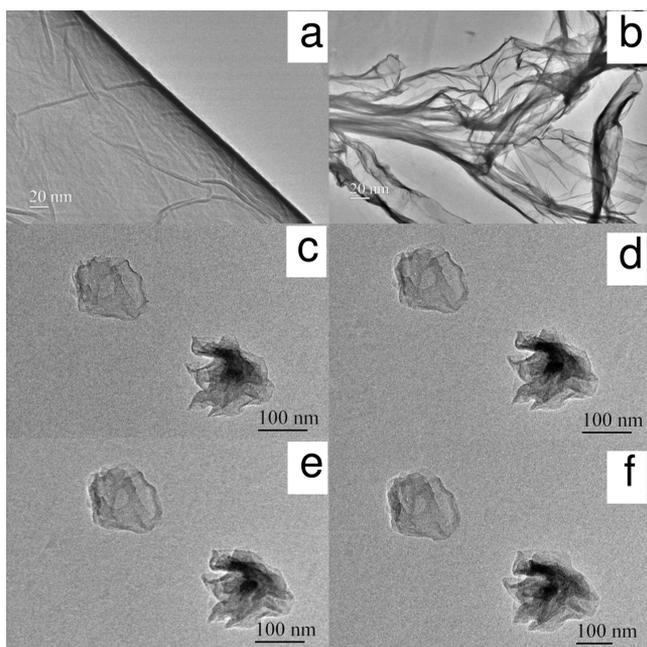
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the crumpled GO nanosheets in an aqueous solution showed a size distribution from 200 nm to 1000 nm with a peak maximum at 600 nm.

The radius of a crumpled ball is dependent on the initial sheet radius, the confining force applied to the sheet, and, the sheets physical properties such as its Young's modulus and spring constant relative to the sheet thickness. Calculations of self-avoiding sheets have shown that the application of a confining force crumples the sheet into a ball diameter with about 60% void volume.<sup>3</sup> Further reduction of the ball diameter requires an exponential increase in the confining force, so a large isotropic confinement force applied against a crumpled ball followed by removal of the force and subsequent relaxation would result in a particle where  $D < 3$ . Formation of a particle with  $D = 3$  from a two-dimensional sheet requires a spherical shape with uniform void volume (constant apparent material density) as a confining force is applied.

GO nanosheets can be prepared to adopt multiple conformations through manipulation of deposition conditions or processing temperature, as illustrated in Figure 1a–c. Figure

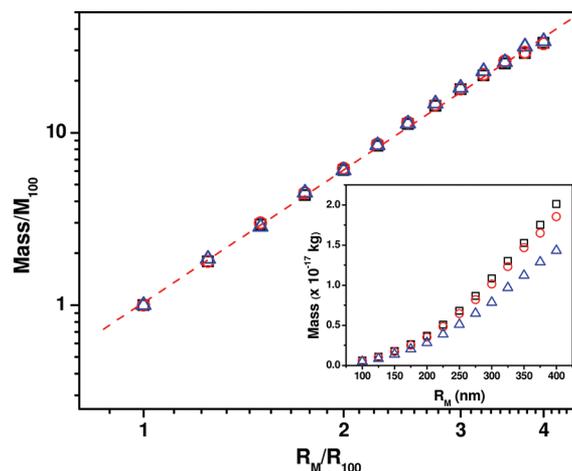


**Figure 1.** TEM images of (a) GO film comprised of multiple nanosheets at slowly dried room temperature, scale is 20 nm, (b) GO film comprised of multiple GO nanosheets slowly dried at room temperature and heated at 250 °C for 3 min, scale is 20 nm, (c) 150 nm mobility diameter GO aerosol formed at room temperature, scale is 100 nm, and same sample heated to (d) 250, (e) 325, and (f) 480 °C.

1a shows a TEM image of a film comprised of multiple overlaid GO nanosheets that form an unsupported continuous two-dimensional film over several micrometers. Images of GO thin films after heating to 250 °C, Figure 1b, show a substantial buckling and crumpling of the film likely due to mass loss from thermal reduction of GO. GO loses intersheet interstitial H<sub>2</sub>O at 130 °C and at >220 °C an additional 30% mass loss to observed, as CO<sub>2</sub> and H<sub>2</sub>O, to form a graphene-like material. Our prior work has shown that reduced GO (r-GO) after 220 °C thermal processing has a carbon/oxygen > 10.<sup>8</sup> A TEM image of 150 nm GO nanoparticles formed at room temperature is shown in Figure 1c, and show that upon drying

GO nanosheets become crumpled at room temperature. No change in conformation is observed for the same GO nanoparticles thermally reduced in situ at 250 °C during the imaging process, nor after reduction at 480 °C, shown in Figure 1d–f.

By plotting the measured GO aerosol mass as a function of mobility diameter we can evaluate eq 1 for the fractal dimension,  $D$ . Results are presented in Figure 2 for three



**Figure 2.** Mass of GO aerosol as function of GO mobility diameter for each processing temperature, data scaled to data at 100 nm. Inset shows aerosol mass versus GO mobility diameter. Room temperature (black square), 250 °C (red circle), and 325 °C (blue triangle).

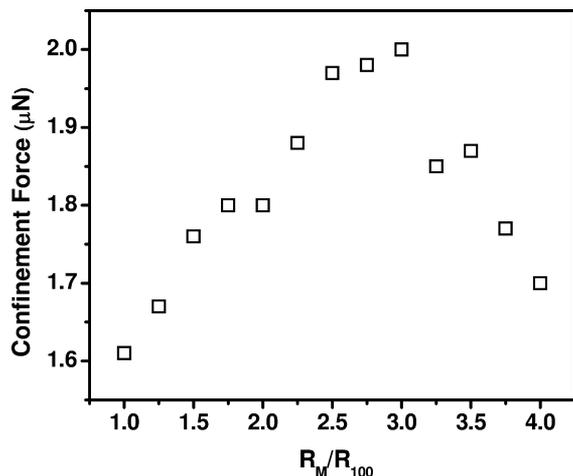
processing temperatures (22, 250, and 325 °C). The inset of Figure shows that we observe a mass loss of 5.5 and 24% at 250 and 325 °C, respectively, consistent with observations of GO mass loss in thin films in our previous work and by others,<sup>8,13</sup> we see a linear relationship of mass as a function of mobility diameter for the entire particle size range that we generate, presented for clarity on a log–log scale in Figure 2. Fitting the data to eq 1 we obtain a  $D$  of  $2.54 \pm 0.04$  for each heating temperature. Values of  $D$  for GO and r-GO (GO after 250 and 325 °C thermal processing) were identical.

The mechanism and forces involved in GO crumpling can be understood from macroscale systems of noninteracting sheets, such as paper and foils. At the nanoscale, the confining force applied to the nanosheet is the capillary force during the drying process. Qualitative methods to ascertain the magnitude of the confinement force can be determined from the particle diameter/initial nanosheet diameter ( $R_M/R_0$ ).<sup>3</sup> The crumpling force in a noninteracting sheet is defined where the particle diameter/flat nanosheet diameter is 0.63.<sup>3</sup> The measurement of the particle mass defines  $R_0$  and  $R_M$  is obtained from the mass measurement, we obtain a value of  $R_M/R_0$  of  $0.12 \pm 0.02$  for the range of particles we form, which suggests that the confinement forces here are much larger than required to initiate crumpling of GO nanosheets. In the case of irreversible folding the confinement force ( $C$ ) is related to the Young's modulus and material thickness by<sup>2</sup>

$$\rho = \rho_m \left( \frac{C}{Yh} \right)^{\delta D} \left( \frac{R}{h} \right)^{3-D} \quad (2)$$

where  $\rho$  is the mass density of a spherical particle,  $\rho_m$  is density of GO (1800 kg/m<sup>3</sup>),<sup>7</sup>  $Y$  is the two-dimensional Young's modulus,  $R$  is the mobility radius,  $h$  is the material thickness

( $0.7 \times 10^{-9}$  m for single sheet GO),  $D$  is the measured fractal dimension of GO (2.54), and  $\delta$  is the force scaling exponent for a noninteracting sheet (0.25).<sup>2</sup> For  $Y$ , we used the two-dimensional elastic constant of a single graphene oxide sheet (150 N/m).<sup>14</sup> The density,  $\rho$ , is evaluated directly from our mass–mobility diameter measurement. As shown in Figure 3,

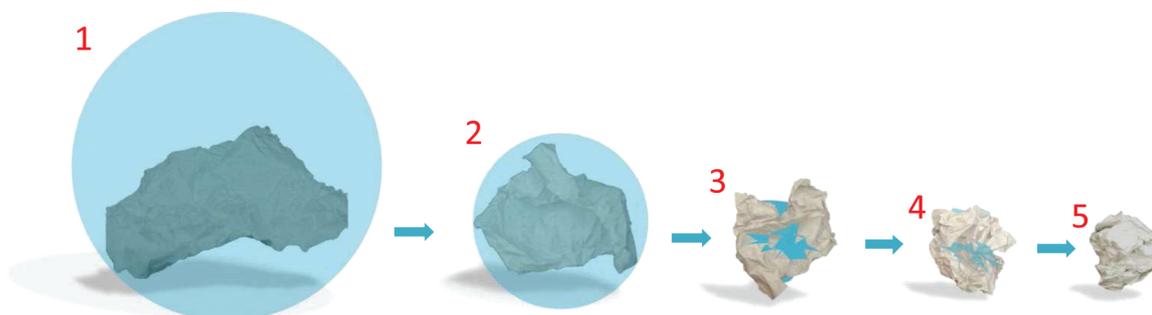


**Figure 3.** Calculated confinement force as function of GO mobility diameter, scaled to data at 100 nm.

the confinement force is around  $2 \mu\text{N}$ . The confinement force increases monotonically as the mobility diameter becomes larger and maximizes at 250–300 nm, which corresponds to the largest size of single nanosheets in our sample. Dynamic light scattering (DLS) data of the solution used to form GO nanosheets show the size distribution maximum is 600 nm and extends to 1000 nm. Using a GO density of  $1800 \text{ kg/m}^3$ ,<sup>7</sup> the width of an uncrumpled 100 nm mobility diameter GO particle is 660 nm, making it likely these particles exist as single nanosheets in aqueous solution, where  $D = 2.15$ . The largest single sheets in solution (1000 nm) correspond to mobility diameters of 250 nm. So larger particles are likely composed of multiple weakly interacting, parallel nanosheets, as observed by Luo et al. of aerosolized r-GO sheets.<sup>9</sup>

We also investigated the effect of drying on the final conformation of GO. TEM images of aerosolized GO nanosheets that were slowly desiccated on a TEM grid, by bypassing the drying and the furnace stages, reveal a heterogeneous mix of flat structures, spherical shapes, and some crumpled sheets, showing the rate of  $\text{H}_2\text{O}$  loss supporting GO nanosheets influences the final conformation. During aerosolization, GO sheets are solvated in  $\text{H}_2\text{O}$  droplets with a

diameter of a few hundred nanometers. It is envisioned that the drying process occurs rapidly to form an unsupported particle comprised of one or more crumpled GO nanosheets. TEM and aerosol mass data each suggest that the crumpling of GO nanosheets is independent of heating, and therefore the chemical composition, of the nanosheet but is most likely due to the loss of solvent stabilization, shown schematically in Figure 4. Initially GO nanosheets are contained in droplets that are rapidly desiccated until the sheets are unsupported and coated in a thin  $\text{H}_2\text{O}$  layer. At this point, additional removal of  $\text{H}_2\text{O}$  will exert a capillary force on the nanosheet crumpling the sheet as the remnants of  $\text{H}_2\text{O}$  are removed. Determination of the capillary force exerted on the nanosheet is complex due to the large number of physical and geometric uncertainties such as the nanosheet conformation, roughness,  $\text{H}_2\text{O}$  contact angle, and partial pressure. However, the calculated capillary force associated with drying nanometer scale  $\text{H}_2\text{O}$  droplets is on the order of  $2.5 \mu\text{N}$ ,<sup>15</sup> and similar capillary force measurements of the  $\text{H}_2\text{O}$  layer sandwiched between two hydrophilic surfaces as a function of relative humidity suggest  $\text{H}_2\text{O}$  removal from a nanosheet drives the crumpling of GO nanosheets.<sup>15</sup> We can conclude that compared to slowly dried nanosheets that rapid drying crumples GO nanosheets into a conformation consistent with shapes observed in comparable noninteracting macroscopic materials. Once a nanosheet conforms to the crumpled shape even the loss of nearly a quarter of its initial mass does not alter the particle shape, or  $D$  of the crumpled sheet. In noninteracting macroscale sheets  $C$  can be used to vary  $R_M/R_0$ , although  $D$  (2.5) is material dependent and thus will not change as  $C$  is increased above the crumpling force. At the nanoscale, we investigated a method to alter  $D$  through variation of the stability of the GO nanosheet conformation in solution. Dynamic light scattering studies have measured  $D = 3$  for GO nanosheets in an aqueous 10% (v/v) acetone solution.<sup>4,6</sup> Using an identical solution we measured  $D = 2.68 \pm 0.02$ . Crumpled GO nanosheets are less spherical than measured in solution, but nevertheless demonstrate that initial conditions can be used to vary  $D$  at the nanoscale, a property not observed in macroscale systems where  $D$  is an intrinsic material property independent of  $C$ . Our results seem to imply that GO is an ideal model for a noninteracting material at the nanoscale. Aerosolization and rapid drying of GO nanosheets crumples the material into shapes observed in the macroscale, such as crumpled paper balls. Heating and chemical transformation of the nanosheets do not change the crumpled conformation. The extent of crumpling can be influenced by the conformation of the nanosheet in solution.



**Figure 4.** Schematic illustrating rapid  $\text{H}_2\text{O}$  loss and subsequent crumpling of GO nanosheets. Numbers represent relative time in diffusion drier.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Aerosol mass data used to determine  $D$  are shown in Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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