Atomic Force Microscopy Study on the Reduction of Graphene Oxide

Introduction

Graphene is a single atomic sheet of carbon atoms arranged in a hexagonal network and has become a widely researched material due to its extraordinary electrical, magnetic, thermal and mechanical properties.[1] An established route for the large scale production of graphene is through the reduction of graphene oxide (GO) through chemical reaction with hydrazine or by thermal annealing.[2,3] The product of this route, reduced graphite oxide (rGO), exhibits properties similar to pristine graphene. Therefore, the objective of this study is to use atomic force microscopy (AFM) to investigate how the geometry and topology of GO sheets change after reduction. Here, we report that chemical reduction and thermal reduction in inert atmosphere both preserve the shape and size of single layer sheets, with the chemical process achieving a greater extent of deoxygenation compared to the thermal process. On the other hand, thermal reduction, if carried out in air, results in burning up of single layers sheets and the breakage of multilayer sheets into globular structures.

Experimental

AFM was carried out on the Dimension ICON from Veeco. Tapping mode was used to capture height and phase images 512 X 512 pixels in size, at a scan rate of 1.5Hz. The same GO sheets were imaged before and after reduction. For chemical reduction, the samples were exposed to hydrazine vapor in a petri dish and heated at 100C for 10 min. After 10 min, the hot plate was turned off and the apparatus was allowed to cool naturally to room temperature before the lid was removed to retrieve the samples. Thermal reduction was carried out in a tube furnace. A heating rate of 10C/min was used to ramp up the temperature to the annealing temperature of 600C, which was held for 30 min. Thermal reduction was carried out either with a 100 sccm flow of Ar gas or with an open tube exposed to air.

Results and Discussion

Chemical reduction of GO with hydrazine

Fig. 1 is a height image of a GO sheet before (1a) and after reduction (1c). The soft nature of the GO is readily apparent from the presence of wrinkles and overlaps. For thickness measurements, we found a discrepancy between the step height measured from substrate to GO (2nm) and the step height of a GO-on-GO overlap (1nm). This discrepancy could be due to SiO_2 and GO exerting different attraction/repulsion forces on the AFM probe. Therefore, the step height of an overlap presents a more accurate measurement of sheet thickness. The thickness of single-layer GO has been previously reported as 1.1± 0.2 nm,[4] which is in agreement with our results.

The same sheet of GO was imaged after chemical reduction and the height profile (Fig. 1d) reveals that, although the shape and size of the GO sheet was preserved, the thickness of the sheet has halved during the reduction process. However, the removal of oxygen-containing functional groups, which are sized in the ~100 picometer range, cannot fully account for the observed decrease in step height, which was about 0.5nm for the overlapping edge. Nevertheless, it is well known that a thin layer of water exists for all AFM experiments conducted at ambient air. We thus attribute the higher than expected decrease in step size primarily to a decrease in the layer of water associated with the surface due to the loss of hydrophilic oxygen-containing functional groups. Using the overlap, the measured thickness of rGO was ~0.5nm, which is close to that of pristine graphene from mechanical exfoliation, ~0.4nm. [5]

To study the effect of chemical reduction on wrinkles, the entire GO sheet was imaged (Fig. 2). The overlay is the height (Fig. 2 a,b) or phase (Fig. 2 c,d) profile along the middle of the sheet. The height of the wrinkles drastically reduced from 2-5nm to 1-2 nm, which can be explained by the loss of hydrophilic groups and thus moisture trapped within the wrinkles.

Although the height images are capable of showing physical changes to the GO sheet, phase imaging (Fig. 2c,d) provides complementary information on the chemical changes to the GO sheet during reduction.[6] Phase images are generated by monitoring the phase lag of the cantilever oscillation during tapping mode. Therefore, they can be

thought of as a measure of damping. The phase difference between GO and the substrate is ~8° (Fig. 2c). However, after reduction, the phase of the rGO sheet and the substrate is the same (Fig. 2d). This supports our hypothesis that the decrease in the apparent thickness of GO is due to the loss of moisture on the GO sheet, which can cause damping to the oscillating cantilever.

Thermal reduction of GO in inert atmosphere

Fig. 3 shows the changes to the GO sheet before and after thermal reduction in an inert atmosphere. The changes observed are similar to that of chemical reduction. There is no change in sheet shape or size, but the apparent thickness is approximately halved and the wrinkles have shrink (Fig. 3a,b). The difference in phase between the substrate and the sheet has also reduced after thermal reduction (Fig. 3c,d). However, while the phase of the chemically reduced GO sheet is the same as that of the substrate (Fig. 2d), the phase of the thermally reduced GO sheet is slightly lower than that of the substrate (Fig 3d). This is indicative of residual hydrophilic groups on the GO sheet, implying that thermal reduction is less effective in removing these hydrophilic groups from GO than chemical reduction.

Thermal reduction of GO in air

The size and shape of single layer GO sheets do not change when GO is thermally reduced under the protection of an argon gas flow. However, when the same reduction process is carried out in air, the landscape of the GO-coated wafer is drastically changed. Fig. 4a and b show the surface of the GO wafer before and after reduction respectively, as viewed through optical microscopy. The single layer sheets had completely burned off and disappeared, while a few multilayer sheets remain. We investigated the morphology of the surviving multilayer GO sheets.

AFM of the surviving multilayer GO sheets reveal that the GO sheet had been broken down into globular particles of rGO (Fig. 4c). The dotted rectangle indicates the region of interest in which the topology is elucidated by a 3D rendering (Fig. 4d). The GO sheet also seemed to break down specifically along wrinkle lines to create trenches in the remnant sheet. The same region of interest was used for particle analysis (Veeco Nanscope Analysis version 1.20). Using a threshold height of 6.06911 nm, and a sample size of 70 particles, the mean diameter was found to be 34 nm, while the mean height of the particles was 1.1 nm. The height (Fig. 4e) and diameter (Fig. 4f) histograms show that the geometry of the globular structures is highly polydisperse.

While the mechanism behind the formation of these globular structures is still the subject of ongoing investigation, we suggest that a combination of combustion and strain imposed upon the multilayer sheets give rise to these structures. When thermal reduction is carried out in air, oxygen attacks defect sites in GO, causing the sheet to break down into fragments. The bonds in the wrinkle lines are already under high strain, so they break down more readily to form trenches. In addition to the combustion process, GO and SiO_2 have different coefficients of thermal expansion, Therefore, they contract at different rates during the cooling process. The resulting strain on the GO fragments caused them to warp into the globular structure observed.

Conclusion

In this study, we found that reduction of GO using hydrazine was a more efficient process compared to thermal reduction in an inert atmosphere. There is a greater change in phase difference between the substrate and GO/rGO sheet for chemical reduction, which takes place at a lower temperature and shorter time than thermal reduction under the flow of argon. However, a novel result is obtained when thermal reduction in carried out in air: multilayer GO sheets break down in to nano-sized globules. This study has shown the different efficacies of chemical and thermal reduction on altering the morphology of the GO sheets, and we anticipate these results to be assimilated in developing techniques for one-step reduction of GO in conjunction with morphological control of the product.

References

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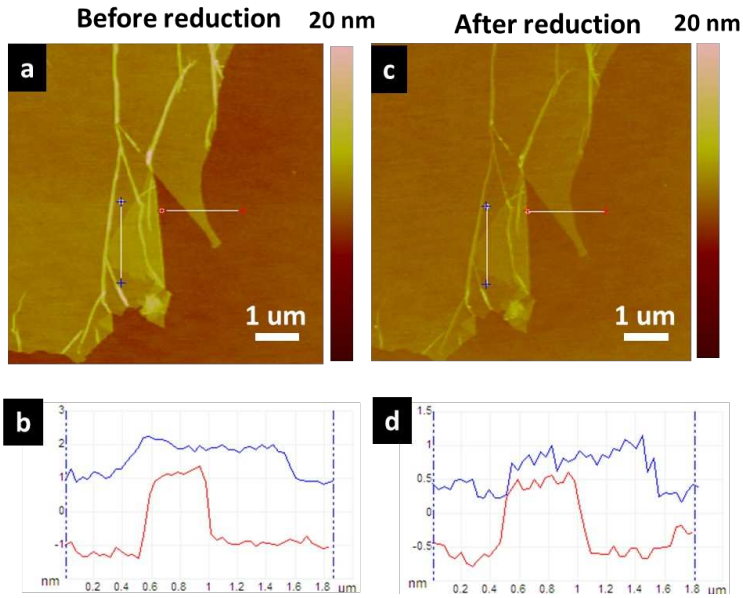

Figure 1: AFM height images of GO before (a) and after (b) chemical reduction, and the respective height profiles (b,d).

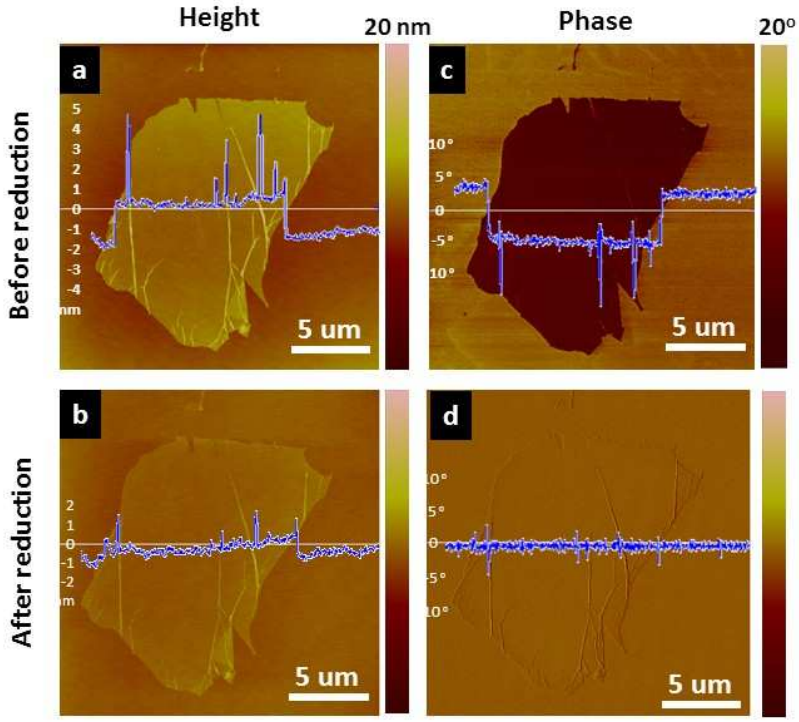

Figure 2: Height (a,b) and phase (c,d) images of GO before (a,c) and after (b,d) chemical reduction

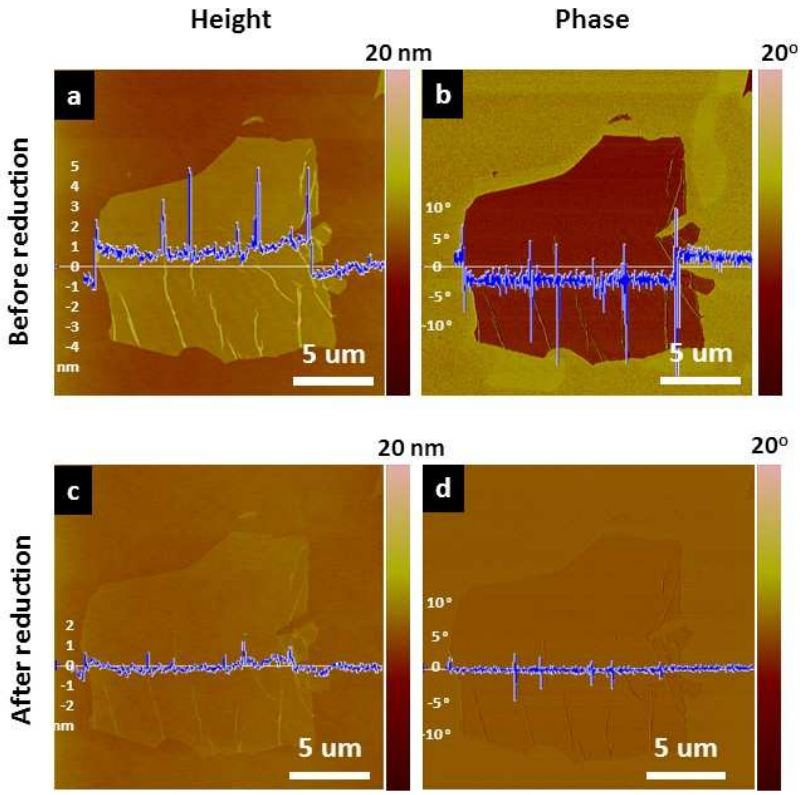

Figure 3: Height (a,b) and phase (c,d) images of GO before (a,c) and after (b,d) thermal reduction

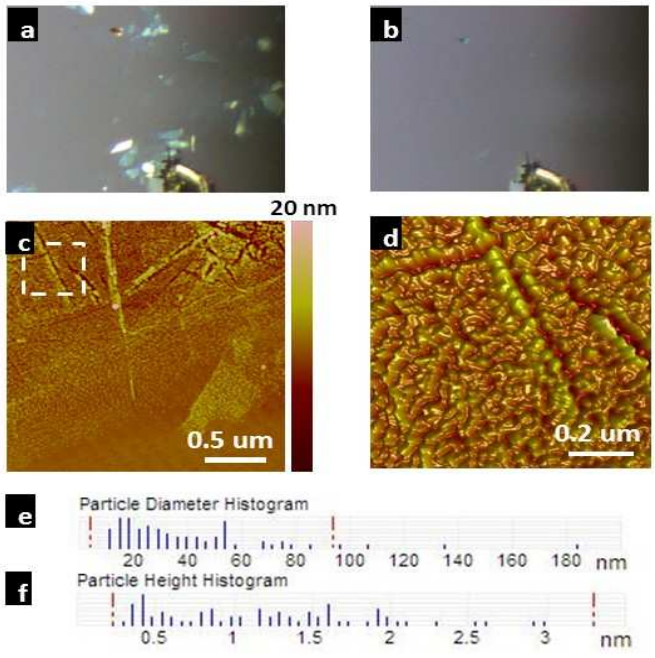

Figure 4: Optical microscopy photos of GO on the substrate before (a) and after (b) thermal reduction in air. (c) is the AFM height image of a multilayer sheet after reduction, and (d) is the 3D rendering of the region of interest indicated in the dotted rectangle of (c). (e) and (f) are diameter and height histograms respectively, calculated from the region of interest.