https://doi.org/10.2352/ISSN.2169-4451.2017.32.466

Controlling "coffee staining" effect of inkjet-printed droplets from graphene oxide inks

Pei He*[1]*, Brian Derby*[1]**

[1] School of Materials, University of Manchester, Oxford Rd., Manchester M13 9PL, U.K.

E-mail: Brian.Derby@manchester.ac.uk

Abstract

Here, we investigate the formation of inkjet-printed graphene oxide (GO) droplets with different flake size. It is shown that the size of GO flakes has strong influence to the drop morphology and can be used to control the CRE. The CRE was eliminated gradually with increased mean GO flake size (from 0.68 to ~ 36 μm). The result suggests a new strategy to control the CRE, and our observation about the morphology of inkjet-printed droplets with different flake size will be very effective to print uniform two-dimensional materials based patterns.

Motivation

When a sessile drop of liquid containing suspended particles dries on a solid surface, it may leave a ring-like structure around the periphery of the drop after the completion of liquid evaporation. This phenomenon is commonly known as the coffee ring [1]. This phenomenon is commonly observed in systems with diverse constituents, ranging from nanoparticles, to colloids and molecules in solution [2]. A mechanism for the coffee-ring effect (CRE) was first described by Deegan et al.,[1] which proposed that the dispersed materials in the droplet are transported to the contact line of the drop by radial flow generated during the evaporating process. Although the ubiquitous nature of the CRE has made it hard to avoid, achieving morphology uniformity from evaporated drops is critical in many practical applications, such as graphics inkjet printing, micro-arrays, coatings, biosensors, and the self-assembly of particles.

In the last decade, Graphene, an atom thick carbon layer with a honey-comb lattice, has attracted particular interest in both academic and industry fields because of its unique chemical, mechanical, thermal, and electrical properties [3]. Graphene was observed by isolating graphite to single-atom-thick crystallites through micromechanical cleavage method in 2004 [4]. Since the discovery of graphene, many techniques have been developed to produce single or few-layered graphene, including mechanical cleavage, epitaxial growth, chemical vapor deposition, liquid phase exfoliation (LPE) [5]. Among these, LPE is promising suited for produce high yield of graphene due to its advantage of solution process. Graphene-based dispersions can be obtained by exfoliation of graphite or graphite oxide in aqueous [6] or organic solvents [7] through an ultrasonication process. Several groups have reported using inkjet printing technique to deposit graphene dispersions for electronic applications [8, 9].

Problem

Inkjet printing of two-dimensional graphene-based inks, which based on pristine few layer graphene sheets or reduced graphene oxide formed by liquid phase exfoliation, have attracted much interest in the field of printed electronics. It has been generally believed that inks containing small diameter graphene or other 2D material flakes may be beneficial for inkjet delivery allowing for a more stable ink and reducing agglommeration or blocking of the fine nozzles used with inkjet printing. However, during drying of printed droplets, inks containing 2D materials such as graphene or GO show a behaviour similar to that observed during the drying of inks made from nanoparticles or nanotubes, i.e. they show a clear CRE with the dried 2D flakes arranged at the contact line of the dried droplets forming a characteristic ring-like structure [8]. Although the CRE can be suppressed by using a combination of two solvents or adding surfactant and a high boiling point solvent, the harsh post-treatment condition required and restrictions to the use of some organic solvents limits these mitigating techniques for large area applications.

Approach

In this work, we will investigate the morphology formation of inkjet-printed graphene oxide droplets with different flake size after drying. GO inks with a range of mean flake size were obtained by ultrasonically milling inks with very large flake size for a range of process times, with increasing sonication time leading to a smaller mean flake size. GO inks of the initial large flake size were obtained using a modified Hummers' method to produce GO dispersions with mean flake size 35.9 μm. This method allowed us to produce a range of GO inks with mean flake size ranging from 0.68 to 35.9 μm. The GO suspensions are highly stable against sedimentation in deionised water and these were then used, after appropriate dilution, directly as inks in this study. It is shown that the size of graphene oxide flakes has strong influence to the drop morphology and can be used to control the CRE. The CRE was eliminated gradually with increased graphene oxide flake size. Inks with GO flake size > 10.3 μm did not show a CRE when drops with a contact diameter of ~ 340 μm dried. The result suggests a new strategy to control the CRE, and our findings about the morphology of printed droplets with different flake size will be very effective to print uniform two-dimensional materials based pattern.

Experimetal method

The preparation of the GO sheets is based on a modified Hummers' method [10]. Briefly, nature graphite flakes (1.5 g, grade 9842, Graphexel Ltd., Epping, UK) were dispersed in concentrated sulfuric acid (200 ml, > 95%, >17.7 mol, Fisher Scientific) by stirring in an ice bath. Then a total of 6.0 g

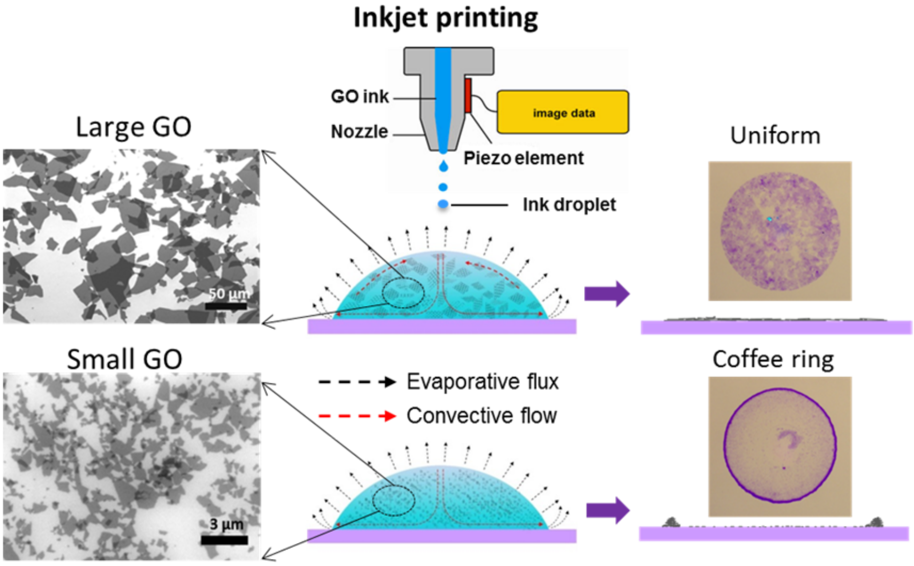

Figure 1. Left: SEM images of large (top) and small (bottom) size of GO sheets. Middle: Schematic representation of the deposition of printed droplets with large GO and small GO. The dash lines shows the capillary flow during the drying process. The droplet cantaining of large GO flakes gives a uniform distribution after drying, while the droplet containing of small GO flakes shows a ring-like structure after drying.

$KMnO_4$ (Lot # MKBK7079V, Sigma-Aldrich) were added at 24 hour intervals over 4 days (1.5 g each time). The prepared GO flakes was break-down to smaller size by treating with tip sonication for different times.

The prepared GO inks were printed on pre-cleaned Si/SiO_2 substrates by using an in-house designed and built laboratory inkjet printer (MPP 1000) was equipped with drive electronics (JetDrive III, Microfab, Plan, TX, USA) interfaced to a PC and controlled in a LabVIEW (National Instruments, Austin, TX, USA) system. The diameter of printhead is 60µm and the temperature of substrate was set to 30 ° C.

The images of dried GO droplets were captured using an Olympus BH-2 optical microscope (Olympus, Tokyo, Japan). The morphology and structure of the GO sheets and GO droplets were characterized by scanning electron microscopy (SEM, XL30 FEG-SEM, FEI, Eindhoven, Netherlands). The size distribution of GO sheets was calculated from SEM images by the software ImageJ (NIH, Bethesda, MA, USA).

Results

Figure 1 shows the schematic of the deposition of printed droplets with large and small GO flakes. The large GO flakes was prepared by a modified Hummers' method as decribed in experimental section, while the small GO flakes was obtained by treating the GO ink with tip sonication for 30 mins. By analysing more than 200 flakes from serval SEM images as shwon in Figure 1 left, the mean size of large and small GO flakes are 35.9±23.2, and 0.68±0.31µm, respectively. It mentioned that the drying GO droplets from large flakes showed a uniform distribution, while the GO droplets form small flakes were stacked at the edge of the drying drop which showed a CRE like structure (shown in Figure 1 right).

Figure 2 shows the typical SEM images of drying GO droplets. It is noticed that the GO droplets with large flakes showed a uniform distribution. The intensity profile of the corresponding area further indicated the uniformity of the droplet. The higher intensity area is due to the overlap of large flakes or folded flakes. On the other hand, the droplet with small flakes showed a very strong CRE at the edge of the droplet. A high intensity and shape edge was observed from the intensity line profile.

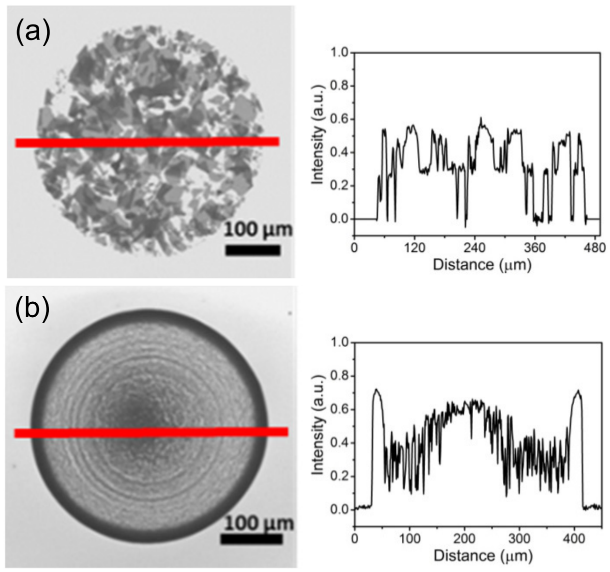

Figure 2. SEM images of printed GO droplets from large (a) and small (b) flake size. Intensity line profiles of the corresponding SEM images are shown to demonstrate this phenomenon.

To further investigate the effect of flake size to the final morphology of drying GO droplets, we prepared four types of

GO dispersions in water with different lateral sheet sizes. The mean flake size of these GO inks is 0.68±0.31, 2.32±1.54, 10.3±9.6, and 35.9±23.2 µm, respectively. Figure 3 shows the optical images of drying GO droplets on Si/SiO_2 substrates with increasing GO flake size. It is noticed that the droplet based on smallest flakes (0.68 µm) showed a ring edge with high contrast colour to substrate which indicated the high degree stacking of GO flakes. With increasing flake size to 2.32 µm, the colour of the edge of the droplet was weaken, which means less stacking of GO flakes. With the flake size increasing to 10.3 µm, the morphology of the droplet became uniform and no obviously stacking of flakes. Further increasing the flake size to 35.9 µm, the CRE phenomenon was completely disappeared and a uniform distribution of GO flakes was observed.

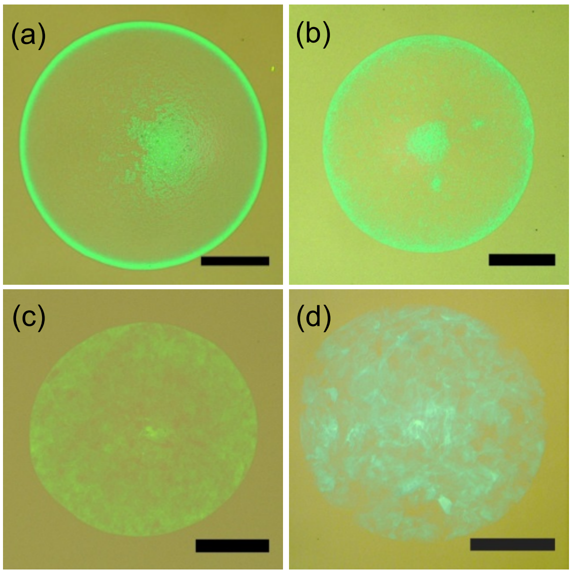

Figure 3. *Optical microscopy image of drying GO droplets on Si/SiO_2 with different flake size: (a) 0.68±0.31, (b) 2.32±1.54, (c) 10.3±9.6, and (d) 35.9±23.2 µm. All scale bars are 100 µm.*

Conclusions

The GO ink with mean size of 36.9 µm was synthesised from nature graphite by modified Hummers' method. By further treated with tip sonication for different time, the mean size of GO flakes was break-down to smaller size to 0.68 µm. It was found that when printed drops with diameter around 340 µm drying on Si/SiO_2 substrates at 30 °C, the coffee ring effect could be overcome when the GO flake size larger than 10.3 µm. Therefore, the coffee ring effect for drying GO droplets can be overcome through increasing the GO flake size.

References

[1] Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A., Capillary flow as the cause of ring stains from dried liquid drops. *Nature* 1997, 389, 827-829.

[2] Yunker, P. J.; Still, T.; Lohr, M. A.; Yodh, A. G., Suppression of the coffee-ring effect by shape-dependent capillary interactions. *Nature* 2011, 476, 308-311.

[3] Zhuang, X.; Mai, Y.; Wu, D.; Zhang, F.; Feng, X., Two-dimensional soft nanomaterials: a fascinating world of materials. *Adv Mater* 2015, 27, 403-27.

[4] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., Electric field effect in atomically thin carbon films. *Science* 2004, 306, 666-669.

[5] Zheng, Q.; Li, Z.; Yang, J.; Kim, J.-K., Graphene oxide-based transparent conductive films. *Prog Mater Sci* 2014, 64, 200-247.

[6] Lotya, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De, S.; Wang, Z. M.; McGovern, I. T.; Duesberg, G. S.; Coleman, J. N., Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions. *J Am Chem Soc* 2009, 131, 3611-3620.

[7] Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z. Y.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N., High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat Nanotechnol* 2008, 3, 563-568.

[8] Torrisi, F.; Hasan, T.; Wu, W. P.; Sun, Z. P.; Lombardo, A.; Kulmala, T. S.; Hsieh, G. W.; Jung, S. J.; Bonaccorso, F.; Paul, P. J.; Chu, D. P.; Ferrari, A. C., Inkjet-Printed Graphene Electronics. *Acs Nano* 2012, 6, 2992-3006.

[9] Su, Y.; Du, J.; Sun, D.; Liu, C.; Cheng, H., Reduced graphene oxide with a highly restored π-conjugated structure for inkjet printing and its use in all-carbon transistors. *Nano Res* 2013, 6, 842-852.

[10] Dimiev, A.; Kosynkin, D. V.; Alemany, L. B.; Chaguine, P.; Tour, J. M., Pristine graphite oxide. *J Am Chem Soc* 2012, 134, 2815-22.

Biography

Pei He graduated from Xidian University with a BEng in Telecommunication Engineering, China, in 2009. Then he studied in organic electronic devices at Shanghai Jiao Tong University under the supervision of Prof. Xiaojun Guo and obtained his MEng degree in Electronic Engineering in 2012. Je started the PhD program in nanostructured materials at the University of Manchester under the sulpervision of Prof. Derby since September, 2012. His research now is focused on inket printing of graphene-baseed dimensional materials for electronic applications