

# Dielectrophoretic Deposition of Graphite Oxide Soot Particles

Seunghyun Hong<sup>1</sup>, Sehun Jung<sup>2</sup>, Sunjung Kang<sup>2</sup>, Youngjin Kim<sup>1,2</sup>, Xinqi Chen<sup>3</sup>,  
Sasha Stankovich<sup>4</sup>, S. Rodney Ruoff<sup>4</sup>, and Seunghyun Baik<sup>1,2,\*</sup>

<sup>1</sup>SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, KyungGi-Do, 440-746, Korea

<sup>2</sup>School of Mechanical Engineering, Sungkyunkwan University, Suwon, KyungGi-Do, 440-746, Korea

<sup>3</sup>NUANCE Center, Northwestern University, Evanston, IL 60208, USA

<sup>4</sup>Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208-3111, USA

Alternating current dielectrophoresis in water was used to position graphite oxide soot (GO-soot) particles generated by rapid thermal expansion of graphite oxide under inert gas. The dielectrophoretic deposition was carried out at a frequency of 10 MHz and a peak-to-peak voltage of 10 V, and the deposited particles were analyzed using scanning electron microscopy. The vertical cross section, obtained by focused ion beam cutting, shows the wrinkled layers of the GO-soot particles and cavities between the layers. The electrical transport measurements show typical characteristics of metal-like pathways. The improved electrical contact between electrodes and GO-soot, probably due to the thin platelet structure of GO-soot, makes the material favorable for electrical device applications. The results demonstrate that AC dielectrophoresis can be used to selectively deposit graphite oxide soot particles at desired locations.

**Keywords:** Dielectrophoresis, Graphite Oxide Soot, Positioning, Electrical Transport Measurement.

Graphene, a single carbon layer of the graphite structure, has received considerable attention for its excellent thermal, mechanical, and electrical properties. The in-plane thermal conductivity and Young's modulus of graphite are  $\sim 3,000 \text{ Wm}^{-1} \text{ K}^{-1}$  and 1,060 GPa, respectively.<sup>1</sup> Recent work has shown that individual layers of graphite ('graphene sheets') have extraordinary electronic transport properties.<sup>2</sup> However, graphene has not been produced on a large scale. Thermally expanded graphite oxide 'soot' (GO-soot) is one route to having electrically conductive thin platelets potentially available in large quantity.<sup>1</sup> GO-soot consists of thermally reduced graphene oxide layers that are connected with each other to some degree, but having no appreciable inter-layer ordering.<sup>3</sup> The exact morphology and chemical composition of such "GO-soots" are a function of the graphite precursor used to prepare the graphite oxide, the method of preparation of the graphite oxide, and quite importantly, the time-temperature profile of the rapid thermal expansion used to "popcorn" the graphite oxide so that it undergoes an enormous volumetric expansion. It is thought that this material might serve as a useful nanofiller in composite materials,<sup>3</sup>

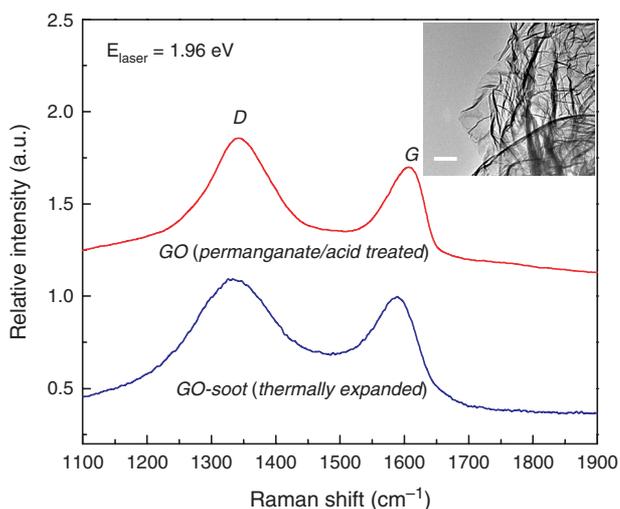
but the individual particles or aggregates of them even without a surrounding matrix material might have important functions. Since the controlled positioning of nanoparticles from liquid suspensions into or onto devices offers certain advantages both for configuring experiments for fundamental research and for achieving practical applications, several manipulation methods such as chemical functionalization to create patterned surfaces and electrical field-assisted deposition have been developed.<sup>4-6</sup> Dielectrophoresis (DEP) is one of the methods that has been used for positioning nanoparticles including carbon nanotubes (CNTs).<sup>7-10</sup> Here, we firstly demonstrate controlled positioning of GO-soot particles at specific locations using alternating current dielectrophoresis.

GO-soot was prepared by rapid thermal expansion of graphite oxide that had been made by the Hummers method, in which the synthesis of graphite oxide (GO) involves treatment of graphite with potassium permanganate in concentrated sulfuric acid.<sup>11</sup> The product was filtered, washed with 5% HCl aqueous solution, and dried at 50 °C for 24 hours. The graphite oxide was then thermally expanded by rapid insertion from room temperature into a vertical oven held at 300 °C, where it was held for 10 minutes under nitrogen gas. A Raman microscope (Renishaw, inVia Reflex) was employed to analyze the

\*Author to whom correspondence should be addressed.

thermally expanded graphite oxide material, which we here refer to as GO-soot. A He-Ne laser with a grating of 1,800 grooves/mm was used for 632.8 nm ( $E_{\text{laser}} = 1.96$  eV) excitation. The laser power at the sample was 20 mW, and the spot size was about  $1\sim 2$   $\mu\text{m}$  in diameter. Figure 1 compares Raman spectra of GO (before the thermal expansion) and GO-soot. The peak at  $1334\text{ cm}^{-1}$ , which is called as the disorder-induced mode (or D band), indicates the presence of  $\text{sp}^3$  hybridized carbon due to the covalently bonded surface functional groups while the Lorentzian peak at  $1582\text{ cm}^{-1}$  is the G band related to the tangential mode vibration of the  $\text{sp}^2$  hybridized C atoms.<sup>12–14</sup> The Raman spectrum of graphite oxide, which shows both G and D bands, thus shows evidence of both regions of  $\text{sp}^2$ -bonding as well as covalently bonded surface functional groups. The Raman spectrum of GO-soot is similar to that of GO. However, the D/G intensity ratio was slightly decreased from 1.16 to 1.09 after the thermal expansion. This indicates the thermal pyrolysis of the oxygen-containing functionalities during the thermal expansion process, as will be discussed shortly.<sup>15</sup> The inset to Figure 1 provides the high resolution transmission electron microscopy (TEM) image of GO-soot. The crumpled sheet looks very similar to that observed previously for GO.<sup>16</sup>

The GO-soot particles were dispersed in a sodium dodecyl sulfate (SDS)-based water solution using ultrasonication. For the preparation of a suspension, 50 mg of GO-soot powder was dispersed in 100 ml of DI water containing 1 wt% of SDS. The mixture was then ultrasonicated at 490 W for 15 minutes using a probe-tip sonicator (Ulsso-High Tech). Although the presence of functional groups on the layer makes GO-soot partially hydrophilic, which per our experience allows the material to disperse in water to a certain degree, surfactant-assisted dispersion helps for a more effective exfoliation of GO-soot in water.

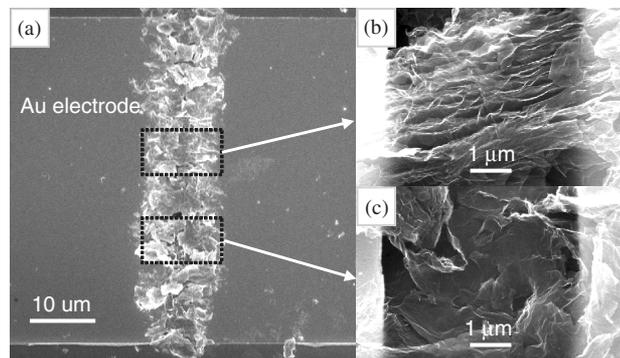


**Fig. 1.** The Raman spectra of GO (which is permanganate and acid-treated graphite) and GO-soot (which is thermally expanded GO). A high resolution TEM image of GO-soot is shown in the upper right corner (scale bar is 100 nm).

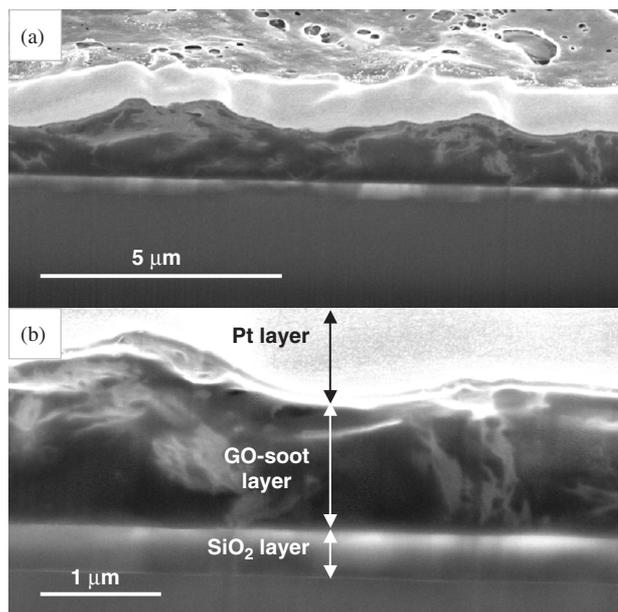
Electrodes were fabricated with a gap of 5  $\mu\text{m}$  and a length of 50  $\mu\text{m}$  using a conventional photolithographic method as shown in Figure 2(a). A 5-nm thick titanium (Ti) layer and then a 200-nm thick gold (Au) layer were vapor-deposited on a  $\text{SiO}_2$  layer (that had been thermally grown on a silicon wafer) as top-electrode materials. 20  $\mu\text{l}$  of the liquid (surfactant suspended GO-soot) was dropped onto the electrode after a function generator (Agilent 33220A, maximum field strength = 20  $\text{V}_{\text{p-p}}$ ) was first switched on at a frequency of 10 MHz and a peak-to-peak voltage of 10 V. The average electric field in the center of the gap is about 2  $\text{V}/\mu\text{m}$ . After 10 minutes, the drop on the electrodes was blown away by a stream of nitrogen gas (99%, 2 bar), and the function generator was switched off.<sup>7–9</sup>

DEP refers to the force exerted on the induced dipole moment of a dielectric particle in a dielectric fluid when it is subjected to a non-uniform electric field.<sup>7, 17–18</sup> The dielectrophoretic mobility depends on the electrical properties of the particle and surrounding fluid, the particle geometry, and the frequency of the electric field. Particles move toward the regions of high electric field strength (positive DEP) if the polarisability of the particles is greater than that of the suspending medium whereas particles move in the opposite direction (negative DEP) when the polarisability of the particle is less than that of the suspending medium.<sup>18</sup> An SEM image of dielectrophoretically deposited GO-soot particles between two parallel electrodes is shown in Figure 2(a). Higher magnification images are shown in Figures 2(b) and (c). The GO-soot particles are deposited in an ordered fashion in some regions (Fig. 2(b)). However, the GO-soot particles are randomly positioned in most regions.

Figure 3(a) shows an SEM image of the vertical cross-section of the deposited GO-soot particles obtained after focused ion beam cutting (DBFIB, NOVA200, FEI; the acceleration voltage of the Ga ion was 30 kV). The cross-section was chosen as parallel to the long edge of the electrode. Figure 3(b) shows a higher magnification image.



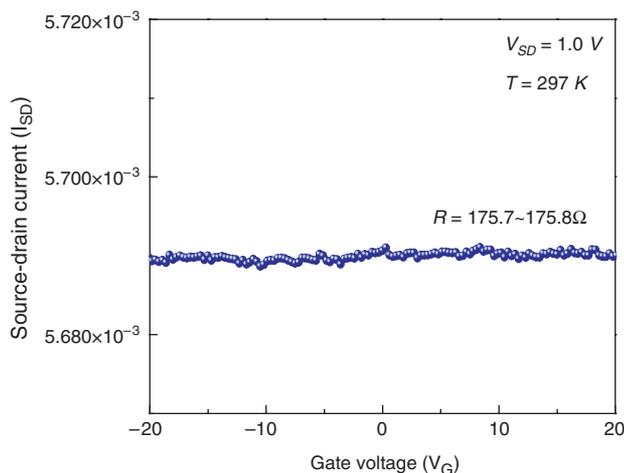
**Fig. 2.** (a) SEM image of GO-soot particles deposited between two metal electrodes with a gap size of 5  $\mu\text{m}$ , and (b) higher magnification image. GO-soot particles are deposited in an ordered fashion in some regions. (c) Magnified image in other regions where GO-soot particles are deposited with random orientation.



**Fig. 3.** (a) SEM image of the vertical cross-section of the deposited layer of GO-soot particles, obtained after FIB cutting. (b) Higher magnification SEM image; the thickness of the deposited layer of GO-soot particles is about 1  $\mu\text{m}$ .

The platinum layer was thermally deposited on top of the GO-soot layer to protect the surface during the cutting process. The thickness of the GO-soot particle layer was about 1  $\mu\text{m}$ . The cross-sectional image shows a wrinkled layer of GO-soot particles. As shown, cavities are observed inside the deposited GO-soot layer although the layer looked densely packed from the top view image (Fig. 2(a)).

Graphite oxide (GO) is an electrically insulating material which limits electrical device applications.<sup>19</sup> The thermal treatment of GO above a certain temperature leads to loss of CO and CO<sub>2</sub>. As a result of this, the C:O ratio increases for the rapidly thermally treated GO (GO-soot) resulting in an increase in electrical conductivity.<sup>15, 19</sup> Here we report the electrical transport characteristics of the dielectrophoretically deposited layer of GO-soot particles using a semiconductor parameter analyzer (Agilent E5262A) and a probe station (CASCADE RF-1). The source-drain current at a source-drain voltage of 1 V was monitored as a function of the back gate voltage. As shown in Figure 4, the layer of GO-soot particles did not show any modulation as the back gate voltage was changed from  $-20$  V to  $20$  V, thus the layer behaves like a metal. The deposited GO-soot layer exhibited much lower electrical resistance ( $\sim 175$   $\Omega$ ) compared with the typical resistance ( $\sim 10^6$   $\Omega$ ) of dielectrophoretically deposited single-walled carbon nanotube arrays for similar deposition conditions.<sup>20</sup> The high electrical resistance of the deposited nanotube arrays is mainly caused by the contact resistance between metallic electrodes and nanotubes. Considering the thin platelet structure of GO-soot, the higher surface area of contact from the face-to-face interaction between the



**Fig. 4.** Electrical transport behavior of a layer of GO-soot particles. The source-drain current was measured at a fixed source-drain bias ( $V_{SD}$ ) of 1.0 V as a function of the back gate voltage. The dielectrophoretically deposited GO-soot particles showed no gate dependence, characteristic of the response of a metal.

electrodes and GO-soot particles makes the material potentially favorable for electrical device applications. Furthermore, GO-soot may have higher surface-to-volume ratio than nanotubes (particularly multi-walled carbon nanotubes) due to the inaccessibility of the inner nanotube surface(s) to external materials.<sup>1</sup>

In summary, alternating current dielectrophoresis has been employed to selectively deposit electrically conductive GO-soot particles at desired locations. The thickness of the dielectrophoretically deposited layer of GO-soot particles was about 1  $\mu\text{m}$ , and cavities could be observed inside the layer by SEM imaging after FIB cutting. Electrical transport measurements showed that the deposited particles exhibited typical characteristics of metal-like pathways, with a lower electrical contact resistance between electrodes and the GO-soot particles compared with that between CNTs and metal electrodes. GO-soot particles can be selectively deposited by dielectrophoresis as potential components for device applications.

**Acknowledgment:** This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2006-331-D00043). XC, SS, and RSR gratefully acknowledge the grant support from the NASA University Research, Engineering, and Technology Institute on Bio Inspired Materials (BIMat) under award No. NCC-1-02037, and (for RSR) by the National Science Foundation (NIRT Program, Grant No. 0304506, Dr. Ken P. Chong, Program Director).

## References and Notes

1. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, *Nature* 442, 282 (2006).
2. A. K. Geim and K. S. Novoselov, *Nature* 6, 183 (2007).

3. S. Stankovich, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, *Carbon* 44, 3342 (2006).
4. X. Q. Chen, T. Saito, H. Yamada, and K. Matsushige, *Appl. Phys. Lett.* 78, 3714 (2001).
5. K. Yamamoto, S. Akita, and Y. Nakayama, *J. Phys. D* 31, L34 (1998).
6. S. G. Rao, L. Huang, W. Setyawan, and S. Hong, *Nature* 425, 36 (2003).
7. Y. Kim, S. Hong, S. Jung, M. S. Strano, J. Choi, and S. Baik, *J. Phys. Chem. B* 110, 1541 (2006).
8. R. Krupke, F. Hennrich, H. v. Löhneysen, and M. M. Kappes, *Science* 301, 344 (2003).
9. S. Baik, M. Usrey, L. Rotkina, and M. S. Strano, *J. Phys. Chem. B* 108, 15560 (2004).
10. H. Seo, C. Han, D. Choi, K. Kim, and Y. Lee, *Microelec. Engineer* 81, 83 (2005).
11. W. S. Hummers and R. E. Offeman, Jr., *J. Am. Chem. Soc.* 80, 1339 (1958).
12. M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho, and R. Saito, *Carbon* 40, 2043 (2002).
13. M. J. Bronikowski, P. A. Willis, D. T. Colbert, K. A. Smith, and R. E. Smalley, *J. Vac. Sci. Technol. A* 19, 1800 (2001).
14. R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London (1998).
15. A. Lerf, H. He, M. Forster, and J. Klinowski, *J. Phys. Chem. B* 102, 4477 (1998).
16. R. J. Beckett and R. C. Croft, *J. Phys. Chem.* 56, 929 (1952).
17. T. B. Johns, *Electromechanisms of Particles*, Cambridge University Press, Cambridge (1995).
18. H. Morgan and N. G. Green, *AC Electrokinetics: Colloids and Nanoparticles*, Research Studies Press, Baldock (2003).
19. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleihammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, *Carbon* 45, 1558 (2007).
20. S. Hong, S. Jung, J. Choi, Y. Kim, and S. Baik, *Langmuir* 23, 4749 (2007).

Received: 9 April 2007. Revised/Accepted: 24 July 2007.

Delivered by Ingenta to:  
SUNG KYUN KWAN UNIVERSITY  
IP : 61.72.109.184  
Mon, 18 Feb 2008 06:57:41