doi:10.1246/cl.2011.54

Submillimeter-scale Graphene Patterning through Ink-jet Printing of Graphene Oxide Ink

Yong Min Jo,[1] Seyoung Yoon,[2] Ji-Hoon Lee,[2] Sung-Jun Park,*[1] Sung Ryong Kim,*[2] and Insik In*[2]
[1]*Department of Mechanical Engineering, Chungju National University, Chungju 380-702, Korea*
[2]*Department of Polymer Science and Engineering, Chungju National University, Chungju 380-702, Korea*

(Received September 17, 2010; CL-100798; E-mail: in1@cjnu.ac.kr)

Patterning of reduced graphene is successfully demonstrated through ink-jet printing of *graphene oxide (GO) ink* and subsequent reduction with hydrazine vapor in submillimeter scale. GO plate size is the most critical parameter for the success of facile ink-jet printing of *GO ink*. Prepared graphene lines show conductivity of $1.1\,\mathrm{S\,m^{-1}}$, which is a fifth of typical conductivity of graphene film, which might result from decreased percolation of graphene plates in ink-jet printing.

Graphene has been utilized in various electronic applications due to its fascinating electrical properties which originate from its ideal sp^2-conjugated molecular structure.[1–5] To fully utilize graphene in the formulation of graphene-based electronic devices, pattern formation of graphene layers is requisite. Transfer printing,[6–8] chemical vapor deposition (CVD) on patterned transition-metal layers,[9] and soft-lithography such as micromolding in capillary (MIMIC)[10] have proven that patterned graphene layers can be obtained in small or large dimensional scale. Recently, preparation of vapor sensors through ink-jet printing of reduced graphene oxide (RGO) on flexible substrate has been successfully demonstrated.[11] Here, we demonstrate the first ink-jet printing of *GO ink* instead of *RGO ink*. When *RGO ink* is utilized for ink-jet printing, subsequent removing of polymer additive is required because insulating polymer additive is typically used for the solubilization of RGO in solvent media. In the case of GO ink, no stabilizer is required becase GO itself is readily soluble in water. While a further chemical reduction step is required to render the insulating printed GO pattern to conducting graphene, the fact that facile chemical reduction of GO layer is possible even by using hydrazine vapor prompted us to test GO ink instead of RGO ink.[12–15] The use of GO ink might minimize any structural deformation of the graphene pattern in the process of solvent washing in the use of RGO ink.

For the ink-jet printing of *GO ink*, GO plate size was carefully examined by dynamic light-scattering (DLS) analysis of aqueous GO solution (1 mg in 10 mL of deionized water) and AFM or SEM analysis of drop-casted GO layers. While DLS analyses show GO plate dimension of more than 1 µm initially, ultrasonication of GO solution showed much decreased plate size to 200 nm.[16] This DLS result correlates with the dimension of GO plates either in AFM or SEM images (Figures 1a and 1b). Without sonication, ink-jet printing of *GO ink* was not feasible due to clog formation inside of the nozzle. Next, ink-jet printing of sonicated GO solution was attempted. The smaller plate dimension of sonicated GO enabled facile ink-jet printing of GO either on Si wafer, glass slide, or overhead PET film. Definitely, ink-jet printing of prepared *GO ink* on PET film or glass slide produced GO films with several wrinkles on their surface (Figures 1c and 1d). The surface roughness of graphene layer is higher in PET film than glass slide, indicating wetting of GO is more favorable on hydrophilic glass.

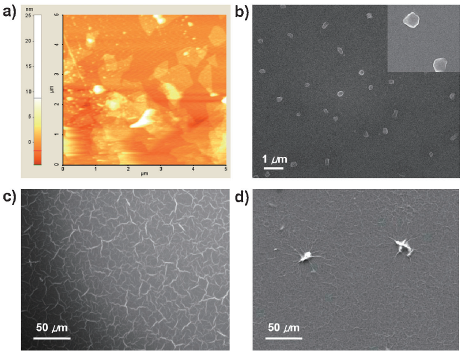

Figure 1. Images of GO plates a) in AFM (before sonication) and b) in FE-SEM analysis (after ultrasonication), and images of ink-jet printed GO layers c) on PET film and d) on glass slide.

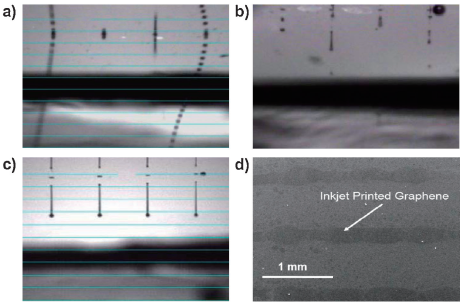

Figure 2. Captured images of ink-jetted ink droplets through several nozzles using *GO ink* a) without optimization and b) after optimization, and c) using commercial ink. d) Patterned reduced graphene through ink-jet printing of *GO ink* on Si wafer.

Next, patterned ink-jet printing of *GO ink* was attempted on Si wafer. There was one significant problem for precise ink-jet printing. Very low solvent viscosity of GO solution induced curved jetting of solution though the nozzle (Figure 2a). Optimization of ink-jetting condition showed rather straightened jetting of ink, but there was clear variation of jetting speed in each nozzle (Figure 2b).[17] While prepared *GO ink* is not ideal compared with a commercial ink which shows both straight and constant jetting of ink (Figure 2c), patterning of GO was successfully demonstrated in submillimeter scale through ink-jet printing (Figure 2d). In FE-SEM images of ink-printed GO lines, most GO plates in initially printed line percolate with each other, which is confirmed by observing current passage along the line after reduction. But some part of the GO line in delayed ink-

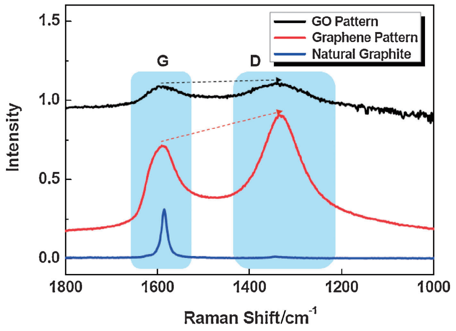

Figure 3. Raman spectra of GO pattern, graphene pattern, and pristine graphite powder.

jet printing was not percolated probably due to the formation of significant amount of clogs in the nozzle and subsequent dilution of GO in the ink. The discontinuous region in GO line showed some bigger GO aggregates more than 8 µm, which is possibly a clog detached from the nozzle head. These GO aggregates were also observed in the FE-SEM images of GO layers on PET film and glass slide (Figure 1d). Another possibility for this GO aggregate is the self-aggregation of GO plates on solvent drying after ink-jetting. We controlled surface temperature of substrates to enhance water evaporation, but it did not decrease the amount of GO aggregates. Therefore, we suppose that the origin of the clog formation on the graphene pattern comes from the formation and detaching of GO clogs on the inner membrane filter inside of ink-jet nozzle. Using *fragmented GO ink* after extensive sonication showed less clog formation compared with *original GO ink* without sonication.

Then, patterned GO lines were chemically reduced to RGO lines by reduction with hydrazine vapor at 80 °C for 24 h. The sheet resistance of prepared graphene lines was dependent on the number of printing. While multiple ink-jet printing increases height and thickness of RGO lines, this will also recover percolation between neighboring RGO plates. Graphene lines (thickness of 50 nm) after five times of printing showed sheet resistance around $1.8 \times 10^7\ \Omega$/sg. Because carbon nanotube can show certain anisotropic conductivity due to its anisotropic 1D structure such as liquid-crystalline structures, anisotroptic sheet resistance of patterned graphene lines was examined in the parallel or vertical direction to the printed grahene lines. Parallel or vertical measurement of sheet resistance was almost identical within an error range ($\pm 0.3 \times 10^7\ \Omega$/sg), revealing that 2D graphene could not form any anisotropic morphology in the ink-jet printing process. The calculated conductivity of RGO line is $1.1\ \mathrm{S\,m^{-1}}$, which is a fifth of the conductivity of RGO film which is obtained by reduction of spin-coated GO film using hydrazine vapor.[18] Decreased conductivity of RGO lines compared with RGO films might result from the decreased percolation of graphene plates in ink-jet printed RGO lines compared with typical spin-coated RGO film. The detailed structural and compositional features of prepared RGO pattern were characterized by Raman spectroscopy (Figure 3). While the pristine graphite does not show any D peak around $1350\ \mathrm{cm^{-1}}$, both GO pattern and graphene pattern showed evident G and D peaks around 1580 and $1350\ \mathrm{cm^{-1}}$, which show the presence of disorder which results from exfoliated plate structure. The increased intensity ratio of D and G peaks, I(D)/I(G) is much higher in graphene pattern (1.29) than GO pattern (1.05), which confirms the reduction to graphene pattern from GO pattern by hydrazine vapor is almost completed.[19]

In summary, facile ink-jet printing of *GO ink* was demonstrated through size control of GO plate by ultrasonication. While this *GO ink* is not comparable with other commercial ink, patterned GO lines were successfully ink-jet printed on substrates in submillimeter scale. Further chemical reduction of prepared GO lines effectively produced conducting RGO lines with conductivity of $1.1\ \mathrm{S\,m^{-1}}$.

This research was financially supported by the Ministry of Education, Science Technology (MEST) of Korea through the Human Resource Training Project for Regional Innovation and the Regional Innovation Center (RIC) Program conducted by the Ministry of Knowledge Economy of the Korean Government. We also specially thank Ms. Hee Won Seo in Research Support Team (KAIST, Central Research Instrumental Facility) for kind help with Raman experiments.

References and Notes

1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
2 D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* **2007**, *448*, 457.
3 A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
4 J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718.
5 M. Freitag, *Nat. Nanotechnol.* **2008**, *3*, 455.
6 M. A. Meitl, Z.-T. Zhu, V. Kumar, K. J. Lee, X. Feng, Y. Y. Huang, I. Adesida, R. G. Nuzzo, J. A. Rogers, *Nat. Mater.* **2006**, *5*, 33.
7 J.-H. Chen, M. Ishigami, C. Jang, D. R. Hines, M. S. Fuhrer, E. D. Williams, *Adv. Mater.* **2007**, *19*, 3623.
8 X. Liang, Z. Fu, S. Y. Chou, *Nano Lett.* **2007**, *7*, 3840.
9 K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706.
10 Q. He, H. G. Sudibya, Z. Yin, S. Wu, H. Li, F. Boey, W. Huang, P. Chen, H. Zhang, *ACS Nano* **2010**, *4*, 3201.
11 V. Dua, S. P. Surwade, S. Ammu, S. R. Agnihotra, S. Jain, K. E. Roberts, S. Park, R. S. Ruoff, S. K. Manohar, *Angew. Chem., Int. Ed.* **2010**, *49*, 2154.
12 S. Watcharotone, D. A. Dikin, S. Stankovich, R. Piner, I. Jung, G. H. B. Dommett, G. Evmenenko, S.-E. Wu, S.-F. Chen, C.-P. Liu, S. T. Nguyen, R. S. Ruoff, *Nano Lett.* **2007**, *7*, 1888.
13 S. Gilje, S. Han, M. Wang, K. L. Wang, R. B. Kaner, *Nano Lett.* **2007**, *7*, 3394.
14 H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, Y. Chen, *ACS Nano* **2008**, *2*, 463.
15 G. Eda, M. Chhowalla, *Nano Lett.* **2009**, *9*, 814.
16 S. Yoon, I. In, *Chem. Lett.* **2010**, *39*, 1160.
17 All ink-jet printing was performed by using Dimatix Materials Printer DMP-2800 of Dimatix, Inc. Initial printing condition: cartridge temperature of 28 °C and voltage of 40 V. Optimized printing condition: cartridge temperature of 30 °C voltage of 31 V, purge time of 10 s. 20 nozzles with diametier of 23 µm eject ink with volume of 10 pL.
18 G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **2008**, *3*, 270.
19 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007**, *45*, 1558.