Journal Name RSCPublishing

COMMUNICATION

3D scaffold for ultra-sensitive reduced graphene oxide gas sensor

Cite this: DOI: 10.1039/x0xx00000x

Yong Ju Yun,[a] Won G. Hong,[b] Nak-Jin Choi,[a] Hyung Ju Park,[a] Seung Eon Moon, [a] Byung Hoon Kim, [c] Ki-Bong Song, [a] Yongseok Jun,[d] and Hyung-Kun Lee[*a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

An ultra-sensitive gas sensor based on a reduced graphene oxide nanofiber mat was successfully fabricated using a combination of an electrospinning method and graphene oxide wrapping through an electrostatic self-assembly, followed by a low-temperature chemical reduction. The sensor showed excellent sensitivity to NO_2 gas.

The fabrication of ultrasensitive gas sensors is critically important in various areas including semiconducting industries, chemical and material industries, medical welfare, and military defense.[1] A wide variety of nanostructured materials such as silicon nanowires, carbon nanotubes, various metal oxide nanofibers and nanoparticles have been explored to fabricate ultrasensitive gas sensors.[2-6]

More recently, graphene, a single atomic planar sheet of carbon atoms that are densely packed into a honeycomb crystal lattice, has been greatly attracted owing to its exceptional structural, mechanical, and electrical properties.[7] Since every atom of graphene can be considered as a surface atoms, a graphene is capable of interacting with even a single molecule. This gives graphene ultra-sensitive gas sensing property.[8] Various types of graphene and chemically derived graphene have been used to fabricate gas and vapor sensors.[9] Among them, the reduced graphene oxide (RGO) based gas sensor has become a promising candidate for chemical sensing because of easy control of defect density and functional group on graphene, and large scale production at a relatively low cost.[10-17]

Despite these advantages, the low response of a sensor consisting of RGOs have to be improved to compete with conventional sensors include semi-conductive metal oxides applied in practical applications.[18-21] Researchers have developed nano-structured materials such as graphene-based woven fabric,[22] a 3-dimensional (3D) graphene foam network,[23] and a graphene nanomesh[24] to overcome the low response of graphene-based gas sensors. Such studies have demonstrated that the design or tailoring of the RGO with nanostructures is an important factor for the development of ultra-sensitive sensors. In this communication, we present a new 3D nanostructured RGO scaffold for ultrasensitive RGO gas sensor using an electrostatic self-assembly between graphene oxides (GOs) and electro-spun nanofibers, followed by reduction at room temperature. It demonstrates that the wrapping of interwoven electrospun nanofibers using molecular sheets of GO is a viable approach toward the fabrication of a graphene-based ultra-sensitive gas sensors. These sensors show a 3.5 times stronger response toward NO_2 gas than the RGO film based sensor.

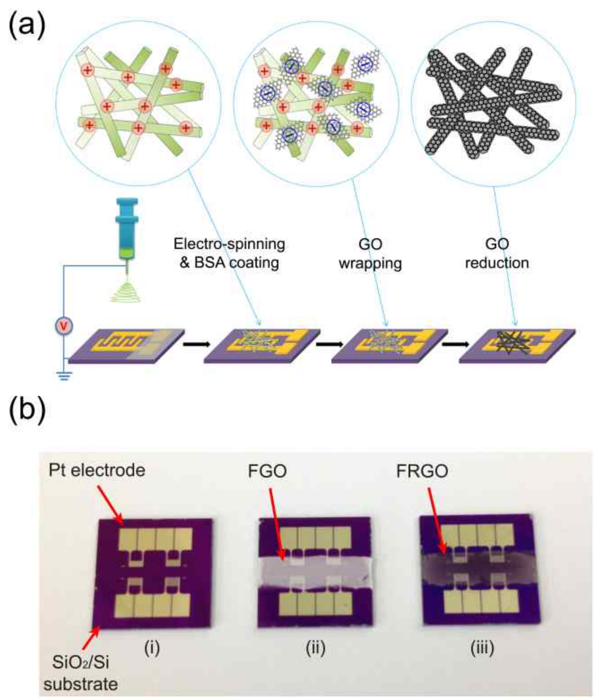


Fig. 1 (a) Schematic illustration of the fabrication steps of FRGO gas sensors. (b) Optical images of bare device (i), GO/Nylon-6 device, FGO (ii), and gas sensing device based on reduced GO/Nylon-6, FRGO (iii).

The scheme in Fig. 1 illustrates the procedure used to fabricate a RGO gas sensor based on a 3D scaffold. We used an electrospinning method to produce a nylon-6 nanofiber scaffold, which is one of the simplest, versatile, and low-cost methods for producing fibers of organic and inorganic materials.[25] First, nylon-6 solution is directly electro-spun onto SiO_2/Si substrate with platinum (Pt) interdigitated electrode (IDE) arrays (Fig. 1(b)(i) and Fig. S1). The device was carefully masked with Kapton tape such that a blank space of 10 mm x 3 mm was made available for the deposition of the electro-spun polymer nanofibers. Second, the electro-spun nylon-6 fiber mats were functionalized using bovine serum albumin (BSA) molecules which induced positive charges on the surface of the nanofibers. Herein, BSA molecules served as a molecular glue for improving the adsorption of the GO sheets into the electro-spun nanofibers.[26-29] To form a GO network (FGO) based on interwoven fibers, GO suspension (0.1 mg/ml, pH 4) was dropped onto a BSA-functionalized nylon-6 nanofiber mat placed on the IDEs (Fig. 1(b)(ii)). The GO sheets are highly negative charged at all pH ranges.[29] Therefore, a uniform coating of GO sheets was formed on the positively charged BSA-functionalized nylon-6 nanofibers via electrostatic self-assembly. Finally, GO/Nylon-6 nanofiber mats were reduced using a low-temperature chemical reduction method.[30] As a result, highly sensitive RGO gas sensors fabricated on electro-spun nanofibers (FRGO) were obtained. (Fig. 1(b)(iii)) Further details on the preparation of the RGO gas sensors are provided in the supporting Information.

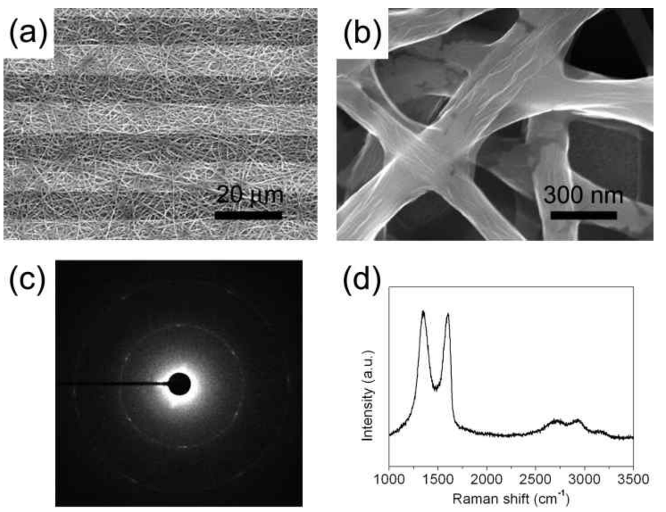


Fig. 2 (a) SEM image of RGO nanofibers on Pt IDE for gas sensing (scale bar = 20 μm). (b) Magnification of Fig. 2(a) (scale bar = 300 nm). (c) SAED pattern of an edge of a RGO nanofiber. (d) Raman spectrum of a RGO fiber.

The thickness of the as-synthesized GO sheets was measured as 0.9 to 1.1 nm with an average lateral size of 350 ± 50 nm by atomic force microscopy (AFM) (Fig. S2); these values are in agreement with those of the GO monolayers.[30-32] A scanning electron microscope (SEM) image of the FRGO on the IDEs shows that the sensor has a porous interwoven structure composed of randomly oriented nanofibers with a diameter of 150 ~ 200 nm (Fig. 2(a)), and is free of impurities and supporting materials. The conformal wrapping of RGO sheets on the nylon-6 fibers was also confirmed through high-resolution SEM (HRSEM), as shown in Fig. 2(b). The RGO sheets were uniformly coated onto the nylon-6 fibers and junctions between fibers, providing continuous conducting pathways. The selected-area electron diffraction (SAED) pattern of the RGO on the nanofiber was similar to that of the RGO film on a flat substrate, suggesting that the outer coatings of the nanofibers are composed of a few layers of RGO (Fig. 2(c) and Fig. S3). The Raman spectrum of the FRGO on the IDEs shows a *D* band at 1350 cm^{-1}, a *G* band at 1584 cm^{-1}, a 2*D* band at ~2700 cm^{-1}, and an *S*3 peak at ~ 2930 cm^{-1} (Fig. 2(d)). The spectrum shows that the ratio of the *D* and *G* bands is well matched with that of the RGO, and is consistent with the previous report for chemically converted graphene.[30]

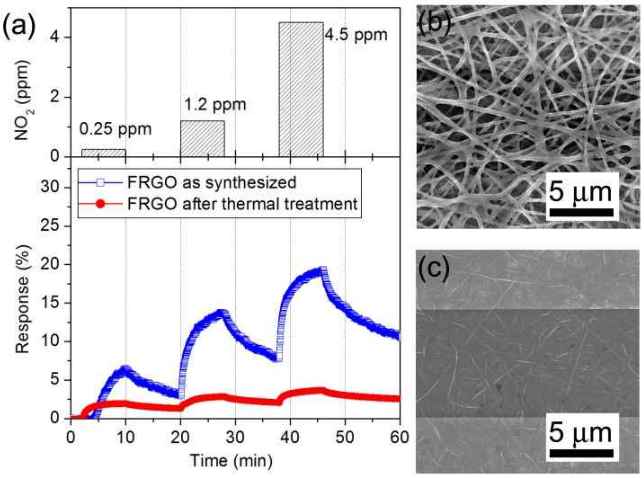


Fig. 3 (a) Gas responses of the devices consisting of FRGO as synthesized (blue line) and FRGO after thermal treatment at 300°C (red line). SEM images of (b) FRGO as synthesized and (c) FRGO after thermal treatment at 300°C.

The sensor devices were exposed to dry air as a balance gas of 1000 cc/min at 100°C, and the resistance changes were measured to investigate the gas responses of the devices by an HP 34970A data acquisition system and BenchLink Data Logger 3 (Fig. S4). An analyte, NO_2 gas, was mixed with a balance gas to achieve a concentration of 0.25 to 4.5 ppm (Fig. 3(a)). The resistances of the devices were decreased upon exposure to NO_2 gas. The FRGO gas sensor shows a 7% response at 0.25 ppm of NO_2 gas, which is significant compared with the 2% response at the same NO_2 concentration of RGO prepared using a spin-coating on a flat substrate without a 3D scaffold composed of electro-spun nanofibers (Fig. 4). These significantly increased responses are expected to result from the high surface-to-volume ratio of porous electro-spun nanofibers, which act as templates for effective wrapping. To prove the contribution of the high surface-to-volume ratio to the increased sensitivity of the FRGO sensor, a device consisting of FRGO was thermally treated at 300°C at which the nylon-6 nanofibers wrapped with RGOs melt away. After thermal treatment at 300°C, the morphology of the device with the FRGOs was changed into a flat surface without chemical change in the RGO, as confirmed by Raman spectroscopy (Fig. S5), and the device's response to NO_2 gas was 2% at a NO_2 concentration of 0.25 ppm (Fig. 3(a), Fig 4). Furthermore we also compared the response of spin-coated rGO on flat surface and found that the morphology of the scaffold for RGO is crucial for strong response (Fig. S6). The morphological change of the sample from a porous interwoven structure into a flattened structure caused a decrease in the surface-to-volume ratio of the sensing material (Fig. 3(b) and 3(c)). The surface area of FRGO can be approximately π(~3.14) times higher than that of flatten fiber, which makes enhanced adsorption of gas molecules and sensing reaction of reduced graphene oxides.[33] increased gas response of FRGO having the 3D nanostructure resulting from interwoven nanofibers is well-matched with the previous reports such as a hollow ZnO nanofiber network fabricated from electro-spun fibers and a macroporous TiO_2 from colloidal templates as sacrificial templates.[34-36]

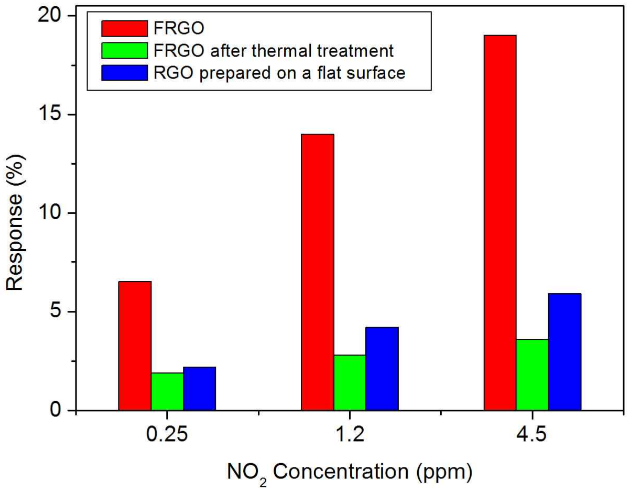


Fig. 4. Comparison of gas response depending on graphene-based gas sensor devices.

Conclusions

In summary, we presented an ultra-sensitive gas sensor composed of a nanofiber mat prepared by electro-spinning and wrapping with RGO through an electrostatic self-assembly. It demonstrated that porous interwoven nanofibers can be used as an efficient 3D scaffold of graphene-related materials for the preparation of ultra-sensitive gas sensors due to the increased surface-to-volume ratio and the introduction of a junction between nanofibers. This method for wrapping nanowires and nanofibers with graphene-related materials as molecular sheets can be useful for the fabrication of 3D heterogeneous functional nanostructures composed of graphene-related and organic/inorganic nanowires or nanofibers through various noncovalent chemical modification methods for reduced graphene oxide.[37-39] Furthermore, this approach can be extended to the preparation of a flexible gas sensor by combining electrospinning on a plastic substrate with the simple GO wrapping technique. We are conducting along this line.

Notes and references

[a] *Electronics & Telecommunications Research Institutes (ETRI), 218 Gajeongno, Yuseong-gu, Daejeon, South Korea. Fax: 82 42 860 5608; Tel: 82 42 860 5857; E-mail: hklee@etri.re.kr*
[b] *Division of Material Science, Korea Basic Science Institute (KBSI), 52 Yuseong-gu, Daejeon, Republic of Korea.;E-mail: hongwg79@kbsi.re.kr.*
[c] *Department of Physics, Incheon National University, Incheon 406-840, Republic of Korea. Tel: 82 32835 8229; E-mail: kbh37@incheon.ac.kr*
[d] *Department of Materials Chemistry and Engineering, Konkuk University, Seoul 143-701, Republic of Korea.Tel:82 2 450 0440; E-mail:yjun@konkuk.ac.kr*

† The gas response of the sensor is defined as follows:

$$\text{Response (\%)} = (R_a\text{-}R_g)/R_a \text{ x100}$$

where R_a is the resistance of the sensor upon exposure to air and R_g is the resistance of the sensor upon exposure to NO_2 gas. We observed the increased response of reduced graphene sensor by increasing the measurement temperature. The response of the sensor became double by increasing measurement temperature from 25°C to 100°C, which is summarized in Fig. S7.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/kbh

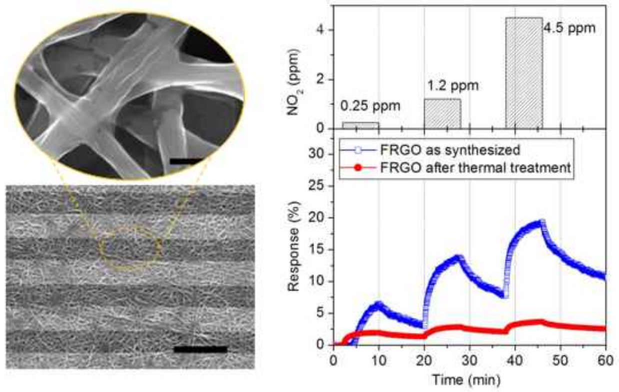
Acknowledgment

This research was supported by the Converging Research Center Program funded by the Ministry of Education, Science and Technology (2013K000367), the New & Renewable Energy Core Technology Program of the KETEP (No.20133030000140) and the IT R&D program of MOTIE/KEIT (10035570, Development of self-powered smart sensor node platform for smart & green building).

1. G. Korotcenkov, Handbook of Gas Sensor Materials, Springer, New York, London, 2013.
2. M. C. Mcalpine, H. Ahmad, D. Wang, J. R. Heath, *Nat Mater.,* 2007, **6**, 379-384.
3. J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science,* 2000, **287**, 622-625.
4. J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, M. Meyyappan, *Nano Lett.,* 2003, **3**, 929-933.
5. I. D. Kim, A. Rothschild, *Polymers advanced technologies,* 2011, **22**, 318-325.
6. J.-H. Lee, *Sens. Actuators, B: Chemical,* 2009, **140**, 319-336.
7. A. K. Geim, K. S. Novoselov, *Nat Mater*., 2007, **6**, 183-191.
8. F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, *Nat Mater*., 2007, **6**, 652-655.
9. F. Yavari, N. Koratkar, *J. Phys. Chem. Lett.,* 2012, **3**, 1746-1753.
10. J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, P. E. Sheehan, *Nano Lett*, 2008, **8**, 3137–3140.
11. J. D. Fowler, M. J. Allen, V. C. Tung, Y. Yang, R. B. Kaner, B. H. Weiller, *ACS Nano*, 2009, **3**, 301-306.
12. 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**, 2154-2157.
13. W. Li, X. Geng, Y. Guo, J. Rong, Y. Gong, L. Wu, X. Zhang, P. Li, J. Xu, G. Cheng, M. Sun, L. Liu, *ACS Nano*, 2011, **5**, 6955-6961.

14. G. Lu, S. Park, K. Yu, R. S. Ruoff, L. E. Ocola, D. Rosenmann, *ACS Nano*, 2011, **5**, 1154-1164.
15. 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**, 2154-2157.
16. W. Yuan, A. Liu, L. Huang, C. Li, G. Shi, *Adv. Mater.*, 2012, **25**, 766-771.
17. A. Lipatov, A. Varezhnikov, P. Wilson, V. Sysoev, A. Kolmakov and A. Sinitskii, *Nanoscale*, 2013, **5**, 5426-5434.
18. N. J. Choi, H.-K. Lee, S. E. Moon, W. S. Yang, *Sens. Actuators, B: Chemical*, 2012, **175**, 132-136.
19. H.-K. Lee, W. S. Yang, N. J. Choi, S. E. Moon, *ETRI Journal*, 2012, **34**, 713-718.
20. S. E. Moon, H. Y. Lee, J. Park, J. W. Lee, N. J. Choi, S. J. Park, J. H. Kwak, K. H. Park, J. Kim, G. H. Cho, T. H. Lee, S. Maeng, F. Udrea, W. I. Milne, *J. Nanosci. Nanotechnol.*, 2010, **10**, 3189-3192.
21. S. E. Moon, H.-K. Lee, N. J. Choi, J. Lee, W. S. Yang, J. Kim, J. J. Jong, D. J. Yoo, *J. Nanosci. Nanotechnol.*, 2012, **12**, 5543-5546.
22. X. Li, P. Sun, L. Fan, M. Zhu, K. Wang, M. Zhong, J. Wei, D. Wu, Y. Cheng, H. Zhu, *Sci. Rep.*, 2012, **2**, 395.
23. C. Li and G. Shi, *Nanoscale*, 2012, **4**, 5549-5563.
24. R. K. Paul, S. Badhulika, N. M. Saucedo, A. Mulchandani, *Anal. Chem.*, 2012, **84**, 8171-8178.
25. A. Greiner, J. H. Wendorff, *Angew. Chem. Int. Ed.*, 2007, **46**, 5670-5703.
26. M. Rabe, D. Verdes, S. Seeger, *Adv. Colloid Interface Sci.*, 2011, **162**, 87-106.
27. A. A. Shemetov, I. Nabiev, A. Sukhanova, *ACS Nano*, 2012, **6**, 4585-4602.
28. J. Liu, S. Fu, B. Yuan, Y. Li, Z. Deng, *J. Am. Chem. Soc.*, 2010, **132**, 7279-7281.
29. Y. J. Yun, W. G. Hong, W.-J. Kim, Y. Jun, B. H. Kim, *Adv. Mater.*, 2013, **40**, 5701-5705.
30. I. K. Moon, J. Lee, R. S. Ruoff, H. Lee, *Nat Commun.*, 2010, **1**, 73.
31. D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat Nano.*, 2008, **3**, 101-105.
32. K. P. Loh, Q. Bao, G. Eda, M. Chhowalla, *Nat. Chem.*, 2010, **2**, 1015-1024.
33. S. J. Choi, I. Lee, B. H. Jang, D. Y. Youn, W. H. Rye, C. O. Park, I. D. Kim, *Anal. Chem.*, 2013, **85**, 1792-1796.
34. H. G. Moon, Y.-S. Shim, H. W. Jang, J.-S. Kim, K. J. Choi, C.-Y. Kang, J.-W. Choi, H.-H. Park and S.-J. Yoon, *Sens. Actuators B: Chemical*, 2010, **149**, 116-121.
35. S. H. Choi, G. Ankonina, D. Y. Youn, S. G. Oh, J. M. Hong, A. Rothschild, I. D. Kim, *ACS Nano*, 2009, **3**, 2623-2631.
36. A. Rothschild, H. Tuller, *J.Electroceram.*, 2006, **17**, 1005-1012.
37. H. C. Cheng, R. J. Shiue, C. C. Tsai, W. H. Wang and Y. T. Chen, *ACS Nano*, 2011, **5**, 2051-2059.
38. V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.* 2012, **112**, 6158-6214.
39. J. Lee, E. Hwang, E. Lee, S. Seo and H. Lee, *Chem. Eur. J.* 2012, **18**, 5155-5159.

TOC graph



Ultra-sensitive RGO gas sensors with a facile preparation method are presented. The gas sensor composed of RGO nanofiber showed excellent sensitivity to NO_2 gas.