Review on Fabrication of Graphene Nanoholes

P. A. Silpa,[†] N. M. Sivamangai

Department of Electronics and Communication, Karunya Institute of Science and Technology, Coimbatore, India

[†] Corresponding author: silpapulickal@gmail.com

Received: 31 December, 2018; Accepted: 3 February, 2019; Published: 28 February, 2019

Graphene, an ultra-thin derivative of carbon, has hindered a lot of applications because of its unique characteristics. It was found that superb improvements on properties can be made on further by creating nanopores or nanoholes on the surface of the graphene film. Such holed graphene can be used in energy storage, fuel cells, bio-sensors, biochemical applications, plasmonic tweezers, etc. This is because pores can contribute toward more surface area and eventually toward transportation and storage for electron/ion, gas, and liquid. This paper is a review of graphene nanohole fabrication methods.

Keywords Graphene nanoholes; Graphene nanomesh; Electron beam lithography; Nano imprint lithography; Block copolymer

I. INTRODUCTION

Graphene is having very fascinating properties. Its unique conductivity, mechanical strength, and numerous other properties drew the attention of researchers. It was found that the surface area of graphene can be increased with holes. Such graphene nanoholes find a wide variety of applications in various disciplines. Porous graphene is used as an atmospheric filter with high selectivity in favor of H₂ and He as reported by Blankenburg *et al.* [1]. Magnetic nanostructures are designed with patterned nanoholes [2, 3]. Nanohole graphene structures can drastically improve the capacitance. Actually, super capacitor concepts come into reality because of these holey graphenes [4, 5]. When coming to the optics applications, electron lenses were designed using porous graphene sheet [6, 7] and also it is already found that graphene nanoholes can induce plasmonics mechanism. Recently, many nanohole arrays were fabricated to couple surface plasmons successfully motivated by intense study of light in holes. In Ref. [6], they find unexpected optical properties especially enhanced transmission when the hole size is less than sub-wavelength. It is also found that each hole will act as a source of excitation. The shape and dimension also affect the transmission spectrum, and the isolated holes also can contribute to the surface plasmonics spectrum. Graphene nanohole based tweezers are developed and reported in Refs. [8, 9]. Flexible conductors have been developed by using

nanohole arrays. When coming to the discussion of bioapplication, deoxyribonucleic acid (DNA) translocation through nanoholes has been achieved [10]. Biosensing and biofuel applications have been developed [11]. Graphene nanohole based electrocatalysts have been developed [12]. Tetrahertz polarizer is reported in Ref. [13]. It is found that nanoholed graphene can act as a ferromagnetic semiconductor.

Graphene nanomesh (GNM) is reported in Ref. [14], which is a highly interconnected form of nanomesh with holes in it and was used to replace channel in graphene field effect transistor. It is found that the change in radius which leads to increase in the band gap is the reason behind the large on/off ratio of nanomesh made up transistor. In Ref. [15], such transistor was also reported and found that it was having a high optical response. Various parameters such as a center-to-center distance (periodicity) and the smallest edge-to-edge distance (neck width) have been defined in Ref. [16] for designing nanomesh.

Graphene nanoholes were studied using a lot of different theoretical approaches such as density functional theory [17, 18]. In Ref. [19], mechanical properties of graphene nanoholes are investigated by molecular dynamic (MD) solutions, and it is found that the holes have a negligible effect on Young's modulus of graphene. In Ref. [20], it is found that porous graphene is a direct band gap semiconductor with a band gap of 2.35 eV. Effect of sp carbon chains on nanohole

Figure 1: Graphene nanomesh using block copolymer technology. (a) Graphene flake on the top of substrate. (b) Graphene is covered by a thin film of SiO_2 and a thin film of spin-coated block copolymer. (c) Formation of porous matrix as a template. (d) Reactive etching for forming hard mask. (e) Graphene is etched away. (f) Chemical etching using HF to remove oxide mask. (g) Etching the substrate to obtain free-standing graphene. Adapted from Ref. [16].

is studied [21]. Surface-enhanced Raman scattering is a good technique to study the hole structure experimentally [22–24]. Band structures in the presence of nanoholes have been studied with atomic modeling [25]. Magnetic behaviors of nanoholes are detailed using extensive first principle calculations [26].

Stabilization of graphene nanopore is one issue. It was found that graphene nanoholes healed itself automatically at a high temperature in the presence of a carbon source. But this healing can be prevented by stabilizing it with edge techniques [27, 28].

II. FABRICATION METHODS

In Refs. [14, 16, 29], GNM was manufactured using block copolymer lithography technology and the neck width was controlled using over-etching and block copolymers having different molecular weights. In Figure 1, block polymer technology is illustrated. It consists of mainly two steps preparing block copolymer template and formation of graphene nanomesh. The process starts with depositing graphene into silicon followed by a SiO_x deposition. This oxide was functionalized with polystyrene-*r*-methyl methacrylate [P(S-*r*-MMA)] random copolymer. This film was annealed to anchor oxide after that rinsed with toluene to remove unanchored polymer and a polymethyl methacrylate (PMMA) deposition was done followed by spinning and annealing. After that with ultraviolet (UV) radiation, PMMA removal was done. A reactive ion etching was done to re-

Figure 2: Fabrication sequence: (i) CVD graphene is transferring. (ii) Covering up with silicon oxide and spherical block copolymer. (iii) Removing the spheres. (iv) Oxygen plasma is used to etch polystyrene nanomask. (v) Etching with fluorine based plasma. (vi) HF dip to remove remaining plasma. Adapted from Ref. [30].

move the exposed film randomly. The prepared nanomesh was used for making the GNM transistors and it is found that the performance was improved when compared with the GNR transistor

In Ref. [30], a block copolymer method was also discussed by using spherical block copolymer (s-BCP). At first, graphene covered with electron beam evaporated silicon dioxide (SiO_x). After that, poly-BCP is spin-cast on the top. The PMMA spheres segregate on the top in hexagonal order. Then PMMA spheres are removed using UV exposure and acetic bath leading to nanoporous polyester film. Reaction ion etching (RIE) was used to etch remaining polystyrene layer. It will serve as a nanomask. The SiO_x layer is etched using a plasma of CH_3/CF_4 . After this, an oxygen plasma removes remaining BCP and etches graphene through holes. Afterward a dip in HF solution removes the residual SiO_x . The sequence is shown in Figure 2. The manufactured structure was successfully used for ultra-sensitive gas sensor.

In another discussion [31], GNM was synthesized with a different approach. The first three-dimensional (3D) graphene gel was produced by hydrothermal treatment of graphene oxide (GO). The gel was immersed into an aqueous solution to form a poly-pyrrole/graphene composite with encapsulated FeCl_3 residues. At high temperatures, N atoms were doped. At this time, the remaining FeCl_3 was converted into Fe_2O_3 nanoparticles which can etch graphene basal planes to form nanoporous GNM.

In another method [15], chemical vapor deposition (CVD) grown graphene layer transferred to Si/ SiO_2 substrate and electron beam lithography is used to drill the holes. This also used for making high on/off transistor.

Helium and gallium ion milling methods of different materials are discussed in Ref. [32], and it was found that helium can drill small holes. The milling process was modeled using Stopping and Range of Ions in Matter (SRIM) software. Fabrication of nanohole drilling with using ion im-

Figure 3: The fabrication sequence of porous graphene. Adapted from Ref. [36].

Figure 4: Illustration of a macroporous bubble graphene film formation. Adapted from Ref. [37].

Figure 5: Illustration of the procedure for obtaining macroporous graphene. Adapted from Ref. [39].

plantation was studied using MD simulations and find that Au ions can form accurate nanoholes on graphene sheet [33].

In Ref. [34], large area gate tunable graphene nanoholes with operating range in mid IR wavelength was developed for plasmonics applications. The nanohole array was fabricated using electron beam lithography (EBL). It is found that only limited control over the structure was there and hexagonal lattice was obtained. In the EBL method, double side polished silicon substrate with silicon dioxide was used as the substrate. Graphene made through CVD was transferred to Si/SiO₂ substrate. An electron resist was spin coated. Using CRESTEC 50 keV electron beam lithography system, holes were exposed to different aspect ratios. A resist has been developed and nanoholes were etched using RIE. The resist was then removed. In a nanoimprint lithography (NIL) method, a silicon substrate with a native dry oxide having metal contacts (chrome and gold) was used. The chip was spin coated, baked and thermally imprinted using CNiV2 (NIL Technology). The pattern used was the same as that of the EBL. The chip was subjected to plasma to remove the residual resist and etch the graphene. The remaining resist was removed by annealing.

Nanoimprint lithography was discussed also in Ref. [35]. The fabricated structure was used for optical purposes and it is found that light transmittance improved a lot.

In Ref. [36], nanomesh was formed on the insulating substrate. A beginning anodic aluminum oxide (AAO) template

was fixed on an optical glass with adhesive thermal tapes. A thin film of Au was deposited on this using sputtering followed by PMMA spin coating. An Ag film was deposited further for avoiding wrinkles. Thermal tapes were pulled out. The AAO was dissolved using NaOH. After rinsing with deionized water. It was scooped with Si/SiO₂ and dried in an oven. To dissolve residual PMMA wafer was dipped in acetone. Samples were inserted into CVD chamber under H₂ gases. The procedure is as shown in Figure 3.

As shown in Figure 4, a bubble graphene film was explored for supercapacitor [37]. PMMA latex spheres were used as hard templates. The GO hydrosol was mixed with a PMMA suspension. Vacuum filtration was then conducted. A composite film was then peeled off and dried to remove the PMMA templates.

In another method [38], gold nanoparticle (AuNp) embedded porous graphene was prepared for electrochemical sensing. In this 3D AuNp porous graphene film by electrostatic layer bilayer assembly of bis(trimethylsilyl) acetamide (BSA) functionalized graphene nanosheets and AuNps with thermal annealing. A good improvement in sensitivity was observed.

In Ref. [39], 3D microporous graphene framework for the application of super capacitors was discussed. A mixture of chemically modified graphene and polystyrene suspension was dispersed in solution under controlled pH. When pH was raised to 6 and polystyrene spheres were assembled due to electrostatic interactions and hydrophobic characteristics.

Figure 6: Steps for illustrating the mechanism for the chemical conversion from porous carbon to 3D graphene. Adapted from Ref. [40].

These were integrated into graphene/polystyrene films as shown in Figure 5.

3D graphene electrodes were fabricated with a hole size of 500 nm [40]. These exhibit superior electrochemical behavior. The steps are as shown in Figure 6. 3D amorphous carbon structures are sputtered with nickel and annealed which converts the material into 3D graphitic monoliths. Acidic etching removes the excess nickel leaving the hollow structure

Graphene based porous flexible architectures are described in Ref. [41] through self-assembly techniques. Hydrothermal reduction of GO dispersion can produce a mechanically strong hydrogel. This hydrogel can be converted into aerogel by freezing. A cork-like graphene microporous structure will obtain. The entire process is as shown in Figure 7. A similar process for producing carbon nanosheets are described in Ref. [42].

Size tunable nanopores are discussed in Ref. [43]. The structure was fluorinated and the nanopores are drilled using fast ion beam/electron beam (FIB/EB) drilling. It is found

Figure 7: Schematic illustration of the preparation of graphene monolith. Adapted from Ref. [41].

Figure 8: Fabrication of nanohole-structured with palladium-embedded 3D porous graphene (3D Pd-E-PG). Step 1 shows microwave exfoliate graphene oxide (MEGO). It is then mixed with palladium acetate and ethanol to make a catalyst. In Step 2, MEGO A and palladium acetate is mixed with C_2H_5OH for 3 h with the help of magnetic stirring. In Step 3, microwave irradiation for a long time. Adapted from Ref. [44].

that the size can be varied precisely using this technique.

Palladium embedded nanoporous graphene (3D Pd-E-PG) is synthesized through microwave irradiation method. It works directly by coupling with polar molecules in a material which causes the particle to move and rotate [44]. The details are given in Figure 8. This structure can be used in various applications such as catalytic engineering, molecule trapping, and energy storage.

A way of making porous graphene by chipping quantum dots is illustrated in Ref. [45]. The process flow is shown in Figure 9. It is achieved by etching of graphene by hydrogen

Figure 9: The process involved in the conversion of graphene to graphene quantum dots and porous graphene. Adapted from Ref. [45].

Figure 10: Schematic diagram of an illustration of porous graphene nanosheet formation. Adapted from Ref. [46].

peroxide, which causes chipping of flakes in nanometer sizes resulting in the formation of graphene quantum dots (GQD) and porous graphene simultaneously.

Thermoplastic phenolic-formaldehyde resin and copper nitrate were mixed in the presence of a curing agent. The mixture was solidified and carbonized to get copper embedded nanosheets. It was further treated by hydrogen peroxide and hydrochloric acid to remove Cu nanoparticles. Vacuum filtering and drying were carried out. Thereafter graphitization was carried out to obtain nanoporous graphene sheets [46]. The procedure is illustrated in Figure 10.

A different study of photoreduction of graphene sheet to form graphene nanosheets was discussed in Ref. [47]. The TiO_2 particles and UV radiation were used for reduction. In Ref. [48], plasma etching is carried out to produce zigzag graphene edges. This can be extended to drill holes on the surface of graphene.

III. CONCLUSIONS

A number of methods have been developed to fabricate graphene nanoholes with different properties. Still, the size

control and volume control are challenging. When considering single volume graphene, not much success stories are reported. 3D graphene nanoholes are more discussed in the literature. Since they are used for biosensing where the pore structure needs to be more accurate, we need good control over the size and volume of nanoholes. The doping of graphene changes the conductivity. So using doping we can improve the sensitivity of electrochemical sensors. But more research is needed on this topic. Also, optical properties and plasmonics effects of holes need much more attention. Stabilization is another issue that requires further studies.

References

- [1] S. Blankenburg, M. Bieri, R. Fasel, K. Müllen, C. A. Pignedoli, and D. Passerone, *Small* **6**, 2266 (2010).
- [2] X. Cui, R. Zheng, Z. Liu, L. Li, B. Delley, C. Stampfl, and S. Ringer, *Phys. Rev. B* **84**, 125410 (2011).
- [3] D. Yu, E. Lupton, H. Gao, C. Zhang, and F. Liu, *Nano Res.* **1**, 497 (2008).
- [4] X. Han, M. R. Funk, F. Shen, Y.-C. Chen, Y. Li, C. J. Campbell, J. Dai, X. Yang, J.-W. Kim, Y. Liao, J. W. Connell, V. Barone, Z. Chen, Y. Lin, and L. Hu, *ACS Nano* **8**, 8255 (2014).
- [5] M. Pumera, *Energy Environ. Sci.* **4**, 668 (2011).
- [6] L. Gerhard, E. Moyan, T. Balashov, I. Ozerov, M. Portail, H. Sahaf, L. Masson, W. Wulfhekel, and M. Hanbücken, *Appl. Phys. Lett.* **100**, 153106 (2012).
- [7] Y. Lin, Y. Liao, Z. Chen, and J. W. Connell, *Mater. Res. Lett.* **5**, 209 (2017).
- [8] J.-D. Kim and Y.-G. Lee, *Carbon* **103**, 281 (2016).
- [9] Y. Yuan, Y. Lin, B. Gu, N. Panwar, S. C. Tjin, J. Song, J. Qu, and K.-T. Yong, *Coord. Chem. Rev.* **339**, 138 (2017).
- [10] C. Merchant, *Biophys. J.* **100**, 521A (2011).
- [11] H.-J. Qiu, Y. Guan, P. Luo, and Y. Wang, *Biosens. Bioelectron.* **89**, 85 (2017).
- [12] X. Qiao, J. Jin, H. Fan, Y. Li, and S. Liao, *J. Mater. Chem. A* **5**, 12354 (2017).
- [13] S. M. Raees-Zadeh and S. Safavi-Naeini, *2015 IEEE International Symposium on Antennas and Propagation & USNC/URSI National Radio Science Meeting (Vancouver, 2015)* pp. 1640–1641.
- [14] Q. Guo, J. Zhang, Y. He, J. Kang, H. Qian, Y. Wang, and Z. Yu, *10th IEEE International Conference on Solid-State and Integrated Circuit Technology (Shanghai, 2010)*.
- [15] M. Dragoman, A. Dinescu, and D. Dragoman, *Nanotechnology* **28**, 015201 (2016).
- [16] J. Bai, X. Zhong, S. Jiang, Y. Huang, and X. Duan, *Nat. Nanotechnol.* **5**, 190 (2010).
- [17] S. Mehdi Aghaei and I. Calizo, *MRS Adv.* **1**, 1613 (2016).
- [18] H. Jippo, M. Ohfuchi, and C. Kaneta, *Phys. Rev. B* **84**, 075467 (2011).
- [19] A. L. Sellerio, A. Taloni, and S. Zapperi, *Phys. Rev. Appl.* **4**, 024011 (2015).
- [20] Y. Ding, Y. Wang, S. Shi, and W. Tang, *J. Phys. Chem. C* **115**, 5334 (2011).
- [21] I. E. Castelli, N. Ferri, G. Onida, and N. Manini, *J. Phys.: Condens. Matter* **24**, 104019 (2012).
- [22] Q. Hao, B. Wang, J. A. Bossard, B. Kiraly, Y. Zeng, I.-K. Chiang, L. Jensen, D. H. Werner, and T. J. Huang, *J. Phys. Chem. C* **116**, 7249 (2012).

- [23] J. Jiang, R. Pachter, T. Demeritte, P. C. Ray, A. E. Islam, B. Maruyama, and J. J. Boeckl, *J. Phys. Chem. C* **120**, 5371 (2016).
- [24] A. Mahigir, T.-W. Chang, A. Behnam, G. L. Liu, M. R. Gartia, and G. Veronis, *Sci. Rep.* **7**, 14044 (2017).
- [25] R. Sako, N. Hasegawa, H. Tsuchiya, and M. Ogawa, *2012 IEEE Silicon Nanoelectronics Workshop (SNW) (Honolulu, 2012)* pp. 1–2.
- [26] D. Yu, E. M. Lupton, M. Liu, W. Liu, and F. Liu, *Nano Res.* **1**, 56 (2008).
- [27] J. Lee, Z. Yang, W. Zhou, S. J. Pennycook, S. T. Pantelides, and M. F. Chisholm, *Proc. Natl. Acad. Sci. U.S.A.* **111**, 7522 (2014).
- [28] Y. Ito, T. Ohto, D. Hojo, M. Wakisaka, Y. Nagata, L. Chen, K. Hu, M. Izumi, J.-I. Fujita, and T. Adschiri, *ACS Catal.* **8**, 3579 (2018).
- [29] L. Jiang and Z. Fan, *Nanoscale* **6**, 1922 (2014).
- [30] A. Cagliani, D. M. A. Mackenzie, L. K. Tschammer, F. Pizzocchero, K. Almdal, and P. Bøggild, *Nano Res.* **7**, 743 (2014).
- [31] Y. Zhao, C. Hu, L. Song, L. Wang, G. Shi, L. Daic, and L. Qu, *Energy Environ. Sci.* **7**, 1913 (2014).
- [32] M. Ananth, L. Stern, D. Ferranti, C. Huynh, J. Notte, L. Scipioni, C. Sanford, and B. Thompson, *Proc. SPIE* **8036**, 80360M (2011).
- [33] W. Li, L. Liang, S. Zhao, S. Zhang, and J. Xue, *J. Appl. Phys.* **114**, 234304 (2013).
- [34] K. K. Gopalan, B. Paulillo, D. M. A. Mackenzie, D. Rodrigo, N. Bareza, P. R. Whelan, A. Shivayogimath, and V. Pruneri, *Nano Lett.* **18**, 5913 (2018).
- [35] J. Liu, G. Xu, C. Rochford, R. Lu, J. Wu, C. M. Edwards, C. L. Berrie, Z. Chen, and V. A. Maroni, *Appl. Phys. Lett.* **99**, 023111 (2011).
- [36] I. Jung, H. Y. Jang, and S. Park, *Appl. Phys. Lett.* **103**, 023105 (2013).
- [37] C.-M. Chen, Q. Zhang, C.-H. Huang, X.-C. Zhao, B.-S. Zhang, Q.-Q. Kong, M.-Z. Wang, Y.-G. Yang, R. Cai, and D. S. Su, *Chem. Commun.* **48**, 7149 (2012).
- [38] Q. Xi, X. Chen, D. G. Evans, and W. Yang, *Langmuir* **28**, 9885 (2012).
- [39] B. Qiu, M. Xing, and J. Zhang, *Chem. Soc. Rev.* **47**, 2165 (2018).
- [40] X. Xiao, T. E. Beechem, M. T. Brumbach, T. N. Lambert, D. J. Davis, J. R. Michael, C. M. Washburn, J. Wang, S. M. Brozik, D. R. Wheeler, D. B. Burckel, and R. Polsky, *ACS Nano* **6**, 3573 (2012).
- [41] X. Wang and G. Shi, *Energy Environ. Sci.* **8**, 790 (2015).
- [42] L. Peng, Y. Feng, Y. Bai, H.-J. Qiu, and Y. Wang, *J. Mater. Chem. A* **3**, 8825 (2015).
- [43] H. Wang, K. Kurata, T. Fukunaga, H. Takamatsu, X. Zhang, T. Ikuta, K. Takahashi, T. Nishiyama, H. Ago, and Y. Takata, *Carbon* **99**, 564 (2016).
- [44] R. Kumar, J.-H. Oh, H.-J. Kim, J.-H. Jung, C.-H. Jung, W. G. Hong, H.-J. Kim, J.-Y. Park, and I.-K. Oh, *ACS Nano* **9**, 7343 (2015).
- [45] T. Palaniselvam, M. O. Valappil, R. Illathvalappil, and S. Kurungot, *Energy Environ. Sci.* **7**, 1059 (2014).
- [46] R. Song, B. Cao, D. Zhang, and H. Song, *RSC Adv.* **6**, 63373 (2016).
- [47] O. Akhavan, M. Abdolabad, A. Esfandiar, and M. Mo-hatashamifar, *J. Phys. Chem. C* **114**, 12955 (2010).
- [48] A. E. B. Amend, T. Matsui, H. Sato, and H. Fukuyama, *e-J. Surf. Sci. Nanotechnol.* **16**, 72 (2018).

All articles published on e-J. Surf. Sci. Nanotechnol. are licensed under the Creative Commons Attribution 4.0 International (CC BY 4.0). You are free to copy and redistribute articles in any medium or format and also free to remix, transform, and build upon articles for any purpose (including a commercial use) as long as you give appropriate credit to the original source and provide a link to the Creative Commons (CC) license. If you modify the material, you must indicate changes in a proper way.

Published by The Japan Society of Vacuum and Surface Science