

How Can the Nanomaterial Surfaces Be Highly Cleaned?

Viet Phuong Pham^{1,2}

¹SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University (SKKU), Suwon, Republic of Korea; pvphuong85@ibs.re.kr (V.P.P.).

²Center for Multidimensional Carbon Materials, Institute for Basic Science, 44919, Ulsan, Republic of Korea.

1. Introduction

The induced contaminations (e.g polymer residues or impurities in air) on nanomaterial surfaces have been a serious problem to probe their intrinsic properties and for unique applications in surface chemistry, electronic, and optoelectronic. The polymer residues still presented on chemical vapor deposited graphene surface after its wet transfer (e.g. poly(methyl methacrylate) (PMMA)) on the arbitrary substrates tends to cause problems such as electrical degradation and unwanted intentional doping. Polymer residues (e.g PMMA), defects, and other contaminations are commonly leaving the thin layers or the particles as residues on nanomaterials.

Nowadays, the nanomaterials are receiving broad interests. Among them, grapheme [1-36], hexagonal-boron nitride (h-BN) [37-40], carbon nanotubes (CNTs) [41,42], and graphene oxide [43] are emerging as many promising potential materials with novel properties in electronics and optoelectronics (Figure 1). These nanomaterials have attracted a huge research interest in recent decades due to its anomalous properties such as very high carrier mobility, extremely high mechanical strength and optical transparency, electrical conductivity, chemical stability and thermal conductivity [1-43] and that is the reason above nanomaterials are being observed as a potential material for next-generation semiconductor devices that would replace silicon-based technology. Due to being an atomically thin material, every atom of nanomaterials has an access to surface that is directly responsible for its electronic and chemical activity. However, for many applications, the nanomaterials in pristine form cannot be used due to high resistance and performance degradation on poor nanomaterial quality.

Thereby, the exploration of new methods in order to mitigation as much polymer residues as possible on nanomaterials (CVD Graphene, CNT, GO, h-BN) is highly desirable (Figure 2). For instance on CVD graphene material, many reports have demonstrated to remove poly(methyl methacrylate) (PMMA) residues and other impurities on surface achieved the significant achievements such as wet chemical by acetone [25,26], cleaning by chloroform or toluene [44] by N-methyl-2-pyrrolidone [45] by diazonium salt [46] a modified RCA cleaning process and mechanically sweeping away the contamination [47] oxygen plasma and reactive ion etching treatment for a short time [25,26,46] mechanical method: AFM tip can remove all resist (theoretically without damaging the sample) in a contact mode [34] annealing in high temperature [18,25,26,48] current annealing [49] by acetic acid [50] by electrostatic force [16] by lithography resist [17] by annealing [18] by electric current [19] by electrolytic [20] by titanium sacrificial layer [22] by heat treatment in air and vacuum [23] by dry-cleaning [24]. Very recently, a superior technique for cleaning of nanomaterials using plasma (Ar, oxygen) proved extremely efficient in residue cleaning from graphene surface and tuning the graphene properties [25-29,51].

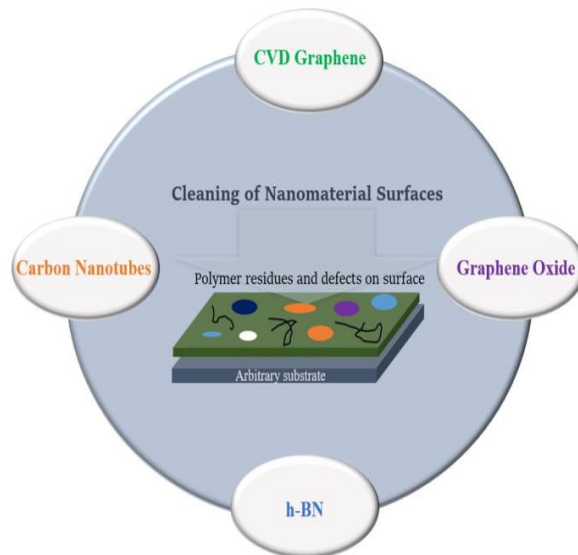


Figure 1.

Schematic of cleaning of various nanomaterial surfaces (CVD graphene, CNTs, GO, h-BN) by chemistry, physic, nanotechnology, and engineering for tuning their electronics and optoelectronics.

The cleaning of CNT materials surface by cyclic Ar plasma and nitric acid treatment for enhancing the electrical conductivity of flexible transparent conducting film [41] or by RF-PECVD technique [42] has also well-investigated. Or the surface of the h-BN material was cleaned greatly by wet chemical (HF solution) and annealing in vacuum at 10500C [52] or annealing at 4500C in air and ozone [40]. In addition, the contamination on GO surface was removed significantly assisted by an oxidation process and washing-centrifugation cycles which is controlled by pH of the supernatant.

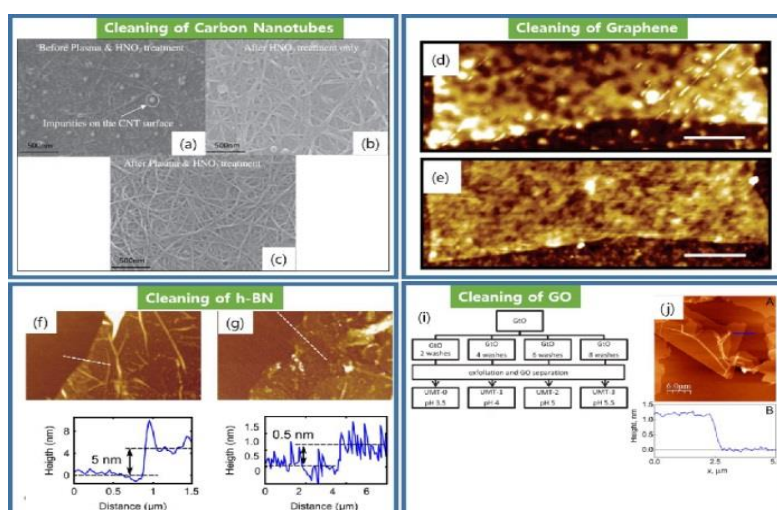


Figure 2. Cleaning process of various nanomaterial surfaces such as carbon nanotubes (a-c), graphene (d-e), h-BN (f,g), and GO (i,j). (a-c) reproduced with permission from [41]. (d,e) reproduced with permission from [17]. (f,g) reproduced with permission from [40]. (i,j) reproduced with permission from [43].

The cleaning of nanomaterials (CVD Graphene, CNT, h-BN, GO) using various strategies related to chemistry, physic, nanotechnology, and engineering in order to obtain the ultra-clean material layer and resulting in improving their electrical characteristics is highly desiring with targeting toward practical applications in the industry to serve human society. The enhancing of electrical properties of cleaned nanomaterials would be raising up the current on-off ratio, photoluminescence, and other unexploited and unexplored exotic properties. Consequently, it could unlock and take a leap forward on developing superior plasma-based cleaning methods [15,32] for other TMDs and low-dimensional materials in various advanced devices and applications.

References

- [1] K. S. Novoselov *et al.*, "Electric field effect in atomically thin Carbon films," *Science*, vol. 306, no. 5696, pp. 666-669, 2004. <https://doi.org/10.1126/science.1102896>
- [2] V. P. Pham, H.-S. Jang, D. Whang, and J.-Y. Choi, "Direct growth of graphene on rigid and flexible substrates: Progress, applications, and challenges," *Chemical Society Reviews*, vol. 46, no. 20, pp. 6276-6300, 2017. <https://doi.org/10.1039/c7cs00224f>
- [3] V. P. Pham *et al.*, "Chlorine-trapped CVD bilayer graphene for resistive pressure sensor with high detection limit and high sensitivity," *2D Materials*, vol. 4, no. 2, p. 025049, 2017. <https://doi.org/10.1088/2053-1583/aa6390>
- [4] V. P. Pham, K. N. Kim, M. H. Jeon, K. S. Kim, and G. Y. Yeom, "Cyclic chlorine trap-doping for transparent, conductive, thermally stable and damage-free graphene," *Nanoscale*, vol. 6, no. 24, pp. 15301-15308, 2014. <https://doi.org/10.1039/c4nr04387a>
- [5] V. P. Pham, K. H. Kim, M. H. Jeon, S. H. Lee, K. N. Kim, and G. Y. Yeom, "Low damage pre-doping on CVD graphene/Cu using a chlorine inductively coupled plasma," *Carbon*, vol. 95, pp. 664-671, 2015. <https://doi.org/10.1016/j.carbon.2015.08.070>
- [6] V. P. Pham, A. Mishra, and G. Y. Yeom, "The enhancement of Hall mobility and conductivity of CVD graphene through radical doping and vacuum annealing," *RSC advances*, vol. 7, no. 26, pp. 16104-16108, 2017. <https://doi.org/10.1039/c7ra01330b>
- [7] V. P. Pham *et al.*, "Low energy BCl₃ plasma doping of few-layer graphene," *Science of Advanced Materials*, vol. 8, no. 4, pp. 884-890, 2016. <https://doi.org/10.1166/sam.2016.2549>
- [8] V. Pham, "Chemical vapor deposited graphene synthesis with same-oriented hexagonal domains," *Eng Press*, vol. 1, pp. 39-42, 2018.
- [9] K. N. Kim, V. P. Pham, and G. Y. Yeom, "Chlorine radical doping of a few layer graphene with low damage," *ECS Journal of Solid State Science and Technology*, vol. 4, no. 6, p. N5095, 2015. <https://doi.org/10.1149/2.0141506jss>
- [10] V. P. Pham and G. Y. Yeom, "Recent advances in doping of molybdenum disulfide: Industrial applications and future prospects," *Advanced Materials*, vol. 28, no. 41, pp. 9024-9059, 2016. <https://doi.org/10.1002/chin.201651225>
- [11] A. Ferrari, F. Bonaccorso, and V. Fal'ko, "Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems," *Nanoscale*, vol. 7, pp. 4587-5062, 2015.
- [12] S. Z. Butler *et al.*, "Progress, challenges, and opportunities in two-dimensional materials beyond graphene," *ACS Nano*, vol. 7, no. 4, pp. 2898-2926, 2013.
- [13] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials*, vol. 6, no. 3, pp. 183-191, 2007.
- [14] H. Zhang, P. Yang, and M. Prato, "Grand challenges for nanoscience and nanotechnology," *ACS Nano*, vol. 9, pp. 6637-6640, 2015.
- [15] K. S. Kim *et al.*, "Atomic layer etching of graphene through controlled ion beam for graphene-based electronics," *Scientific Reports*, vol. 7, no. 1, p. 2462, 2017. <https://doi.org/10.1038/s41598-017-02430-8>
- [16] W. J. Choi *et al.*, "A simple method for cleaning graphene surfaces with an electrostatic force," *Advanced Materials*, vol. 26, no. 4, pp. 637-644, 2014. <https://doi.org/10.1002/adma.201303199>
- [17] M. Ishigami, J.-H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams, "Atomic structure of graphene on SiO₂," *Nano Letters*, vol. 7, no. 6, pp. 1643-1648, 2007.
- [18] Y.-C. Lin, C.-C. Lu, C.-H. Yeh, C. Jin, K. Suenaga, and P.-W. Chiu, "Graphene annealing: How clean can it be?," *Nano Letters*, vol. 12, no. 1, pp. 414-419, 2012. <https://doi.org/10.1021/nl203733r>
- [19] J. Moser, A. Barreiro, and A. Bachtold, "Current-induced cleaning of graphene," *Applied Physics Letters*, vol. 91, no. 16, p. 161513, 2007.
- [20] J. Sun, H. O. Finklea, and Y. Liu, "Characterization and electrolytic cleaning of poly (methyl methacrylate) residues on transferred chemical vapor deposited graphene," *Nanotechnology*, vol. 28, no. 12, p. 125703, 2017. <https://doi.org/10.1088/1361-6528/aa5e55>
- [21] J. D. Wood *et al.*, "Annealing free, clean graphene transfer using alternative polymer scaffolds," *Nanotechnology*, vol. 26, no. 5, p. 055302, 2015. <https://doi.org/10.1088/0957-4484/26/5/055302>

- [22] C. A. Joiner, T. Roy, Z. R. Hesabi, B. Chakrabarti, and E. M. Vogel, "Cleaning graphene with a titanium sacrificial layer," *Applied Physics Letters*, vol. 104, no. 22, p. 223109, 2014. <https://doi.org/10.1063/1.4881886>
- [23] M. Tripathi *et al.*, "Cleaning graphene: Comparing heat treatments in air and in vacuum," *Physica Status Solidi (RRL)–Rapid Research Letters*, vol. 11, no. 8, p. 1700124, 2017. <https://doi.org/10.1002/pssr.201700124>
- [24] G. Siller-Algara, O. Lehtinen, A. Turchanin, and U. Kaiser, "Dry-cleaning of graphene," *Applied Physics Letters*, vol. 104, no. 15, p. 153115, 2014.
- [25] N. Peltekis, S. Kumar, N. McEvoy, K. Lee, A. Weidlich, and G. S. Duesberg, "The effect of downstream plasma treatments on graphene surfaces," *Carbon*, vol. 50, no. 2, pp. 395–403, 2012. <https://doi.org/10.1016/j.carbon.2011.08.052>
- [26] N. McEvoy, H. Nolan, N. A. Kumar, T. Hallam, and G. S. Duesberg, "Functionalisation of graphene surfaces with downstream plasma treatments," *Carbon*, vol. 54, pp. 283–290, 2013. <https://doi.org/10.1016/j.carbon.2012.11.040>
- [27] V. Prudkovskiy, K. Katin, M. Maslov, P. Puech, R. Yakimova, and G. Deligeorgis, "Efficient cleaning of graphene from residual lithographic polymers by ozone treatment," *Carbon*, vol. 109, pp. 221–226, 2016. <https://doi.org/10.1016/j.carbon.2016.08.013>
- [28] F. Hadish, S. Jou, B.-R. Huang, H.-A. Kuo, and C.-W. Tu, "Functionalization of CVD grown graphene with downstream oxygen plasma treatment for glucose sensors," *Journal of The Electrochemical Society*, vol. 164, no. 7, p. B336, 2017. <https://doi.org/10.1149/2.0601707jes>
- [29] H. Al-Mumen, F. Rao, W. Li, and L. Dong, "Singular sheet etching of graphene with oxygen plasma," *Nano-Micro Letters*, vol. 6, pp. 116–124, 2014. <https://doi.org/10.1007/bf03353775>
- [30] H. Sun *et al.*, "High quality graphene films with a clean surface prepared by an UV/ozone assisted transfer process," *Journal of Materials Chemistry C*, vol. 5, no. 8, pp. 1880–1884, 2017.
- [31] W. Choi, M. A. Shehzad, S. Park, and Y. Seo, "Influence of removing PMMA residues on surface of CVD graphene using a contact-mode atomic force microscope," *RSC Advances*, vol. 7, no. 12, pp. 6943–6949, 2017. <https://doi.org/10.1039/c6ra27436f>
- [32] K. S. Kim *et al.*, "Surface treatment process applicable to next generation graphene-based electronics," *Carbon*, vol. 104, pp. 119–124, 2016. <https://doi.org/10.1016/j.carbon.2016.03.054>
- [33] Y. Jia *et al.*, "Toward high carrier mobility and low contact resistance: Laser cleaning of PMMA residues on graphene surfaces," *Nano-Micro Letters*, vol. 8, pp. 336–346, 2016. <https://doi.org/10.1007/s40820-016-0093-5>
- [34] A. Goossens, V. Calado, A. Barreiro, K. Watanabe, T. Taniguchi, and L. Vandersypen, "Mechanical cleaning of graphene," *Applied Physics Letters*, vol. 100, no. 7, p. 073110, 2012. <https://doi.org/10.1063/1.3685504>
- [35] H. M. Choi, J. A. Kim, Y. J. Cho, T. Y. Hwang, J. W. Lee, and T. S. Kim, "Surface cleaning of graphene by CO₂ cluster," *Solid State Phenomena*, vol. 219, pp. 68–70, 2014.
- [36] K. Kumar, Y.-S. Kim, and E.-H. Yang, "The influence of thermal annealing to remove polymeric residue on the electronic doping and morphological characteristics of graphene," *Carbon*, vol. 65, pp. 35–45, 2013. <https://doi.org/10.1016/j.carbon.2013.07.088>
- [37] C. R. Dean *et al.*, "Boron nitride substrates for high-quality graphene electronics," *Nature Nanotechnology*, vol. 5, no. 10, pp. 722–726, 2010.
- [38] C. Elbadawi *et al.*, "Electron beam directed etching of hexagonal boron nitride," *Nanoscale*, vol. 8, no. 36, pp. 16182–16186, 2016. <https://doi.org/10.1039/c6nr04959a>
- [39] Y. Liao *et al.*, "Oxidative etching of hexagonal boron nitride toward nanosheets with defined edges and holes," *Scientific Reports*, vol. 5, no. 1, p. 14510, 2015. <https://doi.org/10.1038/srep14510>
- [40] S. J. Cartamil-Bueno, M. Cavalieri, R. Wang, S. Hourii, S. Hofmann, and H. S. van der Zant, "Mechanical characterization and cleaning of CVD single-layer h-BN resonators," *npj 2D Materials and Applications*, vol. 1, no. 1, p. 16, 2017. <https://doi.org/10.1038/s41699-017-0020-8>
- [41] V. P. Pham *et al.*, "Effect of plasma–nitric acid treatment on the electrical conductivity of flexible transparent conductive films," *Japanese Journal of Applied Physics*, vol. 52, no. 7R, p. 075102, 2013. <https://doi.org/10.7567/jjap.52.075102>
- [42] H. Di, M. Li, H. Li, B. Huang, and B. Yang, "Purification and characterization of carbon nanotubes synthesized by RF-PECVD," *ECS Transactions*, vol. 44, no. 1, pp. 499–504, 2012. <https://doi.org/10.1149/1.3694360>
- [43] I. Barbolina, C. Woods, N. Lozano, K. Kostarelos, K. Novoselov, and I. Roberts, "Purity of graphene oxide determines its antibacterial activity," *2D Materials*, vol. 3, no. 2, p. 025025, 2016. <https://doi.org/10.1088/2053-1583/3/2/025025>
- [44] N. Patra, M. Salerno, A. Diaspro, and A. Athanassiou, "Effect of solvents on the dynamic viscoelastic behavior of poly (methyl methacrylate) film prepared by solvent casting," *Journal of Materials Science*, vol. 46, pp. 5044–5049, 2011.
- [45] X. Liang *et al.*, "Toward clean and crackless transfer of graphene," *ACS Nano*, vol. 5, no. 11, pp. 9144–9153, 2011. <https://doi.org/10.1021/nn203377t>
- [46] X.-Y. Fan, R. Nouchi, L.-C. Yin, and K. Tanigaki, "Effects of electron–transfer chemical modification on the electrical characteristics of graphene," *Nanotechnology*, vol. 21, no. 47, p. 475208, 2010. <https://doi.org/10.1088/0957-4484/21/47/475208>
- [47] C. Y. Stephen, P. R. Krauss, and P. J. Renstrom, "Nanoimprint lithography," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, vol. 14, no. 6, pp. 4129–4133, 1996.
- [48] L. S. Wei, C. T. Nai, and J. T. Thong, "What does annealing do to metal–graphene contacts?," *Nano Letters*, vol. 14, no. 7, pp. 3840–3847, 2014. <https://doi.org/10.1021/nl500999r>
- [49] H. Michael, R. Beams, and L. Novotny, "Graphene transfer with reduced residue," *Physics Letters A*, vol. 377, no. 21–22, pp. 1455–1458, 2013. <https://doi.org/10.1016/j.physleta.2013.04.015>
- [50] Y.-D. Lim, D.-Y. Lee, T.-Z. Shen, C.-H. Ra, J.-Y. Choi, and W. J. Yoo, "Si-compatible cleaning process for graphene using low-density inductively coupled plasma," *ACS Nano*, vol. 6, no. 5, pp. 4410–4417, 2012. <https://doi.org/10.1021/nn301093h>
- [51] S. W. King, R. J. Nemanich, and R. F. Davis, "Cleaning of pyrolytic hexagonal boron nitride surfaces," *Surface and Interface Analysis*, vol. 47, no. 7, pp. 798–803, 2015. <https://doi.org/10.1002/sia.5781>