Md. Zakir Hossain
Natsuhiko Shimizu and Suzuka Oana
International Research and Education Center for Element Science, Graduate School of Science and Technology, Gunma University, Kiryu City, Gunma 376-8515, Japan
zakir@gunma-u.ac.jp

Covalent binding of metal nanoparticles on graphene through thiol functionalization

Abstract
Combination of the extraordinary electrical and opto-electrical properties of graphene and the binding potential of metal nanoparticles (MNPs) with various small molecules and biological targets can lead to the development of ultrasensitive chemical and biological sensors [1][2][3]. Here, we carried out the covalent immobilization of different MNPs (e.g. gold and silver) on the surface of graphene through thiol (-SH) functionalization. We also investigated the further reaction of MNP decorated graphene with two target molecules and fabricate the interdigital electrode for testing its potential for application in sensor. Epitaxial graphene (EG) on SiC was functionalized with −SH groups through the in situ primary amine diazotization reaction [4]. The –SH functionalized EG/SiC was then treated with noble metal ion during the conventional synthesis of MNPs via the $NaBH_4$ reduction process at 80 °C. The noble metal ion treatment resulted in the decoration of graphene with covalently bonded (through −S−M bonding). We found that the immobilized MNPs can be further reacted with other reactive molecules such as hexanedithiol ($HSC_6H_{12}SH$) and pentachlorobenzenethiol (Cl_5C_6SH), which is a step forward for the development of graphene based sensor. To see the performance of this MNP-graphene composite materials for the sensor device, we will also demonstrate the fabrication of interdigital electrode on MNP decorated graphene and its electrical response.

References

[1] Bollella, P.; Fusco, G.; Tortolini, C.; Sanzò, G.; Favero, G. Gorton, L.; Antiochia, R. *Biosens. Bioelectron.* **2017**, 89, 152-166.
[2] Bahadir, E. B.; Sezgintürk, M. K. Applications of Graphene in Electrochemical Sensing and Biosensing. *TrAC, Trends Anal. Chem.* **2016**, 76, 1-14.
[3] Krishnan, S. K.; Singh, E.; Singh, P.; Meyyappan, M.; Nalwa, H. S.; *RSC Adv*, **2019**, 9, 8778-8881.
[4] Hossain, M. Z.; Shimizu, N. *J. Phys. Chem. C*. **2017**, 121, 25223−25228.
[5] Hossain, M. Z.; Shimizu, N. *J. Phys. Chem. C*. **2018**, 121, 6, 3512-3516.

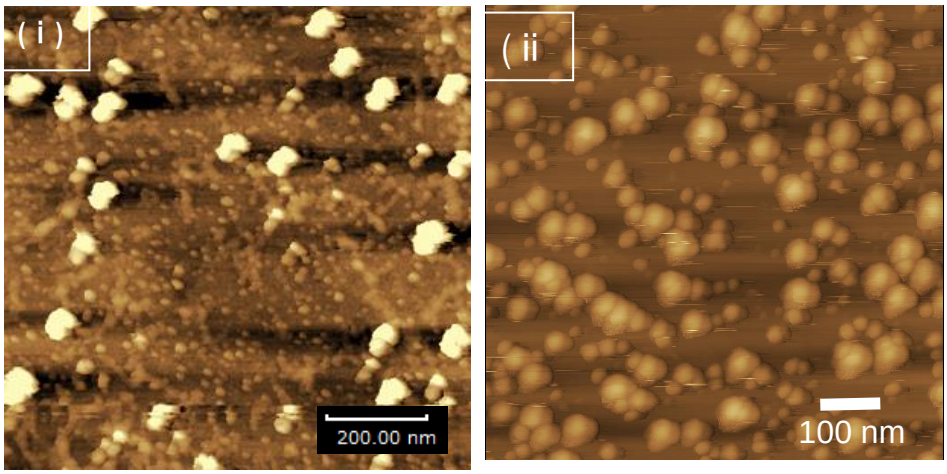

Figure 1: AFM images of nanoparticles on EG/SiC. (i) silver nanoparticles on graphene (ii) gold nanoparticles on graphene.