Dynamics of the graphene-metal nanoparticle catalyst interface during catalytic channeling

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Abstract

The catalytic hydrogenation and reduction of graphene has received renewed attention as one feasible route for the patterning of graphene structures at the nanoscale [1–5] which is applicable to suspended graphene and does not require the use of lithographic resists. An enhanced understanding of the dynamics of this process is required to see where metal nanoparticle channeling might prove technologically applicable, and to enable control of the process - the exact mechanism of the etching process is difficult to ascertain without the help of in-situ studies capable of resolving the dynamics at sufficient spatial and temporal resolution.

We describe the results of in-situ nanoparticle channeling carried out by silver nanoparticles on suspended graphene *in-situ* in an environmental transmission electron microscope. Along with an understanding of the energetics and rate of the process [1] we have also made observations of the metal nanoparticle-graphene interface [2], including the three-dimensional structure of the nanoparticles. In contrast to some of the assumptions of recent studies [3], we find that the morphology of the nanoparticles is dynamic, and changes over time in response to the type of graphene edge it is in contact with. This behavior is particularly pronounced during turning of the nanoparticles, where a loss of crystalline faceting (but not of bulk crystallinity) is observed in our in-situ experiments. These observations highlight the importance of dynamic in-situ studies in the understanding of this process, and contradict assumptions about the metal-graphene interface and therefore the energetics of the system. By combining our observations with DFT calculations, we are able to provide a model for the long straight channels that we observe which are perfectly oriented with the graphene zig-zag direction.

References

[1] T.J. Booth, F. Pizzocchero, H. Andersen, T.W. Hansen, J.B. Wagner, J.R. Jinschek, R.E. Dunin-Borkowski, O. Hansen, P. Bøggild, Nano Lett. **11** (2011) 2689.
[2] F. Pizzocchero, M. Vanin, J. Kling, T.W. Hansen, K.W. Jacobsen, P. Bøggild, T.J. Booth, J. Phys. Chem. C **118** (2014) 4296.
[3] L. Ma, J. Wang, J. Yip, F. Ding, J. Phys. Chem. Lett. 5 (2014) 1192.
[4] M. Lukas, V. Meded, A. Vijayaraghavan, L. Song, P.M. Ajayan, K. Fink, W. Wenzel, R. Krupke, Nat. Commun. **4** (2013) 1379.
[5] G. Melinte, I. Florea, S. Moldovan, I. Janowska, W. Baaziz, R. Arenal, A. Wisnet, C. Scheu, S. Begin-Colin, D. Begin, C. Pham-Huu, O. Ersen, Nat. Commun. **5** (2014).

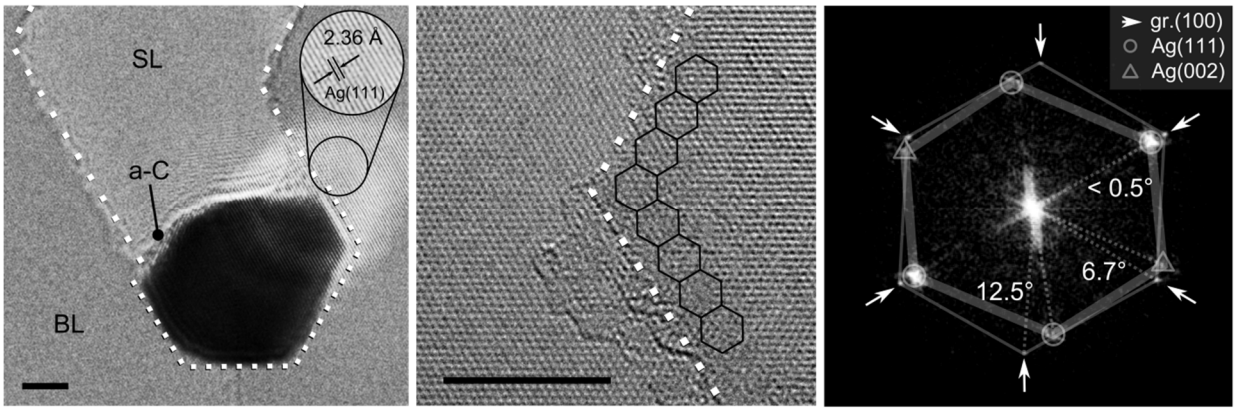

Figure 1. Left – HRTEM image of channeling nanoparticle. Center – HRTEM image of graphene corner at a turning point. Right – FFT of nanoparticle and graphene with angular mismatch between the graphene (100) and Ag (111) and (002) planes.