

Plasmonic Enhancement at Metal Atoms on Graphene Edges revealed by EFTEM

W Pierce¹, R Zan¹, Q M Ramasse², C B Boothroyd³ and U Bangert¹

¹School of Materials, The University of Manchester, Manchester, UK

²SuperSTEM, STFC Daresbury Laboratory, Warrington, UK

³Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Gruenberg Institute, Juelich Research Centre, D-52425 Juelich, Germany

william.pierce@postgrad.manchester.ac.uk

Abstract. Palladium atoms have been deposited onto graphene where they catalyse etching processes in conjunction with the e-beam, during/after which they reside at the edges of the holes, which have formed in the graphene. Energy filtered imaging reveals that the low loss feature at 2-4 eV constituting the shoulder of the graphene π -plasmon, is up to 10 times enhanced at Pd-decorated graphene edges compared to clean monolayer graphene, rendering it a useful feature for electric field enhancement applications in the optical regime

1. Introduction

Graphene is an extremely versatile material for applications in photodetectors, solar cells and plasmonics, as transparent electrode, light enhancer and wave guide. In all these cases graphene needs to be nano-sculpted, i.e., hole and functional impurity atom patterns need to be controllably introduced. Following work by Zhou et al [1], who have shown that individual impurity atoms (in their case Si) can act as atomic antennae, enhancing the graphitic σ -plasmon in graphene, we investigate the possibility of enhancement and energy red-shifting of the π -plasmon and thereto coupled single particle excitations in the visible wavelength regime. For this purpose we introduce metal atoms, which mediate graphene nano-etching under the electron beam [2, 3], and are also expected to enhance absorption and emission within the visible EM spectrum. We concentrate on the case of Pd-adatoms, which induce electron absorption features in the energy regime 2-4 eV, especially at single and double layer graphene edges, scrolls or kinks of one layer above the other.

2. Experimental

We employ two different techniques for graphene preparation, exfoliation from HOPG graphite [4] and the CVD method, in which graphene is grown on copper [5]. Metal impurities have been introduced using electron beam and thermal evaporators, depositing 2 Å of various metals at room temperature. Graphene layer numbers have been identified from electron diffraction patterns by



comparing the first and second ring intensities; atomic resolution imaging of metal atoms and clusters on the graphene surface has been carried out in stationary transmission electron microscopy mode (TEM) as well as in high angle annular dark field (HAADF) scanning mode (STEM), the former in a Tecnai F30, the latter in an aberration corrected dedicated STEM (Daresbury SuperSTEM). Atomic sites of singular metal atoms and clusters on graphene have been directly revealed in HAADF imaging mode by their approximate Z^2 dependence, and by relating HAADF with simultaneously obtained electron energy loss (EEL) spectrum images. Further lattice resolution phase contrast images in conjunction with low loss/ plasmon images were obtained in a monochromated and triple aberration corrected Titan PICO. For this purpose stacks of TEM images were obtained, where the same region was successively imaged with an electron beam that has lost increasing amounts of energy. The stacks then consist of a number of energy filtered images (EFTEM images) taken at energy losses typically ranging from -2 eV (energy gain) to 8 eV, in steps of 0.2 eV (in this case the number of images in the stack is 51). A stack can be viewed as a 3-D array, where the x- and y-axis assign the 2-D image dimensions and the z-axis is the energy. Each x-y slice (image) consists of a certain number of pixels (e.g., 512x512); EEL spectra can then be extracted by plotting the intensities of vertically stacked pixels against energy (projection of the pixel intensity onto the z- or energy-axis).

3. Results and Discussion

Metal atom mediated graphene nano-etching [2] is catalysed by an electron beam in a (S)TEM (however, knock-on and ionization effects are not believed to be the mechanisms for this). The HAADF image in fig. 1a shows hole formation for the case of Pd, the elemental nature of which was established by single-atom EELS (fig. 1b). The Pd atoms, due to the larger binding energy at graphene edges [6], decorate the forming hole. Pd- atoms are expected to enhance absorption and emission

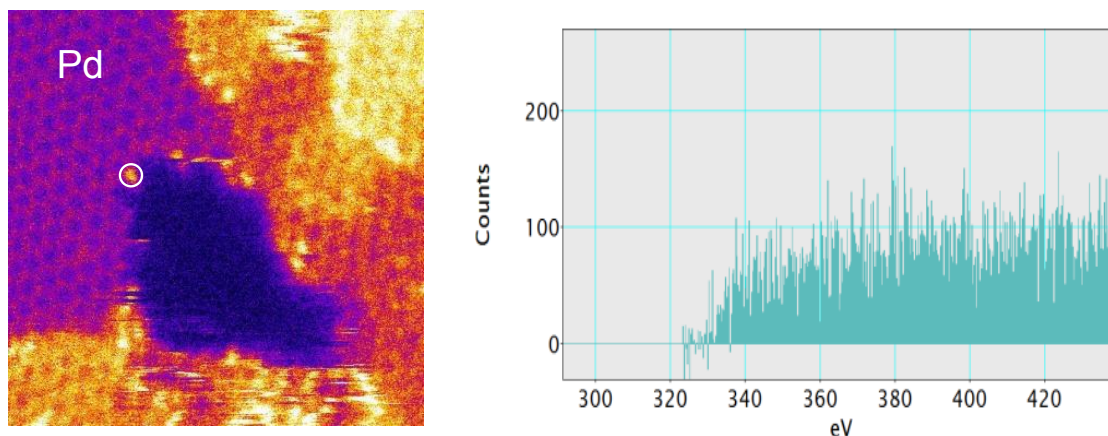
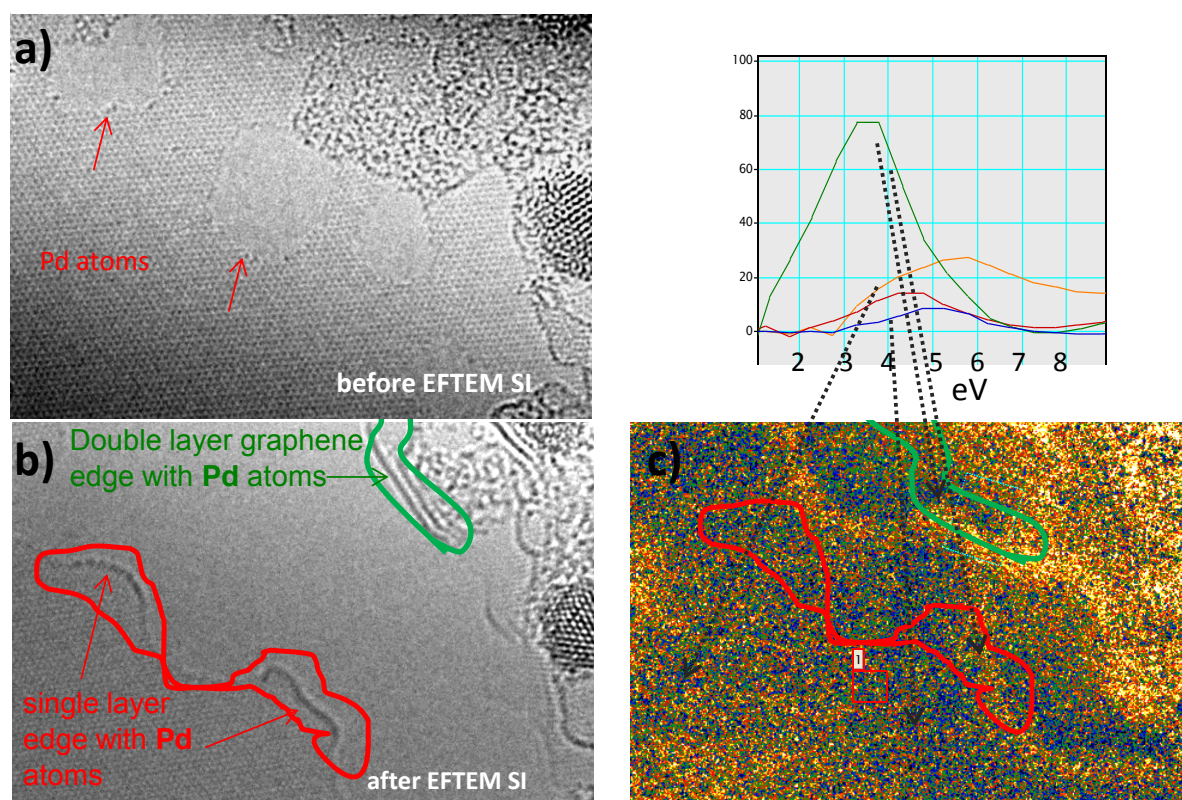


Figure 1. a) HAADF image of 2Å Pd evaporated single layer graphene (false colour: graphene purple, Pd yellow, vacuum dark blue); b) EEL spectrum of the encircled atom in (a) revealing the fingerprint of the Pd L-edge.

within the visible EM spectrum. As can be seen from the EEL spectrum in fig. 2, which was extracted from an EFTEM stack in positions indicated by the arrows, Pd atoms induce electron absorption features at 2-4 eV, especially at single and double layer graphene edges, scrolls or kinks of one layer above the other; judging from the phase contrast in the BF images (figs 2a and b) there appear to always be Pd atoms present (often in chains) when there is an edge-intensity enhancement in fig. 2c. In greater detail: figure 2a was obtained before the acquisition of the EFTEM stack, from which the plasmon map (fig. 2c) comprising of the sum of EFTEM images with losses 3, 3.2, 3.4, 3.6, 3.8 and 4

eV was extracted. The image in fig. 2b was taken after the acquisition of the EFTEM stack. It becomes clear that during the long electron exposure damage to the graphene occurred resulting in the expansion of the three original holes (fig. 2a) to merge into one (fig.2b). The EFTEM image in fig. 2c shows the intermediate stage. It can nevertheless be seen that Pd-atoms (dark dots and dotted lines in the underfocus phase contrast images) are lining the graphene edges. Fig. 2c shows a clear enhancement of the EEL spectrum feature at 2-4 eV, i.e., at uv/vis energies, at Pd atoms along the



hole. Spectra (green) extracted from the EFTEM stack at the hole's edge (arrowed positions) show

Figure 2. a) 2 Å Pd evaporated on graphene predominantly present as nanocrystals in the ubiquitous contamination but also as individual atoms at the edges of holes; b) changes in the graphene topography under exposure to the electron beam after EFTEM: the 3 separate holes in (a) have merged into one large hole; c) residual intensity of absorption features at 3-4 eV after subtracting the zero loss peak and the π -plasmon at 4.7 eV from an EFTEM stack acquired of the area as in the BF images (a) and (b) showing enhancement in the UV/vis regime at graphene edges; this is further proven by the spectra extracted from the merely zero loss peak subtracted EFTEM stack. Images and energy loss measurement were obtained in a monochromated and triple aberration corrected Titan PICO at 80 keV

enhancement by a factor of ~ 10 compared to spectra (blue) obtained from pure graphene (arrowed position). The top edge of the hole in fig. 2b consists of a double layer; the enhancement for mono- and double-layer edges is similar.

The existence of plasmons in graphene is still disputed, hence the issue of whether the observed feature is a ‘true’ plasmon or an exciton albeit coupled to a plasmon, or even a collective exciton, i.e., an interband transition, requires further investigation. However, since the absorption feature is a strong one, this issue does not defer from its usefulness for potential light -coupling and -enhancing applications.

4. Conclusions

In conclusion, it appears that individual Pd atoms at edges of holes in graphene, the latter being a consequence of metal-mediated etching, give rise to considerable enhancement of absorption features in the uv/vis wavelength regime. Together with the nano-topographic aspect of these features the observed phenomenon could lead to real applications in nano-photonics and –plasmonics.

References

- [1] Zhou, W., Lee, J., Nanda, J., Pantelides, S. T., Pennycook, S. J. and Idrobo, J.-C., *Nature Nanotech* **2012**, 7, 161.
- [2] Ramasse, Q. M., Zan, R., Bangert, U., Boukhvalov, D. W., Son, Y.-W. and Novoselov K. S., *ACS Nano* **2012**, 6 (5), 4063
- [3] Zan, R.; Bangert, U.; Ramasse, Q.; Novoselov, K. S., *J. Phys. Chem. Lett.*, **2012**, 3 (7), 953.
- [4] Novoselov, K. S.; et al. *A. Science* **2004**, 306 (5696), 666.
- [5] Li, X.; et al. *Science* **2009**, 324 (5932), 1312.
- [6] Hardcastle T., Seabourne, C. R., Zan, R., Brydson, R. M. D., Bangert, U., Ramasse, Q. M., Novoselov, K. S. and Scott, A. J., *Phys. Rev.B* **2013**, 87, 195430.