Decoupling Epitaxial Graphene from Metals by Potential-Controlled Electrochemical-Oxidation of the Substrate

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High-quality epitaxial graphene can be efficiently grown on metal substrates. Unfortunately, the strong interaction with the supporting metal quenches graphene's outstanding properties, thus transfer protocols to insulating surfaces are nowadays routinely used. These transfer processes are cost inefficient and some can severely degrade the properties of graphene by introducing structural and chemical defects. In this work we have used cyclic voltammetry to decouple epitaxial graphene from Pt(111) and polycrystalline Cu metal surfaces. A multi-technique structural characterization (STM, AFM and Raman) combined with theoretical studies (ab-initio calculations) of the different steps of the process show that an atom thick metal-oxide layer is intercalated on the interface between the Ultra High Vacuum (UHV) grown graphene and the surface.

Epitaxial graphene has been grown in UHV by thermal decomposition of aromatics, following the procedure described in [1]. Fig. 1a shows a representative STM image of a wide scan area as well as the typical LEED pattern obtained for Gr on Pt(111) [2, 3]. It is possible to clearly distinguish a wrinkle, some nanobubbles and the contour of the Gr domains. Fig. 1b shows a high resolution STM image acquired on a terrace, where the representative $\zeta(\sqrt{44}x\sqrt{44})R15°_{Gr}$ Moiré superstructure is observed with atomic resolution. The Moiré superstructure is a fingerprint for single-layer graphene on the platinum surface [2]. Thus, the STM together with the LEED confirm the high quality of the graphene layer used for the experiments.

After in-situ characterization the sample was removed from UHV and characterized by AFM, SEM and Raman spectroscopy before and after electrochemical treatments. Fig. 2 shows important changes in the Raman spectra of the graphene layer induced by the electrochemical treatment. In the untreated sample only atmospheric O_2 and N_2 bands can be observed, and no evidence of the characteristic graphene bands (G and 2D) are found, clearly due to the strong electronic coupling between graphene and the Pt surface. After electrochemical treatments, the most important features of graphene emerge: the G-band and the 2D band, along with a D-band that varies in relative intensity as a function of the electrochemical conditions employed. The AFM overall topography shows that about 90% of the surface is decoupled, and ab-initio calculations clearly show that intercalation of a single atom-thick oxide layer can induce a structural separation of the graphene with respect to the surface. Same results have been obtained for the more technologically interesting polycrystalline Cu substrate suggesting that carefully controlled electrochemical oxidation can provide an alternative and cleaner method to the transfer of graphene.

References

[1] Otero, G. et al., Phys. Rev. Lett. 105 (2010) 216102.
[2] Merino, P. et al., ACS Nano 5, (2011) 5627.
[3] Preobrajenski, A. et al., Phys. Rev. B 78, (2008) 073401.

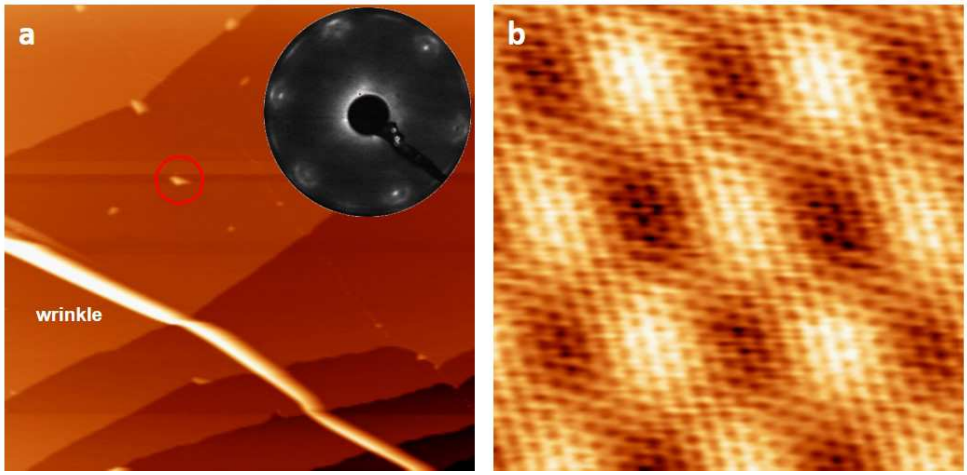

Figure 1: a) STM image of a wide scan area ((200x200)nm^2, I=0.15nA, V=750mV). The graphene layer covers the whole surface. The image shows a wrinkle and several nanobubbles (like that marked in red). The inset shows the characteristic LEED pattern of graphene on Pt(111) surface. b) High resolution STM image acquired on a flat terrace ((4x4)nm^2, I=4nA, V=10mV) showing a characteristic Moiré superstructure with atomic resolution.

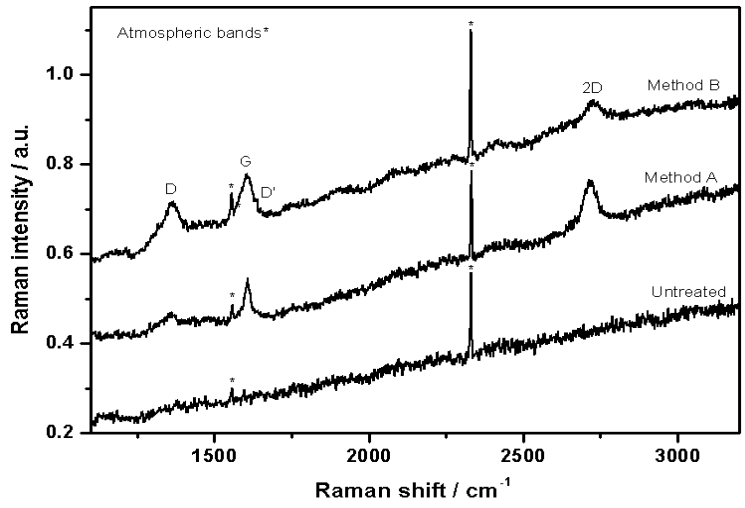

Figure 2: Raman spectra of graphene epitaxially grown on Pt(111) before treatment (lower spectrum), and after two different electrochemical treatments (method A: less aggressive, method B: more aggressive). G, D and 2D bands of graphene emerge after treatment.