



# Surface assisted synthesis, characterization and electronic properties of pristine and oxygen-exposed graphene nanoribbons on Ag(110)



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## INTRODUCTION

Graphene is well-known for its exceptional electronic, mechanical, and thermal properties<sup>1,2</sup>, yet its intrinsic zero-gap reduces its potential for those applications in nanoelectronics for which a band-gap is required<sup>3</sup>. For this reason, attention has shifted towards graphene-based nanostructures and, in particular, towards the so-called graphene nanoribbons (GNRs). If narrower than 10 nm, GNRs possess semiconducting properties due to one-dimensional electron confinement and edge structure effects<sup>4</sup>. GNRs can be produced by either top-down or bottom-up approaches. The former ones give nanostructures with rough edges, sequentially reducing their charge-carrier mobility<sup>5</sup>. The latter ones make use of the surface-catalysed covalent coupling mechanisms occurring between suitable precursors<sup>6,7</sup> and provide, in general, more ordered and uniform patterns of GNRs.

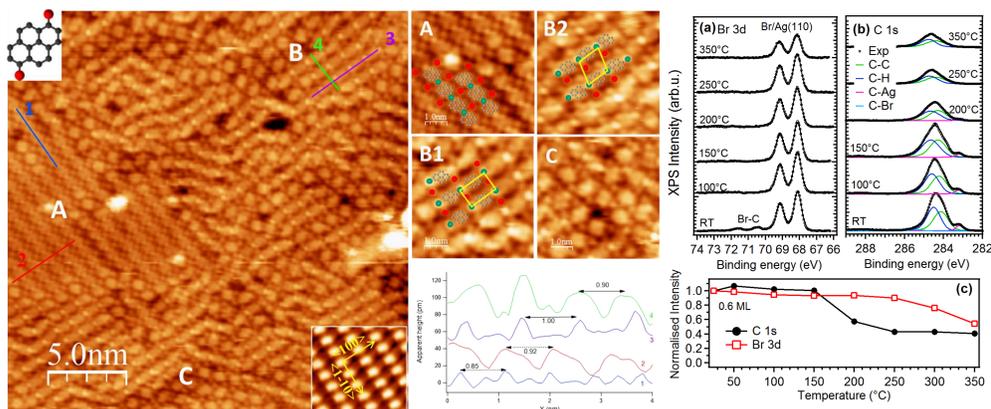
We report our recent results on the formation, characterization, electronic properties and possible chemical

activity of low dimensional graphene nanoribbons on Ag(110)<sup>8,9</sup>. By a combination of scanning tunneling microscopy & spectroscopy (LT-STM & STS), spectroscopic techniques and density functional theory calculations (DFT), we have previously demonstrated the formation of extended patterns of parallel graphene nanoribbons by surface assisted Ullmann coupling and de-hydrogenation of 1,6-dibromo-pyrene (DBP). The GNRs are monodispersed in width and show alternated zig-zag and armchair sites at the edges. Now, we report on the characterization of the electronic band structure of such GNRs by STS and the stability of the GNRs under oxygen exposure using XPS. Our results indicate a characteristic narrow band gap of ~530 meV with the presence of quantum confined states along the length of the GNR. We also demonstrate that oxygen exposure deeply affects the overall system by interacting both with the nanoribbons and with the substrate. These effects severely affect the properties of supported GNRs and must be taken into consideration when using these nanostructures under operative conditions.<sup>10</sup>

## EXPERIMENTAL DETAILS



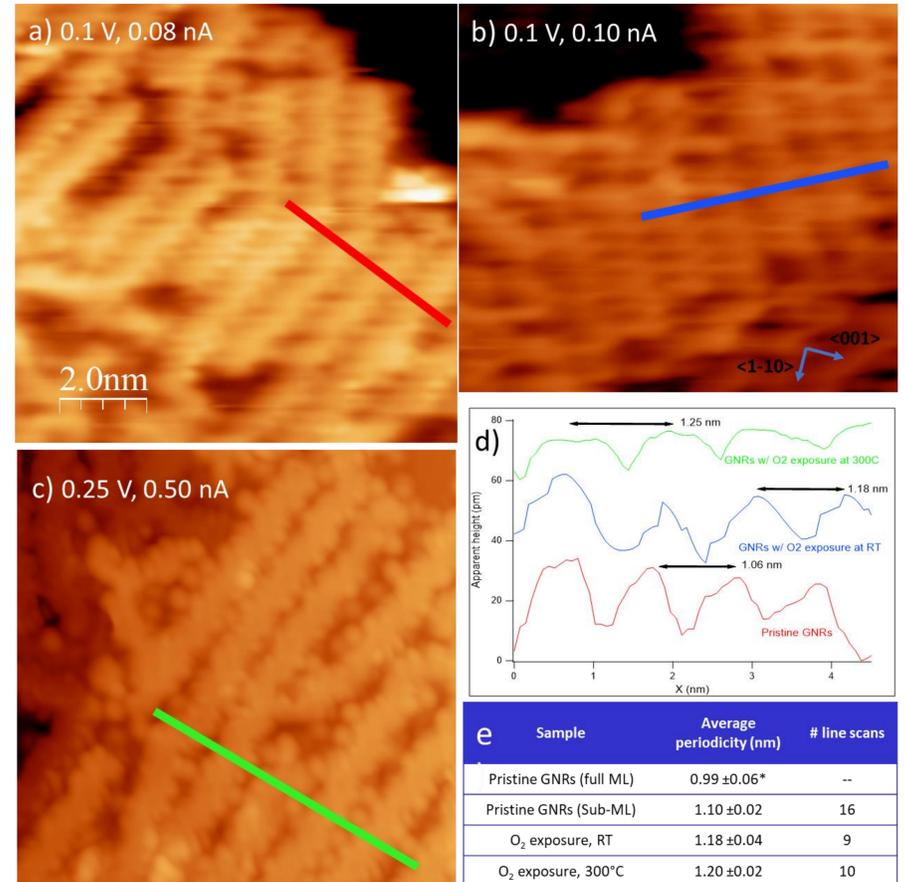
## Synthesis and characterization of pristine GNRs



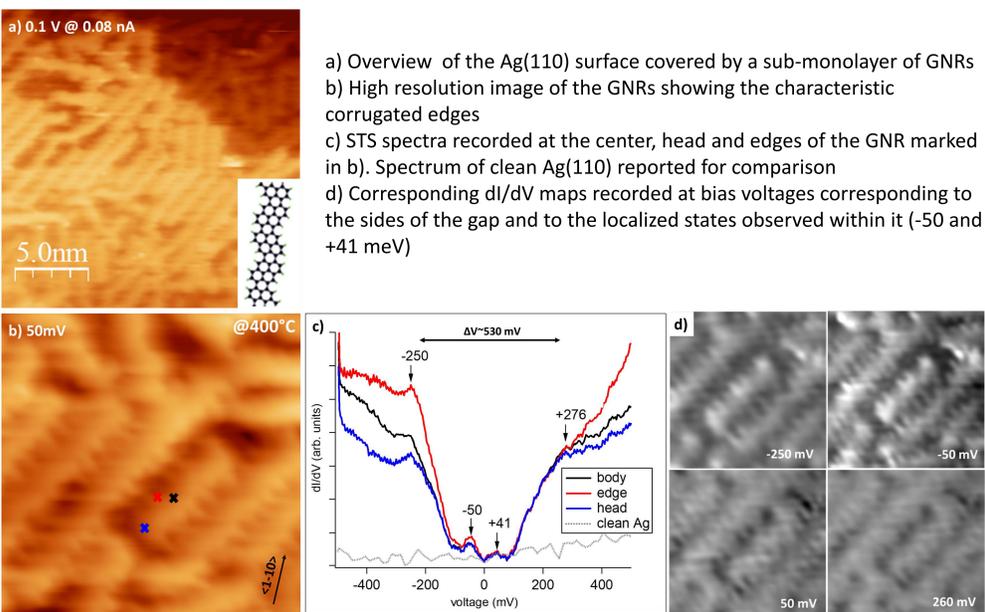
- Left: STM overview of the organometallic structures upon deposition of DBP on Ag(110) at RT ( $V = 150$  meV,  $I = 0.3$  nA). Three different self-assembled geometries (labelled as A, B, C) co-exist on the surface
- Top right: enlarged image of each domain (A, B1, B2, C). Empirical models deduced from the periodicities of the self-assembled structures and from XPS results are superimposed on them (grey: de-brominated pyrene units; blue: Ag adatoms; red: Br atoms)
- Bottom right: line scans cut across the paths marked in the overview for structures A and B1 (color coded)

(a) Br 3d and (b) C 1s core level XPS spectra of 0.6ML DBP deposited on Ag(110) at RT and after annealing the sample at the indicated temperatures. (c) Br 3d and C 1s total intensity as a function of the annealing temperature normalized to the intensity of the corresponding spectra at RT.

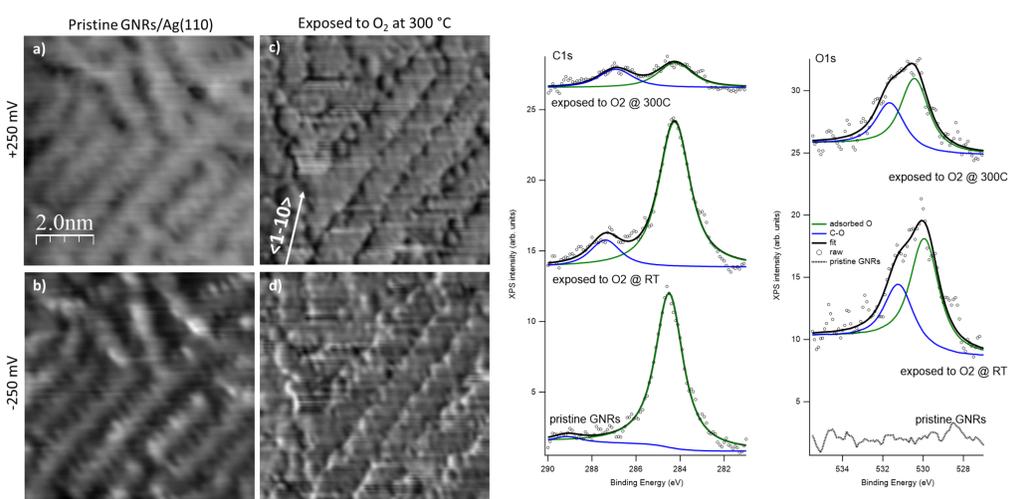
## Oxygen exposure on GNRs



STM images of the Ag(110) surface covered by a sub-monolayer of GNRs and subject to different treatments: (a) pristine GNRs; (b) same as (a) after exposure to O<sub>2</sub> at room temperature; (c) same as (a) after exposure to O<sub>2</sub> at 300°C. Additional small round features appear in between the GNRs and on the bare Ag(110). The nominal O<sub>2</sub> dose is always 900 L. (d) Line scans cut along the paths marked in panels (a-c) showing that the separation between adjacent GNRs increases after O<sub>2</sub> exposure. Table (e) summarizes the average separation between GNRs in ordered arrays with the number of line scans for each preparation (corresponding to the number of GNRs arrays considered). Values are given with their standard error. Data indicated with \* are taken from ref. 8.



Images and STS curves were recorded at  $T=6$  K. Features in the STS reflect the LDOS of the sample and are similar for different parts of the nanoribbon. Our GNRs present a gap of ~530 meV around the Fermi level, with a few states inside (c and d), in particular, a localized state at -50 meV. The behavior is coherent with previous literature on GNRs. Changes in the dI/dV map show differences in contrast when changing the bias voltage (applied to the sample).



Comparison of the dI/dV maps of GNRs pristine and after exposure to oxygen at 300°C. Bias voltages corresponding to the edges of the energy gap measured for the pristine sample are presented.

XPS spectra of the C 1s (left) and O 1s (right) regions recorded on the GNRs/Ag(110) surface before and after O<sub>2</sub> exposure at increasing T. The growth of a C 1s component at 287.4 eV is evident and suggests the formation of C-O bonds and hence oxygen interaction with the GNRs.

## CONCLUSION

We have studied by STM, STS and XPS the formation of graphene nanoribbons synthesized on Ag(110) by surface assisted oligomerization of 1,6-di-bromo-pyrene. Starting from DBP, we observe the formation of achiral graphene nanoribbons with local (2,1) zigzag and armchair edge sites. Such structures have a semiconducting nature with an energy gap of ~530 meV with localized states possibly due to quantum confinement as demonstrated by STS. Significant modification of the surface is observed after exposure to oxygen especially at high temperature. Indeed, the average distance between adjacent nanoribbons increases and the formation of C-O bonds is witnessed by XPS. In parallel, a modification of the surface morphology with the appearance of widespread dots (probably due to Ag-O complexes) is seen in STM images.

These results demonstrate that care must be taken about the modification of supported GNRs upon exposure to reactive gases, not only for their possible interaction with the nanostructures, but also for the changes induced by the reactant on the whole system. This insight opens important perspectives for the optimization of the transfer procedure of the nanoribbons on a different substrate, as well as for operating nanostructure-based devices under realistic conditions.

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