Electronic transport in epoxide and methyl functionalized graphene nanoribbons

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The grafting of chemical groups on the graphene surface strongly modifies the sp^2 hybridization of carbon atoms, thus inducing important modifications on electronic and transport properties, of which the most important is a metal-insulator transition. Possible applications range from carrier mobility engineering to innovative nanolithography techniques. In this context, graphene functionalization has attracted much attention thanks to its reversibility and the possibility of controlling the adsorbate density. However, most of the literature focuses on the functionalization of 2D graphene, without considering the possible role of lateral confinement and edges in nanoribbons.

Here, we present a systematic study of electronic transport in nanoribbons functionalized with two groups of different nature, i.e. epoxide and methyl, see fig.1. We consider ribbons of width W between 5 nm and 20 nm with adsorbate density n between 0.1% and 0.5%. The simulations are based on the Keldysh-Green's function formalism within the tight-binding framework, with Hamiltonians obtained from accurate *ab initio* calculations [1,2]. The results are summarized by fig.2 and fig.3, which show the mean free path ℓ_e as a function of the electron energy E for armchair nanoribbons composed of 41, 83 and 125 dimer lines, corresponding to W=5 nm, 10 nm and 12.5 nm.

As seen from fig.2, methyl functionalization has an almost symmetric impact on the nanoribbon transport properties, which are slightly more degraded for holes (E<0). This trend can be explained in terms of the single defect renormalized Hamiltonian, which is approximately equivalent to that of a vacancy. Conversely, epoxide defects asymmetrically affect ℓ_e, which is markedly reduced for electrons (E>0), see fig3. Again, this originates from the carbon hybridization degree, on whose account the adsorbates are equivalent to divacancies for electrons and to coupled pentagonal rings for holes.

At low methyl density (n=0.1%), for the same number of active conduction modes, ℓ_e decreases with the width of the ribbon, see fig.2(a). For larger ribbons, the dependence of the mean free path on W becomes weaker. Contrariwise, for epoxide functionalization, ℓ_e increases as W increases, see fig.3(a). On the electron side, the mean free path for W=12.5 nm is about 1.5 times that for W=10 nm. This almost linear scaling might be related to the short mean free path (comparable to W), or to the graphene sublattice symmetry preservation. For holes, ℓ_e is almost independent of W. This suggests a more pronounced electron-hole asymmetry in larger ribbons.

When varying the defect density, ℓ_e roughly scales as $1/n$ for both types of defect if n<0.3%, see fig.2(b) and fig.3(b). However, at higher epoxide densities, ℓ_e scales faster than $1/n$ for holes, thus indicating possible correlation effects or the rise of bound states.

In conclusion, epoxide and methyl defects have markedly different impact on nanoribbon transport properties. The differences are consequence of carbon hybridization degree and graphene sublattice symmetry breaking or preservation. The electron-hole asymmetry observed for epoxide functionalization suggests applications in mobility gap engineering [3] with prospects for graphene-based logic devices.

References

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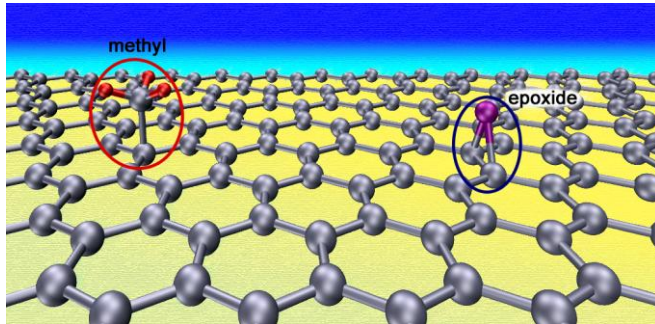
Figures

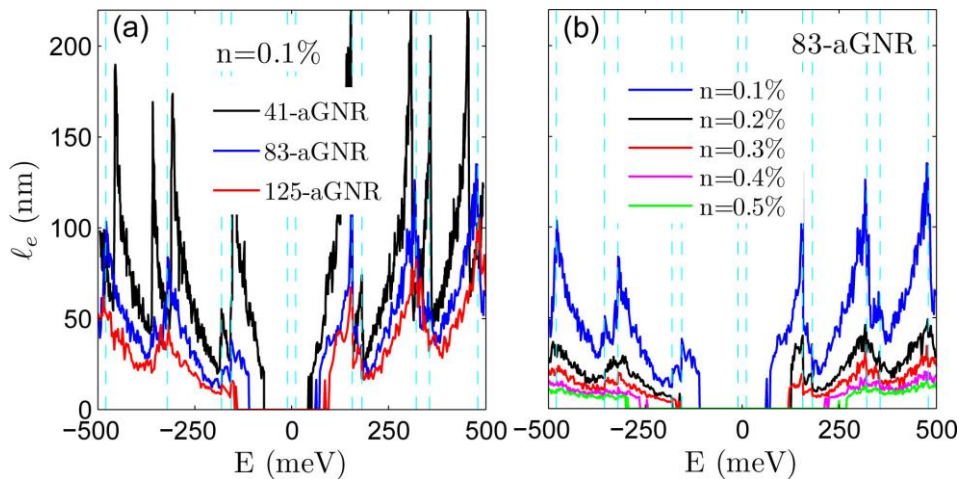*Figure 1: Methyl and epoxide groups on the surface of a graphene nanoribbon.*

Figure 2: Mean free path for methyl functionalized armchair nanoribbons as a function of the electron energy for (a) impurity density n=0.1% and different ribbon width between 5 nm and 12.5 nm (the energy refers to the 10 nm wide ribbon and it is elsewhere rescaled to make the region with the same number of conduction modes coincide) and (b) for width 10 nm and densities between 0.1% and 5%. Vertical lines indicate the activation of conduction modes.
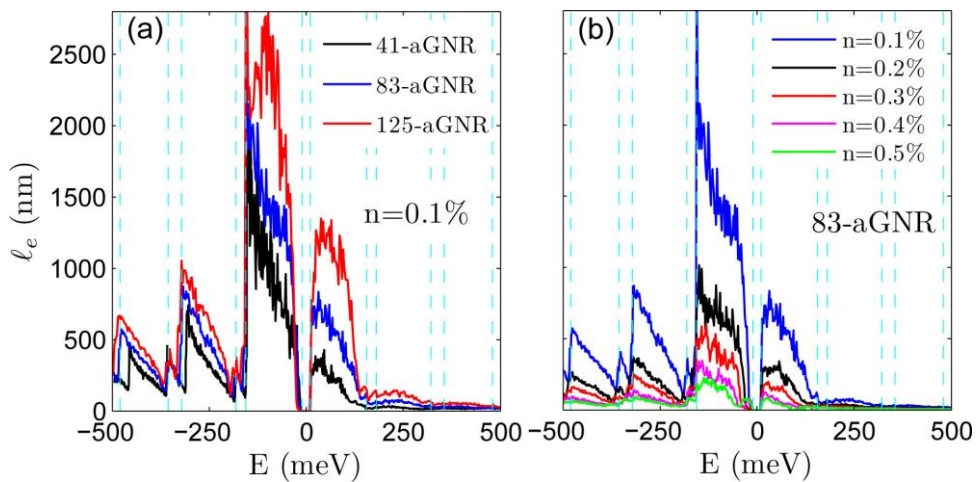

Figure 3: The same as fig.2 but for epoxide functionalized armchair nanoribbons.