Unravelling the growth mechanism of (3,1) graphene nanoribbons on a Cu(111) surface

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Graphene nanoribbons (GNRs) are 1D graphene stripes which are widely investigated due to their remarkable electronic properties compared to 2D graphene. To achieve GNRs with well-defined edge configuration and width, and accordingly control these electronic properties, growth was performed from wisely-chosen molecular building-blocks and was optimized thanks to atomic-scale characterizations using scanning probe microscopies under ultra-high vacuum (UHV). Non-halogenated 9,9'-bianthryl derivatives lead to chiral (3,1)-GNRs, but only on a copper surface. After few controversies, the currently accepted reactional mechanism for the growth of chiral (3,1)-GNRs on a Cu(111) surface is based on a first thermal annealing leading to a protopolymer thanks to on surface-assisted generation of a 2,2'-diradical species. [1] Then, further heating gives the targeted chiral (3,1)-GNR as result of ring-closure driven by a cyclodehydrogenation. Most of the reaction intermediates involved in this mechanism have been observed. Here, we investigate the growth of laterally functionalized (3,1) chiral GNRs by thermal-induced reaction of 10,10'-di(aryl)-9,9'-bianthryl on a Cu(111) surface underUHV by scanning tunnelling microscopy (STM). We find that the growth of GNRs is not possible when the 10,10' positions of the starting building blocks are substituted by aryl groups. Therefore, we revisit the commonly accepted reaction mechanism accounting for the growth of (3,1) GNR on a Cu(111) surface to explain this phenomenon. [2]

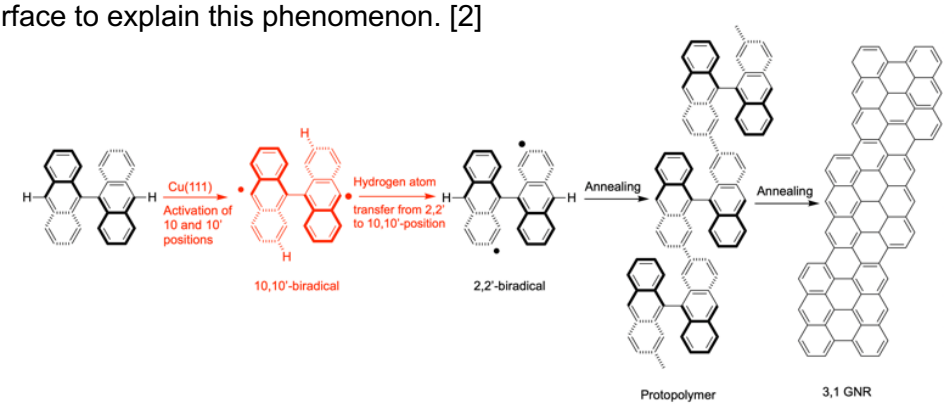

Figure: Completed reaction mechanism for the growth of (3,1) GNR induced by a two-step annealing of BA molecules on a Cu(111) surface. The formation of 10,10'-biradical (in red), followed by radical transposition, is added as initial step.

References

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[2] Geagea, E.; Jeannoutot, J.; Morgenthaler, L.; Lamare, S.; Palmino, F.; Rochefort, A.; Chérioux, F. *Chem. Commun.* **57**, 6043 (2021)

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