Unconventional fabrication of 2D nanostructures and graphene edges

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Citation

Bellunato, A. (2018, December 11). *Unconventional fabrication of 2D nanostructures and graphene edges*. Retrieved from https://hdl.handle.net/1887/67524

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Title: Unconventional fabrication of 2D nanostructures and graphene edges
Issue Date: 2018-12-11

CHAPTER 8

Summary, Conclusions & Outlook

8.1 Summary and general conclusions

Despite a series of promising first and conceptual results, the widespread use of graphene encountered a series of bottlenecks. Beyond the difficulties concerning the agile handling and cheap synthesis of this material, also the nanofabrication and the limited control over its chemistry represent serious limitations. The most promising devices still rely on extremely complicated production processes, which can hardly meet the standardization requirements of large scalability. Furthermore, chemical functionalization is often referred to as the most powerful tool towards the next generation of sensing devices, entitled of advanced molecular selectivity. Still, little or few is achieved concerning the selective functionalization of graphene films, particularly at the edges. Edge functionalities can finely tune the chemical-physical properties of graphene, particularly of nanostructures, where the amount of edges becomes significant over the amount of carbon atoms composing the lattice of graphene. At the state of the art, only chemical synthesis yields highly controlled chemically designed graphene nanostructures, still facing the impossibility of their integration into sensing devices. On the other hand, top down approaches demonstrated the possibility to chemically functionalize graphene, however with limited selectivity between the basal plane and the edges.

This thesis focuses on the unconventional nanofabrication of graphene based nanostructures, while maintaining a strong control on the edge chemistry of graphene. By means of mechanical approaches such as microtomy, in combination with bulk methods such as reactive ion etching or cyclic voltammetry, we fabricated nanopores, nanogaps and nanoribbons architectures, avoiding conventional lithographic procedures. The presented nanofabrication strategies, also, are implemented towards an improved control over the chemistry of the edges of graphene. Accordingly, the thesis is divided in two main parts, first the edges of graphene, their chemistry and application in Chapter 2, Chapter 3, and Chapter 4. Second, we focused on the unconventional fabrication of graphene nanostructures in Chapter 5, and 2D nanoarchitectures in polymeric and metallic supports, in Chapter 6 and Chapter 7. The results demonstrated a first step towards the achievement of scalable, unconventional nanofabrication processes capable of fabricating graphene nanostructures while maintaining and controlling the edge chemistry. We believe that the implementation of these technologies, singularly, and their integration into a unique device is paramount for the next-generation sensing platforms based on graphene. In the near future, for instance, nanogaps and nanopores will merge into a sole nanofluidic system equipped of tunnelling electrodes, where the chemistry at the edges of graphene will be tailored for specific sensing applications.

In Chapter 2, we begin providing an extensive literature review about the chemistry at the edges of graphene. This chapter aims to highlight the state of the art in the field, referring to the most recent literature. The chapter illustrates the importance of the chemistry at the edges of graphene to fine tune the electrical properties of graphene.

Inspired by the outcome of this literature research, in Chapter 3 we investigate the chemical functionalization of the edges of a chemically vapour deposited, CVD, graphene monolayer. The selective functionalization of CVD graphene remains hardly achievable because of the competitive reaction sites provided by the basal plane, primarily at defects and grain boundaries. In order to achieve selective reactions on the edges, we encapsulated graphene within a polymer matrix that was subsequently sectioned via microtomy. Microtomy opens an edge exposed through the sliced interface of the polymeric embodiment. We then built an electrochemical cell for the wet functionalization of this edge. In fact, the edge of graphene is addressed by cyclic voltammetry, where graphene works as the working electrode against an Ag/AgCl reference electrode. Interestingly, we demonstrated the possibility of addressing the chemistry at the edges of graphene without any conventional nanofabrication nor atomic characterization, introducing an innovative approach to the current literature.

The controlled formation of edges in graphene using bulk methods was further explored employing reactive ion etching. Starting from the etching of a suspended CVD film of graphene, in Chapter 4, we successfully built a tunnelling junction between the edges of two graphene electrodes precisely interfaced at sub nanometric distances. This approach yielded the first dynamic tunnelling junction across two single carbon atoms at the edges of two supported graphene monolayers. Our architecture comprises a nanogap composed of two independently supported graphene films interfaced by means of piezoelectric actuators. The edges are interfaced with a twisted configuration crossing in a single point and forming a tunnelling junction across two single carbon atoms. Our adjustable junction allowed also to explore the dynamics of what we speculate being the electrical fingerprint of carbon-carbon bonds forming across the two extremities of the junction upon contact.

Employing a similar approach, in Chapter 5 we used reactive ion etching to address the edge chemistry of another class of graphene nanostructures: graphene nanoribbons. First, we used microtomy to slice metallic nanorods employed as inert masks for the lithography of graphene nanoribbons. Precisely aligned nanorods avoid the application of polymeric resists common in conventional lithography. This, in first instance, prevents polymeric contaminations on the surface of the graphene. Secondly, metallic masks withstand within harsh chemical conditions, for instance during prolonged etching times or, as we attempted, during solution functionalization in organic solvents, incompatible with polymeric resists. Additionally, we employed different etching atmospheres in order to control the edge chemistry of graphene. Despite a poor of control on the crystal structure of the edges of the graphene nanoribbons, we still could observe a modification of the Raman fingerprint, characteristic of doping induced by the chemical functionalization of the edges.

The microtomy of nanorods from metallic thin films is a powerful nanotechnology tool. Beyond the lithography of graphene nanoribbons, microtomy can produce series of metallic nanorods aligned in a parallel fashion and regularly spaced. The coupling of pairs of nanorods at nanometric distance directly yields nanogaps between two metallic electrodes, namely the pair of nanorods. In Chapter 6, multilayered films of polyelectrolytes were grown via Layer-by-Layer deposition and were used as polymeric spacers between gold thin films further converted into nanogaps via microtomy. Microtomy slices the gold films separated at nanometric distance, yielding a nanogap between two nanorods. The flexibility of the Layer-by-Layer deposition and ease of preparation yield a versatile method to assemble thin layers of polyelectrolytes between electrodes with controllable interlayer distance down to 1.5 nm.

In the previous chapters, we extensively worked on the nanostructuring of graphene and its chemical functionalization. The previous work has been performed aiming to fabricate a graphene device integrated into fluidic system able to deliver analytes to the graphene sensing element. Therefore, in Chapter 7, we proposed an innovative nanopore/nanocapillary fluidic system, composed of layered polymeric slabs, which would allow in the future to integrate a nanopore device with a pair of tunnelling electrodes. Similarly to inert mask lithography, we slice metallic thin films embedded in polymeric matrices via microtomy, yielding metallic nanorods supported by polymer slabs. Two nanorods are deposited on top of each other in a crossed configuration. Subsequently, we etch the metallic rods opening two crossing slits through the polymeric supports. The trenches form two nanofluidic channels sharing an aperture: a nanopore. Notably, the overlapping of the two slits forms a nanopore of zero-depth. This capillary, in principle, has the geometrical advantages of atomically thin materials such as graphene, without demanding for extremely complicated fabrications.

Briefly, the present thesis focuses on the unconventional design of nanostructures and the chemical functionalization of graphene edges. This work is the outcome of the attentive analysis of the factors representing a bottleneck in the state of the art in the nanofabrication and chemical functionalization of graphene, which often cannot proceed further than the prototyping phase. Our findings propose a new approach to the field, attempting in a simplification of the current standards of both fabrication, functionalization, and characterization.

We successfully demonstrated the innovative and unconventional achievement of some of the most common nanostructures such as nanopores, nanoribbons and nanogaps, while first proposing a simple, yet effective, way to address the chemistry of the edges of a graphene CVD film. These results, we believe, are of primarily importance to push forward the advancement of the nanotechnology community, particularly for the exploration of non-standard solutions to shape graphene in devices while controlling the chemistry of this material to a larger extent.

8.2 Outlook

Our work explored the fabrication and the chemical functionalization of graphene nanostructures composing sensing devices, and comprising nanopores, nanoribbons and nanogaps.

We already begun exploring the behaviour of tunnelling junctions in water and in presence of buffer solutions and biomolecules. Similarly, lithographic steps were attempted to deliver molecular junctions through gold nanorods separated by multilayered films of polyelectrolytes.

More interestingly, we would like to offer an overview on the shared horizon of these starting results. In fact, in the introduction we highlighted how nanopores, nanoribbons and nanogaps are reunited into sensing devices, even though often only in theoretical simulations. The results and the nanostructures we achieved, instead, can be assembled into real devices. For instance, the multilayered polymeric slabs composing the zero-depth nanopores can host graphene layers in between the two polymer slabs. Etching first the rods and then graphene through the resulting slits, can deliver what is the first graphene nanogap embedded in a nanopore, first joining the electrical device to the fluidic system, Figure 8.1.

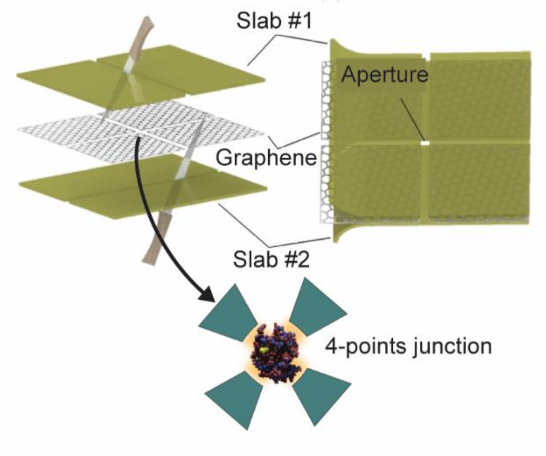

Figure 8.1. Embedding of a nanogap into a nanopore. A four point nanogap is opened in a graphene layer via reactive etching through the slits composing the zero-depth nanopore.

Interestingly, our experiments on reactive etching are the starting point to determine the chemistry of the graphene electrodes, which once immersed into the nanofluidic systems can be addressed for instance via electrochemical approaches, as demonstrated by the electrografting experiments presented in Chapter 3.

In this direction, it is of particular interest to know the characteristic of a tunnelling junction in graphene, and its behaviour when immersed into a liquid environment, similarly to what performed and illustrated in a system such as the twisted nanogaps in Chapter 4.

Thus, we believe that the integration of these nanopore and nanogap components is possible, and we already begun its development. We assembled the very first zero-depth nanopores embedding graphene films and attempted to open a nanometric gaps across the pore, Figure 8.2.

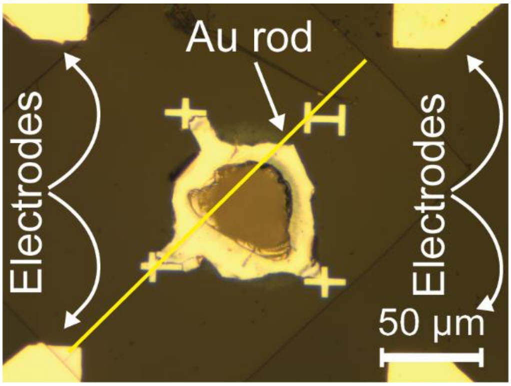

Figure 8.2. Zero depth-nanopore/nanogap. A supported gold nanorod is deposited on a micrometer window as first layer of a zero-depth nanopore embedding a graphene nanogap.

We believe that our work is an important starting point towards the fabrication of graphene based tunnelling junctions and that further investigation can lead to the assembly of real sensing devices operating in water with graphene and other two dimensional materials as the main sensing element.

8.3 General perspectives

Since its discovery, graphene promised to revolutionize many aspects of technology, varying from electronics, to composites and building materials. Particularly, the 2D nature of graphene and its outstanding thermal, mechanical, and electronic properties pointed straight to its application at the nanometre scale, reaching atomistic control over the topology and chemical structure of the carbon atoms composing its lattice. Eventually, graphene could be tailored in size and properties for almost any imaginable application.

Through this work, graphene demonstrated itself as a flexible and powerful platform, which can be adapted to an extended variety of processing techniques, fulfilling the long-told promise of applicability that too often fatigues to be translated into actual technology (especially out of the lab). In fact, the promise of a flexible material, easily tailored in various architectures at the nanoscale and chemically defined, inspired the different chapters composing this thesis. Indeed, graphene demonstrated a great degree of flexibility, that successfully applied to different architectures such as nanoribbons, embedded transistors and nanogaps. Outstandingly, the high workability of such a simple layer of carbon atoms allowed the investigation of extremely complex problems with fairly easy approaches, designed to adapt to graphene at the nanoscale, while being simple and innovative. Whereas graphene appears as the only common element connecting the dots through this work, it actually demonstrates its ability to adapt and to be incorporated in completely different systems expected to compose extremely different devices addressing problems that range from highly scientific platforms for the study of tunnelling currents across nanogaps and molecules, to small transistors which might one day compose any electronic device. Based on the major research interest of our working group, a great focus was pointed to the potential of these graphene architectures into biomolecular sequencing devices, as suggested also by the innovative work performed on layered nanopores architectures, meant to integrate graphene nanogaps and nanopores.

In our perspective, graphene maintained its promise of being a robust and flexible material, with outstanding properties and the potential of interesting many aspects of science and technology. Huge efforts were spent in the attempts of modulating also the chemistry at the edge of graphene. This subject is of rising interest in the scientific community as it represents a valuable tool in order to specifically address the properties of graphene both in terms of its physical properties and chemical interactions. Graphene, thanks to the extended aromaticity, is often imaged as an inert material. Edges, nonetheless, offer excellent reactivity and ideal reaction sites for the chemical functionalization of graphene. The edge functionalization of graphene is too often explored from the perspective of chemically synthetized graphene, or exfoliated graphene, where the process solution also addresses the chemistry of this material. Nonetheless, most of the technological application of graphene in the near future are expected to interest CVD graphene in the form of top-down processed graphene, starting from large graphene films which original edge chemistry is uncontrollable. Is this a limit of graphene? Do its flexibility and ability of being widely processed and structured encounter a bottle neck when dealing with its chemistry? Is its edge chemistry controllable also in top down approaches and on large area CVD films? We demonstrated at least two different transistor architectures, on completely different substrates and prepared accordingly to two completely different protocols which answer these questions. Yes, the chemistry at the edge of graphene can be controlled and can be addressed even when not processed through organic synthesis nor solution-based exfoliation. The chemistry of the edges of graphene becomes accessible at large, thin film scale, with immediate repercussion on its properties, and for the first time studied with bulk characterization methods, rather than hardly accessible atomistic approaches such as scanning probe microscopy. We functionalized CVD graphene films that can be transferred, isolated, and processed out of synthesis solutions and CVD exfoliation media. In this research, the chemistry at the edges of graphene at last encounters graphene samples which can be translated into actual devices and practical technologies.