## Bottom-up Synthesis and Characterization of Nanoporous Graphene Structures with Graphene or Biphenylene-type Fusion

**Ignacio Piquero-Zulaica**<sup>1,2</sup>, Paula Angulo-Portugal<sup>1</sup>, Martin Irizar<sup>3</sup>, Longfeng Huang<sup>4</sup>, Mamun Sarker<sup>5</sup>, Mustafa A. Ashoush<sup>6</sup>, Zakaria M. Abd El-Fattah<sup>6</sup>, Johannes Barth<sup>4</sup>, Frederik Schiller<sup>1</sup>, Dimas G. de Oteyza<sup>7</sup>, Alexander Sinitskii<sup>5</sup>, Aran Garcia-Lekue<sup>3</sup> and Martina Corso<sup>1</sup>

<sup>1</sup> Centro de Física de Materiales CSIC/UPV-EHU, Manuel Lardizabal 5, 20018 San Sebastian, Spain. <sup>2</sup> IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain

<sup>3</sup>Donostia International Physics Center (DIPC), Manuel de Lardizabal 4, E-20018 San Sebastian, Spain. <sup>4</sup> Physics Department E20, TUM School of Natural Sciences, Technical University of Munich, James-Franck-Straße 1, D-85748 Garching, Germany.

<sup>5</sup> Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska – Lincoln, Lincoln, Nebraska 68588, United States

<sup>6</sup> Physics Department, Faculty of Science, Al-Azhar University, Nasr City, E-11884, Cairo, Egypt.

<sup>7</sup> Nanomaterials and Nanotechnology Research Center (CINN), CSIC-UNIOVI-PA, El Entrego, Spain Contact: ignacio.piquero@ehu.eus

The application of graphene derivatives in semiconductor devices such as field-effect transistors requires band gap tuning, which can be achieved, for instance, with the insertion of nanopores<sup>1</sup>. The bottom-up on-surface synthesis in ultra-high vacuum, using haloarene precursors on catalytic noble metal surfaces, allows for the synthesis of atomically well-defined nanoporous graphene (NPG) structures<sup>2,3</sup> suitable for such device applications.

Here we use a new approach to synthesize novel NPG structures. Firstly, we synthesize porous graphene nanoribbons (p-GNRs) on Au(111) and Au(788) using 7,10-dibromo-1,4-diphenyl-triphenylene (DBDT)<sup>4,5</sup>. LT-STM/STS, NC-AFM and ARPES measurements show that p-GNRs grow with low-number of defects and exhibit semiconducting character.

When the p-GNR coverage is high on Au(111), a subsequent thermal annealing to 500°C induces the formation of diverse NPG structures with either graphene-type or biphenylene-type fusion (see Figure 1). The structural and electronic properties of these intriguing NPG structures are characterized with LT-STM/STS, NC-AFM and supported with density functional theory (DFT) calculations. DFT shows that while graphene-type NPGs are direct bandgap semiconductors, biphenylene-type NPGs bear an indirect bandgap. In addition, the insertion of biphenylene into the NPG induces a reduction of the bandgap as compared to the purely graphene-type counterparts.

These interesting results add an additional control-knob towards engineering the electronic properties of NPGs suitable for prospective device applications.

- [1] T. G. Pedersen et al., Phys. Rev. Lett., 100 (2008) 189905
- [2] C. Moreno et al., Science, **360** (2018) 199
- [3] I. Piquero-Zulaica et al., Nat Commun, 15 (2024) 1062
- [4] Q. Fan et al., Nano Lett., 24 (2024) 10718
- [5] M. Sarker et al., J. Am. Chem. Soc., 146 (2024) 14453



Figure 1: LT-STM and NC-AFM images of Graphene-type and Biphenylene-type NPG structures.