Theoretical and experimental characterization of sp-, sp^2- carbon 2D networks obtained via on-surface synthesis

Simona Achilli[1]
Guido Fratesi[1], Nicola Manini [1], Giovanni Onida[1], Andi Rabia[2], Alberto Milani[2], Andrea Li Bassi[2], Francesco Tumino[2], Alessio Orbelli Biroli[4], Alberto Bossi[3], Valeria Russo[2], Nicolò Bassi[2], Wei Xu[5], Carlo S. Casari[2]
[1]*Dept. of Physics, Università degli Studi di Milano, Via Celoria 16,20133 Milano (Italy)*
[2]*Dept. of Energy, Politecnico di Milano,via Ponzio 34/3 – 20133, Milano (Italy)*
[3] *Istituto di Scienze e Tecnologie Chimiche "G. Natta" del CNR (CNR-SCITEC), SmartMatLab Centre, Via Golgi 19, 20133 Milano (Italy)*
[4]*Dipartimento di Chimica, Università di Pavia, via Taramelli 12 - 27100 Pavia, (Italy)*
[5] *Interdisciplinary Materials Research Center, College of Materials Science and Engineering, Tongji University, Shanghai 201804, (P. R. China)*
Simona.achilli@unimi.it

Network formed by sp- and sp2-hybridized carbon atoms with high degrees of π conjugation, namely graphynes and graphdiynes, are stimulating intense research efforts for their potential use in nanoelectronics, catalysis and photo-conversion, due to their high charge carrier mobility and tunable band gaps and band structures [1, 2,3]. The significant advancement in the synthesis of these materials through on-surface assembly of molecular precursors opens the way to the design of novel carbon networks, displaying different geometries and physical properties. Nevertheless, the fabrication of extended ordered 2D monolayers, their characterization and the definition of protocols for their manipulations represent challenging steps in view of their applications. We present a multidisciplinary characterization of sp-, sp^2- and hybrid sp- sp^2 2D systems obtained by on-surface synthesis of brominated molecular precursors on Au(111) surface. By combining *ab initio* calculations based on Density Functional Theory (DFT) and different experimental techniques, such as Scanning Tunneling Spectroscopy and Microscopy (STS and STM) and Raman spectroscopy we give a thorough description of nanoscale linear structures and 2D materials, as carbyne and graphdiyne, and of their interaction with the underlying metal substrate [4-8]. In particular we analyze the evolution of the structural, electronic and vibrational properties during the different stages of the formation, passing from the as deposited metallorganic network to pure sp-/ sp^2- nanostructures during annealing, and we show the effect of the substrate coupling on their semiconducting properties.

References

[1] Y. Fang, Y. Liu, L. Qi, Y. Xue and Y. Li, Chem. Soc. Rev 51, 2681 (2022).
[2] Casari, C. et al., Nanoscale 8, 4414 (2016).
[3] C.S. Casari et al. MRS Communications 8(2), 207-219 (2018).
[4] Fratesi, G. et al., Materials 11, 2556 (2018).
[5] Rabia, A. et al., Nanoscale 11, 18191 (2019).
[6] Rabia, A. et al., ACS Appl. Nano Mater. 3, 12178 (2020).
[7] S. Achilli et al. 2D Materials 8 044014 (2021).
[8] S. Achilli et al. Phys. Chem. Chem. Phys. 24, 13616-13624 (2022).

Figures

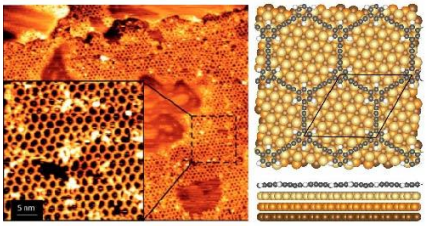

Figure 1: 2D sp-sp2 carbon network on Au(111). STM and theory model