

STM Study of Exfoliated Few Layer Black Phosphorus Annealed in Ultrahigh Vacuum

A. Kumar¹, F. Telesio¹, S. Forti², A. Al Temimy², C. Coletti², M. Serrano-Ruiz³, M. Caporali³, M. Peruzzini³, F. Beltram¹, and S. Heun¹

¹INEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza San Silvestro 12, 56127 Pisa, Italy, ²Centre for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 Pisa, Italy, ³Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

Exfoliated black phosphorus (bP) has found a prominent place in the family of van der Waals materials, thanks to its direct band-gap, tunable with layer number, and to its strong in-plane anisotropy. Another peculiarity of bP is its high reactivity, especially with oxygen and moisture, which results in water-soluble phosphorus oxiacids. This represents a major drawback for surface science studies of this material. Here, we investigate surface modifications on exfoliated bP flakes upon subsequent annealing steps, focusing on the temperature range around 375 °C, when sublimation starts and a controlled desorption from the surface occurs with the formation of well-aligned craters. There is an open debate in the literature about the crystallographic orientation of these craters, i.e. whether they align along the zigzag¹ or armchair² direction. Thanks to the atomic resolution provided by STM, we can directly identify the crystallographic orientation of the craters with respect to the crystal, solving the controversy³: the long axis of the craters is aligned along the zigzag direction. The authors thank the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 670173) for funding the project PHOSFUN by an ERC Advanced Grant to MP. References: [1] M. Fortin-Deschenes et al., *J. Phys. Chem. Lett.*, 7, 1667 (2016) [2] X. Liu et al., *J. Phys. Chem. Lett.*, 6, 773 (2015) [3] A. Kumar et al., *2D Materials* 6, 015005, (2019)

TELESIO Francesca
Istituto Nanoscienze-CNR and Scuola Normale Superiore
NEST Laboratory
Piazza San Silvestro 12
56127
Italy
+39050509470
francesca.telesio@nano.cnr.it