

## Palladium/black phosphorus nanohybrid: what surface techniques tell us about the Pd-P interaction

Matteo Vanni,<sup>a,h</sup> Manuel Serrano-Ruiz,<sup>a</sup> Francesca Telesio,<sup>b</sup> Stefan Heun,<sup>b</sup> Martina Banchelli,<sup>c</sup> Paolo Matteini,<sup>c</sup> Antonio Massilimiliano Mio,<sup>d</sup> Giuseppe Nicotra,<sup>d</sup> Corrado Spinella,<sup>d</sup> Stefano Caporali,<sup>e</sup> Andrea Giaccherini,<sup>f</sup> Francesco d'Acapito,<sup>g</sup> Maria Caporali,<sup>a,\*</sup> Maurizio Peruzzini<sup>a,\*</sup>

<sup>a</sup>CNR-ICCOM, Via Madonna del Piano10, 50019 Sesto Fiorentino, Italy

<sup>b</sup>NEST Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza S. Silvestro 12, 56127 Pisa, Italy

<sup>c</sup>CNR-IFAC, Via Madonna del Piano10, 50019 Sesto Fiorentino, Italy

<sup>d</sup>CNR-IMM Istituto per la Microelettronica e Microsistemi, VIII strada 5, I-95121 Catania, Italy.

<sup>e</sup>Department of Industrial Engineering, University of Florence, Via di S. Marta 3, Florence, 50139, Italy

<sup>f</sup>Department of Earth Sciences, University of Florence, Via La Pira 4, Firenze, 50121, Italy

<sup>g</sup>CNR-IOM-OGG, c/o European Synchrotron Radiation Facility - LISA CRG, Grenoble, France.

<sup>h</sup>Department of Biotechnology, Chemistry and Pharmacy, University of Siena, 53100 Siena, Italy

matteo.vanni@iccom.cnr.it

Since the discovery of graphene in 2004 the interest in 2D materials has grown dramatically due to their peculiar electronic, thermal and optical properties.<sup>1</sup> One of the latest member to join this family is black phosphorus, which in contrast to graphene, exhibits a unique puckered honeycomb structure based on sp<sup>3</sup> hybridized atoms, each bearing a lone pair. Thanks to this feature black phosphorus (bP) is an excellent support to immobilize metal nanoparticles and much work has been done recently to prepare M NPs/bP heterostructures (M: Co,<sup>2a</sup> Pt<sup>2b</sup>) mainly addressed to electrocatalytic and photocatalytic applications. However, no deep experimental investigations to highlight the nature of the bond between black phosphorus nanosheets and surface metal atoms has ever been carried out. We prepared a new Pd-bP nanohybrid by growing bare Pd nanoparticles on exfoliated black phosphorus and tackled the problem of elucidating the Pd-P interaction with different surface technique (EXAFS, XPS, EELS). Our material was also tested as a catalyst for the selective hydrogenation of chloronitrobenzene to chloroaniline showing a far superior chemoselectivity compared to other heterogeneous systems based on palladium nanoparticles.

### Acknowledgements

Thanks are expressed to EC for funding the project PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" (ERC ADVANCED GRANT to M.P.). MIUR is kindly acknowledged for financial support through Project PRIN 2015 (grant number 20154X9ATP).

### References

- 1 H. Liu, K. Hu, D. Yan, R. Chen, Y. Zou, H. Liu, S. Wang. *Adv. Mater.*, **2018**, *30*, 1800295.
- 2 a) F. Shi, Z. Geng, K. Huang, Q. Liang, Y. Zhang, Y. Sun, J. Cao, S. Feng. *Adv Sci.*, **2018**, *5*, 1800575 b) L. Bai, X. Wang, S. Tang, Y. Kang, J. Wang, Y. Yu, Z.-K. Zhou, C. Ma, X. Zhang, J. Jiang, P. K. Chu, X.-F. Yu. *Adv. Mat.*, **2018**, *30*, 1803641.