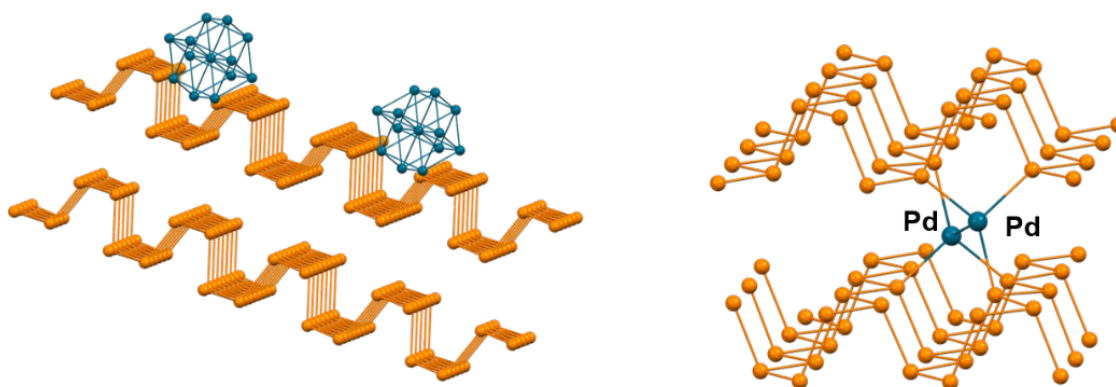


Reactivity of Black Phosphorus with Pd Compounds

Matteo Vanni¹, Marco Bellini¹, Silvia Borsacchi^{2,3}, Lucia Calucci^{2,3}, Maria Caporali¹, Stefano Caporali⁴, Francesco D'Acapito⁵, Marco Geppi^{2,6}, Andrea Giaccherini⁷, Andrea Ienco¹, Gabriele Manca¹, Antonio Massimiliano Mio⁸, Giuseppe Nicotra⁸, Werner Oberhauser¹, Manuel Serrano-Ruiz¹, Martina Banchelli⁹, Francesco Vizza¹, Maurizio Peruzzini¹

¹CNR-ICCOM, Sesto Fiorentino, Italy ²Center for Instrument Sharing of the University of Pisa (CISUP), Pisa, Italy ³CNR-ICCOM, SS Pisa, Italy ⁴Department of Industrial Engineering, University of Florence, Italy ⁵CNR-IOM-OGG, c/o ESRF, Grenoble, France ⁶Department of Chemistry and Industrial Chemistry (DCCI), University of Pisa, Italy ⁷Department of Earth Sciences, University of Florence, Italy ⁸CNR-IMM, Catania, Italy ⁹CNR-IFAC, Sesto Fiorentino, Italy

Since its first reported exfoliation in 2014, the interest in 2D black phosphorus (2D BP) and its chemical functionalization has grown dramatically [1], though a satisfactory structural description of the modified materials is seldom achieved. Herein, the functionalization of 2D BP starting from molecular Pd precursors is presented, leading either to supported Pd NPs (Pd/BP) or to interlayer Pd–Pd discrete units (Pd₂/BP). An in-depth solid-state characterization of the new materials was carried out by means of XPS, HAADF-STEM, XRD, NMR MAS and XAS. Remarkably, XAS analysis, backed up by DFT modelling, was crucial in revealing the existence of Pd₂ moieties stacked amidst BP layers in Pd₂/BP. The potential application of these heterogeneous systems as catalysts was demonstrated in distinct processes, namely the selective hydrogenation of chloronitrobenzene to chloroaniline and the hydrogen evolution reaction (HER) from acidic medium.



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[1] S. Thurakkal, X. Zhang, *Adv. Sci.*, **2020**, 7, 1902359.