

TITUTO DI CHIMICA DEI COMPOSTI ORGANOMETALLICI

Immobilization of Palladium Nanoparticles on Exfoliated Black Phosphorus

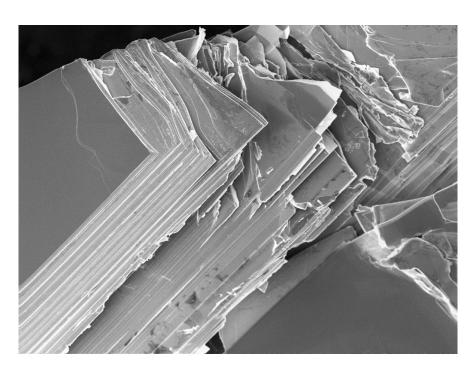


Matteo Vanni,^{a,b} Manuel Serrano-Ruiz,^b Francesca Telesio,^c Stefan Heun,^c Maria Caporali,^{b*} Maurizio Peruzzini^{b*}

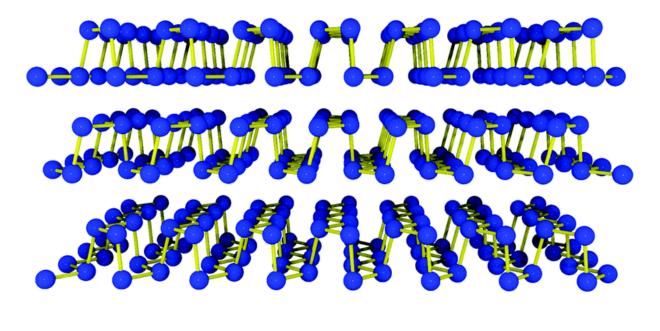
^aDipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, via A. Moro, 2, 53100 Siena, Italy. ^b CNR ICCOM, Via Madonna del Piano 10, 50019 Sesto Fiorentino (Firenze), Italy. ^c NEST, Istituto Nanoscienze–CNR and Scuola Normale Superiore, Piazza San Silvestro, 12, 56121 Pisa (Italy).

mvanni@iccom.cnr.it

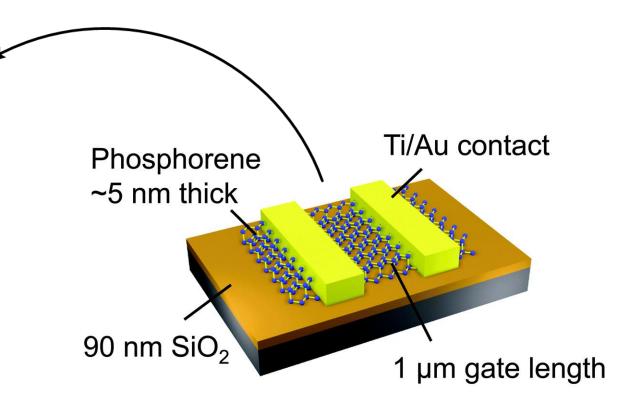
One of the latest member to join the family of 2D materials is few layer black phosphorus. Black phosphorus (bP) is a natural semiconductor which exhibits band gap tunability upon variation of the layer thickness (from 0.3 eV of the bulk BP to 1.8 eV of the monolayer *phosphorene*) and a strong anisotropy in both its electric and mechanical properties along different directions in the layer. A surface made of sp³ hybridized phosphorus atoms seems excellent as a support to anchor metal nanoparticles. We thus decorated 2D bP with Pd nanoparticles grown *in situ* and tested the resulting nanohybrid Pd/bP in the catalytic reduction of nitroarenes. The effect of 2D bP is a dramatic enhancement of the selectivity.



SEM of black phosphorus

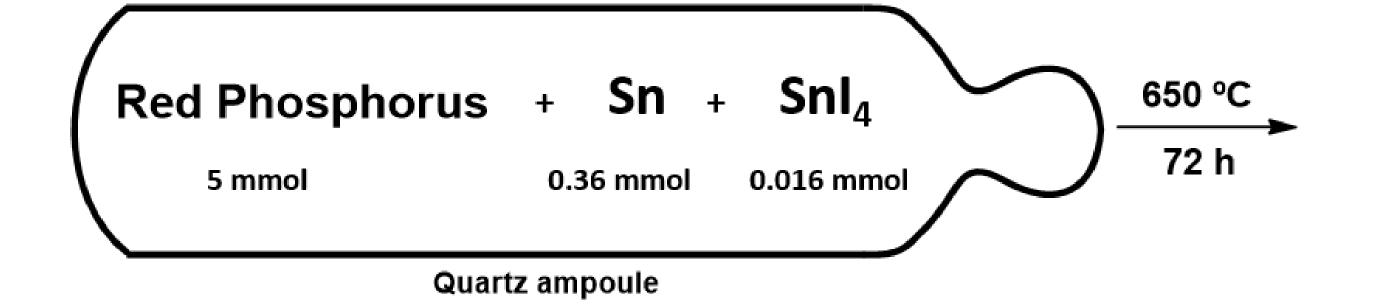


Black phosphorus structure

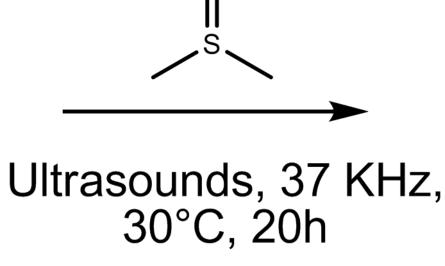


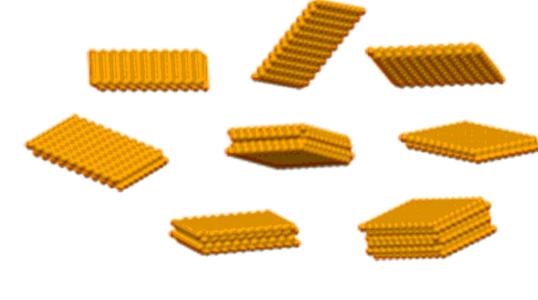
Black phosphorus based FET

Black Phosphorus: Synthesis and Exfoliation





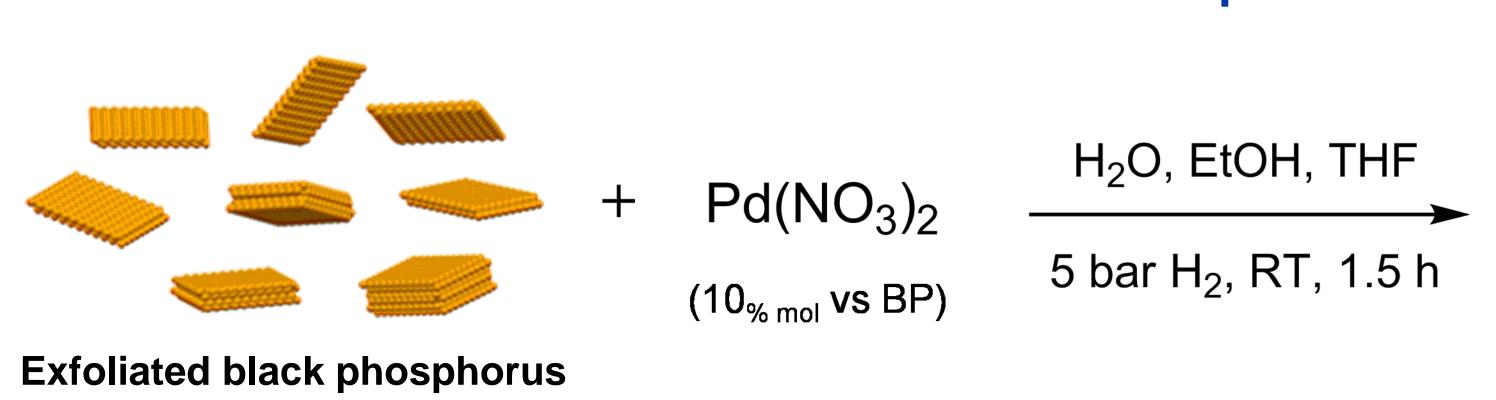


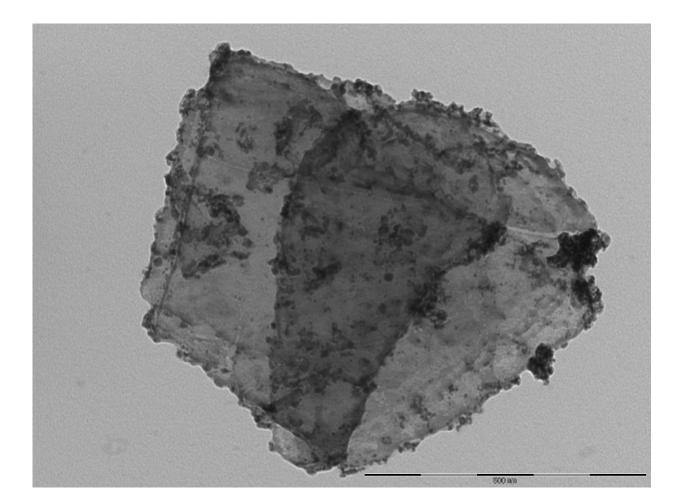


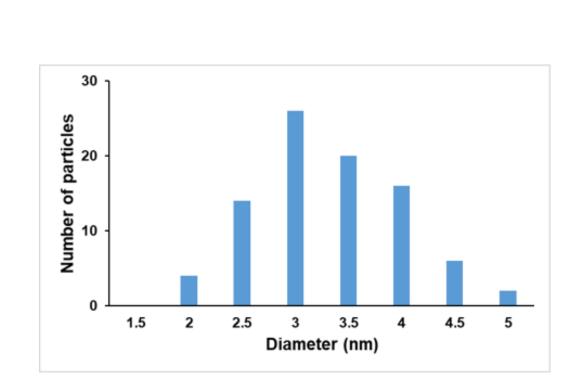
Black phosphorus crystals

Exfoliated black phosphorus

Palladium Nanoparticles Growth on 2D BP







A_{1g} B_{2g} A_{2g} Si BP

A_{1g} A_{2g} Pd/BP

300 350 400 450 500 550 600

Raman shift (cm⁻¹)

Raman spectra of pristine bP (up) and Pd/bP (down)

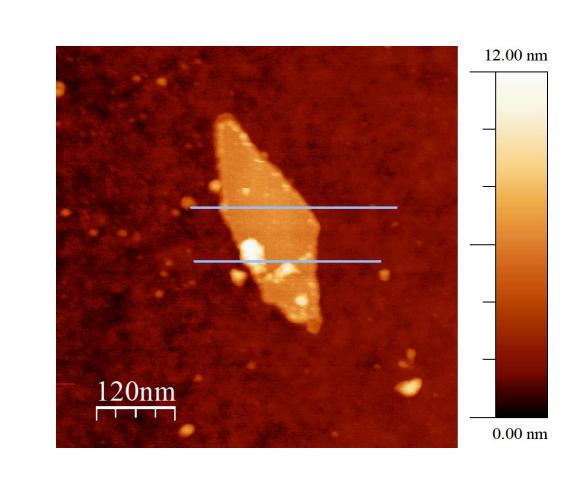
BP (020) BP (040)

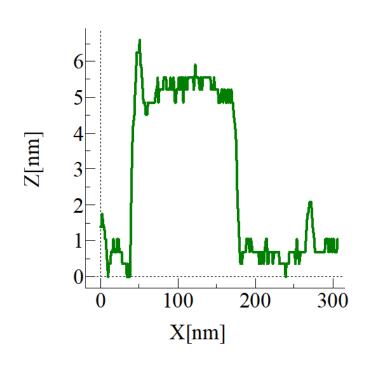
Pd (111) BP (060)

1 14 24 34 44 54 64 74 84 28°

Powder XRD spectrum of Pd/bP

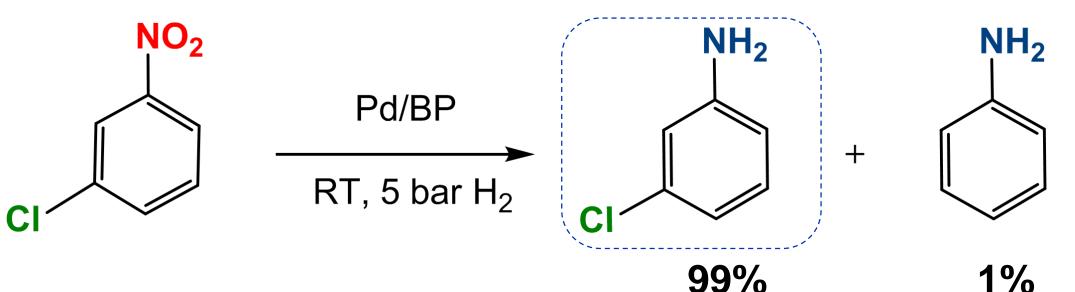
TEM image of Pd NPs on BP





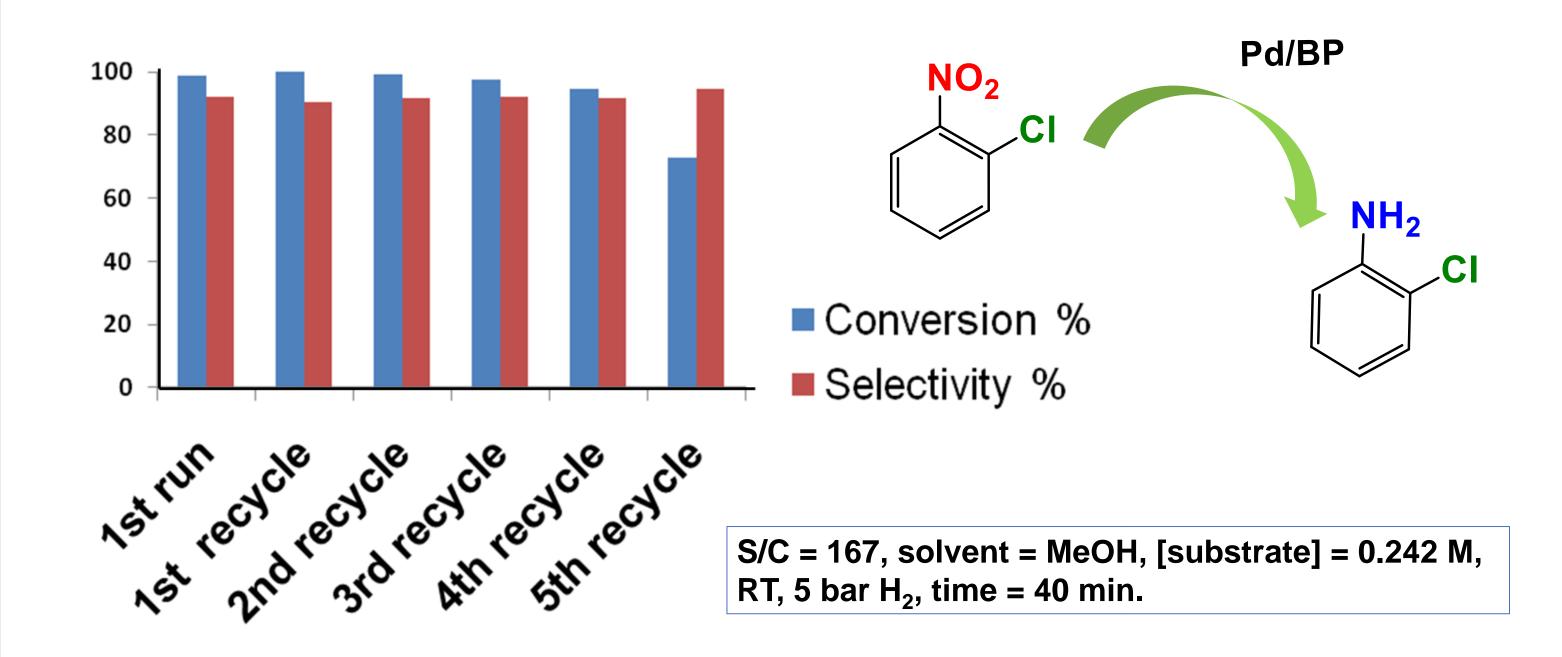
AFM image of a flake

Selective reduction of nitroarenes with Pd/bP



			99% 19		%	
Substrate	Catalyst	S/C	Time (min)	Conversion %	Selectivity %	
1-chloro-3- nitrobenzene	Pd/BP	110	60	98	99	
1-chloro-2- nitrobenzene	Pd/BP	167	60	100	95	
1-chloro-2- nitrobenzene	Pd/ BP light fraction	167	40	99	97	
4-nitrobenzaldehyde	Pd/BP	110	90	99	100	
1-chloro-2- nitrobenzene	Pd/C	167	40	86	72	

o-chloronitrobenzene: recycle test



Acknowledgements

This work was supported by an ERC Advanced Grant PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" (Grant Agreement No. 670173) to M. P.