Palladium/Black Phosphorus Nanohybrid

Unraveling the Nature of Pd-P Interaction and Application in Catalysis

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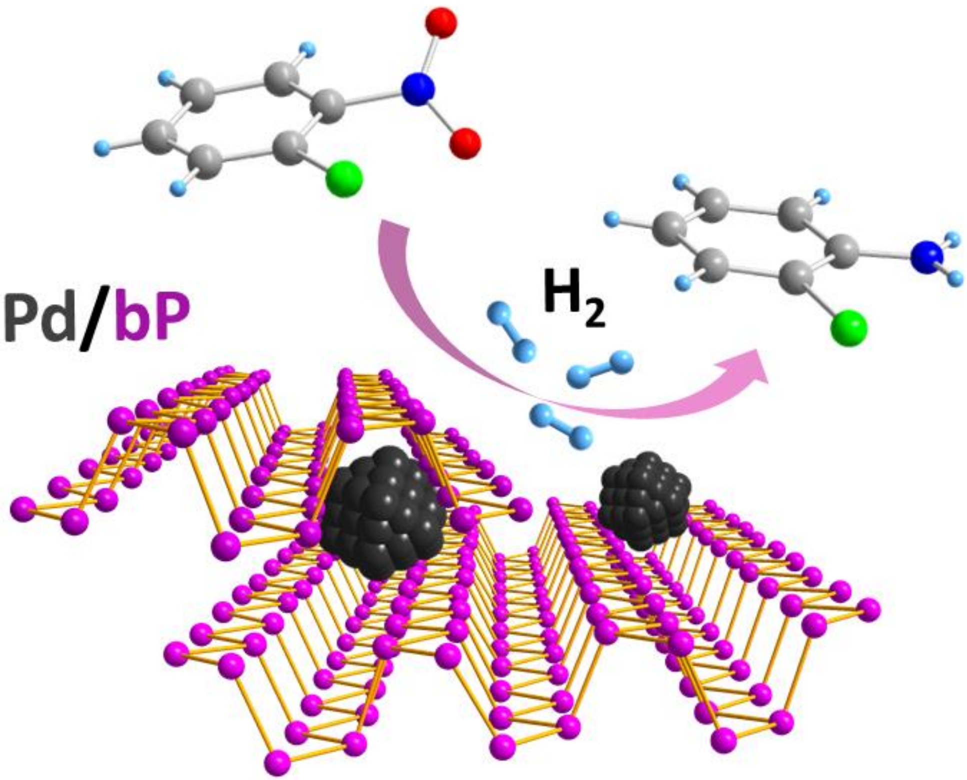

Matteo Vanni

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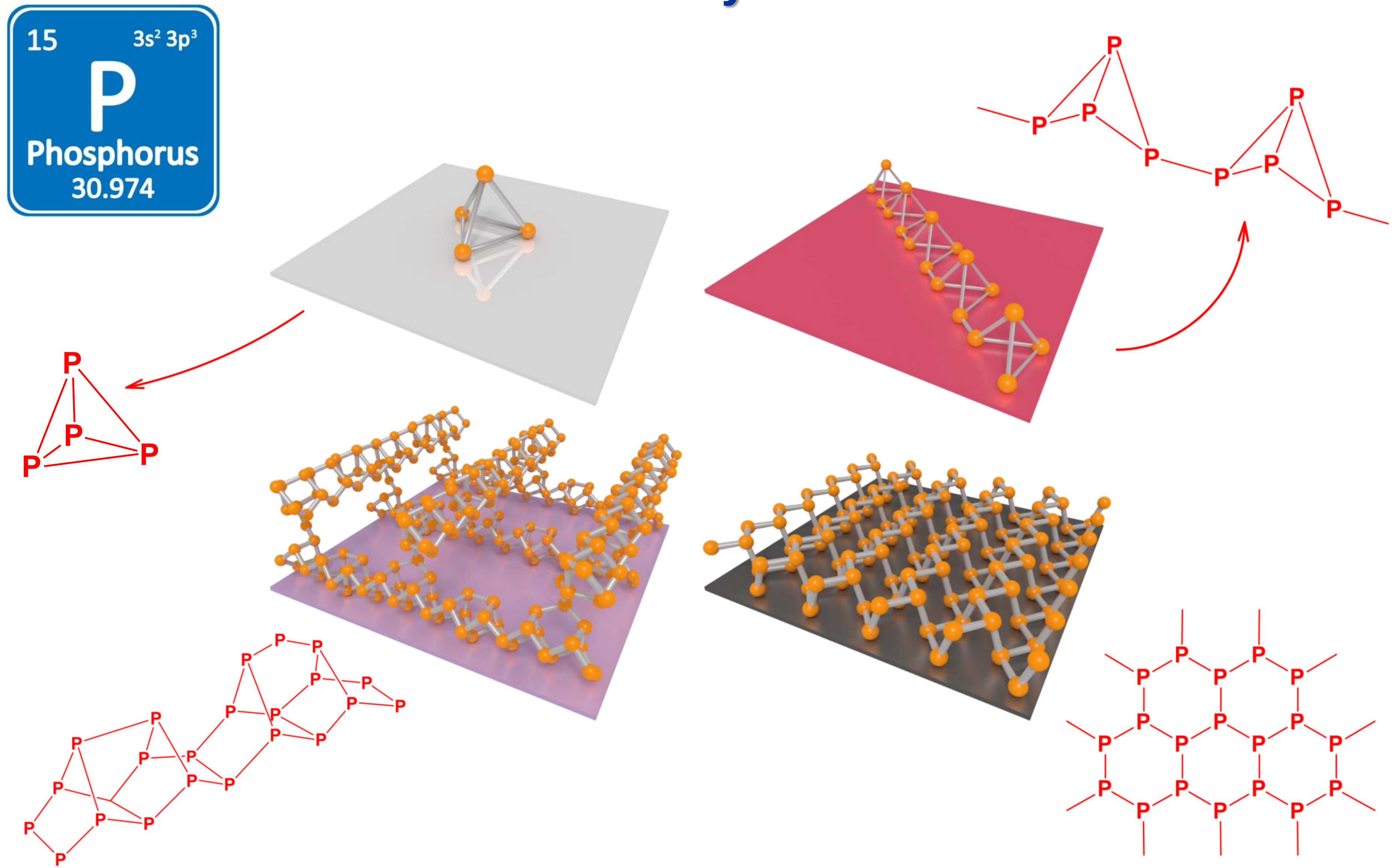
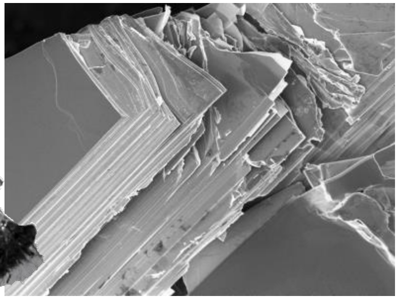
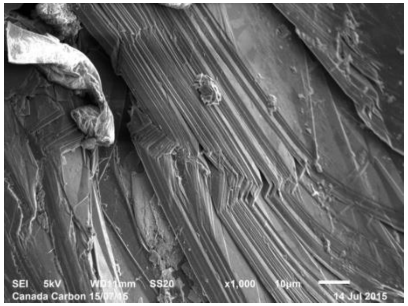


Black Phosphorus (bP) as a P counterpart of Graphite

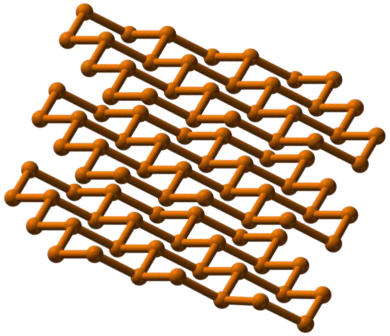
Black phosphorus crystals.



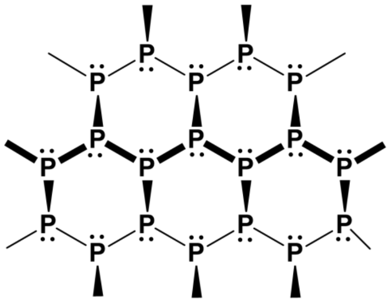
SEM image highlighting the laminar structure



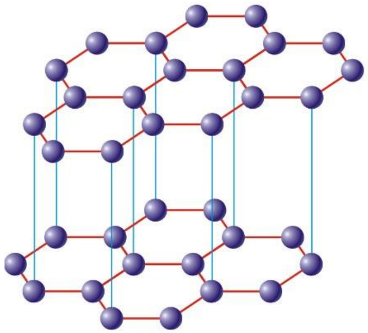
SEM image of a graphite crystal

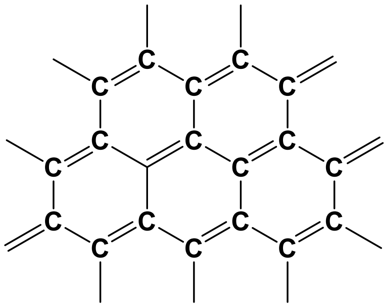


Puckered honeycomb structure of black phosphorus.



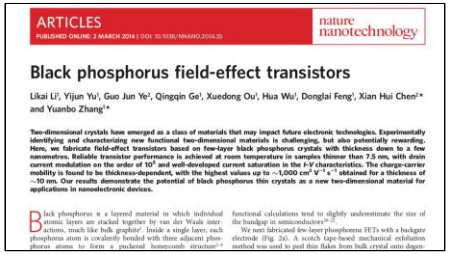
sp^3 hybridized P atoms





sp^2 hybridized C atoms

Black phosphorus exfoliation



ARTICLES
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nature nanotechnology

Black phosphorus field-effect transistors

Likai Li[1], Yijun Yu[1], Guo Jun Ye[2], Qingqin Ge[1], Xuedong Ou[1], Hua Wu[1], Donglai Feng[1], Xian Hui Chen[2]* and Yuanbo Zhang[1]*

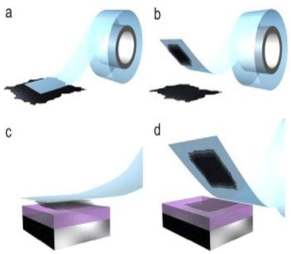
Two-dimensional crystals have emerged as a class of materials that may impact future electronic technologies. Experimentally identifying and characterizing new functional two-dimensional materials is challenging, but also potentially rewarding. Here, we fabricate field-effect transistors based on few-layer black phosphorus crystals with thickness down to a few nanometres. Reliable transistor performance is achieved at room temperature in samples thinner than 7.5 nm, with drain current modulation on the order of 10^5 and well-developed current saturation in the *I–V* characteristics. The charge-carrier mobility is found to be thickness-dependent, with the highest values up to ~1,000 $cm^2 V^{-1} s^{-1}$ obtained for a thickness of ~10 nm. Our results demonstrate the potential of black phosphorus thin crystals as a new two-dimensional material for applications in nanoelectronic devices.

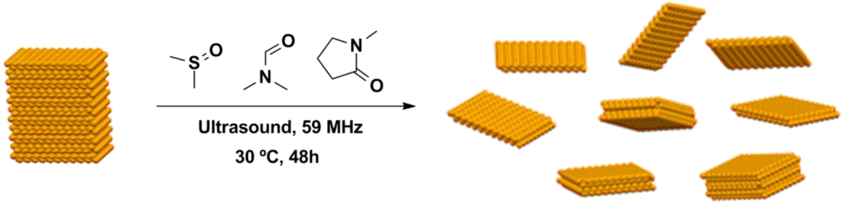
Black phosphorus is a layered material in which individual atomic layers are stacked together by van der Waals interactions, much like bulk graphite[1]. Inside a single layer, each phosphorus atom is covalently bonded with three adjacent phosphorus atoms to form a puckered honeycomb structure[2–4]

functional calculations tend to slightly underestimate the size of the bandgap in semiconductors[20–22].

We next fabricated few-layer phosphorene FETs with a backgate electrode (Fig. 2a). A scotch tape-based mechanical exfoliation method was used to peel thin flakes from bulk crystal onto degen-

X. H. Chen, Y. Zhang *et al.*, *Nat. Nanotechnol.* **2014**

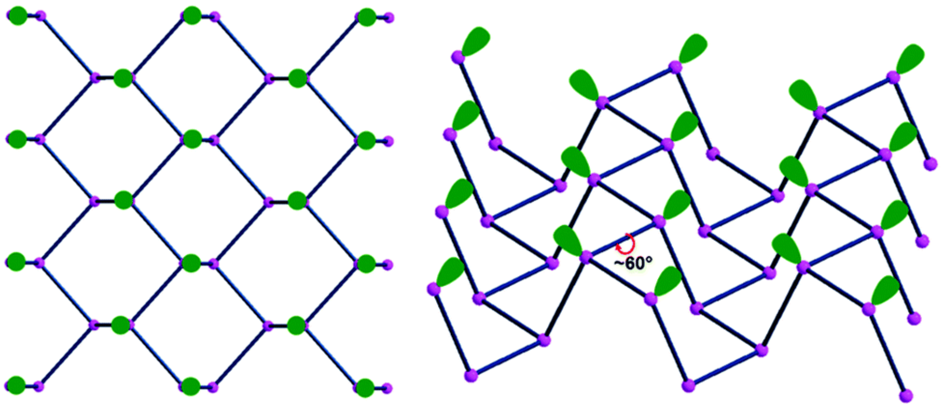




mechanical exfoliation

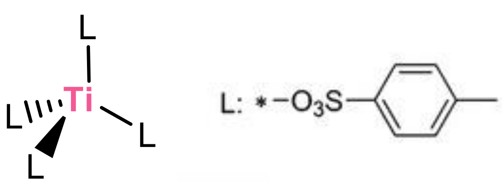
solvent assisted exfoliation

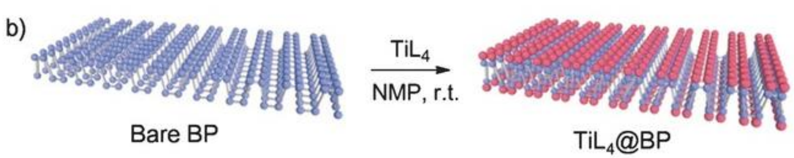
Anchoring Metal Fragments: Coordinative Abilities of bP



Top view and side view of phosphorene lone pairs (green)

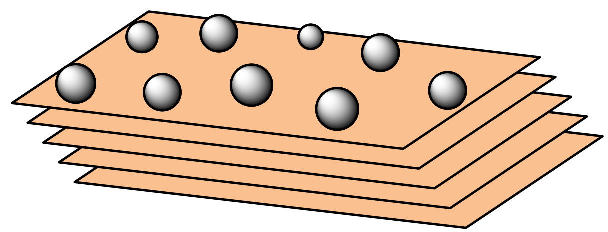
Functionalization with molecular fragments

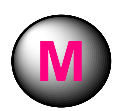




H. Wang, X.-F. Yu, P. K. Chu *et al.*, *Angew. Chem. Int. Ed.*, **2016**

Functionalization with M NPs

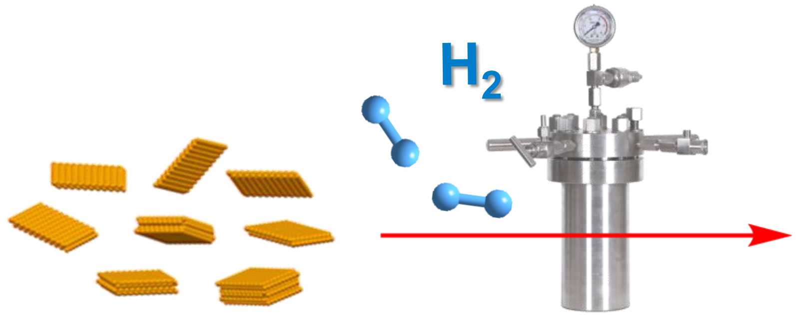




= **Au, Pt, Co, CoP, Co_2P, Ni**

Pd/bP: a New M/bP Nanohybrid

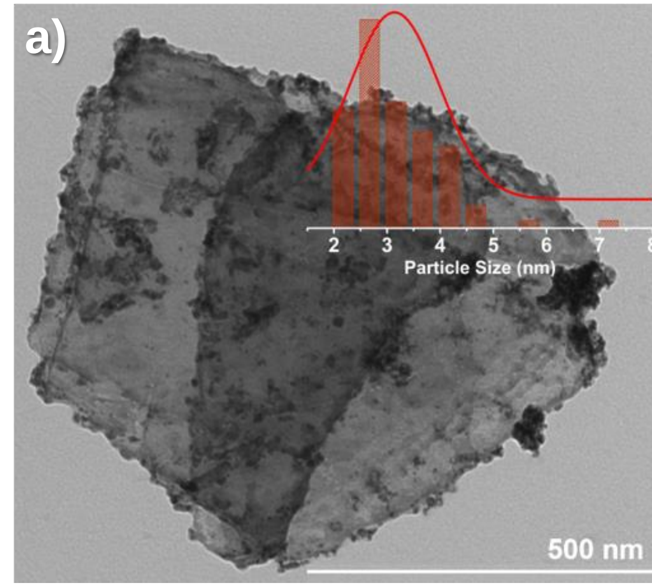
$Pd(NO_3)_2$ +

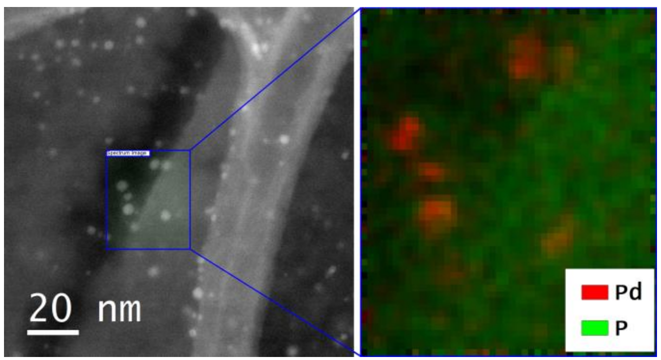


exfoliated bP

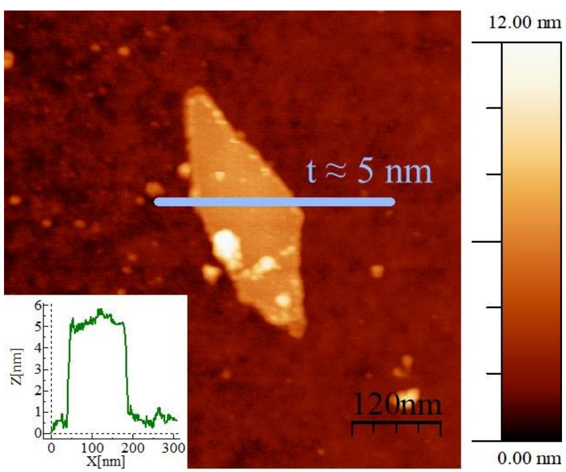
H_2O, EtOH, THF

P_{H_2}= 5 bar, RT, 1h

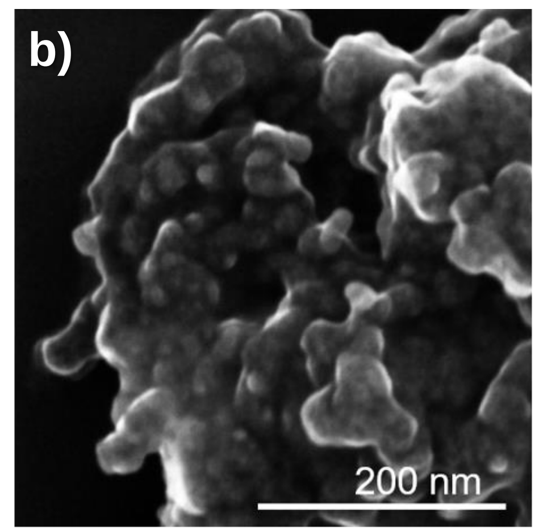




EDS elemental mapping of the highlighted area

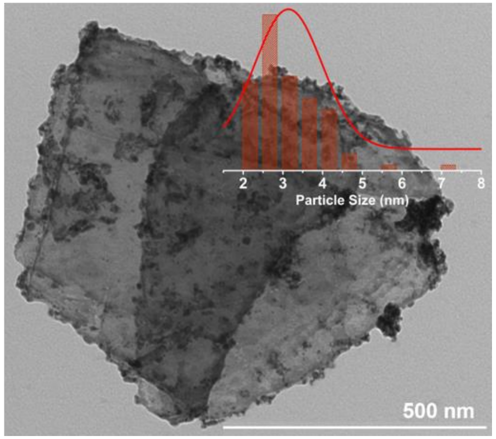


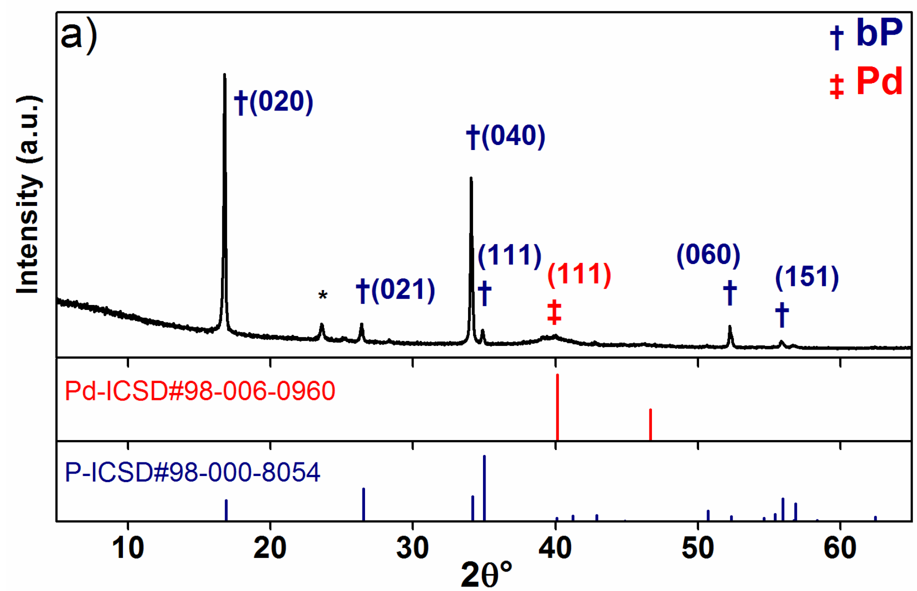
AFM height profile of a Pd/bP flake

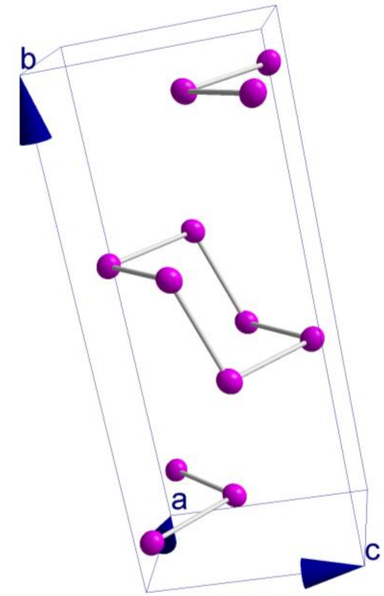


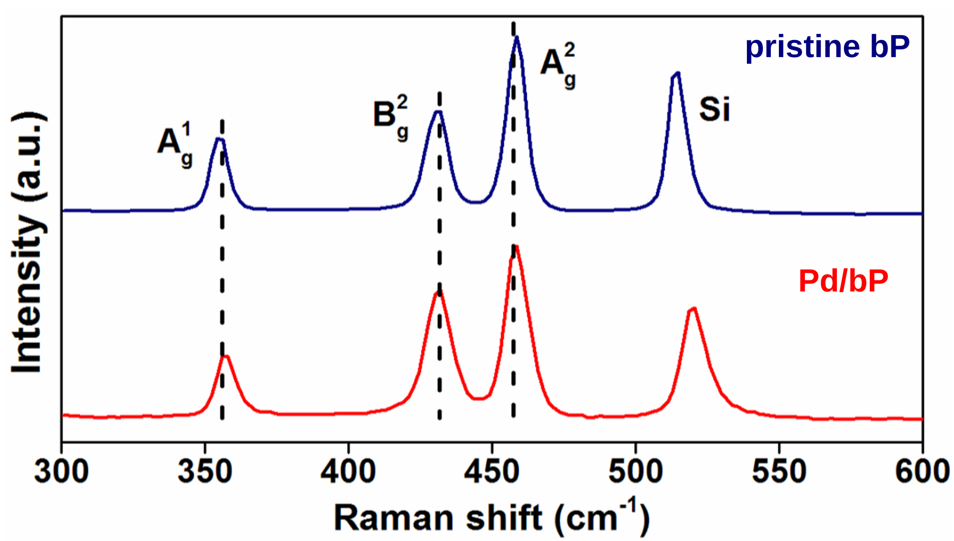
TEM (**a**) and **SEM** (**b**) image of a Pd/bP flake

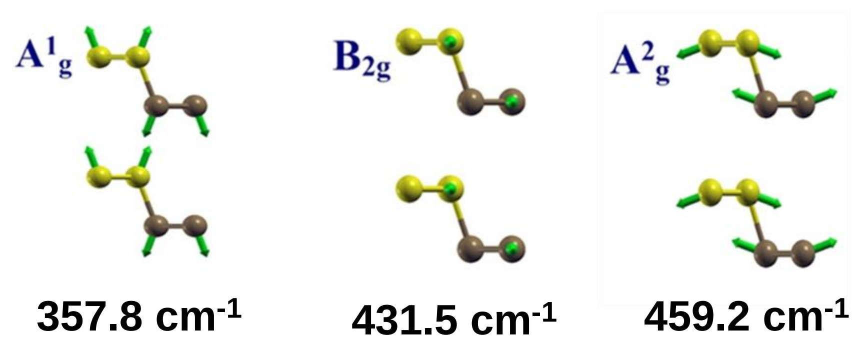
Preliminar Characterization





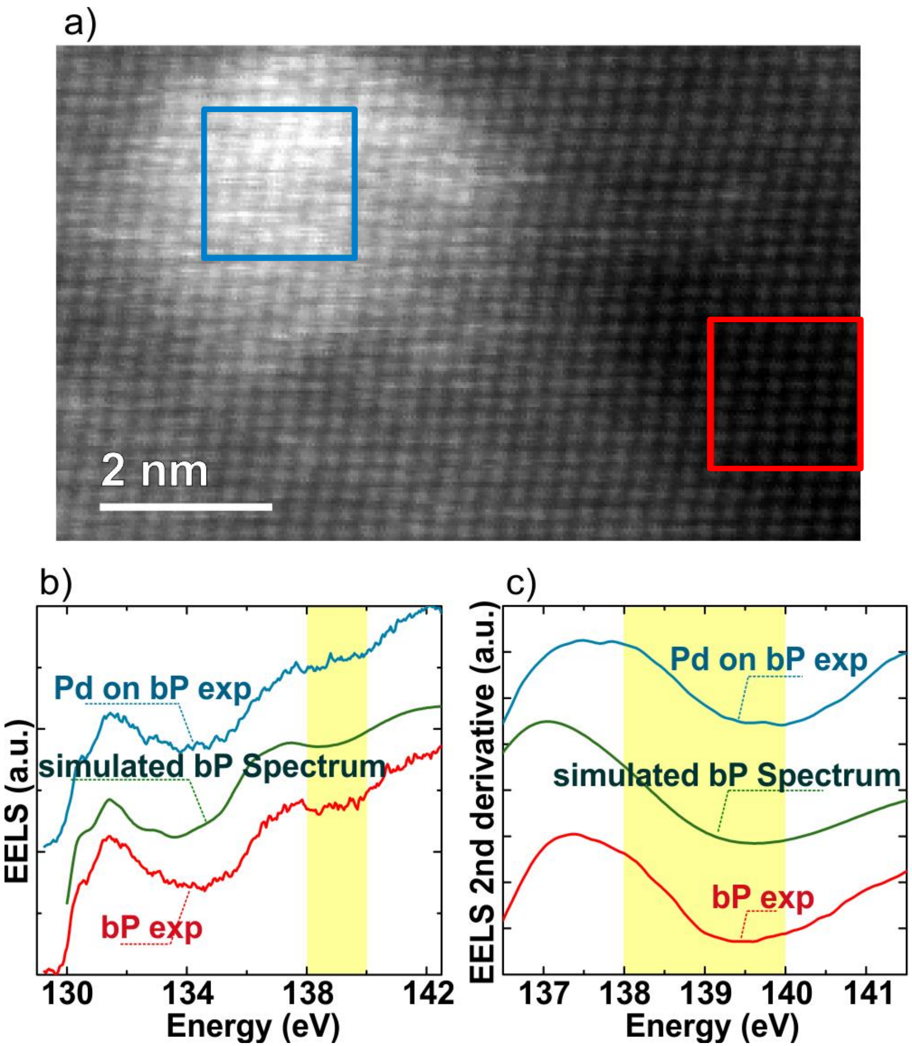


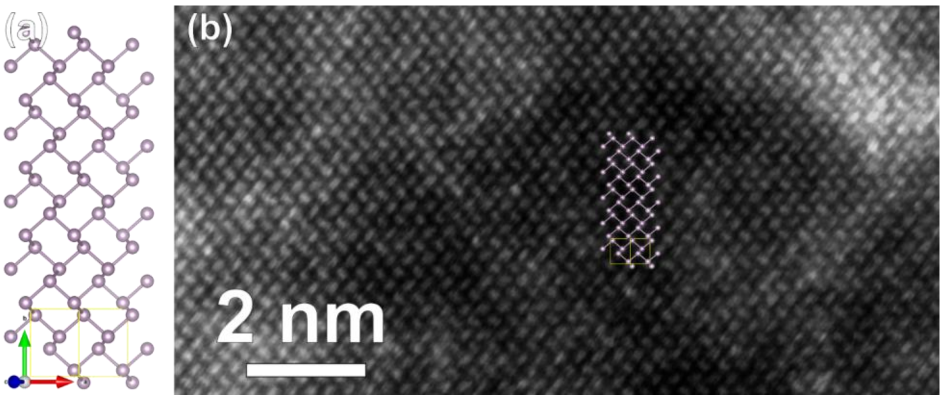




Raman active modes of black phosphorus

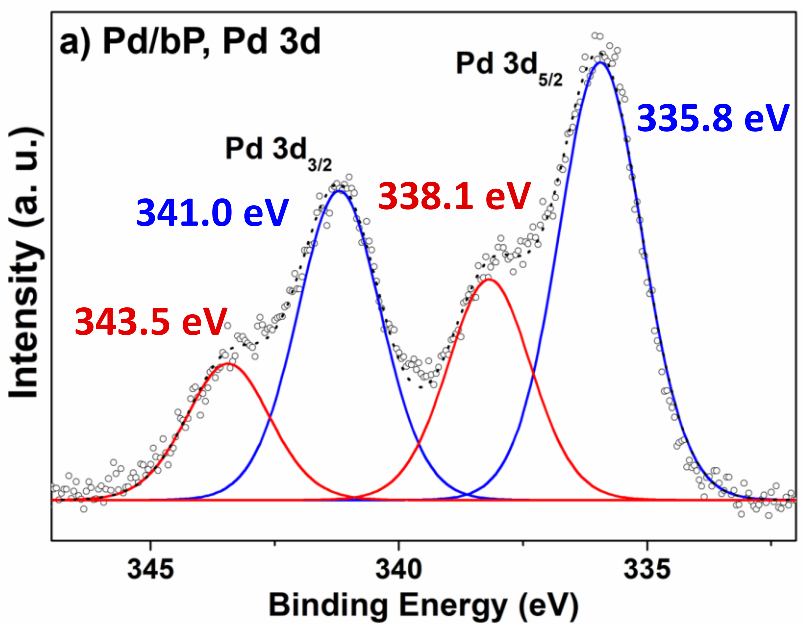
HRTEM-EELS
First Evidence of Strong P-Pd Interaction

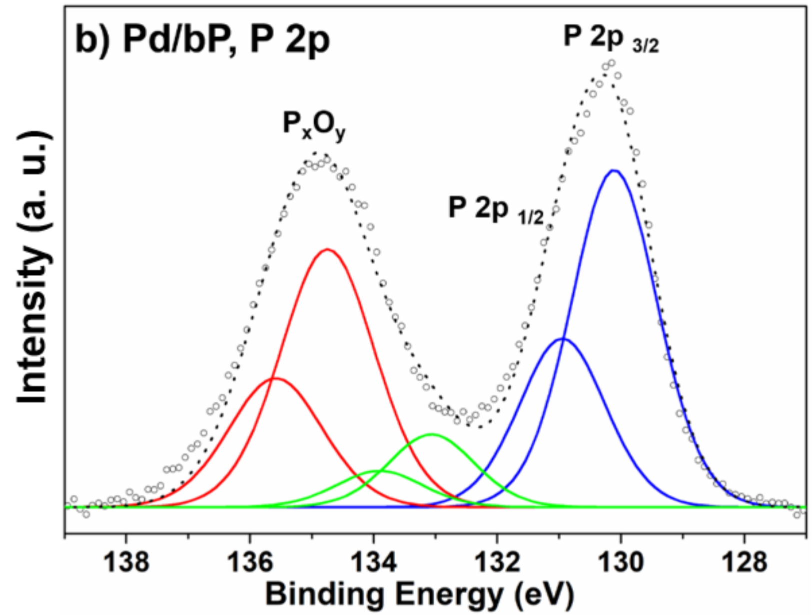




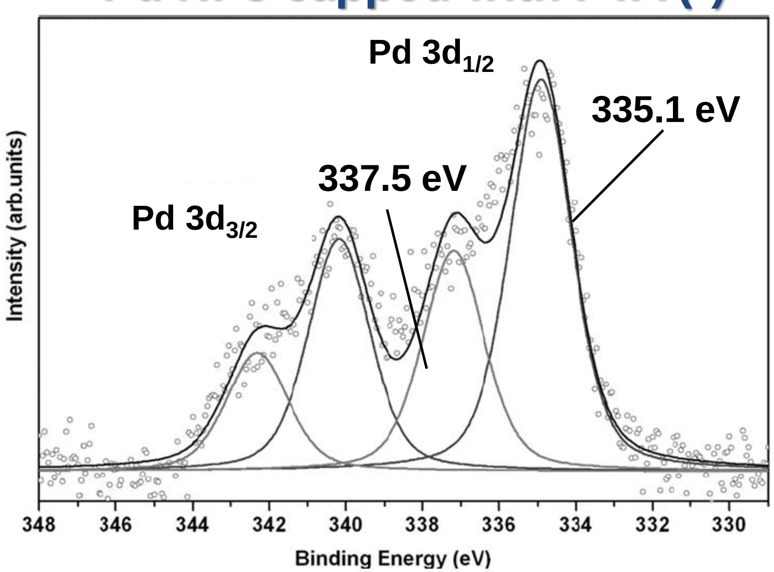
Comparative analysis of the **P_L edge** between Pd free regions (red area) and Pd/bP regions (blue area) reveals **modification in the EELS profile around 137-140 eV**

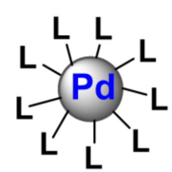
XPS



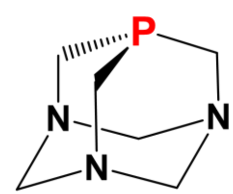


Pd NPs capped with PTA (*)





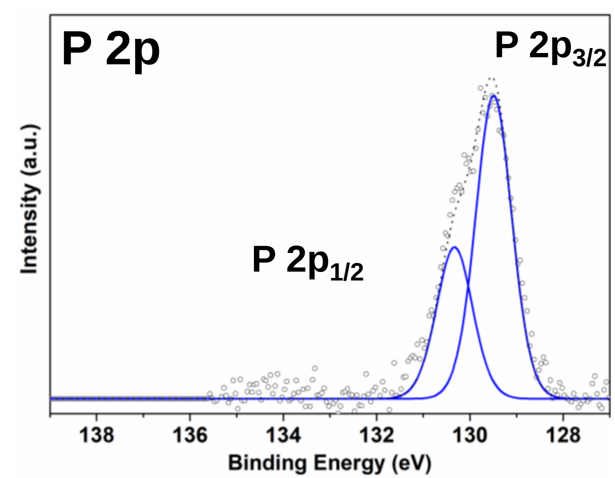
L =



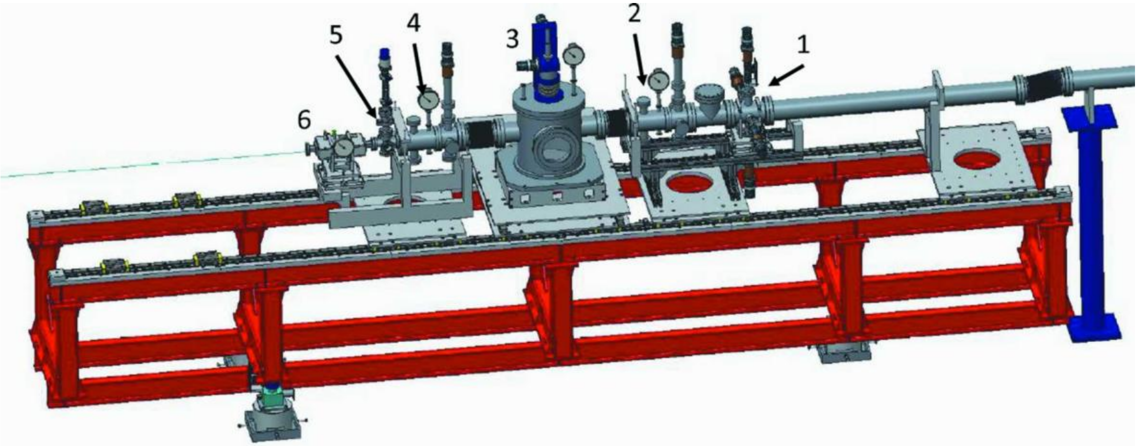
PTA

(*) M. Caporali, L. Gonasalvi *et al.*, ChemCatChem 2013

pristine black phosphorus

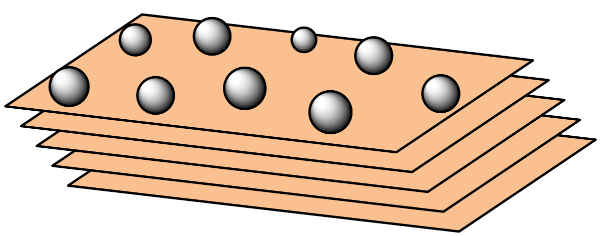


Going Further
Gaining Structural Insights from EXAFS



The LISA beamline. Side view of the EH2 cabin. 1, slits; 2, ion chamber I0; 3, sample chamber; 4, ion chamber I1; 5, reference foils holder; 6, ion chamber (D'Acapito *et al., J. of Sync. Rad.*, 2019).

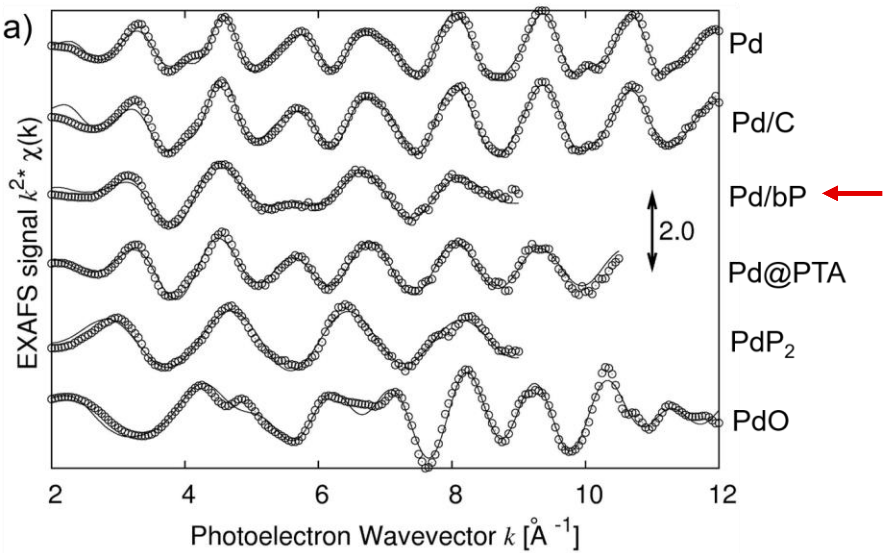
ESRF, Grenoble

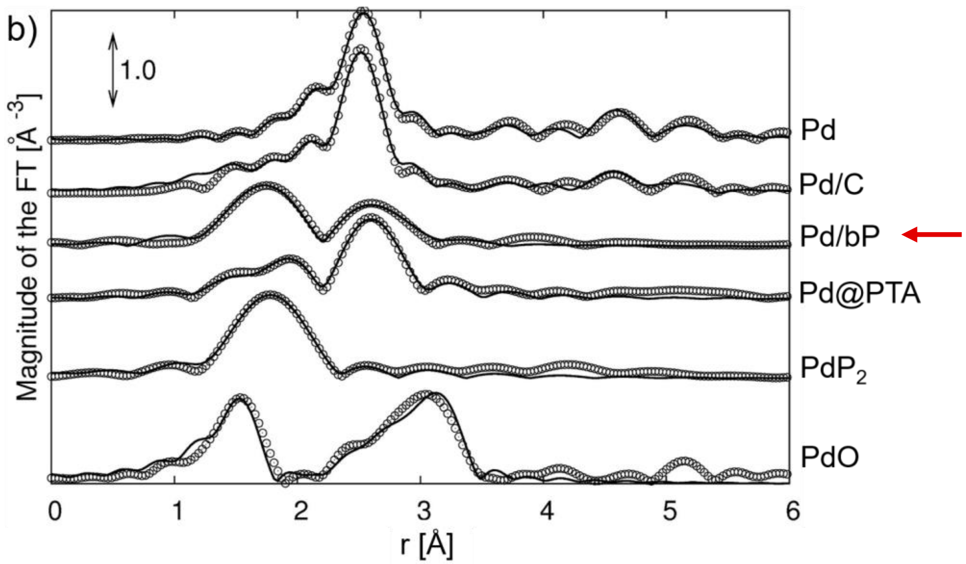


Pd/bP

The new nanohybrid Pd/bP was studied by XAS comparing it with **Pd**, **PdO, PdP_2** and **Pd@PTA**.

EXAFS Study

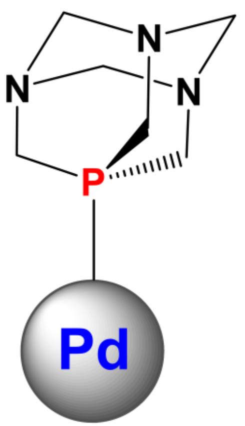




Sample	CNs Pd-Pd	R_{PdPd}(Å)	σ^2_{PdPd} (Å^2)	CNs Pd-P	R_{PdP}(Å)	s^2_{PdP} (Å^2)
Pd foil	12	2.74(1)	0.0059(4)	-	-	-
Pd/C	7(2)	2.73(1)	0.0065(5)	-	-	-
Pd/bP	8(2)	2.77(3)	0.016(4)	1.7(6)	**2.26(3)**	0.0018(6)
Pd@PTA	8(2)	2.73(2)	0.009(2)	0.7(2)	**2.25(3)**	0.004
PdP_2	-	-	-	3.8(6)	2.32(2)	0.004(2)
PdO	4 O	2.01(2)	0.002(1)	-	-	-

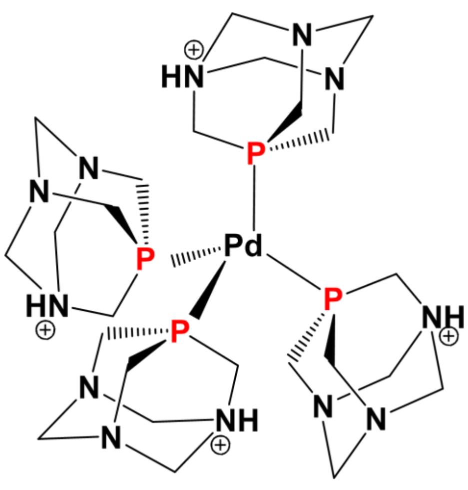
Conclusions from the EXAFS study

EXAFS data confirmed the presence of a strong coordinative bond of covalent nature between Pd and P, with a bond distance of **2.26(3) Å** comparable to that of **Pd@PTA** and to the molecular cation **$Pd(PTAH)_4^{4+}$**



Pd@PTA NPs

d_{Pd-P} = 2.25(3) Å



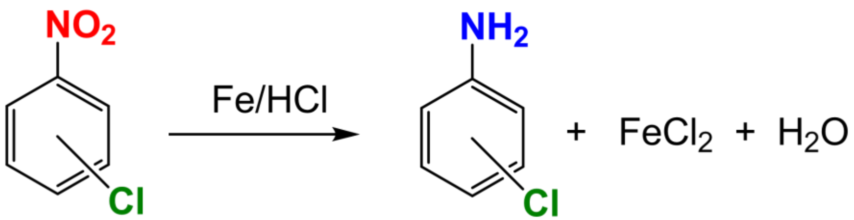
$Pd(PTAH)_4^{4+}$

d_{Pd-P} = 2.203(3) Å(*)

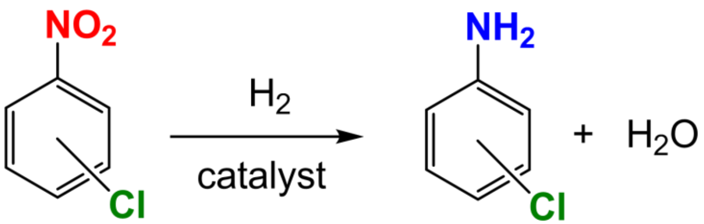
(*) D. J. Darensbourg *et al.*, *Inorg. Chem.*, 1997

From Chloronitrobenzene to Chloroaniline

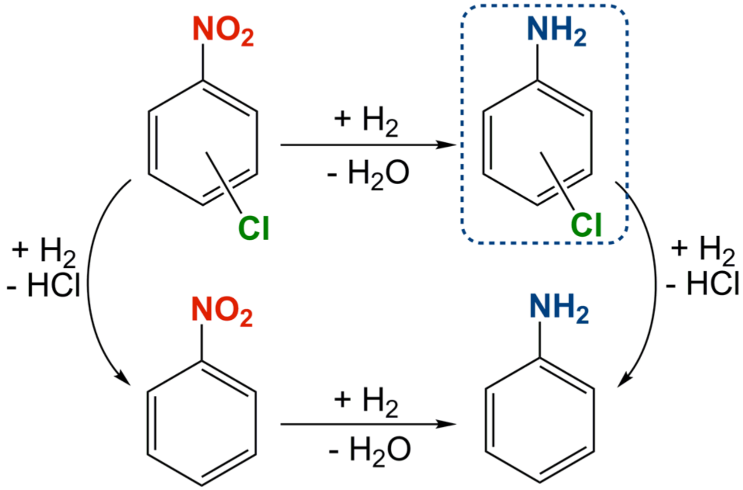
Stoichiometric Route



Catalytic Conversion



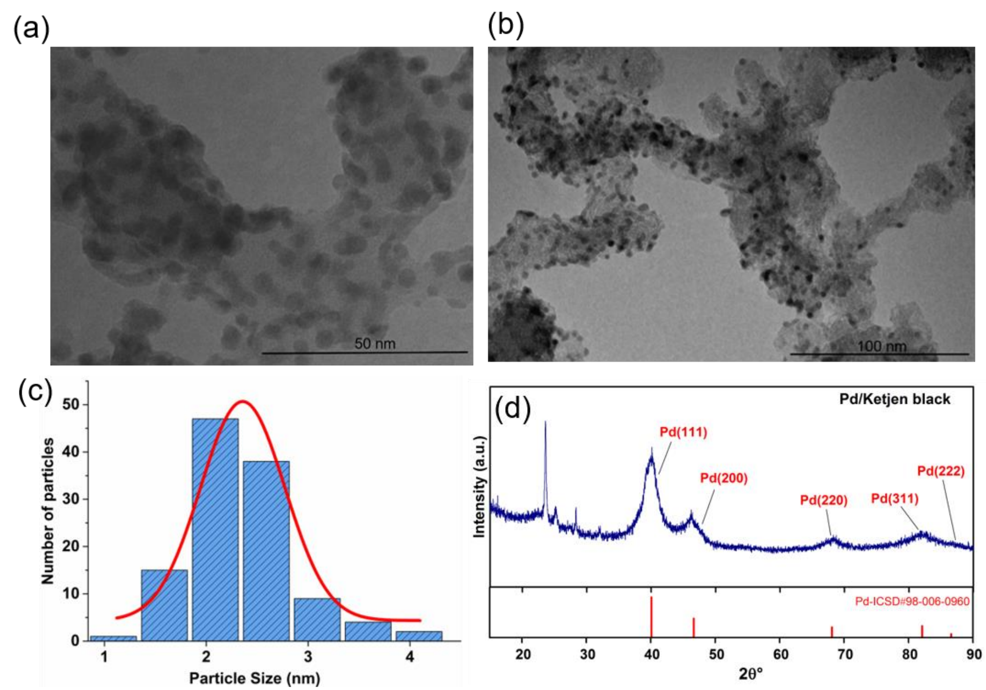
Selective Hydrogenation with Pd/bP



Dehalogenation scheme

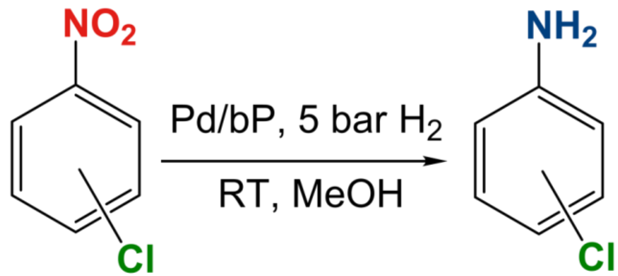
drawback of catalytic hydrogenations:
C-Cl hydrogenolysis

Pd/bP was compared with Pd/C (Ketjen black)



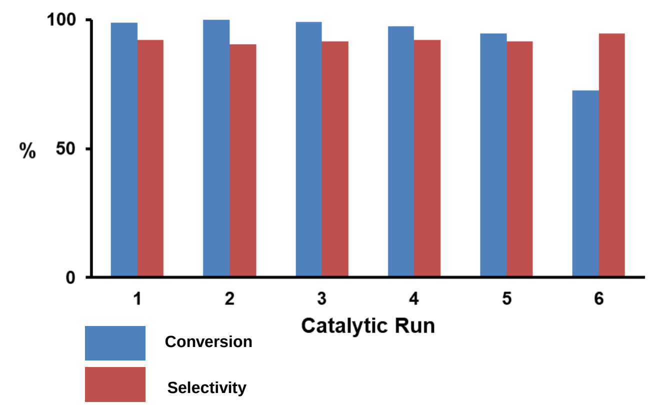
Characterization of **Pd/C** catalyst prepared under the same reaction conditions used for bP

Selective Hydrogenation with Pd/bP



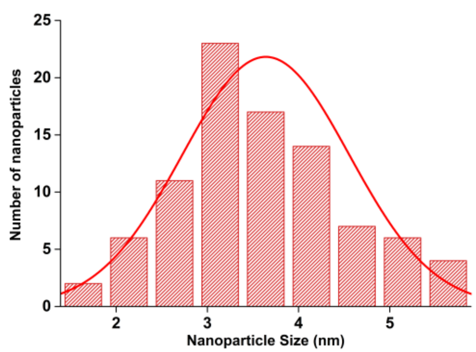
Catalyst	Substrate	Time	S/C	Conv. %[a]	Select. %	TOF[b] (h^{-1})
Pd/bP	1-chloro-3-nitrobenzene	30’	162	99.1	97.7	313
	1-chloro-2-nitrobenzene	40’	162	99.5	97.3	235
Pd/C	1-chloro-2-nitrobenzene	30’	191	99.9	78.1	298

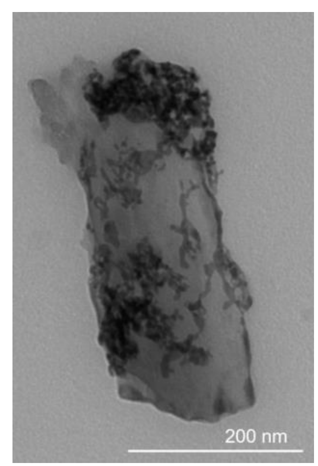
Recycling test



- **Pd/bP** remained active and selective for 6 consecutive runs.

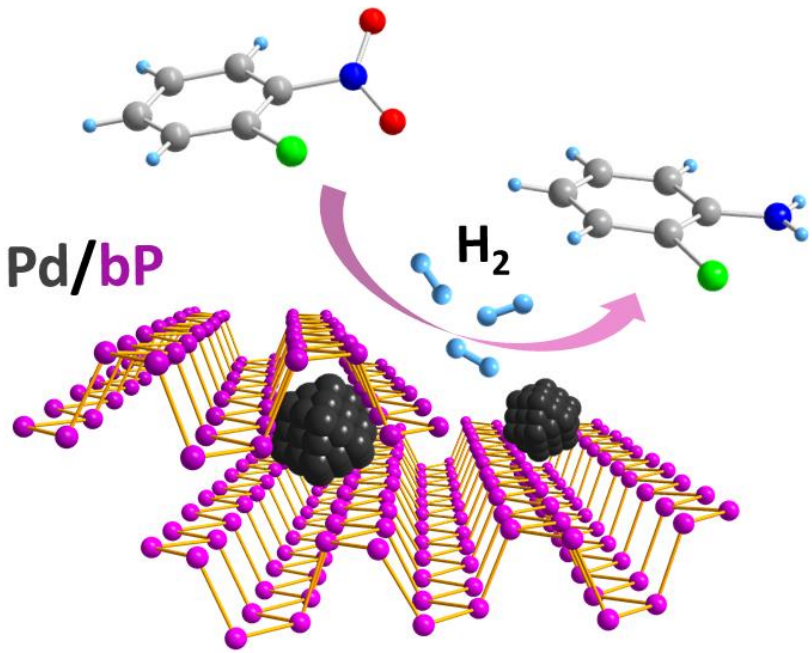
- **Pd/bP** was stable toward NPs agglomeration.





TEM image of a Pd/bP flake after a catalytic run.

Conclusions



- Synthesis of a new Pd/bP nanohybrid

- Detailed experimental study of the Pd-P interaction

- Successfull application as catalyst in the hydrogenation of chloronitrobenzene

The Phosfun group

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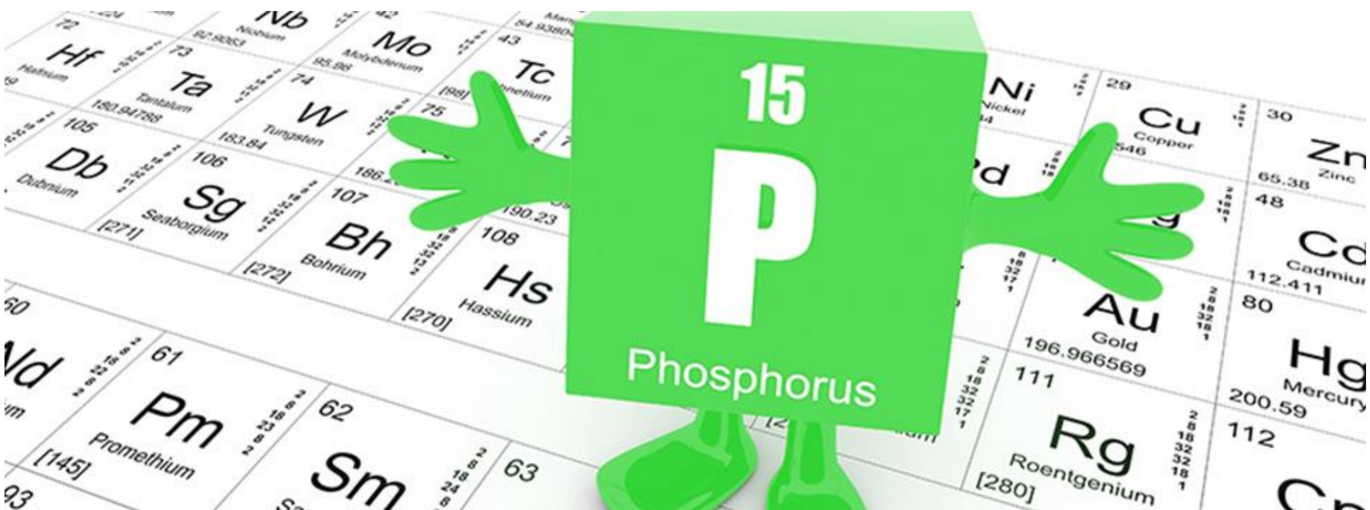

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Prof. Matthias Driess
Prof. Lyndon Emsley
Prof. Sylviane Sabo-Etienne
Prof. Muriel Hissler
Prof. Torben René Jensen
Prof. Aziz M. Muzafarov
Prof. Paul G Pringle
Dr. Anna Tampieri
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