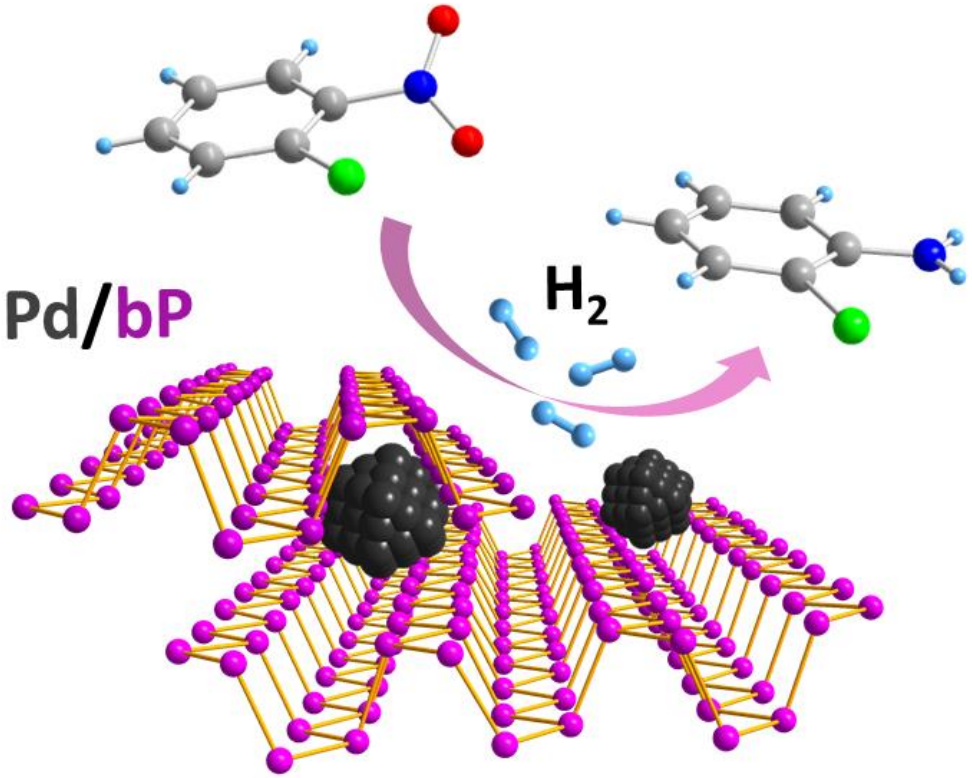
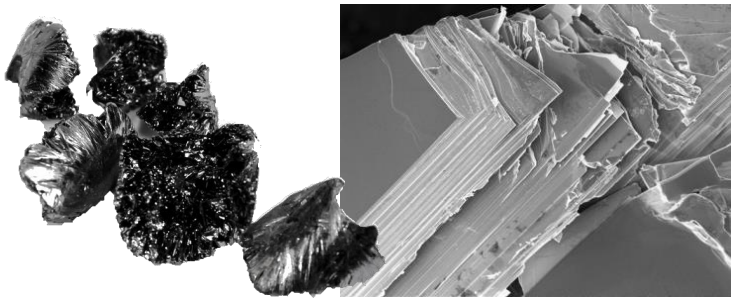
Phosphorene: a rising star in the 2D world



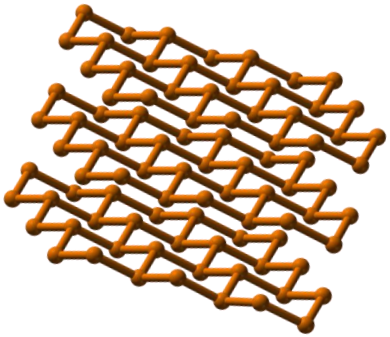
Maria Caporali
CNR ICCOM, Istituto di Chimica dei Composti Organometallici, Firenze (ITALY)

Black Phosphorus (bP) as a P counterpart of Graphite

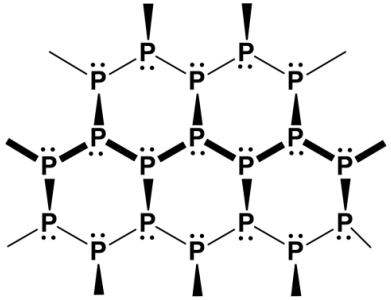


bP crystals

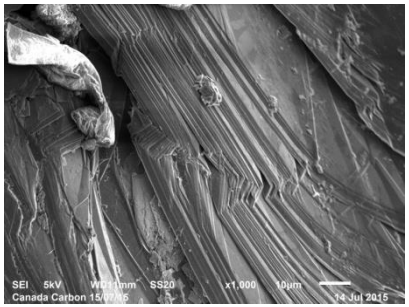
SEM image of bP



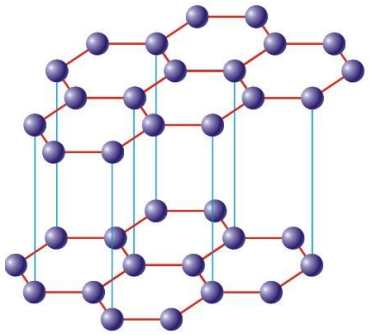
Puckered honeycomb structure of bP

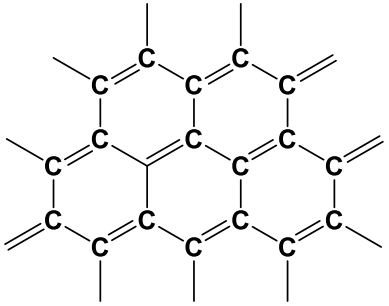


sp^3 hybridized P atoms



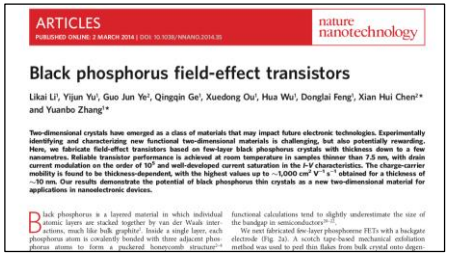
SEM image of graphite





sp^2 hybridized C atoms

Black phosphorus exfoliation

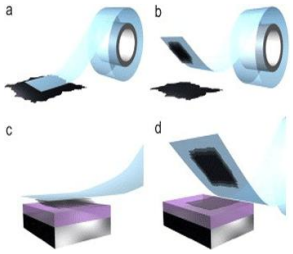


ARTICLES
nature nanotechnology

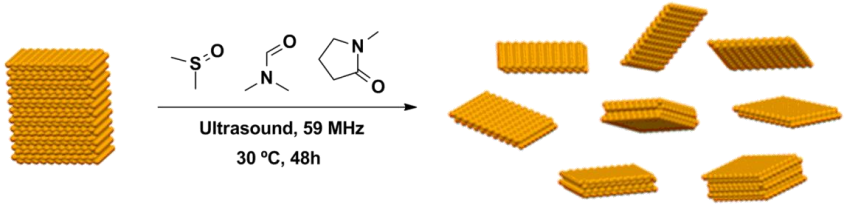
Black phosphorus field-effect transistors

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]*

Nat. Nanotechnol. **2014**

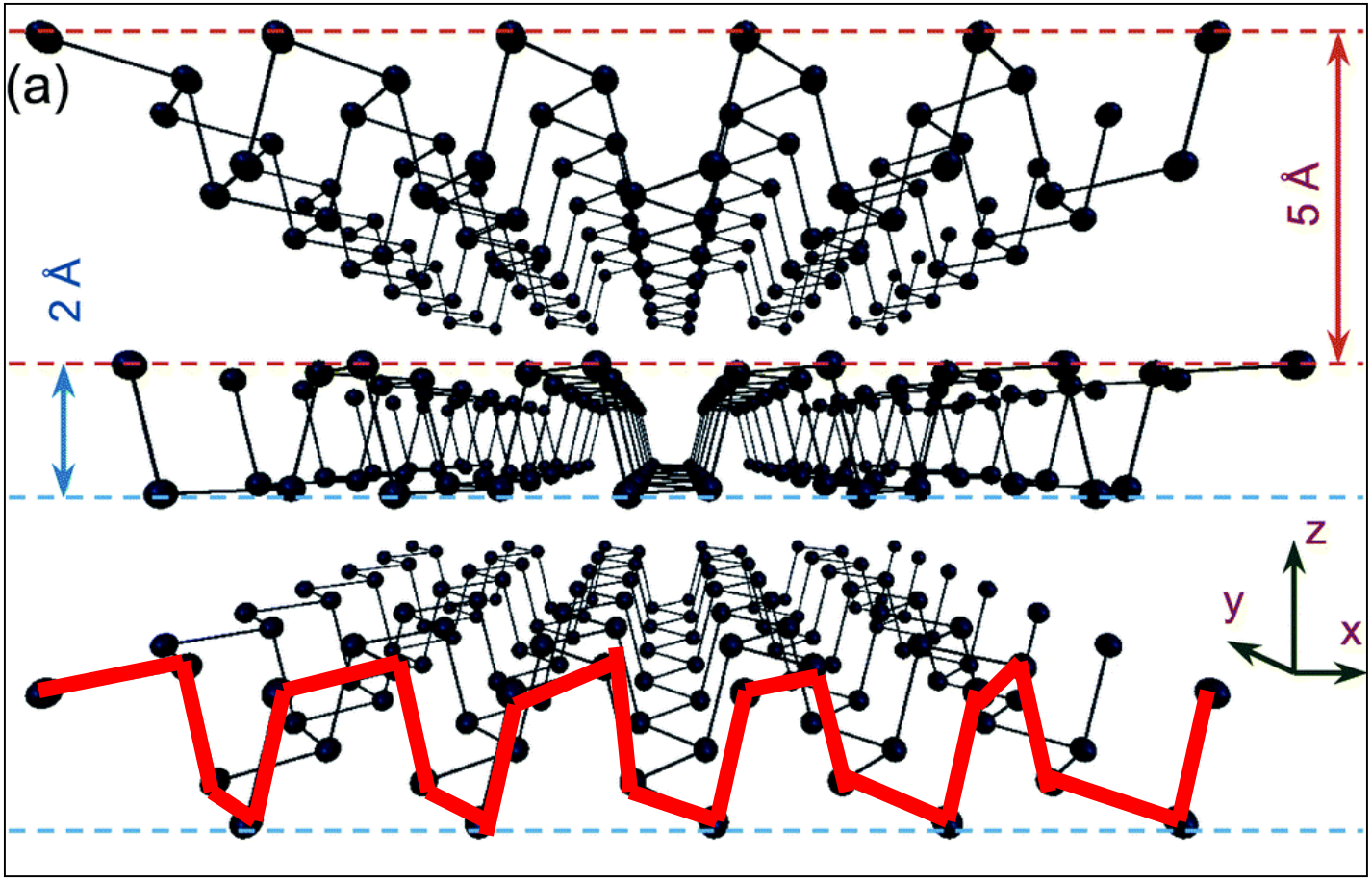


mechanical exfoliation



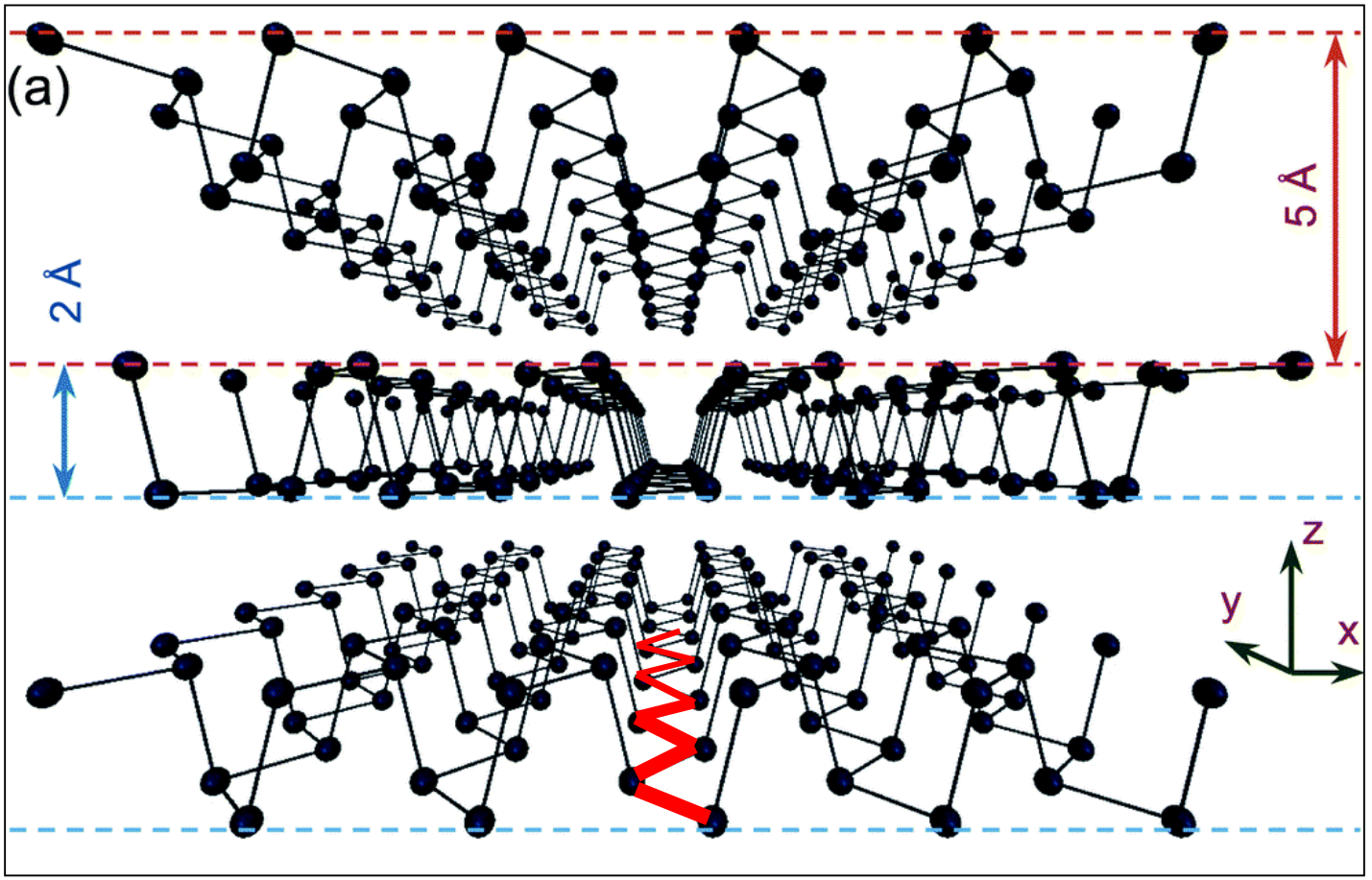
solvent assisted exfoliation

Anisotropic structure of black phosphorus



Armchair (x-axis)

Anisotropic structure of black phosphorus



Zig-zag (y-axis)

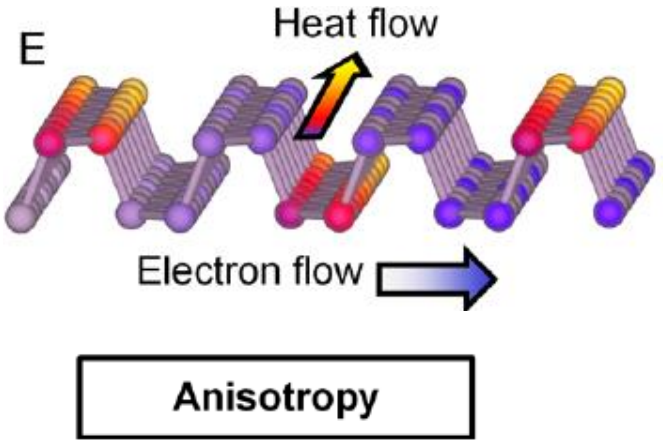
Physical properties of 2D black P

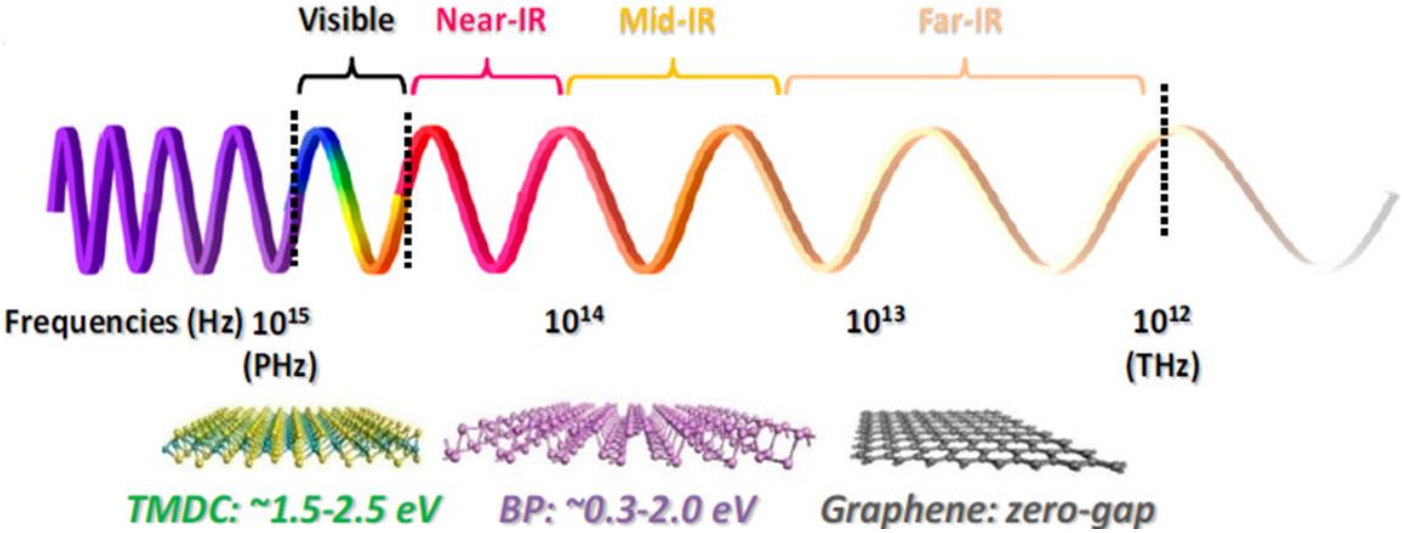
✓ High carrier mobility: 1000 cm^2/Vs

✓ On / off ratio: $10^3 – 10^5$

✓ Thermal conductivity (300 K):

30 W/m K (zig-zag); 13.7 W/m K (armchair)

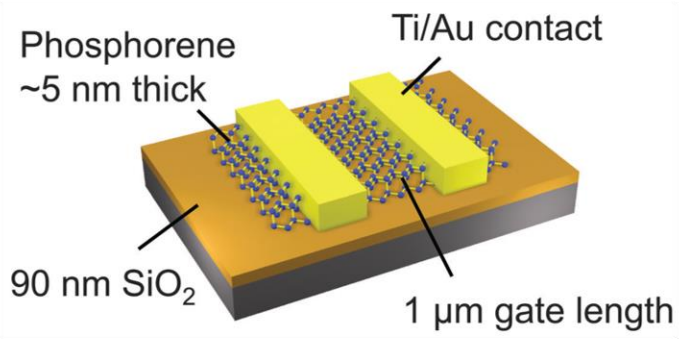




✓ *p*-type semiconductor, with a thickness-depending direct band gap (0.3-2.0 eV)

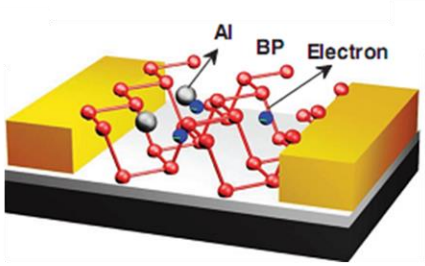
✓ The band gap can be modulated either applying an electrical field or by strain.

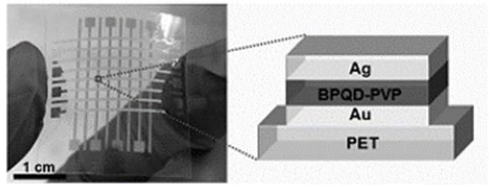
Applications of black phosphorus



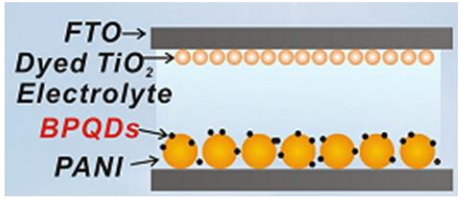
2D BP-based *p*-FET

Al-doped 2D BP *n*-FET

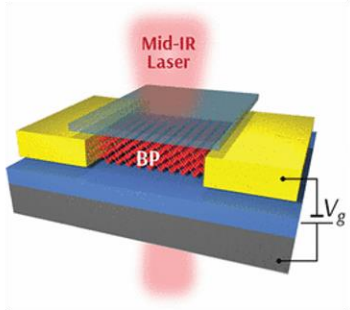


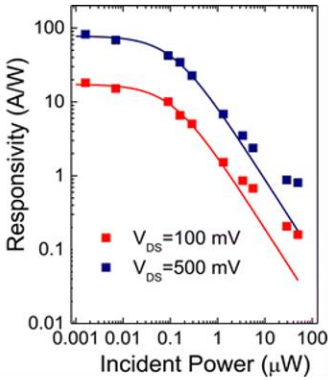


2D BP-based memory device

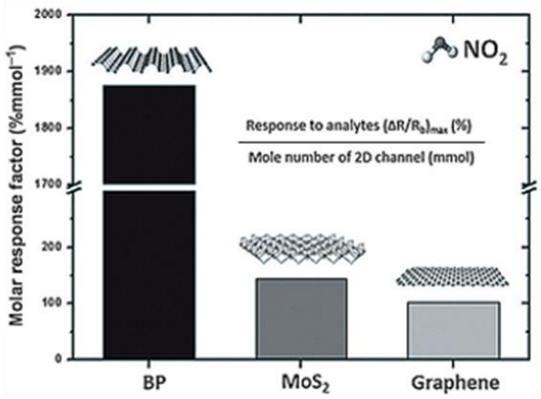


BP QDs-based solar cell



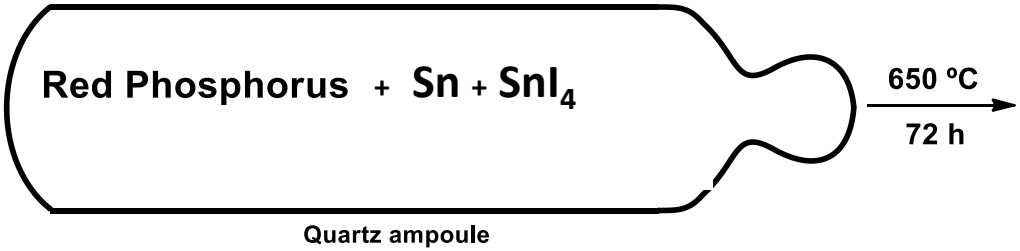


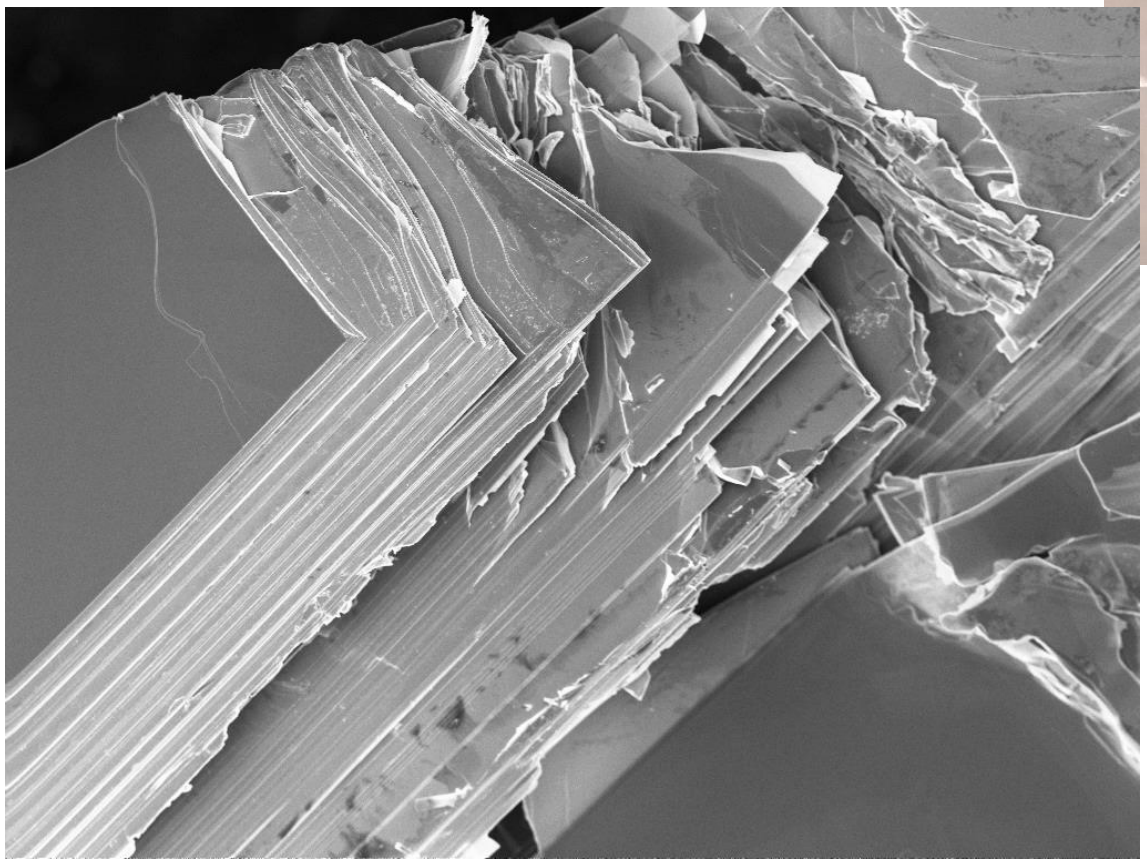
2D BP-based photodetector



NO_2-sensor based on 2D BP

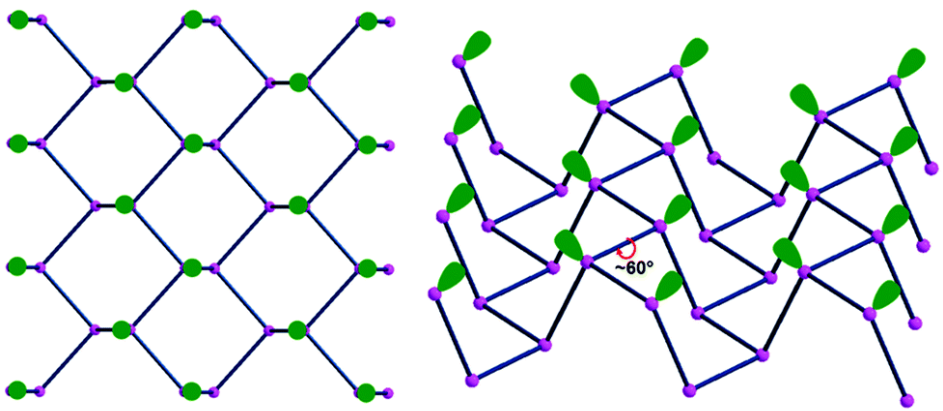
Synthesis of black phosphorus





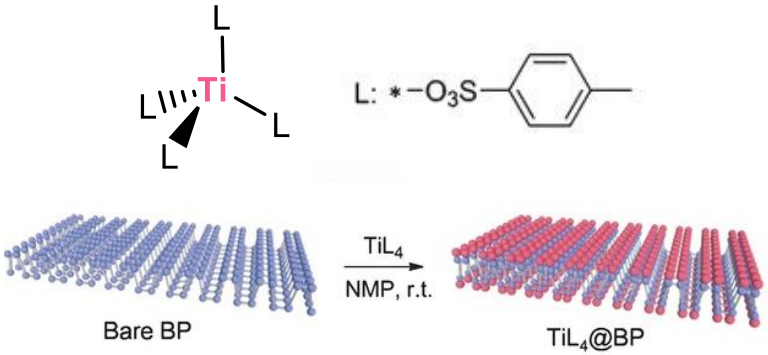
J. Crystal Growth **2014**, *405*, 6

Anchoring Metal Fragments: Coordinative Abilities of bP

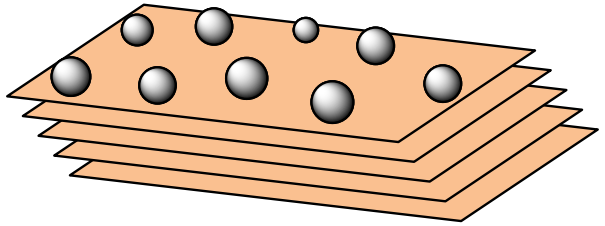


Top view and side view of phosphorene lone pairs (green)

Functionalization with molecular fragments



Functionalization with M NPs

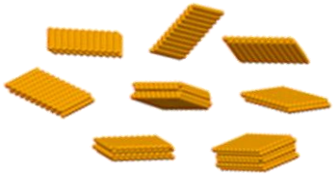


M = **Au**, **Pt**, **Co**, **CoP**, **Co_2P**, **Ni**

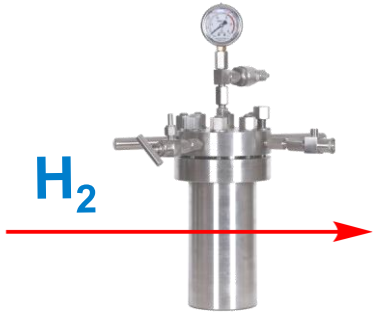
P. K. Chu *et al.*, *Angew.Chem.Int.Ed.*, **2016,** 5003.

Pd/bP: a New M/bP Nanohybrid

$Pd(NO_3)_2$ +

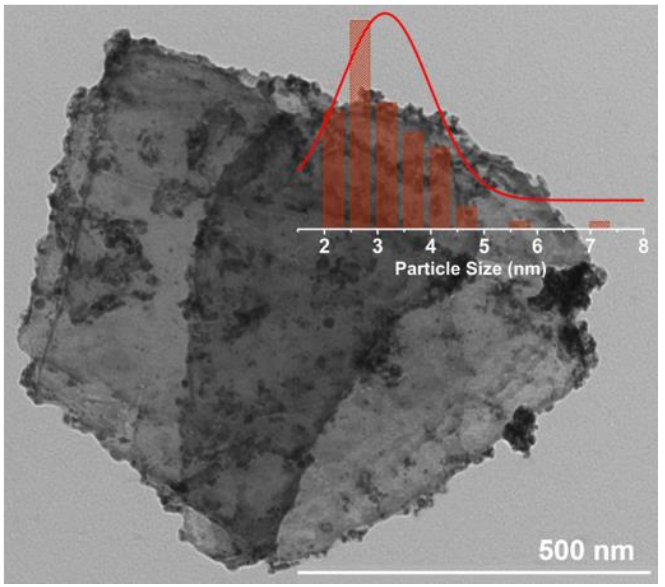


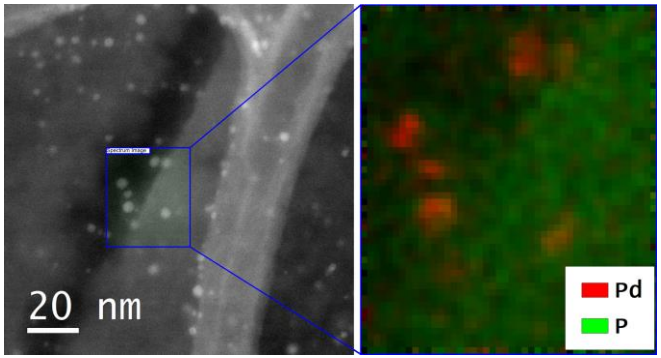
exfoliated bP



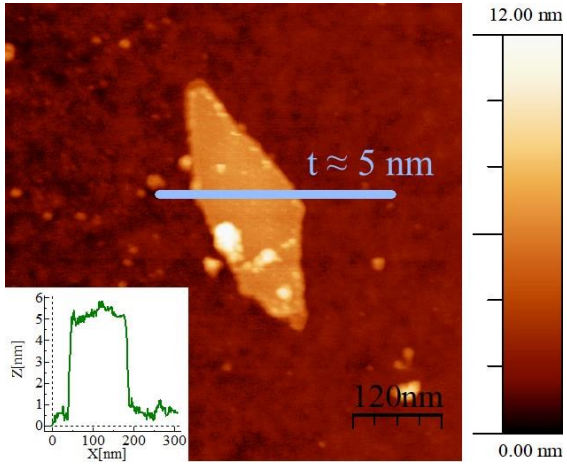
H_2O, EtOH, THF

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

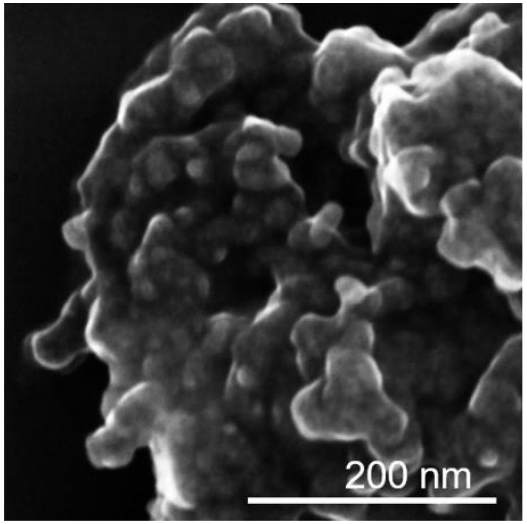




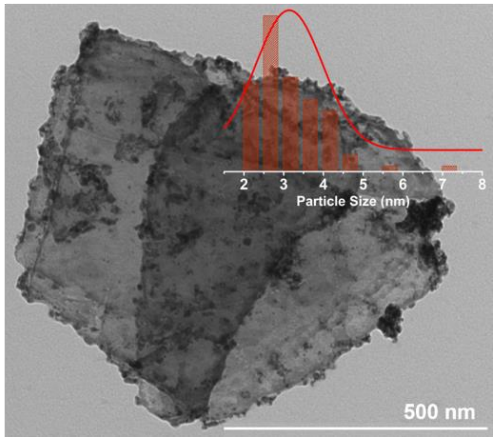
HR-TEM
EDS

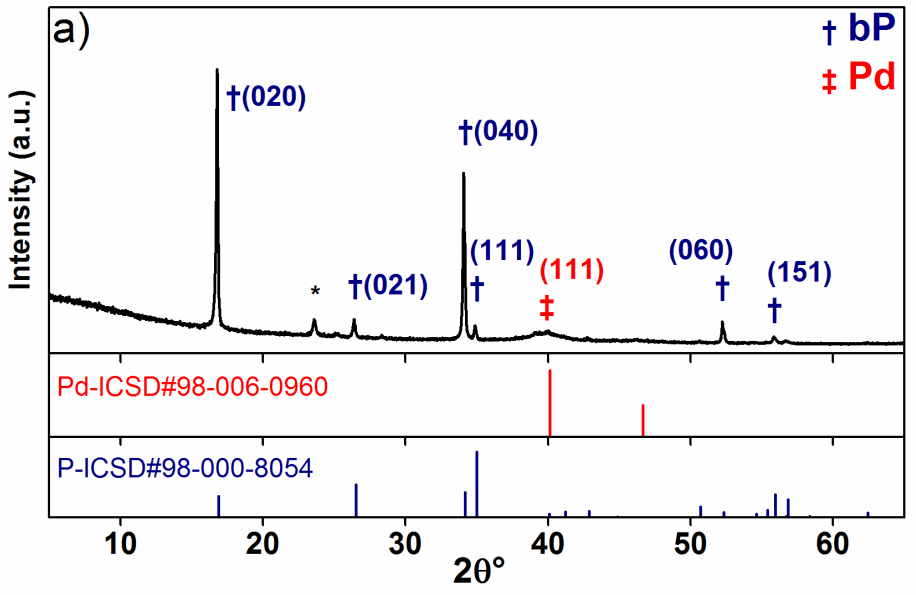


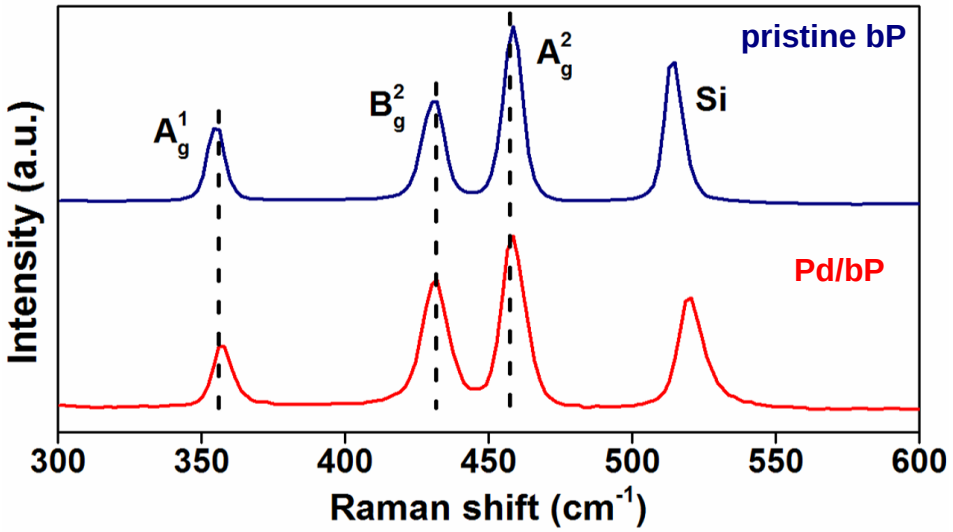
AFM height profile of a Pd/bP flake

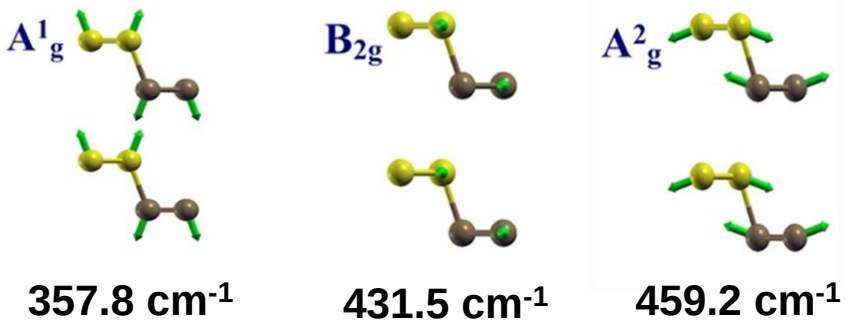


PXRD and Raman



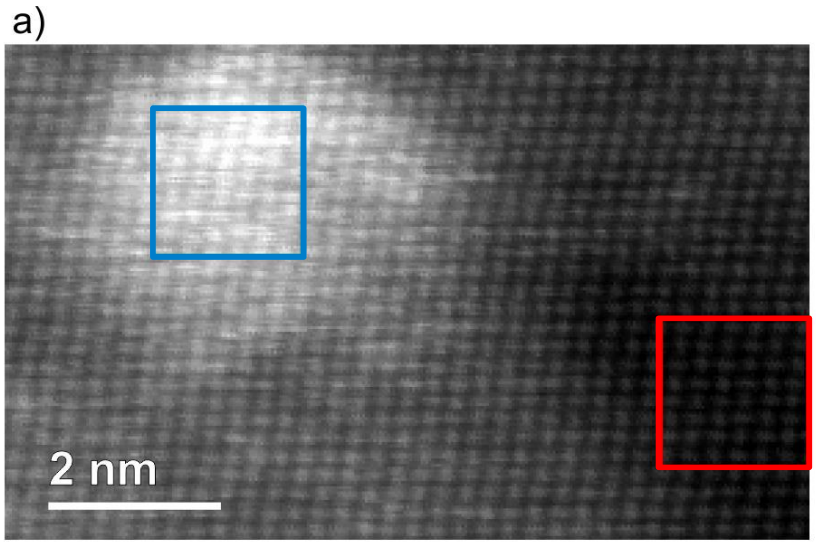


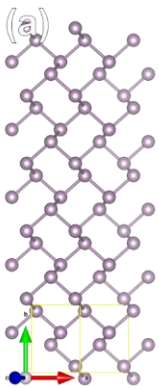


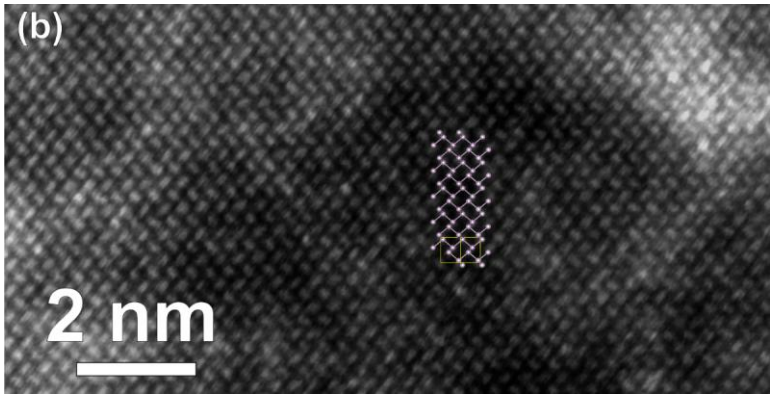


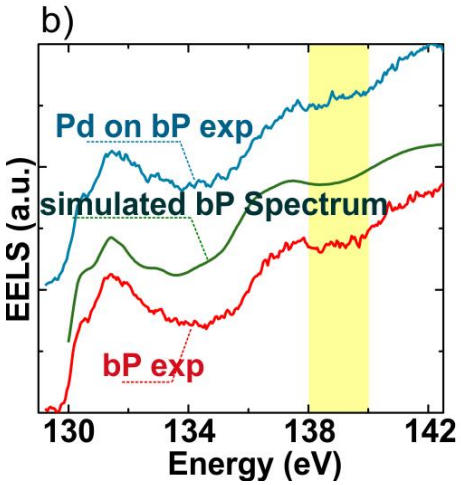
Raman active modes of black phosphorus

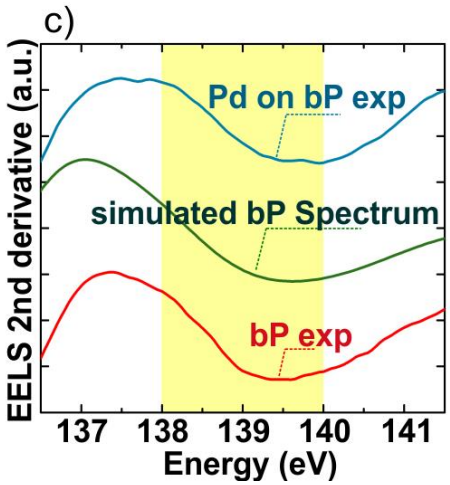
HRTEM-EELS
First Evidence of Strong P-Pd Interaction



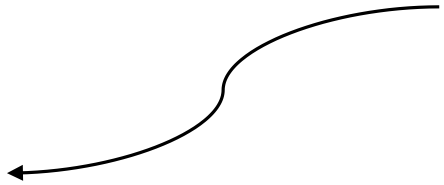




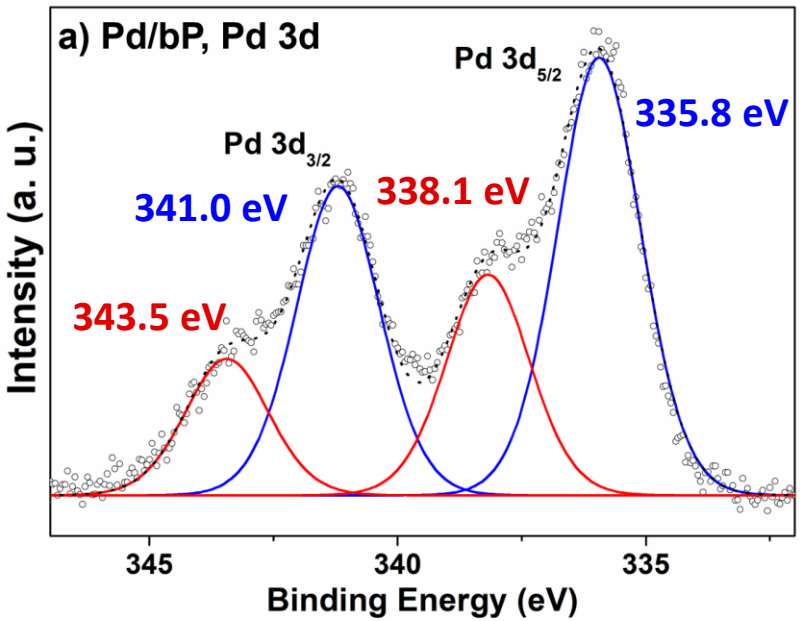


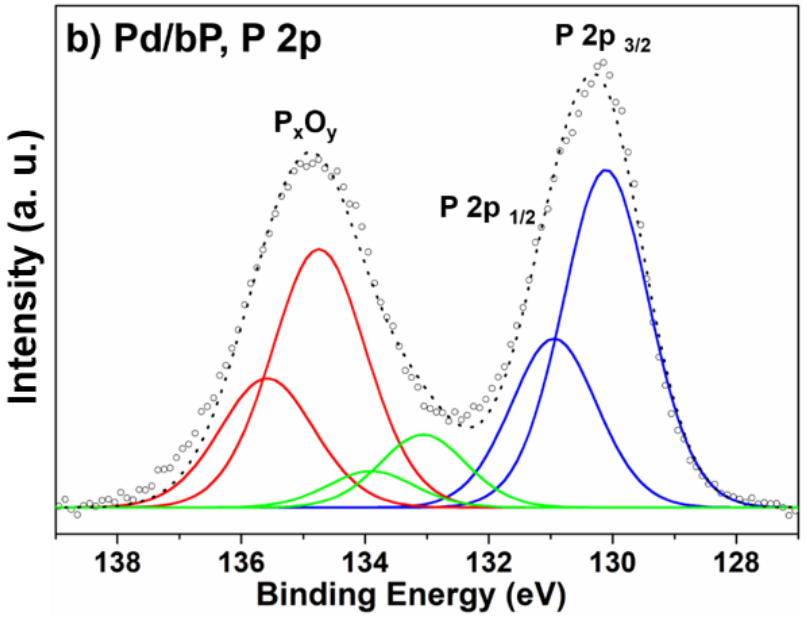


Comparative analysis of the **P_L edge** between Pd free regions (red area) and Pd/bP regions (blue area) reveals **modification in the EELS profile around 137-140 eV**

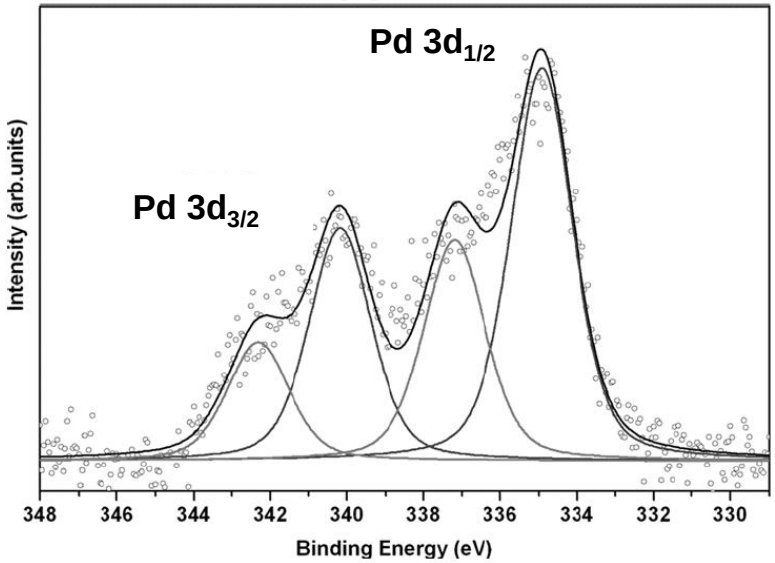


XPS

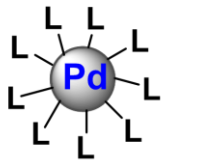


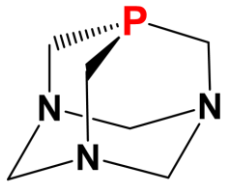


Pd NPs capped with PTA*



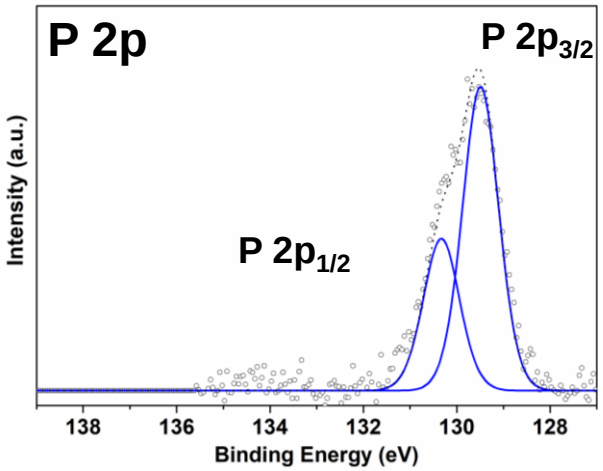
L =





PTA

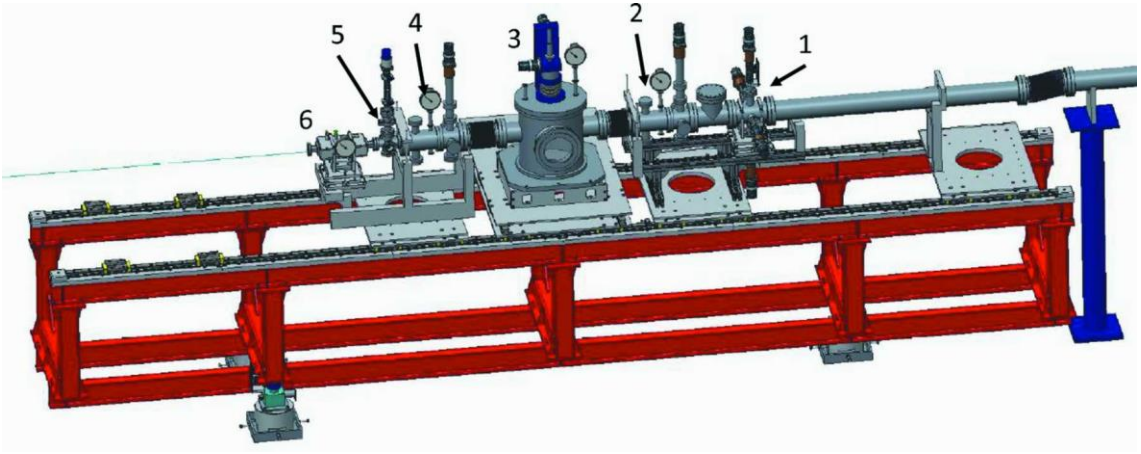
pristine black phosphorus



*M. Caporali *et al.*, *Chem. Cat. Chem*. **2013**, 5, 2517.

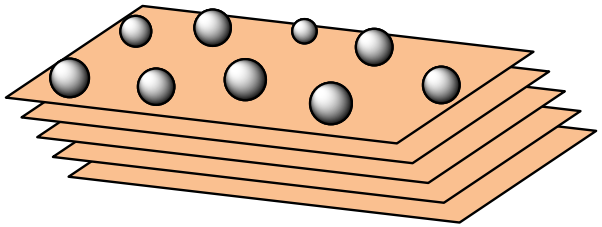
Going Further

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).

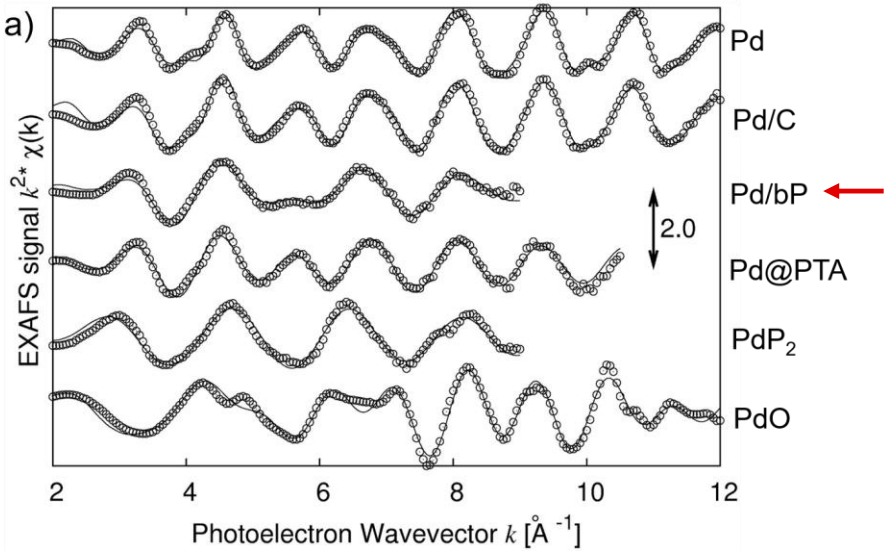
ESRF, Grenoble

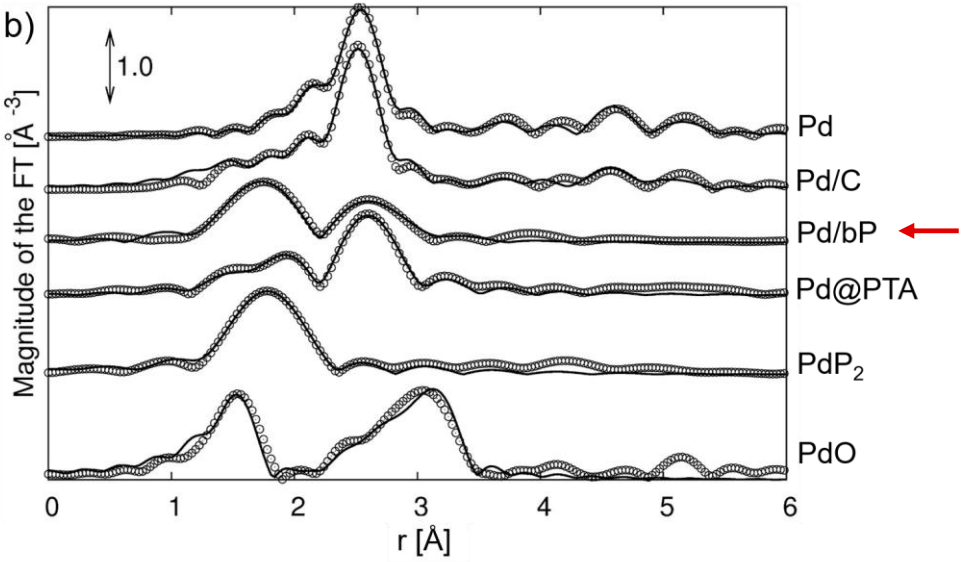


Pd/bP

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

EXAFS Study

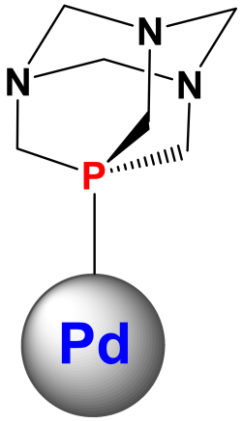




Sample	CNs Pd-Pd	R_{PdPd}(Å)	σ^2_{PdPd} (Å^2)	CNs Pd-P	R_{PdP}(Å)	s^2_{PdP} (Å^2)
Pd foil	12	2.74(1)	0.0059(4)	-	-	-
Pd/C	7(2)	2.73(1)	0.0065(5)	-	-	-
Pd/bP	8(2)	2.77(3)	0.016(4)	1.7(6)	**2.26(3)**	0.0018(6)
Pd@PTA	8(2)	2.73(2)	0.009(2)	0.7(2)	**2.25(3)**	0.004
PdP_2	-	-	-	3.8(6)	2.32(2)	0.004(2)
PdO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

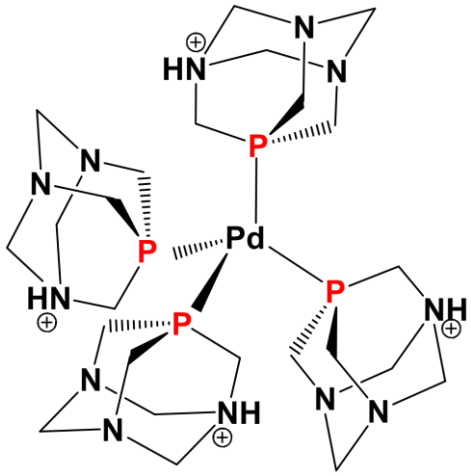
Conclusions from the EXAFS study

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 **$Pd(PTAH)_4^+$**



Pd@PTA NPs

d_{Pd-P} = 2.25(3) Å



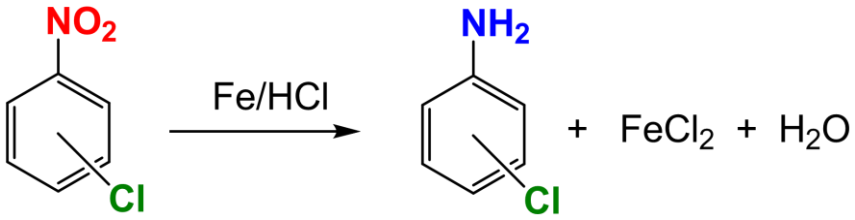
$Pd(PTAH)_4^+$

d_{Pd-P} = 2.203(3) Å(*)

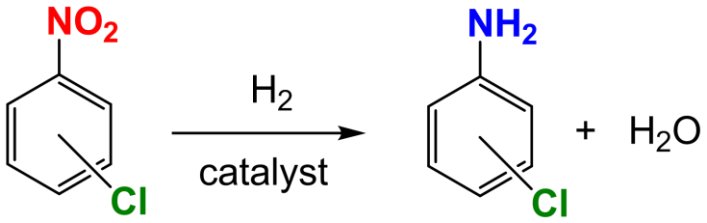
(*) D. J. Darensbourg *et al.*, *Inorg. Chem.* 1997,

From Chloronitrobenzene to Chloroaniline

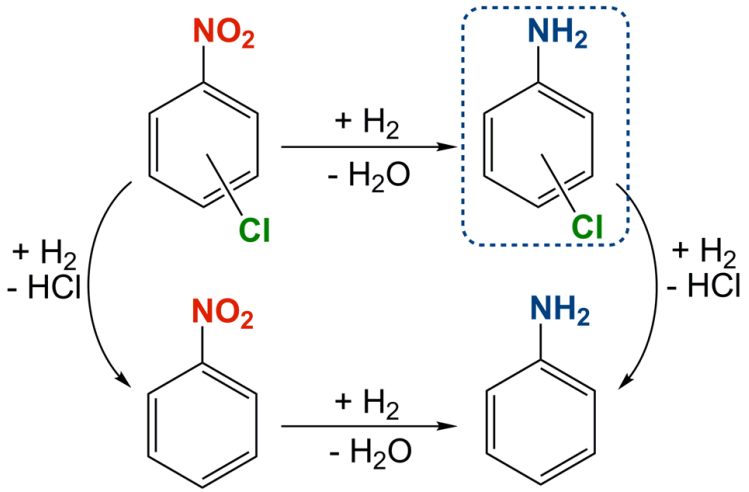
Stoichiometric Route



Catalytic Conversion

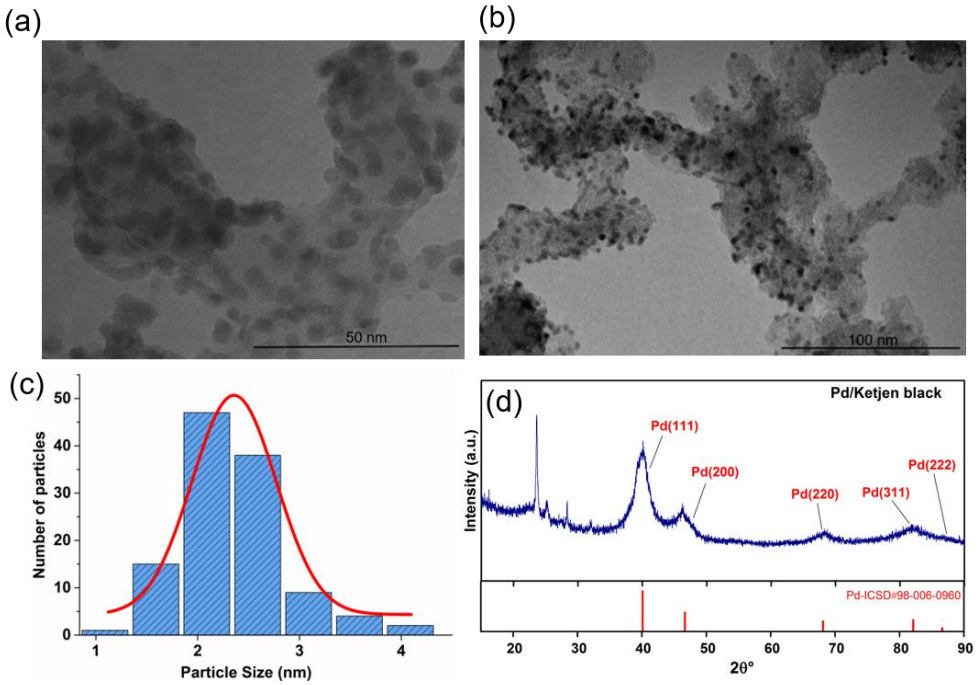


Hydrogenation with Pd/bP



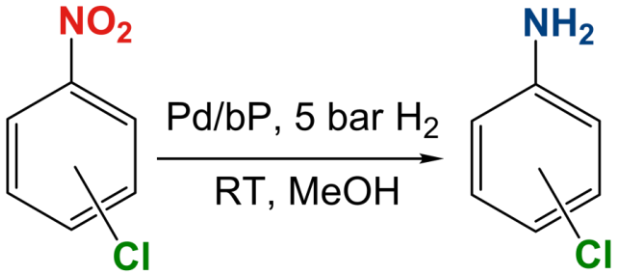
drawback of catalytic hydrogenations:
C-Cl hydrogenolysis

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



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

Hydrogenation with Pd/bP

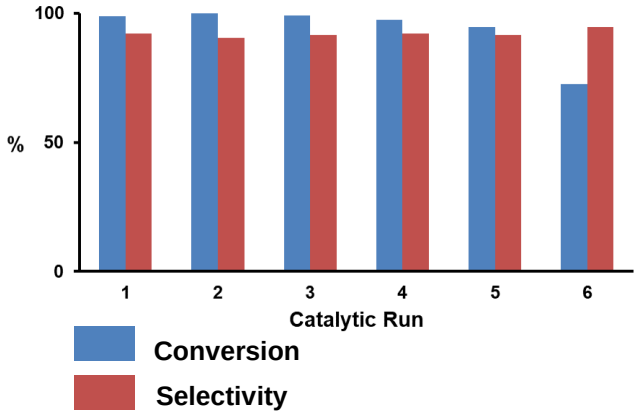


Catalyst	Substrate	Time	S/C	Conv. %[a]	Select. %	TOF[b] (h^{-1})
Pd/bP	1-chloro-3-nitrobenzene	30'	162	99.1	97.7	313
	1-chloro-2-nitrobenzene	40'	162	99.5	97.3	235
Pd/C	1-chloro-2-nitrobenzene	30'	191	99.9	78.1	298

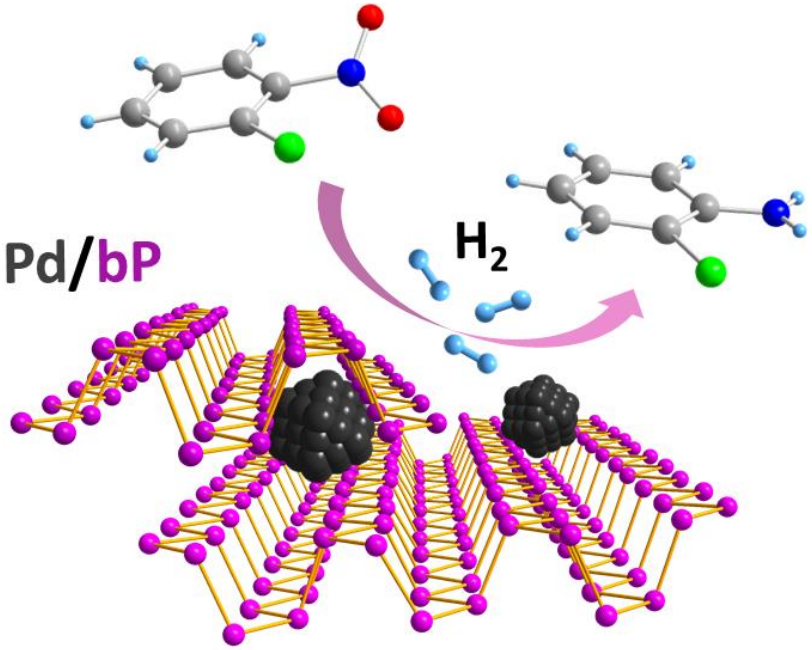
- **Pd/bP** remained active and selective for 6 runs.

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

Recycling test



Conclusions



- Synthesis of a new Pd/bP nanohybrid

- Detailed experimental study of the Pd-P interaction

- Successfull application as catalyst in the selective hydrogenation of chloronitrobenzene

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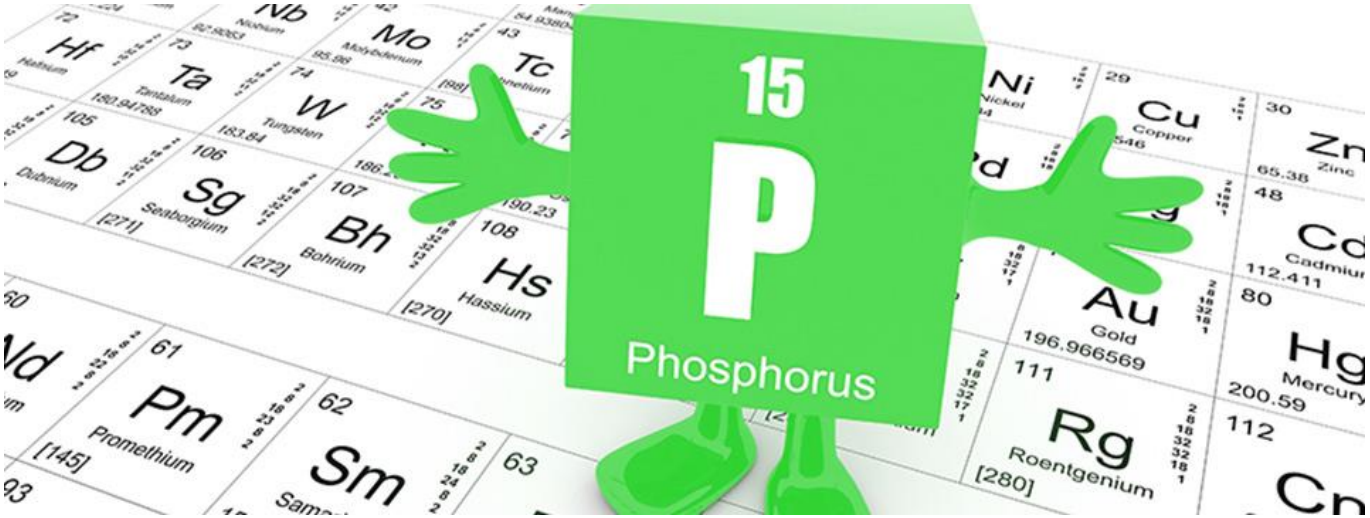

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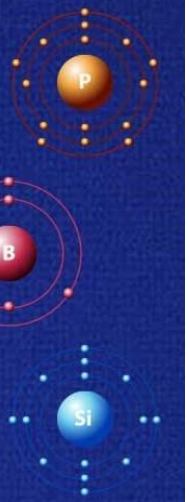

Dec 2-4, 2019 | Rome

Plenary speakers

Prof. Simon Aldridge
Prof. Guy Bertrand
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
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