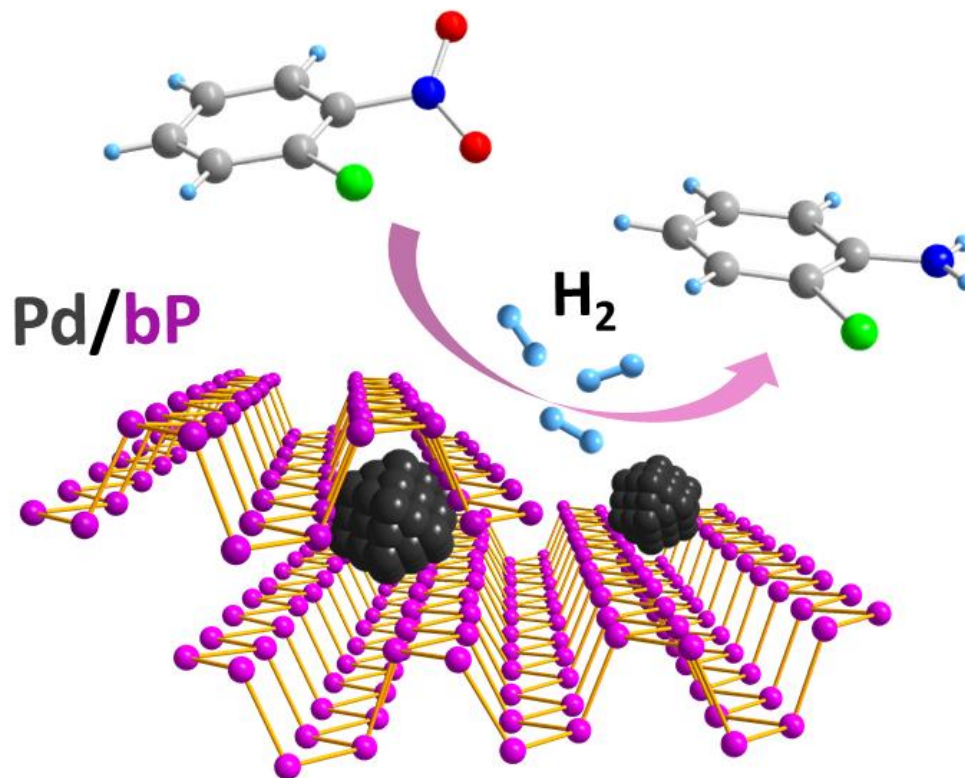


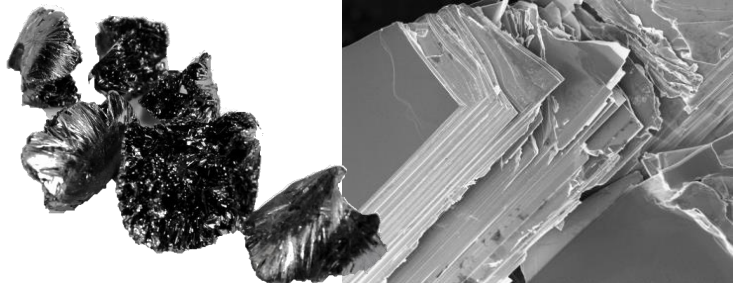
Phosphorene: a rising star in the 2D world



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

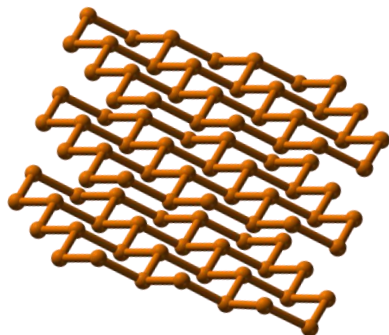


Black Phosphorus (bP) as a P counterpart of Graphite

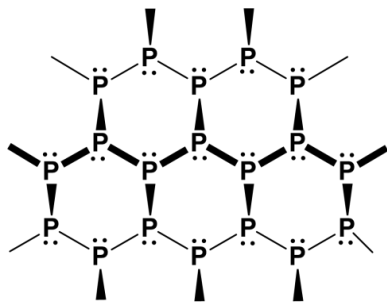


bP crystals

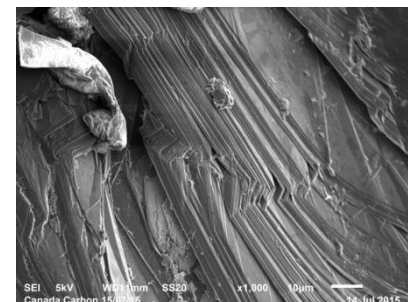
SEM image of bP



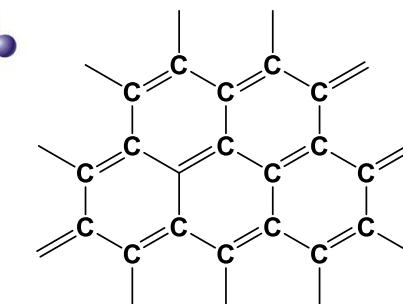
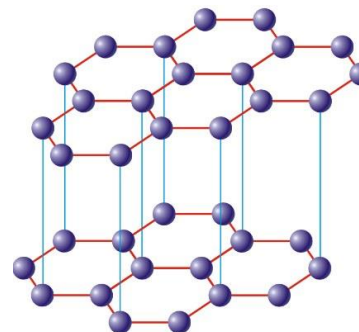
Puckered honeycomb structure of bP



sp^3 hybridized P atoms



SEM image of graphite



sp^2 hybridized C atoms

Black phosphorus exfoliation

ARTICLES
PUBLISHED ONLINE 2 MARCH 2014 | DOI: 10.1039/C3NN00163A

Black phosphorus field-effect transistors
Likai Li, Yijun Yu, Guo Jun Ye, Qingjin Ge, Xuodong Ou, Hua Wu, Donglai Feng, Xian Hui Chen* and Yuanbo Zhang*

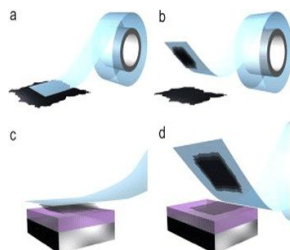
Two-dimensional crystals have emerged as a class of materials that may impact future electronic technologies. Experimentally identifying and characterizing new functional two-dimensional materials is challenging, but also potentially rewarding. Here, we fabricate field-effect transistors based on few-layer 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_D characteristics. The charge-carrier mobility is found to be thickness-dependent, with the highest values up to $\sim 1,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ 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 functional layers tend to slightly underestimate the size of atomic layers are stacked together by van der Waals interactions, much like bulk graphite. Inside a single layer, each phosphorus atom is covalently bonded with three adjacent phosphorus atoms to form a puckered honeycomb structure.

We now fabricated few-layer phosphorene FETs with a buckled phosphorene atom is covalently bonded with three adjacent phosphorus atoms to form a puckered honeycomb structure.

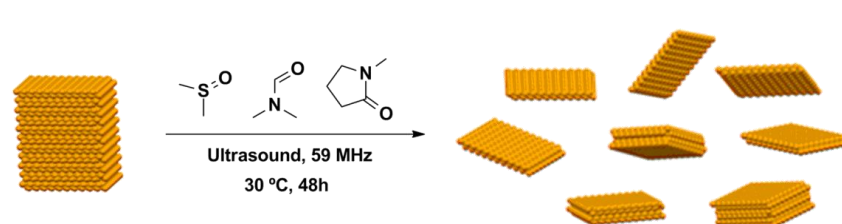
method was used to peel thin flakes from bulk crystal onto silicon

the bandgap is semiconductor²⁰.



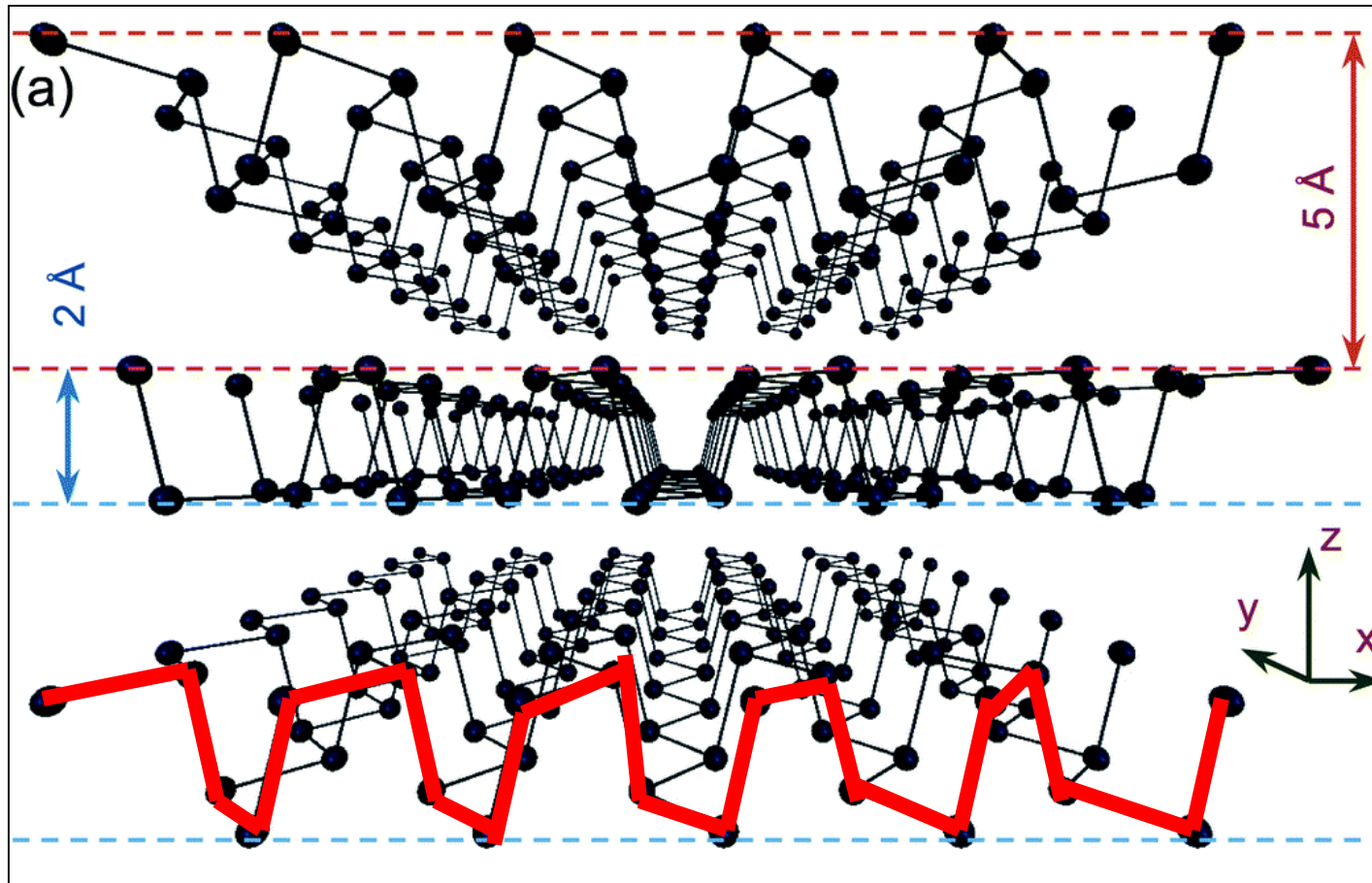
Nat. Nanotechnol. 2014

mechanical exfoliation



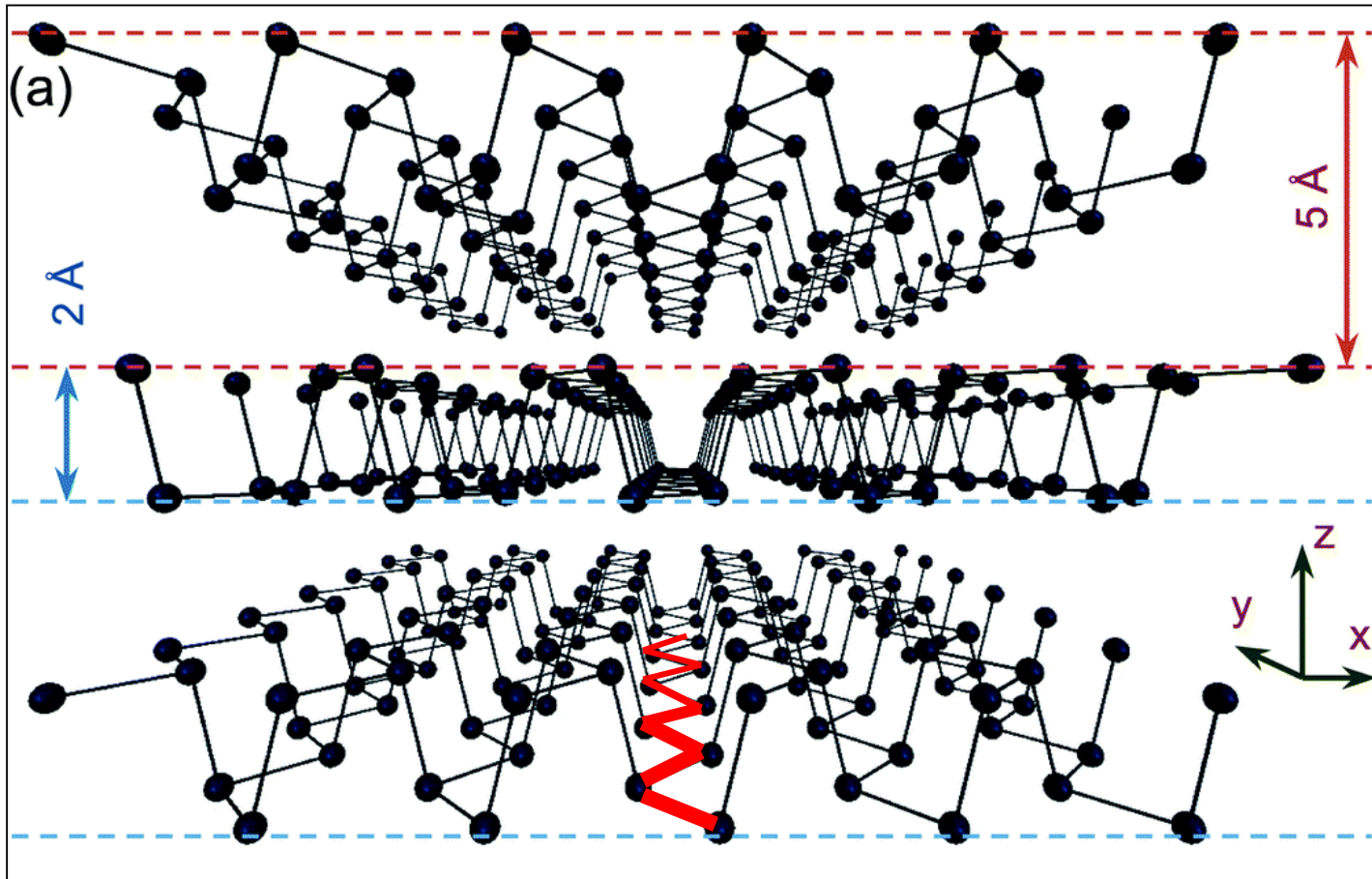
solvent assisted exfoliation

Anisotropic structure of black phosphorus



Armchair (x-axis)

Anisotropic structure of black phosphorus



Zig-zag (y-axis)

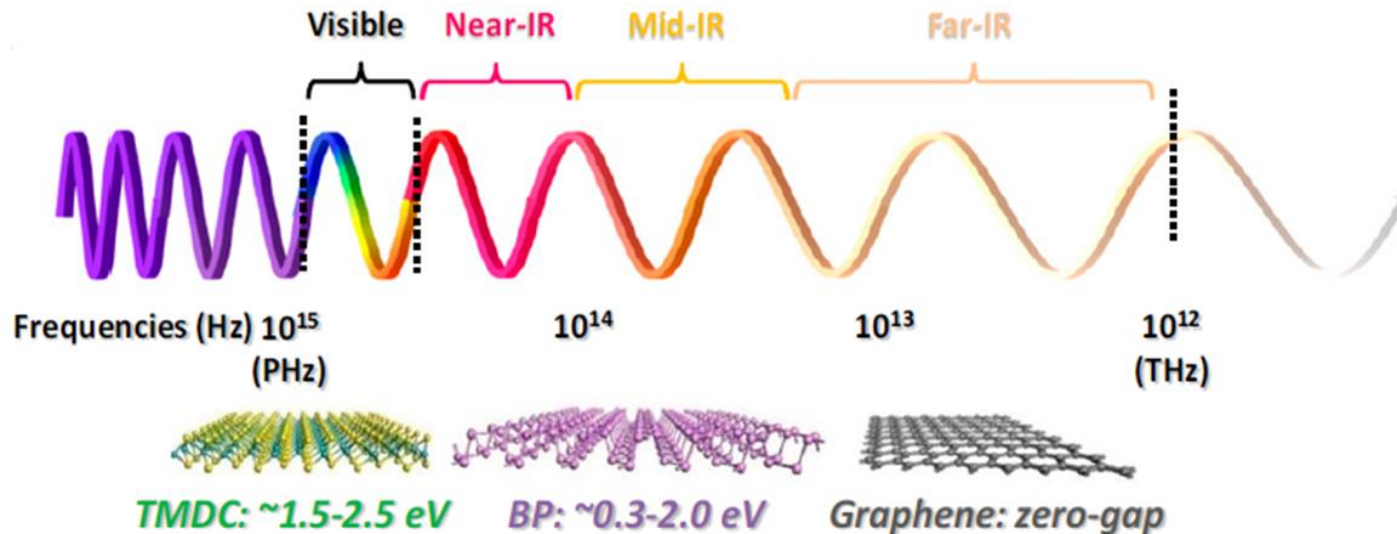
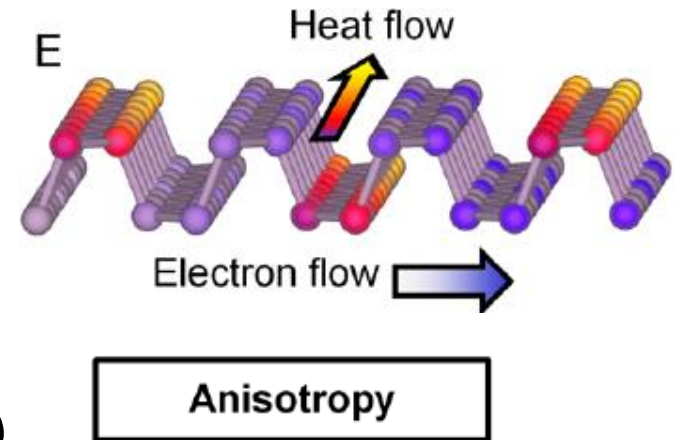
Physical properties of 2D black P

✓ High carrier mobility: $1000 \text{ cm}^2/\text{Vs}$

✓ On / off ratio: $10^3 - 10^5$

✓ Thermal conductivity (300 K):

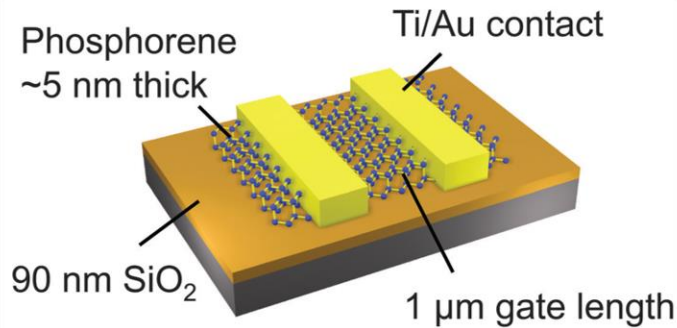
30 W/m K (zig-zag); 13.7 W/m K (armchair)



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

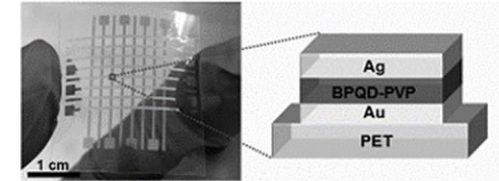
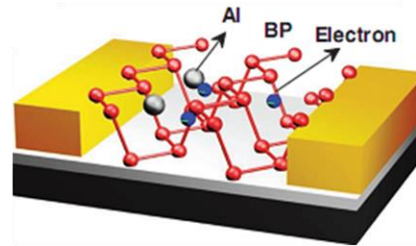
✓ The band gap can be modulated either applying an electrical field or by strain.

Applications of black phosphorus

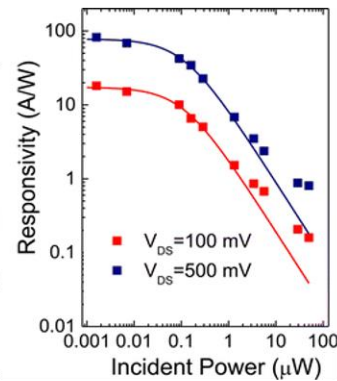
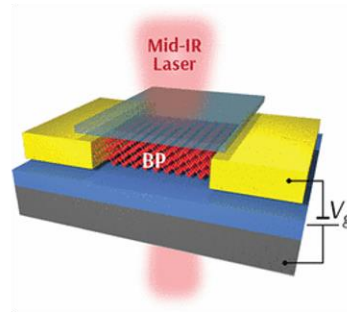
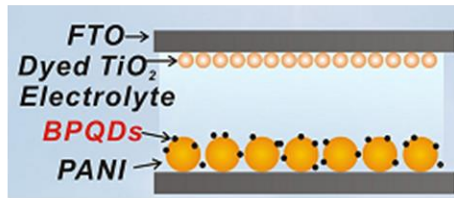


2D BP-based *p*-FET

Al-doped 2D BP *n*-FET

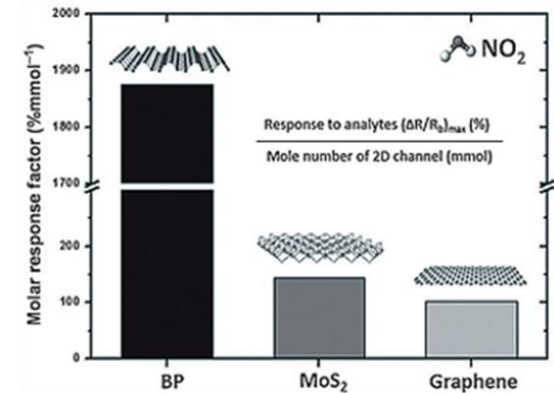


2D BP-based memory device



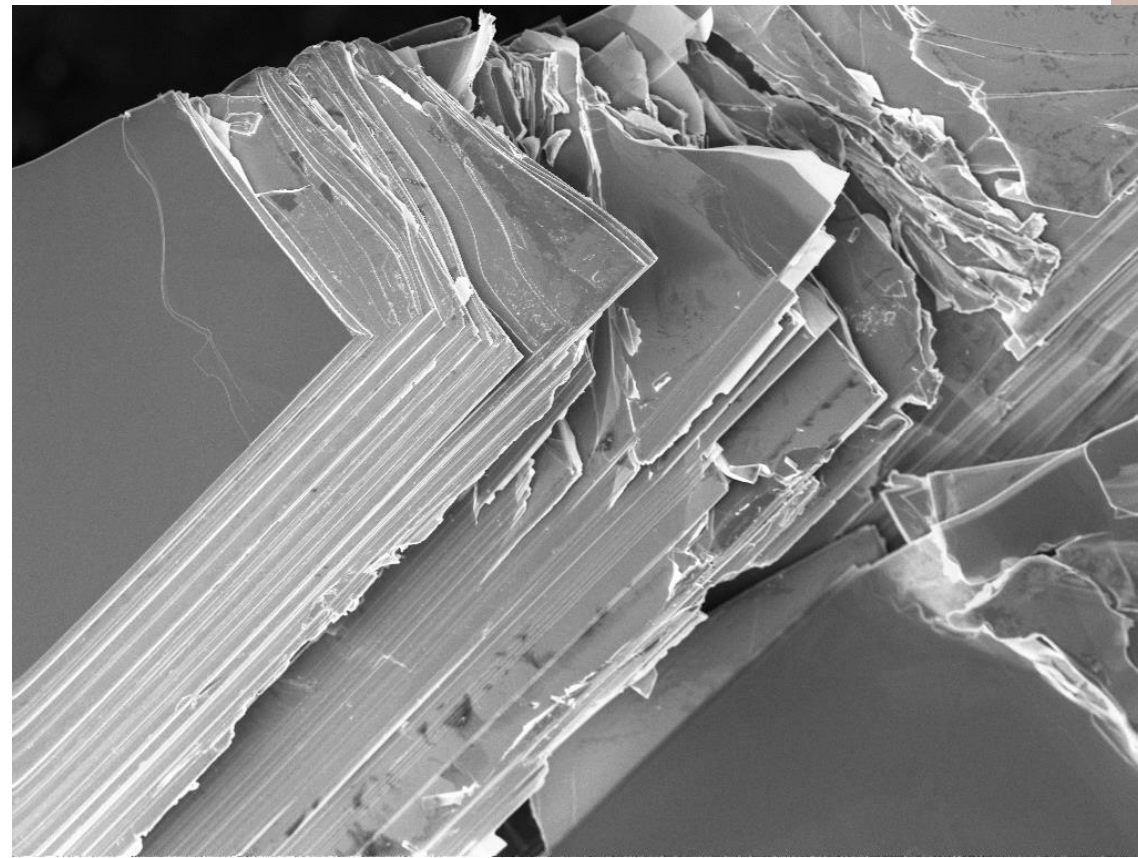
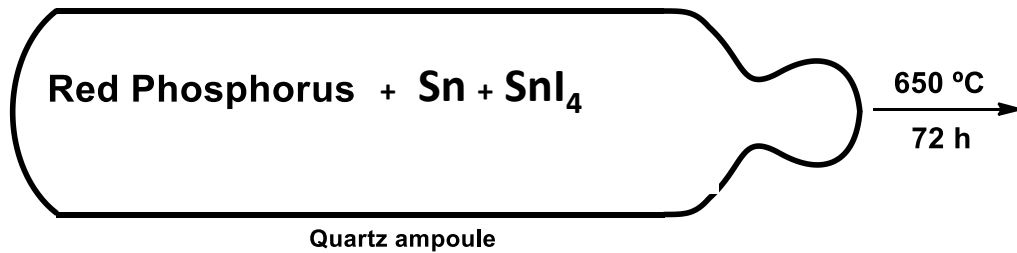
BP QDs-based solar cell

2D BP-based photodetector

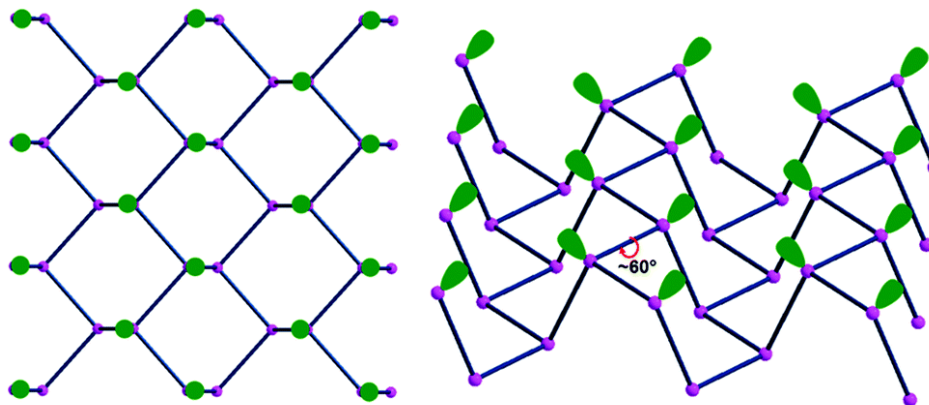


NO₂-sensor based on 2D BP

Synthesis of black phosphorus

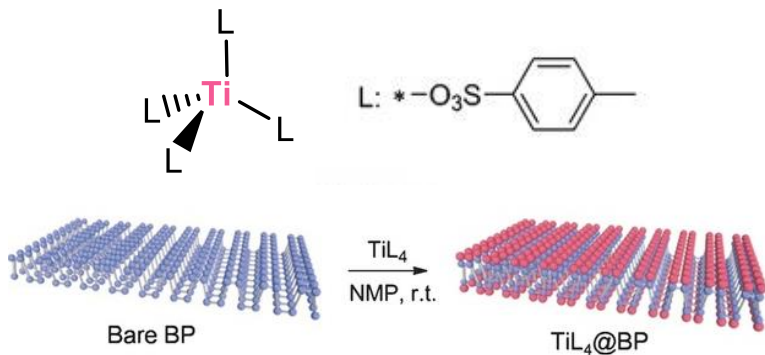


Anchoring Metal Fragments: Coordinative Abilities of bP

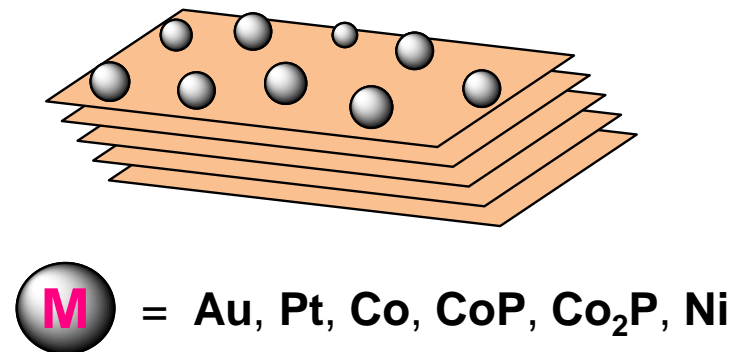


Top view and side view of phosphorene lone pairs (green)

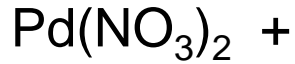
Functionalization with molecular fragments



Functionalization with M NPs



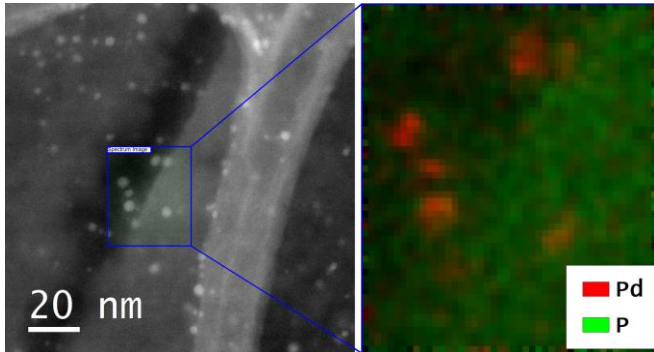
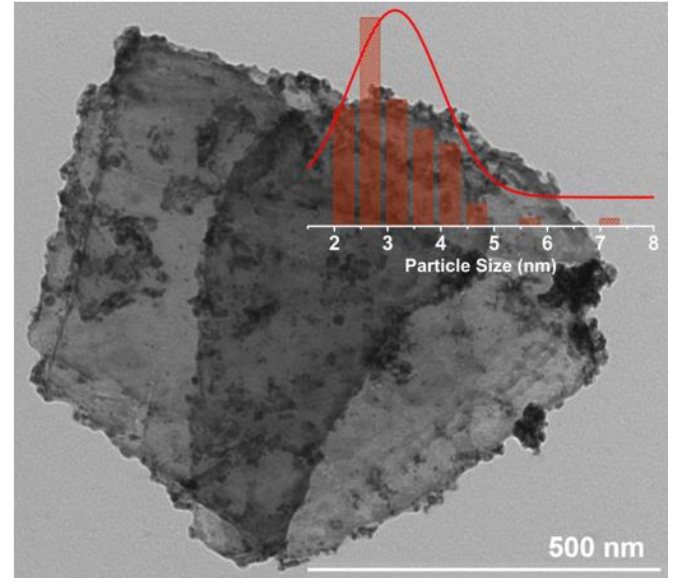
Pd/bP: a New M/bP Nanohybrid



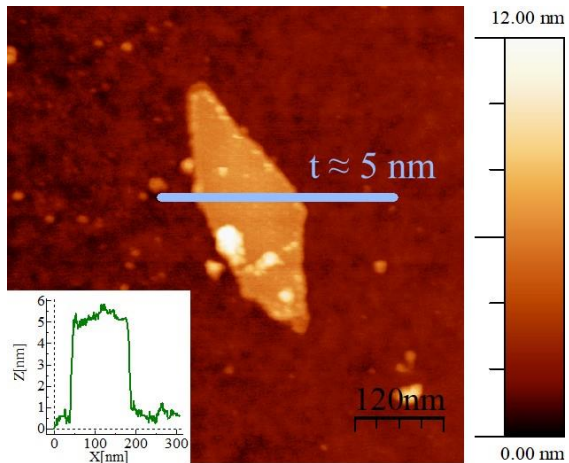
exfoliated bP



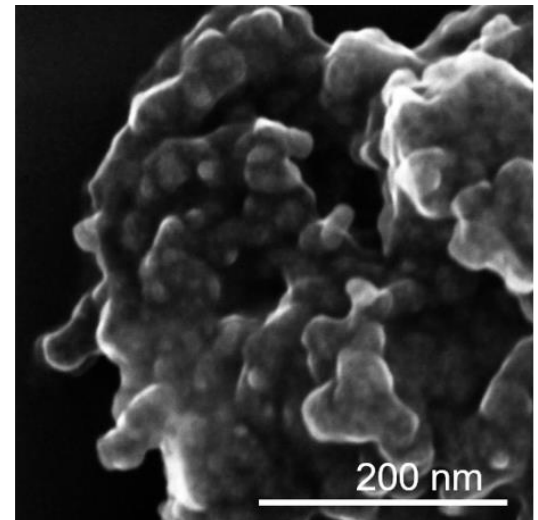
H_2O , EtOH, THF
 $P_{\text{H}_2} = 5$ bar, RT, 1h



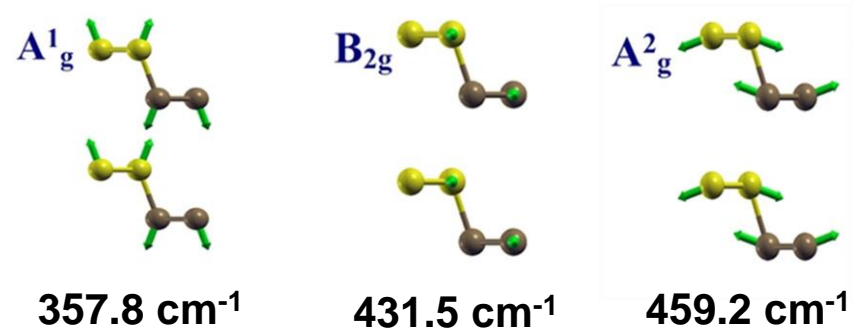
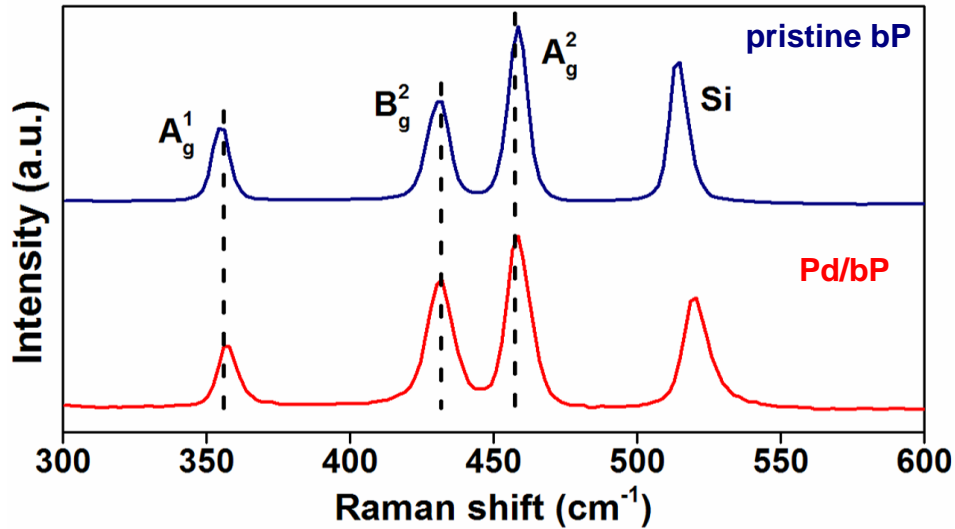
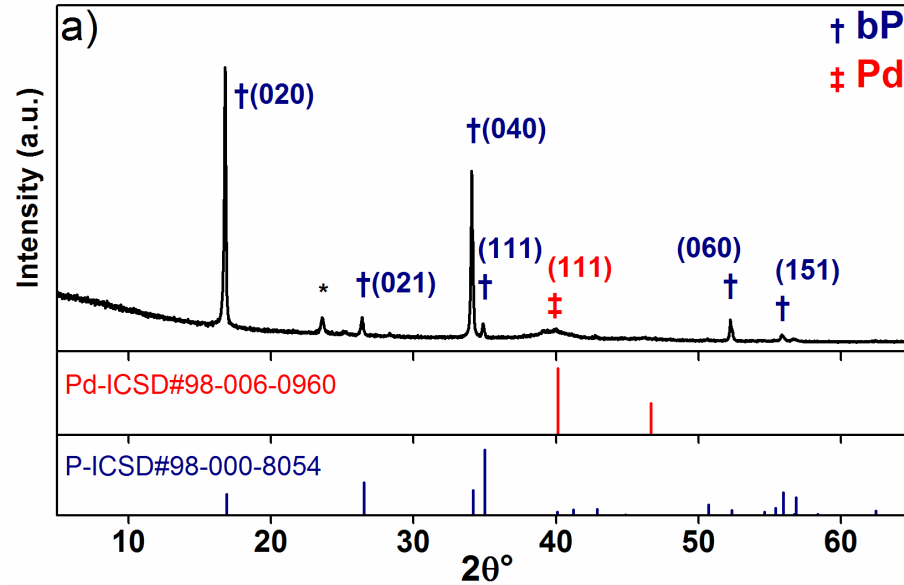
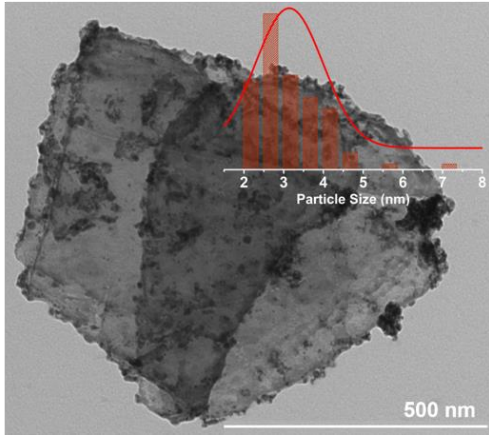
HR-TEM
EDS



AFM height profile
of a Pd/bP flake



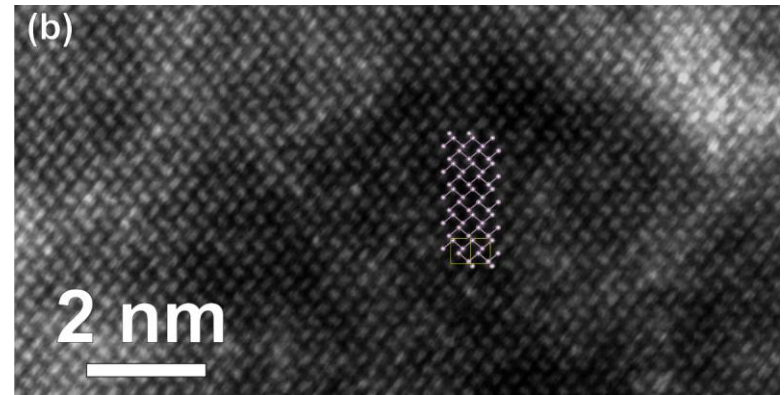
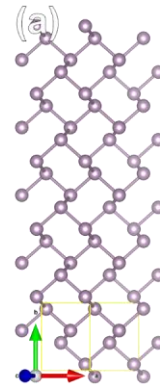
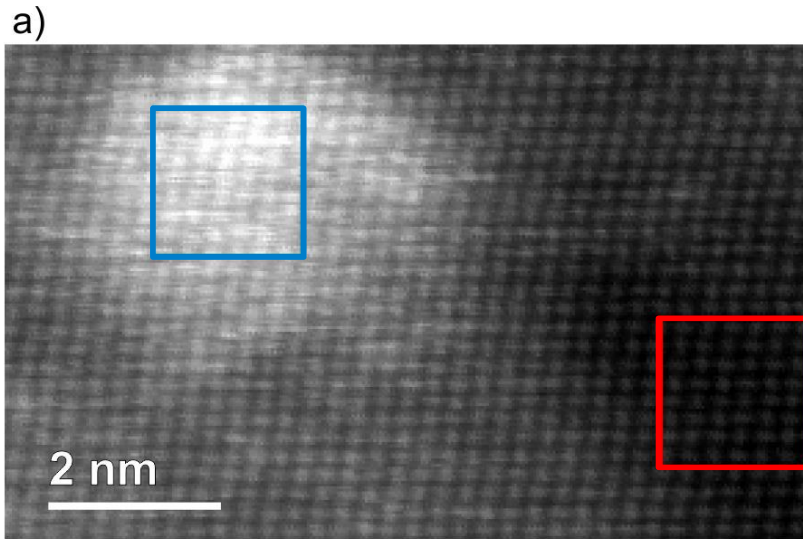
PXRD and Raman



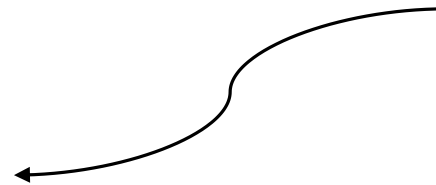
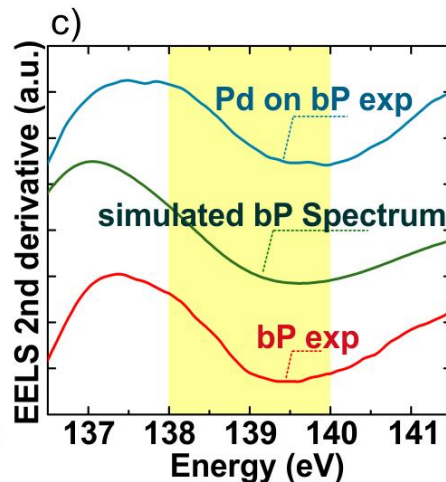
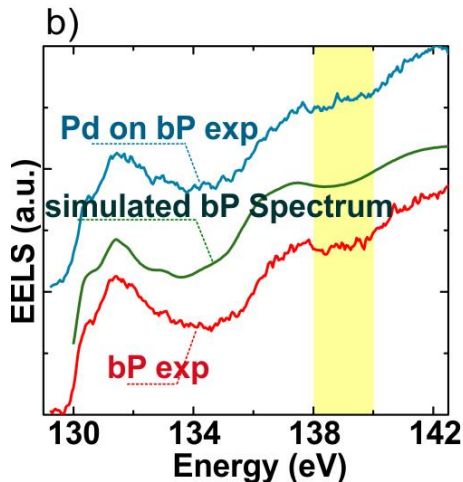
Raman active modes of black phosphorus

HRTEM-EELS

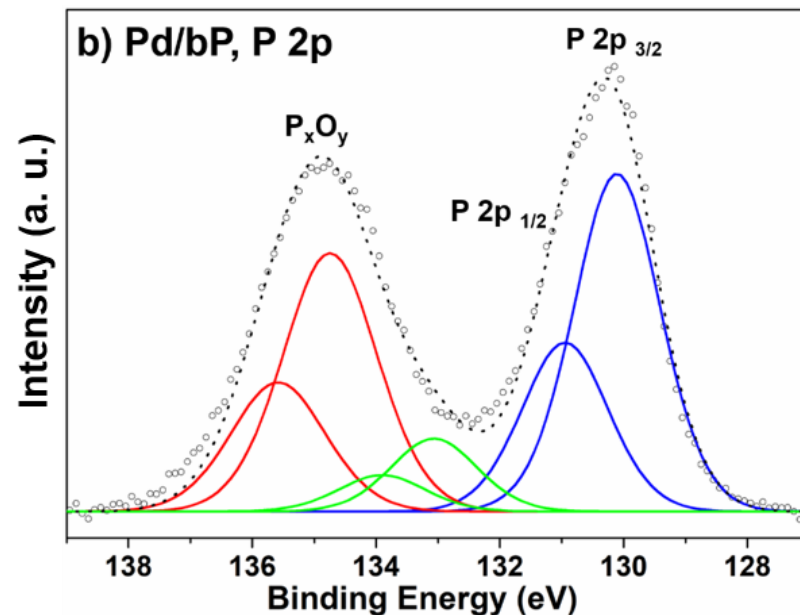
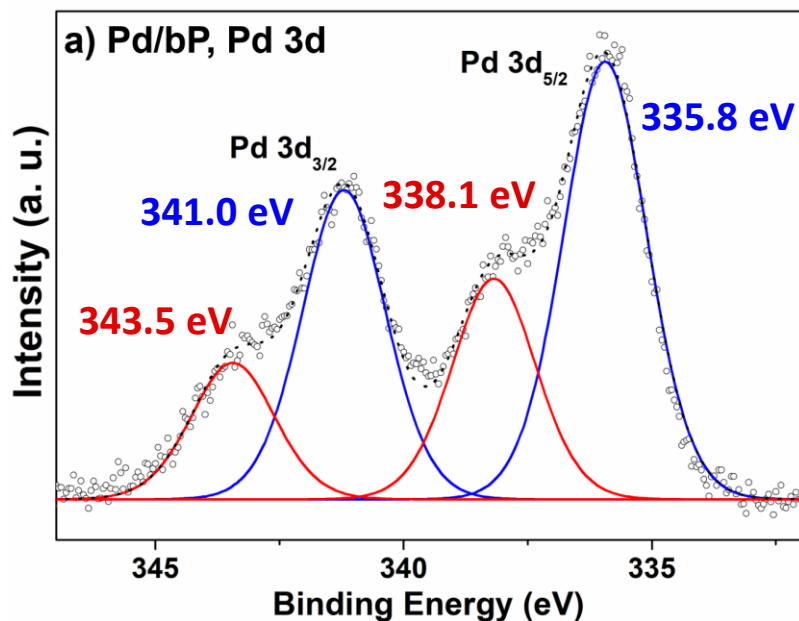
First Evidence of Strong P-Pd Interaction



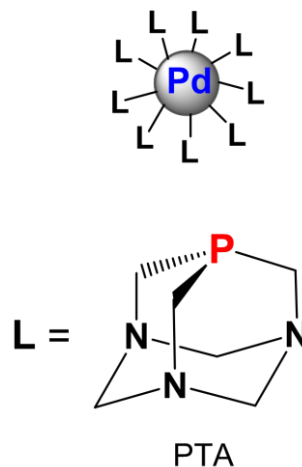
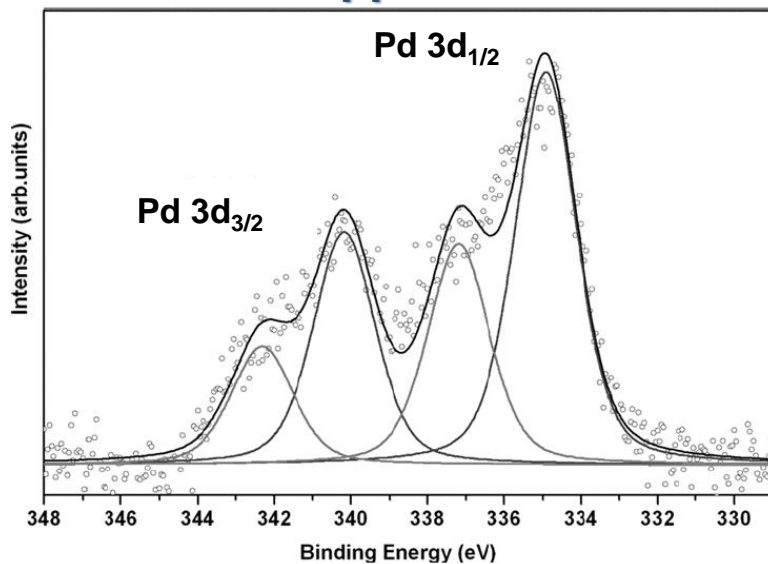
Comparative analysis of the P_L edge between Pd free regions (red area) and Pd/bP regions (blue area) reveals **modification in the EELS profile around 137-140 eV**



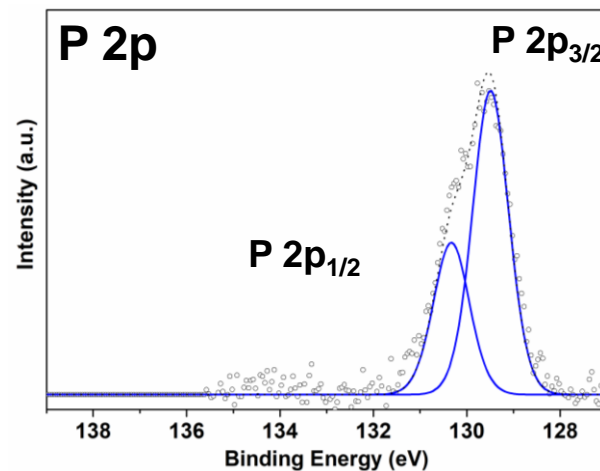
XPS



Pd NPs capped with PTA*



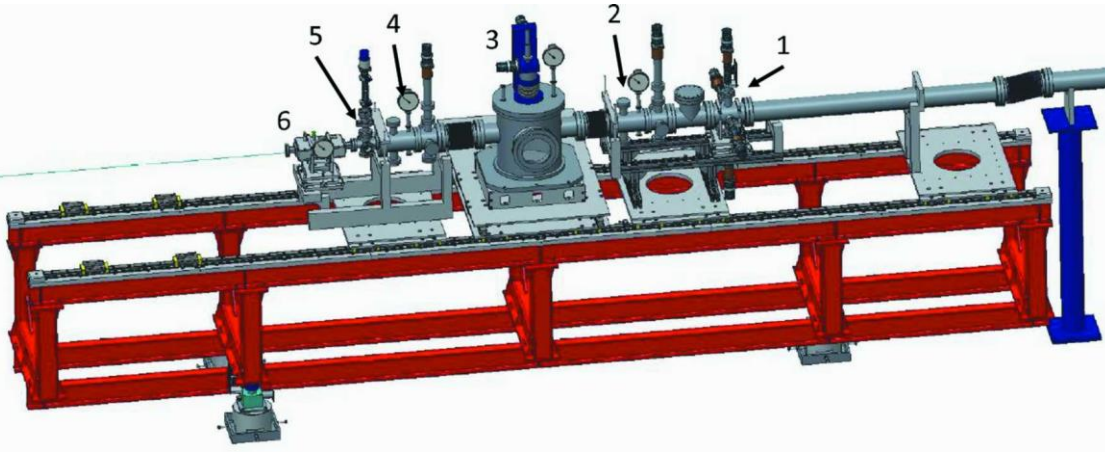
pristine black phosphorus



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

Going Further

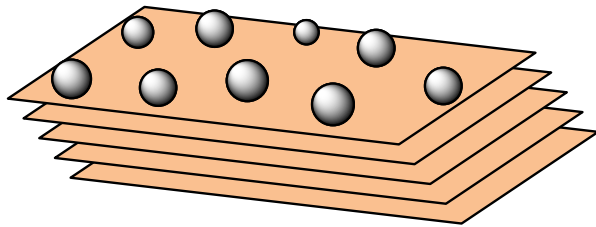
Gaining Structural Insights from EXAFS



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).



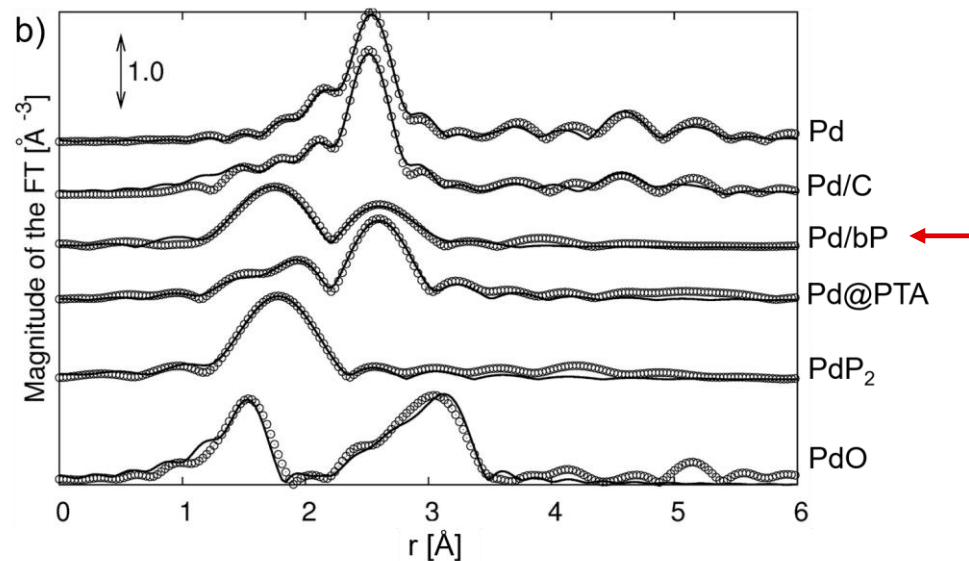
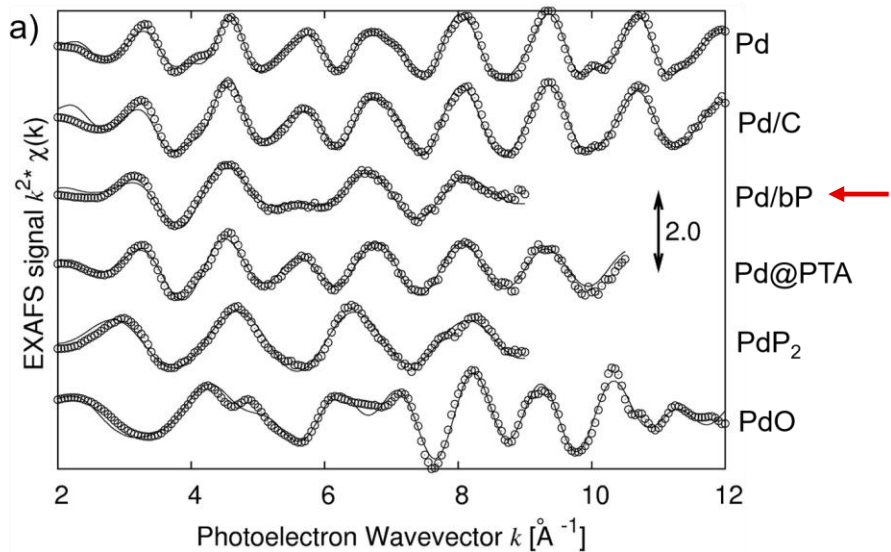
ESRF, Grenoble



Pd/bP

The new nanohybrid Pd/bP was studied by XAS comparing it with Pd, PdO, PdP₂ and Pd@PTA.

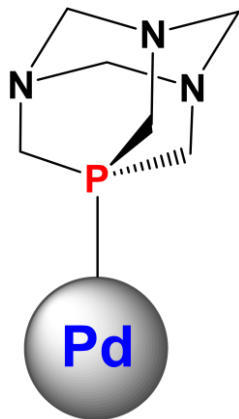
EXAFS Study



Sample	CNs Pd-Pd	R_{PdPd} (\AA)	σ^2_{PdPd} (\AA^2)	CNs Pd-P	R_{PdP} (\AA)	s^2_{PdP} (\AA^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)	-	-	-

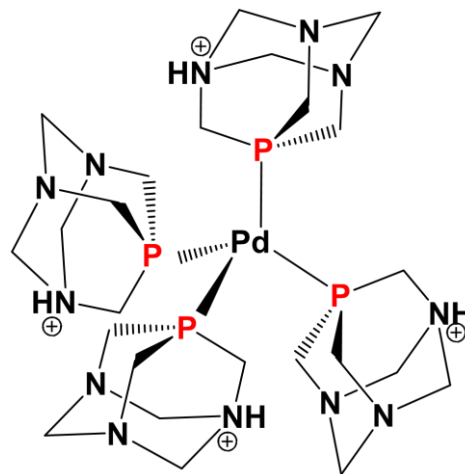
Conclusions from the EXAFS study

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

$$d_{\text{Pd-P}} = \mathbf{2.25(3) \text{ \AA}}$$



Pd(PTAH)₄⁺

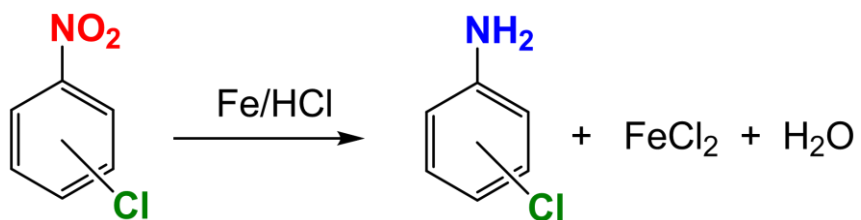
$$d_{\text{Pd-P}} = \mathbf{2.203(3) \text{ \AA}^{(*)}}$$

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

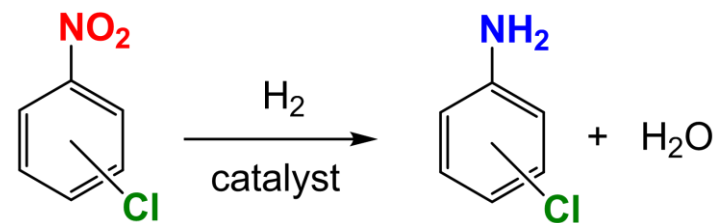
From Chloronitrobenzene to Chloroaniline



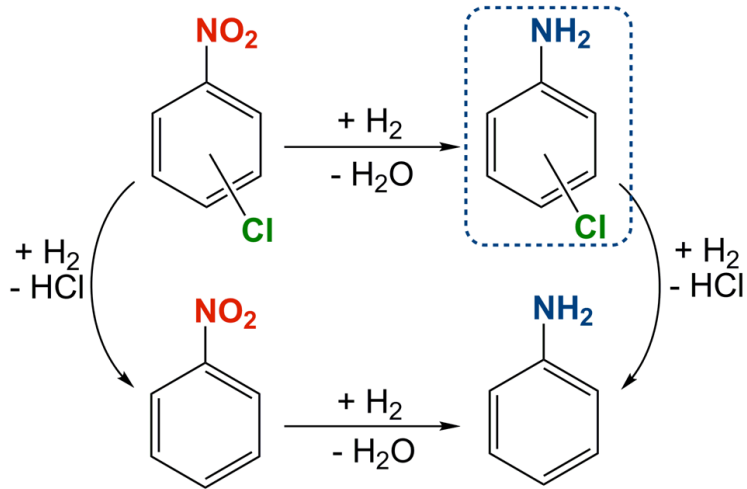
Stoichiometric Route



Catalytic Conversion

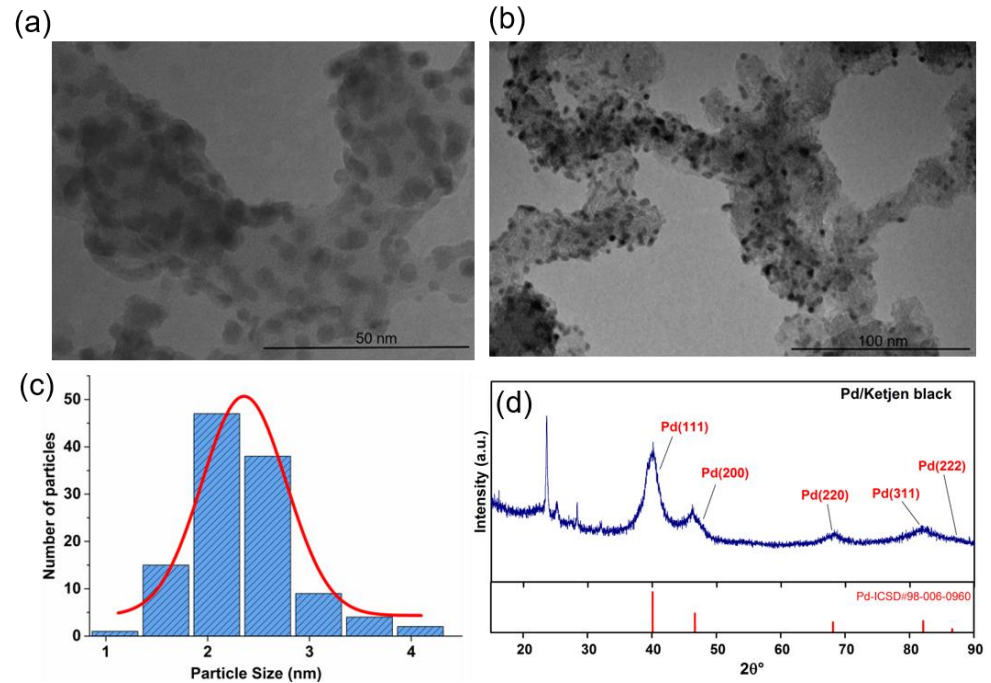


Hydrogenation with Pd/bP



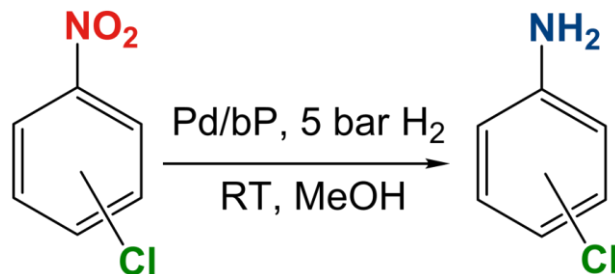
drawback of catalytic hydrogenations:
C-Cl hydrogenolysis

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



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

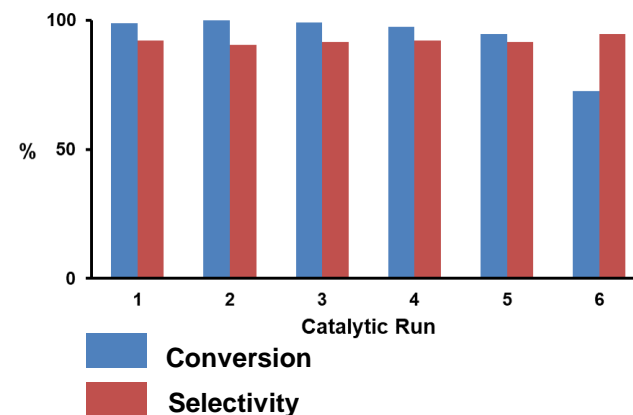
Hydrogenation with Pd/bP



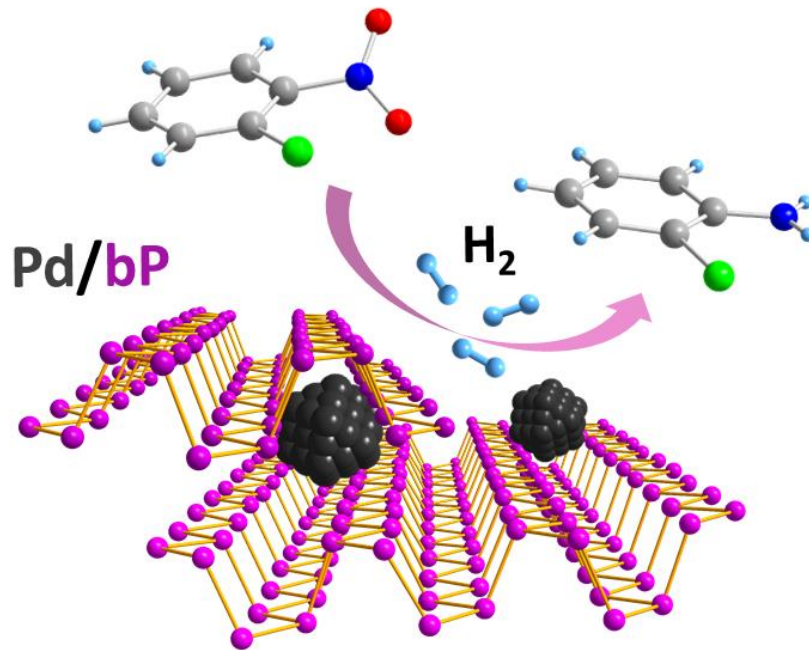
Catalyst	Substrate	Time	S/C	Conv. % ^a	Select. %	TOF ^b (h ⁻¹)
Pd/bP	1-chloro-3-nitrobenzene	30'	162	99.1	97.7	313
	1-chloro-2-nitrobenzene	40'	162	99.5	97.3	235
Pd/C	1-chloro-2-nitrobenzene	30'	191	99.9	78.1	298

- Pd/bP remained active and selective for 6 runs.
- Pd/bP was stable towards NPs agglomeration.

Recycling test



Conclusions

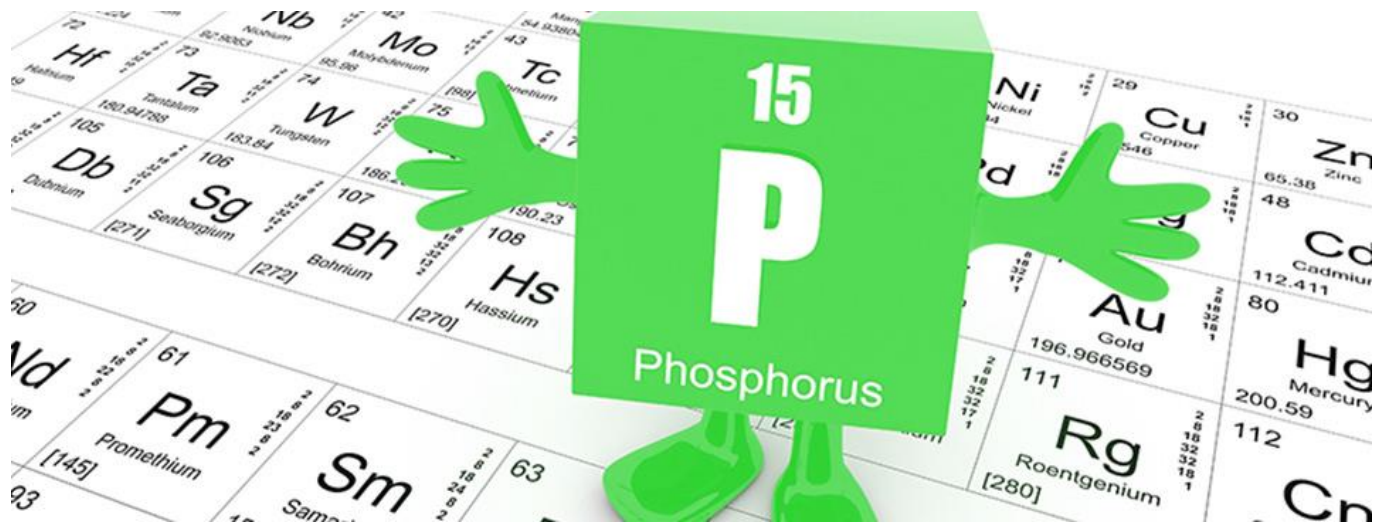


- **Synthesis of a new Pd/bP nanohybrid**

- **Detailed experimental study of the Pd-P interaction**

- **Successful application as catalyst in the selective hydrogenation of chloronitrobenzene**

OUR INSTITUTE



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