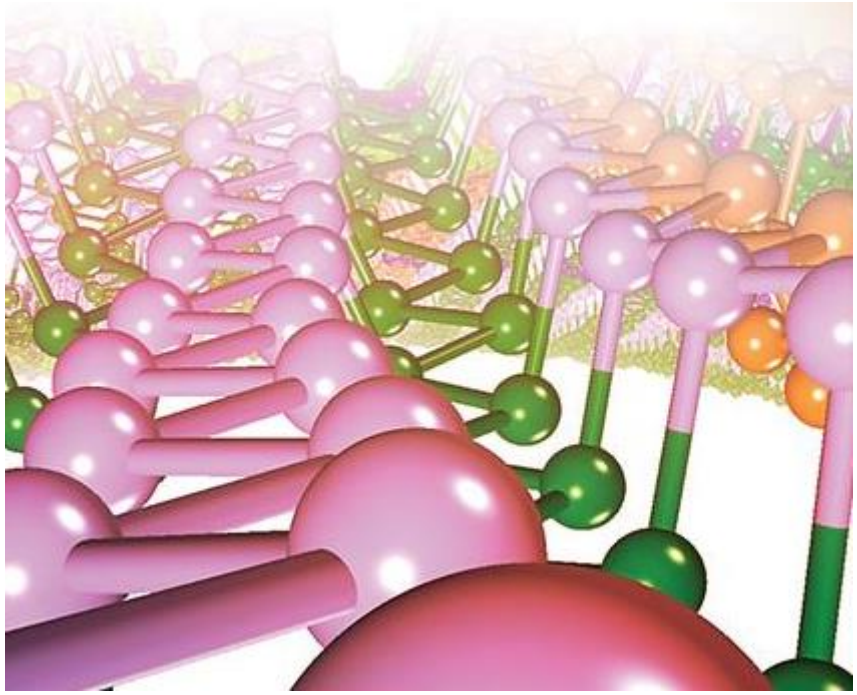
ISTITUTO DI CHIMICA DEI COMPOSTI ORGANOMETALLICI

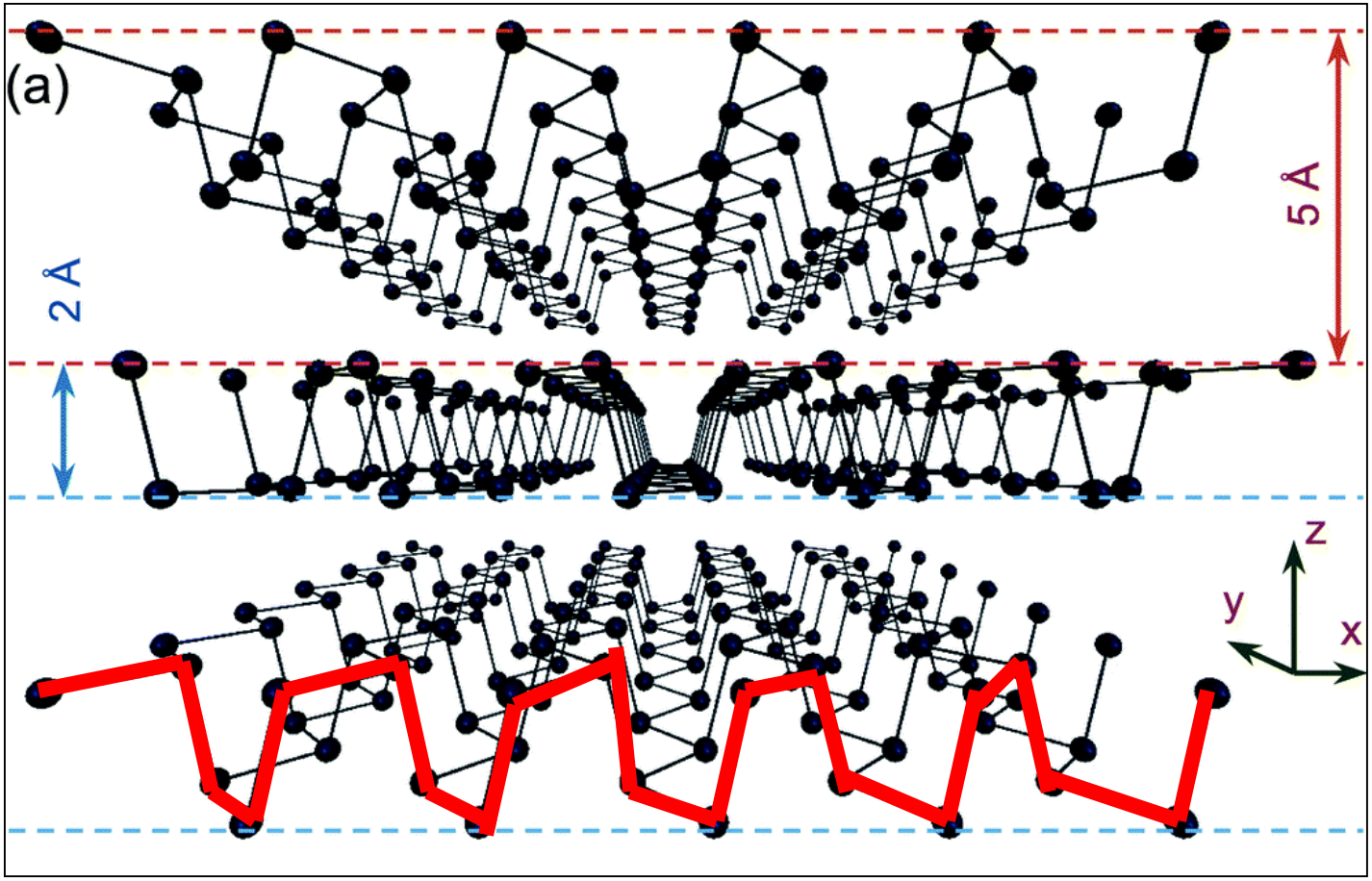
European Research Council

Surface functionalization of exfoliated black phosphorus with transition metal nanoparticles: enhancement of ambient stability and selectivity in chemical processes



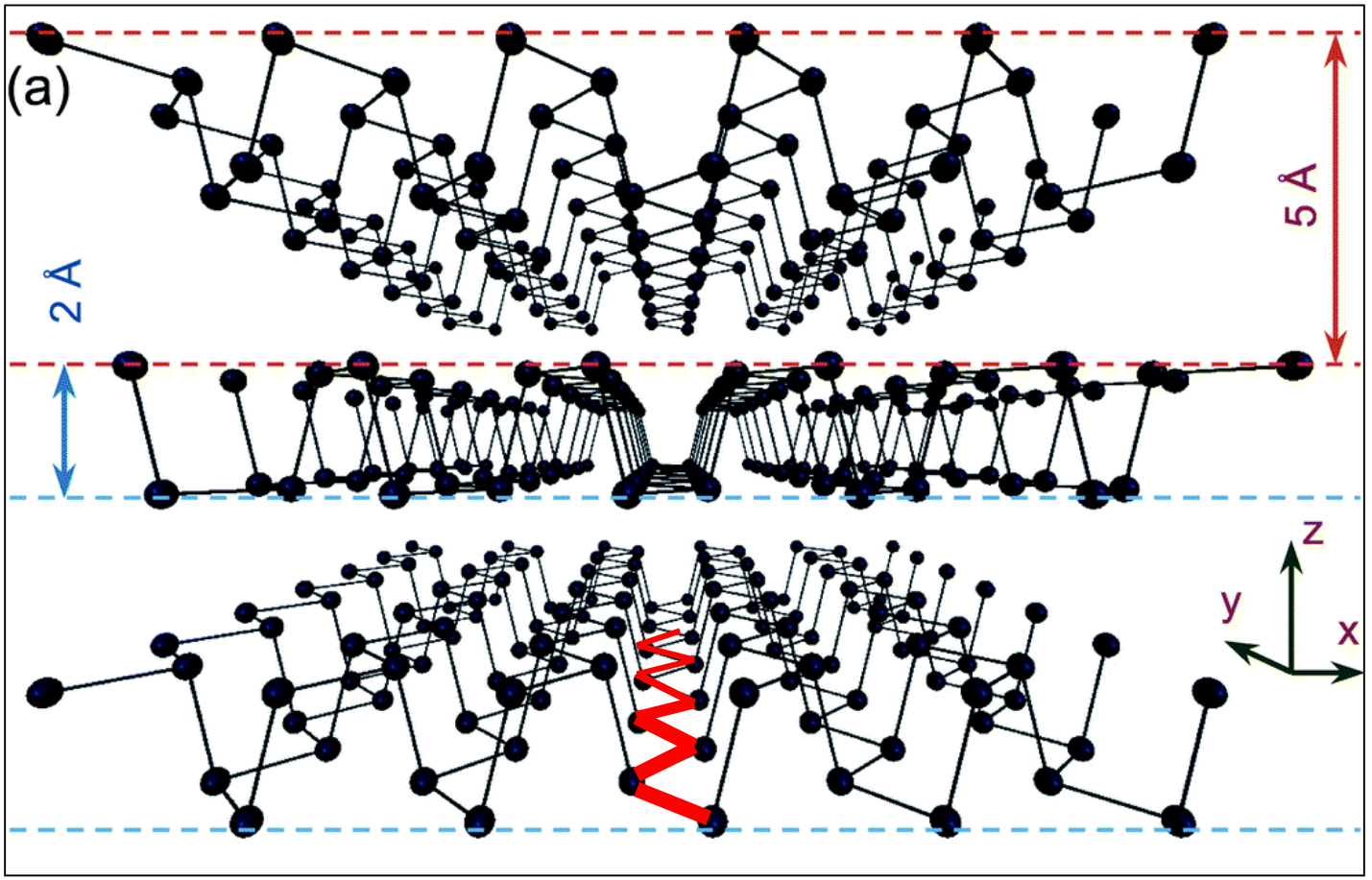
Maria Caporali
CNR ICCOM, Florence (ITALY)

Anisotropic structure of black phosphorus



Armchair (x-axis)

Anisotropic structure of black phosphorus



Zig-zag (y-axis)

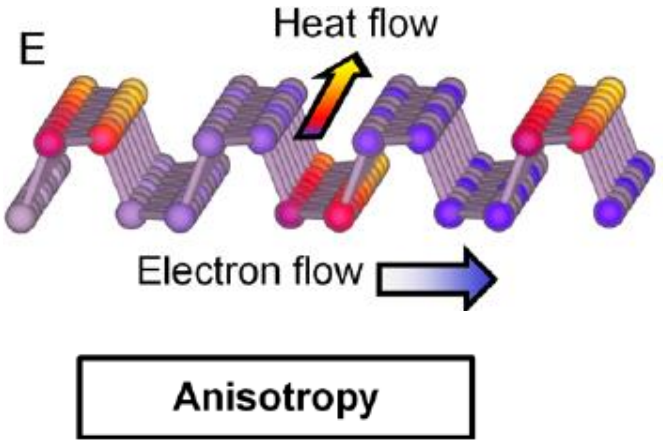
Physical properties of few-layer bP

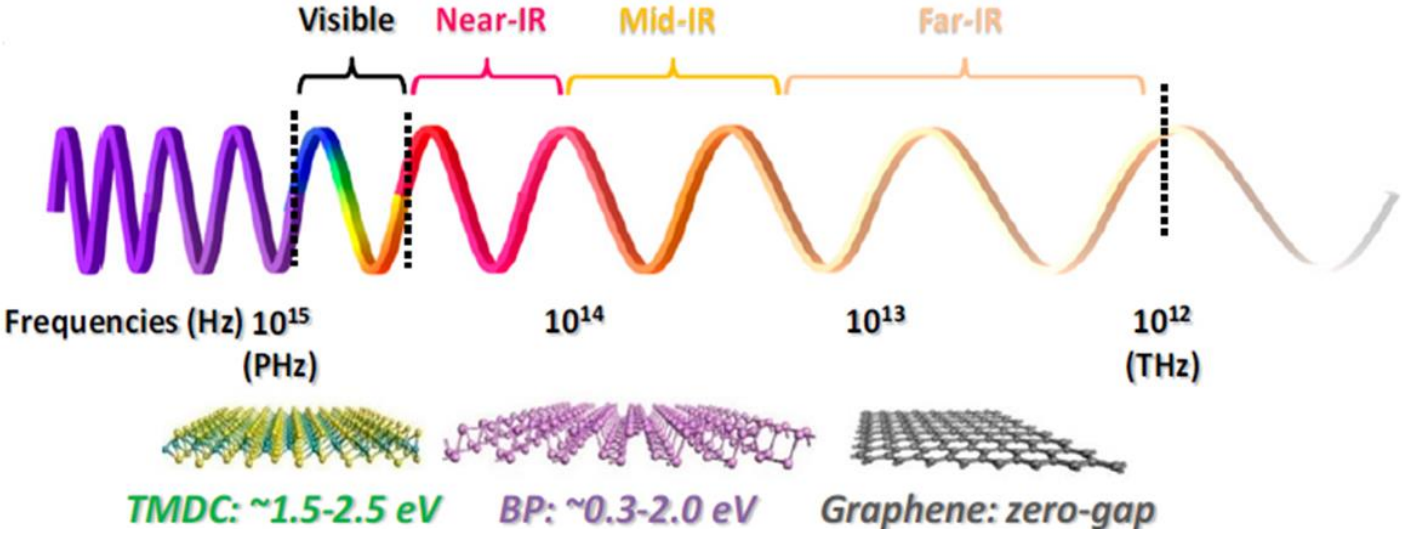
✓ High carrier mobility: 1000 cm^2/Vs

✓ On / off ratio: 10^3 – 10^5

✓ Thermal conductivity (300 K):

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

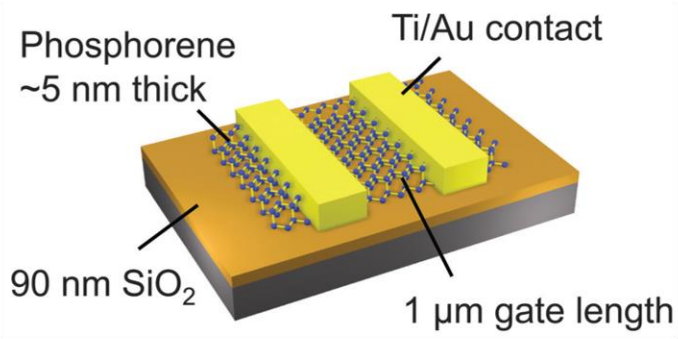




✓ *p*-type semiconductor, with a thickness-depending direct band gap (0.3-2.0 eV)

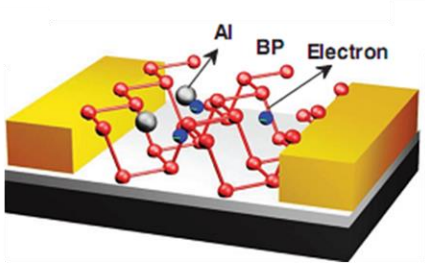
✓ The band gap can be modulated either applying an electrical field or by strain.

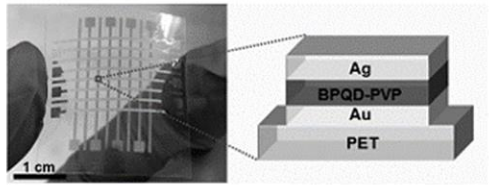
Applications of black phosphorus



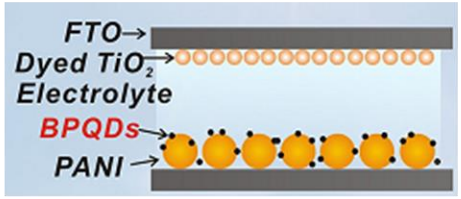
2D BP-based *p*-FET

Al-doped 2D BP *n*-FET

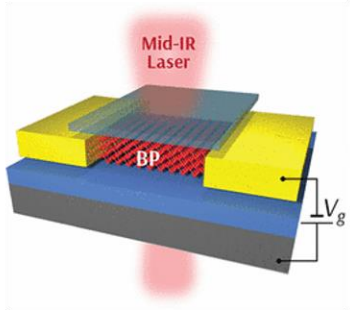


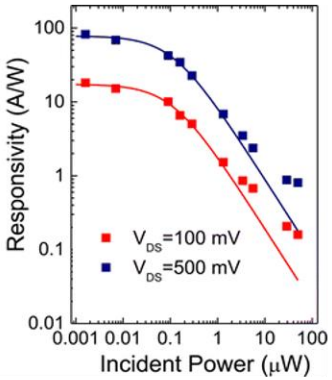


2D BP-based memory device

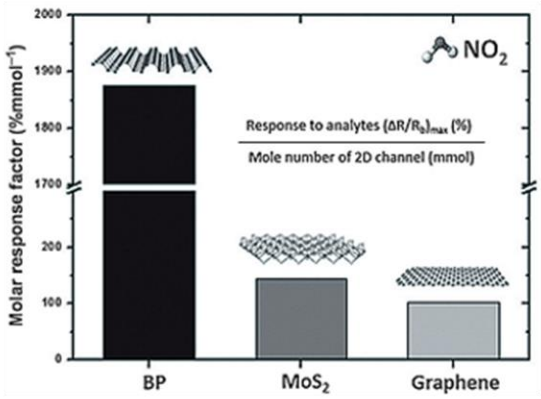


BP QDs-based solar cell



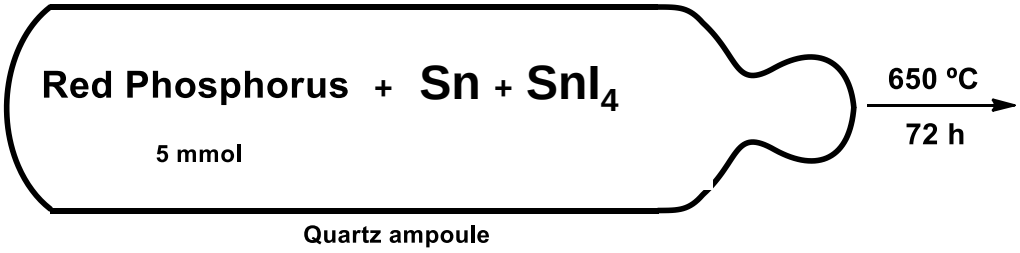


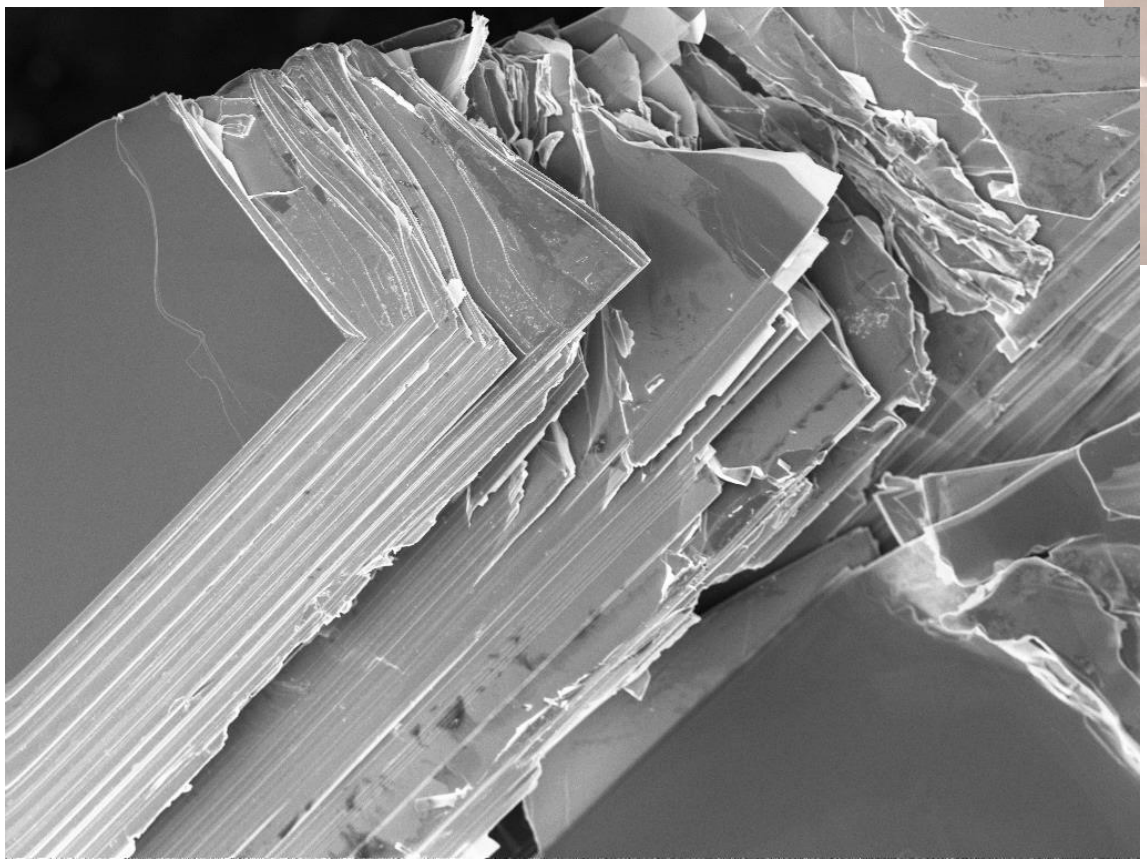
2D BP-based photodetector



NO_2-sensor based on 2D BP

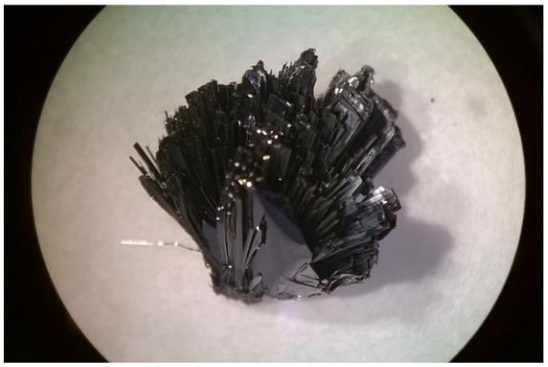
Synthesis of black phosphorus

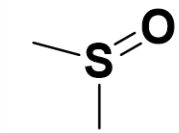




J. Crystal Growth **2014**, *405*, 6.

Liquid-phase exfoliation



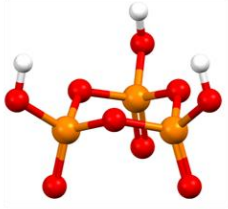


Ultrasound, 37 kHz

30 ºC, 20h

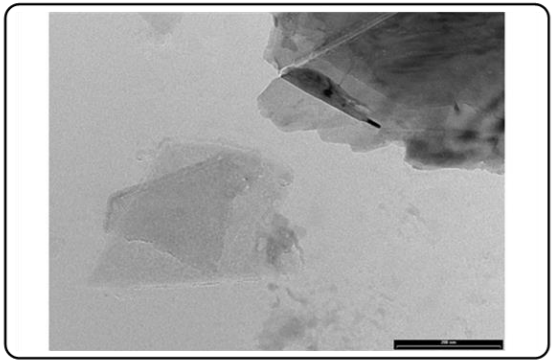
P/H_2O

≥ 15

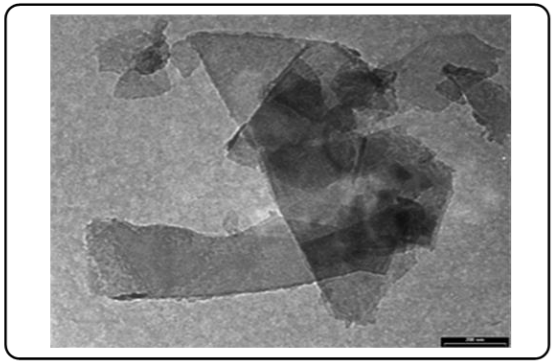


trimetaphosphoric acid

14 - 1.5

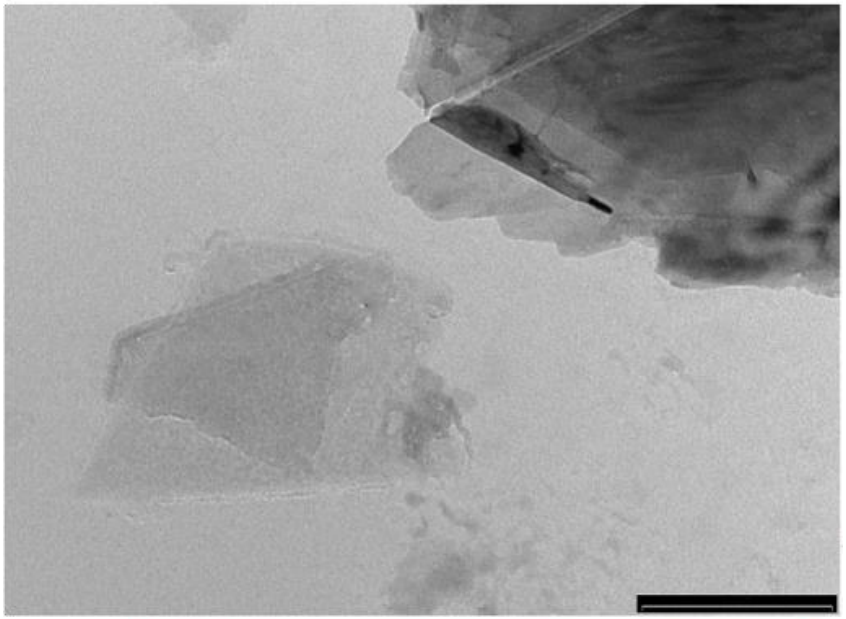


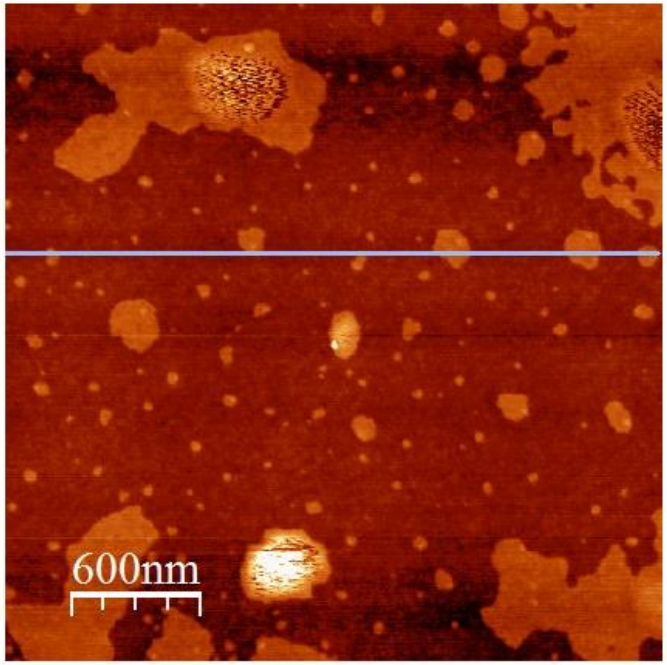
1.4 - 0.3

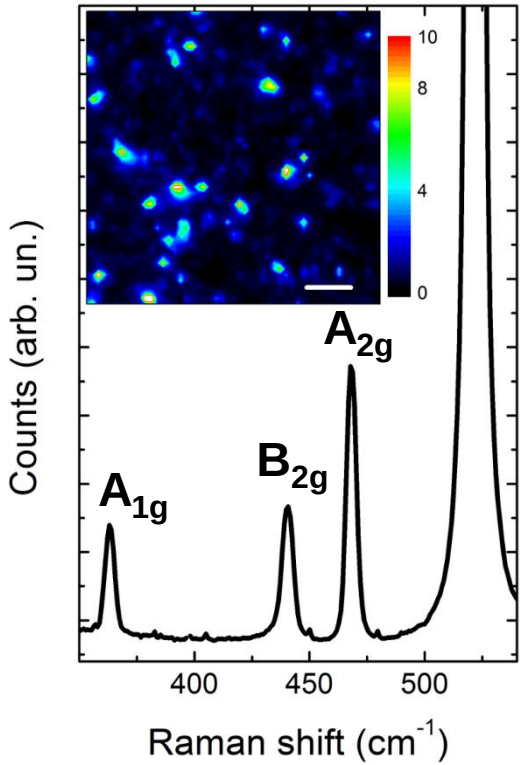


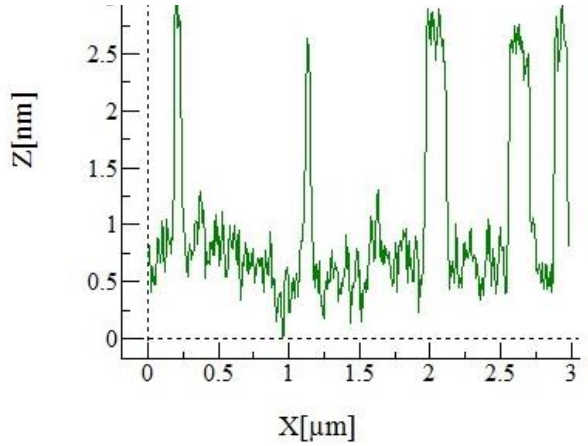
M. Serrano-Ruiz, M. Caporali, M. Peruzzini *et al*. , *Adv. Mat. Interfaces* **2016**, 3, 1500441.

2D black phosphorus: characterization



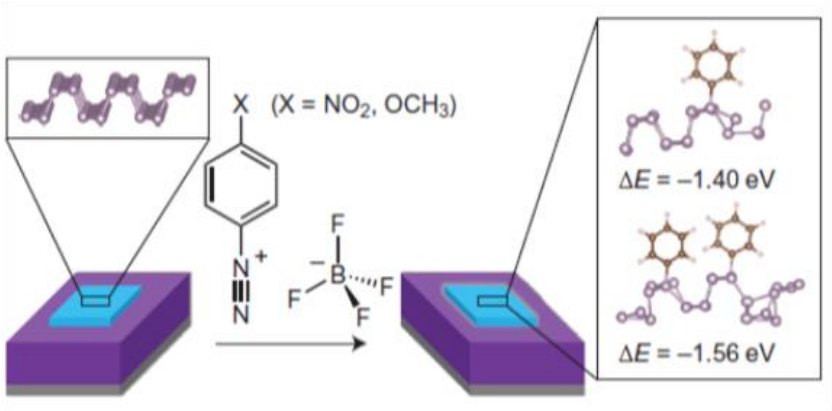




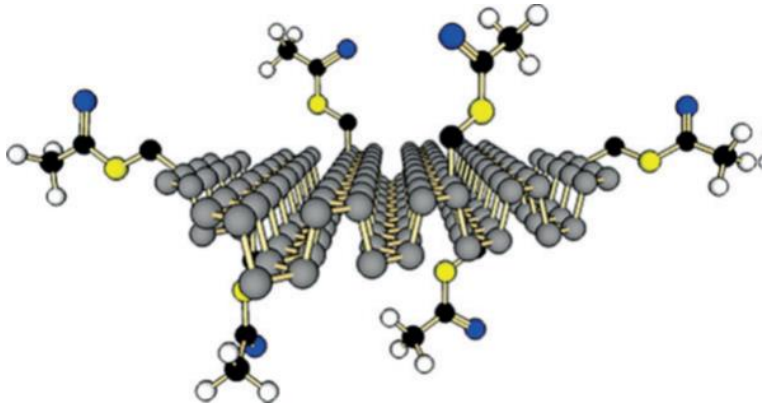


Why is the chemistry of 2D bP important?

- ✓ improve the **processability** and the **solubility** of the nanomaterial;
- ✓ contribute to its **stabilization** in ambient conditions;
- ✓ provide the opportunity for **modulations** and **fine tuning** of the physical properties;
- ✓ serve as a basis for the development of **devices**.



Nat. Chem. 2016, 8, 598.



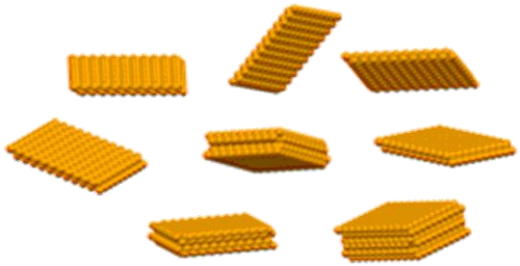
Angew. Chem. Int. Ed. 2017, 56, 9891.

Surface functionalization of 2D bP with Ni NPs

$Ni(acac)_2$ + 10 OA + 0.8 TOP $\xrightarrow[\text{2 h, 100\% yield}]{\text{T = 220°C, inert gas}}$ Ni(L)$_{10}$

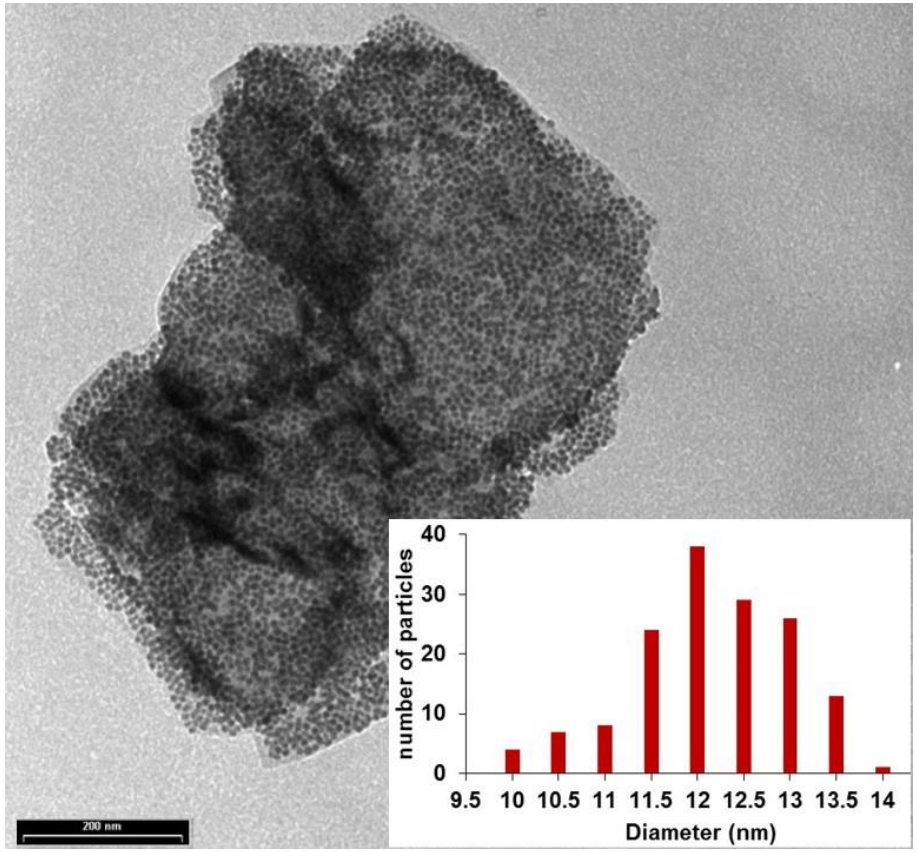
OA : oleylamine
TOP: trioctylphosphine (L)

NiNPs



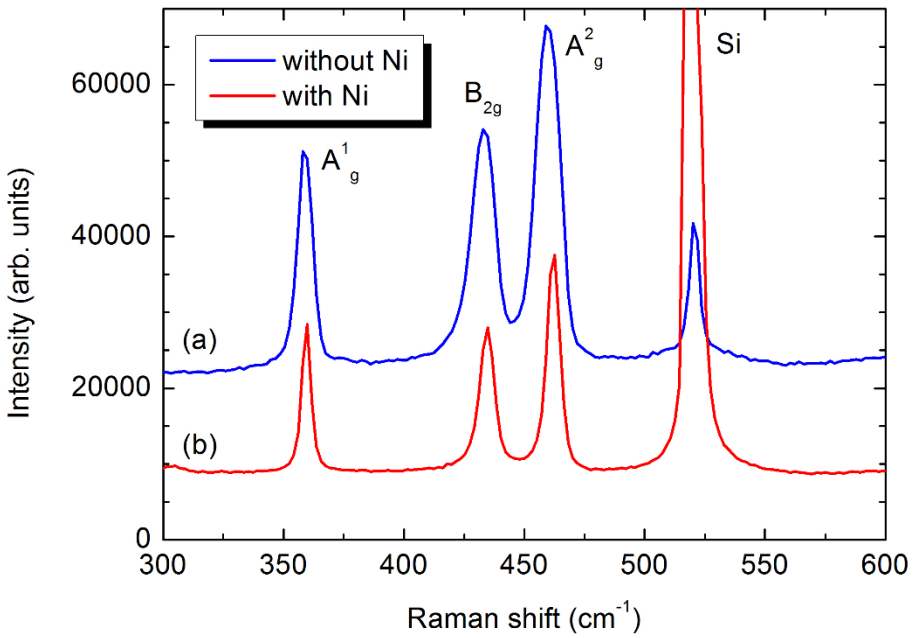
Ni NPs

P: Ni = 3

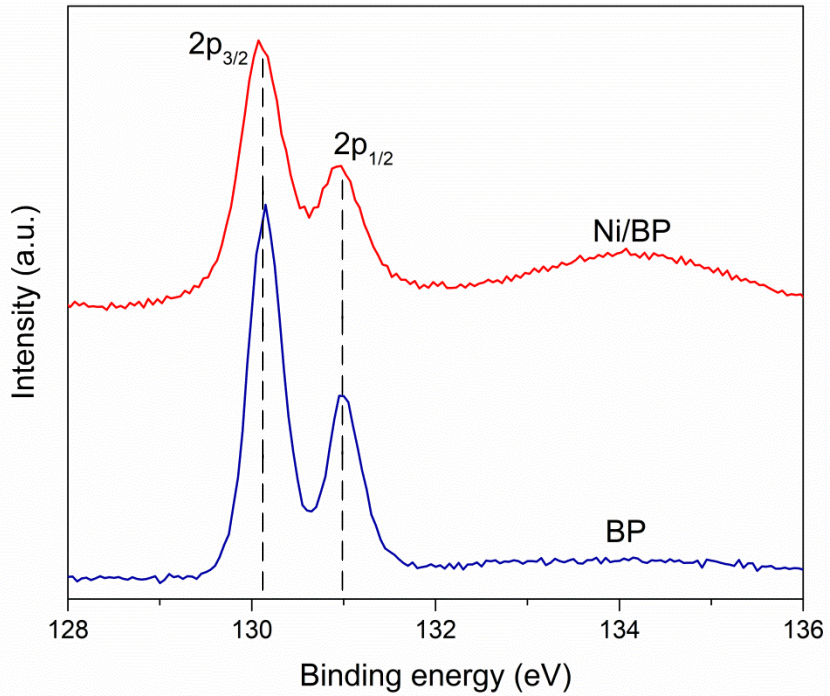


M. Caporali, M. Serrano Ruiz, M. Peruzzini *et al. Chem. Commun*. **2017**, 53, 10946.

Raman



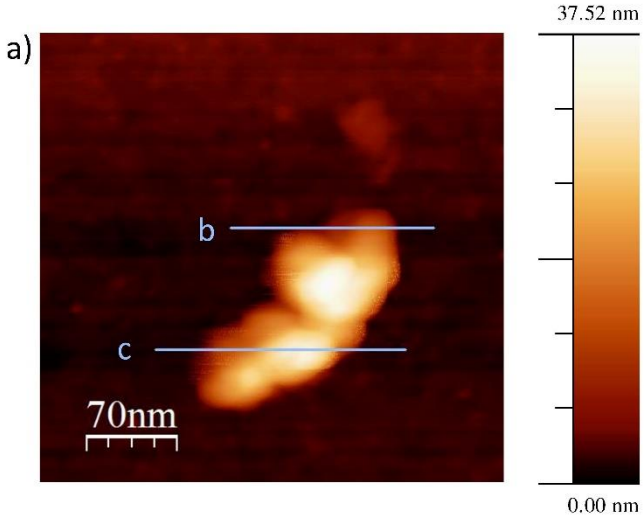
High Resolution XPS

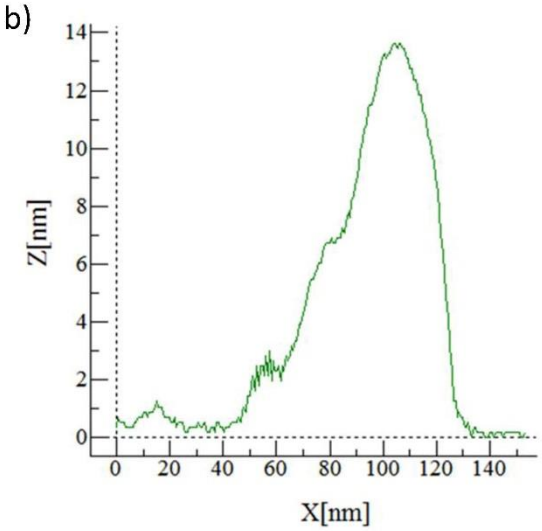


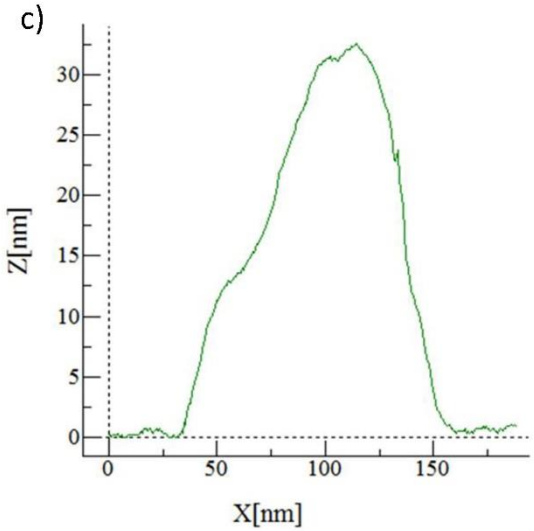
CNRNANO PISA NEST

Elettra Sincrotrone Trieste

Atomic Force Microscopy







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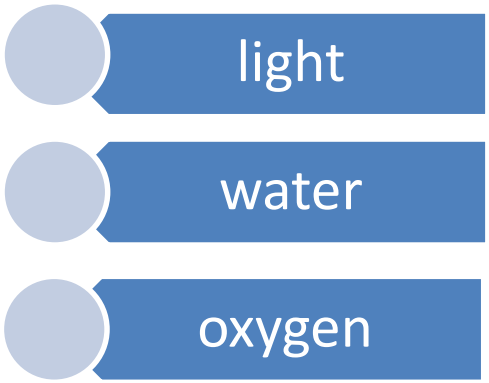
Ambient instability of 2D bP

The degradation is influenced by the following key-factors:



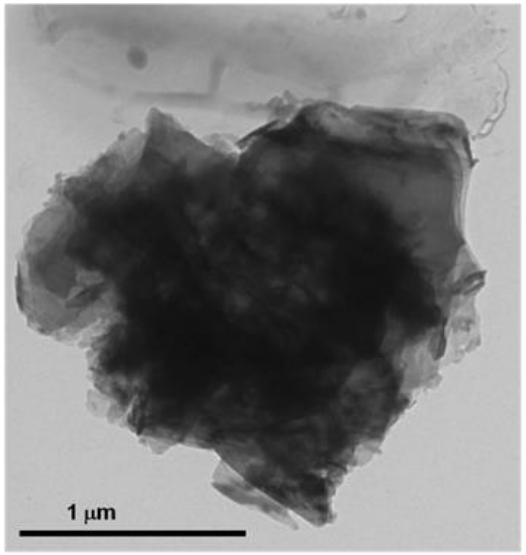
Passivation strategies

The solution to avoid degradation is capping 2D bP to minimize its interaction with the ambient:

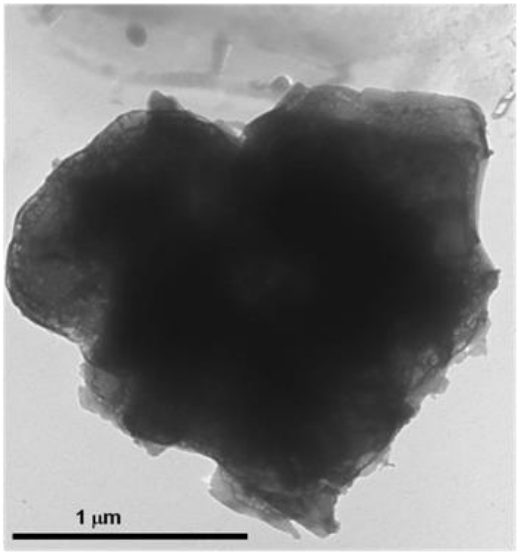
- ✓ passivation with Al_2O_3, SiO_2, PMMA, ionic liquis, $AgNO_{3;}$
- ✓ surface coordination and covalent functionalization;
- ✓ sandwiched 2D bP heterostructures with graphene, *h*-BN.

Ambient degradation of 2D bP

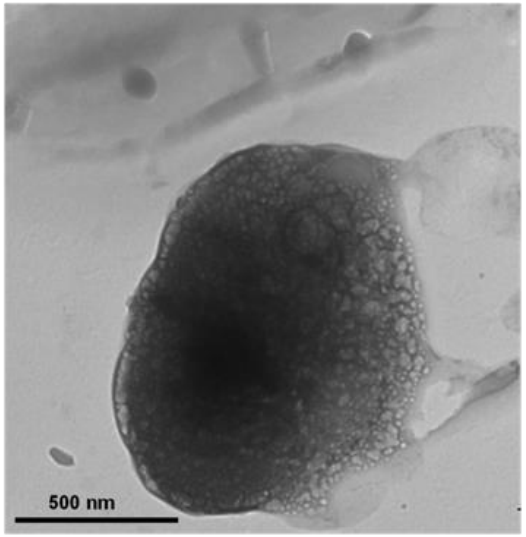
fresh sample



aged 1 week



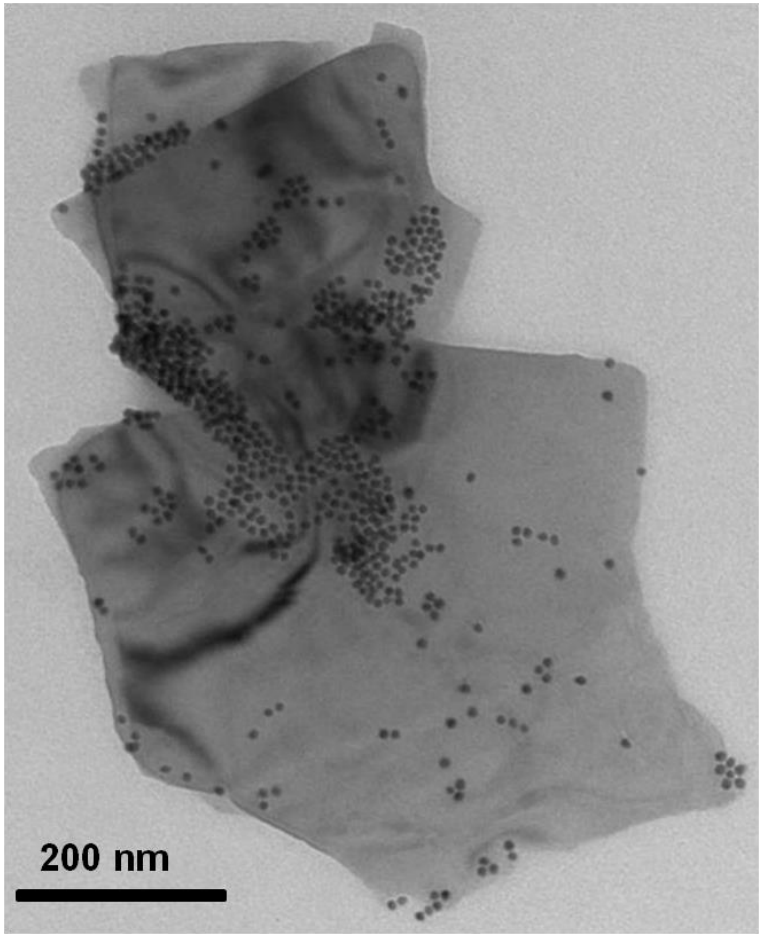
aged 2 weeks

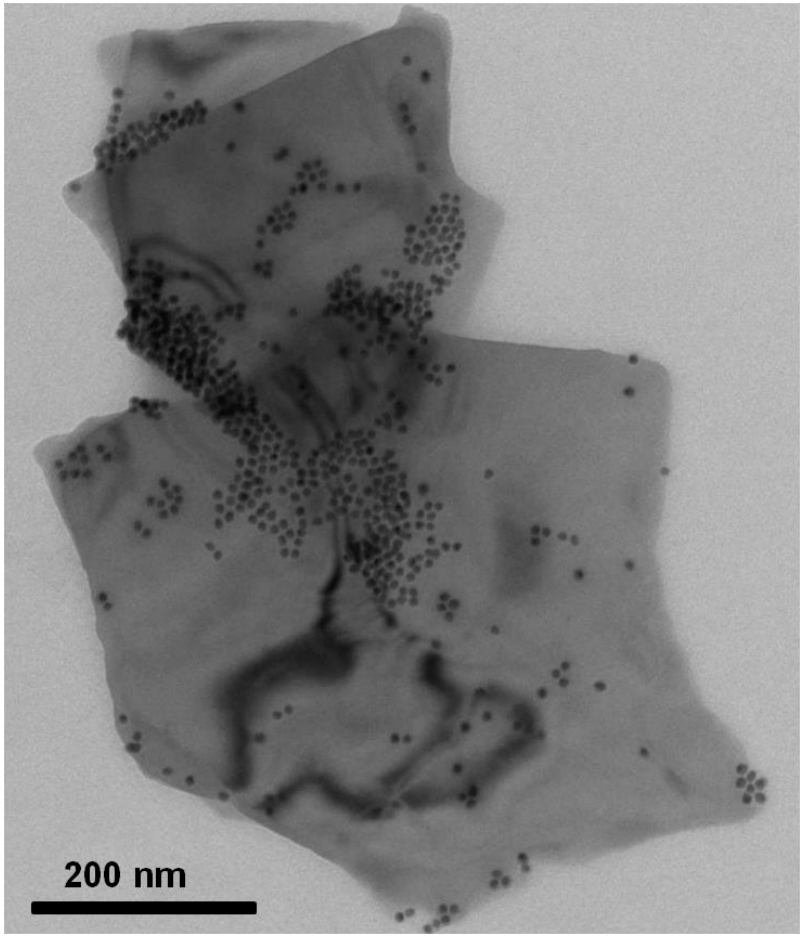


Ambient degradation of Ni/2D bP

fresh sample

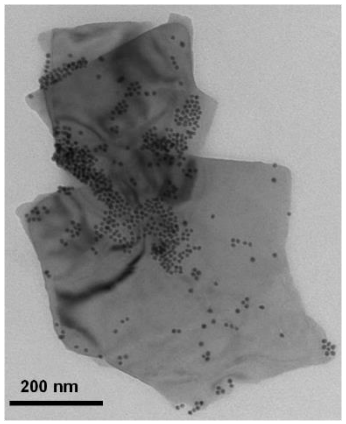
aged 1 week



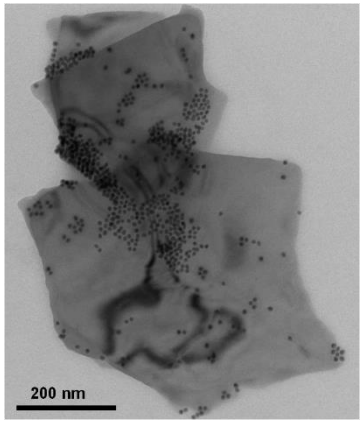


Ambient degradation of Ni/2D bP

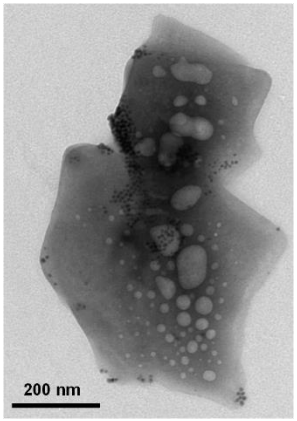
fresh sample



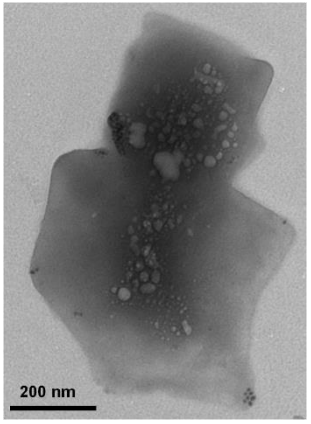
aged 1 week



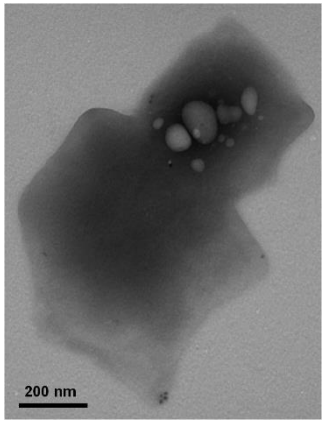
aged 18 days



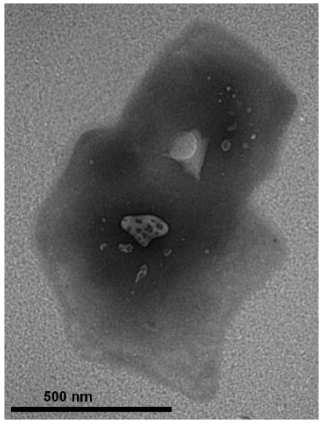
aged 2 months



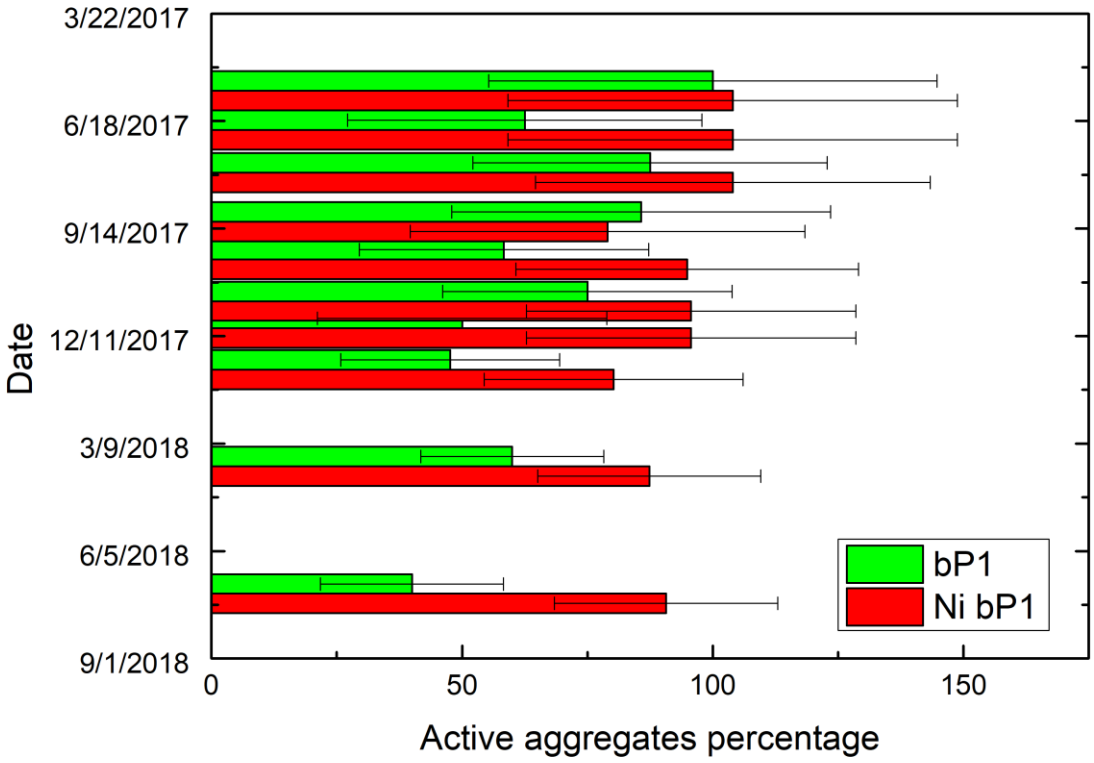
aged 3 months



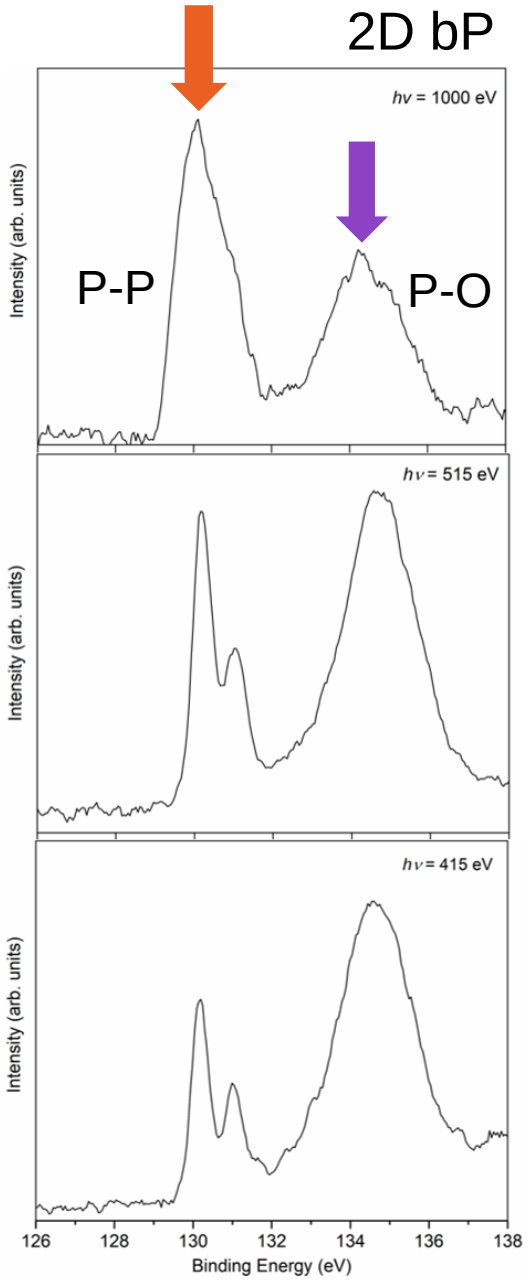
aged 7 months



Raman analysis of aging process



XPS after aging 18 days



Thickness of P-oxide layer, d

$$d = \lambda \ln (I_{oxide} / I_{bP} + 1)$$

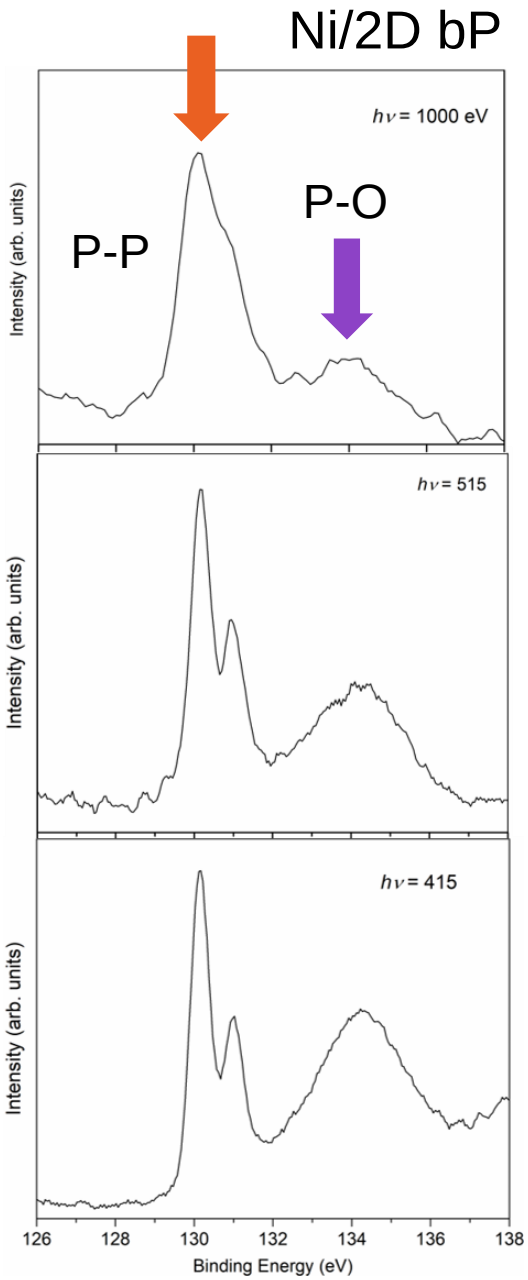
λ = electron mean free path

I_{oxide}, I_{bP} = area underneath curve

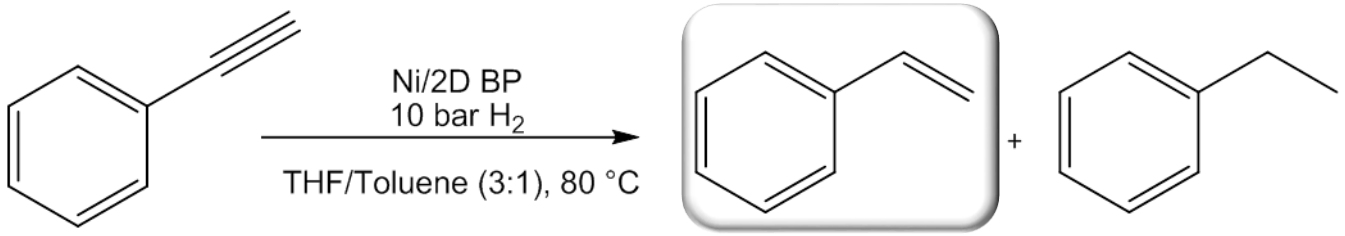
d = 13.9 Å P-oxide in bP

d = 6.2 Å P-oxide in Ni/bP

Elettra Sincrotrone Trieste



Semihydrogenation of phenylacetylene



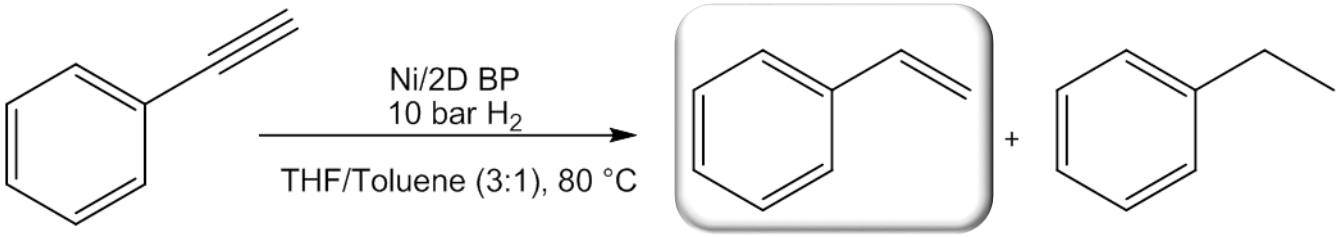
Entry	*Conversion (%)*	*Selectivity to styrene (%)*	*S/cat*	*T (°C)*
Ni NPs	100.0	78.6	56.0	80
2D BP	0.0	-	-	80
Ni/2D BP	93.2	92.8	56.0	80
Ni/Al_2O_3	99.6	0.7[a]	16.5	100
Ni/MgO	98.5	36.0[b]	15.0	50
Ni@C	99.8	59.6[c]	-	100-150

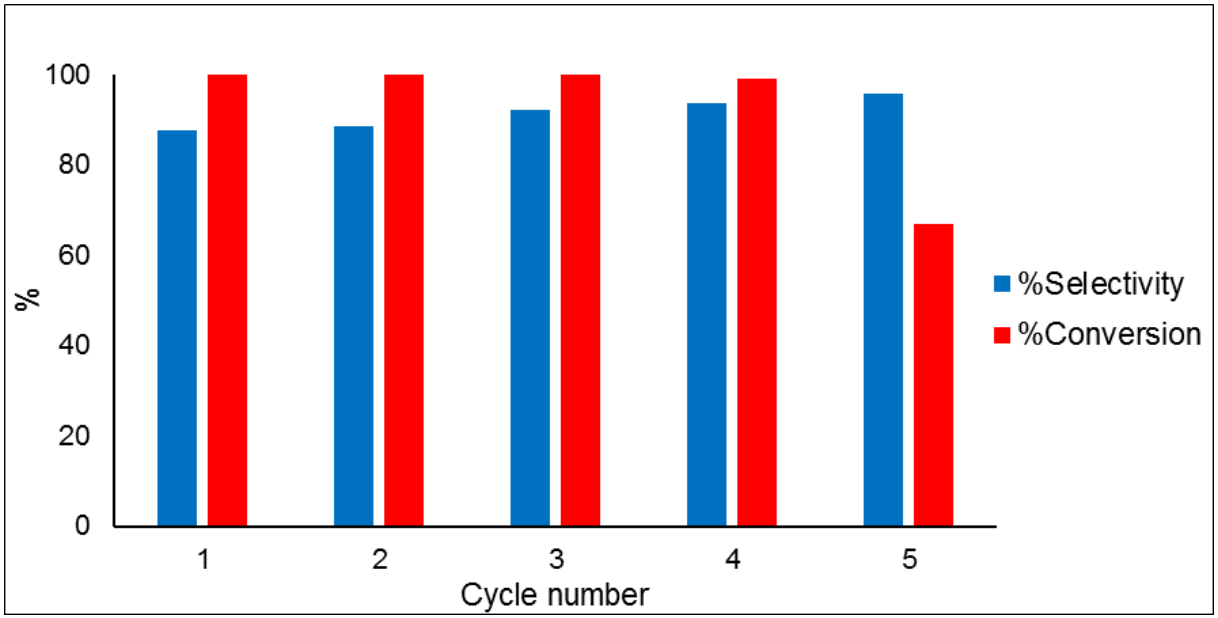
[a] *ACS Catal*. **2015**, *5*, 5756: 2 hours, 3 bar H_2

[b] *Chem. Cat. Chem*. **2014**, 6, 824: 5 bar H_2, 2 h

[C] *Carbon* **2014**, 74, 291: flow bed reactor.

Recycling Ni/2D BP

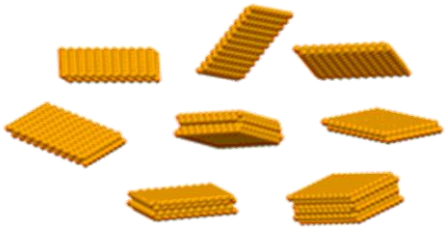




ICP-AES: no leaching of nickel

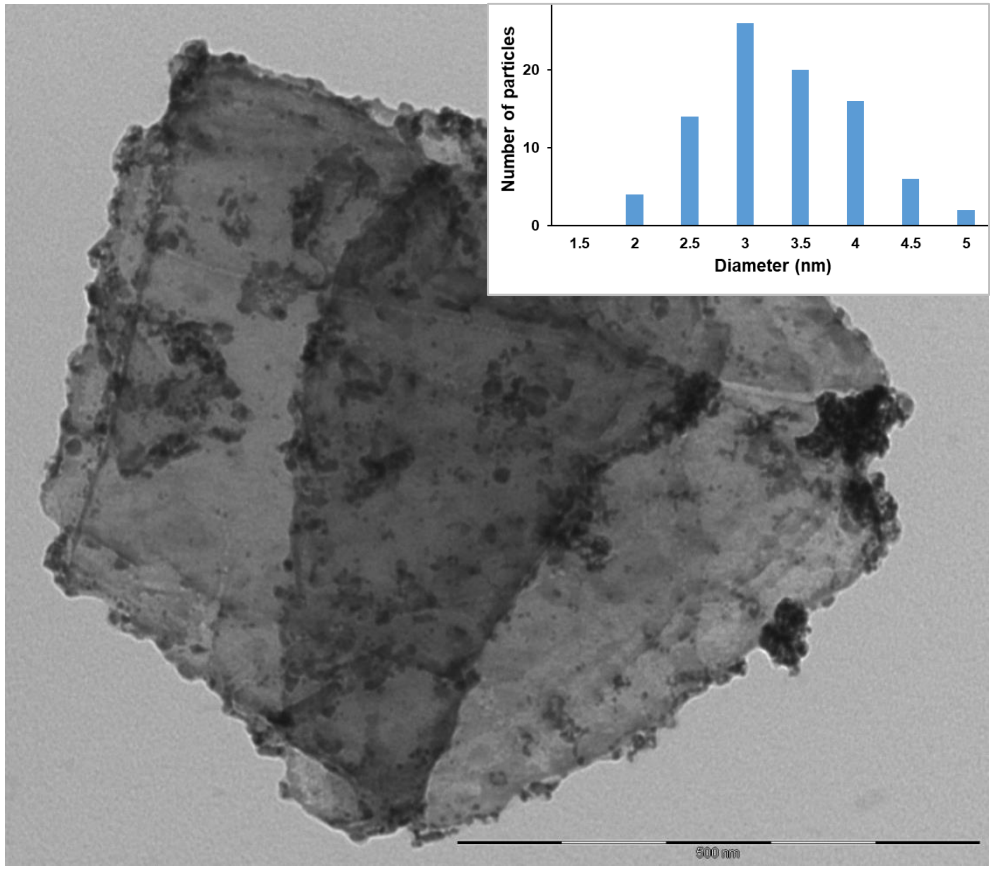
In-situ growth of Pd NPs on 2D bP

- Reducing agent: H_2

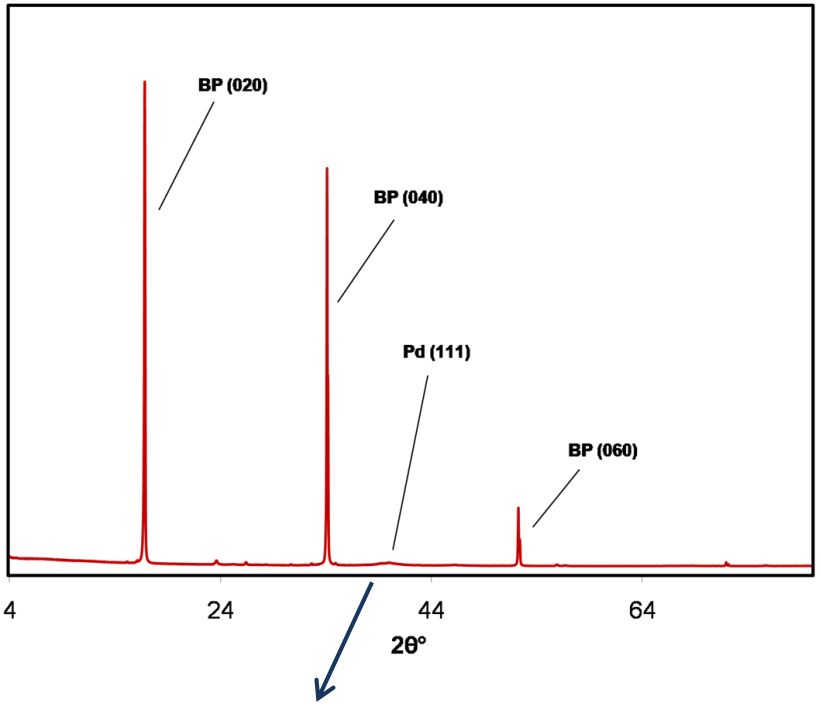


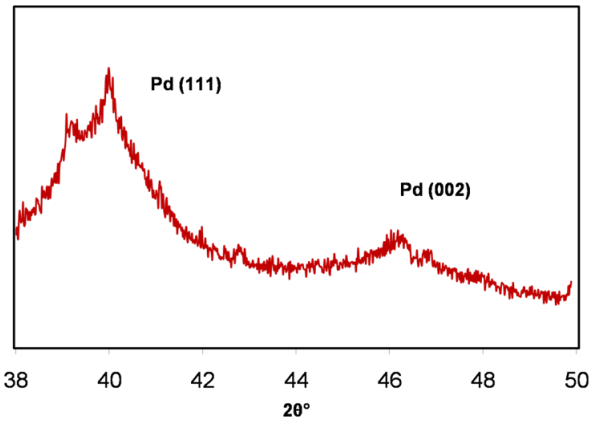
$Pd(NO_3)_2$, H_2O/THF

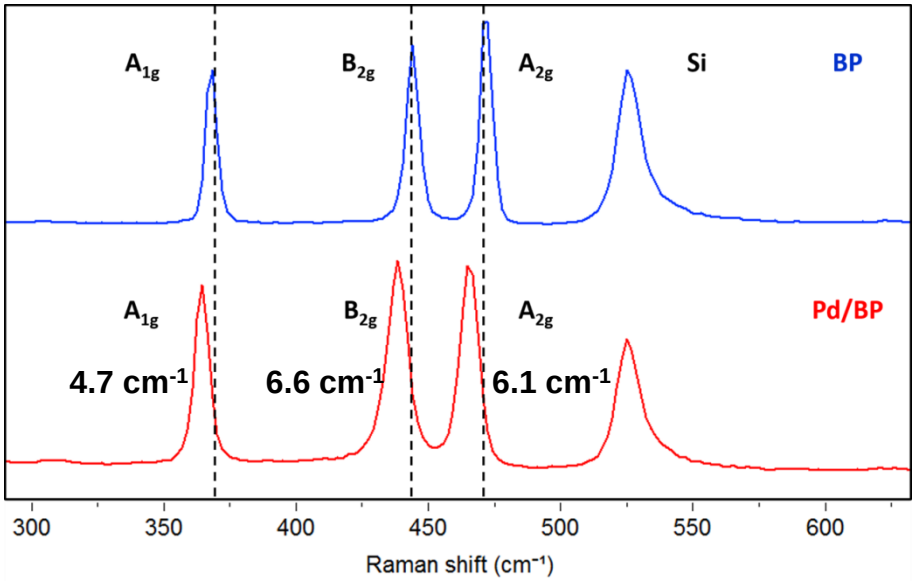
5 bar H_2, RT, 45 min



PXRD and Raman of Pd/2D bP

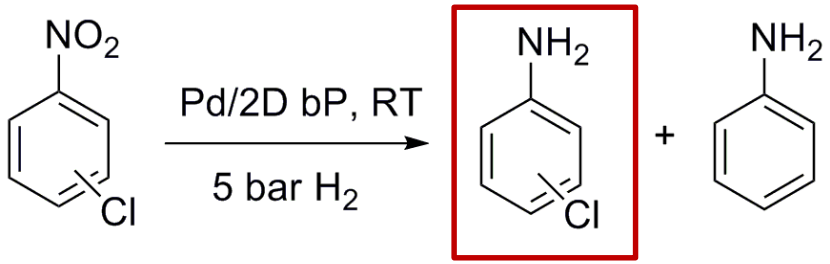






Chem. Mater. **2017**, *29*, 7197;
AIP ADVANCES **2015**, *5*, 057133.

Selective reduction of nitroarenes to anilines

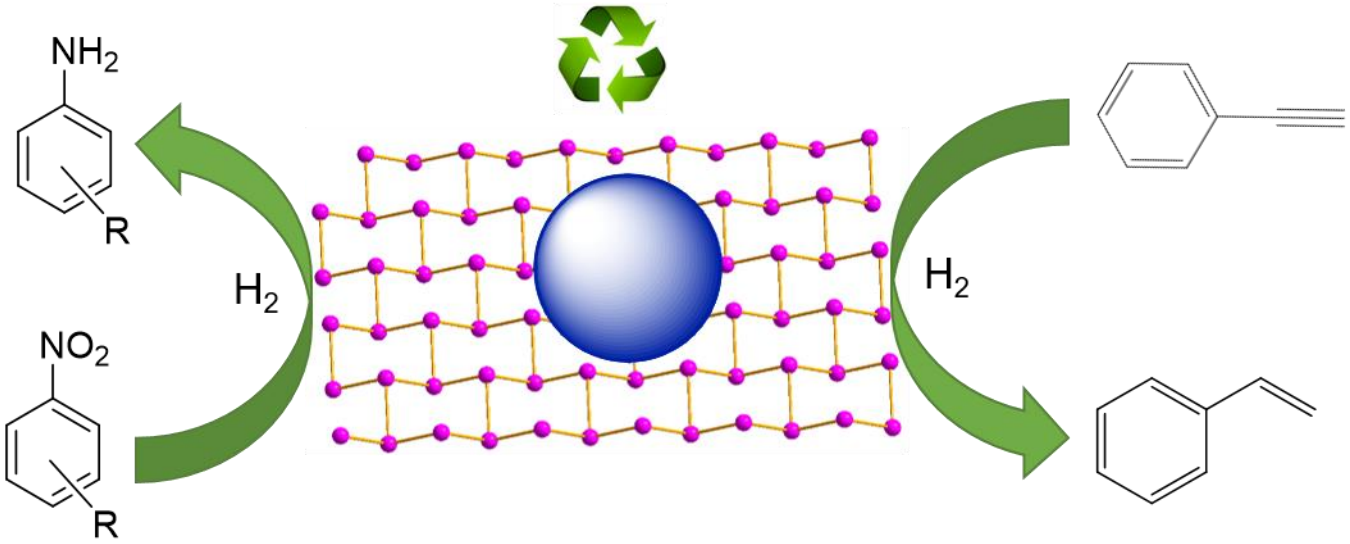


Catalyst	Substrate	Conversion (%)	Selectivity (%)
Pd/Zr-phosphonate*	1-chloro-3-nitrobenzene	99.7	84.0
Pd/C (ketjen black)	1-chloro-3-nitrobenzene	100.0	64.0
Pd/bP	1-chloro-3-nitrobenzene	98.0	**99.0**
Pd/bP	1-chloro-2-nitrobenzene	99.5	**97.3**
Pd/bP	4-nitrobenzaldehyde	99.5	**100.0**
Pd/bP	1-fluoro-3-nitrobenzene	99.9	**100.0**

ICP-AES: no leaching of palladium

*M. Caporali, F. Liguori *et al. ACS Appl. Nano Mater*. **2018**, *1*, 1750-1757.

Summary



- Ni/2D bP catalyzed successfully the semihydrogenation of phenylacetylene and showed high selectivity to styrene.
- An improved ambient stability was observed in presence of Ni NPs.

- Pd NPs were grown onto 2D bP and the resulting catalyst showed remarkable selectivity in the reduction of halo-arenes to halo-anilines.

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2D semiconductors: applications and perspectives

Deadline for abstract:

15 January 2019.