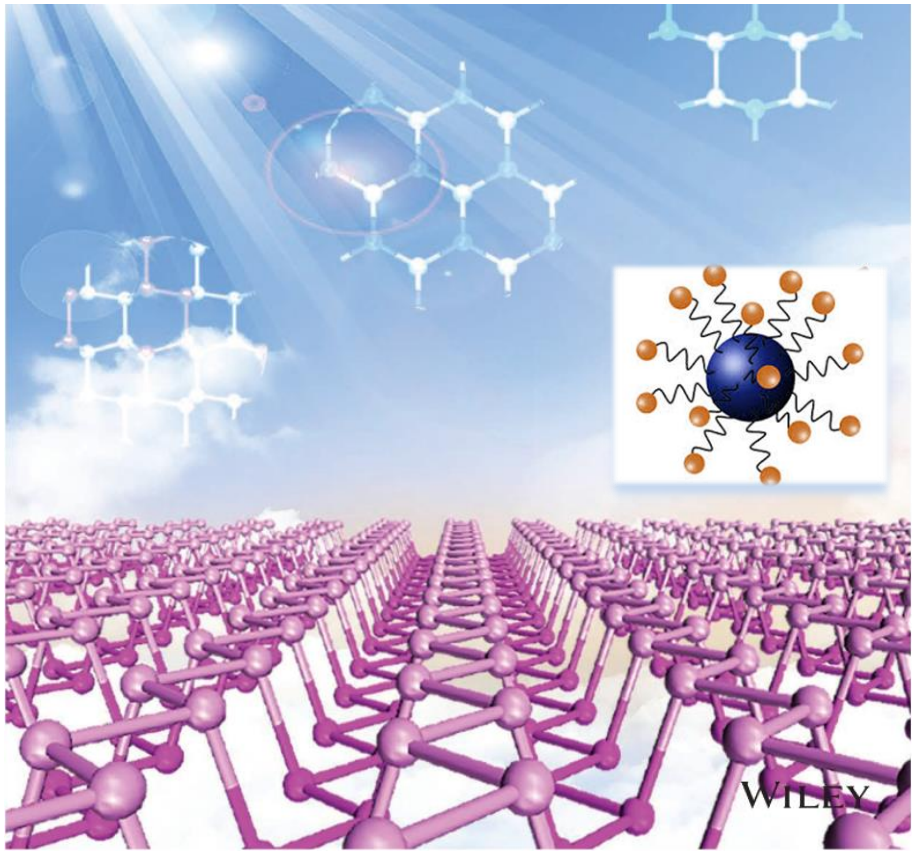
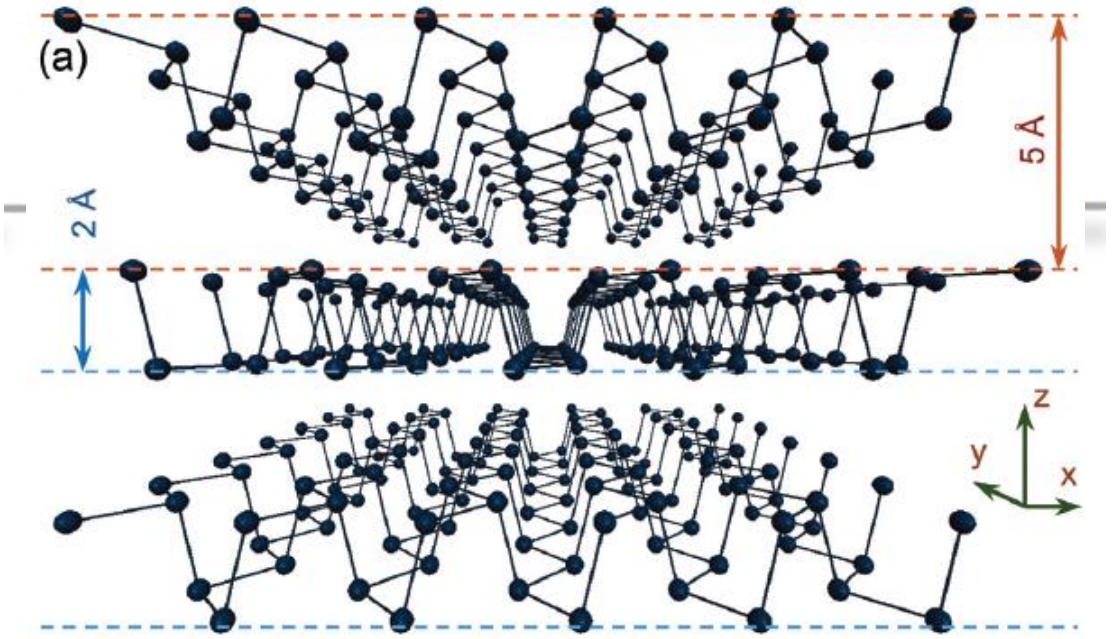
DECORATING FEW-LAYER BLACK PHOSPHORUS WITH NICKEL NANOPARTICLES AND APPLICATION OF THE NANOHYBRID IN CATALYSIS



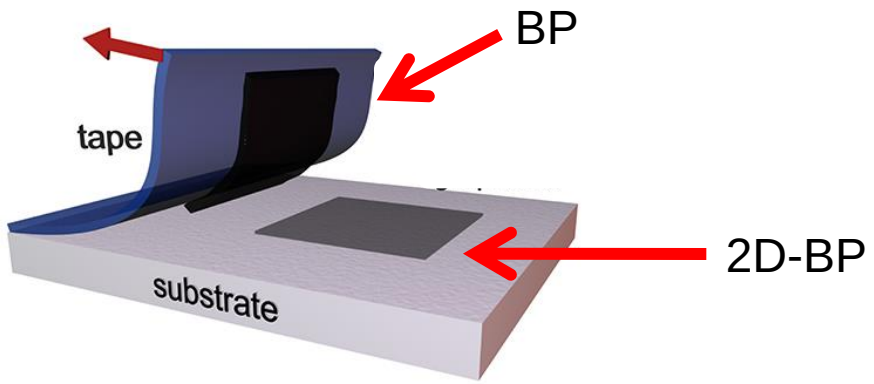
Maria Caporali
CNR ICCOM, Florence (ITALY)

ISTITUTO DI CHIMICA DEI COMPOSTI ORGANOMETALLICI


(a)
5 Å
2 Å
z
y
x

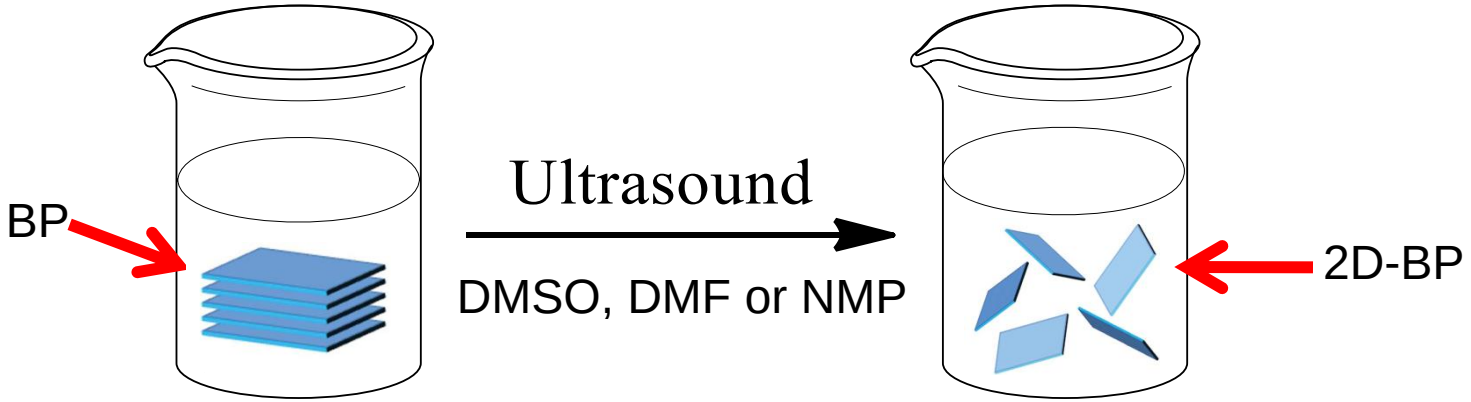
Preparation of few-layer BP

✓ **Mechanical exfoliation**



Ye et al. *ACS Nano* **2014**, *8*, 4033; Zhang, *Nat. Nanotechnol*. **2014**, *9*, 372

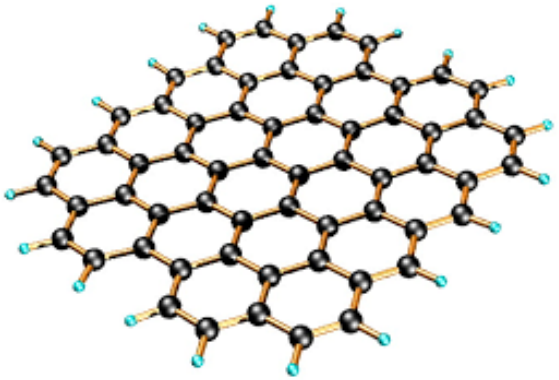
✓ **Liquid phase exfoliation**



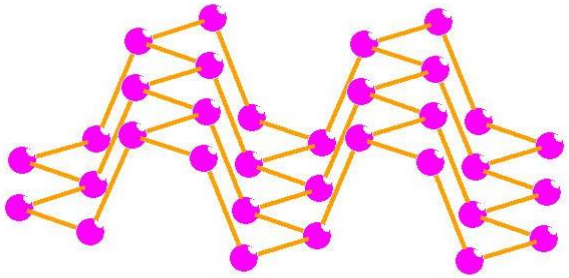
Chem. Commun. **2014**, 50, 13338; *Nano Lett.* **2014**, *14*, 6964; *ACS Nano* **2015**, *9*, 3596; *Adv. Mat*. **2015**, *27*, 1887; *2D Materials,* **2014**,*1*,11002.

2D Materials

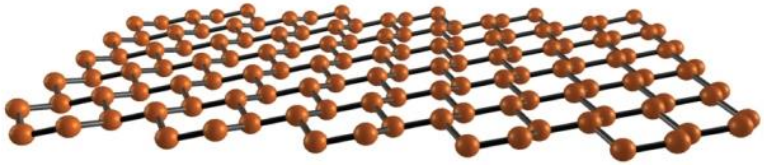
Elemental 2D materials



graphene

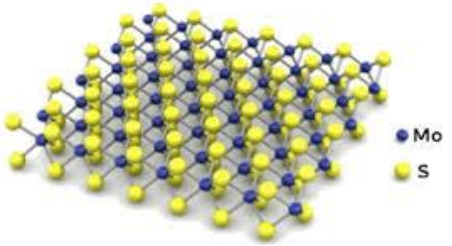


phosphorene

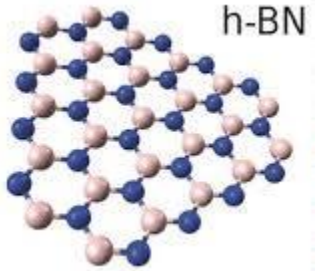


silicene, germanene, stanene

2D Materials composed by two (or more) elements

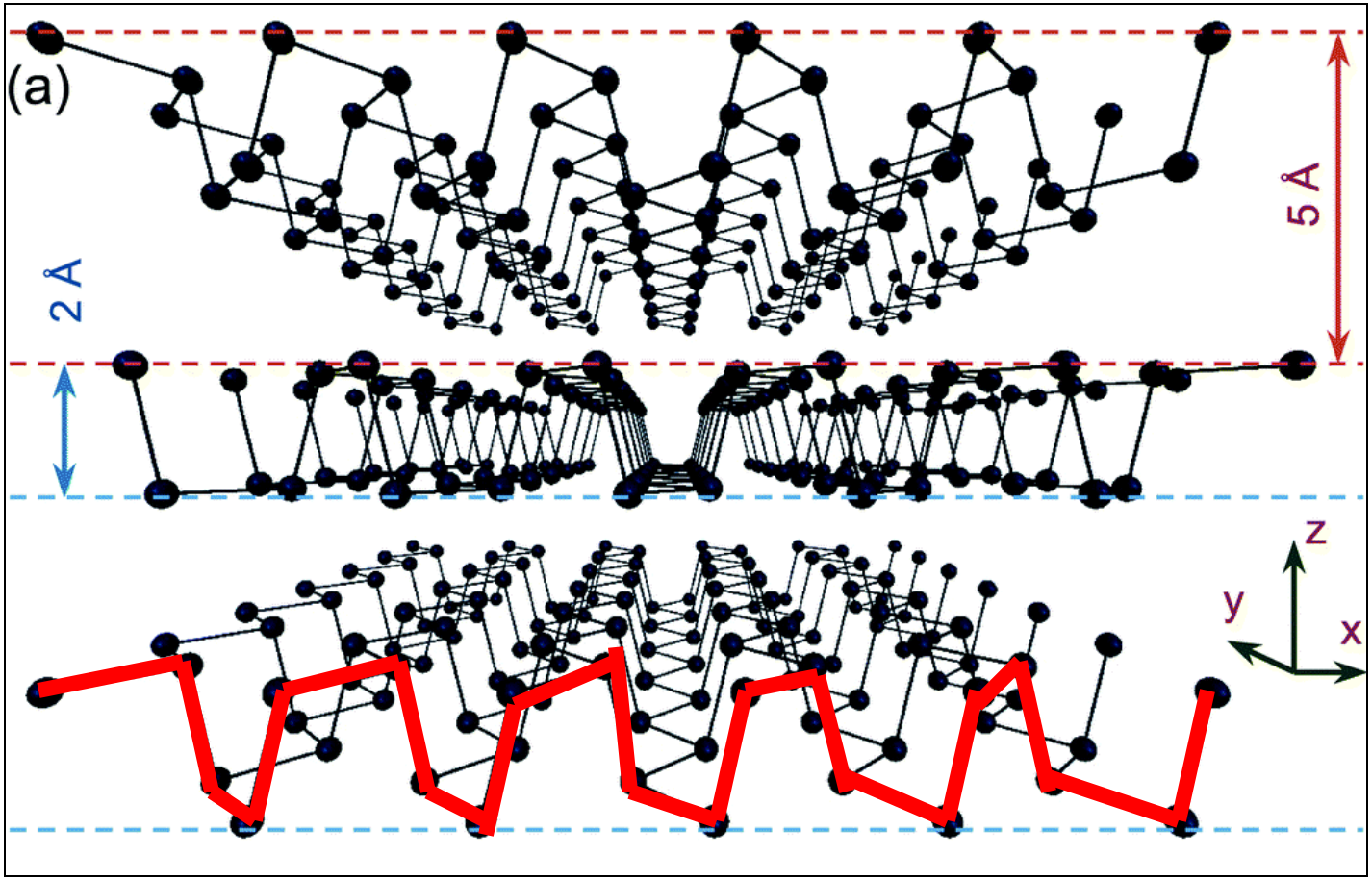


Molybdenum disulfide (MoS_2)



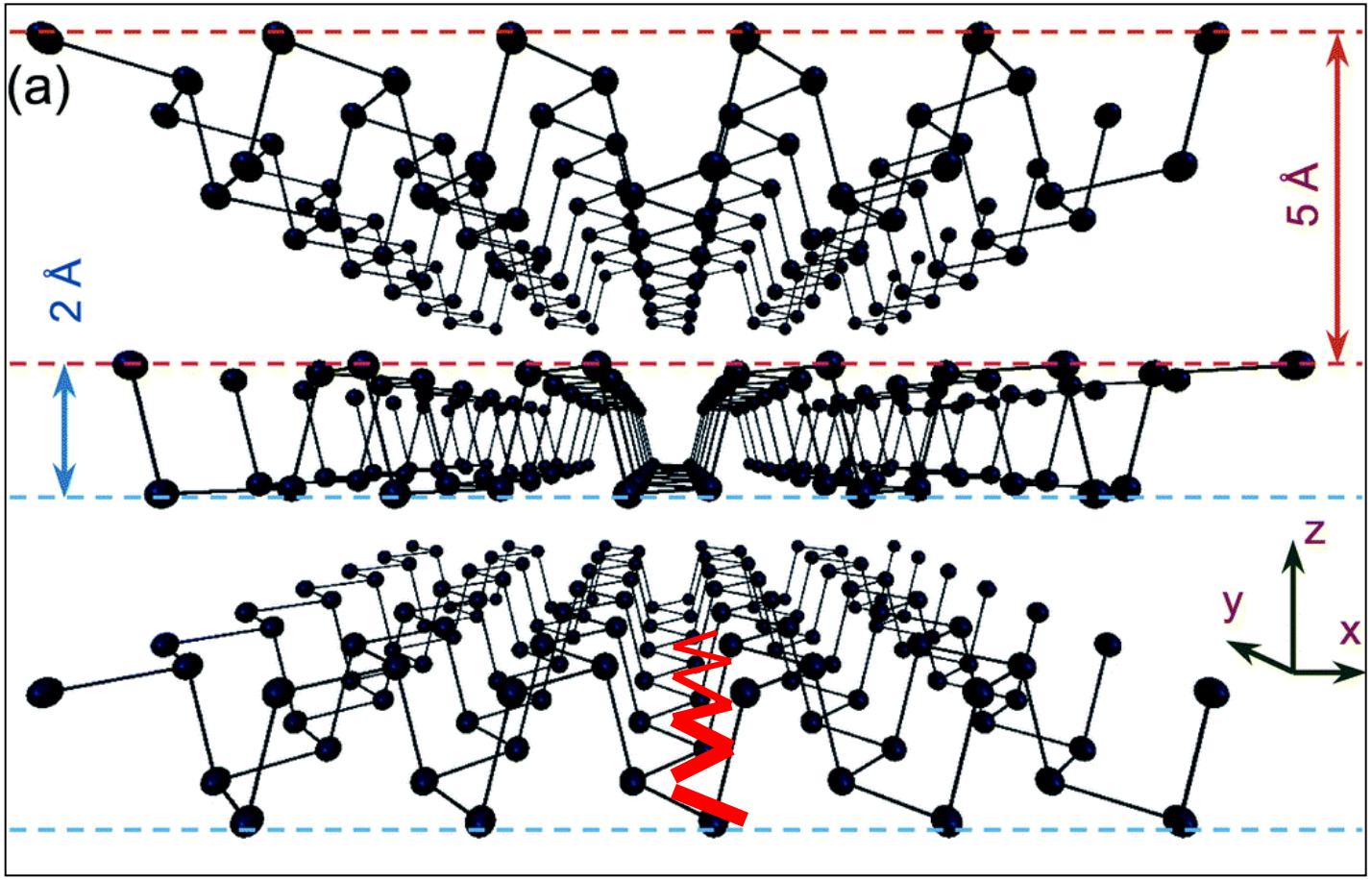
Hexagonal boron nitride (*h*-BN)

Anisotropic structure of black phosphorus



Armchair (x-axis)

Anisotropic structure of black phosphorus



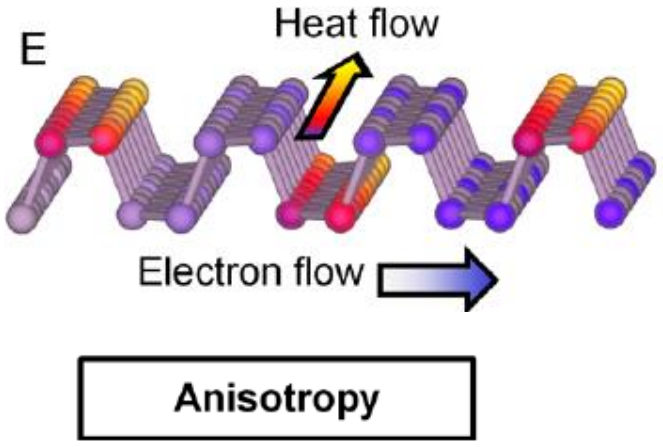
Zig-zag (y-axis)

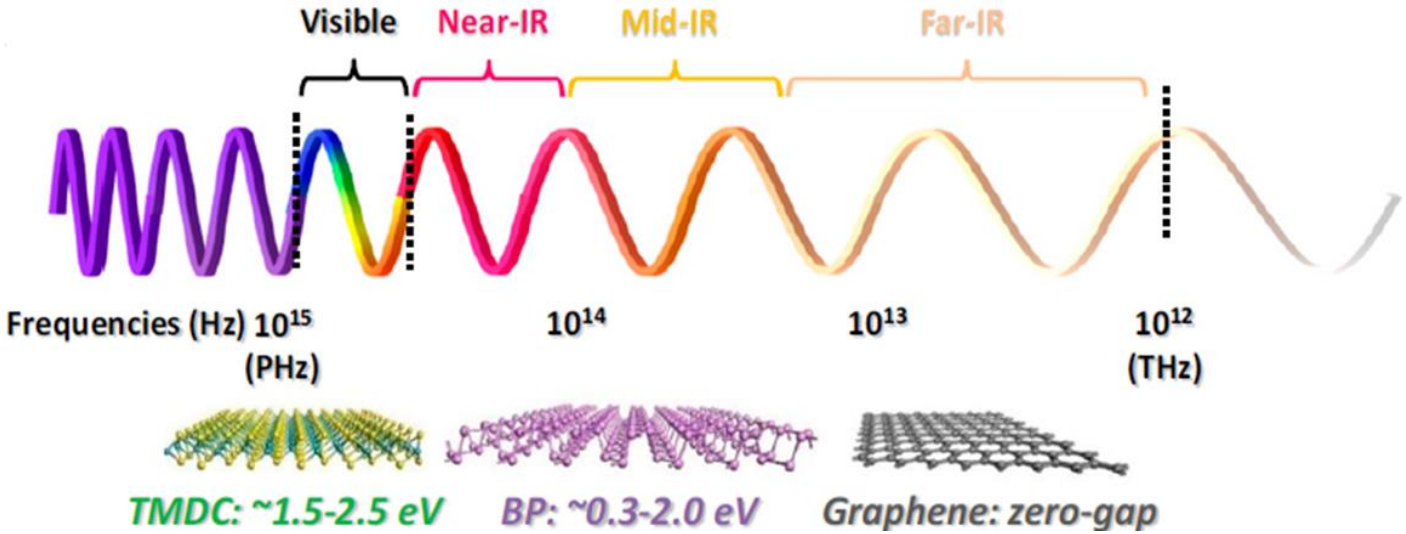
✓ High carrier mobility: 1000 cm^2/Vs

✓ On / off ratio: $10^3 – 10^5$

✓ Thermal conductivity (300 K):

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

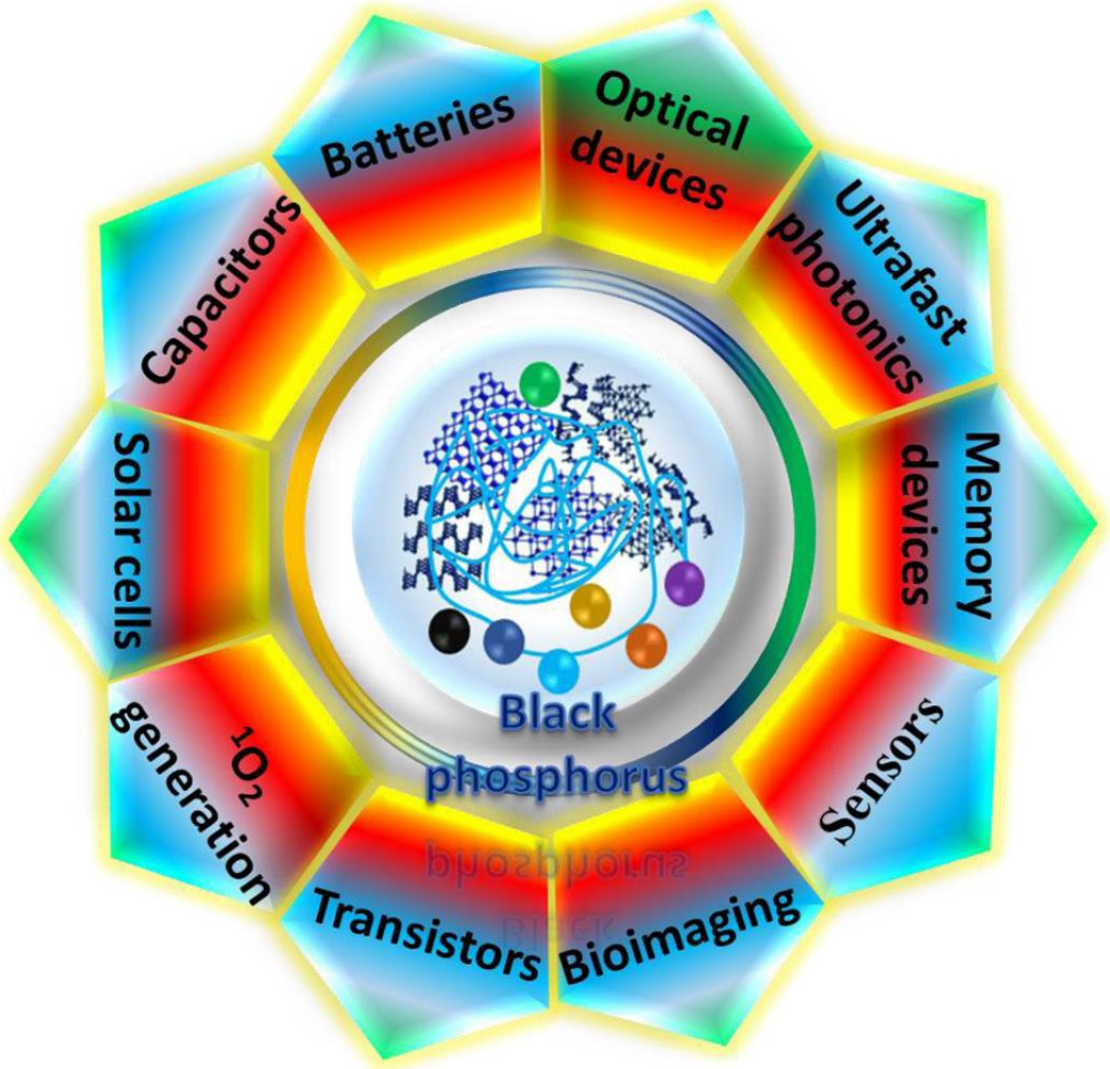




✓ *p*-type semiconductor, with a thickness-depending direct band gap (0.3-2.0 eV)

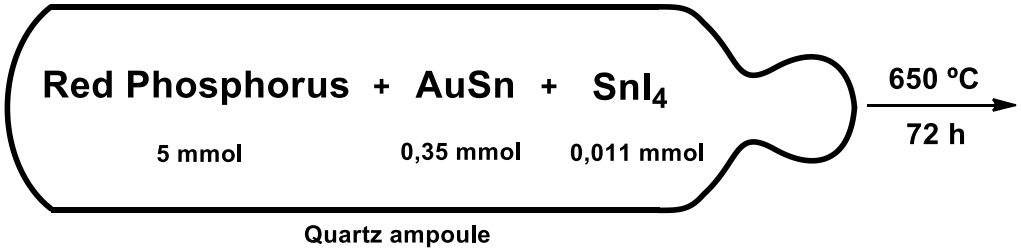
✓ The band gap can be modulated either applying an electrical field or by strain.

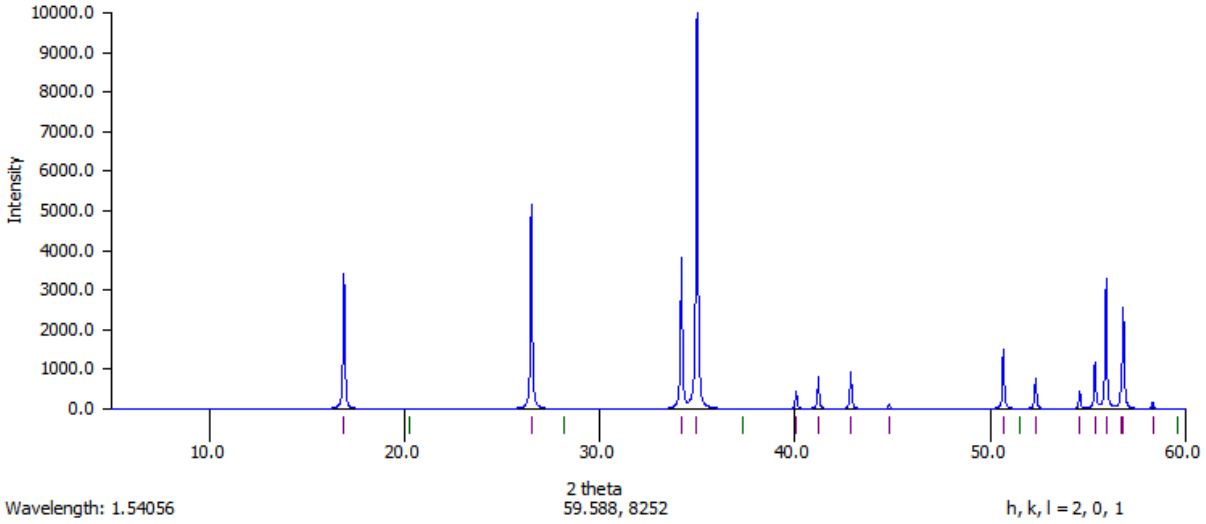
Applications of black phosphorus



FlatChem. **2017**, *2*, 15-37

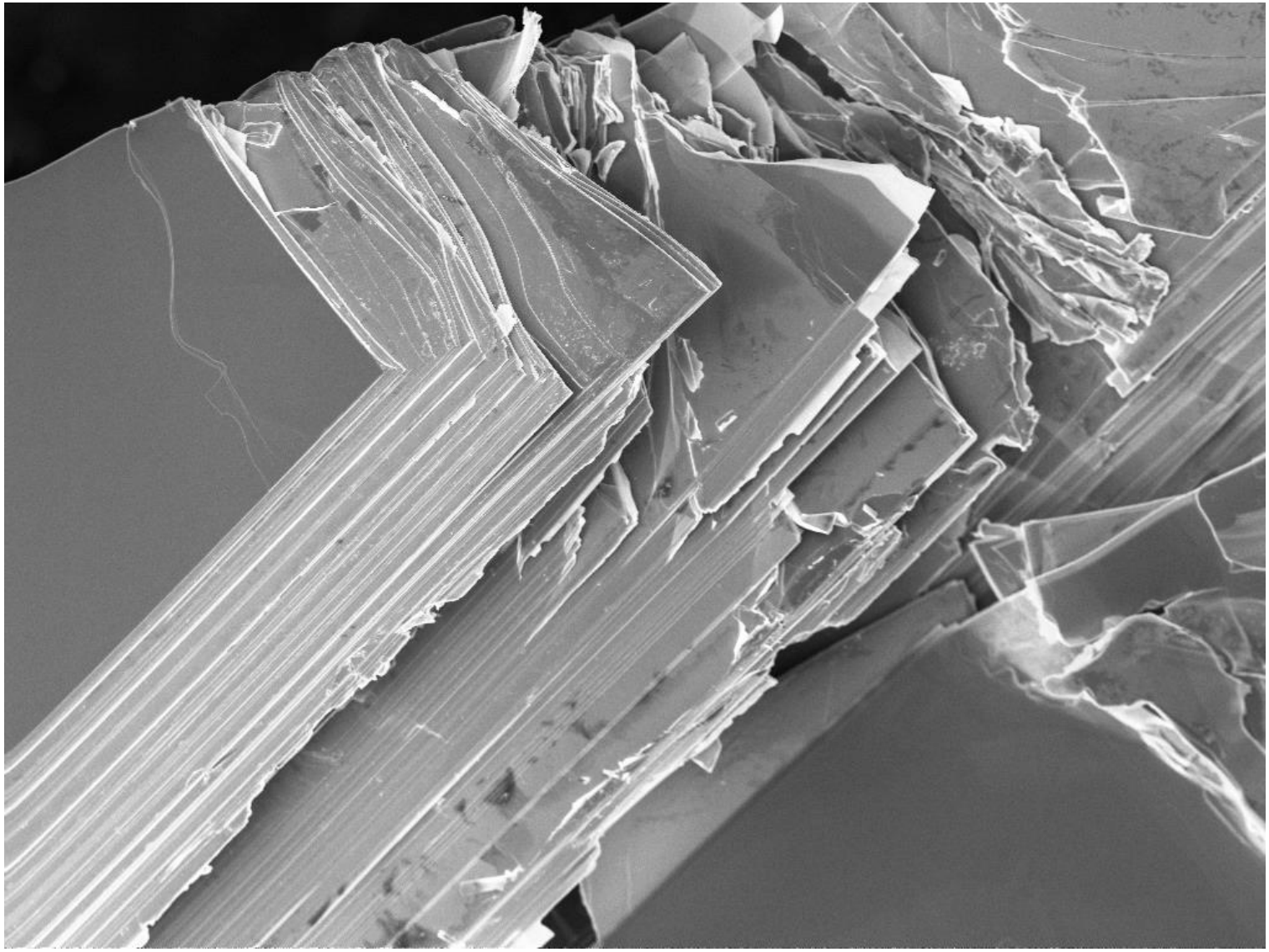
Synthesis of Black Phosphorus



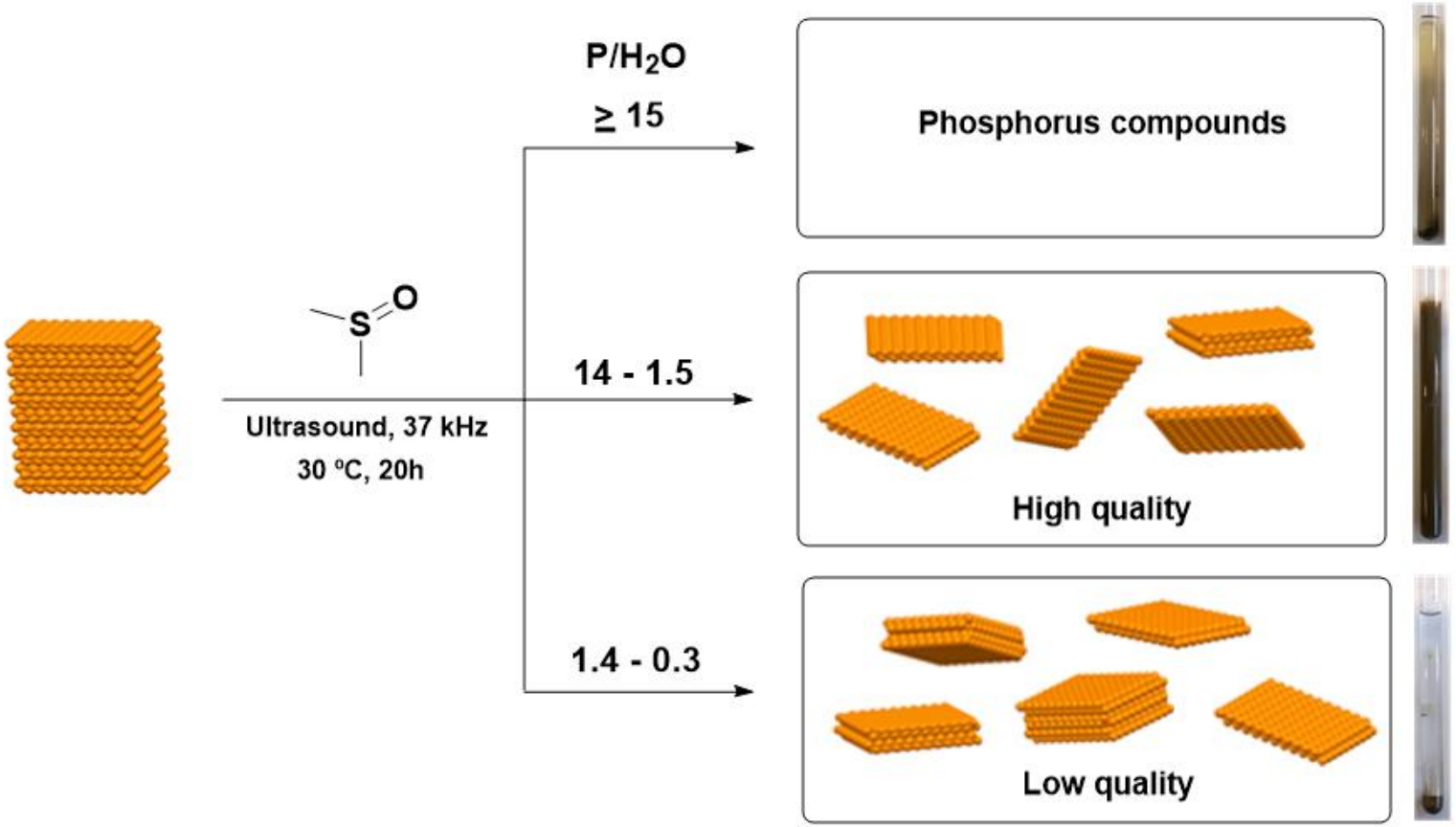


Inorg. Chem. **2007**, *46*, 4028;
J. Solid State Chem. **2008**, *181*, 1707.

Micro-mechanical exfoliation

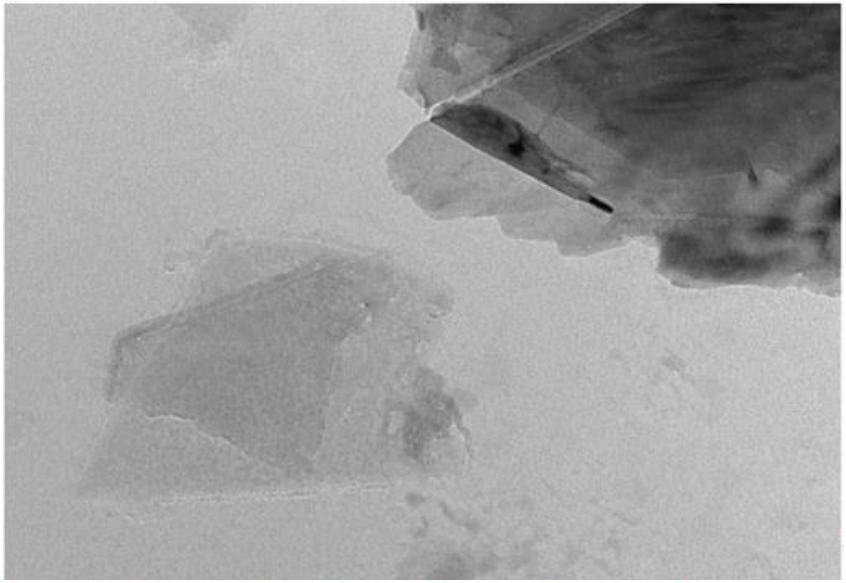


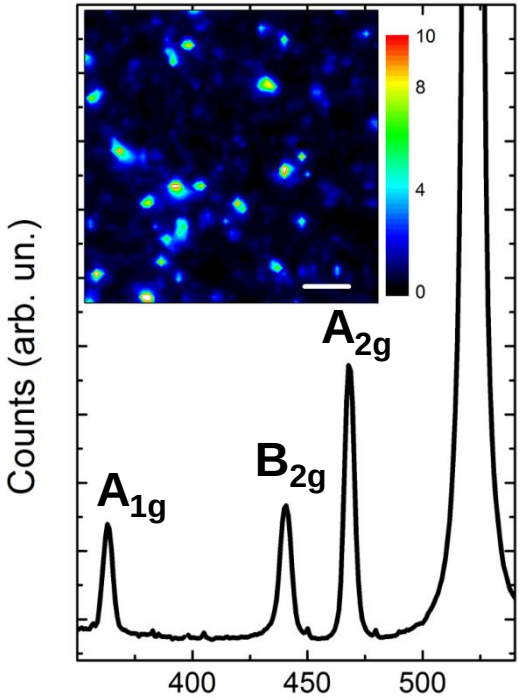
Liquid-phase exfoliation

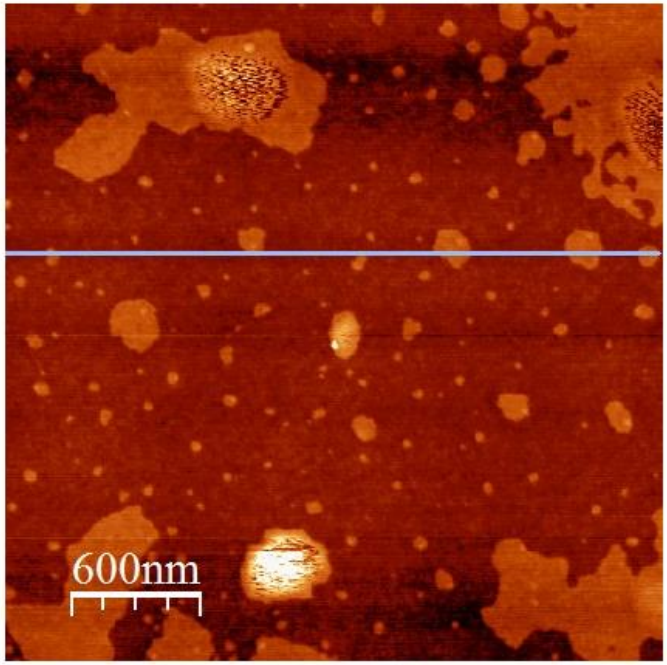


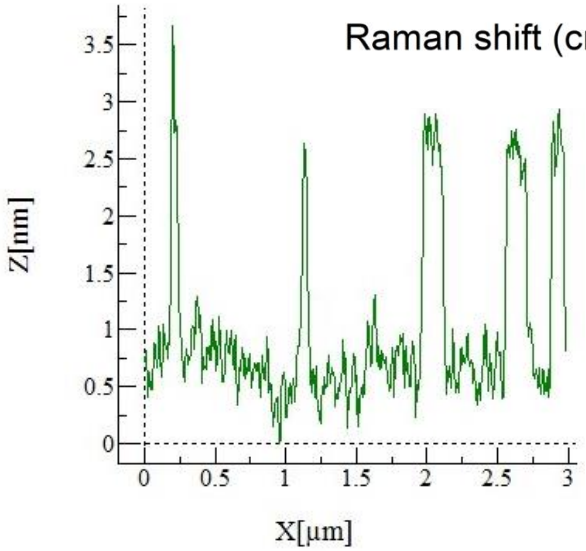
M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv. Mat. Interfaces* **2016**, 3, 1500441.

2D Black Phosphorus: characterization

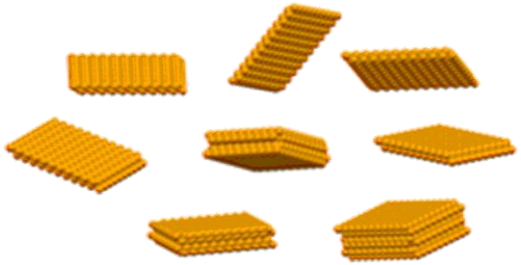








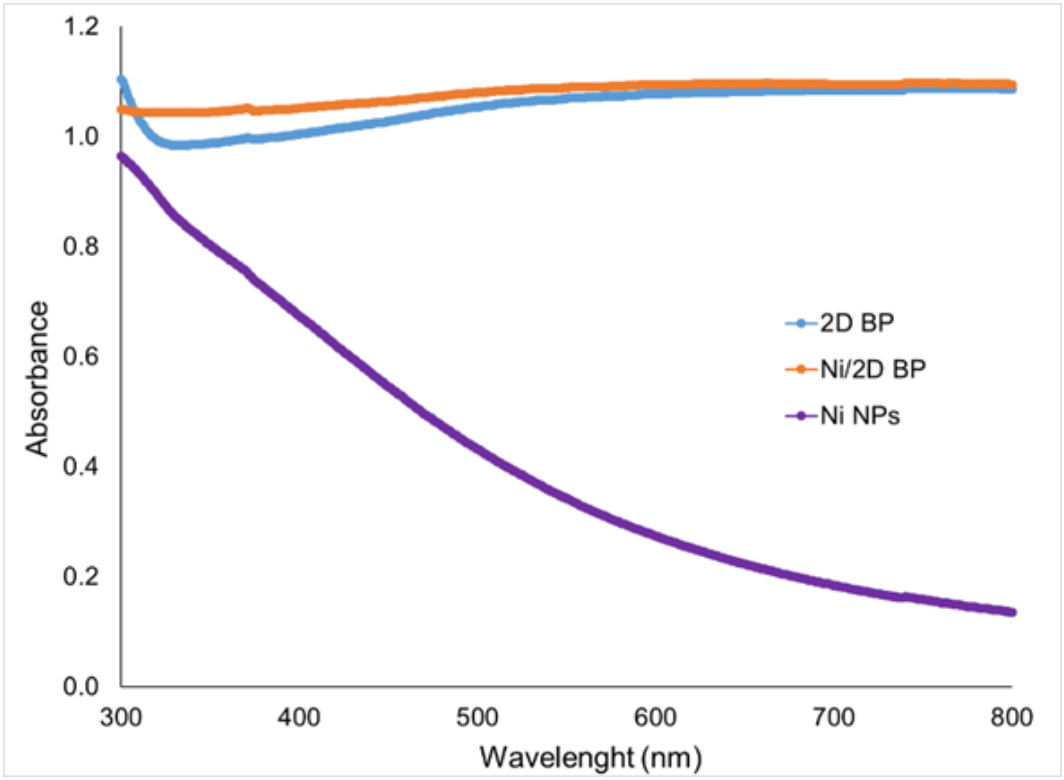
Surface functionalization of 2D black P



Ni NPs in toluene

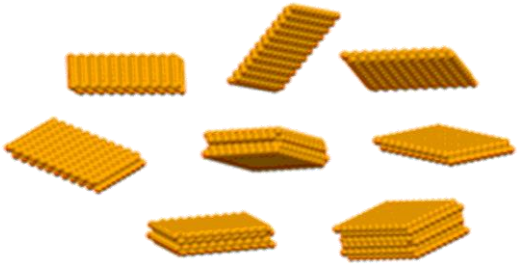
P:Ni = 10, 7, 3

Ni/2D BP



Mezailles *et al. Chem. Mater.* **2010**, *22*, 1340.

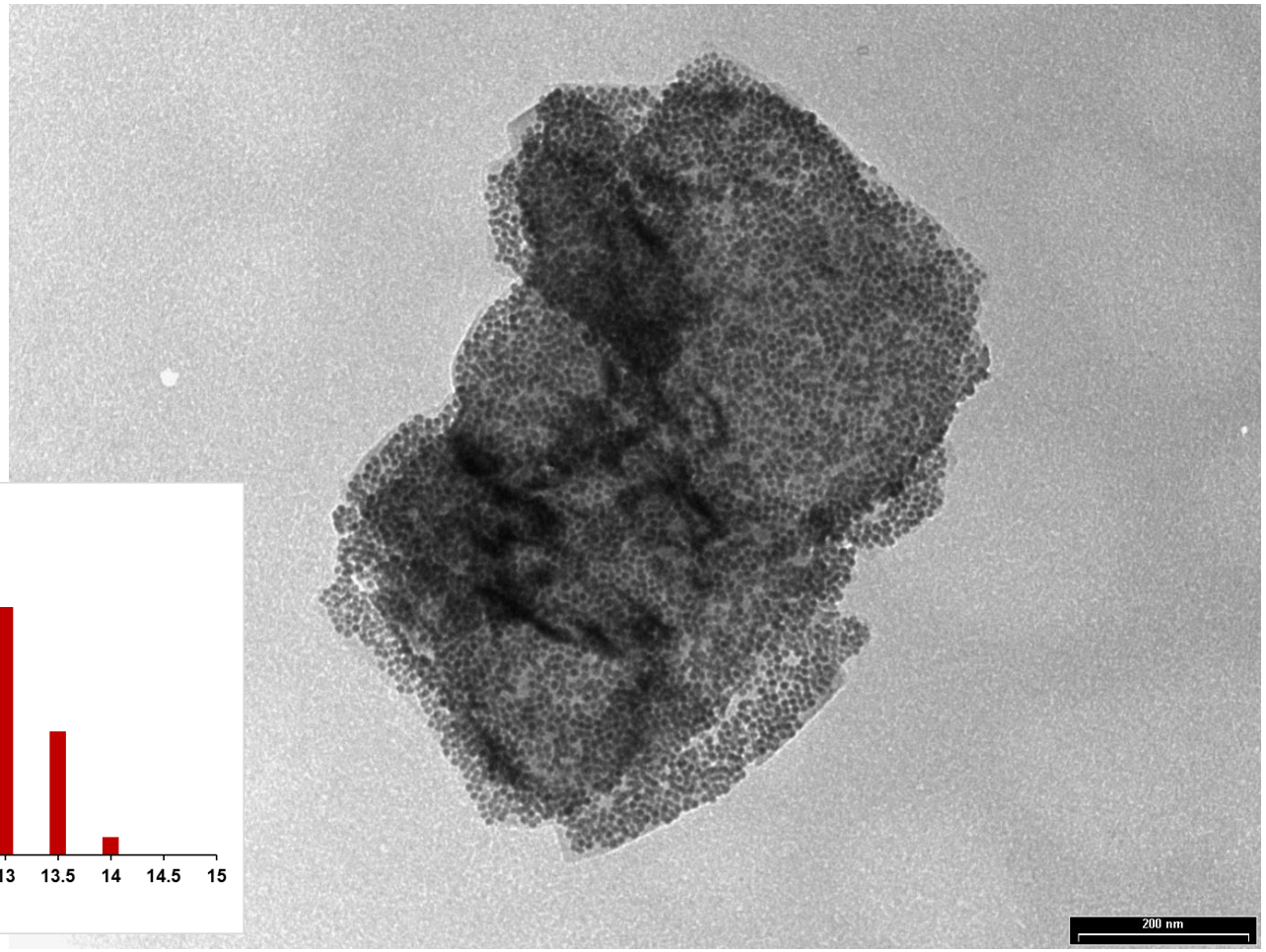
Surface functionalization of 2D black P

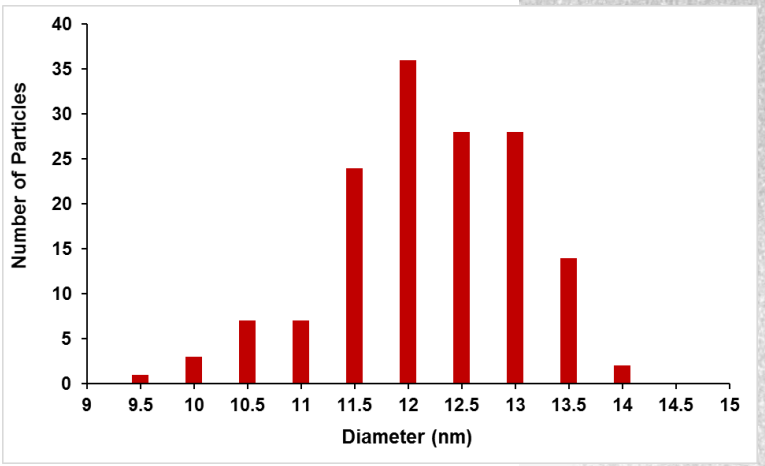


Ni NPs in toluene

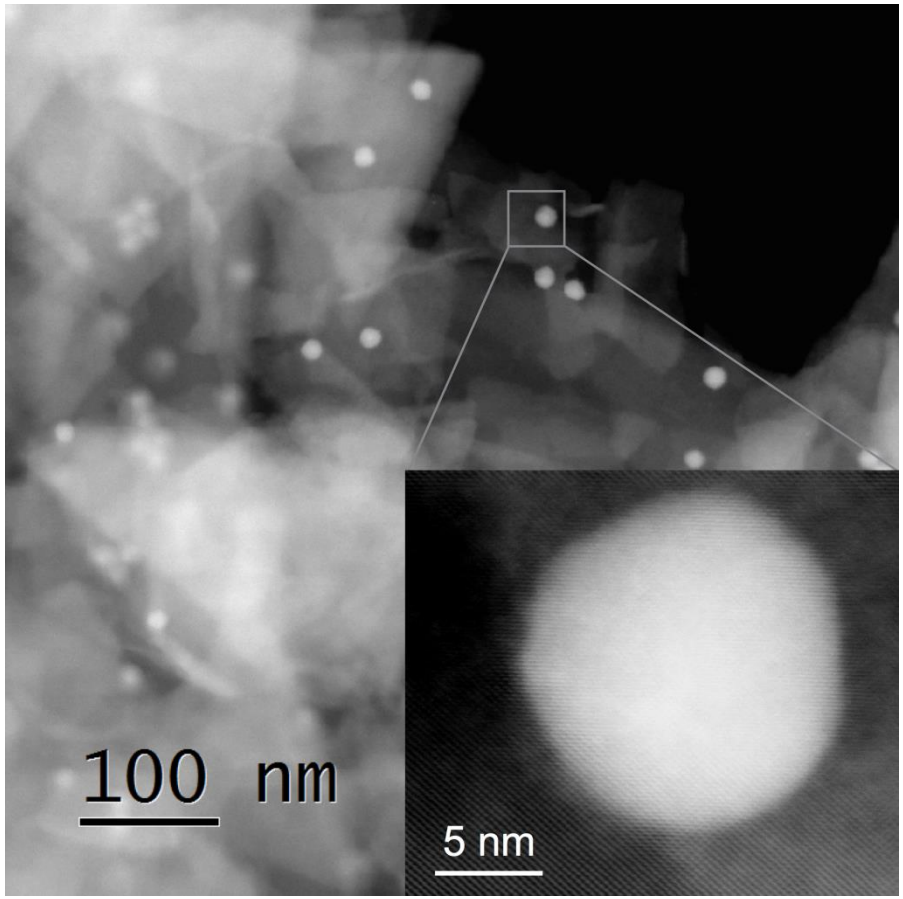
P:Ni = 10, 7, 3

Ni/2D BP





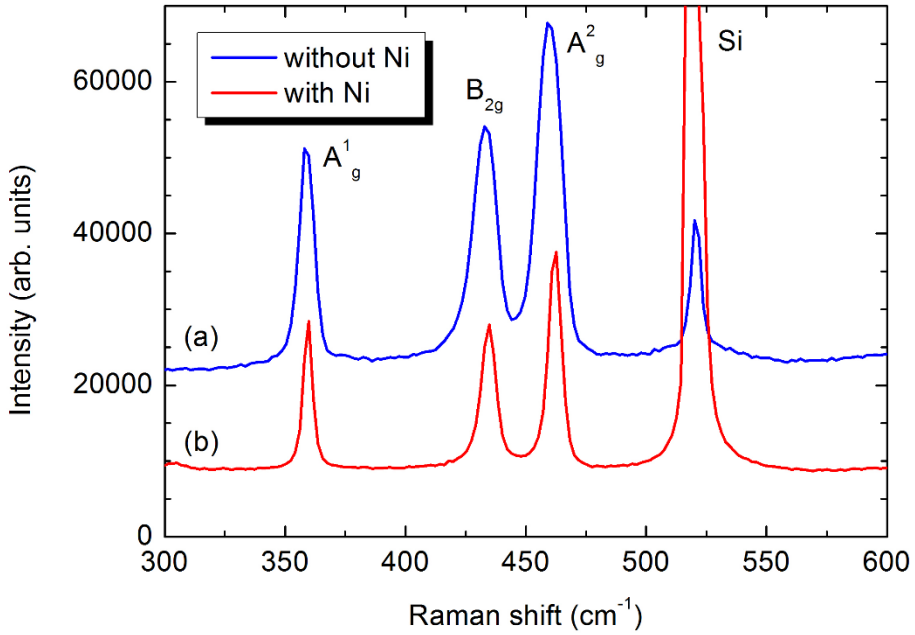
HAADF STEM on Ni/2D BP



STEM-EELS gave chemical information of the surface of the nanohybrid.

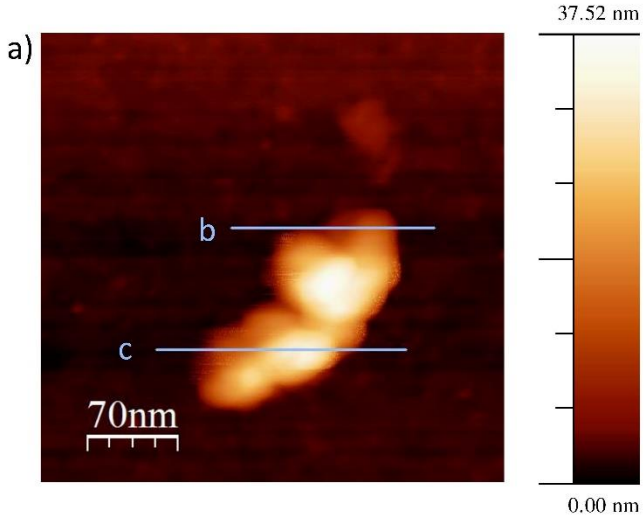
IMM
ISTITUTO PER LA MICROELETTRONICA
E MICROSISTEMI

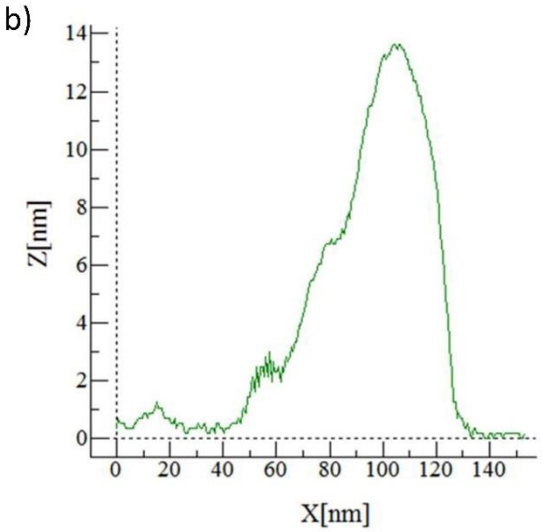
Raman: comparison between pristine 2D BP and Ni/2D BP

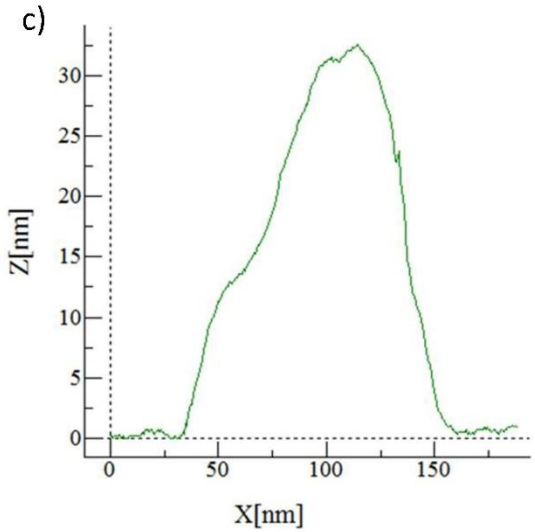


CNRNANO PISA NEST

Atomic Force Microscopy

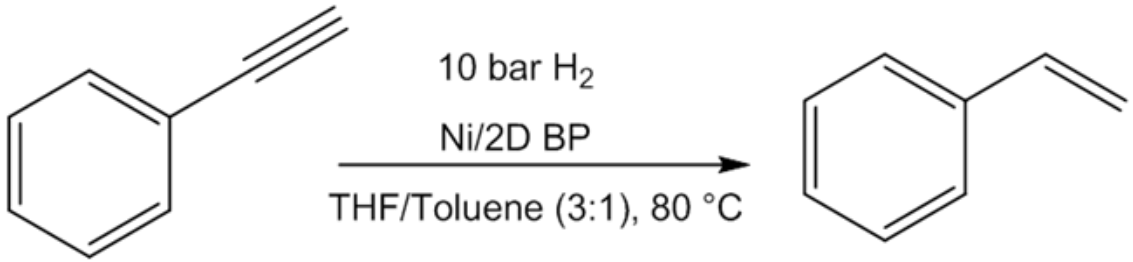






CNRNANO PISA NEST

Semihydrogenation of phenylacetylene



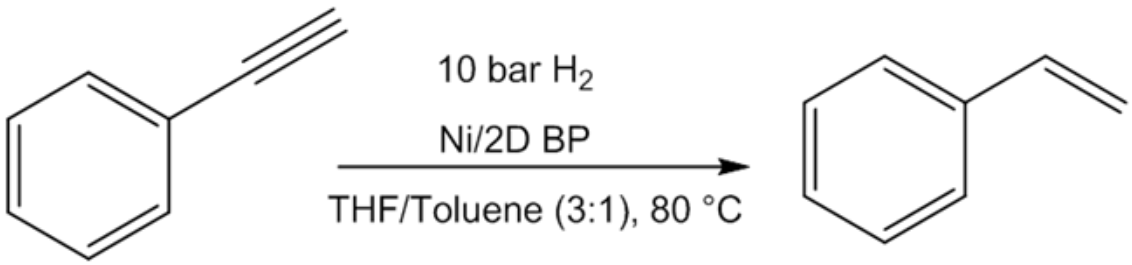
Entry	*Conversion (%)*	*Selectivity to styrene (%)*	*S/cat*	*T (°C)*
Ni NPs	100.0	78.6	56.0	80
2D BP	0.0	-	-	80
Ni/2D BP	93.2	92.8	56.0	80
Ni/Al_2O_3	99.6	0.7[a]	16.5	100
Ni/MgO	98.5	36.0[b]	15.0	50
Ni@C	99.8	59.6[c]	-	100-150

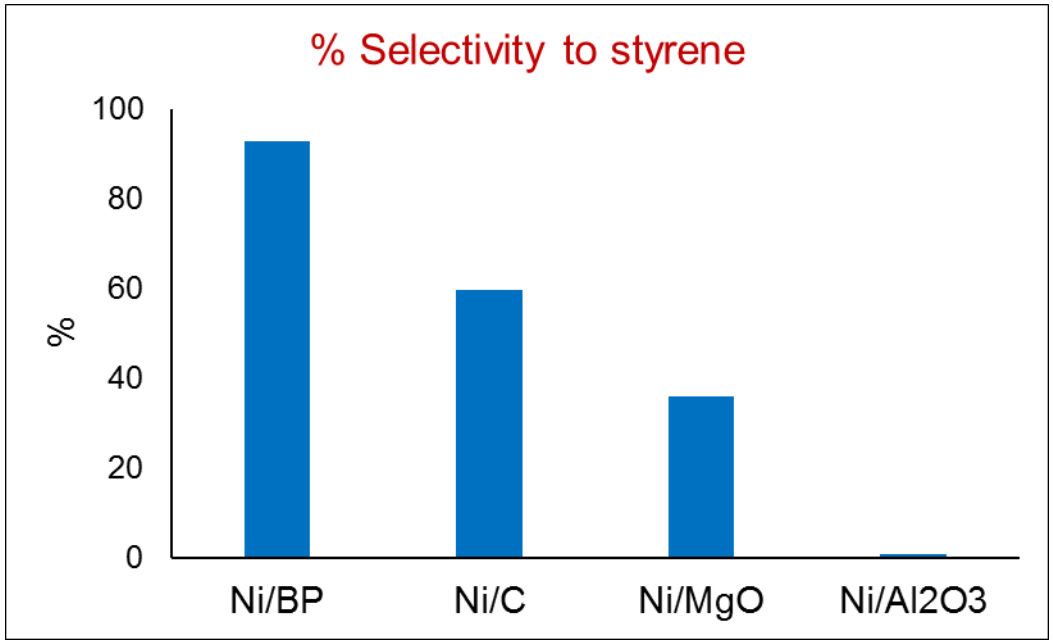
[a] *ACS Catal*. **2015**, *5*, 5756: 2 hours, 3 bar H_2

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

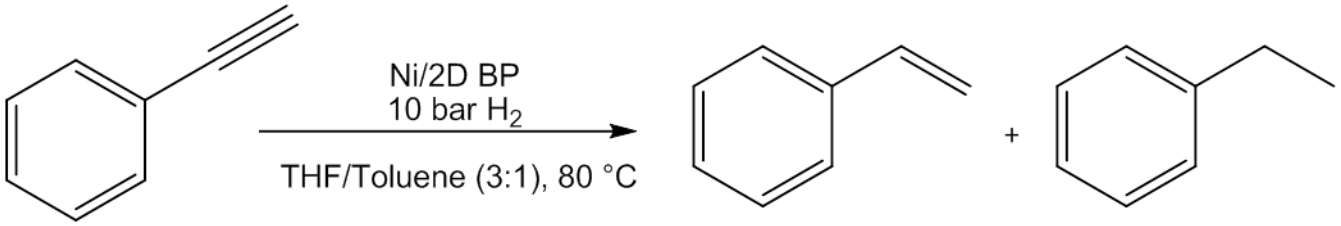
[C] *Carbon* **2014**, 74, 291: flow bed reactor.

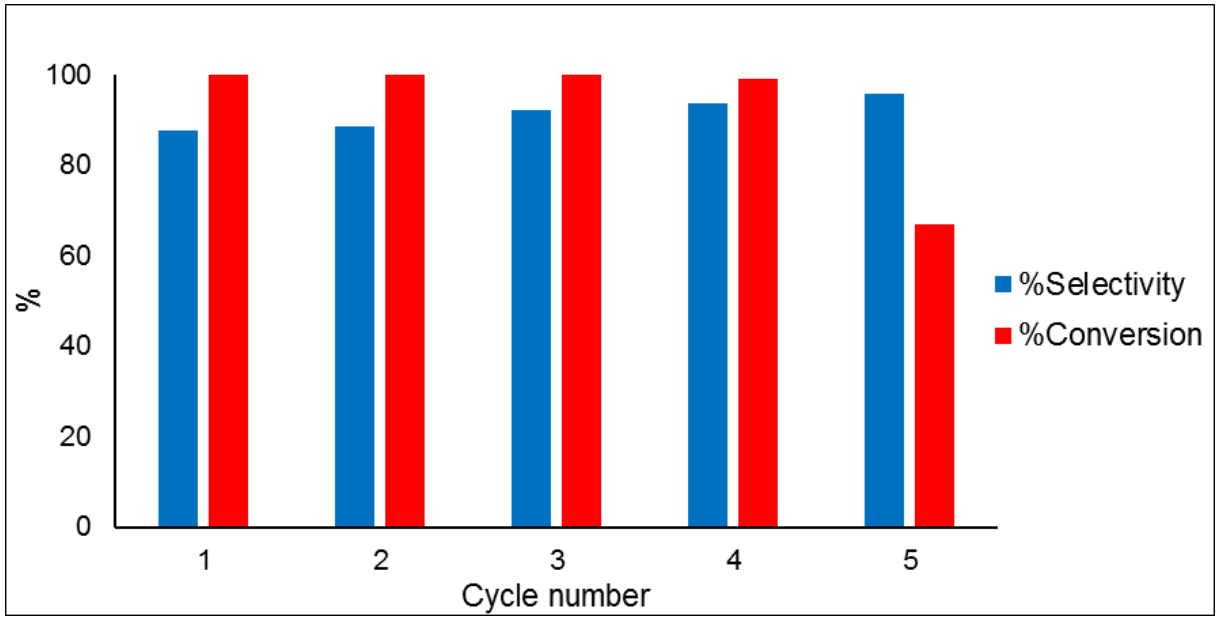
Semihydrogenation of phenylacetylene





Recycling Ni/2D BP



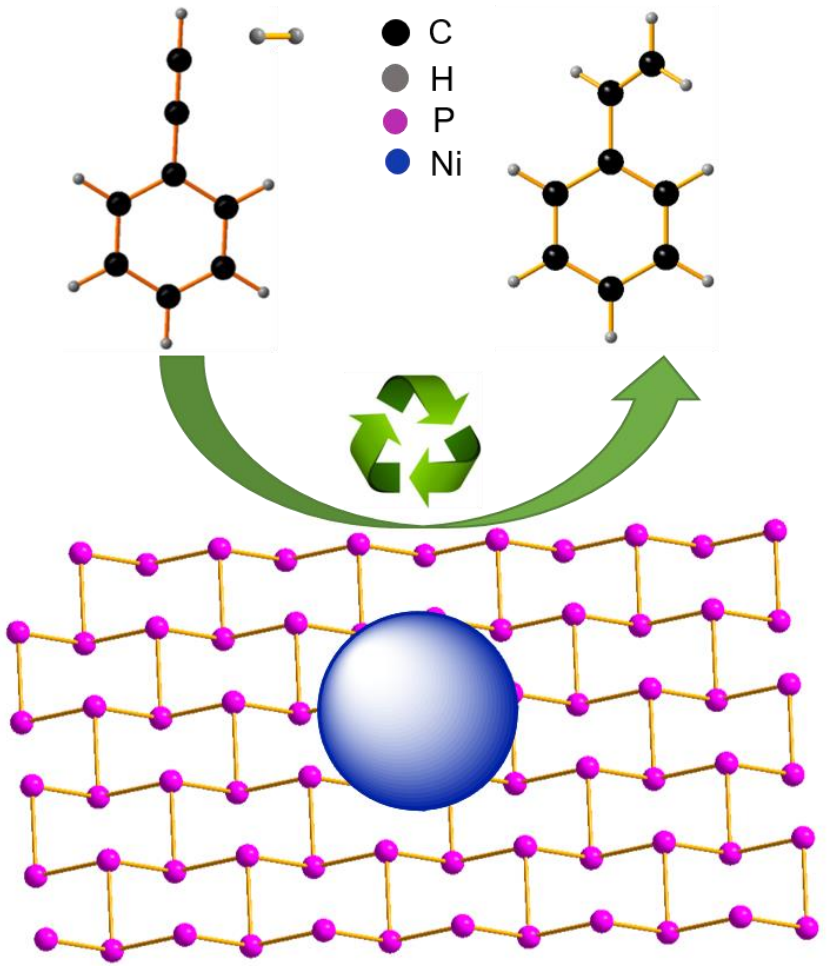


ICP-AES: no leaching of nickel

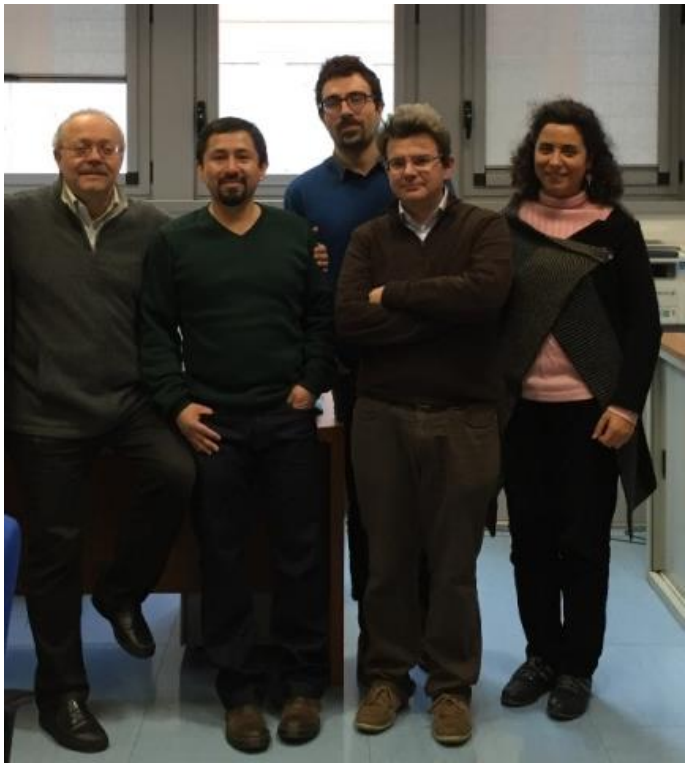
Summary

- Nickel nanoparticles were dispersed on the surface of few-layer black phosphorus achieving a new nanohybrid Ni/2D BP.

- Ni/2D BP catalyzed the semihydrogenation of phenylacetylene and showed good catalytic activity and much higher selectivity than similar systems bearing Ni NPs supported on MgO, Al_2O_3 or graphene.
- The catalytic activity and selectivity remained unaltered after recycling tests.



Acknowledgements



CNR-ICCOM (Firenze):

Maurizio Peruzzini

Manuel Serrano Ruiz

Matteo Ceppatelli

Andrea Ienco

Gabriele Manca

CNR-NANO (Pisa):

Stefan Heun

Francesca Telesio

Shaohua Xiang

CNR-IMM (Catania):

Giuseppe Nicotra

Corrado Spinella

The authors thank the European Research Council for funding the project PHOS*FUN* "*Phosphorene functionalization: a new platform for advanced multifunctional materials*" (Grant Agreement No. 670173) through an ERC Advanced Grant to MP.