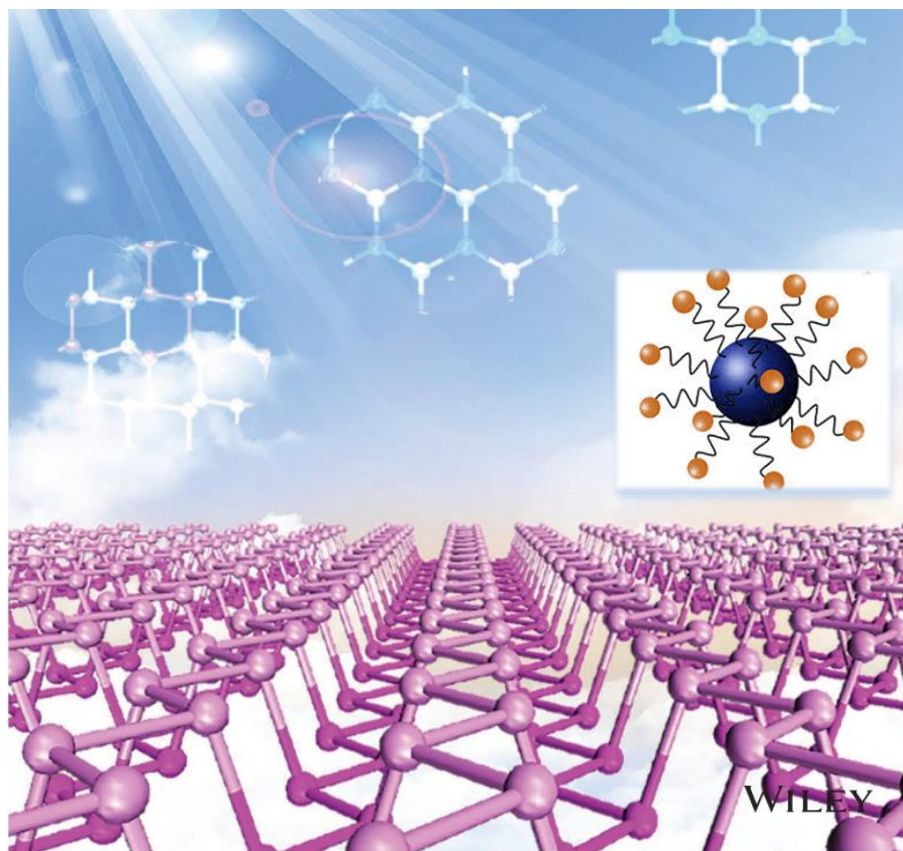
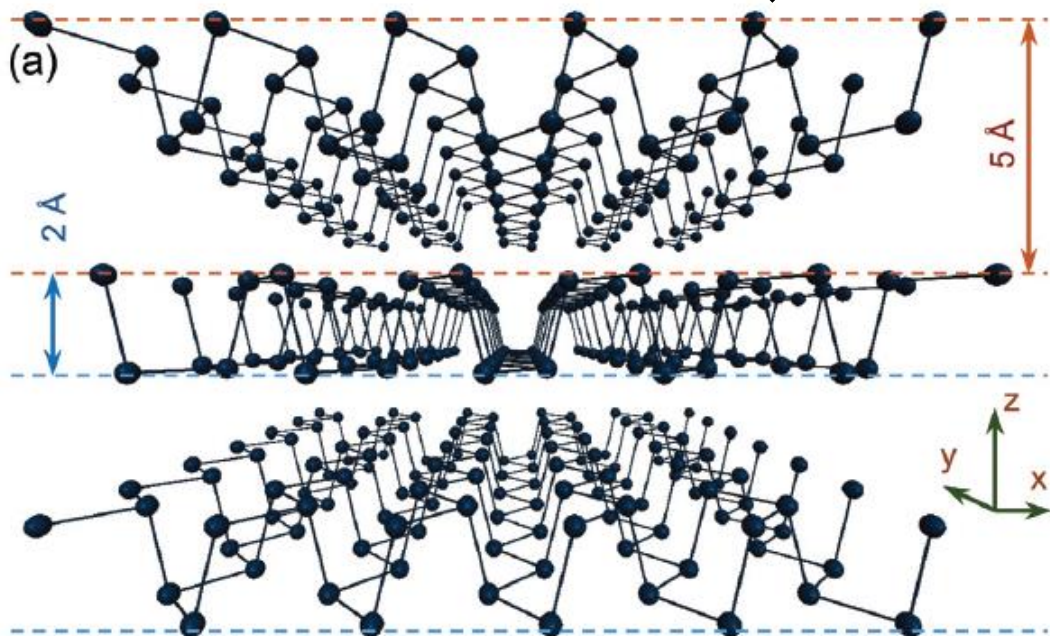
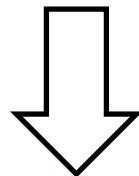


NONCOVALENT FUNCTIONALIZATION OF 2D- BLACK PHOSPHORUS WITH METAL NANOPARTICLES AND ITS APPLICATION IN CATALYSIS



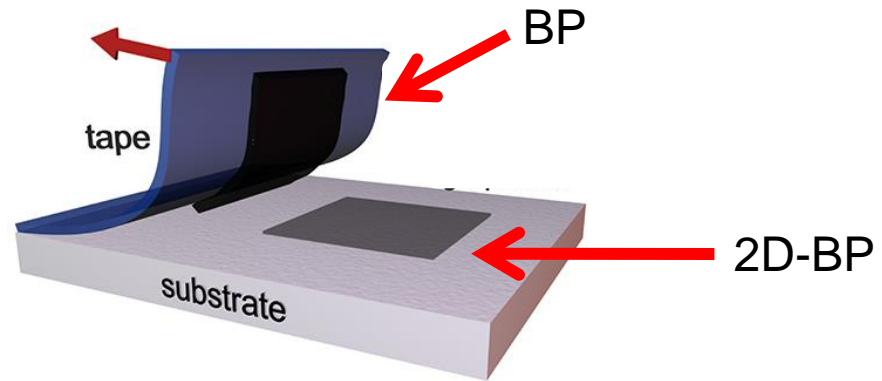
Maria Caporali
CNR ICCOM, Florence (ITALY)





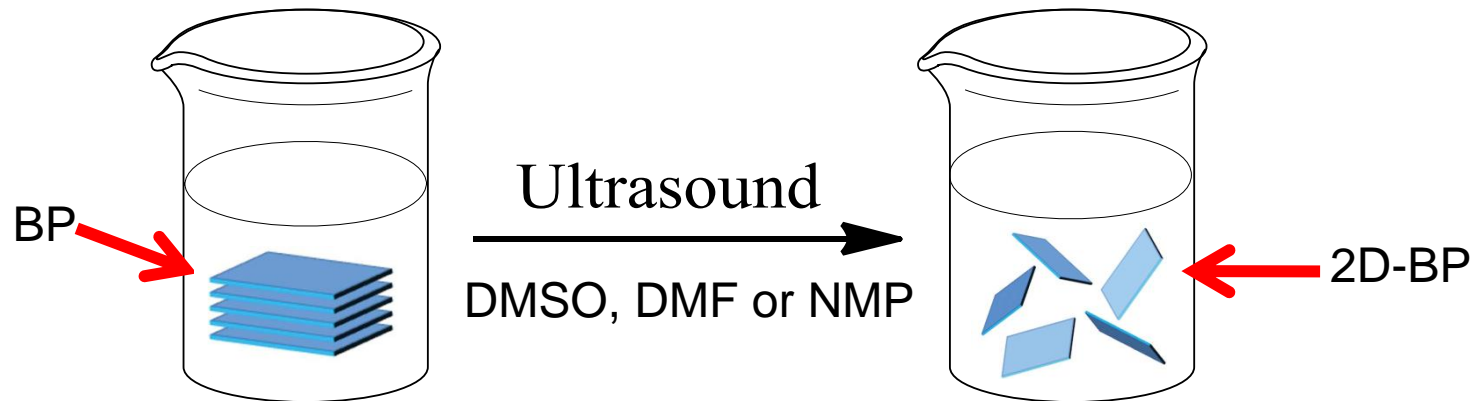
Preparation of few-layer BP

✓ Mechanical exfoliation

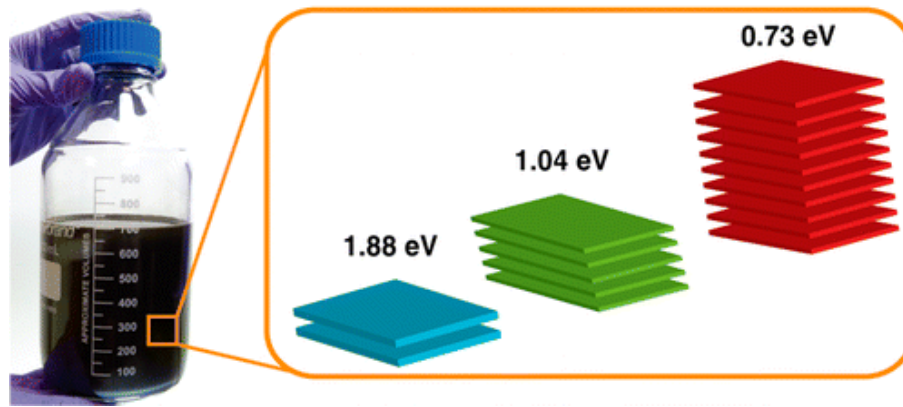


Ye et al. *ACS Nano* **2014**, 8, 4033; Zhang, *Nat. Nanotechnol.* **2014**, 9, 372

✓ 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.



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

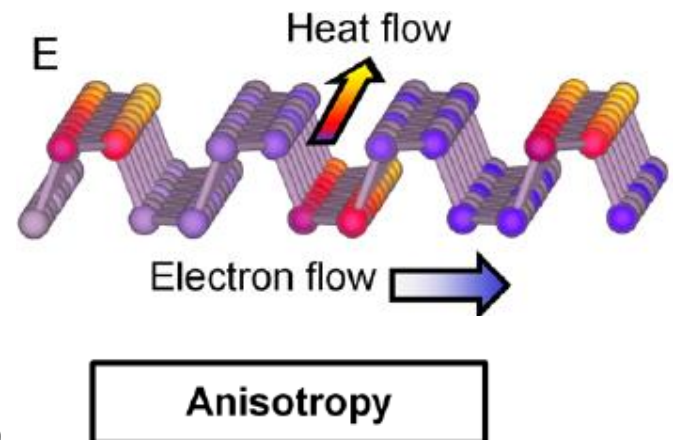
✓ The band gap can be modulated either applying an electrical field or by strain.

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

✓ On / off ratio: $10^3 - 10^5$

✓ Thermal conductivity (300 K):

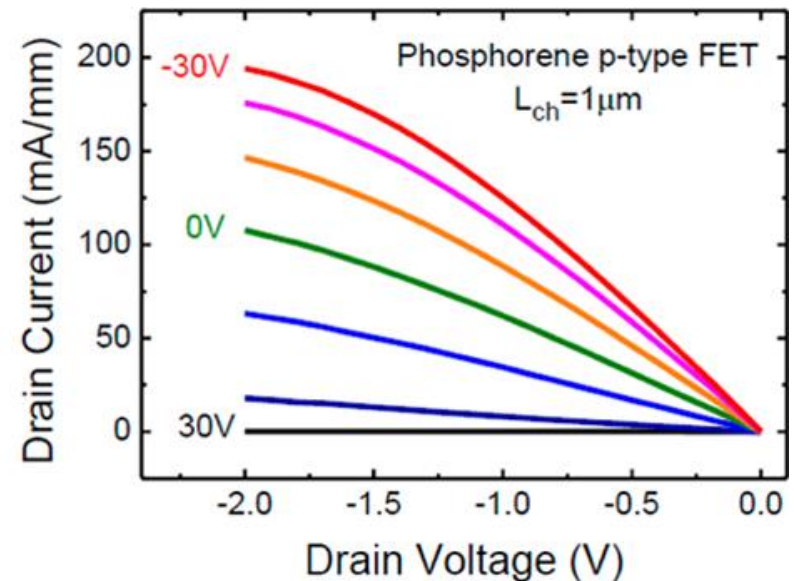
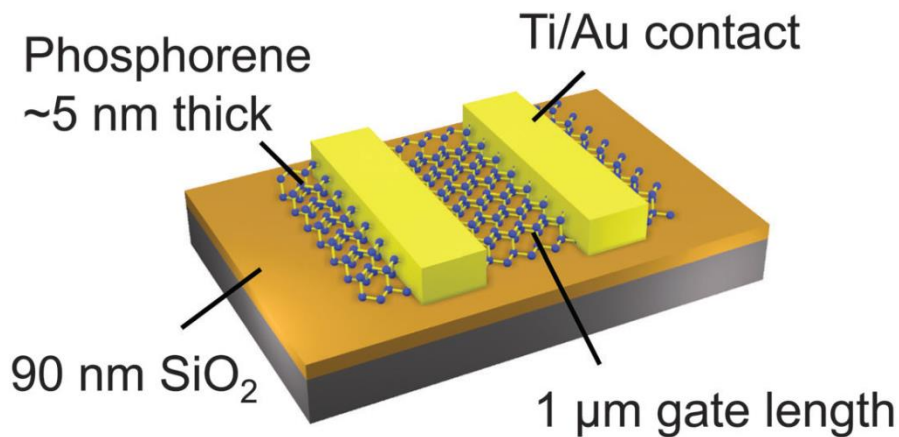
30 W/m K (zig-zag); 13.7 W/m K (armchair)



Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility

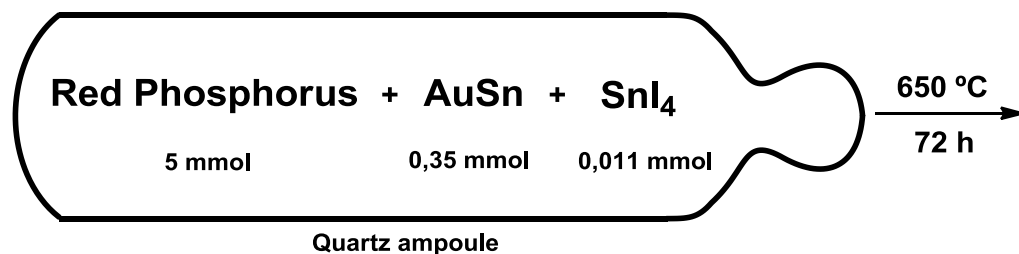
Han Liu,^{†,‡} Adam T. Neal,^{†,‡} Zhen Zhu,[§] Zhe Luo,^{‡,⊥} Xianfan Xu,^{‡,⊥} David Tománek,[§] and Peide D. Ye^{†,‡,*}

[†]School of Electrical and Computer Engineering and [‡]Birk Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, United States, [§]Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824, United States, and [⊥]School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, United States



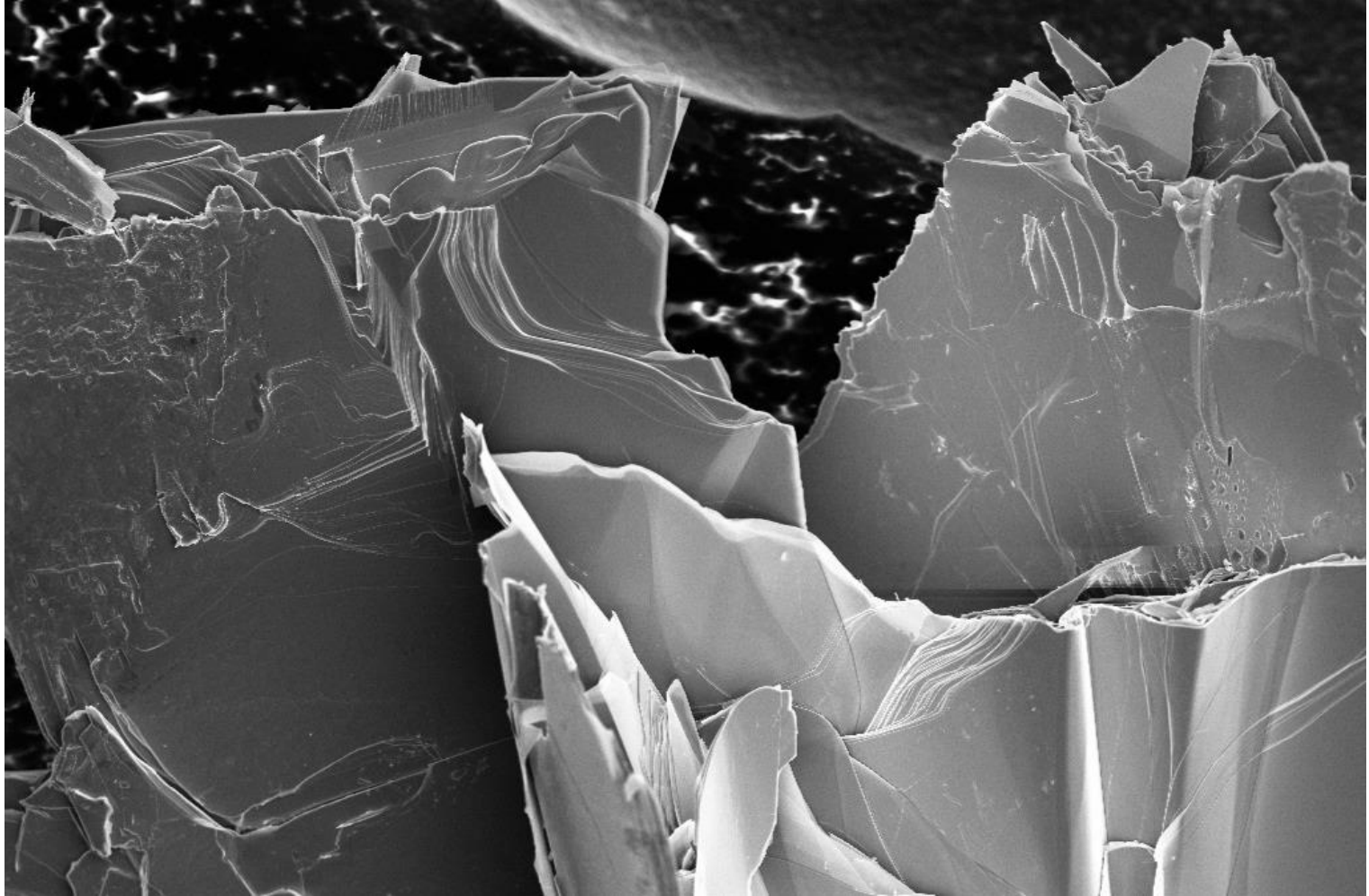
ASC Nano, **2014**, 8, 4033.

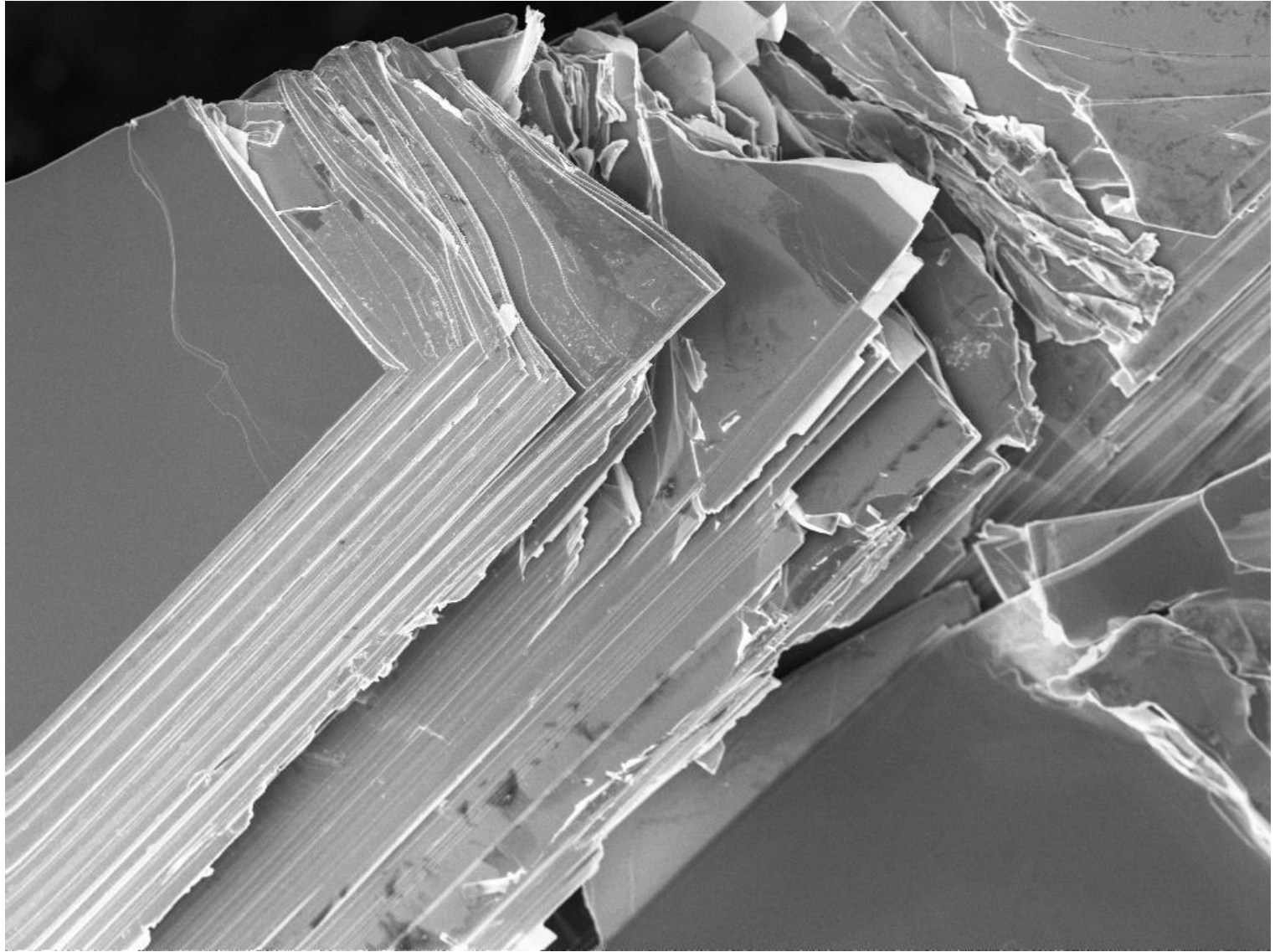
Synthesis of Black Phosphorus



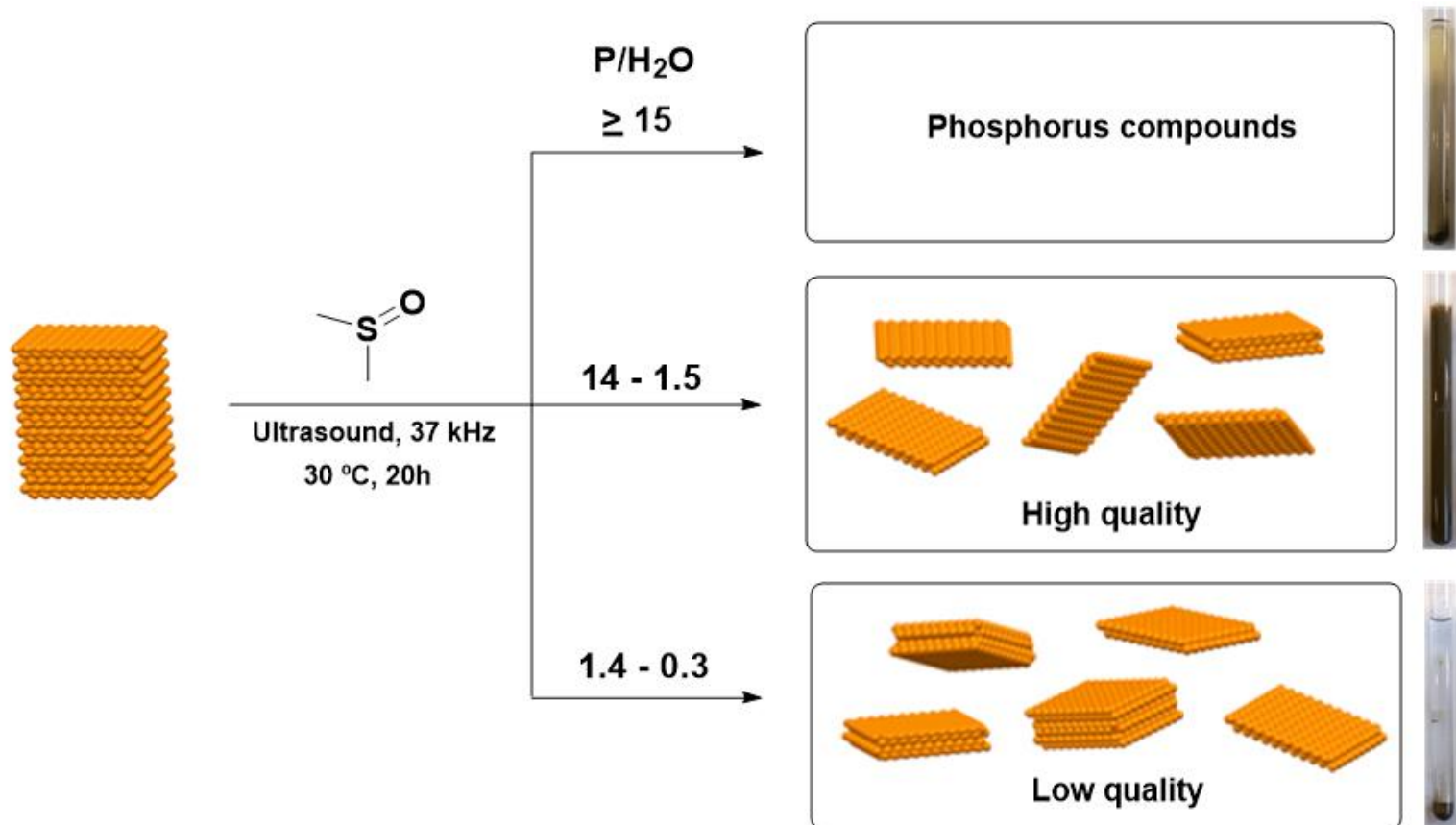
Inorg. Chem. **2007**, 46, 4028; *J. Solid State Chem.* **2008**, 181, 1707.

micro-mechanical exfoliation



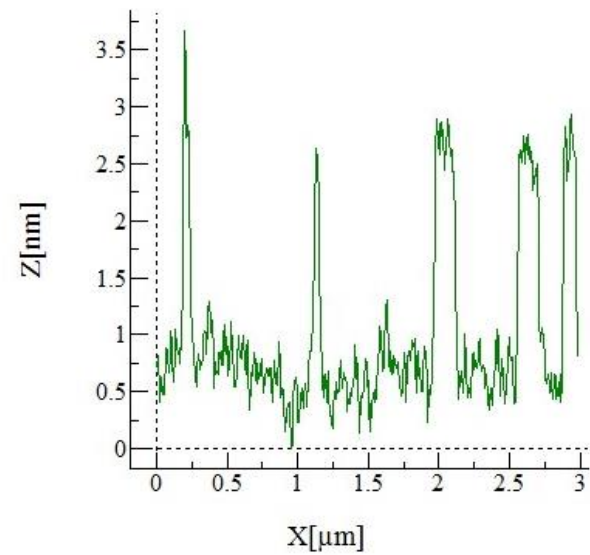
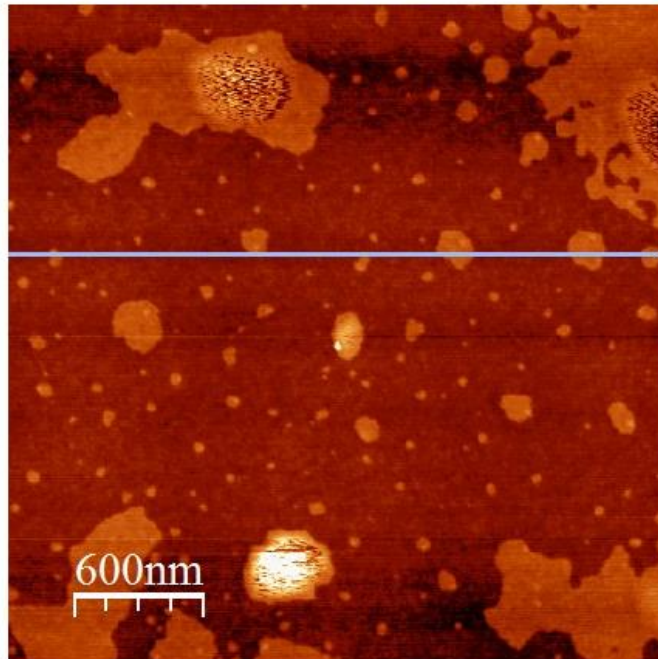
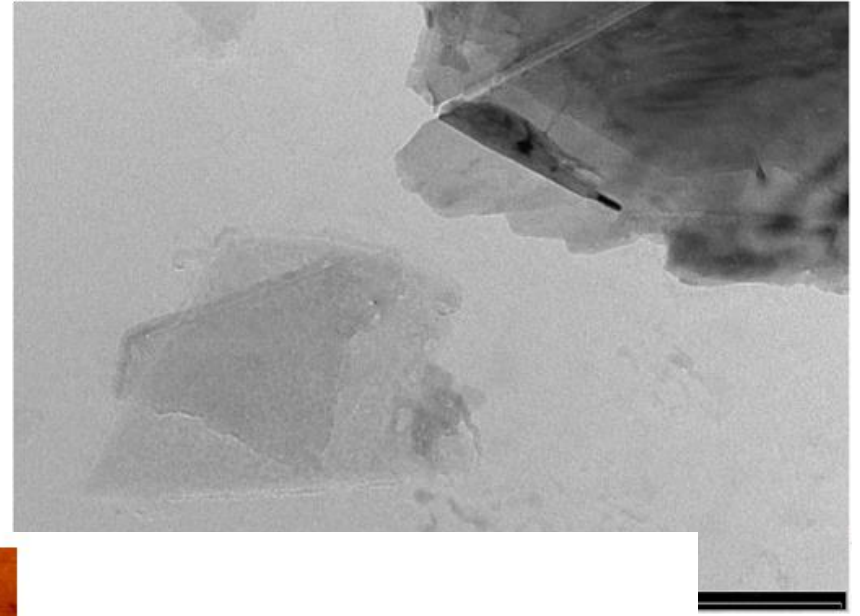
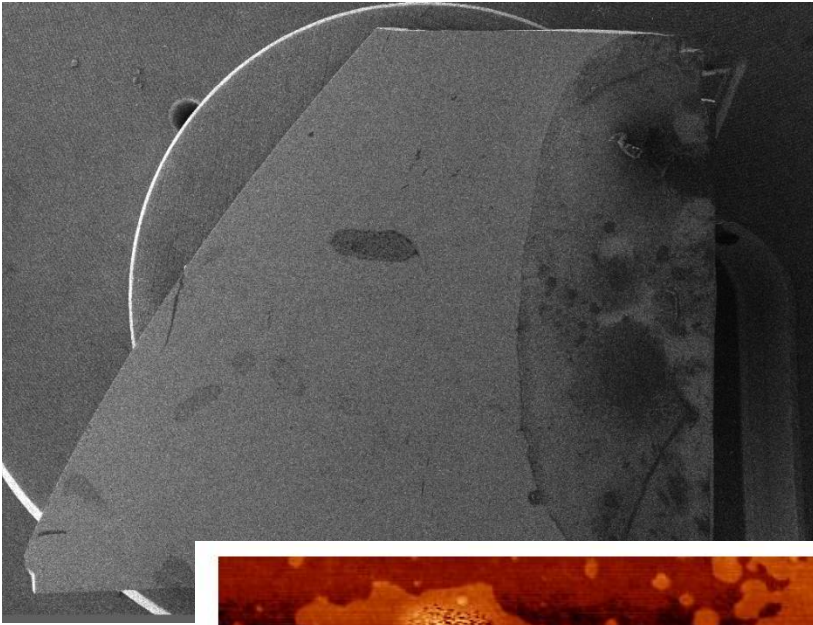


Optimised liquid exfoliation in our labs



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

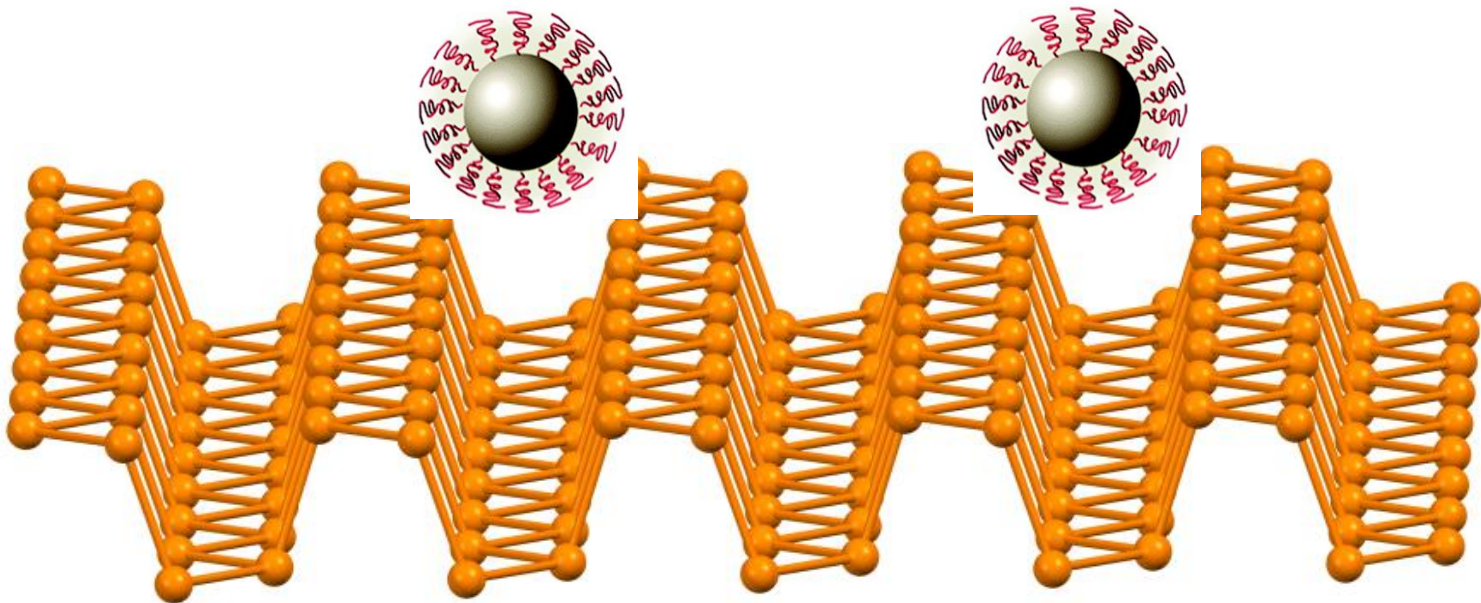
Liquid exfoliation



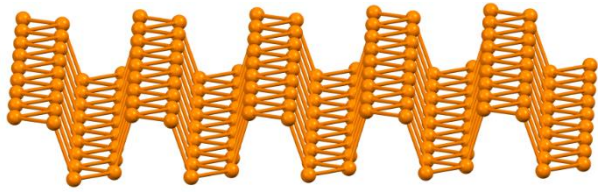
Functionalization of few-layer BP

Each P atom has a free electron pair, may react with:

- ✓ coordinatively unsaturated metal complexes
- ✓ metal nanoparticles



NiNPs supported on 2D-BP

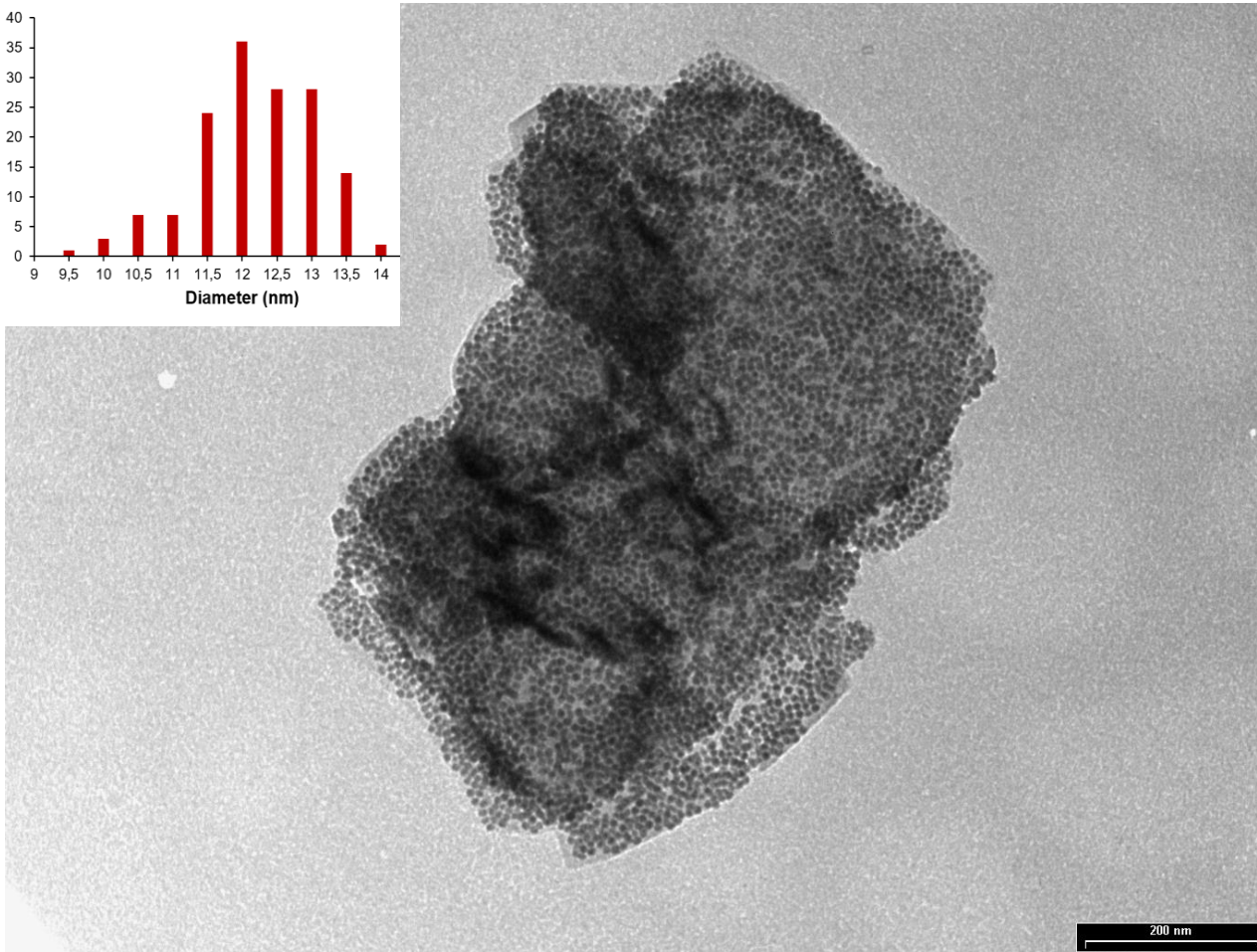
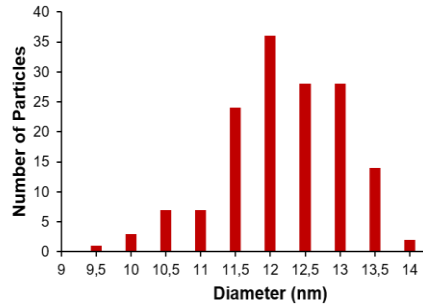


NiNPs in hexane

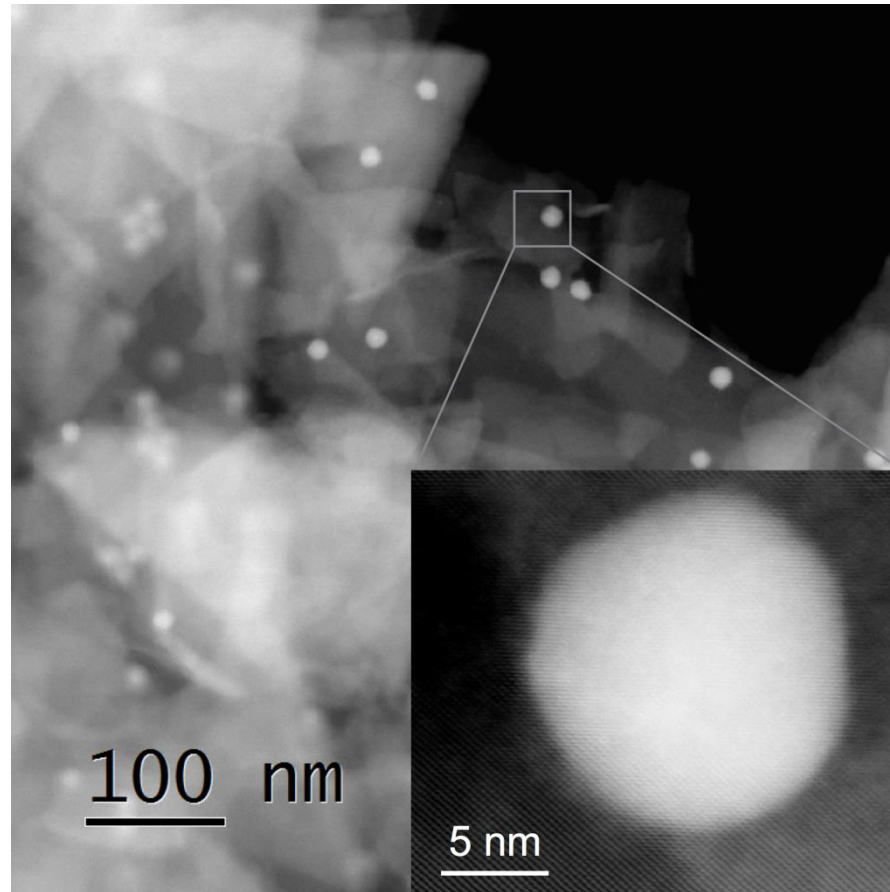
P : Ni = 10, 6, 2

(suspended in THF or

NiNPs/2D-BP

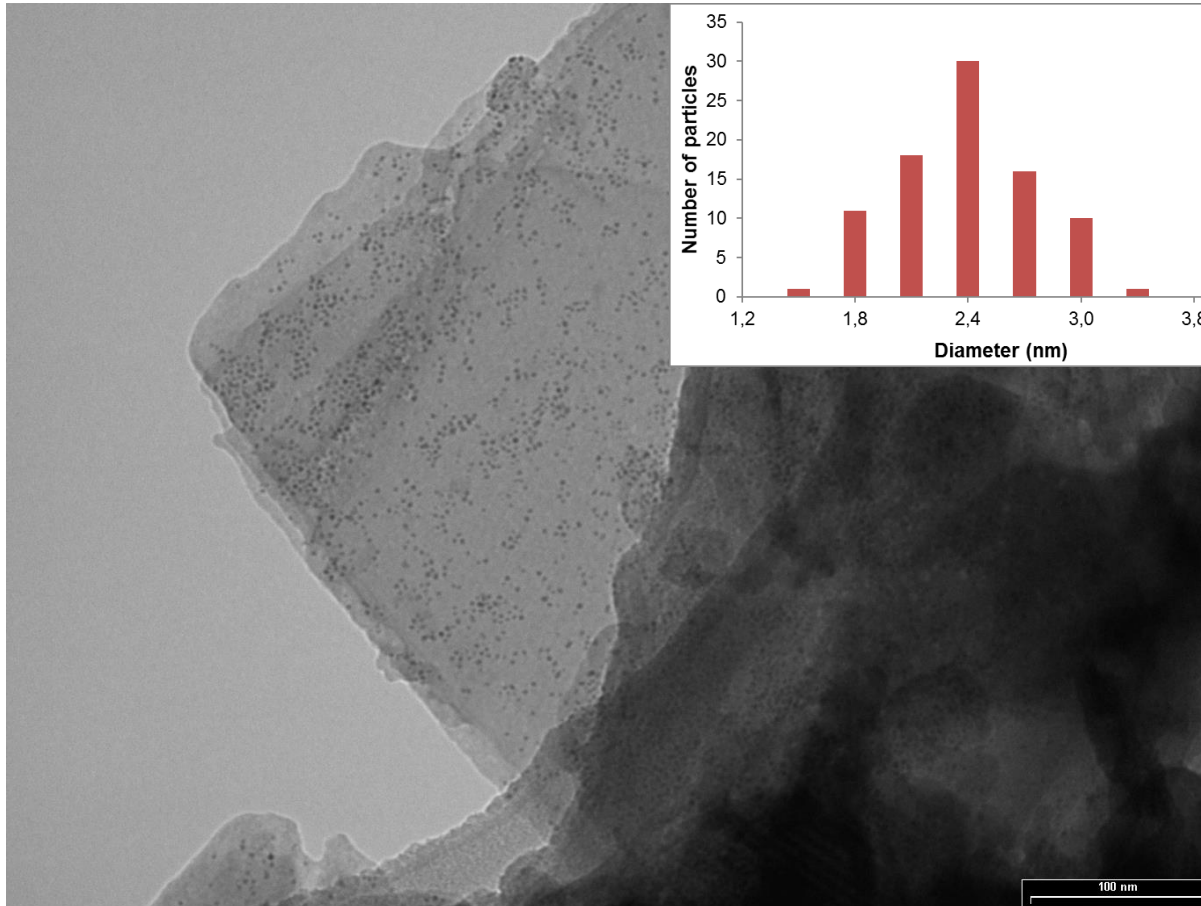
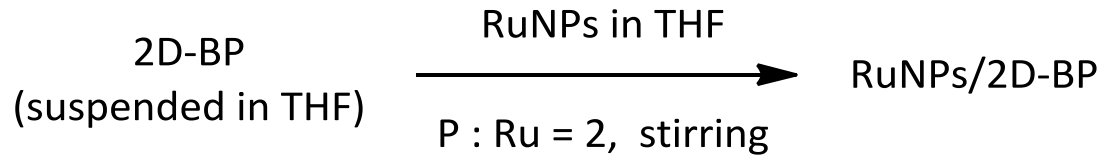


HAADF STEM on NiNPs / 2D BP



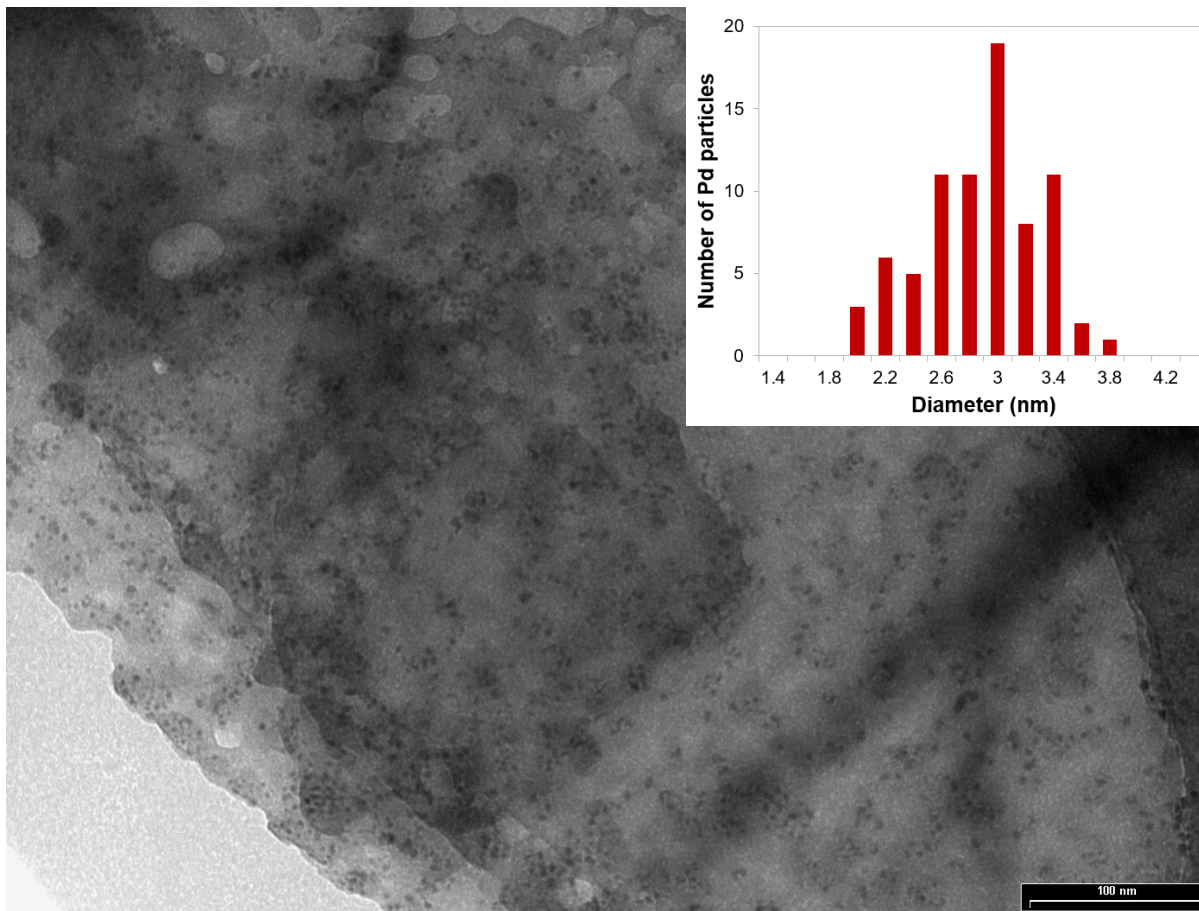
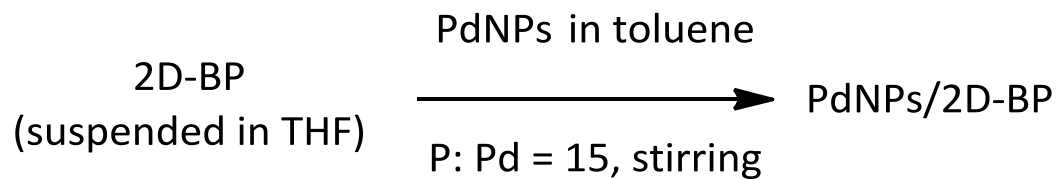
STEM-EELS gave chemical information of the surface of the nanocomposite

RuNPs supported on 2D-BP



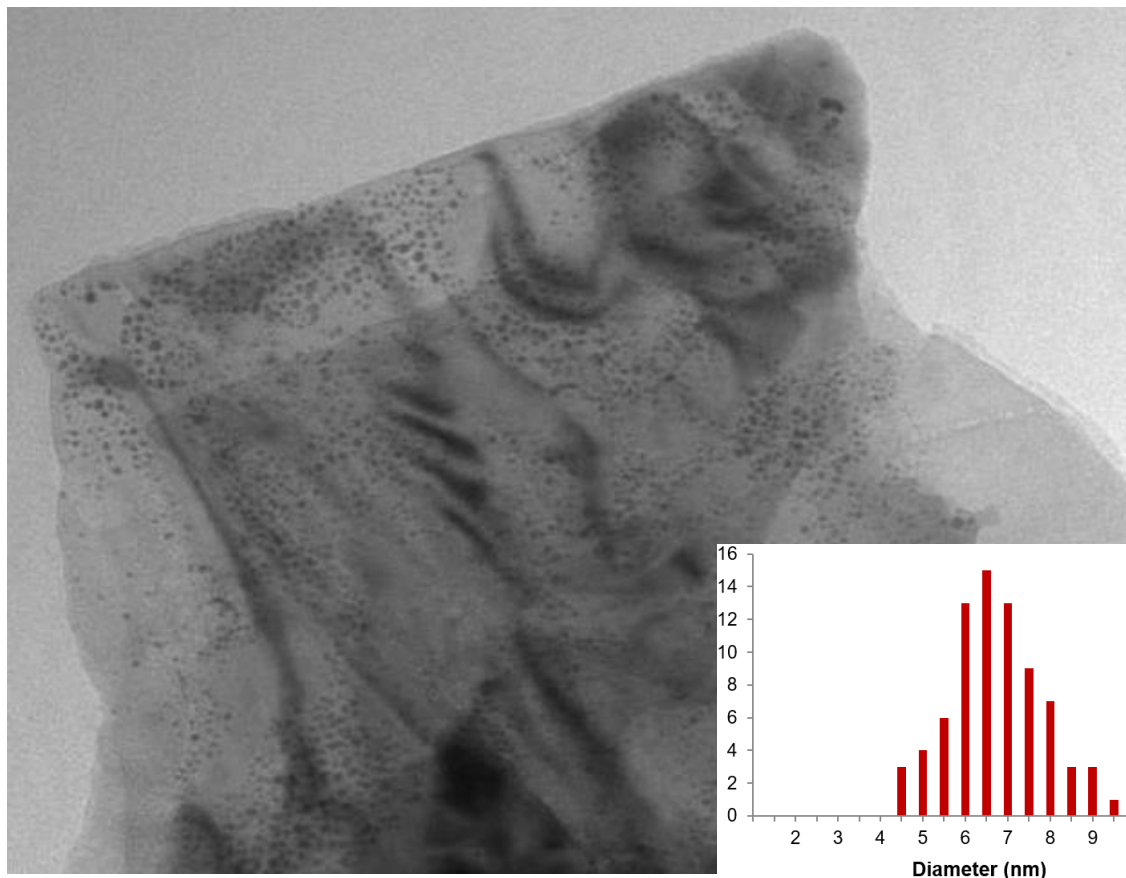
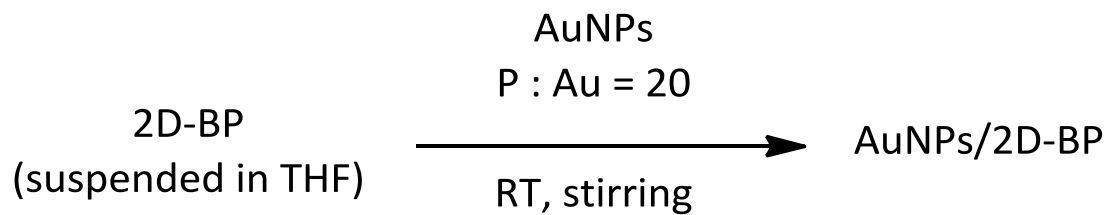
H. Can, Ö. Metin, *Appl. Cat. B-Environ.* **2012**, *125*, 304-310.

PdNPs supported on 2D-BP



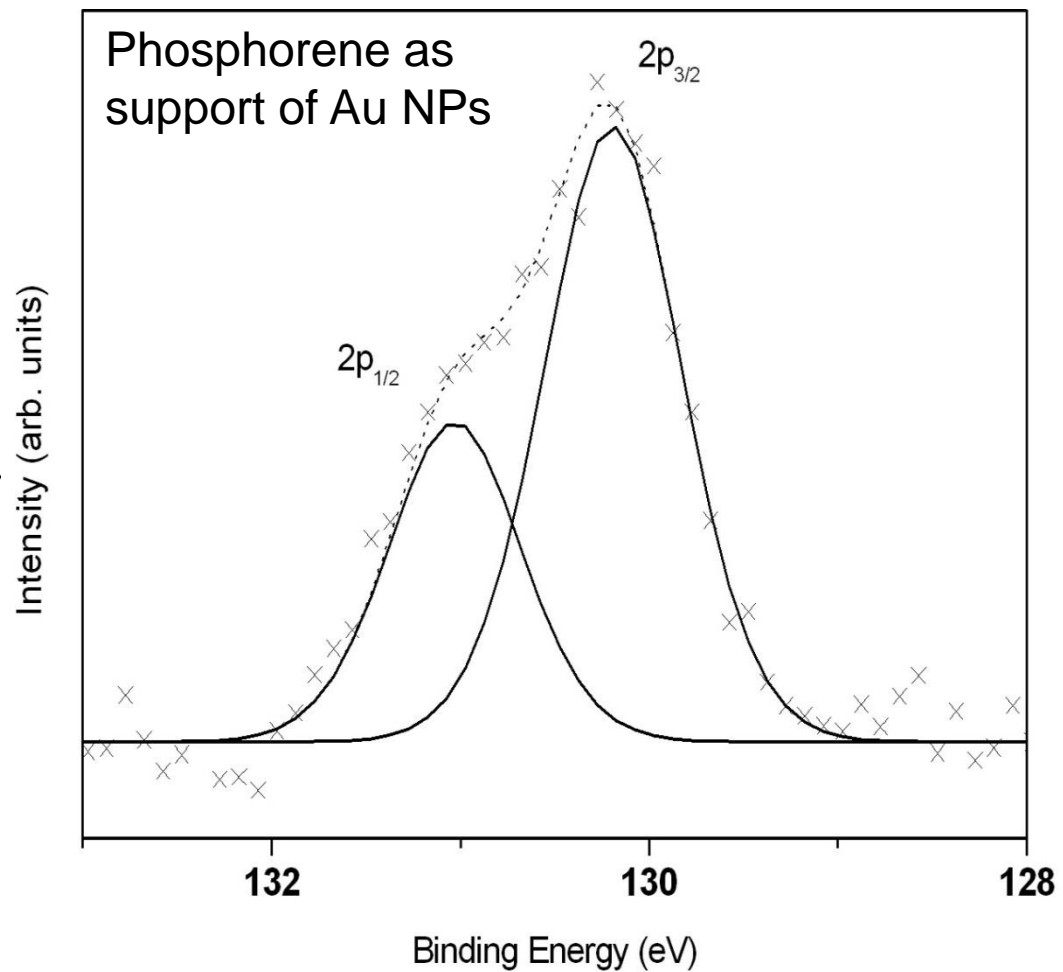
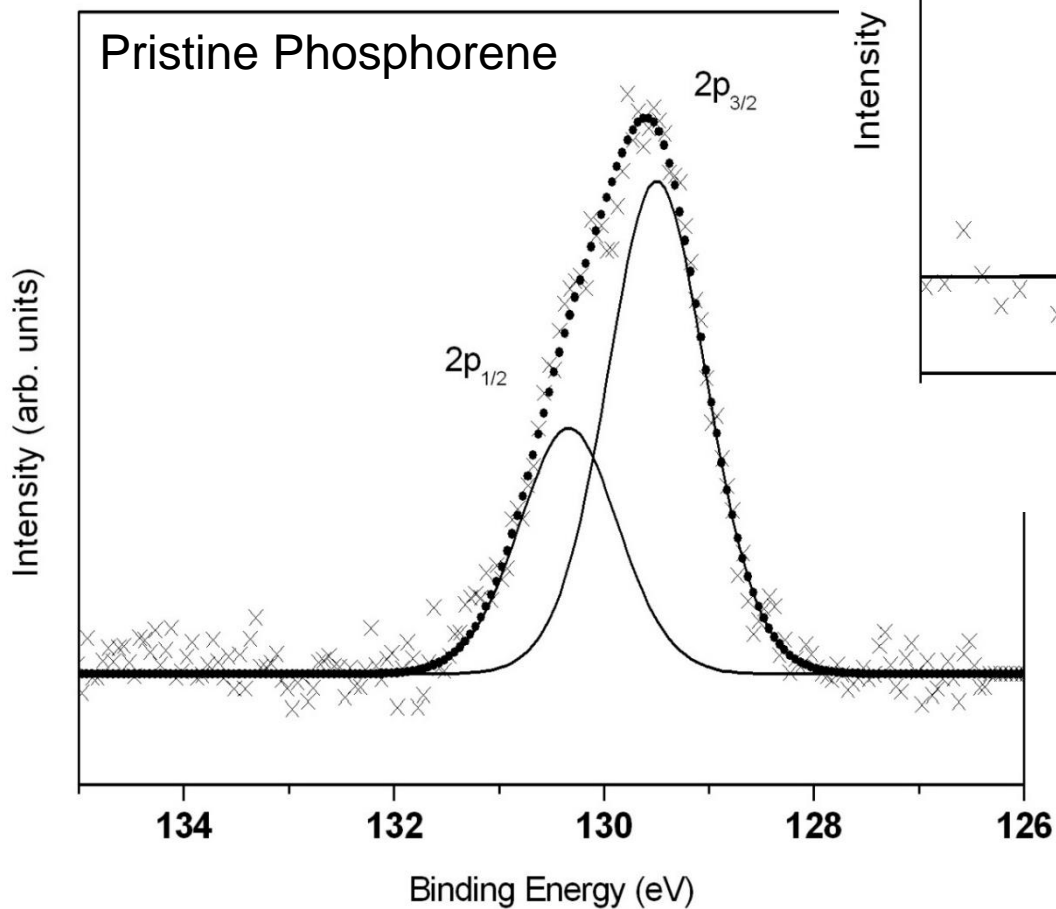
Coronado *et al.*, *J. Mat. Chem.* **2008**, *18*, 5682

Au NPs supported on 2D-BP

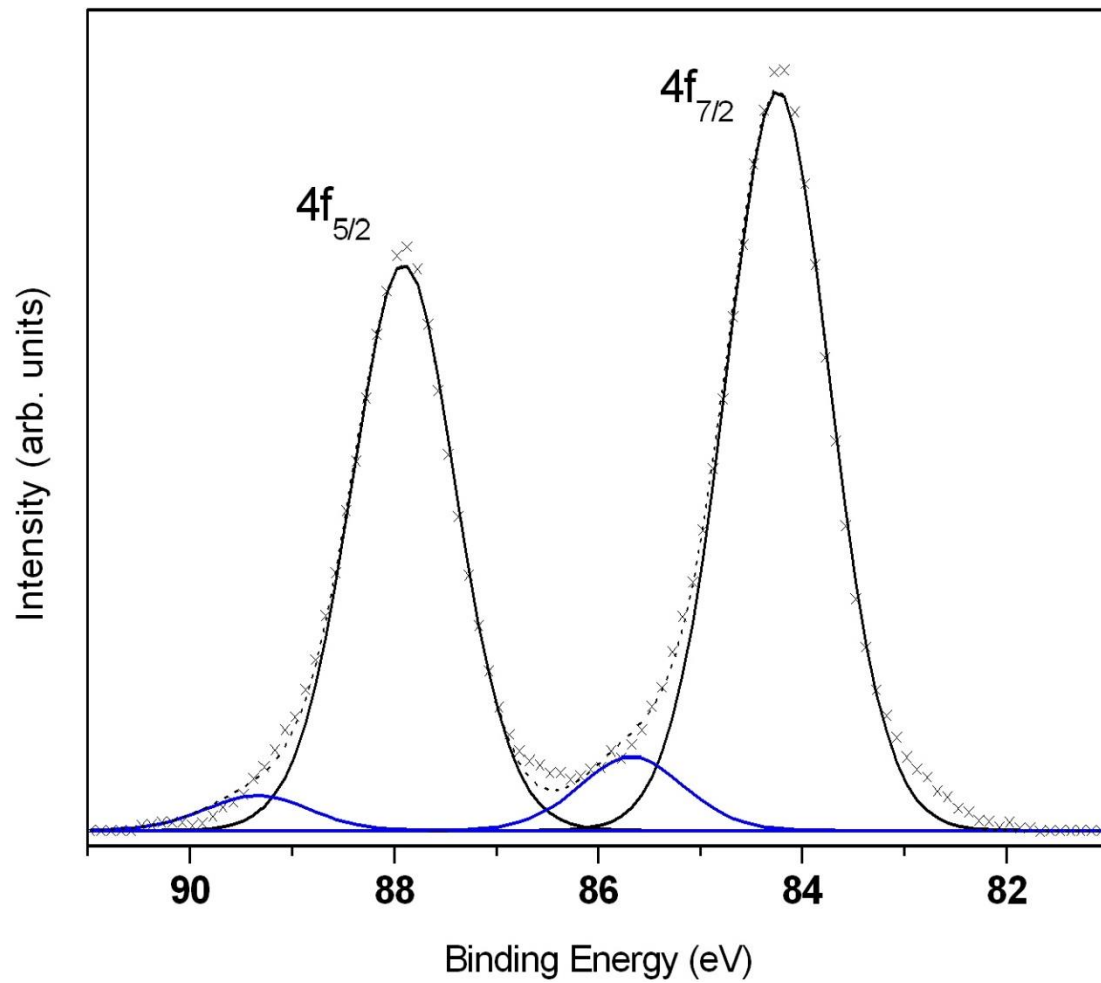


S. Dai *et al*, *Catal. Lett.* **2010**, 136, 209.

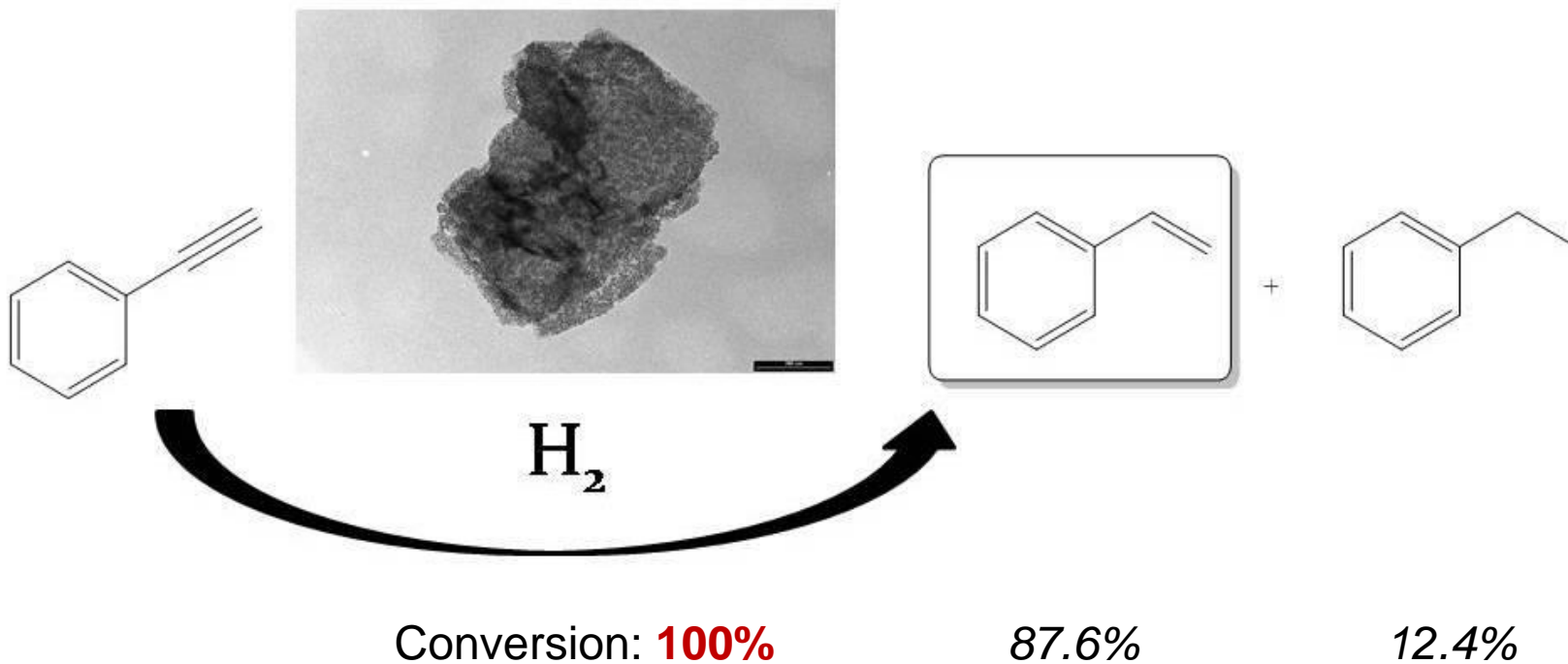
XPS



XPS

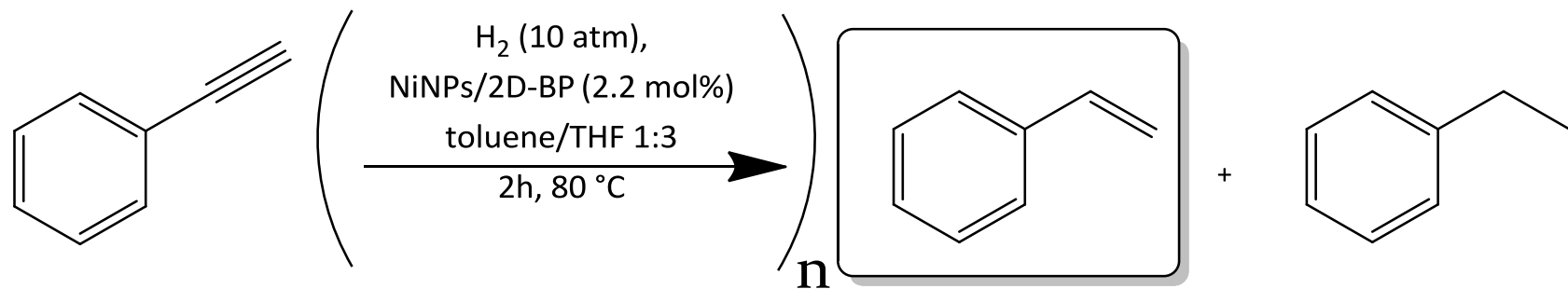


Hydrogenation of Phenylacetylene



Ni NPs 2.2 mol%, P:Ni = 6 molar ratio, Tetrahydrofuran:Toluene = 3, H₂: 10 bar, 80°C, 2 h.

Recycling the catalyst NiNPs/2D-BP

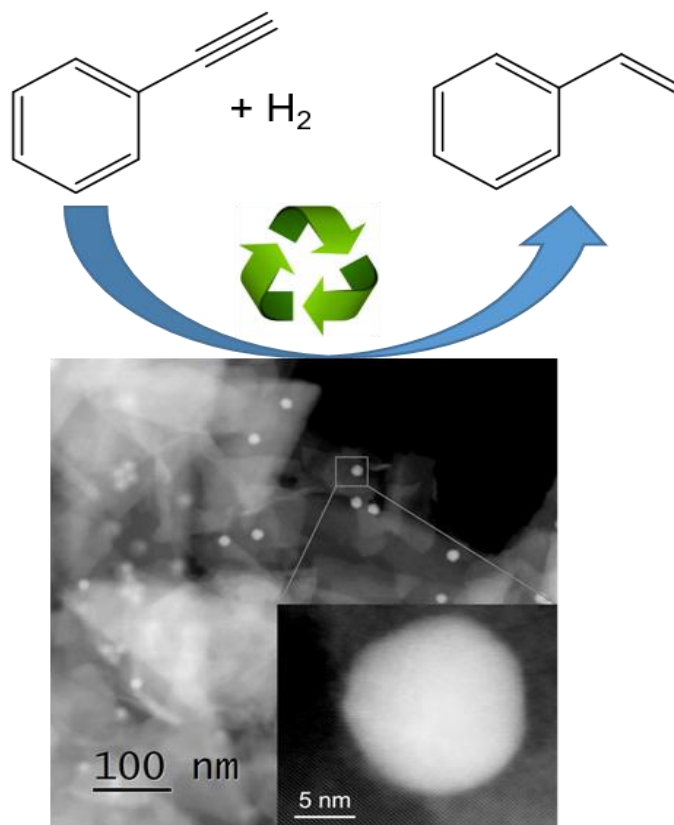


Run	Conversion (%)	Selectivity to styrene (%)
0	100.0	87.6 (12.4)
1	100.0	88.5 (11.5)
2	100.0	92.2 (7.8)
3	99.2	93.1 (6.1)

Summary

- Nanoparticles of nickel, palladium, ruthenium and gold were dispersed on the surface of few-layer black phosphorus (2D BP) achieving new nanocomposite 2D materials.

- The nanocomposite Ni NPs/ 2D BP was tested as catalyst in the hydrogenation of phenylacetylene and showed good catalytic activity that remained unaltered also after recycling tests.



M. Caporali, M. Serrano-Ruiz, F. Telesio, S. Heun, S. Caporali, M. Peruzzini *et al.* <http://arxiv.org/abs/1609.05010>

Acknowledgements



CNR-ICCOM (Florence):

- Maurizio Peruzzini
- Maria Caporali
- Manuel Serrano Ruiz
- Andrea Ienco
- Gabriele Manca
- Matteo Ceppatelli



CNR-IMM (Catania):

- Giuseppe Nicotra



CNR-NANO (Pisa):

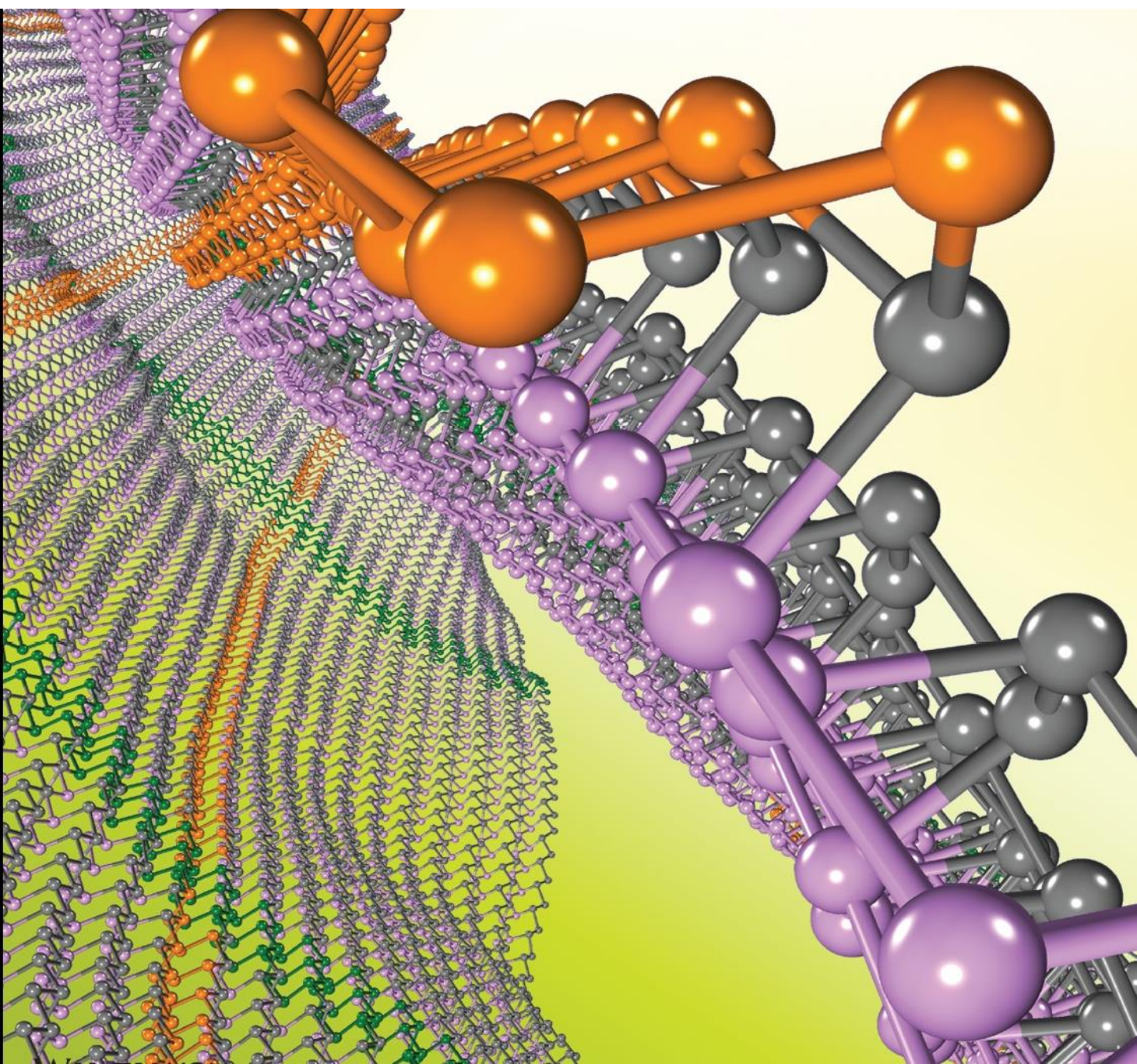
- Stefan Heun
- Francesca Telesio
- Shaohua Xiang



Funding:



erc PHOSFUN “*Phosphorene functionalization: a new platform for advanced multifunctional materials*”
ERC Advanced Grant to MP.



Thank you!!