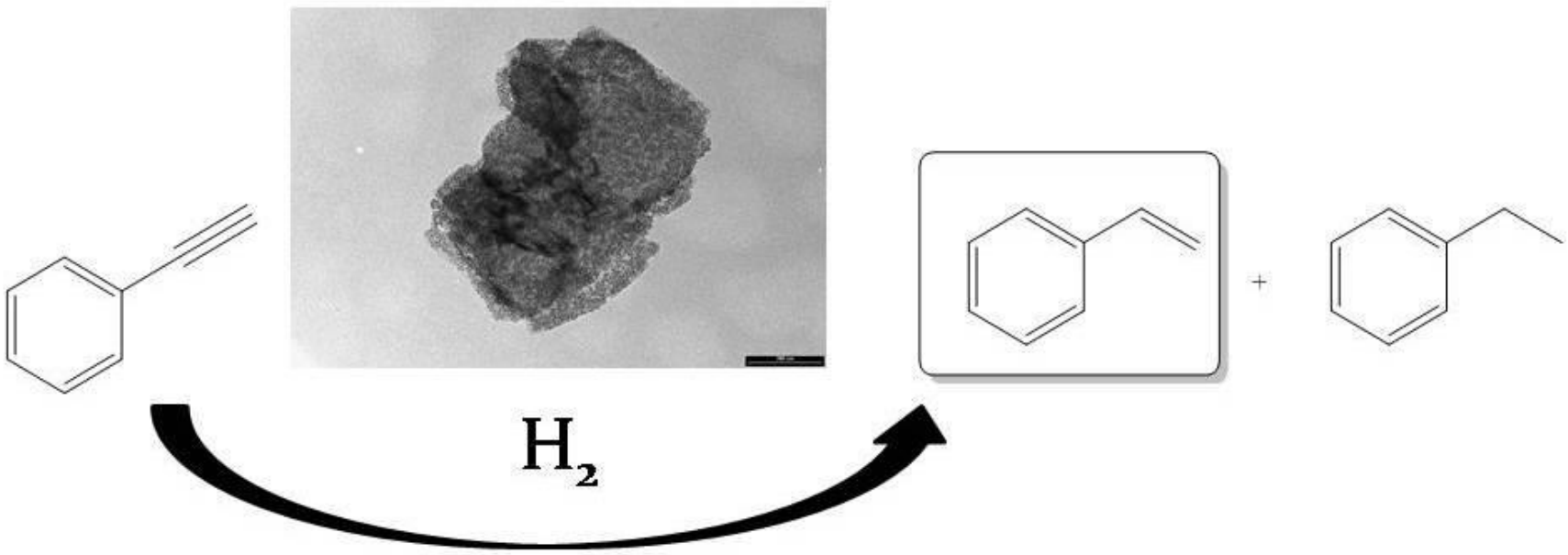
# 2D-BLACK PHOSPHORUS FUNCTIONALIZED WITH METAL NANOPARTICLES: FULL CHARACTERIZATION AND CATALYTIC ACTIVITY ON HYDROGENATION REACTIONS




**EWPC-13**
Freie Universität Berlin

Salvatore Interlandi
**CNR-ICCOM** Sesto Fiorentino (Florence)

# Outline

**Intro**

- 2D-black phosphorus (BP): a new wonder material
- 2D-BP as novel support for metal nanoparticles

**Experimental section**

- Preparation and characterization of 2D-BP functionalized with TM nanoparticles
- Preliminary study on phenylacetylene hydrogenation catalyzed by NiNPs/2D-BP

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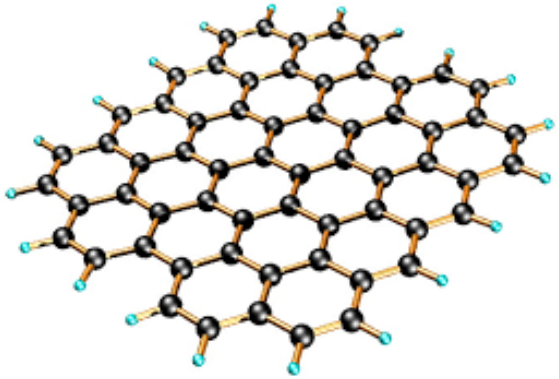
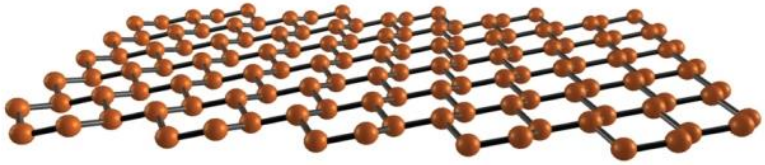
# 2D-Materials

**Elemental 2D-materials**



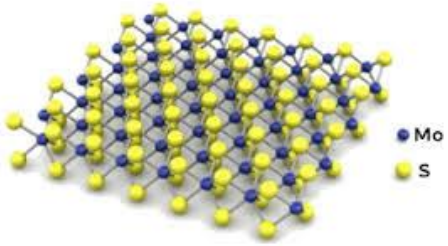
**Graphene**



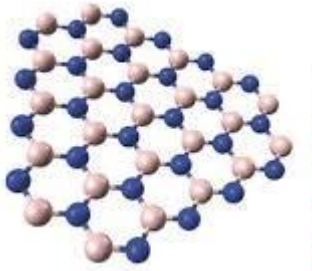
**Silicene**

**……**

**2D-Materials composed by two (or more) elements**




**Molybdenum disulfide ($MoS_2$)**



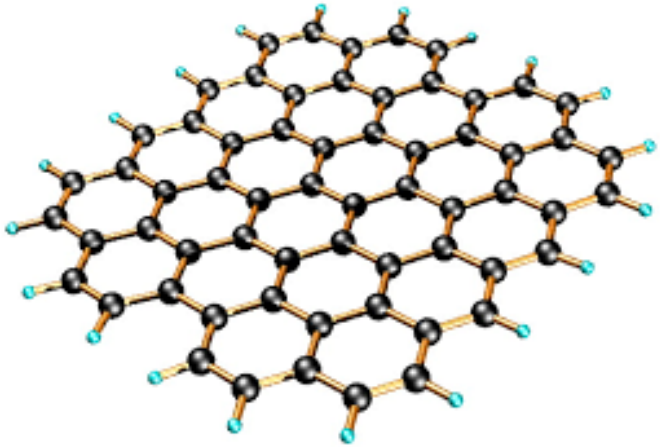
**Hexagonal boron nitride (*h*-BN)**

**……**

# 2D-Materials

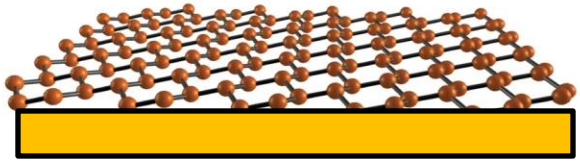
-Microelectronics
-Optoelectronics
-Catalysis
-Chemical and biological sensors
-Supercapacitors
-Solar cells
-Lithium ion batteries

# Elemental 2D-Materials



**Graphene**

Isolated through exfoliation



**Other elemental 2D-materials**

Epitaxially grown onto specific substrates

# 2D-black phosphorus (BP): a new wonder material?

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APS March Meeting 2013
Volume 58, Number 1
Monday–Friday, March 18–22, 2013; Baltimore, Maryland

Session J6: Growth, Structure, Properties, and Defects
2:30 PM–5:30 PM, Tuesday, March 19, 2013
Room: 302

Sponsoring Unit: DMP
Chair: Paola Barbara, Georgetown University

Abstract ID: BAPS.2013.MAR.J6.13

Abstract: J6.00013 : Electronic Properties of Few-layer Black Phosphorus
4:54 PM–5:06 PM

Preview Abstract

Abstract: J6.00013 : Electronic Properties of Few-layer Black Phosphorus
4:54 PM–5:06 PM

(Hefei National laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China)

X.H. Chen
(Hefei National laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China)

Yuanbo Zhang
(State Key Laboratory of Surface Physics and Department of Physics, Fudan University)

Black phosphorus is a layered allotropy of phosphorus that closely resembles graphite. In a single atomic layer, phosphorus atoms are covalently bonded into a puckered honey comb structure. All five valence electrons are localized, so unlike graphene monolayer black phosphorus is a semiconductor with a band gap of ~ 2 eV. In a bulk crystal the interlayer coupling reduces the band gap to ~ 0.3 eV. Using mechanical exfoliation method, we have successfully fabricated few layer black phosphorus field effect transistors. Our samples exhibit bipolar behavior with on-off ratio up to $10^6$, and a low off-state current. Electronic mobilities up to ~ 1000 $cm^2 V^{-1} s^{-1}$ are currently achieved, with possibilities for further improvement. Such characteristics make black phosphorus a potential candidate for future nanoelectronic applications.

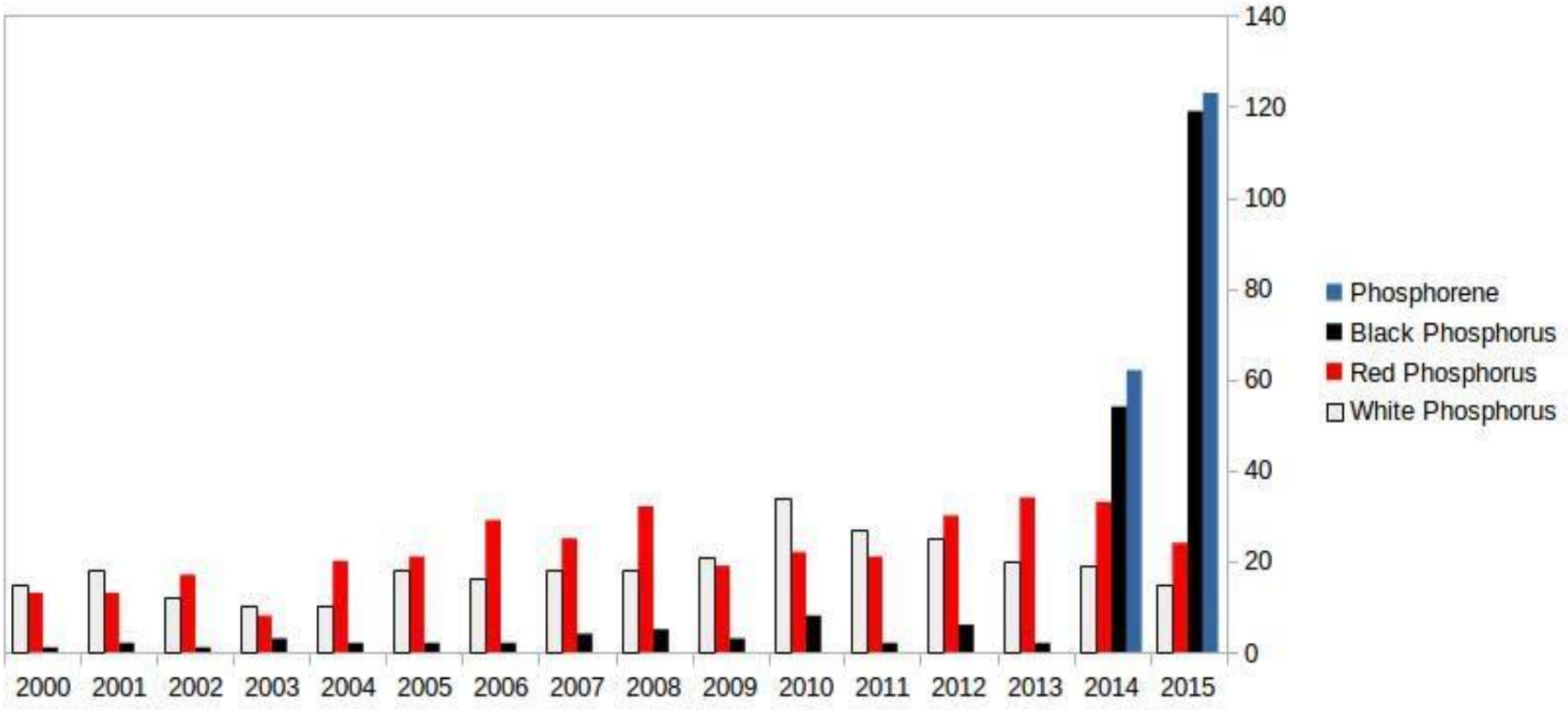
Li, L.; Yu, Y.; Ye, G. J.; Chen, X. H.; Zhang, Y. Electronic Properties of Few-Layer Black Phosphorus. In APS March Meeting; American Physical Society: College Park, MD, 2013; abstract ID Most of the breakthroughs in this field are still to come. The Journal of Physical Chemistry Letters Perspective DOI: 10.1021/acs.jpclett.5b01686 J. Phys. Chem. Lett. 2015, 6, 4280−4291 4286 BAPS.2013.MAR.J6.13, http://meetings.aps.org/Meeting/MAR13/Session/J6.13.

# 2D-BP: a new wonder material?

## The renaissance of black phosphorus

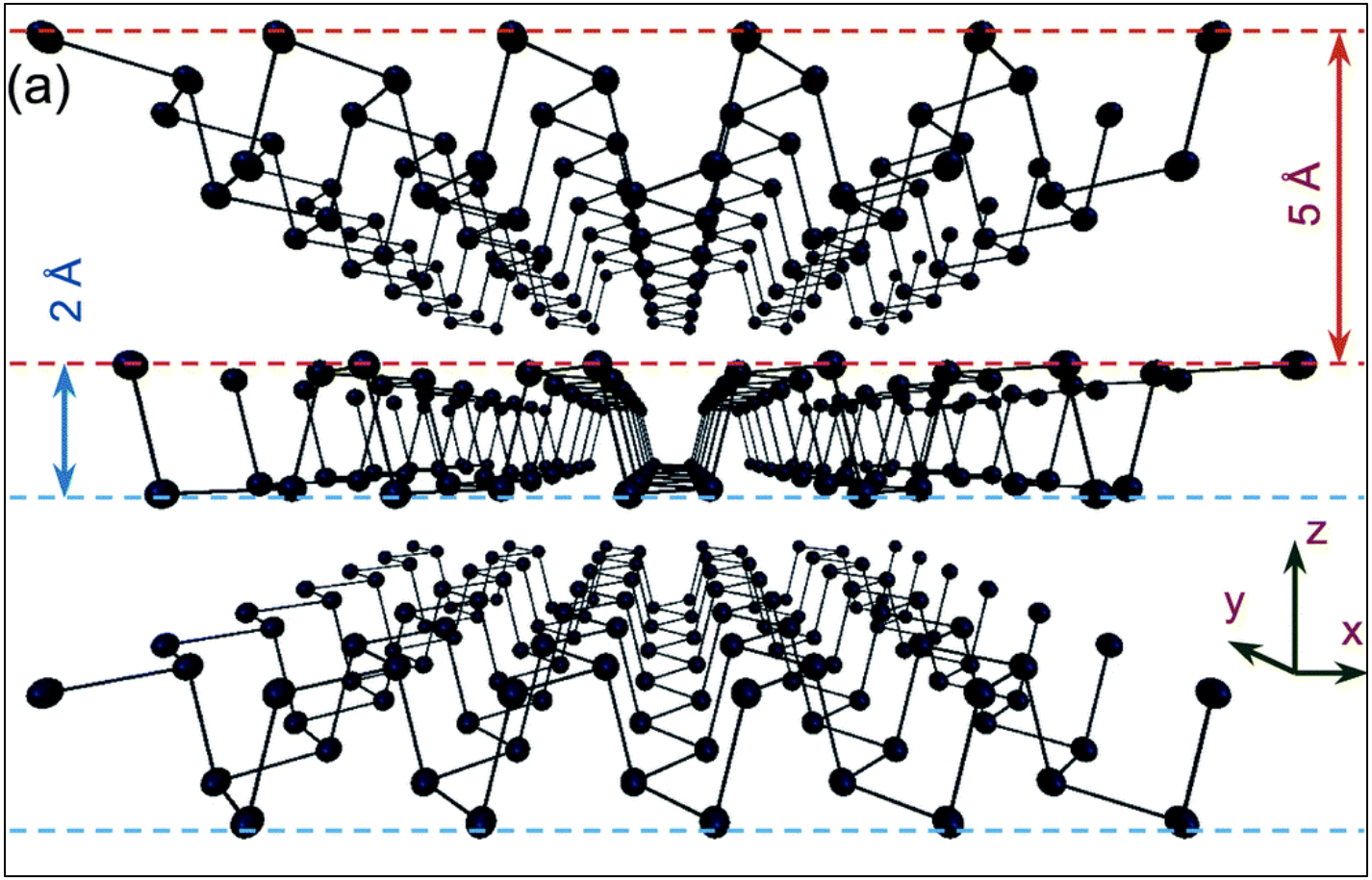
**Xi Ling[a], Han Wang[b,1], Shengxi Huang[a], Fengnian Xia[c], and Mildred S. Dresselhaus[a,d,1]**

*[a]Department of Electrical Engineering and Computer Science and [d]Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139; [b]Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, CA 90089; and [c]Department of Electrical Engineering, Yale University, New Haven, CT 06511*

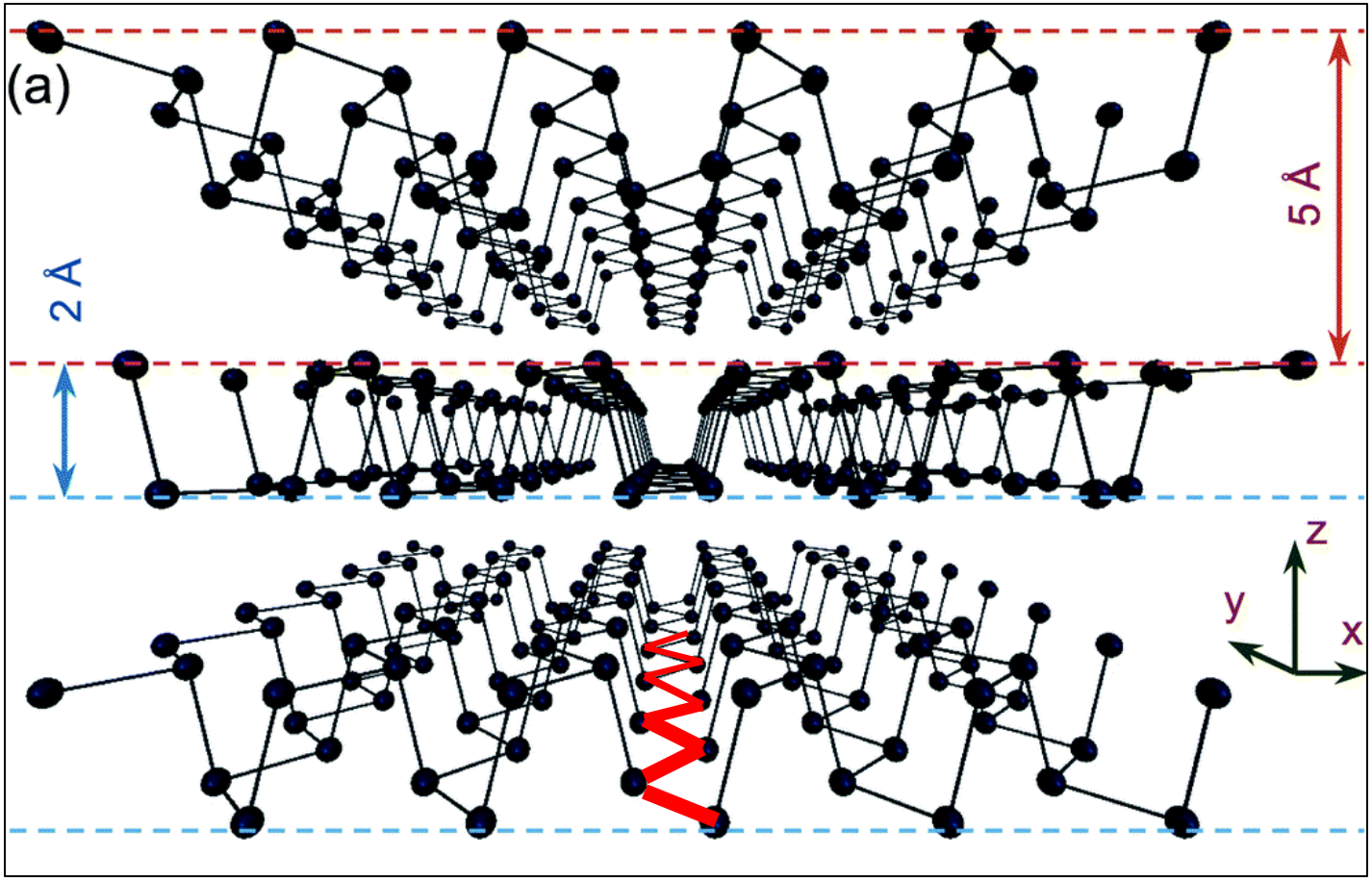



www.pnas.org/cgi/doi/10.1073/pnas.1416581112 PNAS | April 14, 2015 | vol. 112 | no. 15 | 4523–4530

# Crystal structure of BP

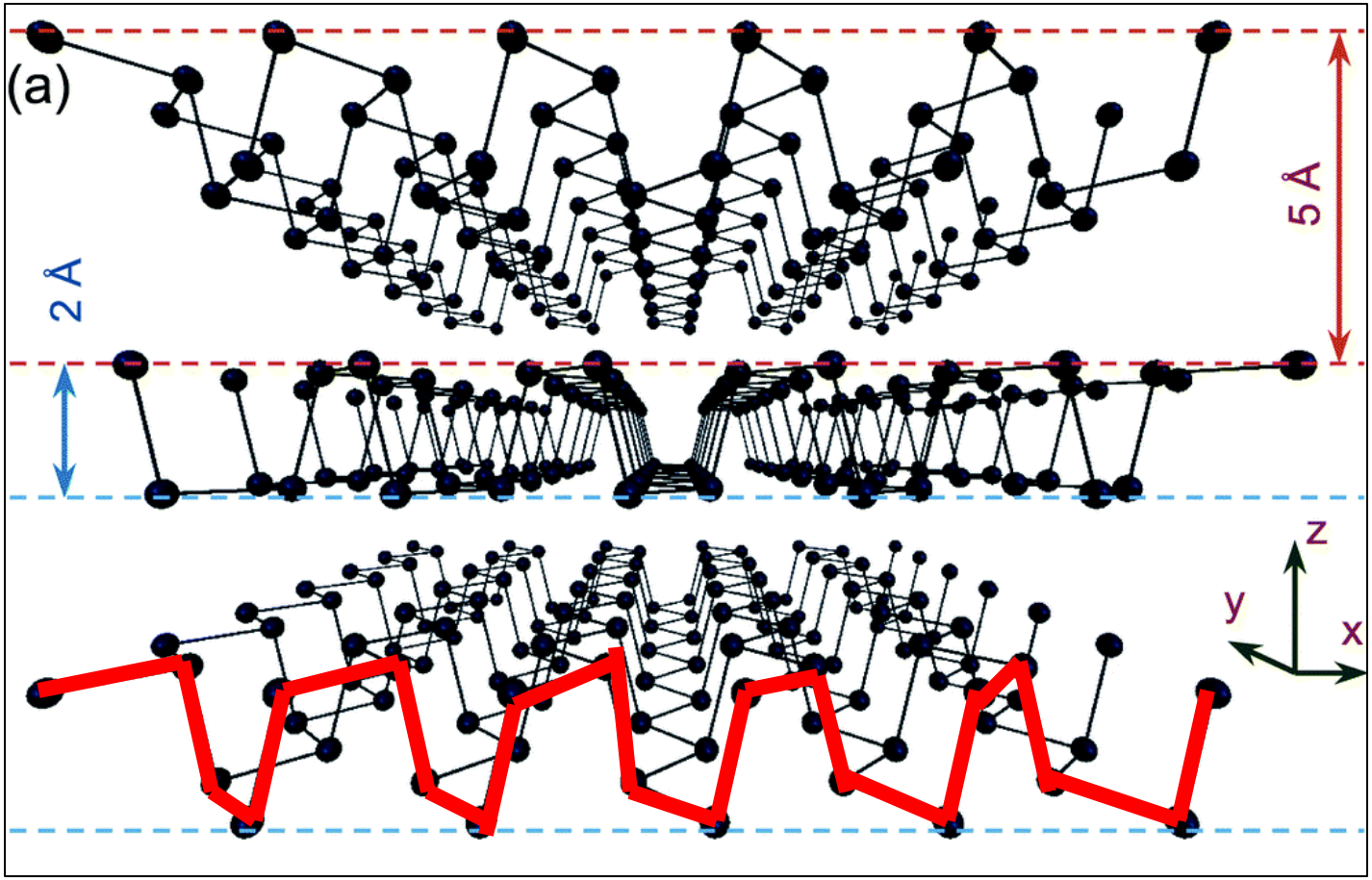


# Anisotropic structure of BP




**Zig-zag (y-axis)**

# Anisotropic structure of BP




**Armchair (x-axis)**

# 2D-BP: highlights

✓Semiconductor, with a thickness-dipendent direct band gap (∼ 2 - 0.3 eV)

✓Good carrier mobility (∼1000 $cm^2 V^{-1} s^{-1}$ at room temperature)

✓High surface area

✓Higher chemical reactivity compared to other 2D-materials stable in free standing form

- Careful handling in inert environments/encapsulation/passivation
- Controllable/mild chemical functionalization (not possible for graphene)

# 2D-BP: highlights

✓Semiconductor, with a thickness-dipendent direct band gap (~ 2 - 0.3 eV)

**-Communication**
**-Light vision goggles**
**-Thermal infrared imaging**
**-Astronomy**
**-Medicine**
**-Document security systems**
**-DVD players**
**-Display**
**-LED, OLED**

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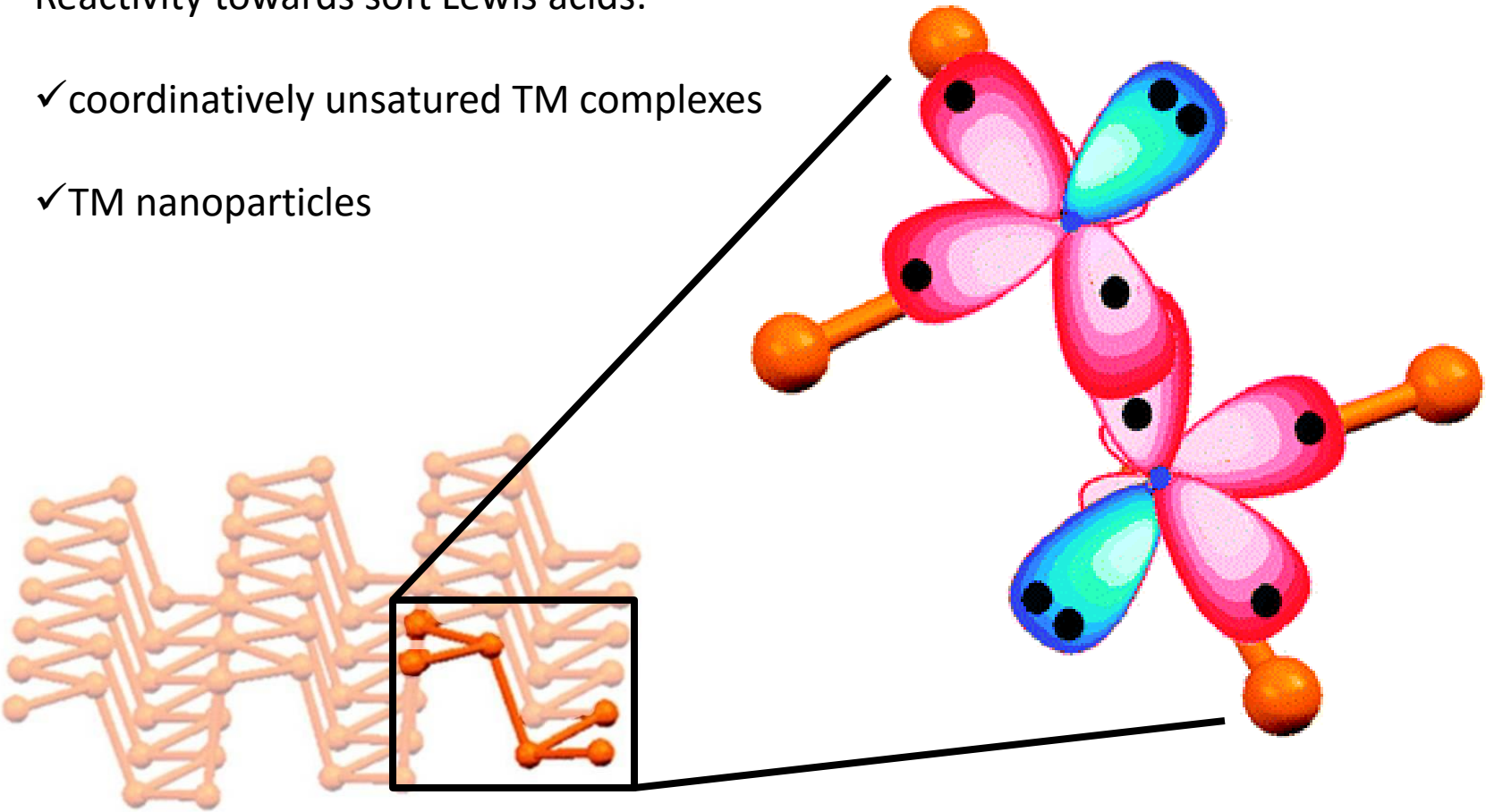
# 2D-BP functionalization: a coordination approach?

Reactivity towards soft Lewis acids:

✓coordinatively unsatured TM complexes

✓TM nanoparticles



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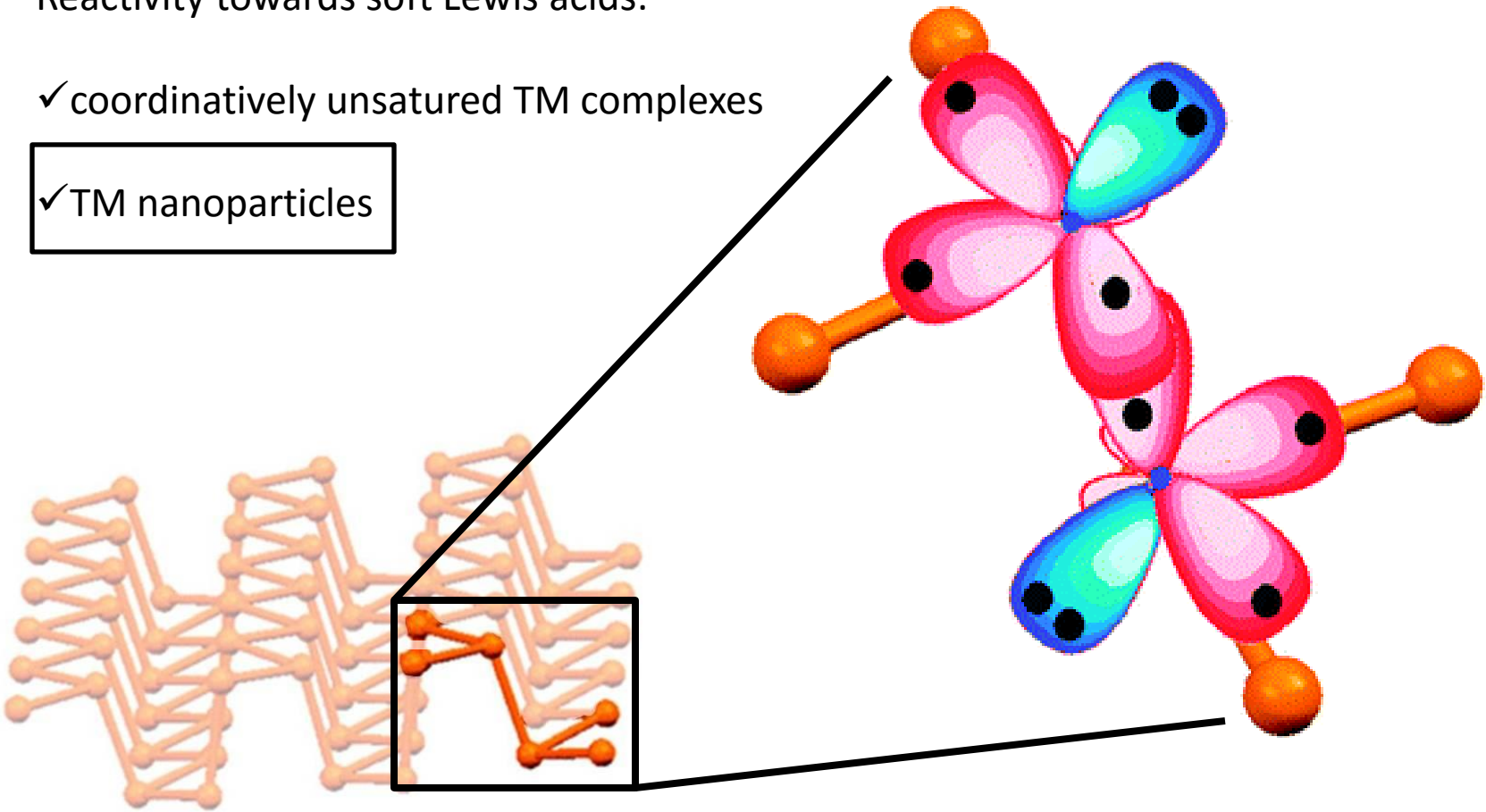

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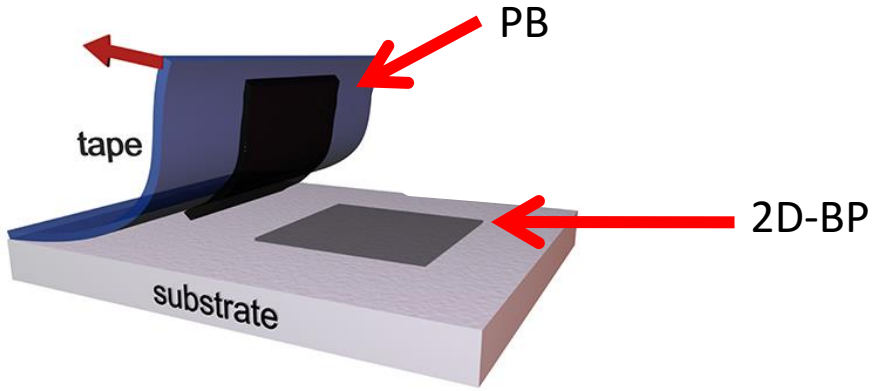
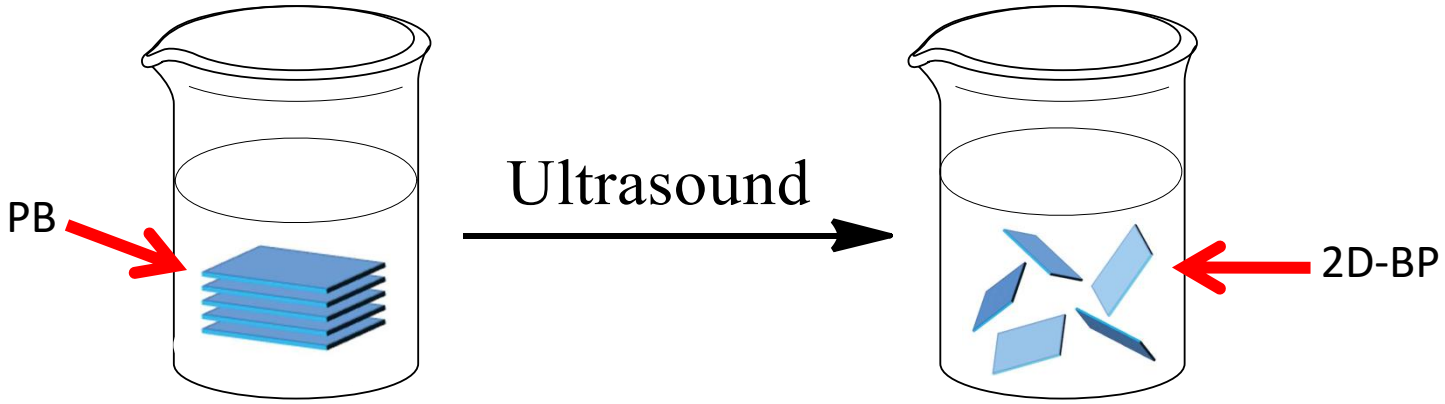
# Preparation of 2D-BP

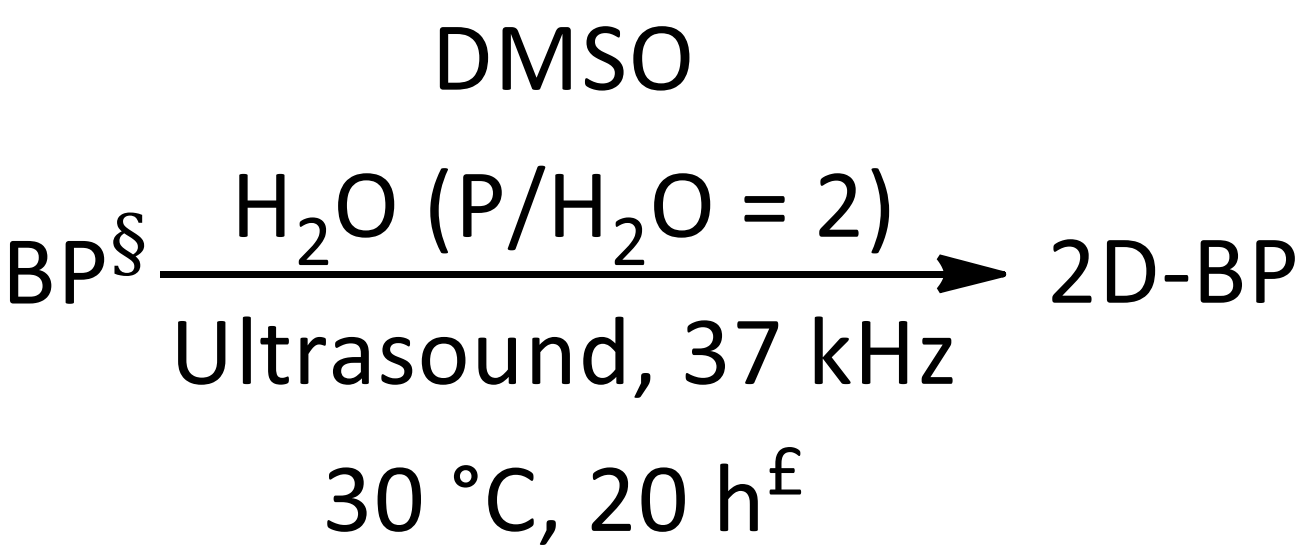
✓**Mechanical exfoliation**




✓**Liquid phase exfoliation**



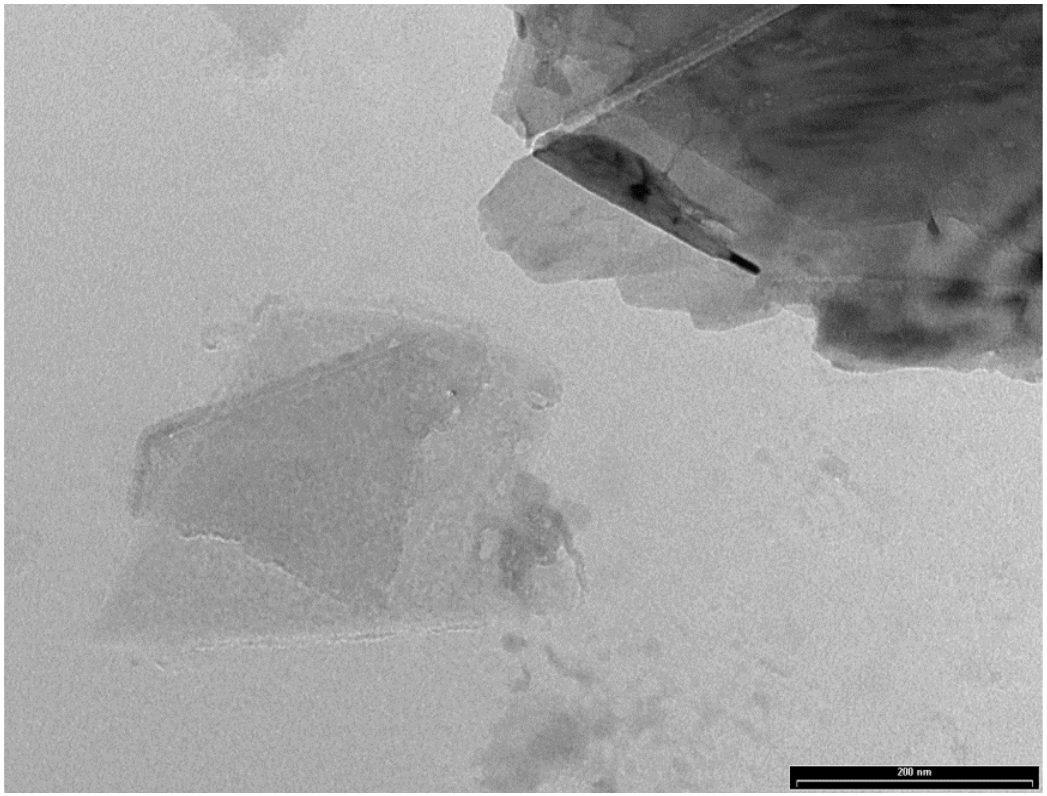
## Preparation of 2D-BP in our lab




§Prepared as described in: T. Nilges, M. Kersting, T. Pfeifer, *J. Solid State Chem*. **2008**, *181*, 1707-1711.

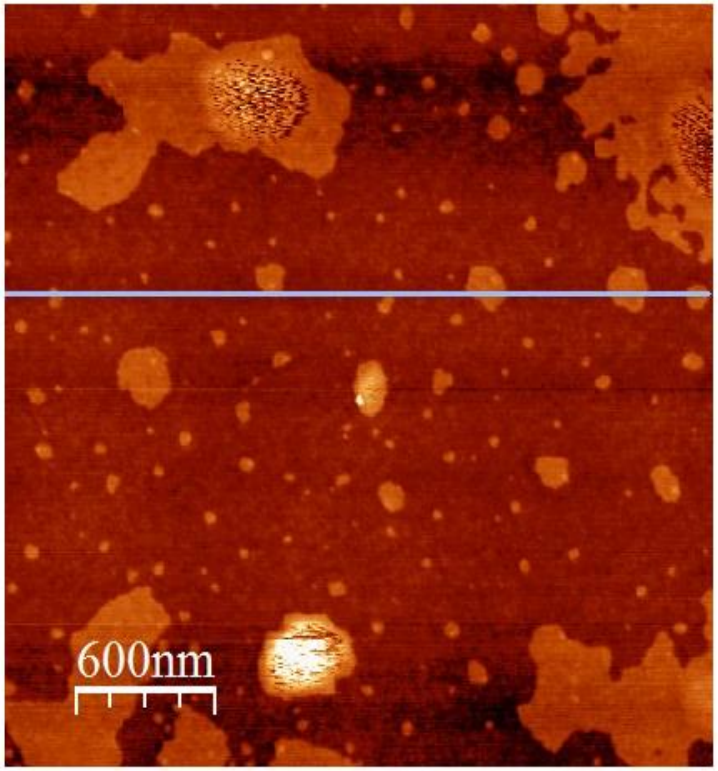
£Exfoliation conditions as described in: M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv, Mat. Interfaces* **2015**, 3, 1500441.

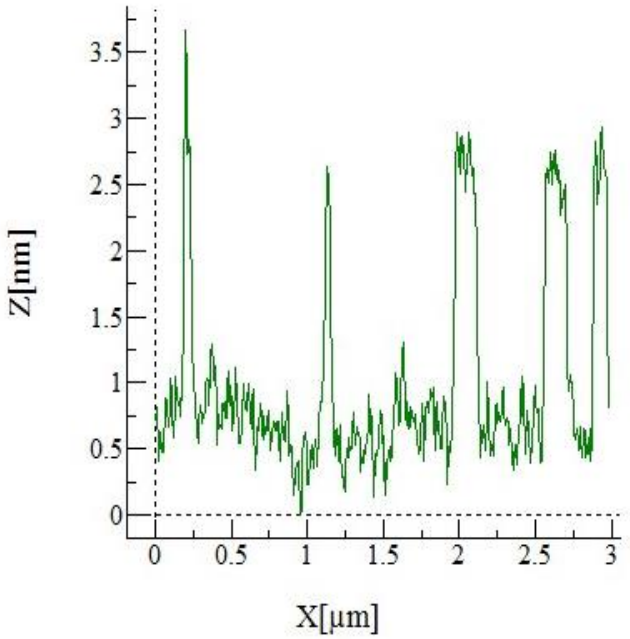
# Bright-field TEM image of 2D-BP




M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv, Mat. Interfaces* **2015**, 3, 1500441.

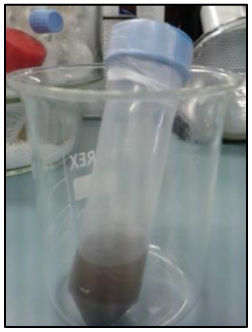
# AFM analysis of 2D-black phosphorus



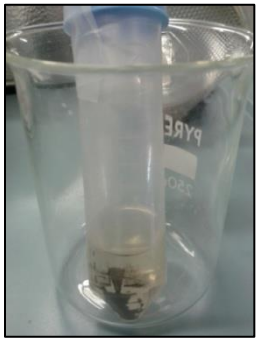



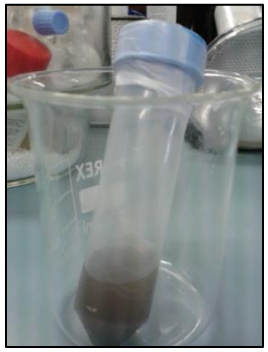

M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv, Mat. Interfaces* **2015**, 3, 1500441.

# Extraction of 2D-BP from the DMSO of exfoliation



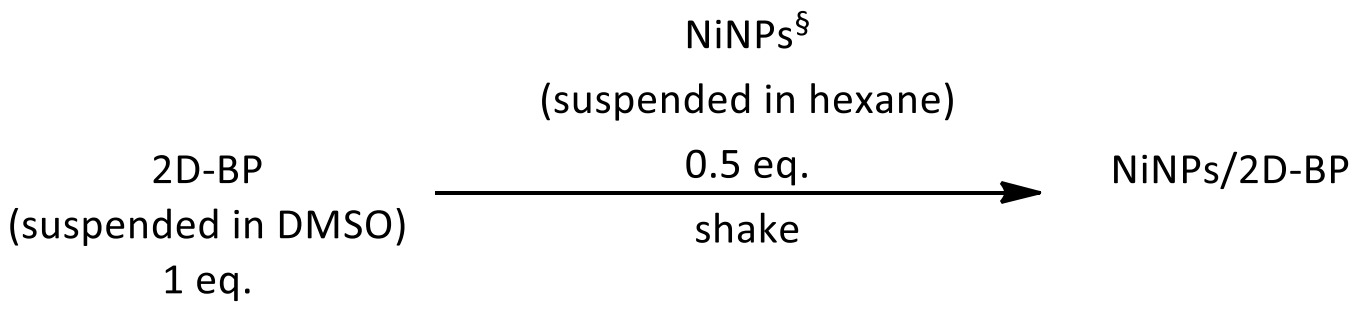
Acetone
Centrifugation (6000 rpm x 2)

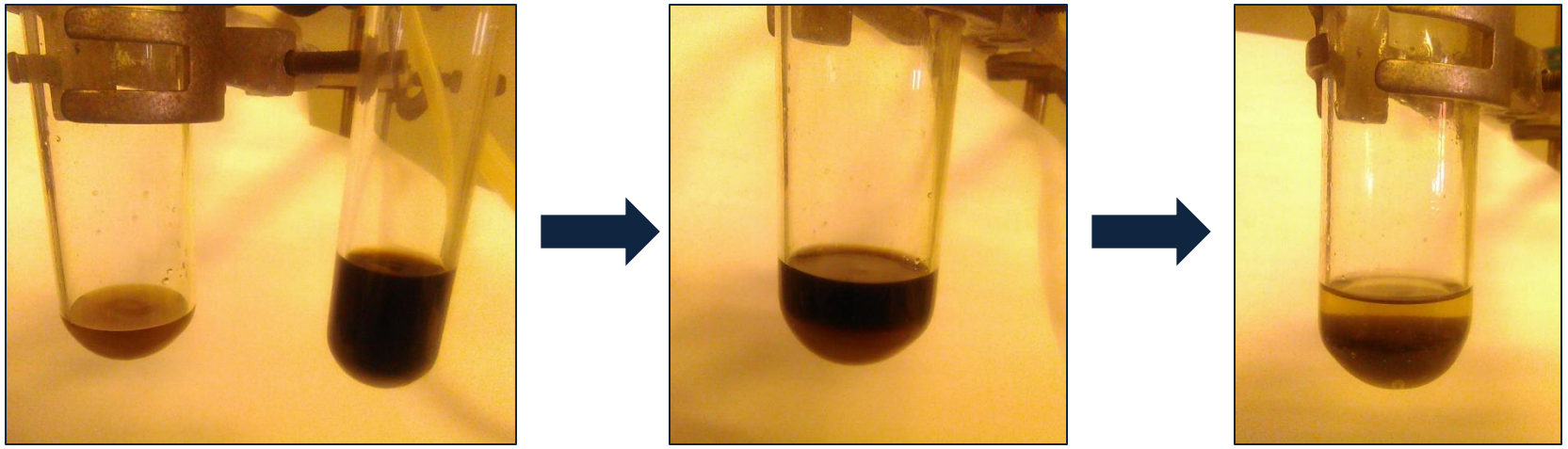




Solvent, Ultrasound 37 kHz, 30''

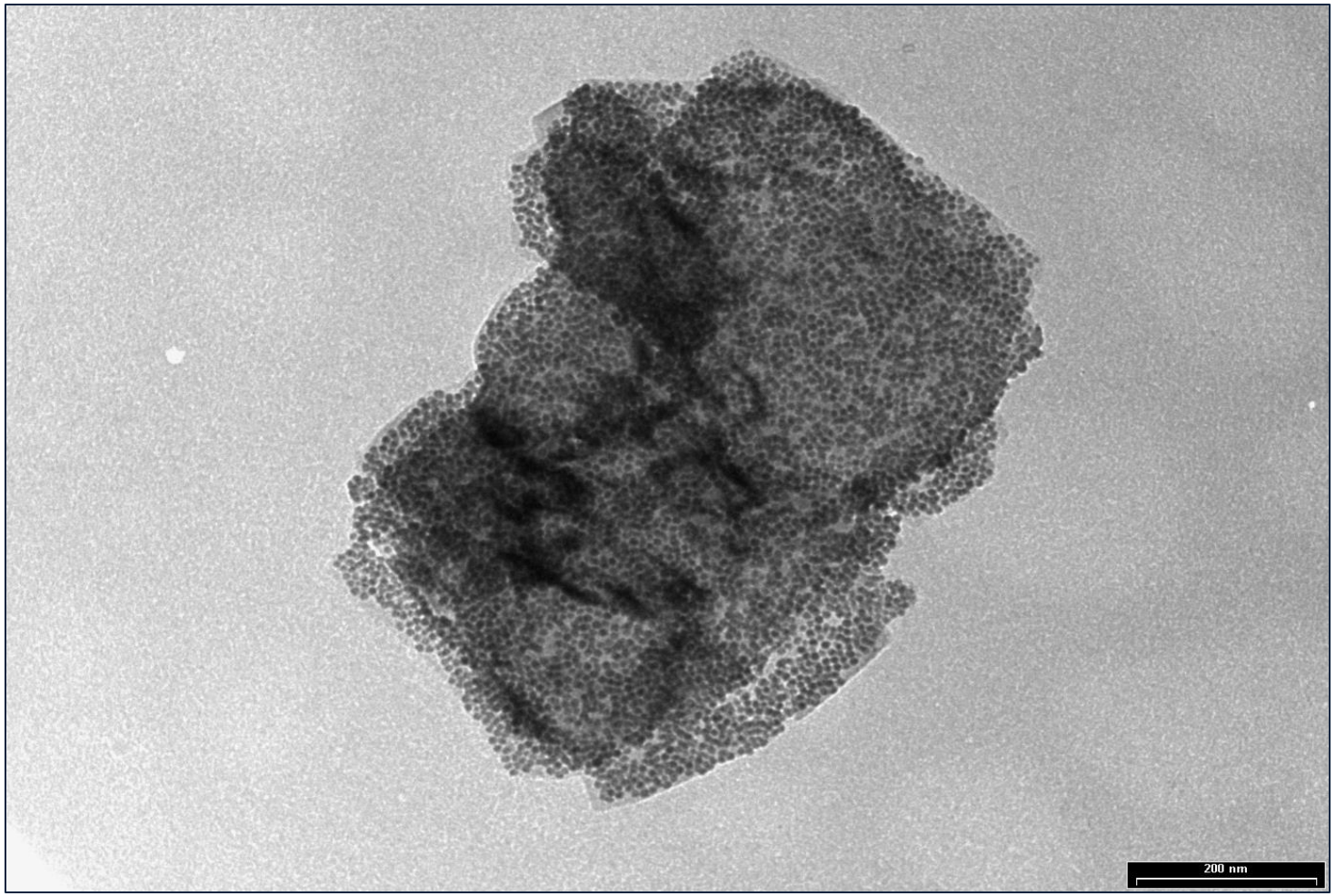
# Preparation of NiNPs/2D-BP



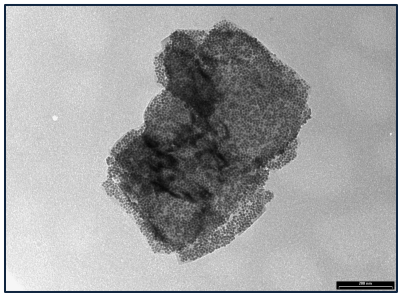



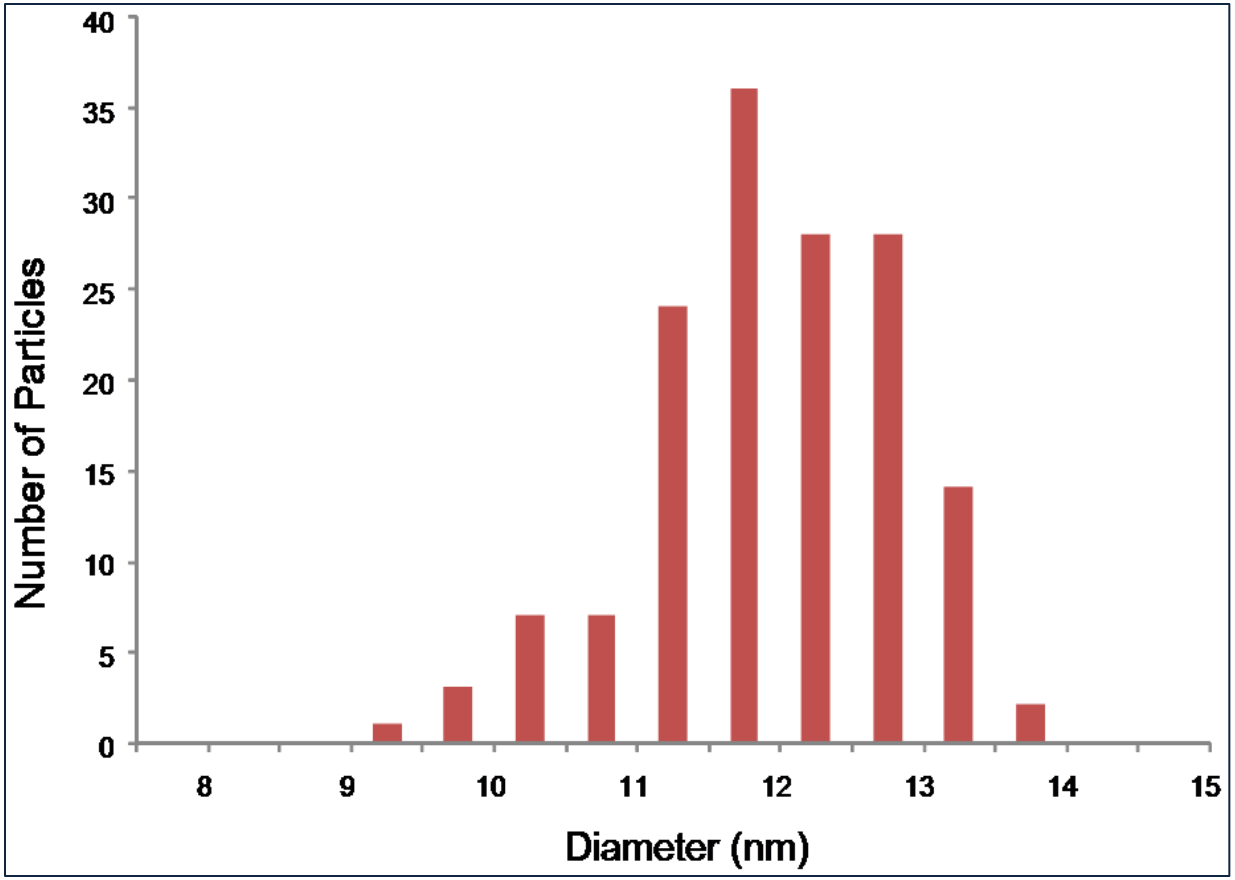
§ Prepared as described in: N. Mezailles *et al. Nano Today* **2012**, 7, 21.

# TEM image of NiNPs/2D-BP

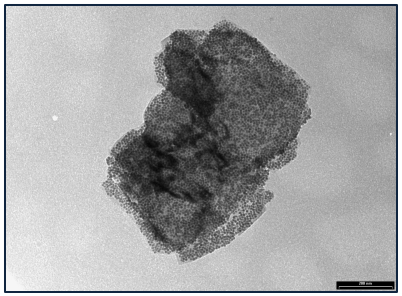


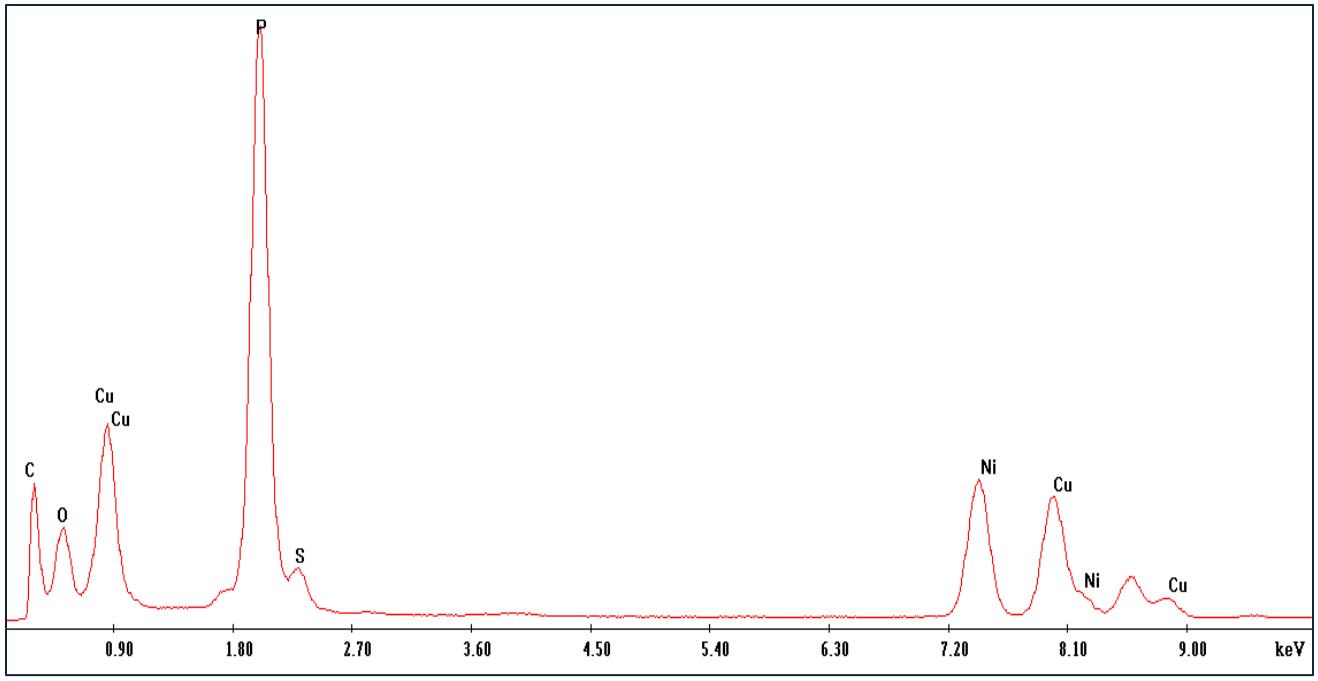
# Size distribution of NiNPs anchored on 2D-BP



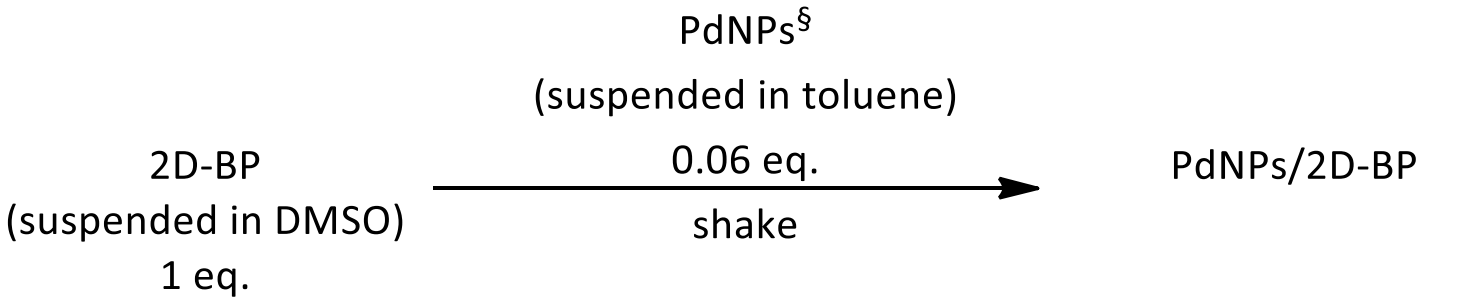


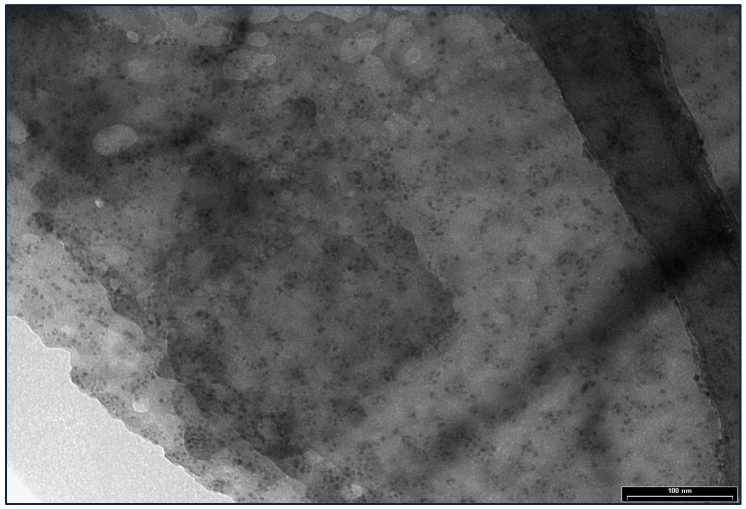
# EDX analysis of NiNPs/2D-BP

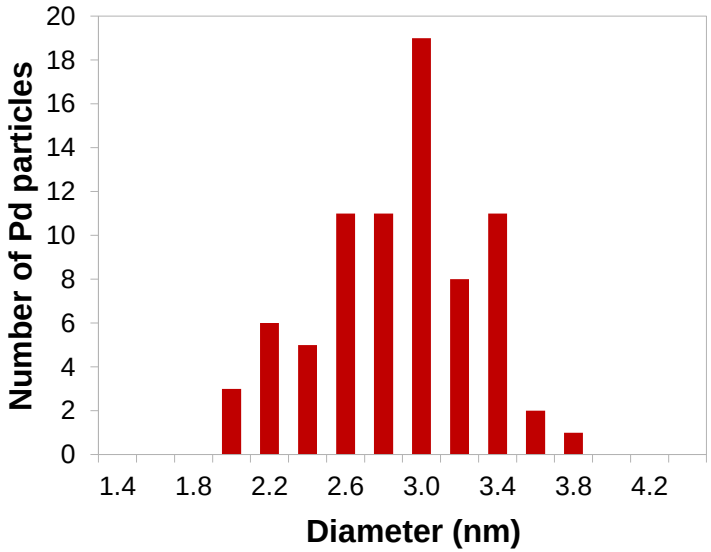




# Preparation and TEM analysis of PdNPs/2D-BP






§Prepared as described in: Coronado *et al. J. Mater. Chem*. **2008**, *18*, 5682.

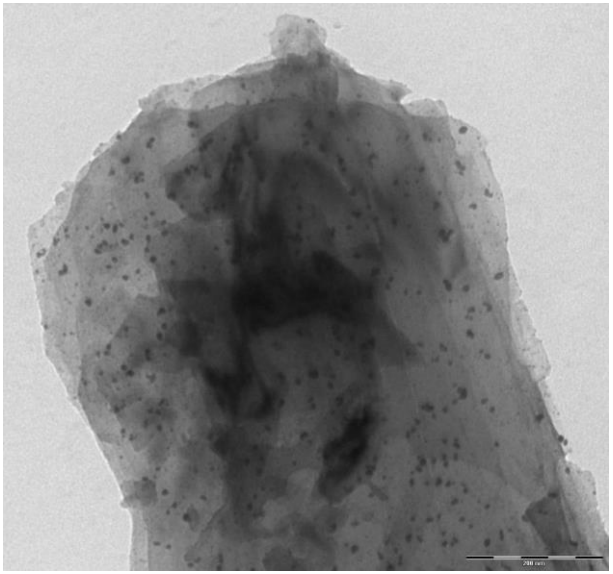
# Preparation and TEM analysis of AuNPs/2D-BP

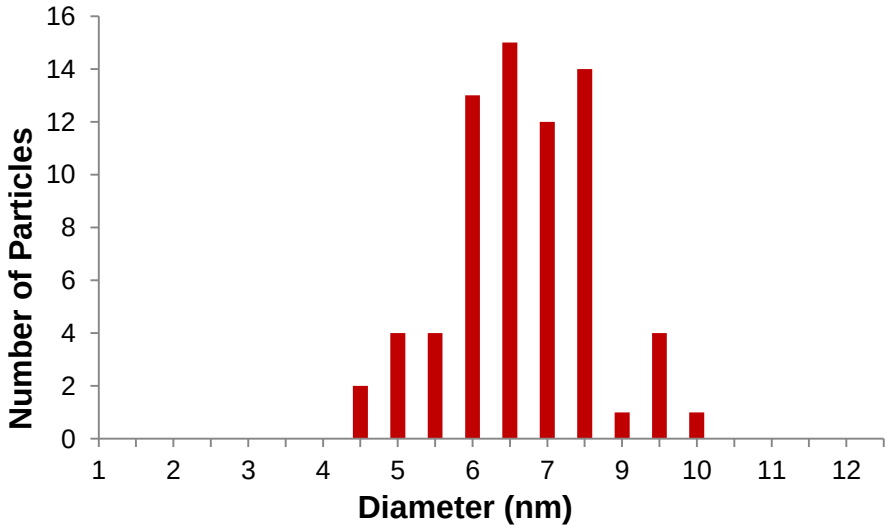
2D-BP
(suspended in DMSO)
1 eq.

AuNPs[§]
(suspended in water)
0.2 eq.
shake

→

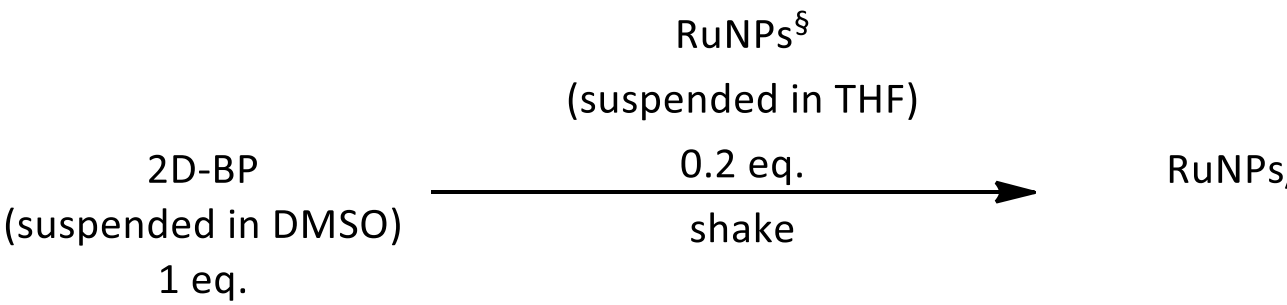
AuNPs/2D-BP

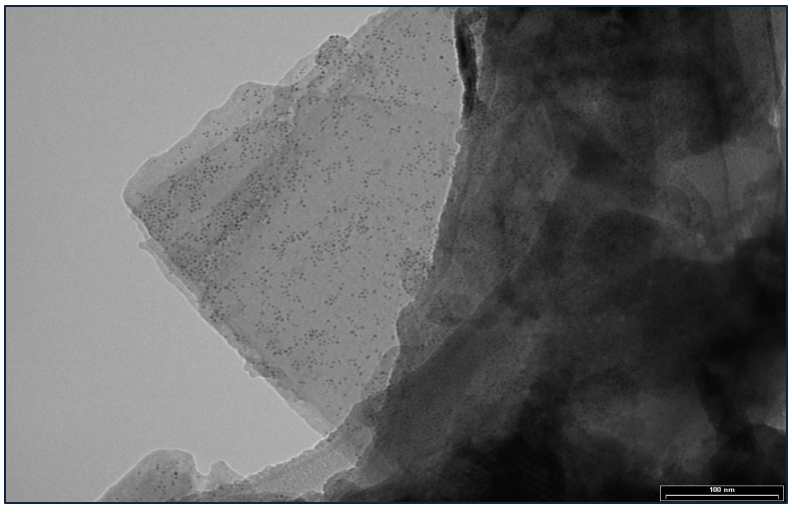


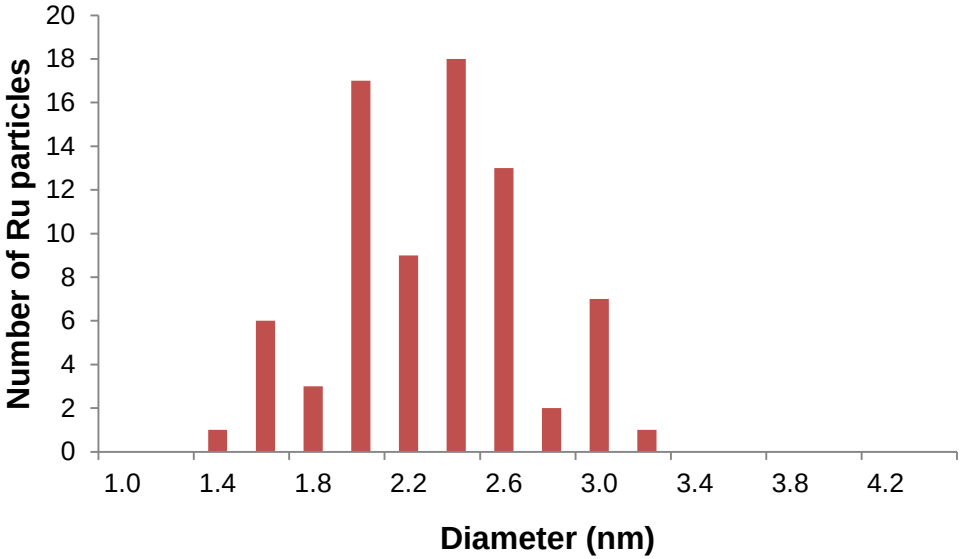



[§]Prepared as described in: Yang, J. Dong, Z. Yao, C. Shen, X. Shi, Y. Tian, S. Lin, X. Zhang, *Sci. Rep*. **2014**, 4, 4501.

# Preparation and TEM analysis of RuNPs/2D-BP






§Prepared as described in: H. Can, Ö. Metin, *Appl. Cat. B-Environ*. **2012**, *125*, 304-310.

# Outline

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- 2D-black phosphorus (BP): a new wonder material
- 2D-BP as novel support for metal nanoparticles

**Experimental section**

- Preparation and characterization of 2D-BP functionalized with TM nanoparticles
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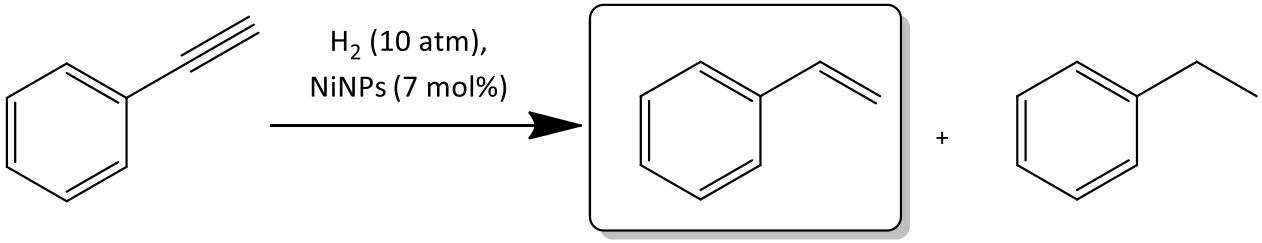
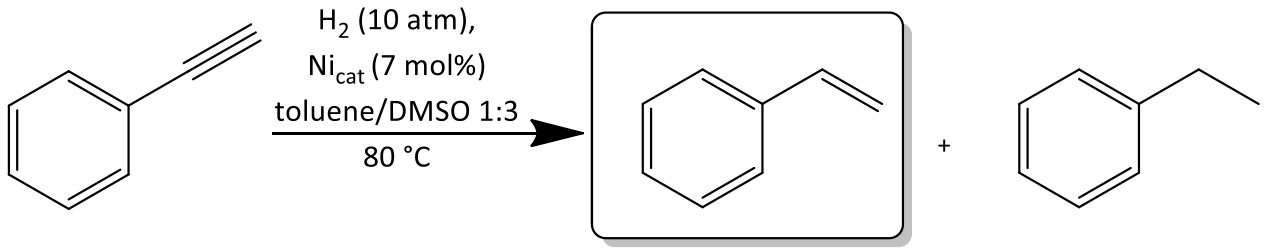
# Phenylacetylene hydrogenation catalyzed by NiNPs




| Solvent | Temperature (°C) | Time (h) | Conv. (%)* | Selectivity toward styrene(%)* |
|---|---|---|---|---|
| toluene | 80 | 2 | 2.2 | 51.1 |
| toluene/DMSO 1:3 | 80 | 1 | 77.9 | 94.3 |
| toluene/DMSO 1:3 | 80 | 2 | 99 | 96.1 |

* Evaluated by GC

# Phenylacetylene hydrogenation catalyzed by NiNPs(TOP)/2D-BP




**Nicat = NiNPs**

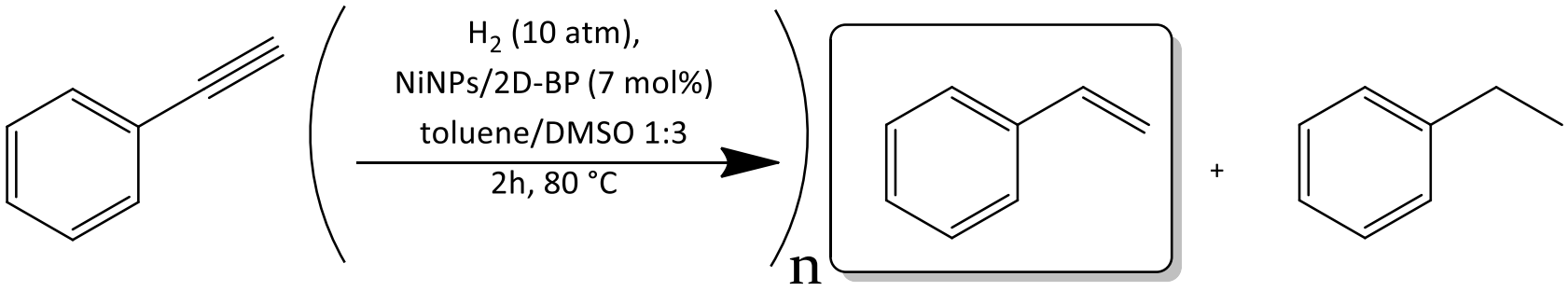
| Time (h) | Conv. (%)* | Selectivity toward styrene(%)* |
|---|---|---|
| 1 | 77.9 | 94.3 |
| 2 | 99 | 96.1 |

**Nicat = NiNPs/2D-BP (P:Ni = 2)**

| Time (h) | Conv. (%)* | Selectivity toward styrene(%)* |
|---|---|---|
| 1 | 45.4 | 94.3 |
| 2 | 96.2 | 94.9 |

* Evaluated by GC

# Recycling the catalyst NiNPs/2D-BP




| n | Conversion (%)* | Selectivity towards styrene(%)* |
|---|---|---|
| 1 | 96.2 | 94.9 |
| 2 | 91.9 | 94.7 |
| 3 | 86.9 | 95.1 |
| 4 | 73.2 | 95.2 |
| 5 | 66.6 | 95.6 |

$Catalyst was isolated by centrifugation (6000 rpm x 2 with acetone) before every recycling test

* Evaluated by GC

# Future work and perspectives

✓Evaluate the effective heterogeneity of the studied catalytic system NiNPs/2D-BP (hot filtration tests, leaching tests…) and run a comparison of 2D-BP with other 2D-supports for metal nanoparticles (graphene, carbon nanotubes…).

✓Explore the catalytic activity of the other nanocomposites, RuNPs/2D-BP, PdNPs/2D-BP and AuNPs/2D-BP in several reactions.

✓Clarify the nature and strenght of the interactions between TM nanoparticles and 2D-BP, using appropriate instrumental techniques (Raman, XPS spectroscopy ...).

✓Study the chemical and physical properties of the nanocomposites, in order to expand their uses in other fields (e. g. microelectronics, optoelectronics).

# Outline

**Intro**

- 2D-black phosphorus (BP): a new wonder material
- 2D-BP as novel support for metal nanoparticles

**Experimental section**

- Preparation and characterization of 2D-BP functionalized with TM nanoparticles
- Preliminary study on phenylacetylene hydrogenation catalyzed by NiNPs/2D-BP

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