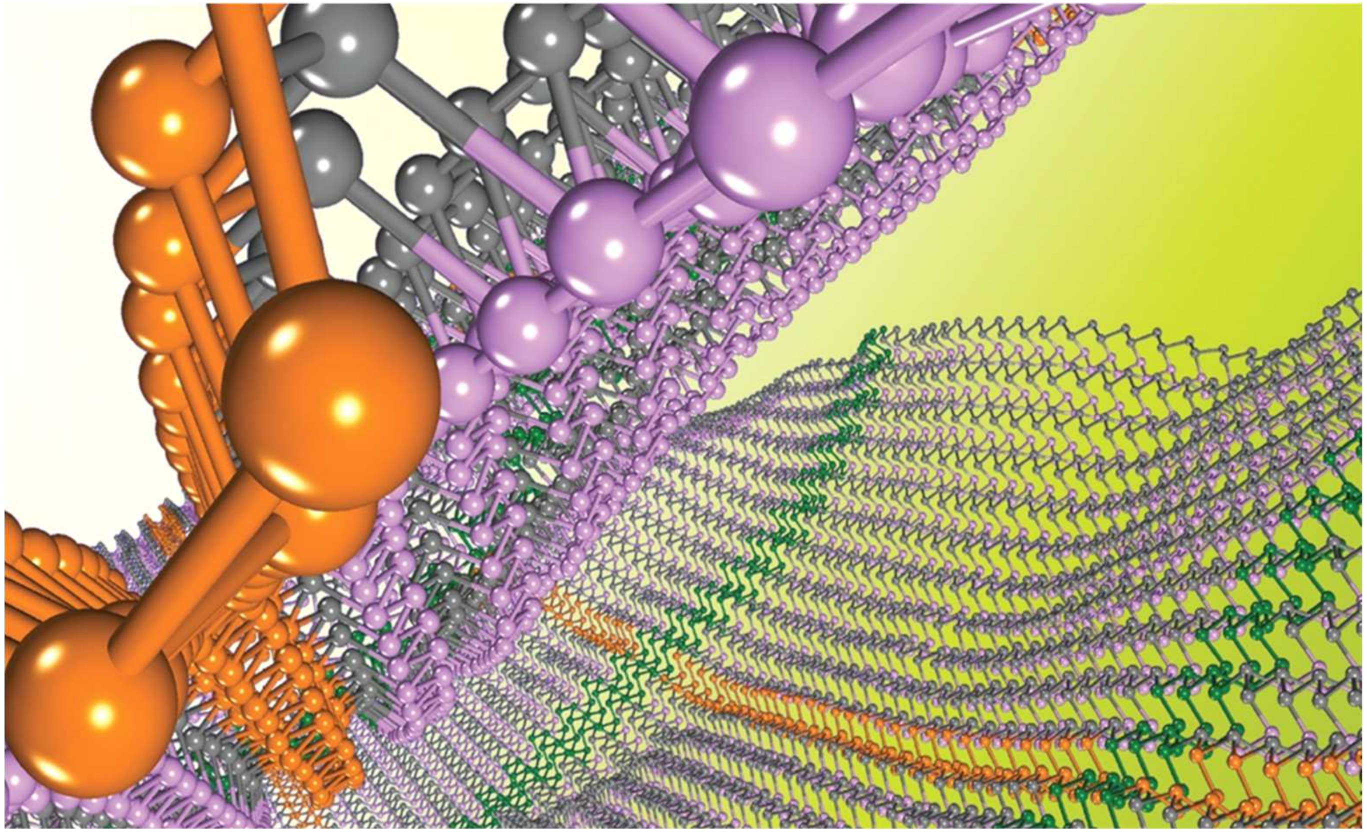
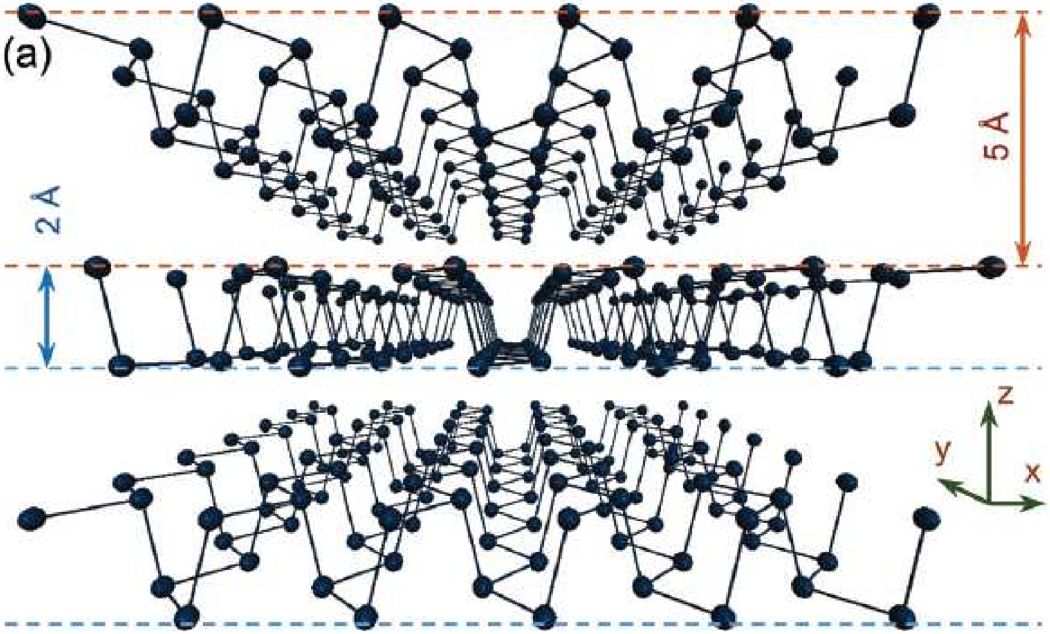
FEW-LAYER BLACK PHOSPHORUS AS NOVEL SUPPORT FOR METAL NANOPARTICLES

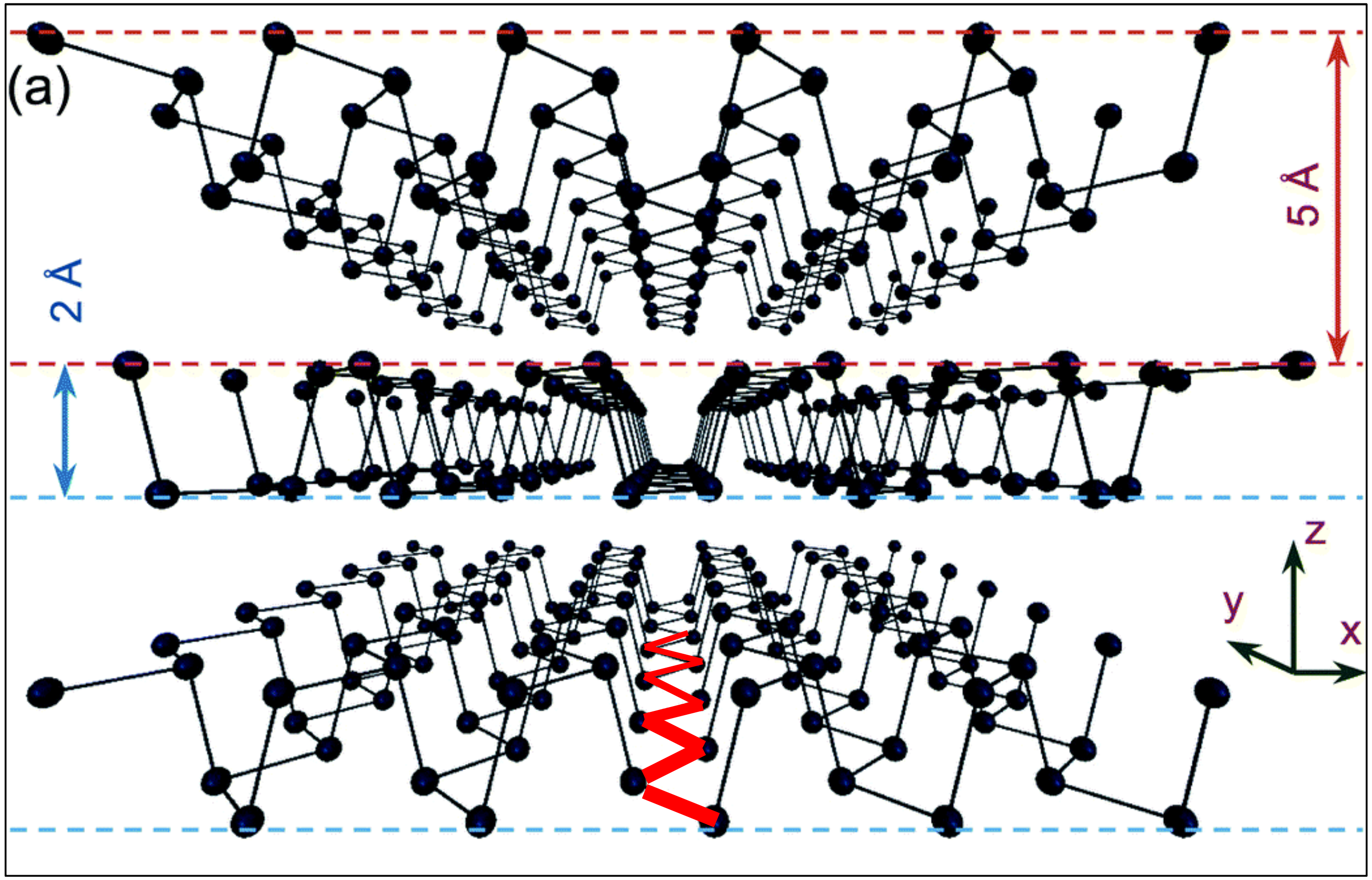
Maria Caporali
CNR ICCOM, Florence (IT)



ICCOM
ISTITUTO DI CHIMICA DEI COMPOSTI ORGANOMETALLICI

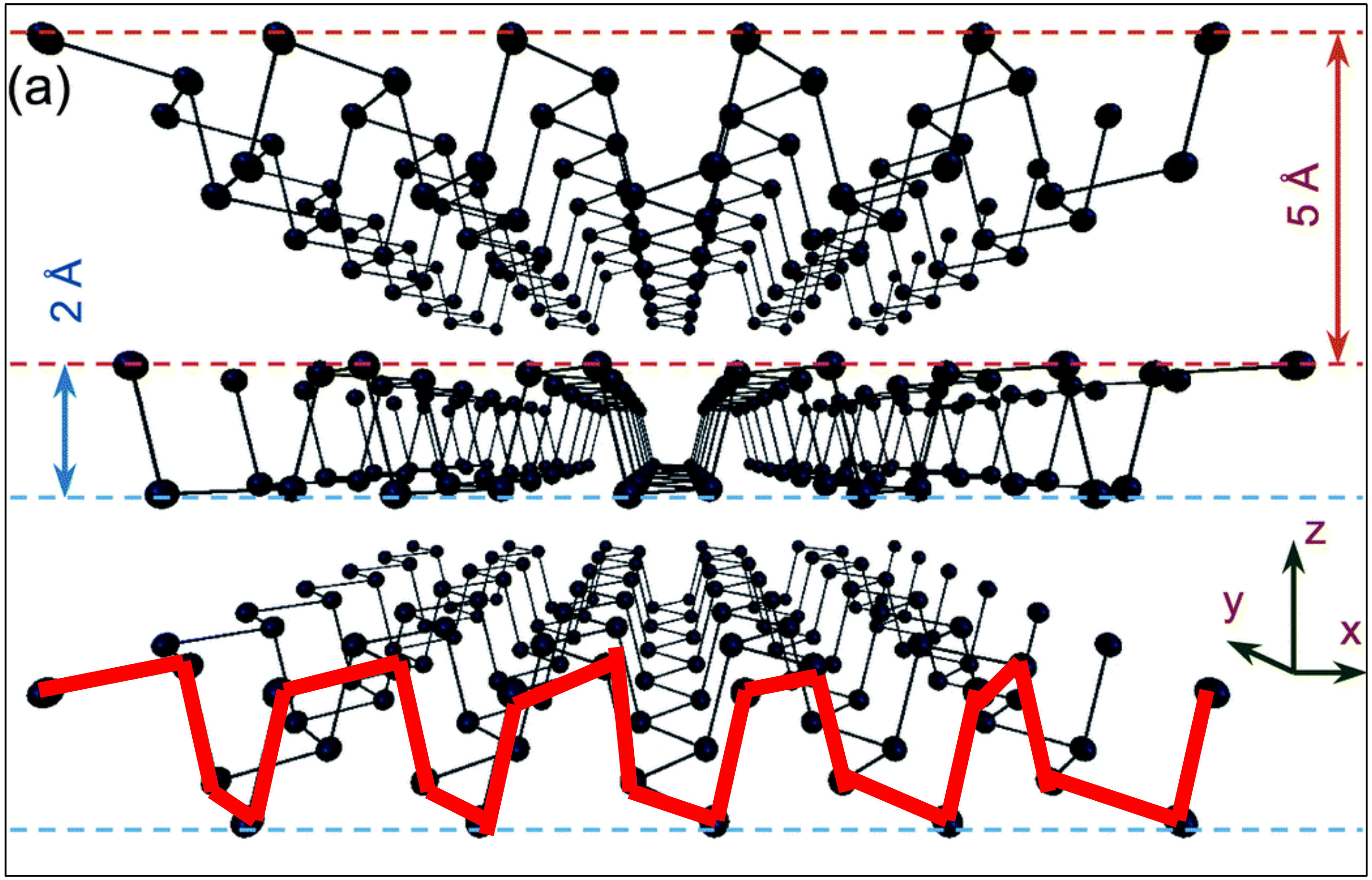

(a)
5 Å
2 Å
z
y
x

Anisotropic structure of BP



Zig-zag (y-axis)

Anisotropic structure of BP

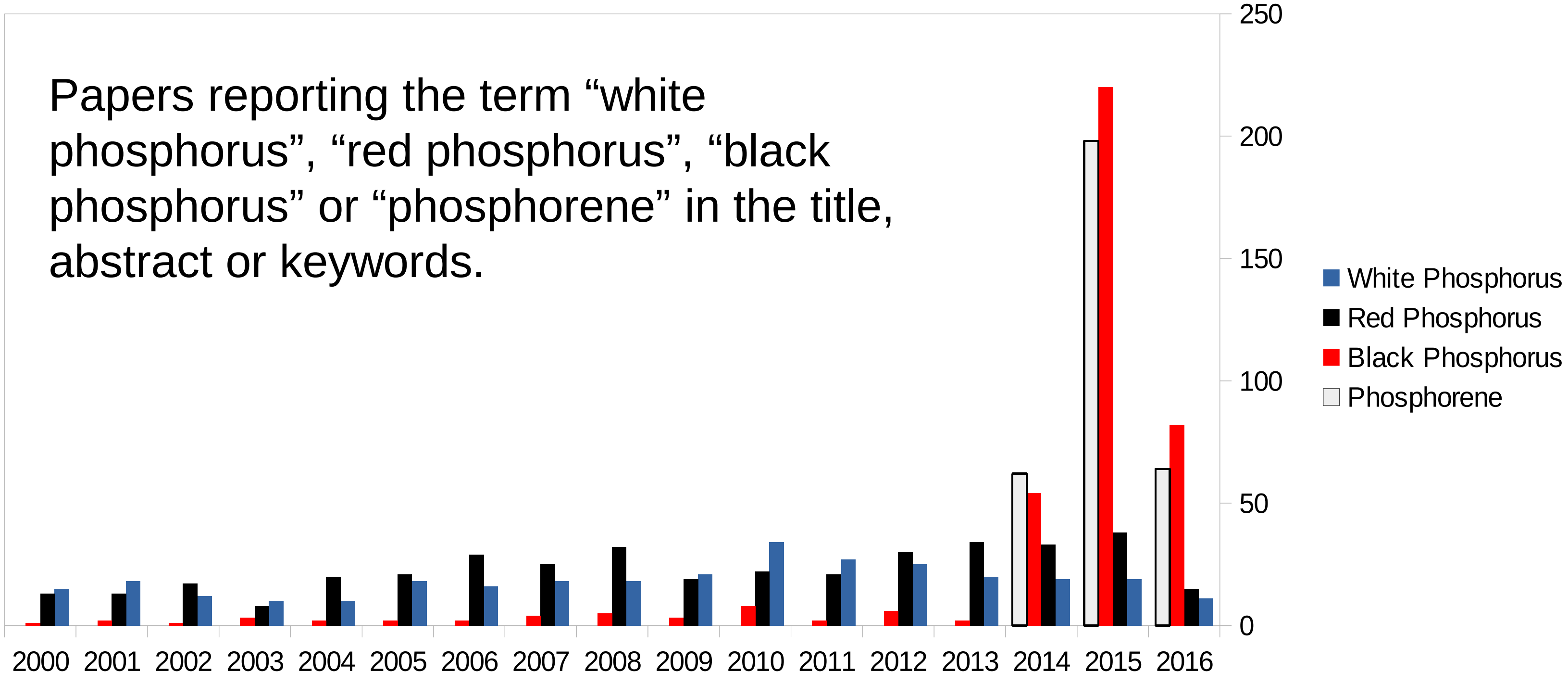


Armchair (x-axis)

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



Papers reporting the term “white phosphorus”, “red phosphorus”, “black phosphorus” or “phosphorene” in the title, abstract or keywords.

PNAS | April 14, 2015 | vol. 112 | no. 15 | 4523–4530

Available online at www.sciencedirect.com

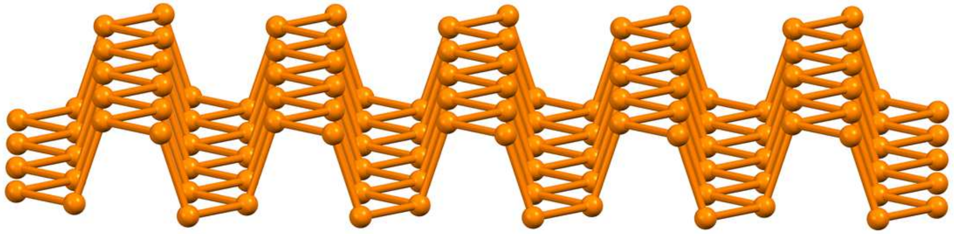
ScienceDirect

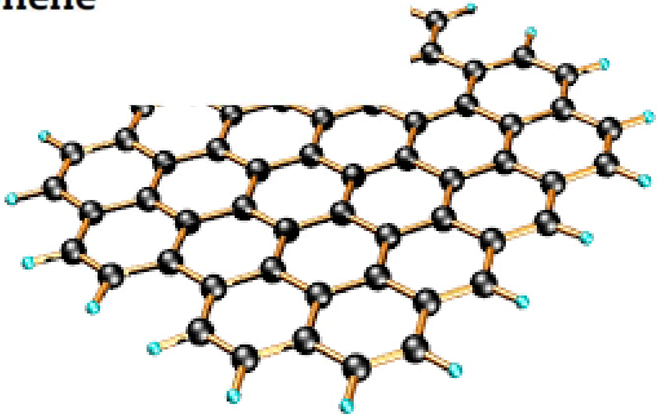
journal homepage: www.elsevier.com/locate/he

Review article

Phosphorene: A new competitor for graphene

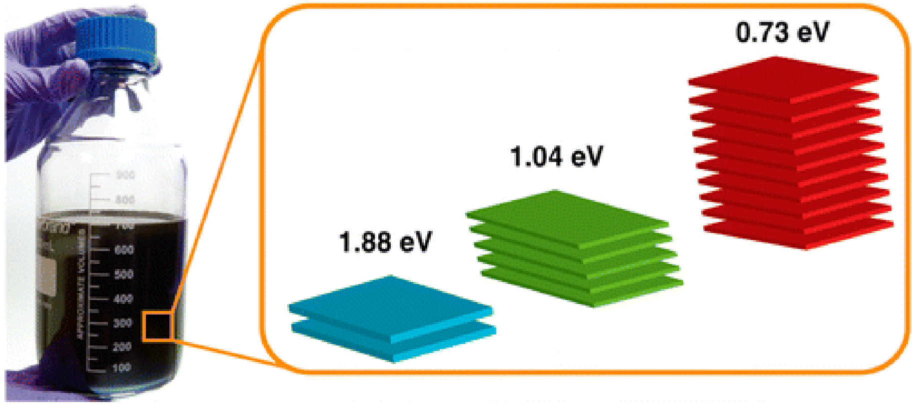
Samira Bagheri [a,*], *Negar Mansouri* [a], *Ermia Aghaie* [b]





Black P: 0.3 – 2.0 eV

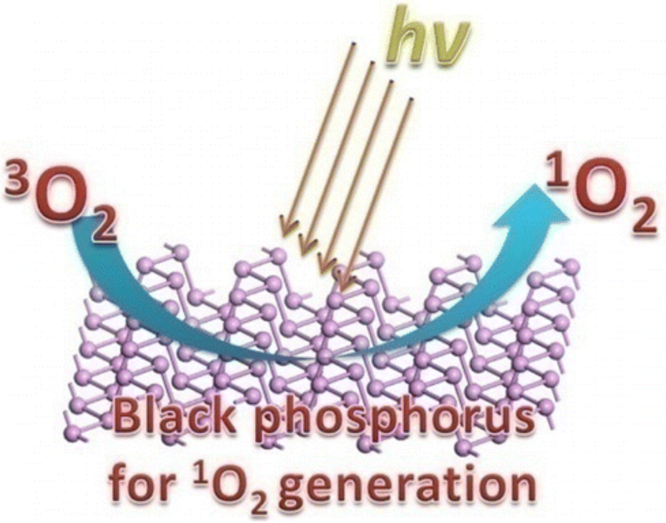
Graphene: zero-gap



✓Semiconductor, with a thickness-dipendent direct band gap (∼ 0.3-2.0 eV)

Ultrathin black P for efficient singlet oxygen production:

Application in catalysis
and photodynamic therapy



Xie et al. JACS **2015**, *137*,11376–11382

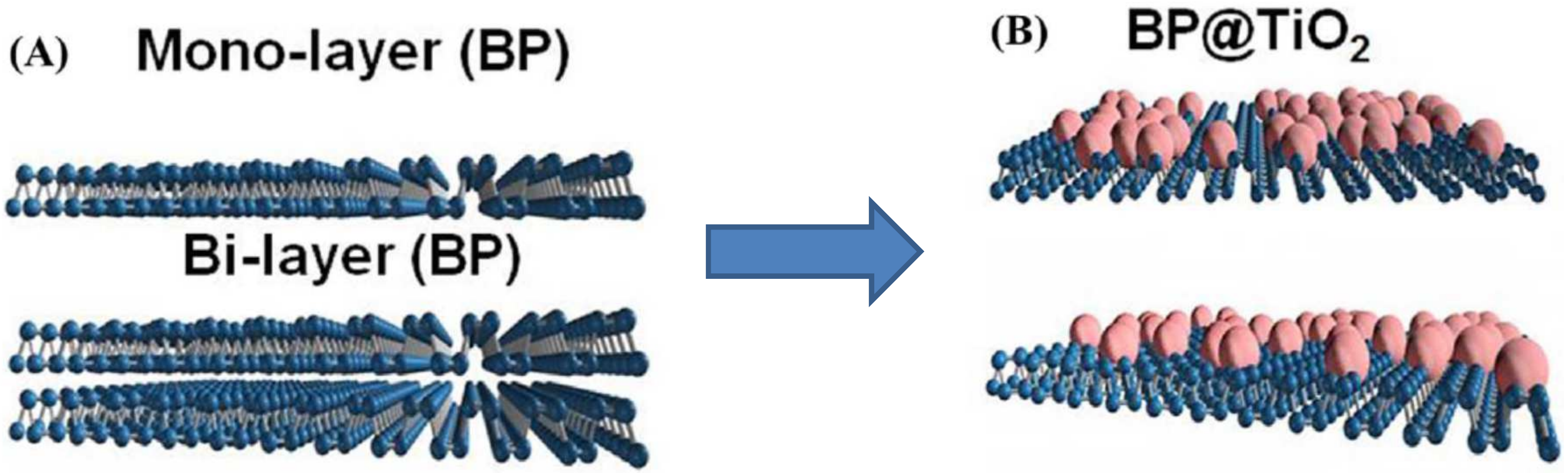
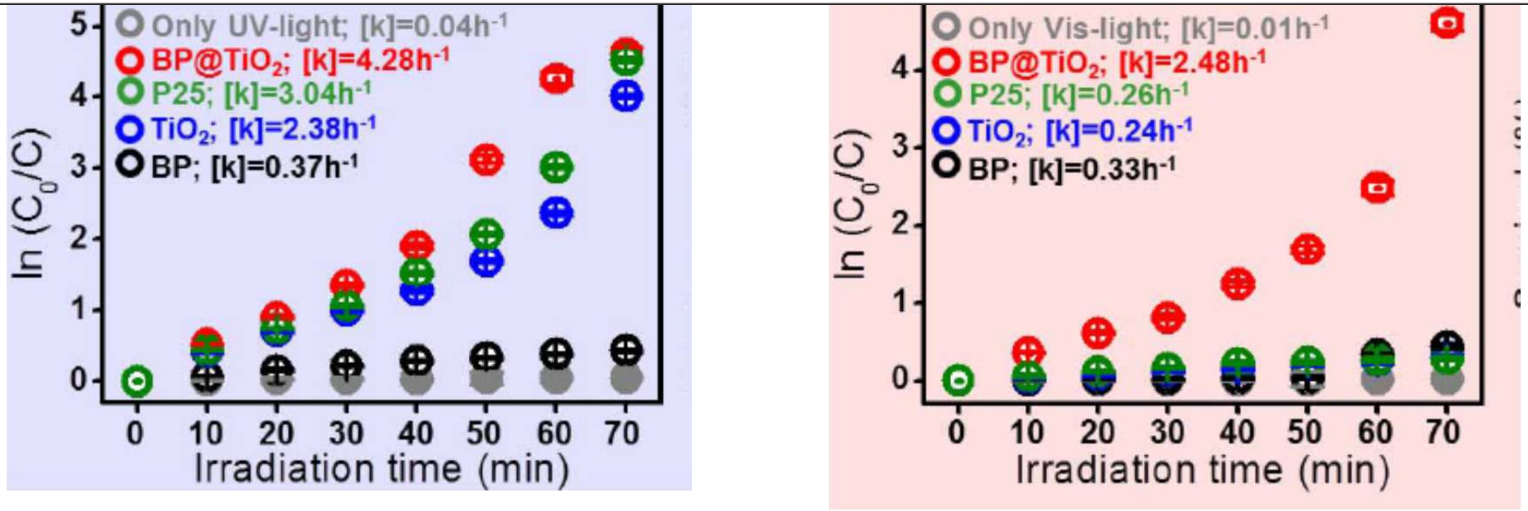


Figure 4 | **Photocatalytic performances.** Relative concentrations and apparent reaction rate constants of RB 5 and Rho B of BP@TiO$_2$ hybrid, P25, and few layered BP photocatalysts under UV- (A) and visible-light (B) irradiation, and antibacterial activities (C) and apparent reaction rate constants of *E. coli* and *S. aureus*.



Scientific Reports 2015, 5, 8691.

PROPERTIES OF FEW-LAYER BLACK PHOSPHORUS

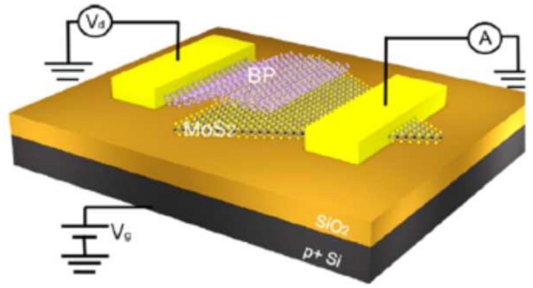
✓Semiconductor, with a thickness-dipendent direct band gap (∼ 2 -0.3 eV)

✓High surface area

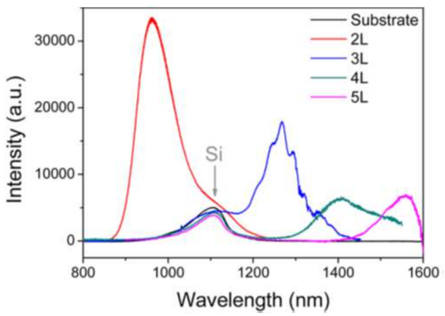
✓Higher chemical reactivity compared to other 2D-materials stable in free standing form

- Careful handling in inert environments/encapsulation/passivation

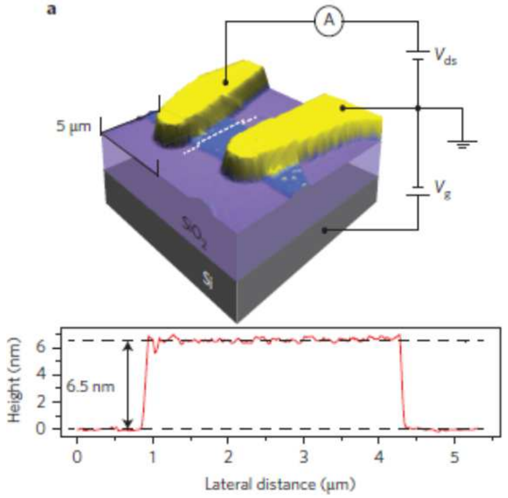
- Controllable/mild chemical functionalization (not possible for graphene)

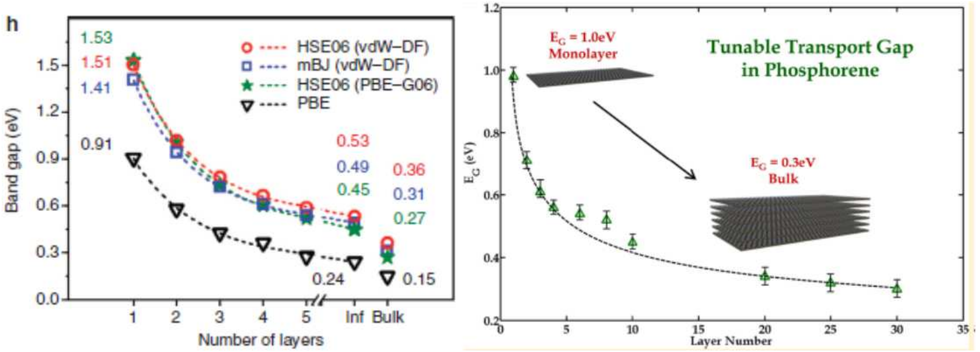


Heterojunction MoS_2-phosphorene

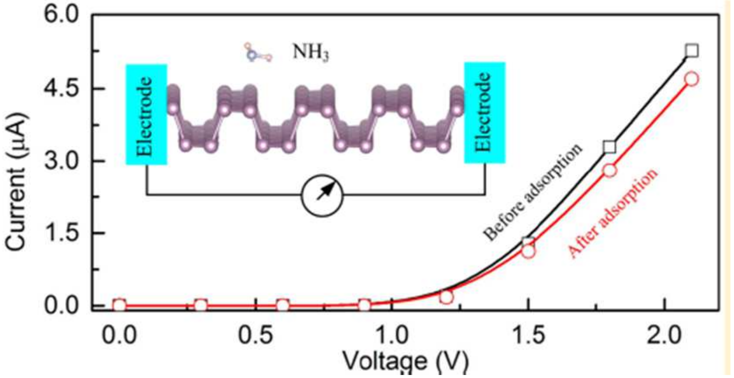


Photoluminiscence

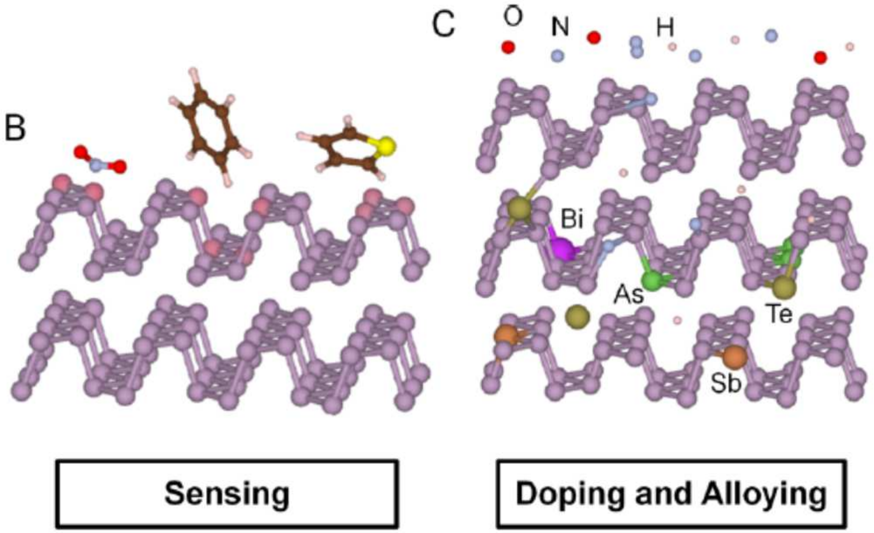


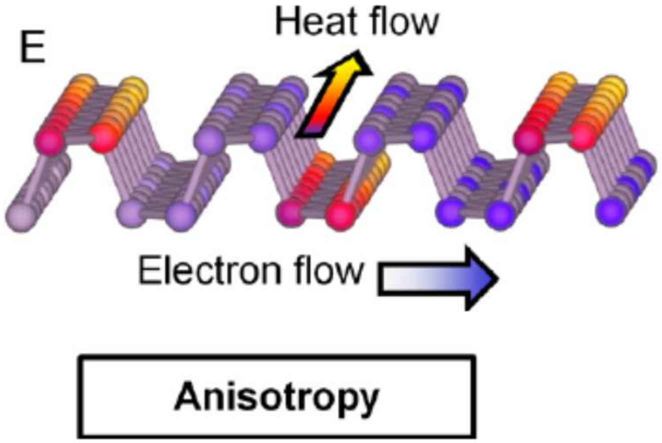


Theoretical and experimental study Band gap



Gas sensor (CO, CO_2, NH_3, NO, NO_2)


B
Sensing
C
O
N
H
Bi
As
Te
Sb
Doping and Alloying


E
Heat flow
Electron flow
Anisotropy

A phosphorene–graphene hybrid material as a high-capacity anode for sodium-ion batteries

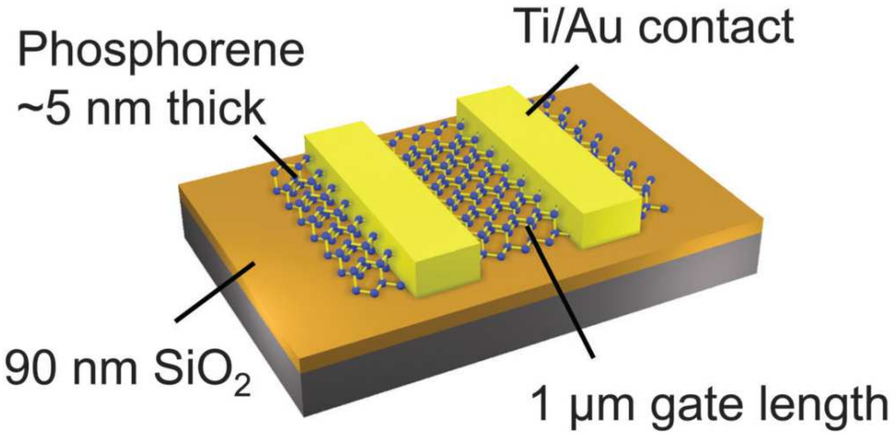
Jie Sun1†, Hyun-Wook Lee1†, Mauro Pasta1 , Hongtao Yuan2,3, Guangyuan Zheng4, Yongming Sun1 , Yuzhang Li1 and Yi Cui1,3*

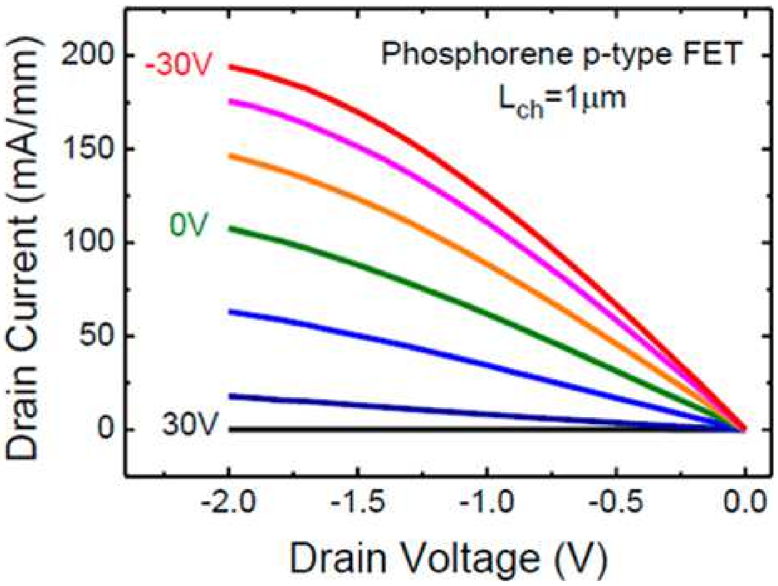
Sodium-ion batteries have recently attracted significant attention as an alternative to lithium-ion batteries because sodium sources do not present the geopolitical issues that lithium sources might. Although recent reports on cathode materials for sodium-ion batteries have demonstrated performances comparable to their lithium-ion counterparts, the major scientific challenge for a competitive sodium-ion battery technology is to develop viable anode materials. Here we show that a hybrid material made out of a few phosphorene layers sandwiched between graphene layers shows a specific capacity of 2,440 mA h g^{-1} (calculated using the mass of phosphorus only) at a current density of 0.05 A g^{-1} and an 83% capacity retention after 100 cycles while operating between 0 and 1.5 V. Using in situ transmission electron microscopy and ex situ X-ray diffraction techniques, we explain the large capacity of our anode through a dual mechanism of intercalation of sodium ions along the x axis of the phosphorene layers followed by the formation of a Na_3P alloy. The presence of graphene layers in the hybrid material works as a mechanical backbone and an electrical highway, ensuring that a suitable elastic buffer space accommodates the anisotropic expansion of phosphorene layers along the y and z axial directions for stable cycling operation.

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 [‡]Birck 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

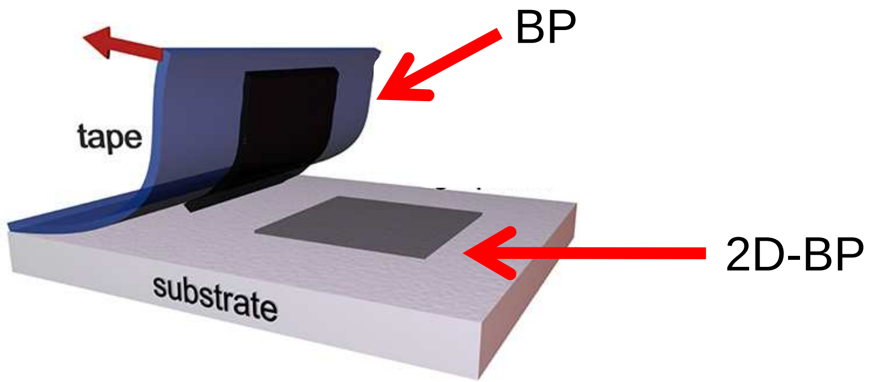




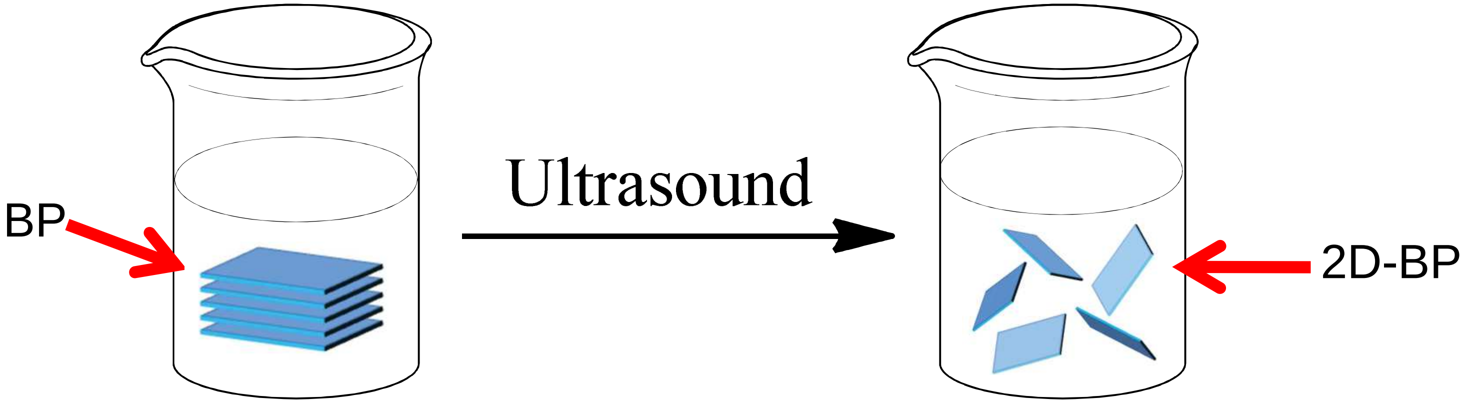
ASC Nano, **2014**, *8*, 4033.

Preparation of few-layer BP

✓ **Mechanical exfoliation**

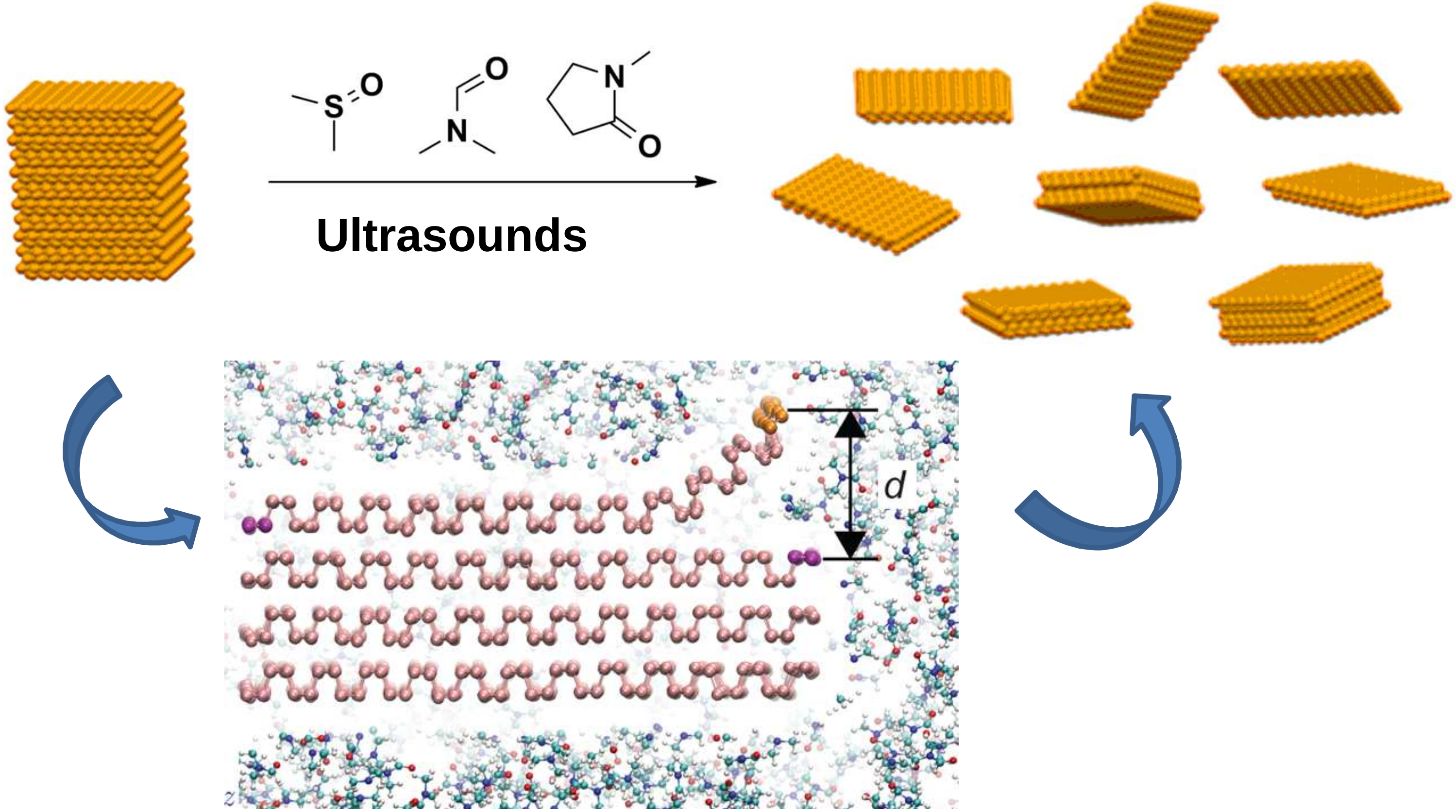


✓ **Liquid phase exfoliation**



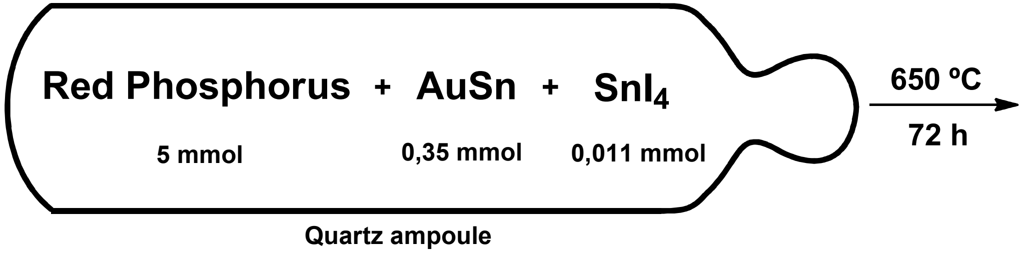
P. D. Ye et al. *ACS Nano* **2014**, *8*, 4033
Y. B. Zhang, *Nat. Nanotechnol*. **2014**, *9*, 372
A. Castellanos-Gomez *et al. 2D Materials,* **2014**,*1*,11002.

Liquid Exfoliation by ultrasounds



O’Brien, *Chem.Commun*, **2014**, *50*,13338; Xie, JACS. **2015**,doi:10.10121.jacs.5b06025
Hersam, *ACS nano* **2015**, 9, 3596; Salehi-Khojin, *Adv. Mater*. **2015**, 27, 1887
Warren, doi:10.10121/acsnano.5b02599; Serrano, Caporali, Peruzzini et al. Submitted.

Synthesis of Black Phosphorus (BP)

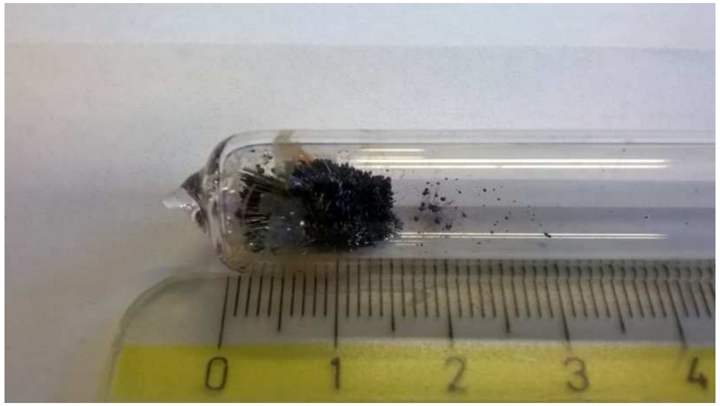


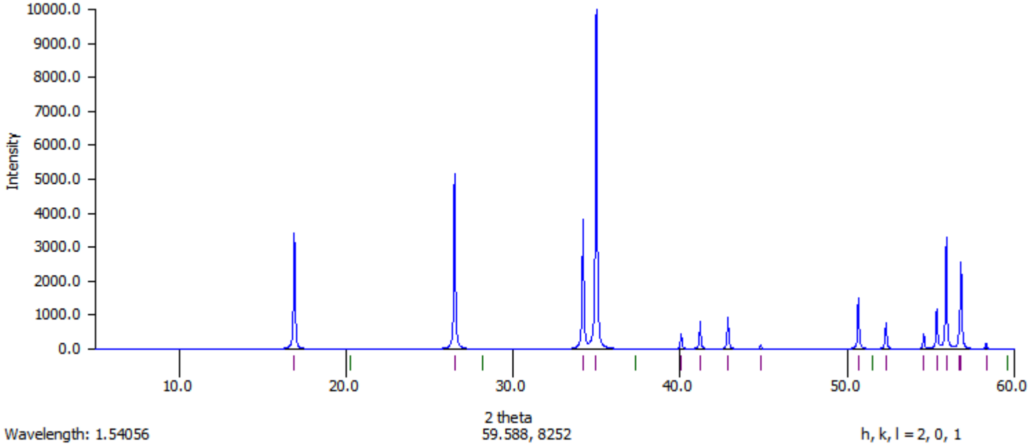
Red Phosphorus + **AuSn** + **SnI_4**

5 mmol **0,35 mmol** **0,011 mmol**

Quartz ampoule

$\xrightarrow[\text{72 h}]{\text{650 °C}}$





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

Exfoliation in DMSO

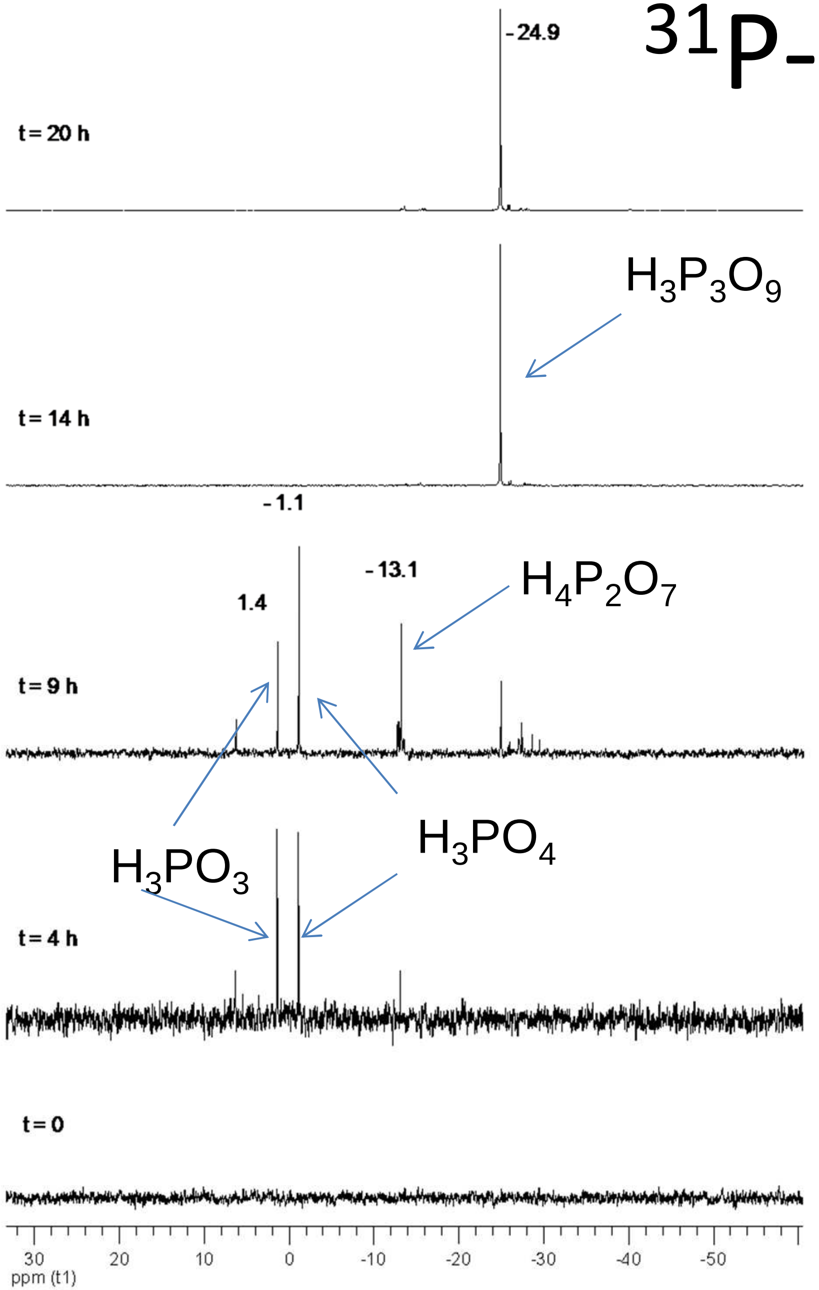
DMSO has:

- high dielectric constant
- high surface tension

➢we found an important influence of the amount of water in the exfoliation

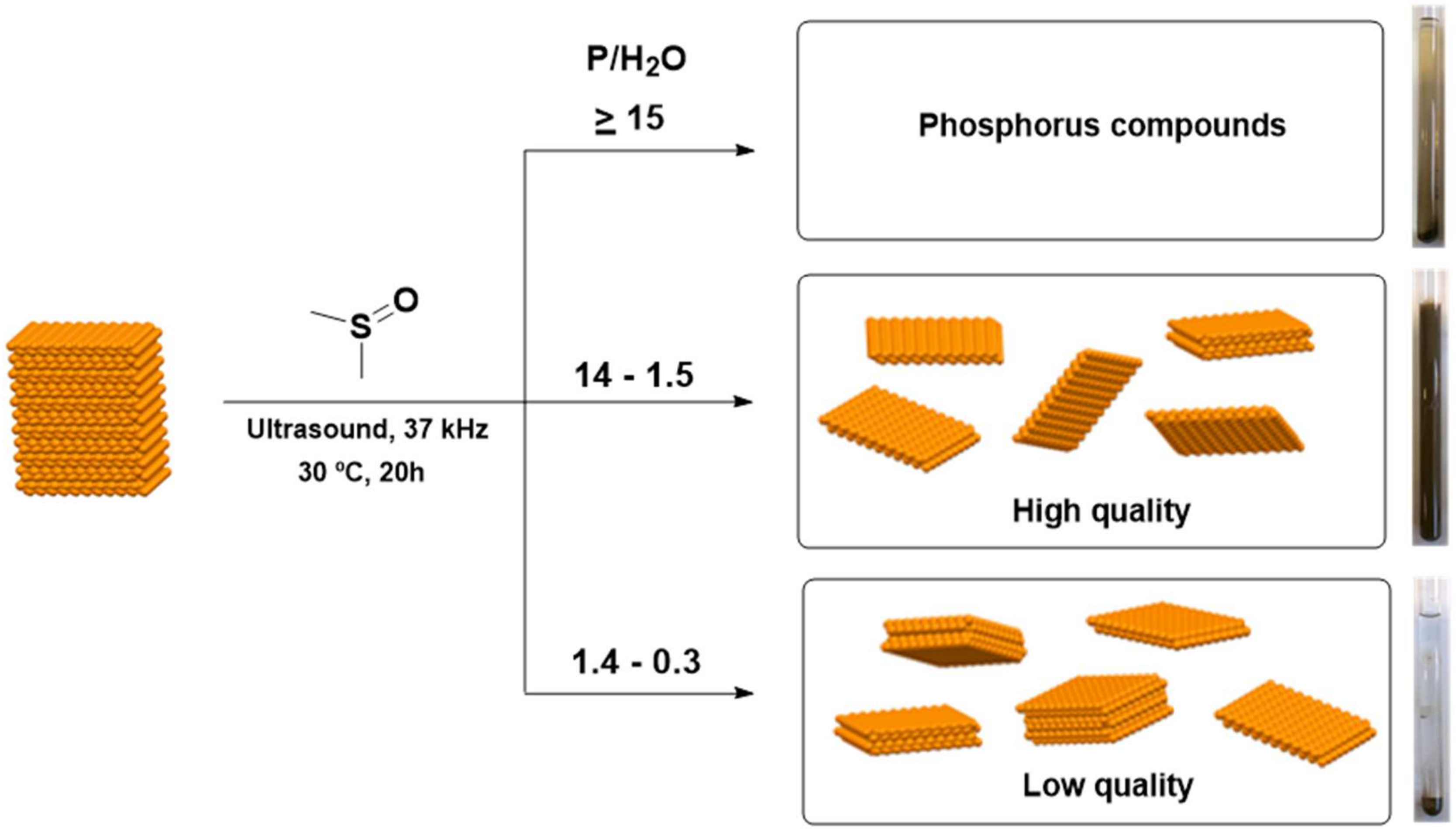
➢ In particular three different ranges of molar ratio between black phosphorus and water were studied.

^{31}P-NMR

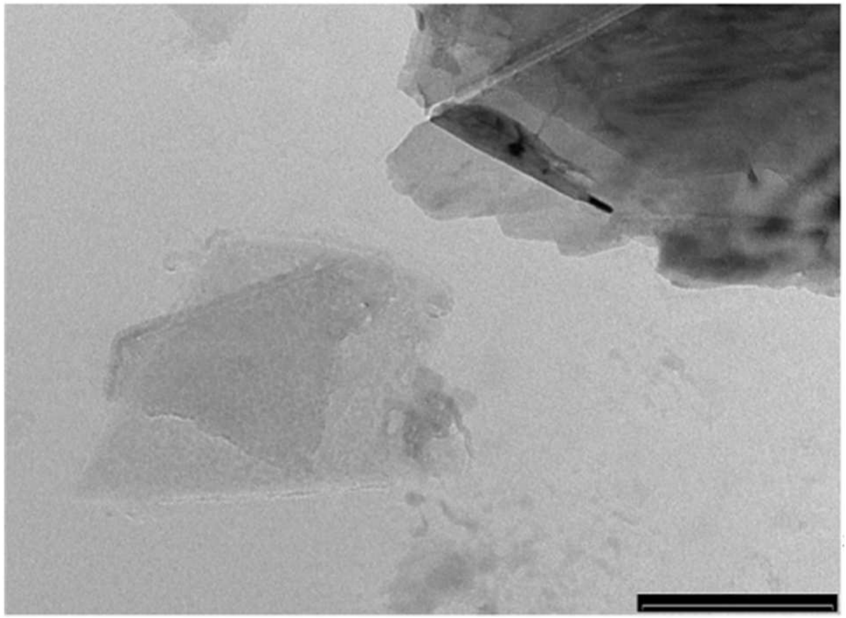


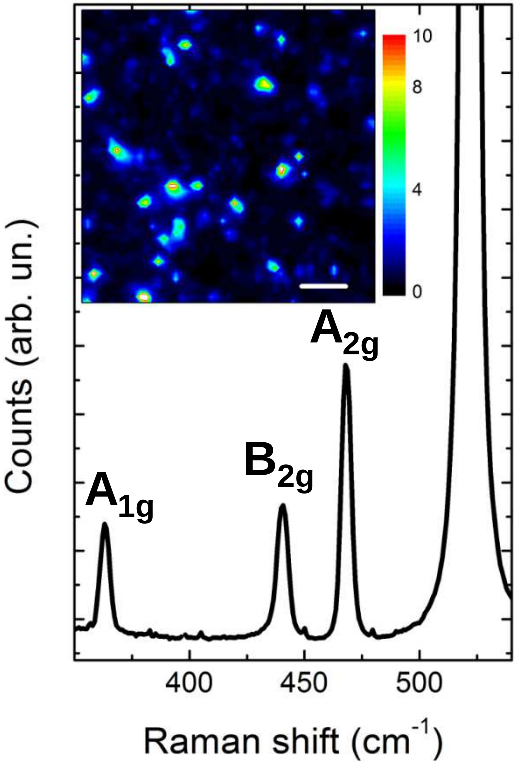
The degradation products resonating at - 13.1 and -24.9 ppm were assigned to pyrophosphate, [$H_4P_2O_7$], and to trimetaphosphate [$H_3P_3O_9$] respectively, on the basis of high resolution ESI MS

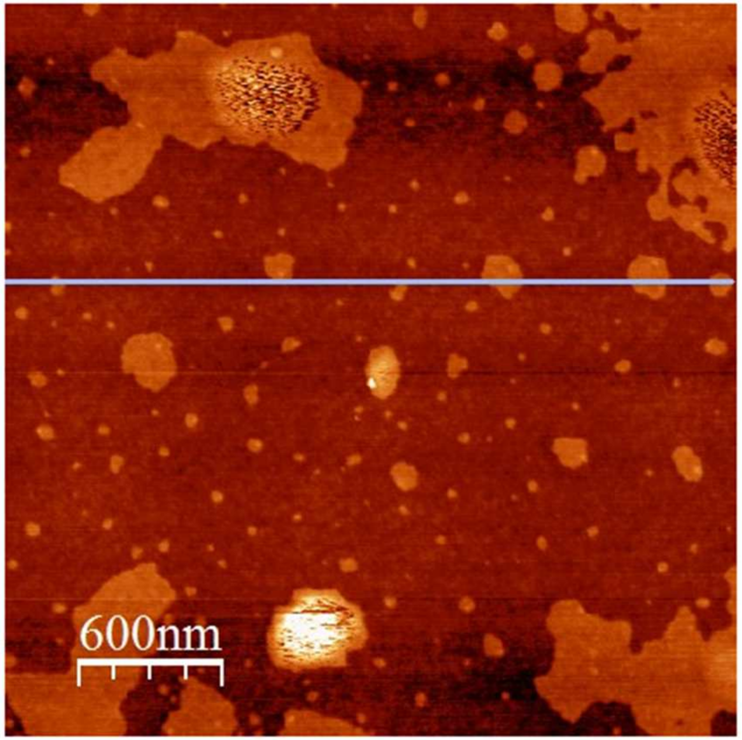
Optimised exfoliation in our labs:

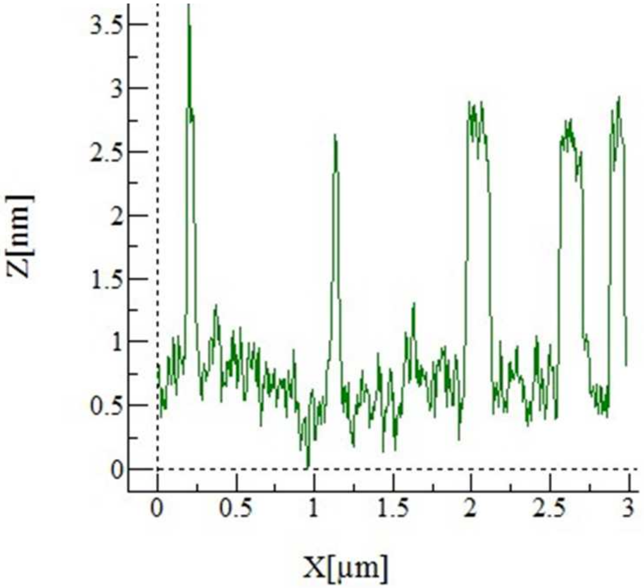


M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv. Mat. Interfaces* **2016**, 3, 1500441.



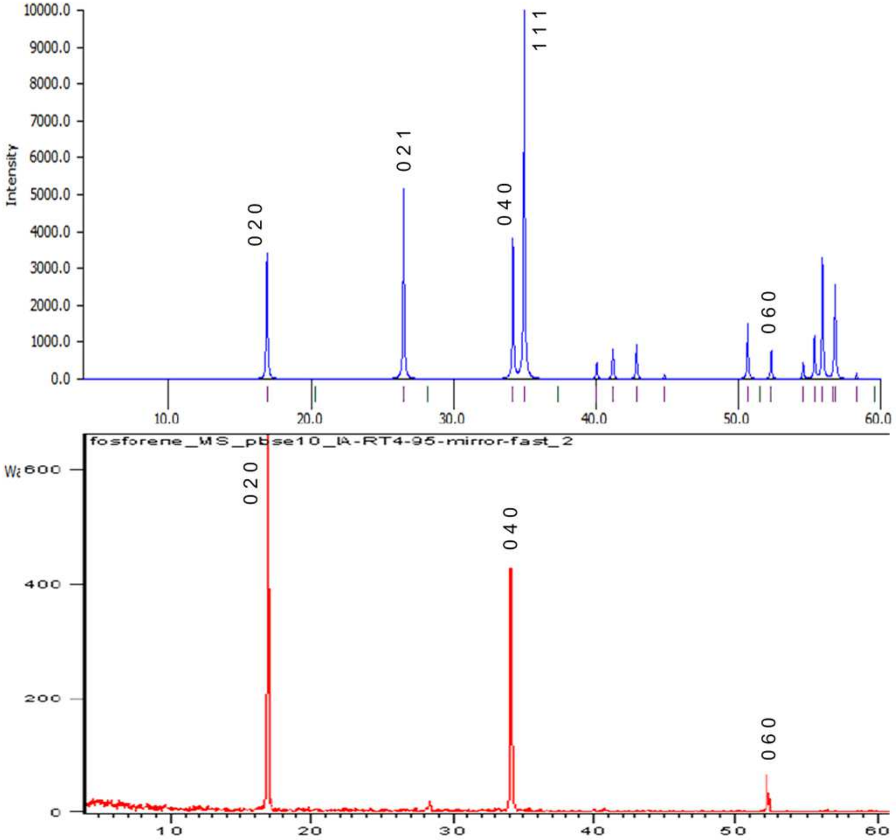

10
8
4
0
A$_{2g}$
B$_{2g}$
A$_{1g}$
Counts (arb. un.)
400
450
500
Raman shift (cm^{-1})

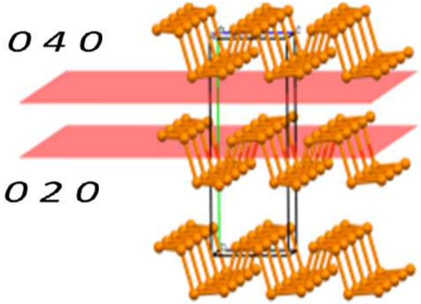

600nm


3.5
3
2.5
2
1.5
1
0.5
0
Z[nm]
0
0.5
1
1.5
2
2.5
3
X[μm]

PXRD

- X-ray powder diffractogram of exfoliated and calculated diffractogram of black phosphorus.





PROCESSING the 2D Black Phosphorus:

Acetone
Centrifugation (6000 rpm x 2)

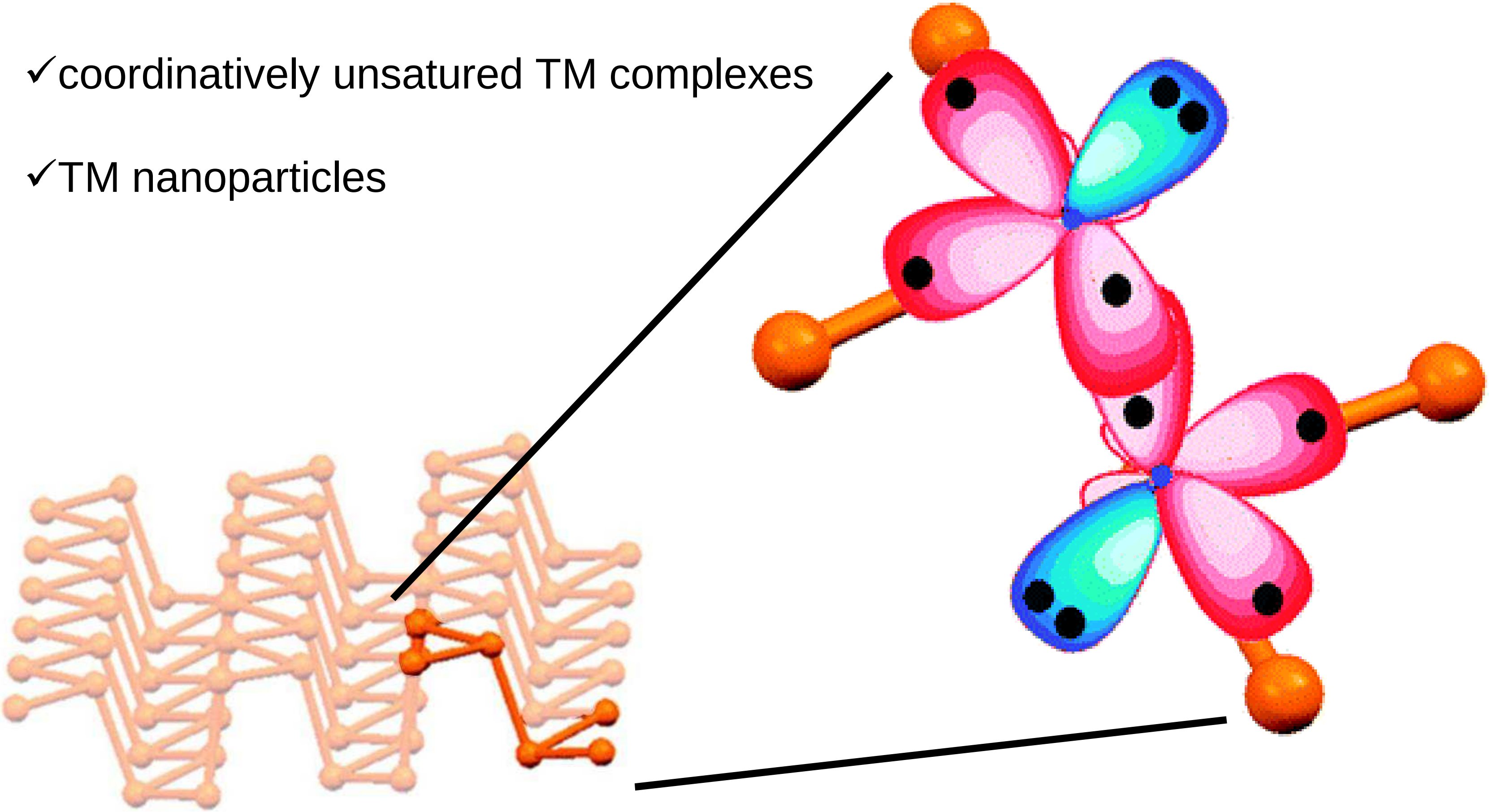
Solvent, Ultrasound 37 kHz
1 minute!!!

2D-BP functionalization: a coordination approach?

Reactivity towards soft Lewis acids:

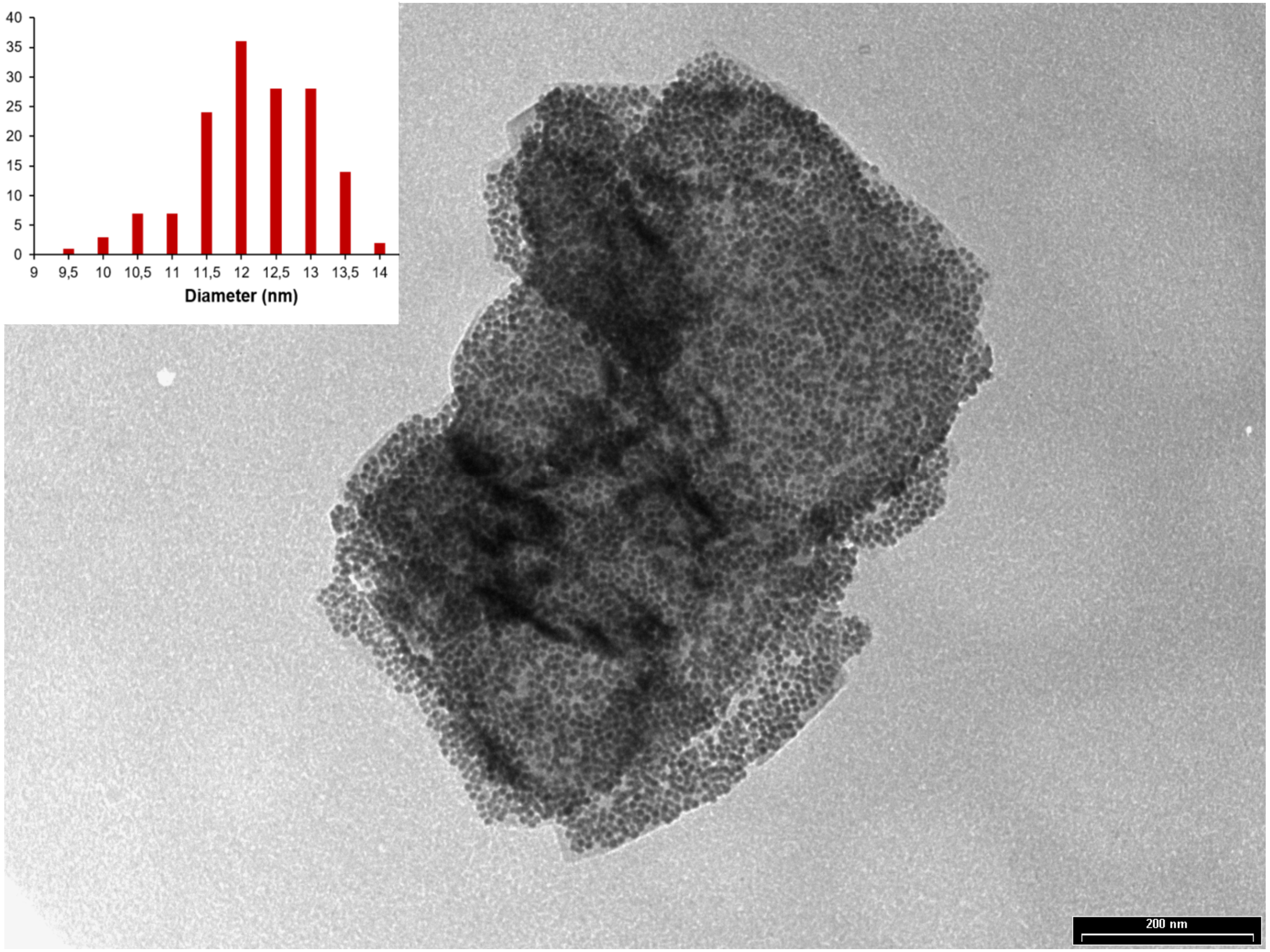
✓coordinatively unsatured TM complexes

✓TM nanoparticles



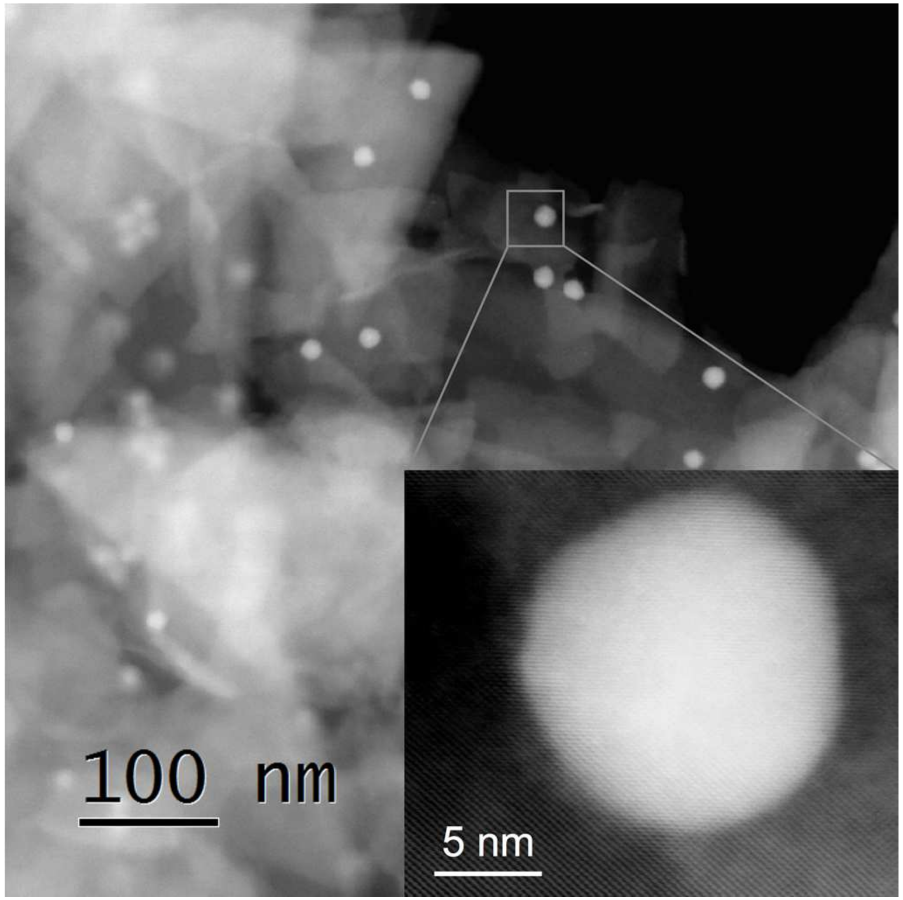
Preparation of NiNPs/2D-BP

$$\underset{\text{(suspended in DMSO)}}{\text{2D-BP}} \xrightarrow{\substack{\text{NiNPs in hexane} \\ \text{P : Ni = 2}}} \text{NiNPs/2D-BP}$$

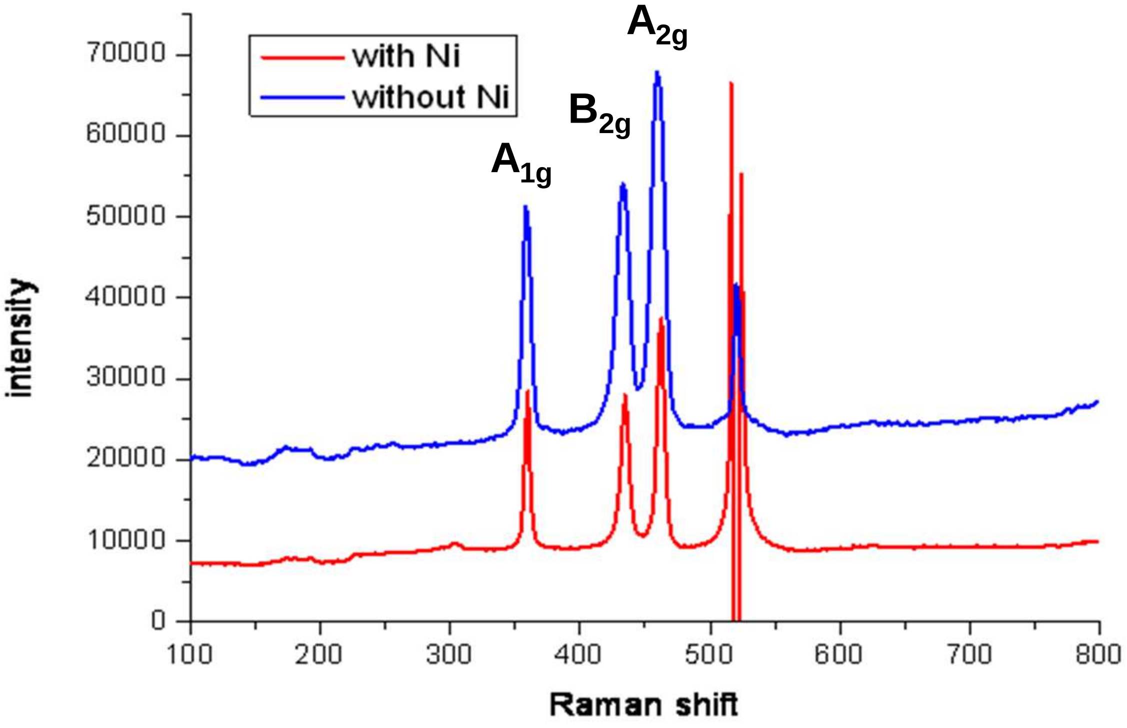


§ Mezailles *et al. Chem. Mater.* **2010**, *22*, 1340.

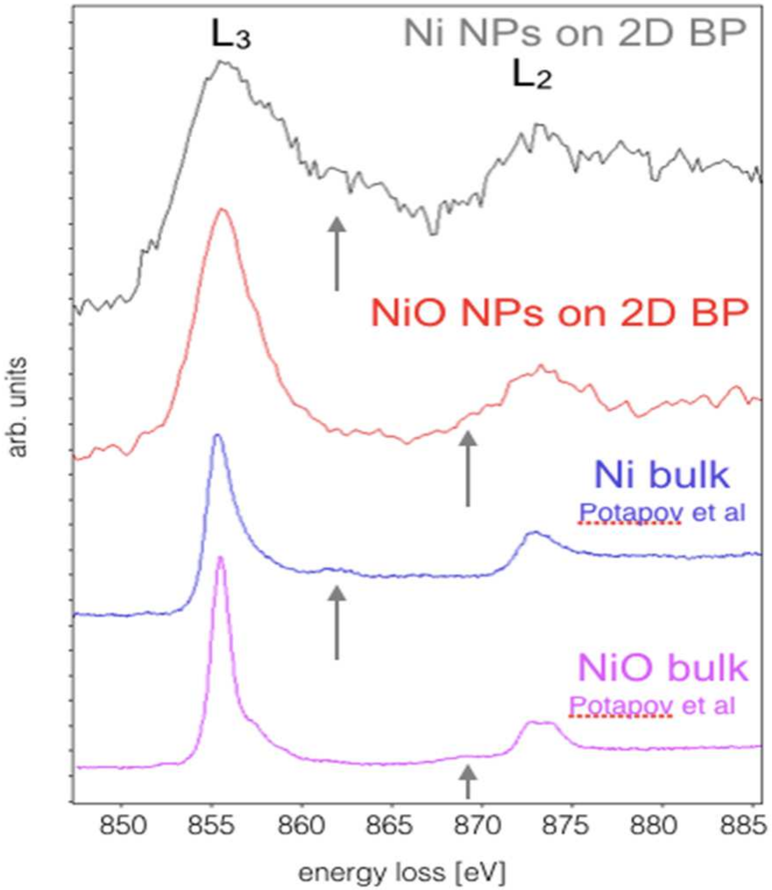
HAADF STEM on NiNPs / 2D BP



Raman of NiNPs -2D Black P



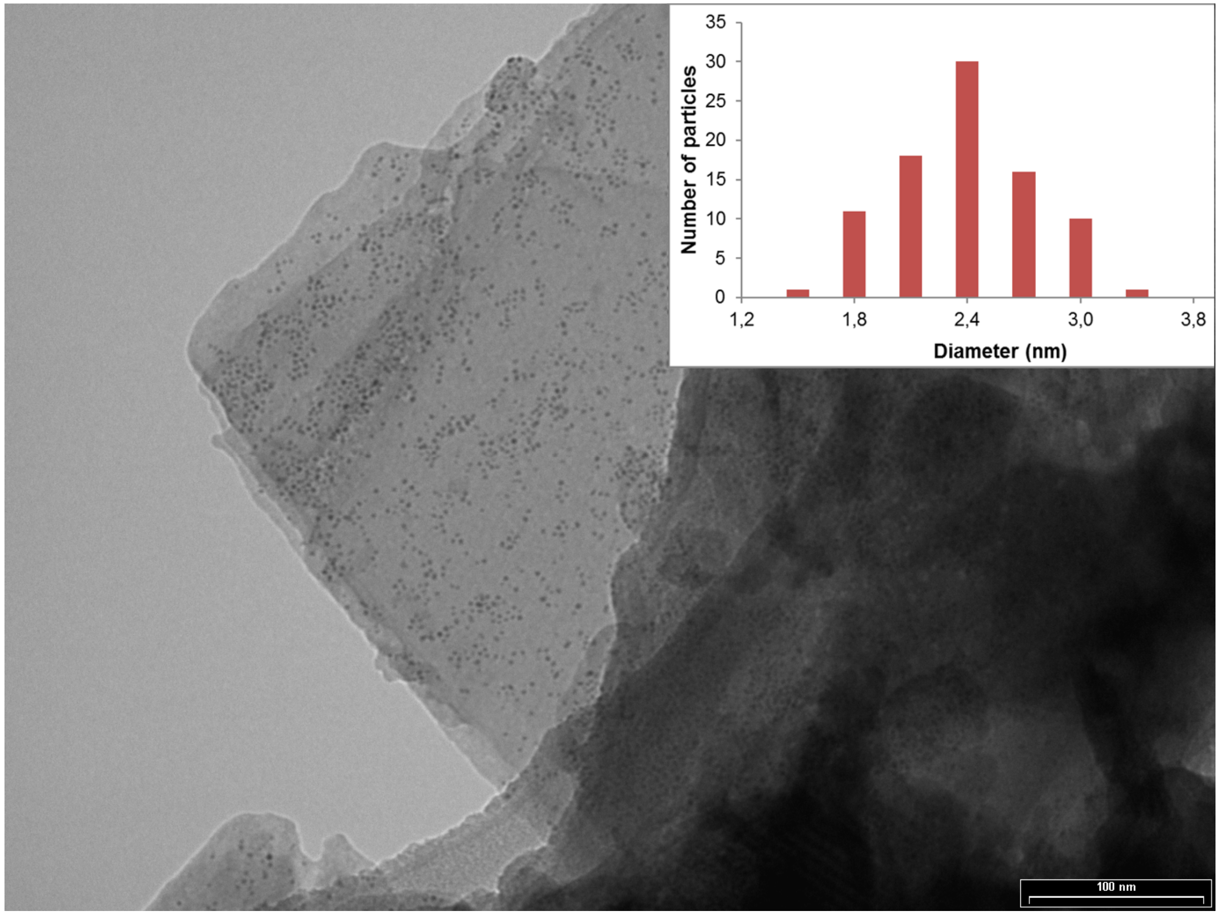
Energy Loss Near Edge Structure (ELNES)



IMM
ISTITUTO PER LA MICROELETTRONICA
E MICROSISTEMI

Preparation of RuNPs/2D-BP

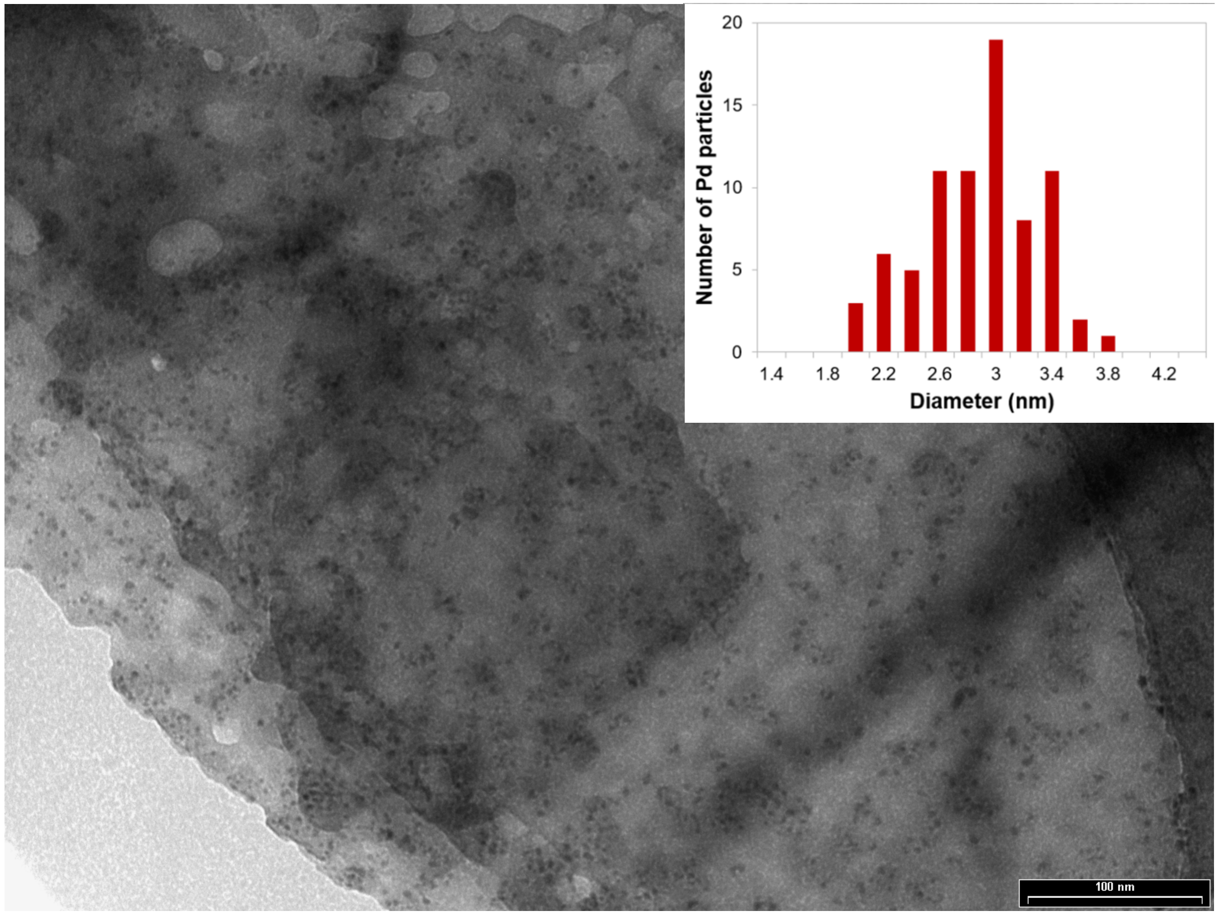
$$\underset{\text{(suspended in DMSO)}}{\text{2D-BP}} \xrightarrow[\text{P : Ru = 2, stirring}]{\text{RuNPs in THF}} \text{RuNPs/2D-BP}$$



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

Preparation of PdNPs/2D-BP

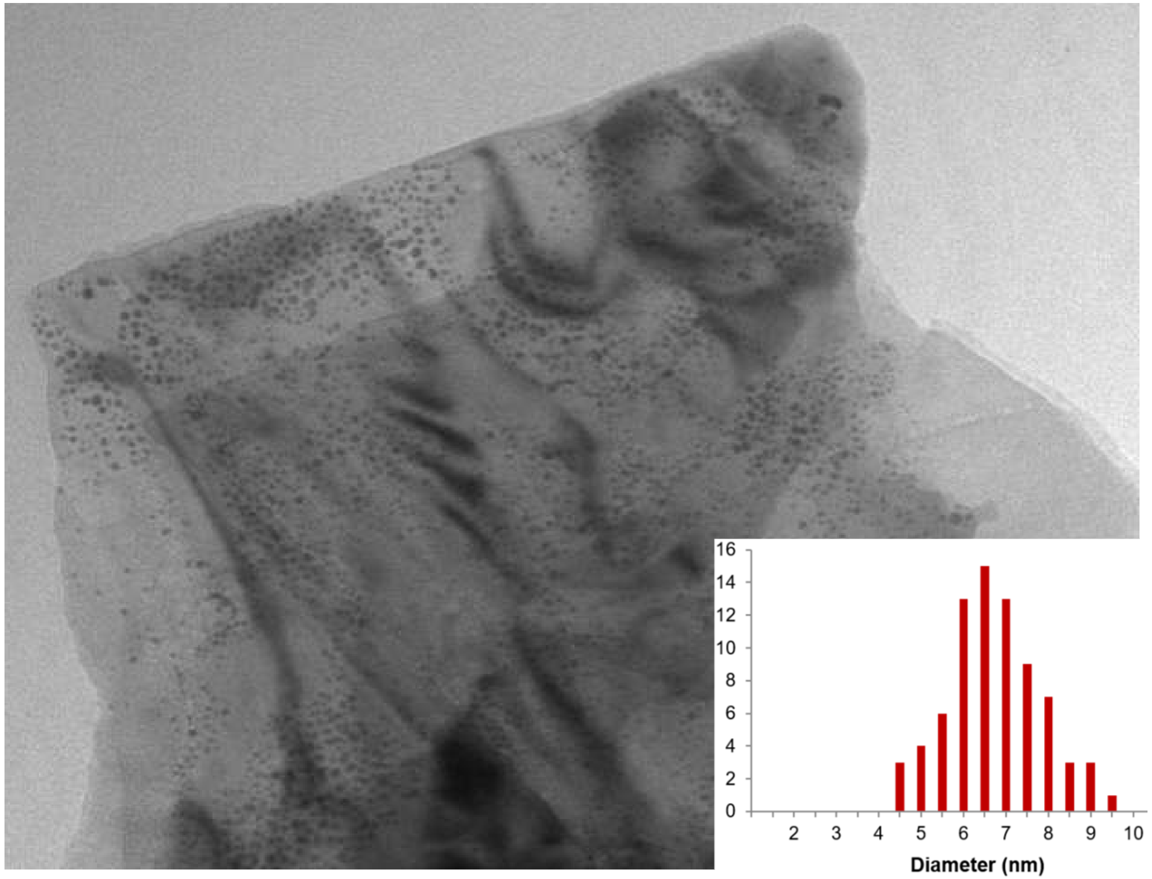
$$\begin{array}{c}\text{2D-BP}\\ \text{(suspended in DMSO)}\end{array} \xrightarrow[\text{P: Pd = 15, stirring}]{\text{PdNPs}^{\S}\text{ in toluene}} \text{PdNPs/2D-BP}$$



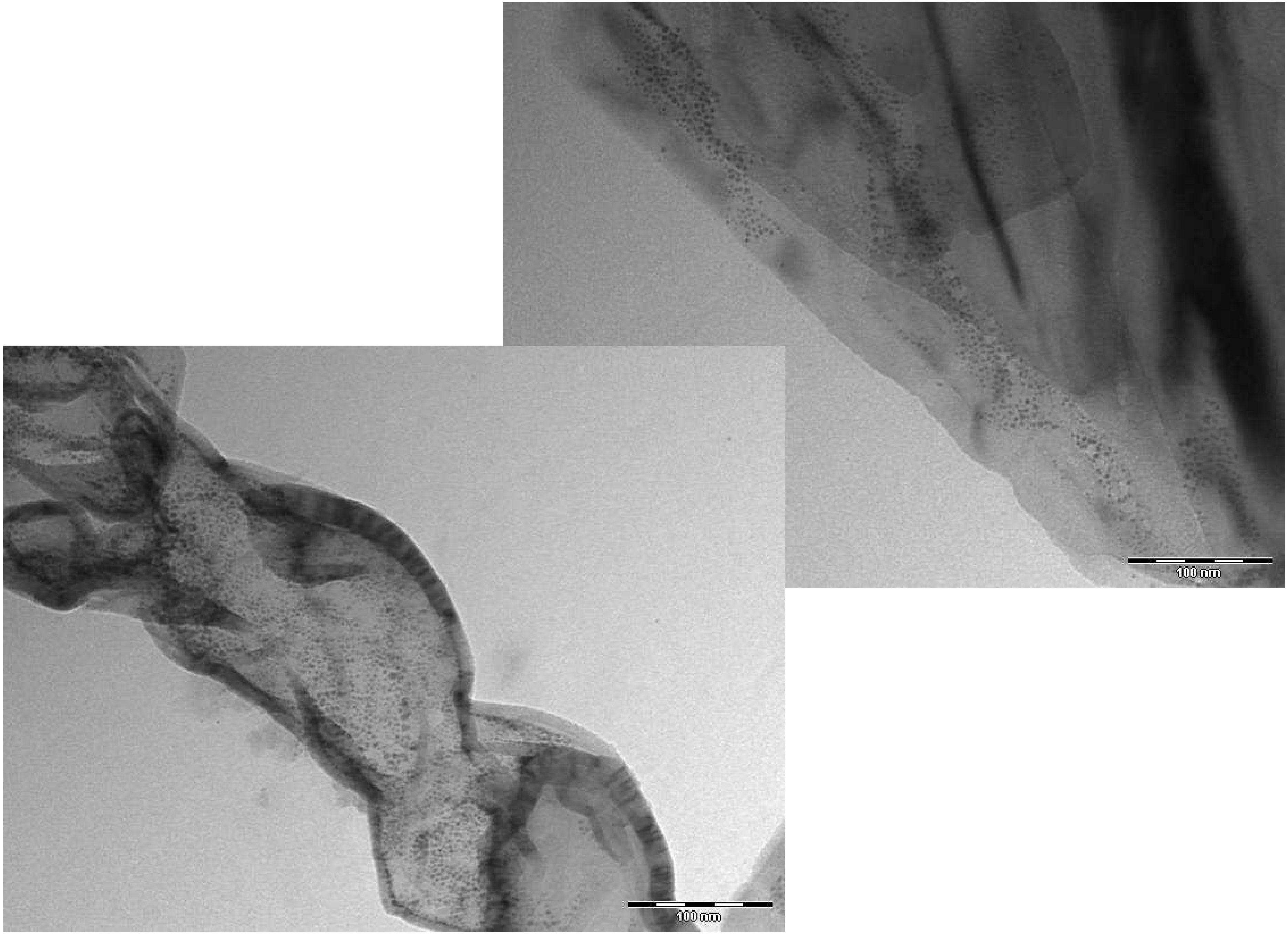
Coronado *et al*., *J. Mat. Chem*. **2008**, *18*, 5682

Preparation of AuNPs/2D-BP

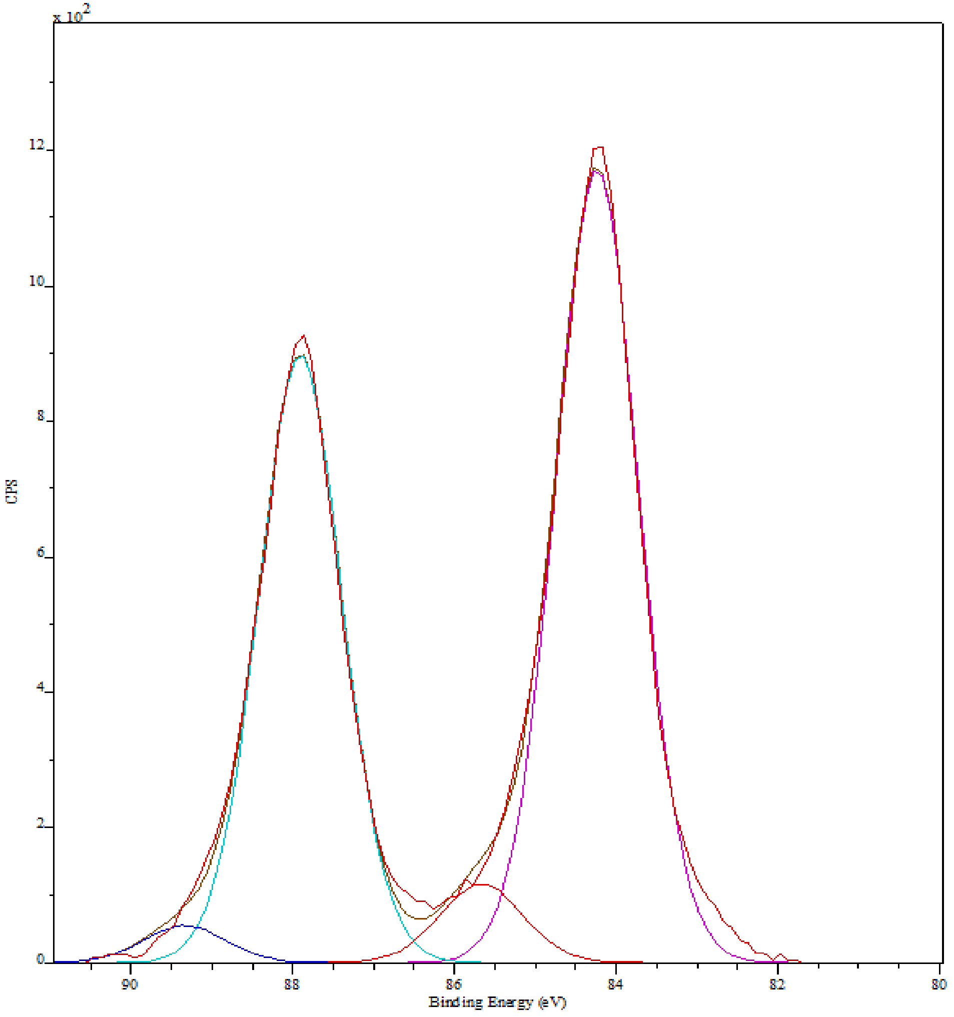
$$\underset{\text{(suspended in DMSO)}}{\text{2D-BP}} \xrightarrow[\text{RT, stirring}]{\text{AuNPs}^{\S}\quad \text{P : Au = 20}} \text{AuNPs/2D-BP}$$

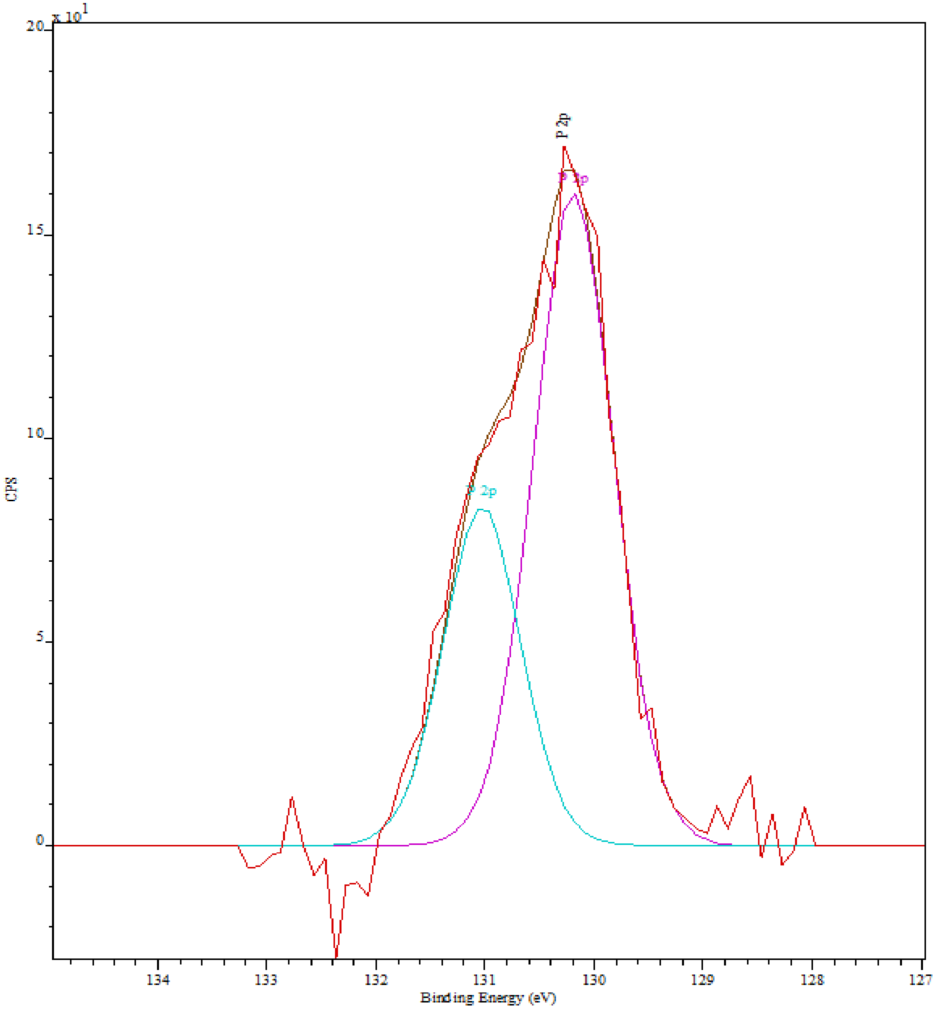


§ S. Dai *et al*, *Catal. Lett*. **2010**, *136*, 209.

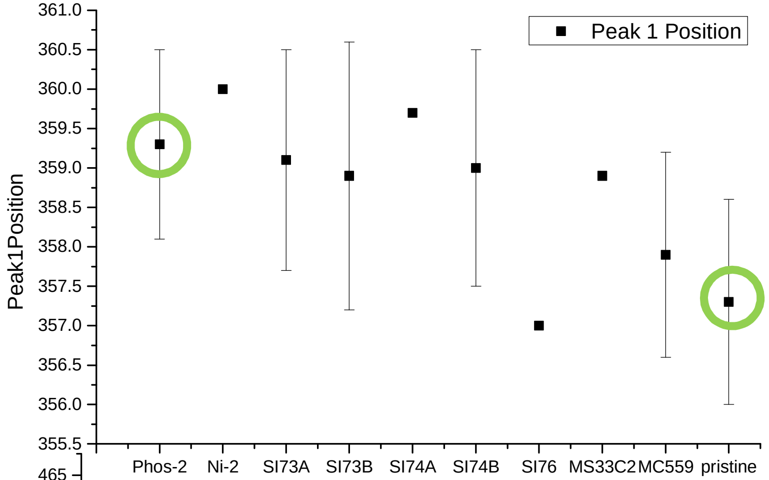

100 nm
100 nm

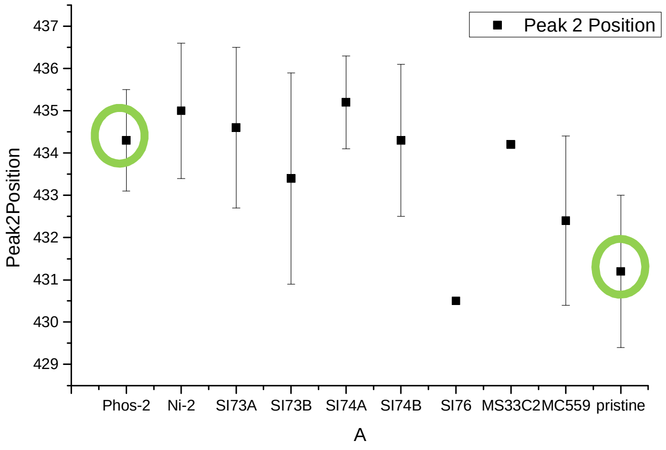
XPS

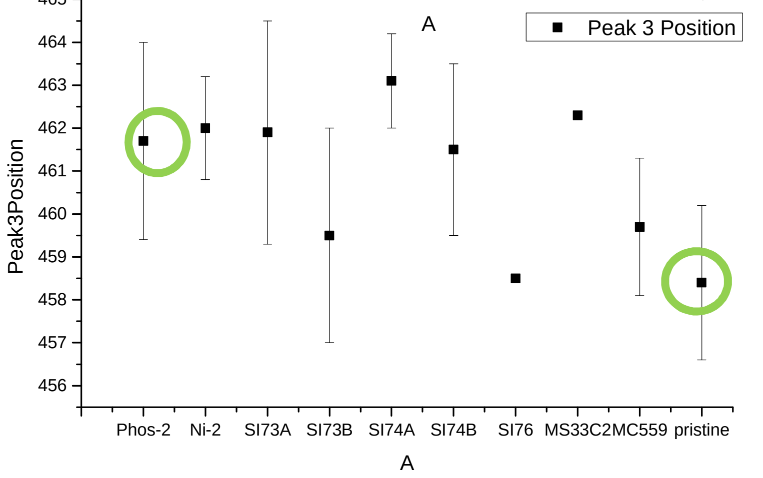

x 10^2
12
10
8
6
4
2
0
CPS
90
88
86
84
82
80
Binding Energy (eV)


x 10^1
20
15
10
5
0
CPS
P 2p
P 2p
P 2p
134
133
132
131
130
129
128
127
Binding Energy (eV)

Raman: comparison



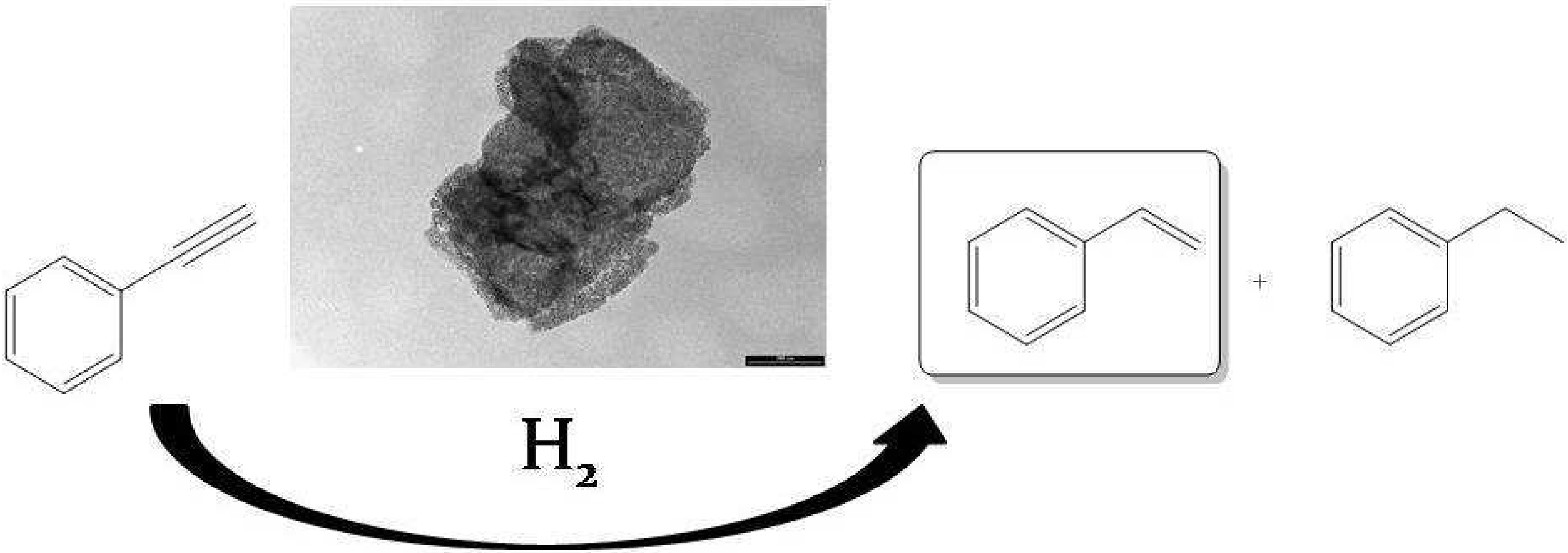




○ Raman signal of pristine phosphorene

- All samples are within the error bar, so we cannot state that there is a Raman shift.

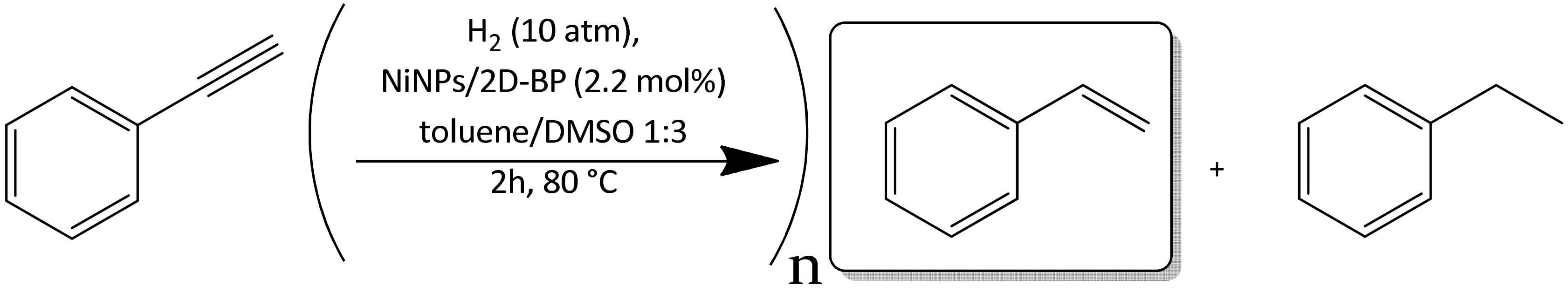
Hydrogenation of Phenylacetylene



Reaction conditions: NiNPs 2.2 mol%, P:Ni = 6, DMSO:Toluene = 3, H_2: 10 bar, 80°C, 2 h.

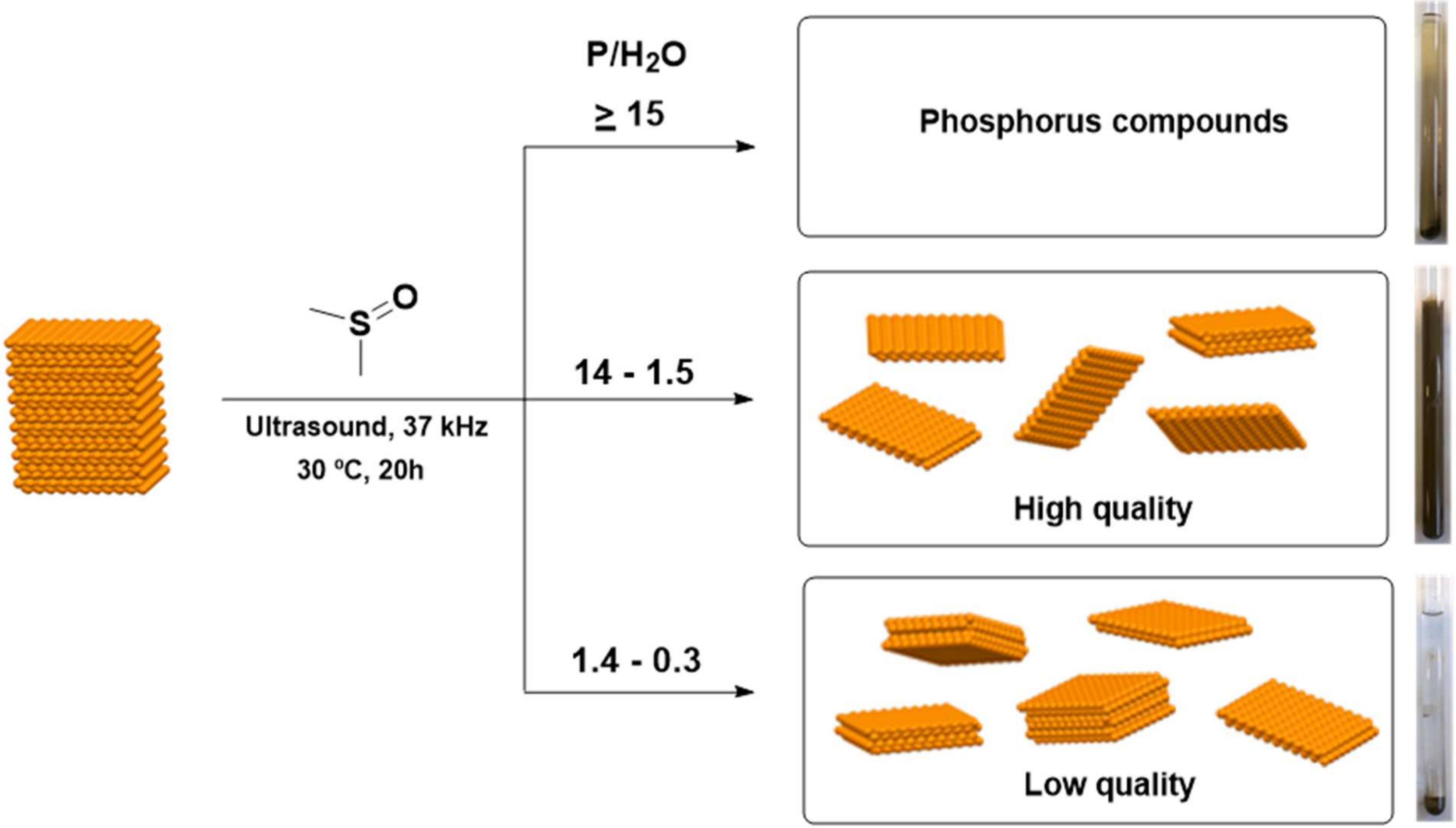
Time (h)	Conv. (%)*	Selectivity toward styrene(%)*
1	45.4	94.3
2	96.2	94.9

Recycling the catalyst NiNPs/2D-BP



Run	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

Summary.....



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

…..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.

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

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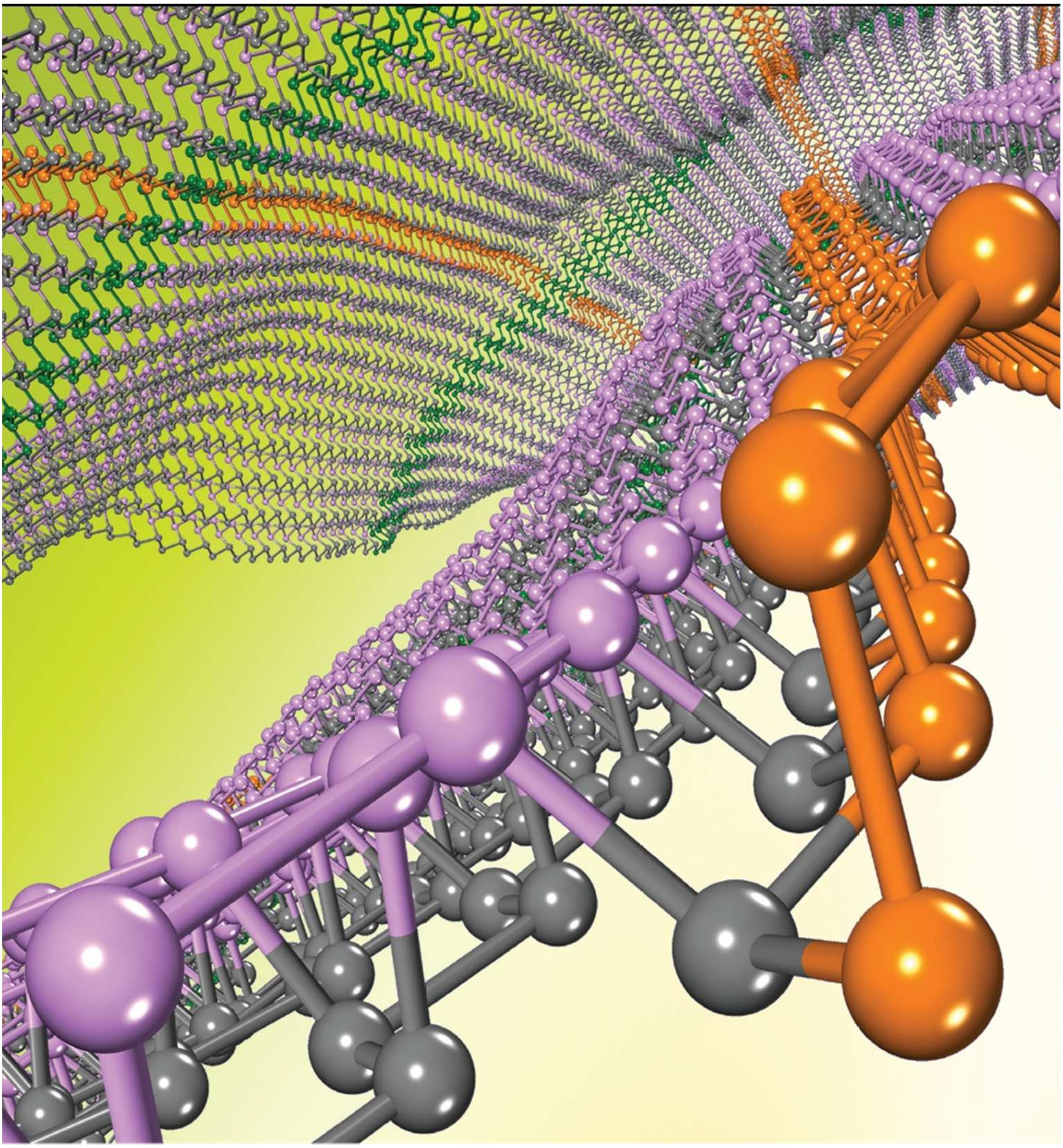

Thank you!!