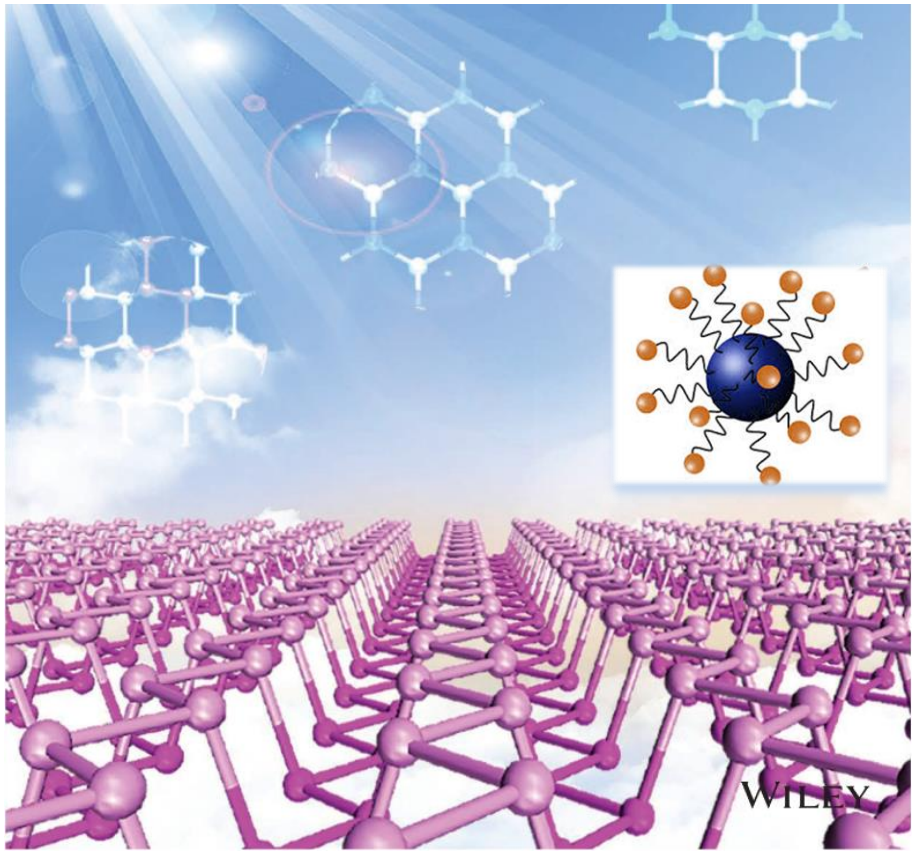
Phosphorene: a new member of 2D family with multifaceted applications in material science

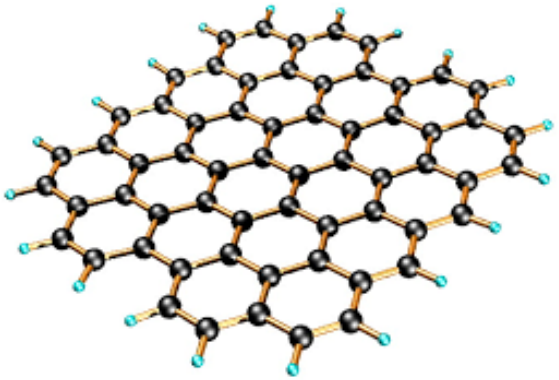


Maria Caporali
CNR ICCOM, Florence (ITALY)

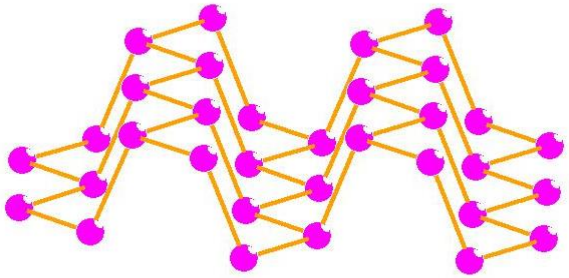
ISTITUTO DI CHIMICA DEI COMPOSTI ORGANOMETALLICI

2D Materials

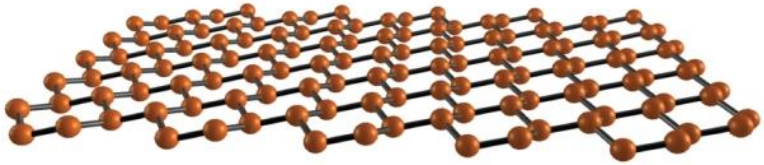
Elemental 2D materials



graphene

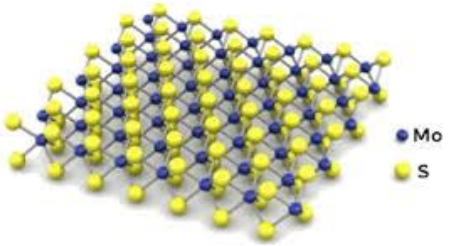


phosphorene

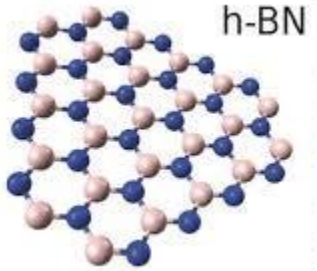


silicene, germanene, stanene

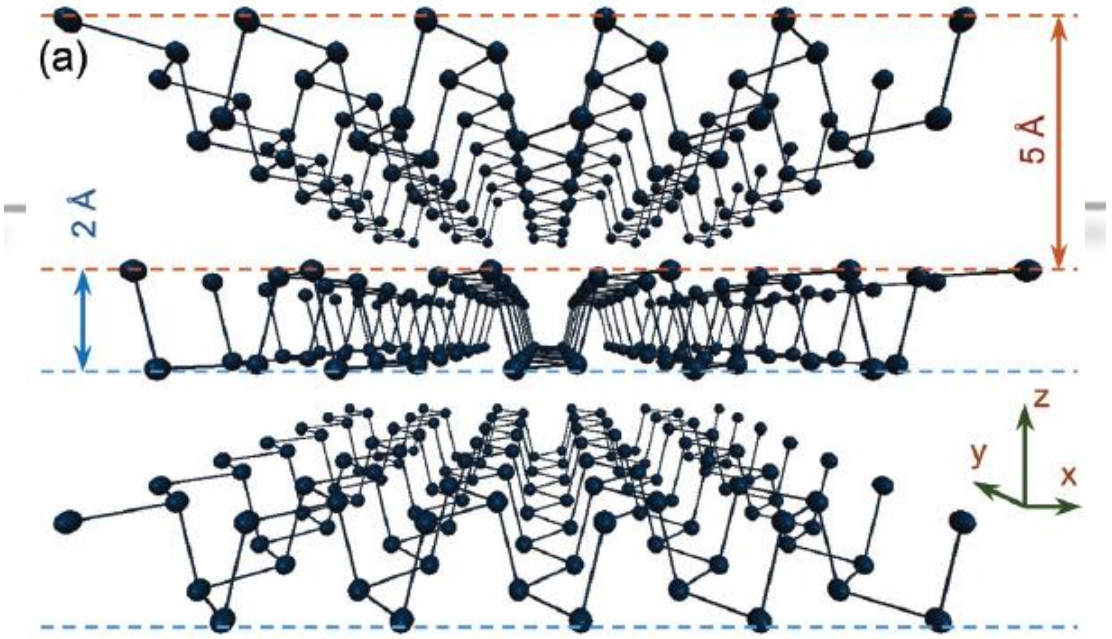
2D Materials composed by two (or more) elements



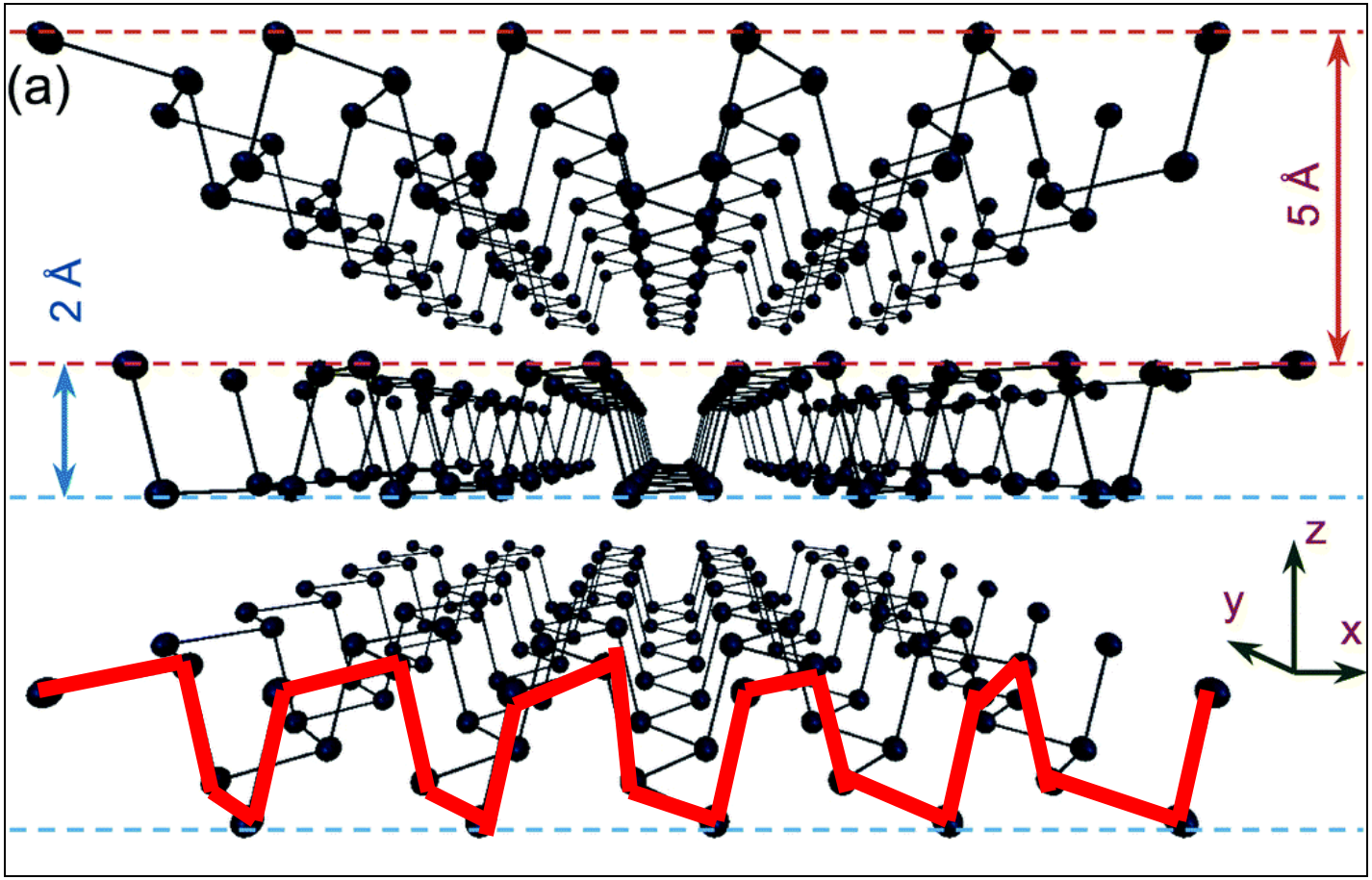
Molybdenum disulfide (MoS_2)



Hexagonal boron nitride (*h*-BN)

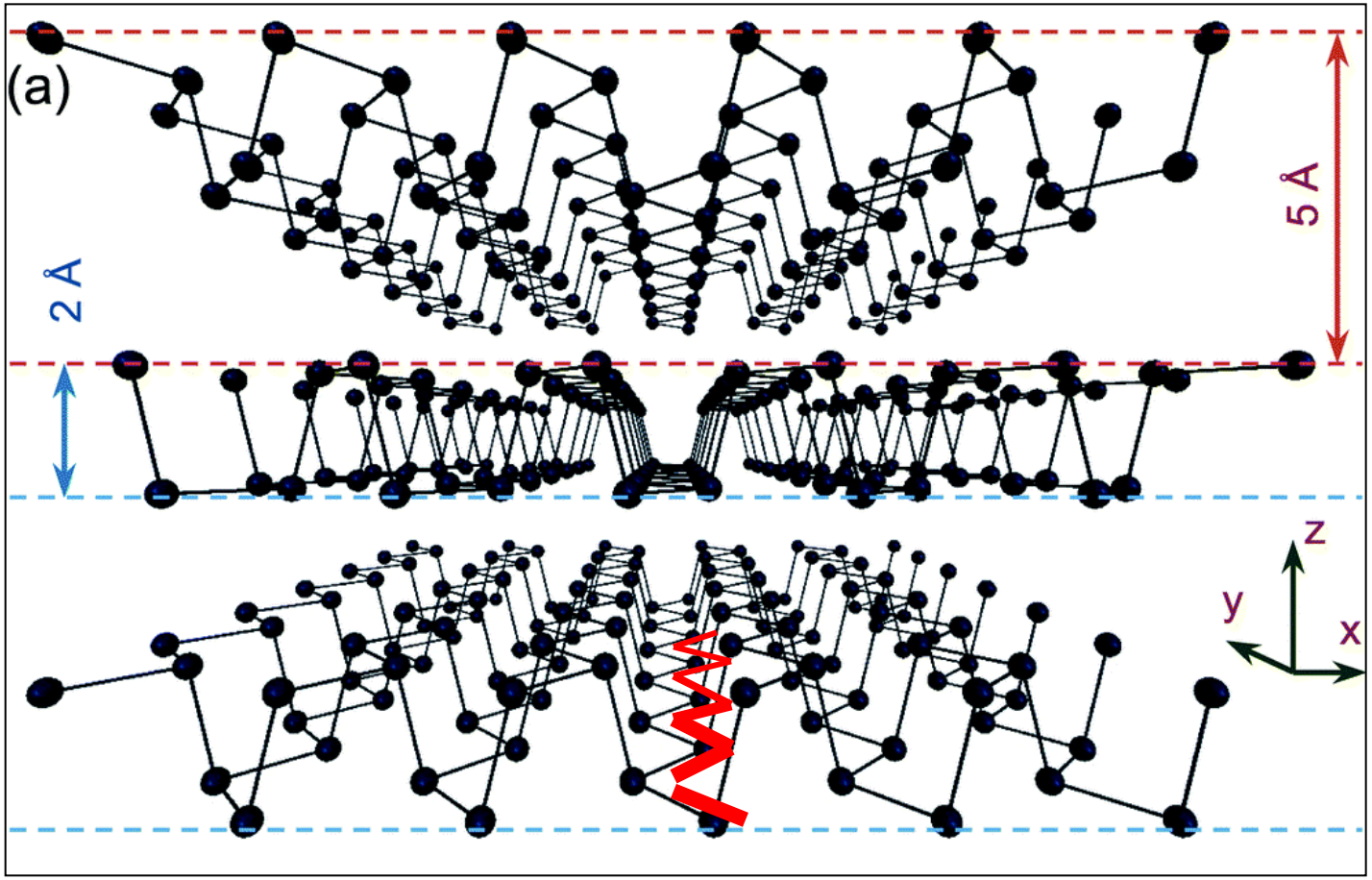

(a)
5 Å
2 Å
z
y
x

Anisotropic structure of black phosphorus



Armchair (x-axis)

Anisotropic structure of black phosphorus



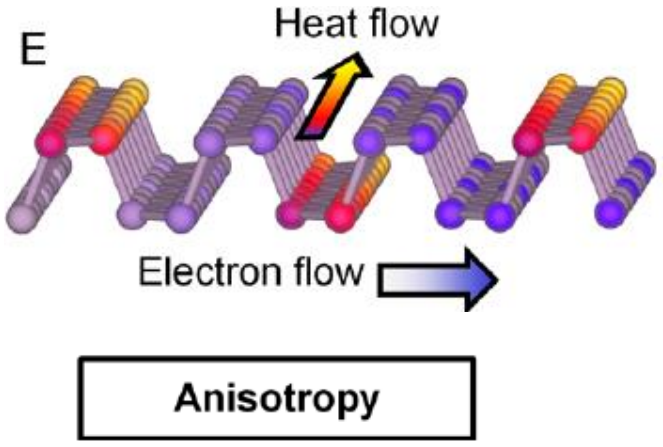
Zig-zag (y-axis)

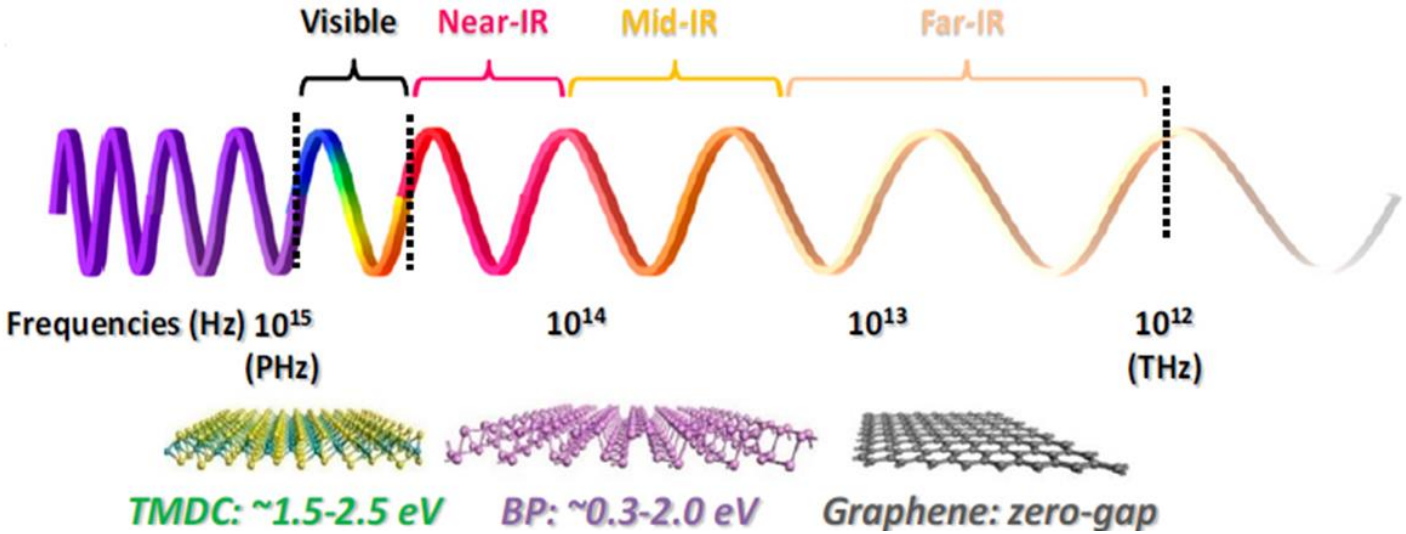
✓ High carrier mobility: 1000 cm^2/Vs

✓ On / off ratio: $10^3 – 10^5$

✓ Thermal conductivity (300 K):

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

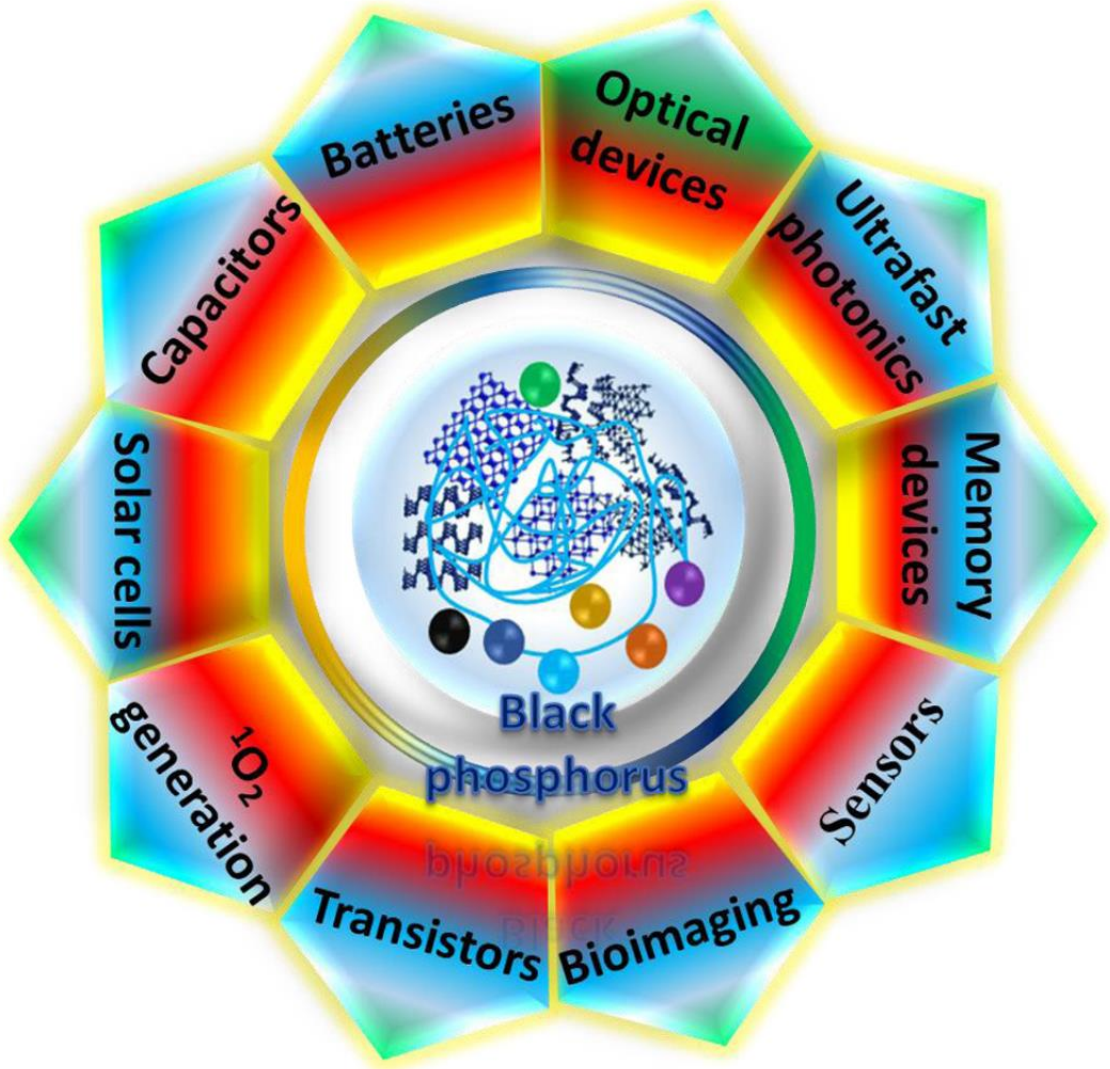




✓ *p*-type semiconductor, with a thickness-depending direct band gap (0.3-2.0 eV)

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

Applications of black phosphorus

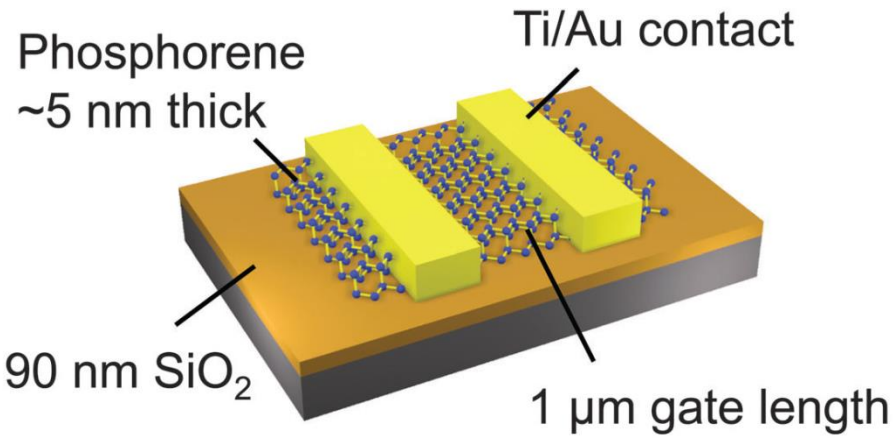


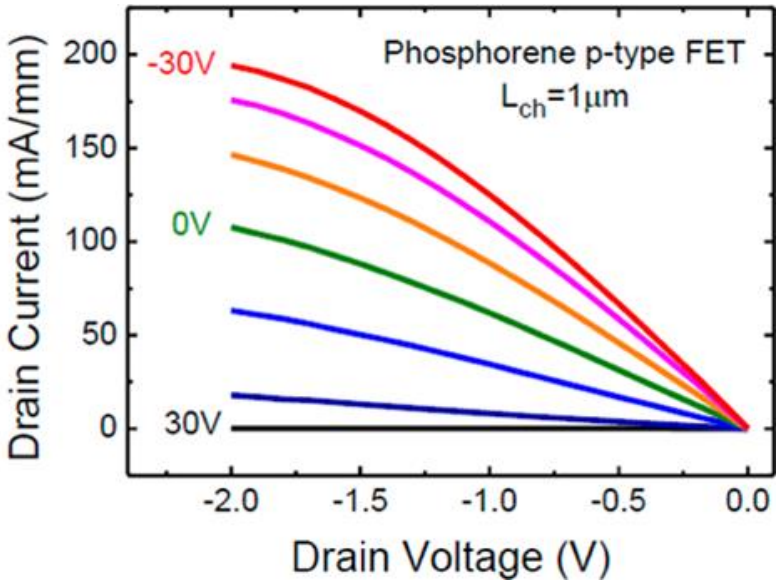
Flat.Chem. **2017**, *2*, 15-37

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

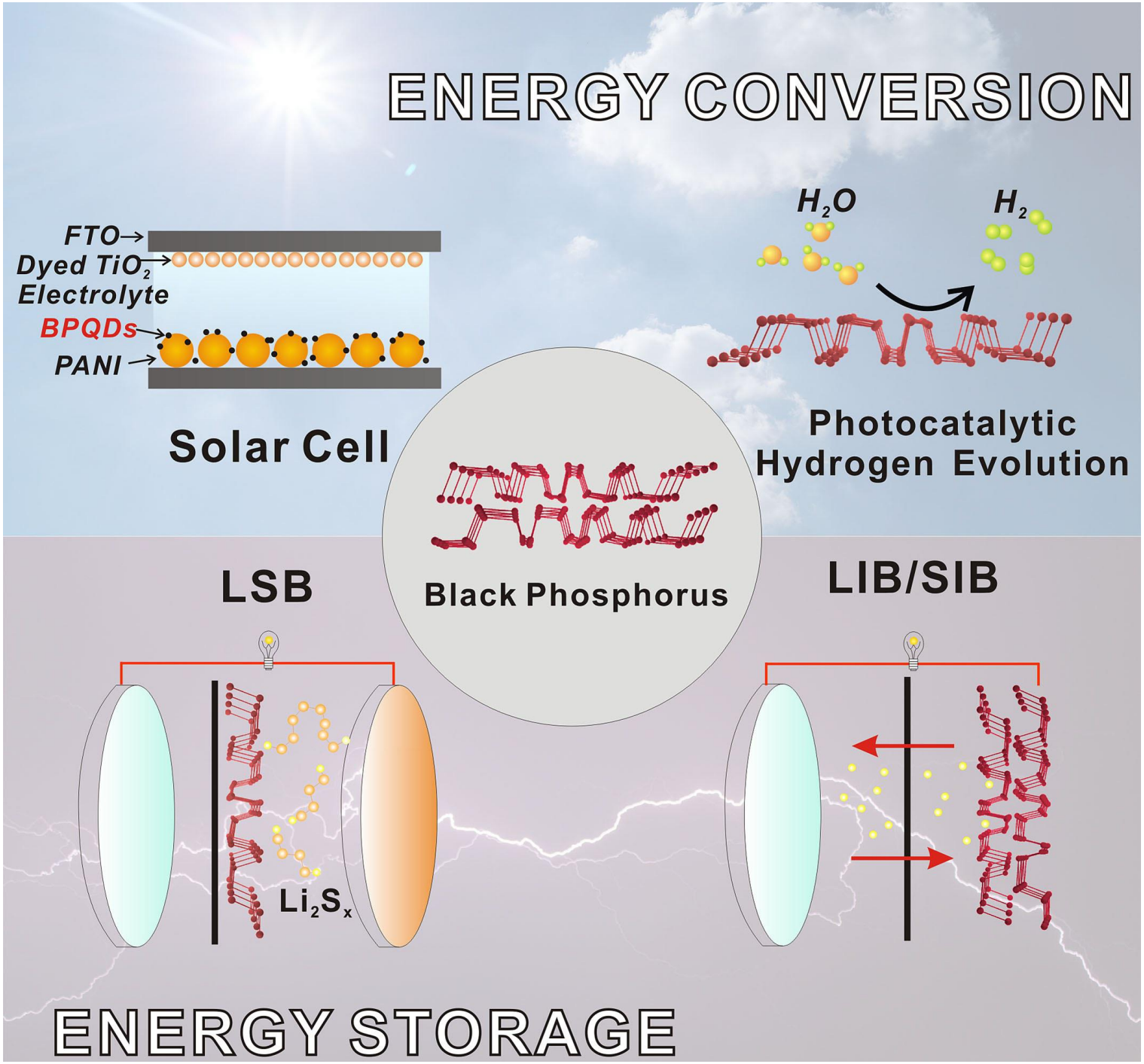
Han Liu,[†,‡] Adam T. Neal,[†,‡] Zhen Zhu,[§] Zhe Luo,[‡,⊥] Xianfan Xu,[‡,⊥] David Tománek,[§] and Peide D. Ye[†,‡,*]

[†]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

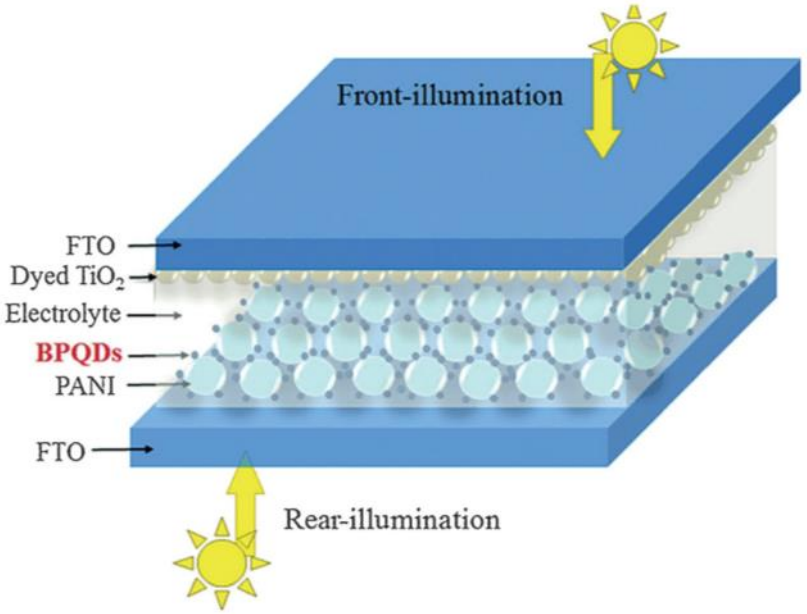


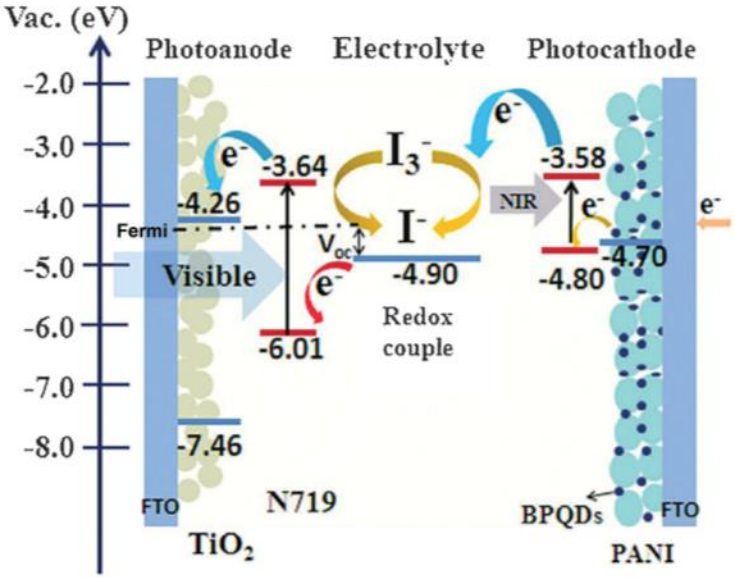


ASC Nano, **2014**, *8*, 4033.


ENERGY CONVERSION
FTO
Dyed TiO2
Electrolyte
BPQDs
PANI
Solar Cell
H2O
H2
Photocatalytic
Hydrogen Evolution
Black Phosphorus
LSB
LIB/SIB
Li2Sx
ENERGY STORAGE

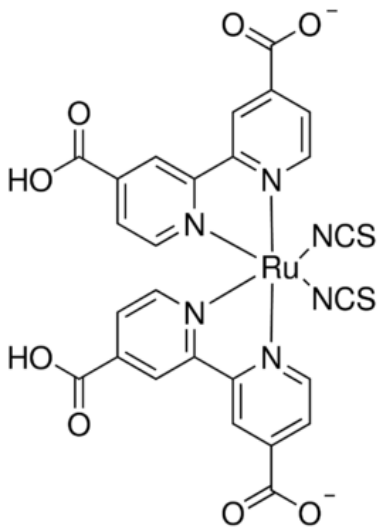
DSSC based on black phosphorus quantum dots

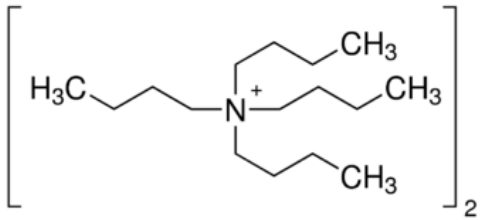




FTO: fluorine-doped tin oxide
PANI: polyaniline film

PCE: 6.8%, increase of 20% in presence of BPQDs

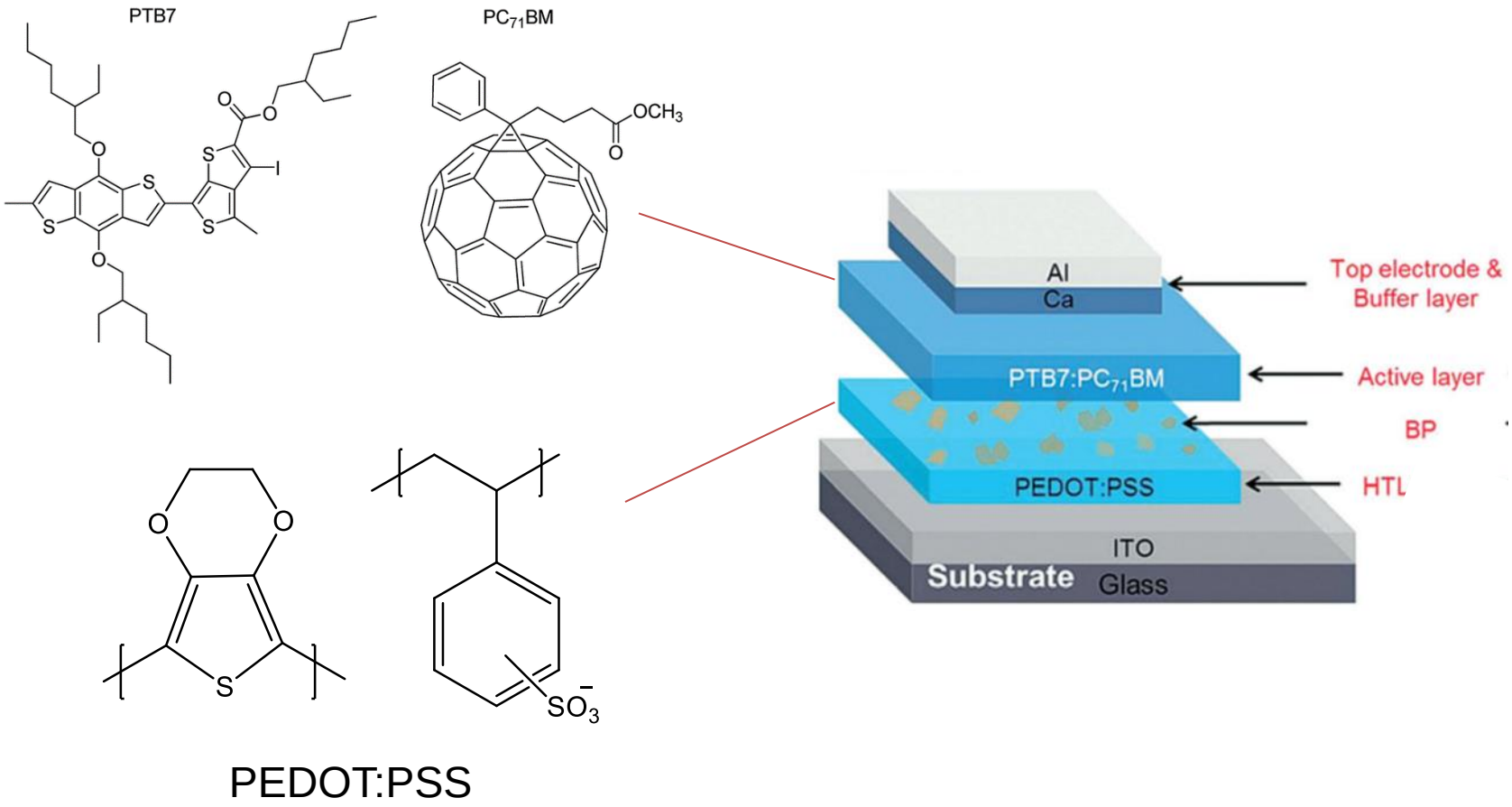




N719

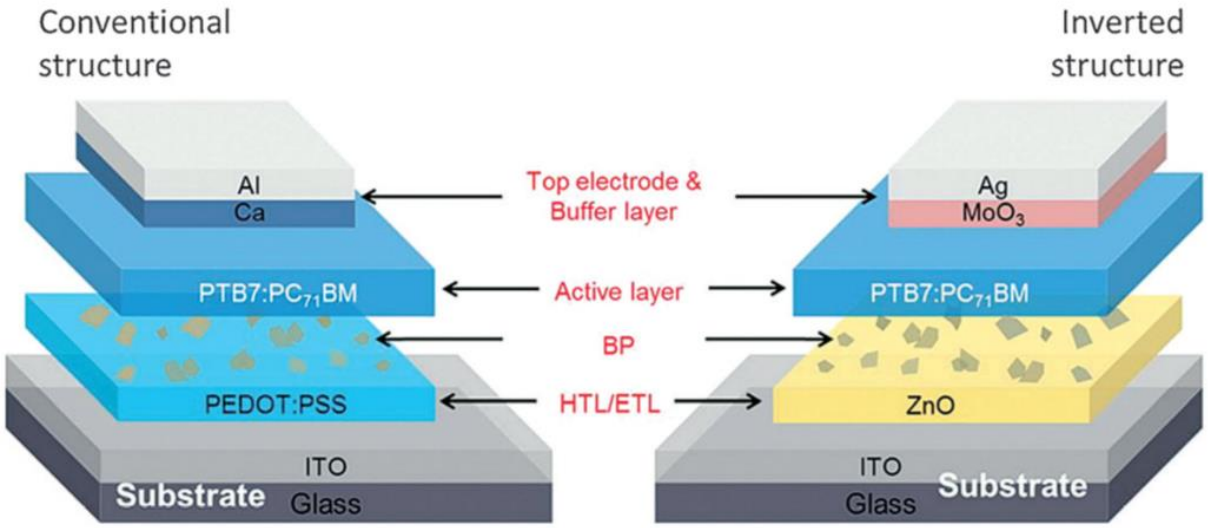
Adv. Mat. **2016**, *28*, 8937-8944.

OPVs based on black phosphorus quantum dots

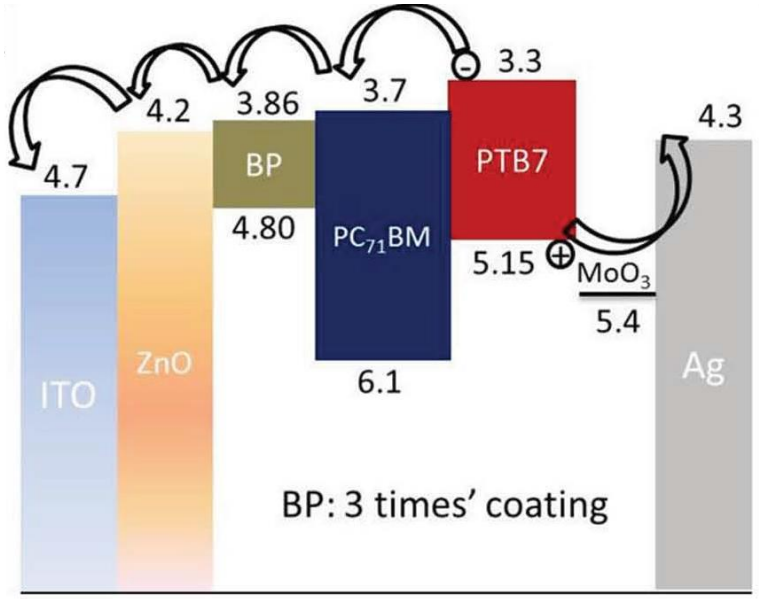


Adv. Funct. Mat. **2016**, *26*, 864-871.

OPVs based on black phosphorus quantum dots

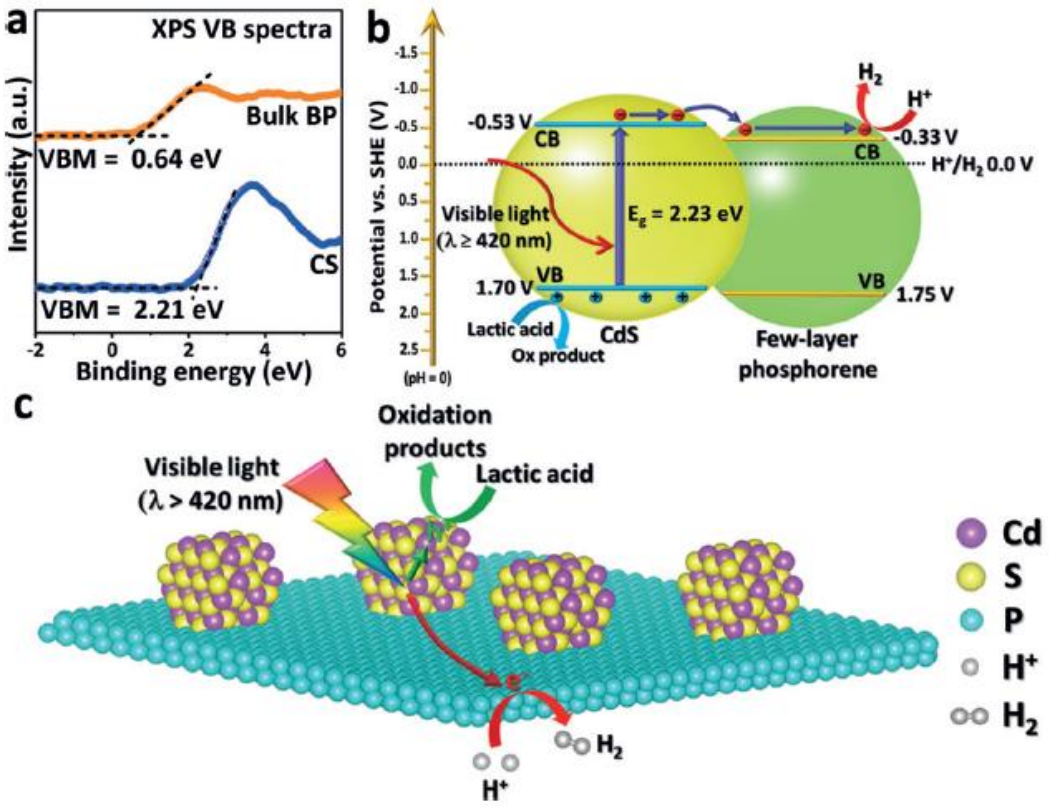


PCE: 8.2%, increase of 11% in presence of BPQDs



Adv. Funct. Mat. **2016**, *26*, 864-871.

Phosphorene as co-catalyst in H_2 production

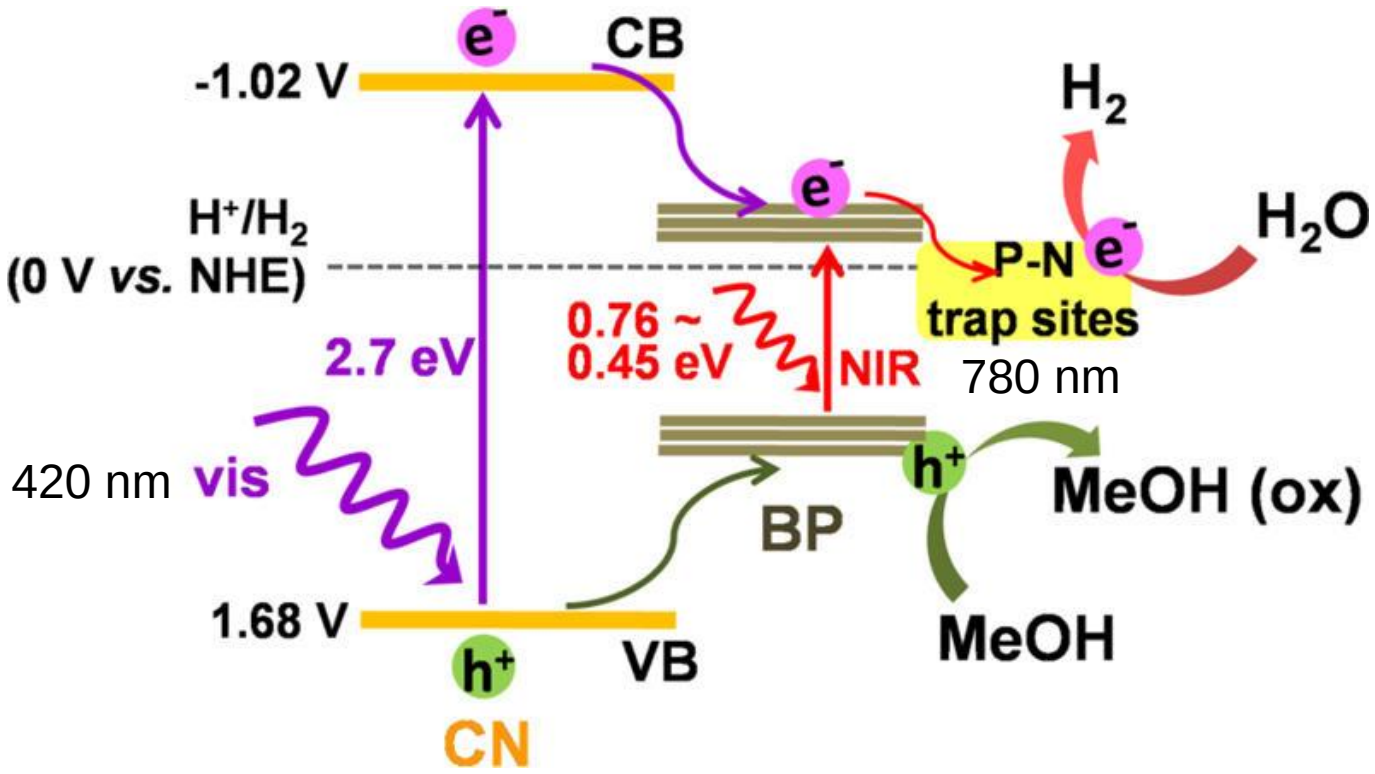


Quantum yield of 34% at 420 nm!!

Zhang Qiao *et al., Angew. Chem. Int. Ed.* **2017**, doi: 10.1002/anie.201703827

Phosphorene as co-catalyst in H_2 production

2D BP and *g*-C_3N_4 (graphitic carbon nitride) as metal-free photocatalyst in water:

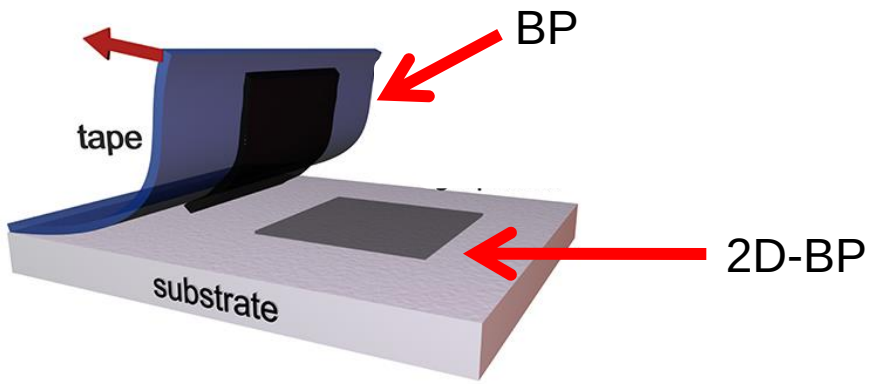


Metal-free photocatalyst

JACS 2017, doi:10.1021/jacs.7b08416

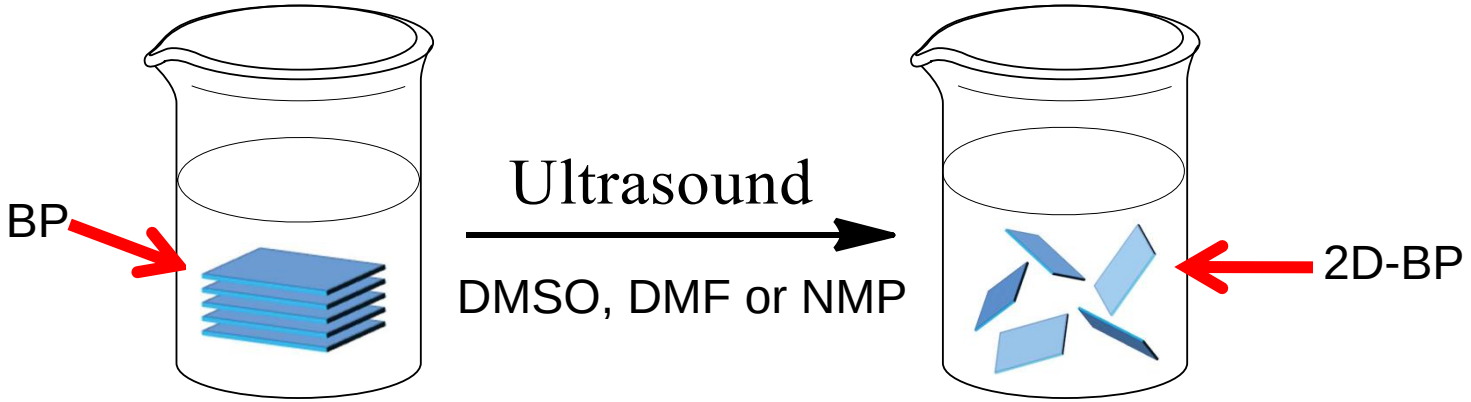
Preparation of few-layer BP

✓ **Mechanical exfoliation**



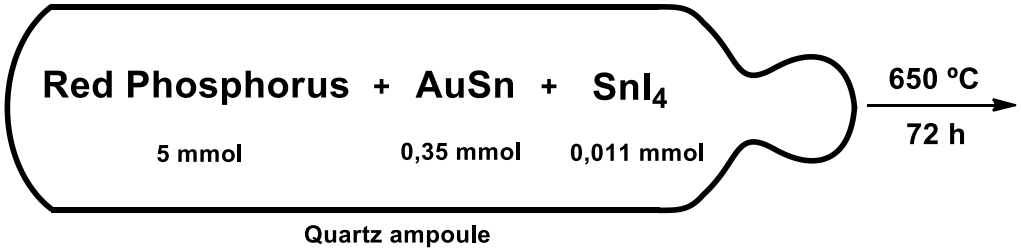
Ye et al. *ACS Nano* **2014**, *8*, 4033; Zhang, *Nat. Nanotechnol*. **2014**, *9*, 372

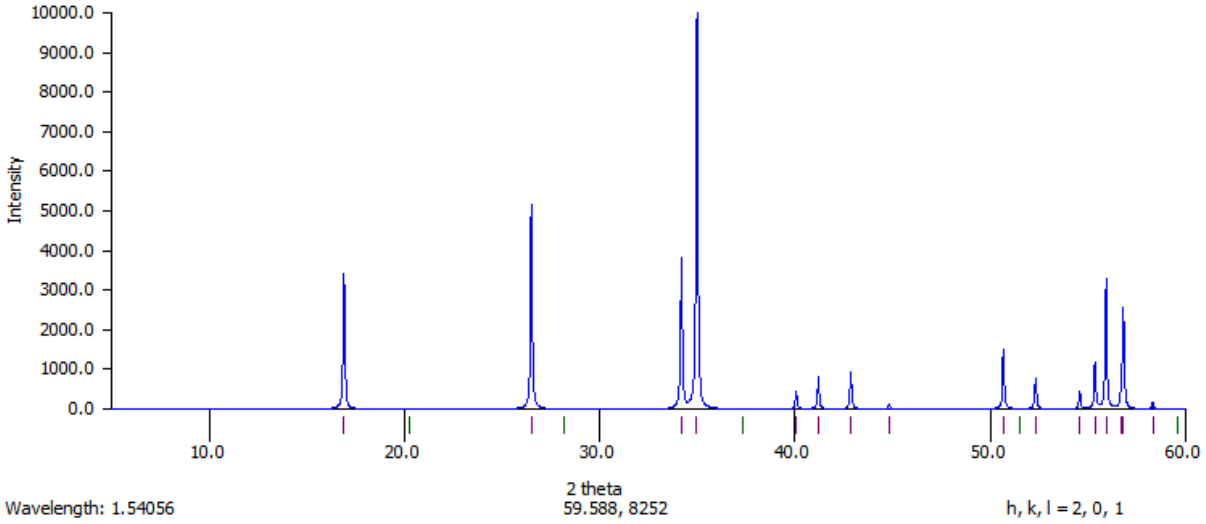
✓ **Liquid phase exfoliation**



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.

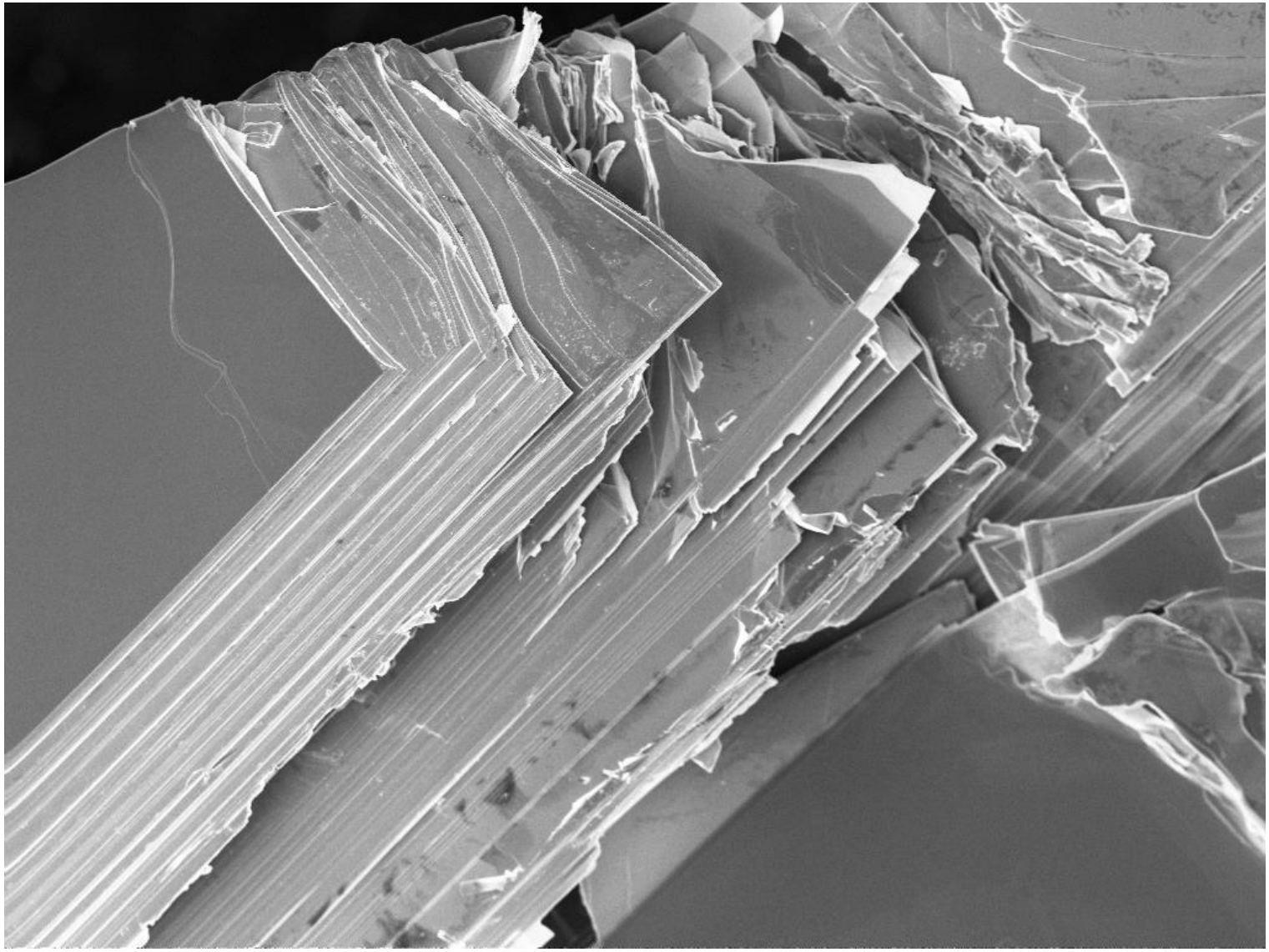
Synthesis of Black Phosphorus



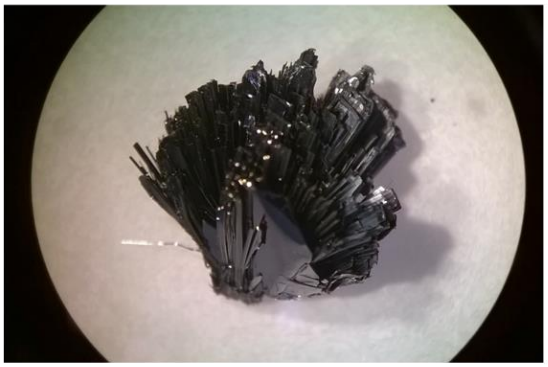


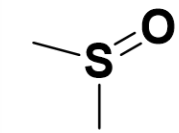
Inorg. Chem. **2007**, *46*, 4028;
J. Solid State Chem. **2008**, *181*, 1707.

SEM of black Phosphorus



Liquid-phase exfoliation



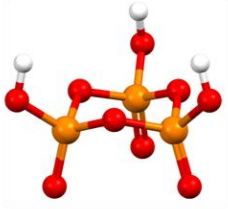


Ultrasound, 37 kHz

30 ºC, 20h

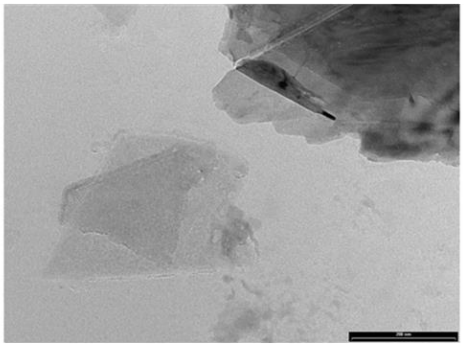
P/H_2O

≥ 15

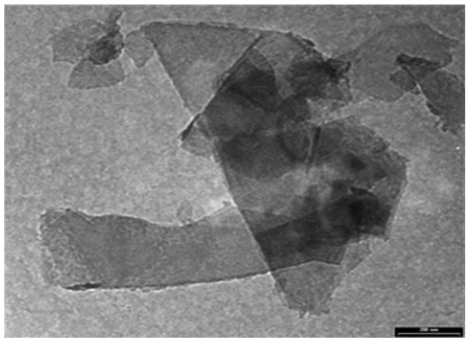


trimetaphosphoric acid

14 - 1.5

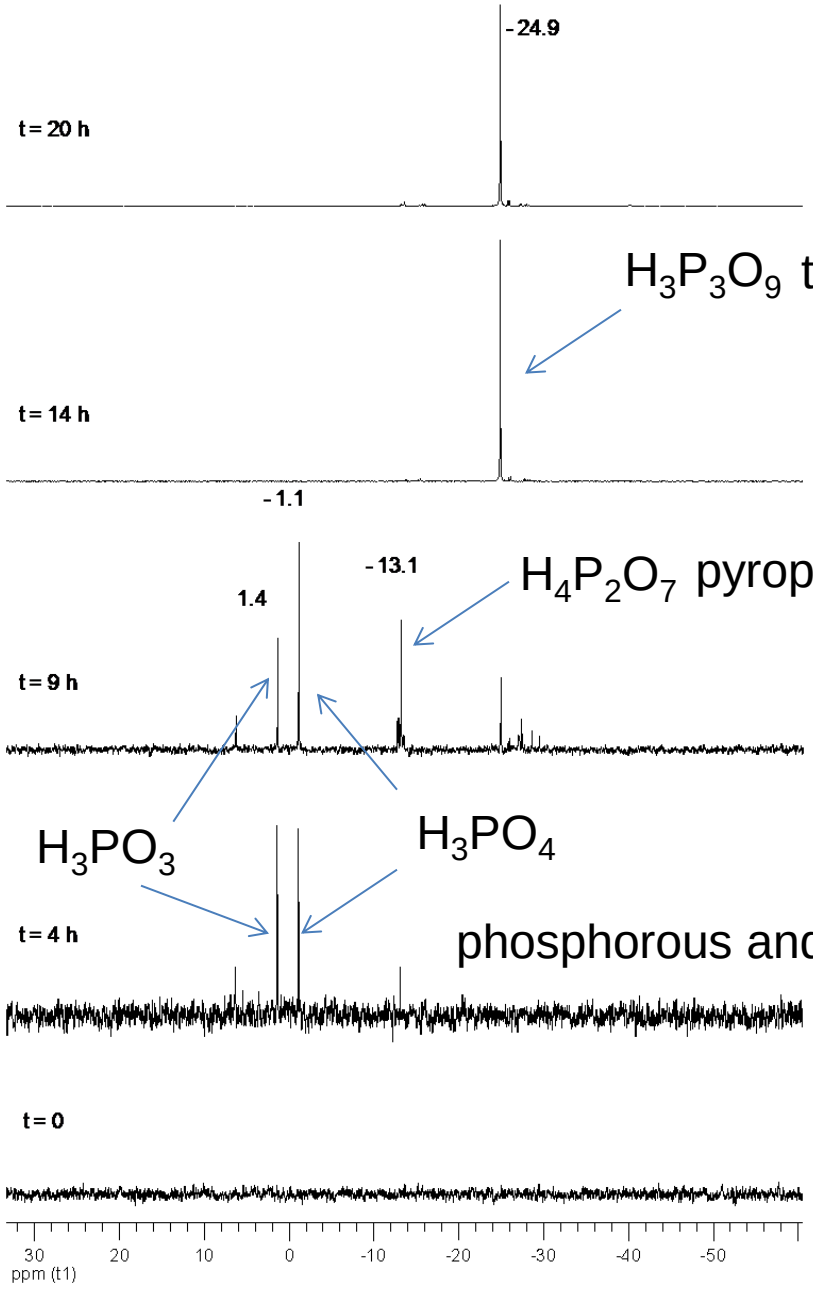


1.4 - 0.3

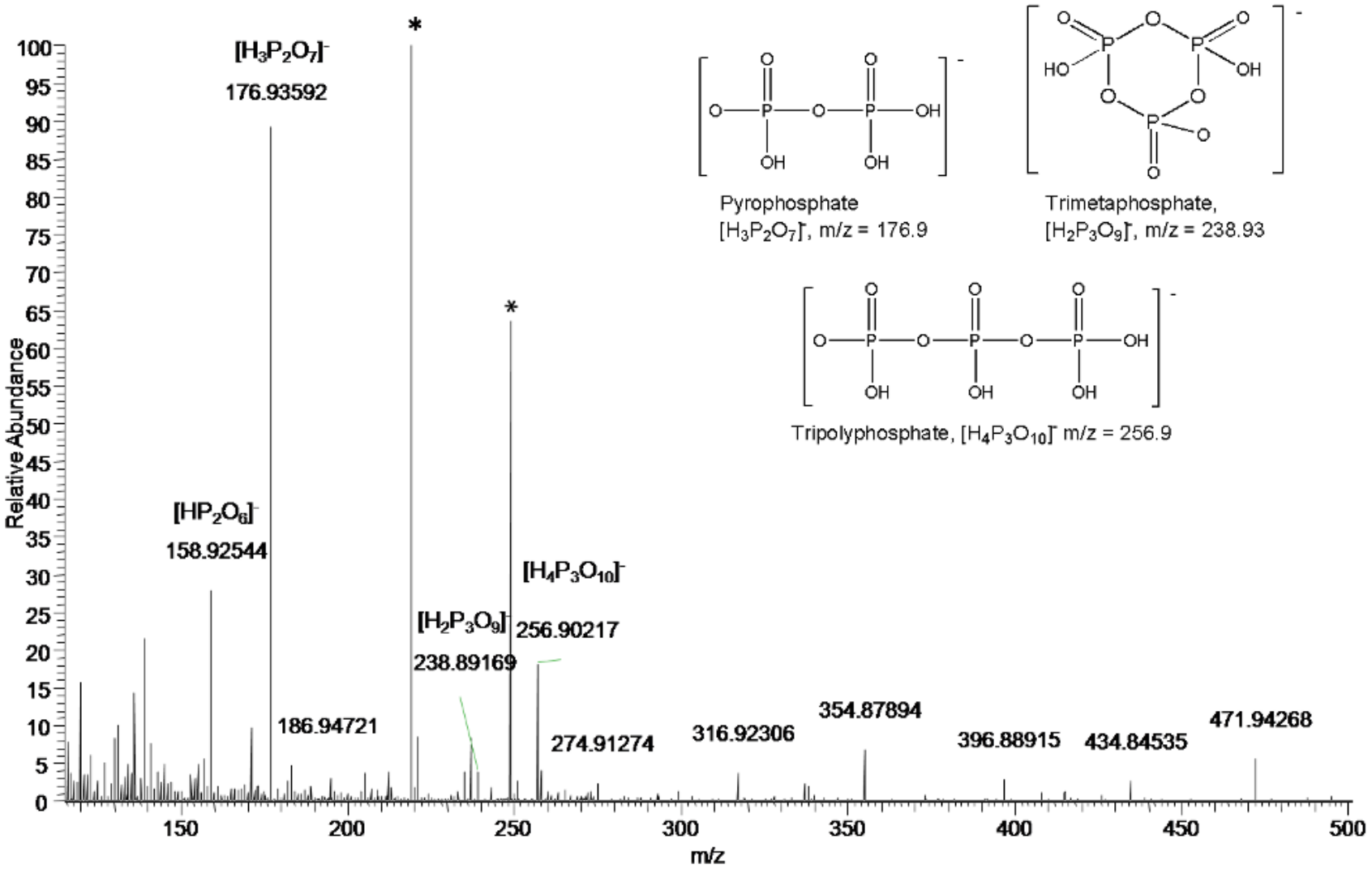


M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv. Mat. Interfaces* **2016**, 3, 1500441.

^{31}P-NMR


-24.9
t = 20 h
$H_3P_3O_9$ trimetaphosphate
t = 14 h
-1.1
-13.1
1.4
$H_4P_2O_7$ pyrophosphate
t = 9 h
H_3PO_3
H_3PO_4
t = 4 h
phosphorous and phosphoris acid
t = 0
30
20
10
0
-10
-20
-30
-40
-50
ppm (t1)

High Resolution ESI-MS

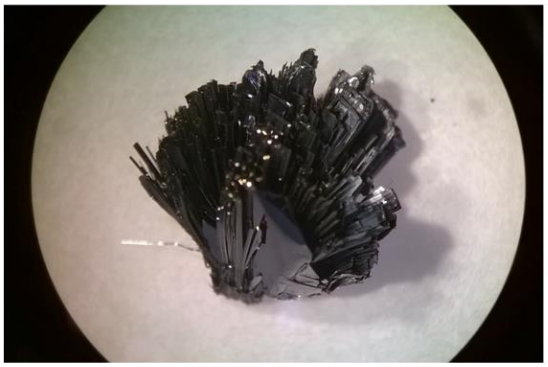


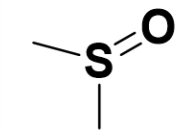
Pyrophosphate
$[H_3P_2O_7]^-$, m/z = 176.9

Trimetaphosphate,
$[H_2P_3O_9]^-$, m/z = 238.93

Tripolyphosphate, $[H_4P_3O_{10}]^-$ m/z = 256.9

Liquid-phase exfoliation



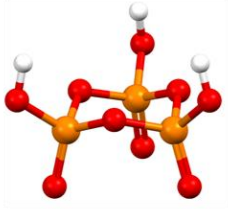


Ultrasound, 37 kHz

30 ºC, 20h

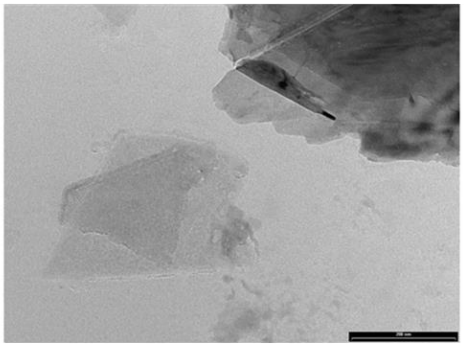
P/H_2O

≥ 15

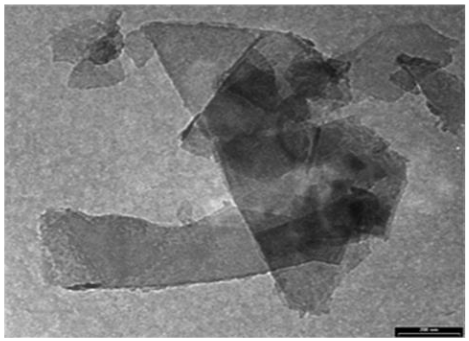


trimetaphosphoric acid

14 - 1.5

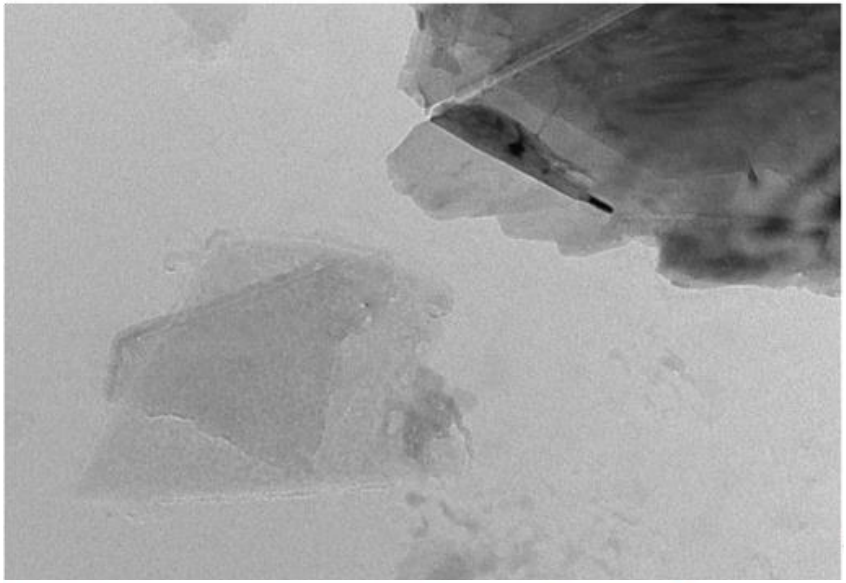


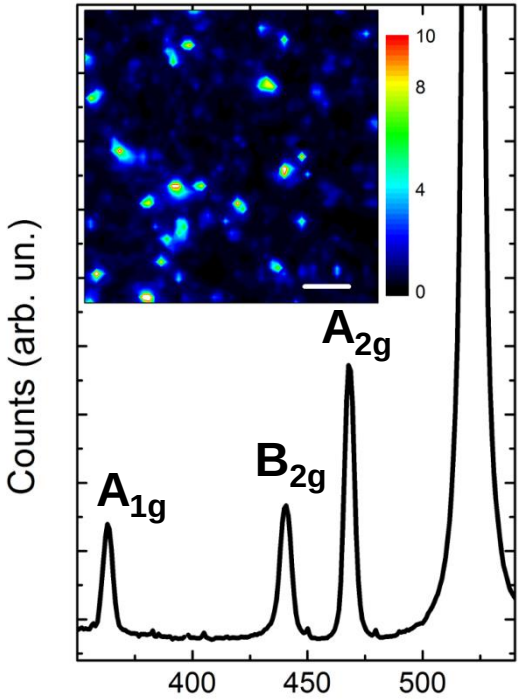
1.4 - 0.3

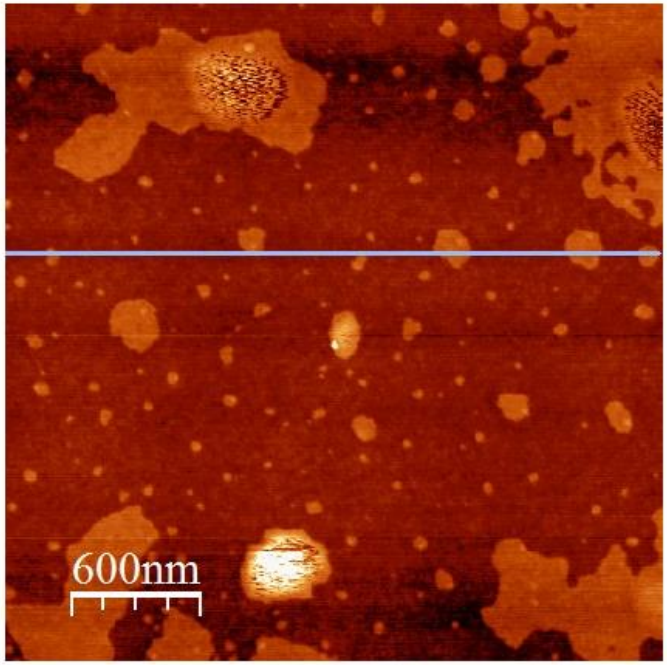


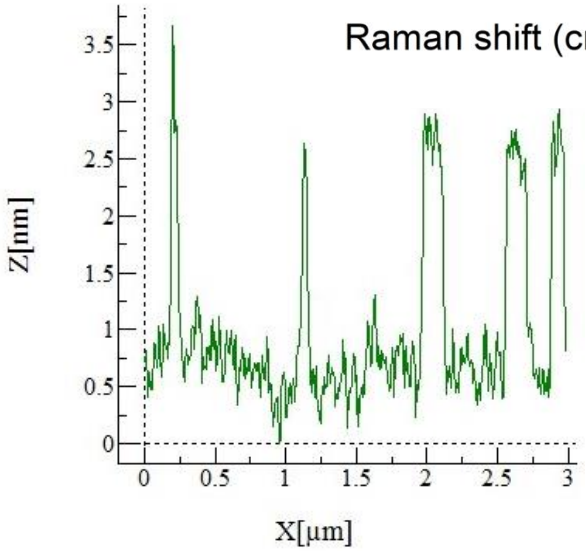
M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv. Mat. Interfaces* **2016**, 3, 1500441.

2D Black Phosphorus: characterization

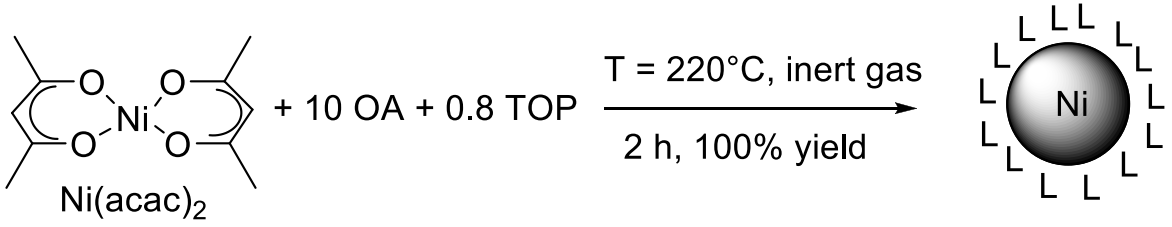






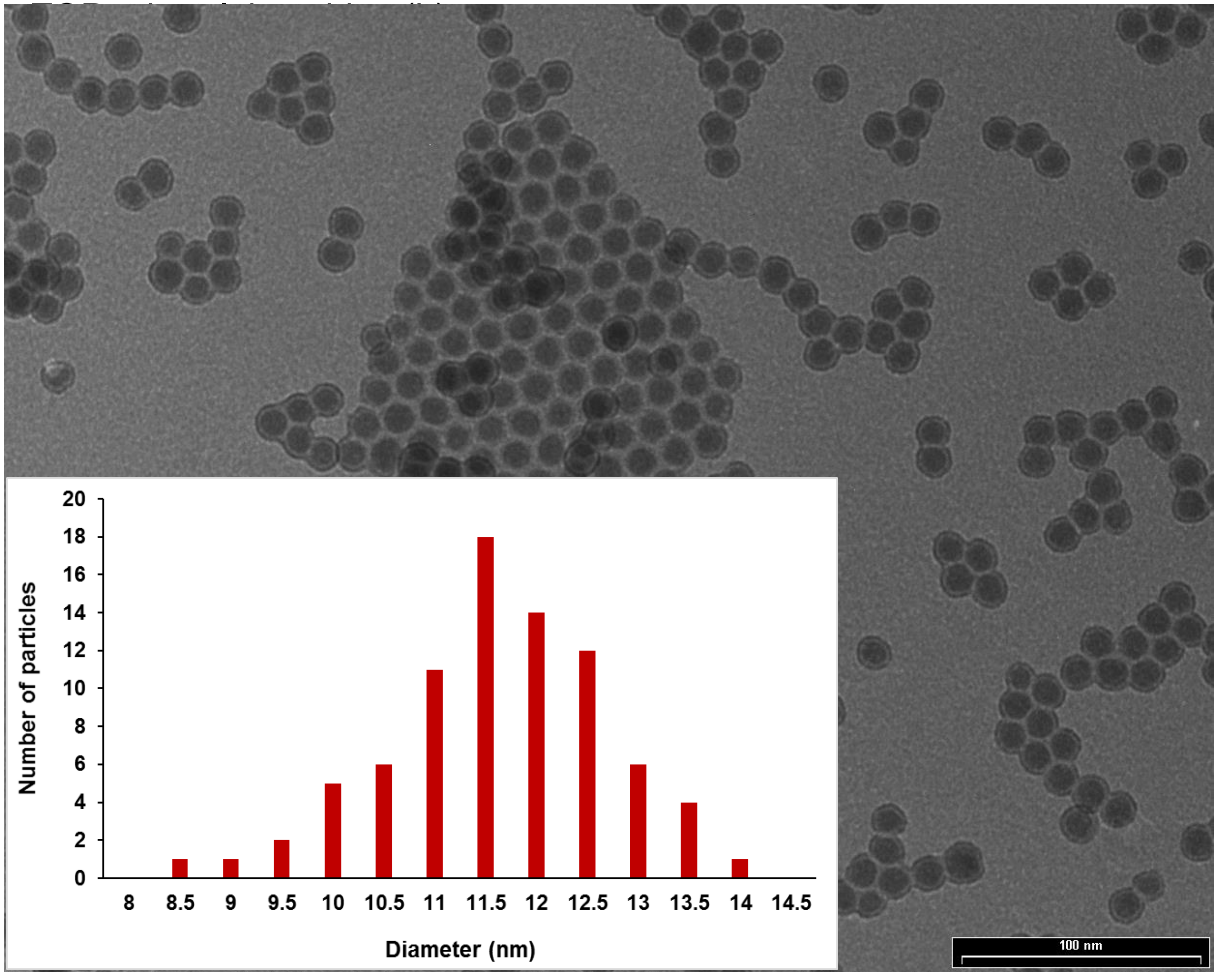


Surface functionalization of 2D black P

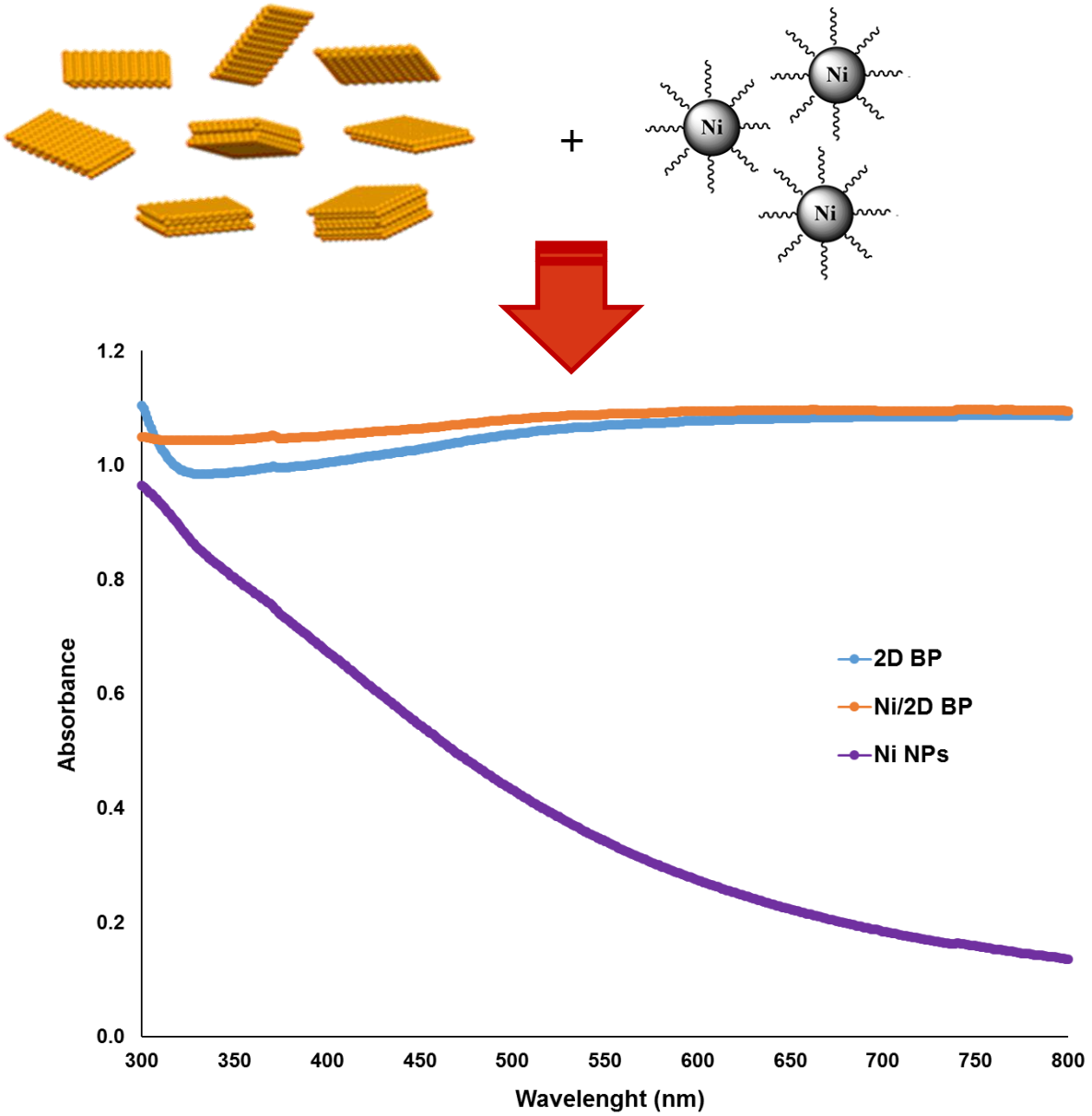


OA : oleylamine

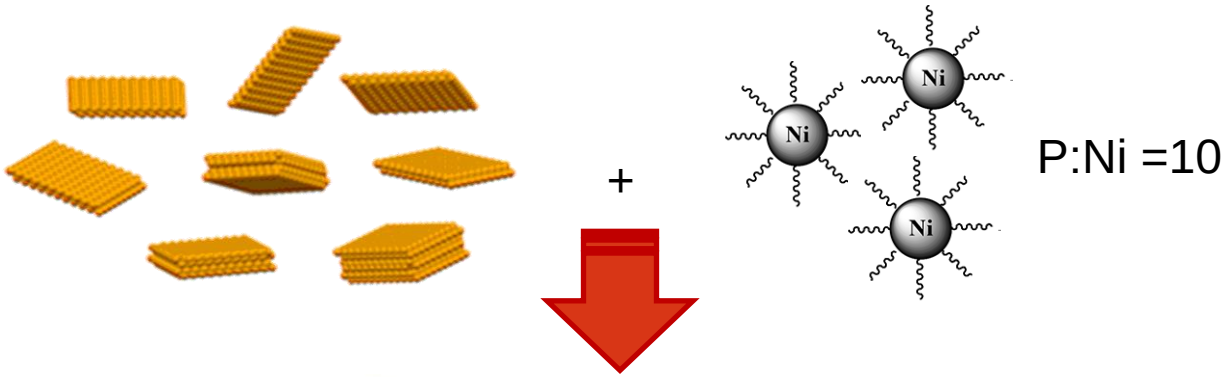
NiNPs

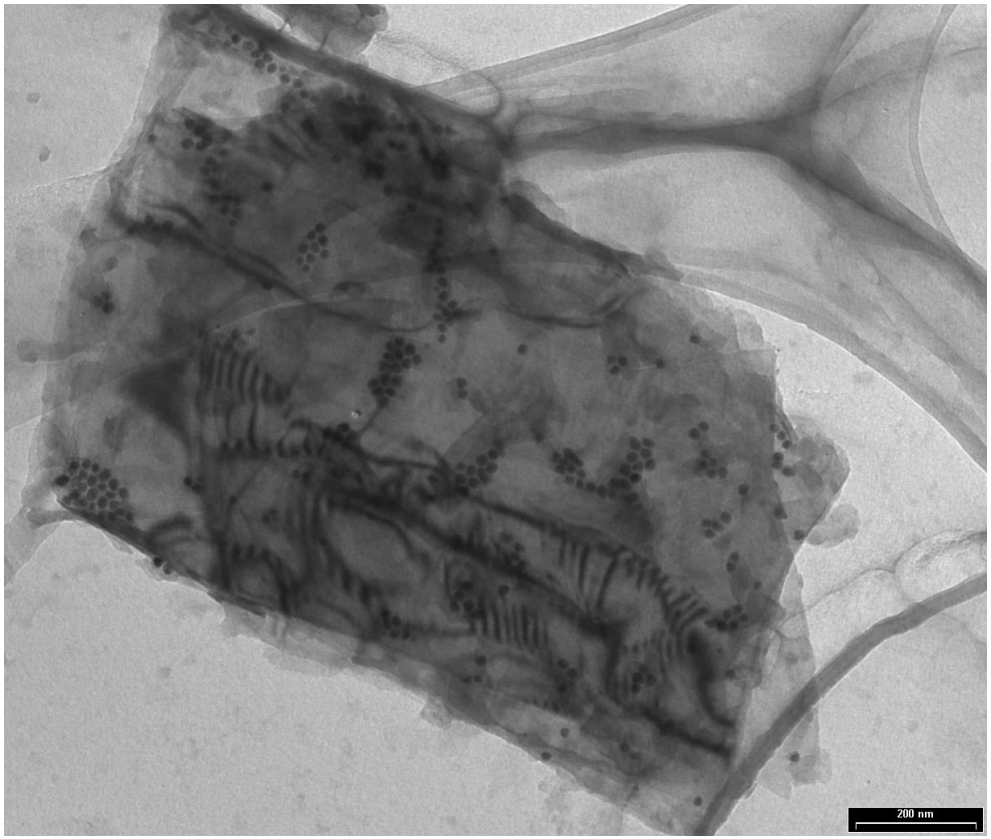


Surface functionalization of 2D black P

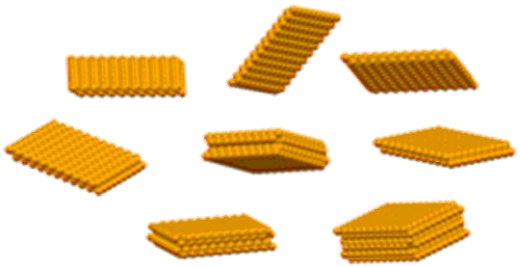


Surface functionalization of 2D black P



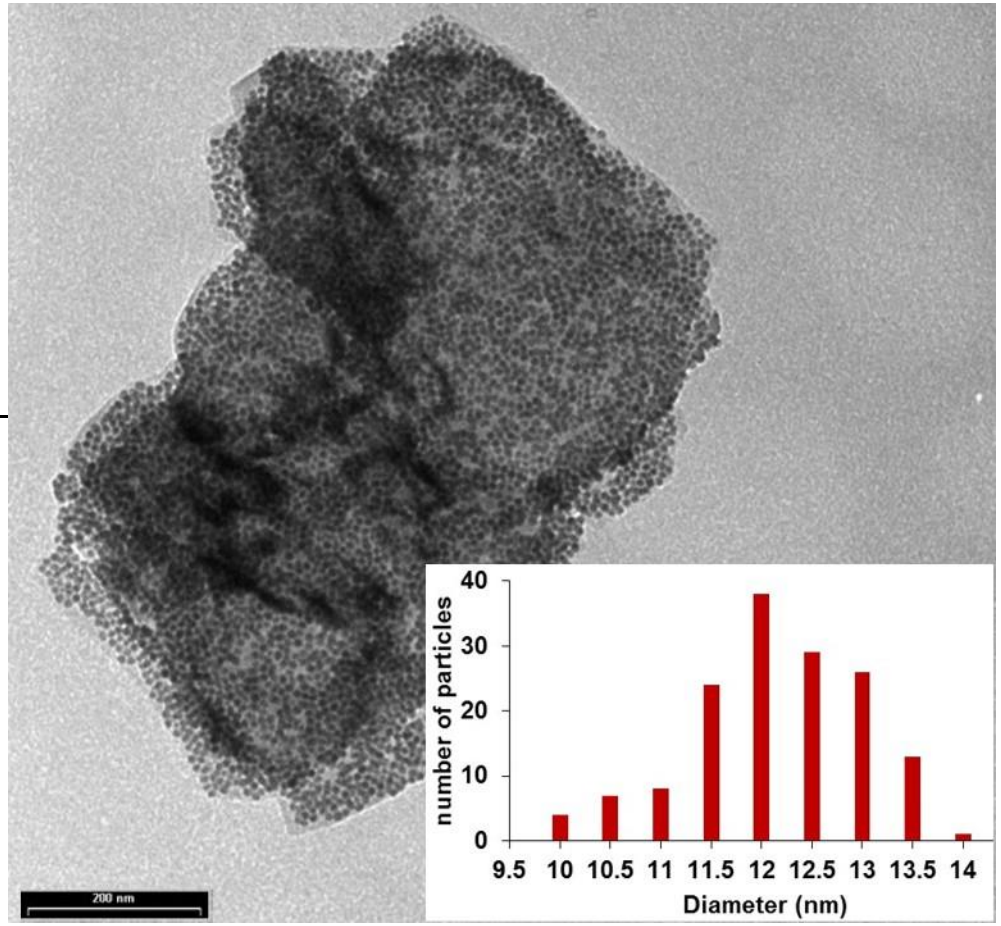


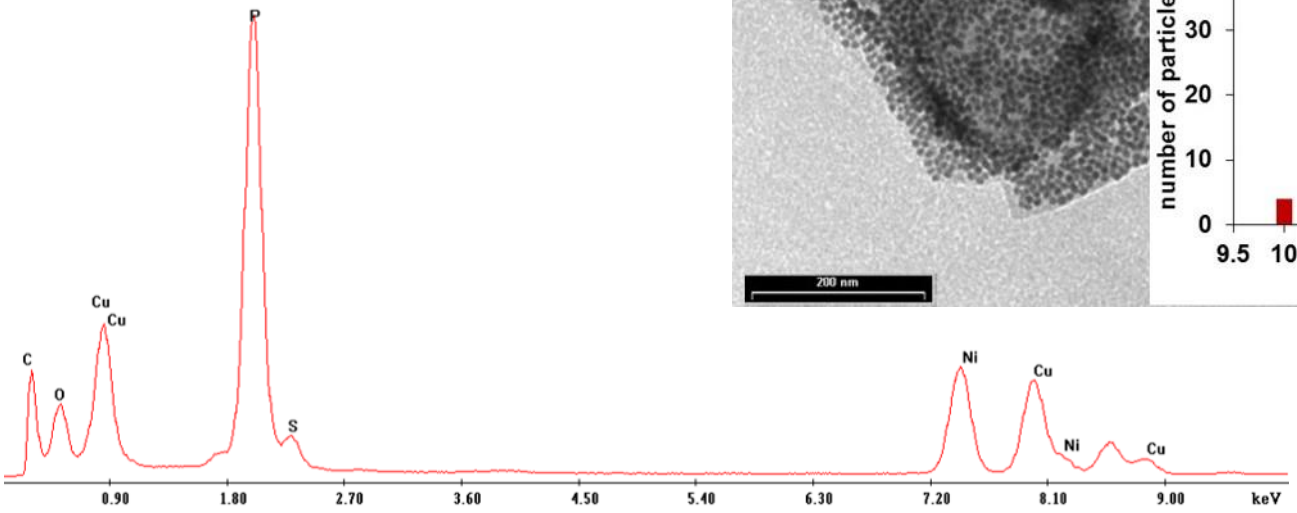
Surface functionalization of 2D black P



Ni NPs

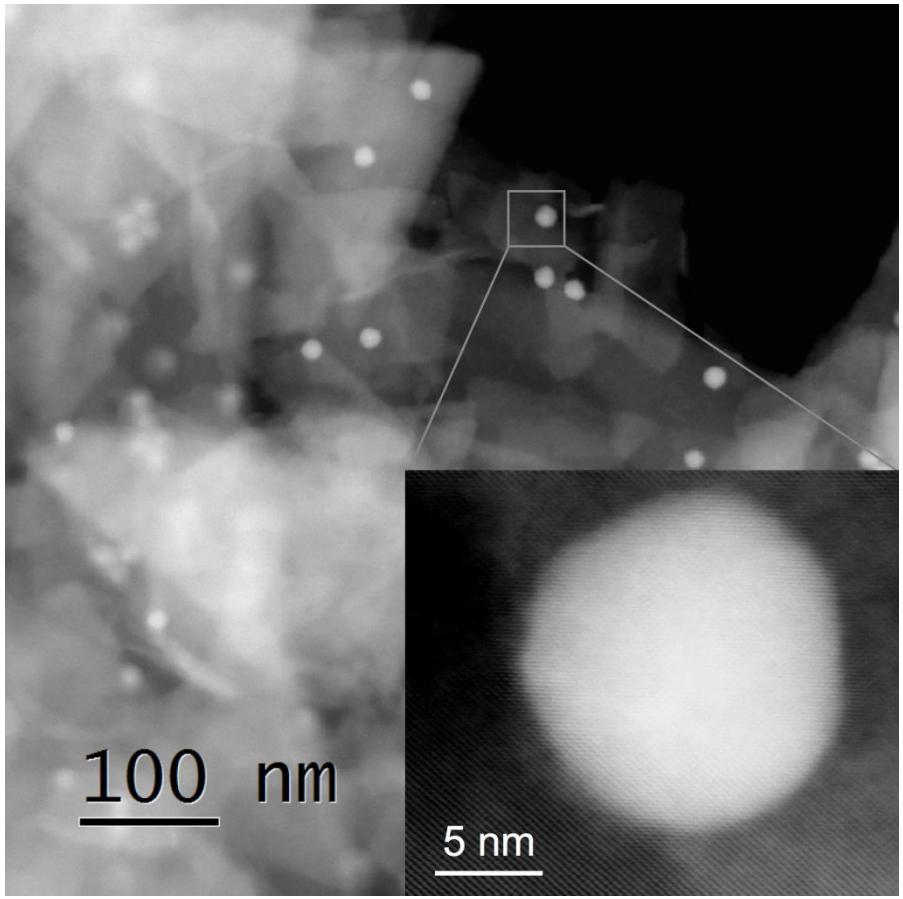
P: Ni = 3





M. Caporali, M. Serrano Ruiz, M. Peruzzini *et al. Chem. Commun*. **2017** in press.

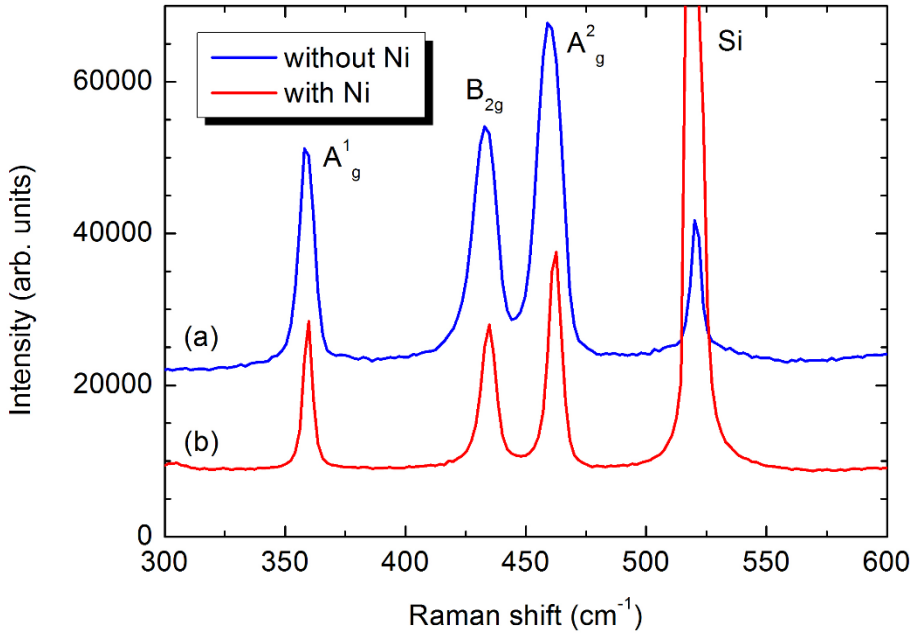
HAADF STEM on Ni/2D BP



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

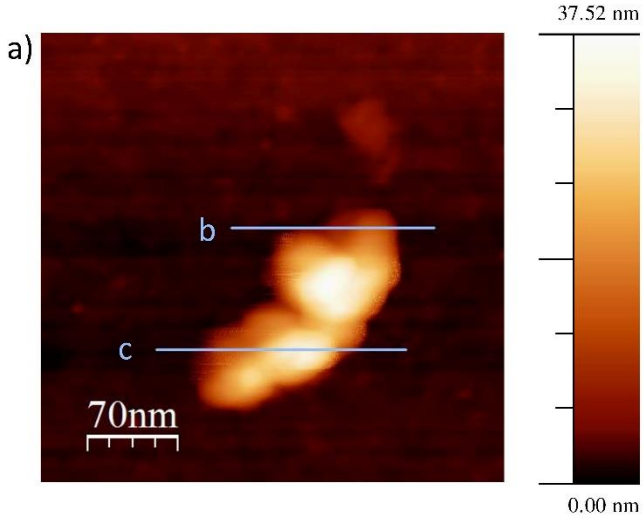
IMM
ISTITUTO PER LA MICROELETTRONICA
E MICROSISTEMI

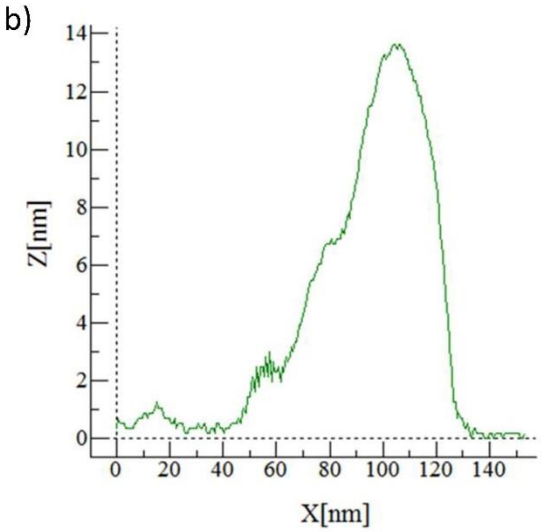
Raman: comparison between pristine 2D BP and Ni/2D BP

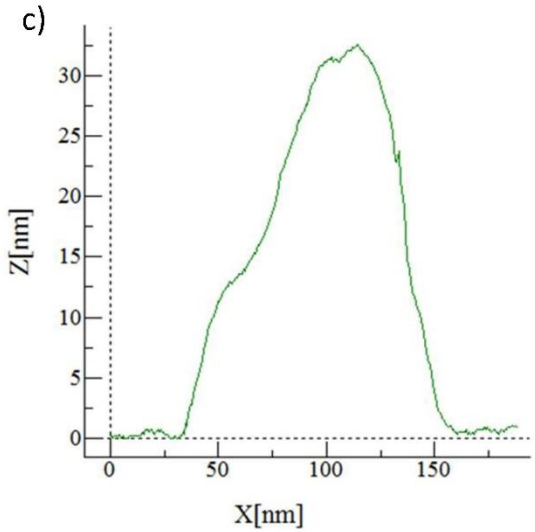


CNRNANO PISA NEST

Atomic Force Microscopy

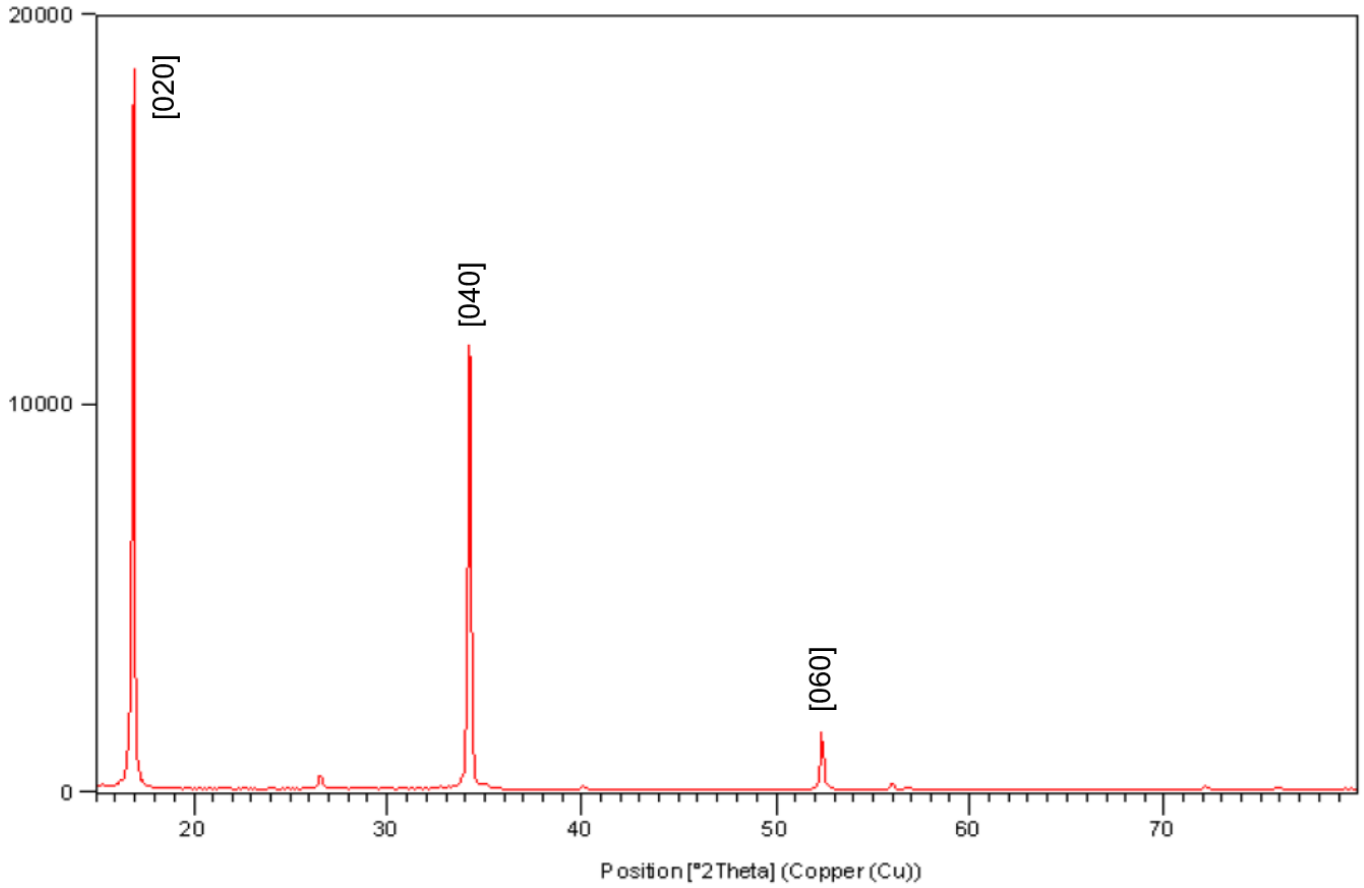




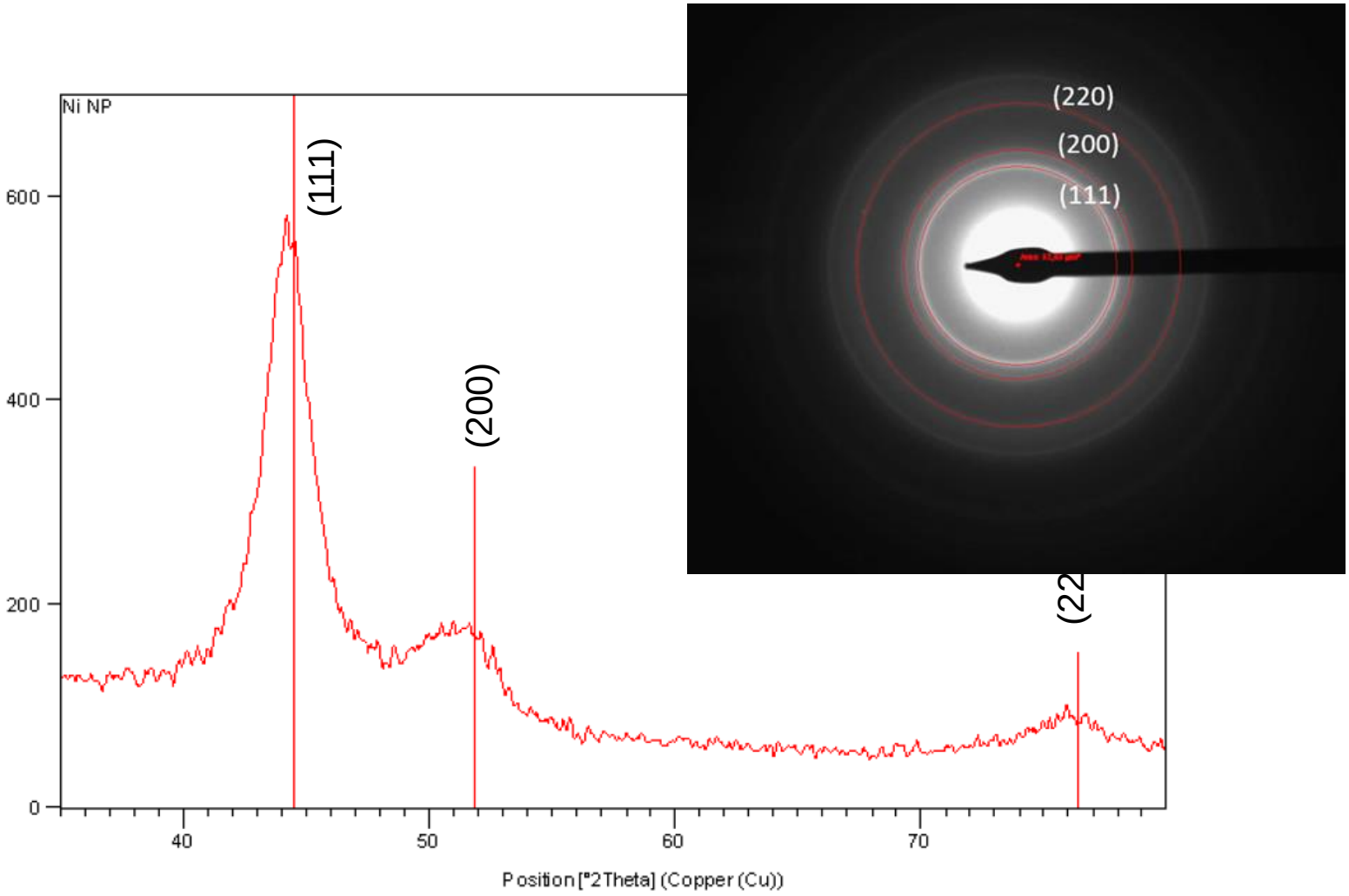


CNRNANO PISA NEST

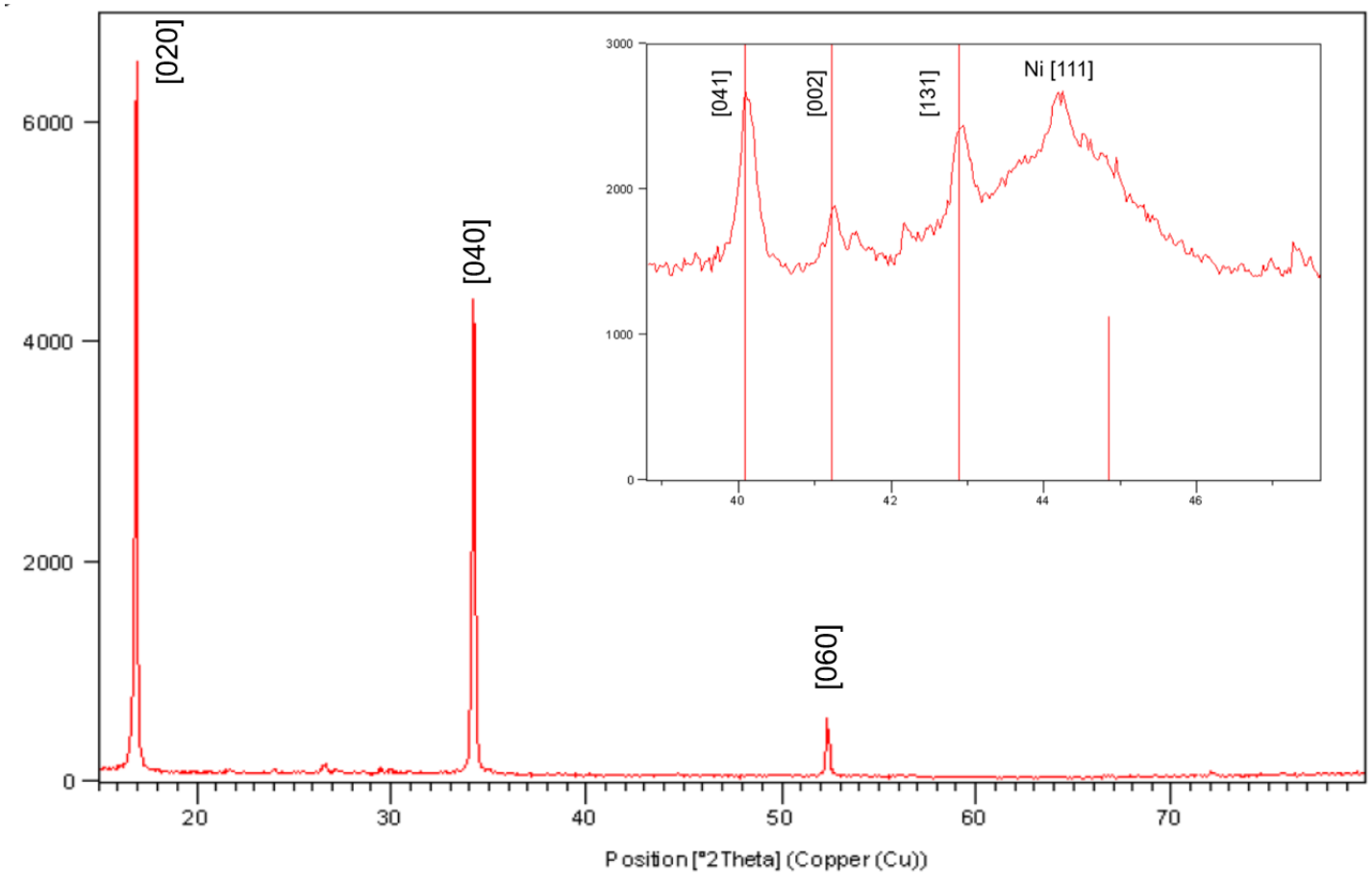
XRD: 2D black P



XRD: Ni NPs


Ni NP
(111)
(200)
(220)
(200)
(111)
600
400
200
0
40
50
60
70
Position [°2Theta] (Copper (Cu))

XRD: Ni/2D BP


[020]
[040]
[060]
[041]
[002]
[131]
Ni [111]
6000
4000
2000
0
20
30
40
50
60
70
3000
2000
1000
0
40
42
44
46
Position [°2Theta] (Copper (Cu))

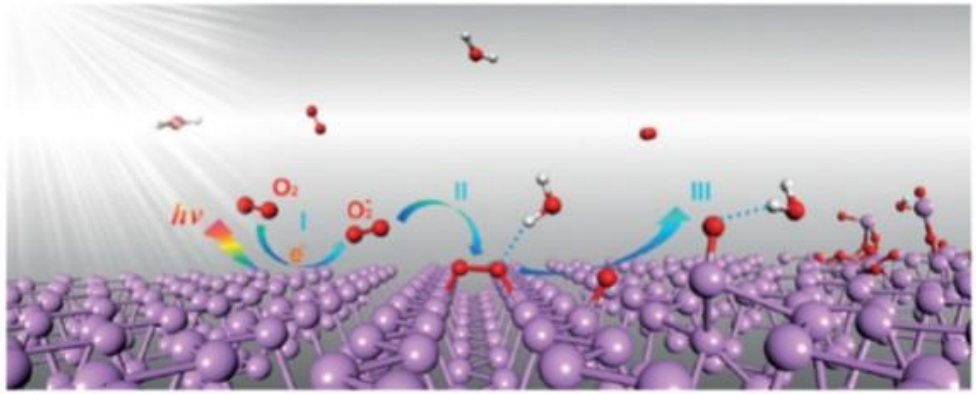
Ambient stability of Ni/2D BP

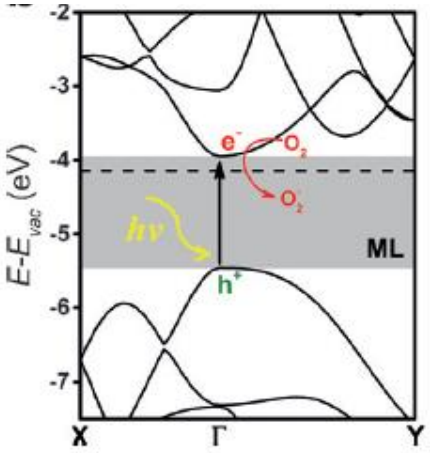
Environmental instability of black Phosphorus hampers its application:

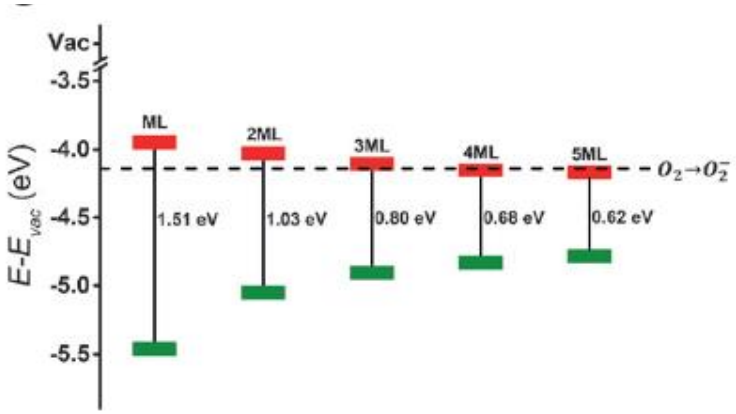
see *2D Mater*. **2015**, 2, 011002.

The degradation is influenced by the following key-factors:

- light
- water
- oxygen







Angew. Chem. Int. Ed. **2016**, 55, 11437 –11441

ACS APPLIED MATERIALS & INTERFACES

Research Article

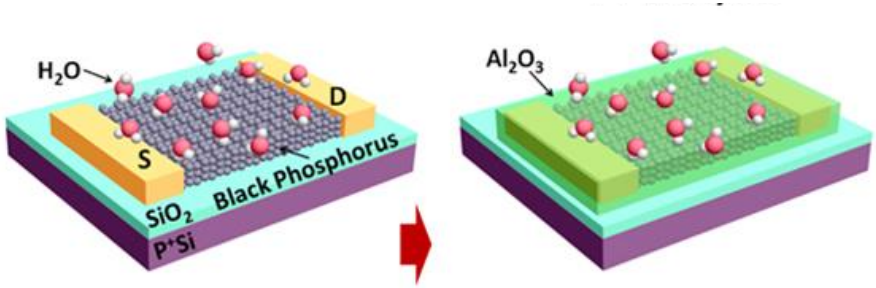
www.acsami.org

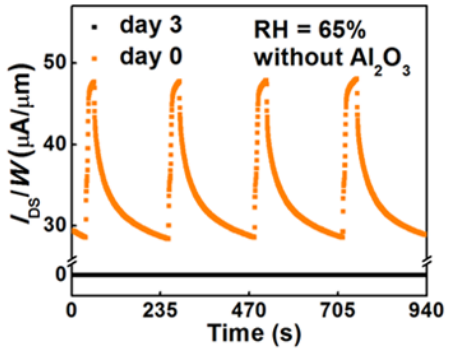
Air-Stable Humidity Sensor Using Few-Layer Black Phosphorus

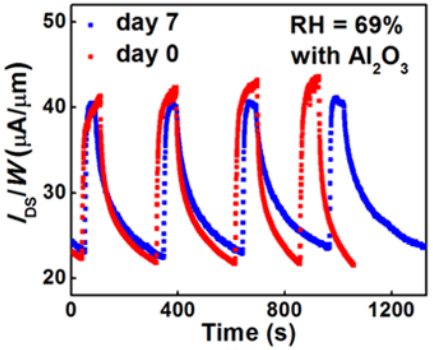
Jinshui Miao,[†] Le Cai,[†] Suoming Zhang,[†] Junghyo Nah,[§] Junghoon Yeom,[‡] and Chuan Wang*[,†]

[†]Electrical and Computer Engineering and [‡]Mechanical Engineering, Michigan State University, East Lansing, Michigan 48824, United States

[§]Electrical Engineering, Chungnam National University, Daejeon 34134, Korea







Passivation strategies

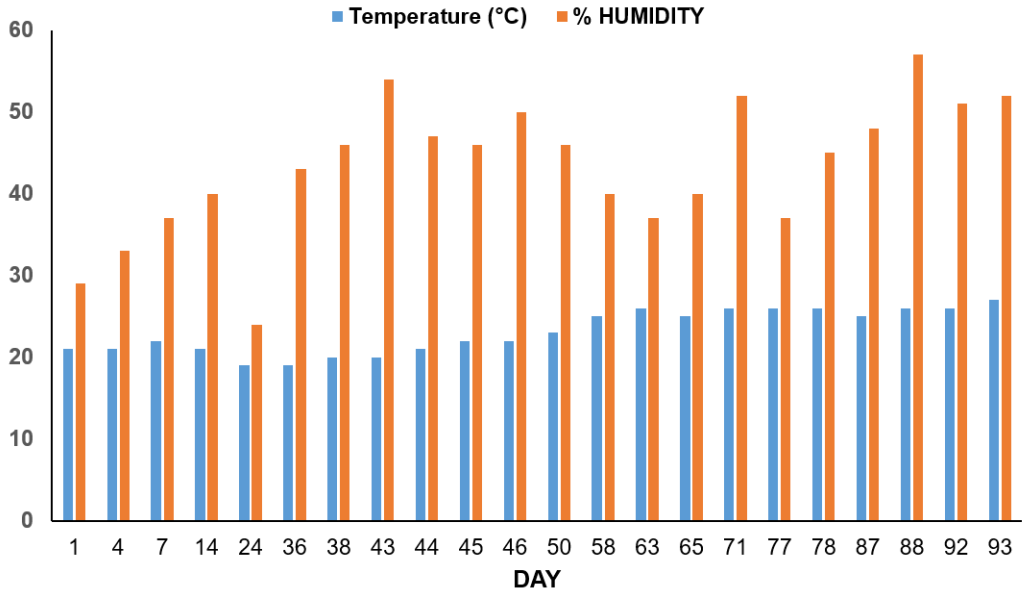
The solution to avoid degradation is capping BP to minimize its interaction with the ambient:

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

- Capping of BP with 2D materials as graphene or *h*-BN have provided a stability for a period of 18 days.

Ambient degradation of Ni/2D BP

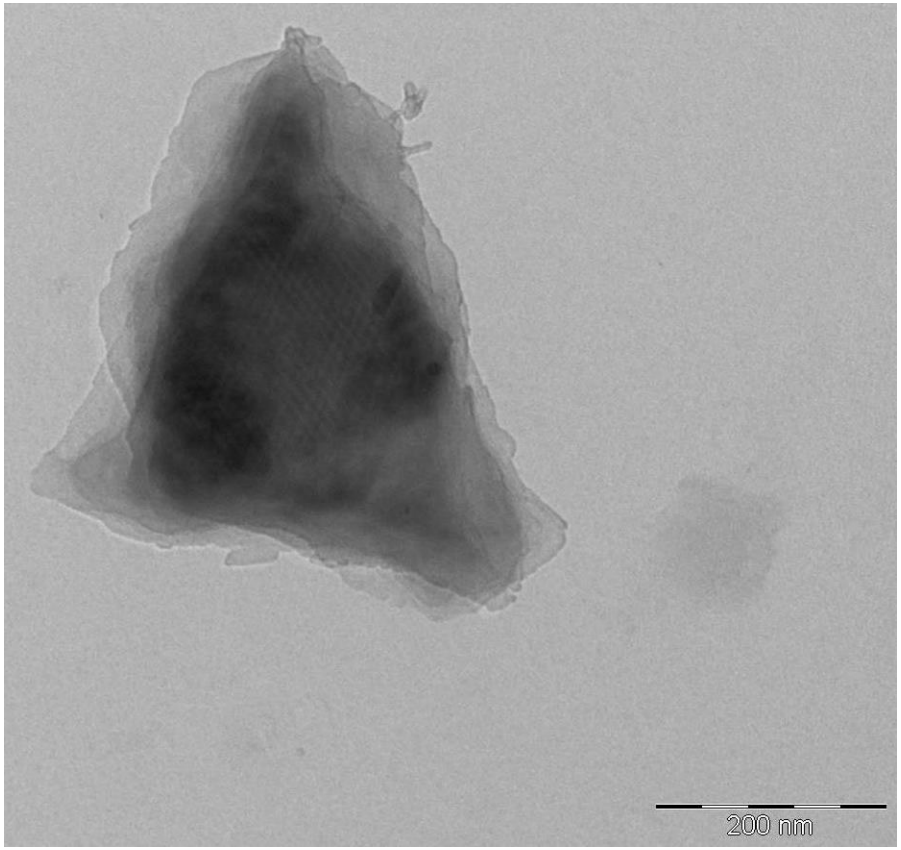
Our conditions: samples exposed to air and humidity, no light



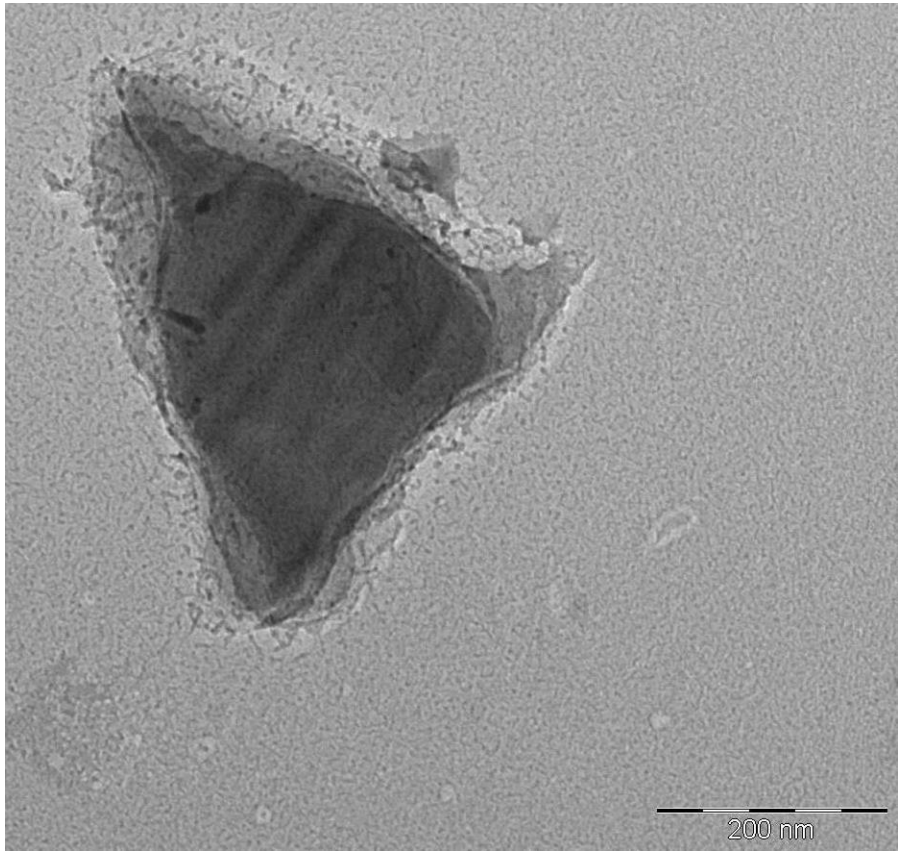
As a comparison, six flakes of Ni/2D BP and of pristine 2D BP kept in the same conditions were observed by TEM along four months.

Ambient degradation of 2D BP

time 0

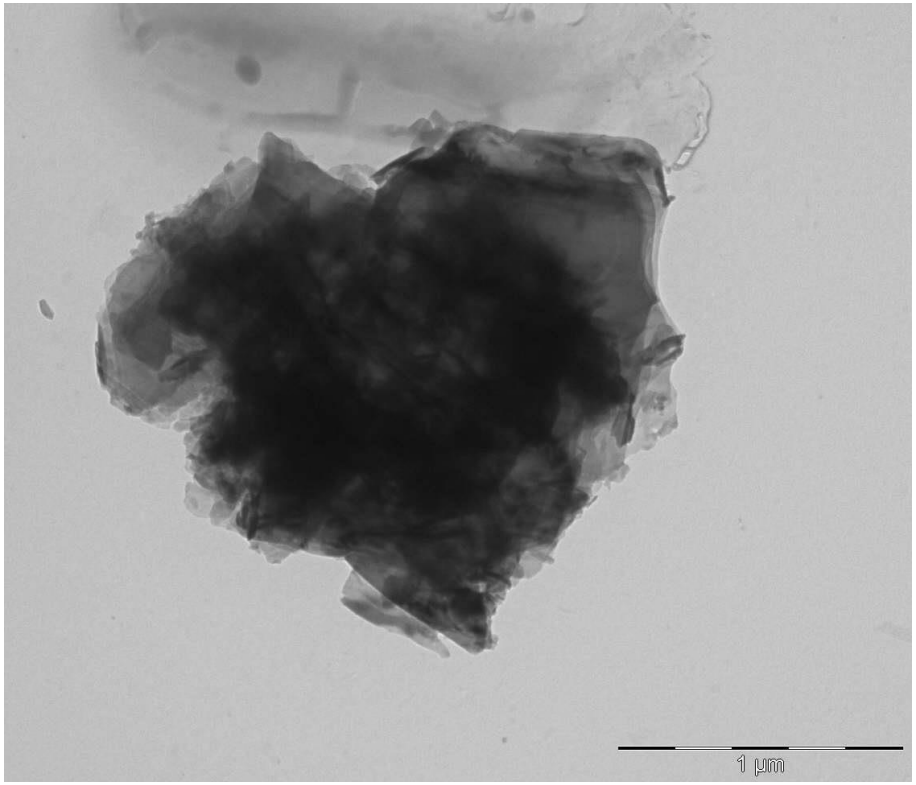


after 2 weeks

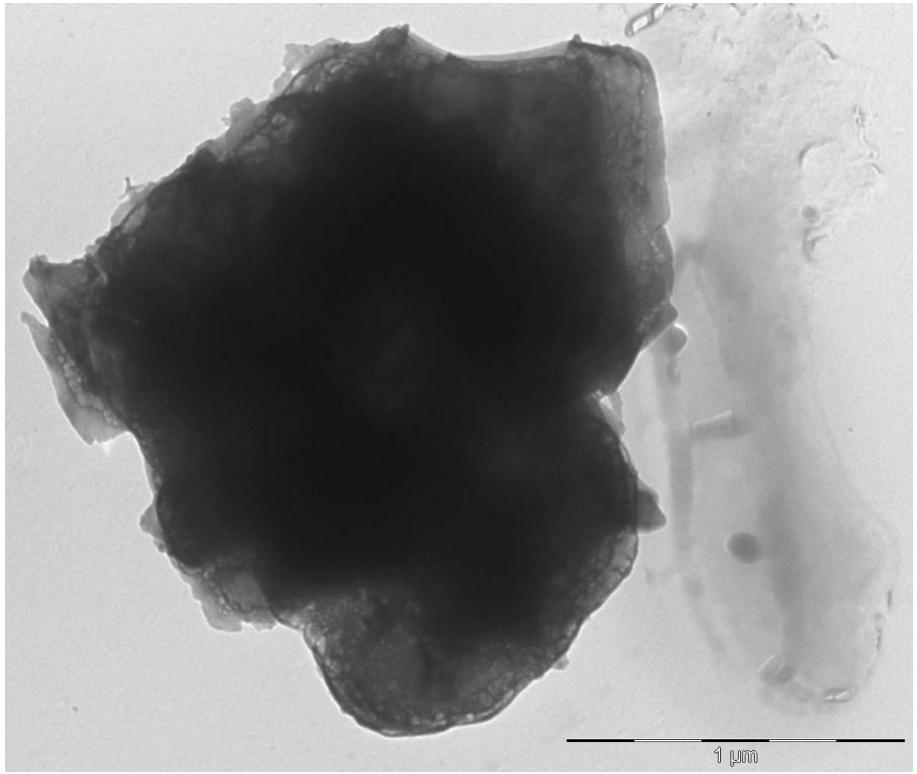


Ambient degradation of 2D BP

time 0



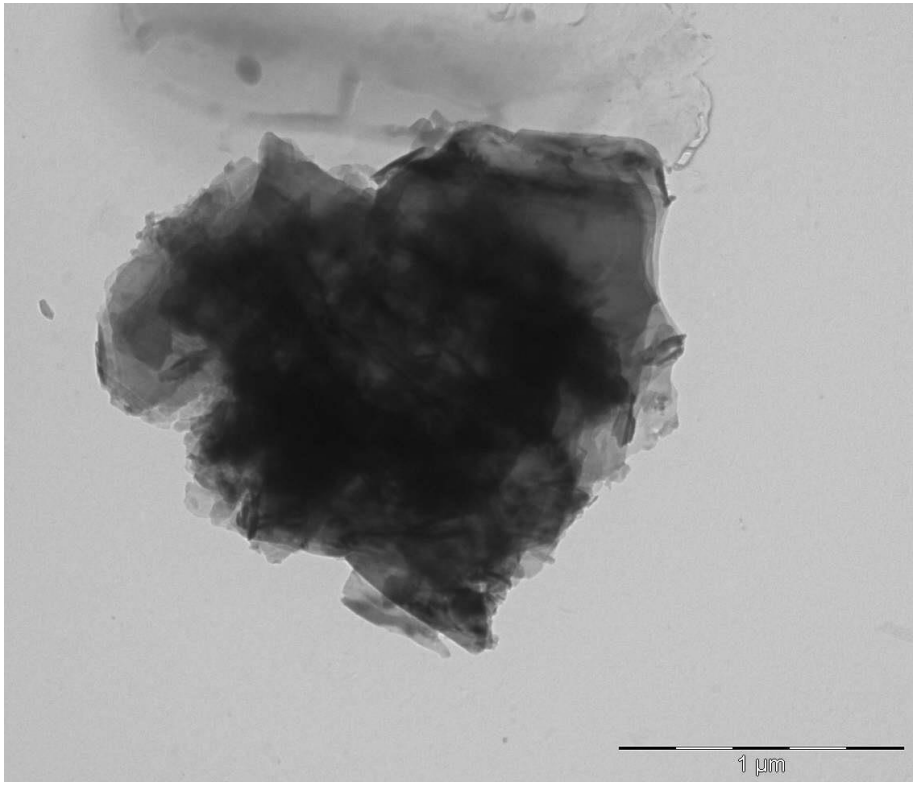
after 1 week



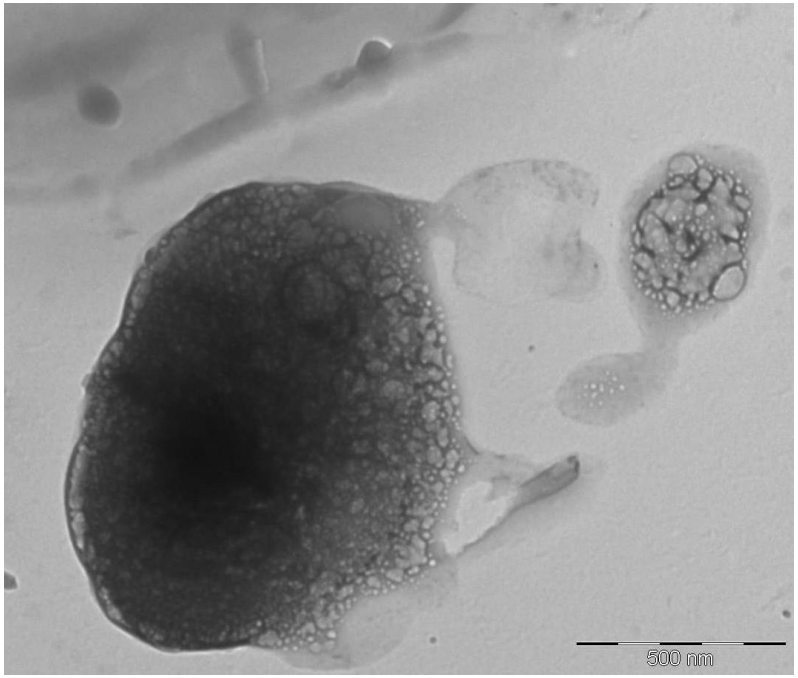
After 8 days, pristine BP flakes degrade completely to molecular phosphates.

Ambient degradation of 2D BP

time 0

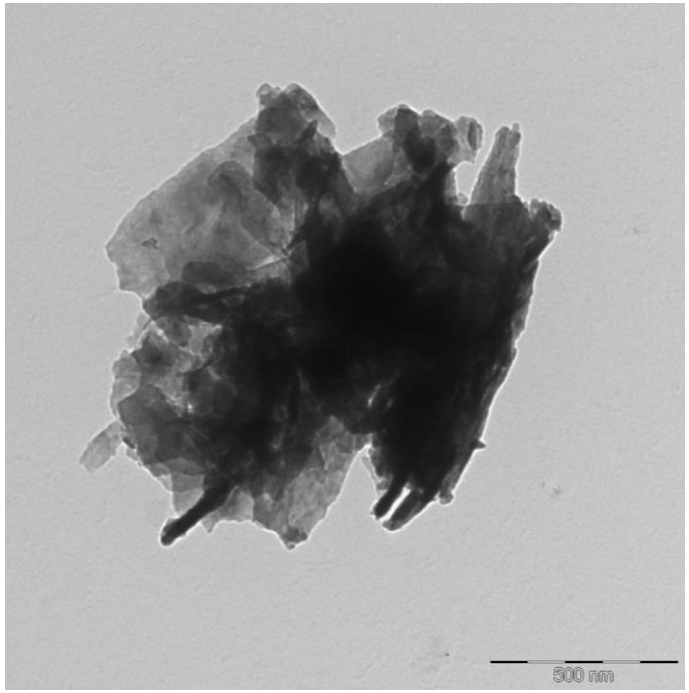


after 2 weeks

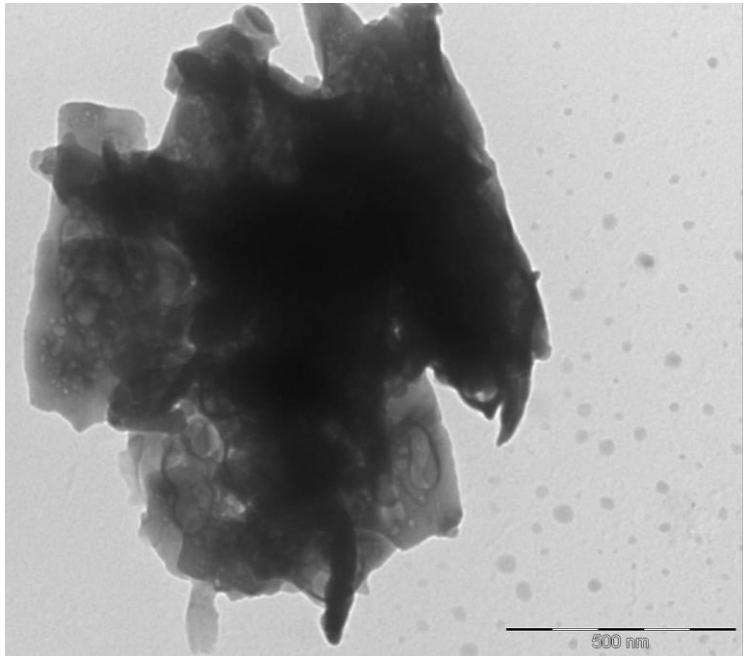


Ambient degradation of 2D BP

time 0

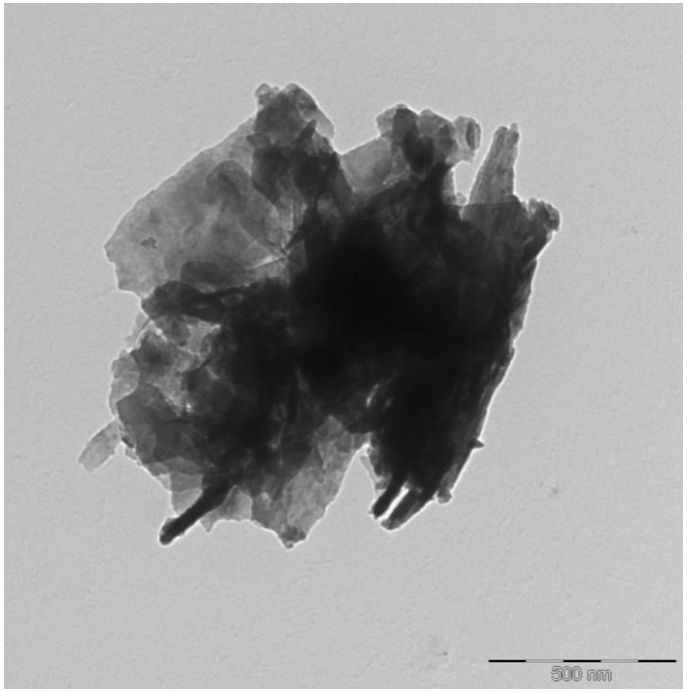


after 1 week

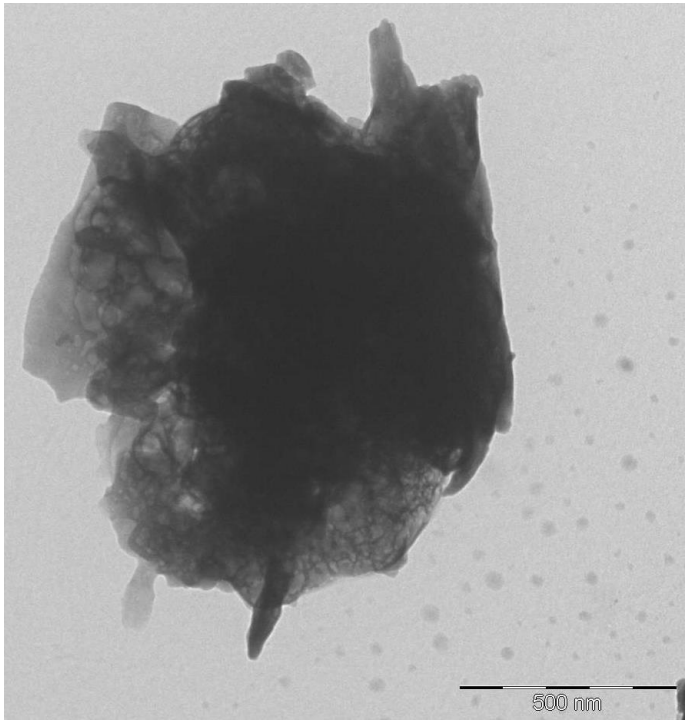


Ambient degradation of 2D BP

time 0

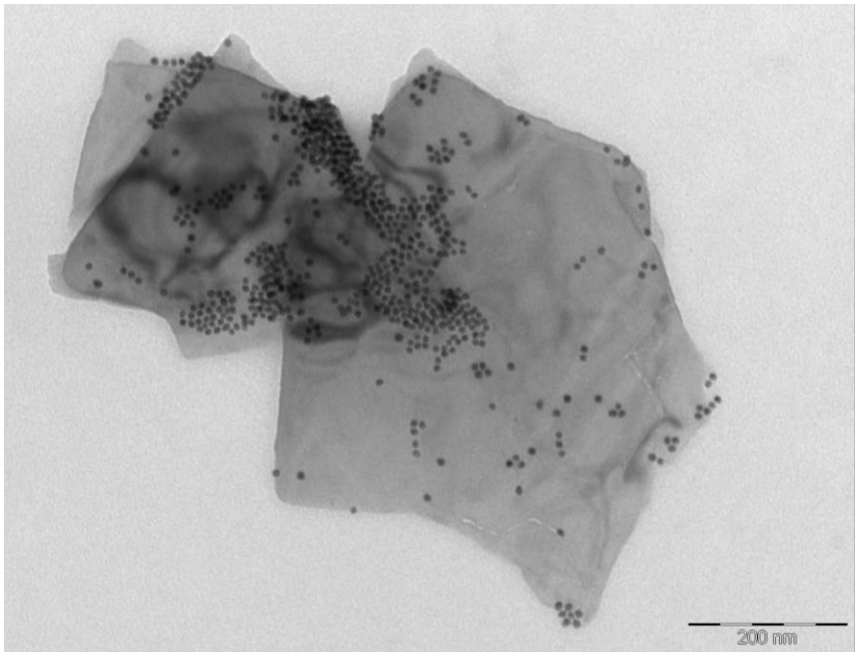


after 2 weeks

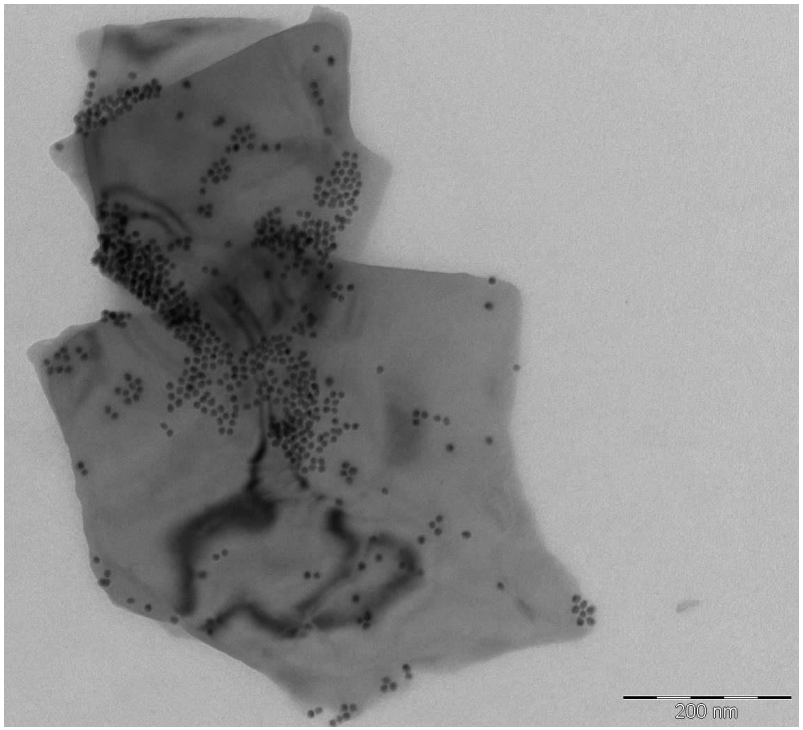


Ambient Degradation of Ni/2D BP

time 0

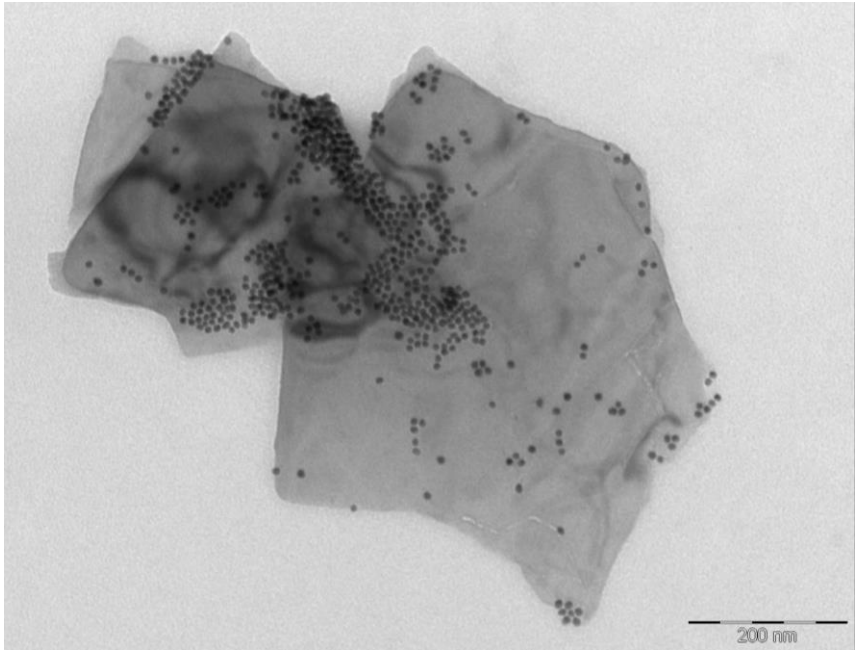


after 1 week

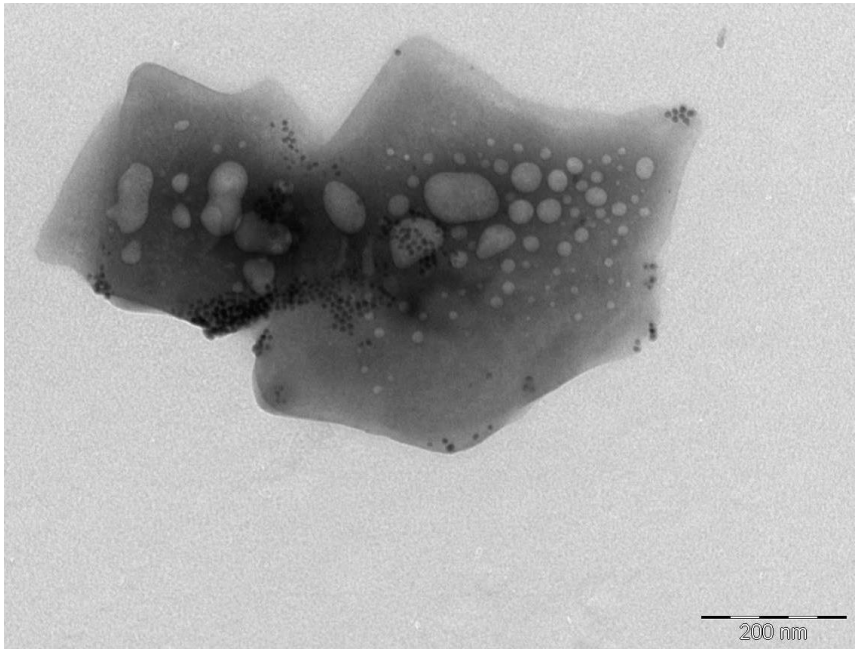


Ambient Degradation of Ni/2D BP

time 0

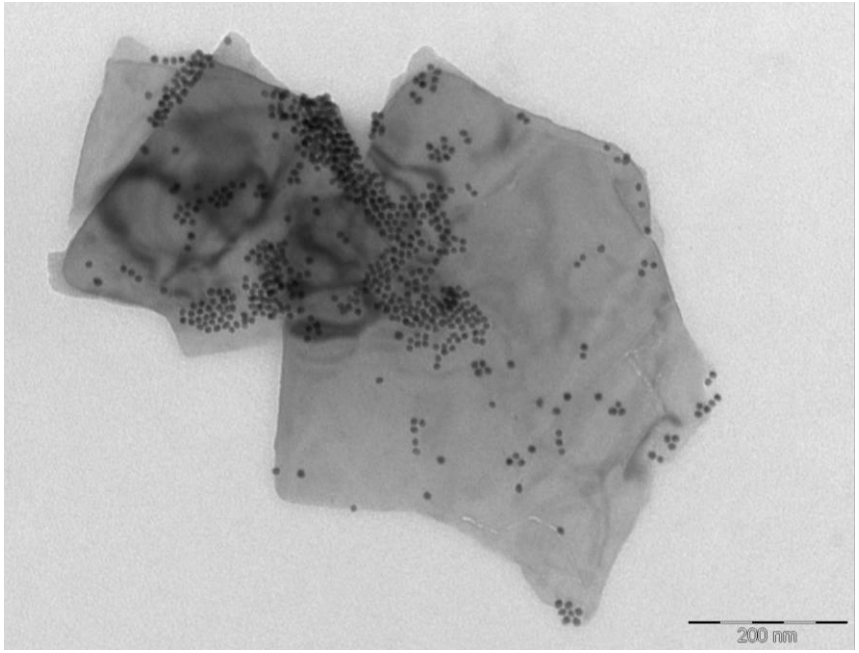


after 2 weeks

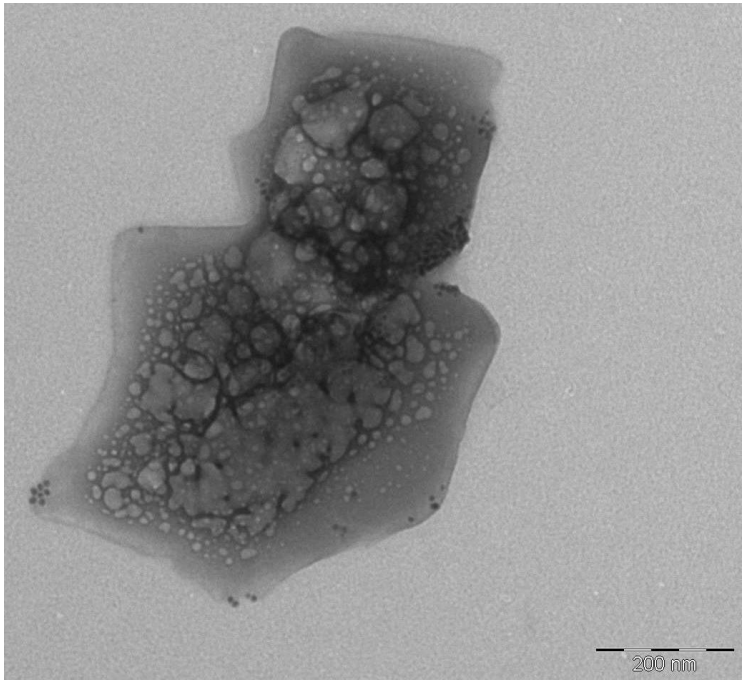


Ambient Degradation of Ni/2D BP

time 0

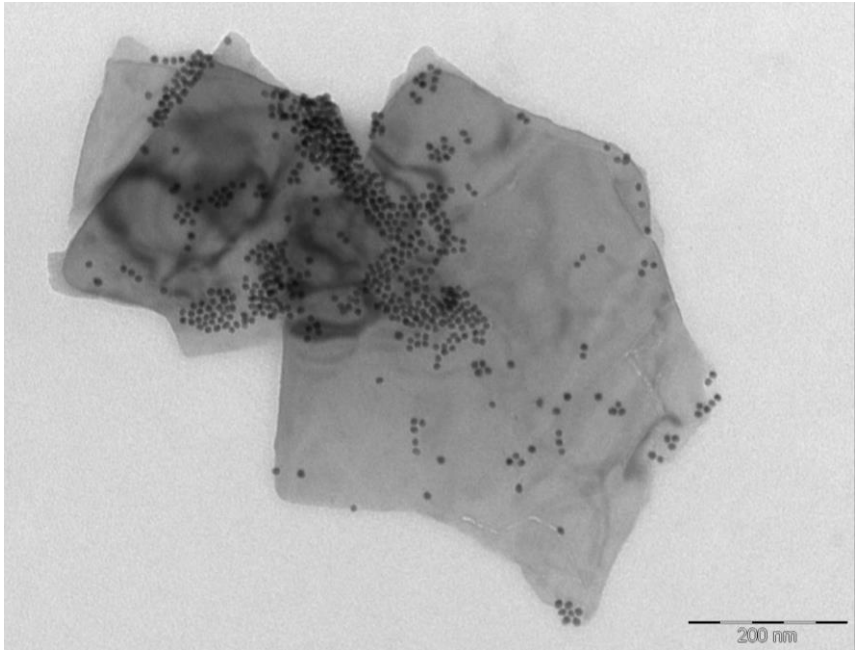


after 2 months

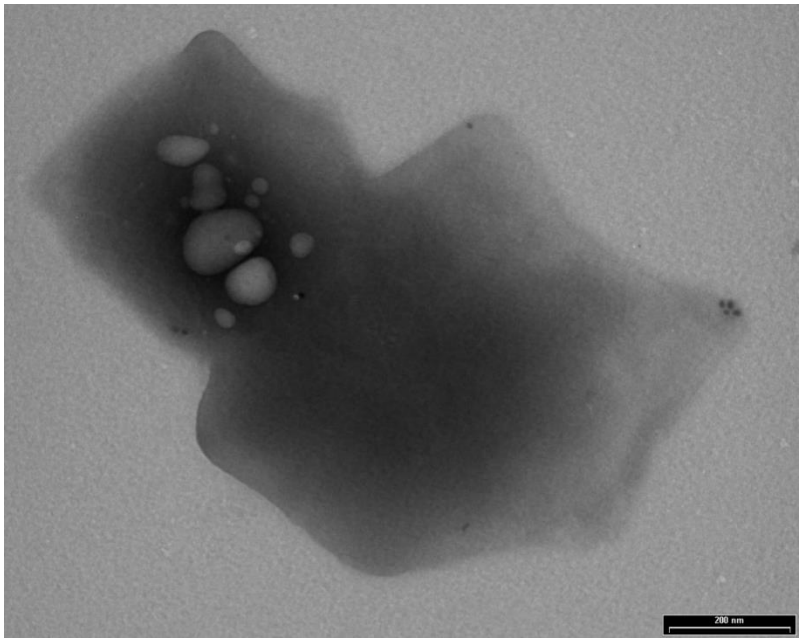


Ambient Degradation of Ni/2D BP

time 0

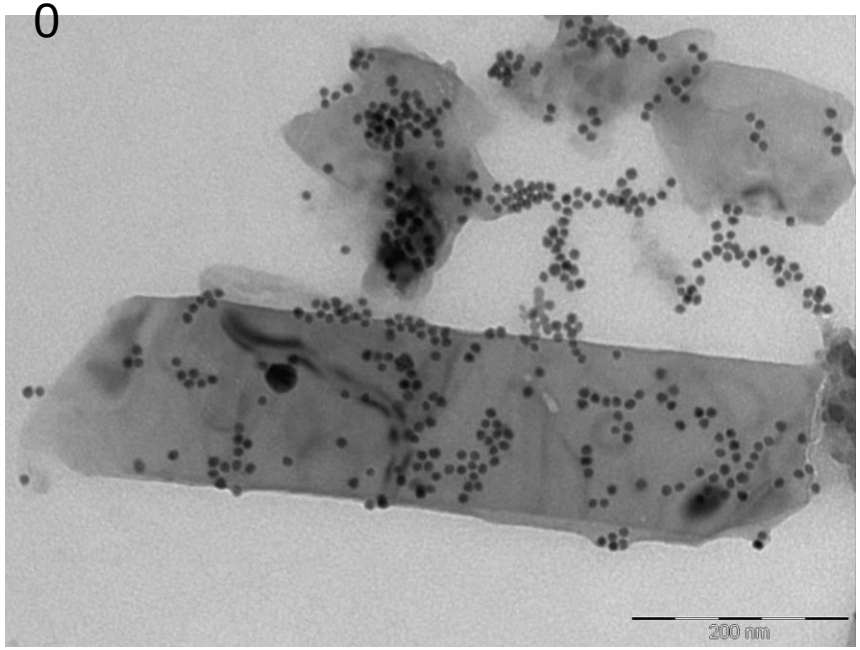


after 3 months

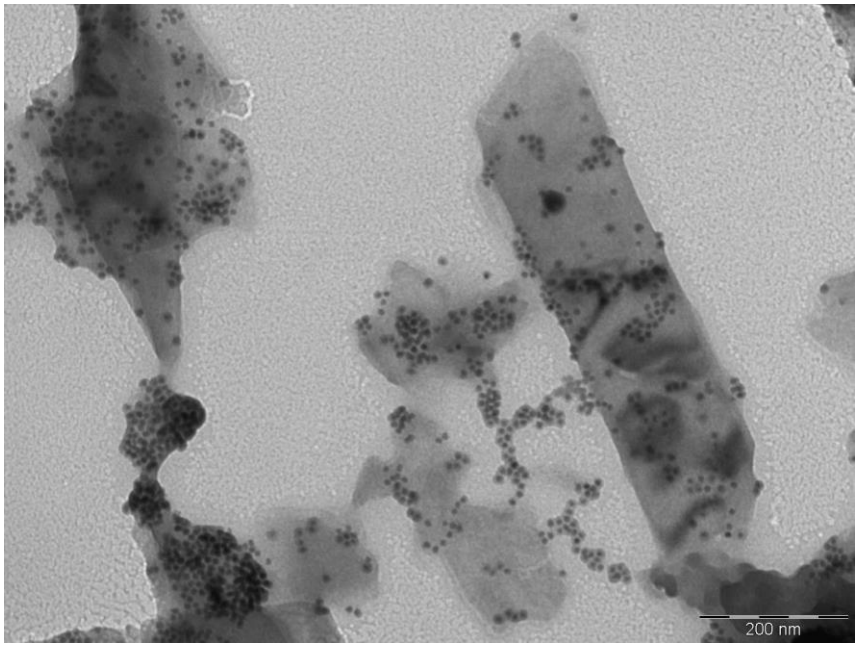


Ambient Degradation of Ni/2D BP

time
0

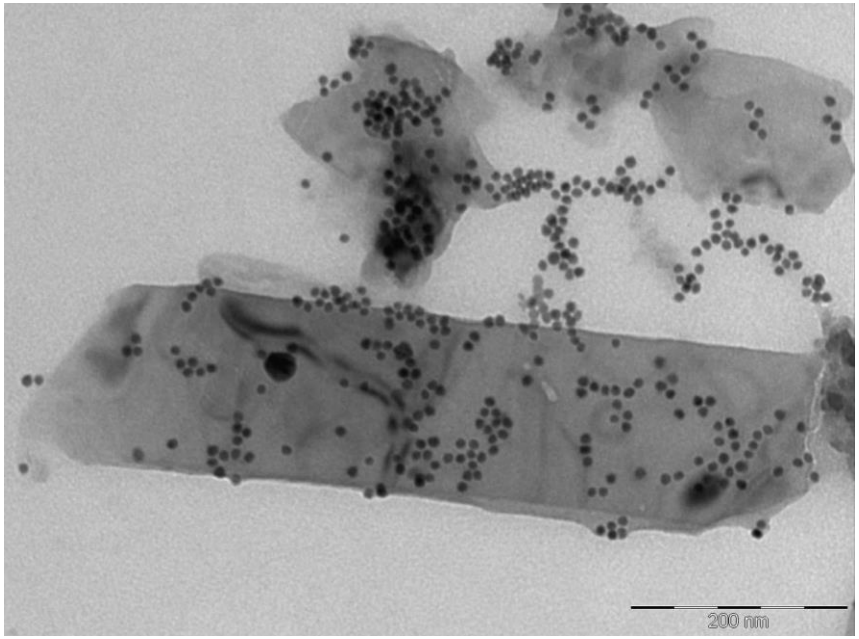


after 1 week

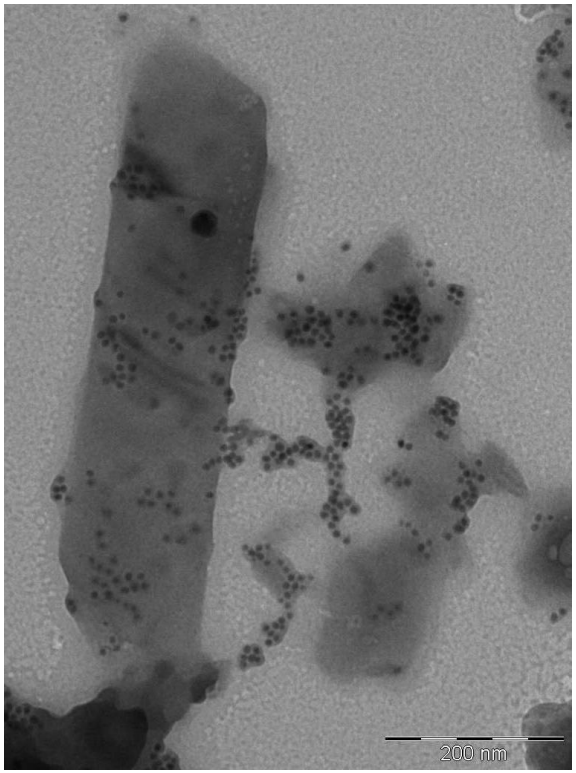


Ambient Degradation of Ni/2D BP

time 0

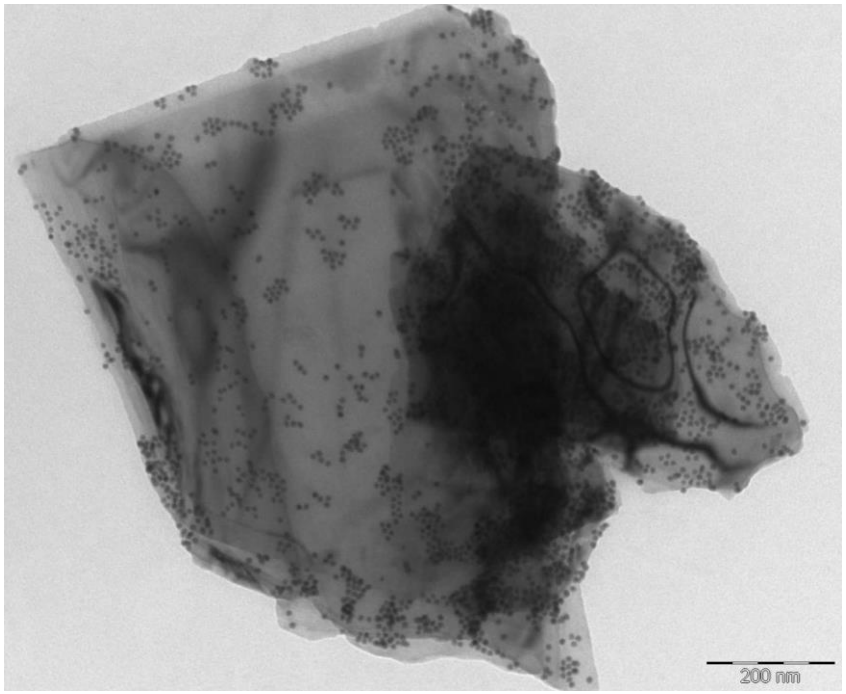


after 24 days

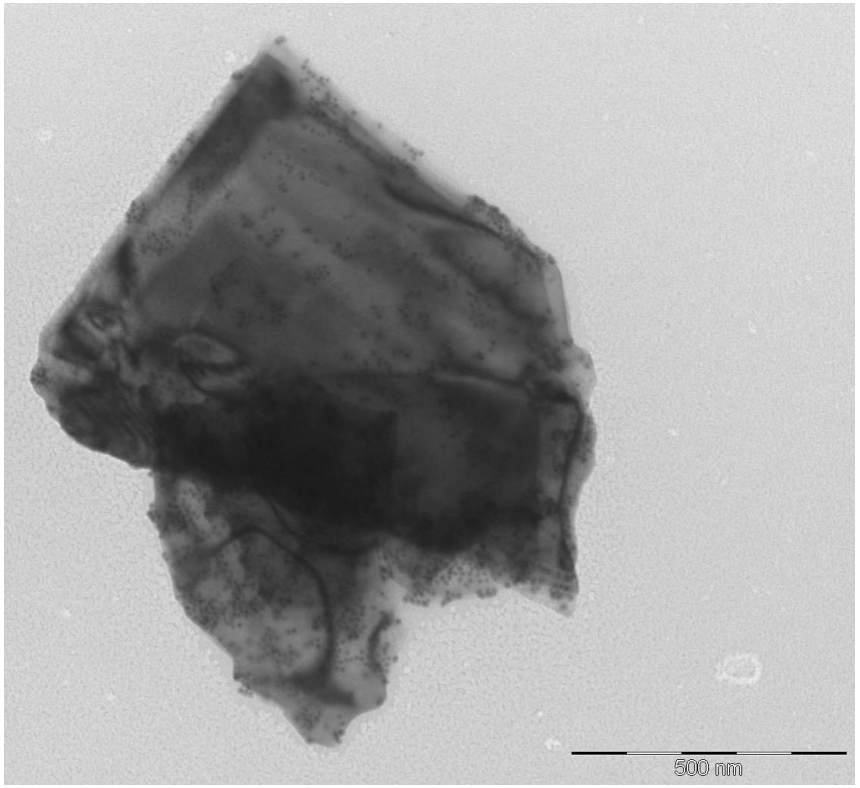


Ambient Degradation of Ni/2D BP

time 0

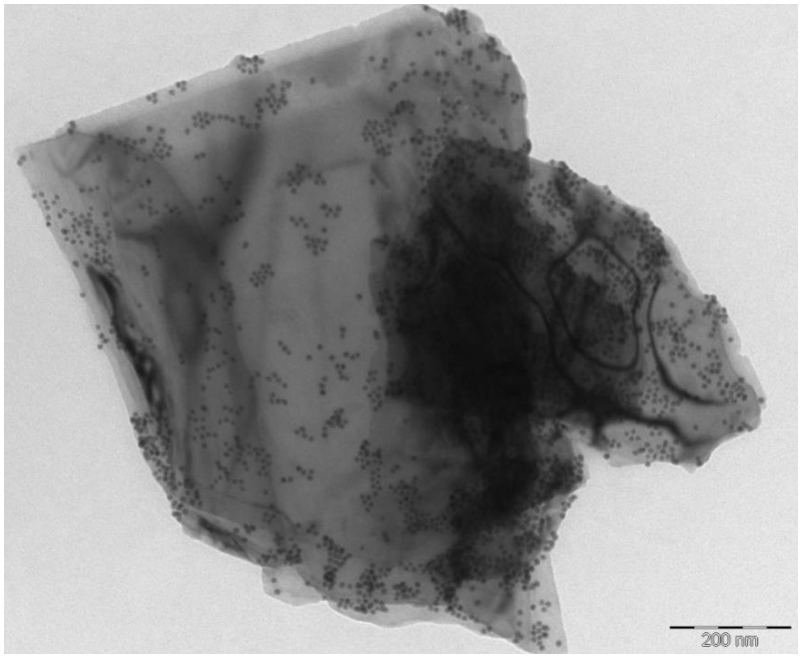


after 1 week

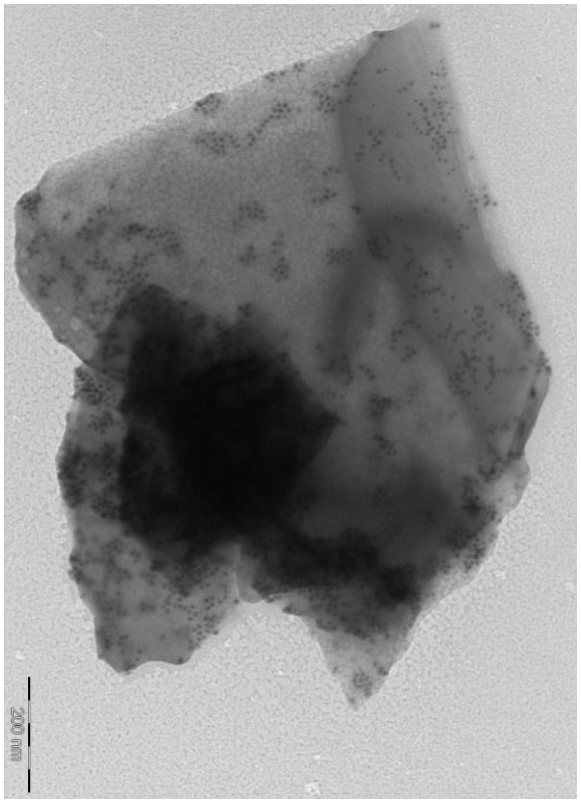


Ambient Degradation of Ni/2D BP

time 0

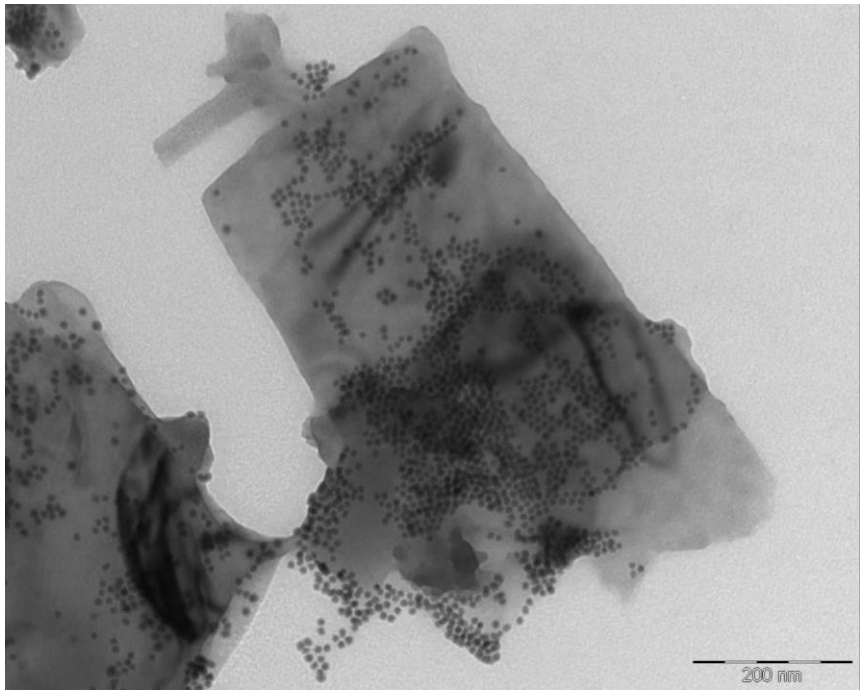


after 2 weeks

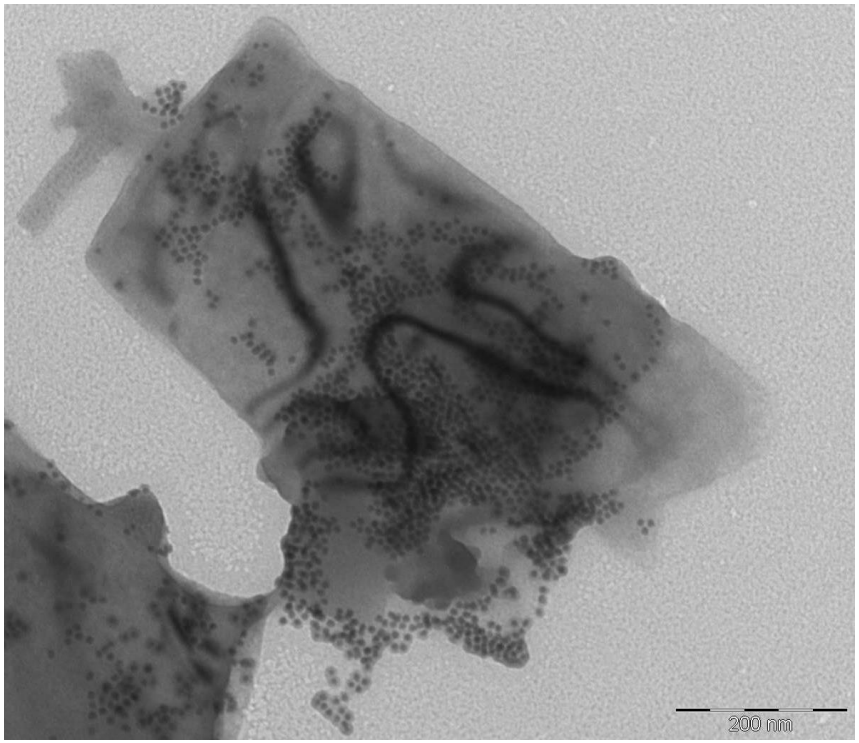


Ambient Degradation of Ni/2D BP

time 0

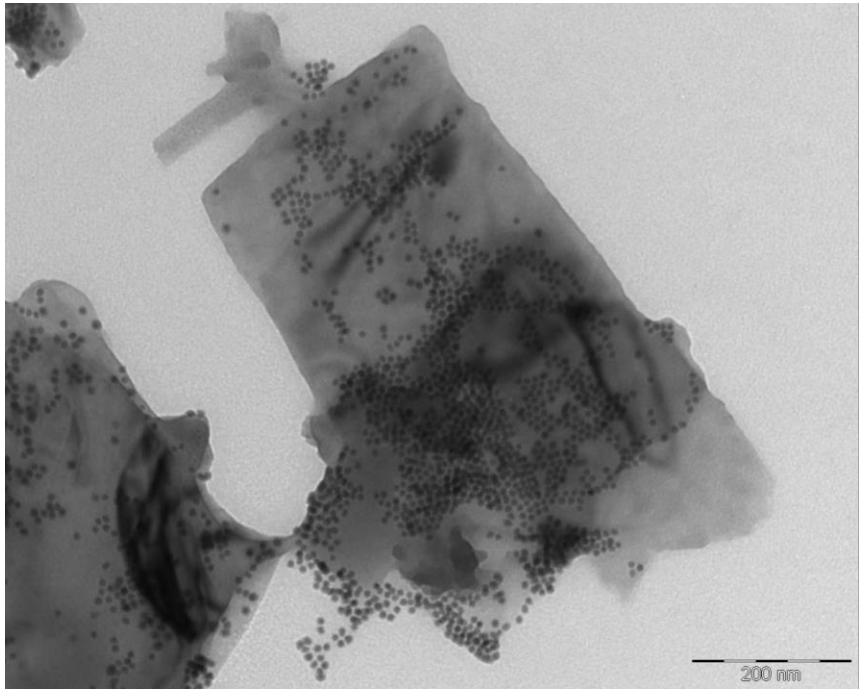


after 1 week

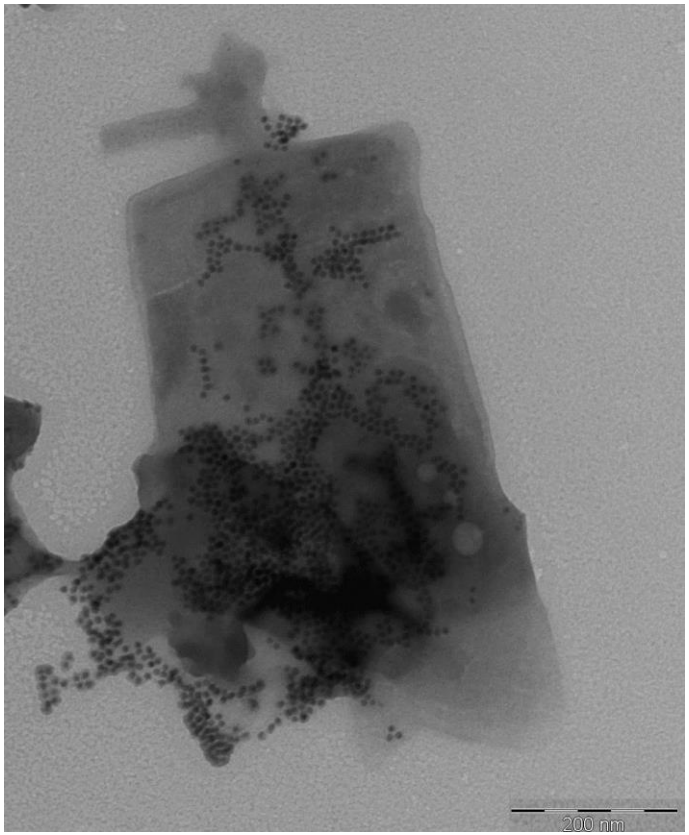


Ambient Degradation of Ni/2D BP

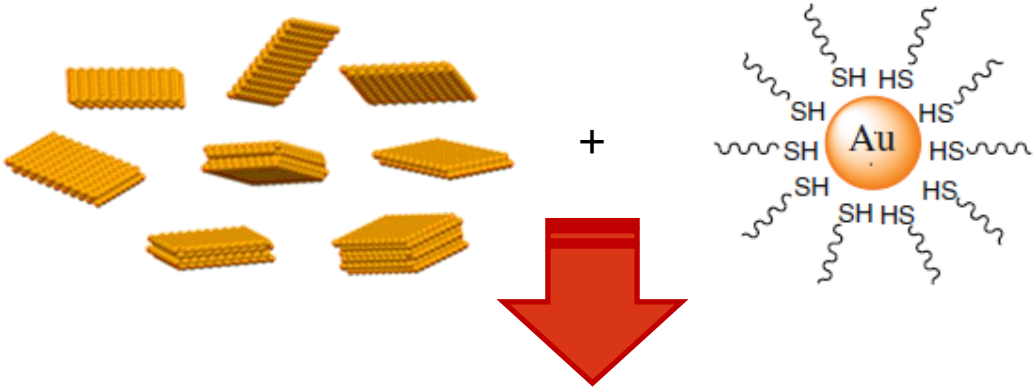
time 0

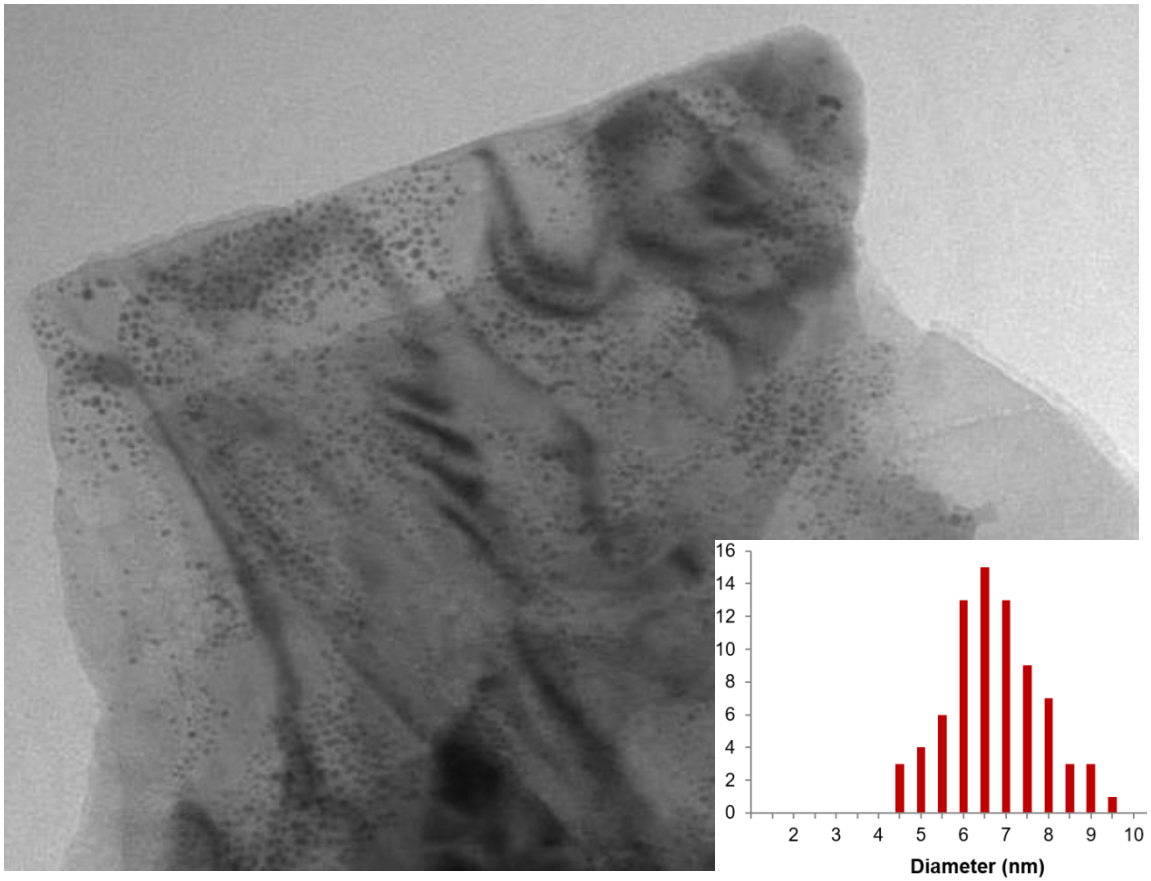


after 2 weeks

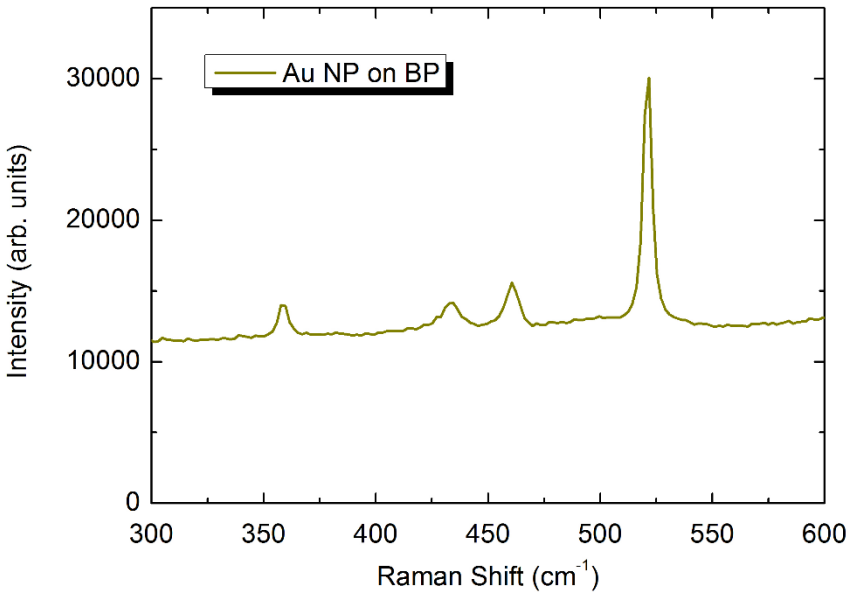


Preparation of Au/2D-BP

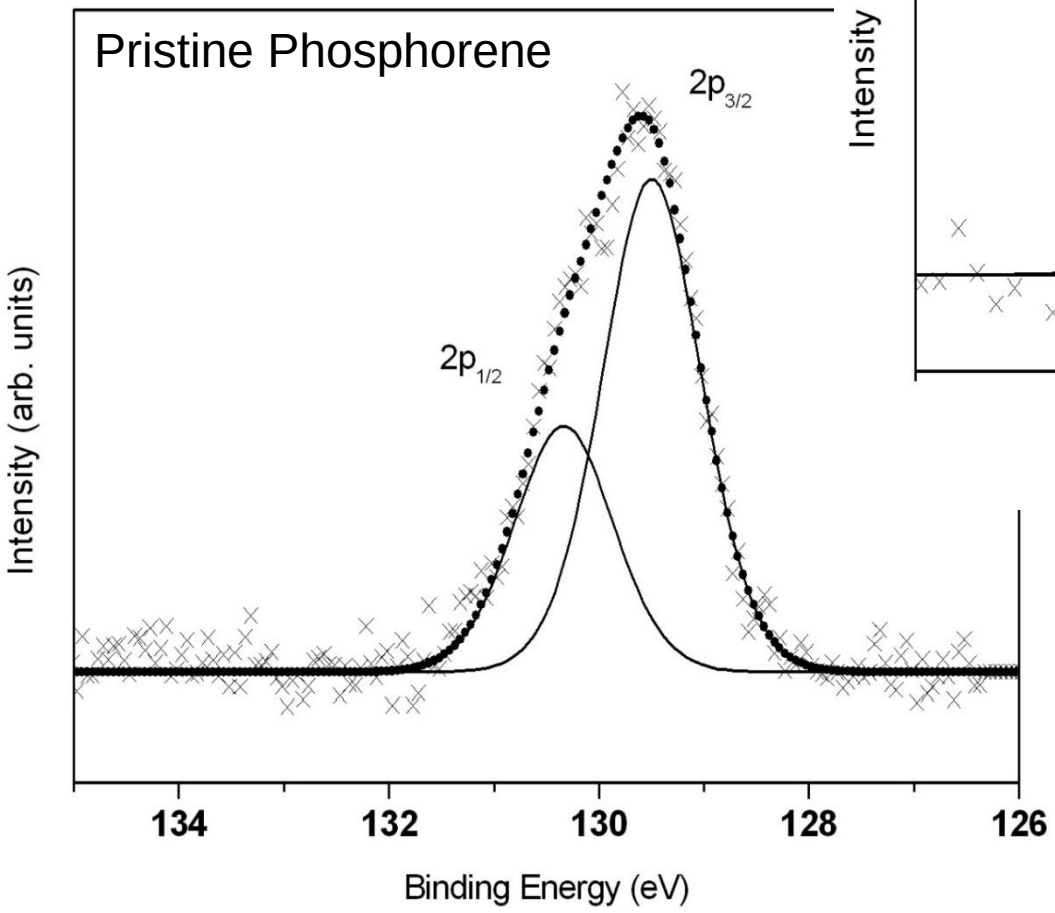


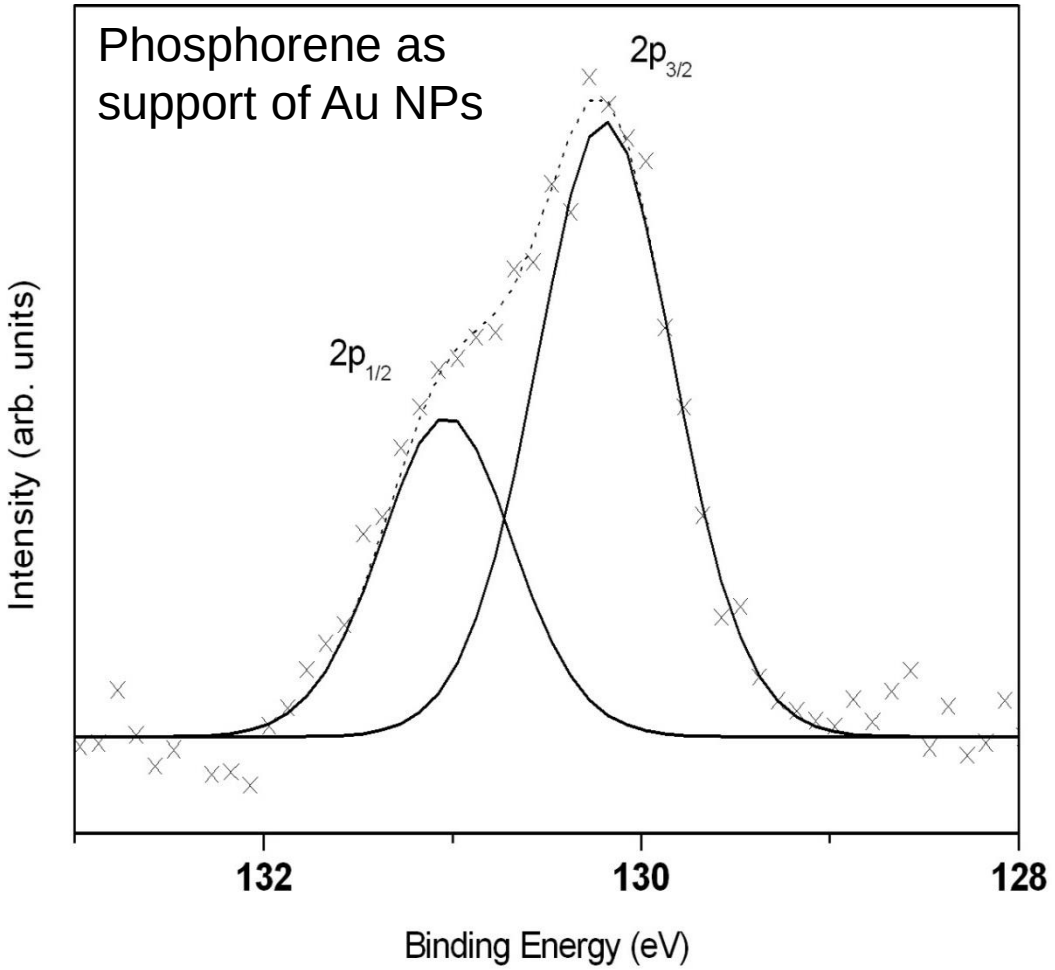


Raman of Au/2D BP

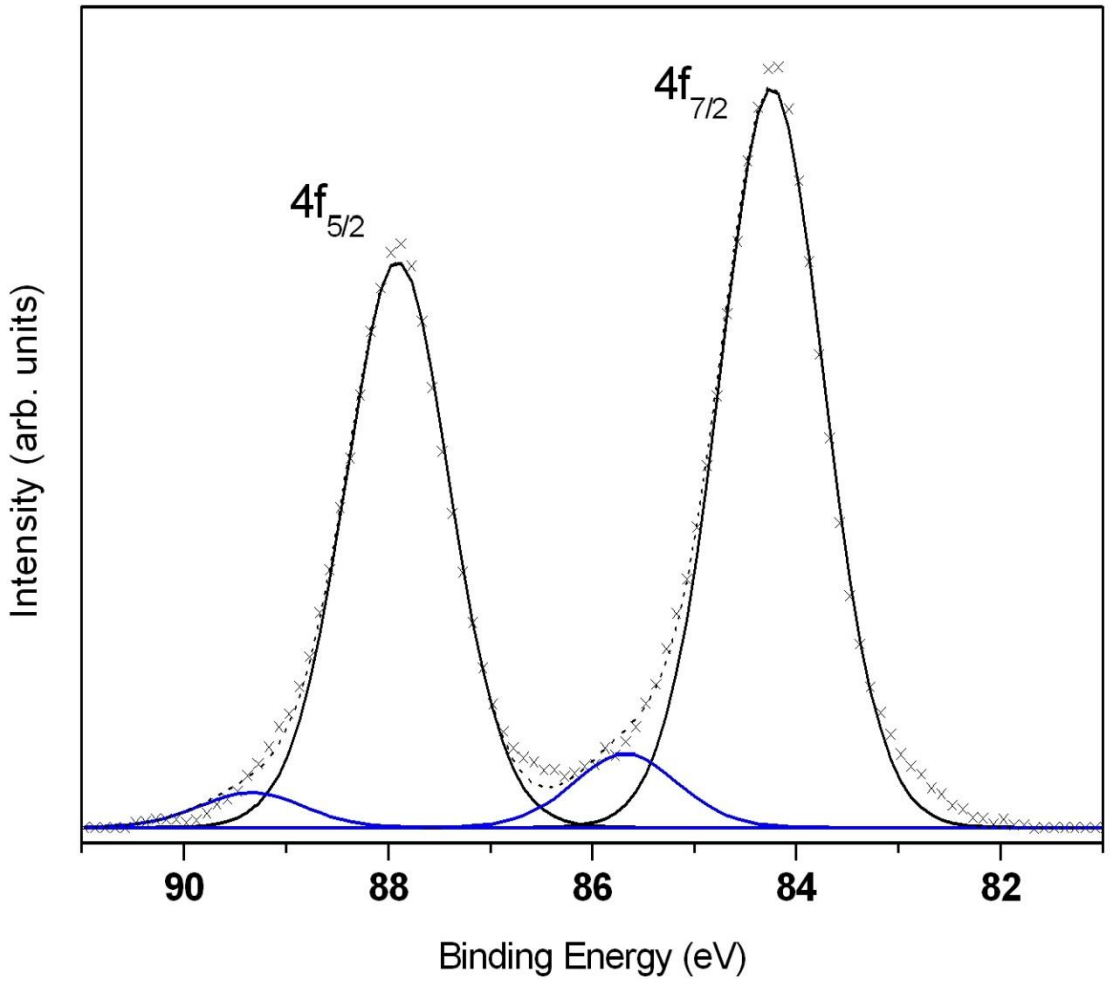


XPS


Pristine Phosphorene
2p3/2
2p1/2
Intensity (arb. units)
134
132
130
128
126
Binding Energy (eV)


Phosphorene as support of Au NPs
2p3/2
2p1/2
Intensity (arb. units)
132
130
128
Binding Energy (eV)

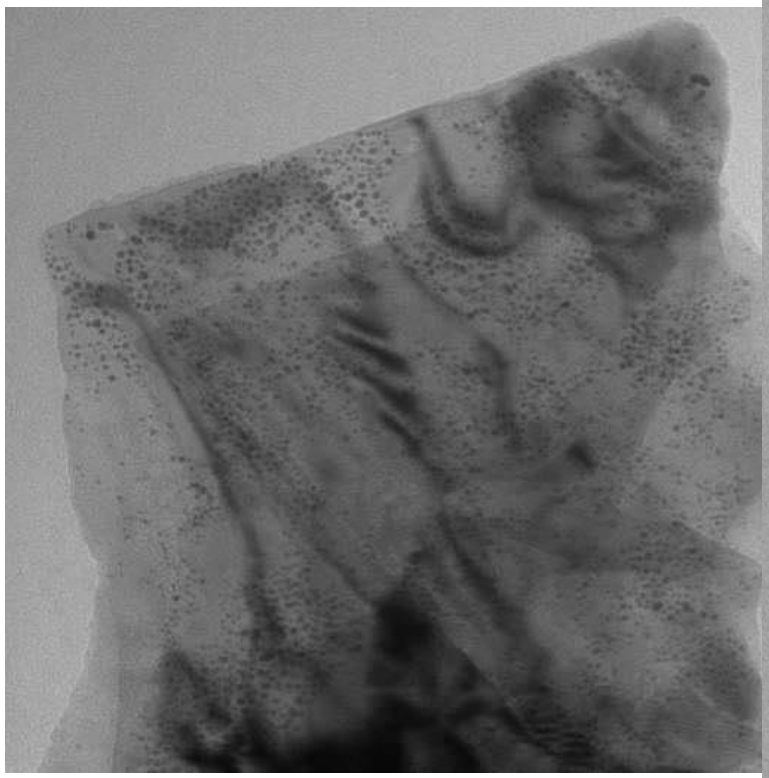
XPS


4f5/2
4f7/2
Intensity (arb. units)
90
88
86
84
82
Binding Energy (eV)

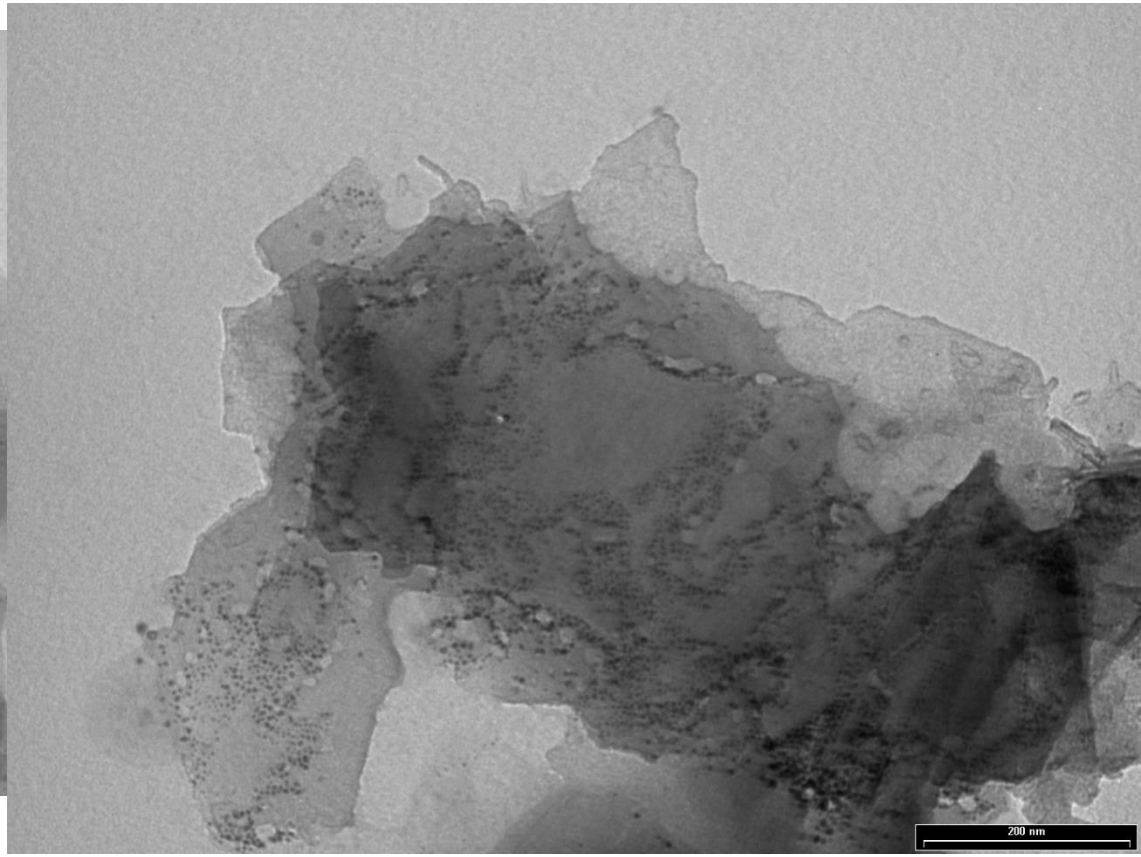
Ambient Degradation of Au/2D BP

Sample kept in ambient conditions, but in absence of light

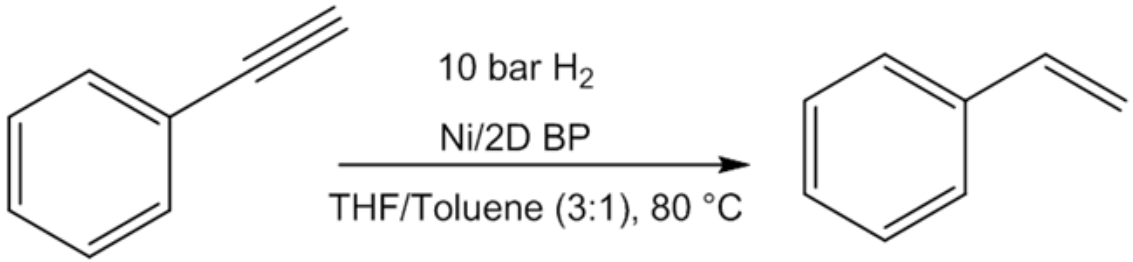
time 0



after 1 year



Semihydrogenation of phenylacetylene



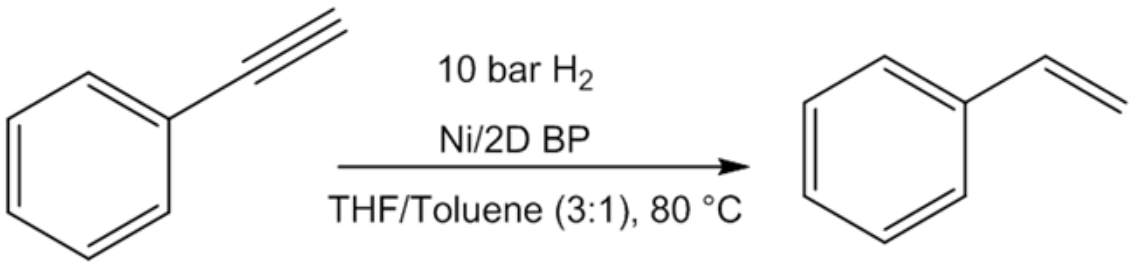
Entry	*Conversion (%)*	*Selectivity to styrene (%)*	*S/cat*	*T (°C)*
Ni NPs	100.0	78.6	56.0	80
2D BP	0.0	-	-	80
Ni/2D BP	93.2	92.8	56.0	80
Ni/Al_2O_3	99.6	0.7[a]	16.5	100
Ni/MgO	98.5	36.0[b]	15.0	50
Ni@C	99.8	59.6[c]	-	100-150

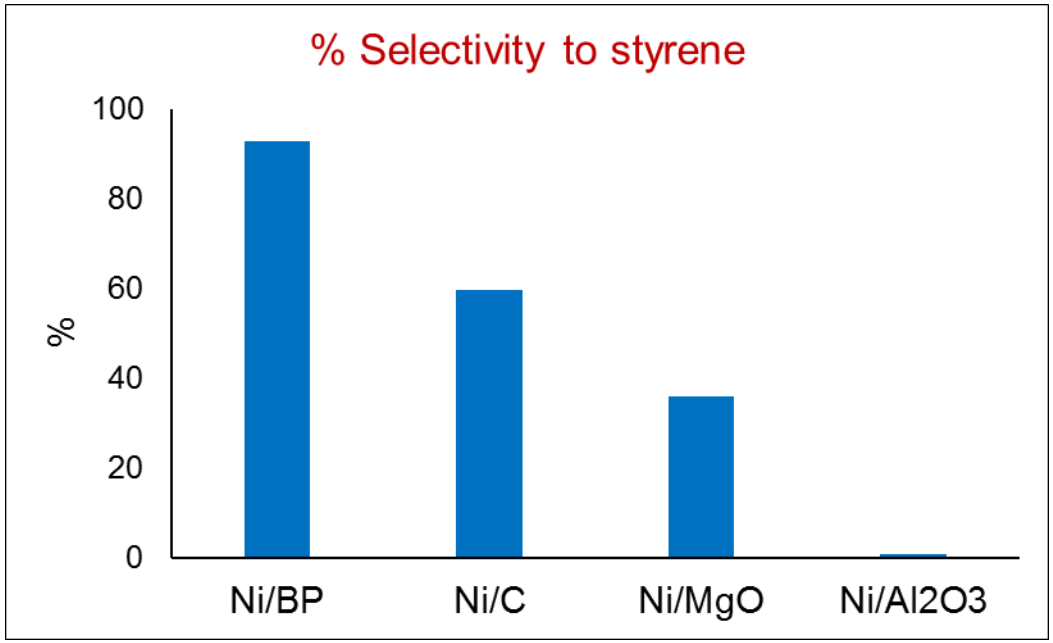
[a] *ACS Catal*. **2015**, *5*, 5756: 2 hours, 3 bar H_2

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

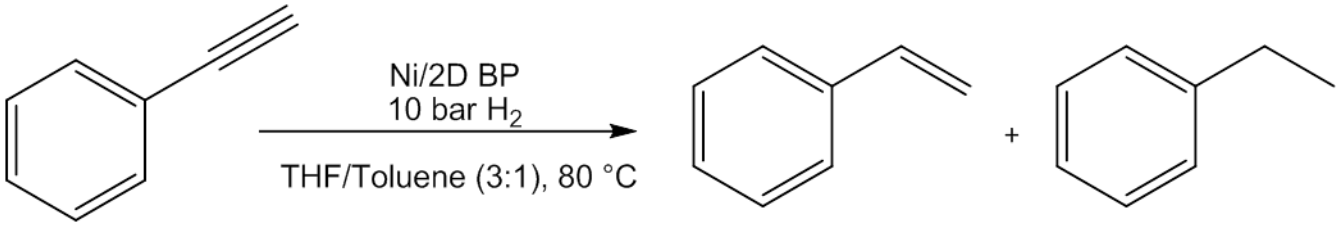
[C] *Carbon* **2014**, 74, 291: flow bed reactor.

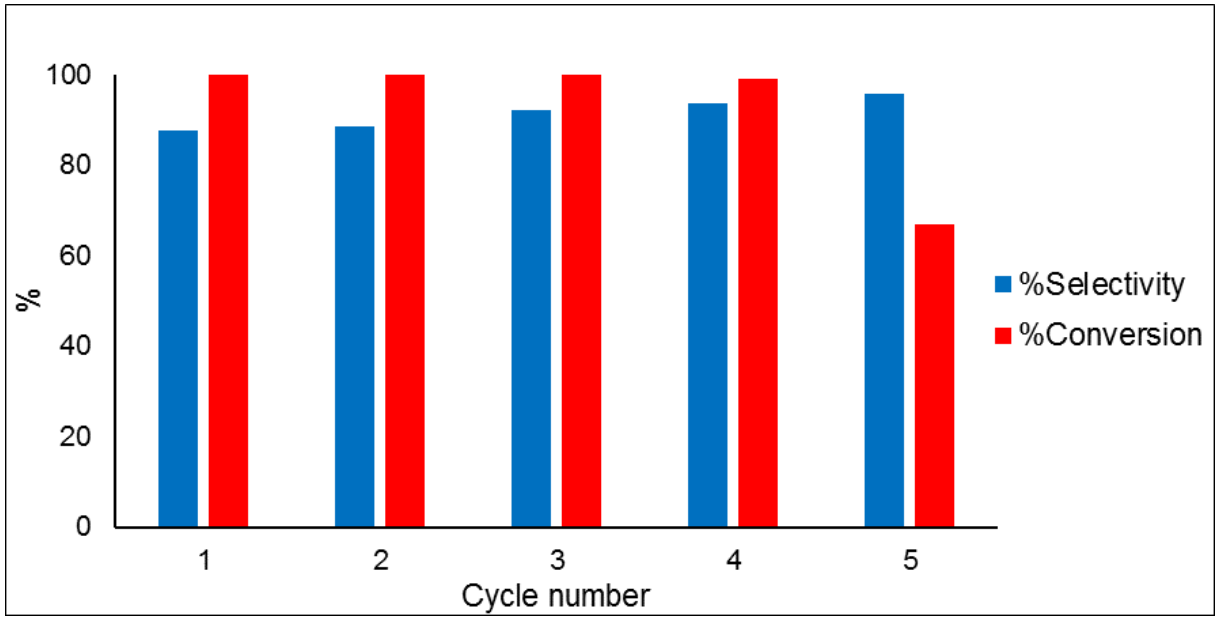
Semihydrogenation of phenylacetylene





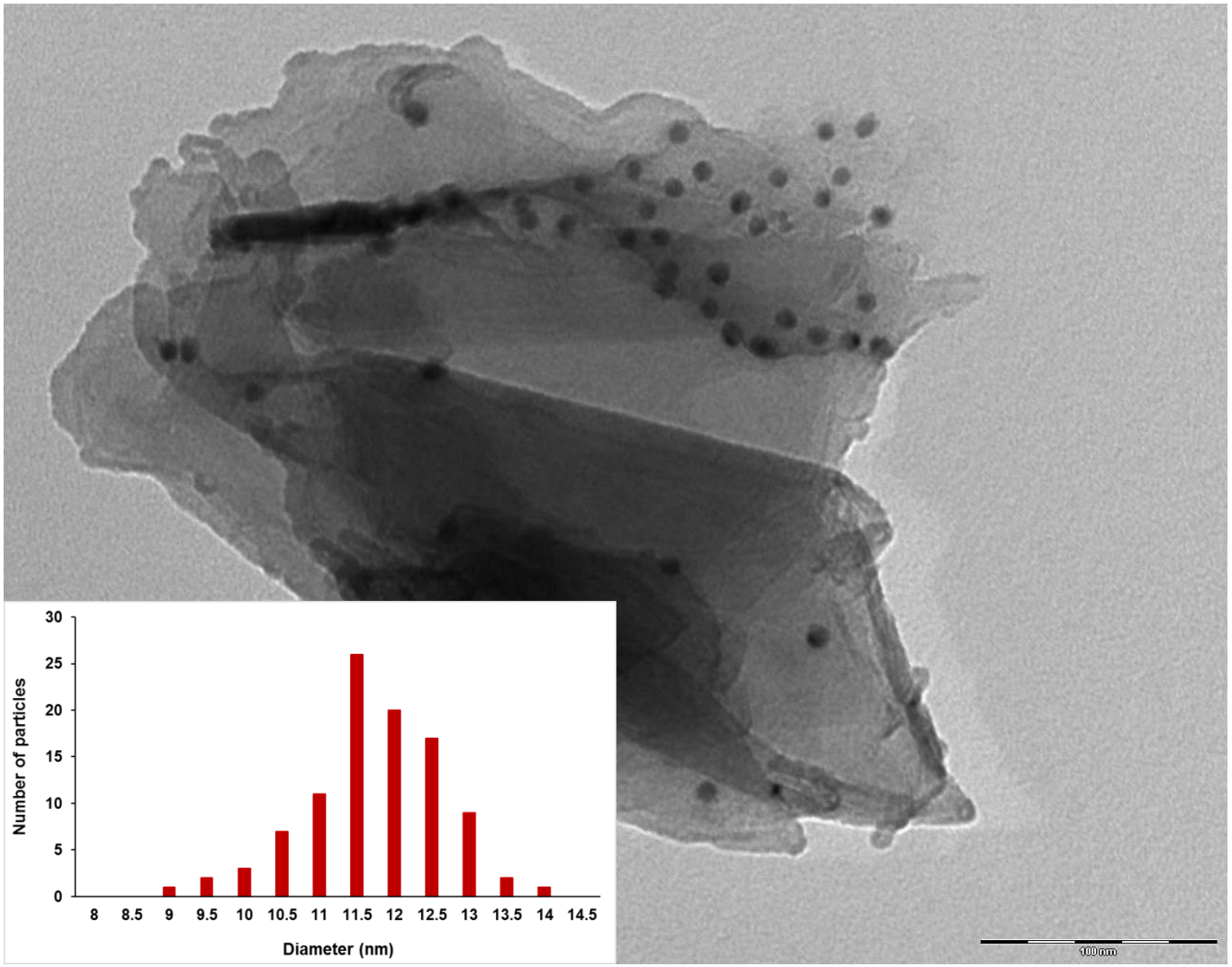
Recycling Ni/2D BP





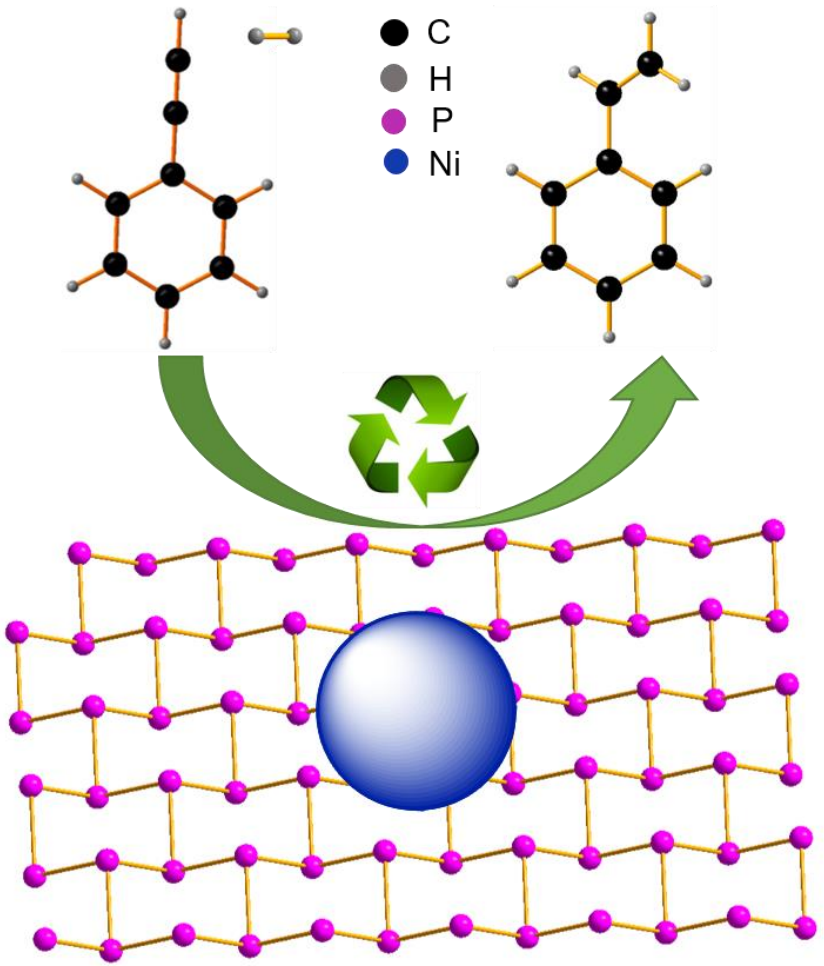
ICP-AES: no leaching of nickel

Ni/2D BP after catalysis

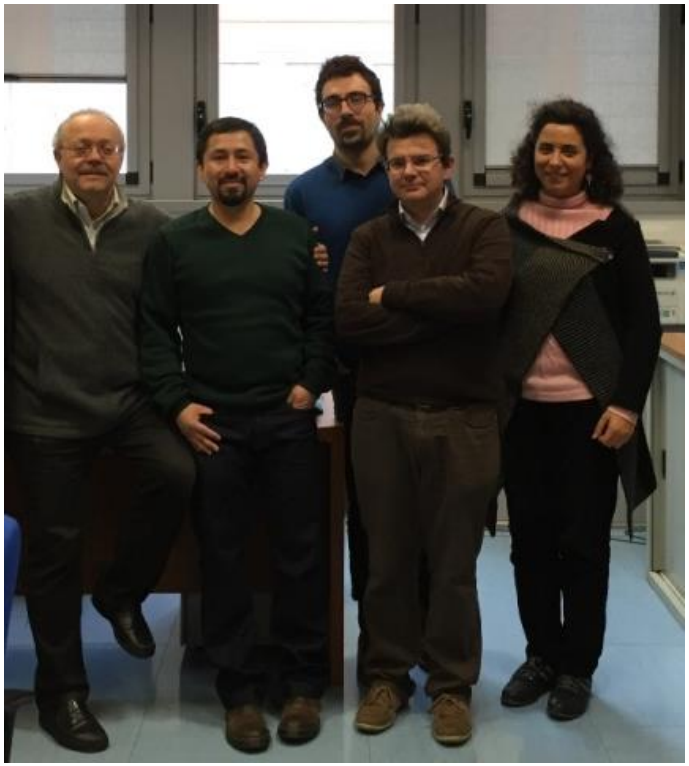


Summary

- Nickel nanoparticles were dispersed on the surface of few-layer black phosphorus achieving a new nanohybrid Ni/2D BP.
- Ni/2D BP catalyzed successfully the semihydrogenation of phenylacetylene and showed high selectivity to styrene.
- The catalytic activity and selectivity remained unaltered after recycling tests.
- The functionalization with Ni NPs inferred high stability to exfoliated black P in ambient conditions.



Acknowledgements



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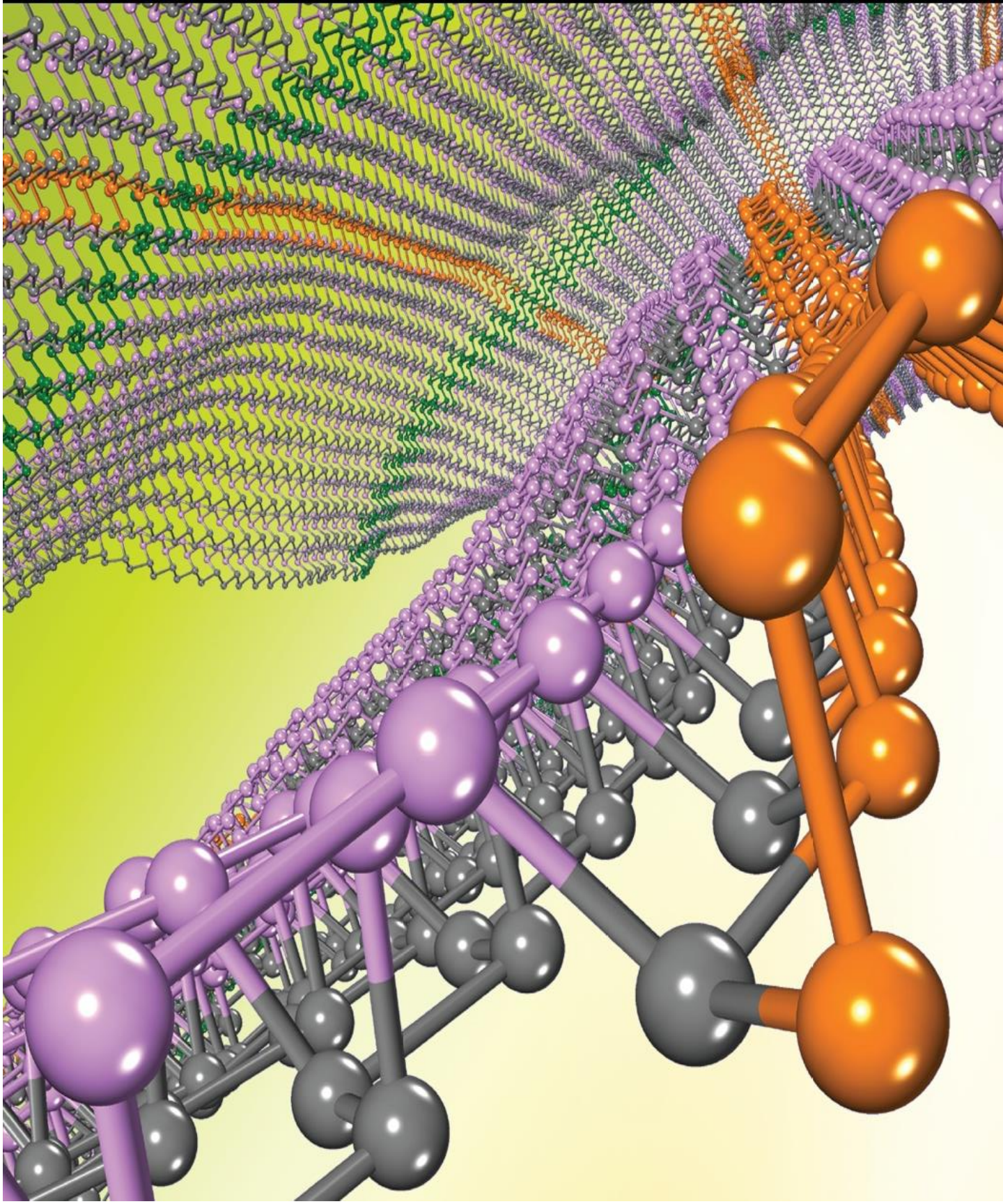

Thank you!!