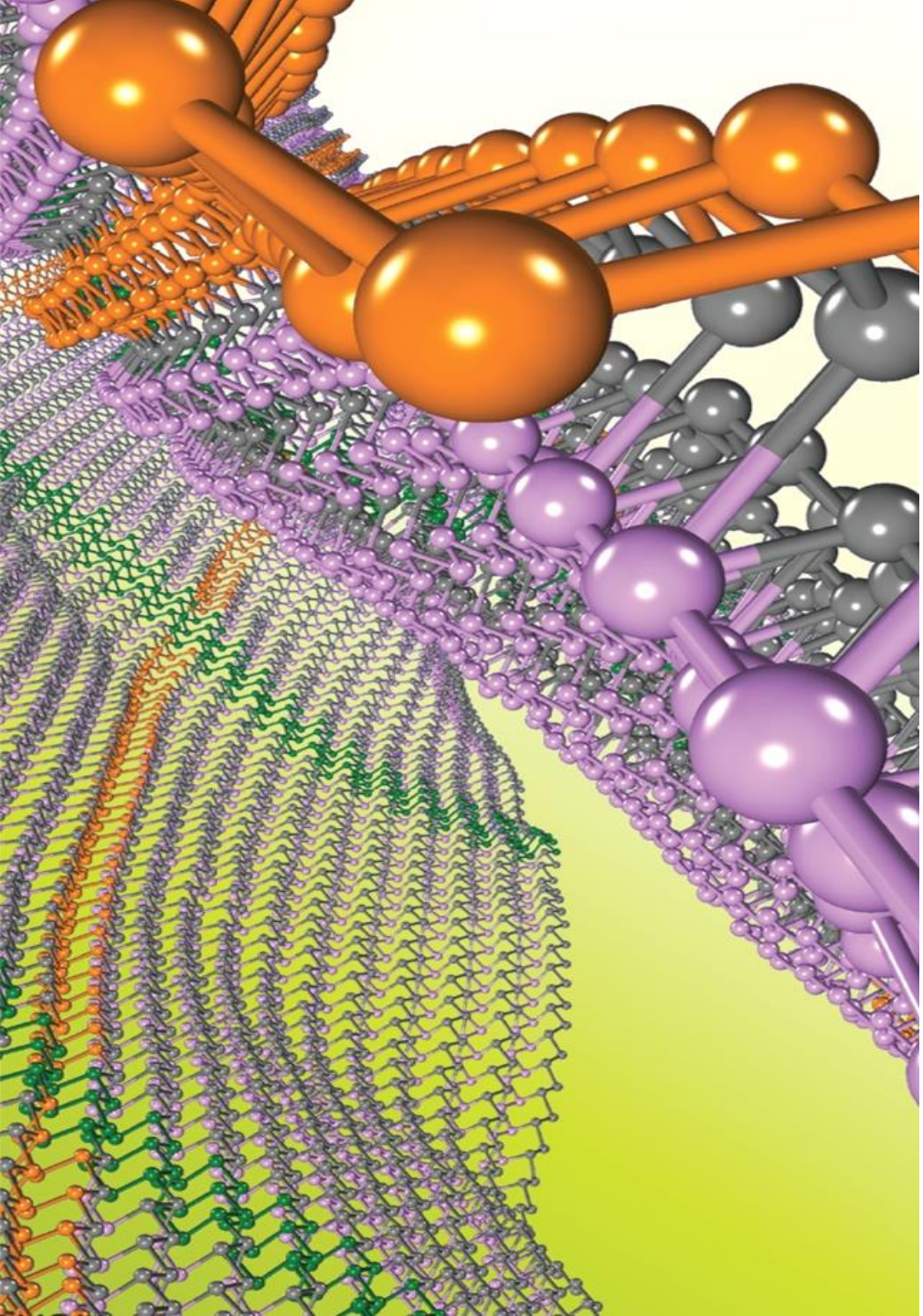
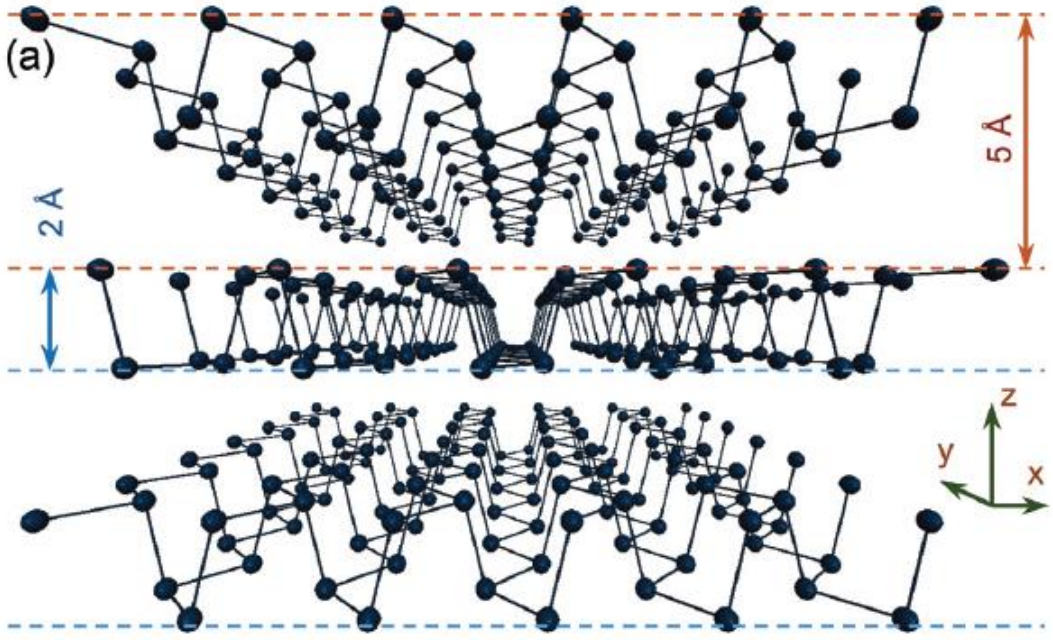


PHOSPHORENE: THE P-ANALOG OF GRAPHENE

Maria Caporali

CNR ICCOM
Florence, Italy

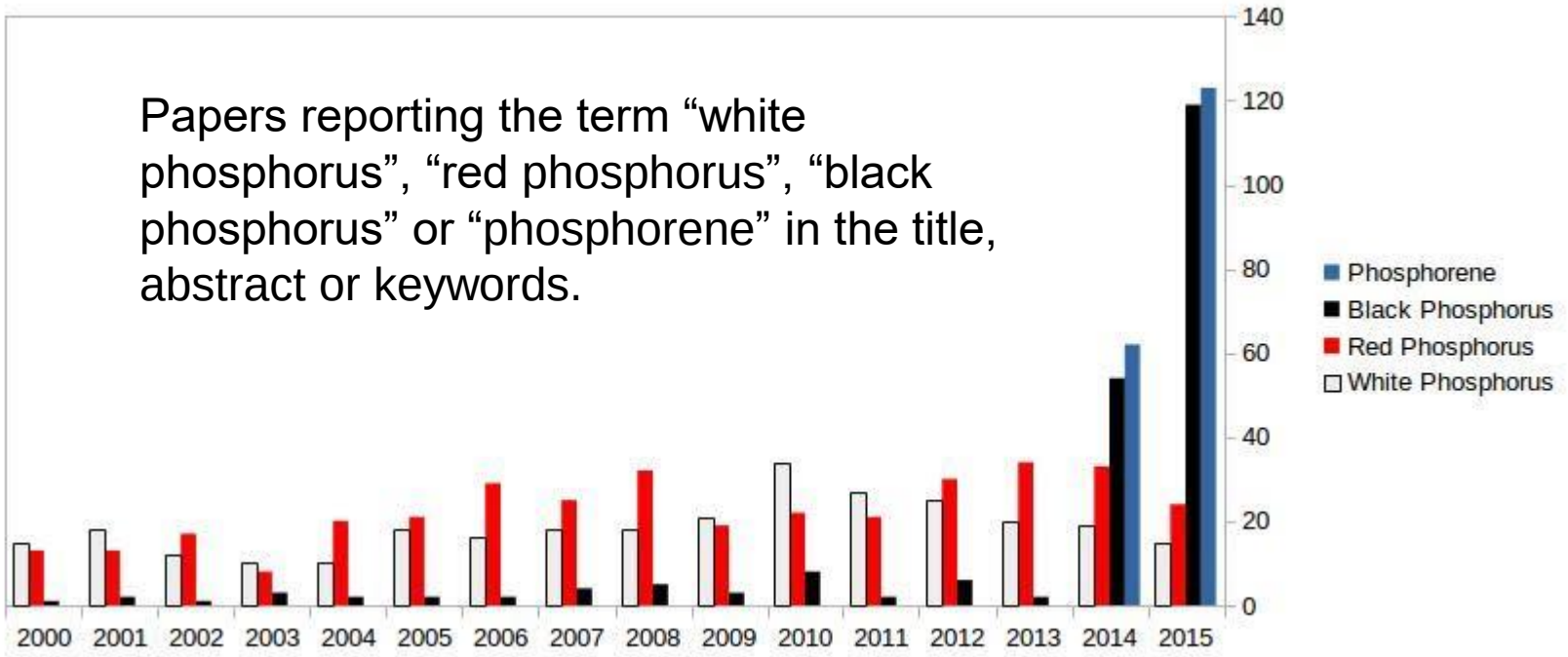
ISTITUTO DI CHIMICA DEI COMPOSTI ORGANOMETALLICI


(a)
5 Å
2 Å
z
y
x

The renaissance of black phosphorus

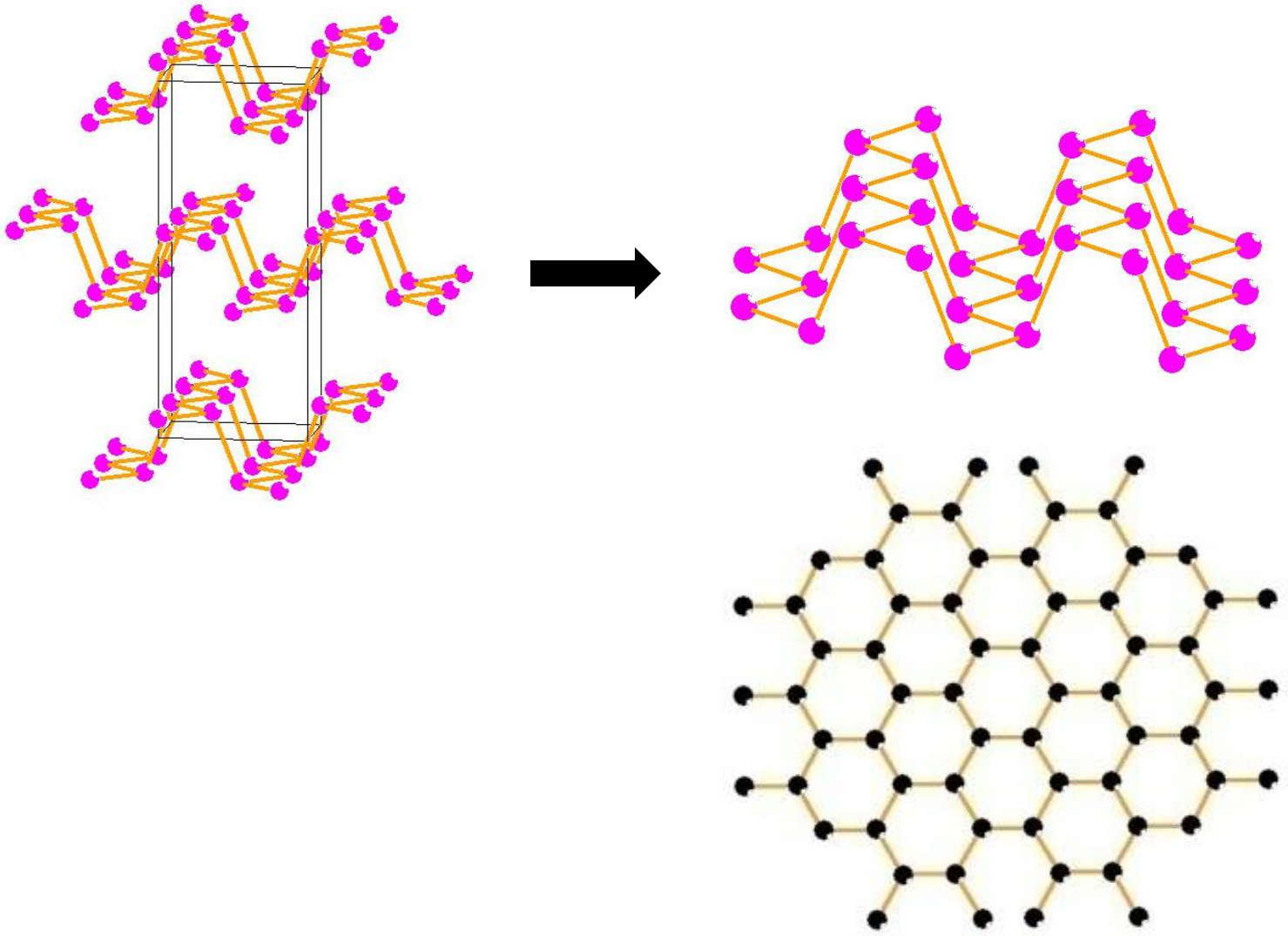
Xi Ling[a], Han Wang[b,1], Shengxi Huang[a], Fengnian Xia[c], and Mildred S. Dresselhaus[a,d,1]

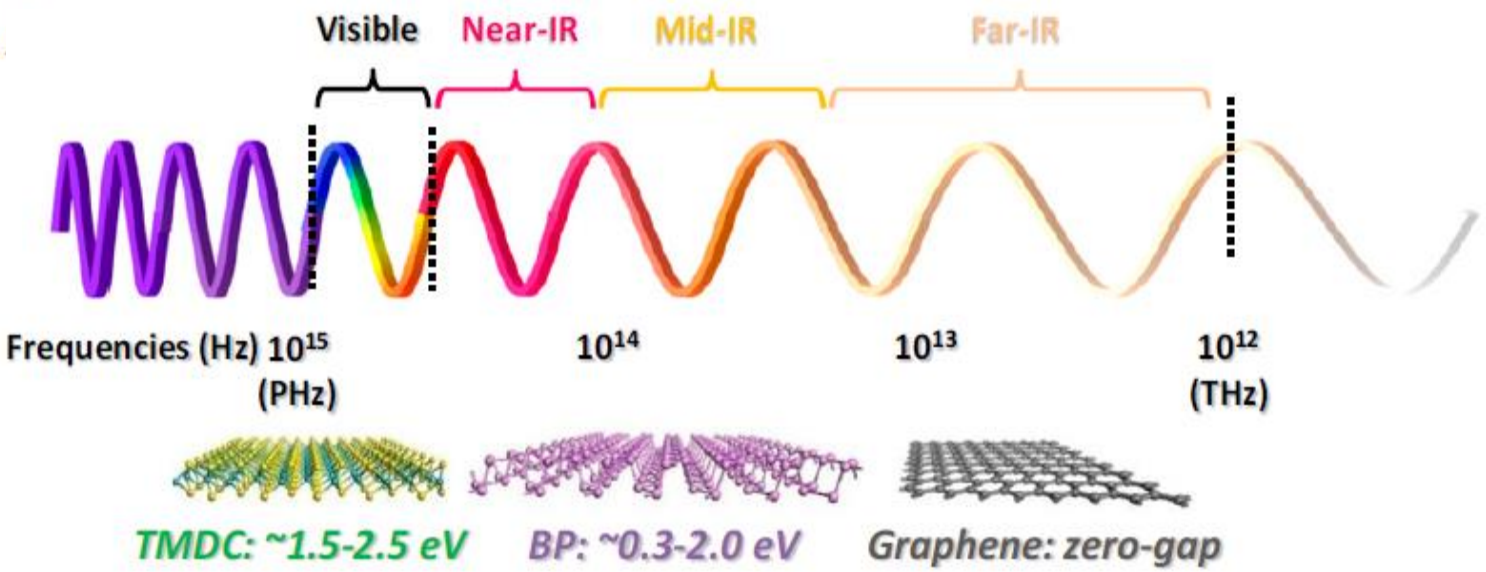
[a]Department of Electrical Engineering and Computer Science and [d]Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139; [b]Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, CA 90089; and [c]Department of Electrical Engineering,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

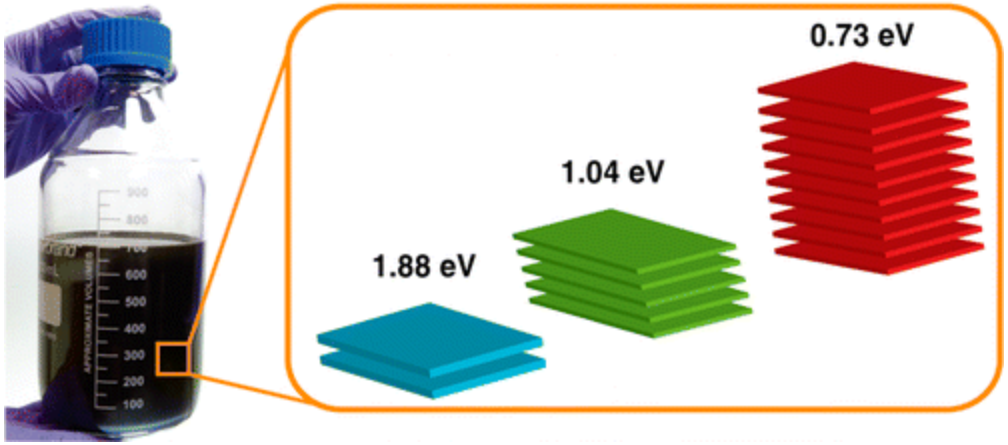


PNAS | April 14, 2015 | vol. 112 | no. 15 | 4523–4530

From Black P to Phosphorene





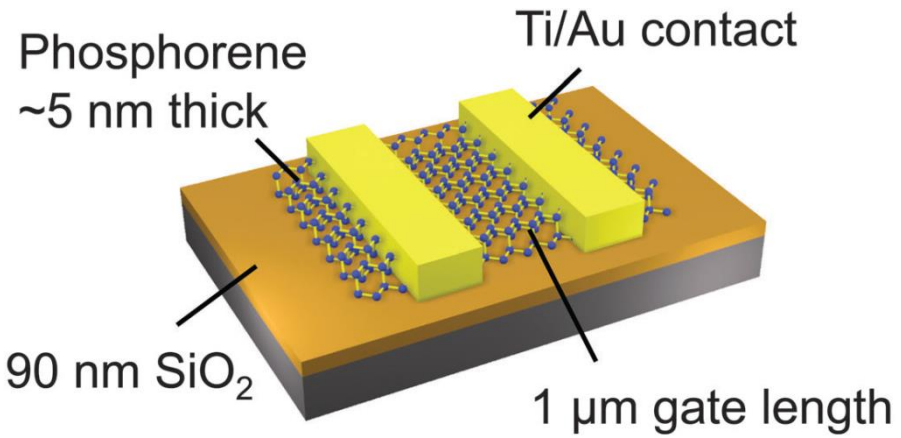


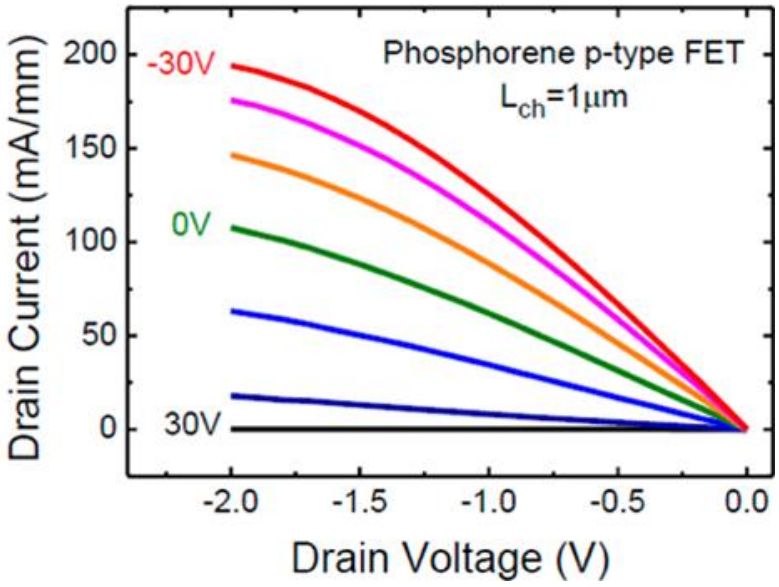
S. Warren *et al*, doi:10.10121/acsnano.5b02599

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

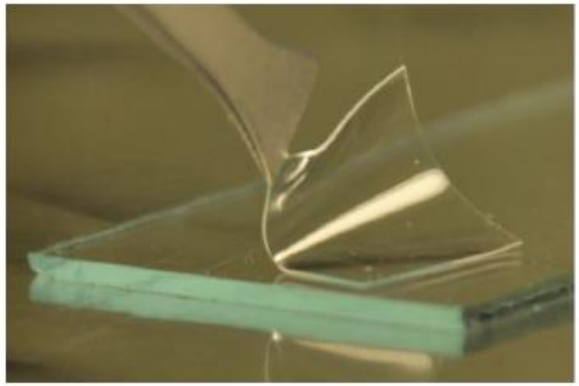


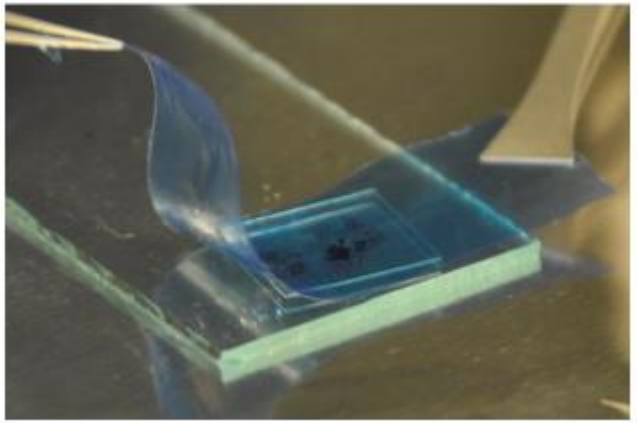


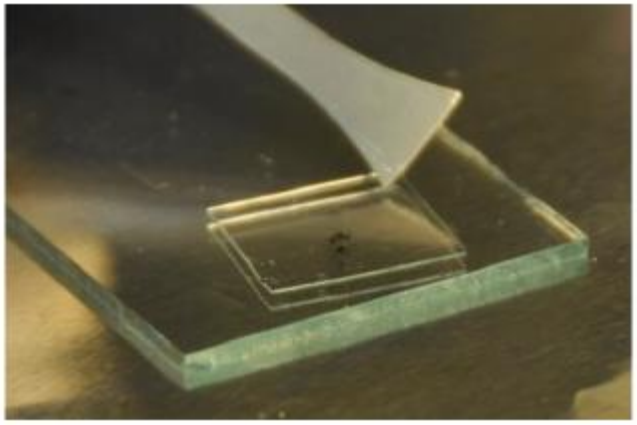
ASC Nano, **2014**, *8*, 4033.

Micromechanical exfoliation

"Scotch-tape method"





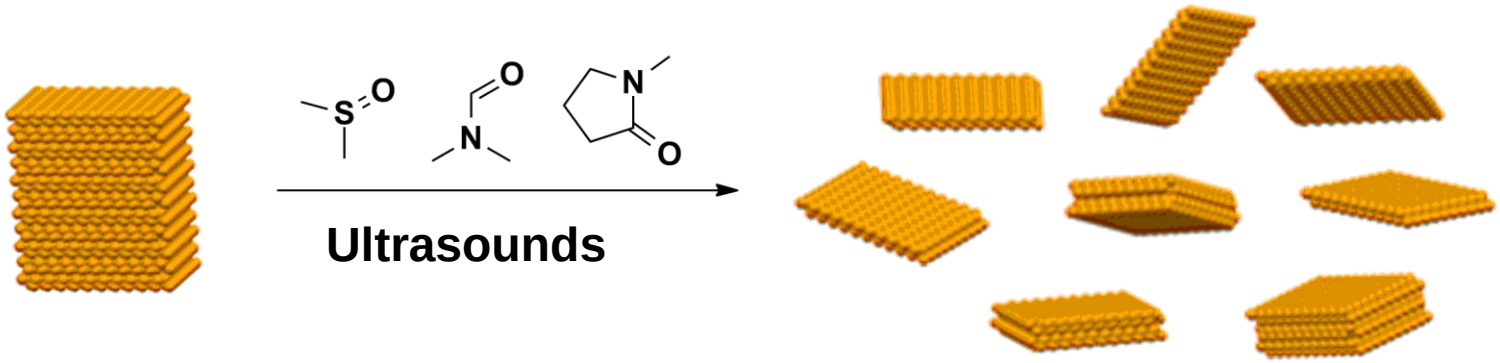


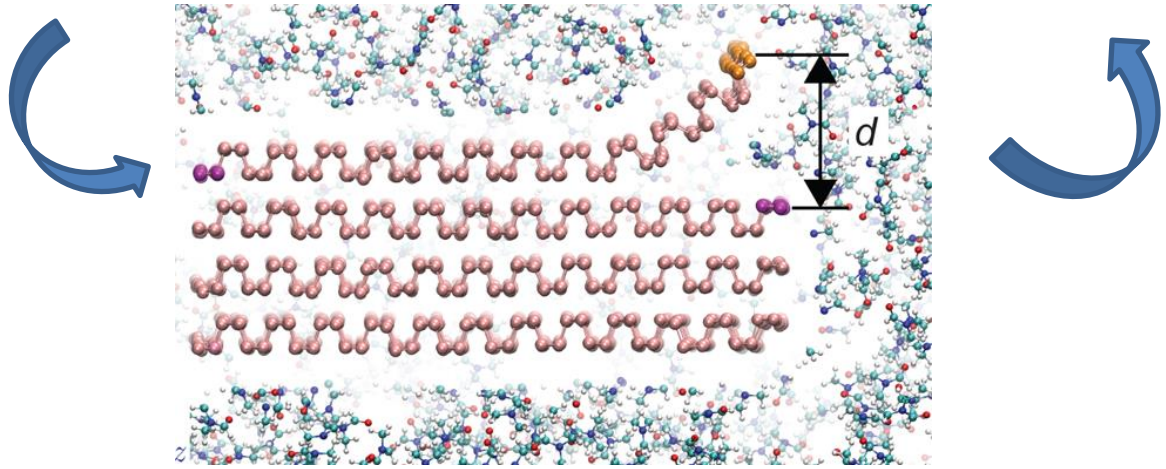
P. D. Ye et al. *ACS Nano* **2014**, *8*, 4033

Y. B. Zhang, *Nat. Nanotechnol*. **2014**, *9*, 372

A. Castellanos-Gomez *et al. 2D Materials,* **2014**,*1*,11002.

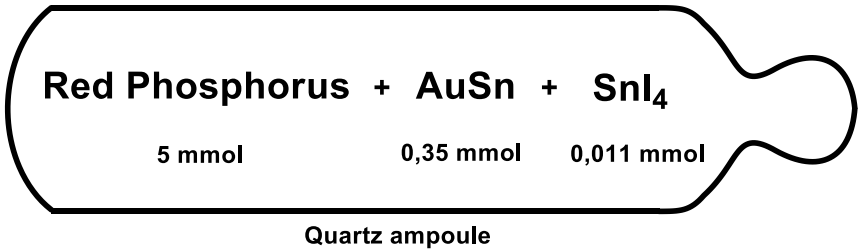
Liquid Exfoliation by ultrasounds

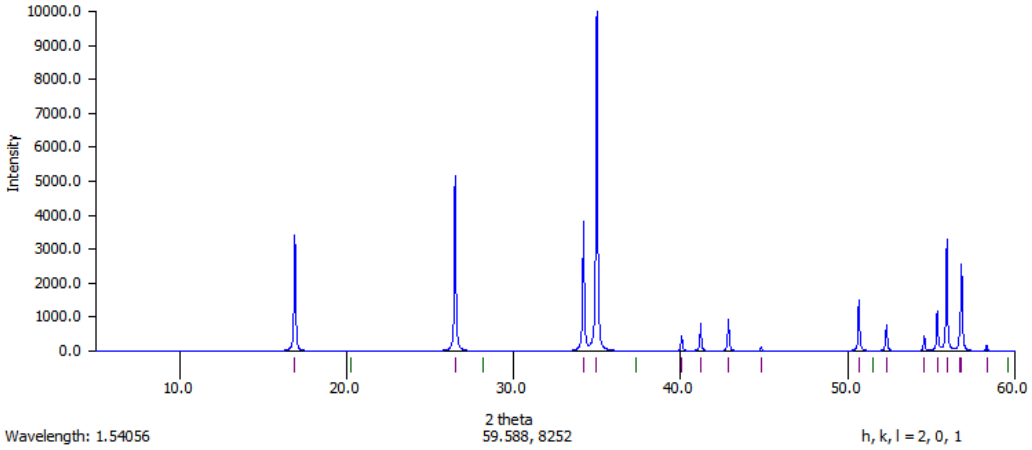


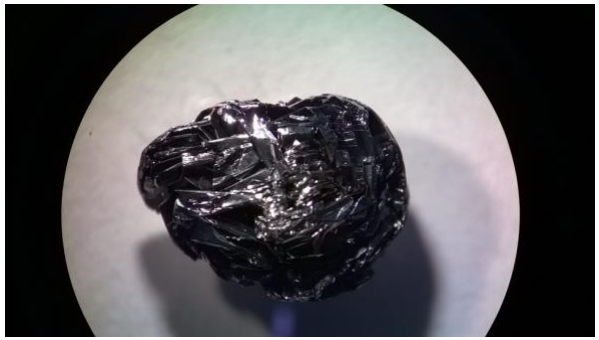


O'Brien, *Chem.Commun*, **2014**, *50*,13338; Xie, JACS. **2015**,doi:10.10121.jacs.5b06025
Hersam, *ACS nano* **2015**, 9, 3596; Salehi-Khojin, *Adv. Mater*. **2015**, 27, 1887
Warren, doi:10.10121/acsnano.5b02599; Serrano, Caporali, Peruzzini et al. Submitted.

Synthesis of Black Phosphorus







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

Exfoliation in DMSO

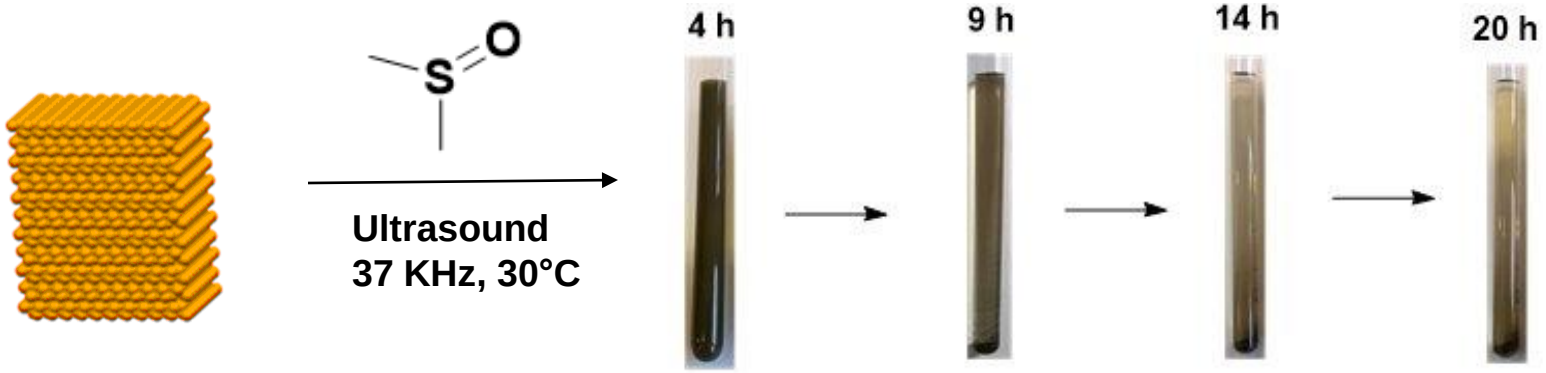
DMSO has:

- high dielectric constant
- high surface tension

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

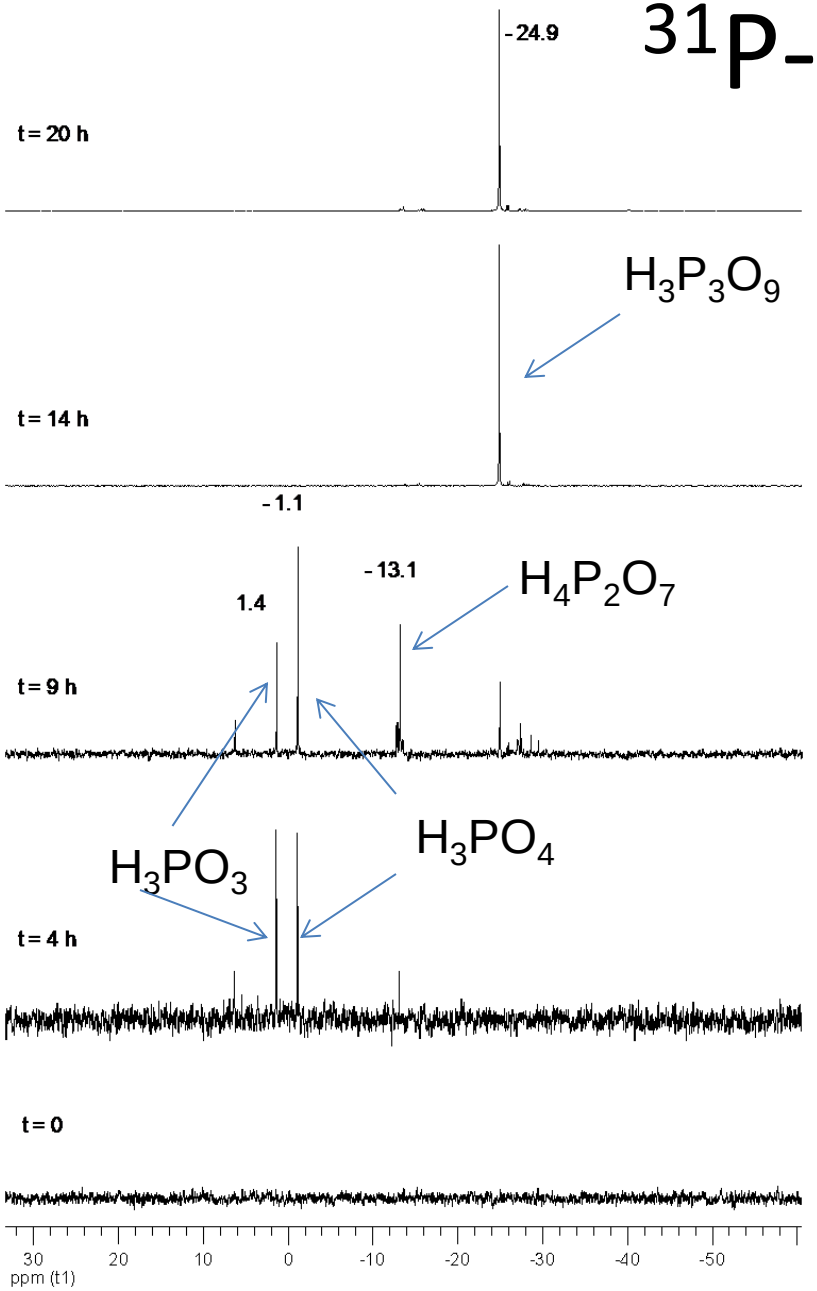
➢ In particular three different ranges of molar ratio between black phosphorus and water were studied.

Range 1: molar ratio (P/H_2O) ≥ 15



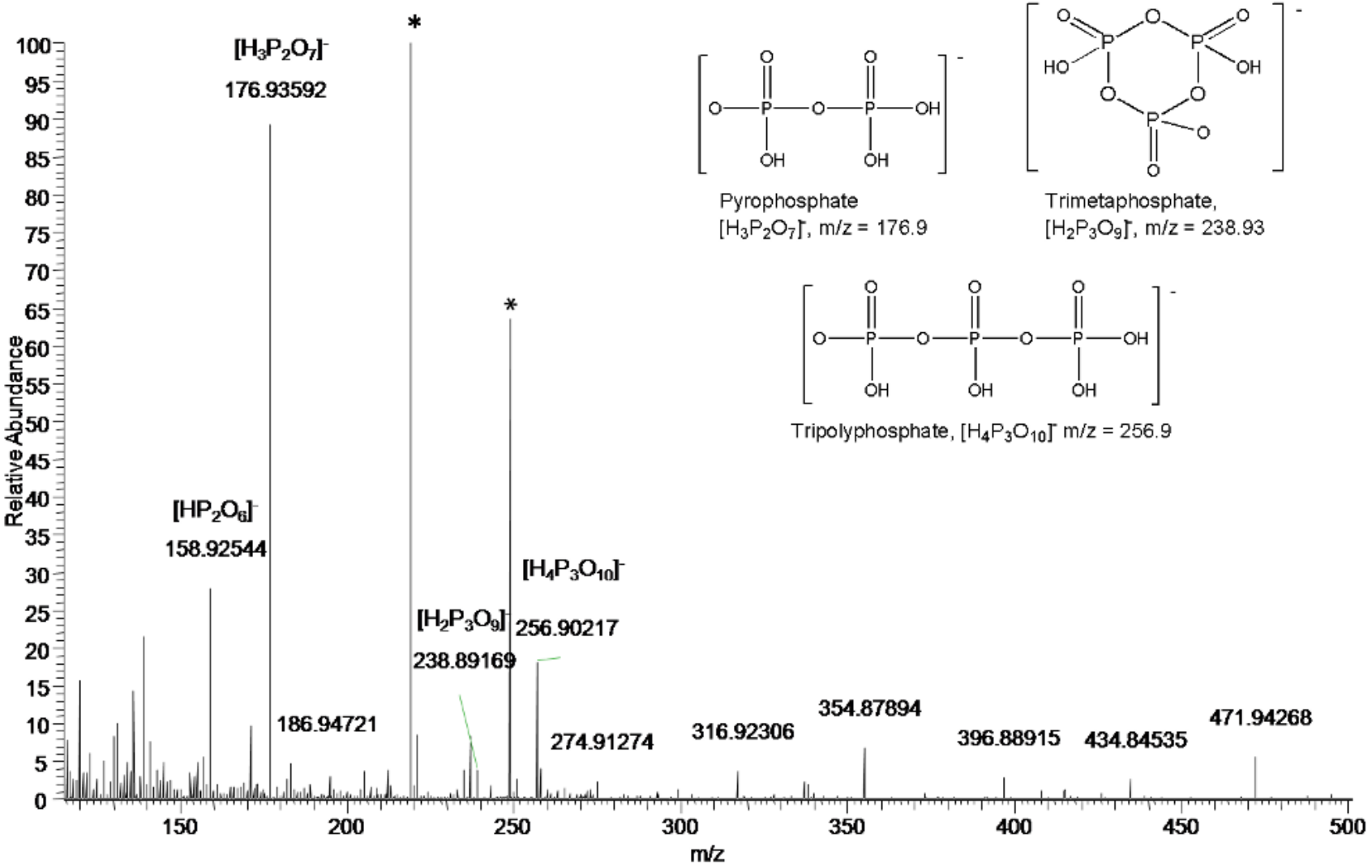
The exfoliation was followed by ^{31}P NMR:

^{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

High Resolution ESI-MS

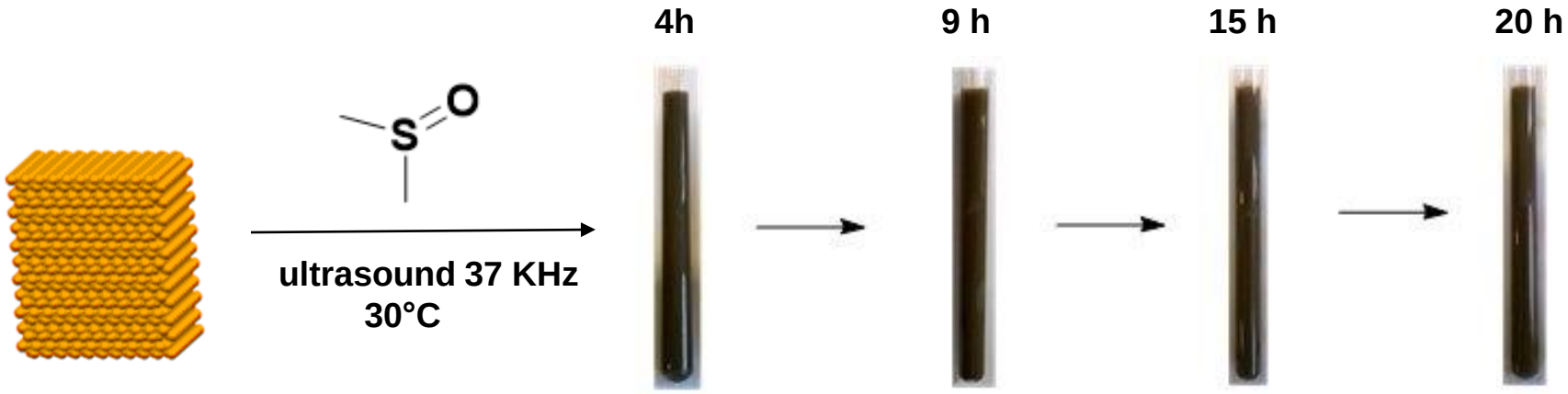


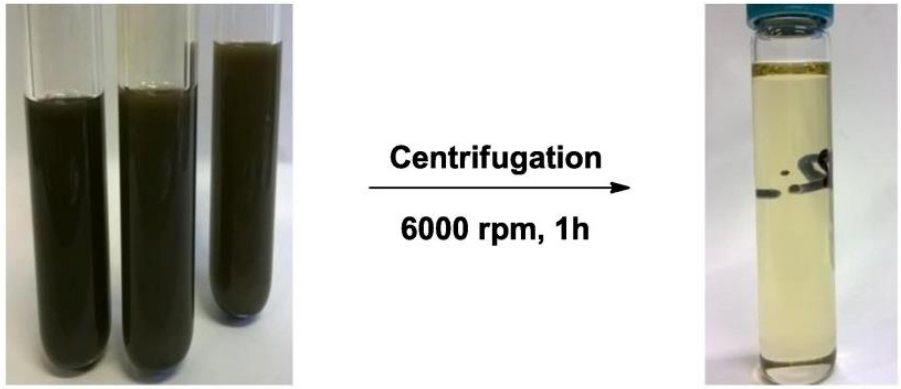
Pyrophosphate
$[H_3P_2O_7]^-$, m/z = 176.9

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

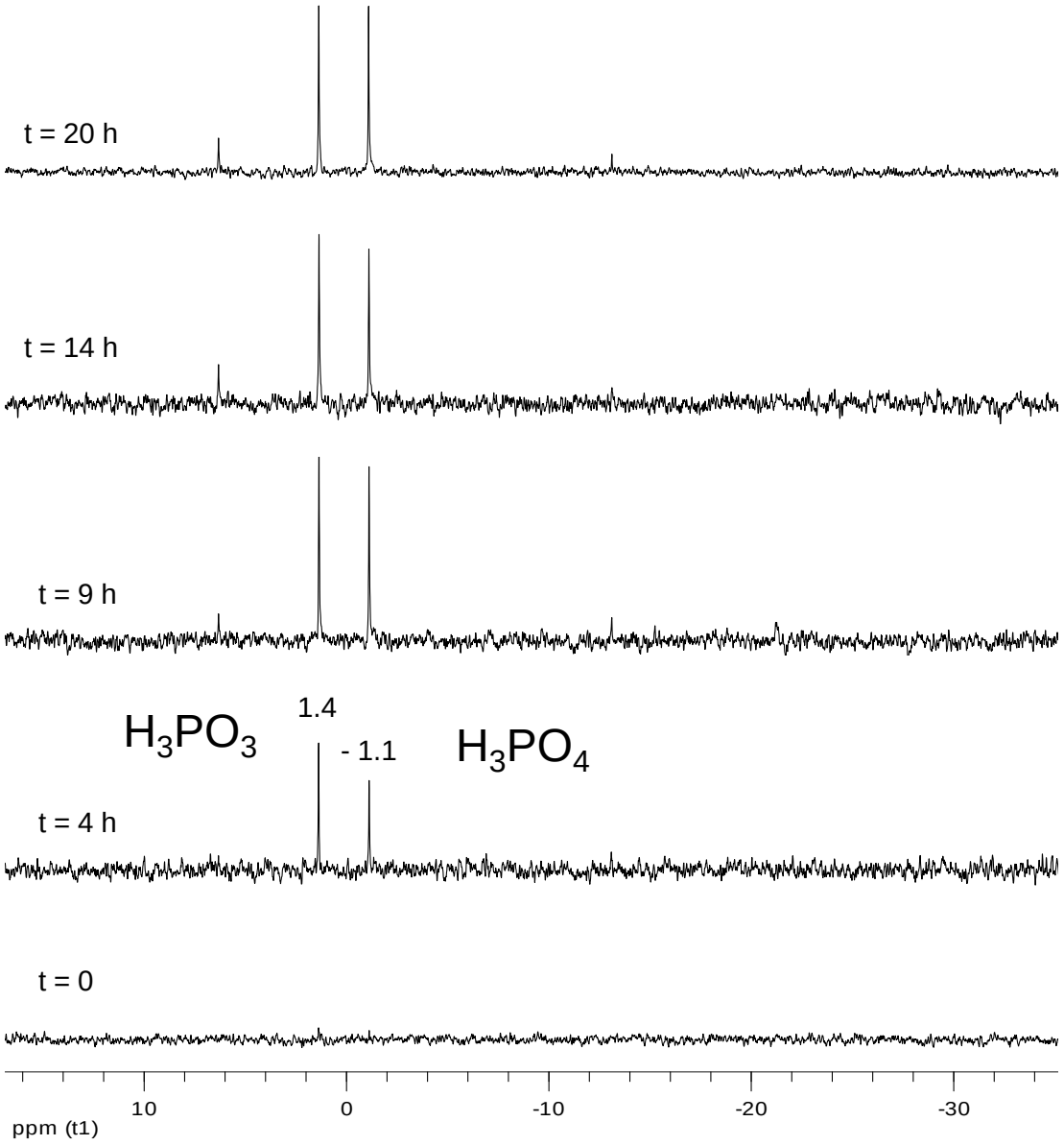
Tripolyphosphate, $[H_4P_3O_{10}]^-$ m/z = 256.9

$1.5 < P/H_2O < 15$

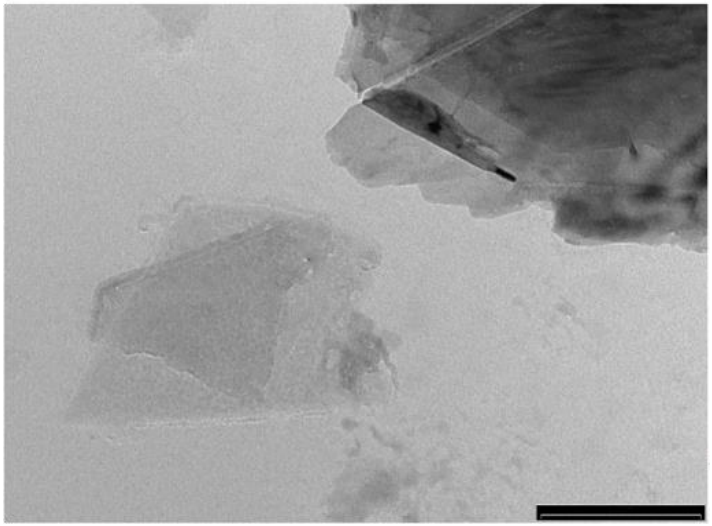

4h
9 h
15 h
20 h
S
O
ultrasound 37 KHz
30°C

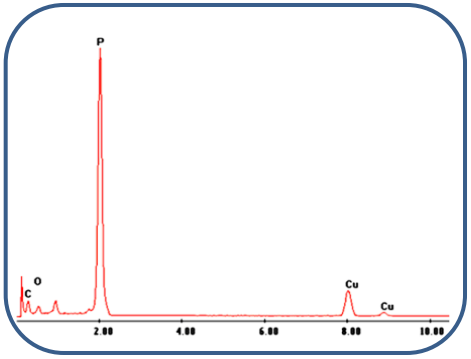

Centrifugation
6000 rpm, 1h

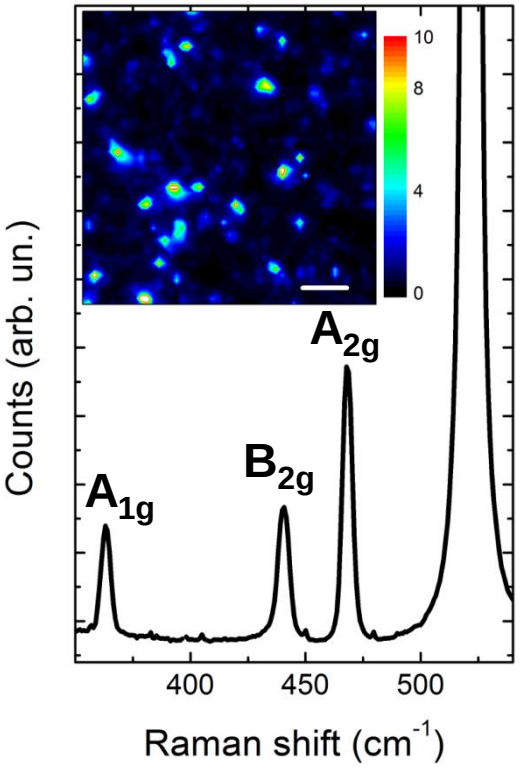
^{31}P-NMR

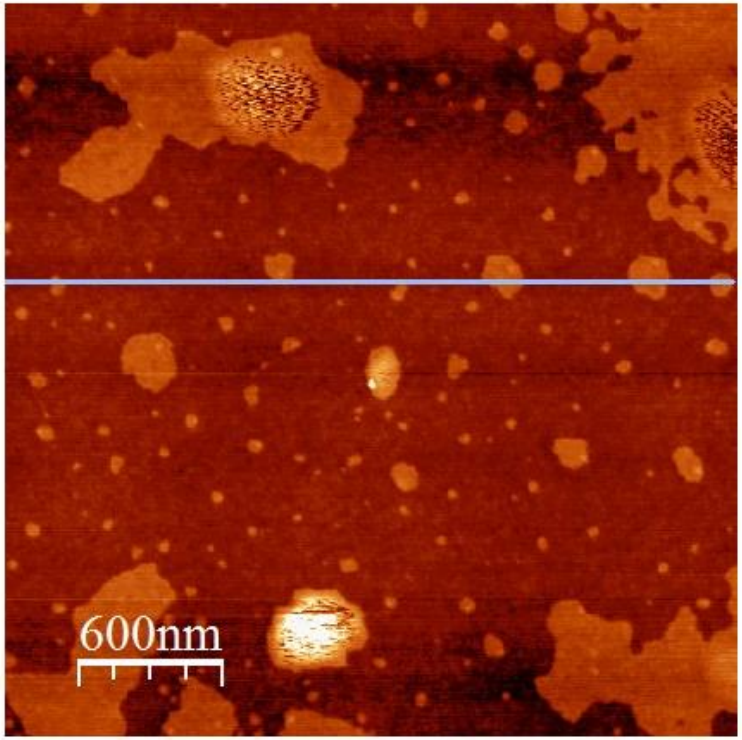


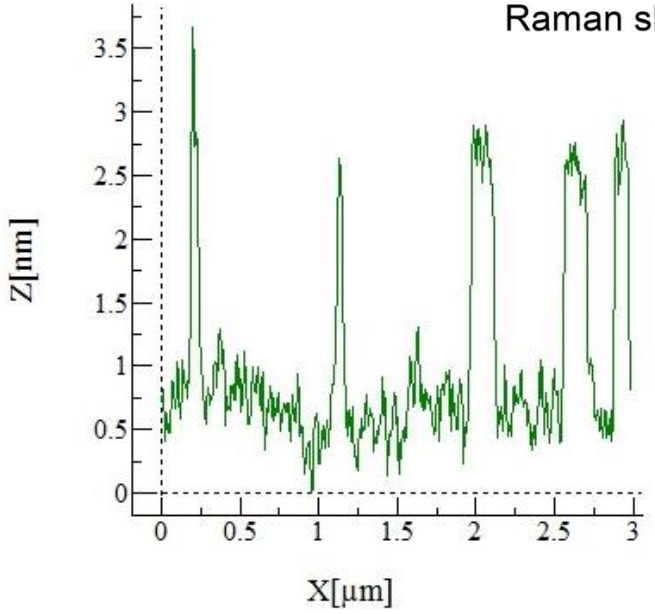
The degradation products were only phosphorous and phosphoric acids.



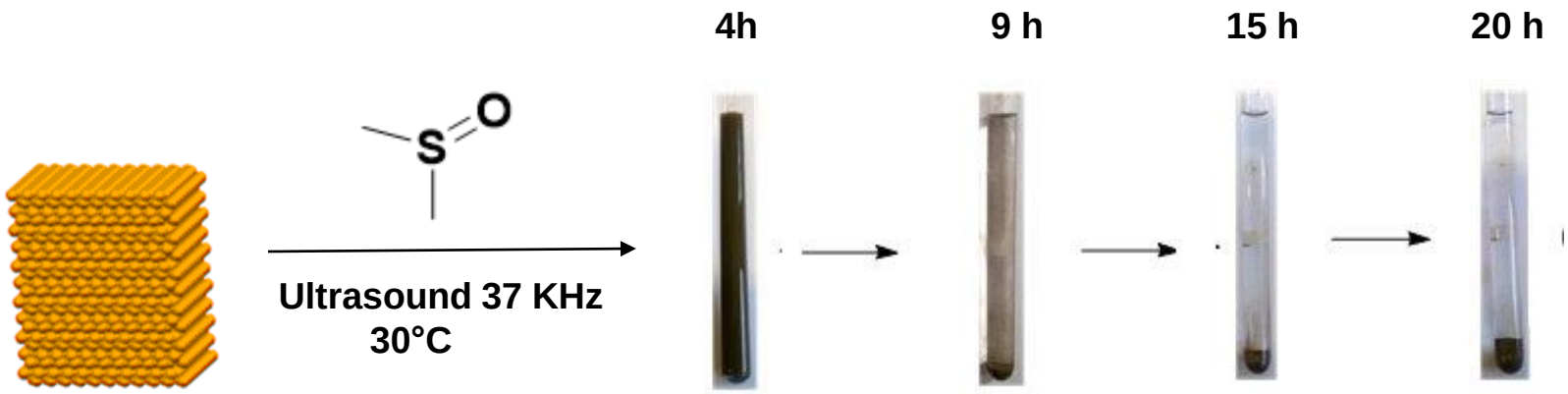

P
O
C
Cu
Cu
2.00
4.00
6.00
8.00
10.00


10
8
4
0
A1g
B2g
A2g
Counts (arb. un.)
400
450
500
Raman shift (cm-1)


600nm

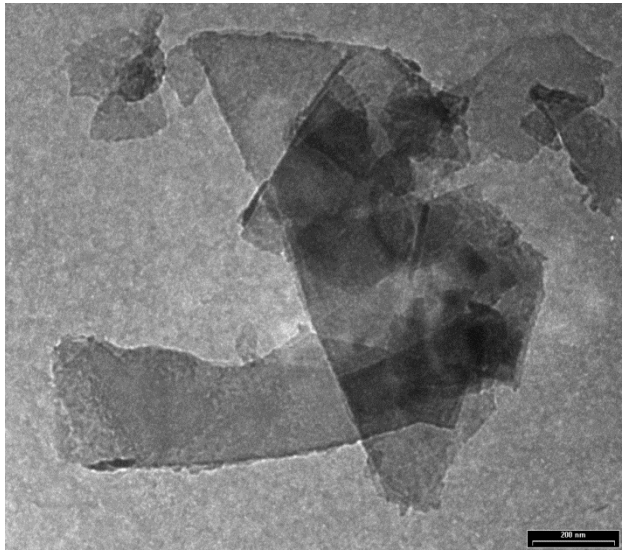

Z[nm]
3.5
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
3
X[μm]

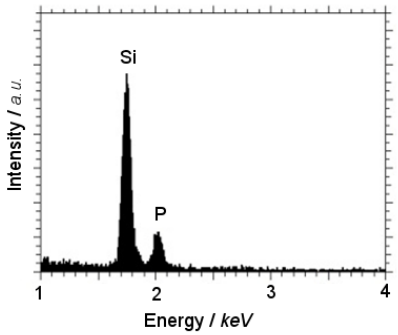
$0.3 < P/H_2O < 1.5$

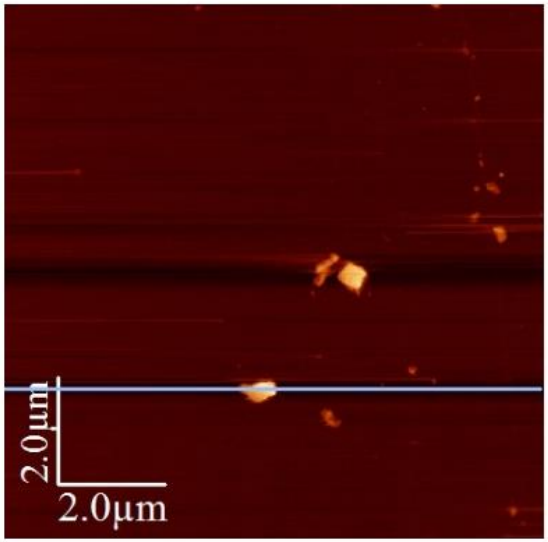


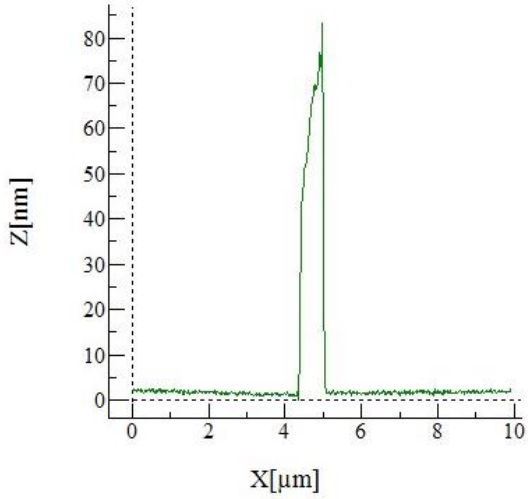
The exfoliation was followed by ^{31}P NMR

AFM – TEM

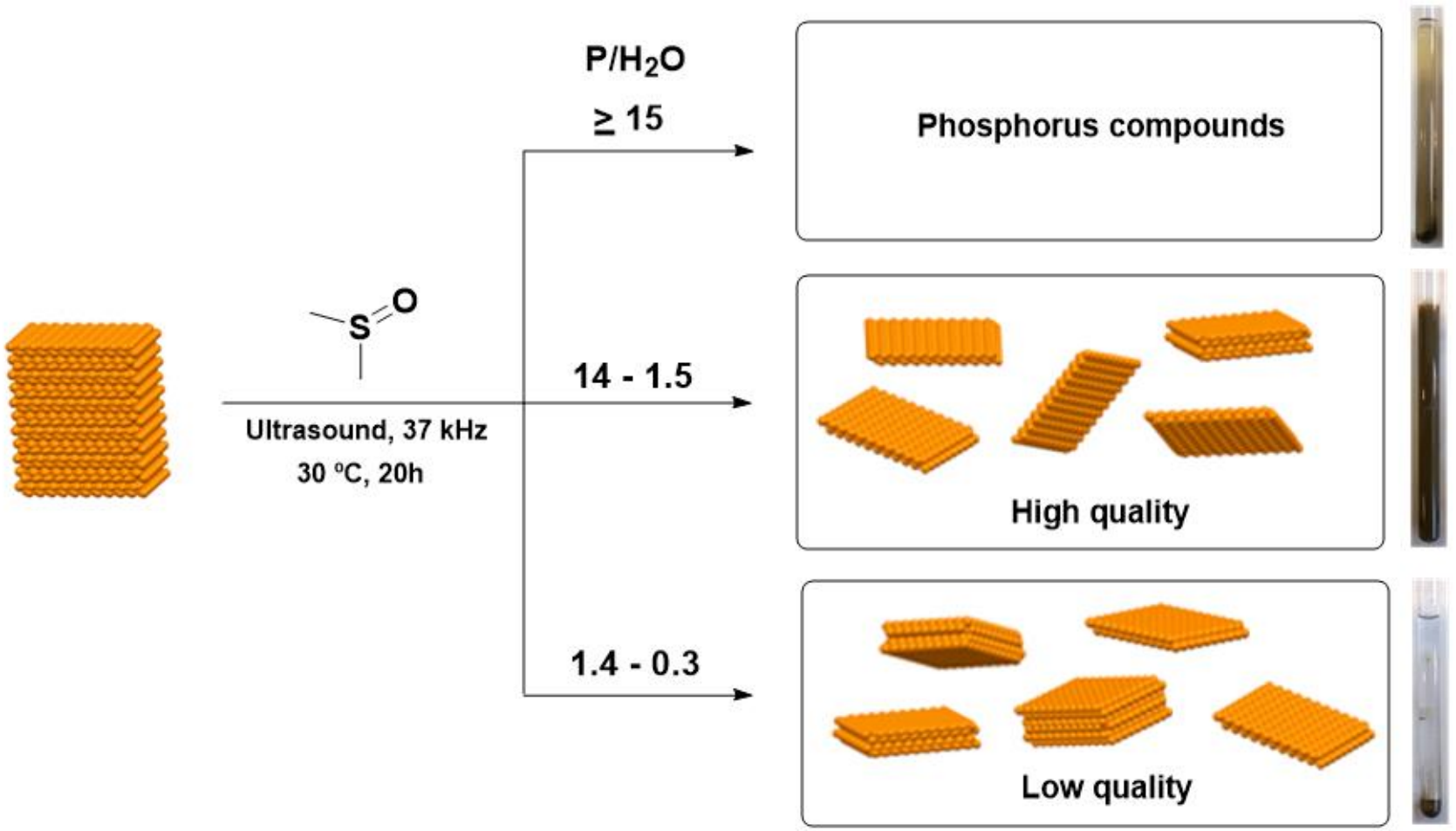



Si
P
Intensity / a.u.
1
2
3
4
Energy / keV


2.0µm
2.0µm


Z[nm]
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
X[µm]

Summary



M. Serrano-Ruiz, M. Caporali, A. Ienco, S. Heun, M. Peruzzini *et al*. submitted.

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Maurizio Peruzzini

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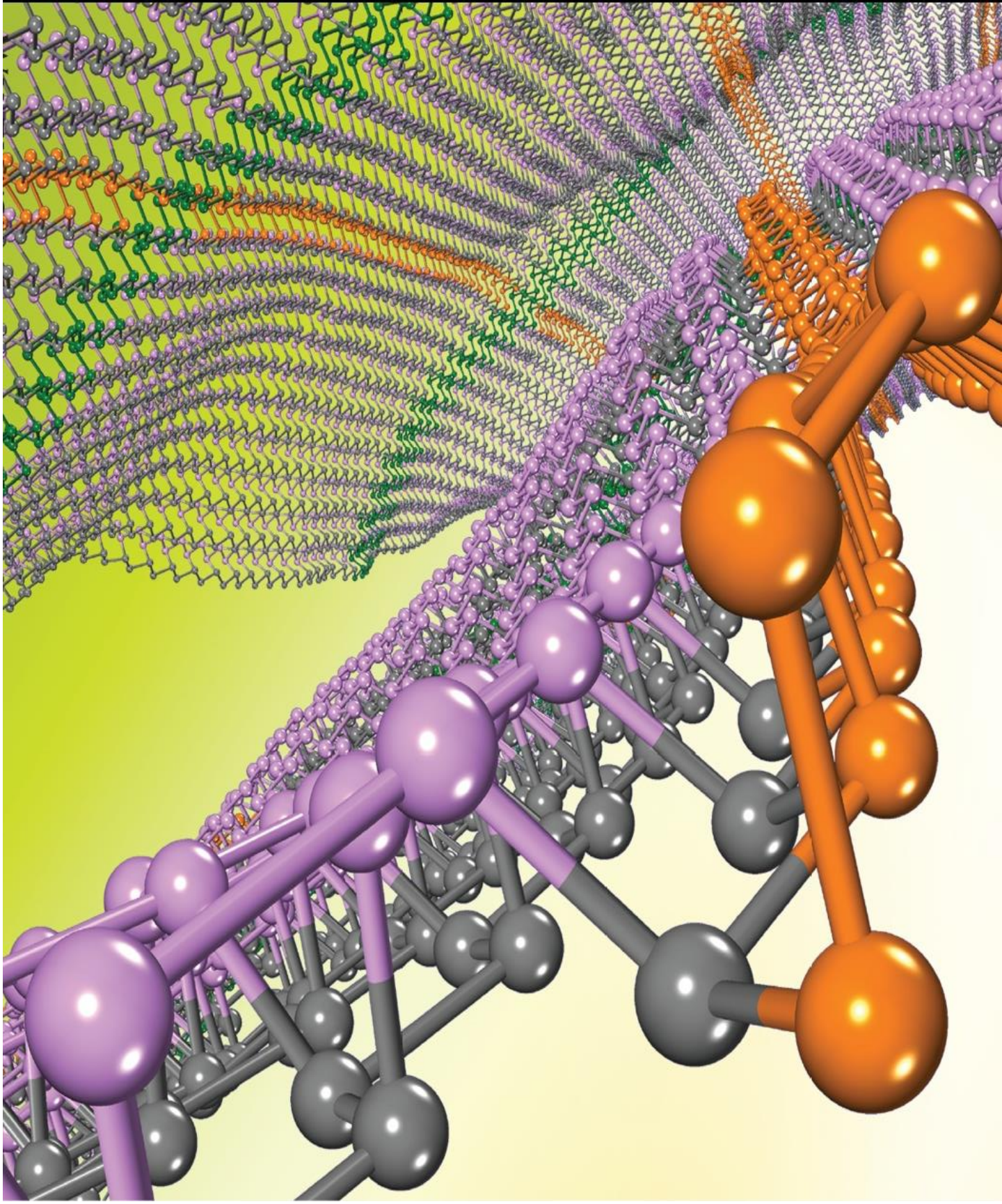
Stefan Heun
Vincenzo Piazza

FUNDING: European Research Council, ERC-2014-AdG 670173 PHOSFUN "*Phosphorene functionalization: a new platform for advanced multifunctional materials*".



Thank you!!