Phosphorene, a new two dimensional platform for advanced materials

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A chemist's view of 2D materials

Organic chemists are masterful at exercising control in zero dimensions ...

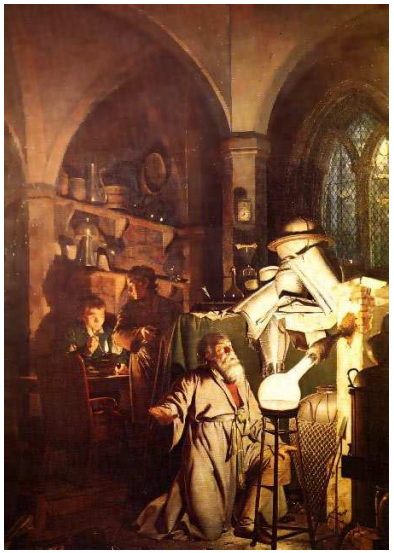
One subculture of organic chemists has learned to exercise control in one dimension. These are polymer chemists, the chain builders ...

But in **two** or **three** dimensions, it's a synthetic wasteland. The methodology for exercising control so that one can make unstable but persistent extended structures on demand is nearly absent. Or to put it in a positive way-this is a certain growth point of the chemistry of the future.

Roald Hoffmann Sci. Am. 1993, 63

Outline

- Phosphorus
- Phosphorene (graphene cousin)
- Synthesis by exfoliation
- The unexpected role of the water
- Conclusions

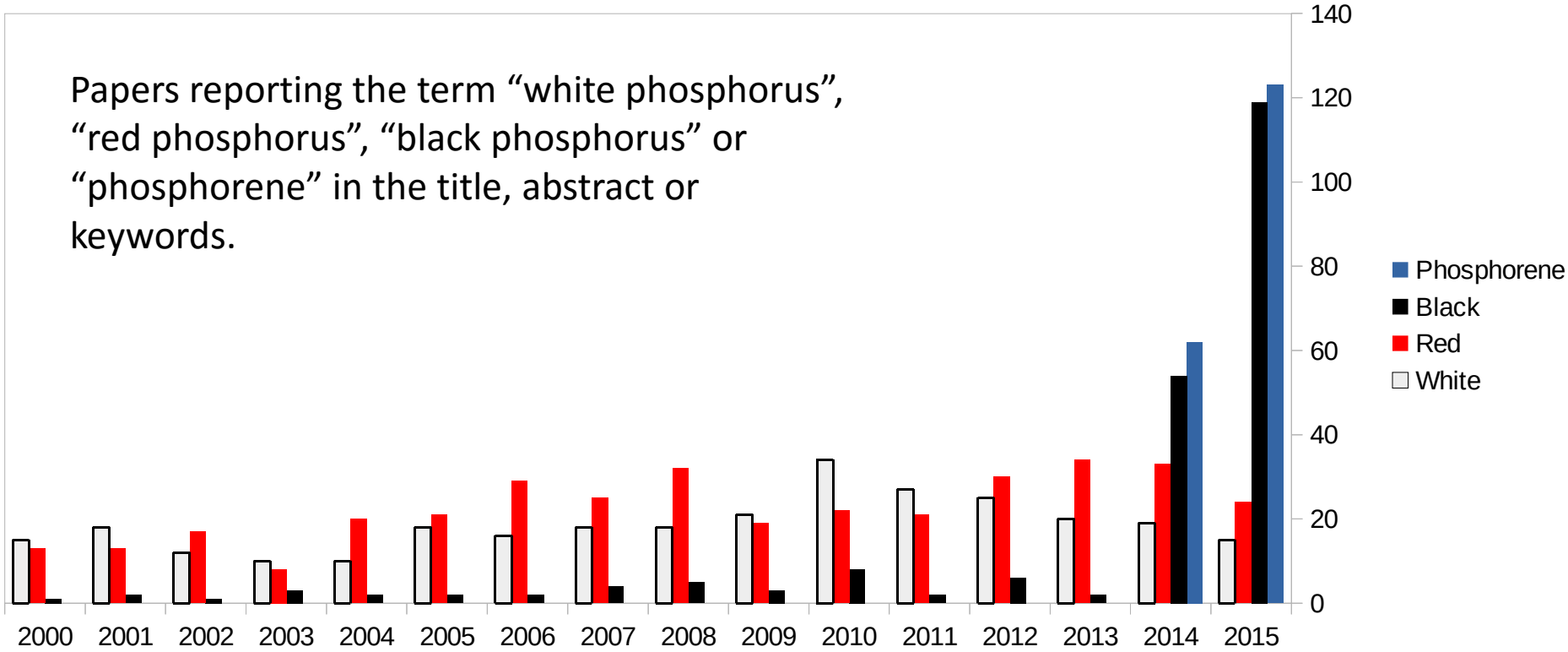


The Rise of 2D Phosphorus

White phosphorus Red phosphorus

Black phosphorus Phosphorene

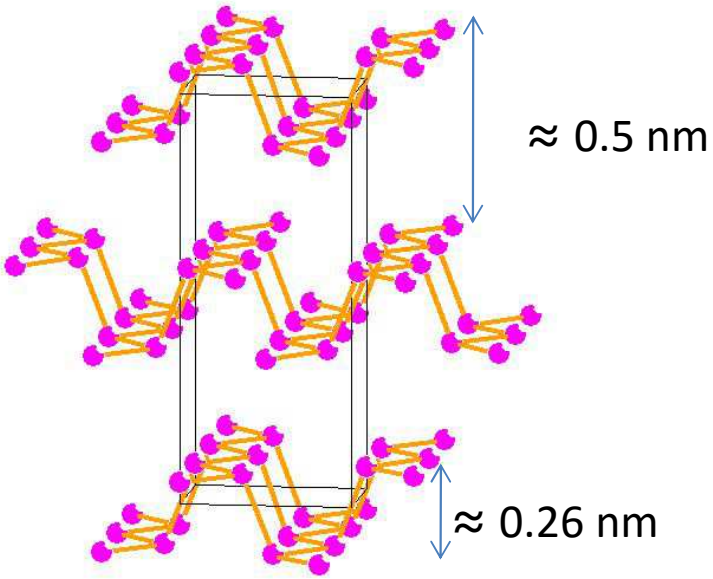
Papers reporting the term “white phosphorus”, “red phosphorus”, “black phosphorus” or “phosphorene” in the title, abstract or keywords.

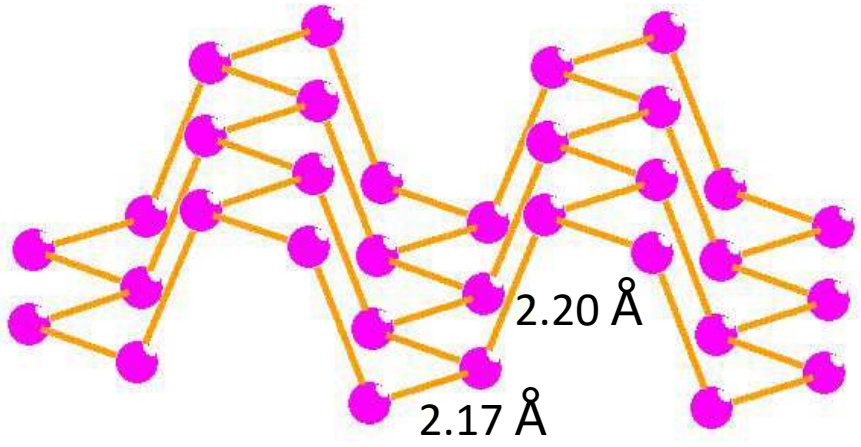


From scopus

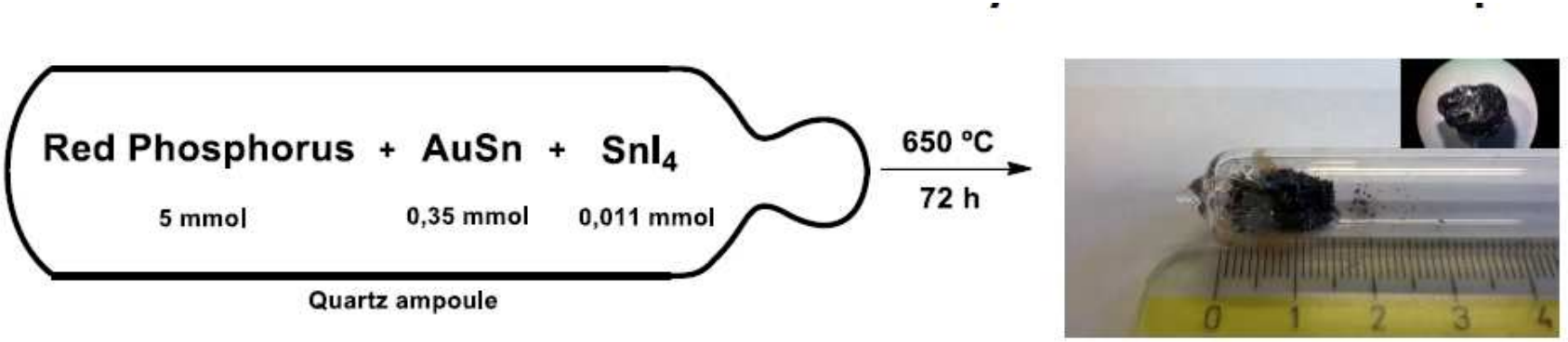
Black Phosphorus

- Black phosphorus has a 2D network;
- It can be exfoliated either by scotch tape method either using solvents.

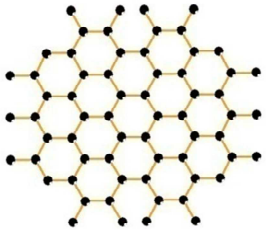




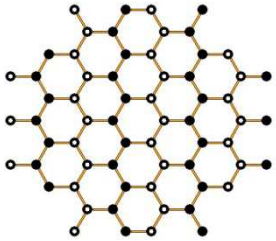
Synthesis of Black Phosphorus

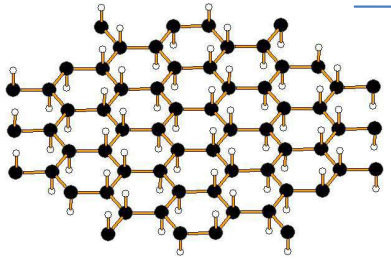


Relationship between Graphene and Phosphorene

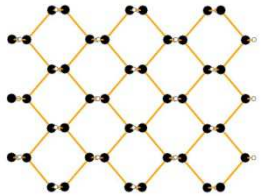


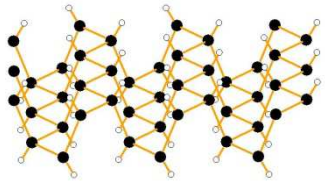
Add an H





Geometric reorganization





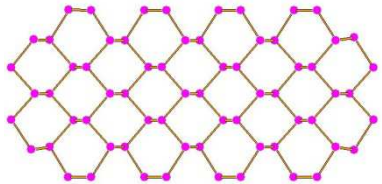
Corrugated Honeycomb network

C sp^2

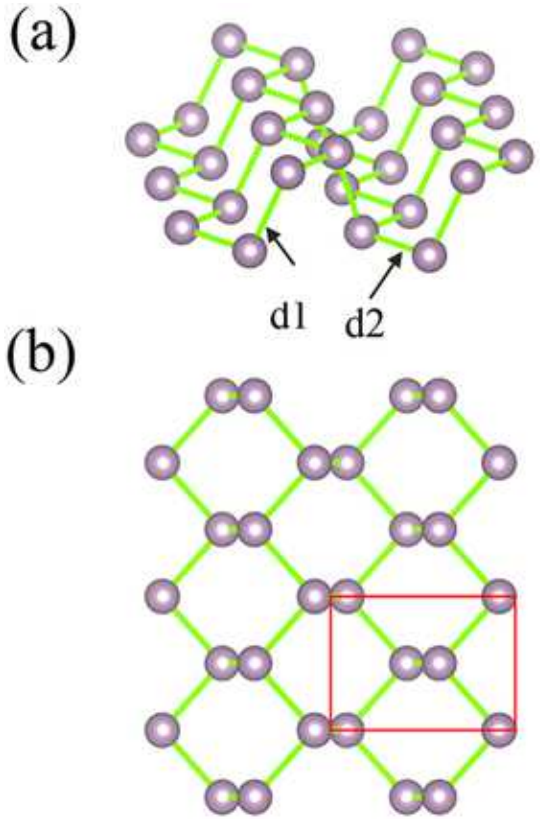
Honeycomb network

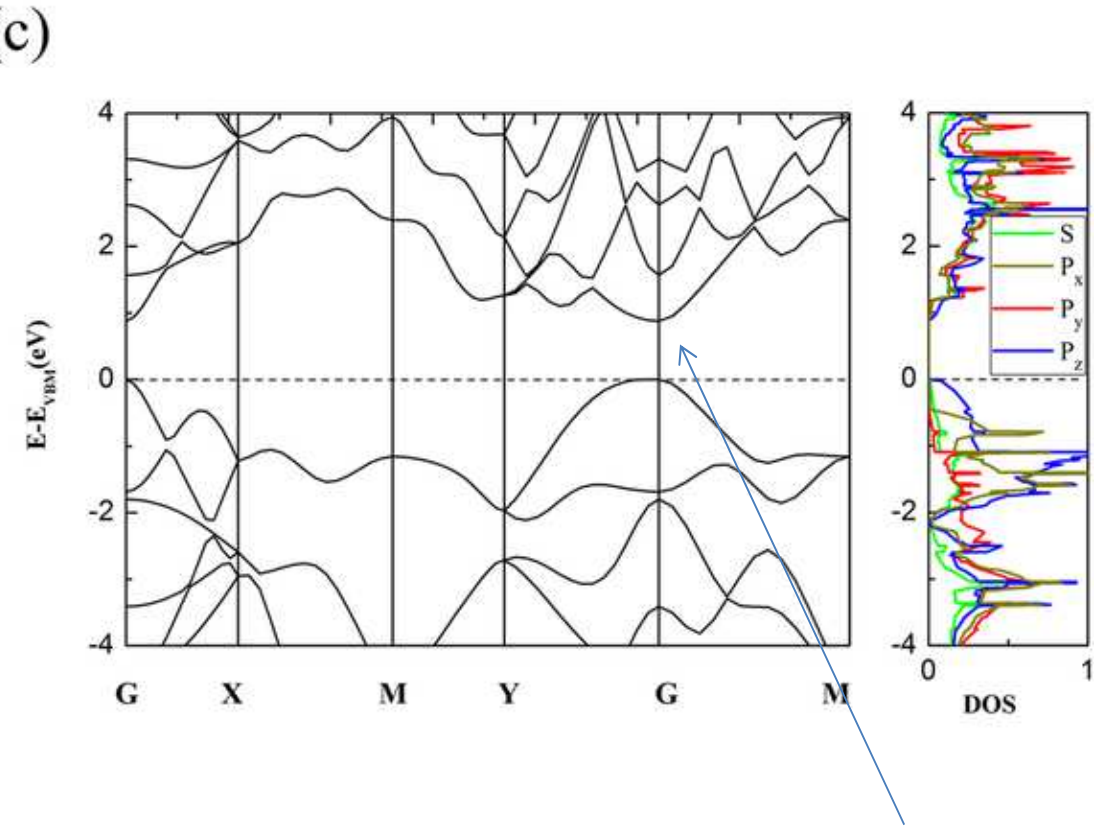
C sp^3

C-H is equivalent to P



Phosphorene Band Structure

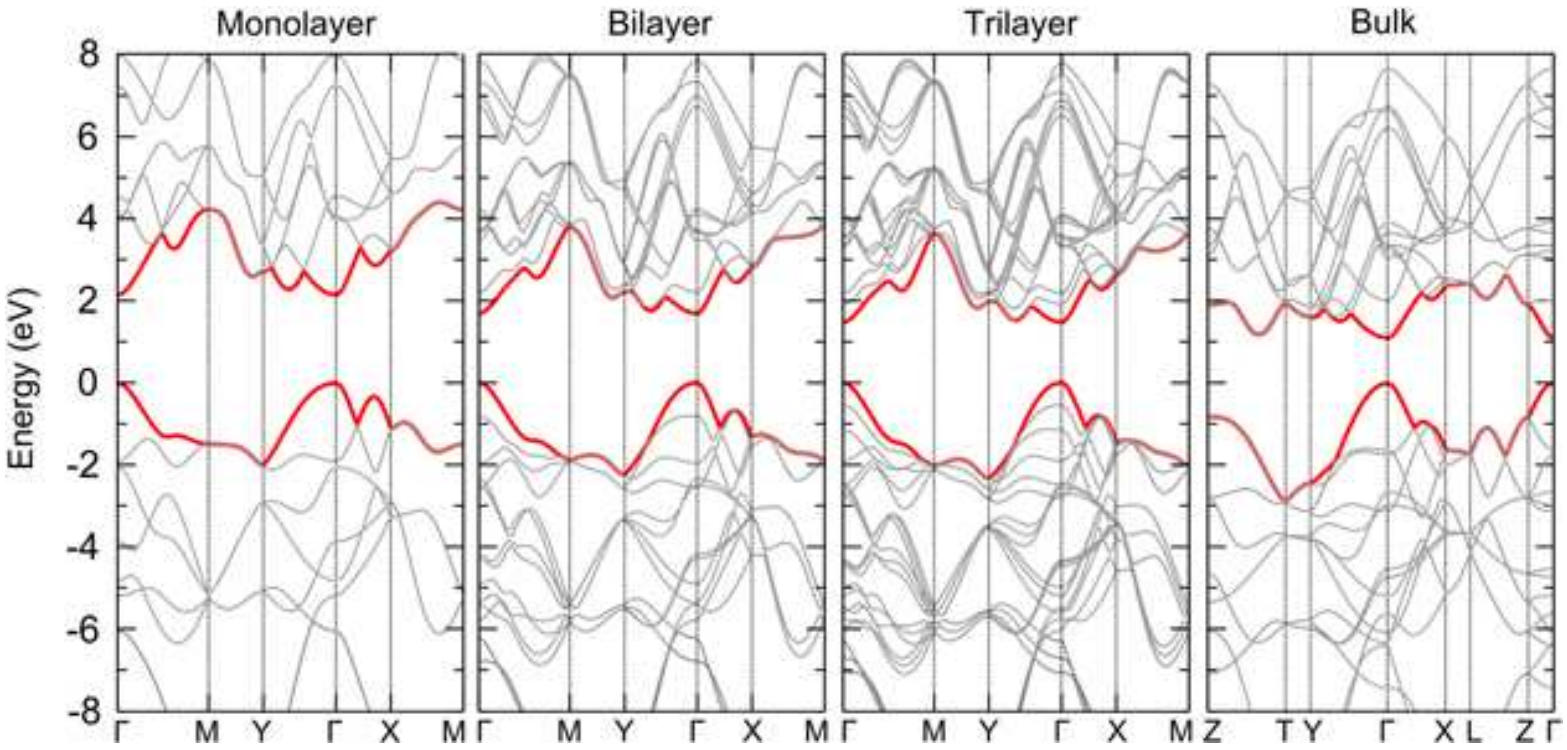




Direct band gap

Li et al. Scientific Reports 2015, 5, 10848

Phosphorene Band Structure



The band gap depends on the number of layers between 2.00 and 0.30 eV depending on the method used to calculate the band gap.

Castellanos-Gomez et al. 2D Materials 1 (2014) 025001

Exfoliation using DMSO

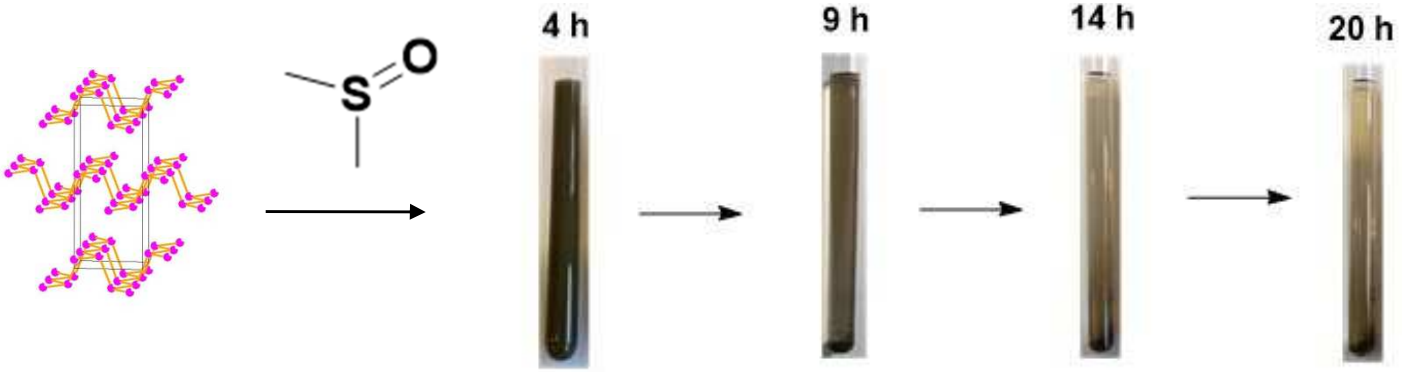
DMSO has:

- high dielectric constant;
- high surface tension;
- the quantity of water could be measured by ^{1}H NMR.

We found an important influence of the amount of water in the liquid exfoliation process.

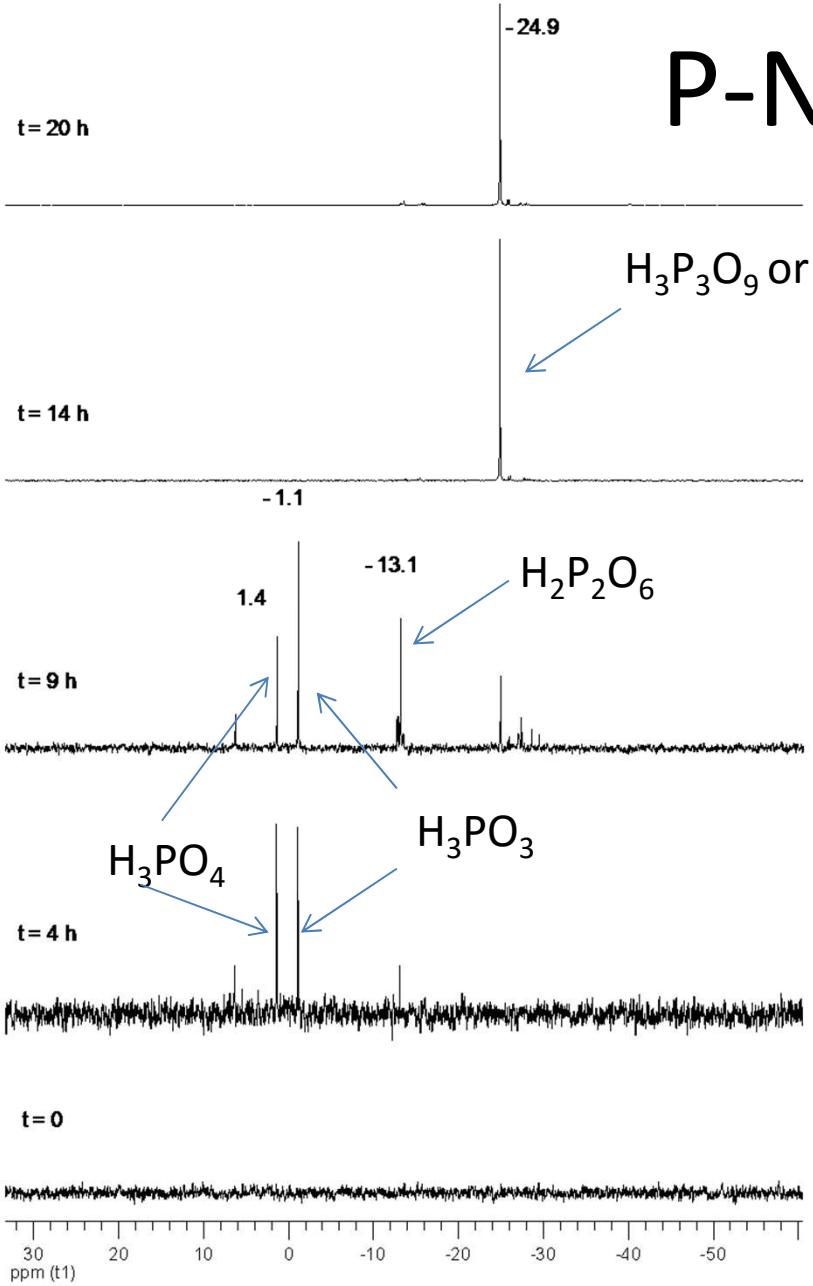
In particular three different ranges of molar ratio between black phosphorus and water were studied.

Range 1: molar ratio (P/H_2O) ≥ 15



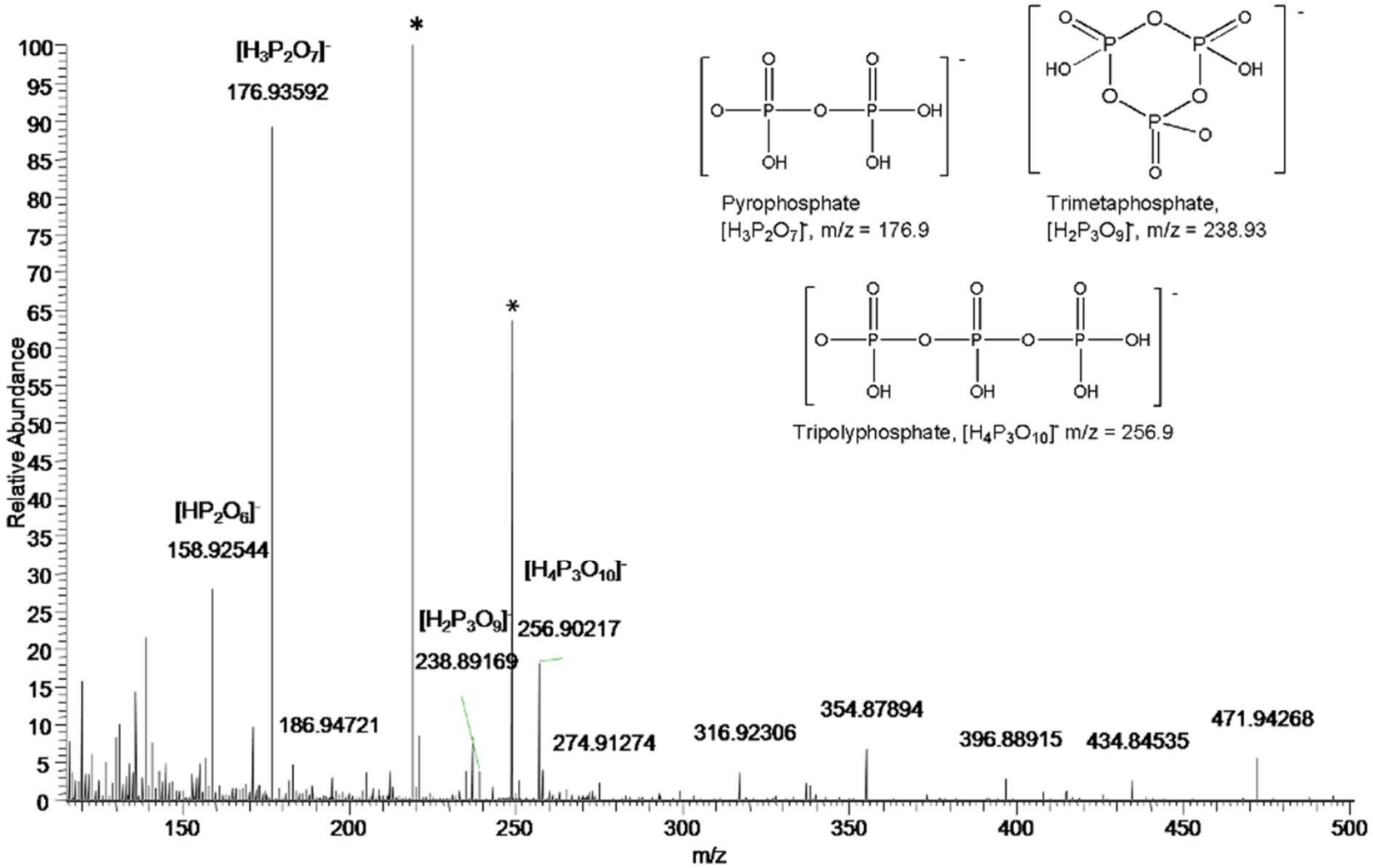
The exfoliation was followed by ^{31}P NMR:

P-NMR

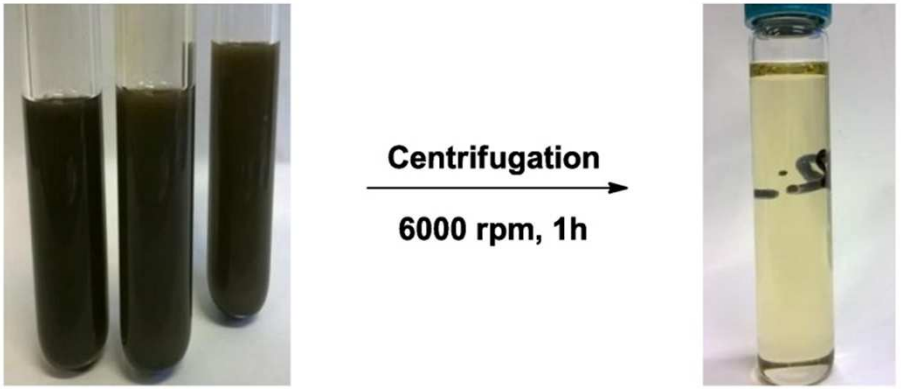


The degradation products resonating at - 13.1 and -24.9 ppm were assigned to pyrophosphate, $[HP_2O_6]^-$, and to trimetaphosphate $[H_2P_3O_9]^-$ respectively, on the basis of high resolution ESI MS

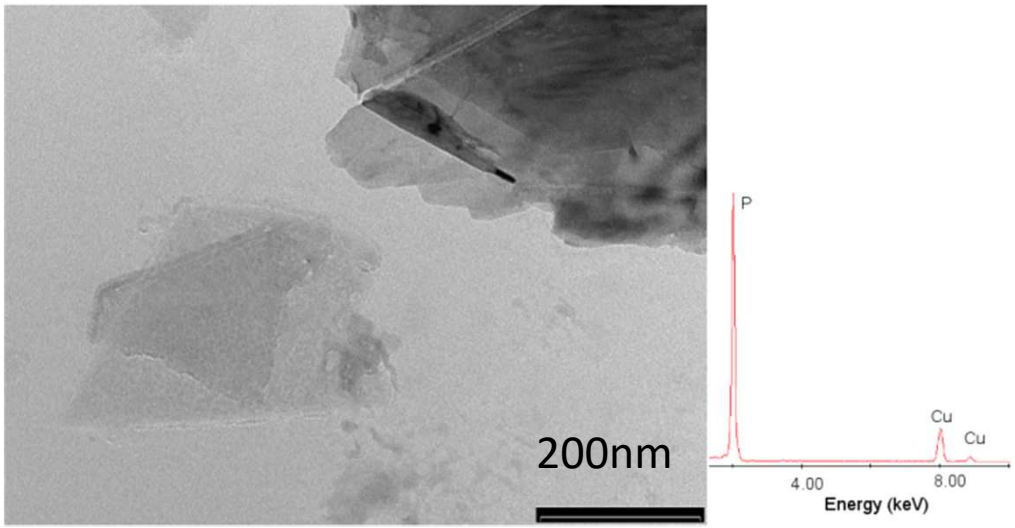
ESI-MS

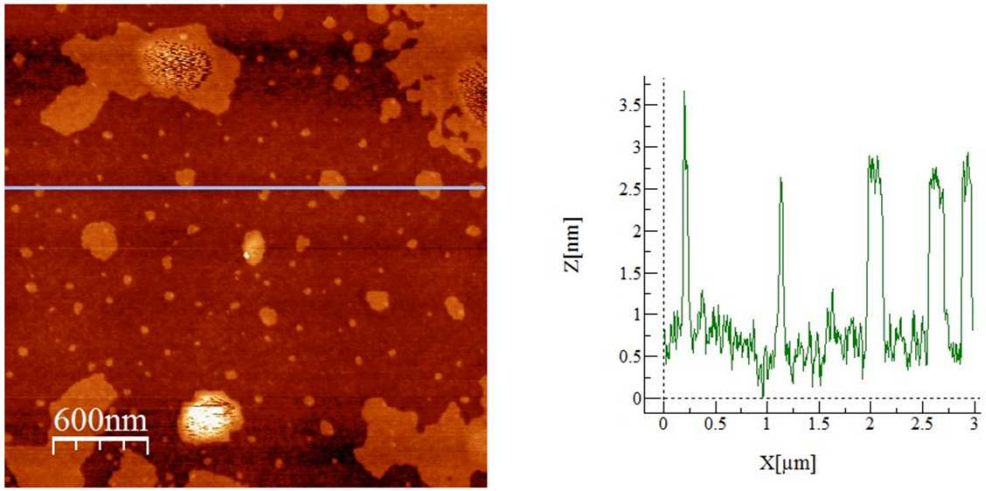

[H3P2O7]-
176.93592
[HP2O6]-
158.92544
[H2P3O9]-
238.89169
[H4P3O10]-
256.90217
186.94721
274.91274
316.92306
354.87894
396.88915
434.84535
471.94268
Relative Abundance
m/z
Pyrophosphate
[H3P2O7]-, m/z = 176.9
Trimetaphosphate,
[H2P3O9]-, m/z = 238.93
Tripolyphosphate, [H4P3O10]- m/z = 256.9

$1.5 < P/H_2O < 15$



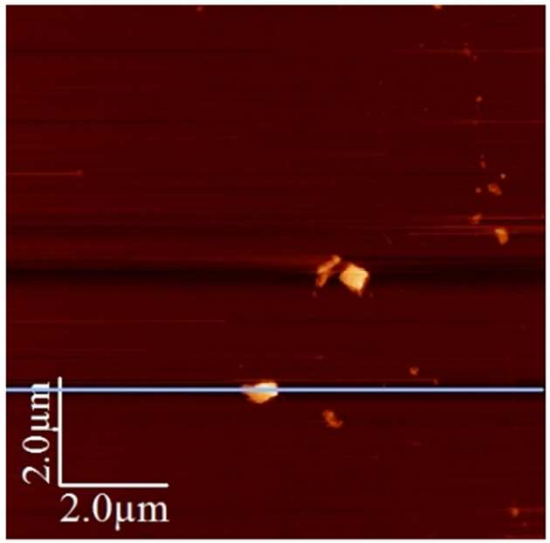
TEM and AFM

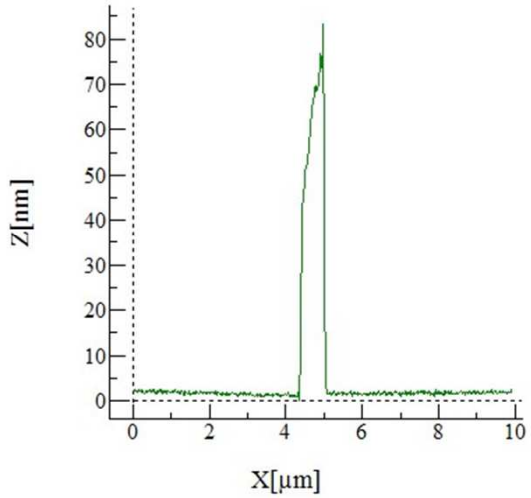


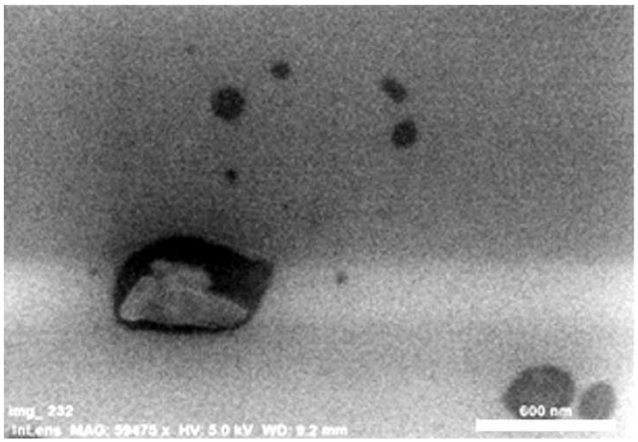


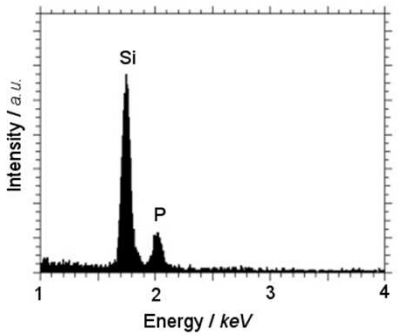
$0.3 < P/H_2O < 1.5$

AFM - SEM

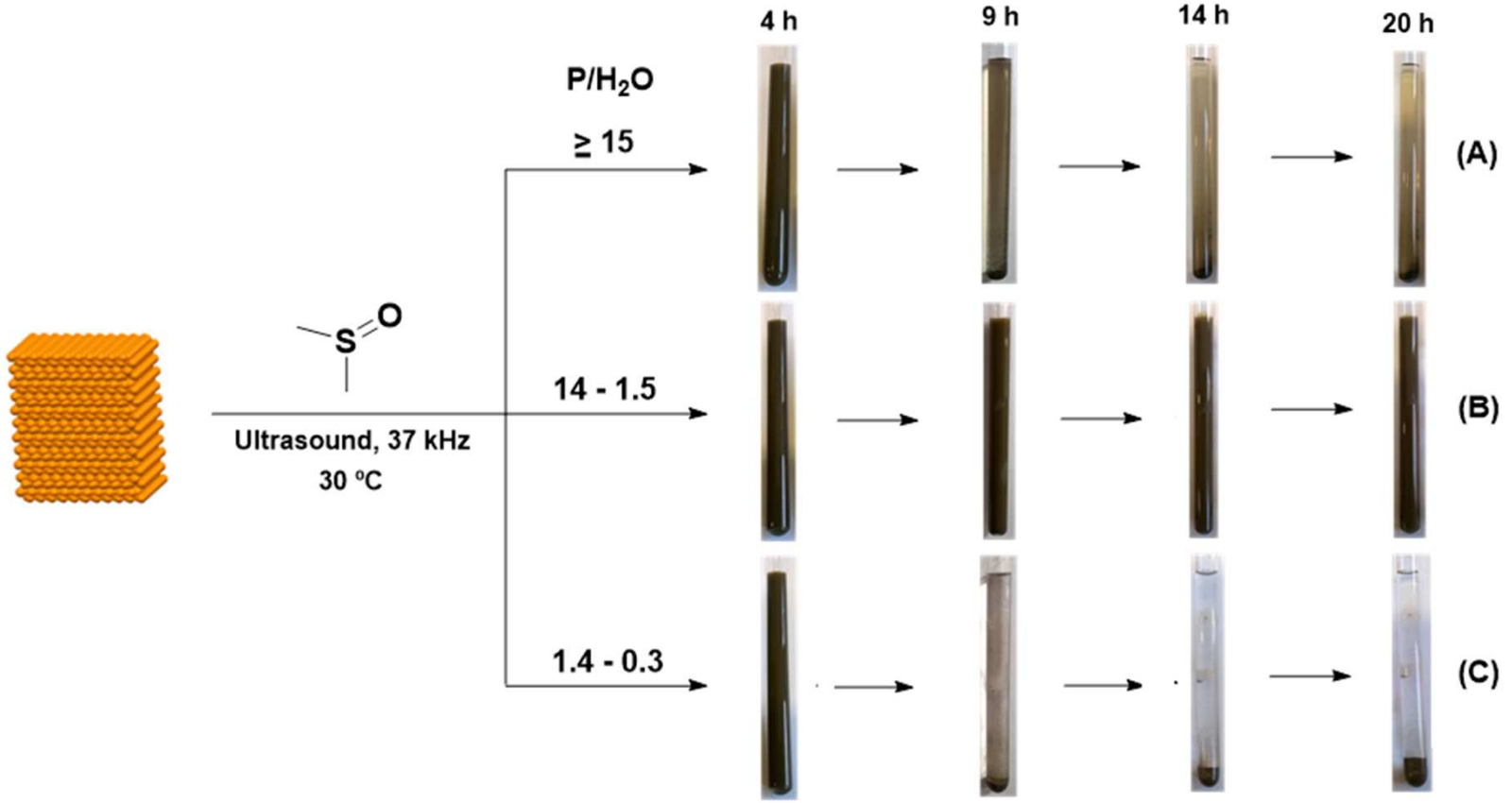

2.0µm
2.0µm

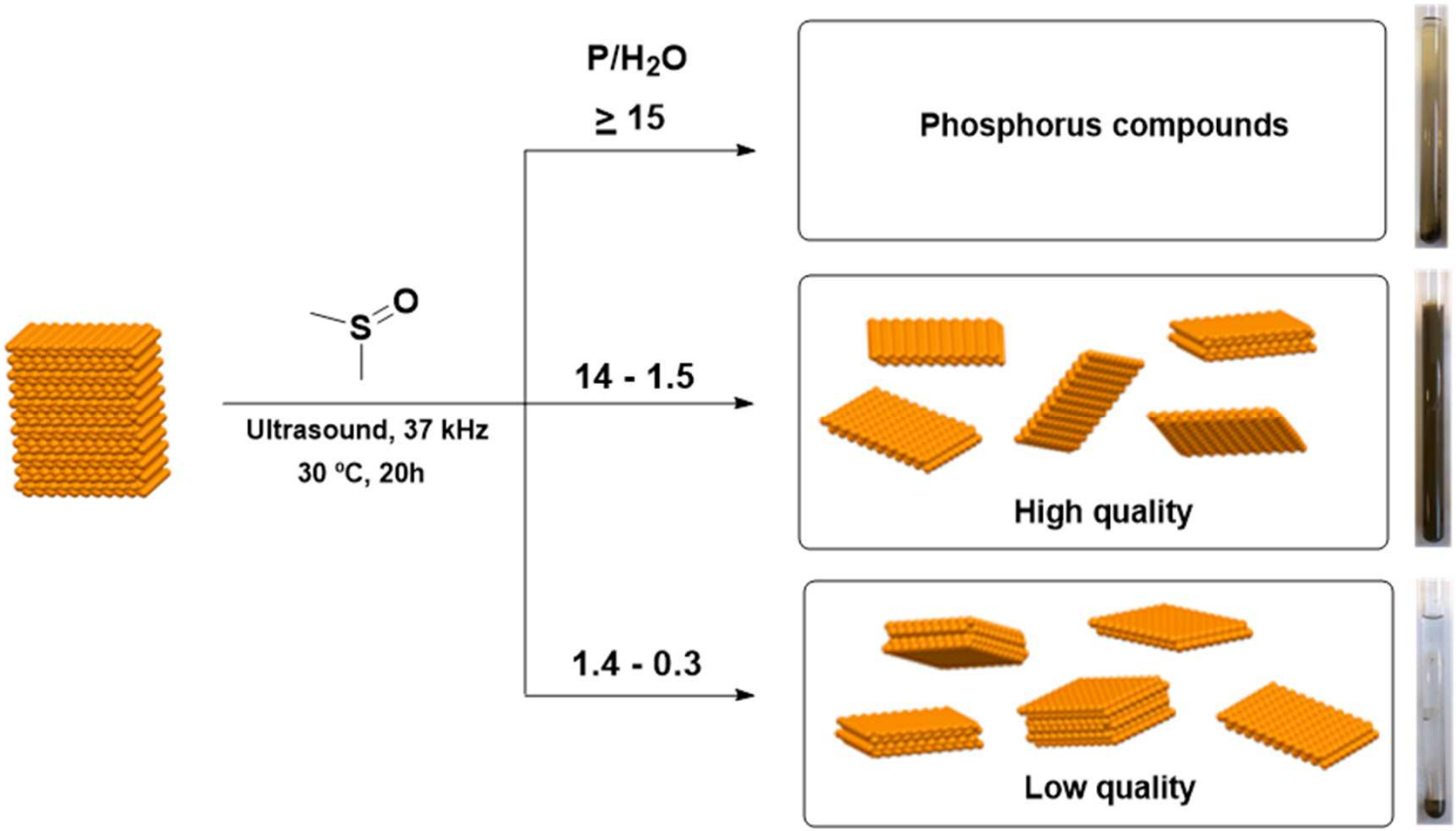

Z[nm]
X[µm]
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10


600 nm


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

Experiment




P/H2O
≥ 15
Phosphorus compounds
S
O
14 - 1.5
Ultrasound, 37 kHz
30 °C, 20h
High quality
1.4 - 0.3
Low quality