2D black phosphorus decorated with palladium nanoparticles. Synthesis, characterization and catalytic applications

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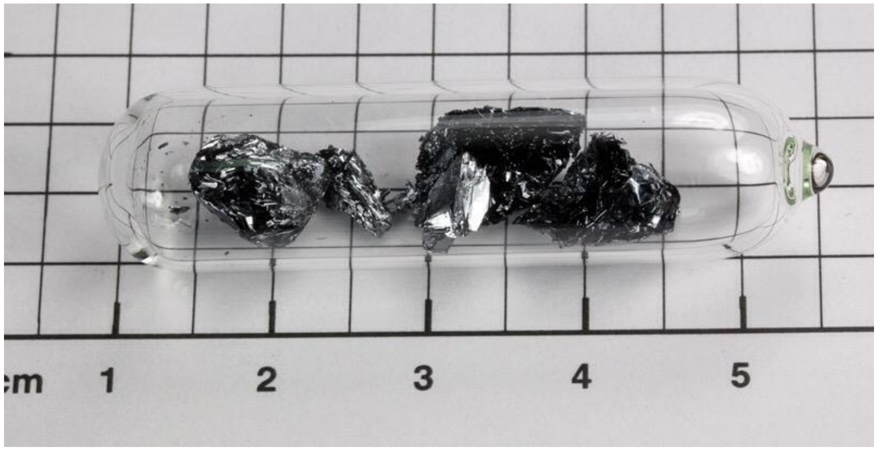
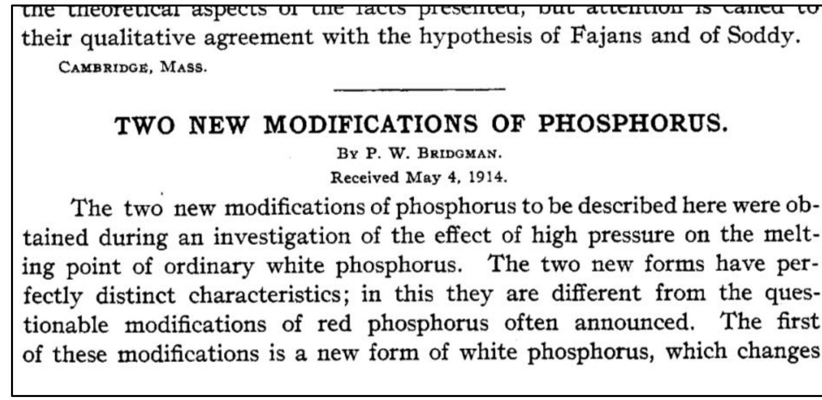
BLACK PHOSPHORUS




the theoretical aspects of the facts presented, but attention is called to their qualitative agreement with the hypothesis of Fajans and of Soddy.

CAMBRIDGE, MASS.

TWO NEW MODIFICATIONS OF PHOSPHORUS.

BY P. W. BRIDGMAN.

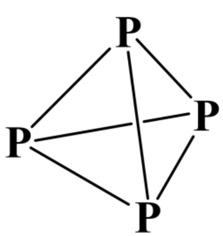
Received May 4, 1914.

The two new modifications of phosphorus to be described here were obtained during an investigation of the effect of high pressure on the melting point of ordinary white phosphorus. The two new forms have perfectly distinct characteristics; in this they are different from the questionable modifications of red phosphorus often announced. The first of these modifications is a new form of white phosphorus, which changes

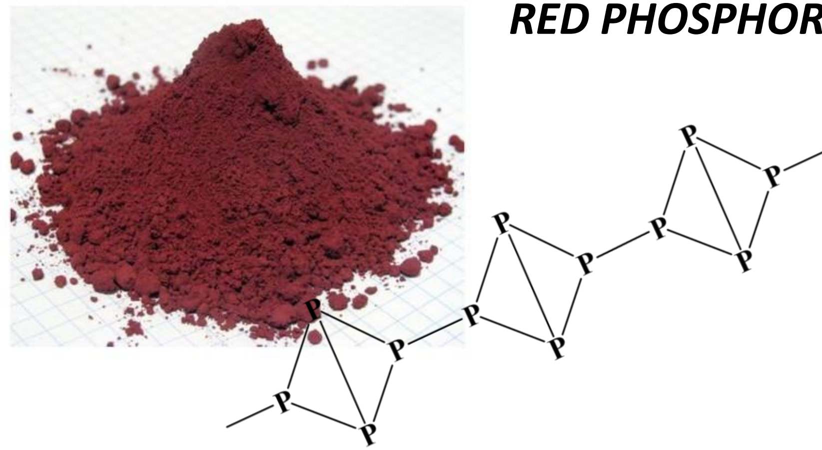
Percy W. Bridgman, 1914

ALLOTROPES OF PHOSPHORUS

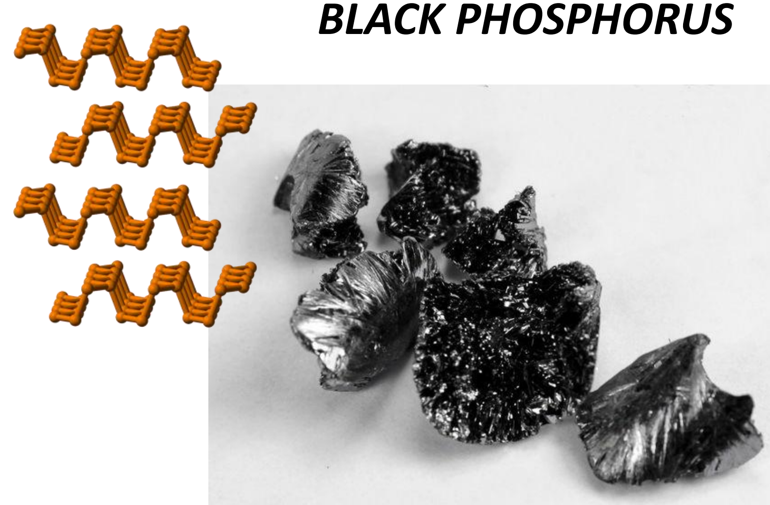
WHITE PHOSPHORUS



RED PHOSPHORUS



BLACK PHOSPHORUS

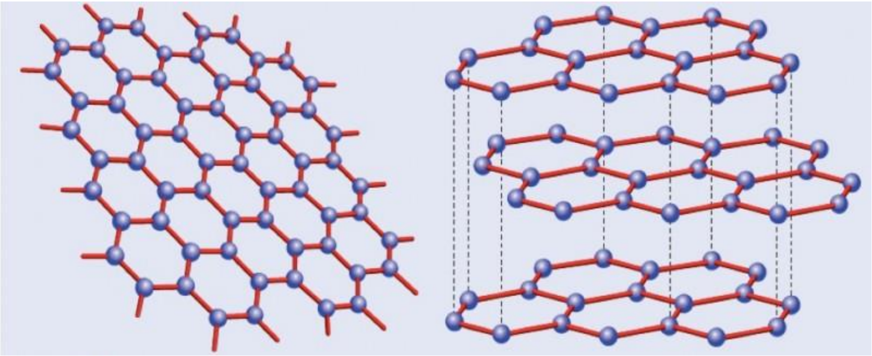


BLACK PHOSPHORUS vs GRAPHITE

BLACK PHOSPHORUS

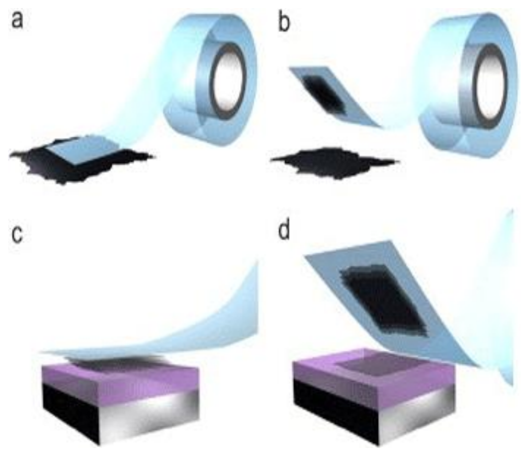
Direct semiconductor

GRAPHITE

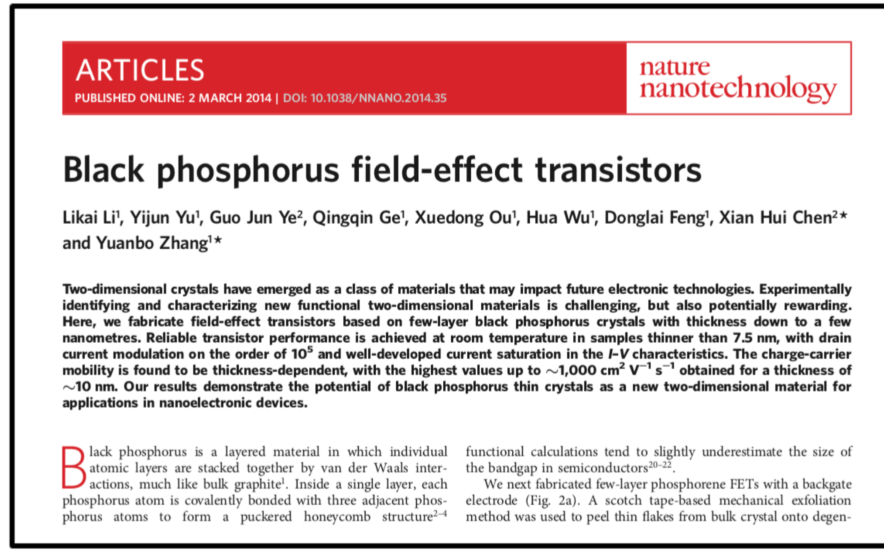


Semimetal

BLACK PHOSPHORUS: MECHANICAL EXFOLIATION



Classical scotch-tape method


ARTICLES
PUBLISHED ONLINE: 2 MARCH 2014 | DOI: 10.1038/NNANO.2014.35
nature nanotechnology

Black phosphorus field-effect transistors

Likai Li[1], Yijun Yu[1], Guo Jun Ye[2], Qingqin Ge[1], Xuedong Ou[1], Hua Wu[1], Donglai Feng[1], Xian Hui Chen[2]* and Yuanbo Zhang[1]*

Two-dimensional crystals have emerged as a class of materials that may impact future electronic technologies. Experimentally identifying and characterizing new functional two-dimensional materials is challenging, but also potentially rewarding. Here, we fabricate field-effect transistors based on few-layer black phosphorus crystals with thickness down to a few nanometres. Reliable transistor performance is achieved at room temperature in samples thinner than 7.5 nm, with drain current modulation on the order of 10^5 and well-developed current saturation in the *I–V* characteristics. The charge-carrier mobility is found to be thickness-dependent, with the highest values up to ~1,000 $cm^2 V^{-1} s^{-1}$ obtained for a thickness of ~10 nm. Our results demonstrate the potential of black phosphorus thin crystals as a new two-dimensional material for applications in nanoelectronic devices.

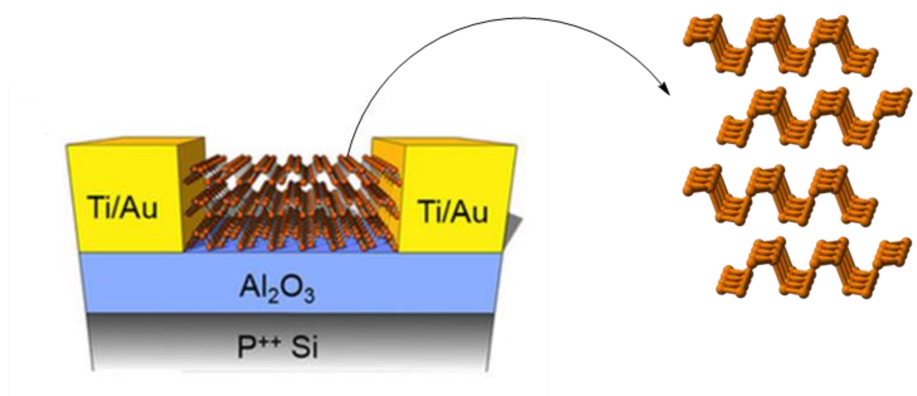
Black phosphorus is a layered material in which individual atomic layers are stacked together by van der Waals interactions, much like bulk graphite[1]. Inside a single layer, each phosphorus atom is covalently bonded with three adjacent phosphorus atoms to form a puckered honeycomb structure[2–4] functional calculations tend to slightly underestimate the size of the bandgap in semiconductors[20–22].

We next fabricated few-layer phosphorene FETs with a backgate electrode (Fig. 2a). A scotch tape-based mechanical exfoliation method was used to peel thin flakes from bulk crystal onto degen-

Nat. Nanotechnol. **2014**, *9*, 372-377

Direct semiconductor with band gap tunability:

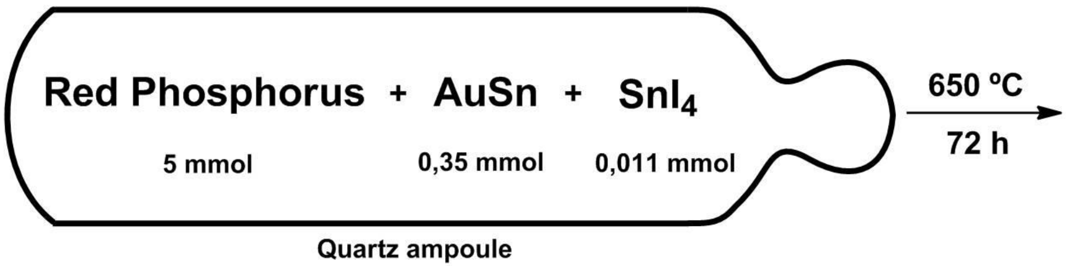
ΔE from **0.3 eV** (bulk BP) to **1.8 eV** (monolayer)



Back-gated black phosphorus FET

(adapted from *Sci. Rep.* 2015, *5*, 08989)

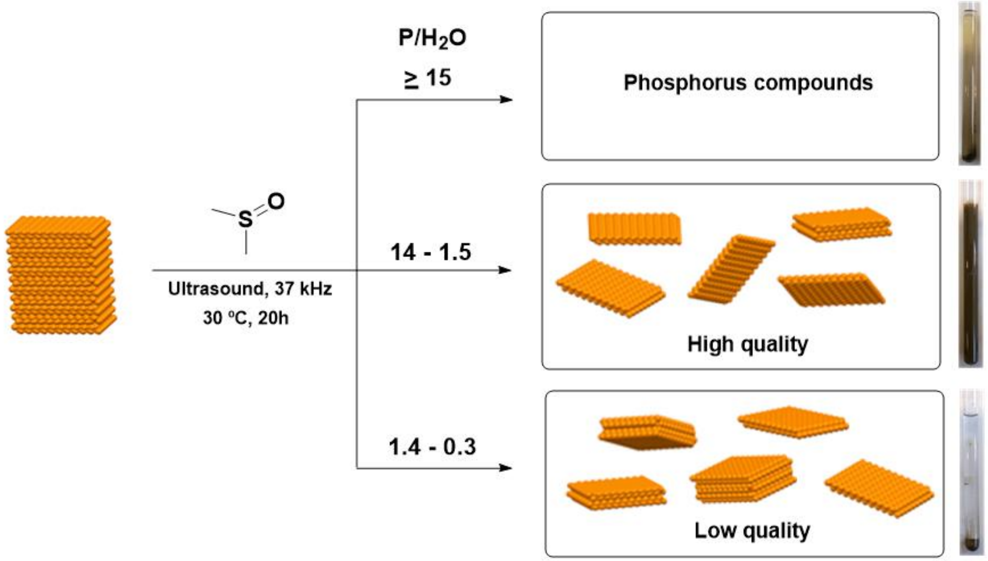
BLACK PHOSPHORUS PREPARATION



Inorg. Chem. 2007, *46*, 4028-4035.

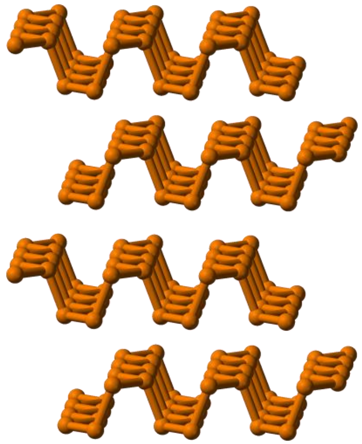
FEW-LAYERS BLACK PHOSPHORUS: WET EXFOLIATION

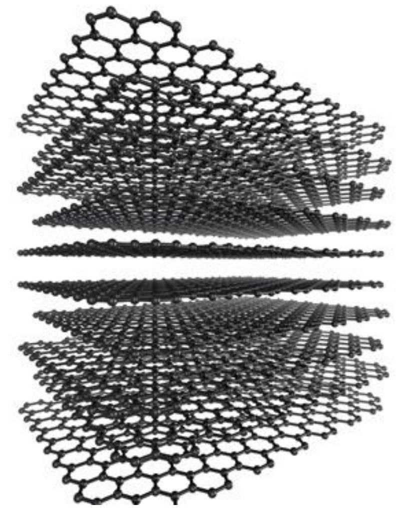
SOLVENT ASSISTED EXFOLIATION WITH ULTRASOUNDS IN DMSO

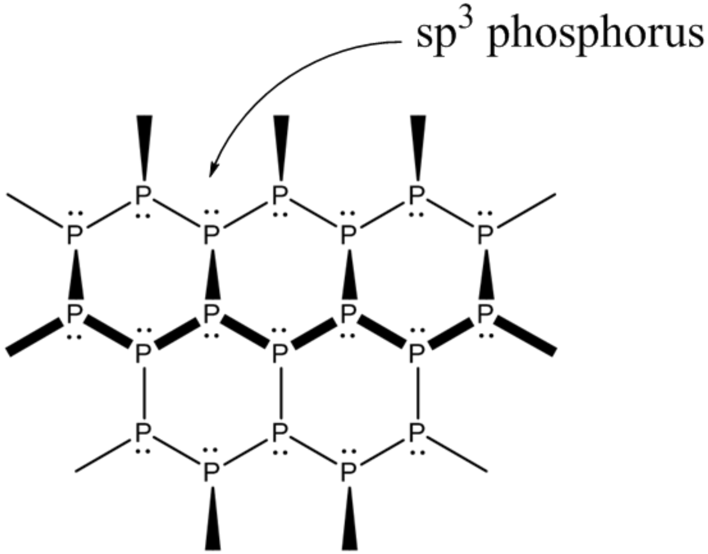


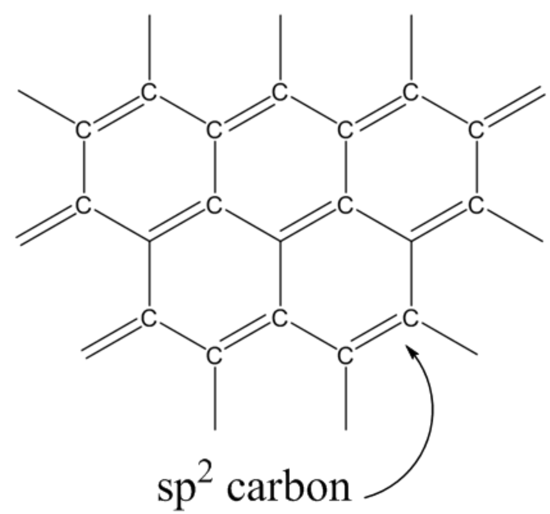
M. Serrano-Ruiz, M. Caporali, A. Ienco, V. Piazza, S. Heun, M. Peruzzini, *Adv. Mat. Interfaces* **2016**, 3, 1500441.

FEW LAYER BLACK PHOSPHORUS:
SURFACE DECORATION

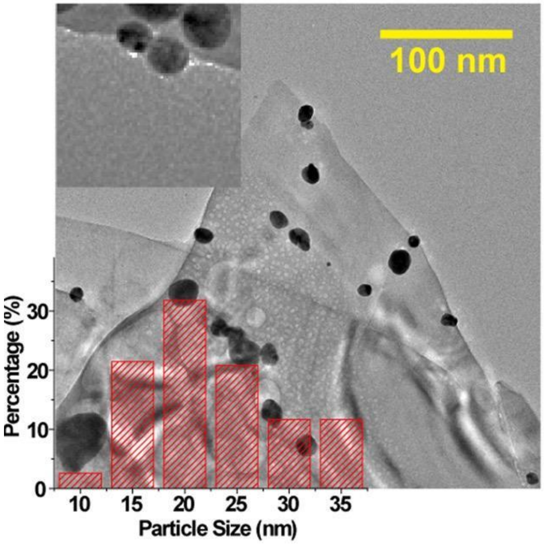




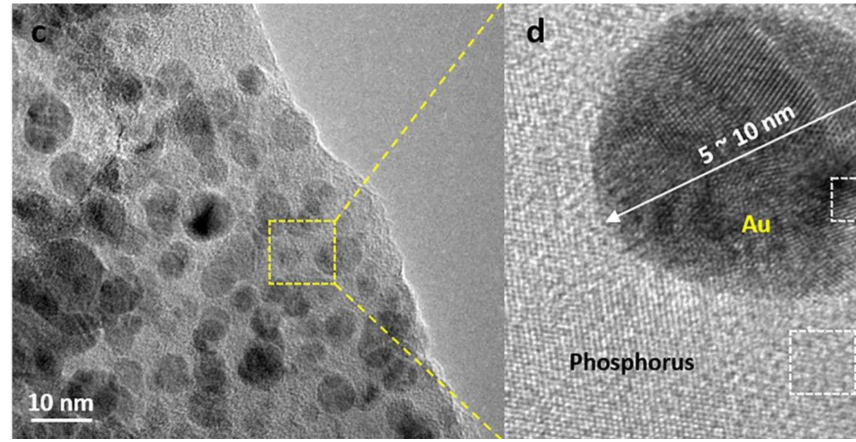




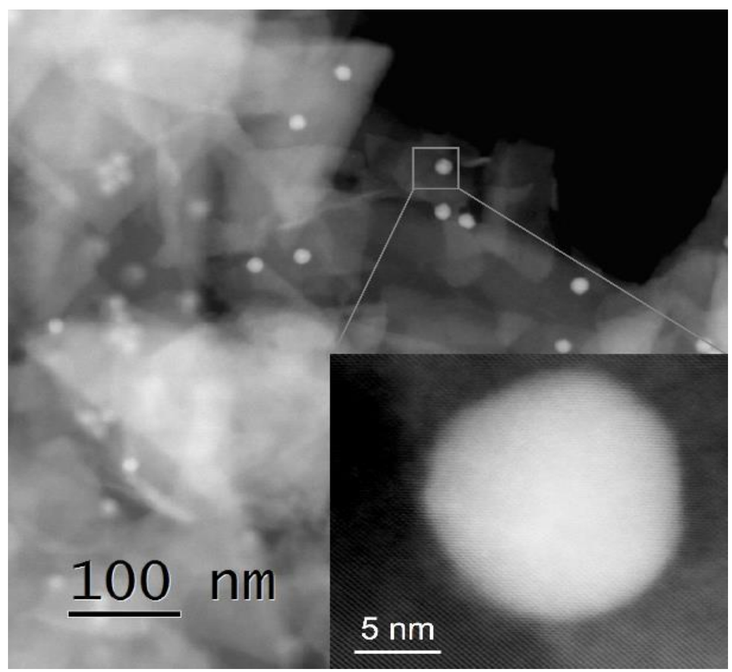
IMMOBILIZATION OF METAL NANOPARTICLES ON BLACK PHOSPHORUS



Ag NPs on BP
(*ACS Catal*. 2016, *6*, 8009−8020)

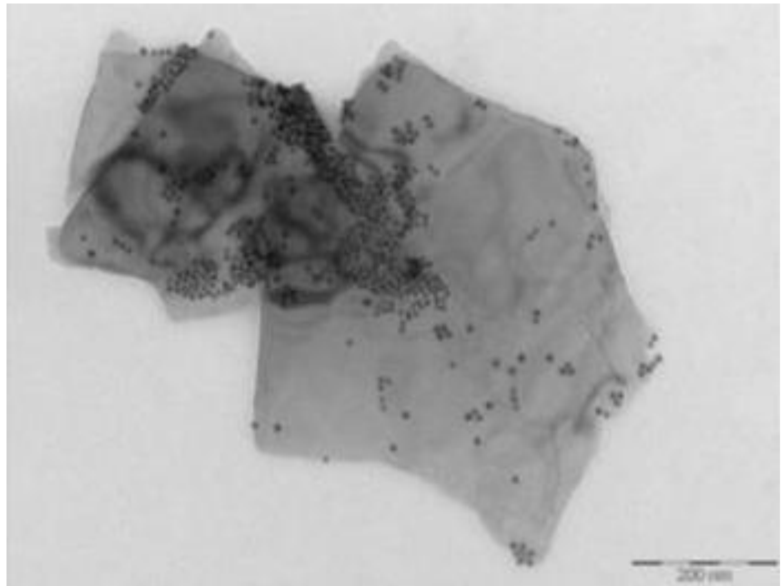


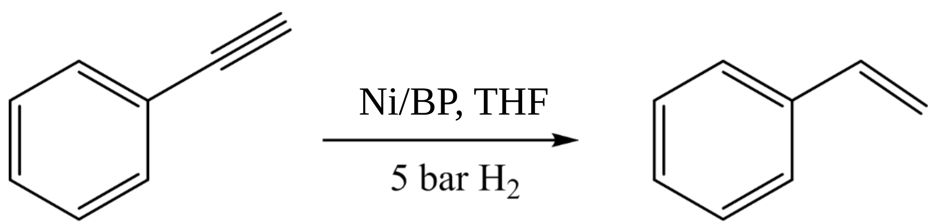
Au NPs on BP
(*Chem.Mater.* 2017, *29*, 7197−7205)



Ni NPs on BP
(*Chem. Commun.* 2017,53, 10946-10949)

METAL NANOPARTICLES ON BLACK PHOSPHORUS: CATALYSIS

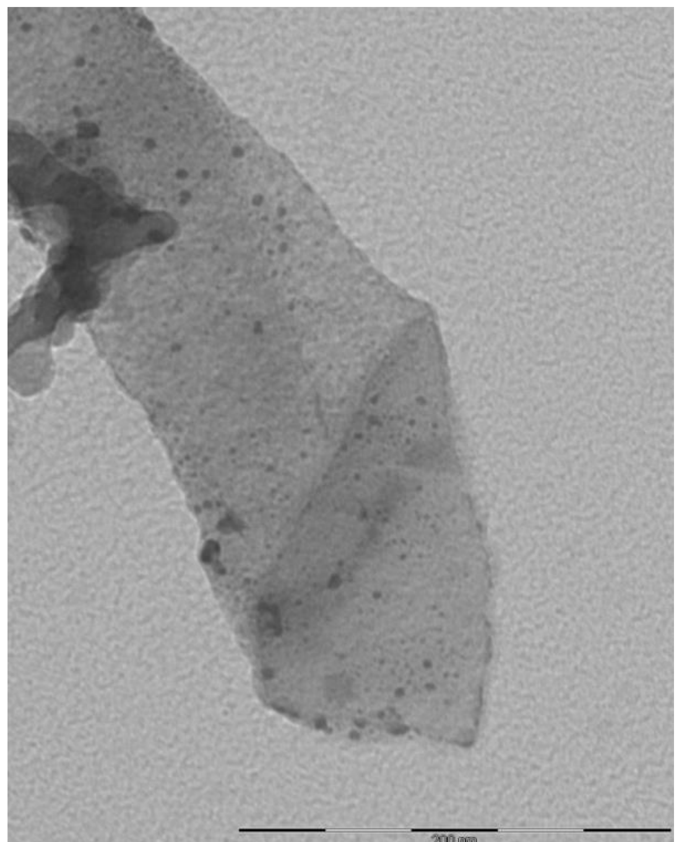




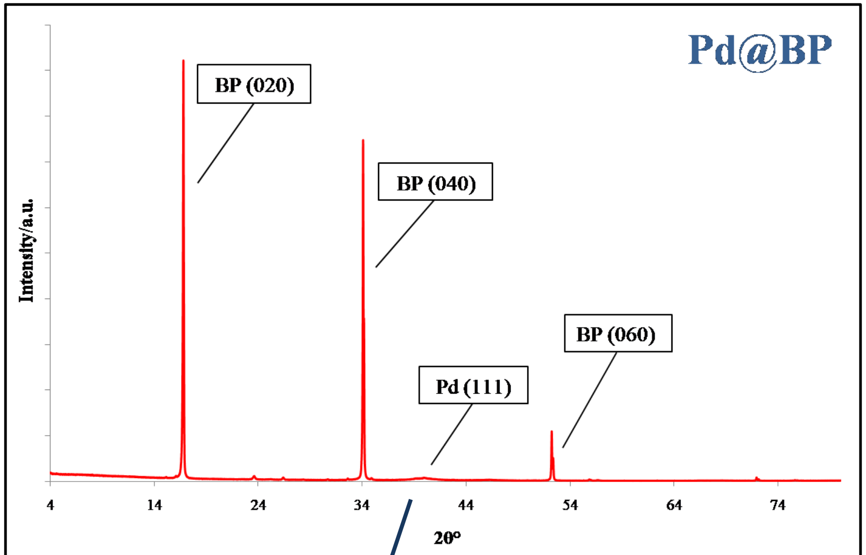
M. Caporali, M. Serrano-Ruiz, F. Telesio, S. Heun, G. Nicotra, C. Spinella and M. Peruzzini, *Chem. Commun.* 2017,53, 10946-10949.

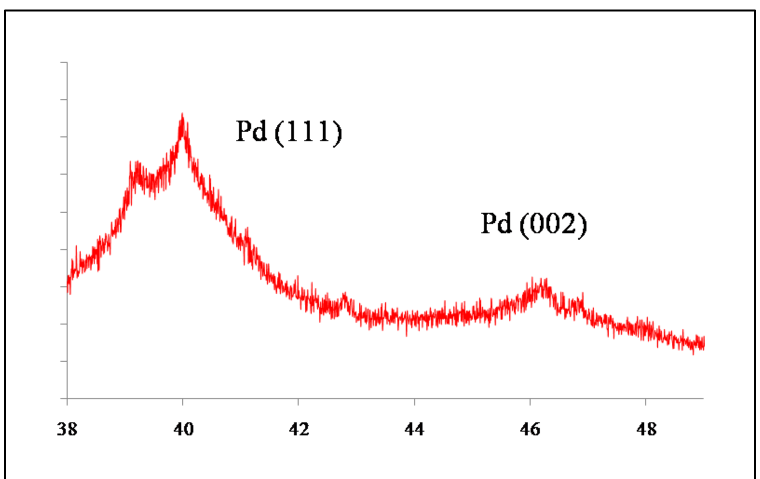
IN SITU GROWTH OF Pd NPs ON BLACK PHOSPHORUS

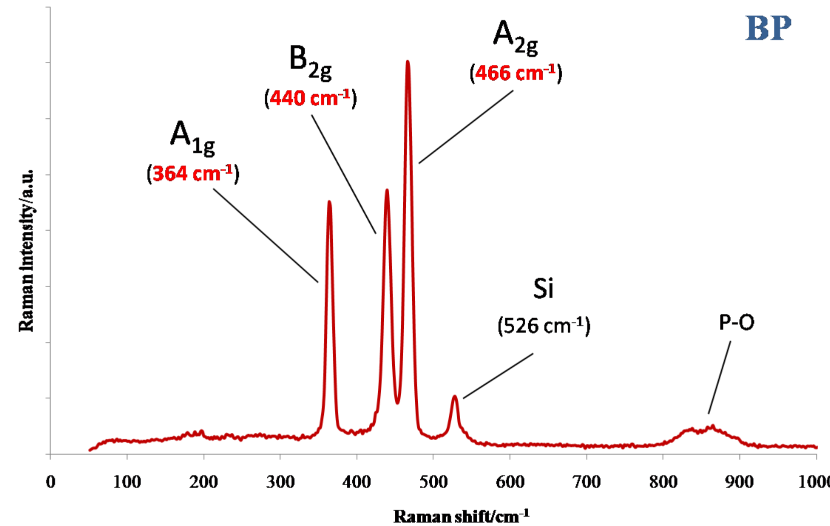
$$\underset{(10\%\ mol)}{Pd(NO_3)_2{\cdot}2H_2O} + BP \xrightarrow[5\ bar\ H_2,\ RT,\ 45']{H_2O/EtOH/THF} Pd@BP$$

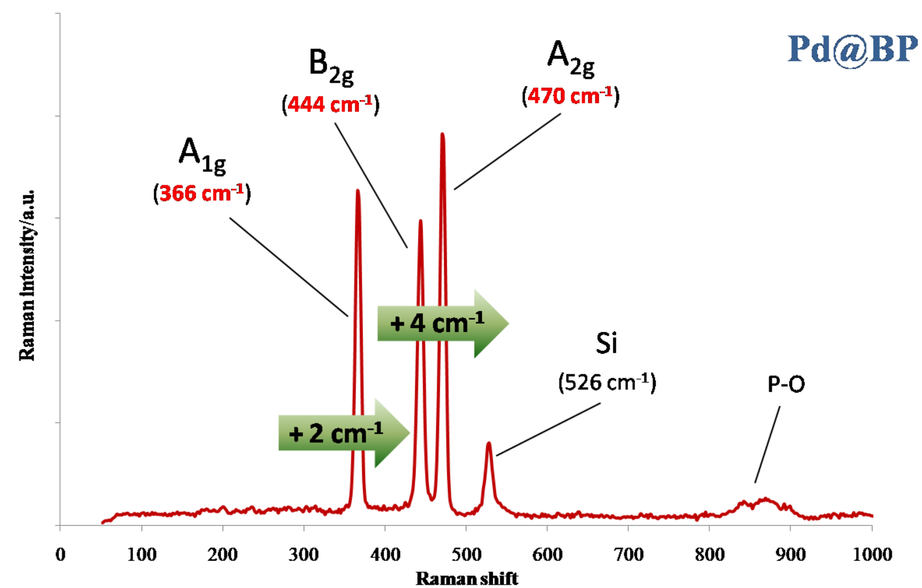


Pd@BP: SOME CHARACTERIZATION

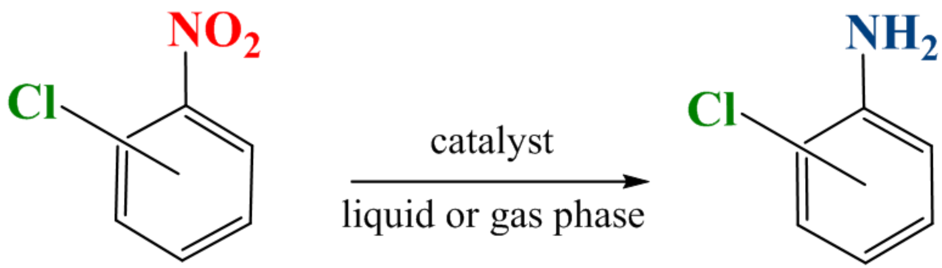


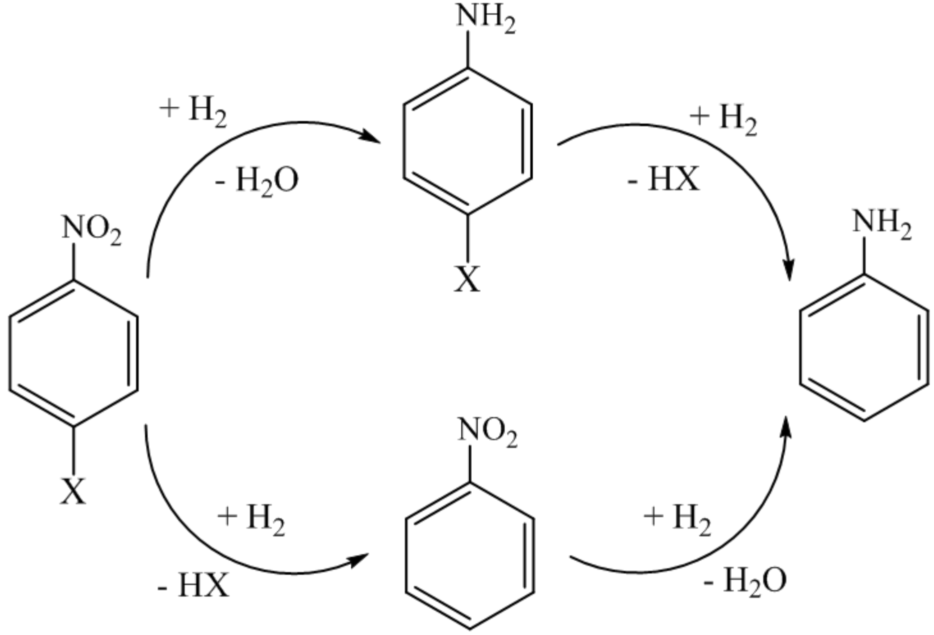






SELECTIVE HYDROGENATION OF CHLORONITROBENZENE



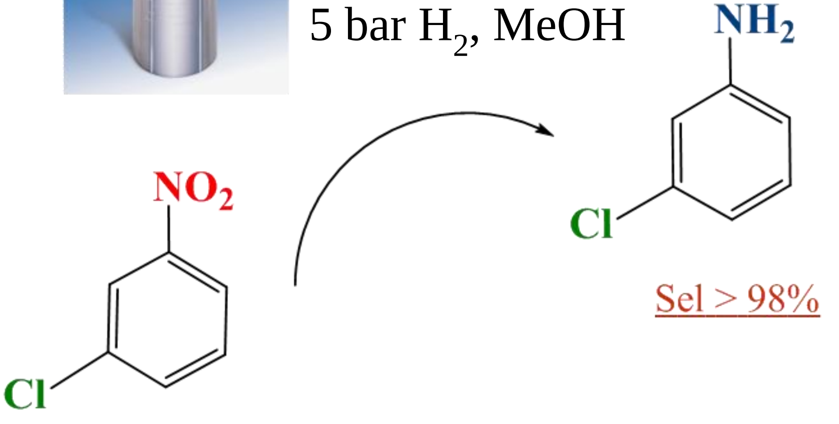


CHLORONITROBENZENE HYDROGENATION ON PALLADIUM

Substrate	Catalyst	Selectivity %	Conversion %	P_{H_2}/bar	T/°C
4-CNB[a]	Pd unsupp.	15	60	1	200*
2-CNB[b]	Pd/C	82	94	5	25
4-CNB[a]	Pd/C - II	74	20	1	200*
3-CNB[b]	Pd/C	87	96	5	25
2-CNB[c]	Pd/TiO_2	86	100	5	250*
4-CNB[d]	$Pd\text{-}PVP/Al_2O_3$	68	100	1	50
4-CNB[a]	Pd/SiO_2	0	20	1	200*
4-CNB[a]	Pd/Al_2O_3	0	40	1	200*
4-CNB[d]	$Pd\text{-}PVP\text{-}Sn^{4+}/Al_2O_3$	97	100	10	50
4-CNB[a]	Pd/ZnO	100	100	1	200*

[a]*ACS Catal.* 2013, *3*, 1386-1396. [b]*Appl. Cat. A-Gen*. 2002, *235*, 225-231. [c] *Catal. Commun*. 2007, *8*, 1999-2006. [d] *J. Mol. Cat. A-Chem.* 2006, *260*, 200-305.
*The catalytic reaction was carried out in a flow reactor

CHLORONITROBENZENE HYDROGENATION WITH Pd@BP



Substrate	n_{SUB}/n_{CAT}	Selectivity %	Conversion %	P_{H_2}/bar	Time/h	T/°C
2-CNB	200	95	100	5	1	25
3-CNB	200	>98	99	5	1	25

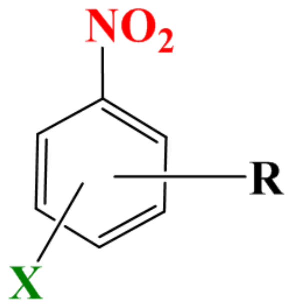
Substrate	Catalyst	Selectivity %	Conversion %	P_{H_2}/bar	T/°C
4-CNB[a]	Pd unsupp.	15	60	1	200*
2-CNB[b]	Pd/C	82	94	5	25
4-CNB[a]	Pd/C - II	74	20	1	200*
3-CNB[b]	Pd/C	87	96	5	25
2-CNB[c]	Pd/TiO_2	86	100	5	250*
4-CNB[d]	Pd-PVP/Al_2O_3	68	100	1	50
4-CNB[a]	Pd/SiO_2	0	20	1	200*
4-CNB[a]	Pd/Al_2O_3	0	40	1	200*
4-CNB[d]	Pd-PVP-Sn^{4+}/Al_2O_3	97	100	10	50
4-CNB[a]	Pd/ZnO	100	100	1	200*
2-CNB	Pd@BP	95	100	5	25
3-CNB	Pd@BP	>98	99	5	25

OUTLOOKS

IMPROVE

a) THE PREPARATION OF THE CATALYST
b) THE CHARACTERIZATION OF THE CATALYST: **XPS, SS-NMR, XAS**

EXTEND THE SCOPE OF THE REACTION



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- Manuel Serrano Ruiz

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-Stefan Heun
- Francesca Telesio

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