Palladium Nanoparticles Immobilized on Exfoliated Black Phosphorus

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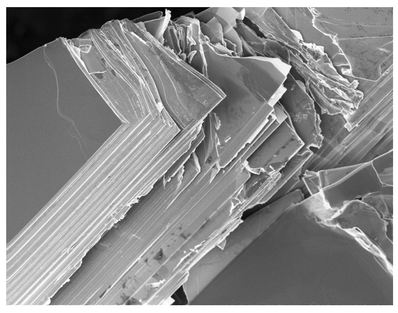
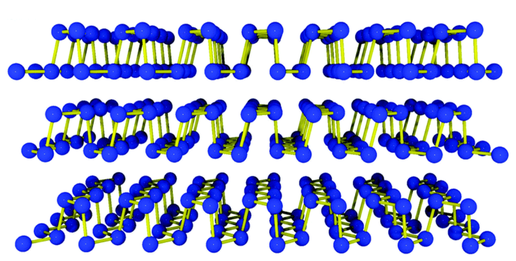
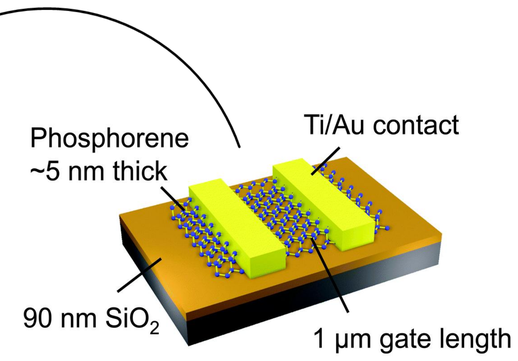
One of the latest member to join the family of 2D materials is few layer black phosphorus. Black phosphorus (BP) is a natural semiconductor which exhibits band gap tunability upon variation of the layer thickness (from 0.3 eV of the bulk BP to 1.8 eV of the monolayer *phosphorene*) and a strong anisotropy in both its electric and mechanical properties along different directions in the layer. A surface made of sp^3 hybridized phosphorus atoms seems excellent as a support to anchor metal nanoparticles. We thus decorated 2D BP with Pd nanoparticles grown *in situ* and tested the resulting nanohybrid Pd/BP in the catalytic reduction of nitroarenes. The effect of 2D BP is a dramatic enhancement of the selectivity.



SEM of black phosphorus

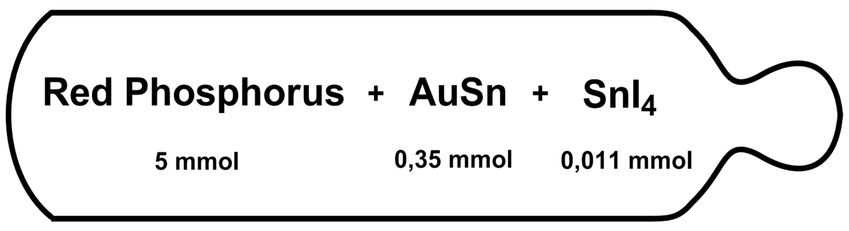


Black phosphorus structure

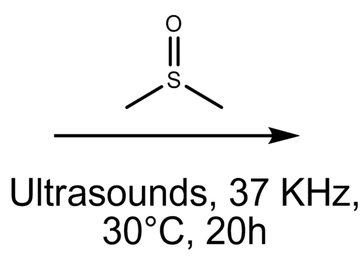


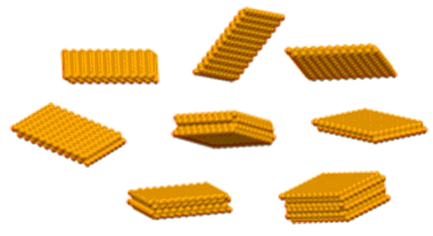
Black phosphorus based FET

Black Phosphorus: Synthesis and Exfoliation



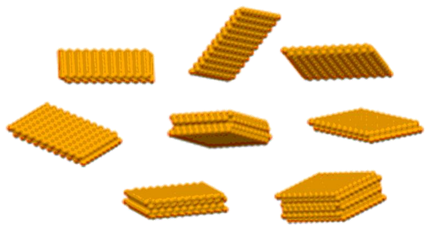
Black phosphorus crystals



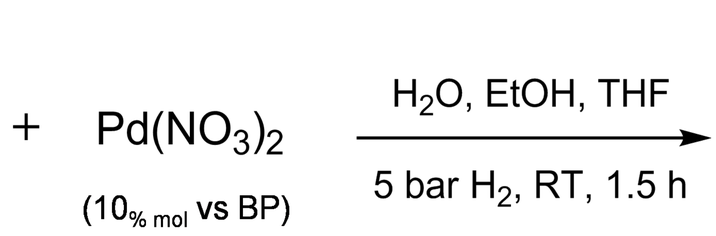


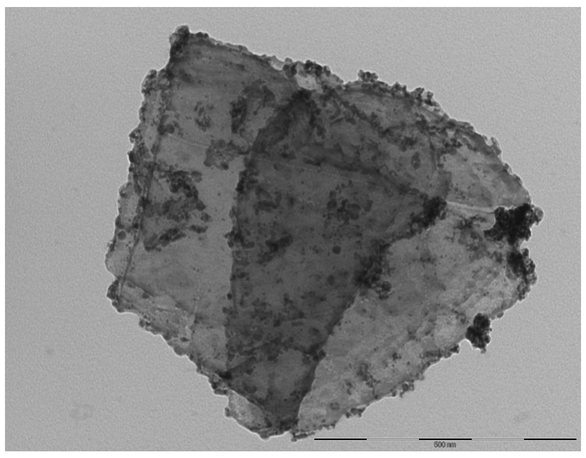
Exfoliated black phosphorus

Palladium Nanoparticles Growth on 2D BP

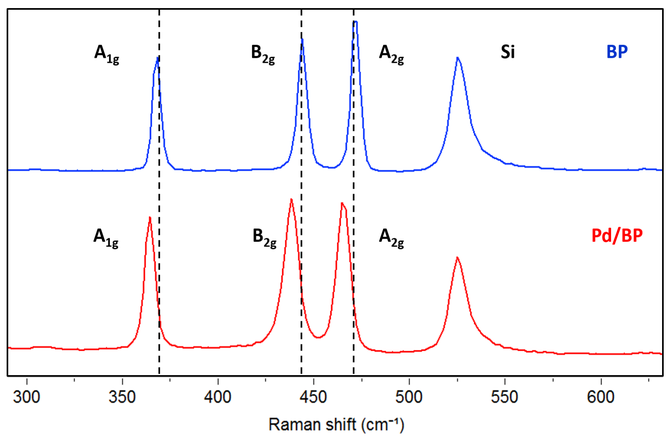


Exfoliated black phosphorus

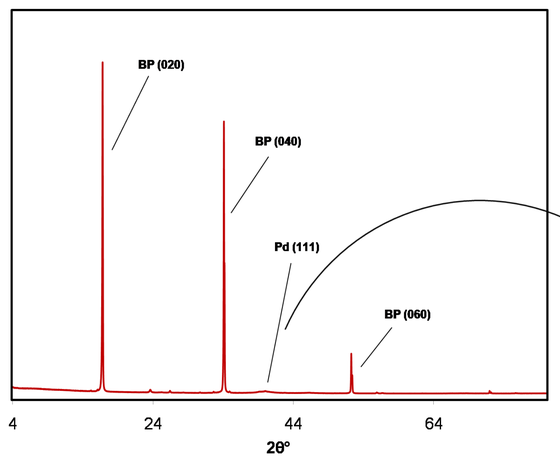




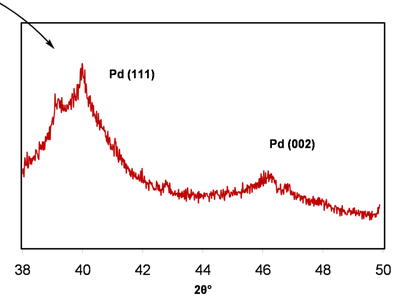
TEM image of Pd NPs on BP

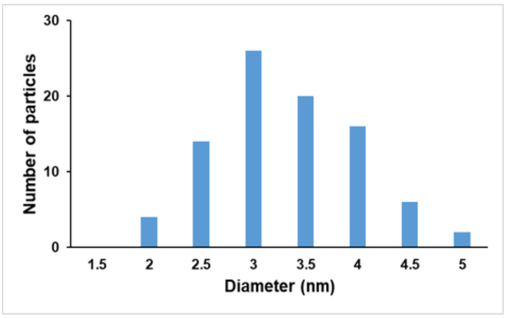


Raman spectra of pristine BP (up) and Pd/BP (down)

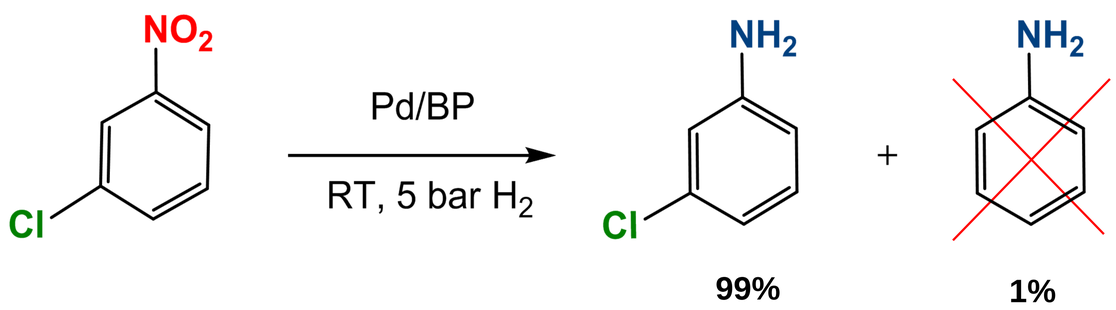


Powder XRD spectrum of Pd/BP





Selective reduction of nitroarenes with Pd/BP



Substrate	S/C	Time (h)	Conversion %	Selectivity %
1-chloro-3-nitrobenzene	200	1	98	**99**
1-chloro-2-nitrobenzene	300	1	100	**95**
4-nitrobenzaldehyde	200	1.5	99.5	**100**
1-fluoro-3-nitrobenzene	100	2	100	**100**

Only minor amounts (1%-5%) of dehalogenation byproducts were detected by GC-MS using Pd/BP. Repeating the catalyst preparation using Ketjen black as support, the selectivity drops dramatically to 72%.

Catalyst	Substrate	S/C	Time (min)	Conversion %	Selectivity %
Pd/BP	1-chloro-2-nitrobenzene	300	60	100	95
Pd/C	1-chloro-2-nitrobenzene	300	40	86	72

Acknowledgements

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