Consiglio Nazionale delle Ricerche - Istituto di Chimica dei Composti Organometallici

Palladium/black phosphorus nanohybrid: what surface techniques tell us about the Pd-P interaction

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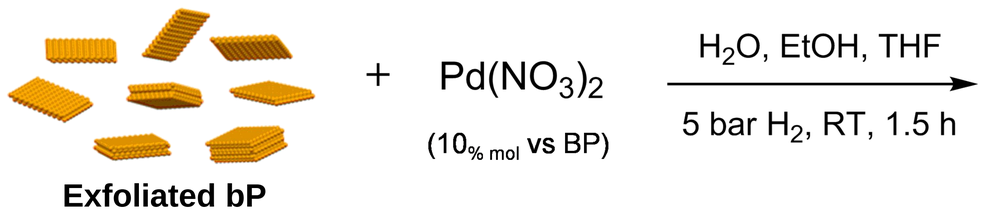
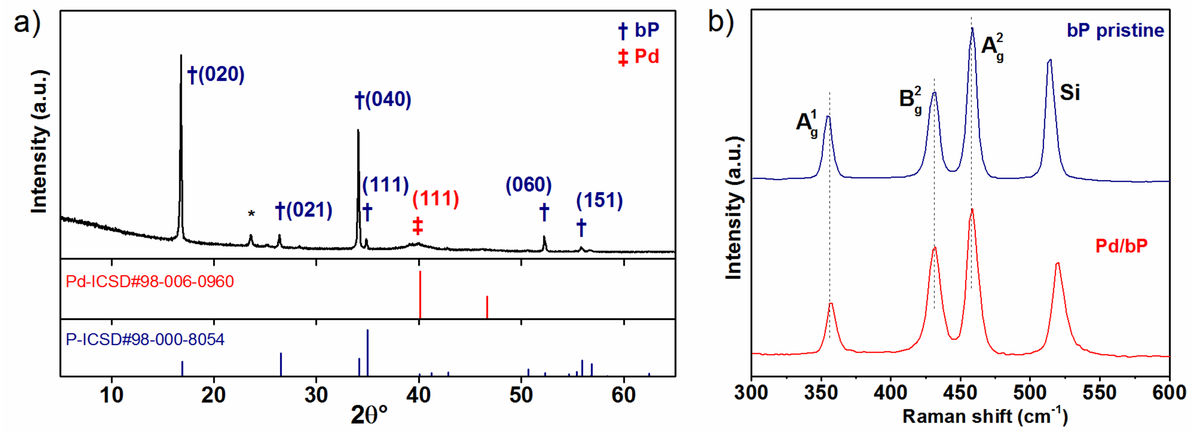
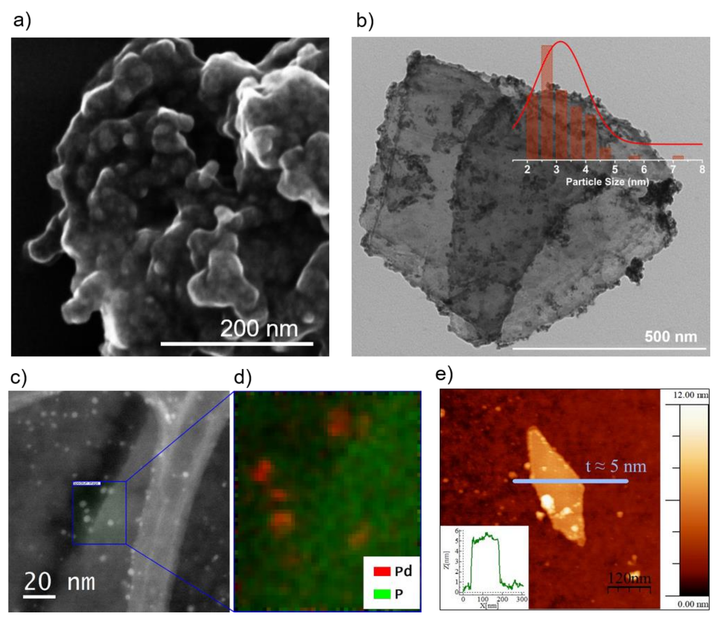
Black phosphorus has drawn major excitement to the 2D-materials community since its first appearance in 2014. Despite its structural resemblance to graphene, each atom in black phosphorus is sp^3 hybridized, bearing a lone pair which may be exploited to achieve the functionalization of its surface. A major problem dealing with surfaces and solid state materials is the elucidation of interactions and structures at a nanometric scale, as common molecular characterization methods are not applicable with these materials. We show here how surface techniques can successfully tackle the problem and tell us a lot about the bonding properties between black phosphorus and palladium nanoparticles.



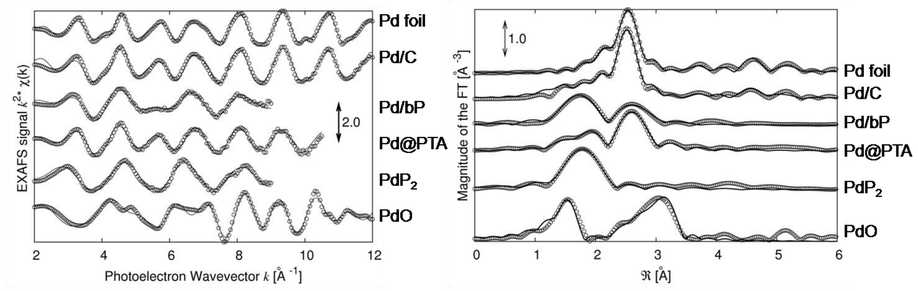


a) XRD spectrum of Pd/bP b) Raman spectrum of pristine bP (blue) and Pd/bP (red).



a) SEM image of Pd/bP. b) TEM image of Pd/bP c) High resolution HAADF STEM image of Pd/bP on a lacey carbon grid. (d) EDS elemental mapping of the selected area on Pd/bP. e) AFM image of a Pd/bP flake on Si/SiO_2. The line corresponds to the cross-sectional profile shown as an inset.

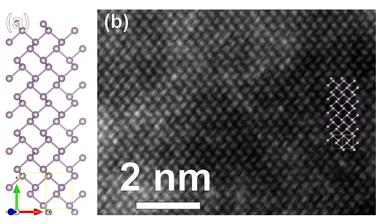
EXAFS



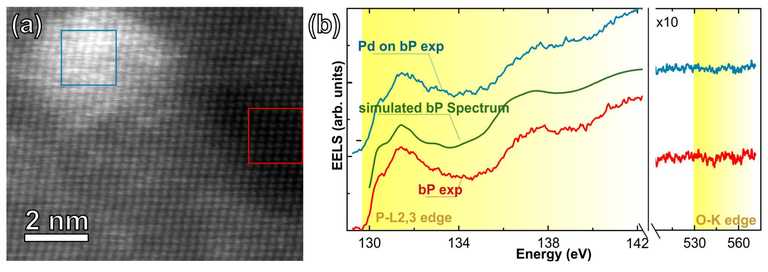
a) EXAFS data at the Pd-K edge; b) the corresponding Fourier transforms.

EXAFS measurements carried out on Pd/bP and on reference materials evidenced the clear presence of a Pd-P bond at a distance of 2.26(3) Å.

HRTEM-EELS



HAADF-STEM-SI of Pd/bP acquired along the [101] zone axis.



A difference in the P_L-edge around 138 eV in Pd/bP compared to pristine bP reveals a modification in the electronic structure of bP after functionalization with Pd nanoparticles.

Acknowledgements

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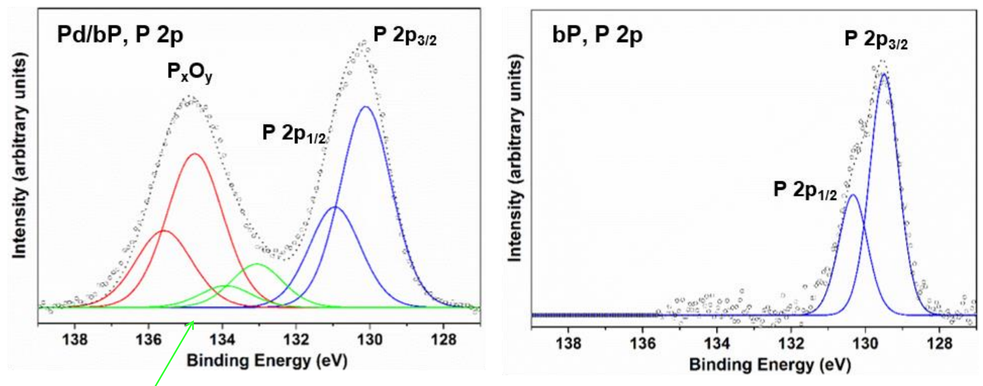
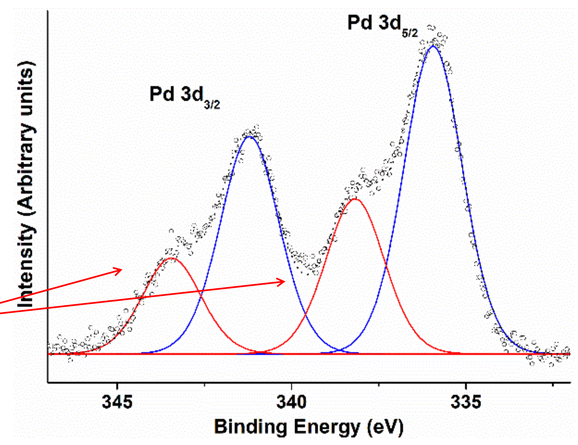
XPS

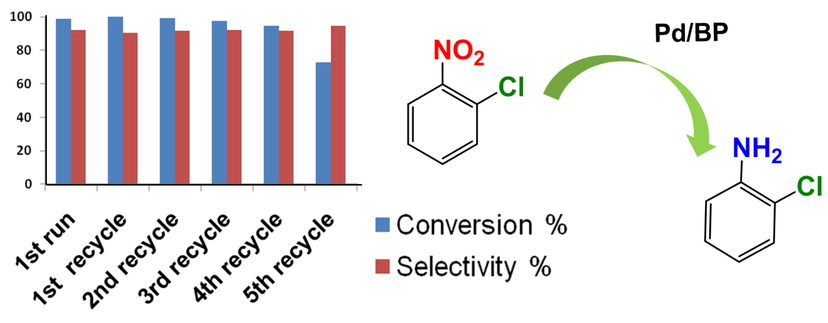


The green peaks correspond to P atoms bound to palladium.

The red doublet at 338.1 eV and 343.5 eV accounts for electrodepleted Pd atoms bound to phosphorus.



o-chloronitrobenzene hydrogenation



Conditions
solvent = MeOH,
[substrate] = 0.242 M,
RT, 5 bar H_2

Catalyst	Substrate	Time (min)	Sub/ Cat	Conversion%	Selectivity%	TOF (h^{-1})
Pd/bP	1-chloro-3-nitrobenzene	30	162	99.1	97.7	313
	1-chloro-2-nitrobenzene	40	162	99.5	97.3	235
Pd/C	1-chloro-2-nitrobenzene	30	191	99.9	78.1	298