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Invited talk

Synthesis, reactivity and catalytic applications of exfoliated black phosphorus

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The chemical functionalization of 2D exfoliated black phosphorus (2D BP) is still attracting great research interest, although a satisfactory structural characterization of the functionalized material is seldom achieved. In our laboratory, we have demonstrated that high quality of phosphorene flakes [1] may be easily decorated with nickel nanoparticles forming nanohybrid Ni/2DBP species showing higher stability with respect to pristine BP [2]. These nanocompounds have been used as catalysts in the selective hydrogenation of phenylacetylene showing high conversion and selectivity towards styrene. These features were preserved after recycling tests revealing the high stability of the nanohybrid. More intriguingly, 2D bP was used as a support for homogeneously dispersed palladium nanoparticles directly grown by a wet chemical process. EEELS-STEM (electron energy loss spectroscopy-scanning transmission electron microscopy) analysis evidences a strong interaction between palladium and P atoms of the bP nanosheets [3]. A quantitative evaluation of this interaction comes from XAS measurements that pointed out a very short Pd–P distance of 2.26 Å, proving for the first time the existence of a previously undocumented Pd–P coordination bond of a covalent nature. The average Pd–P coordination number of about 1.7 revealed that bP acts as a sort of polydentate phosphine ligand toward the surface of the Pd atoms of the nanoparticles, thus preventing their agglomeration and inferring with structural stability. These unique properties result in a very good performance in the catalytic hydrogenation of chloronitroarenes to chloroanilines, with higher chemoselectivity in comparison to other heterogeneous catalysts based on palladium.
Finally, we have demonstrated the first complete structural characterization of 2D BP functionalized with rare discrete Pd_2 units, obtained through mild decomposition of the organometallic dimeric precursor $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ in the presence of exfoliated BP [4]. A multitechnique approach, including HAADF-STEM, Solid State NMR, XPS and XAS spectroscopy, was used to study in detail the morphology of the palladated nanosheets (Pd_2/BP) and to unravel the coordination of the Pd_2 units to phosphorus atoms of 2D BP. In particular, EXAFS spectroscopy, backed up by DFT modelling, revealed the existence of unprecedented interlayer Pd–Pd units, sandwiched between stacked BP layers. Preliminary application of Pd_2/BP as catalyst for the hydrogen evolution reaction (HER) in acidic medium highlighted an activity increase due to the presence of Pd_2 units.

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References:

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