Chemistry and Catalysis Mediated by 2D Black Phosphorus Decorated with Transition Metals Species

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Among 2D-materials exfoliated black phosphorus (*i.e.* phosphorene) [1] is still attracting a great interest mostly as a consequence of its peculiar electronic and optical properties, which encompass a strong anisotropic behavior, a tunable band-gap, dependent on the thickness of the exfoliated phosphorene flake, and a high electron mobility. These intriguing properties follow from the unique corrugated two-dimensional structure of this p-type semiconducting material and have stimulated a huge amount of research mostly addressed to explore and exploit its potential applications in different areas of physics and materials sciences and technologies. [2] In contrast, much less attention has been paid to study the chemical and biologic properties of this innovative material and only recently intriguing results have appeared also in these areas. [3,4]
Here, we present our recent results showing that phosphorene could behave as an extended, flat, molecular platform to be used for catalytic applications. In particular, we have demonstrated that nanoparticles of different transition metals (nickel, copper, palladium, etc.) can decorate the surface of the exfoliated material imparting to phosphorene a higher chemical stability towards air oxidation and forming a sort of inert support to host catalytically active nanoclusters.[5,6] Remarkably, attempts to functionalize the surface of the few-layer exfoliated material with organopalladium precursors do not result in the formation of any organometallic derivative atop the polyphosphorus surface, but affords a very unusual nanocomposite featuring dipallada units covalently bonded amidst two contiguous layers of the exfoliated black phosphorus.[7] The seclusion of the palladium centers in this latter material, makes its catalytic activity in standard hydrogenation reactions dropping to zero, thus indirectly confirming the inaccessibility of the metal centers.

Acknowledgements

Thanks are expressed to the European Research Council (ERC) for funding the projects PHOSFUN “Phosphorene functionalization: a new platform for advanced multifunctional materials” (670173) through an ERC Advanced Grant to MP as PI and PHOSMED “Exfoliated black phosphorus for biomedical applications” (963933) through an ERC POC to MP as PI.
The authors also acknowledge the MAECI Italy−China bilateral project “Graphene related Innovative 2D Materials for Sustainable ENerGetIcs and catalysis (Ginseng PGR00953)

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