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## ABSTRACT:

### 2D Phosphorus on Metals: Growth, Reconstructions and Applications

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After the discovery of graphene, a large number of two-dimensional (2D) materials have been theoretically predicted and experimentally realized. Among them, single-layer Phosphorene—the monolayer form of black phosphorus—has emerged as a particularly promising 2D semiconductor. In addition to layered allotropes, phosphorus can also form ordered reconstructions on metal surfaces, providing structurally well-defined interfaces with properties of potential interest for application in many fields. Here we demonstrate that red phosphorus, a far more accessible and inexpensive precursor than Black phosphorus, produces the same surface structures on metal substrates, offering a practical route for the preparation of phosphorus-based surface phases [1]. On Cu(110) and Cu(111), the resulting phosphorus layers can act as an effective buffer layer, suppressing the electronic interaction between the metallic substrate and adsorbed organic molecules. To investigate this decoupling effect, we studied monolayer films of Zinc Tetraphenylporphyrin (ZnTPP) on Cu(110), both in the presence and absence of a phosphorus buffer layer, using X-ray Photoemission Spectroscopy (XPS) and Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS). Our results show that the formation of phosphorus nanostripes on Cu(110) effectively suppresses charge transfer between the metal surface and the molecular overlayer. We further extend the investigation to Cobalt Tetraphenylporphyrin (CoTPP) and ZnTPP on Cu(111) in the presence of a Blue phosphorus layer, confirming its ability to electronically decouple the molecular films from the substrate. The spectroscopic results are supported by complementary Density Functional Theory (DFT) calculations and Scanning Tunneling Microscopy (STM) measurements, which consistently demonstrate the effectiveness of phosphorus as a decoupling interlayer. By mitigating substrate–molecule electronic hybridization, phosphorus layers preserve the intrinsic electronic structure of organic molecular films deposited on metals. Finally, we present preliminary results on the growth of phosphorus on Pt(111), which emerges as a particularly promising platform for further suppressing substrate–organic interactions. These systems—and phosphorus films more broadly—represent a highly promising platform for engineering 2D interfaces with tailored structural and electronic properties, opening new opportunities for the design of functional hybrid nanostructures.

[1] A. Sala et al., *Nanoscale*, 2022, 14, 16256 - DOI 10.1039/d2nr02657k; Simone Del Puppo et al., *Nanoscale Advances*, 2024, 6(14), pp. 3582–3589 DOI: 10.1039/D4NA00192C