Surface properties and doping of few layer black phosphorus

A broad range of surface science techniques and ab initio simulations are employed to investigate and optimize the properties of exfoliated black phosphorus (bP). The treatment with Ni nanoparticles (NPs) allows to greatly improve the stability of few-layer bP flakes in ambient conditions. Copper deposition is demonstrated to induce charge transfer n-type doping of bP flakes. Exploiting the potential of a local surface investigation by scanning tunneling spectroscopy (STS), intriguing phenomena such as Coulomb blockade, and short-range doping are unveiled.

Among 2D materials, exfoliated black phosphorus (bP) has recently emerged because of its outstanding properties, i.e., modulation of the direct band gap, in-plane anisotropy, high charge-carrier mobility at room temperature, thus having a broad prospect for applications in electronic devices [1,2] and in energy storage. However, it shows higher chemical reactivity in comparison to other 2D materials, implying a lower stability. Moreover, the high concentration of P vacancies makes bP an intrinsically p-type material.

We here report on a relevant enhancement of ambient stability in bP when decorated with Ni NPs [3]. A combined characterization with TEM, Raman and x-ray spectroscopies provides quantitative insight of the oxidation process taking place at the bP surface with and without Ni NPs (work performed in collaboration with Cnr Iccom).

Furthermore, we explore surface charge transfer n-type doping of bP flakes by copper using Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) at room temperature [4], see Fig. 1 a-c. STS reveals a gap opening at Cu islands, tentatively attributed to Coulomb blockade phenomena. Moreover, while n-type doping of bP by Cu is effectively demonstrated, line spectroscopy shows that it is very short-ranged, as shown in Fig. 1d. First-principles simulations give an atomistic understanding of these experimental evidences, allowing us to quantify the role of cluster size for an effective n-type doping of bP and showing that an electronic decoupling of the topmost bP layer from the underlying layers takes place in presence of the Cu cluster (Fig. 1e), consistent with the Coulomb blockade interpretation. Our results provide new routes to reach an ambient stability of bP and a novel microscopic understanding—difficult to retrieve by transport measurements—of the Cu doping of bP, which appears promising for the implementation of bP-based electronic applications.

The work on Cu doping of bP has been carried out within the project SURPHOS – Surface properties of few layer black phosphorus investigated by scanning tunneling microscopy (Cnr Nano SEED collaborative project).

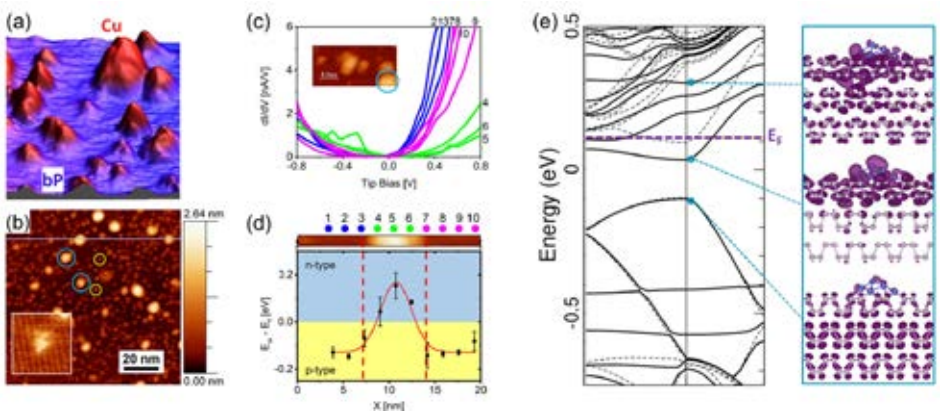

Fig. 1
(a,b) STM images of Cu islands on bP. (c) STS line spectroscopy across one island (blue circle in the inset). Numbers correspond to colored dots in panel d. (d) Midgap value of each spectrum with respect to the Fermi level, plotted as a function of lateral position. The plot field is colored with yellow and blue to indicate p-type and n-type doping regions, respectively. (e) Band structure of adsorbed Cu_n on 3-layer bP (solid line) as compared to pristine bP (dashed line), together with a few relevant Kohn–Sham squared wave functions showing the localization to the topmost bP layer of the states close to the Fermi level (EF).

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