SCIENTIFIC REPORT OF THE RESULTS OBTAINED DURING THE SHORT TERM MOBILITY AT NORTHWESTERN UNIVERSITY

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ATOMIC AND GROUP TRANSFER REACTIONS ON EXFOLIATED BLACK PHOSPHORUS

The exfoliation of the graphite in 2004[1] provided the monolayer, called graphene, opening a new branch of material chemistry, called 2D material chemistry. Starting from graphene, *ca.* 15 new 2D materials[2] have been discovered and, among them, phosphorene, the mono layer of the black phosphorus(BP),[3] is certainly one of the most appealing. In the last years, the attention toward the BP and phosphorene constantly grew up in view of the presence of an inner bandgap associated to the exfoliated material, easily to be tuned, varying the number of the stacked sheets.[4] Conversely the exfoliated BP suffers of a limited stability toward air and moisture, thus, a pre-treatment of the material is necessary before its employment for nanoelectronics applications.
The exfoliated black phosphorus shows on its surface a large number of lone pairs, which are in principle, able to interact with transition metals or molecular fragments. On these basis, in the last years efforts have been devoted towards the functionalization of the material to provide more stability and new target properties. Although some examples of the non-covalent functionalization are already reported in the literature,[5] at the best of our knowledge, the only experimental available covalent functionalization of the exfoliated black phosphorus surface is the one reported by Prof. Tobin Marks at the Northwestern University (NU) in Evanston (Chicago), USA.[6] Thus, the basic idea of my Short Term Mobility visit at NU is to share my computational know-how on the phosphorene chemistry, acquired within the European Research Council Project PHOSFUN, with the expertise at NU in synthetic chemistry on exfoliated black phosphorus. In the last years in Florence, I was involved in the computational investigation on the possible insertion onto the material surface of transition metal groups. Another important research area, related to the ERC Project PHOSFUN, is the possible transfer of single atoms to the phosphorene surface, such as oxygen and sulphur, or small molecular group, such as NR. In the following sections, I will describe the obtained results at NU for the oxygen, sulphur and some preliminary hints on the feasibility of the organic azides activation.

The visit starts with a deep discussion and ideas exchange on the methods used at NU to functionalized phosphorene surface with diazonium salt and the precedent work, done in Florence, on the functionalization of phosphorene with transition metal fragments. In this regards, I have been invited to illustrate the obtained results on metal functionalization in a group meeting of Prof. Tobin Marks and Professor Hersam's groups, the corresponding authors of the first mentioned covalent phosphorene functionalization example.
After the seminary, we set up the action, by choosing the suitable atom and small group sources and we started with the investigation of oxygen insertion on the material surface. The dimethyl sulfoxide has been chosen as oxygen atom source, since it releases in solution a dimethyl sulfide molecule after the oxygen atom transfer. For all the calculations, a bottom-up approach was used, starting from simplified models containing up to 40 atoms, and, the obtained results have been later validated by *ad-hoc* solid state calculations with different O/P ratios, starting with a 1:8 O/P ratio, within CRYSTAL package.[7] At the beginnings, two different conformations for the doping material with oxygen are possible: the former with terminal oxygen bonded to a phosphorus atom and the latter with a bridging oxygen between two centres. The computational investigation revealed that at the very beginning the most stable conformation is the one shows oxygen atoms bonded terminally to the phosphorus atoms, shown in Figure 1, and the energy difference between the two conformation is more than 30 kcal mol^{-1}.

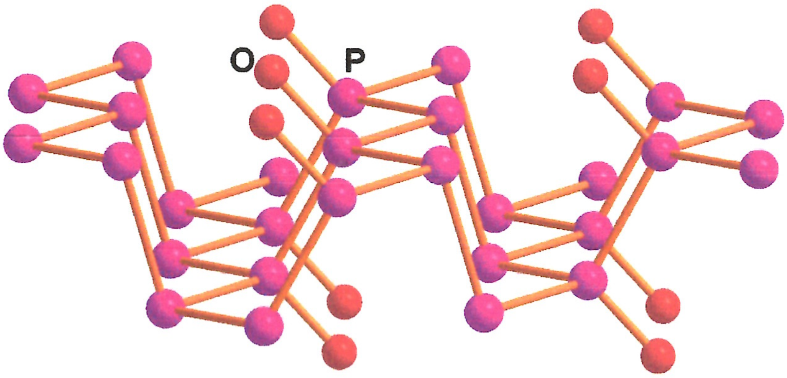

Figure 1. Optimized structure of phosphorene sheet with bonded terminal oxygen atoms.

The simplified models revealed the feasibility of the atom transfer with energy barriers less than 23 kcal mol^{-1}, which are overcompensated by the release of the dimethyl sulfide molecule, being the energy gain *quasi* double than the energy barrier.

The resulted structure does not show any substantial changes compared to the naked monolayer of phosphorene. In order, to better understand the process, we have increased the O/P ratio and we obtained that once obtained adjacent oxidized phosphorus atoms the most favoured conformation shows a third oxygen atom bridging the two terminal PO moieties. This can be seen as the initial step of the phosphorene degradation, toward the formation of tri- or tetra-metaphosphate, suggesting the requirement of strict controlled conditions for the doping of the material.

Similar results were expected also for the introduction of sulphur atoms on the phosphorene surface, although the computational investigation revealed that for the sulphur case only the terminal conformation is possible, without any P-P cleavage associated with the bridging disposition, as shown in Figure 2. As sulphur source we chose for simplicity $SPCl_3$, which releases the PCl_3 moiety, although also the employment of elemental sulphur S_8, as precursor, is still under investigation. Also in this case, the atom transfer seems to be favoured with not so high energy barriers to be overcome.

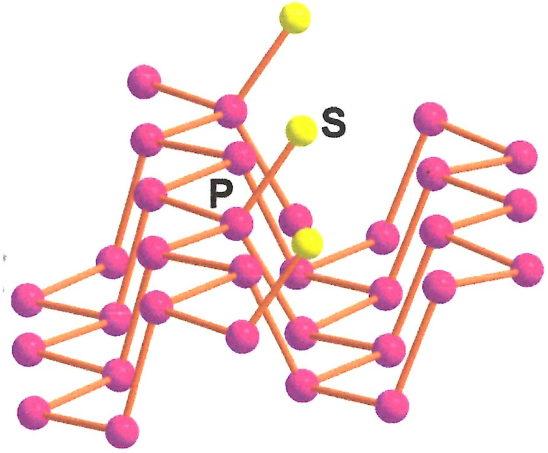

Figure 2. Optimized structure with terminal sulphur atoms.

Other computational tests have been performed to test the feasibility of the activation of organic azides on the phosphorene surface as occurred on the traditional phosphine ligands in the Staudinger reaction, with the dismissal of diatomic nitrogen molecule. This reaction may be considered as correlated to the activation of diazonium salt carried out by Prof. Marks's group.

The preliminary results, obtained at NU during the Short Term visit and carried out on simplified models, seem to suggest the feasibility of the reaction.

The doping of the material with these new moieties not only may increase the stability of the overall system but also may contribute to enhance the not covalent absorption of molecules with interesting electronic properties such as fluorescence. In this regards, also weak interaction between the functionalized material and the absorbed molecules may infer some interesting properties to the overall material.

All these computational results have to be experimentally confirmed and, for these reasons, some *ad-hoc* tests have been already carried out and other are still in progress in order to have strong confirmations of the reactions on the exfoliated BP surface. In particular, it is particular interesting to investigate through a combined experimental/computational approach how the thickness of the material can favour or not the reactivity. This short Term Visit will be the first step in the ongoing collaboration between the CNR-ICCOM of Florence and the group in the Northwestern University of Prof. Marks.

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