Spectroscopy on Black Phosphorus exfoliated down to the monolayer

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Authors: Etienne Gaufrès (1, 2), Alexandre Favron (2), Frédéric Fossard (1), Pierre Lévesque (2), Anne-Laurence Phaneuf-L'Heureux (3), Sébastien Francoeur (3), Richard Martel (2), Annick Loiseau (1)

1. Laboratoire d'Etude des Microstructures, CNRS - ONERA, Chatillon, FRANCE
2. RQMP, Université de Montréal, Montréal, CANADA
3. RQMP, Ecole Polytechnique de Montréal, Montréal, CANADA

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Corresponding email: frederic.fossard@onera.fr
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Black Phosphorus (P(black)) is a 2D semiconductor characterized by a direct band gap associated to high carriers mobility. The crystal is composed by tetravalent P atoms stacked by weak van der Waals interactions that can be exfoliated down to the monolayer using similar procedures than for graphene. Studying pristine thin layers of P(black) is however challenging due to its strong degradation upon exposure to visible light in air.

In this study, we have investigated the chemistry of degradation using *in-situ* Raman spectroscopy, Transmission Electron Microscopy imaging and Electron Energy core-Loss spectroscopy (EELS) of mechanically exfoliated layers prepared in their pristine state in a glove box. The results highlight a thickness dependent photo-assisted oxidation reaction by adsorbed oxygen in water [1]. Using EELS, we have inspected the O K-edge and P L2,3 edge which gets shifted from 130.2 eV in pristine phosphorus to 136 eV in oxidized phosphorus. As shown in Fig.1, the thickness dependence to oxidation has been clearly revealed by comparing layers of different thicknesses before and after a 30s exposure to ambient air and light. On the basis of such experiments, we have proposed an oxidation mechanism involving electron transfer processes based on quantum confinement and found appropriate manipulation procedures opening a route to first Raman measurements on 1 to 5 pristine layers of P(black)[1].

We use also low-loss-EELS spectroscopy to investigate the angular dependence in the Brillouin zone of the dielectric response of exfoliated P(black) in the range [2-40 eV], taking advantages of the TEM-STEM Libra 200 machine at LEM. This machine is equipped with an electrostatic monochromator operating at 80 kV and makes possible the investigation of the angular dependence of the dielectric function at a nm scale and with an energy resolution below 100 meV. To this aim we applied the technique developed in [2] and fully adapted to the machine. Using this technique we have studied the onset of electronic excitations and the dispersion of the plasmons as a function of the q momentum for different crystallographic in plane orientations in mechanically exfoliated P(black) down to 2-3 layers. An example of w - q mapping recorded along the [002] q-direction is displayed in Fig.2 and reveals a large dispersion of the plasmon peak occurring at 19 eV at q= 0. The quantification of this dispersion is obtained by extracting the q dependence of this plasmon peak from the map as shown in Fig.3. Q dependences along two different in plane directions of the layers, namely [200] and [002], are compared in Fig.4 and clearly reveal high anisotropy effects, which will be discussed with the help of suitable ab initio calaculations.

References:

[1] A. Favron, E. Gaufrès et al, Nature Materials, 14, (2015)
[2] P. Wachsmuth et.al., Phys.Rev.B (88), 075433 (2013)

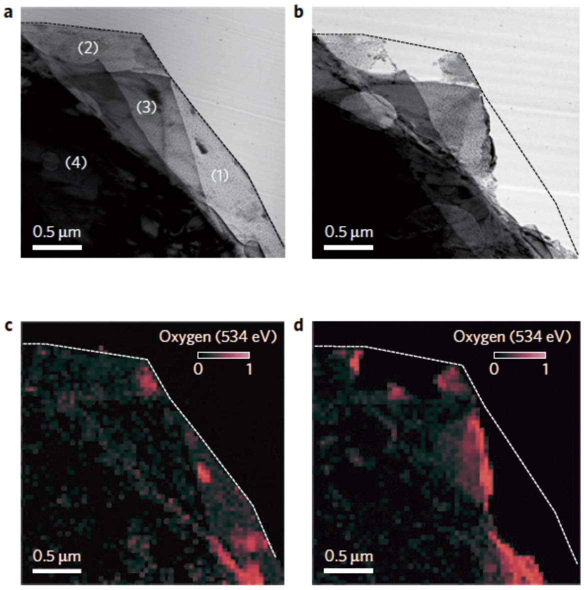

Fig1 : Evolution of the photooxidation reaction of multilayers 2D phosphane by EFTEM. The labels (1) to (4) indicate sheets of different thicknesses from 2 to 10 layers. a) Initial state. b) After an exposition to air and light of a few 10s. O K-edge maps in the initial state in c) and after oxidation in d).

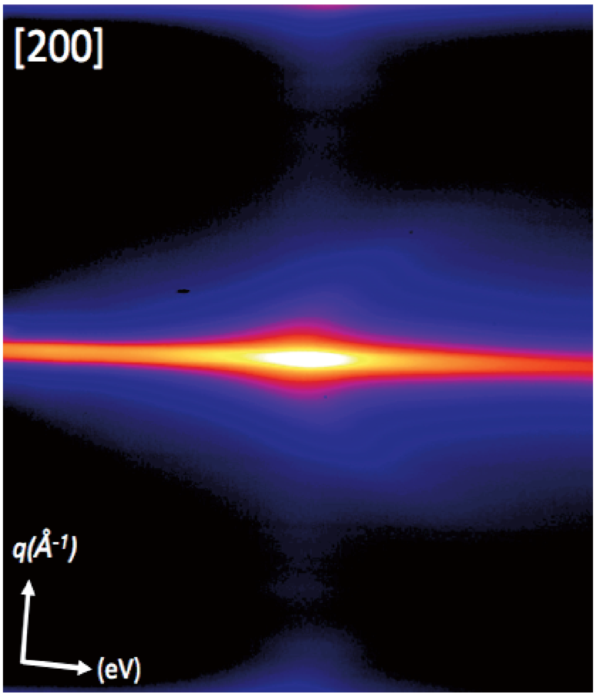

Fig 2 : ω-q map of the energy and momentum dependence along the in-plane [200] q direction of the low losses in a multilayer phosphane.

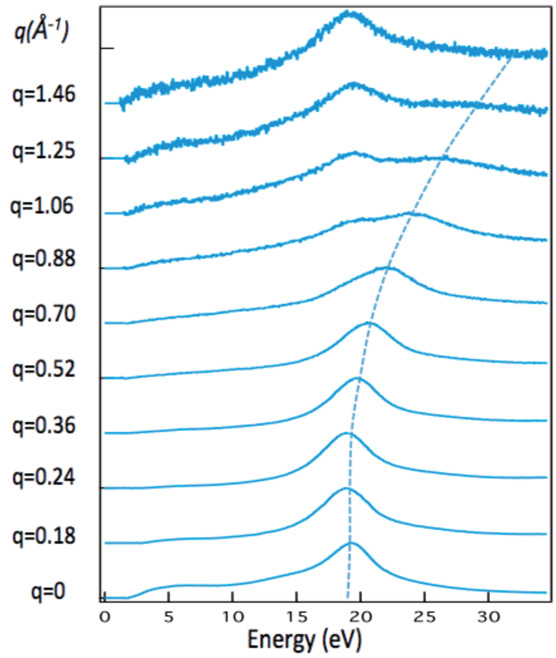

Fig 3 : Evolution of the plasmon peak position as a function of the transmitted momentum in angular resolved EELS along the plane [200] q direction.

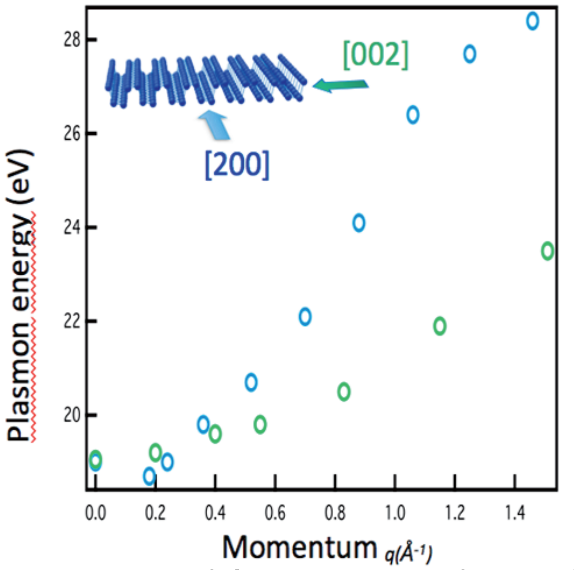

Fig 4 : Dispersion of plasmon energy as a function of the transmitted momentum for in-plane [200] and [002] crystallographic directions.