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Humidity Effects and Anisotropic Etching During Exfoliated Black Phosphorus Degradation ALEXANDRE FAVRON, PATRICIA MORAILLE, ETIENNE GAUFRES, TYCHO ROORDA, PIERRE L. LEVESQUE, RICHARD LEONELLI, RICHARD MARTEL, Universite de Montreal — Black phosphorus, a lamellar structure similar to graphene, is a high mobility semiconductor having a tunable optical band gap from 0.3 eV up to ˜2 eV with decreasing layer thickness. Our previous study has highlighted a fast photo-oxidation in ambient conditions when black phosphorus is exfoliated as thin layers. The kinetics of this degradation is also enhanced by quantum confinement effects and faster for the thinnest layers, which represents an important hurdle to prepare few layers. Here we further investigate the role of water in the process by following the reaction kinetics in different humidity using fast AFM imaging. We report on important changes of wettability of thin layers at room temperature depending on the degradation stages and layer thickness. For a given level of humidity at equilibrium, we observe the formation of water droplets. Those droplets form preferentially on defects sites and cracks and then grow on the thicker parts of the flake to finally accumulate on to the thinnest regions. This sequence of water droplet growth faster from thick to thin layers is interpreted as being due to a lowering of surface tension with decreasing layer thickness. In a second study, the oxidation kinetics of layers completely immersed in water reveal an anisotropic oxidation process with preferential etching in specific orientations of the crystal. This study will be discussed in the context of a reactivity of black phosphorus that appears both anisotropic and thickness-dependent.

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