Ab initio studies of structural, electronic, and optical properties of few-layer black phosphorus encapsulated with hexagonal boron nitride.

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Black Phosphorus (BP) is a rising star of 2D materials [1,2]. Its high hole mobility, tunable band structures, excellent mechanical properties as well as anisotropic properties, leads it to exciting prospects in device applications [1]. Despite the interesting properties, there are many technological challenges to overcome. One of the major issues hindering phosphorene application in modern day devices is its lack of stability under ambient conditions. Black phosphorus is highly reactive to combinations of oxygen, water, and light. Compatibility of black phosphorus with other 2D materials in so-called van der Waals (vdW) heterostructures [3] can offer solution for this important surface degradation problem. Recently, it has been experimentally shown, that black phosphorus encapsulated with hexagonal boron nitride (*h*-BN) becomes resistant to oxidation and exhibits excellent electrical properties [4]. However, little is known about the encapsulation impact on vibrational properties of black phosphorus.

Therefore, in this communication, we report extensive *ab initio* calculations in the framework of density functional Theory (DFT). We examine the structural and vibrational properties (Raman spectra, frequencies and Raman intensities) of few-layer BP (from two to six layers) encapsulated with *h*-BN. Our studies reveal that the structural parameters, as well as the frequency of optical phonons (A_g^1, A_g^2, B_{2g}) are layer dependent. Both non-encapsulated and encapsulated black phosphorus layers, exhibit anomalous evolution of these phonon frequencies, showing red shifted trend. In addition, encapsulation further increases this trend by about 2 cm^{-1}–5 cm^{-1}, depending on the number of black phosphorus layers and the type of the frequency modes. Very recently an elusive peak above the 4 cm^{-1} A_g^1 has been reported [5]. Our studies reveal that this peak is present about 5 cm^{-1} above the A_g^1 mode, which is in good agreement with experimental findings, and its origin can be explained following symmetry considerations. However, this peak is present in both non- and encapsulated cases, where in the latter the intensity is stronger. This and other aspects of structural and optical properties of few layer black phosphorus will be presented and coupled to experimental findings.

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