Effects of Partial Hydrogenation on the Structure and Electronic Properties of Boron Nitride Nanotubes

Supplementary Information

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Structural analysis

In Fig. 2 of the main text we have presented and discussed the structural stability analysis obtained at the HSE level of theory. Here, for completeness, we present similar results obtained using the LDA and PBE functional approximations. As can be seen in Figs. S1 and S2, similar trends are obtained using the (semi-) local functional approximations. The main difference is found in the character of the ground state of some adsorption schemes. For the LDA and PBE functionals, some of the BB and NN adsorption schemes and all of the BN adsorption schemes are of a singlet nature (for the HSE functional the BB and NN families presented exclusively a triplet ground state and the BN family showed both singlet and triplet ground states depending on the angular separation). Another difference is found in the range of calculated relative energetic stabilities where for the HSE calculations the energy differences between the most stable configuration and the highest energy configuration is of the order of 4.3-5.6 eV/unit-cell (depending on the system studied) and for the LDA and PBE it is somewhat lower (4-5 eV/unit-cell).

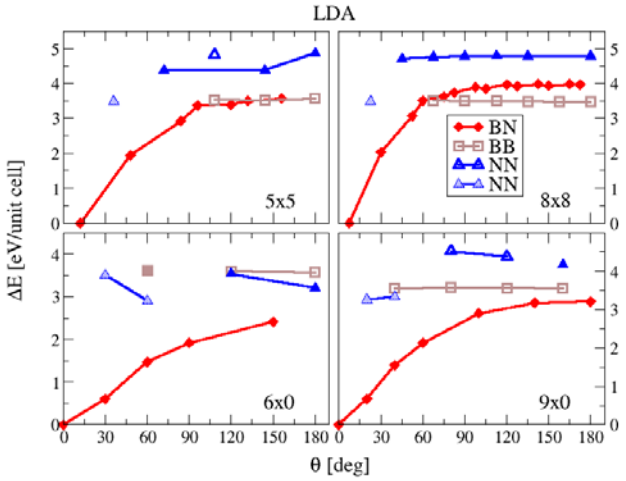

Fig. S1: Relative total energies as a function of inter-hydrogen angular separation (θ) for the (5,5) and (8,8) armchair (upper panels) and (6,0) and (9,0) zigzag (lower panels) BNNTs studied obtained at the LDA/6-31G** level of theory. The total energy of the most stable adsorption scheme of each system is used as reference. For clarity, lines connecting values that belong to the BN (red diamonds), BB (brown squares), and NN (blue triangles) adsorption families were added. Full (open) symbols designate a closed-shell singlet (open-shell triplet) ground state. Dotted triangles represent NN adsorption schemes that form buckling deformations during geometry optimization (see Fig. 5 of the main text).

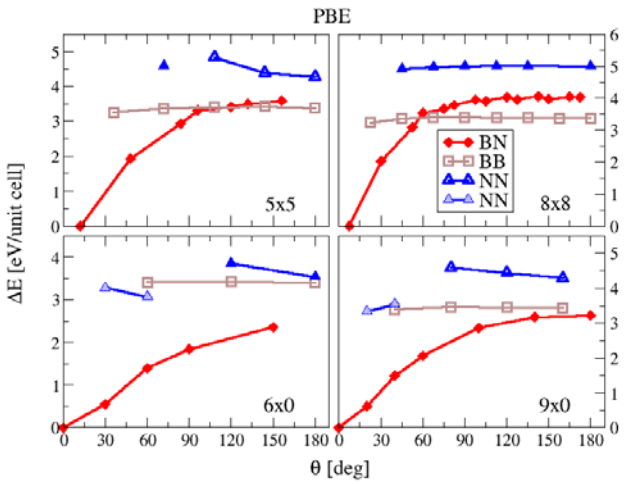

Fig. S2: Relative total energies as a function of inter-hydrogen angular separation (θ) for the (5,5) and (8,8) armchair (upper panels) and (6,0) and (9,0) zigzag (lower panels) BNNTs studied obtained at the PBE/6-31G** level of theory. The total energy of the most stable adsorption scheme of each system is used as reference. For clarity, lines connecting values that belong to the BN (red diamonds), BB (brown squares), and NN (blue triangles) adsorption families were added. Full (open) symbols designate a closed-shell singlet (open-shell triplet) ground state. Dotted triangles represent NN adsorption schemes that form buckling deformations during geometry optimization (see Fig. 5 of the main text).

Electronic properties

In Fig. 6 of the main text we have presented and discussed the analysis of the bandgap calculations of the various structures obtained at the HSE level of theory. Here, for completeness, we present similar results obtained using the LDA (Fig. S3) and PBE (Fig. S4) functional approximations. As can be seen, for positions exhibiting the same ground-state spin configuration as that obtained using the HSE functional approximation, the bandgap dependence on the angular separation presents a similar behavior. As may be expected, the bandgaps predicted using the semi-local functional approximations are somewhat smaller such that for a given structure the bandgap order is usually $E_g^{HSE}>E_g^{PBE}>E_g^{LDA}$. As mentioned above, for some of the adsorption schemes, mainly in the NN family, the ground state obtained using the semi-local functionals presented a singlet character instead of the triplet ground state obtained using the HSE functional. This results in a major reduction of the bandgap where the singlet states present a bandgap in the order of 0-0.2 eV.

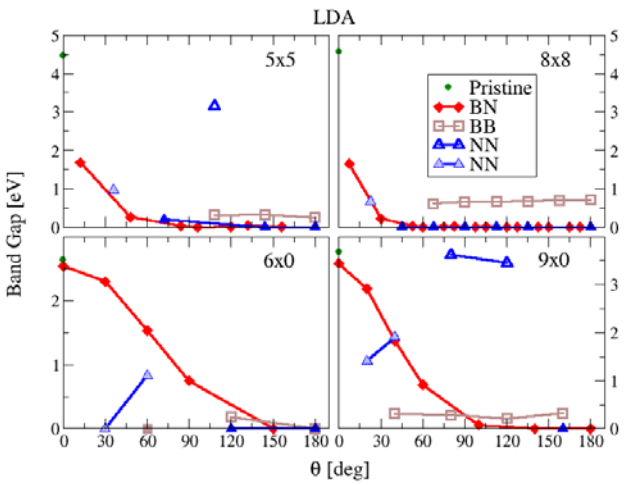

Fig. S3: Bandgap as a function of inter-hydrogen angular separation (θ) for the (5,5) and (8,8) armchair (upper panels) and (6,0) and (9,0) zigzag (lower panels) BNNTs studied obtained at the LDA/6-31G** level of theory. For clarity, lines connecting values that belong to the BN (red diamonds), BB (brown squares), and NN (blue triangles) adsorption families were added. Full (open) symbols designate a closed-shell singlet (open-shell triplet) ground state. Dotted triangles represent NN adsorption schemes that form buckling deformations during geometry optimization (see Fig. 5 of the main text).

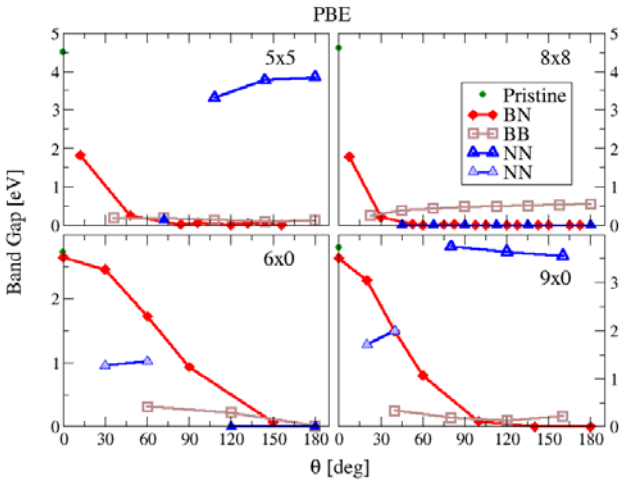

Fig. S4: Bandgap as a function of inter-hydrogen angular separation (θ) for the (5,5) and (8,8) armchair (upper panels) and (6,0) and (9,0) zigzag (lower panels) BNNTs studied obtained at the PBE/6-31G** level of theory. For clarity, lines connecting values that belong to the BN (red diamonds), BB (brown squares), and NN (blue triangles) adsorption families were added. Full (open) symbols designate a closed-shell singlet (open-shell triplet) ground state. Dotted triangles represent NN adsorption schemes that form buckling deformations during geometry optimization (see Fig. 5 of the main text).

Reduced hydrogen density - structural and electronic analysis

Upon reduction of the adsorbed hydrogen density by a factor of two we find that the overall qualitative behavior of the relative total energies and bandgaps as a function of the angular separation remains the same. Nonetheless, there are some quantitative changes. As can be seen in the upper panels of Fig. S5, in the total energies analysis we notice that the range of total energies obtained for the BN family is somewhat reduced and the most stable position of the (5,5,2) system changes from the $\theta=12^{o}$ to $\theta=24^{o}$. Yet, the energetic differences between these two states are merely 0.06 eV/unit-cell. In the bandgap analysis (lower panels of Fig. S5) we find that upon reduction of the hydrogen density the sensitivity of the bandgaps with respect to the angular separation between the two hydrogen adsorbates is considerably lower than the case of the higher adsorption density. We note that, in light of the results obtained using the HSE functional approximation, the LDA and PBE calculations were performed for the BN family alone focusing on the closed-shell singlet spin state.

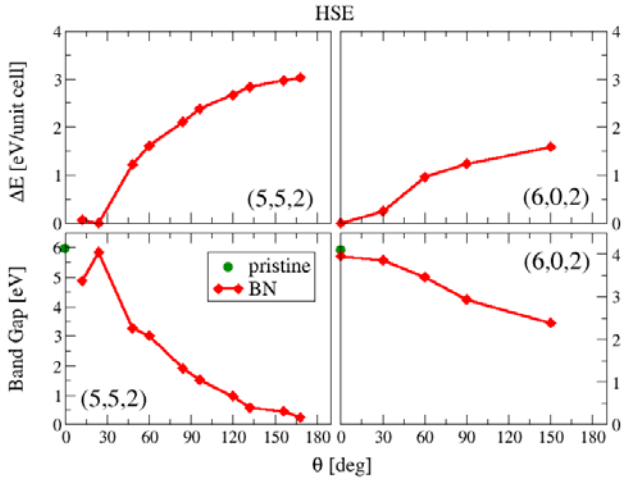

Fig. S5: Relative total energies (upper panels) and bandgap (lower panels) as a function of inter-hydrogen angular separation (θ) for the (5,5,2) armchair (left panels) and (6,0,2) zigzag (lower panels) BNNTs studied obtained at the HSE/6-31G** level of theory. The total energy of the most stable adsorption scheme of each system is used as reference. For clarity, lines connecting the values for the BN adsorption family (full red diamonds) were added.