



Institute for Research in Fundamental Sciences

مقاله نامه ی بیست و هفتمین کنفرانس بهاره فیزیک - ۴ و ۵ تیرماه ۱۳۹۹

شماره (۱۰)

Intercalation of boron nitride quantum dots with Lithium: boron nitride as a protecting layer for a Lithium-ion battery and a spin-dependent photon emission device

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Abstract:

In this study, the electronic properties of pristine and Li-doped BN quantum dots have been studied by the first-principle density functional theory and the B3LYP/6-31G(d,p) level. Accordingly, for pristine flakes, the stability increases as the size increases. For doped flakes, the absolute value of the adsorption energy increases as the size increases. And, for the adsorption near to N-H bonds, we have the highest stability. The distance of the adsorbed Li atom from the BN surface decreases as the adsorption place becomes farther from the symmetry point of the BN flake. For pristine BN the bond lengths do not change as the size increases, and the changes of the bond lengths of Li doped BN are in order of 0.01 Å. About the gap, for pristine BN, the gap increases as the size decreases. Furthermore, for doped structures, a little spin is transferred to the doped BN layer and some states are spin-polarized. A large value of the HOMO-LUMO gap for the pristine and spin-down current leads to this point that we have a wide gap insulator for the pristine BN and spin-down states. While, for spin-up electrons, the gap amounts are between 2 and 2.9 eV possess that we have a semiconductor. Additionally, in doped cases, by the increase of the β gap, the β gap of the spin-up states decreases. Frontier molecular orbitals have also been studied to discuss the ground and excited states. The trends seen in the DOS spectrum and the charge distribution are also observed in the present work. Moreover, doped BN flakes possess non-zero dipole moments due to the asymmetry in the charge distribution. We have also suggested the application of BN as a protecting layer for a Lithium-ion battery. Besides, its photoluminescence properties for optoelectronic applications have been discussed.

Boron nitride (BN) based nanomaterials have shown remarkable physical properties such as high thermal stability and conductivity, high resistance to oxidation, high electrical isolation, and outstanding chemical inertness [1-4]. Because of excellent thermal and chemical stability, BN is a good candidate for high-temperature applications [5]. Moreover, BN has significant potential to be used as a dielectric layer in high-performance 2D material-based electronic and photonic devices [6]. Interaction of BN with alkali metals is a gate of study, as well [7-9]. Interaction of infinite BN with a Lithium (Li) atom has been studied, before [9]. Based on this study, the calculated formation enthalpy of the considered forms of Li intercalated BN is found to be positive that eliminates BN intercalation without externally supplied energy. In Ref. [10], Freeman and Larkindale have discussed that the BN powder reacts with Sodium and Potassium. Accordingly, the interaction of BN film with Potassium is so that the charge transfer between the Potassium and BN bonds is very small. Whereas, no reaction was observed for the case of Li atom [7]. While the interaction of quantum dots of pristine and Li doped BN is still an open issue that we want to discuss it in this article. Based on

our study, we have suggested the BN based protracting layer for Li-ion batteries and a BN based spin-dependent photon emission device.

Here, the studied BN quantum dots are quasi-circular $B_{12}H_{12}N_{12}$, $B_{27}H_{18}N_{27}$, $B_{36}H_{24}N_{36}$, and related Li doped flakes (Fig. 1). The pristine and doped flakes are based on quasi-circular BN with Hydrogen (H) atoms in the boundaries to saturate dangling bonds. Each BN flake has also been doped by one Li atom. We have also selected the Li atom because it is more electronegative compare to other alkali metals.

The method of the study is the density functional theory method as implemented in the Gaussian 03 software [11] that uses the Gaussian type of orbitals basis sets for electronic structure calculations. We have also used the Beke-Lee-Yang-Parr (B3LYP) exchange-correlation hybrid function [12, 13] and polarized 6-31G(d,p) basis set. By this method, stability, the density of states (DOS), highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap, the distance of the Li atom from the BN surface, frontier molecular orbitals (MOs) and the charge distribution of each cluster have been studied.

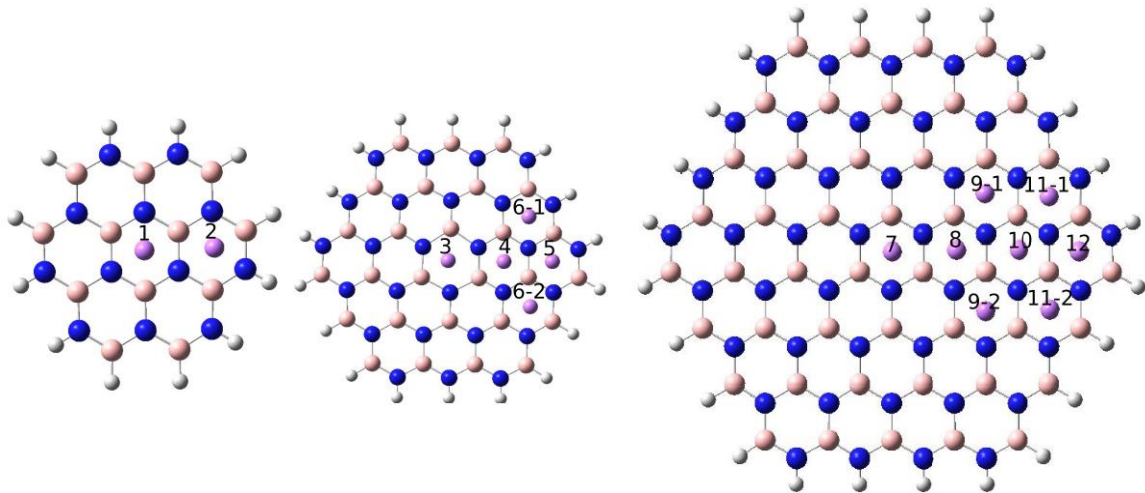


Fig 1. Li doped flakes. Left: two different Li (violet balls) doped $B_{12}H_{12}N_{12}$ systems. Center: flakes NO. 3 to 6-2, $B_{27}H_{18}N_{27}$ related flakes. Right: 8 different doped $B_{36}H_{24}N_{36}$ flakes are depicted. The Li atom in each case has a different place, and the number of each structure is mentioned above the Li atom. Pink, blue and gray balls indicate the place of B, N, and H atoms, respectively.

Based on our results, all doped clusters are stable (flakes NO. 1 to 12 in Fig. 1). Consequently, for the first time, we have shown that a Li doped boron nitride could be stable, and the stability is dependent on the size of the quantum dot and the initial place of the adsorbed Li atom. Furthermore, the stability of all BN flakes, before and after adsorption, have been checked by vibrational calculations where all positive IR frequencies have revealed that BN flakes are stable for all vibrational modes. Additionally, the distance of the adsorbed Li atom from the layer is dependent on its adsorption location. The distance of the adsorbed Li atom from the BN surface decreases as the adsorption place becomes farther from the symmetry point of the BN flake (Fig. 1). About the length of bonds, the increase of the size of pristine BN flake does not affect the bond lengths. And, for Li-doped structures, the change of the bond length is in order of 0.01 Å. Additionally, in doped cases, DOS for HOMO and LUMO molecular orbitals and higher energy levels are spin-polarized. Furthermore, semiconducting for α (spin-up) electrons and insulating for β (spin-down) electrons have happened. Moreover, for pristine BN flakes, HOMO orbitals are delocalized and those are concentrated on the N atoms. Instead, the LUMO molecular orbitals are concentrated on B atoms and MOs are localized. For doped structures, independent of the position of the Li atom, HOMO, and LUMO orbitals of spin-up states and LUMO of spin-down electrons are localized. Besides, for pristine flakes by the increase of the size, the charge distribution interval increases. In doped BN flakes, high charge transfer from

BN surface to the Li atom happens where a Li atom is adsorbed on the edge. We have also found that the alternation in the electronic properties of the adsorbed Li atom in the center of BN flake is less, e.g., there is a little charge transfer (up to 0.04 Mulliken) from the surface to the Li atom. Edge adsorption also increases the charge interval in a cluster. Additionally, the polarity increases as the cluster size increases and the adsorbed Li atom goes to the N decorated edges. So, the polarity comes from the BN size and the position of the adsorbed Li atom relative to the center. It means that if the initial state of the position of a Li atom is near to the center (flakes NO. 3, 7, and 8), the Li goes up far from the plane of BN flake and for other initial places, it goes to the edge.

About the applications of BN flakes, the inorganic 2D layer of BN is attractive for clean energy applications. Additionally, the current Li-ion batteries should never be operated in a thermally insulated case or a high ambient temperature. Consequently, we suggest coating BN on the case of a Li-ion battery. This application grantee the safety of the application of Li-ion batteries in different situations; for example, high temperature and pressure conditions because of the thermal management of the rechargeable Li-ion batteries. Its inertness beside Li atoms and having localized molecular orbitals make BN a good insulator, a protective coating, and a separator for Li atom environments. According to the results of this article, the usage of this cover sheet does not affect reversible Li-ion battery performance. Moreover, according to what we have calculated, the bandgap of pristine BN flakes, including $B_{12}H_{12}N_{12}$, $B_{27}H_{18}N_{27}$, and $B_{36}H_{24}N_{36}$ are 6.9, 6.5, and 6.4 eV, respectively. These bandgap energies are in the range of the deep ultraviolet luminescence. These bandgap energies are also dependent on the size of flakes. And, by the adsorption of the Li atom, only the spin-down electrons can have such a wide bandgap. Hence, the spin-dependent photon emission is possible. For a Li doped BN, emissions change in the order of several Deci eV dependent on the place of the adsorption. Consequently, the BN flakes give such a possibility to study light-matter interaction at the nanoscale especially for nanophotonics applications.

Conclusion

For the first time, we have found that the adsorption of a Li atom by BN flake is possible. Moreover, based on the calculations, the application of BN as an insulator for a Li-ion battery is suggested. We have also suggested that the adsorption of a Li atom as a source of a spin defect in BN for spin-dependent photon emission devices is possible.

Acknowledgments

This work was made possible by the facilities of Computational Nanotechnology Supercomputing Center, Institute for Research in Fundamental Science (IPM).

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