THESIS

STRUCTURAL AND ELECTRONIC PROPERTIES OF BN-DOPED CARBON NANOMATERIALS OBTAINED BY DENSITY FUNCTIONAL CALCULATIONS

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We report here the systematic PBE-DFT studies on the structural and electronic properties of BN-doped carbon nanomaterials grafted with N-nucleophiles. The def-SV(P) basis set and RI approximation implemented in the TURBOMOLE code were used to perform the structural optimization. The single point energy calculations were carried out using Ahlrichs pVDZ basis set implemented in Gaussian03 program. The BN moieties doped onto carbon nanomaterials provide an improvement of their reactivity and conductivity. The degree of grafting the BN-doped (5,5)-SWCNT model with a number of N-nucleophiles (R-groups) was determined by a relative binding energy, which is directly proportional to the magnitude of pK_a. The binding energies lie between 6.9-30.1 kcal/mol and are in the order of guadinine > arginine > ammonia > imidazole > chitosan > pyridine > m-nitroaniline. The conductivity of the complexes was, however, significantly improved by the addition of aromatic molecules. Only m-nitroaniline and pyridine attached to the BN-doped (5,5)-SWCNT can reduce the energy gap (by 0.25 and 0.35 eV with respect to the isolated BN-doped (5,5)-SWCNT, respectively). The BN-doped C_{60} was modified by grafting with bridging heterocyclic molecules, namely, 2,6-Naphyridine, 3,8-Phenanthroline and 2,6-Diazaantracene. The connection of two BN-doped C_{60} molecules with single heterocyclic molecules provides newly improved materials with a very high conductivity. In comparison with C_{60}, the energy gaps were reduced by 1.54, 1.41, and 1.64 eV when using 2,6-diazanapthalene, 3,8-Phenanthroline, and 2,6-Diazaantracene as bridging molecules, respectively. The formation of such complexes is highly exothermic by 52.3, 55.0 and 56.7 kcal/mol, respectively. This suggests that the newly modified materials are thermodynamically stable.

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