Theoretical prediction of adsorption characteristics of cellulose molecules on the surface of carbon nanostructures

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Abstract

Currently, the optical characteristics of nanocomposite materials based on cellulose and carbon nanostructures (CNSs) are being actively studied [1]. Despite intensive studies, several key problems regarding the peculiarities of the interaction of the components of nanocomposites "cellulose-CNSs" still remain unsolved. These are, in particular, the questions regarding the types of bonds formed in the material between components, the mutual influence of the components on their physical (electronic, optical, and other) properties, and the role of individual components' in formation of the properties of material.

Our studies were carried out in the form of the electronic structure calculations performed by the quantum chemical method in the DFT approximation [2]. The calculations revealed the mechanisms of the cellulose molecul adsorption on the surface of carbon nanotubes CNT(5,5) and single-layered graphene sheets, both bare and doped with boron or nitrogen. Binding energies and inter-nuclear distances between components were calculated and analyzed.

Calculation results were discussed in view of the possible influence of doping and surface functionalization of carbon nanostructures on cellulose optical (light absorption) characteristics. Perspectives for the efficient doping and surface functionalization of nanostructured carbon materials are revealed.

Calculation method

Calculations of the electronic structure of cellulose molecules adsorbed on the surface of carbon nanostructures were carried out within the DFT approximation using Gaussian 09 software package with use of 6-31g basis set.

The binding energy between adsorbent (CNS) and adsorbate (MC) was calculated by the formula:

$$E_b = E_{CNS+MC} - E_{CNS} - E_{MC}$$

where E_{CNS-MC} is the calculated total energy of the geometrically-optimized CNS + MC system, E_{CNS} and E_{MC} are the total energies of CNS and MC, calculated separately within the same approximations. If the calculated value of E_b is negative, it is assumed that the MC is adsorbed on the surface of the CNS. If the E_b value is positive, the adsorption is not energetically favorable.

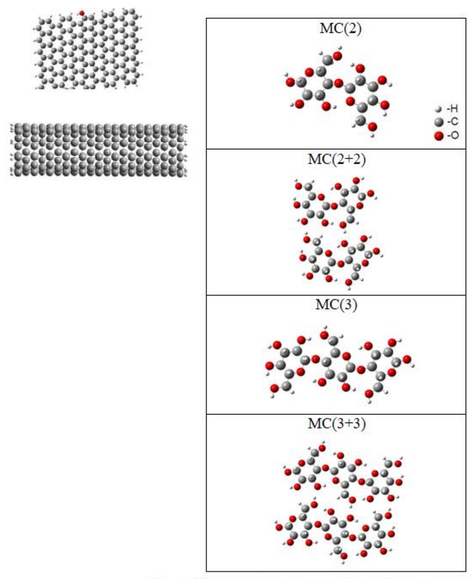

Fig. 1. Optimized structures of the cellulose molecule clusters.

Results

Adsorption of MC on undoped CNS

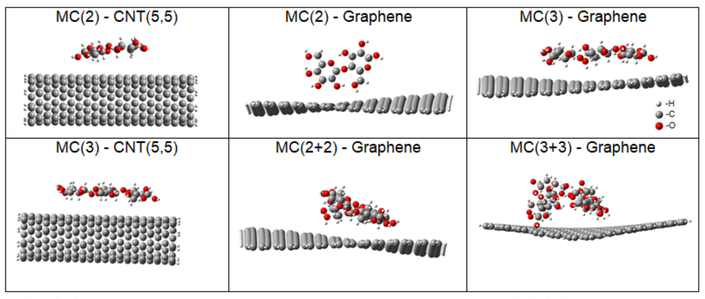

Fig. 2. Optimized geometries of MC clusters adsorbed on the surface CNT(5,5) and graphene.

Table 1. Adsorption characteristics (binding energies and the lowest interatomic distances) calculated for adsorption configurations of two types of MC clusters on the surface of CNT (5,5) and graphene.

Configuration	E_b, eV	R min, Å (type of bond)	Configuration	E_b, eV	R min, Å (type of bond)
MC(2) - CNT(5,5)	-0.002808	3.04743 (H-C)	MC(3) - Graphene	-0.006422	3.09531(H-C) 3.14193(H-C) 2.80632(H-C) 3.05724(H-C) 3.21123(H-C) 3.31243(H-C)
MC(3) - CNT(5,5)	-0.003415	3.06990 (H-C) 3.19104 (H-C) 3.21865 (H-C) 3.24360 (H-C)	MC(2+2) - Graphene	-0.006489	2.94127(H-C) 3.39754(H-C) 3.26849(H-C) 2.87694(H-C) 2.49783(H-C) 2.87694(H-C)
MC(2)-Graphene	-0.005378	3.17756 (H-C) 3.28214 (O-C) 2.47157 (H-C)	MC(3+3) - Graphene	-0.016103	2.55347(O-C) 2.47424(H-H) 2.69401(H-C) 3.65905(H-C) 2.69401(H-C) 2.58950(H-C)

Binding energies are formally negative, but are rather small in absolute value (thousandths of eV). So, covalent bonds between the MC and CNS are not formed.

Adsorption of MC on CNS doped with aliovalent impurities of boron or nitrogen.

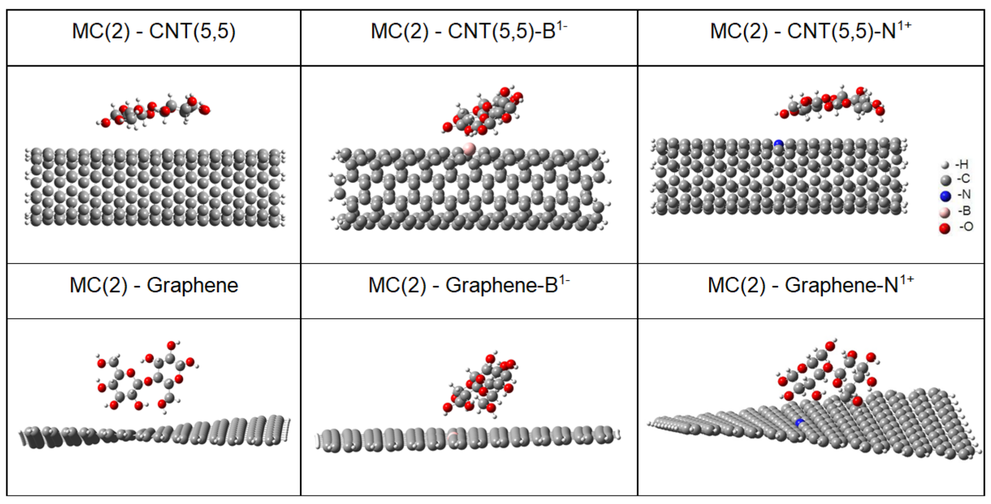

Fig. 3. Optimized geometries of MC clusters adsorbed on the surface of undoped and boron-nitrogen-doped CNT (5.5) and graphene.

Table. 2. Calculated characteristics of adsorption configurations of MC(2) cluster on the surface of undoped, B- or N-doped CNT(5,5) and graphene.

Configuration	E_b, eV	R min, Å (type of bond)	Configuration	E_b, eV	R min, Å (type of bond)
MC(2) - CNT(5,5)	-0.002808	3.39375 (H-C) 3.42555 (O-C) 3.50803 (O-C) 3.04743 (H-C) 3.16473 (H-C) 3.37046 (H-C)	MC(2) - Graphene	-0.005378	3.17756 (H-C) 3.28214 (O-C) 2.47157 (H-C)
MC(2) - CNT(5,5)-B^{1-}	-0.007297	1.83027 (O-B) 3.21072 (O-C) 2.95108 (H-C)	MC(2) - Graphene-B^{1-}	-0.004988	2.68776 (H-C) 3.05471 (H-C) 2.60309 (H-C)
MC(2) - CNT(5,5)-N^{1+}	-0.011816	3.35761 (H-N) 3.45642 (O-N) 3.03750 (H-C) 2.96035 (H-C) 3.47373 (H-C) 2.99882 (H-C) 2.70270 (H-C)	MC(2) - Graphene-N^{1+}	-0.009058	2.84448 (H-C) 3.29699 (O-C) 2.93976 (H-C) 2.54644 (H-C)

Results of our computational modeling suggest that: a) interaction of the cellulose and carbon components of composite materials should be considered as relatively weak if carbon components are *un-doped*; b) such interaction can be enhanced by additional doping of the carbon components surfaces by aliovalent substitution impurities, in particular by boron impurities.

Adsorption of MC on CNS functionalized with oxygen-containing surface groups

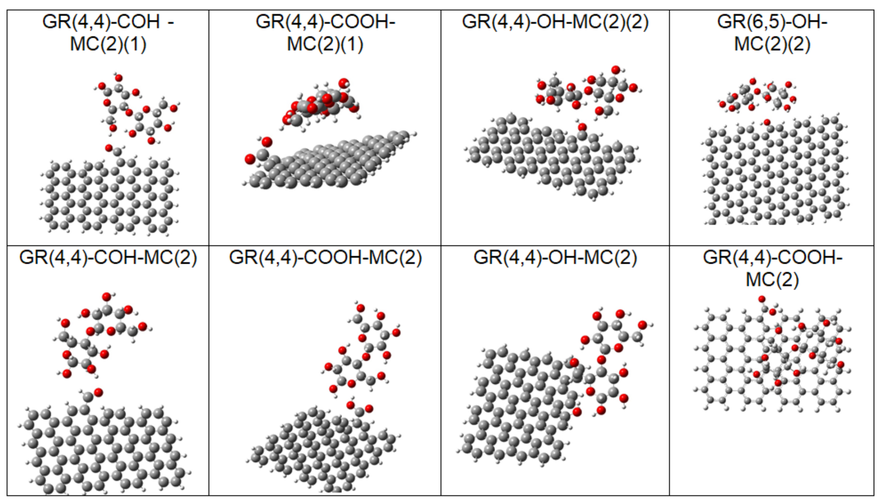

Fig. 3. Optimized geometries of MC clusters adsorbed on the sufrace of graphene sheets functionalized with oxygen-containing surface groups.

Table. 3. Calculated characteristics of adsorption configurations of MC(2) cluster on the surface of functionalized graphene.

Configuration	E_b, eV	R min, Å (type of bond)	Configuration	E_b, eV	R min, Å (type of bond)
GR(4,4)-COH-MC(2)(1)	-0,02958	-	GR(4,4)-COH-MC(2)	-0,015546	[O2'-C1'] 1.79828 (H-C) 2.43939 (O-H)
GR(4,4)-COOH-MC(2)(1)	-0,016124	-	GR(4,4)-COOH-MC(2)	-0,024571	[O5'-O6'] 2.37886 (H-C) 1.66063 (O-H) 2.10768 (H-O)
GR(4,4)-OH-MC(2)(2)	-0,027473	1.79850 (H-O) 1.72490 (H-O)	GR(4,4)-OH-MC(2)	-0,020808	[O1'-O5'] 1.85451 (O-H) 1.83746 (H-O)
GR(6,5)-OH-MC(2)(2)	-0,018091	-	GR(4,4)-COOH-MC(2)	-0,016124	-

Molecular cellulose does not form chemical (covalent) bonds with oxide surface groups of functionalized graphene. However, 1.6 - 1.8 A distances between O and H atoms indicate existence of stable hydrogen bonds between MC and functionalized graphene surface.

Conclusions

The quantum chemical method of electronic structure calculations in the DFT approximation was applied in computational studies of interaction of cellulose and carbon components of composite materials, namely, clusters of cellulose molecules of different structures with surfaces of un-doped and doped with boron or nitrogen carbon nanotube CNT(5.5) and graphene sheet. The following can be derived from analysis of the calculation results:

1) Adsorption of cellulose molecules on the surface of un-doped CNS should generally be considered unlikely, as calculations show the absence of covalent interatomic bonds.

2) Interaction of clusters of cellulose molecules with graphene surface should be more pronounced if compared to the case of nanotube surface because the obtained interatomic distances between cellulose and graphene atoms are significantly shorter (2.2 - 2.4 Å compared to ≥ 3 Å in the case of interaction "MC - CNT").

3) Interaction of cellulose molecules with the surfaces of carbon components of composite materials should be considered as relatively weak. However, this interaction can be somewhat enhanced by additional carbon surfaces doping by aliovalent substitution impurities, in particular boron.

4) Molecular cellulose does not form chemical (covalent) bonds with oxide surface groups of functionalized graphene. However, 1.6 - 1.8 A distances between O and H atoms indicate existence of stable hydrogen bonds between MC and functionalized graphene surface.

Acknowledgements

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References:

[1] Nedilko, S., Barbash, V., Kleshonok, et. al. Morphology, Optical and Electronic Characteristics of Nanocellulose Filled with Microcrystalline Cellulose and Graphene Oxide. In 2020 IEEE 10th International Conference NAP, pp. 01NP06-1, 2020.

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