Nanocomposites and nanomaterials

Modeling of supramolecular interaction of carbon nanotube - cluster of graphite-like structure

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Composites based on the carbon nanotubes with graphite-like clusters and the different polymers ($CNT/C_n/P$) are widely used for the development of the new materials in electronic, mechanical engineering and construction industries. Since the composition and electronic structure of the above-mentioned systems is still unclear, the interaction between graphite-like cluster C_{54} and carbon nanotubes such as $CNT_{8,0}$, $CNT_{10,0}$ and$CNT_{12.0}$ as well as graphite-like clusters C_{96} is considered using a quantum chemical semi-empirical method PM7 (program MOPAC 2016 and Density Functional Theory (DFT) with exchange-correlation function B3LYP including dispersion amendment of Grimme [1] and base set 3-21G(d,p) (program GAMESSUS). The structure of the formed complexes is given in the figure. The radius of curvature 1/R, the ratio of the nanotubes diameters ($D_\perp/D_=$) as well as the binding energy values obtained the semi-empirical $\Delta E(PM7)$ method and DFT without ΔE and included dispersion amendment of Grimme D3 $\Delta E(disp.)$ and charge $\rho(C_{54})$ are presented in the table.

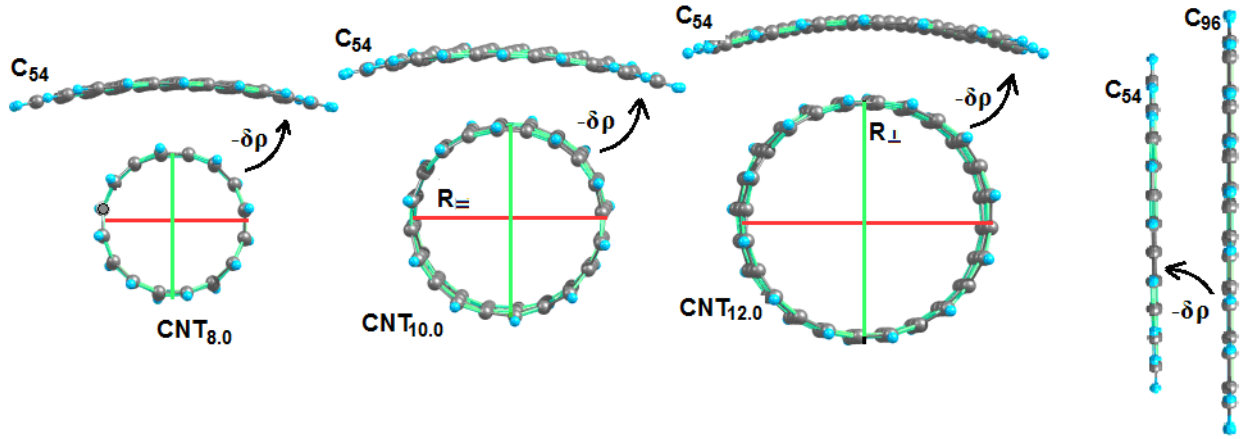

Fig. Structure of C_{54}-$CNT_{8.0}$, C_{54}-$CNT_{10.0}$, C_{54}-$CNT_{12.0}$ and C_{54} – C_{96} (CNT_x, x=8.0, 10.0, 12.0) composites.

Table. Energetic characteristics of C_{54}-CNT_x composites

	1/R(CNT)	$D_\perp/D_=$	ΔE(PM7), kcal/mol	ΔE(disp),kcal/mol	ΔE,kcal/mol	$\delta\rho(C_{54})$
$CNT_{8.0}$-C_{54}	0.31847	0.9791	109.0008	-38.8206	15.6527	0.0495
$CNT_{10.0}$-C_{54}	0.25465	0.9655	101.3127	-42.8272	19.6781	0.0623
$CNT_{12.0}$-C_{54}	0.21229	0.9536	90.6835	-52.0522	19.6644	0.0682
C_{96}-C_{54}	0		-71.7077	-175.6991	-54.9615	-0.0455

Analyzing the obtained data, it follows that:

1) the charge transfer between CHTx and C_{54} where $\delta\rho \sim 0{,}05\text{-}0{,}07$ and their distance exceeded 3,5 Å points on an insignificant overlap of the molecular orbitals of the interacting centers and, thus, inessential contribution in the binding energy in covalent component of CNT_x-C_n composite occurs. Comparison of the binding energy values of CNT_x with C_n taking into account ΔE(disp.) and excluding ΔE dispersion amendment of Grimme D3 supports the suggestion that the electrostatic, hydrophobic and dispersive interactions are determinative during formation of CNT_x-C_n composites. The binding energy (ΔE(disp.)) increase with the increase of R(CNT) radius and the correlation coefficient such as 0.9447 consistent with the increase in the number of contacts between CNT_x and C_n. Hence, the interaction between CNT_x and C_n is determined by entropy (frequency) factor.

2) The interaction between CNT_x and C_{54} leads to the deformation of CNTx diameters in addition to the decrease of $D_\perp$ (perpendicular to the plane C54) while $D_=$ (parallel to the planes C_{54}) is insignificantly increase, the correlation coefficient between $D_\perp/D_=$ and ΔE(PM7) as well as ΔE(disp.) is >0.986. The high correlation coefficient (0.9999) between ΔE(PM7) and ΔE(disp.) values definitely points on the application of semi- empirical PM7 method for the calculation of such systems.

1. *S. Grimme, S. Ehrlich, L. Goerigk*, J. Comp. Chem. **32**(2011) 1456.