Quantum-chemical investigation of the superoxide radical scavenging activity of graphene oxide surface

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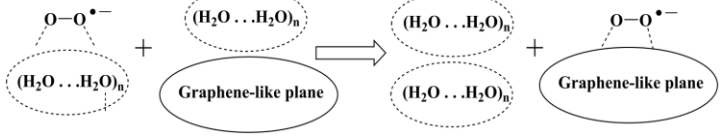
INTRODUCTION

The development of convenient antioxidants remains challenges and opens new questions concerning the origin of the surface in free radical scavenging activity, mechanism of the reaction, optimal conditions of the reaction proceeding, the influence of different factors (temperature, pressure, solvent), etc. For better understanding, all of these questions DFT method could be employed. Carbon-based nanomaterials may show reactive oxygen species scavenging effects, that based on their properties to generate radical adducts at sp2 carbon sites, their possibility to transfer of surface electrons or hydrogen donation from functional groups.

OBJECTS AND METHODS OF THE STUDY

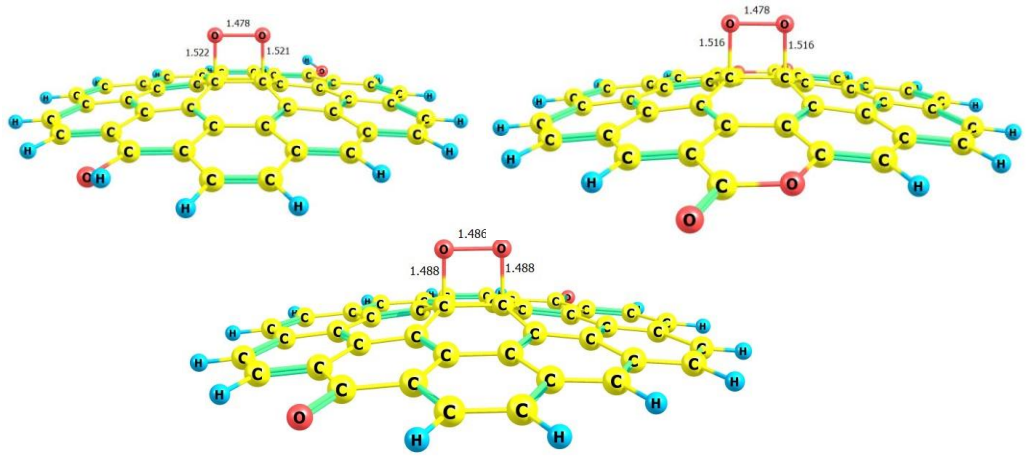
For the modeling of the graphene-like plane (GLP) the polycyclic aromatic cluster ($C_{42}H_{16}$) has been choose. Oxygen atoms were introduced in the graphene plane as hydroxyl, ketone and lactone groups, whereas Nitrogen as quaternary N^+, amine and nitro groups. The calculations were carried out by DFT method with functional B3LYP and basis set 6-31G(d,p) and dispersion correction by Grimme by means of Firefly 8.2.0 program package.

Interaction of the superoxide radical with GLP in aqueous environment was considered as a substitution of the water molecules to superoxide radical on the surface:

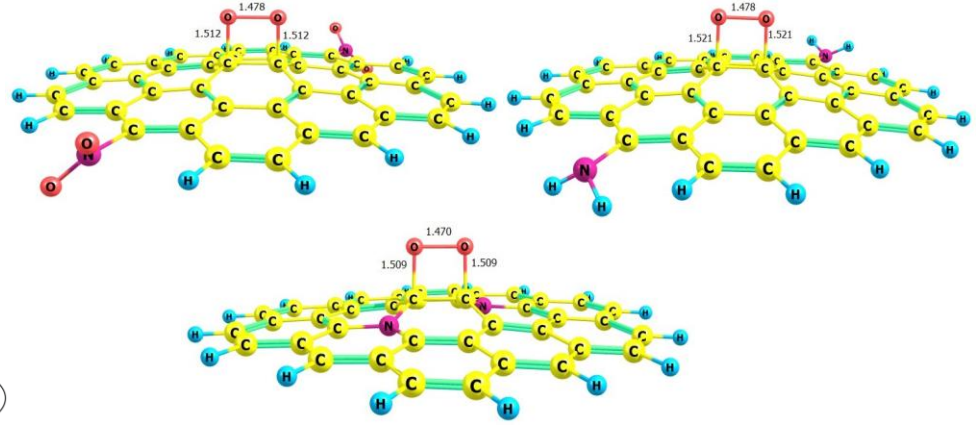


RESULTS AND DISCUSSION

Physically and chemically adsorption complexes of superoxide radical with oxygen-containing GLP



Physically and chemically sorption complexes of superoxide radical with nitrogen-containing GLP



Energy characteristics of the interaction of superoxide radical with GLP

Formula of surface	$\Delta E_{ph.ads}$	$\Delta E_{chem.ads}$
$C_{42}H_{14}(OH)_2$	+32.1	+207.8
$C_{42}H_{14}(O)_2$	-109.7	+123.5
$C_{40}H_{12}(O)_4$	-10.7	+148.6
$C_{40}H_{16}N$	-16.7	-3.4
$C_{42}H_{14}(NH_2)_2$	+9.9	+218.3
$C_{42}H_{14}(NO_2)_2$	-50.1	+138.4
$C_{42}H_{16}$	-8.6	+200.6

CONCLUSIONS

1. Quantum chemical calculations show that the highest energy of physical adsorption (-109.7 kJ/mol) was observed for the GLP with ketone groups on graphene side. The lowest one – (+32.0 kJ/mol) – for the GLP with peripheral hydroxyl groups.

2. The lowest value of the chemical interaction energy (-3.4 kJ/mol) of superoxide radical with GLP is for nitrogen-containing cluster (C40H16N), whereas its highest value (+207.8 kJ/mol) – for GLP with peripheral hydroxyl groups. It could be concluded that superoxide radical physically adsorbed on the surface of the oxygen-containing GLP. Simultaneously, chemical interaction in such case is thermodynamically unlikely.