Adsorption of chemical species on nitrogen-doped [60]fullerene: tight-binding study

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Abstract. We present a theoretical study of the adsorption of common species COOH, H and OH on nitrogen-doped C\textsubscript{60} cage. We find that these radicals tend to bind with the carbon atoms, nearest to the nitrogen defect. Structural and energetical characteristics of functionalized cages are studied in detail. The reactivity of the fullerene is found to be some more than that of graphene.

1. Introduction

In 1973, Russian scientists D.A. Bochvar and Ye.N. Halpern published an article with the results of quantum chemical calculations [1]. It was suggested that there should be a stable form of carbon containing 60 carbon atoms in the molecule. Also in this article was shown the form of such a hypothetical molecule [1]. However, this work was unnoticed. Only in 1985 Kroto and his co-workers found in the mass spectrum of graphite decomposition products under the action of a laser beam an intense peak with a mass of 720 a.m.u. [2]. It was belonged to the C\textsubscript{60} molecule. Another, less intense peak, corresponding to a mass of 840 a.m.u., was belonged to the C\textsubscript{70} molecule. A new allotropic modification of carbon was called as "fullerenes".

The most effective method of obtaining fullerenes is based on the thermal decomposition of graphite. In this process, high-frequency and resistive heating of graphite electrode [3,4], combustion of hydrocarbons [5,6], laser irradiation of the graphite surface [7,8], and evaporation of graphite by a focused solar ray [9] are used. Most often, an arc discharge with graphite electrodes in a helium atmosphere is used to obtain fullerenes [10,11].

The spherical fullerene molecule has unique physical, chemical and biological properties. Therefore, fullerene and its derivatives are widely used in various fields.

The biological activity of fullerenes and their derivatives is actively studied [12–15]. It is shown that representatives of this class are able to inhibit various enzymes [16], cause specific cleavage of DNA molecules [17], actively participate in various oxidation-reduction processes in the body [13]. The study of the metabolism of fullerenes has begun, special attention is paid to antiviral properties [13,18]. It is shown, in particular, that certain derivatives of fullerenes are capable of inhibiting the protease of the AIDS virus [13]. The idea of creating anti-cancer medicines based on fullerenes is widely discussed [19–22].

Also considered the possibility of obtaining super-hard materials based on fullerenes [23–25]. It was shown the possibility of obtaining large diamonds. After the addition of fullerene to graphite, the graphite-diamond phase transition begins at a lower temperature and pressure [26].
Fullerenes can be used as precursors for the growth of diamond films. It is shown that the C\textsubscript{60} fragmentation on C\textsubscript{2} occurs in the microwave discharge. C\textsubscript{60} is a suitable material for the growth of diamond crystals. It is predicted that such a high growth rate will significantly reduce the cost of CVD-grown diamonds [27].

Due to the ability to polymerize under the action of a laser or electron beam and form an insoluble phase in organic solvents, fullerene can be used as a resist for submicron lithography. Fullerene films can withstand considerable heating, they do not contaminate the substrate and they allow a dry manifestation [28].

Fullerene-containing materials are promising for use as materials for nonlinear optics [29]. Fullerites can be used to create a field-effect transistor [30], photovoltaic devices [31], solar cells [32–34]. To use fullerenes effectively, one need to learn how to tune its characteristics. This can be achieved by introducing structural defects in them [35,36], and also by doping them [37]. Another common method of altering the properties of fullerene is substitutional doping, in which some carbon atoms are replaced by atoms of other elements.

Adsorption of adenine to the surface of a Cr or Ni doped fullerene is being studied [38]. These studies can later be used to develop technologies for the delivery of genes, drugs and other biomolecules. The adsorption of hydrogen into fullerene doped with Na and Li [39–41] is investigated, since the development of solid-state fuel cells for storing hydrogen with high gravimetric and bulk density is of great importance in the development of hydrogen energy. Nitrogen-doped fullerene can be used as a cathode catalyst for hydrogen fuel cells [42]. Nitrogen-doped fullerene can also be used as a catalyst that is active for the oxygen reduction reaction and the oxygen evolution reaction and is therefore applicable to energy conversion and storage devices such as fuel cells and metal-air battery systems [43]. Fullerene, doped with rhodamine B, is considered as a material for improving the extraction of electrons when creating organic solar cells [44].

In this study, we investigate the influence of nitrogen doping on reactivity of C\textsubscript{60} cage. Nitrogen-doped fullerene can be synthesized by vaporization of graphite under the atmosphere of nitrogen and helium mixture [45]. The present work is devoted to the investigation of the adsorption of COOH, H and OH radicals onto nitrogen-doped fullerene. The listed radicals are widespread adsorbates: H is interesting from the point of view of hydrogen storage [39–42,46,47]; C\textsubscript{60}(OH) can be useful in biomedicine [48–50]; C\textsubscript{60}(COOH) provides its biocompatibility [51]. In this article, computer simulation is used to study the effect of the nitrogen atom, embedded in the fullerene carbon framework, on the binding energy of fullerene with adsorbents.

2. Computational details
In our study, a computer simulation of the adsorption of the radicals H, OH, COOH on nitrogen doped fullerene. To optimize the molecule and calculate the binding energy, we used a non-orthogonal tight binding model (NTBM) [52,53] with the parameterization [53]. This semiempirical model describes well the interatomic interactions of H\textsubscript{m}C\textsubscript{n}N\textsubscript{m}O\textsubscript{n} compounds. A more accurate method of the density functional theory (DFT) requires too much computer processing power, and the non-orthogonal tight binding model is accurate enough and is often used for fullerenes [54–56], and for systems with a carbon-nitrogen framework [57,58]. Optimization of the geometry of the initial and functionalized nitrogen-doped fullerene was carried out by the method of gradient descent: the atoms were displaced in the direction of the forces acting on them until these forces became less than 0.001 eV / Å.

We define the adsorption energy $E_{\text{ads}}$ as $E_{\text{ads}} = E(C\textsubscript{60}N+R) - E(C\textsubscript{60}N) - E(R)$, where $E(C\textsubscript{60}N+R)$, $E(C\textsubscript{60}N)$ and $E(R)$ are the total energies of functionalized C\textsubscript{60} cage, pristine C\textsubscript{60} and isolated radical R (R= COOH, H or OH), respectively.

3. Results and discussion
We calculated the adsorption energies for each of the radicals COOH, H, OH attached to one of ten different atoms (A0–A9) of the nitrogen-doped fullerene, see figure 1a. These atoms were chosen so...
that they were removed from the nitrogen atom (A0) built into the fullerene framework to the
diametrically opposite fullerene atom (A9). As a result, we obtain oscillation behavior of the binding
energy as a function of the distance between nitrogen atom and absorbent. The figure 1b shows that
the effect of nitrogen defect on the adsorption energy is weaker, when the radical attached far from
nitrogen atom.

![Schlegel diagram of N-doped C₆₀ cage.](image)

**Figure 1.** (a) Schlegel diagram of N-doped C₆₀ cage. A0 position corresponds to the nitrogen
atom. A0-A9 positions are regarded as the adsorption centres. (b) Adsorption energies for different
adsorption positions.

Calculations show that all the selected radicals are capable of adsorbed on nitrogen atom, but this
variant is not of interest to us, since on it the adsorption energy is the lowest of all. The most favorable
position for adsorption was A1: the carbon atom closest to the nitrogen atom. A similar result was
obtained by studying the adsorption of radicals on nitrogen-doped graphene according to our
calculations in the frame of the same tight-binding model. The energy values for adsorption on
graphene on the atom closest to nitrogen were -1.50 eV, -1.91 eV, -2.00 eV for COOH, H, OH,
respectively, and for fullerene -2.32 eV, -2.62 eV, -2.63 eV for the same radicals, respectively. Thus,
one can see a similarity of the adsorption properties of these carbon allotropes. The binding energy
on this atom is higher than on the others. However, the adsorption energy for nitrogen-doped fullerene
was greater than that of nitrogen-doped graphene. Most likely this is due to the fact that the fullerene
can be considered as a convex curved graphene. It was previously shown that the adsorption of atomic
hydrogen onto convex portions of graphene takes place with more energy than on flat or concave ones
[59].

4. Conclusions
In the course of this work, we investigated the adsorption of the radicals COOH, H, OH on nitrogen-
doped fullerene. As a result, we have obtained that the lowest adsorption energy corresponds to
adsorption on the carbon atom, which is adjacent to the nitrogen atom, regardless of the structure and
chemical composition of the adsorbed radical. Therefore, the nitrogen defect enhances the reactivity of
the fullerene. Adsorption of both H and OH species results in the higher energy gain, than that for
COOH. Calculations have shown that the adsorption properties of fullerene are similar to those of
curved graphene on convex portions: the adsorption on fullerene is much more feasible than that on
flat graphene. Thus, we believe that controlling the tunable local curvature of nitrogen-doped graphene
will make it possible to control its adsorption properties.
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