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New approaches for security based on the properties of nanodiamonds

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Abstract

The study has been performed to exhibit the magnetic properties of the hydrogenated nanodimond with nitrogen defect. The results obtained allows us to gain evidence that viruses-sensor employing nanodiamond with paramagnetic centre could be created. The Becke's three-parameter hybrid functional, applying the non-local correlation provided by Lee, Yang, and Parr method with the 6-31G basis was approached. We found that the above compound substituted by banzoic acid possesses unpaired electrons and their magnetic properties are electric field depended. The possibility to create a biosensor employing nanodiamond with paramagnetic centre is foreseen.

Keywords: Nanodimonds; Substituents; Magnetic susceptibility; Density functional approach B3LYP/6-31G.

1. Introduction

Currently, security is defined as freedom from, or resilience against, potential harm or other unwanted coercive change caused by others. Indeed, the meaning of security is very broad. It could be the act of keeping peace within the borders of a sovereign state or other self-governing territories, one against toxic spills, activities to protect personal data or access information on a device, etc. In some cases, the potential harm is predictable and easily identifiable thus it is possible to foresee possible negative consequences, effectively detecting and monitoring it, and create circumstances to protect society from its negative impact. Recent SARS-CoV-2 outbreak exhibits importance as soon as possible to obtain viruses and bacterias causing a pandemic in the early stage of their appearance. On the other hand, to predict the spread and mutation of these biological species, the precise knowledge of their structure and chemical composition must be known in advance.

In recent years, highly sensitive and quantifiable systems have been developed primarily for the detection of viral nucleic acids in the blood or infected fluids and tissues, they have replaced many of the antigen tests. For example, miniaturized chip tests for viral diagnostics have been developed, the predominant genotype of the virus has been determined to develop the resistance tests, a new system for single-virion identification of common respiratory pathogens using a machine learning algorithm trained on changes in current across silicon nanopores has created, too (Arima et al., 2020a).

Currently, biosensors have been increasingly discussed and tested as rapid and sensitive test systems for the detection of various classes of substances and molecules. These sensors are based on various principles thus can be exploited in various conditions. For example, the changes in the oscillation frequency of a quartz crystal coated with antigens indicate positive antibody detection, the potential changes revealed the formation of antigen-antibody complexes. Fluorescence and chemiluminescent are also used for virus detection. There is no doubt that biosensors have expansive applications for diverse targets due to their advantages, such as strong specificity to targets, rapid analysis, high accuracy, easy operation, and low cost (Barbiero et al., 2020 b). Moreover, micro and nanoelectronics and advancements in material sciences allow one to integrate biosensors into healthcare wearable devices for diagnostic and treatment purposes. However, limited applications (for example, to indicate unknown potentially dangerous viruses) the stability, sensitivity, privacy, power source, etc. still are frontier of the sensors used to satisfied the high-security standard to prevent pandemic. Hence, we predicted that sensor employing a nanodiamond with a paramagnetic center indicating magnetic properties change could be a promising tool to obtain viruses, i.e. potential harm. The results of our investigations presented below proved this prediction. It implies, that they could be used for the further development of state-of-the-art devices overcoming the limits of the sensors used today.

The paper is organized followingly: Section 2 shows the contribution to research nanodiamonds as new sensors; Section 3 indicates the method and methodology applied; Section 4 represents the results achieved and their discussion; Section 5 represents the conclusions.

2. State of the art

A model of nanodiamond was investigated as a key compound to achieve our purpose. Nanodiamonds are high hardness, high thermal conductivity, and electrical resistivity, high chemical stability, a tunable surface, resistance to the harsh environment, and, the most important, biocompatible compounds (Basso et al., 2020 c and references herein). The results of our studies exhibited that nanodiamonds possess magnetic properties dependent on the size, shape, and surface functionalization of them (Masys et al., 2019 a, Masys et al., 2019 b). The usage of nanodiamonds for magnetic imaging is also widely described (Barbiero et al., 2020 b, Lin at al., 2019 c]. It proposed to apply these magnetic nanodiamonds together with surface modifications for drug delivery, targeted therapy, localized thermal treatment, and diagnostic imaging. However, the data on the influence of various substitutions to properties of the nanodiamonds are scarce. It is also unknown, how the magnetic properties of the substituent nanodiamond changed in the presence of an electromagnetic field. Hence, we present here our performed investigation on hydrogenated diamond nanocrystal with paramagnetic center (nitrogen atom defect) substituted by benzoic acid (-Ph-COOH) to exhibit their magnetic properties dependence on electric field strength and gain evidence that viruses-sensors based on the magnetic field change could be created. The results obtained shed some light on the influence of -Ph-COOH substitution to magnetic properties of the nanodiamonds with the paramagnetic centre. In addition, we reveal how the magnetic properties of the above nanodiamond are changed in the presence of an electromagnetic field. To our knowledge, such kind investigations have not been published yet.

3. Materials and Methods

The structure of the nanodiamonds was studied by the Becke's three-parameter hybrid functional, applying the non-local correlation provided by Lee, Yang, and Parr (B3LYP) (Becke, 1993 a), i.e. a representative standard DFT method with the 6-31G basis set (Ditchfield et al.1971). The initial structures of nanodiamons under study, possessing elsewhere described crystalline structure of the diamonds. The nanodiamond investigated theoretically consist of 60 C atoms. The total number of the nanodiamond structures modeled and investigated is 12. The structures are different because the defect is in symmetrically different places of the nanodiamond under investigation. The structure of each nanoparticle under the study was optimized without any symmetry constraint. The lowest total energy is obtained taking into account zero-point energy corrections. This energy was approached to select the most probable structure for further investigation. The 12 different structures with benzoic acid (-Ph-COOH) substituent were modeled to obtain the most probable location of them. Actually, all possible different structures of our model used have been created. The above-described procedure for the searching the most probable compound was repeated. Then, the selected structure with the substituent was investigated to evaluate their magnetic properties in electric field. The selected structure with and without a finite field added to the calculation was optimized without any symmetry constraints. An electric dipole field an electric dipole field in the X direction of 0.001 au - 0.026 au was applied to model the electric field influence to magnetic properties of the nanodiamonds. The magnetic susceptibility, indicating the degree of magnetization of a material in response to an applied magnetic field, was evaluated, too. The results of the geometry optimization allowed us to predict the geometric structure changeability due to irradiation and foreseen possibility to used nanodiamonds with adducts for new approach for security. The Gaussian program packages have been applied here (Frisch et al., 2004).

4. Results and Discussion

The results of our investigation indicate that the surface of the nanodiamond if it is not covered by a 'protected layer, possesses disordered form, i.e. it is covered by amorphous carbons, i.e. sp^2 and sp^3 hybridized bonds are present. The relative sp^2 to sp^3 ratios obtained by counting the number of carbon atoms with three bonded neighbors versus those with four bonded neighbors are equal to 25/12. This ratio indicates tetrahedral amorphous carbon on the nanodiamond surface. It is necessary to mention some carbons on the surface of the nanoparticle possessing two neighbor atoms. Some of these atoms form only two or three (from possible four) bonds. It indicates that the nanodiamonds investigated possess atoms having unpaired valence electrons. It allows us to conclude, that the surface of nanodiamonds is covered by polycrystalline materials of diamond or graphite within amorphous carbon. On the other hand, the presence of the atoms with unpaired electrons indicates nanodiamonds as highly chemically reactive towards other substances or even themselves: the surface derivatives could spontaneously dimerize or polymerize. Therefore, it is not a surprise that the N defect is located on the surface of the nanodiamond in the most stable structure obtained and its surface is often covered by hydrogen atoms (Figure 1). On the other hand, this result indicates the possibility of nanodiamond bonding with various species.

We pay attention that the impurities such as nitrogen are implemented to nanodiamonds to improve their magnetic properties because of the unpaired electron, and as consequence, unpaired spin presence because N atom is electron donor in respect of carbon. However, the bonding of two open-shell systems leads usually to the formation of the close shell one. It indicates that nanodiamonds with N impurities substituted by benzoic acid could not have unpaired electrons and lost their magnetic properties. To be sure that there is no other reason for the unpaired electron presence, we have obtained and compared the total energy values of the investigated compound with different multiplicity (M), i.e. a different number of possible orientations of the total spin relative to the total orbital angular momentum to foresee the number of near–degenerate levels that differ only in their spin-orbit interaction energy.

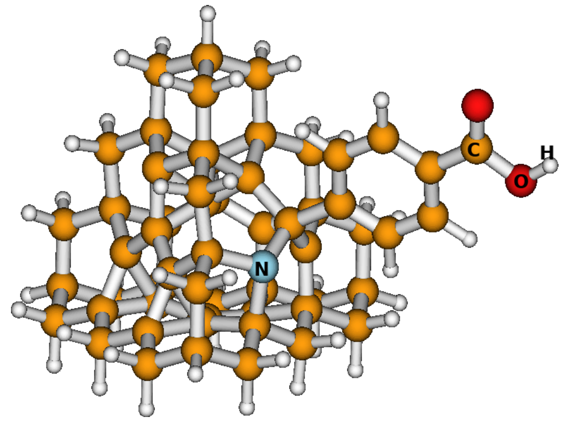

Figure 1. A view of the nanodiamond structure with nitrogen impurity and benzoic acid.

The compounds when M=1, 3, 5 were investigated. The total energy of the compound under study when M=5 is 3.30 eV and higher than that of others and indicates that this electronic state of these compounds is impossible. Additionally, these values reveal higher stability of the compound investigated with multiplicity 3, i.e the total spin S = 1 (Figure 2). Hence, two unpaired electrons filling of degenerate orbitals take place in our investigated compound. It could be due to a static electric field produced by a surrounding charge distribution (anion neighbors). It is interesting, that compound understudy with unpaired electrons remain more stable than that without them (Figure 2) – the total energy of the compound with multiplicity 3 remains lower than that of M=1 Moreover, the external dipole electric field influences the stability of nanodiamonds substituted by benzoic acid what indicate the total energy dependence on this field strength (Figure 2) – within increasing this field strength, the total energy of the compound under study decrease.

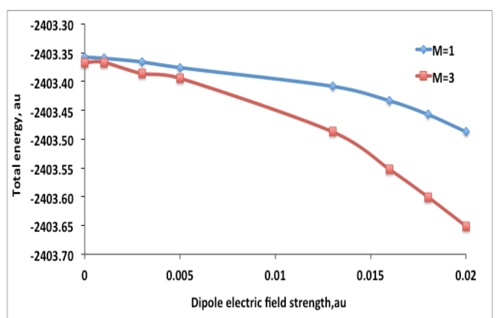

Figure 2. The total energy of the nanodiamond under study dependence on dipole electric field strength and multiplicity.

We obtain, that the nanodiamond substituted by benzoic acid is diamagnetic, which indicates the negative value of magnetic susceptibility obtained by us (Figure 3). In an external dipole magnetic field that strength is higher than 0.003 au, the nanodiamond investigated becomes paramagnetic. The value of magnetic susceptibility rapidly increases with the increase of electric field strength (Figure 3).

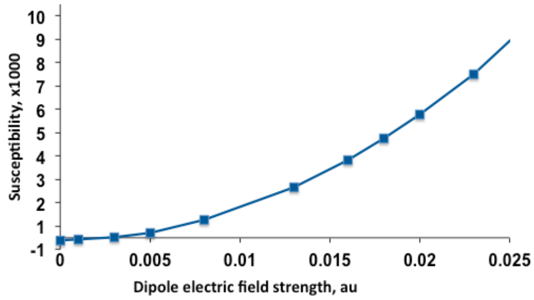

Figure 3. The dependence of magnetic susceptibility on external electric dipole field strength.

Meanwhile, the calculated g-shifts relative to the free-electron yielding significant information about the bound state environment of unpaired electrons, their interactions with an external magnetic field, are presented in Table 1.

Referring to the results presented, we speculate that the spins of the unpaired electrons quenched due to their position in respect to each other. In the external dipole electric field, the electrons are oriented such that spin quenching gradually disappeared.

Table 1. The values of g shifts relative to the free electron (ppm).

Dipole electric field strength	XX	YY	ZZ
0	-1424.2	161.7	418.5
0.001	-1411.9	165	394.4
0.003	-1378.6	166.7	346.8
0.005	-1333.4	177.2	265
0.008	-1170.9	-532.1	201.7
0.013	-1553.3	218	3835.6
0.016	-1524.7	148.3	3489.1
0.018	-1504.4	104.1	3220.5
0.02	-1427.1	14.2	2917.8
0.023	-1433.8	62.9	2455.4
0.026	-2151.8	-1659.4	2755.4

This speculation is proved by the analysis of the geometric structure of the compound at their equilibrium point obtained during the full geometry optimization procedure. These results exhibit the insignificant change of bond length and bond angles and remarkable changes of the electronic structure of the compound under study due to dipole electric field impact. (Figure 4).

In Figure 4 we depicted the gap between the highest singlet occupied (SOMO) and lowest unoccupied (LUMO) molecular orbitals dependence on dipole electric field to demonstrate that the electronic structure of the compound investigated is changed. The presence of SOMO-LUMO gap maxima and minima, as well as different values of g shift, could indicate molecular orbitals splitting due to electric field impact that leads to the appearance of additional unpaired electrons and, as consequence, improving magnetic properties of nanodiamond with a substituent.

Let us remind the main results of investigations of the compound that could represent the nanodiamond and hydrogenated one with paramagnetic center substituted by benzoic acid:

- Compound investigated is highly chemically reactive towards other substances or even themselves.
- The unpaired electrons filling of degenerate orbitals take place even in the hydrogenated compound with substitution.
- The magnetic susceptibility rapidly increases with an increase in electric field strength.

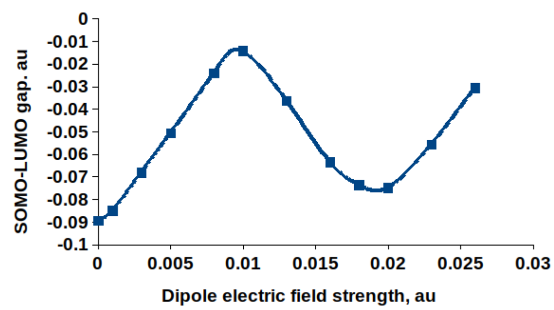

Figure 4. The dependence of SOMO-LUMO gap of the compound investigated on external electric dipole field strength.

These findings allow us to predict the possibility to create a biosensor employing a nanodiamond with a paramagnetic center. When the proposed biosensor had been used, the biological interactions would be detected by using an electric field and measuring changes in magnetic properties or magnetically induced effects such as changes in coil inductance, resistance, or magneto-optical properties.

5. Conclusions

We present here our performed investigation on hydrogenated diamond nanocrystal with paramagnetic center (nitrogen atom defect) and substituted by benzoic acid (-Ph-COOH) to exhibit their magnetic properties dependence on electric field strength and gain evidence that viruses-sensors based on the magnetic properties or magnetically induced effects could be created.

We found that the compound investigated is highly chemically reactive towards other substances or even themselves. The surface of this compound could be covered by polycrystalline materials of diamond or graphite within amorphous carbons. On the other hand, it could be hydrogenated. The hydrogenated compound with nitrogen defect substituted by benzoic acid possesses unpaired valence electrons. However, only in an electric field, that strength is higher than

0.003 au, the compound exhibit ferromagnetic properties.

Referring to the results obtained we predict the possibility to create a biosensor employing nanodiamond with a paramagnetic center.

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