Sensor activity of titanium dioxide nanotubes in relation to acetone molecules

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Abstract. This paper presents the theoretical study results of the possibility of acetone, common volatile organic compound (VOCs) in human respiration, with titanium dioxide nanotubes. The efficiency of interaction of the acetone molecule with the TiO₂ nanotube is analyzed. Recommendations for the creation of highly sensitive sensor devices using titanium dioxide nanotubes for diagnostics of various diseases have been developed.

1. Introduction

Currently, nanotubes made of titanium dioxide are actively studied by scientists around the world. This is due to the possibility of their use in many areas of medicine, electronic engineering and nanoelectronics, the creation of filters and portable sensors of a new generation. The interest is primarily due to the relative ease and variability of creating such structures, as well as useful properties, such as high photocatalytic and sensory activity, biocompatibility, etc. [1-5].

Nanotubes and nanofibers, including titanium dioxide, have a special advantage, since they provide ready access of interacting substances to a high surface area [6]. The use of these materials varies from household to strategic areas. Creating efficient and less energy-consuming devices is the most relevant issue today. One of them is the application of gas sensors using titanium dioxide nanotubes [7-8].

Technologies for creating and using thin films made of titanium dioxide nanotubes as highly sensitive sensors are described in [9-11]. The ability to detect the studied gases at low temperatures and in minimal concentrations is shown, which is extremely important in the analysis of volatile organic compounds (VOCs).

It is known that the exhalation of a person contains many volatile organic compounds. Due to the fact that one of the lungs’ function is the release, the composition of the exhaled air is different in normal and pathological conditions. Metabolic disorders typical of diabetes mellitus are caused by an increased content of acetone in the exhaled air. Acetone (C₃H₆O) is one of the most common VOCs in the respiratory system with concentrations in healthy people in the range of 300-900 parts per billion. Abnormal concentrations exceed 1800 parts per billion. Thus, the selective detection of acetone in the breath is very important for the diagnosis of diseases in a non-invasive way.

However, to date, inexpensive portable gas sensors for breath analysis, especially for clinical diagnostics and monitoring, have not been developed, which can be an alternative to the complex spectrometric systems used. This work is devoted to the study of sensory interaction of an acetone molecule with the surface of titanium dioxide nanotubes. It can be used in devices for analyzing exhaled air and will contribute to the development of diagnostic technologies in medicine.
Theoretical calculations were carried out using one of the most common research methods - density functional theory (DFT), described by Koch and Holthausen [12] using the molecular cluster model.

2. Methods
According to Density Functional Theory, the properties of a many-electron system including energy, can be defined by using an electron density functional. The system is described by electronic density as:

\[ \rho(r) = \int |\psi|^2 d\sigma_x d\sigma_y \ldots d\sigma_z \]

Function is defined in all space. The integral from electronic density on all space gives full number of electrons. Kinetic energy of electrons is described obviously in approach of independent particles, a classical part of potential energy is described on Coulomb's law. Exchange and electronic correlation are considered approximately.

Electronic correlation – the effect caused by instant Coulomb repulsion between electrons. Its account results in lower value of total energy of a system. The specified effect is not considered in Hartree-Fock's method. The energy change caused by these instant Coulomb interactions is called energy of correlation:

\[ E_{cor} = E_{ex} - E_{HF} < 0 \] (2)

Accounting of electronic correlation is especially important at a research of the effects depending on the excited states or which are not clear described in one-determinant approach.

Practical application of DFT resulted in two theorems proved by Hoenberg and Kohn in 1964 and generalized then several authors. The first theorem claims that any property of the main condition of this system is described only by electronic density \( \rho(r) \). It is important to emphasize that this theorem is proved only for the main condition of a molecule and, strictly speaking, DFT is not the exact theory for the excited states. The second theorem establishes the variation principle in DFT: if \( E_0 \) is exact energy of the main state, then for any other electronic density \( \rho \), which can be also approach to the true electronic density of the main state, the ratio of \( E[\rho] \geq E_0 \). This statement, as well as in the methods based on wave function gives a method of stay \( E_0 \) and the corresponding density.

In general, DFT has an excellent ratio of accuracy and computing expenses that allow using this method for solving a huge number of problems of a quantum-chemical research.

3. Results and discussion

3.1. Sensory activity to the side surface of the titanium dioxide nanotube in relation to the acetone molecule
Quantum-chemical modeling of titanium dioxide nanotubes is discussed in detail in [13]. We selected a cluster of three-layer TiO\(_2\) nanotubes of type (6,0), with a diameter of 7 Å, whose open boundaries were closed by pseudoatoms, which were chosen as hydrogen atoms. Modeling of the interaction of a nanotube with an acetone molecule was carried out by step-by-step approximation of the C\(_3\)H\(_6\)O molecule to the oxygen atom of the tube surface located in the middle of the cluster, along the perpendicular to the longitudinal axis of the TiO\(_2\) tubulene. The acetone molecule was oriented to the surface by an oxygen (refer with figure 1).

As a result of the calculations, the surface profile of the potential energy of the system "TiO\(_2\) + C\(_3\)H\(_6\)O nanotube" was constructed (refer with figure 2).
Figure 1. A model of a TiO$_2$ nanotube with a C$_3$H$_6$O acetone molecule.

Figure 2. The energy curve of the interaction of the TiO$_2$ nanotube with the C$_3$H$_6$O acetone molecule.

The energy curve has a minimum at a distance of 3 Å, and the interaction energy is -0.4 eV. This indicates the possibility of an interaction between a titanium dioxide (TiO$_2$) nanotube and an acetone (C$_3$H$_6$O) molecule, which can be called physical adsorption.

3.2. Sensory activity to the end surface of the titanium dioxide nanotube in relation to the acetone molecule

To study the sorption interaction of the end surface of a titanium dioxide nanotube with an acetone (C$_3$H$_6$O) molecule, a molecular cluster of a semi-infinite nanotube was considered, one boundary of which remained open, and the broken bonds at the second boundary were closed by hydrogen pseudoatoms. The interaction was modeled by step-by-step approximation of the acetone molecule to the oxygen atom at the open boundary of the nanotube oriented by the oxygen atom along a straight line parallel to the longitudinal axis of the tube (refer with figure 3). The calculations made it possible to construct an energy interaction curve (refer with figure 4).

Figure 3. A model of a TiO$_2$ nanotube with a C$_3$H$_6$O acetone molecule.

Figure 4. The energy curve of the interaction of the TiO$_2$ nanotube with the C$_3$H$_6$O acetone molecule.

In this case, the characteristic energy minimum was not detected, which indicates the absence of sensory sensitivity of the end of the titanium dioxide nanotube to the acetone molecule.

4. Conclusion

Theoretical studies of the interaction of titanium dioxide nanotubes with an acetone molecule have proved the possibility of creating highly sensitive sensors. These sensors can be used for non-invasive diagnostics of human diseases by analyzing the exhaled air; for example, for the diagnosis of diabetes mellitus.
Nanotubes based on titanium dioxide can be chemical and biological sensors that can detect micro-quantities of a substance. The specified interaction geometry will ensure high accuracy and selectivity of the detection of acetone in a complex mixture of gases, vapors and other volatile organic compounds present in the exhaled air. Taking into account these features of functioning, it is worth noting the importance of creating a device with a sensor based on titanium dioxide nanotubes for non-contact diagnosis of diabetes mellitus.

5. References

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