Study of electrical and optical properties of a new composite material based on carbon nanotubes and titanium oxide

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Abstract. In this regard, the aim of this work is to study the features of the atomic structure and to predict the electronic energy characteristics of the composite material based on carbon nanotube and ceramic particles – titanium oxide using computer simulation methods. To achieve this goal, the following tasks were solved: construction of a geometric model of the rutile nanoparticle; identification of the energy-stable configuration of the composite based on the carbon nanotube and rutile nanoparticles; determination of the electron-energy characteristics of the composite. The structure of the composite was selected so that the total energy of the composite in absolute value was less than that of the individual tube and rutile the enthalpy of the reaction of the tube and rutile becomes negative, which means that the formation of such a nanocomposite is energetically advantageous. One of the most important applications of such composite is to act as photocatalyst for some chemical reactions because of electrical characteristics and high optical absorption.

1. Introduction
Nanostructured optoelectronic components offer large market potentials in the future, e.g. for optical data communication or in the range of consumer electronics (for example mobile and television screens) [1]. Since the discovery of carbon nanotubes began to develop new technological areas aimed at expanding the boundaries of the applicability of existing materials. Consequently, the development of composites based on carbon nanotubes and ceramics is one of the urgent tasks of modern materials science. Recently, ceramics consisting of titanium atoms have been actively used. This is because titanium has been widely used in medicine for many years. The advantage of this material is the strength, corrosion resistance, and high biological compatibility of titanium and its main alloys with living tissue. The above data indicate the relevance of studies of the composite based on carbon nanotubes and ceramic particles. In the process of finding the applied fields of application of new composite materials of paramount importance is the determination of the energetically stable configurations of the material and the study of its physico-chemical properties [2].

2. Atomic structure of rutile nanoparticles
Currently, titanium oxide is a multifunctional material that is used in a wide range of technological fields. In particular, due to its surface properties, titanium dioxide plays a key role in the creation of a number of electronic devices [3,4]. As a crystallographic variety of titanium oxide, we consider the rutile structure with the most stable configuration. In this study, the rutile unit cell presented in
Among the variety of rutile surfaces, preference is given to low-index surfaces (110), (100) and (001) because of their high stability. The most stable surface is rutile (110), which is confirmed by theoretical and experimental studies. The rutile nanoparticle with the surface (110) constructed on the basis of the presented unit cell is also shown in figures 1, 2.

![Figure 1. The unit cell of rutile (TiO₂).](image)

![Figure 2. Atomic structure of rutile nanoparticles.](image)

3. Energy stability of the composite based on carbon nanotube and rutile

The search for a stable configuration of the atomic structure of a nanocomposite based on carbon nanotube and rutile was carried out in two stages. The first stage consisted in the selection of optimal from the energy point of view of the geometric parameters of the nanotube (length and diameter) for the composite. The second stage consisted in choosing the most optimal in terms of the energy of the tube and rutile connection in the composite [5, 6].

The initial model of the composite studied in this work was a structure of a carbon nanotube armchair (5.5) with a diameter of 7.2 Å and a length of 16 Å and a nanoparticle rutile (110) consisting of 254 atoms. The equilibrium configuration of the atomic structure of the carbon nanotube (5.5) and the equilibrium configuration of the rutile nanoparticle were found using the quantum chemical method of strong coupling. The nanotube and the rutile particle were connected by four C–O bonds arranged in one row. The tube was attached to the upper row of titanium atoms located in the center of the rutile surface. The atomic structure of the resulting composite is shown in figure 3.
Figure 3. The first stage is the selection of the optimal geometry of the nanotube for the composite compound, the Initial atomistic model of the nanotube-rutile composite. Structural elements of the composite. Armchair nanotubes (5.5) diameter 7.2 Å; length 16 Å. Rutile (TiO2) Length 16.6 Å; Width 11.5 Å; Height 7 Å.

The energy stability of the composite will be characterized by a change in the total energy of the system $E$, determined by the formula

$$E_{\text{atom}} (eV) = \frac{E_{\text{composite}} - E_{\text{TiO}_2} - E_{\text{tube}}}{N_{\text{atom}}}$$

where $E_{\text{composite}}$ – energy composite, $E_{\text{TiO}_2}$ – энергия наночастицы рутила, $E_{\text{tube}}$ – energy of the nanoparticles of rutile, $N_{\text{atom}}$ – is the atom number of atoms in the composite. The structure of the composite was selected so that the total energy of the composite in absolute value was less than that of the individual tube and rutile. To do this, the diameter of the connecting tube varied in the selected range of values [7, 8].

For figure 4 graph of the dependence of the total energy of the composite on the diameter of nanotubes is presented. The graph shows that with the increase in the diameter of the nanotube, the enthalpy of the reaction between the tube and the rutile nanoparticle, determined by the change in the total energy of the composite structure, monotonically decreases. For nanocomposites based on a nanotube with a diameter of 8.2 Å (7.7) and above, the enthalpy of the reaction of the tube and rutile becomes negative, which means that the formation of such a nanocomposite is energetically advantageous[9,10].

As part of the second stage of the study of the energy stability of the nanotube-rutile composite, various options for joining rutile to the nanotube were considered (see figure 5). The number of C–O chemical bonds and their location varied. The theoretical study found that the energy stability of the nanotube-rutile composite can be increased by attaching rutile to the nanotube using eight C–O bonds with a length of 3.16 Å, arranged in two rows of 4 bonds each. It is shown that the enthalpy of the reaction of formation of such a compound is $-24 \text{ eV}$ [11, 12].
Figure 4. Graph of the enthalpy dependence of the composite formation reaction ased on carbon nanotube and rutile on the diameter of the nanotube.

Figure 5. The second stage – the choice of the optimal method of connecting the structural elements of the composite. The amount of energy change method composites for this connection nanotubes and rutile using eight C-O bonds was $-24 \text{ eV}$.

Then, we investigated the electron-energy characteristics of the resulting energy-stable composite. The ionization potential and the energy gap determined by the electron spectrum were considered as electron-energy characteristics [13]. The electronic spectrum of the composite was calculated using the strong coupling method. This slide shows a diagram of the energy levels with an indication of the energy gap and the ionization potential. The ionization potential is at the last filled energy level (HOMO), and the energy gap as the interval between the last filled (HOMO) and the first vacant level (LUMO) [14].
Figure 6. Electron-energy characteristics of the composite based on nanotube and rutile.

In table 1 calculations are presented, which show the calculated values of the ionization potential and energy gap for the composite, as well as separately for the tube and rutile. From the tabular data it can be seen that the electron-energy characteristics of the formed composite completely coincide with the similar characteristics of rutile.

Table 1. Electron-energy characteristics of the studied composite and its structural elements.

| Structure                  | IP, eV | IP, eV |
|----------------------------|--------|--------|
| Rutile                     | −6.9   | 0      |
| Nanotube                   | −6.1   | 0.03   |
| Composite nanotube + rutile| −6.9   | 0      |

In this work, we have calculated the density distribution of electronic States (DOS) for the composite nanotube-rutile and separately for the handset and rutile. Figure 7 shows the DOS of rutile nanoparticles. The figure shows the presence of three characteristic peaks of decreasing intensity. The highest density of States is characteristic for the valence band [15].

Figure 8 shows the DOS of the carbon nanotubes (7,7). The figure shows the presence of sharp peaks in the conduction band near the HOMO level, but the total intensity of the peaks for the tube is less than the intensity of the peaks for rutile.

Figure 9 shows the DOS of the composite nanotube-rutile. The figure shows that the nature of the DOS distribution for the composite repeats the dependence obtained for rutile. Consequently, the composite completely adopts the electronic structure of rutile.

4. Summaries
The following results were obtained during the theoretical study of the Studying the electrical and optical properties of titanium carbon nanotubes supported by titanium oxide (rutile):

- Atomistic model of rutile nanoparticle is constructed.
- The model of the composite based on carbon nanotubes was considered in the paper, since in practice the technology of carbon nanotube synthesis is easily implemented and allows obtaining materials on an industrial scale.
- Titanium dioxide was considered as a representative of ceramic materials in our work, since rutile is currently one of the most durable ceramic materials and has high biocompatibility, which makes it a promising candidate for creating highly sensitive touch devices and manufacturing photovoltaic devices for optical electronics.
- The tight-binding method used in this work makes it possible to estimate with high precision both the geometric parameters of the structure and the energy parameters. Also, the strong coupling method allows us to investigate the electronic structure of the material, which is inaccessible for study, for example, by empirical methods.
For the calculation of DOS, the energy spectrum of curvilinear graphene was constructed, in which the energy of each molecular orbital was represented as a spectral line. In this case, the intensities of all lines were taken equal to unity. Then, each line was replaced by a Gaussian distribution with a half width at a given half-height of 0.1 eV. The intensities of all distributions at each energy value were added.

- Determined the energetically stable configuration of the composite.
- The dependence of the energy stability of the composite from the geometric parameters of the nanotubes. It is shown that in this study the most stable configuration is characterized by a composite formed of rutile nanoparticles (254 atoms) and nanotubes 16 Å long and 9.5 Å in diameter.
- The optimal way of connecting nanotube and rutile in the composite is found from the point of view of energy stability. It is established that the compound of nanotube and rutile with the help of eight chemical bonds C–O in 2 rows of 4 bonds in each will contribute to the increase in the energy stability of the composite.

It is found that in the density distribution it is shown that the nanotube-rutile composite is characterized by electron-energy characteristics inherent to a greater extent to the rutile nanoparticle.

- It is established that the energy stable composite is characterized by the ionization potential of 6.9 eV and the absence of an energy gap; the electronic States of the composite are observed to redistribute the peaks of intense energy in the energy range near the HOMO level.
5. References

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