

INTERACTION OF GRAPHENE - CALCIUM COMPOUND WITH TITANIUM DIOXIDE CLUSTERS: AN AB INITIO STUDY¹

INTERAÇÃO DO COMPOSTO GRAFENO-CÁLCIO COM CLUSTERS DE DIÓXIDO DE TITÂNIO: UM ESTUDO DE PRIMEIROS PRINCÍPIOS

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ABSTRACT

Titanium dental implants are frequently used, however, in some cases, their utilization results in problems related to inflammations on the tissue. Hence, studies have proposed the use of nanostructures to increase the success rate of the implant. In this work we have studied, through first principles calculations based on the density functional theory, the interaction of the compound graphene-calcium with titanium dioxide clusters $(\text{TiO}_2)_n$, where n varies from 1 to 3. Graphene was chosen due to its potential applications in several areas of knowledge while the calcium atom is one of the main components of the bones. The obtained results showed a strong interaction between the graphene-calcium system and the $(\text{TiO}_2)_n$ clusters. The calculated values for the adsorption energies vary from 2.41 eV to 4.70 eV. Although the results found have a theoretical character, the graphene-calcium compound is a relevant candidate for the creation of thin films to be used as coating for titanium dental implants.

Keywords: density functional theory, thin films, titanium dental implants.

RESUMO

Implantes dentários de titânio são utilizados há diversos anos na implantodontia. Contudo, em alguns casos, sua utilização tem resultado em problemas relacionados a inflamações no tecido. Devido a isso, estudos da literatura propõem o uso de nanoestruturas com o intuito de aumentar a taxa de sucesso do implante. Neste trabalho estudamos, por meio de cálculos de primeiros princípios baseados na teoria do funcional da densidade, a interação do composto grafeno-cálcio com clusters de dióxido de titânio $(\text{TiO}_2)_n$, com n variando de 1 a 3. O grafeno foi escolhido por ser uma nanoestrutura promissora em diversas áreas de pesquisa, enquanto o cálcio por ser um dos principais componentes dos ossos. A utilização dos clusters de dióxido de titânio se deve ao fato de que a superfície de um implante de titânio, em geral, encontra-se recoberta por óxidos. Os resultados obtidos mostraram que uma interação forte se estabelece entre o sistema grafeno-cálcio e os clusters de $(\text{TiO}_2)_n$. Os valores calculados para as energias de adsorção variam de 2,41 eV a 4,70 eV. Embora os resultados encontrados possuam um caráter teórico, o composto grafeno-cálcio mostra-se um candidato relevante para a criação de filmes finos, a serem utilizados como revestimento de implantes dentários de titânio.

Palavras-chave: teoria do funcional da densidade, filmes finos, implantes dentários de titânio.

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INTRODUCTION

Titanium dental implants are the most used ones because of their biocompatible and structural characteristics. However, the success of its use is not observed in 100% of cases. Buser et al. (2012) evaluated 511 individuals who had titanium implants and in 3% of the cases, some complications were observed. In this sense, a lot of effort has been done by the scientific community in order to create structures that facilitate tissue recovery. Nanotechnology has been considered a promising alternative in this particular area, since dental implants coated with nanomaterials could facilitate the recovery of bone tissue as well as its adhesion to it. Some implant coatings based on nanostructures have already been reported in literature, such as implants coated with silver nanoparticles, which facilitated adhesion (JIN et al., 2014); implants coated with zinc oxide nanoparticles, which showed antibacterial effect (MEMARZADEH et al., 2015) and implants coated with titanium dioxide nanotubes, in which antibacterial effects and cellular compatibility were observed (LIU et al., 2014).

A nanomaterial that has been extensively studied recently is the graphene. Its peculiar characteristics have been explored in several areas of knowledge, such as in regenerative medicine (BRESSAN et al., 2014); in drug transport (YAO et al., 2012); in the production of solar cells (SAHOO et al., 2012); in sensors (PUMERA et al., 2010), etc. The graphene, discovered in 2004 (NOVOSELOV et al., 2004), is a two-dimensional structure, constituted by a single layer of carbons, arranged in benzene rings with sp^2 hybridization (GEIM; NOVOSELOV, 2007). Its high mechanical resistance (LEE et al., 2008) and biocompatibility with some specific cells, such as fibroblasts (CHEN et al., 2008), makes it a potential candidate for implant applications.

In order to investigate the possibility of using graphene as a coating for dental titanium implants, in this work we study, through calculations of first principles based on the Functional Density Theory (DFT), the interaction of the graphene-calcium compound (graf+Ca) with titanium dioxide clusters. The insertion of Ca atoms in graphene is justified because it is one of the main components of bones and teeth (HAYNES, 2015). Titanium implants are represented by TiO_2 clusters since, in general, the surfaces of titanium implants are covered by various titanium oxides, usually TiO_2 as the most common (PALMQUIST et al., 2010).

MATERIAL AND METHODS

The simulations were performed using the SIESTA code (Spanish Initiative for Electronic Simulations with Thousand of Atoms) (SOLER et al., 2002), which is based on DFT (HOHENBERG; KOHN, 1964). The exchange-correlation term was described by the generalized gradient approximation (GGA) (PERDEW; BURKE; ERNZERHOF, 1996), and the interactions between the electrons of the valence shell and the core electrons were treated within the pseudopotential method (TROULLIER;

MARTINS, 1991). The Kohn-Sham orbitals were expanded on a double- ζ basis plus a polarization function (DZP). In our calculations, we used a graphene with 144 carbon atoms inserted in a simulation box with the following dimensions: 25.94 Å x 40.00 Å x 14.98 Å. The calcium atom used is characterized as a neutral atom, with 2 electrons in its valence shell. The adsorption energies of the interacting systems were calculated using the base set superposition error (BSSE) (BOYS; BERNARDI, 1970):

$$E_{ads}^{BSSE} = - [E_{A+B} - (E_A^{ghost} + E_B^{ghost})], \quad (1)$$

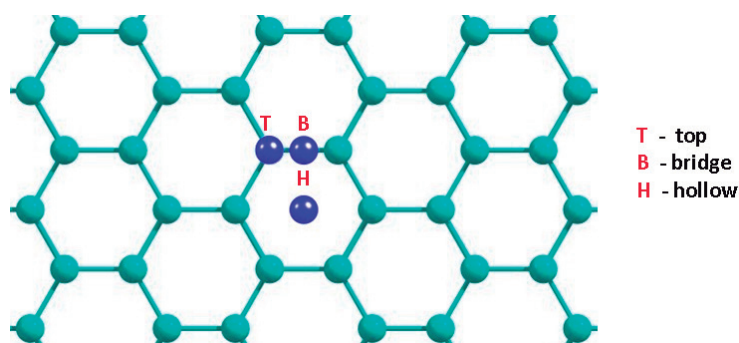
where E_{ads}^{BSSE} is the total interaction energy of structures A and B; E_{A+B} the total energy of the structures A + B; E_A^{ghost} the total energy of the isolated structure A, considering the basis functions of B, but not the presence of the atoms; E_B^{ghost} the total energy of the isolated B structure, considering the basis functions of A, but not the presence of the atoms. Positive values obtained by equation (1) establish an attraction between the structures whereas negative values indicate repulsion between the structures.

RESULTS AND DISCUSSIONS

ADSORPTION OF CALCIUM ON THE SURFACE GRAPHENE

Initially, the adsorption of Ca on the surface of the graphene was carried out. We considered only one calcium atom per unit cell and tested three distinct sites for adsorption: top, bridge and hollow (CHAN; NEATON; COHEN, 2008). Figure 1 shows the three configurations tested. In the top site, the Ca atom was positioned above one of the C atoms; in the bridge site, the Ca atom was positioned above the C-C bond and in the hollow site, the calcium atom was positioned above the center of the benzene ring.

Figure 1 - Adsorption sites for the Ca atom on graphene.

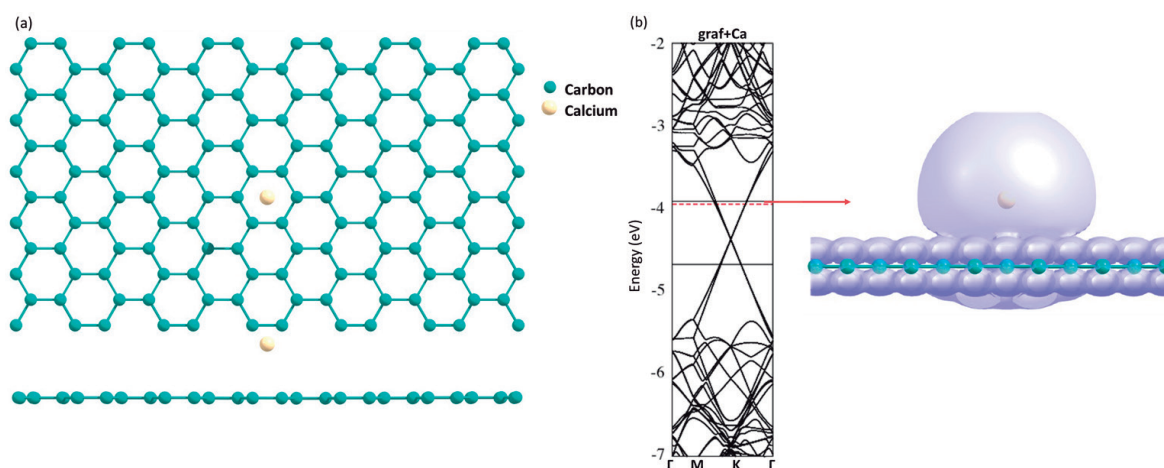


Source: Author's construction.

Among the 3 sites tested, the Ca atom showed to be more stable in the hollow site, at a distance of 3.02 Å from the nearest carbon atom, which is in agreement with the literature results (BEHESHTI;

NOJEH; SERVATI, 2011; CHAN; NEATON; COHEN, 2008; MA et al., 2014; NAKADA; ISHII, 2011). For the most stable configuration of Ca adsorption on graphene, its band structure and the electron density close to the Fermi level are shown in figure 2. As it can be seen, the adsorption of the Ca atom made the final compound into a metallic character material, different from the graphene that has a semiconductor material. The adsorption energy found for this configuration was 0.24 eV.

Figure 2 - (a) Optimized geometry of the most stable configuration adsorption of a unique atom of calcium in graphene in two different views; (b) band structure and electronic charge density of this configuration. The isosurface value used was $0.00005 e/\text{\AA}^3$.

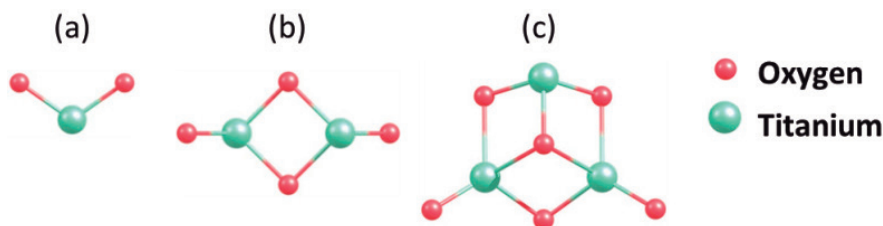


Source: Author's construction.

INTERACTION OF GRAPHENE-CALCIUM COMPOUND WITH TITANIUM DIOXIDE CLUSTERS

For the study of the interaction of the graf+Ca compound with TiO₂ clusters, we start from the optimized geometry of this system that was previously described. Before this, clusters of (TiO₂)_n, with *n* varying from 1 to 3, whose atomic arrangement was constructed according to the work of Qu and Kroes (2006), were optimized according to the methodology of this work. Figure 3 shows the optimized geometry of the studied clusters.

Figure 3 - Optimized configurations of the (TiO₂)_n clusters, where (a) (TiO₂)₁, (b) (TiO₂)₂ e (c) (TiO₂)₃.



Source: Author's construction.

Graf+Ca compound interaction with $(\text{TiO}_2)_1$ cluster

In order to investigate the interaction of the graf+Ca compound with the $(\text{TiO}_2)_1$ cluster it was necessary to determine the configuration that minimizes the total energy of the system. The cluster was then approached by five distinct configurations. The difference between each configuration is due to the positioning of the cluster over the adsorbed atom (hollow site) on the graphene. The bond distances, adsorption energy and charge transfer of the configurations are listed in table 1.

In all studied interactions, the cluster approached the Ca atom to the graphene. Before the optimization, the graf+Ca distance was 3.02 Å, while after the structural relaxation, the distance decreased to approximately 2.8 Å. Such behavior, however, was not exhibited in configuration 1. Again, except for configuration 1, there was a charge transfer from the graf+Ca compound to the cluster.

Table 1 - Bond distances between the C atom and the Ca atom (in Å); bond distances between the cluster and the Ca atom (in Å); adsorption energy (in eV) of the interaction of the compound (graf+Ca) and the $(\text{TiO}_2)_1$ cluster and charge transfer between the studied systems.

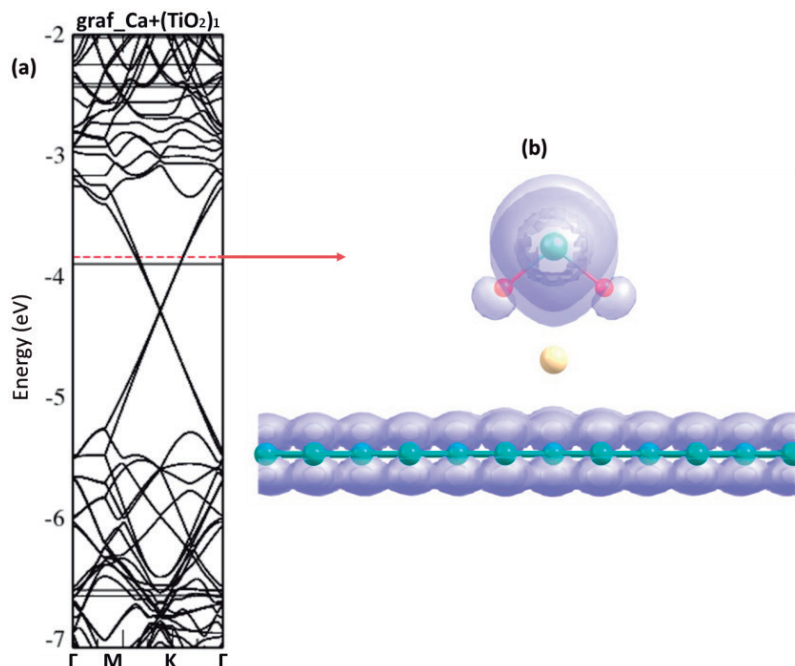
Conf.	$d_{\text{Ca-C}}$ (Å)	$d_{\text{cl-Ca}}$ (Å)	(eV)	Δq (e)
1	3.09	3.48	0.50	-0.02
2	2.79	2.32	3.26	0.56
3	2.82	2.33	3.28	0.55
4	2.84	2.33	2.41	0.56
5	2.83	2.33	3.46	0.55

Source: Author's construction.

From table 1, we observe that the configuration that showed the most stable energy was configuration 5, with an adsorption energy value equal to 3.46 eV. This high value indicates the presence of a chemical bond. For this configuration, the band structure and electric charge densities can be observed in figure 4.

According to figure 4 (a), the band structure of this configuration presented a flat level near the Fermi level from the cluster + Ca, similar to the band structure shown in figure 2 (b). The system has a metallic character, where the Fermi energy is located at approximately -3.90 eV. The electric charge density is concentrated on the cluster and on the graphene, according to figure 4 (b). It can still be observed that there is no charge density on the Ca atom, which may indicate that it has donated its electrons to the other structures.

Figure 4 - (a) Band structure and (b) electric charge density of the most stable configuration of the interaction between the graf+Ca compound and the $(\text{TiO}_2)_1$ cluster. The isosurface value used was $0.00005 \text{ e}/\text{\AA}^3$.



Source: Author's construction.

Graf+Ca compound interaction with $(\text{TiO}_2)_2$ cluster

For the interaction of the graf+Ca compound with the $(\text{TiO}_2)_2$ cluster, we consider three different configurations. In this case, notable structural changes were observed only in configuration 3, where, initially, the O atom in the center of the cluster was approximated to the compound and, after the optimization calculations, the O atom in the corner of the cluster is closer to the Ca atom.

The calculated values for the bond distances, adsorption energy and charge transfer are shown in table 2. For configurations 1 and 3, the cluster approximated the Ca atom to the graphene, as in the previous case of the $(\text{TiO}_2)_1$ cluster. For all 3 configurations, there was a charge transfer from graf+Ca to the cluster.

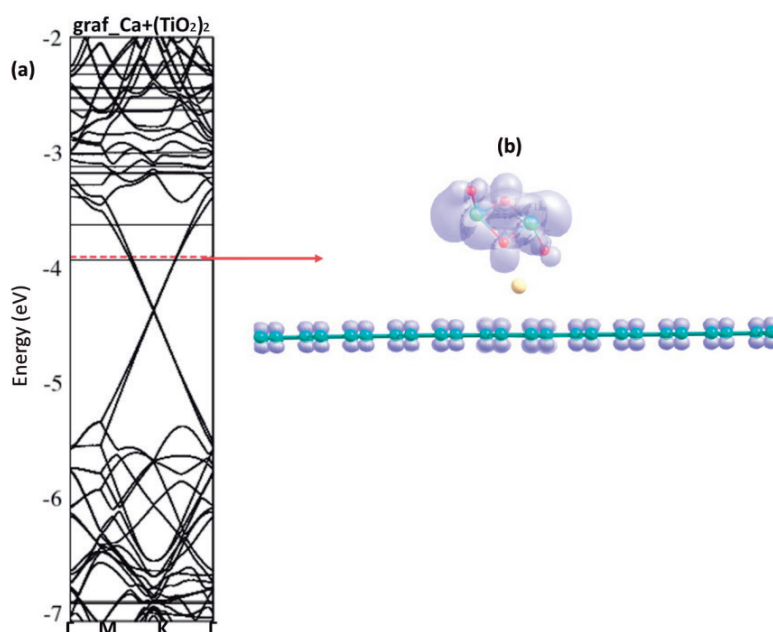
Table 2 - Bond distances between the C atom and the Ca atom (in \AA); bond distances between the cluster and the Ca atom (in \AA); adsorption energy (in eV) of the interaction of the compound (graf+Ca) and the $(\text{TiO}_2)_2$ cluster and charge transfer between the studied systems.

Conf.	$d_{\text{Ca-C}}$ (\AA)	$d_{\text{cl-Ca}}$ (\AA)	(eV)	Δq (e)
1	2.75	2.22	1.44	0.36
2	3.03	3.48	0.49	0.17
3	2.75	2.33	2.41	0.44

Source: Author's construction.

Configuration 3 presented the highest stability among the three analyzed configurations, with adsorption energy of 2.41 eV. Among these conformations, the one that presented the lowest adsorption energy value was the configuration 2, since it was the only one that tried to force interaction between two metallic atoms, Ti and Ca. The band structure and the electric charge densities of the most stable configuration can be seen in figure 5. As in the case of graf+Ca interacting with the $(\text{TiO}_2)_1$ cluster, the band structure shows that the system has a metallic character, where the Fermi energy is located around -3.90 eV. Again, in this case, the charge density is concentrated in the cluster and graphene.

Figure 5 - (a) Band structure and (b) electric charge density of the most stable configuration of the interaction between the graf+Ca compound and the $(\text{TiO}_2)_2$ cluster. The isosurface value used was $0.00005 \text{ e}/\text{\AA}^3$.



Source: Author's construction.

Graf+Ca compound interaction with $(\text{TiO}_2)_3$ cluster

Finally, we studied the interaction of the graphene-Ca compound interacting with the $(\text{TiO}_2)_3$ cluster. For this system, we tested six configurations. The calculated values for the bond distances, adsorption energy and charge transfer are shown in table 3. We observed some significant structural changes in configurations 2, 4 and 5, where both the O atoms of the extremities approached the Ca atom adsorbed on the graphene. These configurations are the ones that presented the highest adsorption energies between the studied configurations, as it can be seen in table 3.

Table 3 - Bond distances between the C atom and the Ca atom (in Å); bond distances between the cluster and the Ca atom (in Å); adsorption energy (in eV) of the interaction of the compound (graf+Ca) and the (TiO₂)₃ cluster and charge transfer between the studied systems.

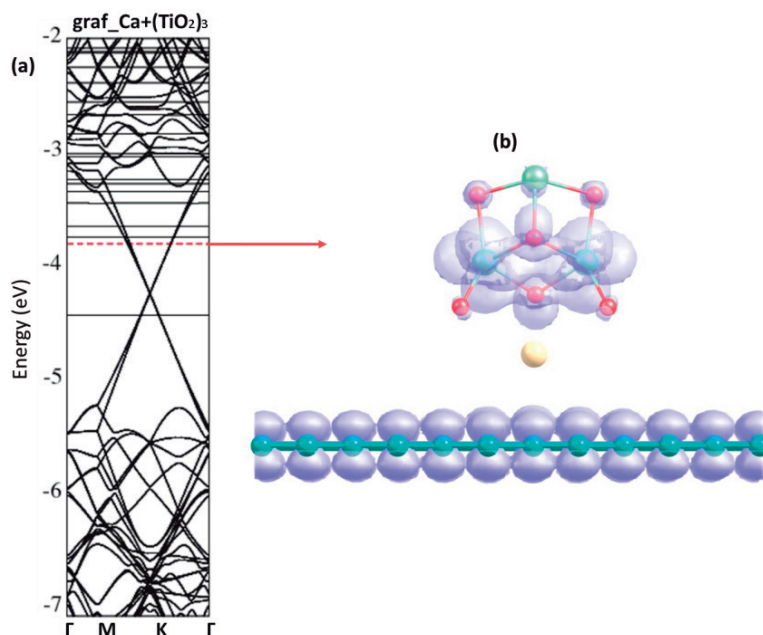
Conf.	$d_{\text{Ca-C}}$ (Å)	$d_{\text{cl-Ca}}$ (Å)	(eV)	Δq (e)
1	3.01	3.47	0.80	0.25
2	2.87	2.44	4.70	0.62
3	2.77	2.22	2.93	0.58
4	2.86	2.42	4.55	0.59
5	2.65	2.40	4.62	0.60
6	2.78	2.22	2.82	0.53

Source: Author's construction.

As we have already mentioned, the most stable systems were observed in configurations 2, 4 and 5, but with greater stability in configuration 2, where the value found for the adsorption energy was 4.7 eV. Also, it is possible to observe that the electrons flow is given from the graf+Ca compound to the cluster. The band structure and the electric charge densities are shown in figure 6. The band structure of the interacting system has a similar behavior to the case of interactions with (TiO₂)₁ e (TiO₂)₂ clusters, only with the energy of Fermi slightly shifted to a higher energy (-3.80 eV). The charge density is located on the cluster and graphene.

So, it is important to note that, as in this study we only study cluster with n varies from 1 to 3, it is not possible to observe a tendency of the adsorption energy as a function of n . However, we observe that the adsorption energy is higher when n is odd. Thus, a systematic study for higher values of n would be required to establish a more appropriate tendency.

Figure 6 - (a) Band structure and (b) electric charge density of the most stable configuration of the interaction between the graf+Ca compound and the (TiO₂)₃ cluster. The isosurface value used was 0.00005 e/Å³.



Source: Author's construction.

CONCLUSIONS

In this work, calculations of the first principles based on the Density Functional Theory were performed to study the interaction of the graphene-calcium compound with titanium dioxide clusters, aiming at a strong interaction between the utilized structures, in such a way that the interacting systems could be applied in the area of implantology. Initially, the adsorption of the calcium atom on pure graphene was carried out. The results showed that the Ca atom is more stable when positioned in the center of the benzene ring (hollow site). The adsorption energy found was 0.24 eV. For the interaction of the graphene-calcium compound with the clusters, the adsorption energies were 3.46 eV, 2.41 eV and 4.70 eV, for clusters with n equal to 1, 2 and 3, respectively. The presence of the cluster caused the Ca atom to approach graphene for all analyzed systems. The obtained high values for the adsorption energies coupled with the fact that the three structures approached indicate the occurrence of a strong interaction, a fundamental characteristic for effective implant adhesion, which is the motivation of this study. Although we cannot establish a tendency for larger clusters, which is important from an experimental point of view, our results show that the graphene adsorbed with the calcium atom may be a potential candidate for the creation of thin films to be used in the coating of titanium implants.

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