Disciplinarum Scientia. Série: Naturais e Tecnológicas, Santa Maria, v. 20, n. 3, p. 301-311, 2019.
Recebido em: 09.09.2019. Aprovado em: 25.10.2019.

ISSN 2176-462X

COMPUTATIONAL SIMULATION OF THE INTERACTION BETWEEN TITANIUM CLUSTER AND GRAPHENE OXIDE: A THEORETICAL STUDY[1]

SIMULAÇÃO COMPUTACIONAL DA INTERAÇÃO ENTRE CLUSTER DE TITÂNIO COM ÓXIDO DE GRAFENO: UM ESTUDO TEÓRICO

Estuardo Salazar[2], Luiza Goulart[3] e Jussane Rossato[4]

ABSTRACT

The replacement of teeth in humans is a technique that has been used since ancient civilizations such as the Mayas. The loss of one or more teeth entails several problems such as aesthetic appearance, speech defects and loss of quality of chewing. Nanomaterials are used effectively in different areas of dentistry. A nanostructure that seems promising in a wide range of areas of knowledge and has been little explored for this purpose is graphene oxide (GO). Thus, the aim of this study is to analyze the structural, electronic and energetic properties of the interaction between GO doped with calcium (Ca), phosphorus (P) and silver (Ag) atoms with TiO_2 cluster. The bioatoms were chosen due to their compatibility with bone tissue (Ca and P) and antibacterial properties (Ag). Titanium was chosen because it is the most commonly used material in dental implant. For this, calculations of first principles, which is based on the Density Functional Theory (DFT) were used, this theory associated to the method of pseudopotencias is implemented in the SIESTA computational code. The most stable interactions between the doped GO with P, Ca and Ag associated with TiO_2 showed binding energies of 3.16, 4.20 and 4.42 eV, respectively. There was chemical adsorption in the interactions with P and Ag. The results of this study show that GO doped with P and Ag may be a candidate for the creation of ultrathin films, and it can be used in implantology.

Keywords: DFT, graphene oxide (GO), TiO_2.

RESUMO

A substituição de dentes nos seres humanos é uma técnica utilizada desde civilizações antigas como os Maias, as perdas de um ou mais dentes acarreta diversos problemas como a aparência estética, defeitos na fala e perda da qualidade de mastigação. Os nanomateriais são empregados com eficácia em distintas áreas da odontologia. Uma nanoestrutura que tem se mostrado promissora em uma ampla gama de áreas do conhecimento e que tem sido pouca explorada para este fim, é o óxido de grafeno (GO). Sendo assim, o objetivo deste estudo é analisar as propriedades estruturais, eletrônicas e energéticas da interação entre o GO dopado com átomos de cálcio (Ca), fósforo (P) e prata (Ag) com cluster de TiO_2. Os bioátomos foram escolhidos por apresentar compatibilidade com o tecido ósseo (Ca e P) e propriedades antibacterianas (Ag). Já o titânio foi escolhido por ser o material mais comumente utilizado como implante dentário. Para isso, utilizaremos cálculos de primeiros princípios, o qual baseia-se na Teoria do Funcional da Densidade (DFT), esta teoria associada ao método de pseudopotenciais está implementada no código computacional SIESTA. As interações mais estáveis entre o GO dopado com P, Ca e Ag associados ao TiO_2 apresentaram as energias de ligação de 3,16, 4,20 e 4,42 eV, respectivamente. Houve adsorção química nas interações do TiO_2 com GO

[1] Study performed as undergraduate research scholarship PROBIC/CNPq.

[2] Undergradute Student of Chemical Engineering - Universidade Franciscana. E-mail: estuardo.salazar@ufn.edu.br

[3] Master of Nanoscience- Universidade Franciscana. E-mail: lgoulartf@gmail.com

[4] Advisor. Professor at the Nanoscience Graduate Program - Universidade Franciscana. E-mail: jussaner@gmail.com

dopado com P e Ag. Os resultados deste estudo mostram que GO dopado com P e Ag podem ser um candidato para a criação de filmes ultrafinos, podendo ser usado na implantodontia.

Palavras-chave: *DFT, óxido de grafeno (GO),* TiO_2.

INTRODUCTION

Over the years, dentistry has been developing new technologies involving nanotechnology with emphasis on tissue engineering. Tissue engineering is the science that aims to correct failures in regeneration and replacement of damaged organs or tissues, based on the development and manipulation of cells, tissues or organs grown in laboratories, thus serving as a more effective medical instrument for the treatment of serious diseases (MACIEL, 2016).

In dentistry, periodontium is the set of tissues that support and surround the teeth with the jaw. These tissues include the periodontal ligament, gum, cementum, and alveolar bone. Patients with periodontal disease may have severe bone loss (FERNANDES *et al*., 2017). The increasing occurrence of this disease attracted the attention of scientists since researchers have shown interest in use nanotechnology to develop materials for the treatment and prevention of these oral diseases (KONG *et al*., 2006).

Several studies show the application of nanostructures in dentistry, such as the use of PLGA (poly-lactic acid-glycolic acid-encapsulated) nanoparticles encapsulated with photoactive drugs in antimicrobial endodontic treatment (PAGONIS *et al*., 2010). Titanium nanotubes doped with zinc oxide have cellular compatibility and results show that this doped nanomaterial has more effective antibacterial properties than the pristine titanium nanotube (LIU *et al*., 2014). Mesoporous nanoparticles of calcium silicate functionalized with chlorhexidine are used as an intra-canal medication against common bacteria called Enterococcus faecalis due to its effective results (FAN *et al*., 2016).

Graphene oxide (GO) is another nanomaterial with great potential that has been widely studied for applications in several areas (YADAV *et al*., 2018; ZICA, 2017). However, its potential for implant dentistry applications has not been explored yet. As there are no studies in the literature on the use of GO doped with bioatoms, such as phosphorus, calcium, and silver, associated with the TiO_2 cluster, it is extremely important to understand the electronic and structural properties of these interactions. Thus the aim of this study is to analyze the structural, energetic and electronic properties of the interaction between doped GO and TiO_2 cluster.

MATERIAL AND METHODS

To study the interactions between GO and TiO_2 cluster it is used first-principle calculations based on the Density Functional Theory (DFT) (HONENBERG; KOHN, 1964), which studies the electronic properties of many-body systems. This theory associated with the Troullier-Martins conserved norm pseudopotential method (TROUYLLIER; MARTINS, 1991) is implemented in SIESTA code (Spanish Initiative for Electronic Simulations with Thousand of Atoms) (SOLER *et al.*, 2002). The electron exchange and correlation potential was treated with the Local Density Approximation (LDA) (CEPERLEY; ALDER, 1980).

In this study we used the GO with distributed functional groups based on the study of Martinez (2013). The GO consists of 164 atoms, 144 carbon atoms of graphene sheet and 20 atoms of functional groups, which include three hydroxyls (OH), two epoxies (O) and three carboxyls (COOH).

The binding energies between the interaction of GO and TiO_2 cluster were calculated using equation (1):

$$E_L = [E_T(GO+ TiO_2) - E_T(GO) - E_T(TiO_2)], \quad (1)$$

where $E_T(GO + TiO_2)$ represents the total energy of the interaction between GO and the TiO_2 cluster; $E_T(GO)$ represents the total energy of isolated GO, and E_T (TiO_2) represents the total energy of the isolated titanium dioxide cluster.

The adsorption energies between GO and biocompatible atoms were calculated using equation (2):

$$E_{ads} = [E_T(GO+ \text{átomo}) - E_T(GO) - E_T(\text{átomo})] \quad (2)$$

Where: E_T (GO + atom) represents the total energy of GO doped with bioatoms (calcium, phosphorus or silver); E_T (GO) represents the total energy of GO isolated, and E_T (atom) is the total energy of the respective atom.

Also, the interaction between doped GO with biocompatible atoms and the TiO_2 cluster was analyzed. The binding energies between the doped GO and the TiO_2 cluster were calculated using equation (3):

$$E_L = [E_T(GO_{ads}+ TiO_2) - E_T(GO_{ads}) - E_T(TiO_2)] \quad (3)$$

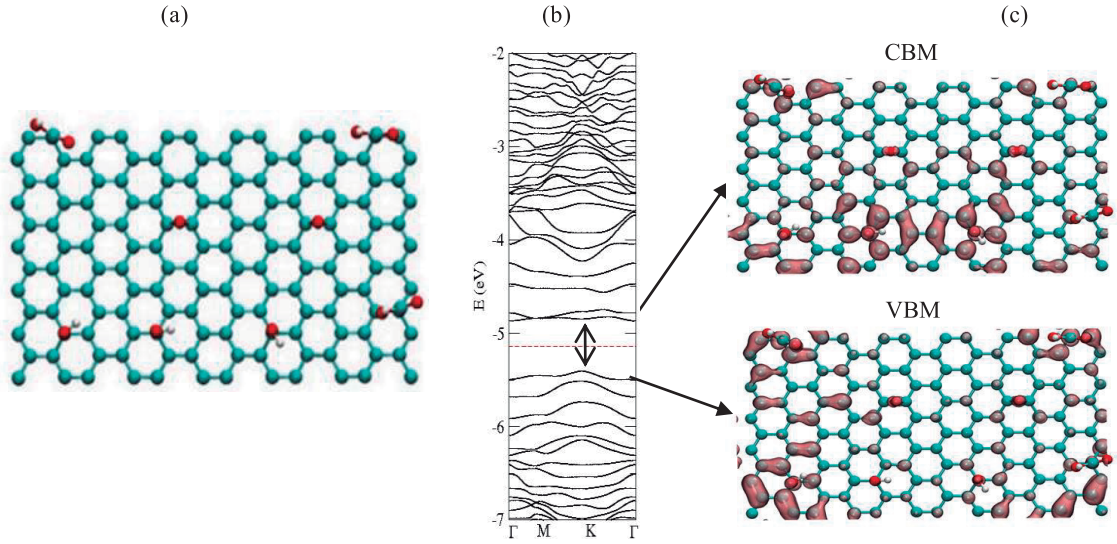
Where the first term represents the total energy of the interaction between the doped GO and the TiO_2 cluster; E_T (GO_{ads}) represents the total energy of the doped GO and $E_T(TiO_2)$ represents the total energy of the titanium dioxide cluster.

RESULTS AND DISCUSSIONS

GRAPHENE OXIDE

Figure 1 shows in (a) the optimized geometry, in (b) the electronic band structure, and in (c) the electronic charge density plot of GO.

Figure 1 - (a) Optimized geometry of GO, (b) electronic band structure and (c) electronic charge density plot.



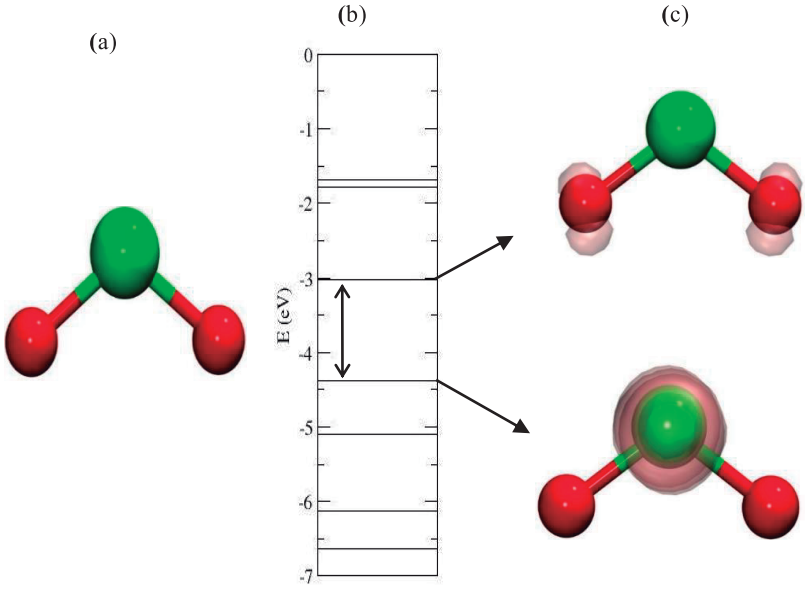
Fonte: Construção do autor.

Figure 1 (b) shows that the GO has a gap of 0.62 eV that characterizes it as a semiconductor material. Figure 1 (c) shows that the electronic charge density associated with CBM (Conduction Band Minimum) is concentrated in the hydroxyl region, and for VBM (Valence Band Maximum) it is concentrated on carboxyl groups. These results indicate the regions most likely to be considered to interact with the TiO_2 cluster.

TiO_2 *CLUSTER*

Figure 2 shows in (a) the optimized geometry, in (b) the energy levels and in (c) the electronic charge density plot of TiO_2 cluster.

Figure 2 - (a) Optimized geometry of TiO_2, (b) energy levels and (c) electronic charge density plot.



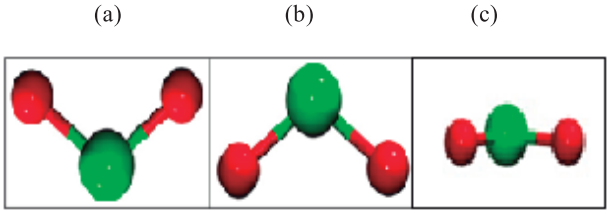
Fonte: Construção do autor.

Figure 2 (b) shows that the TiO_2 cluster has a difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 1.32 eV. Figure 2 (c) shows that the electronic charge density associated with LUMO is concentrated only in oxygen atoms, and for HOMO it is concentrated in titanium atom.

CONFIGURATIONS FOR THE INTERACTION BETWEEN GO AND TiO_2 CLUSTER

Three different configurations were considered for the interaction between the GO and TiO_2 cluster. Two configurations with TiO_2 vertical (Figure 3 (a) and (b)) and one planar (Figure 3 (c)) in relation to the GO sheet. All configurations were approximated by carboxyl and GO hydroxyl, which are the groups with a higher charge. In total, 6 interactions between the GO and TiO_2 cluster were studied. Figure 3 presents the difference between conf.1, conf.2 and conf.3.

Figure 3 - (a) Conf.1, (b) Conf.2 (c) Conf.3 of the TiO_2 cluster used in the interaction with GO.



Fonte: Construção do autor.

Tables presented in the next sections have in the first column the optimized configuration; in the second column the smallest distance between atoms after the interaction; in the third column the binding energy of the interaction; and in the fourth column the charge transfer.

GO INTERACTING WITH TiO_2 CLUSTER

Table 1 presents the results for the interaction between GO and TiO_2 cluster.

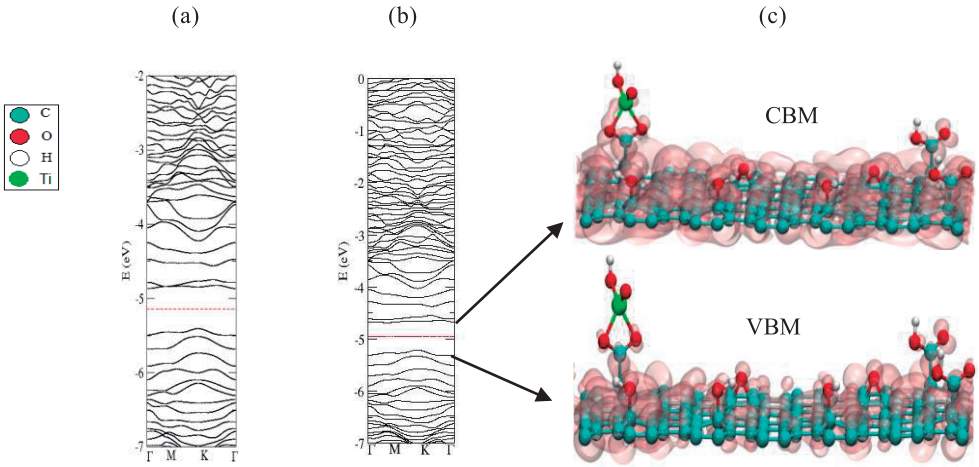
Table 1 - Smallest distance between GO and TiO_2 (Å), binding energy (E_b) and charge transfer (ΔQ). *Most stable interaction.

Optimized Configuration	d (Å)	E_b (eV)	ΔQ (e^-)
COOH (H)_Conf1*	O - Ti = 2.00	4.55	-0.12
COOH (H)_Conf2	H - O = 2.16	1.16	-0.08
COOH (H)_Conf3	H - Ti = 3.29	0.59	-0.05
OH (H) _ Conf1	H - C = 2.28	1.70	-0.05
OH (H) _ Conf2	H - O = 1.57	2.28	-0.01
OH (H) _ Conf3	O - Ti = 1.83	1.71	-0.03

It is observed that binding energy values range from 0.59 to 4.55 eV. The most stable interaction is Conf1 approximated of carboxyl, which has a binding energy of 4.55 eV, smallest distance of 2.00 Å between O and Ti atoms, which is in the range of the typical O-Ti distance of 2.00 Å. The charge transfer of this interaction occurs from the TiO_2 cluster to the GO with the value of -0.12 e-. In Figures 4 (b) - (c) are shown the electronic band structure and the electronic charge density of this interaction.

In Figure 4 (b) it is possible to observe the electronic band structure of the interaction between the carboxyl of GO and the TiO_2 cluster, with a gap of 0.30 eV. There was no significant change in band structure when compared to pristine GO, the system remains as semiconductor after the interaction. The electronic charge density shown in Figure 4 (c) is concentrated on GO and TiO_2 cluster for CBM, and for VBM it is concentrated on VBM. Therefore, this interaction is classified as a chemical interaction because there is a chemical bond between the oxygen and titanium.

Figure 4 - (a) Band structure of the pure GO, (b) band structure of the most stable interaction between GO and the TiO_2 cluster and (c) electron charge density plots.



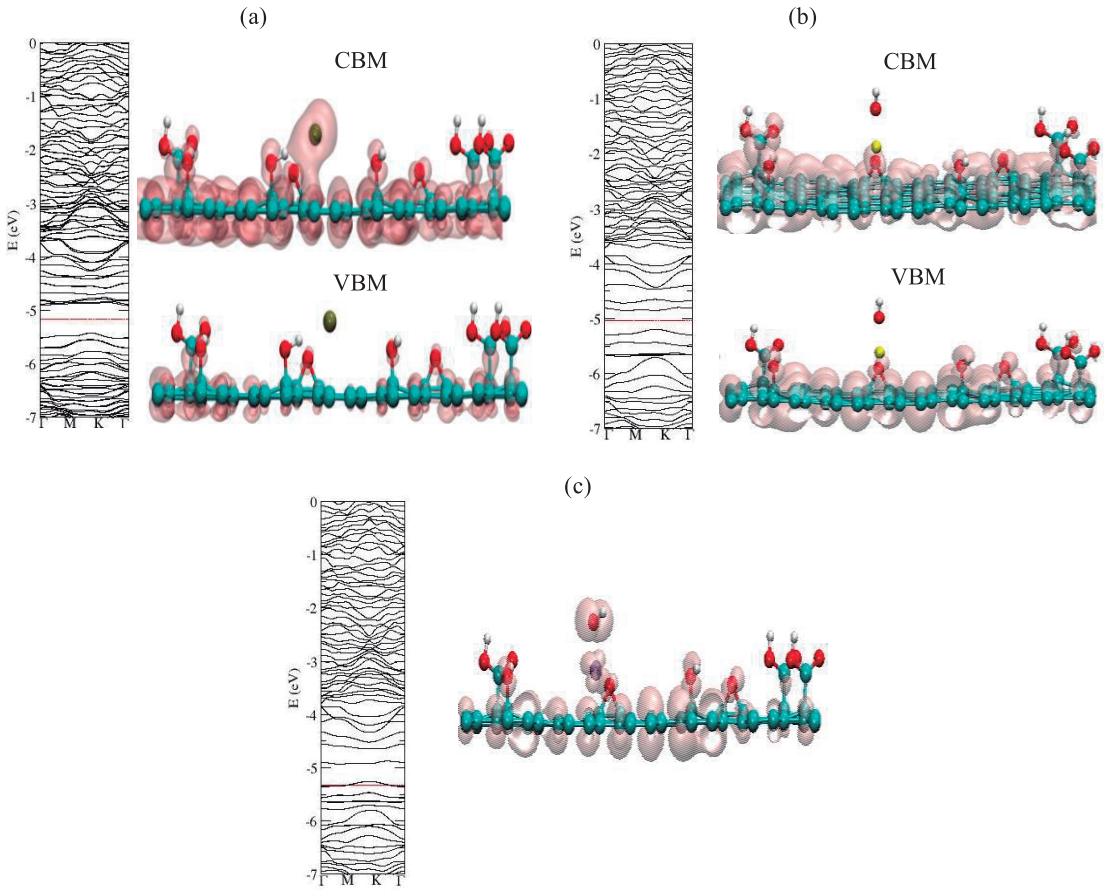
Fonte: Construção do autor.

GO DOPED WITH BIOATOMS

Three regions of the benzene ring were considered to adsorb atoms on GO, which are in agreement with Chan, Neaton and Cohen (2008). These are: the top region (over the carbon atom), hollow region (in the center of the benzene ring), and bridge region (over the C-C bond).

Figure 5 shows the electronic band structures and the electronic charge density plot for the most stable adsorption site for GO doped and P (a), GO doped with Ca (b) and GO doped with Ag (c). For the P atom, the most stable adsorption site was bridge position with adsorption energy of 0.49 eV. This result is in agreement with the results obtained by Solon (2018). For Ca atom, the most stable adsorption site the top region and the adsorption energy was 4.07 eV. The results found in literature indicates that the most stable interaction of this atom and GO is at the hollow region with adsorption energy of Solon (2018). The most stable adsorption site for Ag atom was the top region, which presented adsorption energy of 2.26 eV, which is in agreement with the literature Solon (2018).

Figure 5 - Electronic band structure and the electronic charge density plot for the most stable adsorption site for GO doped and P (a), GO doped with Ca (b) and GO doped with Ag (c).



Fonte: Construção do autor.

DOPED GO INTERACTING WITH TiO_2 *CLUSTER*

The doped GO was approximated by the three previously mentioned TiO_2 cluster configurations, totalizing nine interactions. Table 2 presents the results of these interactions.

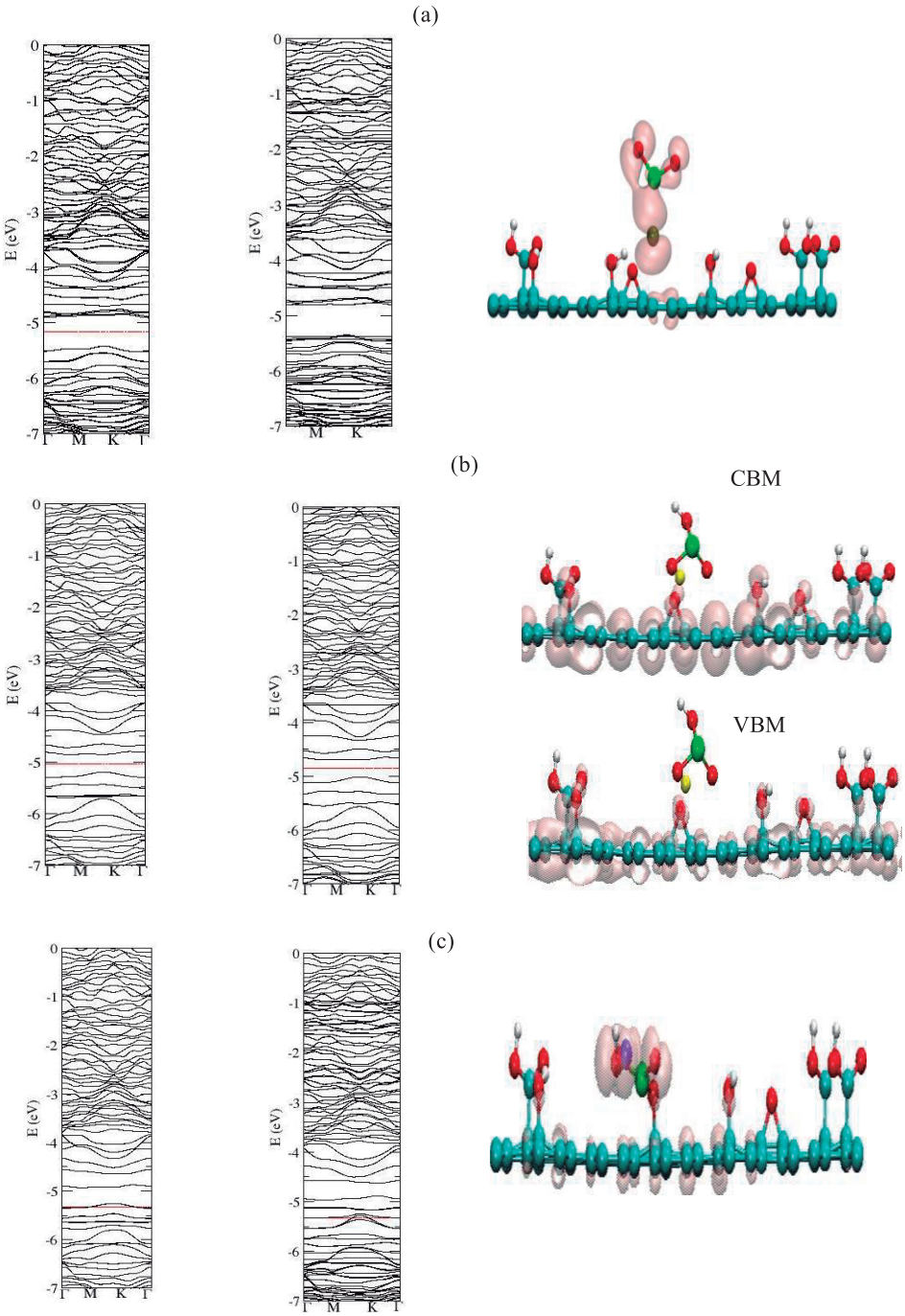
Table 2 - Smallest distance between doped GO and TiO_2 (Å), binding energy (E_L) and charge transfer (ΔQ). *Most stable interaction.

Optimized Configuration	d (Å)	E_b (eV)	ΔQ (e^-)
GO_P_Conf1*	H - P = 2.09	3.16	-0.20
GO_P_Conf2	H - P = 2.15	1.75	-0.11
GO_P_Conf3	P - O = 1.69	1.53	-0.15
GO_Ca_Conf1	O - Ti = 1.90	3.92	-0.05
GO_Ca_Conf2*	O - Ti = 2.17	4.20	-0.18
GO_Ca_Conf3	Ca - O = 2.27	4.02	-0.03
GO_Ag_Conf1	Ag - O = 2.05	4.27	-0.04
GO_Ag_Conf2	Ag - O =2.18	4.18	-0.19
GO_Ag_Conf3*	O - Ti = 2.00	4.42	-0.26

In Table 2 it is observed that the values of binding energy range from 1.53 to 4.42 eV. The most stable interaction between P doped GO and TiO_2 is Conf1, with a binding energy of 3.16 eV, and smallest distance between the P doped GO and H is 2.09 Å, while the typical H-P distance is 1.42 Å. The most stable interaction between Ca doped GO and TiO_2 is Conf2, with a binding energy of 4.20 eV, with a binding distance between O and Ti atoms of 2.17 Å, which is close to the typical O-Ti bond distance of 2.00 Å. The most stable interaction between Ag doped GO and TiO_2 is Conf3, with binding energy of 4.42 eV, the smallest distance between O and Ti atoms was 2.00 Å, the same value as the typical O-Ti bond distance. Charge transfer occur from TiO_2 to the nanomaterial. Figure 6 shows the electronic band structure and electronic charge density plot for the most stable interactions for each dopant.

Figure 6 (a) shows charge density concentration in the doping site and in the TiO_2 cluster. In Figure 6 (b) it is possible to observe that the charge density is concentrated only on the nanomaterial. Figure 6 (c) shows that the charge density is concentrated in the nanomaterial, in the doping site and in the TiO_2 cluster.

Figure 6 - (a) Electronic band structure of the most stable interaction between P doped GO, following up the electronic band structure of the most stable interaction between P doped GO and TiO_2 and electronic charge density plot. (b) Electronic band structure of the most stable interaction between Ca doped GO, following up the electronic band structure of the most stable interaction between Ca doped GO and TiO_2 and electronic charge density plot. (c) Electronic band structure of the most stable interaction between Ag doped GO, following up the electronic band structure of the most stable interaction between Ag doped GO and TiO_2 and electronic charge density plot (c).



Fonte: Construção do autor.

CONCLUSIONS

The interactions between the doped GO with the TiO_2 cluster were analyzed using first principle calculations, to indicate if the systems under study could be used as ultrathin coatings for dental implants.

For phosphorus doped GO interacting with the TiO_2 cluster, the binding energy for the most stable interaction was 3.16 eV. This interaction presented is characterized as semiconductor with semiconductor level at the Fermi level, while the P doped GO is a semiconductor with a gap of 0.35 eV. These results and the presence of electronic charge density after the interaction, indicates a strong interaction, which is necessary for the implant adhesion to be effective.

The binding energy for the most stable interaction between Ca doped GO and TiO_2 cluster was 4.20 eV. Despite the high value there was also no change in the electronic properties so there is no chemical interaction between the systems, which is not interesting for this proposal.

The binding energy for the most stable interaction between Ag doped GO with the TiO_2 cluster was 4.42 eV. There were no changes in electronic properties after the interaction; however, it was observed a charge density and a chemical bond between Ti - O atoms which indicate a strong (chemical) interaction, ideal for the purpose of this study.

These results show that P and Ag doped GO could be candidates for the development of ultra-thin coatings for use in dentistry.

REFERENCES

CEPERLEY, D. M.; ALDER, B. J. Ground State of the Electron Gas by a Stochastic Method. **Phys. Rev. Lett.**, v. 45, p. 566-569, 1980.

FAN, W. *et al.* Calcium-silicate mesoporous nanoparticles loaded with chlorhexidine for both anti--Enterococcus faecalis and mineralization properties. **Journal of nanobiotechnology**, v. 14, n. 1, p. 72, 2016.

FERNANDES, L. D. *et al.* Tratamento ortodôntico em pacientes com comprometimento periodontal. **Revista uningá**, v. 29, n. 1, 2017.

HOHENBERG, P.; KOHN, W. Inhomogeneous electron gas. **Physical Review**, v. 136, n. 3B, p. 864-871, 1964.

KONG, L. X. *et al.* Nanotechnology and its role in the management of periodontal diseases. **Periodontology 2000**, v. 40, n. 1, p. 184-196, 2006.

LIU, W. *et al.* Synthesis of TiO_2 nanotubes with ZnO nanoparticles to achieve antibacterial properties and stem cell compatibility. **Nanoscale**, v. 6, n. 15, p. 9050-9062, 2014.

MACIEL, M. M. **Desenvolvimento e otimização de estruturas condutoras de base polimérica para engenharia de tecidos**. Dissertação (Mestrado em biofísica e bionanossistemas) - Universidade do Minho, Braga, 2016.

PAGONIS, T. *et al.* Nanoparticle-based endodontic antimicrobial photodynamic therapy. **Journal of endodontics**, v. 36, n. 2, p. 322-328, 2010.

SOLER, J. M. *et al.* The SIESTA method for ab initio order-N materials simulation. **Journal of Physics:** Condensed Matter, v. 14, n. 11, p. 2745-2779, 2002.

TROULLIER, N.; MARTINS, J. L. Efficient pseudopotentials for plane-wave calculations. **Phys. Rev. B**, v. 43, n. 3, p. 1993-2006, 1991.

YADAV, S. *et al.* Removal of fluoroquinolone from aqueous solution using graphene oxide: experimental and computational elucidation. **Environmental Science and Pollution Research**, v. 25, n. 3, p. 2942-2957, 2018.

ZICA, A. S. **Desenvolvimento de eletrodos de nanocompósitos de óxido de grafeno e óxidos metálicos para aplicação em supercapacitores.** Tese (Doutorado em física aplicada), Universidade Federal de Viçosa, Minas gerais, 2017.

HORN, M. S. C. F.; SCHWEBDTFEGER, C. F.; MEAGHER, E. P. Refinement of the structure of anatase at several temperatures. **Zeitschrift für Kristallographie-Crystalline Materials**, v. 136, n. 1-6, p. 273-281, 1972.