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Computational studies on the interaction of vitamin C (ascorbic acid) with nitrogen modified TiO_2 anatase nanoparticles

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ABSTRACT

Density functional theory calculations were performed to investigate vitamin C interaction with N-doped TiO_2 anatase nanoparticles. The adsorption of vitamin C on the energy favorable fivefold coordinated titanium sites was investigated. Various adsorption geometries of vitamin C towards the nanoparticle were examined. Since the adsorption energies of N-doped nanoparticles are higher than those of undoped ones, the N-doped TiO_2 nanoparticles can interact with vitamin C molecule more strongly. Besides, adsorption on the pristine nanoparticle is less favorable, whereas on the N-doped one, the adsorption process is more energy favorable. The electronic structure analysis was performed in view of the density of states and molecular orbitals of the considered nanoparticles with the adsorbed vitamin C molecule. The significant overlaps between the PDOS spectra of the oxygen atom of vitamin C molecule and titanium atom of TiO_2 confirm the chemisorption of vitamin C on the TiO_2 nanoparticle. After the adsorption, the electronic densities in the HOMOs of the adsorption systems were mainly distributed over the vitamin C molecule, while the LUMOs were dominant at the TiO_2 nanoparticle. Our calculations shed light on understanding the interaction between vitamin C and TiO_2 nanoparticles, which provides an efficient outline for future experimental studies.

Keywords: *TiO_2 anatase nanoparticle; Interaction; Vitamin C; DFT; PDOS, Molecular orbital.*

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INTRODUCTION

TiO_2 is a well-known biocompatible metal oxide with a wide range of practical applications in many fields such as photo-catalysis [1], gas sensor devices, heterogeneous catalysis [2] and photovoltaic cells [3]. In the past few years, a surge amount of interest has arisen in the investigation of the outstanding properties of TiO_2 such as lack

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of toxicity, chemical stability, large band-gap, and excellent surface properties [4-8]. In this regard, many research groups from different fields of science and technology have focused on the study of outstanding properties of TiO_2 [8-15]. The crystal structure of TiO_2 exhibits three important polymorphs, namely rutile, brookite and anatase. Anatase possesses a large band-gap of 3.2eV, which greatly restricts its ability for the absorption of the incoming solar light, and consequently reduces the optical sensitivity. Different strategies have been tried for the enhancement of the photocatalytic properties of TiO_2. Of the most important methods, the nonmetal (nitrogen) doping is an appropriate method, which expands the photo-catalytic properties and absorption abilities of TiO_2. Therefore, the N-doped TiO_2 anatase seems to be highly more efficient than the undoped one in some photocatalytic processes [16-19]. Over the past years, several researchers from different fields of science and technology have focused on studying the N-doped TiO_2 anatase nanoparticles. For example, Liu et al. [20] suggested that the adsorption of NO molecule on the N-doped TiO_2 anatase is more energetically favorable than undoped one. Moreover, nitrogen doping of TiO_2 nanoparticles gives rise to some improvements on the electronic and structural properties, thus making it a promising candidate to be utilized in gas sensor devices [20-25]. In some theoretical works, researchers have focused on the effects of nitrogen doping on the band structure of TiO_2 anatase [26-28]. In our previous works, we have focused on the interaction of TiO_2 and supported TiO_2 with curcumin drug and other toxic gas molecules [29, 30]. Also, Mirzaei et al. studied the adsorption of vitamin C on the Fullerene surface using the DFT computations [31]. Titanium and titanium alloys show an exceptional combination of strength and biocompatibility, which enables their use in medical applications, and indicates that they can be extensively used as implant materials in the last few years. At present, a large number of works were devoted to determine the optimal surface topography for use in bioapplications, and consequently the emphasis is on nanotechnology for biomedical applications [32]. Recently, it was revealed that titanium implants with rough surface topography and free energy increaseed osteoblast adhesion, maturation and subsequent bone formation. Furthermore, the linkage of different cell lines to the surface of titanium implants is affected by the surface properties of titanium; which is known as topography, charge distribution and chemistry [32-34]. Vitamin C, also known as ascorbic acid, is a water-soluble vitamin. It is naturally present in some foods and available as a dietary supplement. Unlike most animals, in the human body, vitamin C cannot be synthesized, therefore vitamin C is an indispensable dietary component. Vitamin C is an essential component in the biosynthesis of collagen, and certain neurotransmitters. Epidemiologic evidence indicates that major consumption of fruits and vegetables is related to minor hazard of cancerous diseases because of their high vitamin C content [35].

In most case-control studies, it has been found that there is an inverse relation between dietary vitamin C intake and cancers of the lung, breast, colon or rectum, stomach, oral cavity, larynx or pharynx, and esophagus [36, 37]. Therefore, it can be concluded that vitamin C acts as a typical drug in the prevention and treatment of some diseases. In fact, research shows that vitamin C can protect the body against a number of cancers by combating free radicals. Several advantages of vitamin C has been proposed including its help in the repair and regeneration of tissues, protection against heart disease, aid in the absorption of iron, and decrease total cholesterol in the human body. Since the discovery of primary nanostructures, an important concern has been the utilization of innovative nanomaterials in living organisms to improve the quality of human life [38]. For this purpose, it is of eminent importance to gain insights into the interactions of nanostructures with biological systems [39-41]. As an alternative, some researchers have performed several computational and experimental studies, describing the main concepts of the interactions between nanostructures and biological systems. Nevertheless, due to the complexity of both biological and nonstructural systems, no clear answer has found for this question. Hence,the implementation of further investigations are increasingly demanded.

In this research, the interaction of vitamin C molecule with N-doped TiO_2 anatase nanoparticles was studied by means of DFT calculations. The electronic properties of the adsorption systems were examined in view of the density of states and molecular orbitals.

COMPUTATIONAL METHODS

Our DFT calculations [42, 43] were carried out using the Open source Package for Material explorer (OPENMX) version 3.8 [44]. In the OpenMX package, pseudo atomic orbitals (PAOs) centered on the atomic sites were used as basis sets. The wave functions were expanded in a Kohn-Sham (KS) schema with a considered cutoff energy of 150 Ry [45]. In order to create the basis sets, we used the following combination of primitive orbitals of the considered atoms (two-s, two-p, two-d, one-f) for the gold atom, (two-s, two-p, two-d) for the titanium atom, two-s and two-p for O, N and C atoms and two-s for H atom. The cutoff radii for the considered atoms were set to the values of 9 for gold, 7 for titanium, 5.5 for H, 5 for O, N and C (all in Bohrs). The cutoff radius (a.u.) is an imperative factor for the generation of pseudopotentials. Although, an optimum cutoff radius is determined so that the generated pseudopotentials has a smooth shape without distinct kinks and a lot of nodes.

Two important parameters can control the accuracy and efficiency of the calculations: a cutoff radius and the number of basis functions. Generally, the results with better convergence can be obtained by increasing the cutoff radius and the number of basis functions. Nevertheless, it is worth noting that the use of a large number of basis orbitals with a great cutoff radius needs a professional computational resource (especially memory size and computational time). The exchange and correlation interactions were treated using the generalized gradient approximation functional (GGA) in the Pedrew-Burke-Ernzerhof (PBE) form [46]. XCrysDen, which is a crystalline and molecular structure visualization program [47] was utilized for visualization of the isosurfaces such as molecular orbitals, and other Figures presented in this work. The adsorption energy was estimated using the following equation:

$$E_{ad} = E(_{particle+adsorbate}) - E_{particle} - E_{adsorbate} \tag{1}$$

where $E_{(\,particle\,+\,adsorbate\,)}$, $E_{\,particle}$ are the total energies of the adsorption system and bare TiO_2 nanoparticle, whereas $E_{\,adsorbate}$ represents the energy of a free vitamin C molecule. TiO_2 anatase nanoparticles were constructed based on a 3×2×1 supercell of anatase along x, y and z axis, respectively. The considered structure of nanoparticle was shown in Figure 1. The unit cell was taken from "American Mineralogists Database" webpage [48] reported by Wyckoff [49]. In the current work, the dispersion correction was examined and described based on Grimme's DFT-D2 method, which corrects the adsorption energies for the dispersion energy [50]. The keyword for the inclusion of the dispersion correction in the calculations was fully analyzed. With the inclusion of dispersion correction, the effects of vdW interactions were taken into account in the calculations. It is worth noting that the adsorption energies were increased after applying the vdW interaction corrections. The results were summarized in Table 1. We chose the size of the studied nanoparticles as 3×2×1 numbers of TiO_2 unit cells along x, y and z axis following Liu et al. [14, 20]. Liu and co-workers suggested that the nanoparticles of TiO_2 with 72 atoms are more stable and more favorable in energy. Thus, the adsorption of different molecules on these stable particles gives rise to the stable adsorption configurations.

Table 1. Bond lengths (in Å), adsorption energies (in eV) and Mulliken charge results for the interaction of vitamin C with TiO_2 anatase nanoparticles.

Complex	Ti-O	Ti-N	C-O	Newly-formed Ti-O	E_{ad} (eV)		ΔQ(e)
					PBE	DFT-D2	
A	1.80	---	1.30	2.10	-4.69	-5.32	-0.716
B	1.82	---	1.31	2.05	-3.50	-4.08	-0.604
C	1.85	---	1.29	2.03	-1.11	-1.86	-0.536
D	1.76	---	1.25	2.27	-4.01	-4.76	-0.480
E	---	1.80	1.26	2.21	-3.60	-4.18	-0.301
F	1.74	---	1.27	2.17	-1.17	-2.02	-0.252

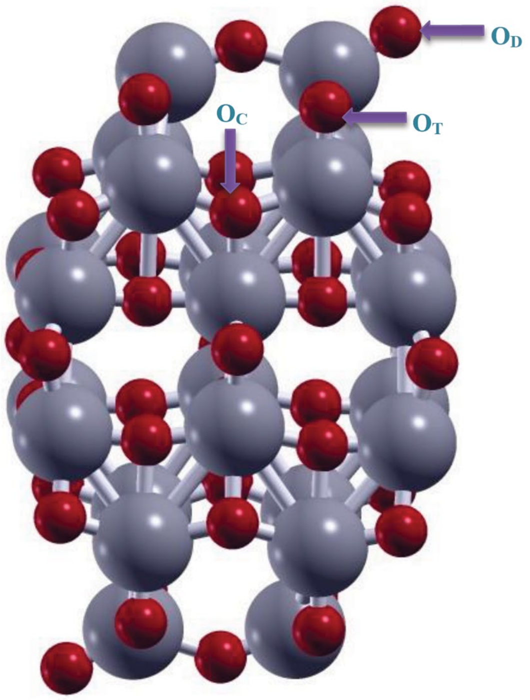

Fig. 1. Optimized geometry of an undoped TiO_2 anatase nanoparticle constructed from the 3×2×1 unit cells. Labels O_C, O_T and O_D indicate threefold coordinated (central oxygen), twofold coordinated oxygen and dangling oxygen atoms, respectively.

We have modeled two N-doped TiO_2 particles according to two doping configurations. In one doping position, a twofold coordinated oxygen atom was replaced by a nitrogen atom, and the other position represents the substitution of a threefold coordinated oxygen atom of TiO_2 by nitrogen atom. The optimized structures of N-doped TiO_2 anatase nanoparticles were represented in Figure 2. Vitamin C molecule interacts with the TiO_2 nanoparticle in both parallel and perpendicular configurations. The fivefold coordinated titanium atoms were found to be the most stable binding sites, and the adsorption was studied over these sites.

RESULTS AND DISCUSSION

Bond lengths, bond angles and adsorption energies

The adsorption configurations of vitamin C molecule on the TiO_2 nanoparticles were studied based on two parallel and perpendicular geometries. In one adsorption geometry, the oxygen atom of vitamin C molecule was positioned toward the TiO_2 nanoparticle in a parallel orientation, and another is that vitamin C molecule was located vertically towards the nanoparticle. The fivefold coordinated titanium sites of TiO_2 were found to be the most energy favorable sites for vitamin C adsorption. Theses interactions both include N-doped nanoparticles in the middle oxygen position and N-doped ones in the twofold coordinated oxygen atom sites. Figures 3-5 show the optimized geometry configurations of vitamin C molecule adsorbed on the undoped and N-doped TiO_2 nanoparticles. The presented configurations were marked by adsorption types A-F. Configurations A-C represent the parallel orientation of vitamin C molecule with respect to the nanoparticle, whereas D-F show the perpendicular adsorption of vitamin C molecule on the considered nanoparticles.

The complexes contained in this figure differ in the position of doped nitrogen atoms of TiO_2 nanoparticle, as well as the relative orientation of vitamin C molecule with respect to the TiO_2. Configuration A shows the parallel adsorption of vitamin C on the O_C-substituted TiO_2 nanoparticle, while B and C show the interaction between O_T-substituted/pristine nanoparticles and vitamin C molecule.

The optimized values of some bond lengths for vitamin C adsorption on the TiO_2 were listed in Table 1. The bond lengths given in this table included Ti-O bond of TiO_2 nanoparticle, nearest C-O bond of vitamin C molecule and newly-formed Ti-O bond between titanium atom of nanoparticle and nearest oxygen atom of vitamin C. Based on the obtained results, we found that the C-O bond of vitamin C molecule was stretched after the adsorption process. This increase in the bond length values can be probably attributed to the electronic density transfer from Ti-O bond of TiO_2 and C-O bond of the vitamin C molecule to the newly formed Ti-O bond between the vitamin C and TiO_2 nanoparticle. Hence, the C-O bond of the vitamin C molecule was weakened after the adsorption process. Table 1 also listed the adsorption energies for vitamin C molecule adsorbed on the undoped and N-doped TiO_2 anatase nanoparticles. The results given in this table indicate that the interaction of vitamin C molecule with N-doped TiO_2 nanoparticle is energetically more favorable than the interaction with undoped one, representing that the N-doped nanoparticle has stronger sensing capability than the undoped one when utilized as a detection device for vitamin C molecule.

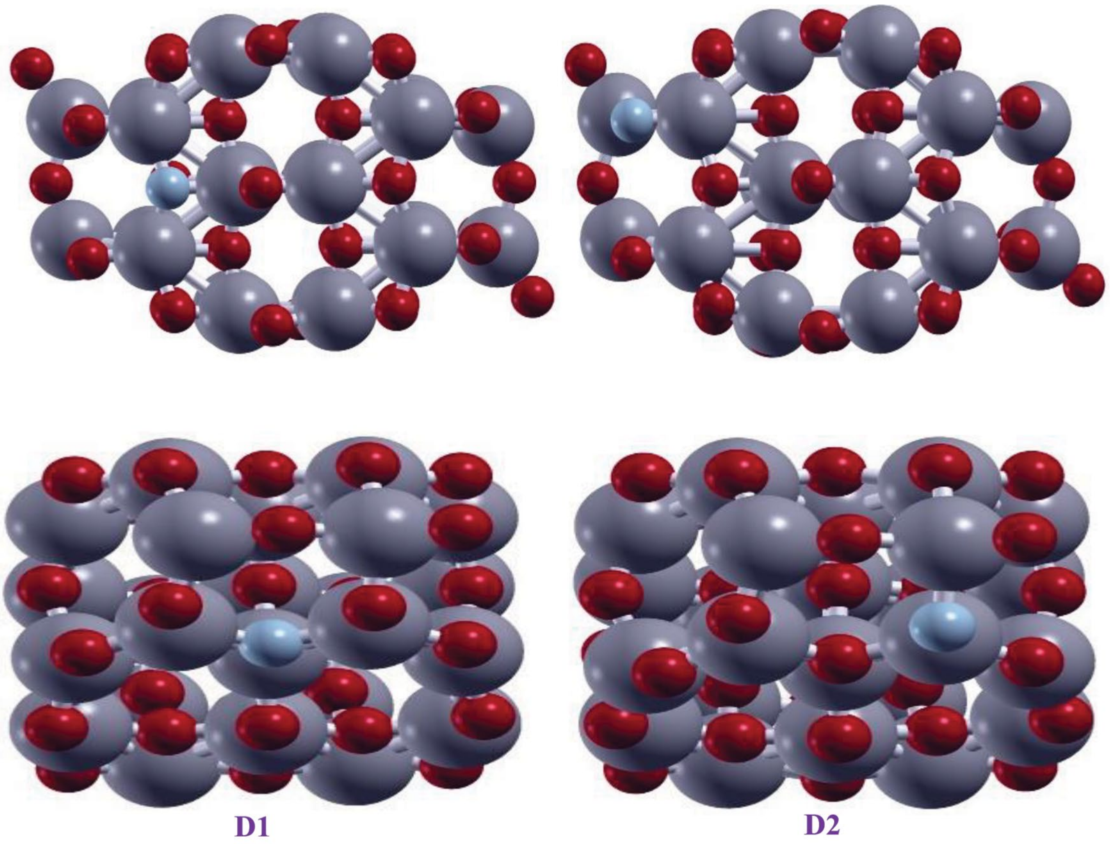

Fig. 2. Different views optimized N-doped TiO_2 anatase nanoparticles constructed using the 3×2×1 unit cells; (D1) O_C-substituted nanoparticle. (D2) O_T-substituted one.

It is worth noting that, in both parallel and perpendicular adsorption geometries, the N-doped configurations were considered as the most energy favorable adsorption configurations.

For parallel configuration (A-C), configuration A (O_C-substituted nanoparticle adsorption system) has the highest adsorption energy value, whereas the lowest adsorption energy belongs to configuration C (pristine nanoparticle adsorption system). Thus, for parallel geometry, we found that configuration C is the most stable adsorption configuration. In the case of perpendicular adsorption geometry, it can be seen from Table 1 that configuration D has the highest adsorption energy value, and the lowest result was found in configuration F. Also, in both cases, it can be seen that the adsorption energy of O_C-substituted nanoparticle is more negative than that of O_T-substituted one, indicating the adsorption process was strongly favored with O_C-substituted TiO_2. Important to note is that the adsorption energies are substantially enlarged when the effects of van der Waals interaction are taken into account. By considering these results, it was found that the N-doped TiO_2 nanoparticles are more sensitive than the pristine ones for the adsorption of vitamin C molecule. Since the adsorption of vitamin C molecule on the N-doped TiO_2 is stronger than that on the pristine one, N-doped particle can react with vitamin C molecules more effectively. Moreover, there are more adsorption sites on the N-doped particles due to their higher activities in the adsorption process, on which the adsorption energies are more negative than those of the pristine particles. It suggests that N doped particles can interact with vitamin C molecule more strongly. Hence, the nitrogen doping behaves as an effectual method in order to adsorb vitamin C molecule in the biological systems, that is, the nitrogen doping strengthens the interaction of TiO_2 with vitamin C molecules [14, 20].

The more negative the adsorption energy, the higher tendency for adsorption, and consequently more energy favorable adsorption. Thus, nitrogen doping strengthens the interaction of vitamin C molecule with TiO_2 anatase nanoparticles. Our calculated results are in reasonable agreement with the computational study of Baniasadi and co-workers, which suggests that vitamin C molecule can be efficiently detected by TiO_2 based and Fullerene based nanosensors.

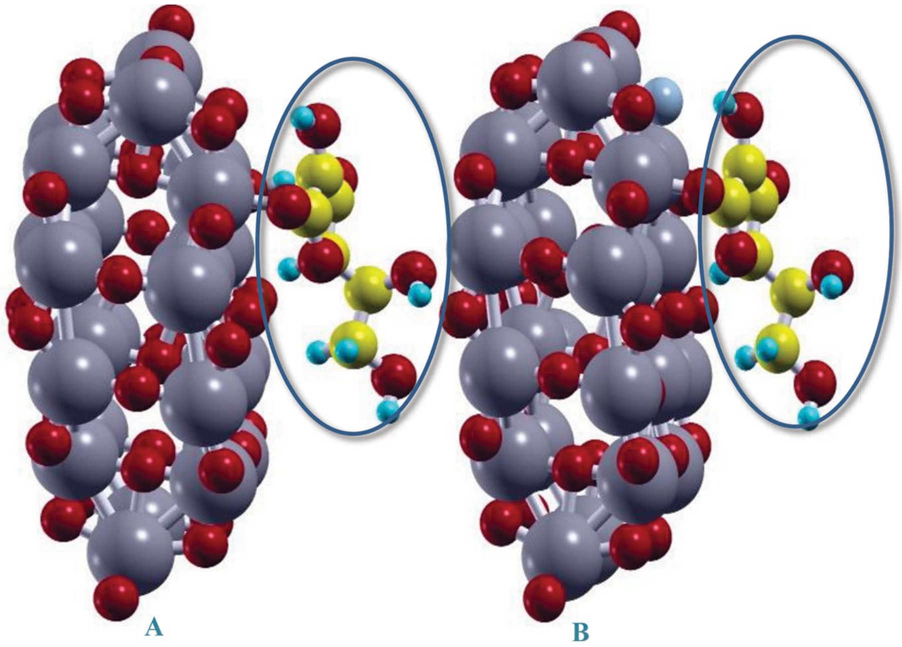

Fig. 3. Optimized geometry configurations of the interaction of vitamin C with N-doped TiO_2 anatase nanoparticles.

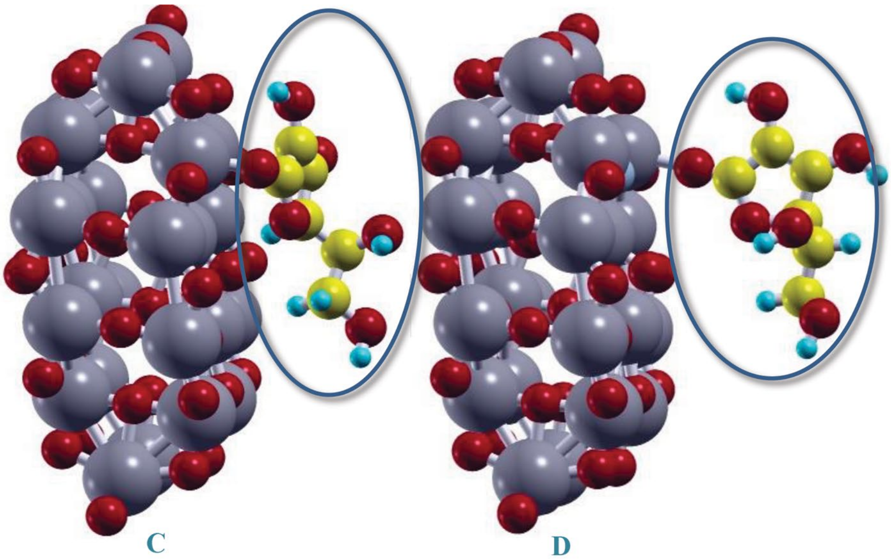

Fig. 4. Optimized geometry configurations of the interaction of vitamin C with undoped and N-doped TiO_2 anatase nanoparticles.

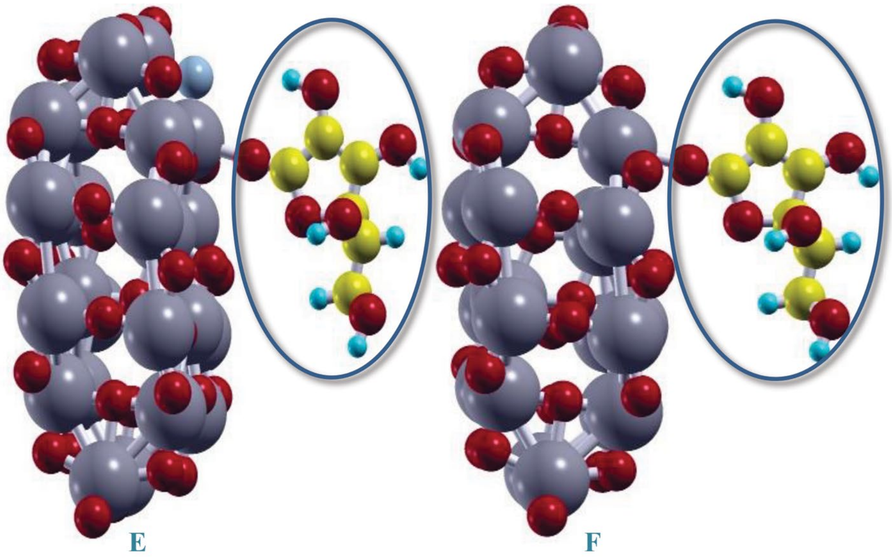

Fig. 5. Optimized geometry configurations of the interaction of vitamin C with undoped and N-doped TiO_2 anatase nanoparticles.

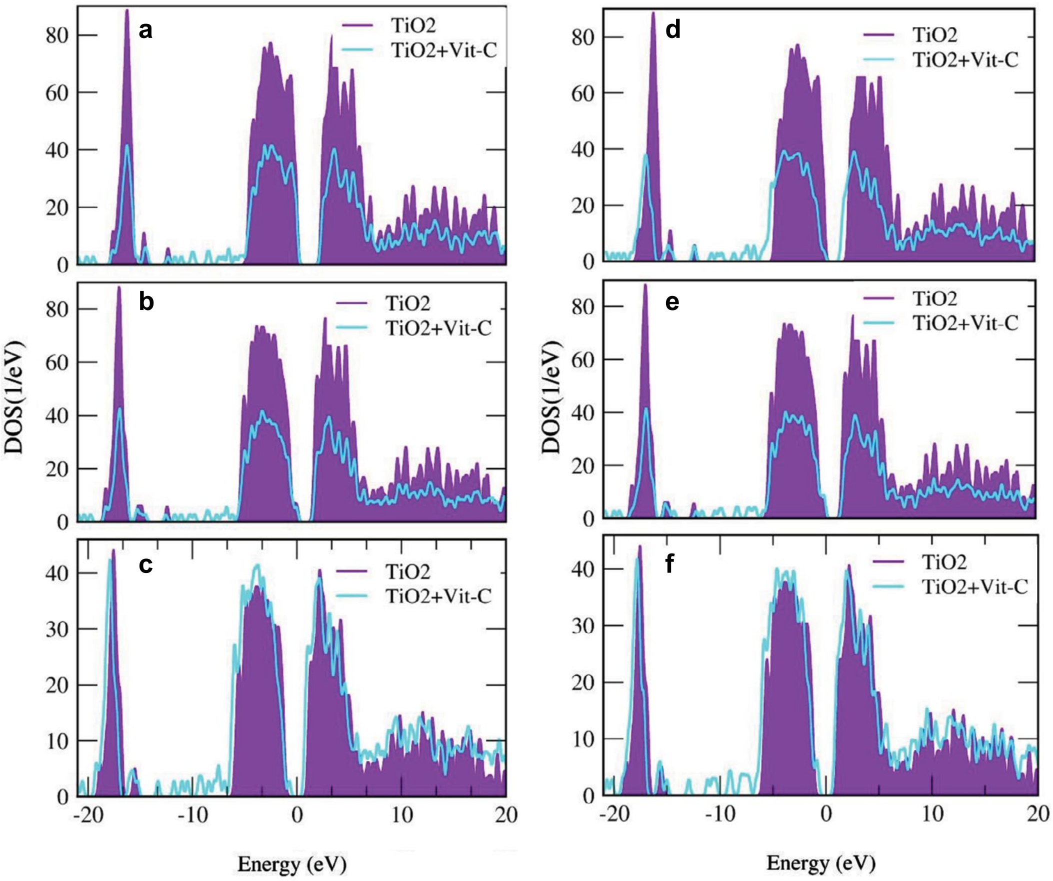

Fig. 6. Total density of states (TDOSs) for the interaction of vitamin C with TiO_2 anatase nanoparticles, (a) configuration A; (b) configuration B; (c) configuration C; (d) configuration D; (e) configuration E; (f) configuration F.

Electronic structures

Figure 6 displays the total density of states (TDOS) for vitamin C adsorption on the TiO_2 anatase. A closer inspection shows that some small peaks appear in the DOS of N-doped TiO_2 at the energy values ranging from -12 eV to -8 eV. Therefore, the DOS spectra show that the differences between DOS of N-doped and undoped TiO_2 are increased by adsorption of vitamin C molecule. It can be seen from this Figure that the adsorption process changes the energies of the states and the density of the states. Consequently, these variations in energy gap of DOS ~~gives~~ rise to some modifications on the electronic transport properties. The projected density of states (PDOSs) for vitamin C molecule adsorbed on TiO_2 nanoparticles was shown in Figure 7. Panels (a-f) display the PDOS spectra for configurations A-F, respectively. It can be seen from these panels that there are significant overlaps between the PDOSs of the oxygen atom of vitamin C molecule and fivefold coordinated titanium atom of TiO_2. Therefore, these overlaps are responsible for the formation of strong chemical bonds between the oxygen and titanium atoms.

Figure 8 represents the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of an isolated vitamin C molecule. Fascinatingly, the HOMO and LUMO of vitamin C molecule exhibit a dominant distribution on the whole vitamin C molecule. The isosurfaces of HOMOs and LUMOs for the adsorption configurations of vitamin C molecule on the TiO_2 anatase nanoparticles were shown in Figures 9 and 10. The HOMOs of the adsorption systems were mostly distributed over the adsorbed vitamin C molecule, while the electronic densities in the LUMOs were dominant over the TiO_2 nanoparticle. This concentration of the HOMOs on the vitamin C molecule confirms that vitamin C adsorption changes the electronic structure of TiO_2 nanoparticle. The charge exchange between vitamin C molecule and TiO_2 nanoparticle was described based on Mulliken population analysis. We can calculate the net charge transfer value using the following equation:

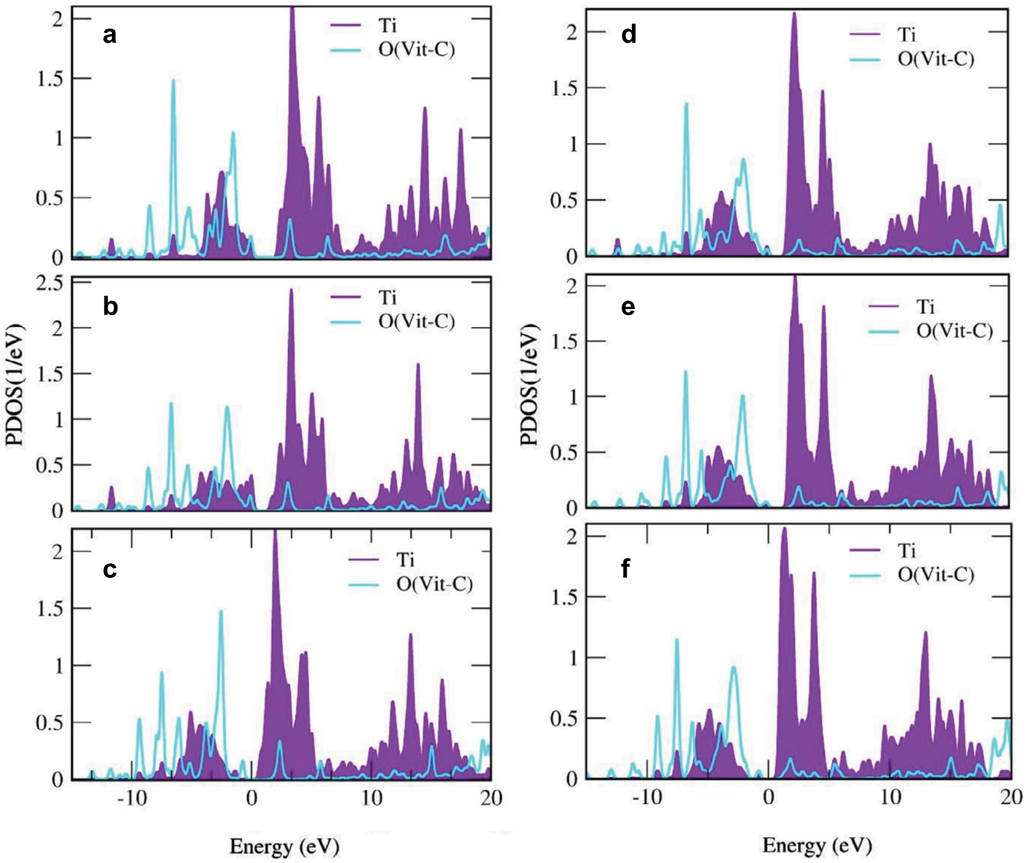

Fig. 7. Projected density of states (PDOSs) for the interaction of vitamin C with TiO_2 anatase nanoparticles, (a) configuration A; (b) configuration B; (c) configuration C; (d) configuration D; (e) configuration E; (f) configuration F.

$$\Delta Q_i = Q_{i\,(in\ complex)} - Q_{i\,(in\ vacuum} \qquad (2)$$

Where Q_i represents the value of Mulliken charge of the i. Subscript “i” refers to the TiO_2 nanoparticle or vitamin C molecule. The charge difference, ΔQi, thus indicates the charge transfer between the TiO_2 nanoparticle and vitamin C molecule. For configuration A, the calculated charge transfer is about -0.716 $|e|$ (e, the electron charge), implying that the charge was transferred from the vitamin C molecule to the TiO_2 nanoparticle. Hence, TiO_2 nanoparticle accepts electron charges from vitamin C molecule.

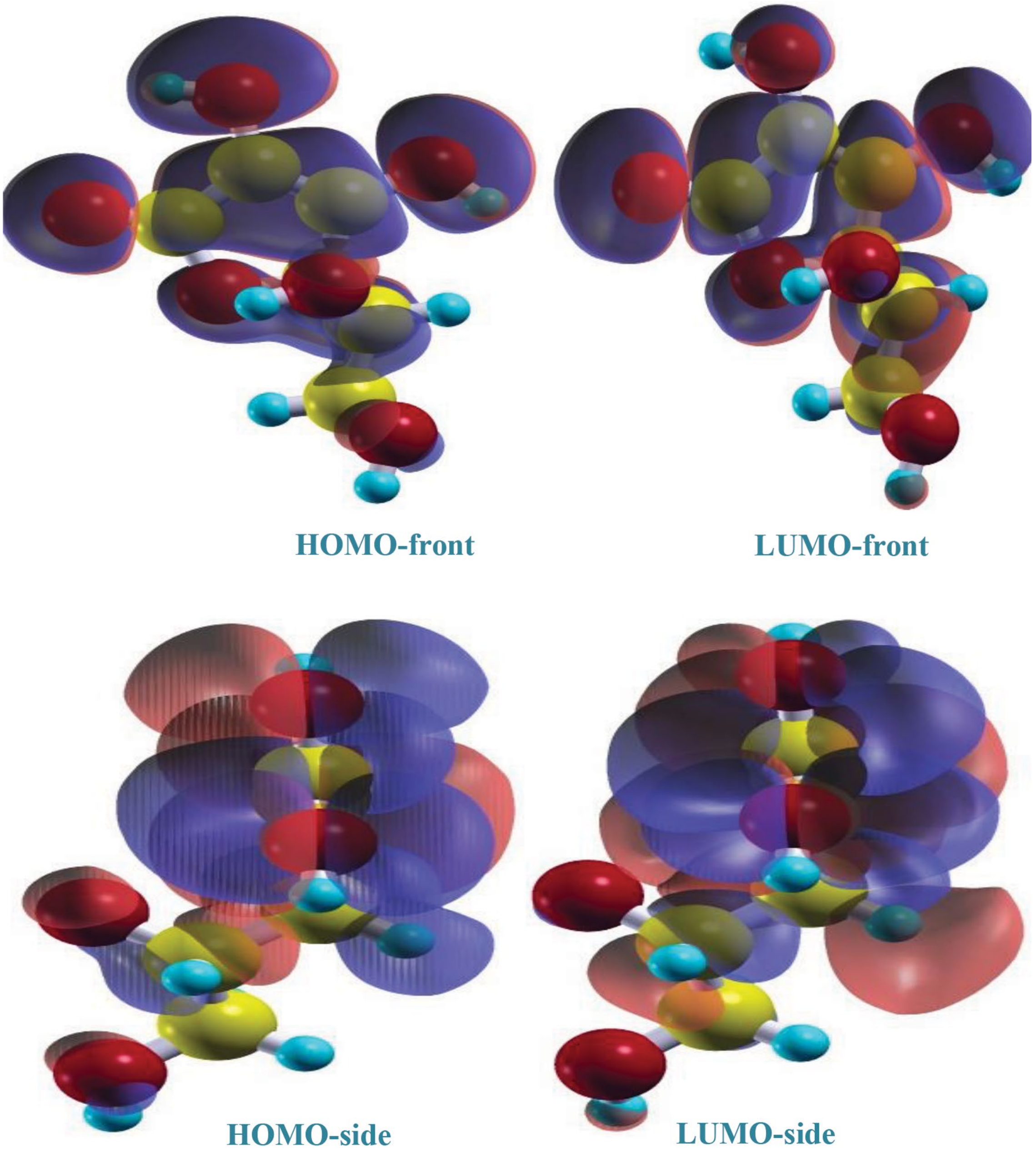

Fig. 8. HOMOs and LUMOs for isolated vitamin C molecule.

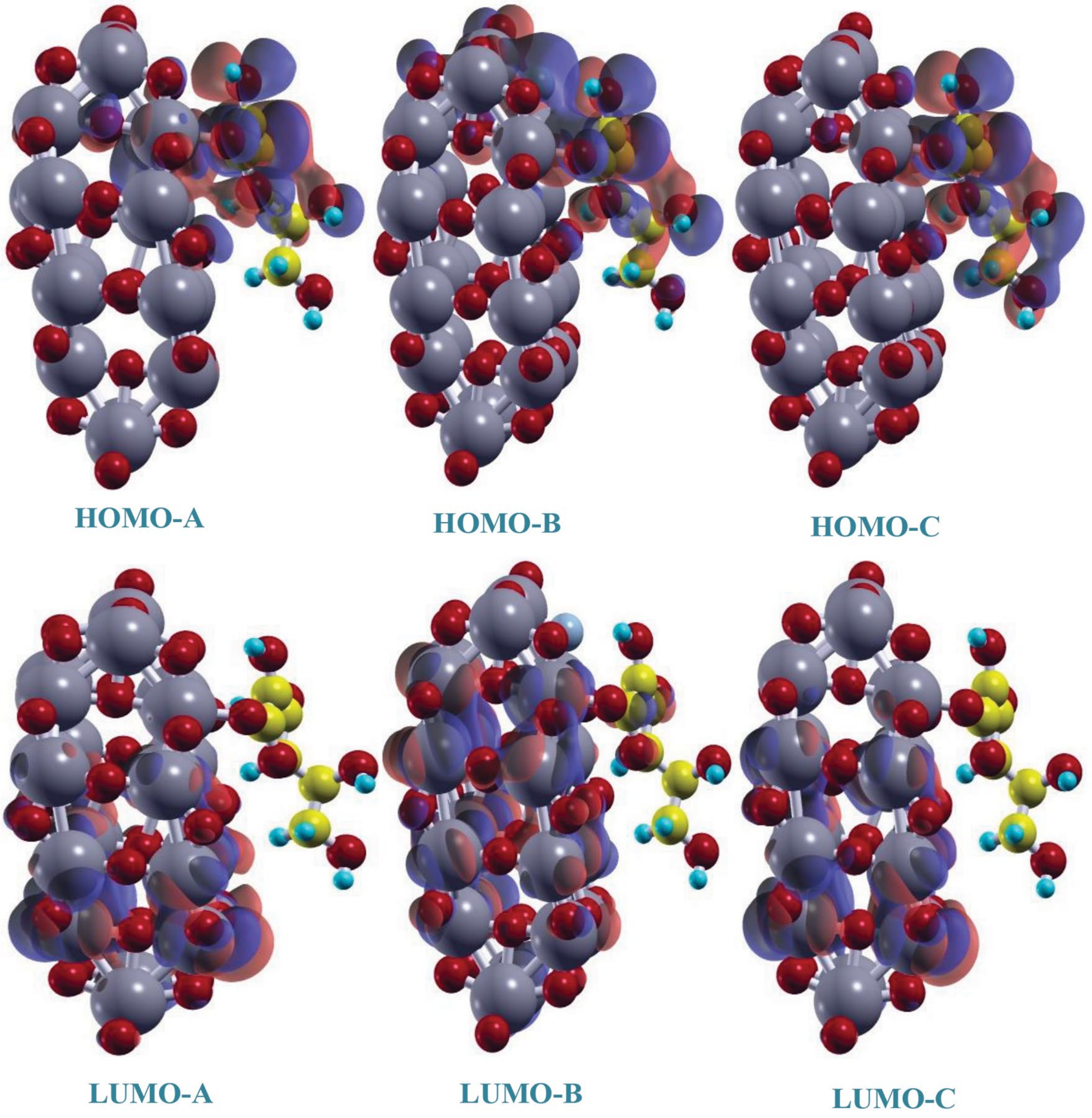

Fig. 9. Isosurfaces of HOMOs and LUMOs for vitamin C molecule adsorbed on the undoped and N-doped TiO_2 nanoparticles (parallel adsorption configurations).

Sensing performance

In order to further examine the sensing ability of TiO_2 based sensors, we have discussed the sensing response of these sensors. The electrons transferred from vitamin C molecule to the TiO_2 nanoparticle will affect the electronic properties of TiO_2 particles. The higher the amount of electrons transferred to the TiO_2, the larger the increase in resistance. This increase in the resistance indicates a better adsorption or sensing performance for TiO_2 based sensors. The sensing performance is normally estimated based on the following formula:

$$\eta = (R_g - R_a)/R_a = \Delta R/R_a \tag{3}$$

Where R_g is the resistance measured in the working circumstances, whereas R_a denotes the resistance in the air. The ΔR is in direct proportion to the electron transfer ΔQ, and the sensing response η is in direct proportion to $\Delta Q/Ra$.

For parallel adsorption of vitamin C on the TiO_2 (configurations A-C), we know that the size order of electron transfer (ΔQ) is: $\Delta Q_A > \Delta Q_B > \Delta Q_C$, where ΔQ_A, ΔQ_B, ΔQ_C represent the electron transfer in adsorption complexes A, B and C, respectively. Thus, the sensing performance of TiO_2 based sensors follows the order: ηA>ηB>ηC, where ηA, ηB, ηC represent the sensing response of sensors based on complexes A, B and C, respectively.

For perpendicular adsorption on the TiO_2, the magnitude order of sensing response is ηD>ηE>ηF, in line with the electron transfer order $\Delta Q_D > \Delta Q_E > \Delta Q_F$. In this case, ηD, ηE, ηF denote the sensing response of sensors based on adsorption complexes D, E and F, respectively.

As a result, it can be inferred that the nitrogen doping is an efficient strategy in order to increase the sensing performance of TiO_2. The increase in the electron transfer upon the adsorption of vitamin C is a major electronic reason taken into account for improving the sensing abilities. Here, a direct relation was found between the adsorption energy and sensing response. The N-doped TiO_2 nanoparticles have a greater sensing response than the pristine ones, in accordance with the higher adsorption energy of N-doped nanoparticles.

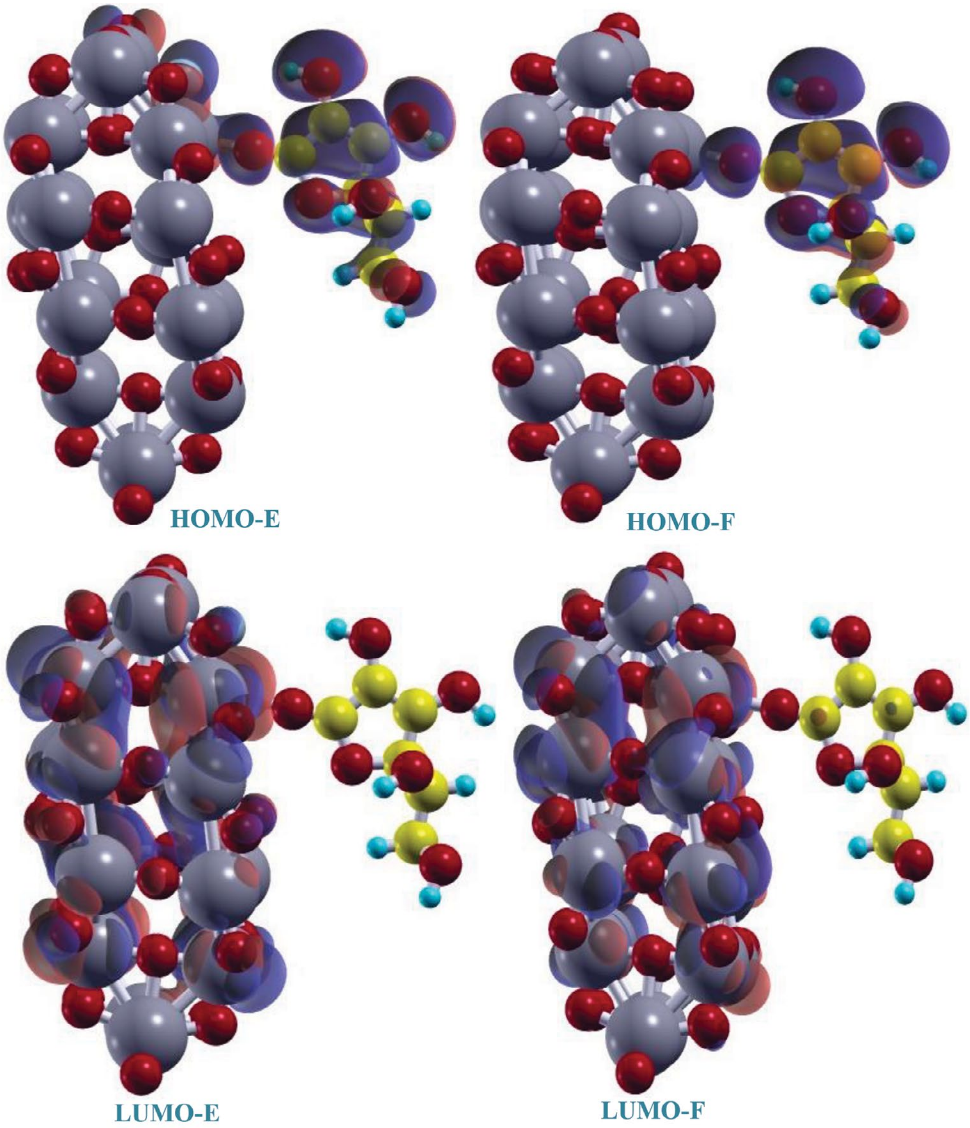

Fig. 10. Isosurfaces of HOMOs and LUMOs for vitamin C molecule adsorbed on the undoped and N-doped TiO_2 nanoparticles (perpendicular adsorption configurations).

CONCLUSIONS

DFT calculations were performed to investigate the adsorption properties of vitamin C molecule on the undoped and N-doped TiO_2 anatase nanoparticles. The adsorption behaviors of the vitamin C on the fivefold coordinated titanium sites of TiO_2 nanoparticles were studied in detail. The results show that the C-O bond of the adsorbed vitamin C molecule was elongated after the adsorption process, giving rise to the weakening C-O bond of the vitamin C molecule. The results also indicate that the interaction of vitamin C molecule with N-doped TiO_2 nanoparticle is energetically more favorable than the interaction with undoped one. Therefore, the N-doped nanoparticle can react with vitamin C molecule more efficiently. With the inclusion of vdW interactions, the adsorption energies were significantly increased. The considerable overlaps between the PDOS spectra of the oxygen atom of vitamin C molecule and titanium atom of TiO_2 nanoparticle indicate that chemical bond was formed between these two atoms. This formation of chemical bonds confirms the chemisorption of vitamin C over the TiO_2 nanoparticle. Mulliken population analysis reveals a significant charge transfer from the vitamin C molecule to the TiO_2 nanoparticle. After the adsorption, the HOMOs of the adsorption systems were dominant over the adsorbed vitamin C molecule, while the LUMOs were mainly concentrated on the TiO_2 nanoparticle.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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