Scientific paper

The Interaction of Acrolein with Pristine and N-doped TiO_2 Anatase Nanoparticles: A DFT Study

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Abstract

Density functional theory calculations were carried out in order to study the effects of the adsorption of acrolein molecule on the structural and electronic properties of TiO_2 anatase nanoparticles. The ability of pristine and N-doped TiO_2 anatase nanoparticles to recognize toxic acrolein (C_3H_4O) molecule was surveyed in detail. It was concluded that acrolein molecule chemisorbs on the N-doped anatase nanoparticles with large adsorption energy and small distance with respect to the nanoparticle. The results indicate that the adsorption of acrolein on the N-doped TiO_2 is energetically more favorable than the adsorption on the pristine one, suggesting that the N doping can energetically facilitate the adsorption of acrolein on the N-doped nanoparticle. It means that the N-doped TiO_2 nanoparticle can react with acrolein molecule more efficiently. The interaction between acrolein molecule and N-doped TiO_2 can induce substantial variations in the HOMO/LUMO molecular orbitals of the nanoparticle, changing its electrical conductivity which is helpful for developing novel sensor devices for the removal of harmful acrolein molecule. The large overlaps in the projected density of states spectra reveal the formation of chemical bond between two interacting atoms. Charge analysis based on Mulliken charges indicates that charge is transferred from the acrolein molecule to the TiO_2 nanoparticle.

Keywords: Acrolein; TiO_2; Electronic properties; Density functional theory; sensor

1. Introduction

Titanium dioxide (TiO_2) has been characterized as one of the most widely used photocatalytic materials with a wide range of applications in photo-catalysis,[1] gas sensor devices, heterogeneous catalysis and photovoltaic cells. It has attracted numerous scientific interests in the recent years because of its outstanding properties such as non-toxicity, chemical stability, abundance and high catalytic efficiency. These unique properties make TiO_2 very interesting material to be utilized in many fields of science and research.[1–8] Numerous attempts have been done in order to develop theoretical aspects of TiO_2 related science and technology including fundamental principles and crucial practical features of TiO_2. [1–15] The photocatalytic activity of TiO_2 has been restricted due to its relatively wide band gap. This large band gap allows the absorption of the small percentage of the incoming solar light. One convenient solution to enhance the optical response and level of photo-efficiency of TiO_2 is non-metal doping such as nitrogen.[16–18] Several computational studies of N-doped TiO_2 nanoparticles have been published in the literature. For example, Liu et al. reported that the N doping can facilitate the adsorption of nitric oxide molecule on TiO_2 anatase nanoparticles.[14] Recently, it has been suggested that the N-doped TiO_2 anatase nanoparticles can react with CO molecules more efficiently, compared to the undoped ones.[19] Moreover, the nitrogen doping of TiO_2 nanoparticles improves its sensing capabilities, thus altering its electronic and structural properties.[20–25] The impacts of N-doping on the photo-catalytic activity and therefore the energy gap of TiO_2 have been inspected in some other works.[26,27] In order to reveal the enhancement of the efficiency of TiO_2 nanoparticles in the adsorption processes, some researchers have analyzed its electronic properties such as density of states (DOS), Mulliken population

analysis and also its structural properties such as bond lengths and adsorption energies.[14,19,28] A material in the atmosphere which causes harmful effects on the public health and the environment is identified as an air pollutant, which can have different forms such as solid particles, liquid droplets or gasses. Acrolein is in the liquid form and has been classified as a hazardous material.[29] It is produced as the result of incomplete combustion in the course of wood and house fires, plastics combustion, fast foods and mobile source emissions. C_3H_4O is mainly generated by cigarette smoking (50–90 ppm of C_3H_4O per cigarette). It can also make detrimental effects on the lung cells and can be also characterized as one of the most dangerous lung irritants.[30] Thus, the removal of C_3H_4O molecule from the atmosphere is an important subject to public health and environmental protection.[31] An admirable gas sensor should have some important properties such as high sensitivity to the harmful material, extensive variety of application and low price fabrication.[32] Solid state sensors such as TiO_2 anatase nanoparticles are one of the most broadly used materials for recognition of toxic molecules in the atmosphere due to their unique response to the air pollutants. In this work, we have studied the adsorption behaviors of undoped and N-doped TiO_2 anatase nanoparticles for chemical sensing of C_3H_4O molecule. We have considered different adsorption configurations of the C_3H_4O molecule on the TiO_2 anatase nanoparticles. The variations of the structural and electronic properties of the considered nitrogen-doped TiO_2 anatase nanoparticles resulting from the adsorption of C_3H_4O were studied in detail. Based on the obtained results, it can be concluded that the electronic properties of TiO_2 anatase nanoparticle are strongly changed by the adsorption of C_3H_4O. This work aims to supply an overall understanding on the adsorption behaviors of TiO_2 nanoparticles for the detection of harmful C_3H_4O molecule in the environment.

2. Details of Computations and Structural Models

2. 1. Computational Methods

The calculations were performed based on DFT[33,34] as implemented in the Open source Package for Material eXplorer (OPENMX3.7),[35] which has been demonstrated to be an efficient software package for the simulation of large atomic systems. The same outer electrons of Ti atom were considered as valence electrons in the self-consistent field iterations. Pseudo atomic orbitals (PAOs) centered on atomic sites were used as basis sets in order to expand the wave functions in a KS scheme with a cutoff energy of 150 Ry (Rydberg).[34] The numerical PAO basis functions were generated by using a basis set of two-s, two-p, one-d for Ti atom, two-s and two-p for O, N and C atoms and two-s for H atom with the considered cutoff radii set to the values of 7 for Ti, 5.5 for H and 5 for O, N and C (all in Bohrs). The generalized gradient approximation (GGA) in the Pedrew-Burke-Ernzerhof (PBE) form was used in order to describe the exchange-correlation energy functional.[36] An open-source program XcrysDen[37] was used for visualization of the data such as molecular orbitals and the other figures. All particles are separated by a vacuum space of about 11.5 Å, which has been tested and proven to avoid the interaction force between neighbor particles. Different adsorption configurations of C_3H_4O on TiO_2 anatase nanoparticles are considered in this work. The configurations included both parallel and perpendicular orientations of the C_3H_4O molecule towards the pristine and N-doped nanoparticles. The adsorption energy was calculated by using the following formula:

$$E_{ad} = E_{(particle + adsorbate)} - E_{particle} - E_{adsorbate} \quad (1)$$

where $E_{(particle + adsorbate)}$, $E_{particle}$ and $E_{adsorbate}$ are the total energies of the complex system, TiO_2 nanoparticle without any adsorbed molecule and free C_3H_4O molecule in the vacuum, respectively. The charge transfer between the C_3H_4O molecule and the TiO_2 nanoparticle was evaluated based on Mulliken charge analysis.

2. 2. Structural Models

The studied TiO_2 anatase nanoparticles were constructed by placing a $3 \times 2 \times 1$ supercell of pristine and N-doped TiO_2 anatase along x, y and z axes, respectively. The considered unit cell of TiO_2 has been reported by Wyckoff, taken from "American Mineralogists Database"

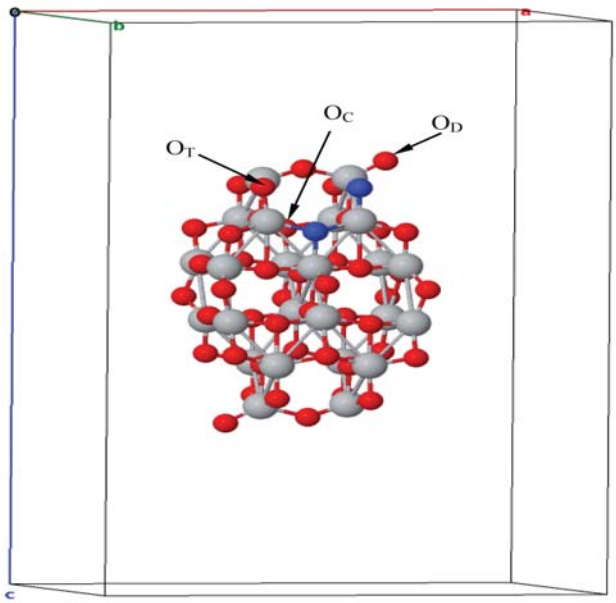

Figure 1. Optimized structure of the 72 atom N-doped TiO_2 anatase nanoparticle constructed from $3 \times 2 \times 1$ unit cells; O_C: central oxygen; O_T: twofold coordinated oxygen; O_D: dangling oxygen.

webpage.[39] Figure 1 displays the optimized structure of 2N-doped TiO_2 anatase located in an appropriate simulation box. The size of the studied nanoparticles has been chosen following Lei et al.[11] and Liu et al.[14]. The results published by Lei et al.[11] indicated that the smaller the particle is, the higher the average energy is. They have demonstrated that the 72 atom TiO_2 nanoparticles have the lowest energy among the different types of nanoparticles.

The size of the box considered in these calculations is $20 \times 15 \times 30$ Å^3, being larger than the size of the chosen nanoparticle. Two oxygen atoms of pristine TiO_2 (twofold coordinated and threefold coordinated oxygen atoms) were substituted by nitrogen atoms to build N-doped nanoparticles. Twofold coordinated and threefold oxygen atoms are denoted by O_T and O_C (middle oxygen), respectively (see figure 1). Acrolein (C_3H_4O) is the simplest unsaturated aldehyde with three carbon, four hydrogen and one oxygen atoms. The acrolein molecule is positioned parallel and perpendicular with respect to the optimized undoped and N-doped nanoparticles on different orientations. The optimization of the complex system shows that the oxygen atom of acrolein molecule preferentially interacts with the fivefold coordinated titanium atom of TiO_2. This reveals a higher activity of oxygen atoms of acrolein, compared to the carbon atoms. The optimized structures of the N-doped nanoparticles were displayed in Figure 2.

3. Results and Discussion

3. 1. Bond Lengths and Adsorption Energies

The acrolein molecule was adsorbed on the fivefold coordinated Ti site of TiO_2. In one orientation, acrolein molecule was placed vertically towards the nanoparticle (perpendicular orientation) and the other is that acrolein was put horizontally on the nanoparticle (parallel orientation). Figure 3 displays the optimized geometry configurations of TiO_2 nanoparticles with adsorbed acrolein molecules. This Figure includes the C_3H_4O-adsorbed complexes, labeled by A1-A5 for perpendicular configuration and A6-A9 for parallel one.

Each complex in Figure 3 differs in the substituted oxygen atom of TiO_2 nanoparticle and/or adsorbed C_3H_4O orientation from the other complexes. For example, complex A2 was constructed from N-doped TiO_2 (at O_C site) and C_3H_4O molecule with perpendicular orientation. The optimized values of some bond lengths before and after the adsorption on the nanoparticle are listed in Table 1. The reported bond lengths in this table include the newly formed Ti-O bond and C-O bond of C_3H_4O molecule. The results indicate that the C-O bond of C_3H_4O molecule was elongated after the adsorption process. These variations of bond lengths are probably due to the transfer of electronic density from Ti-O_D bond of TiO_2 and C-O bond of the adsorbed C_3H_4O molecule to the newly formed Ti-O bond between the titanium atom of TiO_2 nanoparticle and the oxygen atom of the C_3H_4O molecule. The smaller the bond formed between the oxygen atom of acrolein molecule and the titanium atom (Ti-O), the stronger the adsorption of acrolein on the TiO_2 anatase nanoparticle. The most stable adsorption configurations of the acrolein molecule on the undoped and N-doped TiO_2 nanoparticles are shown in Figure 3. The results of adsorption energies indicate that the acrolein molecule is preferentially adsorbed on the fivefold coordinated titanium site of TiO_2 through its oxygen atom. The calculated adsorption energies are listed in Table 1. These results indicate that the adsorption of C_3H_4O molecule on the N-doped nanoparticle is energetically more favorable than the adsorption on the undoped one. The small adsorption distance and great adsorption energy reveal chemisorption of acrolein molecule on the nanoparticles. The results also show that the O_C-substituted nanoparticle adsorbs acrolein

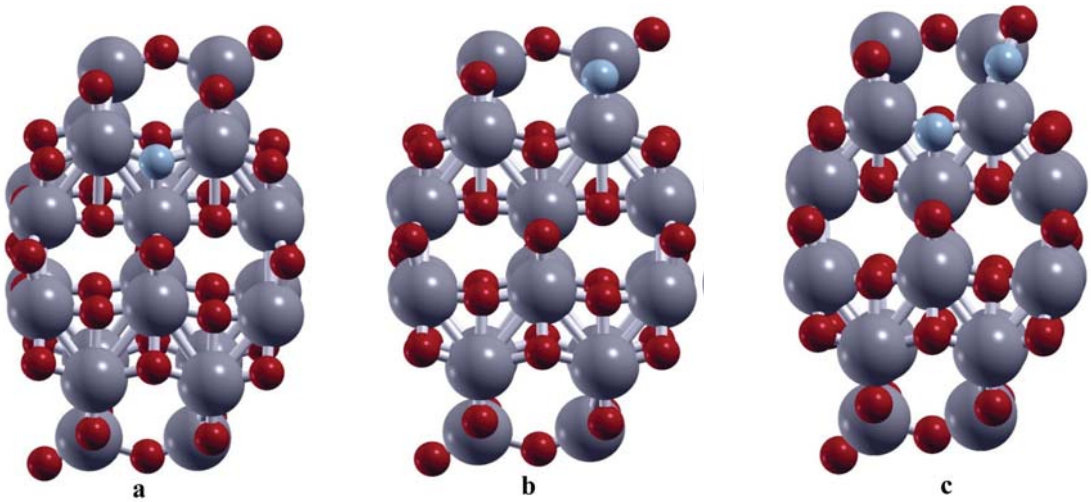

Figure 2. Optimized N-doped TiO_2 anatase nanoparticles, (a) O_C substituted N-doped anatase nanoparticle, (b) O_T substituted and (c) $O_{C,T}$ substituted one. The larger gray spheres are Ti atoms and the small red and blue ones represent O and N atoms, respectively.

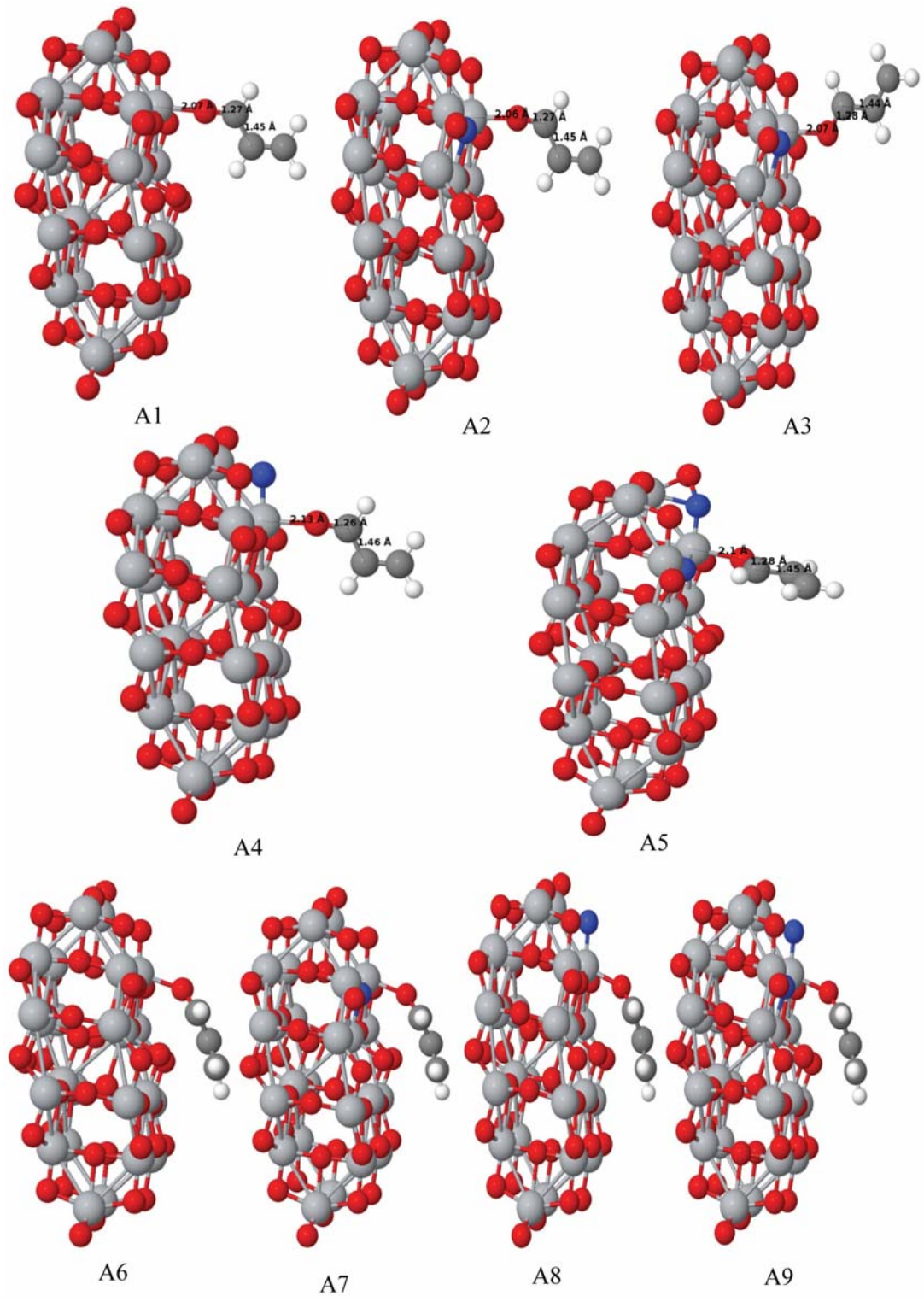

Fig. 3. Optimized geometry configurations of C_3H_4O-TiO_2 complexes. Colors represent atoms accordingly, Ti in light grey, O in red, N in blue, C in dark grey and H in white.

molecule more efficiently, compared to the O_T-substituted one. Besides, the adsorption on the 2N-doped nanoparticle was found to be more energetically favorable than the adsorption on the N-doped nanoparticle, suggesting that the N-doping strengthens the adsorption of C_3H_4O on the TiO_2 nanoparticle. In other words, two doped nitrogen atoms in the nanoparticle make the interaction of C_3H_4O molecule with TiO_2 stronger. The more negative the adsorption ener-

gy, the higher tendency for adsorption, and consequently more energy favorable adsorption. The improvement of both adsorption energy and structural properties of the adsorption of C_3H_4O on TiO_2 resulting from N-doping indicates that the N-doped TiO_2 can be effectively used for the removal of the toxic acrolein molecules in the environment. The increasing of efficiency of the TiO_2 nanoparticles in the adsorption process by N-doping has been recently studied by Liu et al. for adsorption of CO molecule.[19]

3. 2. Electronic Structures

Figure S1 displays the total density of states (TDOS) for the pristine and the N-doped anatase TiO_2 particles before and after the adsorption process. This Figure shows that the differences between DOS of doped and undoped TiO_2 are increased by the adsorption of C_3H_4O molecule. These differences included both increasing shifts of the energies of states and creation of some peaks in the DOS of the pristine TiO_2. The main changes are the creation of some small peaks in the DOS of N-doped TiO_2 at the energy range of –7 eV to –12 eV. As distinct from the DOS spectra, the energies of the states were shifted to the lower values and also the energy gap of TiO_2 was slightly downshifted (especially in panel d), implying that the conductivity of the system was improved upon C_3H_4O adsorption. This improved conductivity increases the sensing capability of TiO_2 nanoparticles for C_3H_4O detection. The changes in DOS states would affect the electronic transport properties of the nanoparticles and this feature can be useful for sensing of C_3H_4O by TiO_2 nanoparticles. The positive variations in the DOS of TiO_2 around the Fermi level improves the sensitivity of the TiO_2 for chemical sensing of C_3H_4O. The titanium and oxygen projected DOSs (Ti-PDOS and O-PDOS) were shown in Figure 4 (panels (a–f) for perpendicular adsorption con-

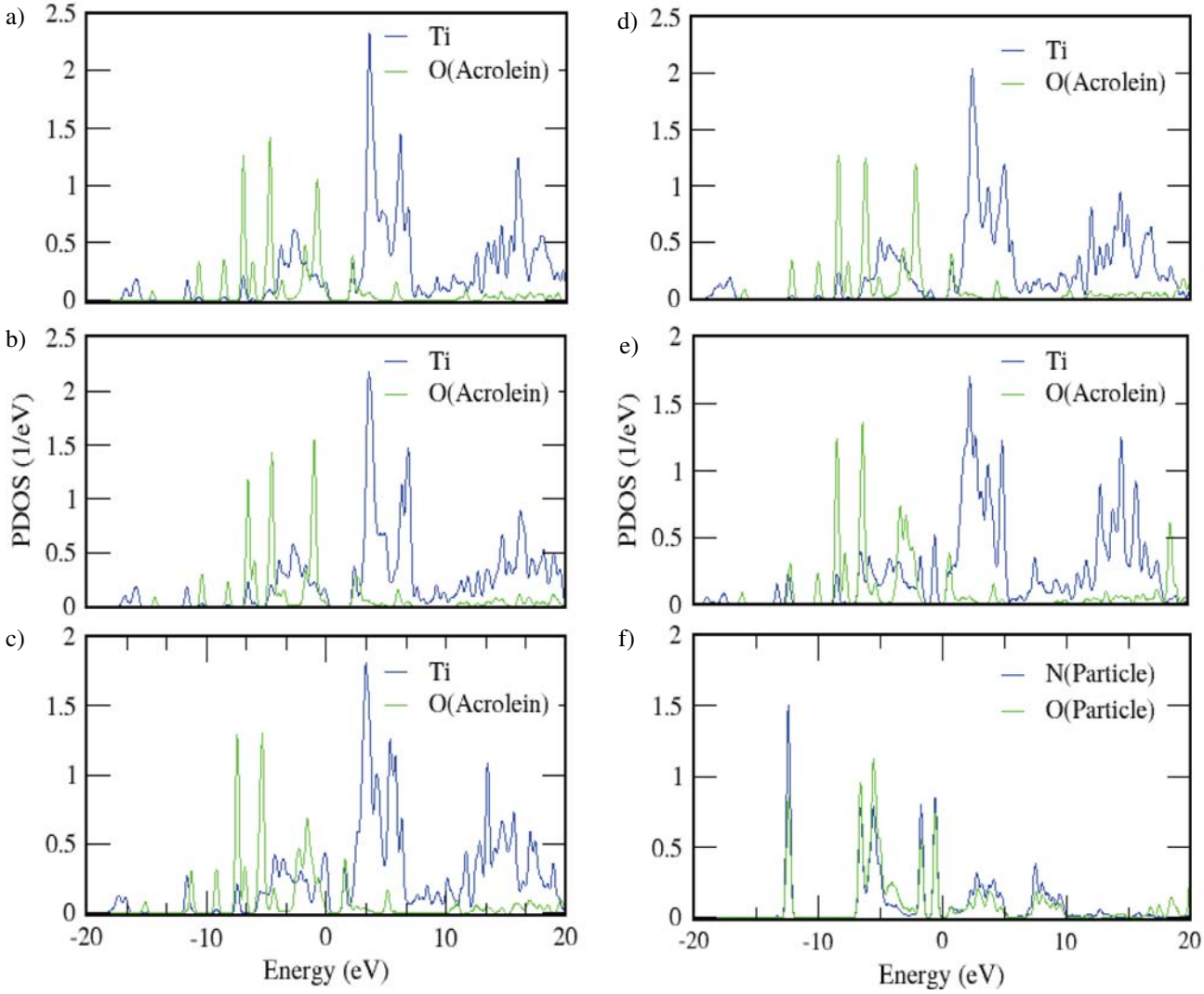

Figure 4. PDOS for the adsorption of C_3H_4O molecule on the N-doped nanoparticles, a: Complex A1; b: Complex A2; c: Complex A3; d: Complex A4; e: Complex A5; f: Complex A5.

figuration). The large overlaps between the PDOSs of these two atoms reveal the formation of new Ti-O bond between the titanium atom of nanoparticle and oxygen atom of acrolein molecule. This implies that the acrolein molecule chemisorbs on the TiO_2 nanoparticle.

The corresponding PDOSs of the titanium and oxygen atoms for parallel configuration were shown in **Figure S2**, indicating considerable overlaps between the PDOSs of titanium and oxygen atoms. This PDOS overlaps represent that the oxygen atom of the acrolein molecule forms chemical bond with the fivefold coordinated titanium atom of TiO_2. For perpendicular configuration, the PDOSs of the titanium and oxygen atoms before and after the adsorption process were presented in **Figure S3**. This figure mainly shows the small shifts in the energy of the states to the lower energy values after the adsorption of acrolein molecule. The variations in the PDOS spectra are expected to make changes on the corresponding electronic properties. As a result, the chemisorbed acrolein on the N-doped TiO_2 gives rise to a considerable increase in the electrical conductivity of the doped TiO_2 particle.

Figure 5 displays the isosurfaces of HOMO and LUMO molecular orbitals for acrolein molecule adsorbed on the nanoparticles. As a matter of convenience, we only presented the molecular orbital calculations for three complexes. These Figures show that the electronic densities in the HOMOs are mainly located on the acrolein molecule, whereas the LUMO's are strongly localized on the TiO_2 nanoparticle. The increasing of the electronic density at the middle of the newly-formed bonds and consequently formation of new bonds were also confirmed by these molecular orbital diagrams.

3. 3. Charge Transfer Analysis

To further investigate the charge transfer between acrolein molecule and TiO_2 nanoparticle, we present in Table 1 the charge analysis based on Mulliken charges for

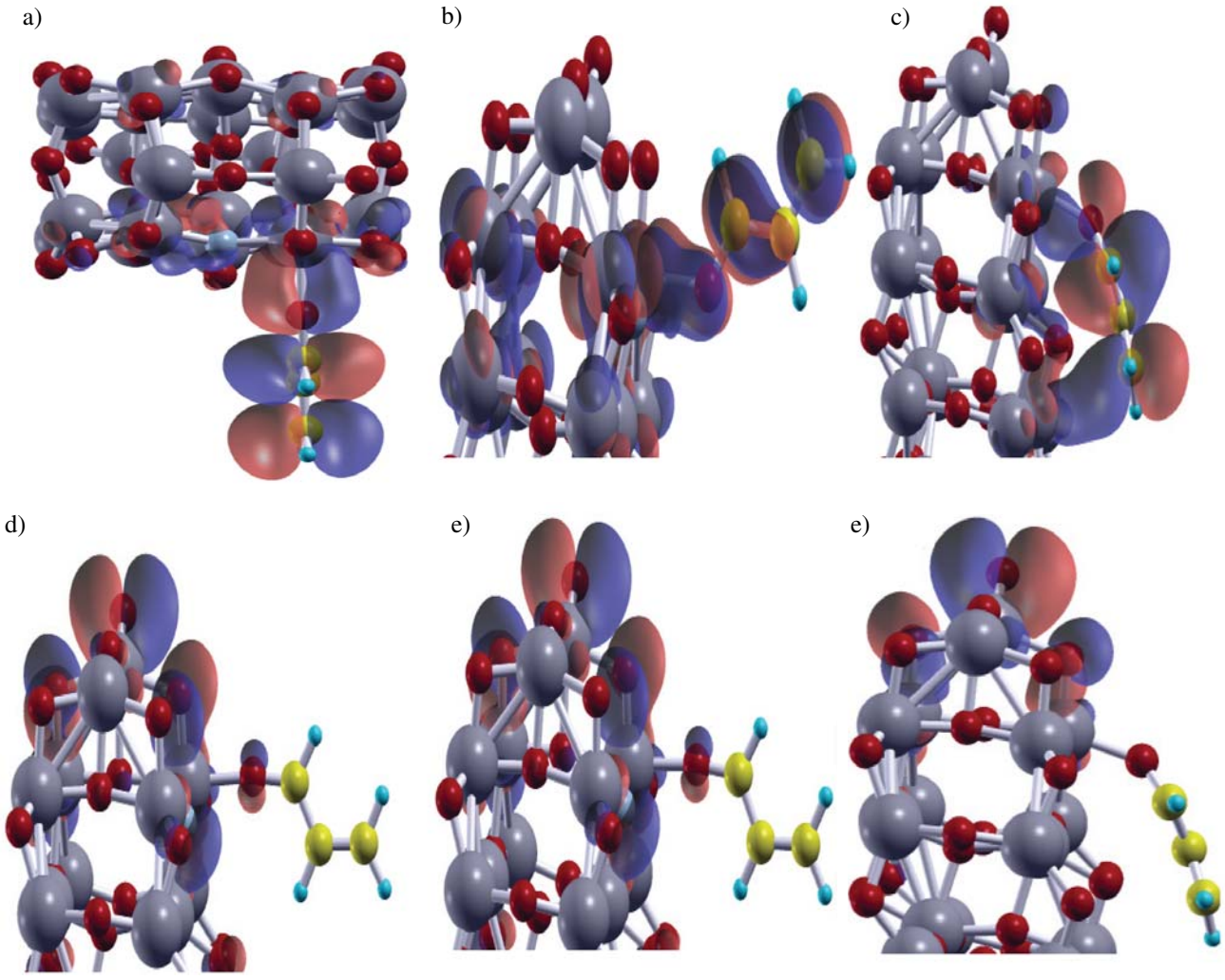

Figure 5. The isosurfaces of HOMO and LUMO molecular orbitals of the systems consisting of the C_3H_4O on the considered nanoparticles, a: Complex A2; b: Complex A1; c: Complex A6; d: Complex A2; e: Complex A1; f: Complex A6.

acrolein molecule. The charge difference for the particle j after and before adsorption, was calculated by using the following formula:

$$\Delta Q_j = Q_{j\,(in\ complex)} - Q_{j\,(in\ vacuum)} \quad (2)$$

where Q_j is the value of Mulliken charge of the j. Subscript "j" means the TiO_2 nanoparticle or acrolein molecule. The charge difference, ΔQj, is a measure of the amount of charge transferred to, or, from the studied nanoparticles from, or, to the acrolein molecule. For configuration A1, the charge analysis reveals that acrolein adsorption induces a relatively considerable charge transfer of about –0.23 |e| (e, the electron charge) from acrolein to the TiO_2 nanoparticle (see Table 1). It implies that TiO_2 nano particle acts as an electron acceptor from the acrolein molecule. The *Δ*Q values for other configurations are listed in Table 1. It should be noted that the charge transfer makes changes on the conductivity of the system. This could be an effective property to help in the design and improvement of TiO_2-based sensor devices for acrolein detection in the environment.

Table 1. Bond lengths (in Å), Mulliken charges (in |e|) and adsorption energies (in eV) for a C_3H_4O molecule adsorbed on the TiO_2 anatase nanoparticles.

Type of complex	Ti-O	C-O	ΔQ	ΔE_{ad}
A1	2.11	1.27	–0.23	–1.88
A2	2.20	1.25	–0.22	–3.58
A3	2.18	1.27	–0.27	–4.17
A4	2.13	1.26	–0.19	–3.17
A5	2.10	1.28	–0.27	–4.20
A6	2.10	1.28	–0.35	–1.48
A7	2.05	1.31	–0.38	–4.11
A8	2.06	1.25	–0.33	–3.95
A9	2.10	1.28	–0.35	–4.15
Non-adsorbed		1.23		

4. Conclusions

The adsorption behaviors of undoped and N-doped TiO_2 anatase nanoparticles for acrolein detection were investigated using the DFT computations. We found that the N-doped nanoparticles have higher efficiency to adsorb toxic C_3H_4O molecule on their surfaces than the pristine ones. It means that the adsorption of C_3H_4O on the N-doped nanoparticles is more favorable in energy than the adsorption on the undoped ones. The effect of adsorption of C_3H_4O on the structural and electronic properties including the adsorption distances, adsorption energies, charge transfers, electronic DOS and PDOSs and molecular orbitals were calculated. It was found that N-doped TiO_2 can be efficiently utilized for removing and sensing of C_3H_4O in the environment. Charge analysis based on Mulliken charges indicates a charge transfer from acrolein molecule to nanoparticle. Adsorption of C_3H_4O molecule leads to significant changes in the electronic properties of TiO_2 nanoparticle, altering its conductivity. Our calculated results present a great potential of N-doped TiO_2 anatase for application as a highly sensitive molecule sensor.

5. Acknowledgement

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6. Supplementary Material

DOS spectra for different adsorption configurations of acrolein molecule on the considered undoped and N-doped TiO_2 nanoparticles and PDOS spectra for in order to reveal the overlap between interacting atoms.

7. References

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Povzetek

Z uporabo funkcionalno gostotne teorije smo preučevali vplive adsorpcije molekule akroleina na strukturne in elektronske lastnosti čistih in N-dopiranih nanodelcev atanasa TiO_2. Izkazalo se je, da se molekula akroleina z veliko energijo in majhno razdaljo kemisorbira na N-dopiranih nanodelcih anatasa. Adsorpcija akroleina na N-dopirani TiO_2 je energetsko ugodnejša od adsorpcije na čist TiO_2, kar pomeni, da lahko N-dopirani TiO_2 nanodelci z molekulo akroleina učinkoviteje interagirajo. Interakcija med molekulao akroleina molekulo in N-dopiranim TiO_2 lahko povzroči znatne spremembe v HOMO/LUMO molekulskih orbitalah nanodelcev ter spremeni električno prevodnost sistema, kar je uporabno za razvoj novih senzorskih naprav za zaznavanje in odstranjevanje škodljivih molekul akroleina. Velika prekrivanja v gostoti napovedani stanj kažejo na možen nastanek kemijske vezi med dvema interagirajočima atomoma. Iz izvedene analize Mullikenovih nabojev lahko sklepamo na prenos naboja od molekule akroleina na nanodelec TiO_2.