

A theoretical study on the adsorption behaviors of Ammonia molecule on N-doped TiO₂ anatase nanoparticles: Applications to gas sensor devices

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Abstract

We have performed density functional theory investigations on the adsorption properties of ammonia molecule on the undoped and N-doped TiO₂ anatase nanoparticles. We have geometrically optimized the constructed undoped and N-doped nanoparticles in order to fully understand the adsorption behaviors of ammonia molecule. For TiO₂ anatase nanoparticles, the binding site is preferentially located on the fivefold coordinated titanium sites. However, we have mainly studied the interaction of NH₃ molecule over the fivefold coordinated titanium sites including the bond lengths, bond angles, adsorption energies, density of states (DOSs) and molecular orbitals. The results indicated that the adsorption of NH₃ molecule on the N-doped nanoparticles is energetically more favorable than the adsorption on the undoped one, suggesting the strong adsorption of NH₃ molecule on the N-doped nanoparticles. Adsorption on the N-doped nanoparticles leads to the more stable and favorable complexes. Our theoretical work represents that the N-doped nanoparticles have higher sensing capability than the pristine ones to remove the hazardous NH₃ molecules from the environment.

Keywords: Adsorption; Density Functional Theory (DFT); Density of states; TiO₂; NH₃.

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INTRODUCTION

Titanium dioxide (TiO₂) has attracted extreme attentions as a promising semiconductor material with wide range of technological applications. It is utilized in heterogeneous catalysis (systems containing metal/TiO₂) as a photocatalyst [1, 2], organic dye-sensitized solar cells [3], gas sensor devices [4] and as a gate insulator for the new generation of MOSFETS (metal oxide semiconductor field effect transistor) [5, 6]. Titanium dioxide is the brightest, nontoxic, whitest pigment available. It has also the highest refractive index of any material known (2.95 for rutile, 2.55 for anatase) and high band gap energy (3.0 eV for rutile, 3.2 eV for anatase). It is also chemically inert, insoluble in polymers, and heat stable under severest processing conditions [5-8], which has aroused many scientific and industrial efforts over

the last few years [8-10]. Important polymorphs (crystalline forms) of TiO₂ exist, namely anatase and brookite, which have low temperature and low pressures, and rutile, the stable polymorph at all temperature and ambient pressure [11]. Several scientific studies have been carried out in order to discover the outstanding properties of titanium dioxide and promising results have been obtained [12-15]. Due to the wide band-gap, it can only absorb a little percentage (4 %) of the solar spectrum. So, the alternative would be the procedure that could extend the optical sensitivity of TiO₂ to the visible area. The nitrogen doping is an appropriate solution, which makes noticeable improvements on the photocatalytic activity and adsorption ability of TiO₂ [16-21]. N-doped TiO₂ anatase nanoparticles have attracted many interests as important candidates for industrial

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and scientific researches. For instance, Liu *et al.* [20] studied the adsorption of NO molecule on undoped and N-doped TiO₂ anatase nanoparticles, in the related work, by Liu *et al.* it has been suggested that the N-doped TiO₂ nanoparticles can react with CO molecule more efficiently [14]. Furthermore, the substitutional doping of TiO₂ with nitrogen leads to improving the electronic and structural properties of TiO₂ particles. The influences of doping of TiO₂ anatase with some elements on its band-gap and photocatalytic activity have been investigated in some other researches [22-29]. The principal strategy towards achieving extensive utility and high efficiency of TiO₂ nanoparticles in the adsorption processes is to perform important investigations on the main structural, optical and electronic properties of TiO₂. In industrial processes, metal oxides especially TiO₂, are commonly utilized as detectors or adsorbents for removing the NH₃ molecules from the environment [12]. In this study, we performed density functional theory (DFT) calculations in order to comprehend NH₃ adsorption on N-doped TiO₂ anatase nanoparticles. Hence, some electronic and structural properties including the total density of states (TDOS), bond lengths, bond angles and adsorption energies have been analyzed. The results indicate that the NH₃ molecule is more efficiently adsorbed on N-doped nanoparticles, compared to the undoped ones. The aim of this study is to theoretically investigate the adsorption behaviors of NH₃ molecule on the modified TiO₂ anatase nanoparticles.

EXPERIMENTAL

Calculation detail

Density functional theory (DFT) calculations [30, 31] are performed using the Open source Package for Material explorer (OPENMX) ver. 3.7 [32] to investigate the energetics of ammonia adsorption on anatase nanoparticles. OPENMX is an efficient software package for nano-scale material simulations based on DFT, norm-conserving pseudopotentials, and pseudo-atomic localized basis functions [33, 34]. Pseudo atomic orbitals (PAO's) centered on atomic sites are used as basis sets in order to expand the wave functions in a KS schema. The PAO's considered here were created by using a basis set (two-s, two-p, one-d) for Ti atom, two-s and two-p for O and N atoms, three-s for H atom within a cutoff radii set to the values of 7 for Ti, 5 for O and N and 5 for H (all

in Bohrs). The generalized gradient approximation (GGA) in the Pedrew-Burke-Ernzerhof (PBE) form [34], was employed for the exchange and correlation functional. The convergence criteria for energy and self-consistent field iterations were set to the values of 10⁻⁴ Hartree/bohr and 10⁻⁶ Hartree, respectively. The spin-polarization was used in the calculations because of odd electron numbers in the N-doped nanoparticles. For visualizing data such as charge densities, adsorption mechanism configurations and the other figures, the open-source program XCrysDen [35] was utilized. The size of the box considered in these computations is 20×15×30 Å³, which contains 72 atom (24 Ti atoms and 48 O atoms) of undoped or N-doped TiO₂ nanoparticles. Ammonia molecule has trigonal bipyramidal structure and the estimated N-H bond length and H-N-H bond angle values in the gas phase state were computed to be 1.08 Å and 106.5°, respectively, in reasonable accordance with previous theoretical results [12]. The real-space grid techniques are applied in numerical integrations and the Poisson equation solution using Fast Fourier Transform (FFT). The computations were carried out by use of a cluster of Ubuntu systems installed on the core-i7 processors with at least 8 GB memory per each computational core. The adsorption energy of NH₃ molecule on TiO₂ anatase particle is calculated using the following formula:

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

Where $E_{(particle + adsorbate)}$ is the energy of the complex system consisting of the NH₃ molecule bound to a TiO₂ anatase nanoparticles, $E_{particle}$ is the energy of the nanoparticles without any adsorbed molecule, and $E_{adsorbate}$ is the energy of isolated NH₃ molecule. According to this definition, a negative E_{ad} value represents that the NH₃ adsorption on the anatase nanoparticles is energy favorable process.

Structural Models

The considered TiO₂ anatase nanoparticles containing 72 atoms were modeled by placing 3×2×1 numbers of TiO₂ unit cells along x, y and z axis, respectively. The pristine 3×2×1 supercell of TiO₂ anatase was shown in Fig. 1.

A distance of 11.5 Å was set between neighbor particles to reduce the interaction between neighbor particles. The unit cell was taken from "American Mineralogists Database" webpage [36]

using x-ray crystallographic structure and reported by Wyckoff [37]. The considered TiO_2 anatase nanoparticles were shown in Fig. 2. N-doped anatase nanoparticles were made by substitution of two appropriate active surface oxygen atoms by nitrogen atoms, introducing a hole in the particle. In one doping configuration, a nitrogen atom substitute an oxygen atom in the middle of the particle and the other is a nitrogen atom substitute an oxygen atom at O_T position. The substituted oxygen atoms are the so-called "Central Oxygen" and "twofold coordinated oxygen" atoms, labeled by O_C and O_T in Fig. 2, respectively. We have geometrically optimized the obtained N-doped nanoparticles and constructed complex systems consisting of the ammonia molecule bound to an optimized TiO_2 nanoparticles. In this study, we have investigated the adsorption on the fivefold coordinated titanium atom site of the considered TiO_2 anatase nanoparticles due to the relatively high activity of this site in the adsorption process, compared to the other sites [14, 20]. The optimized geometrical structures of two kinds of N-doped nanoparticles were displayed in Fig. 3.

RESULTS AND DISCUSSION

Bond lengths and Bond angles

Adsorptions of NH_3 molecule on the active titanium site of undoped and N-doped TiO_2 anatase nanoparticles were discussed here from the structural and energetic points of view. Fig. 4 presents the structure of ammonia molecule before the adsorption process with bond length and angle results. The complexes contained in Fig. 5 differs from in substituted O_C or O_T atom of TiO_2 with respect to the anatase nanoparticles and indicate different orientations of ammonia molecule with respect to the nanoparticles. In adsorption type A, an ammonia molecule is positioned towards the O_C -substituted N-doped nanoparticles. The nitrogen atom is attracted by the titanium atom of nanoparticles with a slightly distortion from its original position. While type B adsorption complex represents the interaction of ammonia molecule over the fivefold coordinated titanium atom of O_T -substituted N-doped nanoparticles.

Fig. 5 also contained one configuration for ammonia adsorption on undoped anatase nanoparticles.

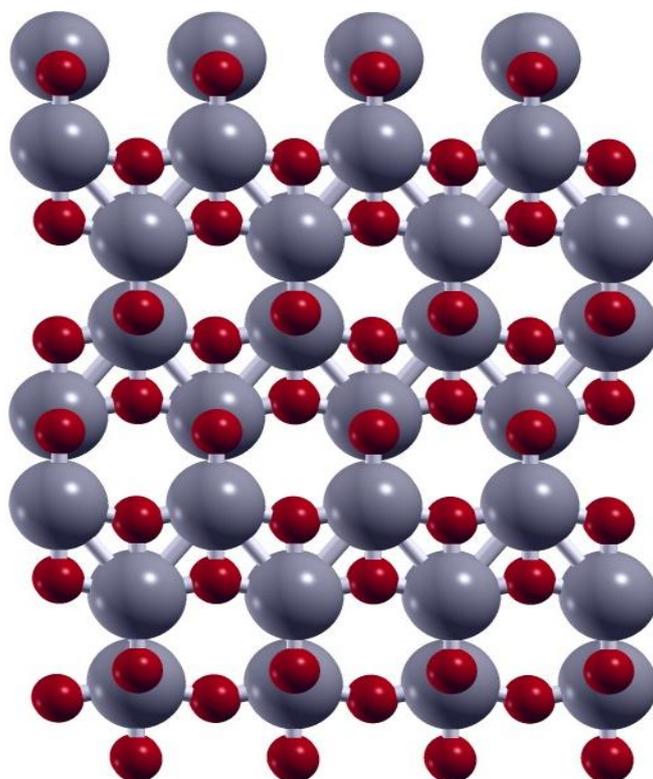


Fig. 1: Representation of a $3 \times 2 \times 1$ supercell of TiO_2 anatase constructed from TiO_2 anatase unit cells along x, y and z directions. Symbols for the individual atoms are: Ti in grey and O in red.

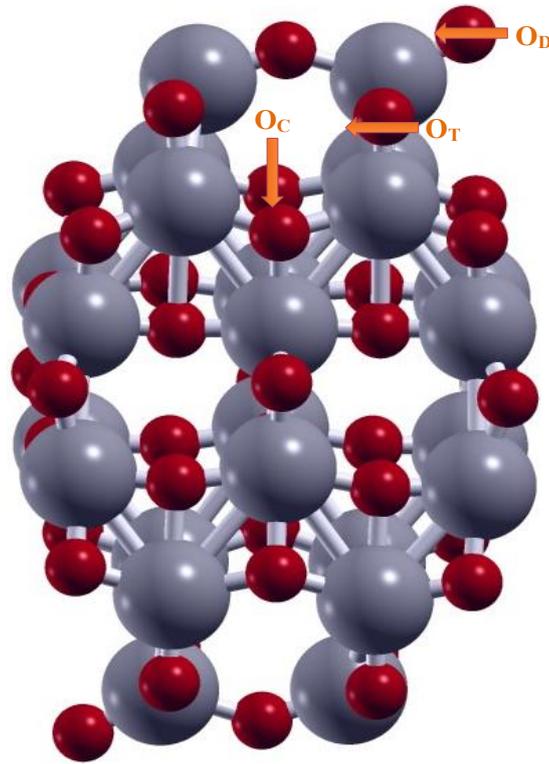


Fig. 2: Optimized structure of an undoped 72 atom TiO₂ anatase nanoparticle constructed from the 3×2×1 unit cells; O_c: Central oxygen; O_T: twofold coordinated oxygen; O_D: Dangling oxygen.

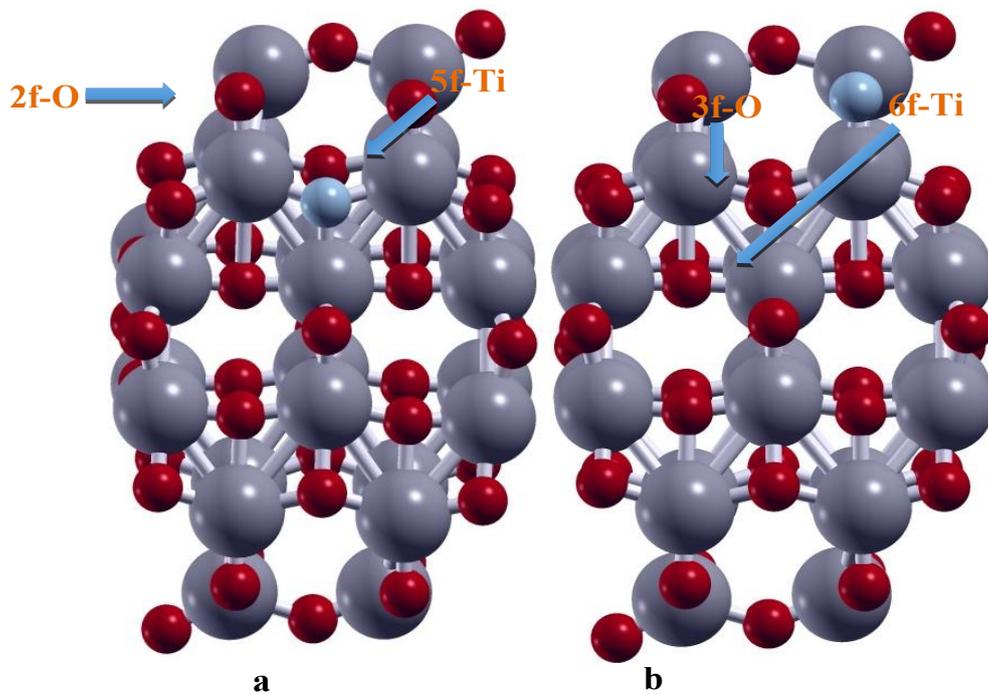


Fig. 3: Optimized N-doped TiO₂ anatase nanoparticles constructed using the 3×2×1 unit cells; (a) O_c-substituted nanoparticle. (b) O_T-substituted one.

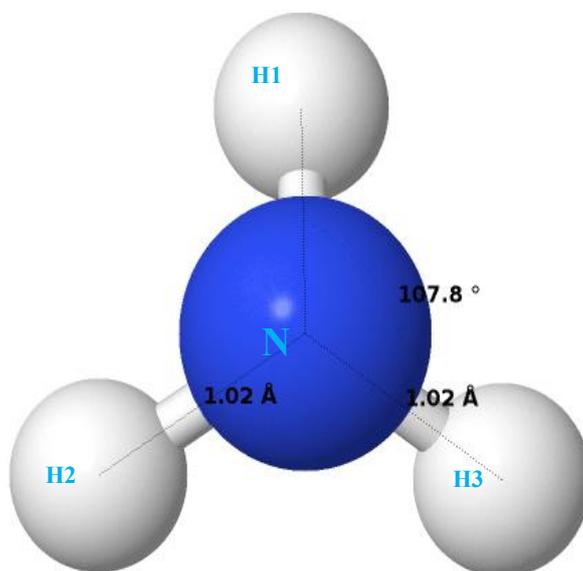


Fig. 4: Representation of the structure of ammonia (NH₃) molecule in an isolated gas phase state.

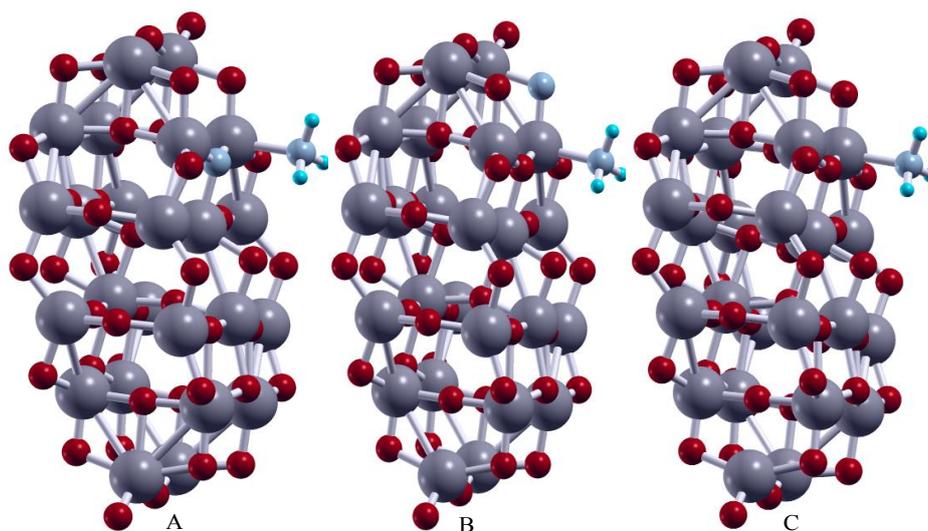


Fig. 5: Optimized geometry configurations of the NH₃ molecule adsorbed on the undoped and N-doped TiO₂ anatase nanoparticles. The larger grey spheres are Ti atoms and the small red, blue and green ones represent O, N and H atoms, respectively.

After the adsorption, one important bond was formed between the titanium atom of TiO₂ nanoparticles and nitrogen atom of the ammonia molecule, namely newly-formed Ti-N bond. Table 1 lists the lengths for N-H bond of the adsorbed NH₃ molecule, H-N-H bond angles and newly-formed Ti-N bond between the nanoparticles and NH₃ molecule, compared to the data before the adsorption process. Based on the obtained results, we found that the lengths for N-H bonds of the adsorbed NH₃ molecule were longer than

those before the adsorption process. The reason could be probably attributed to the transfer of electronic density from the TiO₂ nanoparticles and the N-H bonds of the adsorbed NH₃ molecule to the newly-formed Ti-N bond between the titanium atom of TiO₂ nanoparticles and nitrogen atom of ammonia molecule. The smaller the bond formed between the fivefold coordinated titanium atom of nanoparticles and the nitrogen atom of NH₃ molecule (Ti-N), the stronger the interaction of NH₃ molecule with the TiO₂ nanoparticles.

Adsorption energies

The adsorption energies of NH_3 molecule adsorbed on the different undoped and N-doped anatase nanoparticles are listed in Table 2. The E_{ad} values were computed using GGA exchange-correlation integral approximations. The titanium atom site is considered to be an energy favorable adsorption site. As mentioned above, the relevant configurations are shown in Fig. 5, labeled by A to C complexes. The results of Table 2 indicate that the E_{ad} values for the adsorption of NH_3 on the N-doped nanoparticles are much higher (more negative) than those on the pristine (undoped) one. In other words, the adsorption on the N-doped nanoparticles is energetically more favorable than the adsorption on the undoped one. On the other hand, the adsorption energy of type A is much higher than that of type C, which indicates a more stable configuration in comparison with the undoped system adsorption and other N-doped particles adsorption. This means that the N-doped nanoparticles (Type A or B) can react with NH_3 molecule more efficiently, compared to the undoped one (Type C). This leads to the energy favorable complexes and consequently more efficient adsorption configurations. The more negative the E_{ad} is, the more stable the adsorbed structure. This makes the interaction of NH_3 on the anatase nanoparticles very strong. In view of this conclusion and the improvements of the adsorption energy of TiO_2 nanoparticles obtained by N-doping, it is expected that the N-doped anatase nanoparticles should be more sensitive than the undoped one when utilized as ammonia sensor.

Electronic structures

Fig. 6 shows the total density of states (TDOSs) for N-doped nanoparticles in comparison with the DOS for complex systems consisting of the TiO_2 nanoparticles with NH_3 molecule. Panel (a) of this figure represents the DOS of pristine nanoparticles before and after the adsorption process. Other two panels show the DOS for two types of N-doped nanoparticles. The biggest differences are the creation of some small peaks and also changing the energy of the states to the lower energy values after the adsorption process. Fig. 7 represents the DOSs for NH_3 molecule and TiO_2 nanoparticles after the adsorption of NH_3 , suggesting the high overlaps between the DOS of TiO_2 and NH_3 molecule.

The projected density of states of titanium and nitrogen atoms were also displayed in Fig. 8 as three panels for undoped and two types of N-doped nanoparticles. The large overlaps between the PDOS of titanium and nitrogen atom show the formation of new chemical bond between these two atoms and consequently the transference of electronic density from the old bonds to the newly-formed bond. The isosurfaces of HOMO and LUMO molecular orbitals were shown in Fig. 9 for NH_3 molecule before the adsorption process. The HOMO orbital indicates the positive and negative areas on the nitrogen atom of NH_3 molecule, whereas the LUMO represent the hydrogen and nitrogen atoms as negative and positive areas, respectively.

Fig. 10 displays the isosurfaces of HOMO and LUMO molecular orbitals for the complex systems after the adsorption.

Table 1: Bond lengths (in Å) and bond angles (in degrees) for NH_3 molecule adsorbed on the TiO_2 nanoparticles.

Complex	N-H	Ti-N	H1-N-H2	H1-N-H3	H2-N-H3
A	1.04	2.16	110.3	110.6	111.7
B	1.04	2.17	110.2	111.3	111.1
C	1.04	2.17	110.3	111.1	111.0
Before adsorption	1.02	-	107.8	107.8	107.8

Table 2: Adsorption energies and Mulliken charges for NH_3 molecule adsorbed on the TiO_2 anatase nanoparticle.

Complex	Adsorption energy (eV)	Mulliken charge (e)
A	-4.98	-0.376
B	-4.76	-0.361
C	-2.26	-0.370

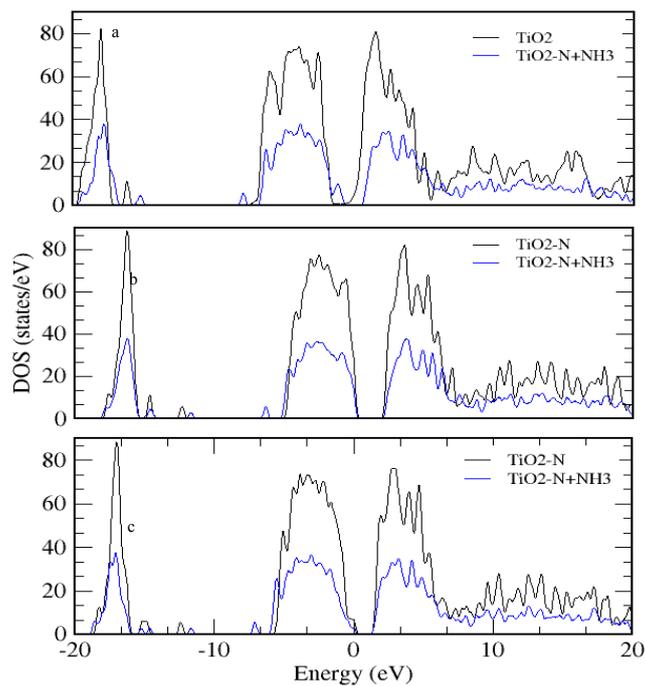


Fig. 6: DOS for the adsorption complexes of N-doped TiO_2 nanoparticles, a: Adsorption type C; b: Adsorption type A; c: Adsorption type B.

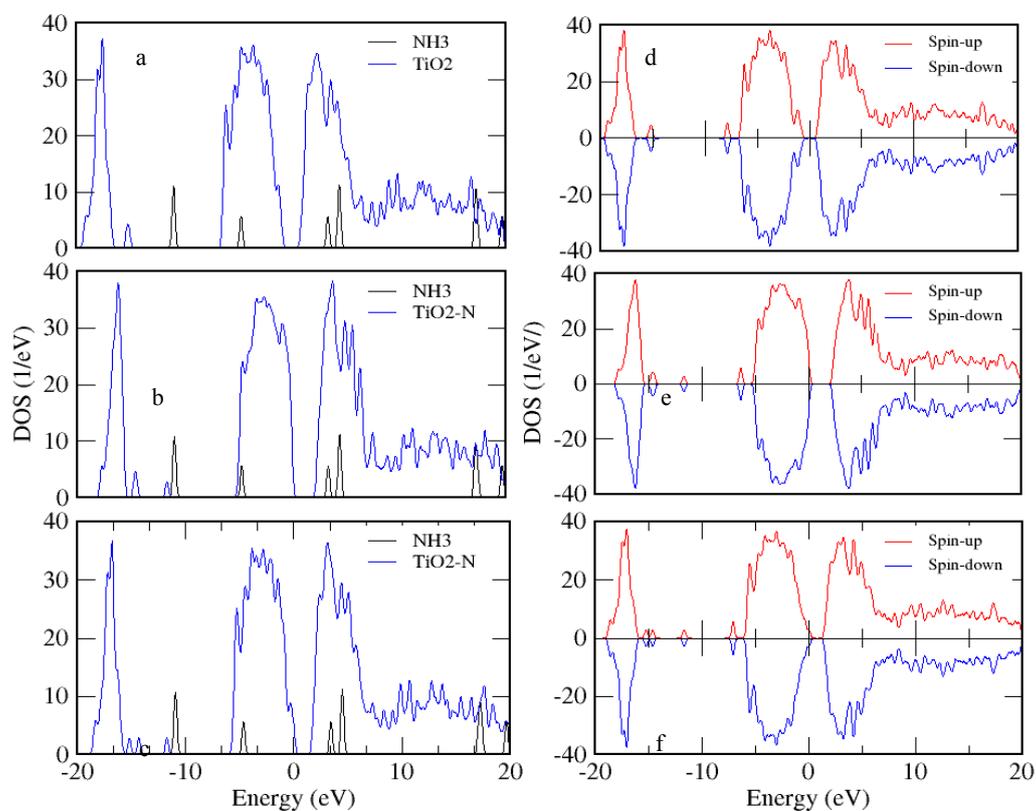


Fig. 7: DOS and spin-polarized DOS for NH_3 adsorption on the TiO_2 nanoparticles, a: Adsorption type C; b: Adsorption type A; c: Adsorption type B; d: Adsorption type G; e: Adsorption type A; f: Adsorption type B.

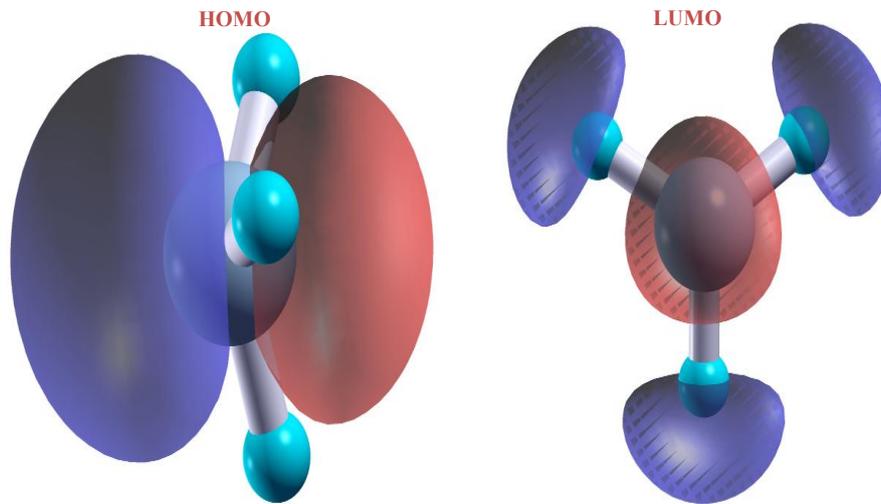


Fig. 9: The isosurfaces of HOMO and LUMO molecular orbitals of NH₃ molecule before the adsorption process.

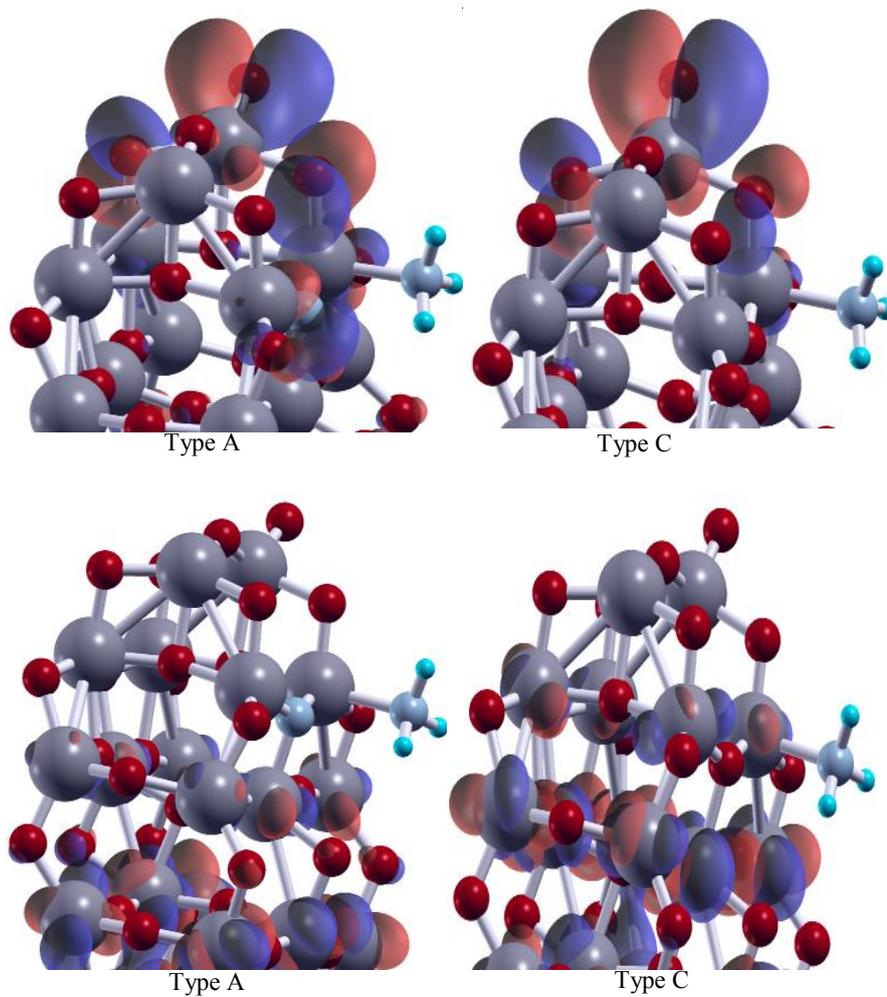


Fig. 10: The isosurfaces of HOMO (First row) and LUMO (Second row) molecular orbitals for different adsorption complexes of NH₃ molecule adsorbed on the TiO₂ nanoparticles, where |0.02| was used as an isovalue of the molecular orbital.

These figures show that the HOMO's are strongly localized on the nanoparticles, whereas the LUMO's are weakly localized on the anatase nanoparticles. These molecular orbital isosurfaces are in the good accordance with the PDOS diagrams.

The spin-polarized density of states and distribution of spin densities were also illustrated in Fig. 11. It was found that the unpaired electron

of the nanoparticles spends most of the time in the adsorption area between the nanoparticles and ammonia molecule. A closer examination of the PDOSs and molecular orbitals for the active sites forming chemical bond in the adsorption process and consequently examining the adsorption energy variations reveal that the N-doping strengthens the interaction of ammonia over the titanium site of TiO_2 nanoparticles.

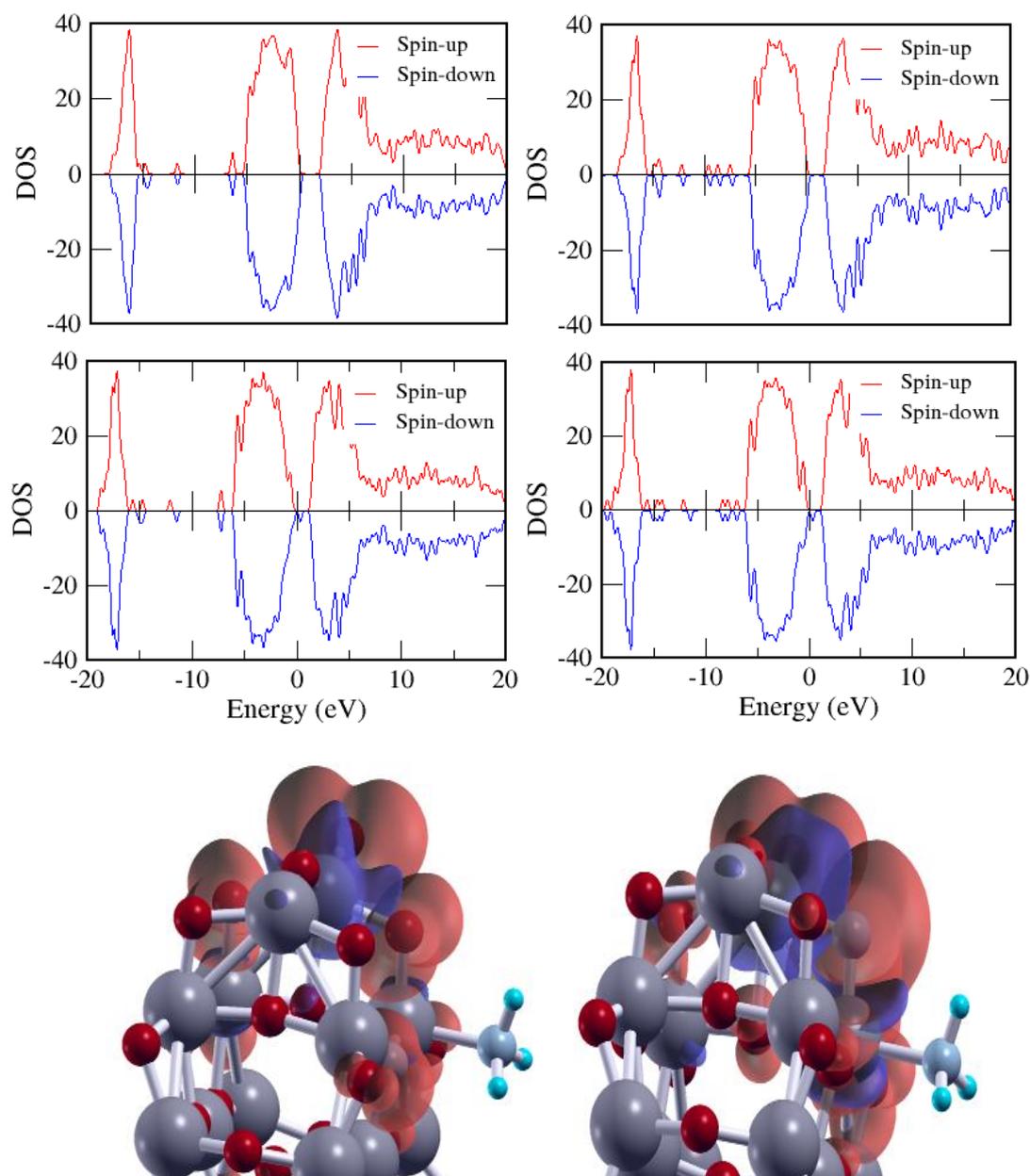


Fig. 11: The spin polarized density of states for spin-up and spin-down states of NH_3 molecule adsorbed on the N-doped TiO_2 anatase nanoparticles with the distribution of spin density plots.

Charge transfer analysis

In order to fully analyze the charge transfer between the nanoparticles and adsorbate, we have mainly performed the charge transfer based on Mulliken charges. The computed values of Mulliken charges for adsorption complexes were listed in Table 2. The following formula is utilized to evaluate the charge transfer process.

$$\Delta Q_i = Q_i (\text{in complex}) - Q_i (\text{in vacuum})$$

where Q_i represents the value of Mulliken charge of the i and subscript “ i ” denotes the TiO_2 nanoparticles or adsorbed molecule. The charge variation, ΔQ , is a measure of the amount of charge transferred to, or, from the studied nanoparticles from, or, to the adsorbed molecule.

For example, the calculated charge value for N-doped TiO_2 (in complex A) is about $-0.376 e$ and that of NH_3 molecule is $+0.376 e$, suggesting that the NH_3 molecule behaves as an electron donor to the nanoparticles. In other words N-doped TiO_2 nanoparticles accept electrons from ammonia molecule. Since the fundamental working principle of a sensing material is that the charge to be exchanged between the adsorbent and adsorbed molecule, this feature could be useful to help in the design of improved sensor materials for NH_3 recognition in the environment.

CONCLUSIONS

In this letter, we have carried out density functional theory calculations on the structural and electronic properties of undoped and N-doped TiO_2 anatase nanoparticles. The results reveal that the N-doped nanoparticles are more energetic than the undoped ones and can react with ammonia molecules more efficiently. Structural analysis of the studied systems represents that the Ti-N bonds of the anatase nanoparticle and N-H bonds of the adsorbed NH_3 were elongated because of the transference of the electronic density from the mentioned old bonds to the newly-formed Ti-N bond between the nanoparticle and adsorbed molecule. We have also commented on the electronic properties of the studied systems including the DOS and molecular orbital plots to understand the electron transport process between the adsorbent and adsorbed molecules. The obtained results indicate that the N-doped anatase nanoparticles are more active than the undoped ones in the adsorption processes. The N doping yields an increased

affinity for TiO_2 nanoparticles to interact with NH_3 molecules in the environment, which could be an efficient property for utilization in sensing and removing applications. Our calculated results thus suggest a theoretical basis for N-doped TiO_2 nanoparticles to be effectively employed in gas sensing applications and give an explanation to help in the design and improvement of amended biosensors for ammonia detection.

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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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