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Structural and electronic properties of N-doped TiO_2 anatase nanoparticles and their effects on the adsorption of Hydrazine (N_2H_4) molecule: A first-principles study

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ABSTRACT: We have performed a density functional theory investigation on the structural and electronic properties of pristine and Nitrogen-doped TiO_2 anatase nanoparticles as the adsorbents for removal and degradation of hydrazine molecules in the environment. We have presented the most stable adsorption configurations and examined the interaction of hydrazine molecule with these doped and undoped nanoparticles. Two nitrogen atoms of hydrazine molecule are more reactive than the hydrogen atoms and tend to be adsorbed on the TiO_2 nanoparticle. It turns out that the hydrazine molecule is preferentially adsorbed on the active fivefold coordinated titanium atom site of nanoparticle. The insights of the computations include the structural and electronic analyses such as bond lengths/angles, adsorption energies, density of states (DOSs) and molecular orbitals. It is found that the adsorption of N_2H_4 on the N-doped nanoparticle is energetically more favorable than the adsorption on the undoped one, representing the higher reactivity of N-doped nanoparticle with hydrazine molecule. It means that the adsorption on the N-doped nanoparticle provides the most stable configurations and consequently the most efficient adsorption processes. Nevertheless, our computational study on the TiO_2 anatase nanostructures suggests that the N-doped nanoparticles are highly sensitive than the undoped ones when utilized as detectors or sensors for hydrazine detection.

Keywords: *Density Functional Theory; Interaction; Molecular orbital; N_2H_4; TiO_2*

INTRODUCTION

TiO_2 has been exhaustively investigated due to its unique properties as a promising semiconductor material, which has wide range of technological applications. Most of the work has been concentrating on anatase and rutile phases because of their relative greater natural abundance. It is developed in heterogeneous catalysis (systems containing metal/TiO_2), as a photocatalyst (Satterfield, 1991, Ando, *et al.*, 1997), in organic dye-sensitized solar cells (Fujishima and Honda, 1972), in sensor devices (Dutta, *et al.*, 1999), It is also used as a gate insulator for the newly developed of MOSFETS (metal oxide semiconductor field

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(*) Corresponding Author - e-mail: a_abbasi@azaruniv.edu effect transistor) (Garfunkel, *et al.*, 1998, Sardroodi, *et al.*, 2015). It has 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 extreme treating conditions (Erdogan, *et al.*, 2010, Zarei, *et al.*, 2013). TiO_2 has gained more scientific and industrial attention over the past few years (Liu, *et al.*, 2012, Landman, *et al.*, 2012). Main polymorphs (crystalline forms) of TiO_2 exist: anatase and brookite, which have low temperature and low pressures, and rutile, the stable polymorph at all temperature and ambient pressure (Banfied and Veblen, 1992). Numerous systematic studies have been implemented in order to determine exceptional properties of titanium dioxide and some advancement have been attained (Wang and Doren, 2005, Wei, *et al.*, 2010, Liu, *et al.*, 2013, Zhao, *et al.*, 2011). Owing to its extensive band-gap, it can only absorb a little fraction (4 %) of the solar spectrum. Thus, the alternative would be the procedure that to spread the optical sensitivity of TiO_2 to the visible area such as nitrogen doping of TiO_2, which causes the improving of photo-activity and adsorptive ability of TiO_2 (Ebrahimzadeh, *et al.*, 2015, Rumaiz, *et al.*, 2009, Chen, *et al.*, 2009, Jia, *et al.*, 2011). N-doped TiO_2 anatase nanoparticles have attracted many interests as important candidates for industrial and scientific researches. For instance, the adsorption of NO molecule on undoped and N-doped TiO_2 anatase nanoparticles has been studied (Liu, *et al.*, 2012), in the parallel work, by Liu group it has been proposed that the N-doped TiO_2 nanoparticles can react with CO molecule more capably in comparison with the undoped ones (Liu, *et al.*, 2013). Carrying out DFT calculations, Ruslan group examined the adsorption of SOx and NOx on anatase supported BaO and Pt overlayers (Hummatov, *et al.*, 2012). Additionally, the substitutional doping of TiO_2 with N leads to the improving of its electronic and structural properties and greatly increases the application of TiO_2 particles as active gas sensors. Hydrazine is a toxic material, which can cause a serious problem in the human body. Thus, controlling its concentration is an important subject to public health (Tafreshi, *et al.*, 2014). The principal strategy towards achieving extensive utility of TiO_2 nanoparticles is to perform important investigations on the electronic properties such as density of states (DOS), molecular orbitals and structural properties such as bond lengths and adsorption energies (Oftadeh, *et al.*, 2015). In industrial processes, metal oxides especially TiO_2, are commonly utilized as detectors or adsorbents to remove the N_2H_4 molecules from the environment. In this study, we performed DFT calculations in order to comprehend N_2H_4 adsorption on N-doped TiO_2 anatase nanoparticles. As also as, some electronic and structural properties including the total density of states (TDOS), band structures, bond lengths, bond angles and adsorption energies for undoped and two kinds of N-doped TiO_2 anatase nanoparticles have been analyzed. The results indicate that the N_2H_4 molecule is more efficiently adsorbed on N-doped nanoparticles, compared to the undoped ones. This work aims to supply an overall understanding on the adsorption configurations of N_2H_4 molecule over TiO_2 anatase nanoparticles.

CALCULATION METHODS

Calculation details

We have carried out all of the calculations based on density functional theory (Hohenberg and Kohn, 1964, Kohn and Sham, 1965) as implemented in the OpenMX3.7 code (Ozaki, *et al.*, 2013) to study the structural and electronic properties of perfect and N-doped TiO_2 anatase nanoparticles with adsorbed hydrazine molecule. OPENMX is an effective software package for nano-scale material simulations based on DFT, norm-conserving pseudopotantials, and numerical pseudo-atomic localized basis functions (Ozaki, 2003, Ozaki and Kino, 2005). Pseudo atomic orbitals (PAO's) adjusted on atomic sites are employed as basis sets in order to expand the wave functions in a Kohn-Sham schema. The local density approximation (LDA) parameterized by Ceperly-Alder (CA) is applied to define the exchange-correlation energy functional (Perdew and Zunger, 1981). The energy cutoff is set at 150 Ry during the calculations. For PAO functions, the database version of 2013 is utilized. The cutoff radii of basis functions are considered to be 7 for Ti, 5 for O and N and 5.5 for H (all in Bohrs). Two s-state radial functions and two p-state radial functions are used for N and O atoms, while three s-state, three p-state and two d-state radial functions are defined for Ti atom. For s-state of H atom, one radial function is assumed. In the calculations related to the electronic properties, 21 k-points along each high symmetry lines are considered. The charge transfer between hydrazine molecule and TiO_2 nanoparticle is evaluated by the help of the Mulliken charge analysis. For visualizing data such as isosurfaces of molecular orbitals, the open-source program XCrysDen (Koklj, 2003) was utilized. The size of the box considered in these computations is 20×15×30 $Å^3$, which contains 72 atoms (24 Ti atoms and 48 O atoms) of undoped or N-doped TiO_2 nanoparticle. 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, E_{ads}, of each configuration is determined by,

$$E_{ads}=E_{nanoparticle+hydrazine}-(E_{nanoparticle}+E_{hydrazine})$$

Where $E_{hydrazine}$ represents the energy of an isolated hydrazine molecule, $E_{nanoparticle+hydrazine}$ and $E_{nanoparticle}$ are the total energies of the nanoparticle with and without hydrazine molecule respectively.

Structural models

The chosen TiO_2 anatase nanoparticles encompassing 72 atoms were constructed by putting 3×2×1 numbers of TiO_2 unit cells along x, y and z axis, respectively. A distance of 11.5 A° was set between neighbor particles to reduce the interaction between neighbor particles. The unit cell was derived from "American Mineralogists Database" webpage and stated by Wyckoff (Wyckoff, 1963). The considered TiO_2 anatase nanoparticles were shown in Fig. 1. N-doped anatase nanoparticles were built via replacement of two appropriate active surface oxygen atoms by nitrogen atoms. 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, which specified by OC and O_T in Fig. 1, respectively.

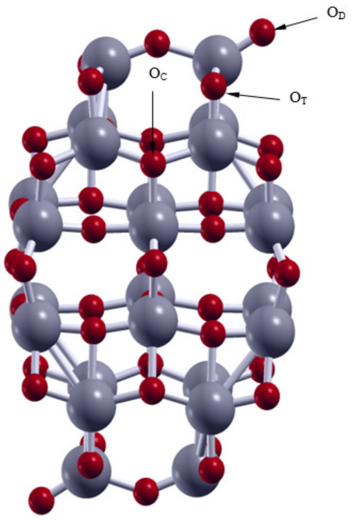

Fig. 1: Optimized structure an undoped 72 atom TiO_2 anatase nanoparticle constructed using the 3×2×1 unit cells; OC: central oxygen; O_T: twofold coordinated oxygen; OD: dangling oxygen

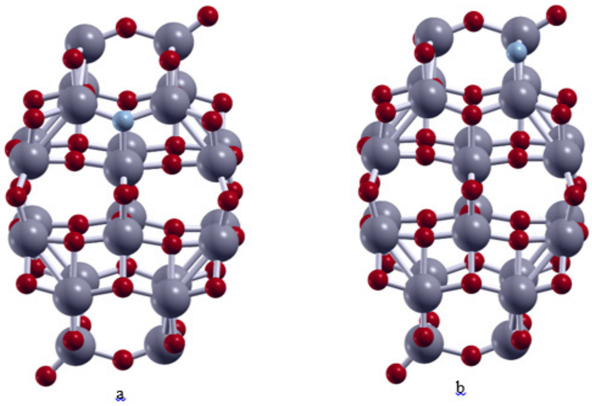

Fig. 2: Optimized N-doped TiO_2 anatase nanoparticles constructed using the 3×2×1 unit cells; (a) O_C-substituted nanoparticle. (b) O_T-substituted one.

The optimized structures for two kinds of N-doped nanoparticles were illustrated in Fig. 2. We have geometrically optimized the obtained N-doped nanoparticles and constructed complex systems consisting of the hydrazine molecule positioned towards the optimized TiO_2 nanoparticle. In this study, we have investigated the adsorption on the fivefold coordinated titanium atom site of the considered nanoparticles due to the relatively high activity of this site in adsorption process, compared to the other surface oxygens.

RESULTS AND DISCUSSION

Bond lengths and bond angles

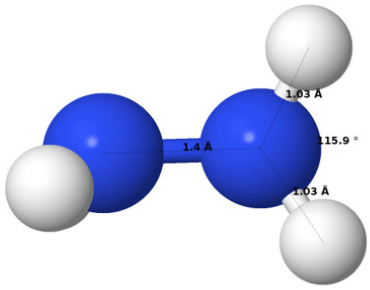

Fig. 3: Representation of the N_2H_4 configuration, Colors represents atoms, N in blue and H in white accordingly.

The interaction of N_2H_4 molecule over the appropriate titanium site of undoped and N-doped TiO_2 anatase nanoparticles were examined here. The structure of hydrazine molecule containing two nitrogen and two hydrogen atoms has been represented in Fig. 3. Hydrazine molecule contains two nitrogen and four hydrogen atoms connecting to each other via covalent bonds. This molecule can be adsorbed on the Ti atom site of TiO_2 nanoparticle by the active nitrogen atoms on its surface.

Fig. 4 also shows the possible configurations of the adsorption of hydrazine on the considered nanoparti-

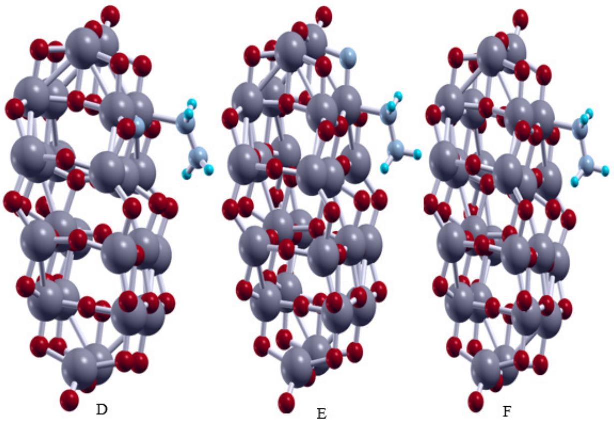

Fig. 4: Optimized geometry configurations of the adsorption of NH_3 and N_2H_4 molecules on the undoped and N-doped TiO_2 anatase nanoparticles. The larger grey spheres are Ti atoms and the small red, blue and green ones represent O, N and H atoms, respectively.

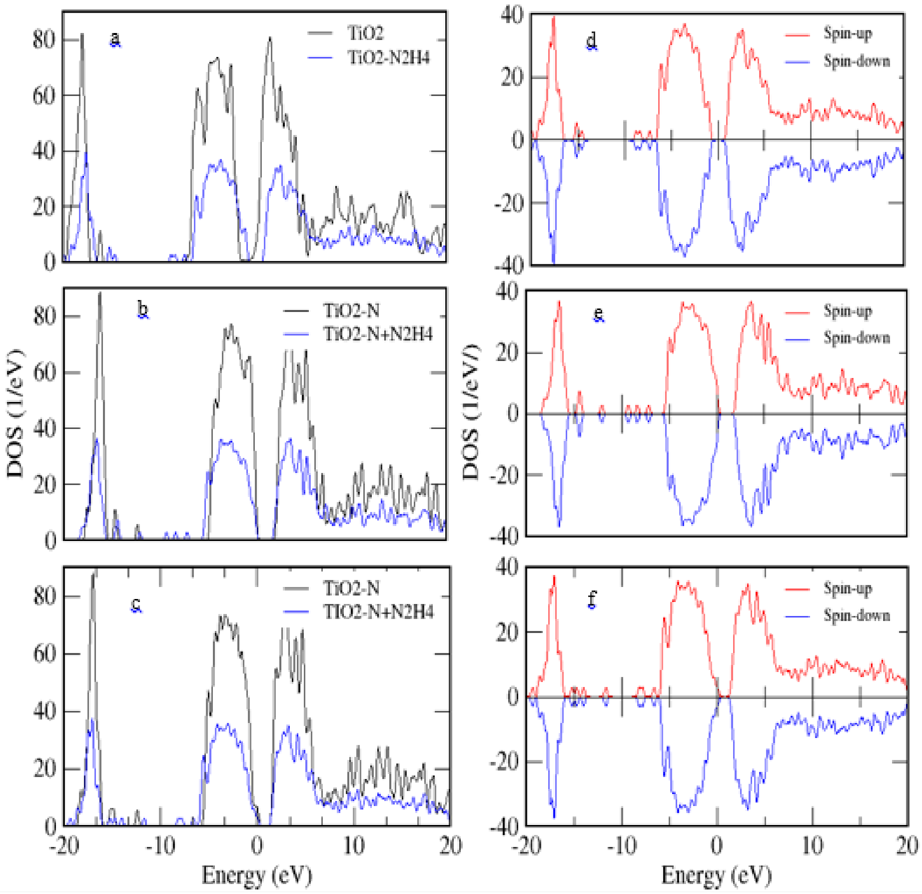

Fig. 5: DOS and spin-polarized DOS for N_2H_4 adsorption on the TiO_2 nanoparticles, a: F complex; b: D complex; c: E complex; d: F complex; e: D complex; f: E complex.

cles. The complexes contained in Fig. 4 differ in substituted OC or OT atom of TiO_2 with respect to the anatase nanoparticles.

For example, type A adsorption configuration presents a hydrazine molecule located in parallel position with respect to the OC-substituted N-doped nanoparticle, while the parallel orientation towards the OT-substituted nanoparticle has been represented in type B configuration. The nitrogen atom of hydrazine molecule is pulled by the titanium atom of nanoparticle with a slight deviation from the original route. Fig. 4 has been also contained one configuration for hydrazine interaction with the undoped nanoparticle. The adsorption of hydrazine on the nanoparticles leads to the formation of one important bond between titanium atom of TiO_2 nanoparticle and nitrogen atom of hydrazine molecule (newly-formed Ti-N bond). The lengths for N-H bonds of the adsorbed hydrazine molecule, Ti-O, newly-formed Ti-N bond and H-N-H bond angles have been tabulated in Table 1, compared to the data before the adsorption process. The results suggest that the lengths for N-H bonds near the particle (hydrazine molecule) and Ti-O or Ti-N bonds of the nanoparticle are stretched after the adsorption, being probably ascribed to the transfer of electronic density from the TiO_2 nanoparticle and hydrazine molecule to the newly-formed Ti-N bond. The shorter the final distance between fivefold coordinated titanium atom of nanoparticle and nitrogen atom of hydrazine molecule (Ti-N), the tougher the adsorption of hydrazine on the TiO_2 nanoparticle. The optimized structure of hydrazine molecule has been displayed in Fig. 3 with bond length and bond angle results. The bond angle variations represent a decrease of the H-N-H bond angle of hydrazine molecule near the titanium site of nanoparticle. This bond angles reduction could be probably due to the formation of new bond between the titanium atom of N-doped nanoparticle and nitrogen atom and consequently changing "sp2" hybridization of nitrogen in N_2H_4 molecule to hybridization with higher p contribution (near sp3). The increasing "p" characteristics of bonding molecular orbitals of adsorbed N_2H_4 molecule leads to enhancing the spatial distribution of orbitals or elongation of measured bonds.

Adsorption energies

The adsorption energies of N_2H_4 molecule on the undoped and N-doped anatase nanoparticles are listed in Table 1. The Ead values have been calculated by use of LDA functional. The hydrazine molecule is preferentially adsorbed on the fivefold coordinated titanium atom site. The corresponding configurations are displayed in Fig. 4, namely A to C. The calculated geometric and energetic parameters suggest that the adsorption of hydrazine on N-doped TiO_2 nanoparticle is almost by strong adsorption in nature whereas on pristine graphene is by somewhat weak adsorption. The Ead values for hydrazine adsorption on the N-doped nanoparticle are much higher (more negative) than those on the pristine one. It means that the adsorption on the N-doped nanoparticle is energetically more favorable than the adsorption on the undoped one. The results of Table 1 indicate that the adsorption energy of type A is higher than that of type C, which means a more stable configuration, compared to the undoped system adsorption. Also, the adsorption on the OC-substituted nanoparticle (complex A) is energetically favorable than the adsorption on the OT-substituted one. The N-doped nanoparticle can react with N_2H_4 molecule more effectively, in comparison with the undoped one. Thus, N-doped TiO_2 nanoparticle is

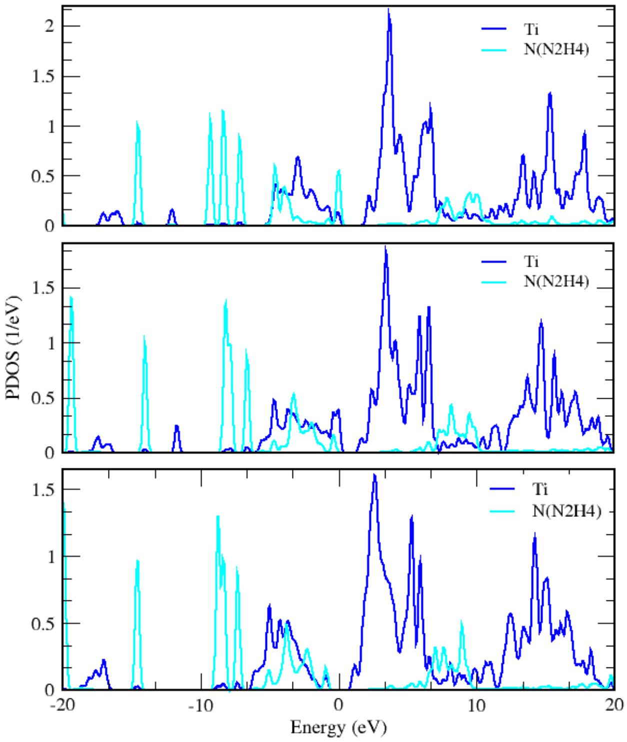

Fig. 6: PDOS of Ti and N atoms for N_2H_4 adsorption on the TiO_2 nanoparticles, a: F complex; b: D complex; c: E complex.

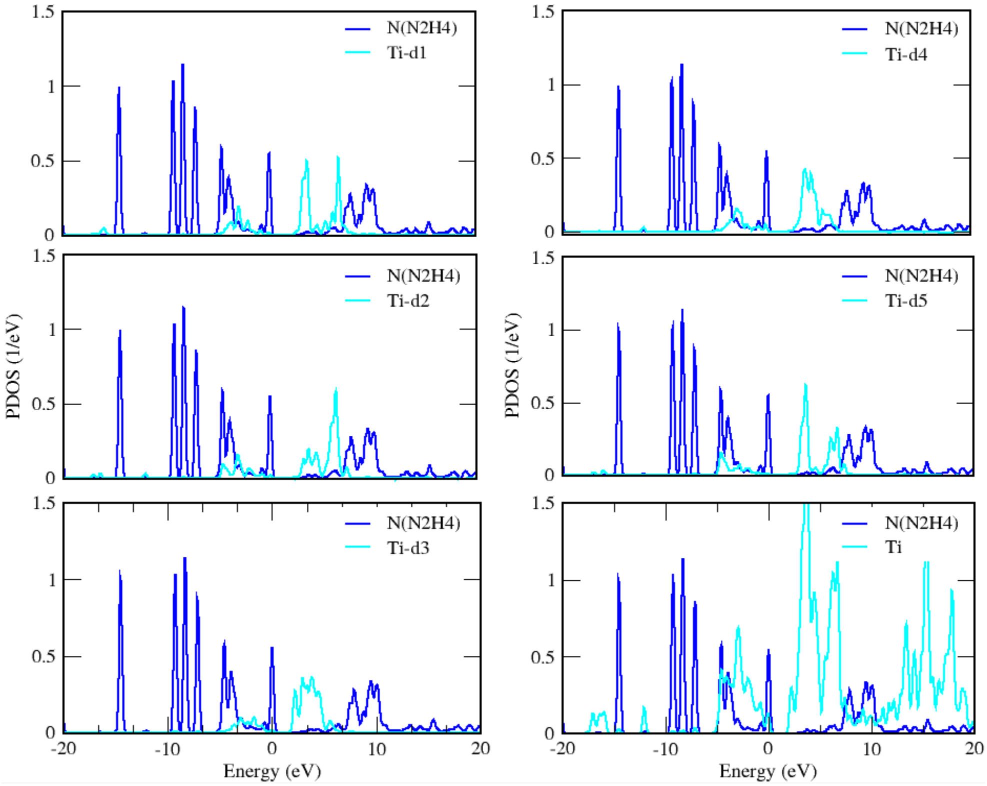

Fig. 7: PDOS of Ti and N atoms with different d orbitals (from d1 to d5) for N_2H_4 adsorption on the TiO_2 nanoparticles, a: F complex; b: D complex; c: E complex

beneficial to design sensors for hydrazine detection. The more negative the Ead, the higher tendency for hydrazine adsorption.

Electronic structures

The electronic densities of states (DOS) of the nanoparticles without and with adsorbed hydrazine molecule have been displayed in Fig. 5, Panel (a) of this Fig. represents the DOS of OC-substituted N-doped nanoparticle whereas panels (b, c) show the DOS for OT-substituted N-doped and undoped nanoparticles respectively. The biggest differences are the creation of some small picks at the energy levels ranging from -7 to -15 eV and also changing the energy of the states to the lower energy values. Panels (d, e, f) tell the spin polarized DOS corresponding to the adsorption complexes.

The projected density of states of titanium and nitrogen atoms have been shown in Fig. 6 as three panels for undoped and two types of N-doped nanoparticles. Fig. 6 represents a significant overlap between the PDOS of titanium and nitrogen atoms, suggesting the formation of chemical bond between these two atoms.

The PDOSs of titanium and nitrogen atoms with different d orbitals of titanium have been also given in Fig. 7, which show a larger overlap between the PDOS of nitrogen atom with that of Ti-d5 orbital.

Thus, the electrons are moved from the nitrogen atom to d5 orbital of titanium. The isosurfaces of HOMO and LUMO molecular orbitals have been shown as Fig. 8 for N_2H_4 molecule before the adsorption process.

The HOMO and LUMO isosurfaces indicate positive and negative areas on the hydrazine molecule. Fig. 9 has been contained the isosurfaces of HOMO and LUMO molecular orbitals for the nanoparticles with adsorbed hydrazine. This Fig. shows that the

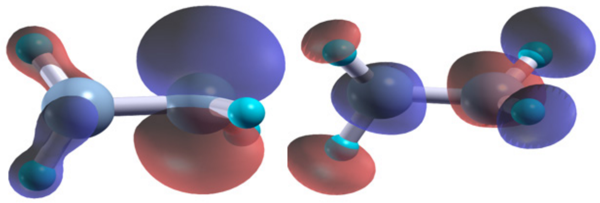

Fig. 8: The isosurfaces of HOMO and LUMO molecular orbitals for free N_2H_4 molecule in the non-adsorbed state.

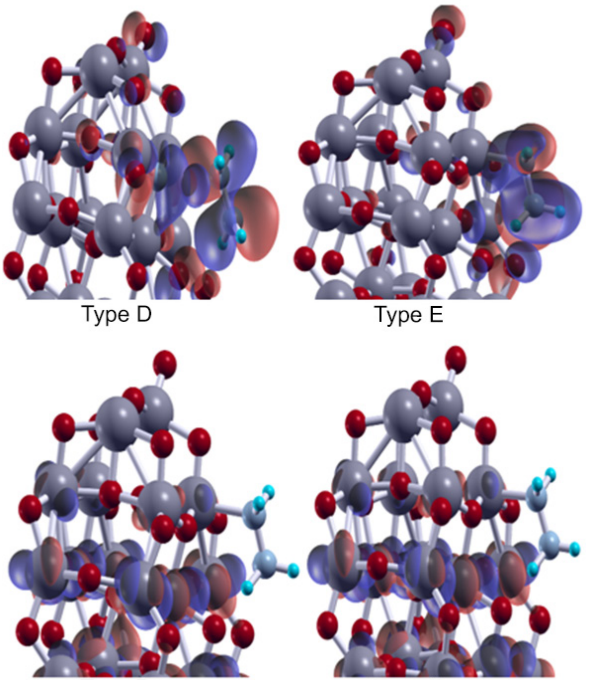
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Fig. 9: The isosurfaces of HOMO (First row) and LUMO (Second row) molecular orbitals for different adsorption complexes of N2H4 molecule adsorbed on the TiO_2 nanoparticles.

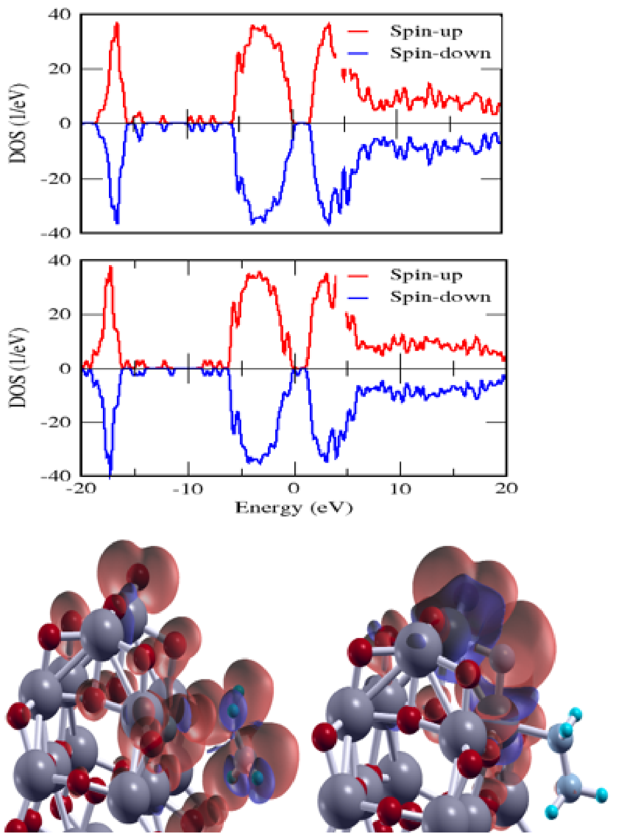
HOMO's are strongly localized on the hydrazine molecule, whereas the LUMO's are mainly localized on the anatase nanoparticle.

The spin-polarized density of states related to the different spin numbers and distribution of spin densities have been also illustrated in Fig. 10.

It is understood that the unpaired electron of the nanoparticle spends most of the time at the intersection of nanoparticle and adsorbed hydrazine molecule. A closer examination of the PDOSs and molecular orbitals reveals that hydrazine adsorption has no substantial effect on the electronic properties of pristine TiO_2 nanoparticle, while the electronic properties of N-doped nanoparticle are sensitive to the presence of hydrazine.

Charge transfer analysis

The charge transfer between the nanoparticle and hydrazine molecule has been also analyzed based on Mulliken charges. Table 1 lists the calculated Mulliken charge values for adsorption complexes shown in Fig. 4. The charge transfer is evaluated using the following formula:



(a) (b)

Fig. 10: The spin polarized density of states and distribution of spin densities for N_2H_4 molecule adsorbed on the TiO_2 nanoparticle, a: D complex; b: E complex.

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

Where Qi represents the value of Mulliken charge of the i and subscript "i" denotes the TiO_2 nanoparticle or hydrazine molecule. The variation of Mulliken charge, ΔQ, represents the amount of charge transferred to, or, from the studied nanoparticles from, or, to the hydrazine molecule.

The calculated charge value for N-doped TiO_2 (in complex A) is about -0.74 e and that of N_2H_4 molecule is +0.74 e, suggesting that TiO_2 nanoparticle works as an electron acceptor. In other words, N-doped TiO_2 nanoparticle accepts electrons from hydrazine molecule. The computed charge value of complex A (N-doped system) is higher than that of complex C (pristine system), which indicates a large amount of charge transfer in the N-doped nanoparticle. The charge transfer is expected to induce changes on the conductivity of the system and this feature could be beneficial to help in the development of enhanced sensor materials for N_2H_4 recognition.

CONCLUSIONS

In this letter, we have carried out density functional theory calculations on 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 hydrazine molecules more efficiently. Structural analysis of the studied systems represents that, after the adsorption, the Ti-N bonds of the anatase nanoparticle and N-H bonds of the adsorbed N_2H_4 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 in order to understand the electron transport phenomena. The obtained results indicate that the N-doped anatase nanoparticles are more active than the undoped ones. The N doping yields an increased affinity for TiO_2 nanoparticles to interact with N_2H_4 molecules in the environment, being an efficient property to be utilized in sensing and removing applications. Our calculated results thus suggest a theoretical basis for N-doped TiO_2 nanoparticles to be effectively employed in sensing and removing applications and give an explanation to help in the design and improvement of amended biosensors for hydrazine detection.

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