

Sensing behavior of acetone vapors on TiO₂ nanostructures — application of density functional theory

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The electronic properties of TiO₂ nanostructure are explored using density functional theory. The adsorption properties of acetone on TiO₂ nanostructure are studied in terms of adsorption energy, average energy gap variation and Mulliken charge transfer. The density of states spectrum and the band structure clearly reveals the adsorption of acetone on TiO₂ nanostructures. The variation in the energy gap and changes in the density of charge are observed upon adsorption of acetone on n-type TiO₂ base material. The results of DOS spectrum reveal that the transfer of electrons takes place between acetone vapor and TiO₂ base material. The findings show that the adsorption property of acetone is more favorable on TiO₂ nanostructure. Suitable adsorption sites of acetone on TiO₂ nanostructure are identified at atomistic level. From the results, it is confirmed that TiO₂ nanostructure can be efficiently utilized as a sensing element for the detection of acetone vapor in a mixed environment.

Key words: *TiO₂, nanostructure, adsorption, acetone, energy gap*

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1. Introduction

The expansion of industries in recent years leads to emission of hazardous gases and vapors into the atmosphere. Moreover, volatile organic compounds (VOCs) are a major source of environmental pollutants and cause a serious impact on humans. For instance, acetone (CH₃COCH₃) is a chemical reagent utilized in laboratories and industries. Besides, this compound is widely used in purifying paraffin, dissolving plastics and in pharmaceuticals. Acetone may cause damages to human noses, eyes and central nervous system when the permissible exposure limit exceeds 1000 parts per million (ppm) according to Occupational Safety and Health Administration [1]. The high exposure to acetone to humans may cause mood swings, respiratory irritation and nausea. In addition, breathing acetone in high ppm value may cause dizziness, respiratory tract irritation and loss of strength [2]. Furthermore, acetone is also highly inflammable. Meanwhile, acetone was found to be the final product for added ketone bodies' metabolism [3]. Among the transition metal oxide semiconductor, titanium dioxide (TiO₂) is extensively investigated as a key material for technological application and fundamental research in the semiconductors, solar cell [4] and lithium-ion batteries [5] owing to its excellent chemical stability and low cost [6]. TiO₂ is also a promising candidate in the field of gas-sensor, photovoltaic, energy storage and photocatalysis due to its photocatalytic properties, long-term stability and low toxicity [7, 8]. Besides, TiO₂ polymorphs are mainly classified into three types, namely anatase, rutile and brookite with corresponding space groups namely $I4_1/amd-D_{4h}^{19}$ (tetragonal), $P4_2/mnm-D_{4h}^{14}$ (tetragonal) and $pbca-D_{2h}^{15}$ (orthorhombic). Besides, only the first two crystal systems play a vital role in industrial applications.

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Experimental work on brookite crystal system is constrained owing to its difficulty in preparation [9]. The optical energy gap values of anatase, rutile and brookite TiO₂ crystal structure are reported as 3.4 eV [10], 3.0 eV [11] and 3.3 eV [12], respectively. The density functional theory (DFT) method has been widely used by the researchers to study rutile and anatase phases of TiO₂ nanostructure [13]. The previous reports on TiO₂ electronic properties were presented in the literature using hybrid-functional schemes [14]. Bhowmik et al. [15] have proposed TiO₂ nanotubes as a good acetone sensor and the authors observed that the response of the sensor reaches 3.35% against 1000 ppm acetone. Chen et al. [16] have reported the sensing performance of acetone based on nanoporous morphology of TiO₂ using a facile hydrothermal method. Rella et al. [17] reported about the sensing properties of ethanol and acetone vapors on TiO₂ nanoparticles prepared from pulsed laser deposition. Chen et al. [18] studied the adsorption properties of acetone on pristine and transition metal doped TiO₂ clusters using DFT study. Thus, from the previous literatures, to our knowledge, there are only limited reports based on DFT method to study the adsorption properties of acetone on rutile TiO₂ nanostructure. The motivation behind the present work is to investigate acetone adsorption properties on TiO₂ nanostructure and to identify the most suitable adsorption site at the atomistic level.

2. Computational methods

The electronic and adsorption properties of acetone on TiO₂ nanostructures are studied using DFT method utilizing SIESTA package [19]. The atomic position in TiO₂ nanostructures has been optimized to their ground state by decreasing their Hellman-Feynman forces [20, 21] supported with conjugated gradient algorithm. Moreover, all interatomic forces of rutile TiO₂ nanostructures are observed to be less than 0.05 eV/Å [22]. The generalized gradient approximation (GGA) combined with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional is utilized to investigate the electron-electron interaction [23, 24]. The energy cut-off of plane-wave basis set was adjusted to 500 eV with energy convergence of 10⁻⁵ eV. The atomic positions in TiO₂ nanostructure were relaxed until the force of 0.02 eV/Å is achieved. The *k*-points in Brillouin zones under the Monkhorst-pack scheme [25], are kept as 10 × 10 × 10 *k*-points with 3 × 3 × 3 super-cell size in the present study. The density of states, charge density, band structure and electron localization function (ELF) of rutile TiO₂ nanostructure were calculated with the help of SIESTA code with Monkhorst-Pack *k*-point meshes of 10⁻³ Å⁻¹. The acetone adsorption properties on rutile TiO₂ nanostructure is also studied using SIESTA package. Furthermore, the electronic wave function of Ti and O atoms is expressed by basis set, which is directly related with the numerical orbitals. The double zeta polarization (DZP) basis set is utilized for relaxation of rutile TiO₂ nanostructure in the present work [26].

3. Results and discussion

3.1. Electronic properties of rutile TiO₂ nanostructure

The present work concentrates on the investigation of electronic properties and adsorption behavior of acetone on TiO₂ nanostructure. Figure 1 represents the schematic diagram of TiO₂ nanostructure with the periodic boundary condition (PBC). The optimized lattice constant and Wyckoff atomic positions, including coordinates of TiO₂ nanostructure are tabulated in table 1. In this work, we have chosen a tetragonal — rutile TiO₂ nanostructure (P4₂/mnm) for calculating the electronic properties and adsorption behavior of acetone on TiO₂ nanostructure.

The electronic properties of TiO₂ base material are described in terms of band structure [27]. Figure 2 illustrates the band structure of an isolated TiO₂ nanostructure. The band gap of TiO₂ base material is observed along the gamma point (G) and it is observed that the band gap value of an isolated TiO₂ nanostructure is found to be 2.43 eV with indirect gap. Moreover, the channels along the conduction band minimum and the valence band maximum are out of phase along the gamma point, which infers the indirect band gap. Furthermore, the calculated band gap of TiO₂ nanostructure is in good agreement with the previously reported work [11]. In addition, based on the selection of exchange-correlation (XC)

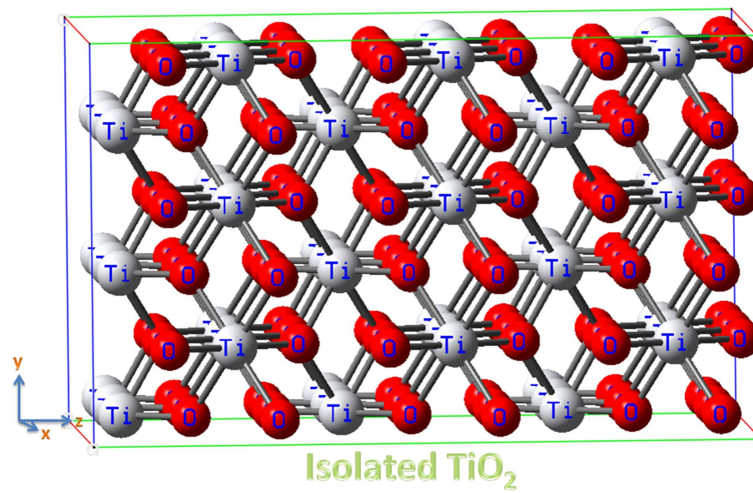


Figure 1. (Color online) Schematic diagram of an isolated TiO₂ nanostructure with periodic boundary condition.

Table 1. The Wyckoff atomic positions of TiO₂ nanostructure.

Structure	Space group	Lattice	Wyckoff atomic positions
Tetragonal — rutile TiO ₂	P4 ₂ /mm (136)	$a = 4.59 \text{ \AA}$ $b = 4.59 \text{ \AA}$ $c = 2.96 \text{ \AA}$	Ti: $2a (0, 0, 0)$ Ti: $16k (0.50, 0.50, 0.50)$ O: $8i (0.31, 0.31, 0)$ O: $8i (0.70, 0.70, 0)$ O: $16k (0.20, 0.81, 0.50)$ O: $16k (0.81, 0.20, 0.50)$

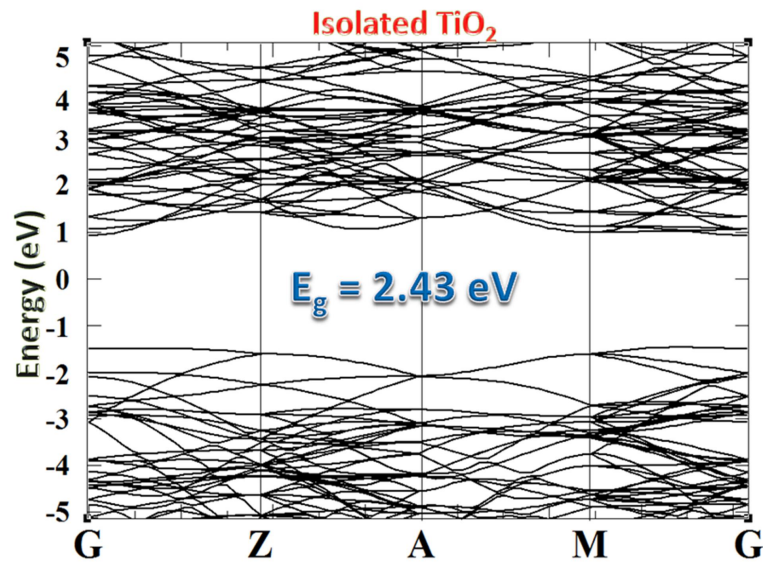
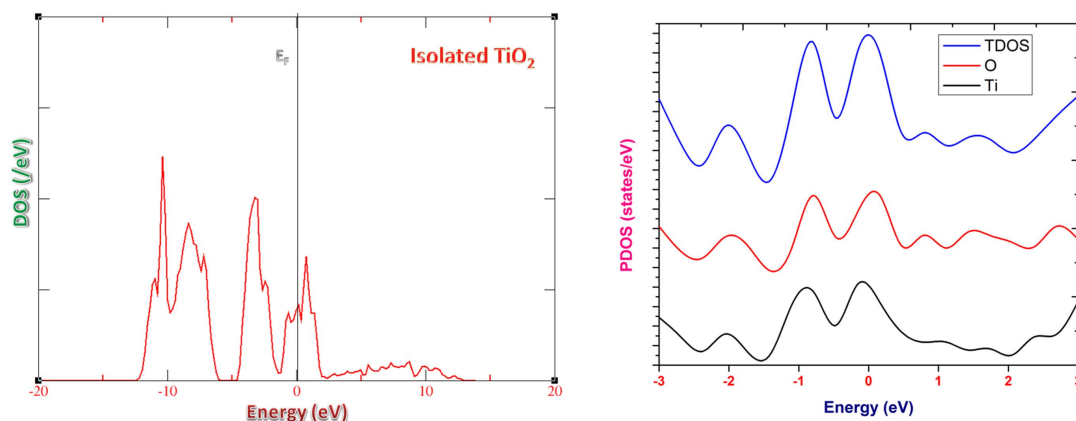


Figure 2. (Color online) Band structure of an isolated TiO₂ nanostructure.

Table 2. Energy gap calculation for isolated TiO₂ nanostructure with various exchange-correlation functional.

XC functional	E_g (eV)	Type
PBE	2.43	GGA
BLYP	2.50	GGA
PBEsol	2.38	GGA
RPBE	2.56	GGA
revPBE	2.48	GGA

**Figure 3.** (Color online) Density of states (DOS) spectrum of an isolated TiO₂ nanostructure.

functional, the electronic properties of TiO₂ nanostructure can be fine-tuned. Previously, Deak et al. [14] reported the electronic band gap of TiO₂ with hybrid HSE06 functional for both anatase and rutile crystal structure, which are overestimated from the present work. Table 2 shows that the energy band gap value of an isolated TiO₂ nanostructure with different exchange correlation functional such as PBEsol, BLYP, RPBE, PBE and revPBE [28]. Kaloni and co-workers [29–33] have suggested that the electronic and structural properties of 2D nanosheets and organic compounds are in oligomer form, which can be fine-tuned with the interaction of transition metal atoms.

The band structure of TiO₂ nanostructure is underestimated in the present work since the density functional theory method with GGA/PBE exchange correlation functional is utilized to calculate the electron-electron interaction in their ground state. Moreover, the electronic and adsorption properties of acetone in TiO₂ nanostructure cannot be disturbed due to underestimation of the band gap, since the isolated TiO₂ base material is compared with acetone adsorbed TiO₂ nanostructures. The density of states (DOS) spectrum gives the insights on localization of charges in different energy intervals along TiO₂ nanostructure. The visualization of band structure, PDOS and DOS spectrum are shown in figures 2 and 3, respectively.

The peak maxima are recorded near the Fermi energy level (EF), which is one of the favorable conditions for the adsorption of target vapor/gas molecules. Thereby, the free electrons can easily transfer between TiO₂ base material and acetone molecules. The peak maximum in different energy intervals arose owing to the orbital overlapping between Ti and O atoms in TiO₂ nanostructure. Generally, for chemiresistive type of vapor/gas sensors, metal oxide semiconducting materials are preferred owing to the fact that the transfer of electrons is facilitated between target gas/vapor and TiO₂ nanostructure and the changes in the resistance can also be observed. From the observations of band structure and DOS spectrum of TiO₂ nanostructure it is inferred that TiO₂ material can be used as a base material for the possible application of chemical nanosensors.

3.2. Adsorption properties of acetone on TiO₂ nanostructure

In the initial stage of acetone adsorption study on TiO₂ base material, acetone vapor should be studied in vapor phase. The bond length between Ti and O atom in TiO₂ nanostructure is 1.98 Å. Figure 4 (a) refers the adsorption of carbon atom in acetone molecules adsorbed on Ti atom in TiO₂ nanostructure and it is referred to as position P. Figure 4 (b) illustrates the adsorption of H atom in acetone molecules adsorbed on Ti atom in TiO₂ nanostructure and it is referred to as position Q. Similarly, positions R and S refer to the adsorption of C and H atom in acetone molecules adsorbed on O atom in TiO₂ nanostructure as shown in figure 4 (c) and (d), respectively. The adsorption energy of acetone on TiO₂ nanostructure can be calculated using equation (3.1)

$$E_{\text{ad}} = [E(\text{TiO}_2/\text{CH}_3\text{COCH}_3) - E(\text{TiO}_2) - E(\text{CH}_3\text{COCH}_3) + E(\text{BSSE})], \quad (3.1)$$

where $E(\text{TiO}_2/\text{CH}_3\text{COCH}_3)$ refers to the energy of TiO₂/CH₃COCH₃ complex. $E(\text{CH}_3\text{COCH}_3)$ and $E(\text{TiO}_2)$ refers to the isolated energy of CH₃COCH₃ and TiO₂ molecules, respectively. BSSE represents the basis set superposition error using counterpoise techniques in order to eliminate the overlapping effect on basis functions during calculations.

When acetone molecules get adsorbed on TiO₂ base material, negative values of adsorption energy (E_{ad}) indicate a strong adsorption of acetone on TiO₂ nanostructure. Besides, in the present work, for all positions namely P–S exhibits a negative value of E_{ad} . This clearly confirms the adsorption of acetone

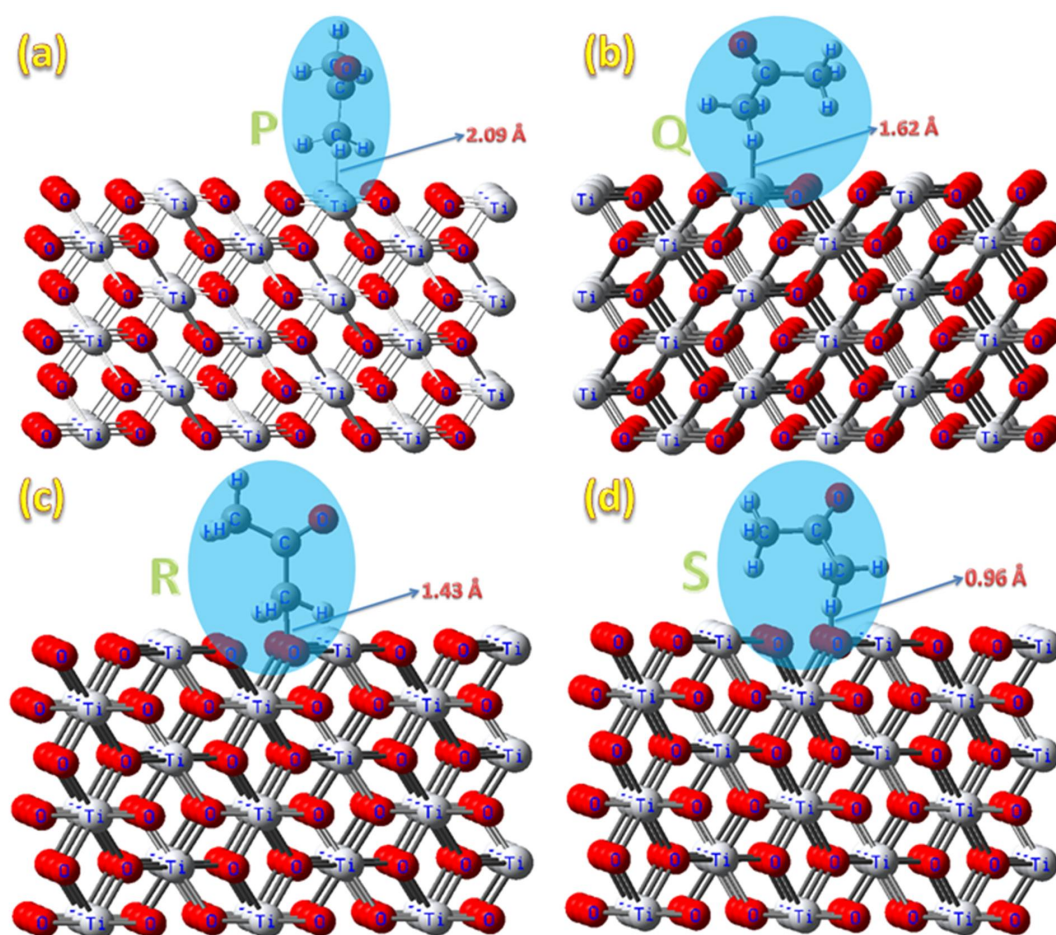


Figure 4. (Color online) (a)–(d) Adsorption of acetone on position P, Q, R and S.

Table 3. Adsorption energy, Mulliken charge and average energy gap variation of TiO₂ nanostructure.

Nanostructures	E_{ad} (eV)	Q (e)	E_g (eV)	E_g^a (%)
Acetone adsorbed on TiO ₂ nanostructure				
Isolated TiO ₂	–	–	2.43	–
P	–1.48	0.012	2.32	4.74
Q	–1.46	0.105	1.32	84.09
R	–1.46	0.171	0.82	196.34
S	–1.29	0.013	0.68	257.35
H ₂ O and O ₂ adsorbed on TiO ₂ nanostructure				
A	–1.62	0.224	2.39	1.67
B	–1.60	0.17	2.41	0.83
C	–1.78	0.029	2.18	11.47
D	–1.71	–0.304	2.36	2.97

molecules on TiO₂ nanostructure. The adsorption energy of TiO₂ nanostructure for position P–S is observed to be –1.48 eV, –1.46 eV, –1.46 eV and –1.29 eV, respectively. In addition, the band gap of TiO₂ nanostructure gets decreased due to the adsorption of acetone molecules on TiO₂ base material owing to the interaction of target VOCs with base material. Thus, the conductivity of TiO₂ nanostructure increases. The resistance of TiO₂ base material decreases when it is exposed to the reducing vapors such as acetone. The trend in the changes of resistance upon exposure towards acetone vapor is in good agreement with the reported work of Sun et al. [34]. The changes in band gap of TiO₂ nanostructure for positions P–S are found to be 2.32 eV, 1.32 eV, 0.82 eV and 0.68 eV, respectively. Besides, the variation in the energy gap and adsorption energy supports that TiO₂ nanostructure can be used for the detection of acetone vapor. Rella et al. [17] reported about the detection of ethanol and acetone vapors using TiO₂ nanoparticles synthesized by pulsed laser deposition method. Chen et al. [16] studied the acetone sensing performance of nanoporous titanium dioxide using a facile hydrothermal method. Epifani et al. [35] reported about the design of an acetone sensor based on titanium dioxide nanocrystals functionalized with tungsten oxide species. From the literature, it is evident that TiO₂ nanomaterial can be utilized as a two probe device for the detection of VOCs upon adsorption, which gives rise to change in the current. The variation in the current is directly proportional to the concentration of acetone molecules present in the atmosphere. From the previous reports, it is inferred that TiO₂ nanostructure can be efficiently used as acetone vapor sensor, which also strengthens the present work. Besides, the present investigation strongly confirms the adsorption of acetone on TiO₂ nanostructure at atomistic level. In addition, the most suitable adsorption site of acetone on TiO₂ base material can be concluded only after studying the percentage of average energy gap variation (E_g^a , %) compared with its isolated counterpart. Table 3 refers the Mulliken charge transfer, percentage of average energy gap variation and adsorption energy. From the results, it is clearly observed that the prominent adsorption sites for acetone molecule on TiO₂ nanostructure are positions Q, R and S. The average energy gap variation is observed to be comparatively higher than P site. The transfer of electron between acetone molecule and TiO₂ nanostructure can be analyzed in terms of Mulliken population analysis (Q) [36–38].

The positive value of Q show that the electrons are transferred from acetone vapor molecule to TiO₂ base material; whereas the negative value of Mulliken charge shows that the electrons are transferred from TiO₂ base material to acetone molecule [39–41]. The Mulliken charge transfer values of TiO₂ nanostructure for positions P–S are found to be 0.012 e, 0.105 e, 0.171 e and 0.013 e, respectively. From the observation, the positive value of Mulliken charge is recorded for all the positions upon adsorption of acetone on TiO₂ base material. Therefore, the concentration of electrons gets increased due to the transfer of electrons from acetone to TiO₂ base material [42–45]. Moreover, the decrease in the energy gap and transfer of electrons from acetone molecule to TiO₂ nanostructures leads to an increase in the current flowing across the two probe TiO₂ device. The TiO₂ base material can be used for the design and development of acetone sensor. Figures 5–7 represents the electron density of an isolated TiO₂ nanostructure and for positions P, Q, R and S.

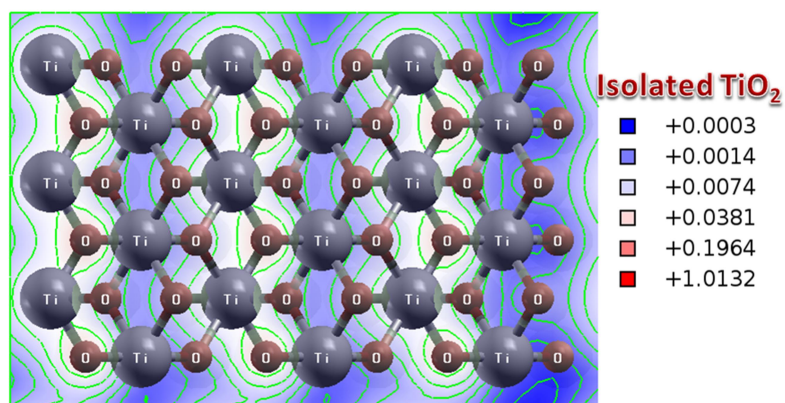


Figure 5. (Color online) Electron density of an isolated TiO₂ nanostructure.

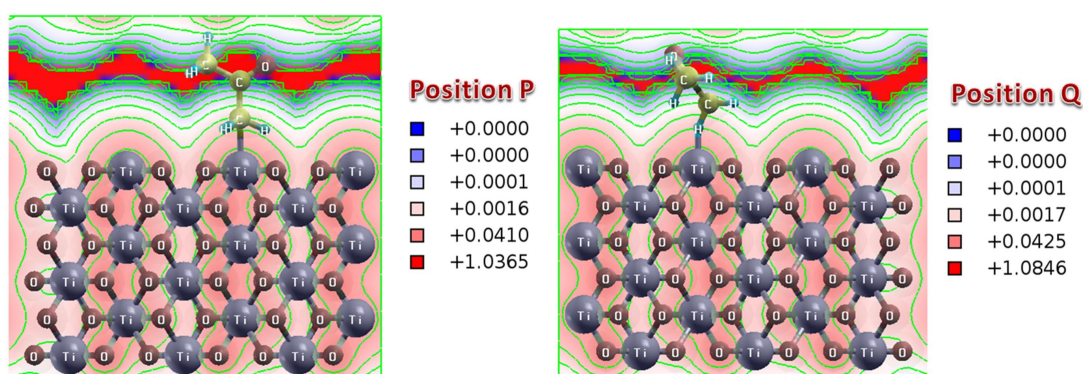


Figure 6. (Color online) Electron density of position P and Q.

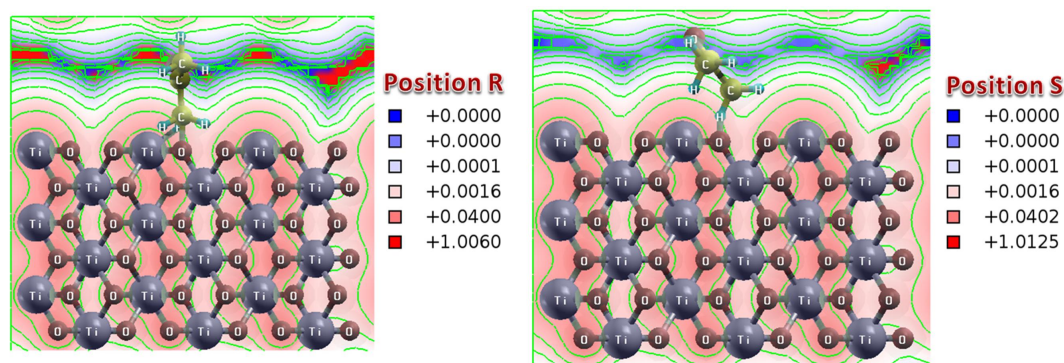


Figure 7. (Color online) Electron density of position R and S.

The variation in the electron density of an isolated TiO₂ nanostructure and acetone adsorbed TiO₂ nanostructure clearly infers that transition of electrons takes place between acetone and TiO₂ nanostructure, which is also in agreement with Mulliken charge transfer. The average energy gap value is found to be high for positions R and S. Also the adsorption energy, Mulliken charge transfer and energy gap variation are found to be favorable for position R. However, for position S, the average energy gap variation is comparatively high with low values of Q and E_{ad} . The Mulliken charge transfer for position P

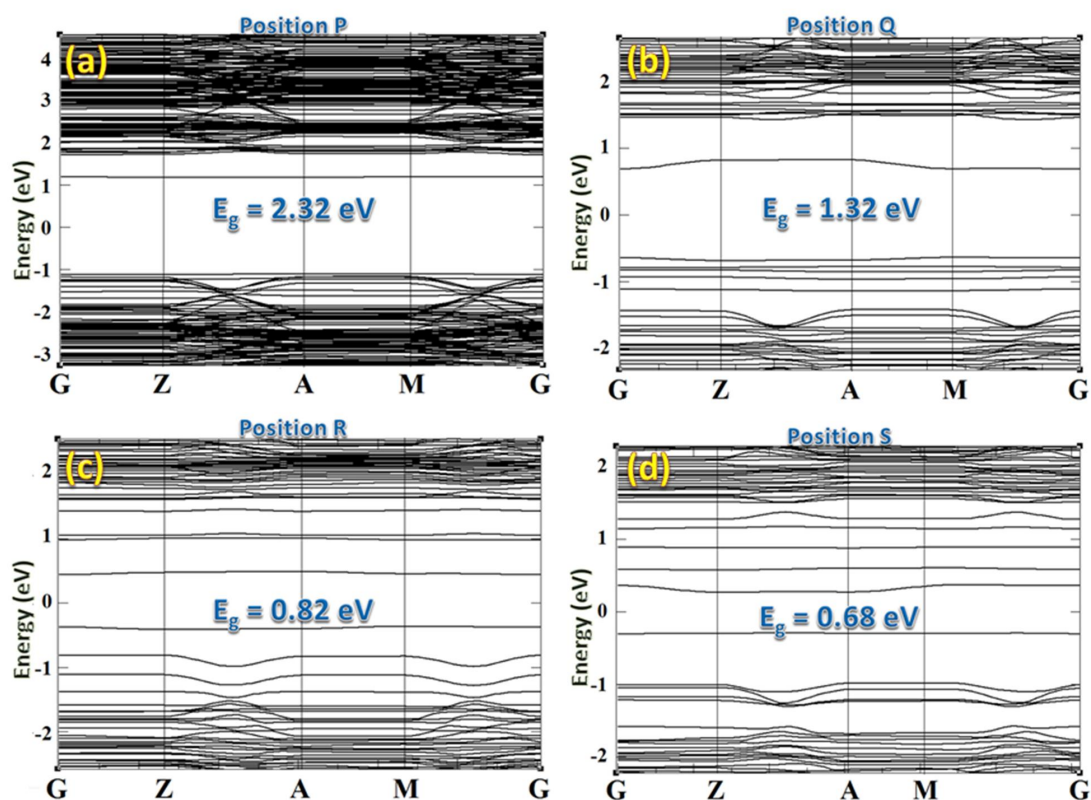


Figure 8. (Color online) (a)–(d) Band structure of TiO₂ nanostructure for position P, Q, R and S.

is almost the same as that of position S, whereas the average energy gap variation is comparatively very low. Figure 8 (a)–(d) illustrates the band structure of TiO₂ nanostructure for positions P–S, respectively. Figures 9–12 represent the corresponding PDOS including DOS spectrum for position P, Q, R and S. From the observation of energy band diagram for positions P and Q, the energy gap is observed to be around 2.32 eV and 1.32 eV, respectively, along the gamma point (G). In the case of position R and S, the energy gap is observed to be around 0.82 eV and 0.68 eV, respectively. Comparing the changes in the energy gap upon adsorption of acetone on TiO₂ nanostructure, the variation is observed to be significant for positions Q, R and S. Meanwhile, on looking at the density of states (DOS) spectrum for positions Q, R and S, the density of charge is observed to be larger than an isolated TiO₂ counterpart. (DOS spectrum is drawn in multi-curve fashion, the magnitude is taken into consideration along y -axis).

An increase in the density of charge is due to the fact that since TiO₂ is n-type semiconductor, the adsorption of acetone molecules consequently gives rise to a transfer of electrons between the acetone vapor and TiO₂ base material. The transfer of electrons will increase the electron concentration in TiO₂ base material, subsequently increasing the density of charge, which is observed in DOS spectrum. The density of states spectrum gives the insight that the electrons can freely transfer between acetone molecule and TiO₂ nanostructure, which can be used as chemical sensor. Thus, the DOS spectrum of TiO₂ nanostructure strongly supports the adsorption of acetone molecule on TiO₂ material. In order to strengthen the above result, the partial (or projected) density of states spectrum (PDOS) of an isolated TiO₂ nanostructure with adsorption sites for the positions P–S is illustrated in figures 9–12. Moreover, the density of charges is noticed to be larger in positions Q, R and S compared to an isolated TiO₂ nanostructure.

Furthermore, a prominent adsorption site of acetone vapor on TiO₂ nanostructure can be concluded only after analyzing the adsorption energy, Mulliken charge transfer, average energy gap variation and energy band gap. From the observations, among all the positions it is found that when hydrogen atom

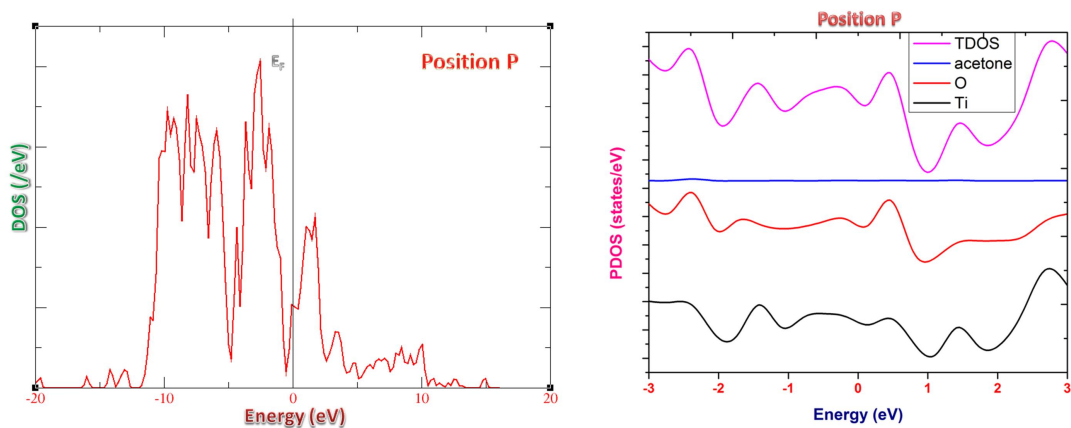


Figure 9. (Color online) Projected density of states (PDOS) and (DOS) spectrum of position P.

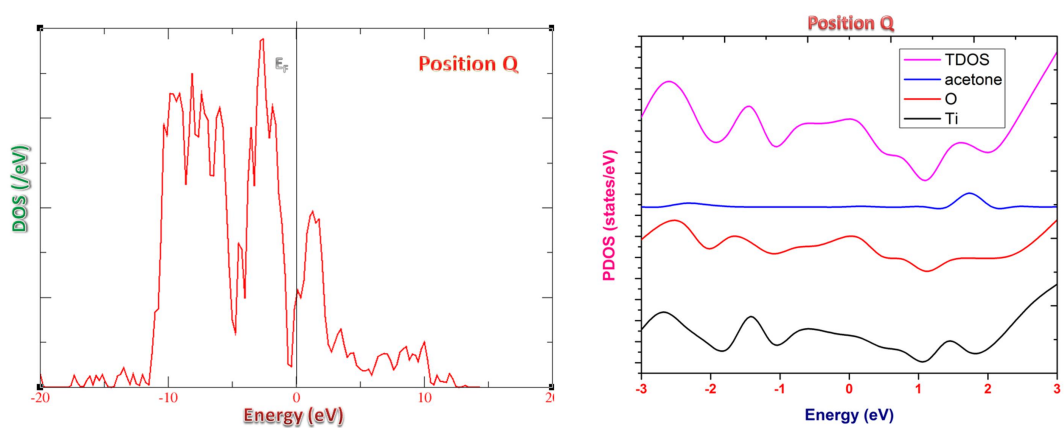


Figure 10. (Color online) Projected density of states (PDOS) and (DOS) spectrum of position Q.

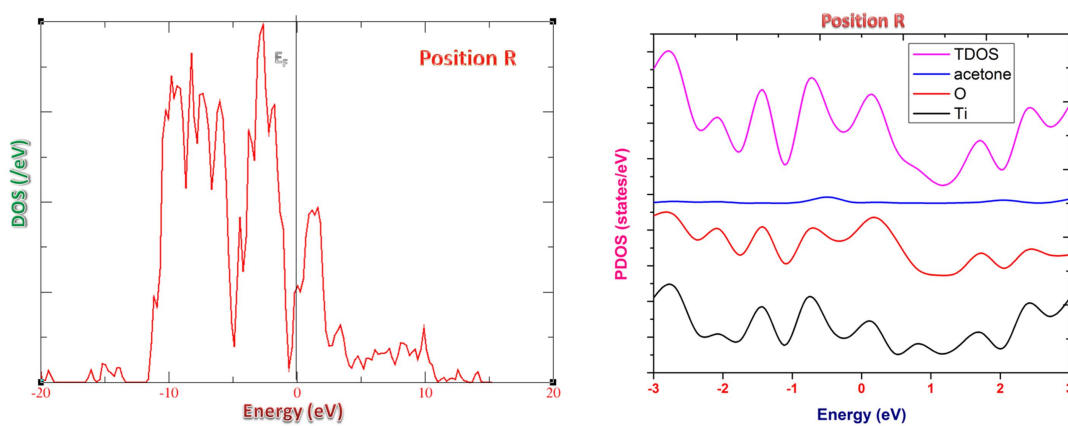


Figure 11. (Color online) Projected density of states (PDOS) and (DOS) spectrum of position R.

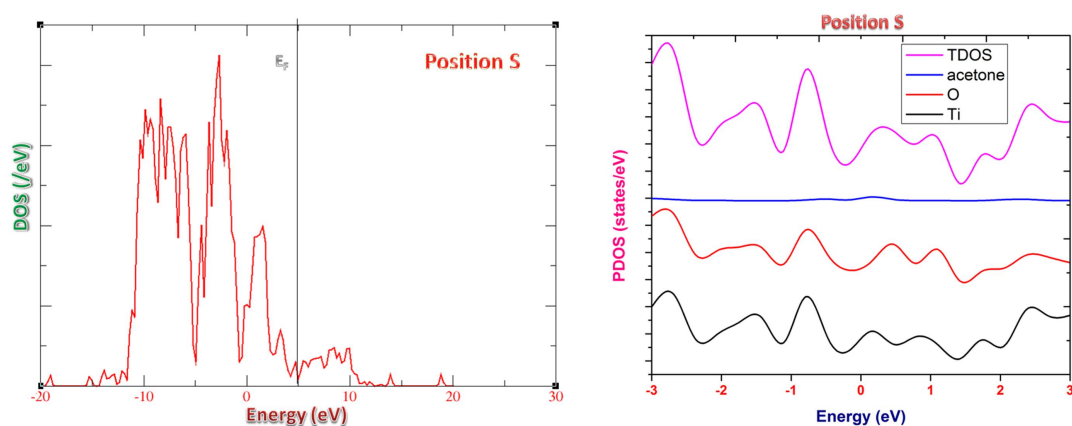


Figure 12. (Color online) Projected density of states (PDOS) and (DOS) spectrum of position S.

in acetone gets adsorbed on O atom in TiO₂ nanostructure, position S is found to be more prominent. Moreover, the selectivity of TiO₂ nanostructure towards acetone in the presence of other interfering gases in the ambient condition is to be ascertained. It is well known to the sensor community that sensitivity, selectivity and stability are important parameters to decide the performance of metal oxide based gas sensors. Figure 13 depicts the selectivity of acetone in ambient condition with other interfering gases, namely H₂O (humidity) and O₂ gas molecules. The adsorption studies of O₂ and H₂O on TiO₂ nanostructure are carried out and the response towards O₂ and H₂O molecules is observed.

The results show that the response of TiO₂ nanostructure towards acetone is found to be relatively high compared with H₂O and O₂ molecules. Besides, band gap variation upon adsorption of H₂O and

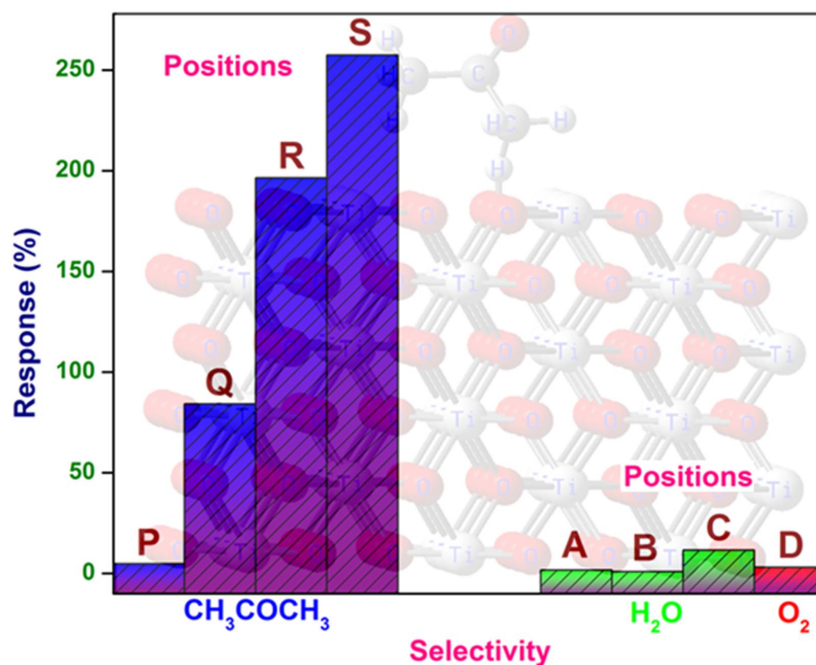


Figure 13. (Color online) The cross-selectivity of acetone in ambient condition with H₂O (humidity) and O₂ gas molecules.

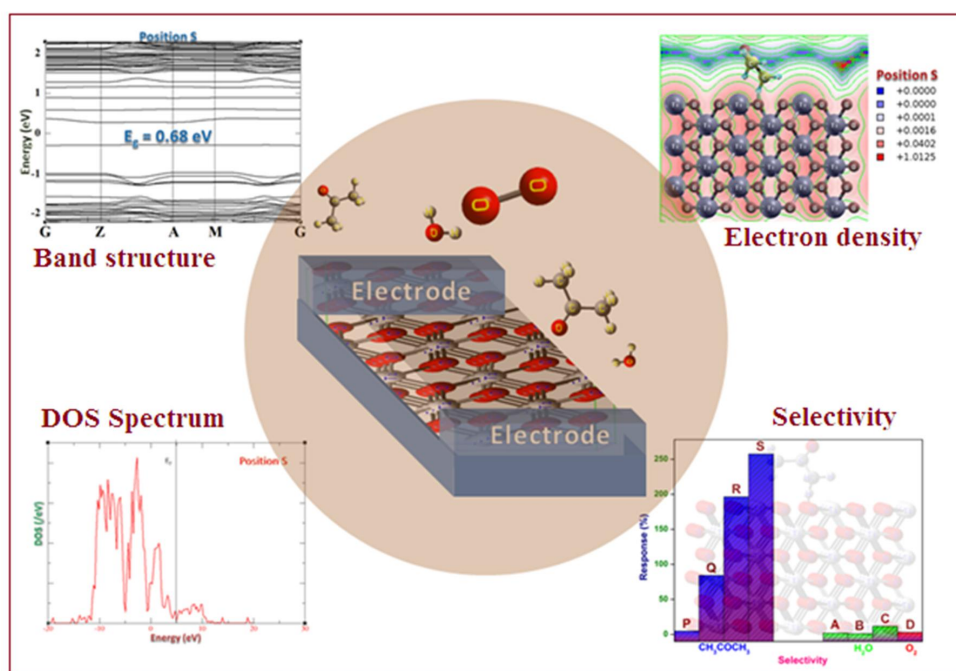


Figure 14. (Color online) The insight on the adsorption behavior of acetone on TiO₂ nanostructure.

O₂ molecules on TiO₂ nanostructure is found to be low. Figure 14 shows the insight on the adsorption behavior of acetone on TiO₂ nanostructure, which can be used to design a simple two probe device for a possible detection of acetone vapors present in the atmosphere.

4. Conclusions

To sum up, the electronic properties and acetone adsorption properties on TiO₂ nanostructure are studied using density functional theory method, which is carried out with GGA/PBE exchange-correlation functional. The band gap of an isolated TiO₂ nanostructure is found to be around 2.43 eV. Furthermore, the adsorption of acetone molecules on TiO₂ nanostructures is confirmed by the change in the adsorption energy, Mulliken charge transfer and average energy gap variation. The results of DOS spectrum clearly reveal that the transfer of electrons takes place between acetone vapor and TiO₂ base material. Furthermore, a prominent adsorption site is explored at atomistic level, which confirms that when a hydrogen atom in acetone molecule gets adsorbed on the O atom in TiO₂ nanostructure, the adsorption is found to be favorable. Furthermore, the selectivity of TiO₂ nanostructure towards acetone molecules with other interfering gases, namely H₂O and O₂, is also studied and reported. The findings from the present investigation strongly support that TiO₂ nanostructure can be efficiently used to detect the presence of acetone vapor in the mixed environment. Thus, we conclude that a properly tailored TiO₂ nanostructure can be used as a two-probe device to detect the presence of acetone vapors.

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Детектор для визначення поведінки випарів ацетону на TiO₂ наноструктурах — застосування теорії функціоналу густини

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Досліджуються електронні властивості TiO₂ наноструктури з використанням теорії функціоналу густини. Властивості адсорбції ацетону на TiO₂ наноструктурі вивчаються в термінах енергії адсорбції, зміни середньої енергії щілини і переносу заряду Муллікена. Спектр густини станів та структура зони чітко вказують на адсорбцію ацетону на TiO₂ наноструктурах. Зміна енергії щілини та зміни густини заряду спостерігаються після адсорбції ацетону на базовому матеріалі TiO₂ n-типу. Результати спектру густини станів показують, що перенос електронів відбувається між парою ацетону і TiO₂ базовим матеріалом. Отримані дані показують, що властивості адсорбції ацетону є більш сприятливими на TiO₂ наноструктурі. Зручні місця для адсорбції ацетону на TiO₂ наноструктурі ідентифікуються на атомарному рівні. Згідно з отриманими результатами, підтверджується, що TiO₂ наноструктуру можна ефективно використовувати в якості чутливого елемента для виявлення випарів ацетону у змішаному довіклі.

Ключові слова: *TiO₂, наноструктура, адсорбція, ацетон, енергетична щілина*
