THEORETICAL STUDY OF THE CARBONE(IV) DOPED ANATASE SURFACES OF TiO$_2$

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Abstract: *In this study photocatalytic activity of TiO$_2$ doped with C(IV) has been investigated using DFT (Density Functional Theory) calculations. This calculations are utilized to illuminate and classify the effect of C(IV)-doping on the electronic and structural properties of TiO$_2$, neutral, stoichiometric clusters Ti$_7$O$_{18}$H$_8$ and Ti$_{25}$O$_{55}$H$_{10}$ cut from the anatase bulk structure and three new models for the C(IV)-doped TiO$_2$ were developed. The DFT calculations were carried out by the hybrid B3LYP functional, by using double-zeta, LanL2DZ basis set. The DFT calculations indicated that C(IV)-doping of TiO$_2$ enhances the visible-light photocatalytic activity.*

Keywords: TiO$_2$, anatase, C-doped, DFT

Introduction

In many studies properties of titanium have been investigated and proved to be the most effective and suitable photocatalyst for the degradation of environment pollutants, selfcleaning and solar cell applications [1]. In [2-4] TiO$_2$ has been proved to be most suitable photocatalyst for application in photocatalysis to degrade refractory organic compounds in water or air. For heterogeneous photocatalysis anates form of TiO$_2$ has also been proved to very effective compared to various semiconductor photocatalysts (WO$_3$, ZnO, ZnS, Fe$_2$O$_3$, CdS and SrTiO$_3$) [5,6]. Although details on the microscopic mechanisms concerning the excited states involved in the process are still a matter of debate [7], under UV irradiation properties of TiO$_2$ are known for many years [8-11]. It is a critical issue to reduce the band gap of anatase TiO$_2$ for improving its photocatalytic applications. Therefore in different studies anatase TiO$_2$ dopped either with nonmetal elements (C, N, F or S) or metal elements (Se, Fe, V etc.) elements aiming to reduce the band gap and improve photocatalytic activity under visible light [12–18].

In this study using DFT (Density Functional Theory) electronic structure, optical and photocatalytic properties of C dopped TiO$_2$ with different substitute sites are analyzed in order to illuminate activity of the photocatalyst in regards to C(IV) the dopant. Using DFT undopped and C(IV) dopped titania cluster models are calculated to elucidate the structural and electronic properties. This study may provide new insights of photoactivity enhancement by C(IV)-doping into the lattice of TiO$_2$.

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Method

The DFT techniques are used to understand the effect of C(IV) dopant on the structural and electronic properties of C(IV)-doped TiO$_2$. Since it is well-known, the Degussa P25 powder has include the anatase phase more than the others. The surface of anatase particles predominantly consists of the (101), (100) and (001) lattice planes. Since (001) surface has the highest photocatalytic activity [19], hence it has been modelled to determine the location and the bonding status of the dopant ion, TiO$_2$ molecules. This model is cut from the anatase bulk structure. The unitcell for anatase has a tetragonal structure with the bulk lattice constants a = b = 3.78 Å and c = 9.51 Å [20]. In the modelled clusters, the unsaturated oxygen atoms were completed with hydrogen's and titanium atoms with OH groups. Using quantum mechanical techniques three new models for the C(IV) doped photocatalyst were developed. The studied three cluster models were Ti$_9$O$_{21}$H$_6$ (Model A) Ti$_{15}$O$_{37}$H$_{14}$ (Model B) Ti$_{25}$O$_{55}$H$_{10}$ (Model C). In these models, replacing one Ti atom whose coordination number was equal to 4 with one C(IV) is performed to constructed the structure of the C(IV) doped TiO$_2$. In the developed cluster models, all the distances were fixed at the bulk values. All the calculations were carried out using the DFT method [21-22] with in the GAUSSIAN 09 package [23] due to the fact that it takes electron correlation in to account. The DFT calculations were performed by the hybrid B3LYP [24] functional. The double-zeta (LanL2DZ) [25] basis set was used. The cluster geometry was frozen throughout all the calculations, but the dopant, terminal hydrogens and the OH groups were relaxed. The geometric parameters, the band edges, the band gap energies and Mulliken charge distributions of the atoms on the undoped, C(IV) doped photocatalyst surfaces were calculated. By changing the location of C(IV) ion with different Ti atoms in the surface for each model A, B and C many models are generated to choose the best photocatalitic activity structure.

Result And Discussion

The Figure 1-3 represents the structures obtained for the C(IV)-doped TiO$_2$ cluster models with minimum energy structure. Electronic structure calculations of the models indicate structures with deviations, which are not as symmetrical as that of the undoped part of TiO$_2$ model. The results indicate that the size and electronegativity difference between the C (IV) cation and Ti (IV) induce structural changes. The calculated results show that the C(11)–O(7) bond length, 1.46 Å was found to be shorter than Ti(2)–O(3) bond length 1.93 Å for Model A, which is consistent with the different electronegativity's and ionic radius of C(IV) (30.0 pm) and Ti(IV) (74.5 pm). The results of shortening of this bond the O(12)–C(11)–O(7) angle from its original value reduced from 116.1^0 to 92.4^0 that in the undoped part while C(11)–O(10) bond lengthens increased from 1.930 Å to 2.48 Å. As a result C (IV) doping causes defacement in the TiO$_2$ lattice. We also experienced same type of changes in Model B and Model C. Depending on the position of the doped C(IV) these bond distances and angles also change. Values that are given in those figures 1-3 belong to the minimum energy structures for Model B and Model C.
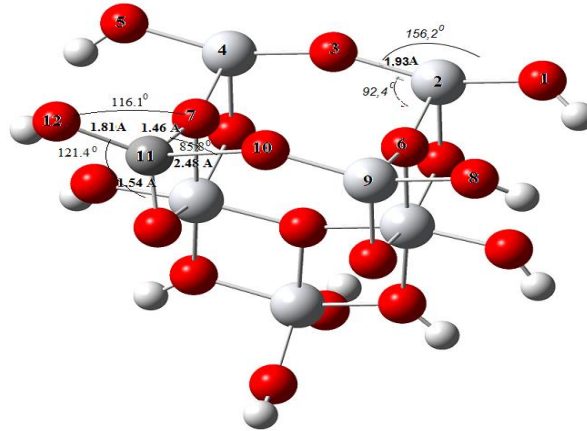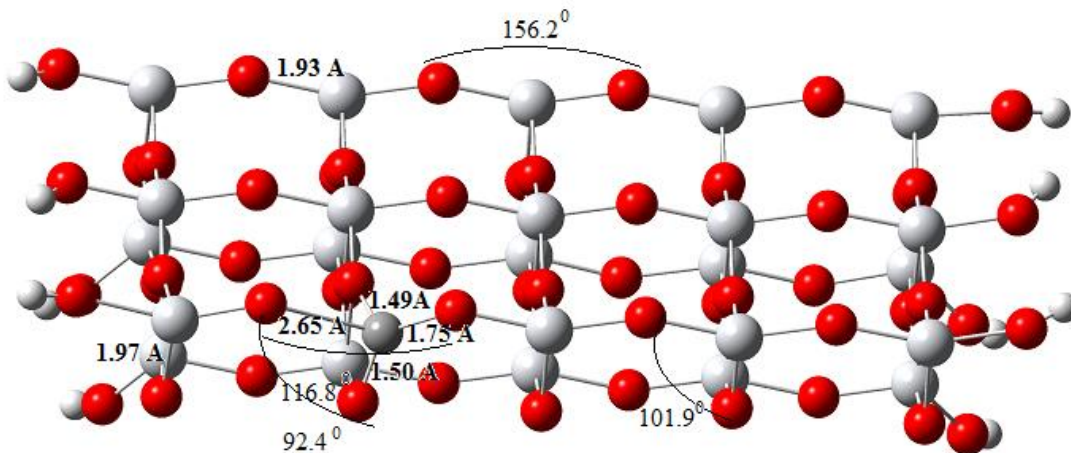
Figure 1: Optimized structure of the C(IV)-doped TiO$_2$ Model A cluster with some distances and angles
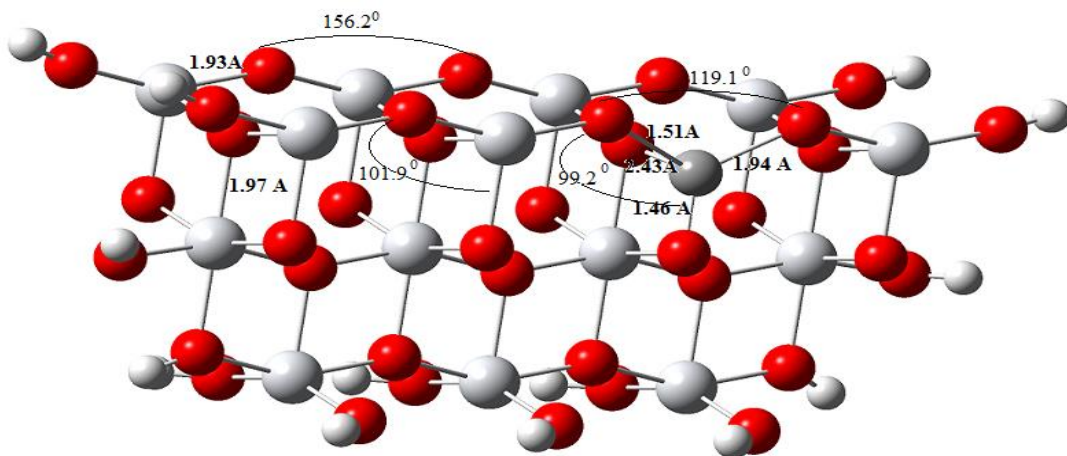
Figure 2: Optimized structure of the C(IV)-doped TiO$_2$ Model B cluster with some distances and angles

Figure 3: Optimized structure of the C(IV)-doped TiO$_2$ Model C cluster with some distances and angles

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The different electronegativity of the C (IV) dopant causes a redistribution of local charges of the surface atoms, which may enhance the photocatalytic activity. Mulliken charge distributions of the surface atoms of Model A showed in Figure 4. reflect the behavior of the dopant in the doped cluster models. In the doped model, the positive charge on surface Ti cations increases to 1.41-1.46 while the dopant C (IV) carries less positive charge 0.9 than the lattice Ti s. The negative charge on Os was found to be increased from 0.9 to 1.4 correspondingly due to C (IV)-doping. The reason may be explained by the fact that the dopant C(IV) is more electronegative.

While four- and fivefold-coordinated titanium atoms shows Lewis acidic characteristics, the two- and threefold-coordinated oxygen atoms behaves as Lewis base sites for the exposed atoms on the (001) surface of Model B and Model C.

A schematic diagram of the electronic energy levels for the undoped and C(IV)-doped anatase models obtained from electronic structure calculations are presented in Figure 5. This figures explains the highest occupied HOMO and the lowest unoccupied molecular orbitals LUMO energies for the studied structures. The valence band (VB) and conduction band (CB) those bands related to HOMO LUMO energies. The experimental band-gap energy of the undoped TiO$_2$ (3.2 eV) was adopted as the benchmark to correct the calculated values of the anatase (001) surface. The calculated band-gap was corrected using an operator that displaces the empty and occupied bands relative to each other by a rigid shift of 0.41 eV for Model C, 0.36 eV for Model B and 0.03 eV for Model A to bring the minimum band-gap in line with experiment for the band-gap of anatase. These intermediate energy levels offer additional steps for the absorption of low energy photons through the excitation of VB electrons to these intermediate energy levels, from where they can be excited again to the CB.
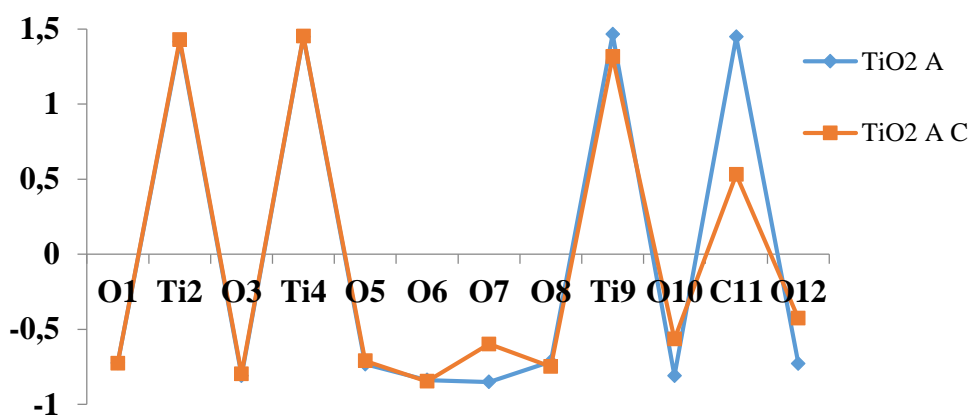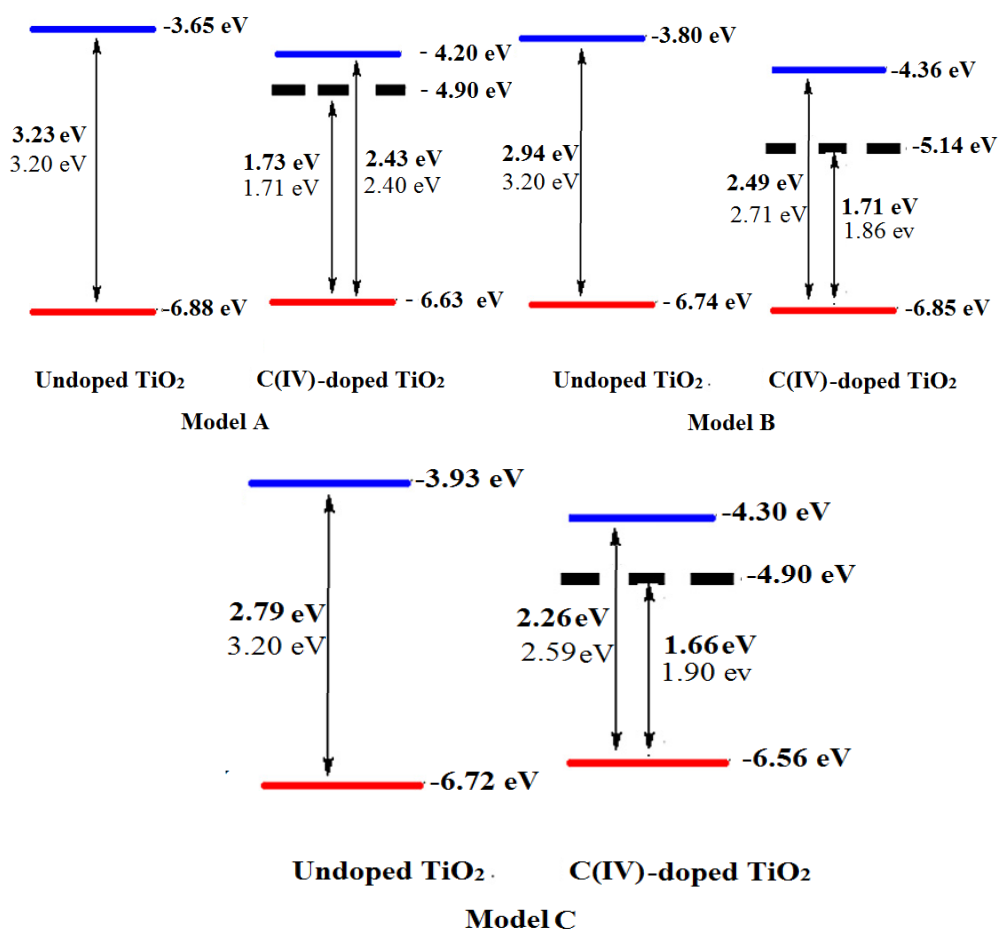

Figure 4: The surface atoms Mulliken charge for undoped and C(IV)-doped TiO$_2$ clusters

Figure 5. The valence band (VB) and conduction band (CB) edges of of C-doped TiO$_2$ molecules

Table 1 Energies of C-doped TiO$_2$ molecules in ev

	Energy	HOMO-1	HOMO	LUMO	LUMO+1	LUMO-(HOMO-1)	LUMO-HOMO	(LUMO+1)-HOMO
TiO2 A	-50158.50	-7.17	-6.89	-3.65	-3.56	3.52	3.23	3.33
TiO2 A C	-49602.01	-6.94	-6.63	-4.90	-4.20	2.04	1.73	2.44
TiO2 B	-99758.11	-6.86	-6.74	-4.01	-3.80	2.85	2.73	2.94
TiO2 B C1	-99200.41	-5.95	-5.87	-4.77	-4.39	1.18	1.10	1.48
TiO2 B C2	-99201.48	-6.99	-6.95	-5.29	-4.46	1.70	1.66	2.49
TiO2 B C3	-99201.55	-7.02	-6.85	-5.14	-4.36	1.89	1.71	2.49
TiO2 C	-152403.20	-6.90	-6.72	-3.93	-3.84	2.97	2.79	2.88
TiO2 C C1	-151845.70	-6.48	-6.44	-5.00	-4.11	1.49	1.44	2.33
TiO2 C C2	-151847.69	-6.74	-6.56	-4.90	-4.30	1.85	1.66	2.26
TiO2 C C3	-151846.81	-6.85	-6.57	-4.87	-4.15	1.97	1.69	2.42
TiO2 C C6	-151844.87	-6.35	-6.06	-4.83	-4.51	1.52	1.23	1.55

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Conclusion

TiO$_2$ was doped with C (IV) ions to obtain a visible light active photocatalyst with high photocatalytic activity. Characterization techniques showed that the C (IV) is in O–C bond is shorter than Ti-O bond in the crystal lattice. Beside this C (IV) charge is less positive than Ti (IV). The absorption threshold of the C (IV)-doped photocatalyst shifted to the visible region of the spectrum. We can understand from the result of DFT calculations that HOMO LUMO band gap has not been effected from that C (IV)-doping of TiO$_2$. However due to C 3p orbitals in the band gap, C (IV)-doping of TiO$_2$ resulted in an additional electronic states. Also these localized mid-gap levels resulted in the visible light photocatalytic activity of the C (IV)-doped TiO$_2$. Changes in the photocatalytic activity of doped TiO$_2$ are due to change in binding position of the C atoms.

Acknowledgments

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