A Density Functional Study of N-Doped TiO$_2$ Anatase Cluster[①]

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ABSTRACT   A systematic study on geometry, electronic structure and vibrational properties of N-doped TiO$_2$ anatase cluster, within the framework of the density functional theory, has been performed in this work. The calculations confirmed that the most structures in substitutional model consist of a two-coordinate bridge structure and a three-coordinate hollow structure. The calculated results can well explain the red shift in N-doped TiO$_2$ observed in experiments. The study provides an illustration for the N-doped anatase from the viewpoint of chemical bonding theory.

Keywords: N-doped TiO$_2$, DFT, HOMO-LUMO gap

1   INTRODUCTION

As an important photocatalyst, titanium dioxide has some evident advantages in applications because of its high efficiency, low price and high thermal stability[1, 2]. However, titanium dioxide photocatalyst can only absorb UV light which is a small fraction of the sun's energy due to its wide band gap (3.2 eV for anatase). Thus, attempts to increase the photoactivity of titanium dioxide catalysts to cover the range of visible light are quite attractive and important.

Some research work is devoted to the application of doping treatments of titania with metal or metal-ions[3, 4]. Recently, non-metal-doped TiO$_2$ was found to be most effective to extend the photoresponse of TiO$_2$ to the visible region[5~11]. Asahi *et al.*[7] showed that TiO$_{2-x}$N$_x$, in which N was substituted on the lattice O by sputtering methods, exhibits enhanced photoactivity in the visible spectral range. Since then, more experimental[12, 13] and theoretical[14,15] resear-

ches on the N-doped TiO$_2$ have been reported. These theoretical calculations under the plane-wave pseudopotential method (LDA or GGA) have evidenced that the substitutional doping of N for O in the anatase TiO$_2$ was effective because N p states contribute to the band gap narrowed by effective mixing with O $2p$ states. Furthermore, the synthesized TiO$_{2-x}$N$_x$ nanoparticles are photoactive, with absorbance that extends into the visible region up to 600 nm. In this regard, *ab initio* cluster model maybe help to provide information for the N-doped anatase system.

The aim of this work is to investigate the effect of N-doping on anatase electron structure and to find cluster models suitable for modeling the electronic structures of doping anatase nano system. We will present the geometric structures and relative energetic and molecular properties of anatase that are modified by N-doping. Moreover, it provides a bonding analysis to make clear how doping N affects the system. Vibrational properties and

HOMO-LUMO gap are also reported.

and Parr (B3LYP).

2   COMPUTATIONAL DETAILS

$TiO_{2-x}N_x$ clusters were computed with the hybrid density functional theory at the B3LYP level[16, 17]. The standard 6-31G(d) basis set[18] for O and N atoms and the small-core RECP (relativistic effective core potential) plus valence double-ζ basis set (LanL2DZ)[19] for Ti were employed. For open shell systems, the spin-unrestricted algorithm was employed. All calculations were performed by using the Gaussian03 program[20]. Geometry optimizations were performed with the BFGS algorithm with no constraints of freedom. Reported stationary points have been confirmed to be local minima by harmonic vibrational analyses at the same theoretical level. The optical energy gap has been performed within the framework of time-dependent density functional theory, employing the hybrid nonlocal exchange-correction functional of Becke, Lee, Yang

3   RESULTS AND DISCUSSION

3.1   Cluster model

Clusters (n = 10, 17, 21, 29) cut out from the anatase structures were considered, as shown in Fig. 1. The information about the stability of the cluster models can be obtained by investigating their energies and HOMO-LUMO gaps (Table 1). For the bare $Ti_{17}O_{34}$ cluster, a HOMO-LUMO gap of 3.58 eV is obtained, with a TDDFT lowest transition of 3.00 eV. Therefore, we simulated the N-doped TiO_2 anatase system with $(TiO_2)_n$ (n = 17, 21) according to the following reasons: (1) Nanostructured anatase contenting 17 or 21 TiO_2 molecules with a size about 1 nm. (2) When N replaces one oxygen atom in this cluster model, the stoichiometry is $TiO_{2-x}N_x$ with x = 0.05～0.06, which is comparable to that used in the experiment. (3) Suitable band gap and inexpensive computing costs.

Table 1.   HOMO-LUMO Gap, TDDFT Optical Band Gap and
Relative Energies of the Cluster Models of Anatase

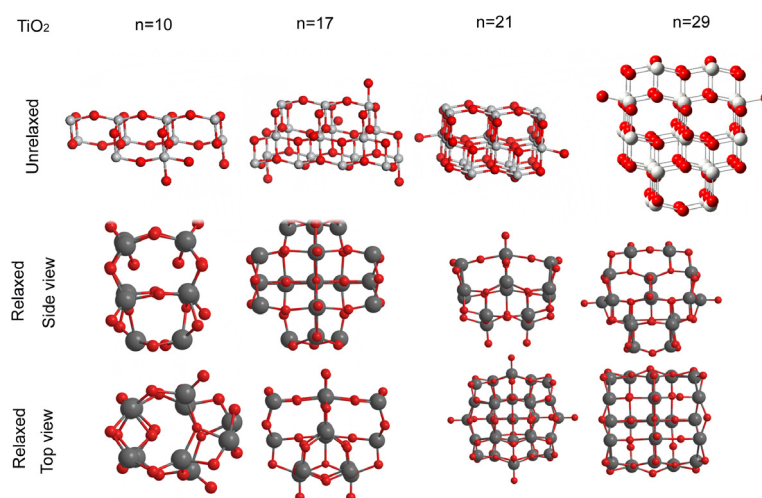| Anatase	Symmetry	HOMO-LUMO gap (eV)	TD gap (eV)	E(TiO$_2$)/n (kcal·mol^{-1})
$Ti_{10}O_{20}$	C_2	3.91	2.97	−105.25
$Ti_{17}O_{34}$	D_{2d}	3.58	3.00	−100.65
$Ti_{21}O_{42}$	D_{2d}	3.69	3.13	−109.21
$Ti_{29}O_{58}$	S_4	3.33	2.79	−113.28

Fig. 1.   Optimized geometries of $(TiO_2)_n$ cluster models, n = 10, 17, 21, 29

3. 2 Geometry and stability of the nitrogen doping in anatase clusters ($TiO_{2-x}N_x$)

Different possible doping geometries for $TiO_{2-x}N_x$ are given from the optimization. The different doping geometries and energies are given in Table 2.

The lowest energy $Ti_{17}O_{33}N$ cluster found by our calculations is a bridge structure, as shown in Fig. 2, cluster 17c which has the Ti–N bond lengths to be 1.77 and 2.02 Å. The next lowest-energy cluster (17b) is a 3-coordinate hollow structure with only 3.30 kcal/mol higher in energy. The lowest energy $Ti_{21}O_{41}N$ cluster is a 3-coordinate hollow structure (21b) and the next lowest-energy cluster (21c) a bridge structure. This indicates that these two structures have relative stability compared with other structures. The Ti–O bond lengths in anatase clusters are from 1.67 to 2.16 Å, and optimized Ti–N bond lengths are 1.73 to 2.24 Å, indicating replacing an O atom with a N atom does not lead to significant structural changes.

Table 2. Geometrical Parameters, Relative Energies and Electronic Properties for $Ti_{17}O_{33}N$ and $Ti_{21}O_{41}N$ Clusters

| Cluster	Structure mode	Ti-N bond length (Å)	N atomic spin	Gap (eV)	Relative energies(Kcal/mol)
$Ti_{17}O_{33}N$	a (1c-chain)	$R_1 = 1.75$	1.33	1.89	10.66
	b (3c-hollow)	$R_1 = R_2 = 2.12$, $R_3 = 2.01$	0.65	2.80	3.30
	c (2c-bridge)	$R_1 = 1.77$, $R_2 = 2.07$	0.90	2.75	0.00
	d (2c-bridge)	$R_1 = 1.82$, $R_2 = 2.02$	0.89	2.38	11.98
$Ti_{21}O_{41}N$	a (1c-chain)	$R_1 = 1.73$	1.00	2.29	11.73
	b (3c-hollow)	$R_1 = R_2 = 2.06$, $R_3 = 2.01$	0.91	2.24	0.00
	c (2c-bridge)	$R_1 = 1.77$, $R_2 = 2.24$	1.00	2.75	2.76
	d (2c-bridge)	$R_1 = 1.80$, $R_2 = 2.12$	0.89	2.40	14.55
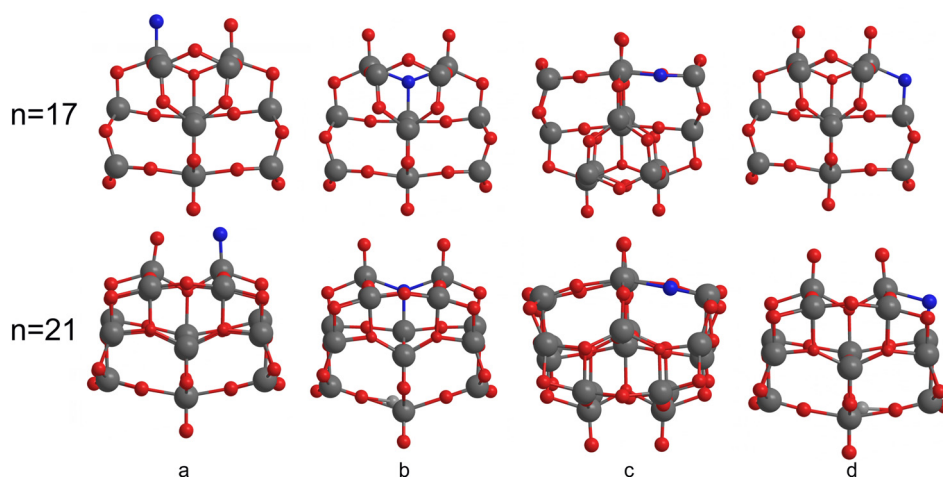
Fig. 2. Optimized geometries of $TiO_{2-x}N_x$

3. 3 Electronic structures and frequencies

To analyze the electronic properties of N-doped anatase clusters, we calculated different structural modes. The calculated HOMO-LUMO gap and atomic spin of $Ti_{17}O_{33}N$ and $Ti_{21}O_{41}N$ structures obtained at the same theoretical level as that used in the optimization processes are listed in Table 2. The calculated energy gap of pure anatase cluster is about 3.60 eV. Asahi *et al.*[7] show Ti 3*d* states to be present throughout the valence band except the very low binding energy region of the valence band, which is attributed almost solely to O $2p_\pi$ states. For N-doped anatase cluster, the calculated results show little changes of LUMO, which is completely consistent with the experimental observation that the conduction band edge remains unchanged by nitrogen-doping. However, the HOMO is mainly attributed to N $2p_\pi$ states, as seen in Fig. 3. It

indicates that N impurities introduce some energy levels above the top of O 2*p* valance state resulting in a reduction of energy gap by about 0.8 eV in contrast with that of pure anatase cluster. The results

are consistent with a previous study and provide a good explanation for the red shift phenomena observed in experiments[8].
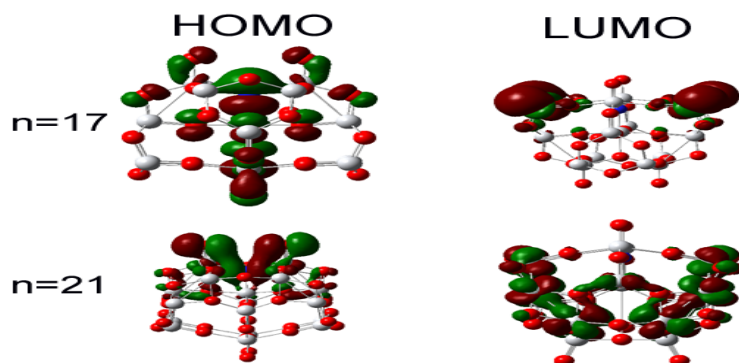

Fig. 3.   Model diagrams showing HOMO and LUMO of Ti$_{17}$O$_{33}$N and Ti$_{21}$O$_{41}$N

In addition, the spin localization on N is demonstrated by the Mulliken population analysis which shows a spin density ≈ 1 on the N atom. EPR investigations of N-doped anatase reveal the presence of paramagnetic centers consisting of single N atoms localized at the bulk oxide lattice[21]. To

investigate the vibrational spectra of doping effect, we also computed vibrational spectra of pure anatase and N-doped anatase, as shown in Fig. 4. Similar to the pure anatase cluster, the dominant vibrations occur at 448, 553, 888, 904, 942 and 1013 cm^{-1}.
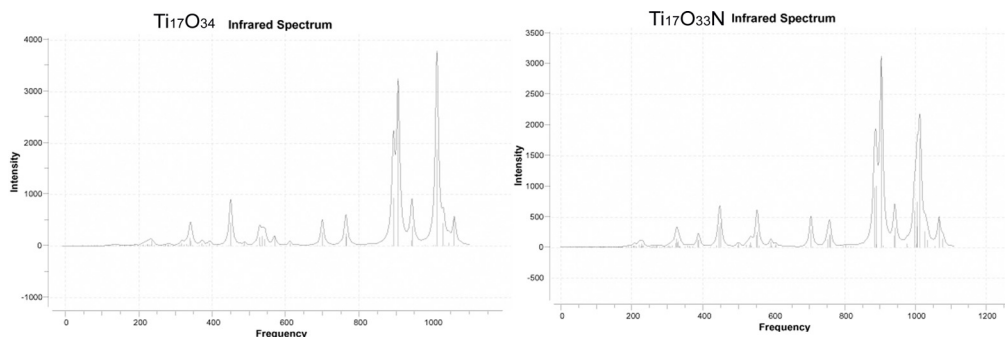

**Fig. 4.   Computed vibrational spectra of pure anatase cluster
(Ti$_{17}$O$_{34}$) and N-doped anatase cluster (Ti$_{17}$O$_{33}$N)**

4   CONCLUSION

N-Doped TiO$_2$ clusters have been studied by using the density functional theory. 3-Coordinate hollow structure and 2-coordinate bridge structure have relative stability compared with other structures. N-doped does not cause significant structural changes. The calculated results show that localized N 2*p* states are located above the O 2*p* state, which

is responsible for the red shift observed in experiments. This localized state leads to a reduction of energy gap of about 0.8 eV. Our calculated results are in good agreement with the experimental data. This cluster model study maybe help to provide useful information about N-doped anatase from the viewpoint of chemical bonding theory for the N-doped anatase nanosystem

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