

Review

Review of First-Principles Studies of TiO₂: Nanocluster, Bulk, and Material Interface

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Abstract: TiO₂ has extensive applications in the fields of renewable energy and environmental protections such as being used as photocatalysts or electron transport layers in solar cells. To achieve highly efficient photocatalytic and photovoltaic applications, ongoing efforts are being devoted to developing novel TiO₂-based material structures or compositions, in which a first-principles computational approach is playing an increasing role. In this review article, we discuss recent computational and theoretical studies of structural, energetic, electronic, and optical properties of TiO₂-based nanocluster, bulk, and material interface for photocatalytic and photovoltaic applications. We conclude the review with a discussion of future research directions in the field.

Keywords: TiO₂; DFT; first-principles; photocatalyst

1. Introduction

Titanium dioxide (TiO₂) is an ideal semiconductor photocatalyst because of its excellent properties (e.g., high activity, good stability, nontoxicity, and low cost), which has many promising applications in the fields of renewable energy and environmental protections [1–5]. However, the larger bandgap of TiO₂ (~3.2 eV for anatase and ~3.0 eV for rutile) makes it inefficient for visible light to excite the electron–hole pairs, which are necessary to initiate a photocatalytic process [2–4]. Therefore, the photocatalytic applications of TiO₂ in the visible light range are heavily limited. To improve the spectra response and photocatalytic activity of TiO₂ in the whole solar spectra, numerous efforts have been carried out [2–4,6–8]. For instance, in recent years, a number of attempts have been made to improve the visible light absorption of TiO₂ by nonmetal doping, which either introduces some impurity states in the bandgap or modifies the fundamental bandgap of TiO₂, and promote the photocatalytic activity of TiO₂ to some degree [4,6–10]. To achieve high photocatalytic efficiency, in addition to increasing the number of photoinduced electron–hole pairs, another approach is to increase the separation rate of photoinduced electron–hole pairs in TiO₂. To do so, increasing efforts are being made to synthesize TiO₂-based materials heterostructures and/or composites that utilize the interfacial charge transfer mechanism to promote the separation rate of electron–hole pairs [11–15]. A high charge separation rate is beneficial not only for photocatalysts, but also for photovoltaic cells in which TiO₂ is often used as electron transport layers as they both use the separated electrons and holes [16–24].

In this review article, we review and discuss recent computational and theoretical progress on the TiO₂ nanoclusters, bulk, and material interfaces from the viewpoints of first-principles calculations. This review is divided into three sections. First, we review the energetic stability and electronic properties of TiO₂ nanoclusters. Second, we focus on the nonmetal doping and co-doping effects on

the electronic structure and optical absorption of TiO₂ along with the relationship between the doping preference of nonmetal atoms and their electronegativities as well as the growth conditions of doped TiO₂. Next, we discuss TiO₂ material interfaces for photocatalytic and photovoltaic applications from first-principles computational perspective. Finally, we conclude this article with several exciting future research directions.

2. Nanocluster

TiO₂ nanoclusters are one class of extensively studied TiO₂ nanostructures for photocatalytic applications because of their high surface to volume ratio [25,26]. Therefore, TiO₂ clusters serve as ideal models to study catalytic properties of nanostructured TiO₂ for pollutants degradation in the first-principles calculations. Qu and co-workers have studied the structural and electronic properties of (TiO₂)_n (*n* = 1–16) nanoclusters in size dependence using first-principles calculations [27–29]. In spite of these earlier studies, to develop a full understanding of the catalytic mechanism of TiO₂ nanoclusters, the first step is generally to choose appropriate structural models with relatively high stability and sizes [25,26,30,31]. For example, in 2016, Arab et al. evaluated the structural stability of (TiO₂)_n (*n* = 1–10) nanoclusters using first-principles approach by analyzing their energetic properties including binding energy, second-order energy difference, and fragmentation energy [31]. The definition of these energetic terms and discussion on their results are below.

(i) The binding energy per atom is defined as $E_b = [nE(\text{Ti}) + mE(\text{O}) - E(\text{Ti}_n\text{O}_m)] / (n + m)$, where $E(\text{Ti})$, $E(\text{O})$, and $E(\text{Ti}_n\text{O}_m)$ are the energies of Ti, O, and Ti_nO_m species, respectively. The calculated E_b increases continuously as cluster size increases, a common phenomenon for nanoclusters [32].

(ii) The second-order energy difference is defined as $\Delta^2 E_n = E(\text{TiO}_2)_{n-1} + E(\text{TiO}_2)_{n+1} - 2E(\text{TiO}_2)_n$, where $E(\text{TiO}_2)_n$, $E(\text{TiO}_2)_{n-1}$, and $E(\text{TiO}_2)_{n+1}$ are the total energies of (TiO₂)_n, (TiO₂)_{n-1}, and (TiO₂)_{n+1} clusters, respectively. The calculated second-order energy difference again cluster sizes show maximum values of $\Delta^2 E_n$ at *n* = 3, 5, and 7, indicating that these clusters are energetically more favorable than their neighboring clusters. Interestingly, the calculated variation of the second-order energy difference shows an odd-even effect as a function of cluster size [32].

(iii) The fragmentation energy is defined as $E_f = E(\text{TiO}_2) + E(\text{TiO}_2)_{n-1} - E(\text{TiO}_2)_n$. The calculated fragmentation energy as a function of cluster size shows again that the (TiO₂)₃, (TiO₂)₅, and (TiO₂)₇ nanoclusters are more stable than their neighboring clusters, as the calculated E_f of these clusters is higher than neighboring clusters.

This work presents an effective approach to evaluate the relative stability of nanomaterials beyond TiO₂ nanoclusters.

Hernandez et al. studied structural and electronic properties of larger (TiO₂)_n (*n* = 15–20) clusters using particle swarm optimization and first-principles calculations [30]. At odd *n* = 15, 17, and 19, these clusters tend to form less stable structures with ionic bond character and relatively low binding energy; at even *n* = 16, 18, and 20, they tend to form more stable structures with large covalent nature and larger binding energy. Interestingly, the (TiO₂)₁₈ cluster is the most stable structure compared to its neighbors and shows the highest value of the electronic energy gap, which is thus likely to be formed via some experimental approach. Additionally, TiO₆ embryo is found to be the common precursor of growth for TiO₂ clusters with high symmetry.

In 2020, Bai et al. carried out first-principle studies on the adsorption mechanism of dimethylbenzoquinones (2,5-DMBQ) onto TiO₂ clusters (*n* = 1–6) [26]. The adsorption ability of 2,5-DMBQ onto the TiO₂ clusters were evaluated from the calculated adsorption energy and changes of Gibbs free energy. The authors found two absorption patterns by searching for the most stable structural configurations: (i) adsorption of the quinone ring on to TiO₂ cluster with the bonding interaction between the C atoms of quinone and Ti atoms and between H atoms of methyl and O atoms, see Figure 1a, and (ii) ketonic O of the 2,5-DMBQ absorbed on the Ti atoms of TiO₂ clusters with the bonding interactions between the O atoms of TiO₂ and H atoms of methyl, see Figure 1b.

By comparing the two absorption patterns (i, ii), the authors found that all these adsorptions are spontaneous and the pattern (ii) is energetically more favorable than the pattern (i) because of more negative adsorption free energy. More interestingly, in both patterns, the $(\text{TiO}_2)_3$ cluster has the most negative adsorption energy among all the adsorption configurations, i.e., approximately -28.44 kcal/mol for pattern (i) and -48.59 kcal/mol for pattern (ii). It is coincidental that, in another independent work, a $(\text{TiO}_2)_3$ cluster with the same size was also proposed as one ideal model to study the fundamental mechanism of TiO_2 photocatalyst, as discussed below. Note that the calculated adsorption energy is much more negative than the typical values of physisorption energies (-1.20 to 9.56 kcal/mol) [33], indicating the chemisorption nature of the two absorption patterns. In addition, the water environment is also found unfavorable for adsorption because gaseous phase has a more negative adsorption energy. This work indicates that the fundamental photocatalytic mechanism of TiO_2 nanoclusters can be well understood from first-principles density functional theory (DFT) calculations. This approach can be applied to evaluate the photocatalytic performance of TiO_2 nanoclusters on other types of pollutant molecules.

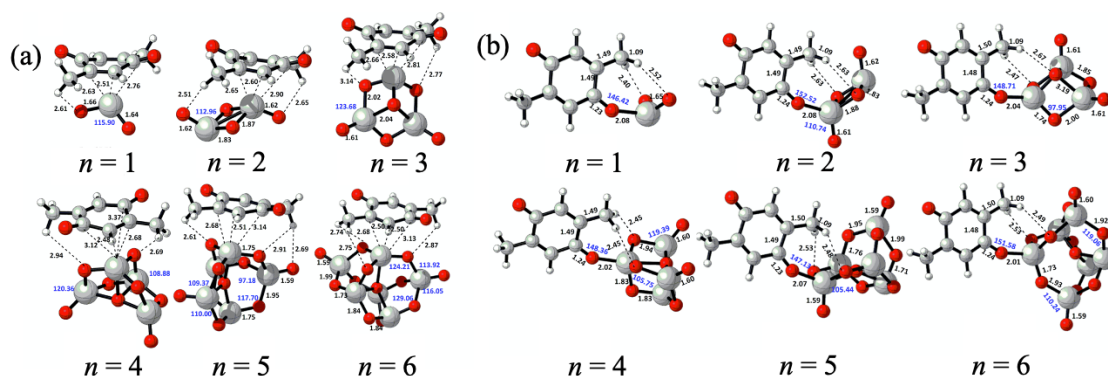


Figure 1. Illustration of adsorption configurations of 2,5-DMBQ onto the surface of $(\text{TiO}_2)_n$ ($n = 1$ – 6) clusters. The left panel (a) shows the absorption pattern of the quinone ring on to the TiO_2 clusters and the right panel (b) shows the absorption pattern of the ketonic O (H) of the 2,5-DMBQ absorbed on the Ti (O) atoms of TiO_2 clusters. Reprinted with permission from Reference [26]. Copyright (2020) Elsevier.

In 2017, Gan et al. reported a first-principles computational study on the mechanism of photo-selective catalytic reduction of 4-bromobenzaldehyde (4-BBA) in different solvents using OH-defected TiO_2 cluster model [34]. In this work, a neutral cluster model of $\text{Ti}_3\text{O}_9\text{H}_6$ was used to represent the reaction sites with photocatalytic activity on TiO_2 surfaces. The authors selected the $\text{Ti}_3\text{O}_9\text{H}_6$ cluster based on three considerations: (i) the dangling bonds of TiO_2 clusters can be saturated by replacing the Ti-O bonds with the Ti-OH bonds without altering Ti^{4+} oxidation state; (ii) the chemical environment of each Ti atom is equivalent and the small cluster size also saves computational cost; and (iii) the surface species such as OH defects on the TiO_2 surface were already involved in the $\text{Ti}_3\text{O}_9\text{H}_6$ cluster. This work shows that the $\text{Ti}_3\text{O}_9\text{H}_6$ cluster is an ideal molecular model to study photocatalytic reactions on the TiO_2 surface, which serves as an important reference in future work.

TiO_2 photocatalysts are usually nanosized materials with highly hydrated surfaces. Hydrogen is thus one of the most common impurities and hydroxyl groups of different nature often appear on TiO_2 surfaces. The size-dependent evolution of the chemical reactivity and site selectivity of $(\text{TiO}_2)_n$ nanoclusters ($n = 5$ – 10) toward hydrogen peroxide were explored from first-principles computational studies by Mohajeri et al. [25]. The adsorption energy of H_2O_2 onto the TiO_2 nanoclusters is found to have a converging trend at $n \geq 8$. After adsorption, the H_2O_2 can be easily decomposed into two OH radicals that can be stabilized through forming bonding interactions with Ti and O atoms on the cluster surface.

The O_2 molecule adsorption on the TiO_2 nanoparticles was also modeled from first-principles DFT calculations [35]. The authors studied two possible adsorption modes: The first one is that O_2 was

adsorbed on TiO_2 nanoclusters via the interaction between H and O atoms. This reduction process of TiO_2 nanoparticles have three following features: (i) forming stable OH group, (ii) low activation energy, and (iii) introducing Ti^{3+} ion related states within the energy gap. Figure 2 shows the structural model, electronic structure diagram, and spin density surface of Ti_8O_{16} cluster. The second one is that O_2 was directly adsorbed on each Ti^{3+} ion of the reduced $\text{Ti}_8\text{O}_{16}\text{H}$ cluster. This process shows three features: (i) formation of stable O_2^- species, (ii) no any energetic barrier, and (iii) no Ti^{3+} defect states within the energy gap. These calculated results are generally consistent with the experimental phenomena of H plasma reduction and interaction between reduced TiO_2 and O_2 .

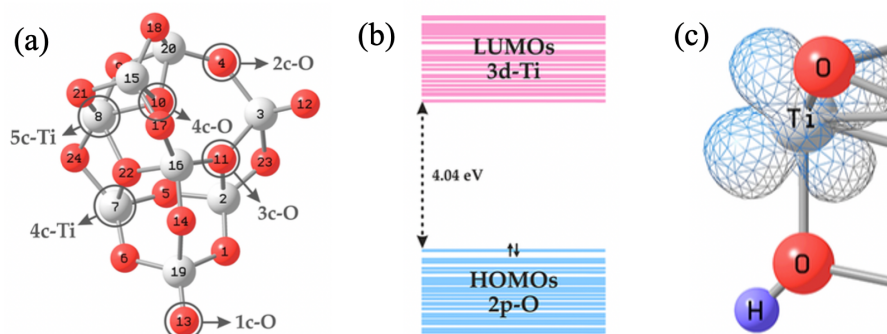


Figure 2. Illustration of (a) geometrical structure, (b) electronic structure diagram, and (c) spin density surface of Ti_8O_{16} cluster. Reprinted with permission from the authors of [35]. Copyright (2012) American Chemical Society.

3. Bulk

In 2001, Asahi et al. reported the visible light photocatalytic activity of nitrogen-doped TiO_2 [9,36]. Soon after, various nonmetal-doped (including B, C, Si, P, S, and halogen elements) TiO_2 were studied to explore their photocatalytic performance under visible light. Although most of these nonmetal-doped TiO_2 show the visible light optical absorption and photocatalytic activity in some degree, there are some “tricky” fundamental issues in their experimental optical absorption spectra and visible light photocatalytic mechanism. For example, what leads to the controversy on the origin of the visible light absorption in N-doped TiO_2 ? Why can B-doped TiO_2 show both redshift and blueshift of the optical absorption edge? What is responsible for the different optical absorption thresholds in C-doped TiO_2 ? Which form (anion or cation) of the Si (P and S) ion in TiO_2 is more effective to promote the visible light absorption? Can F-doping lead to the visible light absorption of TiO_2 ? Why can Cl- and Br-doped TiO_2 show the stronger photocatalytic ability than that of undoped TiO_2 ? What is the difference on the mechanism of the visible light absorption between the I-anion and I-cation doped TiO_2 ? To answer these questions, first-principle theoretical calculation is an effective approach and it has successfully explained many experimental phenomena, including the issues mentioned above. In this section, we review the recent theoretical progress in understanding the electronic structure and optical absorption of nonmetal-doped TiO_2 from first-principles calculations. A brief summary of commonly used nonmetal dopants and the resulting properties of doped TiO_2 is shown in Table 1.

3.1. Formation Energy

First-principles DFT calculations for the relative stability of nonmetal-doped TiO_2 can help us understand the formation of the doped structures and provide useful guidance to prepare samples [37–45]. First, let us focus on the structural stability of substitutional doping models. In principle, there are two possible substitutional doping ways for X-doped TiO_2 , i.e., an X anion at an

O site (X@O) or an X cation at a Ti site (X@Ti). The defect formation energy required for X substituting for either O or Ti in TiO₂ could be calculated from the following formulas, respectively [43–45].

$$E_f^X = E_{X-doped} - E_{undoped} - \mu_X + \mu_O \quad (1)$$

$$E_f^X = E_{X-doped} - E_{undoped} - \mu_X + \mu_{Ti} \quad (2)$$

$E_{X-doped}$ is the total energy of X-doped TiO₂ and $E_{undoped}$ is the total energy of undoped TiO₂. μ_X is the chemical potential of dopant X, and μ_O (μ_{Ti}) is the chemical potential of the O (Ti). The chemical potentials of Ti and O depend on whether TiO₂ is grown under an O-rich or Ti-rich growth condition. Under the Ti-rich condition, the Ti chemical potential can be assumed as the energy of bulk Ti, while the O chemical potential can be obtained by the growth condition:

$$\mu_{Ti} + 2\mu_O = \mu_{TiO_2} \quad (3)$$

Under the O-rich condition, the chemical potential of O can be calculated from the ground-state energy of O₂ molecule, while the chemical potential of Ti is then fixed by condition (3). Therefore, a link between the defect formation energy and the external growth condition of doped TiO₂ can be created.

The relationship between the formation energies of substitutional nonmetal-doped TiO₂ and its growth condition has been studied systematically [38,42–45]. For Si-doped TiO₂, the formation energy of the substitutional Si-cation-doped model is much less than that of the substitutional Si-anion-doped model under both Ti-rich and O-rich growth conditions [44,46,47]. This indicates that Si is energetically more favorable to substitute Ti than O under both Ti-rich and O-rich growth conditions. For S- and P-doped TiO₂, the doping sites of S and P strongly depend on the preparing method and growth condition of the doped TiO₂ [43,48,49]. Under O-rich growth condition, S (P) prefers to replace Ti and form substitutional S (P)-cation doped structure. On the contrary, under the Ti-rich growth condition, S (P) prefers to replace O and form S (P)-anion doped structure. This is consistent with the experiments reported by several independent groups [50–53]. Yu et al. and Ohno et al. used the titanium isopropoxide and thiourea as the titanium and sulfur original materials, respectively, which corresponds to the O-rich growth condition, and prepared the S-cation -doped TiO₂ [50–52]. Moreover, it is further confirmed that replacing Ti by S is energetically more favorable than replacing O under the O-rich growth condition [50]. In contrast, Umebayashi et al. used TiS₂ as the starting material, which corresponds to the Ti-rich growth condition, and prepared S-anion -doped TiO₂ [53,54]. Therefore, the first-principles theoretical calculations demonstrated a basic experimental fact that the ionic form and site of S (P) dopant in TiO₂ can be controlled by the growth condition and preparation method of doped TiO₂ sample [43,48,49]. For C-doped TiO₂, Di Valentin et al.'s theoretical calculations also gave a similar conclusion [38]. In addition, the first-principles theoretical calculations for halogen-doped TiO₂ further revealed the relationship between the doping sites of halogen atoms and their electronegativities as well as the growth condition of doped TiO₂ [45,55]. The following conclusions were drawn [45].

(i) Substitutional X-anion-doped TiO₂ (X = F, Cl, Br, and I) is energetically preferred to form under the Ti-rich rather than under the O-rich growth condition, and the formation energy increases in the order F < Cl < Br < I. This indicates that it is more difficult to replace an O atom using a larger and less electronegative X atom.

(ii) Substitutional X-cation-doped TiO₂ (X = F, Cl, Br, and I) is energetically preferred to form under the O-rich rather than under the Ti-rich growth condition, and the formation energy increases in the order I < Br < Cl < F. This indicates that it is more difficult to replace a Ti atom using a smaller and more electronegative X atom.

(iii) Under O-rich growth conditions, it is energetically more favorable to substitute Ti than O using Br and I, while it is energetically more favorable to substitute O than Ti using F and Cl.

(iv) Under Ti-rich growth conditions, it is energetically more favorable to substitute O than Ti using all the X atoms ($X = \text{F}, \text{Cl}, \text{Br}$, and I).

To qualitatively show the relationship between the formation energy and the growth condition of doped TiO_2 as well as the electronegativities of dopants, we plot the function of the formation energies of nonmetal-doped TiO_2 as the oxygen chemical potential (corresponding to the growth condition of TiO_2), see Figure 3. The following conclusions can be obtained.

(i) For high electronegative F (Cl and N), it is energetically more favorable to substitute O than Ti under both O-rich and Ti-rich conditions.

(ii) For low electronegative Si (Ge), it is energetically more favorable to substitute Ti than O under both O-rich and Ti-rich conditions.

(iii) For other nonmetal main group elements X- ($X = \text{B}, \text{C}, \text{S}, \text{Se}, \text{Te}, \text{P}, \text{As}, \text{Sb}, \text{Br}$, and I) doped TiO_2 , substitutional X-anion-doped TiO_2 is energetically preferred to form under Ti-rich condition while substitutional X-cation-doped TiO_2 is energetically preferred to form under O-rich conditions. This discrepancy can be partially understood from the electronegativity difference between nonmetal dopants and O (Ti) as well as the bond strength of X-O and X-Ti bonds. For high electronegative F (Cl and N), it is preferred to form a F-Ti (Cl-Ti and N-Ti) bond by picking up electrons from Ti rather than form a F-O (Cl-O and N-O) bond by losing electrons. In addition to the bulk doping, a recent computational study shows that F surface adsorption could tune the relative stability of (001) and (101) surfaces of anatase TiO_2 , thus providing one effective approach to synthesize TiO_2 surfaces with desired properties [56–59]. For low electronegative Si (Ge), it is preferred to form a Si-O (Ge-O) bond by losing electrons to O rather than form a Si-Ti (Ge-Ti) bond by picking up electrons. For other nonmetal main group elements X ($X = \text{B}, \text{C}, \text{S}, \text{Se}, \text{Te}, \text{P}, \text{As}, \text{Sb}, \text{Br}$, and I), their electronegativities are between Ge and N, and thus both X-O and X-Ti bonds are possible to form, depending on the growth conditions of doped TiO_2 . These results are expected to provide some useful guidance to prepare nonmetal-doped TiO_2 and other semiconductor oxides.

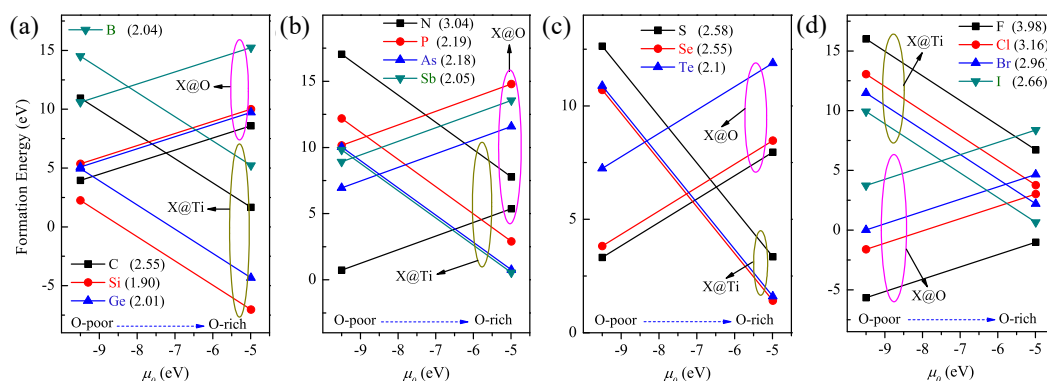


Figure 3. (Color online) Calculated formation energies of substitutional nonmetal-doped TiO_2 as a function of the oxygen chemical potential (μ_{O}). (a) B- and carbon group- (C, Si, and Ge) doped TiO_2 . (b) Nitrogen group- (N, P, As, and Sb) doped TiO_2 . (c) Chalcogen- (S, Se, and Te) doped TiO_2 . (d) Halogen- (F, Cl, Br, and I) doped TiO_2 . X@O and X@Ti represent substitutional X for O and substitutional X for Ti doped structure, respectively. The Pauling electronegativities of these nonmetal dopants are given inside the parentheses.

Next, let us discuss the possibility of interstitial nonmetal-doped TiO_2 . Generally speaking, only the dopant with a small atomic size can easily form interstitially doped structure. Therefore, B, C, and N are most possible to be located at the interstitial site. First-principles theoretical calculations show that substitutional N-anion and interstitial N-doped structures have nearly the same formation energy under O-rich growth condition [40]. Di Valentin et al. found that interstitial C-doped TiO_2 even has lower formation energy than substitutional C-anion-doped TiO_2 under O-rich growth condition [60]. Geng et al. reported that interstitial B-doped TiO_2 has slightly lower formation energy

than substitutional B-anion-doped TiO₂ [61]. Finazzi et al. also suggested that the substitutional-anion doped B dopants can be converted into interstitial B after annealing at high temperature on the basis of the first-principles analysis [62]. In summary, for the nonmetal dopants with small atomic size, both the substitutional (at O site) and interstitial structures are possible to form.

Table 1. Summary of nonmetal dopants and the resulting properties of doped TiO₂. X@Int (X = B and H) denotes that X dopant at an interstitial site.

Dopant	Doping Site	Properties	Ref.
N	N@O	Visible light absorption due to either narrowed bandgap at a high doping level ($\geq \sim 4.2$ at.%) or gap states at a low doping level ($\leq \sim 2.1$ at.%)	[9,40,63]
S	S@O	Redshift of optical absorption edge due to either narrowed bandgap or gap states, depending on doping levels, as in the case of N@O doping.	[43]
P	P@O	Visible light absorption due to reduced optical band gap.	[43]
	P@Ti	Unchanged band gap.	
B	B@O	Redshift due to gap states.	[64]
	B@Int	Blueshift due to Moss–Burstein shift.	
C	C@O	Different optical absorption thresholds due to discrete gap states.	[65]
	C@Ti	Visible light absorption due to narrowed band gap; forming O=C double bond.	
Si	Si@Ti	Visible light optical absorption due to narrowed bandgap by 0.25 eV.	[44]
F	F@O	Nearly unchanged band gap.	[45]
Cl	Cl@O	Bandgap reduces by 0.2 eV; reduced oxidation and reduction ability due to band-edge shift.	[45]
Br	Br@O	Bandgap reduces about 0.3 eV; CBM shifts downwards by 0.3 eV and VBM keeps unchanged.	[45]
I	I@Ti	<i>n</i> -type conductivity, visible light photocatalytic activity due to gap states.	[45]
H	H@Int	<i>n</i> -type conductivity due to interstitial H doping.	[66–69]

3.2. Nonmetal Doping

N Doping

Since the discovery that N doping can promote the visible light photocatalytic activity of TiO₂ [9,36], numerous experimental efforts have been made to study the N doping influence on the optical absorption and photocatalytic properties of TiO₂ [39,70–83]. With the progress of the theoretical and experimental research, the controversy on the origin of the redshift of the optical absorption edge in N-doped TiO₂ appears [7,42,84]. Three different opinions have been proposed to explain the redshift of the optical absorption edge in N-doped TiO₂:

(i) The mixing of N 2*p* states and valence band (VB) leads to the bandgap narrowing. A representative example is Asahi et al.’s theoretical calculation and experiment [9,36], and it is further confirmed by the later experiments [76,78,85].

(ii) N doping introduces isolated impurity states in the bandgap. This is widely confirmed by the experiments [70,71,77,78] and the first-principles theoretical calculations [40,63,86–89].

(iii) N doping creates oxygen vacancies in TiO₂, which introduces defect states in the bandgap, and this leads to the visible light absorption [83,90–92].

In addition, several independent research groups reported that there exists an optimal nitrogen concentration to achieve the highest photocatalytic activity [78,81] or maximize visible light absorption [85]. It is also found that a bandgap narrowing can be realized in high-concentration N-doped TiO₂ [78,85]. As a consequence, it is speculated that the N-doped TiO₂ may show different electronic structure characteristics under different doping concentration, which may lead to the

controversy on the origin of the visible light absorption. This speculation was confirmed through the first-principles electronic structure calculations [40].

Yang et al. analyzed electronic structures of N-doped anatase and rutile TiO₂ at different doping levels and found following conclusions [42].

(i) At lower doping concentration ($\leq \sim 2.1$ at.%), N doping introduces some isolated impurity states above the VB in the bandgap. They act as transition levels, and thus the electronic transition among the VB, conduction band (CB), and impurity states may be responsible for the redshift of the optical absorption edge [63,86–88].

(ii) At higher doping levels ($\geq \sim 4.2$ at.%), more N 2p states are introduced, and they mix with the O 2p states, leading to the bandgap narrowing [9].

Zhao et al. also found similar conclusion from first-principles calculations [84]. Therefore, these results can clarify the controversy on the origin of the redshift of the optical absorption edge in N-doped TiO₂, i.e., bandgap narrowing and N 2p states in the bandgap can be both responsible for the visible light absorption of N-doped TiO₂, which depends on the N doping levels. It is noted that the same conclusion can be drawn using spin-polarized calculations despite some differences of the positions of N 2p states, which is caused by spin split. It also shows that when nitrogen concentration exceeds ~ 2.1 at.%, the optical energy gap has little further narrowing compared with that at lower doping levels. In contrast, increasing the nitrogen concentration leads to larger formation energy [42]. This is well consistent with the experiment, in which the higher nitrogen concentration does not lead to further optical energy-gap narrowing but makes the growth of N-doped TiO₂ more difficult [85]. In addition, nonmetal doping (C, S, and P) can lower the formation energy of oxygen vacancy [38,93–95], and thus the combined effects of the oxygen vacancy and nonmetal doping cannot be excluded to be responsible for the visible light absorption in N- (C-, S-, and P-) doped TiO₂.

TiO₂ has three kinds of crystal phases: anatase, rutile, and brookite. Anatase and rutile are two common phases, and thus they are also generally considered to share similar electronic properties despite the different bandgap (3.2 eV for anatase phase [96] and 3.0 eV for rutile phase [97]). It is known that N doping in TiO₂ can induce a redshift of the optical absorption edge [9,36,39,70–83]. Surprisingly, Diwald et al. observed a blueshift of the optical absorption edge ~ 0.2 eV in N-implanted rutile TiO₂ [98]. Soon after, Di Valentin et al. proposed that the bandgap increasing of approximately 0.08 eV in N-doped rutile TiO₂ can be responsible for the experimentally observed blueshift on the basis of the first-principles calculations [86]. However, this explanation is not in harmony with a basic experimental fact that the redshift is also observed in N-doped rutile TiO₂ [36,72,74,77,82]. In principle, there are three possible N-doping sites, including substitutional N-anion (N at O site, i.e., N@O), N-cation (N at Ti site, i.e., N@Ti), and interstitial N-doped structures. A prior first-principles computational study for all these three possible models shows that N doping either introduces some impurity states in the bandgap for substitutional N-anion-doped and interstitial N-doped TiO₂ or narrows the bandgap for substitutional N-cation doped TiO₂, which both can lead to a redshift of the optical absorption edge [40]. Therefore, the possibility that N doping leads to the blueshift of rutile TiO₂ can be excluded. A phase transition from rutile to anatase by nitrogen doping can easily explain the blueshift of the optical absorption edge ~ 0.2 eV, though Diwald et al. did not observe the anatase phase in N-doped rutile TiO₂ [98]. In contrast, Henderson proposed that the blueshift may be explained according to hole trapping effects [8].

3.3. S Doping

Experiments show that there are two possible substitutional doping sites for S dopants in TiO₂, i.e., S anion at O^{2−} site (S@O) and S cation at Ti⁴⁺ site (S@Ti) [50–54,99–103], and both the S-anion- and S-cation-doped TiO₂ show the high photocatalytic activity under visible light. For example, Umebayashi et al. prepared S-anion-doped anatase and rutile TiO₂ by oxidation annealing of titanium disulfide (TiS₂) and ion implantation in the rutile single crystal, respectively, and observed the visible absorption spectrum in these samples [53,54,99]. Similar visible light absorption property

of S-anion-doped TiO_2 was also reported by several other groups [101,102], and the S doping concentration was found to have a great influence on the visible light photocatalytic activity of S-anion TiO_2 [100]. For substitutional S-cation-doped TiO_2 , interestingly, Yu et al. observed a bactericidal effect under visible light irradiation [50]. Ohno et al. even found that it exhibits stronger visible light absorption than N-, C-, and the S-anion-doped TiO_2 [51,52,103]. As in the case of N-doped TiO_2 , the controversy on the mechanism of the visible light absorption in S-anion-doped TiO_2 also exists. Earlier theoretical calculations indicated that S-anion doped TiO_2 has an obvious bandgap narrowing [53,99,104,105], while the later first-principles calculation shows that S dopants introduce S 3*p* impurity states above the VB, which might be responsible for the redshift of the absorption edge of S-anion doped TiO_2 [106].

First-principles studies revealed that S-anion- and S-cation-doped TiO_2 show different mechanisms for the visible light absorption [43]. For S-anion-doped TiO_2 , different doping levels lead to the different electronic structure characteristics. At lower S doping concentration (≤ 2.08 at.%), the bandgap narrows slightly but some S 3*p* localized states are introduced in the bandgap. Therefore, electron excitations from these occupied S 3*p* states to CB might lead to a more significant redshift of the optical absorption edge than the slight bandgap narrowing [100]. At higher S doping concentration (≥ 4.17 at.%), the mixing of the S 3*p* states with the VB causes an obvious bandgap narrowing (~ 0.7 eV), thus leading to a substantial redshift of absorption spectra.

For S-cation-doped TiO_2 , S dopants introduce some occupied impurity states consisting of S 3*s* and O 2*p* states in the bandgap despite the unchanged bandgap. This indicates that the S dopant has an electron configuration resembling a S^{4+} (s^2p^0) ion in TiO_2 . Therefore, these impurity states can act as transition levels, and the electron excitations from these transition levels to CB may be responsible for the experimental redshift of the optical absorption edge. Similar S doping influence also appear in rutile TiO_2 [43].

3.4. P Doping

Visible light photocatalytic activity was also reported in P-anion- and P-cation-doped TiO_2 , respectively. Shi et al. [107] found that P-cation-doped (P@Ti) TiO_2 nanoparticles exhibit a stronger visible light absorption than undoped sample, which is thought to be induced by the impurity states in the bandgap. Furthermore, their X-ray photoelectron spectroscopy (XPS) measurements also indicated that the doped P ions are in the pentavalent-oxidation states (P^{5+}) [107]. Yu et al. also found that P-doped TiO_2 shows a better photocatalytic ability than that the pure TiO_2 [108]. Li et al. observed a visible light absorption in substitutional P-anion-doped (P@O) anatase TiO_2 , and attributed it to a narrowed bandgap [109]. On the contrary, Yu et al. found a larger bandgap in phosphor-modified TiO_2 than that of pure TiO_2 [110].

To understand the mechanism underlying these inconsistent experimental observations, first-principles calculations for P-anion (P@O) and P-cation (P@Ti) doped TiO_2 were performed [43]. It is found that P-anion doping does not cause a large bandgap narrowing but introduce P 3*p* states in the bandgap. In contrast, P-cation doping neither narrows the bandgap nor introduces impurity states in the bandgap. The first-principles results indicated that the high photocatalytic activity in P-cation-doped TiO_2 may be caused by the large surface area and the crystallinity of TiO_2 instead of the formation of an impurity energy level in the bandgap [108,110].

3.5. B Doping

There are three possible doping sites for boron in TiO_2 , i.e., substitutional B for O (B@O), substitutional B for Ti (B@Ti), and the interstitial B site. The atomic radius of B is larger than that of O (0.85 Å vs. 0.6 Å) but smaller than that of Ti (0.85 Å vs. 1.4 Å). Therefore, substitutional B-anion (B@O) doping and interstitial B doping are expected to cause a lattice expansion of TiO_2 , while substitutional B-cation (B@Ti) doping causes a lattice shrinking. Variable-cell structure optimizations for the three B-doped anatase models were carried out to qualitatively study the B doping influence on the lattice

structure of TiO_2 [64]. Compared with the undoped anatase model, the volumes of the substitutional B-anion and interstitial B-doped models expand approximately 7.7% and 7.0%, respectively. In contrast, the volume of substitutional B-cation-doped model shrinks by ~5%. These results are consistent with Jung et al.'s experiment in which the grain size of anatase phase was enlarged when the incorporation of boron oxides is more than 10% [111]. However, Chen et al. found that the doping of boron ions inhibited the crystal size [112]. Although substitutional B-cation doping can lead to a decrease of the volume of TiO_2 , this kind of structure is not consistent with Chen et al.'s experiment in which the B ions are sited at an interstitial position. Therefore, substitutional B-cation doping cannot account for Chen et al.'s experimental phenomenon.

The calculated electronic properties of three B-doped TiO_2 models show that, for substitutional B-anion-doped TiO_2 , some impurity states mostly consisting of B 2p states are introduced in the bandgap [64]. The electron excitation energy from VB to the unoccupied gap states above the Fermi level decreases about 0.3 eV with respect to the optical bandgap of undoped TiO_2 . This is consistent with the experimental redshift of the optical absorption edge in B-doped TiO_2 [113]. It is noted that the substitutional B-anion doping leads to a spin-polarized electron state [62,64,114,115], and thus forms a paramagnetic defect consisting of B and adjacent Ti ions [62]. A detailed discussion can be found in Section 4. For the substitutional B-cation-doped TiO_2 , its optical bandgap decreases by ~0.3 eV due to the downward shift of the CB. On the contrary, for the interstitial B-doped TiO_2 , its optical bandgap increases by ~0.2 eV for anatase TiO_2 and 0.3 eV for rutile TiO_2 because of the well-known "band-filling mechanism" [116] or "Moss–Burstein shift" [117,118], which is often associated with the optical absorption shift in *n*-type semiconductors. This is in good agreement with the experimental blueshift of the optical absorption edge in interstitial B-doped TiO_2 , in which the optical absorption energy increases by ~0.12 eV. Therefore, the blueshift of optical absorption edge in B-doped TiO_2 can be attributed to the intrinsic property of interstitial B-doped structure instead of the quantum size effects [111,112]. Similar doping effects also occur in B-doped rutile TiO_2 [64,119]. It is also noted that the several different interstitial positions of B dopants should exist [62], and both the standard and hybrid DFT calculations have been carried out to study the trigonal-planar-coordinated $[\text{BO}_3]$ and pseudo-tetrahedral-coordinated $[\text{BO}_4]$ species [62,120]. It is found that the $[\text{BO}_3]$ species leads to an increase in the bandgap, while the $[\text{BO}_4]$ species leads to a decrease in the bandgap [120]. However, the $[\text{BO}_3]$ is shown to be more stable than $[\text{BO}_4]$ [62].

3.6. C Doping

C doping can extend the optical absorption of TiO_2 effectively. Interestingly, different degrees of the reduction of the optical bandgap have been observed in C-doped TiO_2 [10,121–134]. Khan et al. firstly found that C-anion-doped rutile TiO_2 exhibits two optical absorption thresholds at 535 and 440 nm, which corresponds to the optical bandgap decrease of approximately 0.18 and 0.68 eV, respectively [10]. Soon after, more experimental studies confirmed that C-anion doping could induce different degrees of the redshift of the optical absorption edge of TiO_2 . For example, the optical bandgap reduction of approximately 0.3 eV and 0.45 eV was observed [121–125], and more pronounced optical bandgap reduction of approximately 0.72 eV [126], 0.86 eV [127,128], 0.95 eV [129,130], and 1.0 eV [131–133] was also observed. Xu et al. found two regions of photo-response from ultraviolet (UV) to 450 nm and 575 nm in C-doped anatase TiO_2 , which equals to the optical bandgap decrease of 0.45 eV and 1.05 eV, respectively [134]. These experiments both indicate that substitutional C-anion doping can lead to several different optical absorption thresholds in TiO_2 . In addition, carbon can also be incorporated into TiO_2 as a cation at a Ti site because of its low electronegativity, and the C-cation doping influence on the optical absorption spectra of TiO_2 is open. Kamisaka et al.'s first-principle calculations indicate that C-cation doping neither introduces gap states nor induces visible light absorption [135]. On the contrary, Ren et al. observed a visible absorption in the 400–450 nm range in their C-cation-doped TiO_2 sample using UV–Vis diffuse reflectance spectroscopy [136].

Spin-polarized first-principles generalized gradient approximation (GGA) plus U calculations were carried to study the electronic and optical absorption properties of C-anion and C-cation-doped TiO_2 [65]. With respect to the undoped TiO_2 , the calculated bandgap of C-anion-doped TiO_2 changes slightly but some spin-polarized impurity states are introduced in the bandgap. Correspondingly, associated electron excitations among the VB, the CB, and the impurity states can be responsible for the various visible light absorption thresholds in C anion-doped TiO_2 . The electron excitation energy from the occupied gap states just above the valence band maximum (VBM) to the conduction band minimum (CBM) decreases approximately 0.33–0.53 eV, which is consistent with the reduction of the optical absorption energy approximately 0.30–0.45 eV [121–125,134]. The electron excitation energies from the occupied gap states to the CB and from the VB to the empty gap states reduce by approximately 0.63, 0.83, and 1.18 eV. This may be responsible for the large redshift (approximately 0.70–1.05 eV) of the absorption edge in C-doped anatase TiO_2 and TiO_2 nanotubes [126–134]. C-doped rutile TiO_2 also shows same electronic characteristics [65].

Figure 4 shows density of states (DOS) plots of undoped and C-cation-doped anatase TiO_2 . For C-cation-doped TiO_2 , the calculated bandgap in the frame of GGA+ U is approximately 2.85 eV, less than that of the undoped anatase TiO_2 by approximately 0.18 eV [65]. This can explain the experimental redshift of the optical absorption and enhanced visible light absorption in the range of 400 to 450 nm [136]. Similar electronic structure modifications induced by C-cation doping also occur in C-doped rutile TiO_2 . It is worth mentioning that the local structure around the C dopant in anatase TiO_2 significantly influences its electronic properties. Kamisaka et al. performed first-principles calculations for C-cation-doped TiO_2 , in which the cell size and shape were fixed, and found that the C dopant forms a planar CO_3 species. Neither in-gap impurity states nor visible light absorbance is found in their calculations [135]. In contrast, Di Valentin et al. reported a local structure of CO_4 unit and found the bandgap of C-cation-doped TiO_2 shrank slightly approximately 0.1 eV [38]. In Yang et al.'s first-principles calculations, the lattice parameters and all the atomic positions are allowed to relax, in which the doped C atom forms a linear O-C-O unit with a short C-O distance (~ 1.2 Å) like carbon dioxide $\text{O}=\text{C}=\text{O}$. Interestingly, this structural characteristic of linear O-C-O unit was confirmed by experimental X-ray Photoelectron Spectroscopy (XPS) study, in which the XPS measurement of the C1s binding energy (288.6 eV) shows the presence of C=O bonds [136].

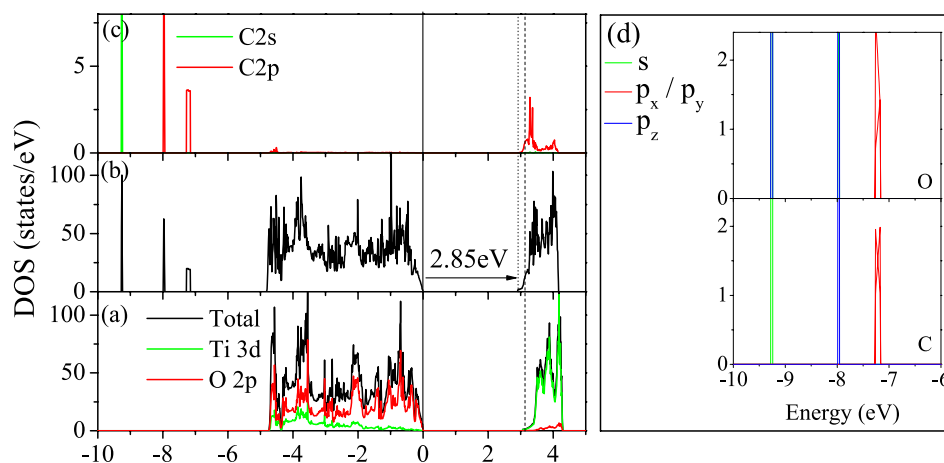


Figure 4. (Color online) (a) Total and projected density of states (DOS) plots calculated for undoped anatase TiO_2 . (b) Total DOS plot calculated for C-cation-doped anatase TiO_2 . (c) Projected DOS plots calculated for the C s and C 2p states of C-cation-doped anatase TiO_2 . (d) Zoomed-in views of the projected DOS plots of the C 2s/2p states and those of the O 2s/2p states for one of the two O atoms forming the linear O-C-O unit. The energy zero represents the valence band maximum (VBM) of the undoped and C-cation-doped anatase TiO_2 , the vertical dashed line the conduction band minimum (CBM) of undoped anatase TiO_2 , and the vertical dotted line the CBM of C-cation-doped anatase TiO_2 . Reprinted with permission from Reference [65]. Copyright (2009) American Chemical Society.

Interstitial C-doped TiO₂ has also been studied using first-principles calculations [38,137]. It is found that the interstitial C dopants introduce impurity states in the bandgap, which can lead to the visible light absorption in C-doped TiO₂.

3.7. Si Doping

Visible light photocatalytic activity of Si-doped TiO₂ has also been reported [138–141]. For example, Oh et al. found that Si doping at low level could improve the photocatalytic activity of TiO₂, while a high doping over 2% could decrease its photocatalytic activity [138]. Yan et al. observed that substitutional Si-cation doping (Si at Ti site) could cause a redshift of the absorption spectra of TiO₂ and favor its photocatalytic activity [139]. Ozaki et al. prepared nitrogen-doped silica-modified TiO₂ and found a high visible light photocatalytic activity [140,141]. First-principles calculations were carried out to understand the mechanism of extended visible light optical absorption [44]. In this work, substitutional Si-anion- (Si@O) and Si-cation- (Si@Ti) doped TiO₂ are modeled, respectively. Compared with the undoped anatase TiO₂, it is found that substitutional Si-cation doping leads to a bandgap narrowing of approximately 0.25 eV, which is consistent with the experimental visible light optical absorption [138–141]. The calculations also show that high silicon concentration doping cannot lead to further bandgap narrowing, but requires larger formation energy [47]. For the substitutional Si-anion-doped anatase TiO₂, visible light absorption is expected because it shows the lower photon absorption energy than that of undoped anatase TiO₂ [142].

3.8. Halogen Doping

In recent years, many attempts have been made to explore whether halogen doping can improve the visible light photocatalytic activity of TiO₂ [143–159]. Among all the halogen elements, F is one of the most extensively studied dopants [143–156]. In particular, whether F doping could lead to visible light absorption is controversial. F-doped TiO₂ has shown an improved photocatalytic activity [143,144] and a stronger absorption in the Ultraviolet/Visible (UV/Vis) region, which corresponds to a slight bandgap narrowing of approximately 0.05 eV [145]. Similar optical bandgap reduction also occurs in F-doped TiO₂ nanotubes [146] and F-ion-implanted TiO₂ [147,148]. On the contrary, more experimental studies show that F-doping neither induces any redshifts of the absorption edge of TiO₂ [149,151–153] nor changes its optical absorption strength [154–156]. The photocatalytic properties of TiO₂ doped with other halogen elements are also reported. Compared with the undoped and F-doped TiO₂, Cl and Br co-doped TiO₂ exhibits a smaller optical bandgap [157], and I-doped TiO₂ shows a much better photocatalytic activity than undoped TiO₂ under both visible light and UV–visible light [158,159].

To clarify the halogen doping influences on the photocatalytic properties of TiO₂ under the UV/Vis light, it is essential to understand whether the doping introduces impurity states in the bandgap and how the doping affects the CB and VB edges, i.e., the CBM and VBM of TiO₂. First-principle calculations of halogen-doped TiO₂ have been done to understand its electronic properties and origin of the associated visible light photocatalytic activity [45]. The calculated bandgap of the undoped anatase TiO₂ is approximately 2.10 eV. For F-, Cl-, Br-, and I-doped TiO₂, the calculated bandgaps are approximately 2.06, 1.90, 1.80, and 1.40 eV, respectively. The calculated bandgap of the F-doped TiO₂ is slightly less than that of the undoped TiO₂ (by approximately 0.04 eV). As a result, it is understandable that either a very slight decrease (~0.05 eV [145]) or no optical bandgap change was found in experiments [149,151–156]. It is also noted each F atom (s^2p^5) requires one less electron from TiO₂ than does each O atom (s^2p^4), and thus the substitution of one F[−] ion for one O^{2−} introduces one additional electron in the TiO₂ lattice. As a result, the treatment of standard DFT calculations for the additional electron leads to the *n*-type conductive property of F-doped TiO₂ [160]. In contrast, in the hybrid DFT or GGA + *U* calculations, the additional electron is shown to reduce one Ti⁴⁺ (d^0) to Ti³⁺ (d^1) ion and introduces localized gap states in the bandgap [161–163]. However, the lack of the visible light absorption in F-doped TiO₂ indicates that the electron transition from these occupied gap states to the CB is not effective to lead to visible light absorption. Therefore, F is not a good dopant to

extend the optical absorption edge of TiO_2 into the visible light region. In contrast, an obvious bandgap narrowing (approximately 0.2 and 0.3 eV) is observed in Cl- and Br-doped TiO_2 , respectively. This is consistent with the experimentally observed reduction of the bandgap by approximately 0.2–0.3 eV in Cl/Br co-doped TiO_2 [157]. For I-doped TiO_2 , the bandgap narrows by approximately 0.7 eV, and thus a significant visible light optical absorption is expected.

The photocatalytic ability of a semiconductor, i.e., the ability to transfer photon-excited electron–hole pairs to the adsorbed species on the surface of the semiconductor, can be partially determined by the relative positions of its CBM and VBM with respect to the redox potentials of the adsorbate [2]. Therefore, the photocatalytic ability of TiO_2 can be qualitatively evaluated by the positions of its CBM and VBM. Thermodynamically, the VBM of a photocatalytic semiconductor should lie below the redox level of the adsorbed species, while the CBM should lie above the redox level, so that the photoinduced hole in VB can capture an electron from the adsorbed species and the photoexcited electron in CB can be transferred to the adsorbed species. Figure 5 shows the comparison of the calculated VBM and CBM positions of X-anion doped anatase TiO_2 ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) with the experimental values of undoped TiO_2 . A scissor operation of 1.10 eV was applied to make the calculated bandgap comparable to the experimental value. The corrected bandgaps for F-, Cl-, Br-, and I-doped TiO_2 are 3.16, 3.00, 2.90, and 2.50 eV, respectively. For F-doped TiO_2 , its CBM and VBM shift downwards by 0.20 and 0.16 eV with respect to the undoped TiO_2 . This indicates that F-doped TiO_2 should have a stronger oxidation ability, which can explain the experimentally observed higher photocatalytic activity in F-doped TiO_2 than that of the undoped TiO_2 [143–145,149,155,156]. For Cl-doped TiO_2 , its CBM shifts downwards by approximately 0.15 eV while the VBM shifts upwards by 0.05 eV relative to the corresponding values of undoped TiO_2 . Therefore, Cl doping may reduce the ability of oxidation and reduction of TiO_2 , which is in good agreement with the experimental fact that Cl-doped TiO_2 shows lower water-splitting power than that of undoped TiO_2 under UV irradiation [157]. For Br-doped TiO_2 , its VBM is nearly same with that of undoped TiO_2 , and thus Br-doped TiO_2 should have the same oxidation ability with that of undoped TiO_2 . In contrast, the CMB of Br-doped TiO_2 shifts downwards by approximately 0.3eV compared with that of undoped TiO_2 , so that Br-doped TiO_2 might show lower ability to reduce H^+ to H_2 than does undoped TiO_2 . For I-doped TiO_2 , its CBM shifts downward slightly but VBM is raised strongly with respect to that of undoped TiO_2 , and thus visible light photocatalytic activity might appear in I-doped TiO_2 . In summary, the changes of the VBM and CBM can qualitatively explain some experimental facts that the photocatalytic ability was improved upon F, Cl, and Br doping [143–145,149,155–157]. In addition, the local internal field induced by the dipole moment is considered to be effective to separate the electron–hole pairs and inhibit their recombination [164,165], and thus the photocatalytic performance of doped TiO_2 can be evaluated from the variation of the dipole moment of TiO_6 octahedron adjacent to the dopants [165].

For I-doped anatase TiO_2 , its VBM and CBM are nearly the same as those of undoped TiO_2 . However, a double-occupied bandgap state above the VBM approximately 0.6 eV is introduced in the bandgap. Its PDOS plot shows that this gap state mostly consists of I 5s states and the 2p states of the neighboring O atoms around the I dopant, and that I 5p states contribute to its CB. This indicates that I dopant exists as an I^{5+} (s^2) cation, as observed experimentally [158,159]. The Fermi level of I-doped TiO_2 is pinned above the CBM approximately 0.2 eV, indicating that iodine is a good *n*-type dopant, as in the case of I-doped ZnTe [166]. Therefore, the optical bandgap of I-doped anatase TiO_2 decreases approximately 0.4 eV with respect to that of undoped TiO_2 . This is mainly responsible for the optical bandgap decrease of I-doped TiO_2 and the improved photocatalytic efficiency in the UV/Vis region [158,159]. For substitutional X-cation ($X = \text{F}, \text{Cl}, \text{and Br}$) doped TiO_2 , unlike the case of I-doped TiO_2 , Cl 3s and Br 4s states do not appear above the VBM. In contrast, singly-filled Cl 3p and Br 4p states appear in the bandgap of Cl- and Br-doped TiO_2 , respectively. This indicates that Cl and Br at Ti sites exist as Cl^{4+} (s^2p^1) and Br^{4+} (s^2p^1) ions, respectively. For F-doped TiO_2 , the F 2p states lie in the VB, and the empty F 2p states lie just above the Fermi level. Therefore, with respect

to the Cl- and Br-doped TiO₂, the doped F atom at a Ti site should exist as a F³⁺ (*s*²*p*²) ion to a first approximation [45].

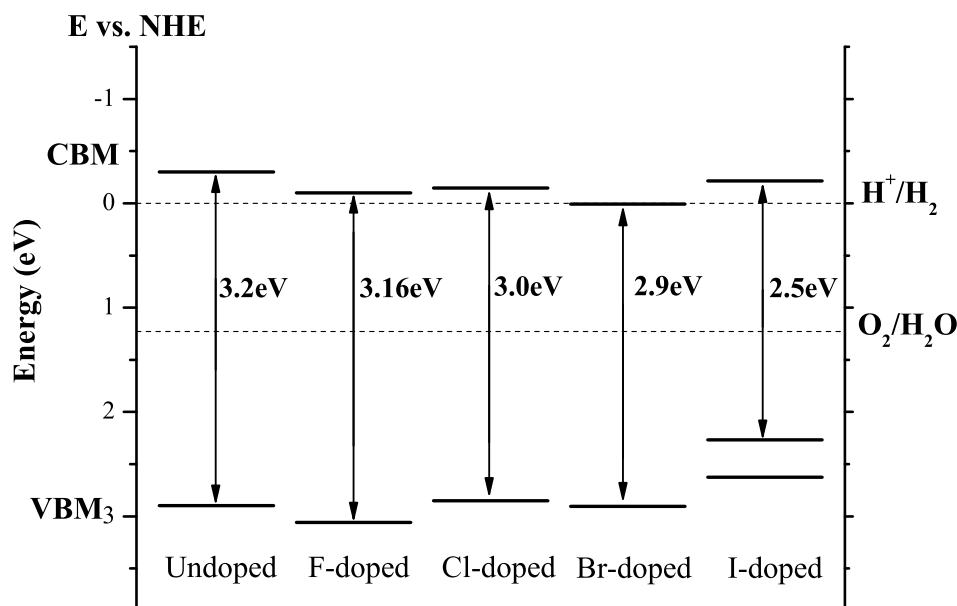


Figure 5. (Color online) Comparison of the calculated VBM and CBM positions of X-doped anatase TiO₂ with X@O (X = F, Cl, Br, and I) from the DFT calculations with the corresponding experimental values of undoped TiO₂. The VBM and CBM values are given with respect to the normal hydrogen electrode (NHE) potential. Reprinted with permission from the authors of [45]. Copyright (2008) American Chemical Society.

3.9. Hydrogen Impurities in TiO₂

As a ubiquitous impurity, hydrogen (H) widely exists in metal oxides, which forms either deep gap states or shallow donor levels [66–69]. Owing to its small ionic radius, H at an interstitial site is more stable than that at a substitutional site [167], though in principle, it can form substitutional structure by replacing the O atom. First-principles calculations show that the interstitial H introduces a shallow donor level in TiO₂ [66–69]. This is consistent with the recent experiments in which the H is identified as either a shallow donor or metastable donor in rutile TiO₂ single crystal [168,169]. Interstitial H introduces an additional electron in TiO₂, and thus the *n*-type conductivity can be understandable. However, recent GGA+*U* and hybrid functional calculations show that the additional electrons can be trapped by the Ti ions, reducing Ti⁴⁺ to Ti³⁺, and introduce the gap states [161,170], although the position of the gap states strongly depends on the choice of *U* parameters [162]. First-principles calculations also show that substitution of H for O can lead to the *n*-type conductivity, though its structure is not stable [167].

It is also interesting to explore the effects of H impurity on the structural stability and electronic property of nonmetal-doped TiO₂ [167,171,172]. With respect to the N-doped TiO₂, the combinational doping of (N, H) can enhance the structural stability and lead to a significant bandgap narrowing for anatase and brookite phases of TiO₂ [167,171]. For N-anion-doped TiO₂, the doped N dopant exists as N^{2−} (*s*²*p*⁵) ion, and introduces an unoccupied N 2*p* impurity state in the bandgap [173]. For (N, H)-doped TiO₂, the interstitial H atom adjacent to the N dopant introduces an additional electron into the lattice, and forms the N-H bond by transferring the additional electron to one empty N 2*p* orbital. As a result, all the N 2*p* impurity states become occupied, leading to either an obvious bandgap narrowing or double-filled N 2*p* impurity states above the VB. This type of charge compensation mechanism also occurs in (N, Ta)- and (N, F)-doped TiO₂ [60,174], in which the substitutional Ta-cation (Ta⁵⁺) and F-anion (F[−]) doping introduce one additional electron into the TiO₂ lattice separately, which fills the empty N 2*p* orbital. For (C, H)-doped TiO₂, it is thermodynamically

more stable than C-doped TiO₂, and a bandgap narrowing also occurs [172]. However, in this case, one electron donated by the interstitial H cannot compensate the two holes of C^{2−} (*s*²*p*⁴) dopant [175], and thus this incomplete charge compensation results in an impurity level just below the CB [172]. It is expected that two interstitial H and one substitutional C at an O site can satisfy full charge compensation. In addition, recent experimental and theoretical studies show that hydrogenation on the surface of TiO₂ can lead to a structural disorder and introduce mid-gap states, which is responsible for the improved solar-driven photocatalytic activity [176,177]. In summary, the influence of hydrogen impurity on the structural stability and electronic property of TiO₂ is one interesting topic, and further work is worthy to be done.

3.10. Co-Doping

Introducing impurity states in the bandgap by nonmetal or metal doping is effective to extend the optical absorption edge of TiO₂ into the visible light region; however, the electron–hole recombination center, which generally refers to the impurity-related states near the middle of the bandgap, inhibits the photocatalytic efficiency of TiO₂. Therefore, narrowing bandgaps without creating mid-gap states is necessary to maximize the photocatalytic performance of TiO₂ under the visible light irradiation [178–181]. To this aim, co-doping can be an effective approach because it has three important effects:

(1) Co-doping can eliminate impurity states in the bandgap via charge compensation between different dopants, which can reduce the number of recombination centers and promote the separation of electron–hole pairs.

(2) Co-doping can facilitate the mixing between the impurity states and VB (CB) by adjusting the position of impurity states in the bandgap, and narrow the bandgap effectively.

(3) Co-doping can reduce the formation energy of the combination defect with respect to the monodoped TiO₂, and thus improving the solution of ideal dopants in TiO₂ or other metal oxides becomes possible.

Herein, we divided the co-doping into three classes, i.e., anion–anion co-doping, anion–cation co-doping and cation–cation co-doping, according to the ionic type (anions or cations) of dopants, and summarized the recent theoretical research progress of the co-doped TiO₂, mainly from the viewpoint of charge-compensation.

3.10.1. Anion–Anion Co-Doping

One typical example of anion–anion co-doping is (N, F) co-doped TiO₂ [60,150,151,182–184], in which N and F both replace O ions. In N-anion monodoped TiO₂, one N at an O site introduces an accept level in the bandgap and exists as a N^{2−} ion, while in F-anion monodoped TiO₂, one F at O site introduces one donor level by donating one additional electron into the TiO₂ lattice. As a result, in (N, F) co-doped TiO₂, this additional electron can occupy the N 2*p* accept level, and then all the N impurity states become occupied. These occupied N 2*p* states are located just above the VB, and do not act as the electron–hole recombination center, thus improving the visible light photocatalytic activity of TiO₂ with respect to that of the N-anion monodoped TiO₂ [60,185]. In addition, (N, F) co-doping reduces the formation energy with respect to that of the N monodoped TiO₂, and thus a higher nitrogen concentration doping can be realized. Similar anion–anion charge compensation effect is expected to occur in (N, Cl), (N, Br), (N, I), (P, F), (P, Cl), (P, Br), and (P, I) co-doped TiO₂.

3.10.2. Anion–Cation Co-Doping

(N, H_{int}) co-doped TiO₂ is a typical example of the anion–cation co-doping, in which N replaces O while H locates at an interstitial site. In this system, one electron donated by an interstitial H occupy the N 2*p* acceptor level, and the bandgap narrows approximately 0.26 eV, much larger than the N-anion monodoped TiO₂ (0.04 eV) [171].

Another two kinds of anion–cation co-doping combinations are (N, X) and (C, Y) [174,179,186,187], in which X can be Ta^{5+} or Nb^{5+} while Y (Herein Y is not element yttrium.) can be W^{6+} or Mo^{6+} . It is known that N dopant exists as N^{2-} (s^2p^5) ion at an O site [173], and introduces one acceptor level in the bandgap, while the pentavalent Ta (Nb) cation at a Ti site donates one electron into TiO_2 lattice, introducing one donor level in the bandgap. As a result, the charge compensation can occur in (N, Ta) [174,186], and (N, Nb) co-doped TiO_2 , and the electron–hole recombination center (i.e., the impurity-related states near the middle of the bandgap) might be removed, thus promoting the rate of electron–hole separation and improving its photocatalytic efficiency. Similarly, the C dopant exists as C^{2-} (s^2p^4) ion at an O site [175], and introduces two acceptor levels in the bandgap. In contrast, the hexavalent W (Mo) cation at a Ti site donates two electrons into TiO_2 lattice, i.e., introducing two donor levels. Therefore, in (C, W) and (C, Mo) co-doped TiO_2 [179,187], the two acceptor levels introduced by C dopant become occupied by capturing the two electrons donated by W and Mo, and C $2p$ impurity states are more close to the VB, reducing the number of electron–hole recombination centers. However, it is noted that the full charge compensation only occurs when the doped anion and cation are bonded together, though this configuration generally possesses the lowest total energy [187,188]. This is reasonable because the doped anion and cation can form a strong bond by a direct charge transfer.

Another kind of anion–cation co-doping, such as (N, Mo) co-doping, has been proposed [188], in which two N anions are bonded to one hexavalent Mo cation, forming a near-linear N–Mo–N unit. For convenience, we refer it to as (N–Mo–N) co-doping. In this case, two electrons donated by one hexavalent Mo cation at a Ti site can compensate two holes introduced by two N anions, thus achieving full charge compensation. Liu et al. further studied the difference of the electronic structures between non-passivated and passivated (N, Mo) co-doping [188]. The local geometrical configurations of N and Mo dopants for these two kinds of (N, Mo) co-doped TiO_2 are shown in Figure 6a,b. Their calculated TDOS and PDOS plots are shown in Figure 6c. For non-passivated (N, Mo) co-doping, one N anion is bonded to one Mo cation, and the doping ratio between N and Mo is 1:1. In this case, one hole introduced by one N cannot compensate two electrons donated by one Mo, thus leading to n -type conductivity. In passivated (N, Mo) co-doped TiO_2 , i.e., (N–Mo–N) co-doped system, the two electrons are fully compensated by the two holes introduced by the two N anions, and the N $2p$ acceptor levels are removed and do not act as an electron–hole recombination centers, thus improving the photocatalytic efficiency. Similar to the case of (N–Mo–N) co-doped TiO_2 , full charge compensation is also expected in (N–W–N), (Ta–C–Ta), and (Nb–C–Nb) co-doped TiO_2 .

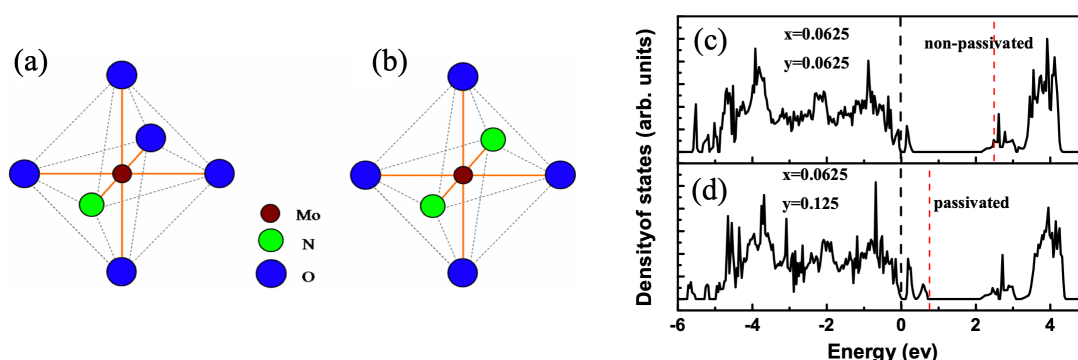


Figure 6. (Color online) Illustration of relative positions of substitutional N anion and Mo cation in TiO_2 : (a) Non-passivated doping and (b) passivated doping, and calculated TDOSs of (Mo + N) co-doped TiO_2 ($\text{Ti}_{1-x}\text{Mo}_x\text{O}_{2-y}\text{N}_y$): (c) non-passivated and (d) passivated. The red dash lines represent the Fermi level. Reprinted with permission from the authors of [188]. Copyright (2011) Elsevier.

3.10.3. Cation–Cation Co-Doping

Cation–cation co-doping has also been proposed to narrow the bandgap of TiO_2 , and two criteria of choosing cations are suggested [180]. First, the cation should have a closed-shell electronic

configuration like d^0 or d^{10} . Second, to keep the semiconductor characteristic of TiO_2 , co-doping with cations A^{x+} and B^{y+} should satisfy a simple rule, i.e., $x + y = 8$. On the basis of the criteria, the cation–cation co-doping combination of (Mo^{6+} , $\text{Zn}^{2+}/\text{Cd}^{2+}$) and (Ta^{5+} , $\text{Ga}^{3+}/\text{In}^{3+}$) is expected to cause an effective bandgap narrowing without introducing gap states. In these two kinds of cation–cation co-doped TiO_2 , the number of the holes introduced by $\text{Zn}^{2+}/\text{Cd}^{2+}$ ($\text{Ga}^{3+}/\text{In}^{3+}$) equals to that of electrons introduced by Mo^{6+} (Ta^{5+}), and thus full charge compensation can be obtained. In addition, the electronic configuration of d^0 or d^{10} of the cations can guarantee that the d states of dopants either are fully unoccupied or occupied, and thus no d -orbital-related impurity states can be created in the bandgap. First-principles calculations show that charge compensation does occur in the (Ta^{5+} , $\text{Ga}^{3+}/\text{In}^{3+}$) and (Mo^{6+} , $\text{Zn}^{2+}/\text{Cd}^{2+}$) co-doped TiO_2 , and with respect to cation monodoped TiO_2 , the mid-gap states are passivated.

In summary, co-doping can be an effective approach to narrow the bandgap of semiconductor photocatalyst and get rid of the electron–hole recombination centers through the full charge compensation. To this aim, the number of the holes on acceptor levels should be equal to that of the electrons on donor levels. Therefore, we can define the following equation to be a basic rule for co-doping:

$$N_a \times N_h = N_d \times N_e. \quad (4)$$

N_a and N_d represent the number of acceptor atoms and donor atoms, respectively. N_h represents the number of introduced holes per acceptor atom and N_e represents the number of donated electrons per donor atom. It is noted that the Ti (O) ions in TiO_2 and SrTiO_3 have same chemical state, and thus the co-doping combinations mentioned above can also be applied in SrTiO_3 [189–191]. For a reference to choose an ideal combination of dopants for co-doping in TiO_2 and SrTiO_3 , we list the common acceptor (donor) atoms as well as the number of the holes (electrons) per acceptor (donor) atom in Table 2.

Table 2. List of the acceptor atoms and donor atoms in TiO_2 . The numbers in the third column represent the introduced holes per acceptor atom (N_h) or donated electrons per donor atom (N_e). H_{int} and Li_{int} represent the interstitial H and Li ions, respectively.

Acceptor Atom		N_h	
Anion	N^{2-} , P^{2-}	1	[43,173]
	C^{2-}	2	[175]
	B^{2-}	3	[115]
Cation	B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , La^{3+}	1	[115,192]
	Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}	2	[115]
	Li^{+} , Na^{+} , K^{+} , Rb^{+} , Cs^{+}	3	[115,193]
Donor atom		N_e	
Anion	F^{-} , Cl^{-} , Br^{-} , I^{-}	1	[45,161]
Cation	H_{int} , Li_{int}	1	[66–68,171]
	I^{5+} , Nb^{5+} , Ta^{5+}	1	[45,174]
	Mo^{6+} , W^{6+}	2	[180]

4. Interface

4.1. TiO_2 /Perovskite Interface

The organic–inorganic halide perovskite solar cells have received significant attention in the recent years because of the low cost, high power conversion efficiency, and the flexibility of halide perovskite materials. In the perovskite solar cells, TiO_2 is widely used as electron transport layers and plays a significant role in achieving high efficiency and stability of photovoltaic devices. One major reason is the conduction band of TiO_2 is lower than that of the halide perovskite such as MAPbI_3 and

MASnI₃ (MA = CH₃NH₃, methylammonium) [16,17]. Therefore, first-principles computational studies of TiO₂/perovskite interfaces have been an emerging topic recently [16–24].

De Angelis's research team has extensively studied the material interfaces between the anatase TiO₂ (denoted as ^aTiO₂) and tetragonal MAPbI₃ and MAPbI_{3–x}Cl_x perovskite from first-principles calculations [18,21,194–196]. To build materials interface models, the first step is generally to choose the most stable surfaces. The authors considered pseudo-cubic (001) and tetragonal (110) perovskite surfaces because they found the (001) surfaces of the cubic and tetragonal phases have an identical topology [21]. That is to say, the (001) surface of the tetragonal phase is essentially same with one of the three equivalent surfaces of the cubic phase. Their calculations show that the isolated (110) surface is energetically more favorable than the (001) surface, with a total energy difference of approximately 0.7 and 0.1 eV for MAPbI₃ and MAPbI_{3–x}Cl_x, respectively. Interestingly, after “depositing” the perovskite on the ^aTiO₂ (101) surface, the (110) perovskite surface are further stabilized against the (001) surface from the energetic analysis; moreover, the interfacial Cl atoms further increases the interfacial binding energy to TiO₂ in MAPbI_{3–x}Cl_x compared to that in MAPbI₃. Later, a combined angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and first-principles calculations by the same research team revealed more details at the MAPbI_{3–x}Cl_x/TiO₂ interface. They found that Cl is preferentially located at TiO₂ interface rather than the bulk perovskite [194], and the interfacial Cl is also found to induce the band bending that creates a directional “electron funnel”, improving the charge collection efficiency of the photovoltaic devices. This conclusion is also consistent with the previous computational study on Cl-doped bulk TiO₂ in which Cl is thermodynamically favorable to replace O [45].

The strong interfacial interaction between TiO₂ and perovskite is essentially attributed to the charge transfer across the TiO₂/perovskite interface. To quantify the charge transfer, De Angelis et al. carried out a charge displacement analysis, as shown by calculated charge displacement curves for TiO₂/MAPbI₃ and TiO₂/MAPbI_{3–x}Cl_x interfaces in Figure 7 [21]. It clearly shows a strong charge displacement variation across the interfacial region in both cases, indicating a strong interaction between TiO₂ and perovskite and a strong polarization. Furthermore, there is a slight increase in charge donation to TiO₂ in the case of MAPbI_{3–x}Cl_x, suggesting an increased charge accumulation at the TiO₂/MAPbI_{3–x}Cl_x interface compared to TiO₂/MAPbI₃ interface. This charge displacement analysis well explains the stronger binding energy for TiO₂/MAPbI_{3–x}Cl_x than that for TiO₂/MAPbI₃. This work indicates that the charge displacement analysis is one effective approach to visualize the charge displacement from the non-interacting two materials fragments to the interacting heterointerface.

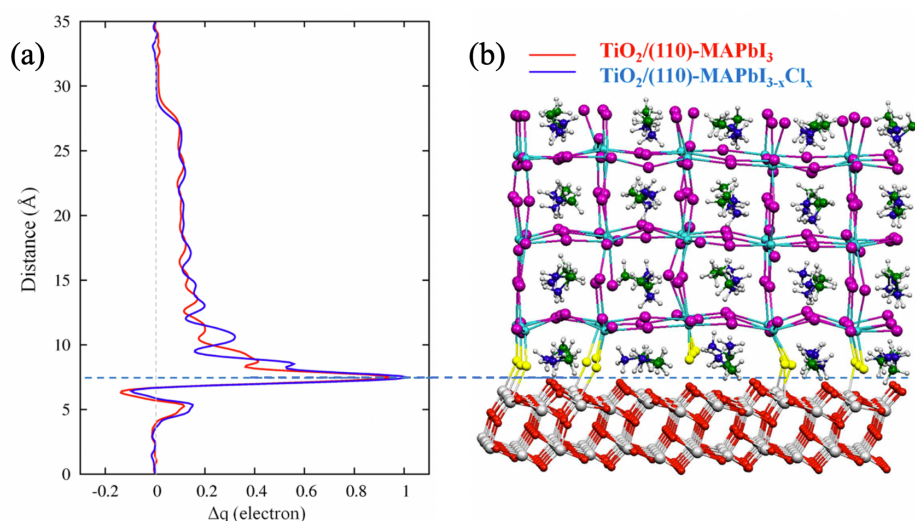


Figure 7. Illustration of (a) calculated charge displacement and (b) geometrical structure for TiO₂/MAPbI₃ (red) and TiO₂/MAPbI_{3–x}Cl_x (blue). Reprinted with permission from the authors of [21]. Copyright (2014) American Chemical Society.

In 2019, Sultana et al. reported first-principles computational studies for the MAPbI₃ perovskite interfaces with TiO₂, ZnO, and SnO₂ [22]. The interface models were built by placing tetragonal MAPbI₃ along its [001] direction on top of rutile (001) TiO₂, wurtzite (1010) ZnO, and rutile (110) SnO₂ slabs. To understand the interfacial charge transport properties of these systems, the authors calculated their charge difference density using the following equation.

$$\Delta\rho = \rho_{interface} - \rho_{MAPbI} - \rho_{MO} \quad (5)$$

The authors analyzed the charge transfer from charge density difference plot and found that the charge accumulation and depletion mainly occur around the interfacial Pb and O atoms, indicating that the charge transfer mostly occurs at the interface. Among the three materials interfaces, the TiO₂-based interface has the highest charge transfer based on the Bader charge analysis, thus suggesting that TiO₂-based interface has the highest efficiency for the perovskite solar cells. However, the authors found that TiO₂ and ZnO have a stronger binding energy with MAPbI₃ than SnO₂, but the strong binding may lead to decomposition of CH₃NH₃ molecules. The authors thus conclude that SnO₂ can be a feasible replacement for TiO₂ and ZnO to improve the stability of perovskite solar cells.

The defect properties at the TiO₂/perovskite interface were also studied from first-principles calculations. In 2017, Haruyama et al. reported the defect properties at the ^aTiO₂(101)/tMAPbI₃(110) interface using first-principles computational approach, in which anatase TiO₂ (001) was placed on the MAPbI₃ (110) plane [20]. They found that the vacancy defects in the TiO₂ layer create undesired defect levels within the bandgap, which serves as hole traps and recombination centers; while most of the vacancy defects in the MAPbI₃ layer produces no additional states, thus having no influence on the electron–hole separation rates. This computational work indicates a possible route to further improve the performance of perovskite solar cells via interface modification.

Yang et al. studied relative stability and charge transport properties of different interfaces between the lead-free MASnI₃ and TiO₂, including anatase and rutile phases from first-principles calculations [24], in which (001) surface of MASnI₃ and (001) surfaces of anatase and rutile were used to build models. The authors considered two types of terminations of MASnI₃ and built four interface models—MAI/A, MA/R, SnI₂/A, and SnI₂/R, in which A and R represents anatase and rutile phases, respectively, as shown in Figure 8. The authors found that SnI₂/A interface is more stable than the other three systems and this interface also has a better separation of photoinduced electron–hole pairs from the analysis of the plane-averaged electrostatic potential and density of states. Similarly, by examining four types of interfaces between MAPbI₃/TiO₂ from first-principles calculations, Gent et al. also concluded that PbI₂/A interface has a stronger interaction but PbI₂/R interface model is most efficient for charge separation from the electrostatic potential analysis, which was attributed to the better lattice and atoms arrangement match between MAPbI₃ and rutile TiO₂ [19].

In addition to the extensively studied materials interfaces between the hybrid halide perovskites and TiO₂, it is noted that the materials heterointerfaces between the classical inorganic perovskite oxides such as SrTiO₃ and TiO₂ has also attracted increasing attention because of the emerging interfacial properties and/or enhanced functionalities [23,197]. One major consideration is that the formed heterointerface has a better stability compared to the isolated bulk materials [23,198]. In 2017, Kitchin's research team explored the possibility to stabilize the epitaxial thin films of anatase and rutile TiO₂ on perovskite (Sr/Ba)TiO₃ by studying relevant bulk and interface energy terms using first-principles calculations [23]. The authors first identified four potential coherent epitaxial interfaces—(001)A/(001)(S/B)TO, (102)A/(011)(S/B)TO, (112)A/(111)(S/B)TO, and (100)R/(111)(S/B)TO—based on the experimental findings, volumetric formation and strain, and areal substrate, and then calculated their interface energies. Their computational models predict a decrease order of anatase stability from (001) to (011) to (111) perovskite substrates, which is in a general agreement with the experimental epitaxial stability investigations. In contrast, rutile is energetically more favorable than anatase on the (111) perovskite substrate. This work indicates that

first-principles calculations of interface energy is a promising approach to predict epitaxial polymorph stability and to search for coherent epitaxial interfaces toward the stability of target materials even beyond TiO_2 polymorphs.

The TiO_2 polymorphic structures exhibit different photocatalytic properties and the synthesis of the specific TiO_2 polymorph with target materials properties are desired. One possible way to stabilize the metastable polymorphs is to use the epitaxial synthesis approach, i.e., materials heterointerfaces.

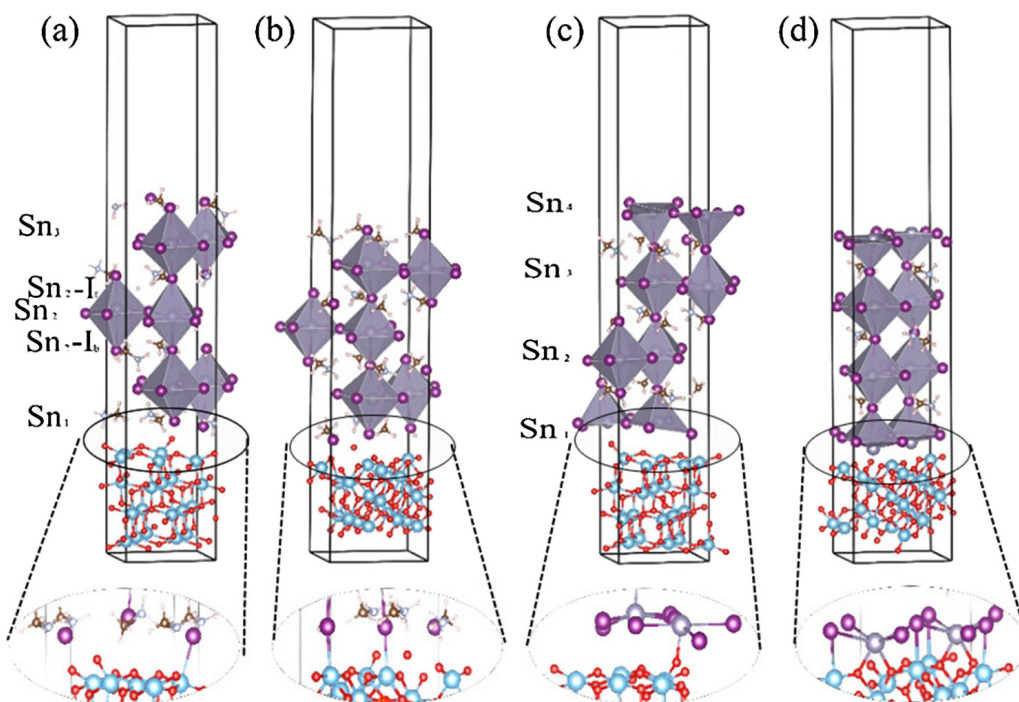


Figure 8. Relaxed geometrical structures of (a) MAI/R, (b) MAI/A, (c) SnI_2 /R, and (d) SnI_2 /A TiO_2 /MASn I_3 interface. Reprinted with permission from the authors of [24]. Copyright (2018) Elsevier.

4.2. TiO_2 /BiOI Interface

Bismuth oxyhalide BiOX ($X = \text{Cl}, \text{Br}, \text{and I}$) has a layer structure and exhibits promising catalytic properties for degrading pollutants under visible light irradiation because of their low bandgaps [22–24,194,195]. However, high electron–hole recombination rates in this class of materials severely inhibit their photocatalytic applications. A heterostructure that combines two different semiconductors could transfer charge carriers between a high energy band and a low energy band, which could effectively separate photoinduced electron–hole pairs, and thus greatly enhance the photocatalytic efficiency of semiconductor heterostructure. In a very recent study [199], Qu et al. studied BiOI/ TiO_2 heterostructure using first-principles electronic structure calculations, in which the heterostructure model was built by “depositing” (001) BiOI slab on the (001) rutile TiO_2 slab. In this work, two types of materials interfaces including I1/TiO_2 and BiO/TiO_2 were modeled, as BiOI has two types of surface terminations along the [001] direction. Note that the authors chose the average value of the two separate lattice parameters of the BiOI and TiO_2 as the lattice parameters of the new heterostructure in order to achieve a high lattice match between BiOI (001) and TiO_2 (001) surfaces, leading to a lattice mismatch of 6.63%. The calculated formation energy is -2.21 eV/A and -2.25 eV for I1/TiO_2 and BiO/TiO_2 models, respectively, suggesting that both two models are likely to be formed and the BiO/TiO_2 is slightly more stable than I1/TiO_2 . More interestingly, the bandgap of I1/TiO_2 heterostructure reduces to 0.28 eV while BiO/TiO_2 heterostructure changes into an n -type semiconductor, see Figure 9a. Moreover, as shown in Figure 9c, the built-in potential of the heterostructure can effectively separate the photoinduced electron–hole pair across the interface, thus potentially improving the photocatalytic performance

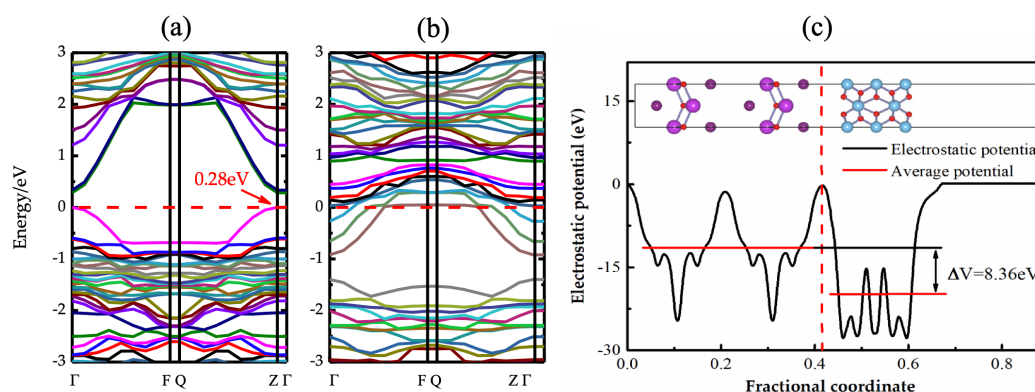


Figure 9. Calculated electronic band structure of (a) 1I-BiOI/TiO₂ and (b) BiO-BiOI/TiO₂ heterojunction and (c) electrostatic potential of 1I-BiOI/TiO₂ model. Reprinted with permission from the authors of [199]. Copyright (2018) Elsevier.

4.3. TiO₂/RuO₂ Interface

Ruthenium oxide (RuO₂) has various technological applications such as being used as electrodes, supercapacitors, and catalysts because of its promising properties [11]. It has a rutile-like structure and exhibits an excellent electrical conductivity. In recent years, TiO₂/RuO₂ heterostructure has been proposed as one efficient photocatalyst for water splitting and decomposition of organics [11–15], which is attributed to the high separation rate of photogenerated electron–hole pairs. In 2015, Wei et al. studied the energetic and electronic properties of the TiO₂/RuO₂ (110) heterostructure in which RuO₂ was “deposited” on the rutile TiO₂ (110) surface using first-principles DFT calculations [200]. The calculated interfacial energy shows that the TiO₂/RuO₂ interface is exothermic, indicating a strong bonding interaction between TiO₂ and RuO₂. The calculated projected DOS plots for the TiO₂/RuO₂ heterostructure show that the valence and conduction band of TiO₂ bend downward toward RuO₂. Interestingly, upon introducing oxygen vacancies at the interface, there exists an upward band bending toward RuO₂, in agreement with the experimental finding [11].

For convenience, a brief summary of these materials interfaces and their critical materials properties are listed in Table 3. However, it is worth mentioning that, in addition to the material interfaces discussed above, there exist many other types of TiO₂-based materials interfaces such as TiO₂/SnO₂ [201], TiO₂/WS₂ [202], TiO₂/WSe₂ [203], TiO₂/Mo₂ [204], TiO₂/ZnS [205], TiO₂/g-C₃N₄ [206], TiO₂/MnO_x [207], TiO₂/Mo₃ [208], TiO₂/C₆₀ [209], and TiO₂-based plasmonic composite [210]. The central idea of these heterostructures is to enhance the charge separation rate of the photoinduced electron–hole pairs via the interfacial charge transfer mechanism, which generally requires the appropriate band alignment. Among these interfaces, it is particularly worth mentioning that plasmonic composites that consist of plasmonic nanoparticles such as noble metals [210,211] and TiO₂ are emerging as one promising photocatalytic system because of their efficient light absorption. Details on this new class of photocatalytic composites can be found in recent review articles [212–220].

Table 3. Summary of TiO₂-based materials interfaces along with their critical interfacial properties. ^aTiO₂ and ^rTiO₂ denote anatase and rutile TiO₂, respectively.

Interface	Properties	Ref.
^a TiO ₂ /MAPbI ₃ & ^a TiO ₂ /MAPbI _{3-x} Cl _x	(110) perovskite surface was stabilized against (001) surface after “depositing” TiO ₂ for both materials interfaces; interfacial Cl atoms increase the interfacial binding energy.	[21]
^r TiO ₂ /MAPbI ₃	Higher interfacial charge transfer rate than ZnO- and SnO ₂ -based interface.	[22]
^a TiO ₂ /MASnI ₃ & ^r TiO ₂ /MASnI ₃	^a TiO ₂ /SnI ₂ interface is energetically most favorable among the four considered systems and has the highest electron–hole separation rate.	[24]
^a TiO ₂ /MAPbI ₃ & ^r TiO ₂ /MAPbI ₃	^a TiO ₂ /PbI ₂ has stronger interfacial interaction but ^r TiO ₂ /PbI ₂ model is most efficient for electron–hole separation.	[19]
^a TiO ₂ /(Ba,Sr)TiO ₃	Stability of anatase TiO ₂ decreases in the order from (001) to (011) to (111) perovskite substrates.	[23]
^r TiO ₂ /BiOX (X = Cl, Br, and I)	BiO/TiO ₂ interface is more stable than I1/TiO ₂ interface; band gap of I1/TiO ₂ interface reduced by 0.28 eV while BiO/TiO ₂ exhibits an n-type conductivity.	[199]
^r TiO ₂ /RuO ₂	Strong bonding interaction at the interface; oxygen vacancies at the interface changes the band bending direction.	[200]

5. Conclusions and Outlook

In summary, this review covered first-principles computational and theoretical understanding on the structural, energetic, electronic, and optical properties of TiO₂-based nanocluster, bulk, and material interface. A fundamental understanding and computational design of novel TiO₂-based materials structures and/or composites is of great importance for developing highly efficient photocatalytic and photovoltaic applications, in which the first-principles computational approach is expected to play an increasing role. Herein, we discuss several possible future research directions from the viewpoint of first-principles calculations:

(i) Nonmetal or metal doping is one effective approach to tune electronic properties of TiO₂, which, however, will also significantly influence the anatase-to-rutile phase transition. A clear computational and theoretical understanding of the phase-transition mechanism will be useful to further optimize the performance of TiO₂ in photocatalytic and other applications. In this regard, future efforts can be devoted to the development of novel computational and analytical approaches based on first-principles calculations.

(ii) Increasing the number of photoinduced electron–hole pairs is one effective way to achieve high photocatalytic performance of TiO₂. Researchers have made great efforts to tune the bandgap of TiO₂ via doping engineering or defect engineering, which essentially utilizes light absorption property of TiO₂ for producing electron–hole pairs. Instead of utilizing generated electron–hole pairs in TiO₂, the emerging TiO₂-based plasmonic composites that utilize the light absorption of plasmonic nanoparticles instead of TiO₂ are one promising approach to achieve high photocatalytic performance. However, the current plasmonic nanoparticles are typically noble metal particles, and thus future direction could be to search for low-cost alternative plasmonic nanoparticles that can work with TiO₂ and exhibit comparable and even superior photocatalytic properties.

(iii) Increase the separation rate of photoinduced electron–hole pairs is another approach to improve the photocatalytic activity of TiO₂-based catalysts. Although several TiO₂-based materials interfaces have been studied from first-principles, future efforts can be on the design of novel TiO₂-based material interfaces such as heterostructures or core-shell structures that can significantly promote the separation rate of electron–hole pairs.

(iv) The emerging high-throughput computational materials design approach is becoming one powerful tool to significantly accelerate the materials discovery and development process, which has been successfully applied in the design of bulk materials [221–224], material interfaces [225,226], and organic–inorganic hybrid materials with target properties [227,228]. It is thus expected that the

application of such an approach in the design of TiO₂-based photocatalysts is likely to yield fruitful results and worth further exploring.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript.

DFT	Density Functional Theory
GGA	Generalized Gradient Approximation
DOS	Density of States
VB	Valence Band
VBM	VB Maximum
CB	Conduction Band
CBM	CB Minimum
2,5-DMBQ	Dimethylbenzoquinones
4-BBA	4-bromobenzaldehyde
XPS	X-ray Photoelectron Spectroscopy
AR-XPS	Angle-resolved XPS
UV	Ultraviolet

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