A strategy of enhancing the photoactivity of TiO_2 containing nonmetal and transition metal dopants*

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An effective structural codoping approach is proposed to modify the photoelectrochemical (PEC) properties of anatase TiO_2 by being doped with nonmetal (N or/and C) and transition metal (Re) elements. The electronic structures and formation energies of different doped systems are investigated using spin-polarized density functional theory. We find that (C, Re) doped TiO_2, with a low formation energy and a large binding energy, reduces the band gap to a large extent, thus it could contribute to the significant enhancement of the photocatalytic activity in the visible-light region. It should be pointed out that, to be successful, the proper proportion of the dopants C and Re should be controlled, so that reasonable PEC properties can be achieved.

Keywords: codoping, photoactivity, density functional theory, formation energy

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1. Introduction

TiO_2 has become one of the most promising photocatalysts for photoelectrochemical (PEC) water splitting due to its high chemical stability and strong catalytic activity. However, its large band gap of 3.2 eV has hindered its usage as an ideal photoelectrode, because it absorbs only the ultraviolet portion of light, which amounts to $\sim 4\%$ of solar energy.[1] To reduce the band gap and thus improve its efficiency under visible light, many efforts have been made by using various dopants.[1–6] Ever since Asahi *et al.*[7] discovered that $TiO_{2-x}N_x$ films and powders exhibited better optical absorption and photocatalytic activity than pure titania under visible light, nonmetal doping, especially N and C, of TiO_2 has been investigated widely as a promising photocatalyst.[8–13] It has been demonstrated that the photocatalytic efficiency of non-metal mono-doping TiO_2 decreases because strongly isolated empty states in the band gap may trap the photo-excited electron–hole pairs and reduce photo-generated current.[14] On the other hand, transition metal doping can promote photocatalytic efficiency[15,17–20] as well. Choi *et al.*[15] reported that doping with transition metals, including Re, in TiO_2 significantly increases the photo-reactivity for both oxidation and reduction. Actually, the transition metal-doped TiO_2 is impeded by the presence of carrier recombination centers and the formation of strongly localized states in the band gap, which is detrimental to carrier mobility.[16] To improve the photocatalytic efficiency of TiO_2, the challenge is to place its band edges at proper positions, thus shifting its absorption edge toward the visible light region.[21–26] Recently, using first-principles calculations, Gai *et al.*[6] have investigated the photocatalytic activity in compensated donor-acceptor, (Mo + C), codoping TiO_2 and found enhanced visible-light photocatalytic efficiency. According to the extensive density functional theory (DFT) band structure calculations, Yin *et al.*[5] predicted that (Ta, N) and (Nb, N) pairs are the optimal codoping combinations in the high-concentration regime, and (Mo, 2N) and (W, 2N) complexes are good candidates in the low-concentration regime for engineering TiO_2. To the best of our knowledge, there is no theoretical study regarding the comparison of the photocatalytic activity between the nonmental N (or/and C) and Re codoped TiO_2.

In the present work, we investigate structural and optical properties of various codoped TiO_2 by N (or/and C) and Re using spin-polarized DFT. We find that codoping results in a more effective band gap narrowing than monodoping, especially (C, Re), (CN, Re), and (3N, Re)-Re codopings obviously reduce the band gap further than other doped cases. Combining their formation and binding energies, we predict that (C, Re) may play an important role in developing the efficient photocatalysts.

2. Computational details

All of the spin-polarized DFT calculations were performed by the PWSCF code based on the plane-wave method.[27] Exchange–correlation effect is treated in the generalized gradient approximation (GGA), and the interaction between the valence electrons and the ionic core is described by the Perdew–Burke–Ernzerhof gradient-corrected functional and ultrasoft pseudopotentials. The k space integration was done with the Monkhorst–Pack grid with $2\times2\times2$ k-points for geometry optimization and $4\times4\times4$ k-points for

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electronic property calculations in the Brillouin zone of the supercell, and the wave functions are expanded with kinetic energy cutoff of 30 Rydberg.[28–31] The optimized lattice parameters for pure anatase were found to be $a = 3.798$ Å and $c = 9.511$ Å, which are consistent with other experimental and theoretical results,[32,33] indicating that our method is reasonable. The supercell consists of 48 atoms with $2 \times 2 \times 1$ repetition of the unit bulk anatase primitive cell. For monodoping, we consider that the N or C atom substitutes for O atoms and the Re atom substitutes for Ti atoms. For codoping, acceptor and donor codoped TiO_2 is modeled by taking into account the different possibilities. The most stable geometries are double checked with the larger $3 \times 3 \times 1$ supercell with 108 atoms.

To see whether the defect pairs can form, we calculate the binding energy of defect pairs in the host lattice. The binding energy E_b of the dopants, such as N_O and Re_{Ti}, is defined as

$$E_b = E(\text{pure}) + E(\text{N,Re}) - E(\text{N}_O) - E(\text{Re}_{Ti}), \quad (1)$$

where $E(\text{pure})$ is the total energy of the pure TiO_2, and $E(\text{N,Re})$, $E(\text{N}_O)$, and $E(\text{Re}_{Ti})$ are the total energies for supercells containing defects (N, Re), N_O, and Re_{Ti}, respectively. A negative value of E_b corresponds to a metastable or a stable bound dopant pair when both are present in the system. Extension of Eq. (1) to charged states is straightforward.

The formation energies of substitutional dopant defects are defined by

$$E_f = E(\text{defect},q) - E(\text{pure}) - \sum_i n_i\mu_i + q(E_v + E_F + \Delta V), \quad (2)$$

where $E(\text{defect},q)$ is the total energy of the system containing the impurity, $E(\text{pure})$ is the total energy of the pure host supercell, n_i and μ_i are the number and chemical potential of the atoms added to (positive n_i), or taken from (negative n_i), the bulk reference supercell in order to create the defect. E_F is the Fermi level, with respect to the valence band maximum (VBM), E_v is the bulk VBM, and ΔV is a correction term, which can be obtained by aligning the reference potential in the defect supercell to that in the bulk.[34] The atom chemical potential, μ_i, depends on the experimental condition under which the material is grown. For a Ti-rich condition, $\mu_{Ti} = E_{Ti}(\text{bulk})$, and for an oxygen-rich condition, $\mu_O = 1/2E(O_2)$, where $E_{Ti}(\text{bulk})$ and $E(O_2)$ are the total energy of a Ti atom in bulk Ti and the energy of an oxygen molecule, respectively. The chemical potential for oxygen (titanium) under Ti-rich (O-rich) conditions can be determined from the assumption of thermal equilibrium: $\mu_{Ti} + 2\mu_O = \mu_{TiO_2}$, where μ_{TiO_2} is the chemical potential of TiO_2, the total energy of a bulk TiO_2 stoichiometric unit. The chemical potentials of μ_N, μ_C, and μ_{Re} are determined by $\mu_N = \mu_{TiN} - \mu_{Ti}$, $\mu_C = \mu_{TiC} - \mu_{Ti}$, and $\mu_{Re} = \mu_{ReO_3} - 3\mu_O$, respectively.

3. Results and discussion

3.1. Structural properties

The optimized local structures of (C, Re) (CN, Re), and (3N, Re) codoped in TiO_2 are shown in Fig. 1. Due to the difference in atomic radius between the dopants and host atoms, it can be seen that dopants induce local lattice distortion in their neighbourhood, otherwise the host lattice remains almost unchanged. The change of the C–Re or N–Re bond length is calculated to be around -1%, corresponding to a small contraction relative to O–Ti distance, and the distance between O and Re along the c axis is extended by $\sim 2\%$.

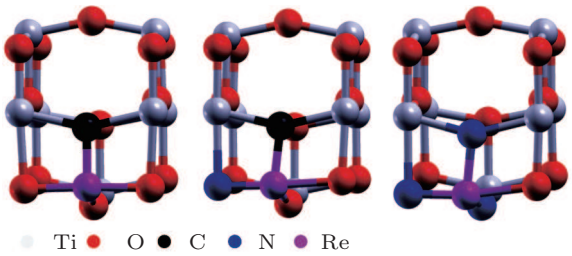


Fig. 1. (color online) Optimized geometries of (C, Re), (CN, Re), and (3N, Re) doped in TiO_2.

The calculated binding energies of considered defect pairs are shown in Table 1. Negative values of E_b indicate that the defect pairs are preferable with respect to the isolated impurities in the host. For the codoped systems, the (C, Re) and (N, Re) complexes each have a tendency to attract an N atom on the nearest-neighbour O sites, forming (CN, Re) and (2N, Re) combinations. The formation of the (3N, Re) complex is also stable.

Table 1. Binding energies, E_b, (in eV) for codoped TiO_2.

	(N, Re)	(2N, Re)	(3N, Re)	(C, Re)	(CN, Re)
E_b	–2.20	–4.63	–6.59	–3.51	—5.78

The formation energy describes the relative difficulty for different ions to be incorporated into the host lattice and is a widely accepted gauge of energetic stability. In Fig. 2 we present the calculated formation energies for the considered defects, each as a function of the Fermi level, E_F, under O-rich (a) and Ti-rich (b) conditions. Under oxygen-rich conditions, Re donor has a low formation energy and thus contributes to the n-type conductivity. Note that, in reality, C_O, N_O, (2N, Re), (CN, Re), and (3N, Re) codoped TiO_2 could be incorporated under a Ti-rich condition, where (N, Re), (2N, Re), and (C, Re) codoping have lower formation energies than the (CN, Re) and (3N, Re) codoping. For (CN, Re) and (3N, Re) codoping, it is clearly a high formation energy indicating that the concentration of such a structure under thermal equilibrium will be low. It is possible that these structures may form under nonequilibrium growth conditions.

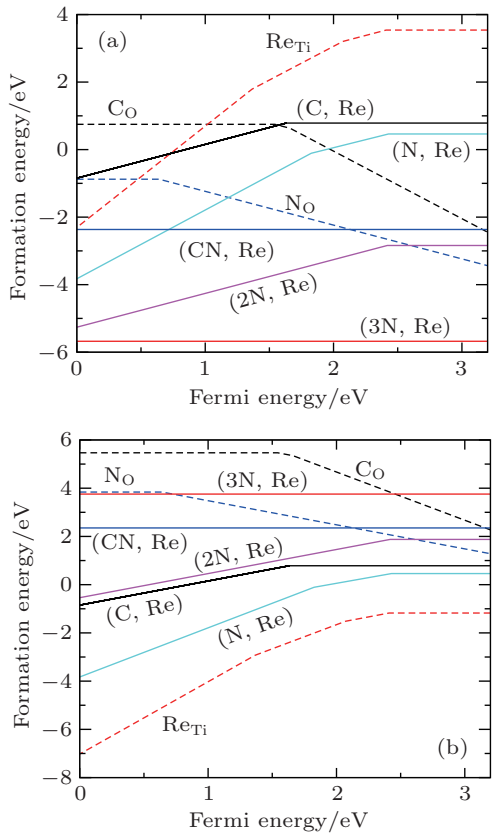


Fig. 2. (color online) Formation energies each as a function of the Fermi level for defects and complexes in TiO_2 for O-rich conditions (a) and for Ti-rich conditions (b). The zero of the Fermi level is at the top of the valence band maximum. Kinks in the curves indicate transitions between different charge states.

3.2. Electronic and optical properties

The calculated band gap of pure anatase TiO_2 is 2.10 eV, which is consistent with other theoretical results, but underestimates the experimental value of 3.2 eV due to well-known limitations in density functional theory. In this study, we focus on the change of the band gap upon doping, and the generalized gradient approximation method is expected to largely cancel the band gap error between different systems. Recent theoretical work of nonmetal codoping with transition metals has shown that standard density functional theory methods can deal fully with these doped systems.[5,26] As shown in Fig. 3(a), the valence band maximum (VBM) of pure TiO_2 is dominated by O-2p states while the conduction band minimum (CBM) consists mainly of Ti-3d states. The substitutional N_O introduces acceptor states, contributed by N-2p orbital, above the valence band maximum [see Fig. 3(b)]. The empty N-2p states may act as traps for excited electrons, which could promote an electron–hole recombination rate. For the carbon mono-doped case, C_O, the 2p states of carbon are localized in the band gap without changing the valence band maximum relative to the undoped case, while its conduction band minimum shifts down [Fig. 3(c)]. The electron in the valence band can be excited into gap states and then subsequently to the conduction band by visible-light absorption. For the Re-doped TiO_2 as shown in Fig. 3(d), the donor states below the conduction band minimum lead to the down shift of the conduction band minimum.

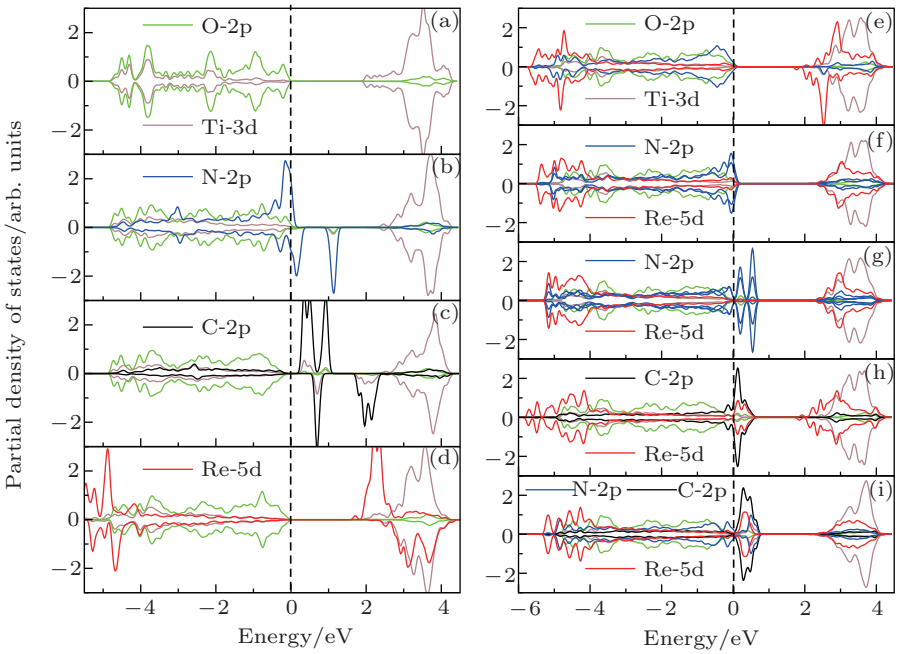


Fig. 3. (color online) Partial densities of states for (a) pure anatase; (b)–(d): monodoping N_O, C_O, and Re_{Ti}, respectively, (e)–(i): (N, Re), (2N, Re), (3N, Re), (C, Re), (CN, Re)-codoped cases. In all cases, the vertical dashed line indicates the VBM of pure TiO_2.

Considering that the defect states of C and N are mainly located at the edge of the valence band, and the Re-5d states only contribute to the lowering of the CBM, it is expected that their codoping would enhance the mixing of N (or C)-2p and O-2p states in the valence band. We find that for the (N, Re)-doped case, the empty minority band of nitrogen vanishes completely from the gap [see Fig. 3(e)]. A small shift of the VBM (relative to the vertical dashed line) (0.18 eV) indicates that (N, Re) doping contributes less to the improvement of photocatalytic efficiency. For the (2N, Re)-doped case [see Fig. 3(f)], similarly, no impurity state exists within the band gap, and the VBM moves further towards a higher energy compared with that of (N, Re) combination. Doping N further to form complex (3N, Re), the non-equivalent N atoms induce VBM to significantly shift up (0.74 eV) as shown in Fig. 3(g). For (C, Re)- and (CN, Re)-doped systems, the VBM increases greatly. There are strongly mixed characteristics from the dopants in the valence band, indicating strong coupling between the dopants. The hybridized states, located mainly at the edge of the valence band, are composed of anionic dopants 2p states and Re-5d states, while other Ti-3d states are at the edge of the conduction band. Particularly, for (C, Re) pair [see Fig. 3(h)], a large upshift (0.67 eV) of VBM and a tiny downshift of CBM are observed. The net band gap reduction is 0.82 eV relative to that of pure TiO_2.

Band-gap narrowing is a highly important factor for the enhancement of optical absorption under visible light irradiation. Since (C, Re), (CN, Re), and (3N, Re)-codoped TiO_2 reduce the band gap to a larger extent than the other codoped systems, we calculate their optical properties by the frequency dependence of the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, which is mainly a function of electronic structure. The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, can be calculated from the momentum matrix elements between the occupied and unoccupied wave functions. The real part $\varepsilon_1(\omega)$ can be evaluated from the imaginary part $\varepsilon_2(\omega)$ by the famous Kramer–Kronig relationship. The corresponding absorption spectrum is estimated using the following equation:

$$I(\omega) = 2^{1/2}\omega[\varepsilon_1^2(\omega) + i\varepsilon_2^2(\omega)]^{1/4} - 2^{1/2}\omega\varepsilon_1(\omega)^{1/2}. \quad (3)$$

The optical coefficients for (C, Re), (CN, Re), and (3N, Re)-codoped TiO_2 are compared with that of bulk TiO_2 as shown in Fig. 4. An electron is taken away from the system to ensure that the system is neutral, and to enable the calculating of the optical absorption spectrum of (C, Re) doping. Obviously, these codopings would lead to much better absorption edges under sunlight. As is well-known, PEC water splitting for hydrogen production using TiO_2 must simultaneously meet three requirements: it must be stable, efficient and energy favorable.[6,25] By comparison, the (C, Re)-codoped anatase TiO_2 has the potential to fit these requirements. Therefore this type of codoped TiO_2 is expected to significantly improve the PEC water-splitting efficiency.

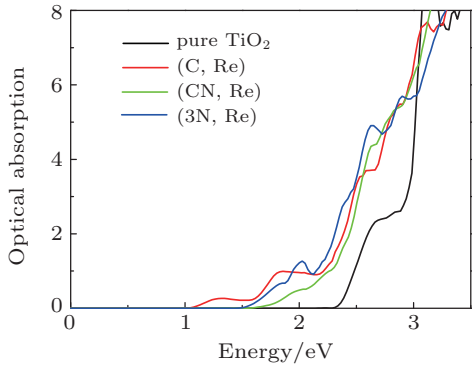


Fig. 4. (color online) Calculated optical adsorption spectra of TiO_2 with a complexes of (C, Re), (NC, Re), and (3N, Re), respectively. The optical adsorption spectrum of TiO_2 is included for comparison.

4. Conclusion

In this paper, according to the first-principles calculations and analysis of electronic structures, we have proposed that the codopings with nonmetal (C or/and N) and transition metal (Re) impurities are used to improve photocatalytic limitation of anatase TiO_2. We find that (C, Re), (CN, Re), and (3N, Re)-codoped systems each could induce a larger band gap reduction than other doped systems. However, for (CN, Re) and (3N, Re) combinations, their high formation energies limit their concentrations under thermal equilibrium. With a relatively low formation energy and a large binding energy, (C, Re) codoping is predicted to be a good candidate for the considerable enhancement of the photocatalytic activity of anatase TiO_2 in the visible-light region.

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