Electronic and optical properties of Cr and Cr–N doped anatase TiO$_2$ from screened Coulomb hybrid calculations

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Abstract

We studied the electronic and atomic structures of anatase TiO$_2$ codoped with Cr and N using hybrid density functional theory calculations. The nonlocal screened Hartree–Fock exchange energy is partially mixed with the traditional semilocal exchange energy. This not only patches the bandgap underestimation but also improves the description of the anion/cation-driven impurity states and the magnetization of the dopants. Cr and/or N doping modifies the valence and conduction band edges of TiO$_2$, leading to significant bandgap reduction. Hence, Cr, N and Cr–N doped TiO$_2$ are promising for enhanced visible light absorbance.

1. Introduction

For photocatalysis, titanium dioxide (TiO$_2$) offers excellent oxidation and charge transport properties together with its wide availability, nontoxicity, and chemical stability. For this reason, it has found many useful applications, such as the photogeneration of hydrogen from water, the degradation of pollutants under visible light irradiation and the production of hydrocarbon fuels and dye sensitized solar cells (DSSC) [1–4]. Among the several polymorphs the anatase phase exhibits the highest photocatalytic activity [5].

One important limitation is that anatase TiO$_2$ has a wide bandgap of $\sim 3.2$ eV [6] and can only absorb in the ultraviolet (UV) region ($\lambda < 380$ nm). This seriously reduces solar energy utilization to $\sim 5\%$. Substitutional cation and/or anion modified titania has been proposed as an effective approach to obtain catalytic activity under visible light irradiation [7–13]. Recent experiments have shown that Cr–N codoping in TiO$_2$ greatly enhances the absorbance [17, 18]. Moreover, Cr and Cr–N doping were reported to increase the visible light reactivity with increasing Cr incorporation [19, 20]. Ferromagnetism has also been observed in Cr doped anatase films [21, 22]. Theoretical studies predicted a magnetization per Cr much larger than experimental findings [23, 24]. Pure density functional theory (DFT) methods unreliable estimate a half-metallic character for Cr doped TiO$_2$ [24, 25]. For the optical properties, hybrid theoretical approaches have been used recently to obtain improved quantitative agreement with the experimental data [18, 26]. Detailed electronic structure investigations are still needed to obtain a proper description of the bandgap features for the doped systems.

In this present work, we used screened Coulomb potential hybrid DFT calculations to investigate the modifications of the bandgap properties of TiO$_2$ induced by Cr and Cr–N dopants and their effect on the corresponding absorption spectra. Formation energies have been calculated as a function of the oxygen chemical potential to compare the thermodynamical stability of the doped structures. We also obtained the magnetic moments and charge states of Cr and N species.

2. Theoretical method

For all systems, our calculations were performed based on the spin polarized hybrid density functional theory as implemented in the Vienna ab initio simulation package (VASP) [28]. Ionic cores and valence electrons were treated by the projector-augmented waves (PAW) method [29, 30]. The kinetic energy cutoff value was determined to be 400 eV. Pure DFT methods have some shortcomings in describing the impurity and defect associated properties of transition
metal oxides. For example, Ti 3d defect states resulting from oxygen vacancies are predicted to occupy the bottom of the conduction band (CB) of TiO$_2$ [31]. However, experimental studies show a semiconducting nature. This failure of the standard DFT functionals lies in the approximations to the exchange–correlation (XC) energy being usually local or semilocal. This flaw can be patched by using hybrid methods where a portion of the nonlocal exact exchange is admixed with the traditional semilocal exchange. One must note that the success of such hybrid functionals with respect to the band structure, and especially the gap, is a consequence of error cancellation and has a semiempirical character.

We used the Heyd–Scuseria–Ernzerhof hybrid XC functional (HSE06) [32–34] based on a screened Coulomb potential to reduce the self-interaction error. Technically, this results in a rapid spatial decay of HF exchange, which improves the convergence behavior of self-consistent iterations. The HSE exchange is derived from the PBE0 [35, 36] exchange by range separation, and then by cancellation of counteracting long-range HF and PBE contributions, as

$$E_{\text{HSE}}^x = a E_{\text{HF,S}}^x(\omega) + (1 - a) E_{\text{PBE,S}}^x(\omega) + E_{\text{PBE,LR}}^x(\omega),$$

where $\omega$ is the range separation parameter for the screening and $a$ is the mixing coefficient. The parameter of $\omega = 0.2 \text{ Å}^{-1}$ is used for the exchange contributions, as suggested for the HSE06 functional [37]. We determined the mixing ratio of the exact exchange to be 22%, so that calculated bandgaps and lattice constants for both the anatase and the rutile polymorphs show good agreement with the experimental values [13].

In order to model the doped systems we constructed a 108-atom supercell by $3 \times 3 \times 1$ replication of the conventional anatase unit cell. This structure (11.33 Å × 11.33 Å × 9.45 Å) is sufficiently large to accommodate spatial separation between the periodic images of the defects. We traced all possible Cr and N doping configurations. In particular, for Cr/N codoping, the structure shown in figure 1 is found to be energetically the most favorable. For geometry optimization and density of states (DOS) calculations we used eight periodic images of the defects. We traced all partitions of the real space delimited by local zero-flux conditions, and especially the gap, is a consequence of error cancellation and has a semiempirical character.

Table 1. Average charge states ($e$) of dopants and their adjacent (nn) Ti and O atoms from Bader analysis.

| Doping | Cr | N | Ti(nn) | O(nn) |
|--------|----|---|-------|-------|
| None   |    |   | 2.84  | −1.43 |
| N@O    | −1.38 | +2.31 |       |       |
| Cr@Ti  | +2.30 |   |       |       |
| Cr/N   | +2.29 | −1.13 | +2.81 | −1.19 |

$\mu_O$ is calculated from $\mu_O = \frac{1}{2} (\mu_{TiO_2} - \mu_{Ti})$. The remaining chemical potentials of Cr and N are taken from their molecular phases ($\mu_{Cr} = \frac{1}{2} (E_{CrO_2} - \frac{1}{2} E_{O_2})$ and $\mu_N = \frac{1}{2} E_{N_2}$).

Bader analysis is useful for determining the charge states of atoms in molecules and solids. It involves integration of Bader volumes around atomic centers. These volumes are partitions of the real space delimited by local zero-flux surfaces of the charge density gradient vector field. We calculated charge states of atomic species (in table 1) using a grid based decomposition algorithm [38].

The frequency dependent dielectric matrix can be computed by using the ground state electronic band structure. The transitions are considered from occupied to unoccupied states within the first Brillouin zone. Then, the imaginary part of the dielectric function $\varepsilon_2(\omega)$ is determined by summing over empty states using the expression

$$\varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,r,k} 2 \mu_k |\delta(\varepsilon_{ck} - \varepsilon_{ck} - \omega)| \times \langle \psi_{ck} \psi_{cq} \psi_{rk}^* \psi_{rk} \rangle,$$

where the summation indices $c$ and $v$ refer to conduction and valence band states respectively, and $u_k$ is the cell k vector of the orbitals at the $k$-point $k$ [39].

3. Results and discussion

The bulk properties of pure anatase were calculated using the 108-atom supercell. Our HSE-predicted lattice parameters ($\alpha = 3.78$ Å, $c = 9.45$ Å) and bandgap value (3.23 eV in figure 2) show remarkable agreement with the experimental data.

The monodoping of TiO$_2$ with N has been extensively studied by theoretical calculations, including various surface models with the possible involvement of bridging oxygen vacancies [14–16]. The appearance of an isolated empty N 2p state above the VBM in our HSE PDOS (figure 2) agrees with the spin restricted (doublet) ultrasoft pseudopotential calculations of Finazzi et al [14] and with the DFT+U results of Ortega et al [16]. Since the N doping case has been discussed in detail elsewhere [13], we will focus on Cr and Cr–N doped anatase to elucidate the role of Cr in the photoelectrochemistry of TiO$_2$.

**Cr-doped TiO$_2$:** Experiments report the incorporation of chromium at substitutional sites forming single-crystalline Cr doped TiO$_2$ [21, 18, 9, 19]. They also conclude that if chromium oxide forms it must be highly dispersed and its size must be undetectably small [17–21, 27]. In order to model the structure we substituted one Cr atom at a Ti site in

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Figure 1. Relaxed geometries and total charge densities of substitutional N (a)–(c), Cr (d)–(f) and Cr–N (g)–(i) in anatase TiO$_2$. 

the anatase supercell, forming sixfold coordination with the nearest neighbor (nn) oxygens as shown in figure 1. All Cr–O bonds are 1.90 Å and slightly shortened relative to those of the undoped TiO$_2$. The disturbance of the substitutional Cr on the lattice is very small, agreeing with the x-ray diffraction (XRD) patterns [27, 20]. Under O-rich conditions, the formation energy of Cr@Ti doping has been calculated to be 1.06 eV (in figure 3). These energetics are sensitive to the choice of the XC functional. For example, McDonnell et al. found a value of 0.36 eV with the HSE06-PBEsol method [18]. Under Ti-rich conditions the formation energy gets as large as 10.21 eV. Therefore, synthesis of substitutional Cr under O-rich conditions must be much easier, as pointed out by previous calculations [26].

Substitutional Cr introduces 3d states which are dominant above the top of the valence band (VB), as presented in the corresponding projected DOS (PDOS) of figure 2. For the minority spin component, fully occupied Cr 3d states appear isolated 1.07 eV above the valence band maximum (VBM). Our calculations are interestingly in agreement with the x-ray photoemission spectra (XPS) of Osterwalder et al [21], who reported the formation of defect states at 1.0 eV above the VBM giving an intensity roughly proportional to the Cr concentration. The HSE06 functional not only gives the relative positions of the defect states in the bandgap, but also better describes the character of these states. For instance, unlike the full-potential linearized augmented plane wave (FLAPW) calculations of Ye et al [23] and the LDA study of Peng et al, our HSE06 results predict Cr doped anatase to be semiconducting, not half-metallic.

Chromium also significantly modifies the conduction band minimum (CBM) by introducing empty Cr 3d states at the bottom of the CB. Widely dispersing Cr-induced states effectively reduce the calculated bandgap from 3.23 eV to a value of 2.16(2.14) eV for the spin up(down) component. This bandgap narrowing agrees well with the decrease of the binding energy of Cr 3d from 3.2 to 2.20 eV observed in the XPS spectra [21]. Depending on the choice of XC flavor, the bandgap reduction was calculated by the previous theoretical studies to be 1.2 eV [23] and 0.34 eV [18] with FLAPW and HSE06-PBEsol methods, respectively.

XPS core level and valence band data show that the majority of Cr is present in the 3+ charge state [21, 9, 19, 18]. In addition, the room temperature magnetization measurements reveal a ferromagnetic state for all Cr doped anatase films, with a saturation magnetic moment of \( \sim 0.6 \) \( \mu_B \) per Cr atom [21]. Similarly, Zhang et al reported Cr$^{3+}$-associated ferromagnetism which increases up to \( \sim 0.42 \) \( \mu_B/\text{Cr} \) on lowering the oxygen pressures [22]. Theoretical studies, on the other hand, predicted a charge state of 4+ with a
Figure 2. Total (left) and projected (right) densities of states (DOS) of pure and doped (with Cr and/or N) anatase TiO$_2$, calculated using the HSE06 functional. Dashed (dotted) line indicates the Fermi energy (the VBM of pure anatase).

Figure 3. Calculated formation energies as a function of the oxygen chemical potential (relative to the value at its molecular gas phase) for Cr, N mono- and Cr/N codoped TiO$_2$ structures.

magnetization of 2 $\mu_B$ [23, 25, 26]. The discrepancy has been attributed to the possible presence of oxygen vacancies, which leave excess charge in the samples, reducing the charge state from Cr$^{4+}$ to Cr$^{3+}$. However, without such a compensation, our HSE-calculated charge state of +2.3 and total magnetic moment of 1.21 $\mu_B$ per Cr show a significant improvement over the existing theoretical estimations.

Cr/N-codoped TiO$_2$: Substitutional codoping of Cr and N in the anatase form has been confirmed by XRD measurements for various impurity concentrations [17, 19, 20, 26]. Initially, we considered all possible doping configurations. After the relaxation, the Cr–N pairing shown in figures 1(g)–(h) yields the lowest total energy. A competing configuration where Cr and N are paired along [001] is energetically less favorable by 0.05 eV. The difference in the supercell energy becomes as large as 0.61 eV, depending on the separation between the Cr and N dopants. The lattice becomes slightly disturbed because of the strong Cr–N interaction, leading to a bond length of 1.62 Å, which is considerably shorter than the Ti–N bonding. The total charge density plots in figures 1(g) and (f) clearly show the covalent character of Cr–N coupling while Ti–N bonding is more polarized.

We calculated the formation energy for Cr/N codoping to be 4.43 eV under O-rich conditions. It rises up to 8.93 eV in an O-poor growth environment, as shown in figure 3. The experimental realization of Cr–N codoping is expected to be energetically viable under an oxidizing atmosphere, in agreement with previous studies [18].

The presence of substitutional N in the codoped anatase phase reduces the calculated magnetic moment to 1.00 $\mu_B$
relative to the case of Cr monodoping. Moreover, it insignificantly alters the charge state of Cr, which is +2.29 as presented in table 1. This indicates a strong delocalization of N 2p states over TiO$_2$ bands. The UV–vis reflectance spectral measurements of Li et al [19] and the x-ray absorption spectroscopy (XAS) of Chiodi et al [17] confirm the presence of Cr$^{3+}$ species. Our HSE-calculated charge state is reasonably closer than the previous DFT+U predicted Mulliken charges (+0.86) on the substitutional Cr when N dopant is present [26].

The strong Cr–N pair interaction exhibits interesting features in the electronic properties in figure 2. First, the isolated impurity states associated with Cr 3d and N 2p in the (Cr@Ti) and (N@O) monodoping cases mutually passivate each other, giving a clean bandgap. This eliminates the possibility of photogenerated charge recombination due to well localized trap states. Secondly, this reduces the electron–hole recombination rate, improving the overall photocatalytic performance.

4. Conclusions

The electronic, magnetic and optical properties of Cr- and Cr/N-doped anatase TiO$_2$ have been investigated by means of screened Coulomb hybrid calculations. Hybrid functionals incorporating exact exchange terms not only improve the description of defect states but also are promising to predict the magnetization properties of d-band dopants. We have shown the dominant character of Cr in modifying the band edges of anatase. Substitutional Cr with or without N is very effective in bandgap reduction, causing a significant red-shift of the absorption edge into the visible spectral region. Isolated N 2p states become delocalized over TiO$_2$ bands due to mutual passivation by Cr 3d states, giving a clean bandgap. These results translate to an enhancement of the optical absorption of Cr/N-codoped TiO$_2$, confirming the experimental observations. Consequently, the disappearance of the bandgap states, the strong delocalization of N 2p unoccupied states over the CB of TiO$_2$ and the absence of other point-defects imply that the substitutional Cr and N pair reduces the electron–hole recombination rate, improving the overall photocatalytic performance.

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Figure 4. Calculated absorption spectra for pure, Cr- and Cr/N-doped anatase TiO$_2$ structures.
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