Band gap engineering of (N, Si)-codoped TiO$_2$ from hybrid density functional theory calculations

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Abstract. We have investigated systematically the influence on electronic properties of anatase-TiO$_2$ of codoping by N and Si at different concentrations using Heyd–Scuseria–Ernzerhof (HSE06) hybrid density functional theory calculations. The optimized total energy shows that TiO$_2$ codoping by N and Si favours a configuration of two substitutional N atoms located at two adjacent O sites, with one substitutional Si atom at their neighbouring Ti site. We show that N–Si codoping can harvest longer-wavelength visible-light than either those of N and Si monodoping, owing to the contribution from N 2p in the ‘forbidden gap’ and Si 3s–3p at the tail of the conduction band. Increasing the N doping concentration leads to a larger extent of gap narrowing, which is directly related to coupling between N atoms. Our results suggest that double-hole coupling plays a key role in similar systems to obtain high visible-light photoactivity in TiO$_2$-based photocatalysts.

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1. Introduction

Titanium dioxide (TiO$_2$), a material involving many and varied applications in the field of renewable energy and photocatalysis, has attracted considerable scientific interest due to its unique properties, which render it a promising photocatalyst material for water splitting and hydrogen production. This is due to attractive properties, such as high photocatalytic activity, resistance to photocorrosion, low cost and non-toxicity [1]. However, its large band gap ($\sim 3.2$ eV) only allows it to absorb a small amount of incident sunlight ($\sim 5\%$). Many experiments and theoretical studies have shown that narrowing of the band gap is the most effective way to achieve higher photocatalytic activity and solar-to-hydrogen conversion efficiency. For instance, the introduction of dopant atoms into the TiO$_2$ lattice is perhaps the most effective method to reduce the band gap. It is well known that the O 2p orbitals dominate the valence band (VB) while Ti 3d orbitals govern the behaviour of the conduction band (CB). Generally, the introduction of dopants with different p orbital energies relative to the O atom shifts the valence band maximum (VBM) upwards, while dopants with different d orbital energies vis-à-vis Ti atoms shift the conduction band minimum (CBM) downwards. Both monodoping at oxygen sites [2–5] and donor-acceptor codoping at Ti and O sites have been attempted to narrow the band gap [6–9], as well as both approaches at Ti sites [10]. However, it is generally believed that two anion acceptor dopants would repel each other; therefore, acceptor–acceptor codoping is not usually considered an effective way to reduce the band gap because it is expected to be energetically unfavourable [8–10]. Recently, Yin et al [11] reported, via standard density functional theory (DFT) calculations, that a double-hole-mediated coupling mechanism can provide an alternative explanation for the high photocatalytic activity of N-doped TiO$_2$ [12]. In particular, Shi et al [13] very recently assessed the effects of N, Si and N/Si doping in titania, and found that hybridization between the codoped states and O 2p orbitals leads to broadening of the VB and possible improvement in mobility of any photo-generated hole. We have investigated systematically the electronic structures of (N, P)-codoped TiO$_2$ involving doping concentration and spin effects using hybrid density functional calculations and found interesting results [14]: double-hole coupling results in a substantial reduction of the band gap with the formation of an N–P chemical bond at high doping concentration, while a spin-double-exchange mechanism is responsible for the relatively large gap narrowing when N and P are separated by a larger distance in the lattice. At low doping concentrations, double-hole-coupling is dominant regardless of the N–P distance.

In this study, we focus our attention on (N, Si)-codoped anatase-TiO$_2$ because this has shown high photocatalytic activity under visible-light irradiation [15]. Owing to N having one less electron than O, substitutional doping by N atoms will provide one hole when the N atom replaces an O atom. Correspondingly, the system will only provide one hole when an N atom locates at an O site and an Si atom locates at a Ti site due to an equal valence electron number so that the N 2p orbitals cannot couple to each other. It is expected that gap narrowing is limited. However, N 2p orbitals can couple to each other when two N atoms are located at adjacent lattice O atoms sites, leading to the formation of an effective N–N bond while the Si atom is located at the Ti site. A key, unresolved question is as to the nature of the resultant behaviour when two N dopants are separated by a larger distance with a very weak, or essentially no, interaction. In this study, we attempt to explore gap narrowing mechanisms arising from both N–Si codoping and monodoping, in addition to the effects of doping concentration, energy-level coupling and spin effects. In particular, key goals are to ascertain: (i) why codoping leads to a larger extent
of gap narrowing vis-à-vis monodoping, (ii) if gap narrowing is related primarily to the doping concentration, or if other dependences are at play, (iii) what influence double-hole coupling contributes towards gap narrowing and (iv) what influences spin effects have on coupling. To address these questions, we have considered systematically many configurations with N and Si located at different sites, with and without spin-polarization (vide infra).

2. Methodology

We carried out spin-polarized DFT calculations using projector-augmented wave (PAW) pseudopotentials, as implemented in the Vienna *ab initio* simulation package (VASP) code [16, 17]. The calculations were performed using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [18, 19]. The exchange-correlation contribution employed in the HSE06 functional is divided into short- and long-range parts; Hartree–Fock (HF) is mixed with Perdew–Burke–Ernzerhof (PBE) [20] exchange-correlation in the short-ranged part. To avoid the expensive calculation of long-range HF, as well as enabling hybrid DFT calculations on metal elements for which conventional HF or global hybrid calculations are intractable, this term is replaced by long-range PBE exchange-correlation:

\[
E_{xc}^{\text{HSE}} = \frac{1}{4} E_{xc}^{\text{HF}, \text{s}} + \frac{3}{4} E_{xc}^{\text{PBE}, \text{s}} + E_{xc}^{\text{PBE}, \text{lr}} + E_{xc}^{\text{PBE}, c},
\]

where (sr) and (lr) refer to the short- and long-range parts of the respective exchange interactions; the range separation of the Coulomb kernel varies typically between 0.2 and 0.3 Å⁻¹. We have used \(\mu = 0.2\) Å⁻¹ for HSE06. The exact exchange contribution of 25% was used and this produced a band gap of 3.20 eV for anatase-TiO₂, in essentially exact quantitative agreement with the experimental value [21], and far superior to previous conventional DFT modelling of titania by both ourselves [7, 8] and others [2, 6, 9, 11, 12]; this exact exchange contribution of 25% was also suggested originally by Becke by fits of atomization energy data of molecules and is reasonably applicable to a wide extent of materials in hybrid-DFT [22]. It should be noted that the use of the hybrid HSE06 functional has led to improved results in recent studies of the electronic properties of a wide variety of materials vis-à-vis previous non-hybrid DFT and DFT + U studies, such as the technologically important SiC [23], NiO [24] and, importantly for this study, titania [10, 14, 25–27]; therefore, this serves as a useful motivation for the use of HSE06 in this study. In addition, Deák et al [28] concluded that the HSE06 functional offers improved accuracy for the energetics of defect levels and associated charge transition levels in a variety of materials, as well as describing group-IV semiconductors well. The electron wave function was expanded in plane waves up to a cutoff energy of 400 eV and a Monkhorst–Pack \(k\)-point mesh [29] of \(2 \times 2 \times 2\) was used for geometry optimization and electronic structure calculations. Both the atomic positions and cell parameters were optimized until residual forces were below 0.01 eV Å⁻¹. We used a 48-atom supercell containing 32 O atoms and 16 Ti atoms to simulate bulk anatase-TiO₂, arising from \(2 \times 2 \times 1\) replication of the anatase unit cell, as shown in figure 1. The optimized lattice parameters are \(a = 3.80\) and \(c = 9.48\) Å, which are in good agreement with experimental values [21].

As shown in figure 1, we denoted one codoped system as NNSi1 when N1, N2 substitute for two O atoms and Si1 replaces Ti at a Ti site, while we dubbed a second codoped configuration NNSi2, for which N2, N3 substitute for O at O sites and Si2 replaces Ti at a Ti site; they correspond respectively to nonspin- and spin-polarized scenarios, and are the lowest-energy configurations amongst the various inter-dopant distances upon optimization for both of these
Figure 1. Supercell for (N, Si)-codoped 48-atom anatase-TiO$_2$ showing the location of the dopants. The N ions’ doping sites are marked by N1, N2 and N3 while Si ions’ doping sites are denoted by Si1 and Si2. The grey, red, blue and yellow spheres represent Ti, O, N and Si atoms, respectively. NSi stands for N1Si1. NNSi1 means N1N2Si1 and NNSi2 denotes N1N3Si2.

situations; we attempted systematically a variety of NNSi configurations and found that these two spin- and nonspin-polarized configurations were the lowest in energy for their respective spin scenarios. For N- and Si-monodoping we also chose the most energetically favorable case when N1 substitutes for O and Si1 substitutes for Ti. To assess system size effects, we also carried out 108-atom supercell calculations for NNSi1- and NNSi2-doped systems, and validated qualitatively similar behaviour (vide infra).

3. Results and discussion

We calculated the density of states (DOS) and projected DOS (PDOS) for N-, Si-, NSi-, NNSi1, and NNSi2-doped TiO$_2$, and these are displayed in figure 2. For comparison, the pure DOS of TiO$_2$ is also plotted in figure 2(a), with a calculated band gap of 3.2 eV. For N-monodoped TiO$_2$ (cf figure 2(b)), the N 2p orbitals split into occupied and unoccupied states, which mix well with O 2p orbitals at the VBM and locate at the ‘forbidden gap’. In particular, N 2p-occupied states mix well with O 2p states at the VBM. These states accommodate five valence electrons of the N dopant. As a result, the other unoccupied N 2p state is responsible for the band gap narrowing, and this finding agrees well with many previous DFT studies [2, 9, 15]. Furthermore, the current calculation of the N defect level agrees well with recent HSE06 results [30] (see figure 5(b) in [30]). This is also in consistent with the experimental observation that N-doped TiO$_2$ samples can extend the absorption edge to 660 nm [31], corresponding to a reduction in band gap by 1.4 eV. It is expected that the band gap will be reduced further if the N-doping concentration increases. For Si-monodoped TiO$_2$ (cf figure 2(c)), Si 3p states reside well inside the valence
The Fermi level is set as zero.

On the other hand, hybrid Si 3s-3p states contribute to the tail of the conduction band and are responsible for the slight gap narrowing of 0.3 eV, in agreement with our and other groups’ theoretical studies [32–34]. This also presents a convincing explanation for experimental observations of optical absorption extending to longer wavelengths in Si (substitutionally)-doped TiO₂ [35], in which Si-doped TiO₂ samples can harvest visible light to wavelengths of 430 nm, corresponding to a decrease in the absorption energy of about 0.28 eV (cf figure 6 in [35]). For NSi-codoped TiO₂ (cf figure 2(d)), it was found that no direct interaction exists between N and Si because N 2p and Si 3s/3p states were located in disparate energy regions. Unoccupied N 2p states still locate at a similar position in the ‘forbidden gap’ vis-à-vis the N monodoping case, while hybrid Si 3s–3p states contribute to the CBM. It would appear that the higher photocatalytic activity of N/Si-codoped TiO₂ relative to that experienced from N- and Si-monodoping arises simply from the contribution of both N and Si [15].

Increasing the N doping concentration further, it becomes appropriate to focus our attention on the electronic structure of NNSi-codoped anatase from the double-coupling perspective [11], particularly in the vicinity of the dopants. Before discussing the electronic structures, we describe briefly the geometries of NNSi1, NNSi2 configurations. The relaxed N–N distance is 1.306 Å in the NNSi1 model, indicating that an effective N-N bond exists. It should be noted
that both N atoms bind to the Si atom, so that the level of interaction between N and Si is an additional consideration, besides the coupling of two N atoms. In the case of NNSi2, the distance between two N atoms is as large as 4.768 Å, and there is no direct interaction between them. However, the large differences in the geometries may result in a substantial difference in electronic properties.

For the NNSi1 case, each of the N atoms can provide one hole and the two holes can couple to each other owing to the existence of an effective N–N bond. As expected, figure 2(e) indicates that the N 2p orbitals couple to each other, forming two distinct occupied states in the ‘forbidden gap’ without spin-polarization. In other words, the coupling of N 2p energy levels leads to upward-shifted, fully filled states, which are designated as the highest occupied molecular orbital (HOMO) and HOMO-1. In the top panel of figure 3, the electron densities show that N 2p states dominate the HOMO and HOMO-1 and come partly from O 2p orbitals. This results in a larger reduction of the band gap than that of NSi-codoped TiO₂. Therefore,
this coupling and higher extent of doping concentration may be regarded as responsible for the large reduction of band gap induced by NNSi codoping vis-à-vis NSi codoping, arising from the formation of an N–N bond.

For the NNSi2 case, it should be noted that the total energy is 2.4 eV higher than that of NNSi1, indicating that it is difficult to obtain experimentally. In order to demonstrate whether double-hole coupling or higher levels of doping concentration dominate large gap narrowing as well as involving the spin effect, we calculated the electronic structures of NNSi2 configuration with inter-dopant separations. The DOS (cf figure 2(f)) shows that spin-polarization occurs in this case so that we can also consider the spin effect in spite of the total energy of NNSi2 being 2.4 eV higher than that of NNSi1. There are three obvious differences from cases with smaller N–N bond lengths. Firstly, impurity states become unoccupied, and therefore more similar to the N-monodoping case. The two N dopants can be regarded as two isolated N atoms which cannot couple to each other. We also plotted the lowest unoccupied molecular orbital (LUMO) and LUMO + 1 at the gamma point to check the orbital components in figure 3 (bottom panel); it displays clearly that each N atom dominates the LUMO and LUMO + 1 and originates partly from O 2p. Secondly, spin-polarization of N 2p occurs, interacting with O 2p states, which leads to the formation of N2p–O2p hybrid states below the CBM. To examine this, the spin charge is plotted in figure 4 and it shows the spin density induced by the N dopant, and also induced spin-polarization on its first- and second-neighbouring O. This suggests that N not only essentially spin-polarized themselves, but also induce spin-polarization on the surrounding O atoms. In this case, the gap narrowing is large if transition occurs between the hybrid states and the CBM. It is difficult to determine, however, if double-hole coupling or high doping concentration plus spin-polarization is the primary reason for the larger extent of gap narrowing.

Figure 5 shows the band structures of pure and N and/or Si-doped TiO2. It indicates that the all of the pure, N- Si-, NSi-doped, and NNSi1-doped TiO2 are direct band gap while NNSi2-doped case is indirect band gap. At the same time, it is valuable to compare the electronic
Figure 5. The HSE06-calculated band structure of pure, N-, Si-, NSi-, NNSi1 and NNSi2-doped 48-atom anatase-TiO2. The Fermi level is set as zero.

structure of NN-doped TiO2 to NNSi-doped TiO2. The DOS of NN case is shown in figure 6(a). The spin-polarization behaviour is similar with the NNSi1 case. However, the CBM and VBM of NNSi1 case downshift significantly relative to the NN case, indicating that addition of Si increase the oxidation ability. The band structure (cf figure 6(b)) shows this case is direct band gap as well.

In order to demonstrate directly the influence of N and/or Si doping on optical properties, we have calculated optical absorption spectra for NNSi1- and NNSi2-codoped anatase-TiO2 to compare with both the NSi-codoped system and the N- and Si-monodoped cases, as well as pure anatase; this is shown in figure 7. This indicates clearly three obvious characteristics: (i) codoping can harvest longer-wavelength visible-light than monodoping; (ii) for increasing N doping concentration, codoped systems’ spin-polarization effects prevail and the double-hole coupling mechanism contributing to harvesting longer-wavelength visible-light; and (iii) at higher N concentrations, this does not arise from simply increasing the doping concentration, from comparison with the absorption spectra of NSi, NNSi1 and NNSi2 cases. However, as discussed above, the total energy of NNSi2 is 2.4 eV higher than that of NNSi1, and therefore it is expected that the NNSi2 configuration is difficult to obtain experimentally. Therefore, this supports further the view that the double-hole coupling mechanism contributes to the larger degree of gap narrowing and harvesting of longer-wavelength visible-light.

To examine the influence of doping concentration on the coupling mechanism, we have also performed HSE06 calculations for a 108-atom supercell of NNSi1- and NNSi2-codoped TiO2. Here, the NNSi2 case is some 2.4 eV less energetically stable than the NNSi1 case, which agrees with results from 48-atom supercell studies. The calculated DOS is shown in figure 8.
Figure 6. (a) The HSE06-calculated total and projected DOS of NN-doped 48-atom anatase-TiO\(_2\) and (b) band structure. The Fermi level is set as zero.

Figure 7. Optical absorption spectra of pure, N-, Si, NSi, NNSi1 and NNSi2-doped TiO\(_2\).

Compared with the 48-atom supercell codoped by N and Si, the effective band gap is larger than that of NNSi-codoped 48-atom supercell because the lower doping concentration gives rise to relatively weaker coupling; however, the behaviour of the electronic structure is consistent with each case and double-hole-coupling is concluded to still be primarily responsible for an appreciable degree of large gap narrowing.
4. Conclusions

In summary, we have calculated the electronic structure of (N, Si)-codoped anatase TiO$_2$ based on HSE06 DFT calculations. The calculated total energies indicate that an (N, Si)-codoped TiO$_2$ configuration is energetically favourable, in which two N dopants occupy two adjacent lattice O atom sites, whilst the Si dopant is located at the adjacent Ti lattice site. The results indicate that NSi-doping can result in a large extent of gap narrowing vis-à-vis N and Si monodoping, as found by Shi et al [13]. Upon increasing the N doping concentration, we found that the larger extent of gap narrowing is directly related to double-hole coupling rather than high doping concentrations and spin effect.

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