



# The electronic and magnetic structure of *p*-element (C,N) doped rutile-TiO<sub>2</sub>; a hybrid DFT study



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## ABSTRACT

We study the electronic and magnetic structure of carbon and nitrogen impurities and interstitials in rutile TiO<sub>2</sub>. To this end we perform *ab initio* calculations of a 48-atom supercell employing the VASP code. In order to obtain a realistic description of the electronic and magnetic structure, exchange and correlation are treated with the HSE06 hybrid functional. Both, atomic positions and cell dimensions are fully relaxed. Substitutional carbon and nitrogen are found to have a magnetic moment of 2 and 1 μ<sub>B</sub>, respectively, with a tendency for anti-ferromagnetic long range order. For C/N on interstitial sites we find that carbon is non-magnetic while nitrogen always possesses a magnetic moment of 1 μ<sub>B</sub>. We find that these interstitial positions are on a saddle point of the total energy. The stable configuration is reached when both carbon and nitrogen form a C–O and N–O dimer with a bond length close to the double bond for CO and NO. This result is in agreement with earlier experimental investigations detecting such N–O entities from XPS measurements. The frequencies of the symmetric stretching mode are calculated for these dimers, which could provide a means for experimental verification. For all configurations investigated both C and N states are found inside the TiO<sub>2</sub> gap. These new electronic states are discussed with respect to tuning doped TiO<sub>2</sub> for the application in photocatalysis.

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## 1. Introduction

TiO<sub>2</sub> plays an important role in the fields of dilute magnetic semiconductors (DMS) and photocatalysis. For both applications TiO<sub>2</sub> requires tailor made electronic properties, which can be manipulated by selectively diluting the system by insertion of dopants.

DMS have been investigated in the past in order to gain new insights in the functional principles and the manipulation of the magnetic and semiconducting properties. The search for magnetic semiconductors or for half-metals used for spin-injection led to the discovery of the new material class of *p*-electron magnets. The prospect of controlling the charge and the electron spin as information carriers would make it possible to combine information processing and storage at the same time [1–3]. The second major application is in the field of photocatalysis, where the favourable electronic gap range of 1.65–3.1 eV can be also achieved by doping [4–6].

Regarding rutile TiO<sub>2</sub> from a photocatalytic point of view we are especially interested in the manipulation of the band gap by

incorporation of impurities. Rutile TiO<sub>2</sub> has a band gap of 3.0 eV, which corresponds to an absorption spectrum in the ultraviolet region. The absorption of photons lead to the creation of electron hole pairs, which are of special relevance for photocatalytic and photoelectrochemical applications like the photo-induced decomposition of water on TiO<sub>2</sub> electrodes demonstrated by Fujishima and Honda [7]. Another line of research regards the photocatalytic properties; due to the creation of electron hole pairs the valence band (VB) becomes oxidative and the conduction band (CB) reductive. Surrounding molecules can therefore be oxidized or reduced and as a consequence form radicals which are harmful to organic compounds like bacteria and fungi. Hence, TiO<sub>2</sub> can be used as a purifier, removing gaseous or aqueous contaminants [8,9]. Beside water- and air-purification there is a wide range of other photocatalytic applications, like antifogging and self-cleaning surfaces [10]. Since UV light only makes up 5% of the sunlight spectrum one aims to shift the absorption spectrum of TiO<sub>2</sub> into the visible region to improve the absorption rate and therefore the photocatalytic efficiency. Several studies have shown that impurities like nitrogen and carbon verifiably modify the band gap. Beside computational studies done by DiValentin et al. [11,12] and Yang et al. [13] there are experimental studies confirming the earlier theoretical results. Diwald et al. [14] reported a blueshift in the band gap after doping with nitrogen. In a second study [15] they observed a redshift by

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inducing nitrogen into the TiO<sub>2</sub> rutile host matrix. For the first case they assumed oxygen atoms being substituted by nitrogen impurities and for the latter nitrogen atoms being placed on interstitial sites. Batzill et al. [16] on the other hand reported to see a redshift when substituting O by N. Motivated by these partly contradictory reports we perform our theoretical investigation in order to interpret the experimental results.

In the present study we investigate TiO<sub>2</sub> rutile doped with carbon and nitrogen atoms, respectively, where we assume C and N either to replace oxygen or to occupy interstitial positions. Although magnetic order is most common in metallic materials with narrow bands of *d*- or *f*- electrons, the carriers of the magnetic moments in doped semiconductors or insulators like TiO<sub>2</sub> are the carbon or nitrogen atoms. The magnetic moment is produced by the *p*-electrons which become polarized because of the flat *p*-bands of these impurity atoms [17]. This is called *p*-electron magnetism and has been investigated intensely during the last years.

## 2. Crystal structure and doping configurations

There are three common polymorphs of titanium dioxide: rutile, brookite and anatase. Rutile is the thermodynamically most stable modification of TiO<sub>2</sub> and is an indirect wide band gap semiconductor with an experimental band gap of 3.0 eV [18].

The rutile structure belongs to the P4<sub>2</sub>/mnm (No. 136) tetragonal space group with unit cell parameters of  $a = b = 4.587$  Å and  $c = 2.954$  Å. In rutile TiO<sub>2</sub> every titanium atom is octahedrally coordinated to six oxygen atoms. The so formed octahedrons show an orthorhombic distortion, with the apical Ti–O bond length being slightly longer than the equatorial Ti–O bond length. Each TiO<sub>6</sub> octahedron is in contact with 10 neighbour octahedrons. The TiO<sub>2</sub> rutile crystal structure therefore can be seen as a chain of edge and corner-sharing TiO<sub>6</sub> units [18,19].

Beside the investigation of the electronic properties of pristine TiO<sub>2</sub>, we examined the effect of C and N atoms incorporated in various concentrations and positions into the host matrix. In total seven different levels and configurations of doping were examined using *ab initio* calculations. Fig. 1 depicts the different positions of the C and N dopants in the TiO<sub>2</sub> 2 × 2 × 2 (48 atoms) supercell. In one of the performed calculations we assumed a single oxygen atom of the host matrix to be replaced by C or N (position (1)). This corresponds to a doping concentration of 2.1%. Further, two substitutional oxygen sites with two C or two N atoms, respectively, were occupied leading to a doping rate of 4.2%. This was done for

two different configurations investigating the effect of increasing distance between the two impurity atoms. In the first configuration of this double substitutional state the distance between the two dopants was chosen to be minimal (position (1) and (2)). In the second one the two dopants were placed on arbitrary oxygen sites (positions (1) and (3)) increasing the distance. Moreover, two different interstitial positions of C and N (positions (4) and (5)) in the TiO<sub>2</sub> host lattice were examined. Finally, we performed a set of calculations exchanging these interstitial dopants by their next nearest oxygen neighbour, so that O and C or N respectively switch position, with a doping concentration of again 2.1%.

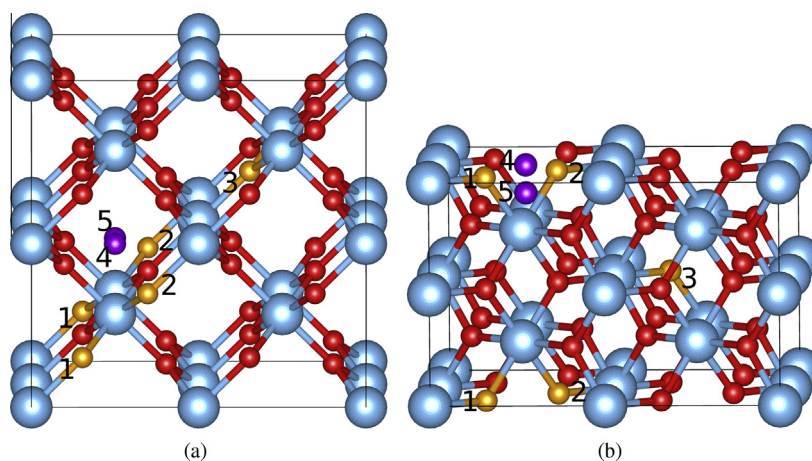
## 3. Computational details

All calculations were performed employing the *Vienna Ab-initio Simulation Package* (VASP) [20–25] which uses projector augmented wave (PAW) pseudopotentials [26] to describe the potential between the ions. The semi-core *s* and *p* states for Ti and the 2*s* states for O, C and N, respectively were incorporated in the calculations. To save computation time, the effects of exchange and correlation were initially treated using the GGA–PBE approximation [27,28], until all force components were smaller than 0.01 eV/Å. During the relaxation we allowed for a change of the atomic positions, shape and volume of the cell. The final convergence was done with the post-DFT HSE06 functional [29] which is known to yield reliable results for the gap size and the position of the impurity bands inside the gap.

Plane waves with an energy up to 530 eV were included in the basis set, in order to avoid Pulay stress and other related problems. The Brillouin-zone integration was performed using a 4 × 4 × 4  $\Gamma$  centred *k*-mesh with Gaussian smearing set to 0.05 eV. The total energy was converged better than 1 × 10<sup>−6</sup> eV for all cases investigated. The limitations of LDA and GGA+U in predicting the equilibrium lattice constant and the proper band gap [30] poses problems in the description of the structural and electronic properties of the pristine and doped system. Thus, predicting the position of the impurity states, crucial for photocatalytic reasons, becomes only possible after extracting the appropriate *U* from experimental data.

## 4. C/N-substitutions

To compare and evaluate the structural changes induced by the impurities calculations on pure TiO<sub>2</sub> were done initially to obtain structural and electronic data that can be used as a reference.



**Fig. 1.** (a and b) shows the 48-atom supercell of TiO<sub>2</sub>. The large blue and the small red spheres represent the Ti and the O atoms. The orange numbered spheres (1–3) denote the positions of O substituted by the C and N dopants and the violet numbered spheres (4–5) notify the interstitial doping positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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