JRDN
Journal of Research and Development on Nanotechnology

First-principles Investigation on the Electronic Structures of *Anatase* TiO_2 codoped with Nitrogen and 3*d* Transition Metals

Ganes Shukri[ab]†, Hasna Afifah[a], Adhitya G. Saputro[ab], Hermawan K. Dipojono[ab]

Received
09 June 2021
Accepted
22 June 2021
Published
21 July 2021

DOI: 10.5614/jrdn.2021.1.1.16510

By means of first-principles density functional theory (DFT) calculations, we study the effect of introducing Nitrogen and 3*d* transition metals (*viz*., Cr, Mn, Fe, Co, Ni) as a pair of co-dopants to the electronic structure of *anatase* TiO_2. Herein, our attempt is to mapped the pattern of the impurity states emergence on the band structures and density of states of *anatase* TiO_2 for spesicif application such as photocatalysis water splitting. Based on the obtained results, TiO_2 codoped with (N,Co) or (N,Fe) pairs are expected to be more active and efficient photocatalyst compared to pristine *anatase* TiO_2 due to their synergistic effect of dopant pairs in lowering the overall anatase TiO_2 band gap and simultaneously hindering the possibility of early charge recombination.

Keywords: anatase TiO_2, transition metal, nitrogen, dopant, density functional theory.

Introduction

The significant increase in predicted global energy demands gives rise to the importance of the continuous availability of energy sources. The centuries-long dependence on fossil fuel has contributed not only to the depletion of world energy reserves but also to the environmental degradation caused by the emission of hazardous chemical compounds formed during fuel extraction and processing (Ali, Ahmad and Yusup, 2020). To achieve energy sustainability, it is imperative to develop new and renewable energy systems with highly abundant and environmentally friendly resources. Hydrogen-based fuel is considered as one of potential alternative to fossil fuel as hydrogen is plentiful in quantity with low pollutant emission (Hashimoto, Irie and Fujishima, 2005). However, hydrogen is only naturally available in the form of compounds, mostly as water (H_2O). Therefore, splitting water molecule to produce hydrogen has attracted huge academic and industrial interest as it offers cheap and clean energy source.

One of the most extensively researched method for water-splitting is through photocatalysis. Among several photocatalysts for water splitting application, TiO_2 is one that most commonly used as a benchmark material (Matsuoka *et al.*, 2007; Ni *et al.*, 2007). However, one significant drawback of TiO_2 is its wide band gap (i.e., ~3,23 eV) that limits its photocatalytic activity only under ultraviolet (UV) light irradiation range. Numerous approaches have been done in order to improve the catalytic activity of TiO_2 under visible light spectrum, such as through the addition of impurities using transition metals (Zhu *et al.*, 2006; Subramanian *et al.*, 2008; Dholam *et al.*, 2009; Eder, Motta and Windle, 2009), nonmetal elements (Di Valentin, Pacchioni and Selloni, 2005; G. Liu *et al.*, 2009; Wang *et al.*, 2009) or the combination of both (Higashimoto *et al.*, 2008; W. X. Liu *et al.*, 2009; Zhang *et al.*, 2010) and the use of organic dye (Mosconi, Selloni and De Angelis, 2012; Ünal *et al.*, 2014; Liu *et al.*, 2018).

In the present work, we systematically investigate the effect of introducing a pair of dopants consist of nonmetal element (i.e., Nitrogen) and 3*d* transition metals (i.e., Cr, Mn, Fe, Co Ni) to the electronic structure of *anatase* TiO_2. As have been mentioned in previous paragraph, previous works have indeed shown that Nitrogen and 3*d* transition metals are able to extend the optical response of TiO_2 into visible light range. Here we shed light onto the details of the electronic structure of the Nitrogen and 3*d* transition metal codoped TiO_2 and discuss their relation to the photoactivity of TiO_2

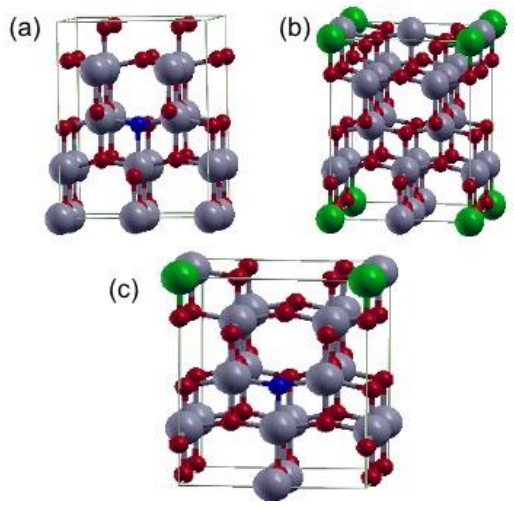

Figure 1. Structure of *anatase* TiO_2 with (a) Nitrogen dopant (blue ball), (b) 3*d* transition metal dopant (green ball) and (c) Nitrogen and 3*d* TM codopant. The grey and red balls represent Ti and O atom, respectively.

[a] *Research Group of Advanced Functional Materials, Faculty of Industrial Technology, Bandung Institute of Technology, Bandung 40132, West Java, Indonesia*
[b] *Research Centre for Nanoscience and Nanotechnology (RCNN), Bandung Institute of Technology, Bandung 40132, West Java, Indonesia*
* Corresponding author: ganes_tf07@itb.ac.id

Computational Details

We carried out density functional theory (DFT) calculations as implemented in the Quantum ESPRESSO package (Giannozzi *et al.*, 2009). Generalized gradient approximation of Perdew-Burke-Ernzerhoff (GGA-PBE) was used to describe the exchange interaction and electronic correlation (Perdew, Burke and Ernzerhof, 1996). To ensure the convergency of electronic total energy, we used 300 eV kinetic cut-off energy. Brillouin zone integrations were done by 3x3x3 k-points grid under the Monkhorst-Pack scheme. We used ultrasoft pseudopotentials to approximate the atomic core region. We modelled anatase TiO_2 bulk by 2x2x1 supercell containing 48 atoms (16 Ti and 32 O). To model the (co)doped anatase TiO_2, one Ti and one O were then replaced by one 3*d* transition metal (i.e., Cr, Mn, Fe, Co and Ni) and one Nitrogen, respectively (**Figure 1a-c**). Note that here we did not use any higher level functionals (e.g., LDA/GGA+*U*, Hybrid-DFT) to deal with the electronic structure calculations of co-doped TiO_2. We are aware that DFT/GGA tends to underestimate the electronic band gap of oxide semiconductors (Perdew *et al.*, 2017). However, in our present work the trends of the emergent impurity electronic states can still be qualitatively well described by our choice of functional. Hence, here we focused only on the results obtained by DFT/GGA.

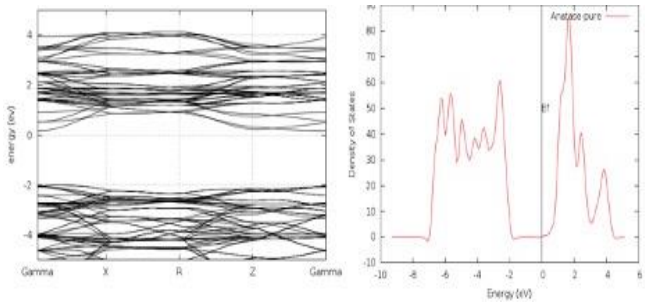

Figure 2. Electronic band structure (left) and Density of States (right) of pristine *anatase* TiO_2. The Fermi level is set at 0 eV.

Results and Discussion

Electronic Structure of Pristine and N-doped Anatase TiO_2

Firstly, we calculated the ground state electronic band structure of pristine anatase TiO_2 and its corresponding density of states (DOS) (**Figure 2)**. Our results show that anatase TiO_2 has an indirect electronic band gap of 2.3 eV. Analysis done on the DOS shows that the valence and conduction band of *anatase* TiO_2 are composed of O 2*p* and Ti 3*d* states, respectively (not shown in detail). In general, our result is consistent with previous DFT-GGA calculated band structure of *anatase* TiO_2 (Long *et al.*, 2006).

For the case of N-doped TiO_2 (hence $TiO_{1.94}N_{0.06}$), we observed two new impurity states: an empty N 2*p* shallow impurity state close to the valence band maximum (VBM) of O 2*p* state and another occupied N 2*p* state **(Figure 3)** . Previous studies have shown that N-doped TiO_2 is photocatalytically active under visible light irradiation (Long *et al.*, 2006; Wang *et al.*, 2009; Varley, Janotti and Van De Walle, 2011). Based on our result, the aforementioned result can be attributed to the emergence of the new impurity states of N 2*p*. This is also consistent to previous theoretical finding of N-doped TiO_2 (Long *et al.*, 2006; Varley, Janotti and Van De Walle, 2011). However, note that the shallow empty N 2*p* gap state can simultaneously act as a recombination centre that possibly limit the overall efficiency of N-doped *anatase* TiO_2 under visible light irradiation.

Electronic Structures of TM-doped Anatase TiO_2

We now turn to the case of 3*d* transition metal (TM = Cr, Mn, Fe, Co, Ni) doped *anatase* TiO_2. The band structures and DOS plots of TM-doped *anatase* TiO_2 are shown by **Figure 4a-4e**, respectively. Starting from the Cr-doped TiO_2 both the band structure and DOS show the emergence of localized 3*d* impurity states located at ~0.1 eV below the conduction band minimum (CBM) of TiO_2. It can be seen as well that some bands of the impurity state are occupied, and the other impurity states are unoccupied though they are located close to each other near the Fermi level. This finding indicates that Cr-doped TiO_2 can possibly activated under visible light irradiation while simultaneously increasing the electronic conductivity of the doped TiO_2 itself. The same qualitative finding can also be observed for Mn-doped TiO_2. As can be seen in **Fig 4b**, some localized Mn 3*d* impurity states are also observed within the band gap of TiO_2. However, notice that the Mn 3*d* impurity states are located deeper within the band gap (relative from the CBM) as compared to the Cr-doped case.

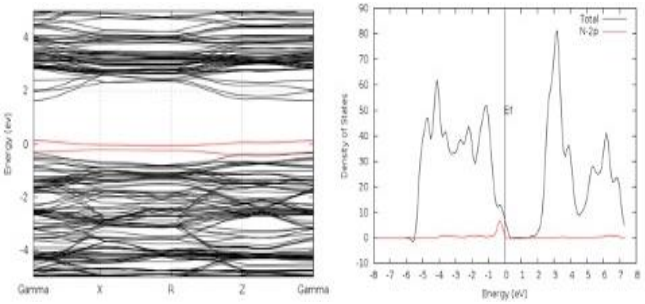

Figure 3. Electronic band structure (left) and Density of States (right) of Nitrogen doped TiO_2. The red line in the band structure and DOS plots represent the N 2*p* state. The Fermi level is set at 0 eV.

For the case of Fe-doped TiO_2 we observed some differences with the case of Cr-doped and Mn-doped cases. Notice that the Fe 3*d* impurity states are split into two different energy levels: the partially occupied ones that are located (localized) deep inside the band gap and the unoccupied states that are located closed the CBM of TiO_2. These states can be the possible reason of why Fe--doped TiO_2 is also photocatalytically active under uv-vis irradiation (Dholam *et al.*, 2009). The same qualitative features also can be observed for the case of Co- and Ni-doped TiO_2. Though, it can be seen that the unoccupied Co 3*d* impurity states are located relatively further from the CBM of TiO_2 as compared to Fe-doped

case. As for the case of Ni-doped TiO_2, different to the cases of Fe- and Co-doped, it can be seen that the lower-level Ni 3*d* impurity states are delocalized. Notice as well that the upper-level unoccupied Ni 3*d* impurity states are also located deep inside the band gap relative to the CBM of TiO_2. In general, our results suggest that the TM-doped TiO_2 introduces impurity states that mostly are located inside the band gap of TiO_2. While those states can possibly activate the optical response of TiO_2 under uv-vis irradiation the overall photocatalytic efficiency may possibly be low. This is because the localized impurity states induced by the TM dopant could serve as recombination centre (Long and English, 2011).

Electronic Structures of N, TM-codoped Anatase TiO_2

We now discuss the N, TM-codoped *anatase* TiO_2 cases. The band structure and DOS plots of N, TM-codoped *anatase* TiO_2 are shown by **Figure 5a-5e**. We first analyse the electronic band structure and DOS of N,Cr-codoped TiO_2 case (**Figure 5a**). Our results reveal that the impurity states closed to the VBM are dominated by the occupied N 2*p* states. This is different to the N-doped TiO_2 case where an unoccupied impurity N 2*p* state is observed. Meanwhile, notice as well that the Cr 3*d* impurity states are located deep inside the band gap and unoccupied. This is also different to the case of the Cr-doped TiO_2 case where some Cr 3*d* impurity states are initially occupied. Combining these finding we argue that Cr donates some negative charges to the Nitrogen, thus filling some N 2*p* states that are initially unoccupied to become occupied states. This is consistent with previous experimental result which observes strong coupling between N and Cr when both are introduced to TiO_2 as a pair of codopant (Kurtoglu *et al.*, 2011). The similar qualitative features are also in general observed for N,Mn-codoped case (**Figure 5b**). Though notice that for N,Mn-doped TiO_2 the unoccupied Mn 3*d* impurity states are located further from the CBM of TiO_2 as compared to the N,Cr-doped TiO_2.

For the N,Fe-case it can be seen that the Fe 3*d* states behave similar to the Fe-doped TiO_2 i.e., the Fe 3*d* states are split into two different energy levels (**Figure 5c**). The lower states are occupied and located closed the VBM of TiO_2 as well as the N 2*p* impurity states. The higher-level states are unoccupied and located close the CBM of TiO_2. This feature is also similarly observed for N,Co-codoped TiO_2 with the higher energy unoccupied Co 3*d* impurity states are slightly lower relative the CBM of TiO_2 compared to the N,Fe-codoped case (**Figure 5d**). However, notice that the two pairs of codopant do not produce any deep impurity states that may possibly act as recombination centre. Instead, the impurity states are mostly located closed to the VBM and CBM of TiO_2 which can effectively reduce the TiO_2 band gap. This reduction of band gap can possibly make the N,Co- and N,Fe-codoped TiO_2 systems as efficient photocatalyst (Wei, He and Cao, 2008; Liu *et al.*, 2013). As for the case of N,Ni-codoped TiO_2 , it can be observed that both the impurity states of Ni 2*p* and Ni 3*d* are located relatively closed to the VBM of TiO_2 with some Ni 3*d* are unoccupied states (**Figure 5e**). This combination of dopants can also possibly activate the optical response of TiO_2 under uv-vis irradiation (Sinhmar *et al.*, 2020). However, our result suggests that the unoccupied Ni 3*d* states within the band gap possibly act as recombination centre that may further reduce the overall efficiency of its photocatalytic activity.

Conclusion

By means of first-principles density functional theory (DFT) calculations, we have investigated the effect of Nitrogen (N), 3*d* transition metal (TM) and combination of N, TM dopants to the electronic structure of *anatase* TiO_2. Our results suggest that all dopants introduce impurity states inside the band gap of anatase TiO_2 that can extent the optical response of TiO_2 to the visible light range. However, our results further reveal that only N,Co and N,Fe pairs that do not show any deep impurity states inside the band gap of TiO_2 possibly hindering the early charge recombination phenomena. Thus, we conclude that N,Co- and N,Fe-codoped TiO_2 are two promising materials for photocatalytic material.

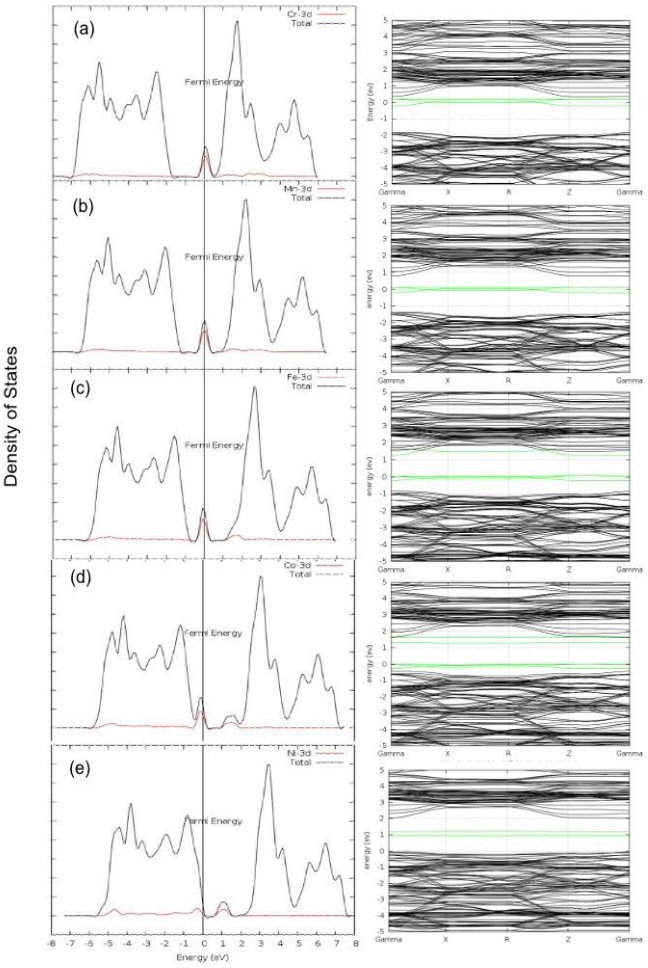

Figure 4. Electronic band structure (right) and Density of States (left) of (a) Cr-doped TiO_2, (b) Mn-doped TiO_2,(c) Fe-doped TiO_2, (d) Co-doped TiO_2 and (e) Ni-doped TiO_2. The red and green lines in the DOS and band structure represent the TM 3*d* impurity state. The Fermi level is set at 0 eV.

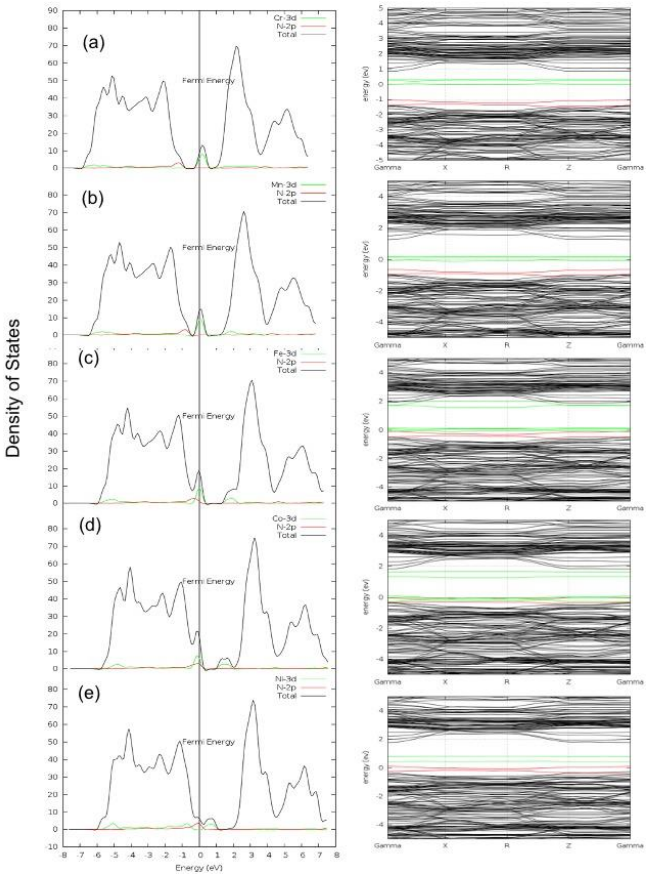

Figure 5. Electronic band structure (right) and Density of States (left) of (a) N,Cr-codoped TiO_2, (b) N,Mn-codoped TiO_2,(c) N,Fe-codoped TiO_2, (d) N,Co-codoped TiO_2 and (e) N,Ni-codoped TiO_2. The red and green lines in the DOS and band structure represent the N 2*p* and TM 3*d* impurity states, respectively. The Fermi level is set at 0 eV.

Conflict of Interest

We have no conflict to declare.

Acknowledgements

This research is supported by the Institut Teknologi Bandung under "Riset Peningkatan Kapasitas (RPK) 2020" scheme.

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