Theoretical Investigation for Neon Doping Effect on the Electronic Structure and Optical Properties of Rutile TiO$_2$ for Photocatalytic Applications by *Ab Initio* Calculations

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Abstract: *The non-metals doping as an anion to alternate the electronic structure and optical absorption property of TiO$_2$, and ultimately, to induce the visible light activity for it have been the purpose of this work. The electronic structure and optical properties of neon-doped rutile TiO$_2$ have been investigated by using the density functional theory with Slater type orbital basis set and correlation. This was done using the PBE96 method as implemented within the HyperChem 7.52 software package with Ne concentration approaching the low level may present in industrial samples of rutile TiO$_2$. Defect states involving substitution of an oxygen atom for a neon atom were studied along with the more stable configuration of one neon substitution. Neon changed the band structure and led to a reduce in the band gap in rutile. This means that neon doping brings the absorption edge into the visible range and therefore increase the photocatalytic activity. A stronger absorption for anionic Ne-doped TiO$_2$ one was predicted, because of the higher position of the impurity state in the band gap. The nonmetal- doped TiO$_2$ could efficiently extend the photo-response of TiO$_2$ to low energy (visible) region.*

Keywords: Rutile TiO$_2$, neon doping effect, ab initio, DFT, photocatalyst

1. INTRODUCTION

Titanium dioxide (TiO$_2$) is widely used as a pigment, catalyst support and photocatalyst.[1] TiO$_2$ crystallises in three different forms: rutile, anatase and brookite. Rutile and anatase are the two most stable forms and are both produced on an industrial scale. TiO$_2$ is a well-known photocatalyst because of its low cost, nontoxic peculiarities and stable, efficient performances in the depuration of air and water.[2] However, it is activated only under UV light irradiation (about 3% of the solar spectrum) because of its large band gap (3.2 and 3.0 eV for anatase and rutile respectively).[3] It is therefore imperative to develop efficient visible-light-driven photocatalysts by modifying TiO$_2$ which allows the main part of the solar spectrum (45%) to be used. Doping with transition metals is one of the methods to tailor the band gap of TiO$_2$, but this kind of doped TiO$_2$ generally has lower photocatalytic activity due to thermal instability and higher carrier recombination

rate.[4] Recently, nonmetal-doped TiO_2 received a lot of attention as the doping of the nonmetals (S, N, C, B, P, F, etc.) could efficiently extend the photo-response of TiO_2 to low energy (visible) region.[2–6] With recent increases in computational power, *Ab Initio* methods such as density-functional theory (DFT) and Hartree-Fock (HF) have become available. These calculations have been performed with DFT and the local-density approximation (LDA), and using the HF approach.[5–8] There have also been some self-consistent calculations that can be done using the linear muffin-tin orbital method, tight-binding models and the extended Huckel molecular-orbital method.

Commonly, as a two-element crystal, TiO_2 could provide three kinds of positions for the impurity to occupy on the O site, the Ti site and the interstitial site. The doping impurity usually displays as an anion on the O site and a cation on the Ti site. The present work will explore non-metals doping as an anion to alternate the electronic structure and optical absorption property of TiO_2, and ultimately, induce the visible its light activity.

The first aim of this paper is to investigate the influence that Ne doping has on the electronic structure of the rutile phase of TiO_2. The second is to understand an expected nature of the spectra of electronic excitations and the optical properties of Ne-doped TiO_2.

2.   EXPERIMENTAL (COMPUTATIONAL METHOD)

The density-functional theory is used throughout; this is widely used for a variety of crystal systems and has been successfully applied to TiO_2. Specifically, it has been used for investigating the impact of dopants on electronic structure. The generalised gradient approximation (GGA) as proposed by Perdew, Burke and Ernzerhof[9] (PBE96) was applied with the Slater type orbital STO-3G basis set.[10] Figure 1 shows the neon-doped/undoped rutile model. Most importantly, the band gap is due to basis-set truncation are therefore small compared to inherent errors associated with DFT. The significant underestimation of the band gap is a concern. However, it does seem to be well behaved, consistently underestimating the gap by 50%.[4] All calculations were performed using the HyperChem-7.52 for Windows Modeling System.[11]

a

b

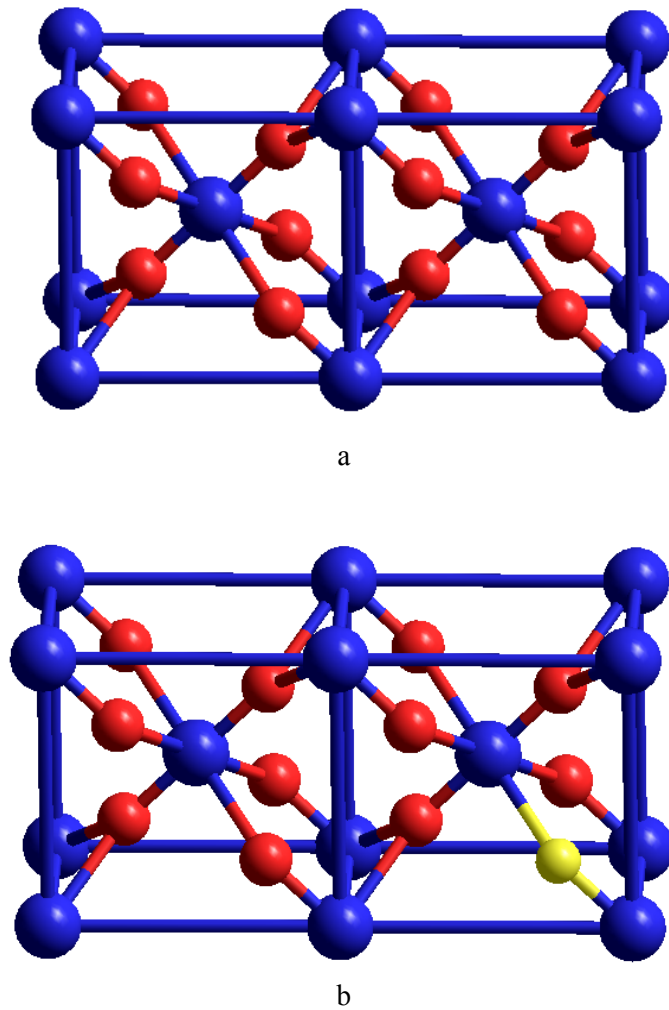Figure 1: Rutile model for a) undoped and b) Ne-doped.

3.   RESULTS AND DISCUSSIONS

Neon atom has ten electrons occupying closed shell $2P^6$ that make neon as an inert element. Based on this, neon is not an active atom and it does not share its electrons with another electronic system, so the neon atom has zero electronegativity. We calculate the eigen value of outer energy level $2P$ by using the PBE96/STO-3G method. The neon $2P$ energy state has the magnitude of –2.69 eV. The oxygen atom has an outer energy state $2P$ with an eigen value of

−3.45 eV, also the electronegativity of about 3.44. Under a compression between neon and oxygen atoms, it is clear that neon has a *2P* energy state [$E_{2P}(Ne)$] higher than this of oxygen atom [$E_{2P}(O)$] by an energy difference $E_d = E_{2P}(Ne) − E_{2P}(O)$ of about $E_d = 0.76$ eV, and beside a zero electronegativity neon atom will act differently to oxygen at TiO_2 system.

The electronic structure and visible/ultraviolet spectrum properties of neon-doped and undoped rutile TiO_2 are explored by the DFT method using PBE96/STO-3G level of theory. The electronic properties of valence band edge (VB), conduction band bottom (CB) and energy band gap (E_g) are showed in Table 1. Also the optical properties of first and second excited states wavelength (1st Ex and 2nd Ex) and their oscillator strength (OS) are displayed.

Table 1: Electronic and optical properties of undoped/neon-doped rutile TiO_2, VB, CB, and E_g in eV, Ex in nm and oscillator strength OS.

	VB	CB	E_g	1st Ex	1st OS	2nd Ex	2nd OS
TiO_2	−12.49	−11.30	1.19	388	0.083	288	0.016
Ne-doped	−13.14	−12.77	0.37	612	0.100	360	0.013

The VB of undoped TiO_2 is shifted for neon-doped TiO_2 toward lower energy by energy amount of 0.65 eV, which is close in magnitude to the energy difference between the neon and oxygen *2P* states (0.76 eV). At the other side, the CB of rutile shifted toward lower energy state by 1.47 eV when it doped with neon atom. The CB is lowered by double amount of E_d. The band gap of neon-doped rutile is narrow than that of pure rutile by 0.82 eV, which is very close to E_d.

All these changes in the electronic properties of rutile TiO_2 induced by neon substitution doping may be interpreted by understanding the difference in the electronic structure between the neon and oxygen atoms. Neon atoms will not be induced into midgap states as in the case of nitrogen or carbon atoms. Rather, they interact with the TiO_2 surrounding system to create a new electronic structure.

Pure rutile TiO_2 has the theoretical light absorption at UV range as well known experimentally. The first excited state has wavelength of 388 nm with an optical energy gap of 3.19 eV (experimental wavelength is 385 nm and with optical energy gap of 3.0 eV), so the PBE/STO3G method is very good level of theory to explore measured data. The optical properties of neon-doped TiO_2 describe the new electronic structure, which has a semiconductor response to the light absorption. The neon-doped system will absorb the visible light at 612 nm

of wavelength which has an optical energy gap of 2.02 eV, while the second excited state keeps the essential rutile UV absorption but with weak oscillator strength. Based on these results, the substitution doping of neon atom makes rutile TiO_2 a good photocatalyst material under a visible light.

4.   CONCLUSION

Electronic structure analysis shows that anionic doped Ne could induce visible light activity for rutile TiO_2 effectively by providing an impurity state on the upper edge of valence band. A stronger absorption for anionic Ne-doped TiO_2 was predicted, because of the higher position of the impurity state in the band gap, which is consistent with experiment results. The potential of anionic Ne-doped TiO_2 for visible light absorption indicates that it can be a good photocatalyst with visible light activity. Positive characteristics and performance of anionic Ne-doped TiO_2 can potentially make it a promising photocatalyst.

5.   ACKNOWLEDGEMENT

6.   REFERENCES

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