

Rational Selection of Transition Metal Co-Dopant in Sulfur-Doped Titanium Dioxide [†]

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Abstract: This paper investigates the general trend in structural, electronic, and optical properties of anatase TiO₂ photocatalysts co-doped with transition metals and sulfur. We attempt to rationalize co-dopant selection by employing molecular dynamics and density functional theory calculations. The structural properties of the first-row transition metal co-dopants were determined. TM-TiO₂ and TM/S-TiO₂ were structurally stable, with minimal changes in their lattice parameters, cell volume, density, and XRD profiles relative to pristine TiO₂. However, only Fe and Mn, among the first-row transition metals, are thermodynamically-favorable, i.e., their substitutional energies are lower relative to pristine TiO₂. Intermediate energy levels (IELs) are formed during transition metals and sulfur co-doping on TiO₂. In particular, Fe and Co form two IELs between the VBM and CBM, resulting in improved optical properties, especially in the visible-light region, mainly attributed to the unsaturated nonbonding transition metal d orbitals and the half-filled Ti–O bonding orbitals. On the other hand, Cu and Ni form three IELs close to each other due to the M–O anti-bond orbitals, half-filled p orbitals of S, and the Ti–S anti-bonding orbitals. These IELs in co-doped systems can serve as “stepping stones” for the photogenerated electrons, facilitating easier charge mobility. Among the investigated co-doped systems, Fe/S-TiO₂ was shown to be the most promising for photocatalytic applications.

Keywords: molecular dynamics; density functional theory; titanium dioxide; co-doping; photocatalysis

1. Introduction

Titanium dioxide, a widely-available metal oxide semiconductor, has been used by many researchers for various applications since the first reports of Fujishima and Honda [1] on UV-induced chemical reactions on its surface. Among its common uses are photocatalytic degradation of organics in water [2,3], treatment of volatile organic compounds (VOCs) in the air [4–6], and photoelectrochemical water splitting and hydrogen production [7–9], among others.

Despite the extensive use of titanium dioxide in literature, commercial applications are minimal due to various key challenges that remain unaddressed to be feasible for large-scale use. Among the issues identified based on a surface science perspective [10], the most important ones are bandgap engineering to alter the optical properties towards the visible light region, thus enabling solar-driven photocatalytic reactions and charge transport engineering to suppress, if not wholly arrest electron-hole recombination.

Doping titanium dioxide is the most popular method to narrow its bandgap. It involves the addition of one or more atoms, called the dopant, within the crystal lattice of titanium dioxide to intentionally alter its electronic and optical properties. Doping can

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either be substitutional or non-substitutional (interstitial and surface doping). Various dopants have been used and are generally categorized as cationic or anionic dopants.

Cationic doping is more widely studied; common cationic dopants are noble metals [11], transition metals [12], and rare earth metals [13]. Doping with a transition metal ion increases the formation of Ti^{3+} ions, enhancing photocatalytic activity. More Ti^{3+} states may cause more oxygen defects, facilitating efficient oxygen adsorption on the titania surface. The formation of O_2^- upon oxygen chemisorption requires a surface defect site which can be enhanced by transition metal ion doping. Since the redox energy states of many transition metal ions lie within the bandgap states of TiO_2 , substituting metal ions into the TiO_2 introduces an intraband state close to the CB or VB edge, inducing visible light absorption at sub-bandgap energies [14]. Previous first-principles calculations revealed that they introduce intermediate energy levels (IELs) that are previously absent in pristine TiO_2 due to the delocalization of $3d$ or $4d$ states of the transition metals and sometimes hybridization of these states with the Ti $3d$ and O $2p$ states, thus altering its electronic structure and improving its visible light absorption ability by narrowing the bandgap [15–17].

On the other hand, anionic dopants such as nitrogen [18], sulfur [19], and halogens [20,21] were also used to enhance visible light photocatalysis to extend the optical absorption edge of TiO_2 . Because anions are less electronegative than O, substitutional doping causes the anionic p -states to be pushed up out of the TiO_2 valence band into the bandgap [10]. For the case of nitrogen doping, the decrease in conduction band minimum (CBM) and the increase in valence band minimum (VBM) causes a narrower bandgap, the extent of which is dependent on the dopant concentration [22]. Nonmetal ion doping is a promising way to avoid the deteriorating thermal stability of the TiO_2 lattice [14].

Despite the effectiveness of doping in extending the photocatalytic range of TiO_2 to the visible light region, various factors should be considered to ensure that it will translate to the desired photoactivity. Issues on cationic doping, such as induced thermal instability and enhanced electron-hole recombination when the metals act as either photogenerated electron traps, such as in p-type doping, or photogenerated hole traps, such as in n-type doping, could be detrimental to the photocatalytic activity of TiO_2 [23]. In the case of anionic doping, post-processing annealing could lead to reduced dopant concentration [24].

Co-doping TiO_2 with two or more elements was done by some researchers [25–27] to address the concerns on individual cationic or anionic doping. The strong interaction between these dopants within the TiO_2 matrix alters the charge carrier transfer-recombination dynamics and shifts the bandgap absorption to the visible region. The coupling of one dopant with a second has been proposed to enable a reduction in the number of carrier recombination centers by the proposed charge equilibrium mechanism, as well as enhance the visible light absorbance by increasing the solubility limit of dopants [14]. In our previous work, we co-doped copper and sulfur to titanium dioxide and showed a significant increase in its photocatalytic activity when used to degrade organic pollutants in water [28].

Although co-doping a transition metal with S enhanced photocatalytic activity, selecting a co-dopant is not trivial. For example, what trends do the bandgap changes follow in the transition metal series? What criteria for selecting a transition metal for co-doping with S that will lead to an enhanced photoactive catalyst? A detailed analysis of the electronic structure change based on different co-doped transition metals with N could provide insight into the underlying physical origin of the photocatalytic activity. Therefore, this paper describes the investigation of the first-row transition metal series co-doped with S using molecular dynamics calculations (MD) and density functional theory (DFT) to elucidate the effect of co-doping on the structural and electronic properties of TM/S (TM represents first-row transition metals) co-doped TiO_2 to reveal the atomic relationship between the band structure and the origin of the enhanced photocatalytic activity.

2. Computational Details

TiO₂ exhibits three crystal phases, among which the anatase phase is the most photocatalytically active. Anatase TiO₂ has a tetragonal structure with a symmetry group of I4₁/AMD and lattice parameters of $a = b = 3.776 \text{ \AA}$ and $c = 9.486 \text{ \AA}$. Doping systems were constructed using a 48-atom anatase supercell with a $2 \times 2 \times 1$ repetition. The (TM, S) co-doped configurations were constructed by replacing one oxygen atom with a sulfur atom and a Ti atom with a TM atom. The atomic ratio of TM to Ti was 0.0625, close to the value used in many experimental studies. The supercell with co-doped TM and S is shown in Figure S1.

For the rational selection of co-dopants, molecular dynamics calculations were performed using the Forcite module of Materials Studio using the Universal forcefield (UFF). Geometry optimization of the supercells was done using a cascade of the steepest descent, adjusted basis set Newton-Raphson (ABNR), and quasi-Newton methods with the total energy, maximum force, maximum stress, and maximum displacement tolerance values set to $2 \times 10^{-5} \text{ eV}$ per atom, $0.001 \text{ eV \AA}^{-1}$, 0.001 GPa , and $1 \times 10^{-5} \text{ \AA}$, respectively. The Ewald summation method was used for the electrostatic and van der Waals interactions with an Ewald accuracy of $1 \times 10^{-5} \text{ eV}$.

Molecular dynamics calculations were then performed using the optimized supercells using the NPT ensemble at 298 K and 1 atm. Pressure and temperature control were achieved using the Berendsen barostat with a decay constant of 0.1 ps and the Nosé-Hoover thermostat with a Q ratio of 0.1, respectively. The simulation was allowed to proceed for 5 ns at a 1.0 fs timestep for 5 million steps; frames are saved every 100 steps. Again, the Ewald summation method was used for the electrostatic and van der Waals interactions with an Ewald accuracy of $1 \times 10^{-5} \text{ eV}$.

Spin-polarized DFT calculations were performed using the CASTEP module of Materials Studio with the GGA-PBE functional. Electron-ion interactions were modeled using ultrasoft pseudo-potentials in the Vanderbilt form. The wave functions of the valence electrons were expanded through a plane wave basis set to a cutoff energy of 400 eV. The Monkhorst-Pack scheme with a $4 \times 4 \times 3$ K-point grid generated k-points for reciprocal space sampling. The convergence threshold for self-consistent iterations was set to $5 \times 10^{-6} \text{ eV}$. In the geometry optimization process, the energy change, maximum force, maximum stress, and maximum displacement tolerance values were set to $2 \times 10^{-5} \text{ eV}$ per atom, 0.05 eV \AA^{-1} , 0.1 GPa , and 0.002 \AA , respectively.

Co-doping of S and a transition metal is expected to alter the oxidation states of Ti atoms surrounding the dopant. The oxidation state of the doped transition metal also depends on its local environment. As such, the DFT + U method was adopted to describe the strong on-site Coulomb repulsion. The DFT + U method has been employed to describe the electronic structures more accurately and strong on-site Coulomb repulsion among the localized transition metal 3d/4d electrons. The spherically averaged Hubbard parameter U describes the increase in energy caused by placing an extra electron at a particular site, and the parameter J (1 eV) represents the screened exchange energy. The effective Hubbard parameter, $U_{\text{eff}} = U - J$, which accounts for the on-site Coulomb repulsion for each affected orbital, is the only external parameter required in this approach. In this work, the corresponding transition metal oxide bandgap was used to determine the suitable Hubbard U parameters used in the calculations.

3. Results and Discussion

3.1. Transition Metal and Sulfur Co-Doped TiO₂: Insights from Molecular Dynamics

Transition metal co-doping of TiO₂ has been used to improve its optical properties to make visible-light-driven photocatalysis a reality. However, as mentioned previously, dopant selection is usually non-trivial. Investigating the effect of various dopants on the photocatalytic activity of TiO₂ is wasteful and experimentally time-consuming. Herein, we demonstrate the use of molecular dynamics calculations to rationalize the selection of

transition metals for co-doping with sulfur in TiO₂. MD simulation was done, and the time-averaged structural properties, i.e., lattice constants, density, and total energy, are tabulated in Tables S1 and S2 for both the TM-TiO₂ and TM/S-TiO₂, respectively. The periodic trend in these properties across the first-row transition metal series of the periodic table is shown in Figure S2.

In general, doping TiO₂ with TMs leads to an overall cell contraction except for Mn, where cell expansion was observed. For the case of TM/S-TiO₂, cell contraction occurred for all TM/S-TiO₂ except for Sc/S-TiO₂. It appears that transition metals can cause structural rearrangement of the cell, leading to volume changes. Meanwhile, an investigation of the cell density revealed that the density of TM-TiO₂ and TM/S-TiO₂ increases from left to right across the first-row transition metals. This may be due to the increasing atomic weight of the TMs coupled with decreasing cell volume across the periodic table. Analysis of the structural parameters showed that all TM-TiO₂ and TM/S-TiO₂ have a relative density difference within $\pm 3\%$ with respect to pristine TiO₂ and $\pm 3\%$ with respect to S-TiO₂, respectively. Moreover, all TM-TiO₂ and TM/S-TiO₂ have a relative cell volume change within $\pm 2\%$ with respect to pristine TiO₂ and S-TiO₂, respectively. This is good because we want to have only small changes in the structure of TiO₂ as it translates to the structural stability of the TM-TiO₂ and TM/S-TiO₂. In this discussion, we neglect the presence of titanium and oxygen vacancies, which have been reported to reduce the energy cost of incorporating the dopant into the host lattice.

To further investigate the structural character of the TM-TiO₂ and TM/S-TiO₂, their respective X-ray diffraction profiles were simulated using the Forcite Module of Materials Studio and are shown in Figure S3 for TM-TiO₂ and Figure S4 for TM/S-TiO₂. The degree of crystallinity for each system was estimated using the VAMP module of Materials Studio and is summarized in Table S3 for TM-TiO₂ and TM/S-TiO₂, respectively. According to the generated results, the XRD profiles of the TM-TiO₂ and TM/S-TiO₂ are not significantly different from that of pristine TiO₂. This is expected because, during substitutional doping, we are only replacing an atom/s with another atom/s, unlike in interstitial doping, where the dopants are distributed within the void spaces of the crystal. As such, it is highly unlikely for new XRD peaks to occur in substitutional doping because the appearance of new peaks occurs when the crystal is non-homogeneous, i.e., there are two or more crystal phases within the material of interest. The most prominent peak observed in the simulated XRD profile of pristine TiO₂ occurred at $2\theta = 25.5^\circ$, corresponding to the (101) plane of anatase. This is consistent with what we have observed experimentally. This is also the most catalytically-active surface of TiO₂ as shown in many studies in the literature. It was observed that doping causes a shift in the (101) plane peak to higher 2θ values by around $\pm 0.15^\circ$ for TM-TiO₂ and $\pm 0.10^\circ$ for TM/S-TiO₂ with corresponding changes in the peak intensity. This is expected because substituting the Ti atom with TM and O atom with the S atom causes structural rearrangement, breaking the crystal symmetry. This can potentially impact the properties and stability of TiO₂.

Substitutional doping involves the breakage and formation of bonds, which requires substitutional energy. This energy barrier should be overcome to synthesize the doped TiO₂ successfully. To understand how TM and TM/S doping affects the energetics of TiO₂ formation, the total energy of the TM-TiO₂ and TM/S-TiO₂ were plotted with varying TM. The results are shown in Figure S2e,f. In general, replacing an atom within the crystal is energetically unfavorable. Therefore, we want to have a dopant or co-dopant that can readily be incorporated within the crystal structure of TiO₂ so that thermodynamic constraints will not be an issue. Our results showed that among the first-row transition metals, only Mn and Fe are thermodynamically-favorable regarding substitutional doping into TiO₂. Mn and Fe can easily be incorporated into the anatase crystal structure without extreme conditions during their synthesis. This stabilization could be due to the formation of the closed-shell structure of these doped systems, which makes it unnecessary the generation of oxygen or titanium vacancies. This is crucial in reducing the formation of point defects during doping, which has beneficial effects with respect to the recombination rate

and, consequently, on the photocatalytic properties of the material [15]. Although other TM-TiO₂ and TM/S-TiO₂ are deemed energetically unfavorable based on our MD calculations, it doesn't necessarily mean that these structures cannot be obtained nor are not stable. These structures can be obtained at high temperatures, which provide the necessary driving force to overcome the energy barrier of TM-TiO₂ and TM/S-TiO₂ formation.

3.2. Late Transition Metal and Sulfur Co-doped TiO₂: Insights from Density Functional Theory

Based on the above discussion, we have shown that Mn/S-TiO₂ and Fe/S-TiO₂ are the most favorable structures among the first-row transition metal series. However, we still do not know whether these structures would result in enhanced photocatalytic activity under visible light illumination, which is the ultimate goal of materials scientists to make solar photocatalysis a reality.

As such, we also performed Density Functional Theory calculations to model the electronic structure and determine the optical properties of late TM/S-TiO₂ (TM = Fe, Co, Ni, Cu). For comparison, the band structure of the late TM-TiO₂ is shown in Figure S5, including that of S-TiO₂. Substitutional TM/S co-doping causes additional partially occupied S-2p states and TM-3d states in the band gap of TiO₂. Two distinct impurity energy levels (IELs) in the electronic structure were observed for Fe/S-TiO₂ and Co/S-TiO₂. The first IEL occurs just above the Fermi level at around 0.6–0.7 eV, followed by another IEL at around 1.5–2.3 eV. Fe/S-TiO₂ and Co/S-TiO₂ have widely-spaced IELs, which can be attributed to the bonding orbital of the Ti–O bonds next to the doped atom. These IELs can serve as “stepping stones” for absorbing low energy photons and promoting electrons from the highest occupied molecular orbital, i.e., the valence band, to the first IEL and then to the second IEL, and lastly to the lowest unoccupied molecular orbital, i.e., the conduction band.

On the other hand, three additional IELs were seen for Ni/S-TiO₂ and Cu/S-TiO₂. The first IEL occurs just above the Fermi level at around 0.6–0.8 eV, followed by another IEL at around 0.8–1.1 eV. The last IEL is seen at around 1.1 eV to 1.8 eV. Ni/S-TiO₂ and Cu/S-TiO₂ have closely-spaced IELs. Although these leads to significant bandgap reduction, these “concentrated” region of IELs may not effectively offer the advantage of “stepping stones” for the low-energy photons [29].

For Fe and Co, the IELs induced by dopants can be divided into two categories: (i) the unsaturated nonbonding d orbitals (mainly d_{xy} , d_{yz} , and d_{xz}) of the doped transition metal located below the CBM, and (iii) the bonding orbitals of Ti–O bond next to the doped transition metal, located close to the Fermi level. For the case of Ni and Cu, the IELs are divided into three parts: (i) states originated from the M–O anti-bonding orbitals, located right below the CBM; (ii) states originated from the S p_z orbital located in the middle of the gap region; and (iii) states originated from electron transfer induced S–Ti anti-bonding orbitals; located right above the Fermi level [15].

The optical absorption spectra of the late TM/S-TiO₂ were also determined from DFT calculations. As shown in Figure S6, pure anatase mainly absorbs light in the ultraviolet region. Upon introducing dopants, the absorption edges are shifted to the visible-light region. For TM/S-TiO₂, the optical spectra were altered, most especially for the case of Fe/S-TiO₂ and Co/S-TiO₂. This supports our hypothesis that distributed IELs between the bandgap of TiO₂ are more effective for absorbing photons than the concentrated IELs observed in Ni/S-TiO₂ and Cu/S-TiO₂. Again, in a TiO₂ system, co-doping transition metal and sulfur led to the formation of IELs between the VBM and CBM, which offer “stepping stones” for absorbing low energy photons and promoting electrons from VBM to the IELs, and then to the conduction band.

3.3. Rational Selection of Co-Dopants

Designing, fabricating, and tailoring the physicochemical and optical properties of TiO₂ is indispensable to utilizing a large fraction of the solar spectrum and realizing the

indoor applications of this photocatalyst [14]. Unfortunately, the selection of co-dopants is usually arbitrary—experimentalists just select a combination of dopants without clearly understanding why they might work. This is frustrating based on the point-of-view of materials scientists. As such, this paper tried to rationalize the selection of transition metal co-dopants by combining computational tools, specifically molecular dynamics and density functional theory, to guide the researchers in rationally selecting the appropriate co-dopants.

There are several factors that we must consider in the selection of a suitable co-dopant. First, co-doping TiO₂ should lead to a visible-light active photocatalyst. Hence, the resulting co-doped TiO₂ should have less than a 3.2 eV bandgap to be optically active under solar illumination. After performing DFT + U calculations, we have shown that co-doping TiO₂ with transition metals and sulfur leads to visible-light active photocatalysts. Second, the resulting photocatalyst should be structurally- and thermally stable. Upon performing molecular dynamics calculations, it was also shown that at low dopant levels considered in this study, the resulting co-doped systems are structurally-stable as evidenced by only small changes in the density, lattice constants, cell volume, and XRD profiles relative to that of pristine TiO₂. Third, substitutional co-doping should be thermodynamically-favorable, i.e., the substitutional energy of the co-doped systems should be lower than that of the pristine TiO₂ to enable its synthesis without requiring tremendous amounts of energy. Based on our molecular dynamics study, only iron and manganese are deemed energetically favorable among the transition metal choices.

A volcano plot is shown in Figure S7 to summarize our findings focusing on late-transition metals. Herein, we show that even though Cu/S-TiO₂ has the narrowest bandgap (thus the most photoactive among the late transition metal co-doped systems), it has a very high relative energy to that of pristine TiO₂. This means it might require severe conditions to overcome the thermodynamic energy barrier to synthesize this photocatalyst. Therefore, among the late transition metals, Fe/S-TiO₂ seems to be the most attractive choice among the co-doped systems because it is structurally stable, thermodynamically favorable, and visible-light active.

4. Conclusions

Herein, transition metal and sulfur co-doped TiO₂ were investigated to rationalize the selection of co-dopants for photocatalytic applications. Molecular dynamics calculations showed that TM-TiO₂ and TM/S-TiO₂ are structurally-stable with minimal changes in their lattice parameters, cell volume, density, and XRD profiles relative to pristine TiO₂. However, not all transition metals lead to thermodynamically-favorable doped and co-doped systems. Our calculations have shown that only iron and manganese, among the first-row transition metals, are thermodynamically-favorable, i.e., their substitutional energy is lower than pristine TiO₂. Further DFT + U calculations on late transition metals and sulfur co-doped TiO₂ revealed that intermediate energy levels (IELs) are formed during co-doping. For example, Fe and Co form two IELs between the VBM and CBM, improving optical properties, especially in the visible-light region. These IELs are mainly due to the unsaturated nonbonding transition metal *d* orbitals and the half-filled Ti–O bonding orbitals. On the other hand, Cu and Ni form three IELs close to each other due to the M–O anti-bond orbitals, half-filled *p* orbitals of S, and the Ti–S anti-bonding orbitals. These IELs in co-doped systems can serve as “stepping stones” where the photogenerated electrons can jump from the VBM to these IELs and then to the CBM. This facilitates easier charge mobility and thus possibly arrests electron-hole recombination, a major issue for semiconductor photocatalyst systems. Therefore, the location of these IELs was of paramount importance that affected the optical properties of the co-doped TiO₂. Among the investigated co-doped systems, Fe/S-TiO₂ was the most promising for various photocatalytic applications, such as solar photocatalysis, such as in pollutant degradation, water splitting, solar cells, and solar fuel production.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, **Figure S1:** Tetrahedral structure of (a) pristine TiO₂ and TM/S-TiO₂. Color coding: Ti = gray, O = red, S = yellow, and TM = purple; **Figure S2:** Calculated cell volume differences of (a) TM-doped TiO₂ relative to pristine TiO₂ and (b) TM/S co-doped TiO₂ relative to S-doped TiO₂; Calculated density differences of (c) TM-doped TiO₂ relative to pristine TiO₂ and (d) TM/S co-doped TiO₂ relative to S-doped TiO₂; and Calculated energy differences of (e) TM-doped TiO₂ relative to pristine TiO₂ and (f) TM/S co-doped TiO₂ relative to S-doped TiO₂; **Figure S3:** Simulated XRD profiles of various TM-doped TiO₂; **Figure S4:** Simulated XRD profiles of various TM/S co-doped TiO₂; **Figure S5:** Electronic structure of: (a) Fe/S-TiO₂, (b) Co/S-TiO₂, (c) Ni/S-TiO₂, (d) Cu/S-TiO₂, and (e) S-TiO₂; **Figure S6:** Optical absorption spectra of: (a) Fe/S-TiO₂, (b) Co/S-TiO₂, (c) Ni/S-TiO₂, (d) Cu/S-TiO₂, and (e) pristine TiO₂; **Figure S7:** Volcano plot of late transition metals and sulfur co-doped TiO₂; **Table S1:** Effect of various transition metals on the properties of TM-doped titanium dioxide; **Table S2:** Effect of various transition metals on the properties of TM/S co-doped titanium dioxide; **Table S3:** Effect of various transition metals on the crystallinity of TM-doped titanium dioxide; **Table S4:** Effect of various transition metals on the crystallinity of TM/S co-doped titanium dioxide.

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