

Article

Adsorption of CuSO₄ on Anatase TiO₂ (101) Surface: A DFT Study

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Abstract: The rapid growth of industrial activities has increased environmental pollution, and solar-driven heterogeneous photocatalysis using TiO₂ has emerged as a promising solution. However, its wide band gap limits its efficiency, prompting research into various optimization strategies. One of these approaches is surface functionalization. Thus, this study investigates the adsorption of CuSO₄ on the anatase TiO₂ (101) surface using density functional theory calculations. The adsorption process induced a magnetic moment of 0.97 μ_B and a slight reduction in overall bandwidth. A preferential adsorption geometry pattern with an energy of -4.31 eV was identified. Charge transfer analysis revealed a net transfer from the TiO₂ surface to the CuSO₄ molecule, with increased net atomic charges for atoms involved in new chemical bond formation, indicating a chemisorption process. These electronic structure modifications are expected to influence the electronic and catalytic properties of the material. The findings provide insights into the CuSO₄ adsorption mechanism on an anatase TiO₂ (101) surface and its impact on the properties of the material, contributing to a deeper understanding of this system.

Keywords: TiO₂ (101); CuSO₄; DFT + *U*; vdW; chemisorption; surface



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1. Introduction

The rapid growth of industrial activities and population has accelerated the dispersion of harmful chemicals into the environment, leading to the presence of persistent organic pollutants even in remote areas [1,2]. This global issue calls for cleaner, more sustainable production and consumption policies, along with the development of innovative technologies for air, soil, and water treatment [3].

In this sense, solar-driven heterogeneous photocatalysis is a promising and sustainable solution for removing organic and biological contaminants from water [4,5]. Among materials, titanium dioxide (TiO₂) is a key material in several high-technology applications, including photocatalysis, biomaterials, and novel photovoltaic solar cells [6–8]. Its use in photoelectrochemical processes is particularly crucial for enabling efficient large-scale solar electricity production, addressing the growing global need for sustainable energy.

TiO₂, particularly in its anatase phase, has proven to be a promising material due to its unique electronic and catalytic properties, making it suitable for applications in

photocatalysis, sensors, solar cells, and environmental remediation [9–11]. The anatase TiO_2 (101) surface is known for its high stability and favorable energetic properties [6,12,13]. Studies have demonstrated that the anatase TiO_2 (101) surface is the most energetically favorable and commonly observed surface in natural and synthetic anatase crystals [14,15]. By examining how different molecules interact with this surface, researchers can develop insights into improving TiO_2 -based materials for various applications [16,17].

However, the wide band gap of anatase-phase TiO_2 (3.2 eV) significantly constrains its photocatalytic efficiency under solar irradiation [18]. To address this limitation, researchers have explored various strategies, including doping [19], morphological engineering [20,21], surface functionalization [22], and synthesis of substoichiometric titanium oxides, specifically Magnéli phases [23,24]. Also, the formation of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterojunctions constitutes another effective strategy, which has been demonstrated to enhance photocatalytic performance by facilitating charge separation and extending light absorption capabilities [25]. These approaches aim to modulate the electronic structure and optical properties of TiO_2 , thereby enhancing its photocatalytic performance across a broader spectrum of light.

Photocatalysis is an advanced oxidation process (AOP) that facilitates the degradation of organic compounds by generating hydroxyl radicals ($\text{HO}\bullet$). Nevertheless, optimizing the efficiency of photocatalysts remains challenging, requiring extensive experimental testing, often based on trial-and-error methods.

Furthermore, the oxygen evolution reaction (OER) mechanism on the anatase (101) surface has been extensively studied, providing valuable insights into the surface reactivity and electron transfer processes involved in photocatalysis. For instance, Patra and Meyerstein [26] reported key aspects of this mechanism through analysis that complemented both experimental and theoretical studies, elucidating the role of anatase (101) in catalytic applications. In this context, computational simulation of molecular adsorption on metal oxide surfaces has emerged as a key tool for understanding catalytic and adsorption mechanisms. This study investigates the adsorption of the copper (II) (CuSO_4) molecule on the anatase (101) surface of TiO_2 using first-principles methods based on density functional theory (DFT).

To the best of our knowledge, no studies based on density functional theory (DFT) have specifically focused on the surface adsorption of this molecule on TiO_2 . Previous research has addressed other related aspects and has experimentally demonstrated that modifying TiO_2 with CuSO_4 (copper sulfate) significantly alters its electronic and catalytic properties [27]. In particular, CuSO_4 has been used as a dopant in TiO_2 with the aim of enhancing its photocatalytic activity under visible light irradiation, especially for the degradation of organic pollutants in water [28]. This line of research emerges from the need to develop more efficient, accessible, and environmentally sustainable catalysts and photocatalysts, both for the reduction of NO_x compounds in industrial emissions and for water pollutant treatment [29].

However, these studies lack an in-depth atomic-level analysis of charge redistribution, and the electronic mechanisms involved in the $\text{CuSO}_4/\text{TiO}_2$ interaction. Therefore, the present study aims to complement the experimental findings by providing a more detailed atomic-scale perspective on the adsorption process and the fundamental interactions governing the $\text{CuSO}_4/\text{TiO}_2$ system.

2. Results and Discussion

2.1. Pristine Surface

To model the anatase (101) TiO_2 surface a slab was constructed using a (3×3) 12-atom primitive unit cell, resulting in a periodic slab containing 144 atoms. The slab consists of

three trilayers, each containing upper and bottom layers of O atoms bonded with a middle layer of titanium atoms. Prior to adsorption, the uppermost trilayer was fully relaxed while the underlying layers were constrained to their bulk positions, as illustrated in Figure 1. The top trilayer was relaxed to capture adsorption-induced effects, while the bottom two trilayers were fixed to bulk positions, consistent with studies showing minimal subsurface relaxation influence [6,30]. Our calculated structural parameters demonstrate excellent agreement with both the experimental surface X-ray diffraction (SXRD) measurements and DFT values reported by Treacy et al. [31]. Specifically, our computed lattice parameters ($a = 10.26 \text{ \AA}$, $b = 3.71 \text{ \AA}$) closely match the SXRD measurements ($a = 10.23 \text{ \AA}$, $b = 3.79 \text{ \AA}$). The atomic displacements within the first trilayer, as illustrated in Figure 1 and quantified in Table 1, show strong concordance with the SXRD experimental data. The only notable exception is the O_2 atom, which exhibits a somewhat larger displacement in our calculations; however, this finding aligns with the DFT results obtained by Treacy et al. This structural consistency validates the robustness of our computational framework for modeling the anatase TiO_2 (101) surface.

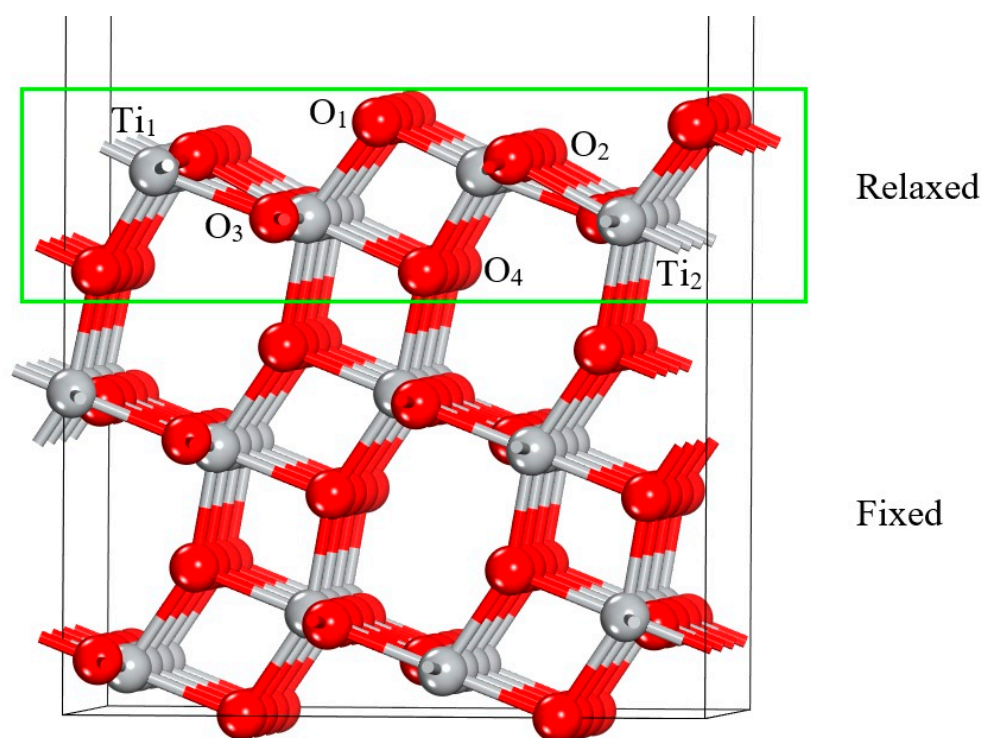


Figure 1. TiO_2 anatase (101) surface structure. Red and gray spheres represent O and Ti atoms.

Table 1. Atomic displacements in the first trilayer of anatase TiO_2 (101): comparison between our computational results, SXRD measurements, and DFT calculations reported by Treacy et al. [31].

Atom	Atomic Displacements ($\text{\AA}$)		
	SXRD	DFT	Present Work
O_1	0.07 ± 0.01	0.14	0.08
O_2	0.15 ± 0.01	0.33	0.39
O_3	0.08 ± 0.01	0.16	0.03
O_4	0.01 ± 0.01	0.07	0.04
Ti_1	0.03 ± 0.01	0.01	0.03
Ti_2	0.15 ± 0.01	0.28	0.15

The computed total density of states (DOS) of the pristine surface is presented in Figure 2. It can observe hybridization between O 2p and 3d states in the valence band (VB) with major contributions of O 2p states. In the case of the conduction band (CB), it is primarily constituted of Ti 3d states, with a small contribution from O 2p states. This composition is consistent with previous works [32,33].

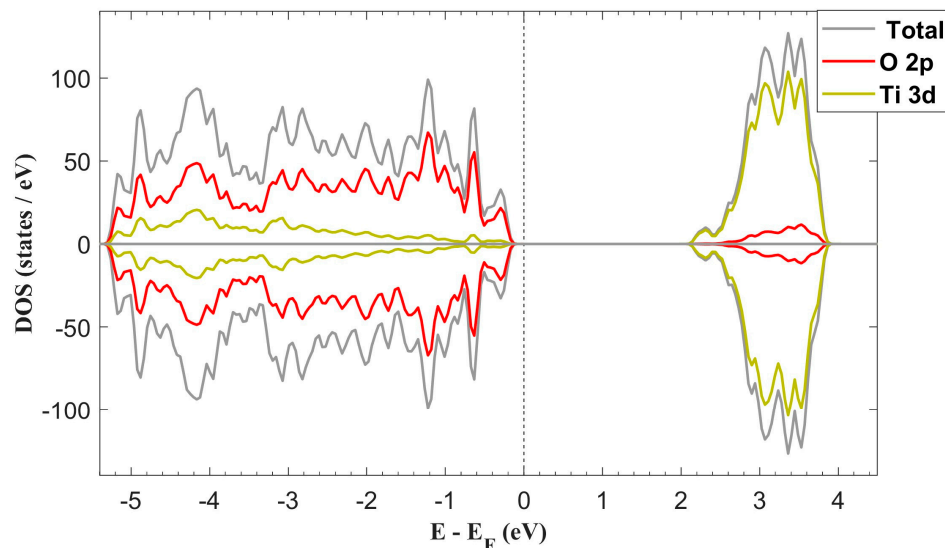


Figure 2. DFT + U total DOS and partial DOS (PDOS) of anatase TiO_2 (101) surface. The band-gap is 2.27 eV.

The computed band gap width was 2.05 eV, which is smaller than the well-established value of 3.2 eV for bulk anatase TiO_2 . This underestimation is a known limitation of DFT methodologies. To address this issue, we implemented the Generalized Gradient Approximation plus Hubbard U (GGA + U) approach with $U = 3.5$ eV. After introducing the U value of 3.5 eV for Ti, we observe only a modest improvement in the calculated band gap of the TiO_2 component, increasing from 2.05 eV to 2.27 eV, compared to the experimental band gap of ~ 3.2 eV for anatase TiO_2 . While larger U values could further widen the band gap to more closely match experimental findings, we retained $U = 3.5$ eV because it was previously optimized for TiO_2 systems and balances multiple properties critical to our study. Higher U values, although improving the band gap, tend to overestimate lattice parameters and distort the structural integrity of TiO_2 surfaces, negatively impacting the accuracy of adsorption energies and geometries for the $\text{TiO}_2 + \text{CuSO}_4$ system.

2.2. Free Molecule

The anhydrous form of CuSO_4 was selected to model the molecule, as it simplifies the adsorption study by avoiding the complexity introduced by hydration water molecules. This approach allows for a more direct evaluation of the interaction between CuSO_4 and the TiO_2 (101) surface, minimizing computational cost and focusing on the fundamental adsorption mechanisms, with its initial geometry based on the experimental crystallographic data reported by Wildner and Giester [34]. The free molecule was constructed by positioning it at the center of a $15 \times 15 \times 15 \text{ \AA}^3$ cubic supercell and subjecting it to full atomic relaxation. The optimized molecular structure is presented in Figure 3 and Table 2.

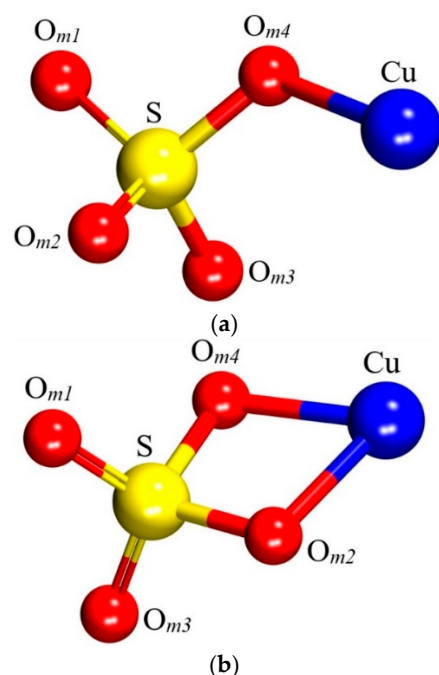


Figure 3. CuSO₄ molecule structure. (a) Experimental and (b) modeled.

Table 2. Interatomic distances and relevant angles of the CuSO₄ molecule comparing the experimental [34] and the modeled structures.

Distance (Å)			Angle (°)		
Atoms	Exp.	Modeled	Atoms	Exp.	Modeled
S–O _{m1}	1.46	1.44	S–O _{m4} –Cu	123.44	94.04
S–O _{m2}	1.46	1.60	O _{m1} –S–O _{m3}	110.52	119.39
S–O _{m3}	1.46	1.44			
S–O _{m4}	1.52	1.60			
Cu–O _{m4}	2.04	1.85			
Cu–O _{m3}	3.71	3.46			
Cu–O _{m2}	3.25	1.85			
Cu–O _{m1}	4.33	3.51			

The atomic relaxation within this model led to the approximation of Cu and its nearest O atom, designated as O_{m2}. Prior to optimization, these atoms were separated by 3.25 Å, and afterwards, the distance is found to be 1.85 Å, indicating significant structural relaxation. The initial geometry of the CuSO₄ molecule was derived from the bulk crystalline structure of chalcocyanite (CuSO₄). In this bulk structure, the Cu–O distances within the CuSO₄ unit, such as the 3.25 Å separation noted here, reflect the influence of the crystalline environment, including coordination with oxygen atoms from adjacent units.

For this study, a single CuSO₄ unit was extracted from chalcocyanite and placed in a large cubic simulation cell (15 × 15 × 15 Å³) to model the free molecule in a gas-phase environment, devoid of periodic lattice effects. During optimization, the Cu–O distance contracted to 1.85 Å, consistent with the expected adjustment to an isolated molecule, where the absence of bulk coordination allows for shorter, energetically favorable bonds. This transition from the bulk-derived starting geometry to the relaxed gas-phase structure underscores the impact of the local environment on the structural parameters of the molecule, aligning with our objective to investigate the properties of free CuSO₄.

2.3. Adsorption on Anatase TiO₂ (101) Surface

The anatase phase of TiO₂ is widely recognized as the most prevalent form in photovoltaic applications [35], with the (101) surface being particularly significant due to its thermodynamic stability [36]. Consequently, this study employs the anatase TiO₂ (101) surface as the substrate for investigating the adsorption behavior of CuSO₄.

To determine the optimal adsorption geometry of CuSO₄ on the anatase TiO₂ (101) surface, seven distinct initial orientations of the CuSO₄ molecule were systematically explored, each positioned over different adsorption sites on the surface. These initial configurations are illustrated in Figure 4.

Following the initial placement of the CuSO₄ molecule, a comprehensive atomic relaxation was performed. This optimization procedure was conducted without imposing any constraints on the atomic displacements of both the adsorbed molecule and the atoms within the uppermost trilayer of the TiO₂ surface. Upon completion of the geometry optimization, the adsorption energy (E_{ads}) for each configuration was calculated using the following equation:

$$E_{ads} = E_{(surf+mol)} - E_{(surf)} - E_{free(mol)}$$

where $E_{(surf+mol)}$ refers to energy of the surface with the adsorbate, and $E_{(surf)}$ is the energy of the pristine surface while $E_{free(mol)}$ represents the energy of the free molecule. Computed adsorption energies are shown in Table 3.

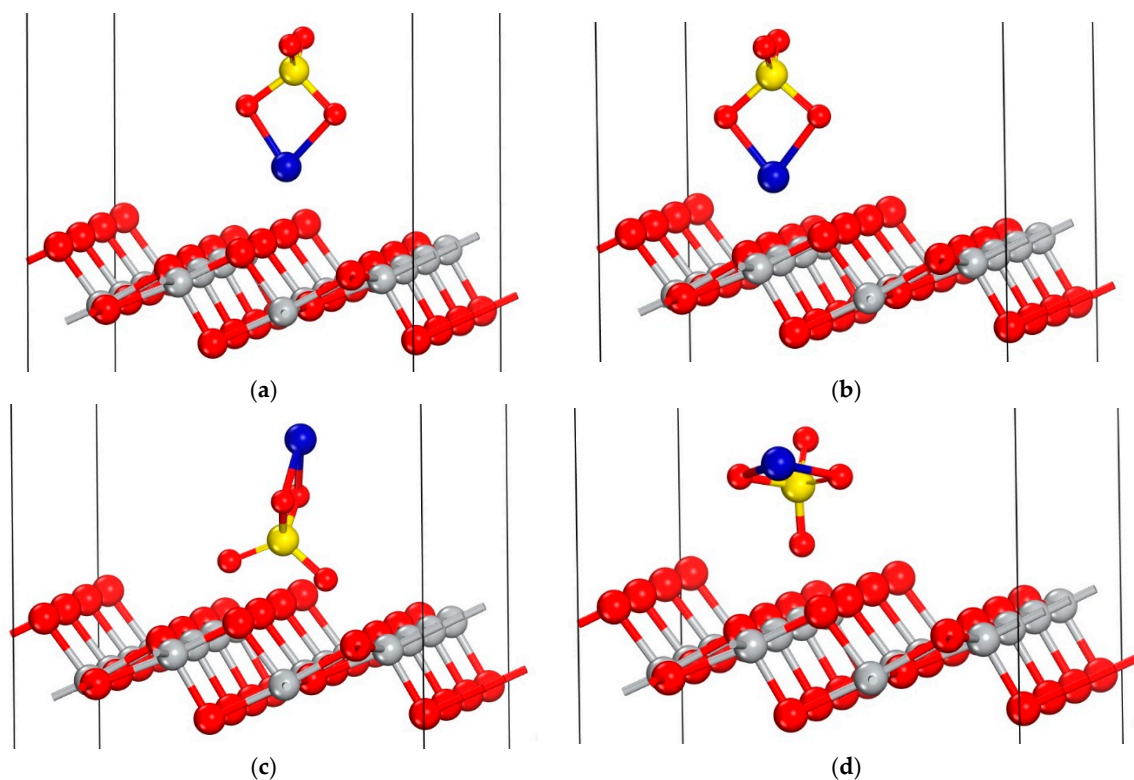


Figure 4. Cont.

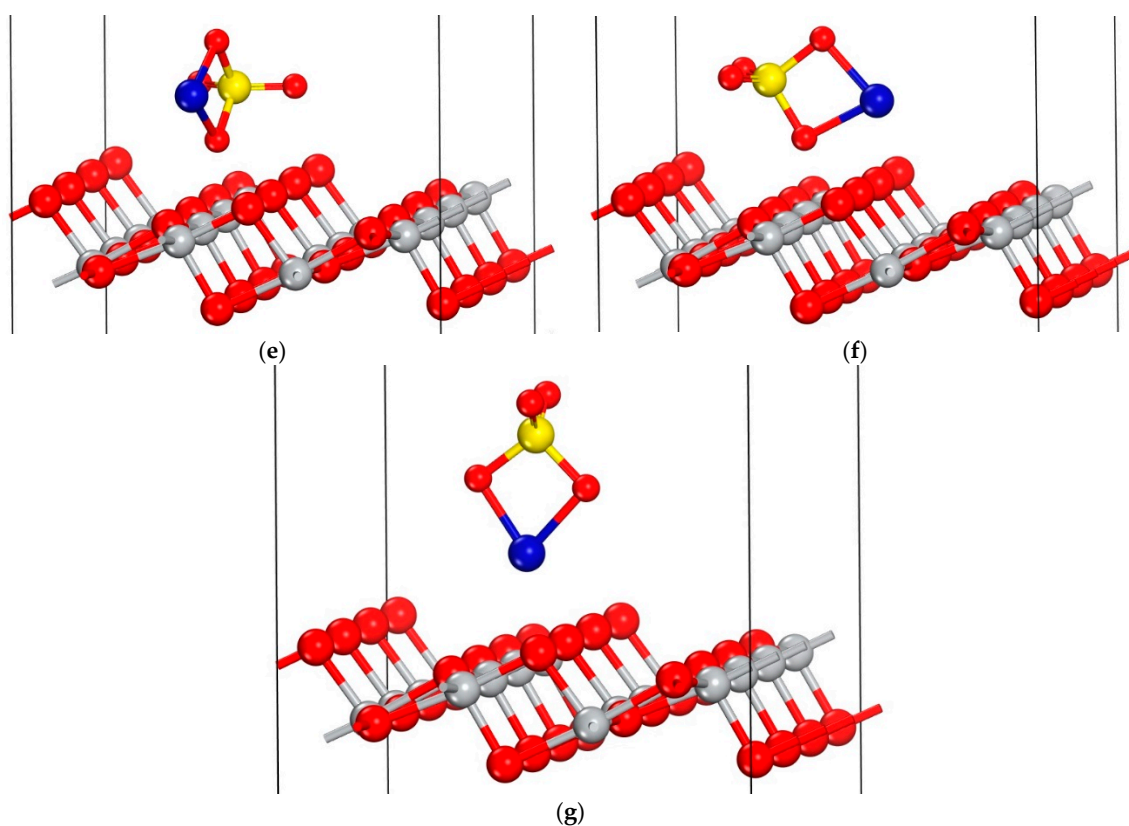


Figure 4. Illustrations (a–g) show the initial adsorption structures of the CuSO_4 on the anatase TiO_2 (101) surface, prior geometry optimization. Atoms are represented by colored spheres: Cu (blue), S (yellow), O (red), and Ti (gray). For clarity, only the uppermost atoms of the TiO_2 surface are displayed.

Table 3. Computed adsorption energies.

Configuration	E_{ads} (eV)
a	−2.06
b	−4.31
c	−1.25
d	−4.31
e	−4.00
f	−4.31
g	−2.67

As can be observed in Table 3, configurations that achieved the lowest adsorption energies are b, d, and f, all of which reach an identical adsorption structure after full geometric optimization. These configurations converge to the same final structure, reinforcing the robustness of the adsorption process. The second most favorable configuration was e, which is depicted in Figure 5.

However, the adsorption geometry with the lowest adsorption energy corresponds to configurations b, d, and f, which has been selected for further analysis due to its higher likelihood of occurrence. Its structure closely resembles configuration e, as is illustrated in Figure 6.

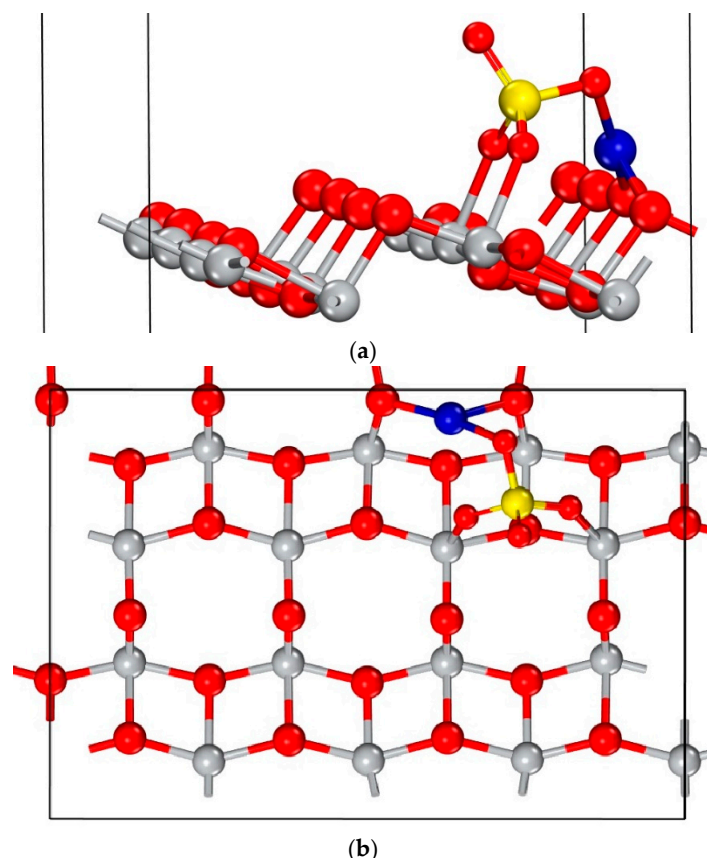


Figure 5. Adsorption geometry of configuration e: (a) side and (b) top views. The blue, yellow, red, and gray spheres represent atoms of Cu, S, O, and Ti, respectively.

Figure 6 illustrates the resulting structure of the adsorption process, highlighting the formation of bonds between the molecule and the surface, which indicates a chemisorption mechanism. Notably, the molecule binds to the surface through its oxygen and copper atoms. This interaction significantly alters the geometry of both the molecule and the uppermost surface layers, inducing atomic displacements in these regions. To quantify these changes, the interatomic distances and angles of the atoms labeled in Figure 6b were measured and are presented in Table 4. The newly formed bonds are between O_{m1} and O_{m3} of the molecule with Ti_1 and Ti_2 on the surface, while the Cu atom interacts with surface oxygen atoms O_1 , O_2 , and O_3 . As a result of this process, the surface atoms tend to displace toward the molecule, predominantly in the upwards direction. Ti_1 and Ti_2 move about 0.13 Å, while O_1 and O_3 show a minor displacement of 0.03 Å. O_2 , located in a deeper layer, experiences a more significant displacement of 0.21 Å.

The bond length between the O_1 and O_2 atoms with the Cu atom is 1.94 Å which is consistent with the 1.95 Å observed in the monoclinic crystal structure of Copper (II) oxide (CuO) [37]. In the case of O_m –Ti bonds measure 2.02 Å, which is close to the experimental within the bulk of 1.98 Å (Table 4) [38].

Atomic charges were calculated using Bader population analysis [39]. Table 5 presents the atomic charge redistribution upon CuSO₄ adsorption onto the TiO₂ surface. While initial observations suggest an increase in the atomic charge for Cu and variations in O and S, a detailed analysis indicates that these changes do not necessarily imply purely ionic bonding.

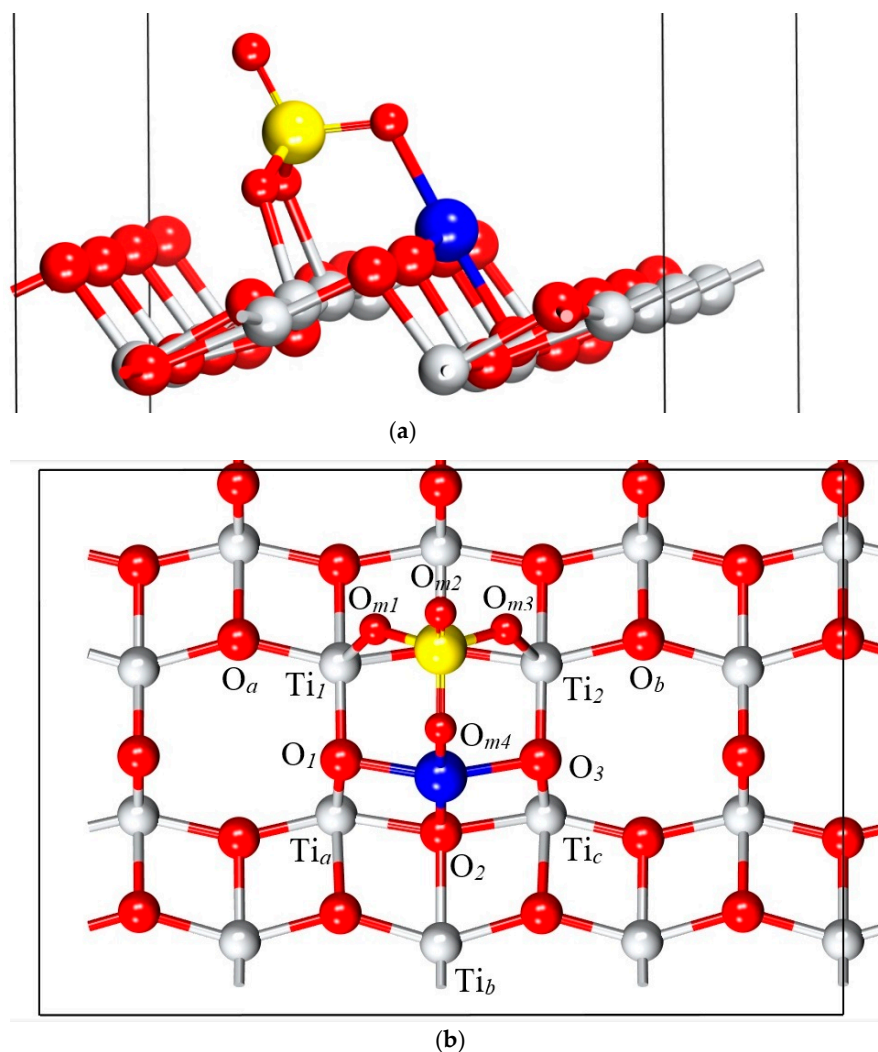


Figure 6. Most favorable adsorption geometry of CuSO_4 on the anatase TiO_2 (101) surface: (a) side and (b) top views. The blue, yellow, red, and white spheres represent atoms of Cu, S, O, and Ti, respectively.

The Cu atom exhibits a slight charge increase from $+1.00 e$ to $+1.14 e$, suggesting partial electron density transfer rather than full charge donation. Similarly, the oxygen atoms (O_{m1} and O_{m3}) experience marginal changes, which are insufficient to confirm a purely ionic character. The sulfur atom retains a high positive charge of $+3.77 e$, aligning more closely with covalent bonding rather than full ionic separation.

To further clarify the bonding nature, the Electron Localization Function (ELF) (Figure 7) reveals that the Cu–O interactions exhibit a predominantly polar covalent nature, while the O–Ti interactions demonstrate a mixed ionic–covalent character. The ELF values (0.47–0.50 for Cu–O, 0.85–0.87 for O–Ti) confirm that these bonds cannot be classified as purely ionic.

Table 4. Interatomic distances and relevant angles for the pristine surface and the surface with the adsorbate. Atoms labels adhere to the notation established in Figure 6b.

Bond Length (Å)			Angle (°)		
Atoms	Free Molecule	Adsorbed Molecule	Atoms	Free Molecule	Adsorbed Molecule
S–O _{m1}	1.45	1.53	Ti ₁ –O _{m1} –S	-	132.57
S–O _{m2}	1.57	1.42	S–O _{m3} –Ti ₂	-	132.62
S–O _{m3}	1.45	1.53	S–O _{m4} –Cu	93.82	112.29
S–O _{m4}	1.57	1.51	O _{m1} –S–O _{m3}	116.04	107.58
Cu–O _{m4}	1.91	1.92			
Atoms	Pristine Surface	Adsorbed Molecule	Atoms	Pristine Surface	Adsorbed Molecule
O _{m1} –Ti ₁	-	2.02	O _a –Ti ₁ –O _{m1}	-	102.16
O _{m3} –Ti ₂	-	2.02	O _{m3} –Ti ₂ –O _b	-	102.24
Ti ₁ –O _a	1.98	1.97	Ti ₁ –O ₁ –Ti _a	100.96	101.53
Ti ₂ –O _b	1.98	1.97	Ti ₂ –O ₃ –Ti _c	100.96	101.52
Cu–O ₁	-	1.94	Ti _a –O ₂ –Ti _c	155.23	152.98
Cu–O ₂	-	2.02	Cu–O ₂ –Ti _b	-	108.19
Cu–O ₃	-	1.94			
O ₁ –Ti _a	1.94	1.96			
O ₂ –Ti _b	2.06	2.16			
O ₃ –Ti _c	1.94	1.96			

Table 5. Atomic charges of the atoms labeled in Figure 6b.

Atomic Charge (e)		
Atom	Free Molecule	Adsorbed Molecule
Cu	1.00	1.14
S	3.58	3.77
O _{m1}	−1.27	−1.26
O _{m2}	−1.00	−1.27
O _{m3}	−1.27	−1.26
O _{m4}	−1.04	−1.23
Atom	Pristine Surface	Adsorbed Molecule
Ti ₁	2.26	2.32
Ti ₂	2.26	2.32
Ti _a	2.30	2.30
Ti _b	2.26	2.24
Ti _c	2.30	2.30
O ₁	−1.03	−1.09
O ₂	−1.18	−1.23
O ₃	−1.03	−1.09
O _a	−1.20	−1.19
O _b	−1.20	−1.19

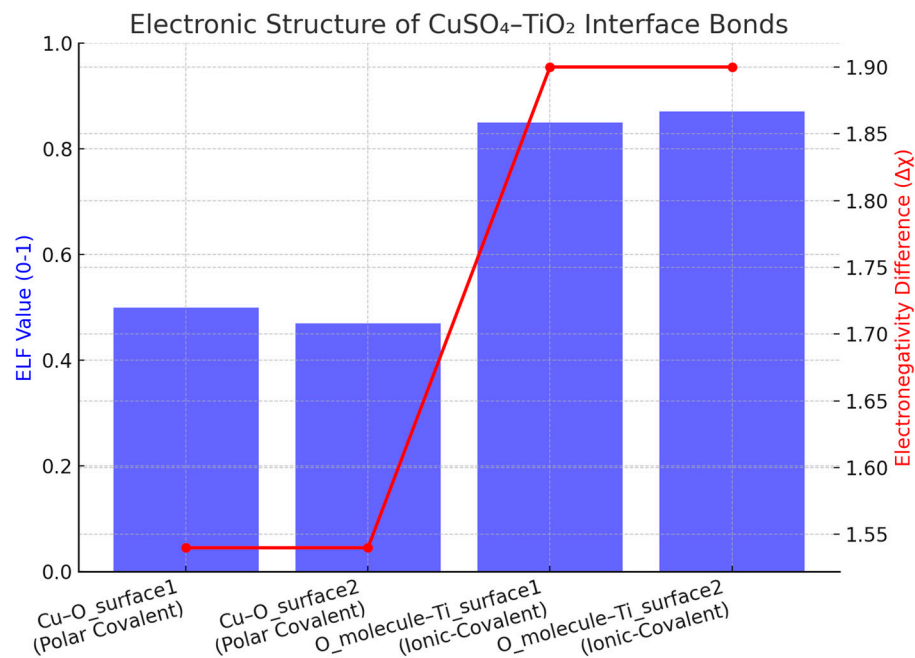


Figure 7. The bar chart represents the ELF values for different bonding interactions at the CuSO₄–TiO₂ interface. The blue bars indicate ELF values, where Cu–O bonds exhibit moderate electron localization (polar covalent nature), while O–Ti bonds display higher ELF values, supporting an ionic–covalent character. The red line represents the trend of ELF variations across different bonding types.

Additionally, bond length data (Table 6) and electronegativity difference comparisons (Table 7) [40], alongside Figure 8, demonstrate significant electron density redistribution, reinforcing the presence of both covalent and ionic contributions. Additionally, S–O interactions within the CuSO₄ molecule exhibit predominantly covalent character, as evidenced by ELF values (0.78–0.80) and an electronegativity difference of 0.86, consistent with the observed structural stability (Table 6). Therefore, the bonding nature at the interface is best described as a combination of polar covalent and ionic–covalent interactions.

Table 6. Bond length analysis: structural stability and bonding nature.

Bond	Covalent Radius (Å) Atom 1	Covalent Radius (Å) Atom 2	Expected Covalent Length (Å)	Observed Distance (Å)	Interpretation
Cu–O _{surface}	1.22 (Cu)	0.64 (O)	1.86	1.94	Covalent, slightly elongated
O _m –Ti	0.64 (O)	1.48 (Ti)	2.12	2.34	Partial ionic character
S–O _m	1.04 (S)	0.64 (O)	1.68	1.72	Very close to covalent

Table 7. Electronegativity differences support hybrid bonding model.

Bond	Electronegativity Atom 1	Electronegativity Atom 2	Δχ	Predicted Bond Type
Cu–O _{surface}	1.90 (Cu)	3.44 (O)	1.54	Polar Covalent
O _m –Ti	3.44 (O)	1.54 (Ti)	1.90	Ionic-Covalent
S–O _m	2.58 (S)	3.44 (O)	0.86	Predominantly Covalent

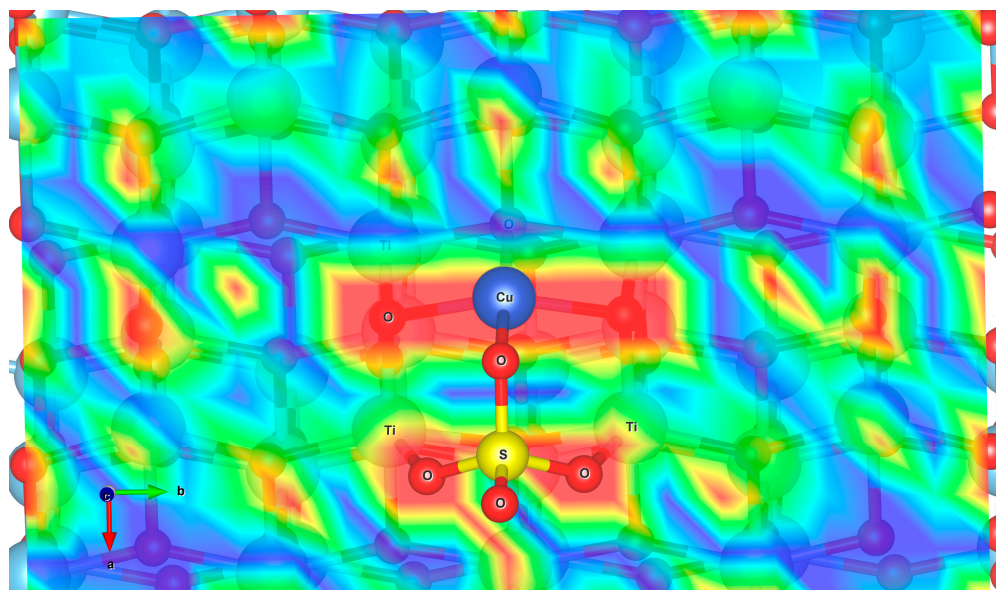


Figure 8. ELF map across the $\text{CuSO}_4\text{-TiO}_2$ interface. Red and yellow regions indicate high ELF values (≥ 0.78), confirming strong covalent bonding, as seen in the S–O interactions (ELF $\sim 0.78\text{--}0.80$). Green regions around the Cu–O bonds suggest moderate electron localization (ELF $\sim 0.47\text{--}0.50$), characteristic of polar covalent interactions. The blue regions surrounding the O–Ti bonds indicate a mixed ionic–covalent interaction.

The computed DOS of the system with the adsorbed molecule is presented in Figure 9. Analysis of these data reveals a band gap width of 2.19 eV, which is narrower than the 2.27 eV observed for the pristine surface. Regarding the band's composition, it can be noticed that the VB exhibits some minor presence of O 2p and Cu 3d states from the molecule. Sulfur states are also present at deep energy levels within the VB, but their intensity is very small and thus not distinguishable in the graph.

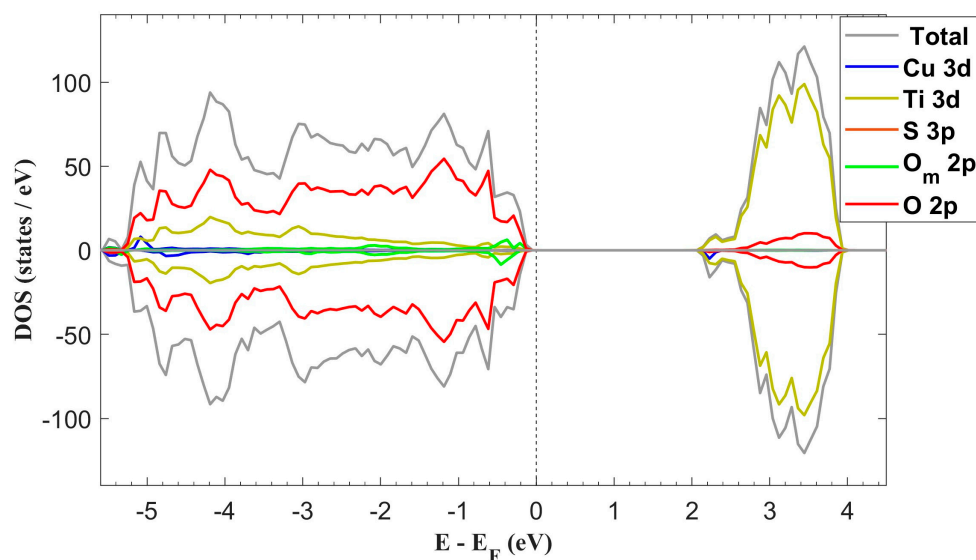


Figure 9. Total DOS and partial DOS (PDOS) of anatase TiO_2 (101) surface with one adsorbed molecule. The corresponding band gap width is 2.19 eV.

The DOS exhibits asymmetrical contributions from the molecular atomic states, indicating the presence of a magnetic moment within the system. The isolated CuSO_4 molecule exhibits a total magnetic moment of $0.90 \mu\text{B}$ prior to adsorption, consistent with the $\text{Cu}^{2+} d^9$ electronic configuration. This moment is primarily distributed among the Cu atom ($0.42 \mu\text{B}$,

predominantly from $3d$ states) and two oxygen atoms (O_{m2} and O_{m4} , each contributing $0.23 \mu_B$, mainly from $2p$ states). Following adsorption, the total magnetic moment of the combined system (molecule and surface) increases to $0.97 \mu_B$. An analysis of the spin density distribution reveals that the Cu $3d$ states contribute $0.72 \mu_B$ to this moment, while the Ti $3d$ and O $2p$ states contribute $0.02 \mu_B$ and $0.23 \mu_B$, respectively, indicating electronic redistribution at the molecule–surface interface.

The induced magnetic moment coupled with band gap narrowing, could alter the optical absorption properties of the material and potentially enhance the catalytic performance. This phenomenon aligns with previous experimental observations, including the favorable influence of CuSO_4 on the catalytic activity observed in [27] and the reported photoexcitation under blue light irradiation [28]. While these studies attribute enhanced activity to the formation of intermediate energy levels within the band gap, our computational analysis suggests that the effect primarily originates from band gap narrowing.

3. Computational Details

The present work was conducted using the Vienna ab initio Simulation Package (VASP) version 6.1.2, a computational framework that implements first-principles methods including DFT, Density Functional Perturbation Theory (DFPT), and various many-body approaches [41,42]. While VASP supports multiple theoretical frameworks such as Hartree–Fock (HF), hybrid functionals, and Green’s function-based methods (GW, BSE), our calculations specifically employed the Generalized Gradient Approximation (GGA) [43]. This choice of functional balances computational efficiency with sufficient accuracy for describing the electron exchange–correlation interactions in our system, though VASP also accommodates more computationally intensive approaches such as hybrid functionals and meta-GGA methods. In this approach, the valence electronic states are represented using a set of periodic plane waves, and the interaction between core and valence electrons is implemented through the projector augmented wave (PAW) method [44]. The Perdew–Burke–Ernzerhof (PBE) [45] parameterized GGA functionals are used to describe the exchange–correlation interaction. The valence configuration employed in our calculations for each atom is as follows: $3p^6 3d^2 4s^2$ for Ti, $3d^{10} 4s^1 4p^6$ for Cu, $2s^2 2p^4$ for O, and $3s^2 3p^4$ for S. Additionally, to account for the strong correlation between d electrons, an intra-site Coulomb repulsion U -term was included in the calculations, specifically, the rotationally invariant (Dudarev) approach to the GGA + U , [46] resulting in the so-called DFT + U method [47]. The utilized U parameters values chosen based on prior optimizations in the literature were 3.5 eV for the Ti atom [48] and 7 eV for the Cu atom [49]. For Ti, $U = 3.5$ eV was adopted from studies of bulk TiO_2 (anatase and rutile) [48] and molecular adsorption on anatase (101) [6] and rutile (110) [7] surfaces, where it was shown to effectively balance electronic properties, such as the band gap, with structural accuracy using the same PAW–PBE pseudopotentials. The U value of 7 eV for Cu, sourced from ref. [49] for CuO , was adopted based on the similar Cu^{2+} (d^9) electronic configuration and oxygen coordination environment in both systems. This approach is justified as the Hubbard correction primarily addresses intra-atomic correlation effects of the Cu $3d$ electrons, which are comparable between these compounds despite their structural differences. Furthermore, spin-polarized calculations within the DFT + U framework were applied throughout the study.

GGA and hybrid functionals have limitations in accurately capturing long-range electron correlations necessary for modeling van der Waals (dispersive) forces. This shortcoming arises because these functionals approximate the exchange–correlation energy based on local or semi-local density gradients and, in the case of hybrid functionals, include a portion of non-local Hartree–Fock exchange [50]. However, they do not inherently account for long-range dispersive interactions, which are essential for accurately modeling

adsorption processes. To address this, we have employed the DFT-D3 dispersion correction method developed by Grimme, which includes a Becke–Johnson damping function [51,52]. This method enhances the accuracy of our adsorption studies by incorporating van der Waals interactions.

This study employed precision settings of VASP (PREC = Accurate) and a cut-off kinetic energy of 550 eV (ENCUT = 550) which was determined by converging the total energy to less than 1 meV/atom. The Brillouin zone sampling was performed using a Γ -centered Monkhorst–Pack (MP) scheme [53]. A $3 \times 2 \times 1$ k-point mesh was used for structural optimization of the 144-atom periodic slab, while a higher-resolution $7 \times 5 \times 1$ mesh was implemented for subsequent static calculation to compute properties. To prevent artificial interactions between periodic slabs, a vacuum space of 20 Å and dipole correction were applied [54,55].

Atomic charges were evaluated using the Bader charge partitioning scheme [39], which decomposes the total electronic charge density into contributions associated with individual atoms based on zero-flux surfaces. This method was applied consistently to the free CuSO₄ molecule, the pristine TiO₂ (101) surface, and the adsorbed system, enabling a robust analysis of charge transfer as presented in Table 4.

To accurately model the isolated CuSO₄ molecule within the context of periodic calculations, it was placed in a cubic supercell with dimensions of $15 \times 15 \times 15$ Å³. The molecule was then geometrically optimized without constraints, using the same kinetic energy cut-off as employed for the slab calculations. This approach ensures consistency in the representation of both the adsorbed and free molecular states.

4. Conclusions

This study presents a first-principles analysis of CuSO₄ adsorption on the anatase TiO₂ (101) surface, employing density functional theory (DFT) calculations. The key findings are as follows:

- (1) **Adsorption Geometry:** A preferential adsorption pattern was identified, characterized by the lowest adsorption energy of -4.31 eV. This configuration was consistently obtained regardless of the initial approach of the molecule to the surface, suggesting its prevalence in real samples.
- (2) **Adsorption Mechanism:** The substantial adsorption energy and the formation of new chemical bonds between CuSO₄ and the TiO₂ surface provide strong evidence for a chemisorption process.
- (3) **Charge Transfer:** Atomic charge analysis reveals a net charge transfer from the TiO₂ surface to the CuSO₄ molecule. Atoms directly involved in forming new chemical bonds exhibit increased net atomic charges, indicating the ionic nature of these bonds.
- (4) **Electronic Structure Modification:** The adsorption process induces a magnetic moment and a slight reduction in the bandwidth. These electronic structure alterations are expected to impact on the electronic and catalytic properties of the material.

Future research could focus on analyzing the photocatalytic implications of CuSO₄-modified TiO₂ surfaces under various environmental conditions, such as changes in pH and light irradiation spectra. Additionally, the experimental validation of computational findings through spectroscopic techniques and surface characterization would contribute to a deeper understanding of the material's behavior. Furthermore, exploring the incorporation of other transition metal salts or co-adsorbates could be relevant to optimizing its electronic and catalytic properties, with a view toward applications in photocatalysis and environmental remediation.

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References

- Pastorino, P.; Prearo, M. High-mountain lakes, indicators of global change: Ecological characterization and environmental pressures. *Diversity* **2020**, *12*, 260. [\[CrossRef\]](#)
- Wang, X.; Wang, C.; Zhu, T.; Gong, P.; Fu, J.; Cong, Z. Persistent organic pollutants in the polar regions and the Tibetan Plateau: A review of current knowledge and future prospects. *Environ. Pollut.* **2019**, *248*, 191–208. [\[CrossRef\]](#)
- Vergragt, P.; Akenji, L.; Dewick, P. Sustainable production, consumption, and livelihoods: Global and regional research perspectives. *J. Clean. Prod.* **2014**, *63*, 1–12. [\[CrossRef\]](#)
- Ren, G.; Han, H.; Wang, Y.; Liu, S.; Zhao, J.; Meng, X.; Li, Z. Recent advances of photocatalytic application in water treatment: A review. *Nanomaterials* **2021**, *11*, 1804. [\[CrossRef\]](#) [\[PubMed\]](#)
- López, M.C.; Fernández, M.I.; Martínez, C.; Santaballa, J.A. Photochemistry for pollution abatement. *Pure Appl. Chem.* **2013**, *85*, 1437–1449. [\[CrossRef\]](#)
- Stashans, A.; Marcillo, F.; Castillo, D. Dopamine adsorption configurations on anatase (101) surface. *Surf. Rev. Lett.* **2015**, *22*, 1550052. [\[CrossRef\]](#)
- Castillo, D.; Ontaneda, J.; Stashans, A. Geometry of dopamine adsorption on rutile (110) surface. *Int. J. Mod. Phys. B* **2014**, *28*, 1450071. [\[CrossRef\]](#)
- Grätzel, M. Dye-sensitized solar cells. *J. Photochem. Photobiol. C Photochem. Rev.* **2003**, *4*, 145–153. [\[CrossRef\]](#)
- Yan, L.; Du, J.; Jing, C. How TiO₂ facets determine arsenic adsorption and photooxidation: Spectroscopic and DFT studies. *Catal. Sci. Technol.* **2016**, *6*, 1526–1538. [\[CrossRef\]](#)
- Eddy, D.R.; Permana, M.D.; Sakti, L.K.; Sheha, G.A.N.; Solihudin; Hidayat, S.; Takei, T.; Kumada, N.; Rahayu, I. Heterophase polymorph of TiO₂ (Anatase, Rutile, Brookite, TiO₂ (B)) for efficient photocatalyst: Fabrication and activity. *Nanomaterials* **2023**, *13*, 704. [\[CrossRef\]](#)
- Gao, J.; Jia, S.; Liu, J.; Yang, X.; Chen, Z.; Wang, X. Enhanced effect of adsorption and photocatalysis by TiO₂ nanoparticles embedded porous PVDF nanofiber scaffolds. *J. Mater. Res.* **2021**, *36*, 1538–1548.
- Li, Y.; Gao, Y. Interplay between water and TiO₂ anatase (101) surface with subsurface oxygen vacancy. *Phys. Rev. Lett.* **2014**, *112*, 206101. [\[CrossRef\]](#)
- Liu, L.; Li, K.; Chen, X.; Liang, X.; Zheng, Y.; Li, L. Amino acid adsorption on anatase (101) surface at vacuum and aqueous solution: A density functional study. *J. Mol. Model.* **2018**, *24*, 107.
- Hengerer, R.; Bolliger, B.; Erbudak, M.; Grätzel, M. Structure and stability of the anatase TiO₂ (101) and (001) surfaces. *Surf. Sci.* **2000**, *460*, 162–169. [\[CrossRef\]](#)
- Diebold, U. Structure and properties of TiO₂ surfaces: A brief review. *Appl. Phys. A* **2003**, *76*, 681–687.
- Sakar, M.; Prakash, R.M.; Do, T.-O. Insights into the TiO₂-based photocatalytic systems and their mechanisms. *Catalysts* **2019**, *9*, 680. [\[CrossRef\]](#)
- Irfan, F.; Tanveer, M.U.; Moiz, M.A.; Husain, S.W.; Ramzan, M. TiO₂ as an effective photocatalyst mechanisms, applications, and dopants: A review. *Eur. Phys. J. B* **2022**, *95*, 184.
- Degefu, D.M.; Liao, Z. Photocatalytic degradation of volatile organic compounds using nanocomposite of P-type and N-type transition metal semiconductors. *J. Sol-Gel Sci. Technol.* **2021**, *98*, 605–614.

19. Xing, M.; Wu, Y.; Zhang, J.; Chen, F. Effect of synergy on the visible light activity of B, N and Fe co-doped TiO₂ for the degradation of MO. *Nanoscale* **2010**, *2*, 1233–1239. [\[CrossRef\]](#)
20. Liu, M.; Piao, L.; Lu, W.; Ju, S.; Zhao, L.; Zhou, C.; Li, H.; Wang, W. Flower-like TiO₂ nanostructures with exposed {001} facets: Facile synthesis and enhanced photocatalysis. *Nanoscale* **2010**, *2*, 1115–1117.
21. Zhang, P.; Shao, C.; Zhang, Z.; Zhang, M.; Mu, J.; Guo, Z.; Liu, Y. TiO₂@carbon core/shell nanofibers: Controllable preparation and enhanced visible photocatalytic properties. *Nanoscale* **2011**, *3*, 2943–2949. [\[PubMed\]](#)
22. Luan, Y.; Jing, L.; Xie, Y.; Sun, X.; Feng, Y.; Fu, H. Exceptional photocatalytic activity of 001-facet-exposed TiO₂ mainly depending on enhanced adsorbed oxygen by residual hydrogen fluoride. *ACS Catal.* **2013**, *3*, 1378–1385.
23. Jagminas, A.; Ramanavičius, S.; Jasulaitiene, V.; Šimėnas, M. Hydrothermal synthesis and characterization of nanostructured titanium monoxide films. *RSC Adv.* **2019**, *9*, 40727–40735.
24. Domaschke, M.; Zhou, X.; Wergen, L.; Romeis, S.; Miehlich, M.E.; Meyer, K.; Peukert, W.; Schmuki, P. Magnéli-phases in anatase strongly promote cocatalyst free photocatalytic hydrogen evolution. *ACS Catal.* **2019**, *9*, 3627–3632.
25. Yang, F.; Zhang, H.; Wu, Z.H.; Xiang, L.; Yu, Y.X. Formation of Monodispersed Anatase TiO₂ Spheres from TiOSO₄ for Enhanced Hydrogen Evolution of TiO₂/g-C₃N₄ Photocatalysts. *J. Environ. Chem. Eng.* **2024**, *12*, 114888.
26. Patra, S.G.; Meyerstein, D. On the Mechanism of Heterogeneous Water Oxidation Catalysis: A Theoretical Perspective. *Inorganics* **2022**, *10*, 182. [\[CrossRef\]](#)
27. Yu, Y.; Miao, J.; Wang, J.; He, C.; Chen, J. Facile synthesis of CuSO₄/TiO₂ catalysts with superior activity and SO₂ tolerance for NH₃-SCR: Physicochemical properties and reaction mechanism. *Catal. Sci. Technol.* **2017**, *7*, 1590–1601.
28. Luna, M.D.G.; Garcia-Segura, S.; Mercado, C.H.; Lin, Y.-T.; Lu, M.-C. Doping TiO₂ with CuSO₄ enhances visible light photocatalytic activity for organic pollutant degradation. *Environ. Sci. Pollut. Res.* **2020**, *27*, 24604–24613.
29. Yadav, S.; Arif, T.; Wang, G.; Sodhi, R.N.S.; Cheng, Y.H.; Filleter, T.; Singh, C.V. Interfacial Interactions and Tribological Behavior of Metal-Oxide/2D-Material Contacts. *Tribol. Lett.* **2021**, *69*, 91.
30. Martsinovich, N.; Jones, D.R.; Troisi, A. Electronic Structure of TiO₂ Surfaces and Effect of Molecular Adsorbates Using Different DFT Implementations. *J. Phys. Chem. C* **2010**, *114*, 22659–22670. [\[CrossRef\]](#)
31. Treacy, J.P.W.; Hussain, H.; Torrelles, X.; Grinter, D.C.; Cabailh, G.; Bikondoa, O.; Nicklin, C.; Selcuk, S.; Selloni, A.; Lindsay, R.; et al. Geometric Structure of Anatase Ti O₂(101). *Phys. Rev. B* **2017**, *95*, 075416.
32. Rafique, M.; Shuai, Y.; Hassan, M. Structural, electronic and optical properties of CO adsorbed on the defective anatase TiO₂ (101) surface; A DFT study. *J. Mol. Struct.* **2017**, *1142*, 11–17.
33. Liu, Q.-L.; Zhao, Z.-Y. DFT study on microstructures and electronic structures of Pt mono-/bi-doped anatase TiO₂ (101) surface. *RSC Adv.* **2015**, *5*, 17984–17992. [\[CrossRef\]](#)
34. Wildner, M.; Giester, G. Crystal structure refinements of synthetic chalcocyanite (CuSO₄) and zincosite (ZnSO₄). *Miner. Petrol.* **1988**, *39*, 201–209.
35. Diebold, U. The surface science of titanium dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
36. Lazzeri, M.; Vittadini, A.; Selloni, A. Structure and energetics of stoichiometric TiO₂ anatase surfaces. *Phys. Rev. B* **2001**, *63*, 155409.
37. Marabelli, F.; Parravicini, G.B.; Salghetti-Drioli, F. Optical gap of CuO. *Phys. Rev. B* **1995**, *52*, 1433–1436.
38. Burdett, J.K.; Hughbanks, T.; Miller, G.J.; Richardson, J.W.; Smith, J.V. Structural electronic relationships in inorganic solids: Powder neutron diffraction studies of the rutile and anatase polymorphs of titanium dioxide at 15 and 295 K. *J. Am. Chem. Soc.* **1987**, *109*, 3639–3646.
39. Henkelman, G.; Arnaldsson, A.; Jonsson, H. A Fast and Robust Algorithm for Bader Decomposition of Charge Density. *Comput. Mater. Sci.* **2006**, *36*, 354–360. [\[CrossRef\]](#)
40. Haynes, W.M. (Ed.) *CRC Handbook of Chemistry and Physics*, 97th ed.; CRC Press: Boca Raton, FL, USA, 2016; ISBN 978-1-4987-5429-3.
41. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
42. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169. [\[CrossRef\]](#)
43. Perdew, J.P.; Chevary, J.A.; Vosko, S.H.; Jackson, K.A.; Pederson, M.R.; Singh, D.J.; Fiollhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1992**, *46*, 6671. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented wave method. *Phys. Rev. B* **1999**, *59*, 1758. [\[CrossRef\]](#)
45. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865. [\[CrossRef\]](#)
46. Dudarev, S.; Botton, G.; Savrasov, S.; Humphreys, C.; Sutton, A. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B* **1998**, *57*, 1505. [\[CrossRef\]](#)

47. Liechtenstein, A.; Anisimov, V.; Zaanen, J. Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators. *Phys. Rev. B* **1995**, *52*, R5467. [[CrossRef](#)] [[PubMed](#)]
48. Stashans, A.; Bravo, Y. Large hole polarons in Sc-doped TiO₂ crystals. *Mod. Phys. Lett. B* **2013**, *27*, 1350113. [[CrossRef](#)]
49. Mishra, A.K.; Roldan, A.; de Leeuw, N.H. CuO Surfaces and CO₂ Activation: A Dispersion-Corrected DFT+U Study. *J. Phys. Chem. C* **2016**, *120*, 2198–2214. [[CrossRef](#)]
50. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799. [[CrossRef](#)]
51. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104. [[CrossRef](#)]
52. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465. [[CrossRef](#)] [[PubMed](#)]
53. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188. [[CrossRef](#)]
54. Neugebauer, J.; Scheffler, M. Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al (111). *Phys. Rev. B* **1992**, *46*, 16067. [[CrossRef](#)] [[PubMed](#)]
55. Makov, G.; Payne, M. Periodic boundary conditions in ab initio calculations. *Phys. Rev. B* **1995**, *51*, 4014. [[CrossRef](#)]

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