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THE ELECTRONIC STRUCTURE MODIFICATION AND PHOTOCATALYTIC ABILITY IMPROVEMENT OF TITANIUM DIOXIDE DOPED WITH SILVER AND COPPER ATOMS

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Abstract: This research employed density functional theory (DFT) calculations to investigate the electronic structure, band characteristics, and bonding properties of pure titanium dioxide (TiO₂) and its silver (Ag)- and copper (Cu)-doped counterparts. The potential of these materials for photocatalytic water splitting to produce hydrogen was assessed. The calculated band gaps were 3.18 eV, 2.3 eV, and 2.1 eV for TiO₂, Ag-TiO₂, and Cu-TiO₂, respectively. Crucially, localized impurity states appeared within the band gap of the doped semiconductors. For Ag-TiO₂, the conduction band edge (-0.73 eV) and valence band edge (1.53 eV) were favorably positioned relative to the redox potentials for water splitting, suggesting promising photocatalytic activity.

Keywords: Ag- and Cu-doped titanium dioxide, DFT, band gap, photocatalysis, electronic characteristics, mobility and lifetime of charge carriers.

I. INTRODUCTION

Titanium dioxide (TiO₂) has been extensively explored as a photocatalyst due to its chemical stability, non-toxic nature, and environmental abundance. However, TiO₂ has limitations that hinder its efficiency under visible light, primarily because of its large intrinsic bandgap (~3.2 eV for anatase phase and ~3.0 eV for rutile) which restricts its absorption to the ultraviolet (UV) region, constituting only a small fraction (~4%) of the solar spectrum. To address this issue, researchers have employed various strategies, including bandgap engineering through doping, surface modifications, and coupling with co-catalysts. Among these approaches, transition metal doping is one of the most promising techniques for enhancing visible-light-driven photocatalysis by altering the electronic properties of TiO₂. In particular, the doping of TiO₂ with silver (Ag) and copper (Cu) has drawn considerable attention due to their unique electronic contributions.

The incorporation of Ag or Cu atoms into the TiO₂ lattice introduces impurity levels within the bandgap, thereby enabling visible-light absorption. Studies report that Ag doping forms shallow donor states close to the conduction band, which lowers the bandgap and enhances light absorption. Moreover, Ag-doped TiO₂ improves electron-hole separation, as silver acts as an electron sink, reducing the recombination of charge carriers and facilitating more efficient photocatalysis [1]. On the other hand, Cu-doping creates mid-gap states, which also reduce the effective bandgap, though the photocatalytic improvement is often limited by issues such as photo-corrosion and reduced long-term stability [2]. These dopants modify not only the optical properties but also influence surface reactions by enhancing adsorption of water and oxygen molecules, which are critical intermediates in photocatalytic processes.

Density Functional Theory (DFT) has become an indispensable tool for understanding the structural and electronic modifications introduced by dopants in semiconductors. Standard DFT calculations often underestimate the bandgap, which can be corrected by employing Hubbard U-corrections or hybrid functionals. In recent studies, DFT has been used to model the effects of Ag and Cu doping on the electronic band structure, density of states (DOS), and charge transfer dynamics in TiO₂ systems [3]. These calculations provide insights into the spatial distribution of charge densities and the interaction between dopant atoms and the TiO₂ host lattice. For instance, Ag-doping shifts the Fermi level closer to the conduction band, resulting in an n-type semiconductor behavior [4]. In contrast, Cu-doping introduces localized states that promote p-type conductivity, a desirable feature for applications in photocatalytic hydrogen production. Charge density analysis obtained through DFT simulations has shown that Cu atoms preferentially bind with oxygen atoms in the TiO₂ lattice, further stabilizing the material and facilitating enhanced surface reactions under visible light [5].

II. COMPUTATIONAL DETAILS

To accurately capture the electronic structure of both pure and doped TiO₂ systems, we employed a comprehensive DFT framework. Geometry optimizations were conducted using the generalized gradient

approximation (GGA) exchange-correlation functional parameterized by Perdew-Burke-Ernzerhof (PBE), renowned for its robustness and accuracy in describing a wide range of materials. This initial optimization step ensured that the atomic positions of each system were relaxed to their equilibrium configurations, providing a reliable foundation for subsequent electronic structure calculations.

For an accurate description of the electronic wavefunctions, we utilized a plane-wave basis set with an energy cutoff of 450 eV, determined through rigorous convergence tests to ensure sufficient precision in our calculations. The Brillouin zone integration, essential for sampling the reciprocal space, was performed using a 9x9x14 k-point mesh, chosen to adequately capture the electronic band structure of the tetragonal anatase TiO₂ lattice. The atomic positions and cell parameters for the pure TiO₂ structure were optimized using the quasi-Newton method, specifically the LBFGS (Limited-memory Broyden-Fletcher-Goldfarb-Shanno) algorithm, achieving a force convergence criterion of 0.03 eV/Å for unconstrained atoms. The optimized structure was then compared with experimental data to ensure accuracy. The lattice dimensions of pure TiO₂ and doped structures, as obtained using the LDA + U method, are presented in Table 1. The calculated lattice parameters of pure TiO₂ ($a = 3.776$ Å, $b = 3.776$ Å, $c = 9.484$ Å) are in good agreement with the experimental values reported in [6] ($a = 3.785$ Å, $b = 3.785$ Å, $c = 9.514$ Å). In the optimized TiO₂ geometry, selected titanium atoms were substituted with silver and copper atoms, and the resulting structures were further optimized using the LBFGS algorithm.

Table 1. Optimized structures and the deviation with experimental results

Unit cell parameter, Å	TiO ₂	Ti _{1-x} Ag _x O ₂	Ti _{1-x} Cu _x O ₂	Experiment [23]	Deviation (%)
a	3.776	3.775	3.776	3.785	+0.23
b	3.776	3.775	3.776	3.785	+0.23
c	9.484	9.486	9.484	9.514	+0.31

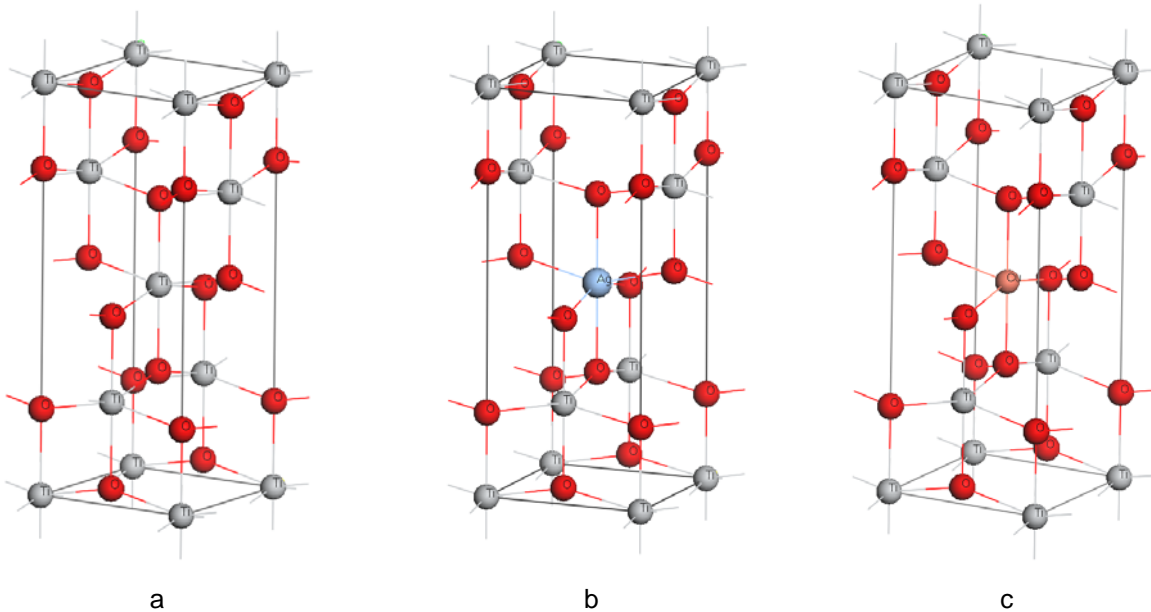


Figure 1. Crystal structures of **a)** TiO₂, **b)** Ag-doped TiO₂, **c)** Cu-doped TiO₂ used in the calculations. Titanium, oxygen, silver and copper atoms are indicated in grey, red, blue and brown, respectively.

In order to mitigate the well-known band gap underestimation issue inherent in standard DFT, we implemented the LDA+U method, a widely adopted approach to correct for the self-interaction error in strongly correlated systems. In this method, the Hubbard U parameter, set to 8.0 eV for the Ti 3d states, accounts for the on-site Coulomb interactions between the localized d electrons of titanium. This correction significantly improves the accuracy of the calculated band gap, bringing it closer to experimental values. To incorporate the effects of valence electrons, we employed ultrasoft pseudopotentials, which significantly reduce the computational cost while maintaining accuracy.

III. RESULTS AND DISCUSSION

The calculated electronic band structures and density of states (DOS) reveal a profound impact of Ag and Cu doping on the electronic properties of TiO_2 (Figure 2). In pure TiO_2 , the valence band is dominated by O 2p states, while the conduction band primarily consists of Ti 3d states, consistent with previous theoretical and experimental studies. This clear separation results in a wide band gap of 3.18 eV, limiting the material's ability to absorb visible light.

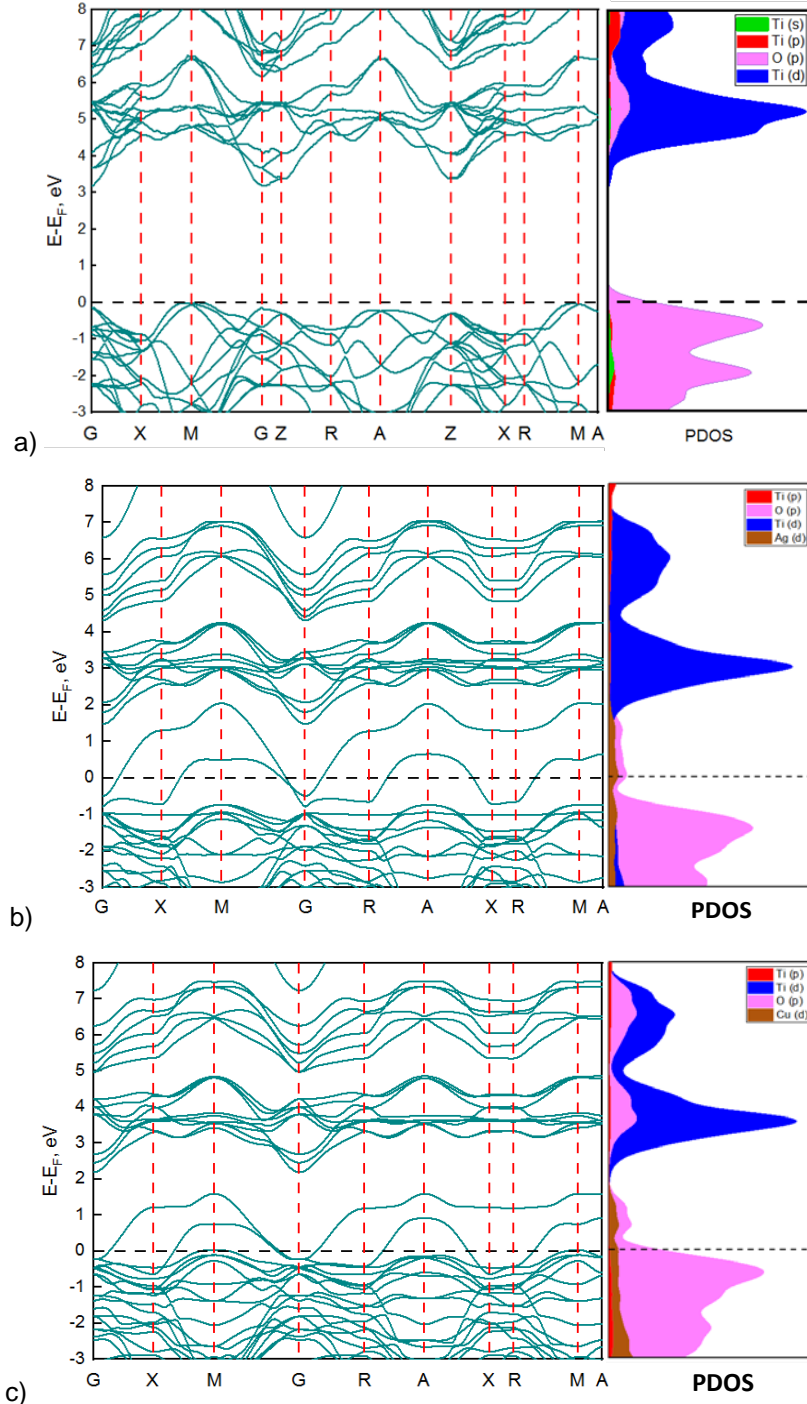


Figure 2. Structure of energy bands and partial density of states of a) TiO_2 , b) Ag-doped TiO_2 , c) Cu-doped TiO_2 structures

Upon doping with Ag, we observe a notable decrease in the band gap to 2.3 eV. The Ag 4d states hybridize with the O 2p states, forming localized impurity states within the band gap. These new states effectively narrow the band gap and introduce additional energy levels that can facilitate the absorption of photons with lower energies, extending the absorption spectrum into the visible range. Additionally, the presence of these

localized states can act as traps for photogenerated electrons and holes, potentially enhancing charge carrier separation and reducing recombination rates, thereby improving photocatalytic efficiency.

Similarly, Cu doping also leads to a reduction in the band gap, albeit to a slightly lower value of 2.1 eV. The Cu 3d states contribute to the formation of impurity states near the valence band edge, further modifying the electronic structure. This band gap narrowing, coupled with the potential for enhanced charge carrier separation due to the impurity states, suggests that Cu-doped TiO₂ could also exhibit improved photocatalytic activity under visible light irradiation.

The band edge positions of the doped systems are of particular interest for photocatalytic water splitting. The calculated conduction band edge of Ag-TiO₂ (-0.73 eV) lies above the H⁺/H₂ reduction potential, while the valence band edge (1.53 eV) is below the O₂/H₂O oxidation potential. This favorable alignment suggests that Ag-TiO₂ possesses the thermodynamic potential to drive both the reduction and oxidation half-reactions of water splitting, a crucial requirement for efficient photocatalytic hydrogen production.

Furthermore, the effective masses of charge carriers are a critical factor influencing carrier mobility and transport properties. Our calculations reveal a decrease in the effective masses of both electrons and holes upon doping with Ag and Cu, indicating enhanced carrier mobility. This improved mobility can facilitate faster charge transport to the surface reaction sites, thereby promoting efficient charge separation and reducing recombination losses.

IV. CONCLUSION

In this comprehensive DFT investigation, we have elucidated the intricate electronic structure modifications induced by Ag and Cu doping in TiO₂. Our findings unequivocally demonstrate the ability of these dopants to engineer the band gap, introduce localized impurity states, and modulate charge carrier dynamics. These alterations hold profound implications for the photocatalytic performance of TiO₂, particularly in the context of water splitting for hydrogen generation.

Specifically, Ag-doping emerges as a promising strategy, significantly narrowing the band gap of TiO₂ and creating favorable band edge alignments for both hydrogen and oxygen evolution reactions. The introduction of localized states within the band gap not only enhances visible light absorption but also promotes charge carrier separation, potentially leading to improved photocatalytic efficiency. Additionally, the reduced effective masses of charge carriers in Ag-doped TiO₂ suggest enhanced mobility, facilitating faster charge transport and further mitigating recombination losses.

While Cu-doping also exhibits a beneficial band gap narrowing effect, the resulting band edge positions may not be as optimal for water splitting as those observed in Ag-doped TiO₂. However, the presence of localized states and reduced effective masses still suggest the potential for improved photocatalytic performance compared to pure TiO₂.

To further optimize the photocatalytic activity of doped TiO₂, future research could explore the effects of varying dopant concentrations, co-doping with multiple elements, and investigating alternative dopants with different electronic configurations. Moreover, experimental validation of these theoretical predictions is essential to assess the practical feasibility and long-term stability of doped TiO₂ photocatalysts.

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МОДИФИКАЦИЯ ЭЛЕКТРОННОЙ СТРУКТУРЫ И ФОТОКАТАЛИТИЧЕСКИЙ ПОТЕНЦИАЛ ДИОКСИДА ТИТАНА (TiO₂), ЛЕГИРОВАННОГО АТОМАМИ СЕРЕБРА И МЕДИ: ИССЛЕДОВАНИЕ МЕТОДОМ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

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Аннотация: В этом исследовании использовались расчеты теории функционала плотности (DFT) для изучения электронной структуры, характеристик зон и свойств связей чистого диоксида титана (TiO₂) и его аналогов, легированных серебром (Ag) и медью (Cu). Была оценена способность этих материалов к фотокалалитическому расщеплению воды с получением водорода. Рассчитанные ширины запрещенных зон составили 3,18 эВ, 2,3 эВ и 2,1 эВ для TiO₂, Ag-TiO₂ и Cu-TiO₂ соответственно. Важно отметить, что локализованные примесные состояния появились в запрещенной зоне легированных полупроводников. Для Ag-TiO₂ край зоны проводимости (-0,73 эВ) и край валентной зоны (1,53 эВ) были выгодно расположены относительно окислительно-восстановительных потенциалов для расщепления воды, что предполагает многообещающую фотокалалитическую активность.

Ключевые слова: Диоксид титана, легированный серебром и медью, DFT, запрещенная зона, фотокалализ, электронные характеристики, подвижность и время жизни носителей заряда.