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Mohammed Benali Kanoun, Faheem Ahmed, Chawki Awada, Christian Jonin, Pierre-François Brevet. Band gap engineering of Au doping and Au -N codoping into anatase TiO<sub>2</sub> for enhancing the visible light photocatalytic performance. *International Journal of Hydrogen Energy*, 2024, 51, pp.907. 10.1016/j.ijhydene.2023.10.244 . hal-04274983

**HAL Id: hal-04274983**

**<https://hal.science/hal-04274983>**

Submitted on 8 Nov 2023

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# **Band gap engineering of Au doping and Au – N codoping into anatase TiO<sub>2</sub> for enhancing the visible light photocatalytic performance**

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## **Abstract**

We investigate anatase TiO<sub>2</sub> doping with Au to determine the change in the band gap energy and optoelectronic properties using experimental and theoretical analysis. The structural analysis using XRD patterns revealed that the synthesized materials primarily exhibited an anatase phase of TiO<sub>2</sub>, with no impurity peaks observed. However, as the concentration of Au increased, additional diffraction peaks corresponding to Au crystalline phases were detected, indicating successful doping. Furthermore, the crystallite size was found to decrease with increasing Au concentration. We observe that the band gap reduces through substitution of Au into the TiO<sub>2</sub> lattice from 3.09 eV to 2.78 eV, demonstrating the feasibility of bandgap tuning of the TiO<sub>2</sub> system. A redshift for Au doped TiO<sub>2</sub> is observed from absorption spectroscopy and optical absorption intensity using hybrid density functional theory, facilitating visible light absorption, although with potential electron-hole recombination limitations. To enhance a visible light photocatalytic activity for water splitting, we extend our work to explore the impact of N and Au codoping into TiO<sub>2</sub> lattice. It reveals that the combination between N and Au leads to a suitable reduction in the band gap width of pure TiO<sub>2</sub>. Interestingly, Au-N codoping may decrease the effect of photogenerated carriers, produce a new optical absorption feature in the visible region, and enhance the photocatalytic performance of TiO<sub>2</sub>. This codoping configuration is also a promising photocatalyst for the decomposition of water using visible light without inducing unoccupied states.

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**Keywords:** Experimental study, first principles computations, Au doped and Au – N codoped TiO<sub>2</sub>, band gap, optical absorption, photocatalytic activity

## 1. Introduction

During the last years, the technology of clean and renewable energy has received wide interest for the development of economic sustainability and decreasing of atmospheric and industrial pollution [1,2]. Currently, semiconductor photocatalysis is an advanced and effective method for degrading organic contaminants and solving the issue of clean energy [3]. Accordingly, photocatalytic materials have been considered for these purposes, especially semiconductor photocatalysts and have gained a lot of attention because of their excellent physical and chemical stability, high photocatalytic activity, nontoxicity, and relatively low cost [4]. Titanium dioxide (TiO<sub>2</sub>), which is the most commonly studied photocatalyst, has a characteristic large bandgap (>3 eV) [5]. This indicates that photocatalytic performance is limited to the ultraviolet (UV) spectral region with the wavelength below 400 nm [6]. Consequently, systematic investigation has concentrated on expanding the light absorption limit of TiO<sub>2</sub> toward longer wavelengths [7-16]. Substitutional doping through various schemes is considered as a practical approach for controlling the optoelectronic properties and extending the functionalities of TiO<sub>2</sub> under visible light irradiation [17]. The nature of the dopant atom has an impact on this activity as the impurities can be incorporated as substitutional, interstitial, or both together. Various doping procedures have been utilized for fabricating doped materials such as the sol-gel process, ultrasonic treatment followed by UV irradiation, chemical vapor deposition or other commercial titania impregnation procedures [13,18-23]. Many experimental [7-14] and theoretical [15-38] investigations were reported to enhance the photocatalytic performance of TiO<sub>2</sub> using various dopant transition metals, alkali metals, p-block metals and nonmetals as well as noble metals. Among them, Au doping has received the most attention in the area of photocatalysis, because of the significant influence on the changes of the electronic properties of TiO<sub>2</sub>. Nobel metal such as Au can boost visible light absorption owing to the surface plasmon resonance effect [13]. Moreover, TiO<sub>2</sub> nanoparticle growth and facet formation can be affected by gold dopants,

creating unusual morphologies and surface structures that can improve photocatalytic performance. The presence of Au dopants can facilitate numerous chemical processes on the TiO<sub>2</sub> surface, extending the potential application of material beyond photocatalysis [36-38]. Some experimental studies have reported that the Au incorporation in TiO<sub>2</sub> could exclude the recombination of electron/holes and yield a significantly enhanced optical absorption in the visible range [38]. It also showed from optical absorption spectrum measurements that a new peak of energy below 3.2 eV presented in Au/Au<sup>3+</sup>-TiO<sub>2</sub> increased optical absorption characteristic in the visible range and allowed it to be activated by visible light [38]. On the theoretical side, it was revealed that Au doping into TiO<sub>2</sub> effectively shifts the absorption band edges of pristine TiO<sub>2</sub> towards the visible range, locating it in the region of 400–1000 nm [30]. Through a combination of first principles computations and several experimental analyses (FESEM, UV–vis spectroscopy, photoluminescence, Raman), in this work we analyze the modifications in morphology structures, electronic structures, and optical properties due to Au doped TiO<sub>2</sub>. The stability of various doping states as well as the optimum growth atmosphere conditions have been demonstrated, which is useful for n-type or photocatalytic applications. We also explored the effect of Au – N codoping on the stability, electronic structure and photocatalytic performance of TiO<sub>2</sub>. The findings suggest that Au – N codoping might have the potential to improve visible light photocatalysis.

## **2. Materials and methods**

### **2.1. Experimental section**

For the preparation of TiO<sub>2</sub>, a homogeneous mixture containing 2 mL of 0.1 M CTAB solution and 30 mL of ethanol was prepared by mixing and stirring with a magnetic stirrer. After proper mixing, 1.02 mL of Ti isopropoxide ( $3.45 \times 10^{-3}$  moles) solution was added to this mixture and then heated to 65 °C with continuous stirring. After heating and stirring for 5 min, a white precipitate appeared, which was continuously stirred and heated. After ~45 minutes, the solution becomes completely white in color. In this stage, HAuCl<sub>4</sub> with different molar fraction of 0%, 0.5% (5.86 mg), 1 % (11.7 mg), and 2 % (23.44 mg), respectively was added to the white solution to prepare pure TiO<sub>2</sub> and Au-doped TiO<sub>2</sub>. Then, 50 mL of di-ionized (DI) water was added under continuous heating and stirring for 15 minutes. After, the formed solution was kept precipitating overnight. The precipitate was collected, washed several times with DI water and

ethanol, and finally centrifuged at 4000 rpm 3 times using DI water. The dried solid white mass was collected, then dried and annealed at 600 °C for 1 hour in an aerated oven. The product was then called as pure TiO<sub>2</sub> and Au-doped TiO<sub>2</sub> and was used for further characterizations. X-ray diffraction (XRD) was used to characterize the crystal structure of the prepared samples. The system consists of X-ray diffractometer (Phillips X'pert (MPD 3040)) with Cu K $\alpha$  radiations ( $\lambda = 1.5406 \text{ \AA}$ ) at voltage of 40 kV and a current of 30 mA. A field emission scanning electron (FESEM) microscope (JEOL-JEM) equipped with EDX has been used to study the surface topography of the synthesized powders. A confocal Raman microscope (LabRAM HR800) was used to perform the Raman measurements, and photo-electron spectra were recorded using a multichannel charge-coupled detector (CCD). Raman spectra were reported at ambient room temperature using a backscattering geometry with a spectral resolution of 0.8 cm<sup>-1</sup>. For the excitation of the samples, a Helium Cadmium blue laser (wavelength 442 nm and an output power 20 mW) was used. The optical characteristics of Au -doped TiO<sub>2</sub> were obtained at room temperature by estimating the UV-Vis absorbance in the wavelength range [200 – 800 nm]. A spectrophotometer (Hitachi UV-3600) with an integrating sphere that enables the measurement of powder absorbance spectra.

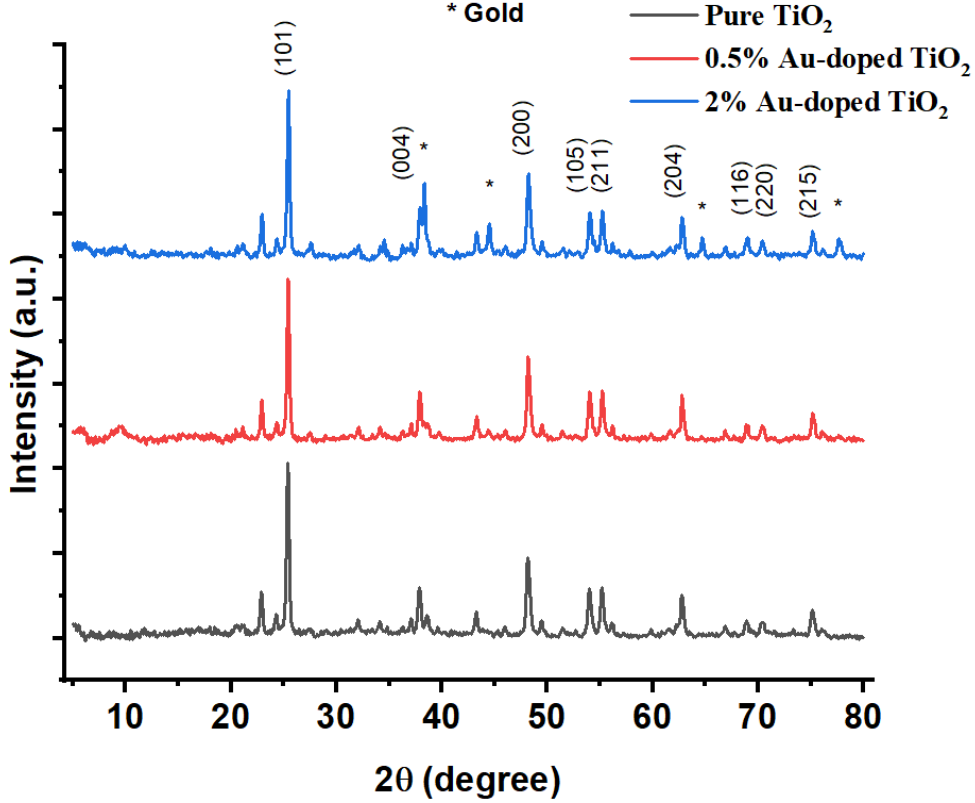
## 2.2. Computational details

Using the linear combination of atomic orbitals method as basis set, the Quantum Atomistix ToolKit (QuantumATK) software package [39] was used to perform theoretical calculations based on the density functional theory (DFT) framework, within the generalized gradient approximation (GGA) exchange-correlation functional of the Perdew, Burke, Ernzerhof (PBE) [40]. The FHI pseudopotential with double zeta polarized considering the medium basis set was adopted. A mesh cutoff energy of 60 Ha is used. With a tolerance value of 10<sup>-4</sup> Ha, the PulayMixer algorithm was used as an iteration control parameter. The structures were completely optimized utilizing the limited-memory Broyden–Fletcher–Goldfarb–Shanno (LBFGS) approach, with force on each atom position less than 0.05 eV/Å. A 4 × 4 × 2 Monkhorst-Pack [41] k-grid was used for geometry structure optimization, while a 8 × 8 × 4 grid was applied for electronic property calculation. The Heyd-Scuseria-Ernzerhof HSE06 hybrid functional was used to calculate all of the electronic structures and optical properties [42-44].

### 3. Results and discussion

#### 3.1. Structural properties

XRD patterns were investigated to present the structure and phase configuration of as-synthesized materials. The analysis of Figure 1 shows that the XRD patterns are attributed to pure TiO<sub>2</sub> and gold doped TiO<sub>2</sub>. The XRD patterns show different diffraction peaks at 2θ angles 25.3, 37.9, 48.05, 53.9, 55.06, 62.4, 68.76, 70.3, 75.06 assigned to the crystal planes of the anatase phase TiO<sub>2</sub> [(101), (004), (200), (105), (211), (204), (116), (220), (215)] (see JCPDS card no. 21-1272). Moreover, there are no impurity peaks to be observed, only clear and sharp peaks. The latter confirms the purity of the synthesized anatase phase of TiO<sub>2</sub>. On the other hand, samples of 0.5% and 2% doped TiO<sub>2</sub> show some diffraction peaks at 2θ angles 38.21, 44.35, 64.7, and 77.7. They belong to the crystal planes of gold (111), (200), (220), and (311), respectively, (JCPDS card No. 04-0784). A significant increase of these peaks is observed with the increase of the Au fraction. To calculate the crystallite size of all the prepared samples, we used the Debye Scherrer equation shown below [45];  $D = \frac{k\lambda}{\beta \cos\theta}$ , where k is a constant, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) parameter and θ is the diffraction angle. It is observed that the crystallite size drops off with the rising of Au concentrations. The crystallite size of pure TiO<sub>2</sub>, 0.5% Au-doped TiO<sub>2</sub>, 2% Au-doped TiO<sub>2</sub> was found to be 52 nm, 41 nm, and 48 nm, respectively. The morphologies studied by FESEM and the EDX plots of pure and Au-doped TiO<sub>2</sub> nanoparticles with various doping concentration of Au were shown in Figure S1 and S2.



**Figure 1:** XRD patterns of pure TiO<sub>2</sub>, 0.5%, and 2% Au-doped TiO<sub>2</sub> nanoparticles.

To support the experimental measurements of the crystal lattices, we carried out first-principles computations on hexagonal TiO<sub>2</sub> anatase with the space group I4<sub>1</sub>/amd. The optimized lattice parameters match the experimentally reported values rather well [46], and previous theoretical works [33,34,47] as listed in Table 1. Then, based on an optimized unit cell, 2 × 2 × 2 supercells were built containing 96 atoms, as illustrated in Figure S3. The substitutional defect was created in the supercell by simultaneous replacement of a Ti atom by an Au atom (equivalent to 3.125% Au composition). The co-doped configurations were produced by simultaneously changing a Ti atom for a Au atom and an O atom for an N atom. The formation energy is computed for Au doped and Au – N codoping TiO<sub>2</sub> configurations according to expression;  $E_f = E_{doped} - E_{undoped} - n_{Au}\mu_{Au} + n_{Ti}\mu_{Ti} + n_O\mu_O - n_N\mu_N$ , where  $E_{doped}$  denotes the total energy of the doped system and dopant, and  $E_{undoped}$  is the total energy of the pure TiO<sub>2</sub> [48,49,50]. The number of added or removed dopant and host ions is represented by  $n$ . The chemical potentials of the Au, Ti, N and O atoms, are defined by  $\mu_{Au}$ ,  $\mu_{Ti}$ ,  $\mu_N$  and  $\mu_O$  respectively, varying depending on the experimental circumstances. In the case of Ti-rich and an O-rich situation,  $\mu_{Ti}$

and  $\mu_O$  can be obtained in the stable state with energy of bulk Ti and O<sub>2</sub> molecule, respectively. The relation,  $\mu_{Ti} + 2\mu_O \approx \mu_{TiO_2}$ , can be used to estimate the chemical potentials of Ti under O-rich environments and O under Ti-rich environments, in which  $\mu_{TiO_2}$  can be thought of as the total energy per TiO<sub>2</sub> formula unit. The chemical potential for Au is known and calculated using the formula,  $2\mu_{Au} + 3\mu_O \approx \mu_{Au_2O_3}$ , where  $\mu_{Au_2O_3}$  is computed from the total energy of the Au<sub>2</sub>O<sub>3</sub> [47,48]. The computed formation energies for doped and codoped TiO<sub>2</sub> systems are gathered in Table 1. According to these findings, Au doped systems form a more energetically preferable structure in O-rich growth circumstances than in Ti-rich growth settings. In the optimized geometry structure of Au doped TiO<sub>2</sub>, it is found that the lattice constants increase slightly with regard to that of pure TiO<sub>2</sub>, as listed in Table 1. The doping with Au in TiO<sub>2</sub> shows that the tetragonal crystalline structure is distorted, resulting in this observed variation.

**Table 1.** The predicted lattice constants, and the formation of energy for pristine, doped and codoped TiO<sub>2</sub>.

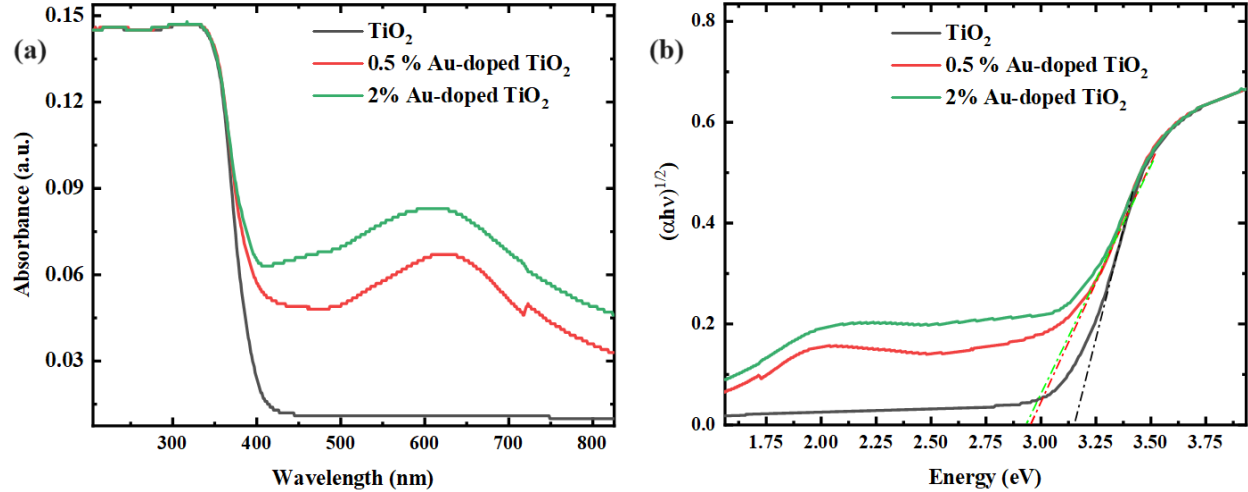
	$a$ (Å)	$c$ (Å)	$E_f$ (eV)	
			Ti-rich	O-rich
Pure	3.782 (3.7842 [46])	9.496 (9.5146 [46])	-	-
Au	3.825	9.512	10.5	4.84
Au - N	3.793	9.485	12.87	3.75

### 3.2. UV-Vis optical absorption properties and electronic structures

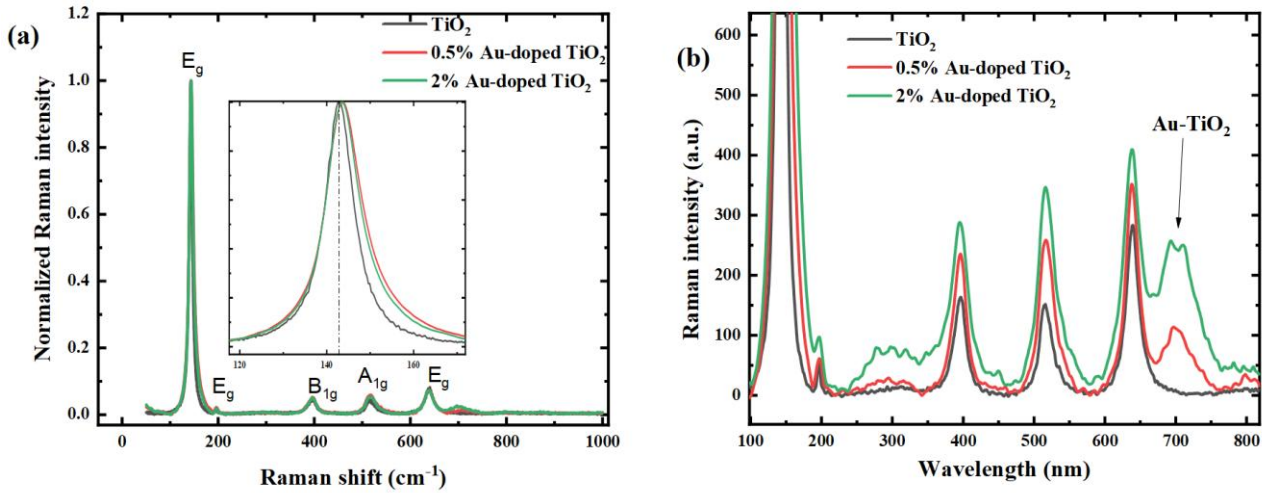
UV-vis diffuse reflectance spectra (DRS) of pure TiO<sub>2</sub> and 0.5 and 2 % Au-TiO<sub>2</sub> was obtained using Kubelka-Munk equation [21], as displayed in Figure 2. Figure 2(a) shows the surface plasmon resonance owing to the collective oscillation of conduction electrons in gold nanoparticles or clusters. A band gap study was performed by plotting Tauc equation  $(\alpha h\nu)^{1/2}$  versus the incident photon energy, see Figure 2(b). Regarding the structural analysis of the samples, we plotted the tauc equation with n=2 that lies to the anatase phase where the band gap is indirect. The obtained band gap values for the samples are 3.09 eV, 2.82 eV and 2.78 eV for



TiO<sub>2</sub>, 0.5% Au-TiO<sub>2</sub> and 2% Au-TiO<sub>2</sub>, respectively. The doping process reduces the band gap marginally, but still potentially increases the system photocatalytic performance.



**Figure 2:** UV-visible absorption spectra for pure TiO<sub>2</sub>, 0.5%, 1%, and 2 % of Au-doped TiO<sub>2</sub>. a) Absorbance versus wavelength. b) Tauc plot of the absorbance versus incident photon energy by using indirect transition of band gap.



**Figure 3:** Raman spectra of pure TiO<sub>2</sub>, 0.5%, and 2 % of Au-doped. Inset shows the shift and the broadening of the E<sub>g</sub> phonon mode. b) Zoom in of the Raman spectra.

Figure 3(a) presents the Raman spectra of pure TiO<sub>2</sub>, 0.5%, and 2% of Au-doped TiO<sub>2</sub>. The observed phonon modes belong purely to anatase phase. This anatase phase crystallizes in tetragonal structure with a space group  $I_{4_1/amd}$  and point group  $D_{2d}$ . The two TiO<sub>2</sub> units

composing the primitive cell give, six Raman-active modes in the Raman spectrum: three  $E_g$ , two  $B_{1g}$ , and one  $A_{1g}$  modes [51]. It is shown a shift toward the high vibrational energy and a broadening of the  $E_g$  mode resulting from the incorporation of the gold atoms into the  $\text{TiO}_2$  matrix. In addition, a new phonon mode located at  $700 \text{ cm}^{-1}$  was observed. The latter may be assigned to the presence of a new phase of  $\text{TiO}_2$ -Au or multiphonon scattering in the disordered anatase phase because of the presence of impurities.

To explore the influence of Au doping and (Au – N) codoping on the variation of the electronic properties  $\text{TiO}_2$ , we calculated the electronic band structures and density of states (DOS) of Au-doped  $\text{TiO}_2$  and (Au – N) codoping with pristine  $\text{TiO}_2$  for comparison, as illustrated in Figure 4. The electronic band structure of pristine  $\text{TiO}_2$  calculated with the HSE06 functional exhibits the upper of valence band (VB) situated at  $\Gamma$ - and X-points and the lower of conduction band (CB) folding at  $\Gamma$ -point, as shown in Figure 4(a). The band gap is found to be indirect in nature with an energy value of 3.58 eV. This is rather consistent with our obtained experimental measurements (3.09 eV) and the previously reported experimental (3.20 eV) [5] and theoretical (3.17-3.59 eV) works [18,32-34,52,53]. When incorporating Au into the  $\text{TiO}_2$  lattice, two new impurity states emerge in the band gap region to form intermediate states just below the minimum of the CB, as displayed in Figure 4(b). It is also observed that both valence and conduction band edges are shifted to lower energies. Our results reveal that the energy separation between the edges of the VB and the CB amounts to 3.18 eV for Au-doping, indicating a reduction in the band gap width. The decreased bandgap favors the absorption of the visible region, while the non-occupied impurity features above the Fermi level act as electron-hole recombination centers and lower the photocatalytic efficiency. To avoid this limitation, the codoping N with Au into  $\text{TiO}_2$  is investigated. As expected, Figure 4(c) demonstrates that for (Au - N)-co-doped configuration, no impurity states are observed close to Fermi level. The predicted band gap has a value of 1.71 eV.

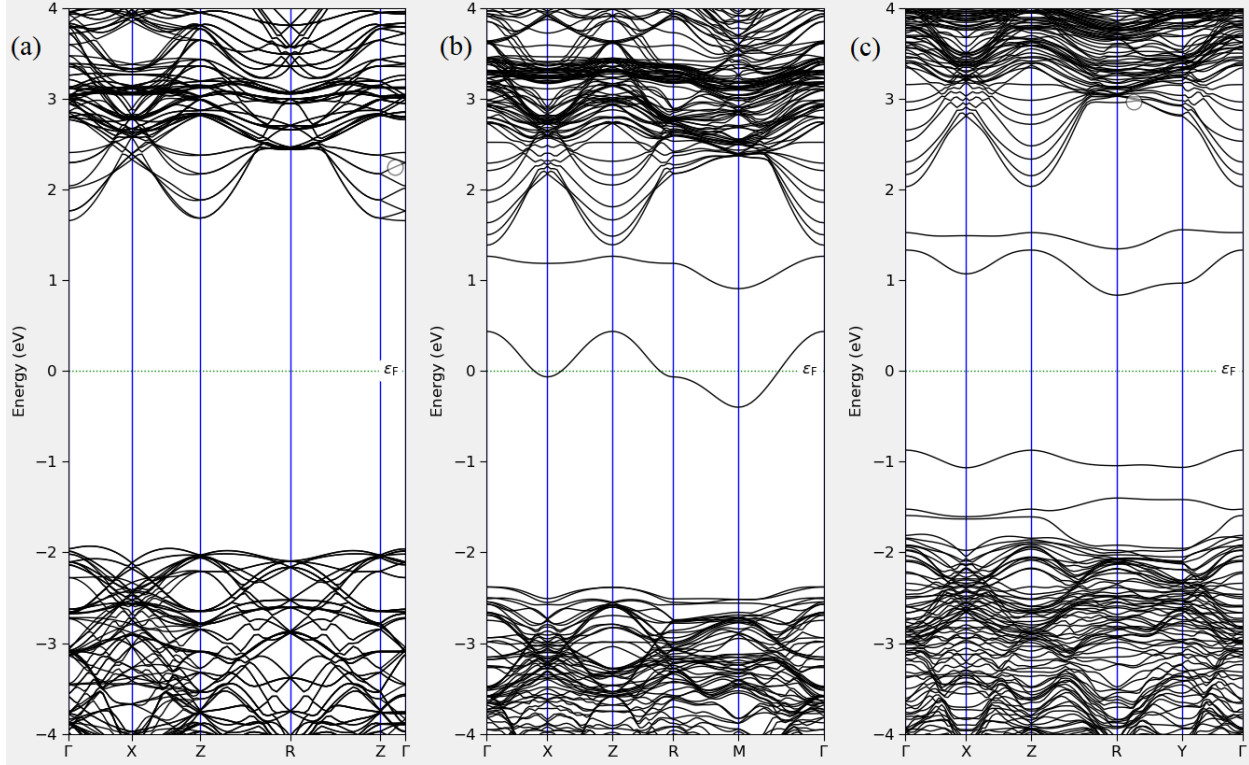
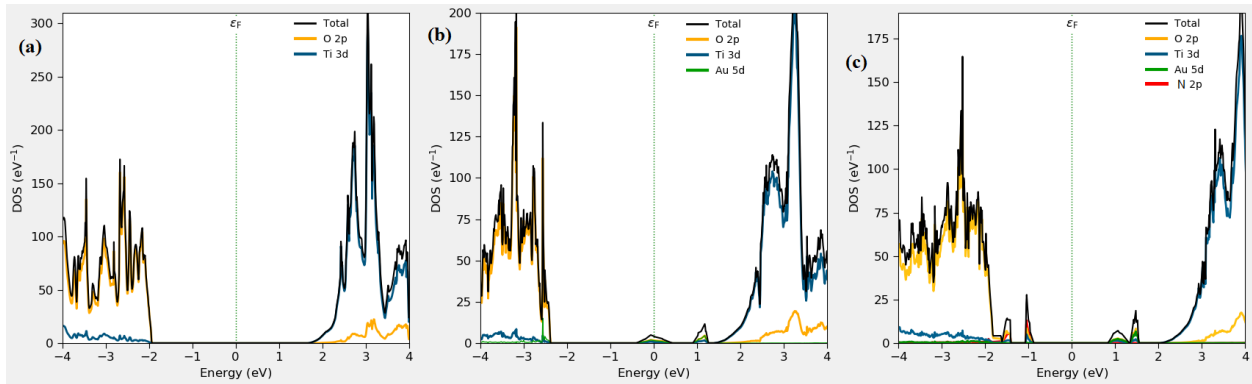


Figure 4. Calculated band structure of (a) pristine  $\text{TiO}_2$ , (b) Au doped  $\text{TiO}_2$  and (c) (Au – N) co-doped  $\text{TiO}_2$ .

An examination of the DOS from Figure 5(a) of pure anatase shows that the edge of the VB is primarily characterized by the O 2p states, indicating that electrons in the VB are primarily localized on O atoms. While the lowermost part of the CB is mostly dominated by empty Ti 3d states, implying that in the absence of any dopants, the excited electrons are promoted from O 2p states to empty Ti 3d states during electronic transitions. For the Au doping into  $\text{TiO}_2$ , it is observed that two separate local DOS peaks emerge in the band gap with the first peak being partially occupied around the Fermi level and the second peak being unoccupied just below the CB (see Figure 5(b)). The presence of these peaks indicates the creation of new energy levels within the band gap due to Au doping. Furthermore, at roughly 0.5 eV from the minimum of the CB, a distinct Au state is added in the bandgap, demonstrating the allowed electron transitions under visible light spectrum. The Au-induced donor state has a high contribution of Au 5d states, as well as small components of O 2p and Ti 3d states, indicating that the O 2p - Au 5d hybridization has occurred. The deep Au states provide sites from which electrons can be triggered in response to light absorption. As a result, there are more charge carriers. In spite of

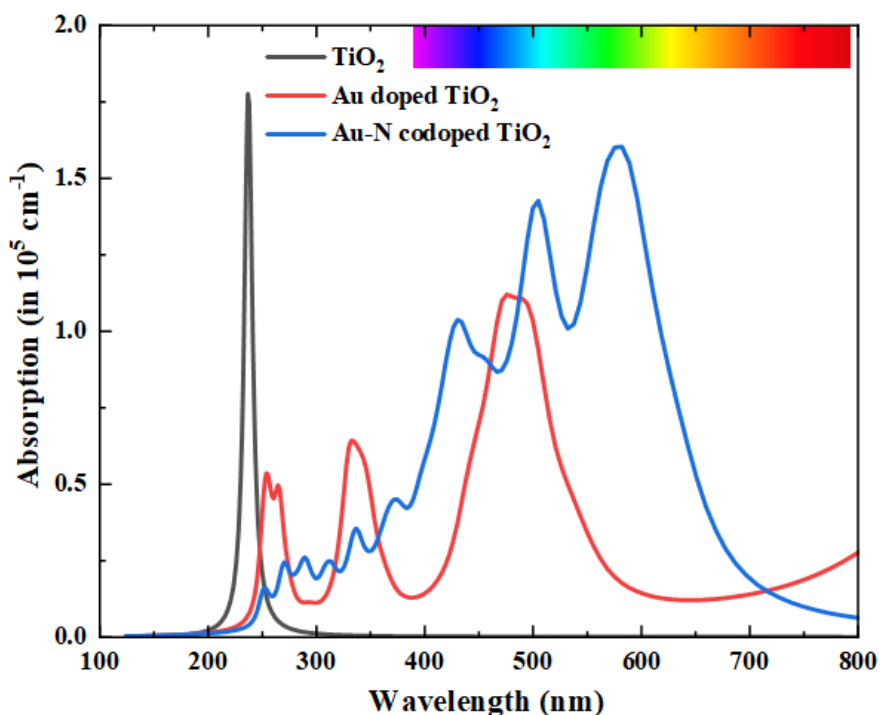
this, they might act as recombination sites for these charge carriers. Thus, the reaction to visible light enhances the optical absorption of Au doped  $\text{TiO}_2$ . When Au and N are combined, as shown in Figure 5(c), Ti 3d states contribute mostly to the lower part of CB, while O 2p and N 2p states make up the maximum of VB. It is also shown that the bandgap is noticeably reduced as a result of the creation of continuous bands just below the lower of the CB and above the edge of the VB. In both instances, the upper of VB is built up from hybridized O2p - N2p states, while the minimum of CB is mostly composed of Ti 3d mixed with Au 5d states. The Au cation at a Ti site provides one electron to the  $\text{TiO}_2$  lattice, while the N dopant ion at an O site generates one acceptor level in the band gap. As a result, the (Au - N) co-doped system experiences full charge compensation, allowing the recombination centers to be eliminated. This modification allows for efficient utilization of visible light, enhancing the photocatalytic performance of the Au-N codoped  $\text{TiO}_2$  system.



**Figure 5.** Calculated total and partial DOS of (a) pristine  $\text{TiO}_2$ , (b) Au doped  $\text{TiO}_2$  and (c) (Au – N) codoped  $\text{TiO}_2$ .

To examine the absorption features in pristine, Au doped  $\text{TiO}_2$  and (Au – N) codoping  $\text{TiO}_2$  systems, we calculated optical absorption coefficient, as a function of the wavelength of incident light using HSE06 functional, as shown in Figure 6. The analysis of Figure 6 of pure  $\text{TiO}_2$  reveals that it can only absorb in the UV range, with no visible range absorption response. The Au doping causes a minor red shift of the edge of absorption because of the in-gap level impurities. This small red shift is consistent with the observed experimental red shift for Au-doped  $\text{TiO}_2$  nanoparticles, caused by a modest band gap reduction rather than gap state excitation. The augmentation of the absorption in the visible light for Au doped  $\text{TiO}_2$  is

consistent with the excitation energy from the dopant states in the band gap to the minimum of the CB. These results indicate that the electrons could be excited from the edge of the VB to the empty gap state, resulting in a new optical absorption in the visible region. According to the absorption curve of codoping configuration indicates that when Au and N are combined, the absorption strength increases and the absorption peak extends throughout the entire visible light spectrum compared with the pure and monodoping TiO<sub>2</sub>. The major difference here may be related to the rise of the dopant energy levels below the lower of CB and above maximum of VB in Au – N codoping as compared with those in pristine and Au doping.



**Figure 6.** The absorption spectra of the pure and Au doped and (Au – N) co-doped TiO<sub>2</sub>.

In addition to possessing the appropriate bandgap to collect visible light, the upper VB and the lower CB of a perfect water-splitting photocatalyst should be positioned correctly. **Figure 7** shows the capacity of monodoping and codoping systems for photocatalytic water splitting. The calculations for the VB and CB edges, which are estimated in relation to the normal hydrogen

electrode (NHE), are described in detail in references [43,54-57] (see supporting information). The VB and CB edge positions of a desirable photocatalyst for overall water splitting must be adjusted in relation to the water redox potentials to allow for the spontaneous release of oxygen and hydrogen. From Figure 7, it can be seen that the CB and VB edge positions of pure  $\text{TiO}_2$  are above and below the redox potential and oxidation potential of water, respectively. This is in line with prior experimental and theoretical findings [58]. Au doping results in the formation of an occupied intermediate band, which may allow charge carriers to move from the valence area to the conduction region. Furthermore, the production of hydrogen and oxygen in au doping is thermodynamically impossible. For Au-N codoping, the maximum of CB is 0.48 eV below the  $\text{H}/\text{H}_2$  level whereas the maximum of VB is 0.96 eV below the  $\text{H}_2\text{O}/\text{O}_2$  energy. This demonstrates that Au-N codoping only has the capacity for spontaneous oxygen generation.

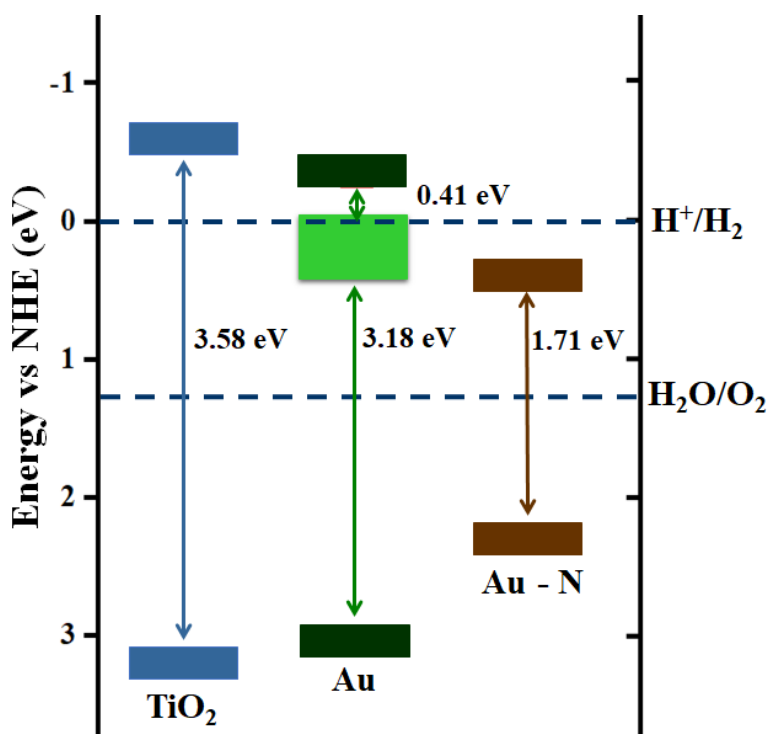


Figure 7. Schematic illustration of computed maximum of VB and minimum of CB of the pure, Au doped and Au - N codoped  $\text{TiO}_2$  with respect to the water reduction and oxidation potentials. (The delocalized impurity bands are identified by the green)

## Conclusions

A combined experimental and computational investigation was used to evaluate the structural, electronic, and optical characteristics of Au doped TiO<sub>2</sub>, improving our understanding of the impact of Au doping into TiO<sub>2</sub> lattice and possibilities for enhancing their properties for visible photocatalytic performances.

The following are the main findings of our thorough analysis.

- (a) The calculated formation energies reveal that Au doped TiO<sub>2</sub> systems form more energetically preferable structure in O-rich growth circumstances than in Ti-rich growth settings.
- (b) Significant band-gap reduction is seen within the replacement of Ti by Au at small concentrations, in which new impurity states appear in the band gap region to form intermediate states just below lower of the CB, thereby displaying the n-type behavior.
- (c) Increasing the Au content in TiO<sub>2</sub> leads to a decrease in the bandgap energy, the main origin in the observed red shift of the absorption edges, inducing an absorption coefficient peak in the visible-light spectral region.
- (d) Passivated Au - N codoping in TiO<sub>2</sub> reveals that the combination between N and Au leads to a suitable reduction in the band gap width of pure TiO<sub>2</sub>. Interestingly, Au-N codoping may deduce the effect of photogenerated carriers, produce a new optical absorption feature in the visible region, and enhance the photocatalytic performance of TiO<sub>2</sub>.

This research therefore contributes to the development of ideas for improving optical absorption and photocatalytic performance in the visible light spectral domain in Au doped and Au – N codoped TiO<sub>2</sub> systems by providing fundamental insights into this important question.

### **Author Contributions**

Conceptualization M.B.K., F.A. and C.A.; Data curation, F.A. and M.B.K.; Formal analysis, M.B.K., F.A. and C.A.; Funding acquisition, C.A.; Computational methodology, M.B.K. (lead), Experimental methodology, F.A. and C.A. (lead); Writing—original draft, M.B.K., F.A. and C.A.; Writing—review & editing, C.A., C.J. and P.-F.B. All authors have read and agreed to the published version of the manuscript.

### **Conflicts of interest**

There are no conflicts to declare.

**Acknowledgments:** The authors extend their appreciation to the Deputyship for Research & Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project number (1063).

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