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A DFT + U study of (Rh, Nb)-codoped rutile TiO₂

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Abstract

A systematic study of electronic structure and band gap states is conducted to analyze the monodoping and charge compensated codoping of rutile TiO_2 with Rh and Nb, using the DFT + U approach. Doping of rutile TiO_2 with Rh atoms induces hybridized O 2p and Rh 4d band gap states leading to a red shift of the optical absorption edge, consistent with previous experimental studies. Since Rh monodoping may induce recombination centers, charge compensated codoping with Rh and Nb is also explored. This codoping induces an electron transfer from Nb induced states to Rh 4d states, which suppresses the formation of Rh⁴⁺, thereby leading to a reduction in recombination centers and to the formation of band gap states that account for recombination centers makes (Rh, Nb)-codoped TiO₂ a more efficient and stable photocatalyst.

S Online supplementary data available from stacks.iop.org/JPhysCM/25/085501/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

The development of a safe, abundant and inexpensive photocatalytic material is an important consideration in solving our imminent energy and environmental crisis [1]. Titanium dioxide (TiO₂) is one such promising material that meets the requirements of a good photocatalyst and has therefore attracted wide attention in recent years for use into solar hydrogen production [2, 3], water decontamination [4] and solar cells [5]. However, TiO₂ is a wide band gap semiconductor (3.0 eV for rutile and 3.2 eV for anatase). This restricts sunlight absorbance in the UV range, accounting for <5% of the full solar spectrum and rendering pure TiO₂ inefficient for solar energy conversion. Suitable reduction of the band gap, either by doping or by surface engineering, can lead to significant improvements in the photocatalytic activity of TiO₂ [6–9]. Doping leads to defect states in the band gap [10] which allow sub-band-gap illumination by electronic transitions from VB to defect states or from defect states to CB, thereby improving visible light activity. Recently, disorder-engineered nanophase TiO₂ involving hydrogenation has been demonstrated to exhibit substantial solar-driven photocatalytic performance [9], due to the introduction

of localized mid-gap states and enhanced photogenerated electron-hole separation [11]. However, these intraband states may also serve as recombination centers leading to a significant drop in the overall photocatalytic efficiency [12].

TiO₂ doped with rare earth metals possesses significantly improved photoactivity owing to the enhanced electron density imparted to the titania surface by the dopant oxide [13]. Despite their potential significance, investigations on doping with rare earth metals have so far been limited. In particular, experimental reports of rhodium (Rh) doping suggest that photocatalytic activity depends on the dopant concentration, its distribution, visible light intensity, and the preparation method [12, 14]. Choi *et al* [12] reported that doping TiO₂ with Rh markedly increases photoreactivity, due to the charge transfer transitions between Rh and TiO₂ CB or VB, or a d–d transition in the crystal field. Kitano *et al* [14] showed that Rh-modified TiO₂ samples exhibit higher level of activity than Cu²⁺-modified and nitrogen-doped samples.

Motivated by the above experimental findings and apparent discrepancy in the role of the Rh-dopant, we performed a detailed investigation of the band structure and electronic properties of Rh-doped, Nb-doped and (Rh, Nb)-codoped rutile. Codoping was investigated in order to understand the potential benefit of charge compensation for eliminating or suppressing the recombination centers that may be present in monodoped rutile structures. First-principles based theoretical investigations were conducted so as to clearly delineate the origin of band gap defect states, the local structural environment around the dopant site and the localization of excess charge due to defects. Furthermore, in order to represent strong d-electron correlation in titania, the present study utilized density functional theory with Hubbard energy correction, i.e. the DFT + U method. An in-depth comparison of our theoretical findings with the above-mentioned experimental data is performed so as to ascertain the effect of rare earth metal doping of rutile in the hope of developing an efficient visible light photocatalyst.

2. Computational details

Rutile has a tetragonal crystal structure, with a space group of p42/mnm containing two Ti and four O atoms. A 2 \times 2×3 supercell consisting of 72 atoms was considered in the present calculations. The Quantum-Espresso [15] software package within the plane-wave pseudopotential approach was utilized throughout. The interaction between the valence electrons and the ionic core was described by the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) formulation [16] with Vanderbilt ultrasoft pseudopotentials [17]. The kinetic energy cutoffs of 544 eV (=40 Ryd) and 5440 eV were used for wave functions and charge density, respectively. Brillouin zone integrations were performed using a Monkhorst-Pack [18] grid of $4 \times 4 \times 6$ k-points. The electronic energy falls by less than 0.06 eV/atom between kinetic energy cutoffs of 544 and 816 eV and less than 6×10^{-5} eV/atom between a Monkhorst-Pack grid of 4 \times 4 \times 6 and 6 \times 6×6 k-points, respectively. All calculations were spin polarized. The structures were relaxed using a conjugate gradient minimization algorithm until the magnitude of residual Hellman-Feynman force on each atom was less than $0.025 \text{ eV } \text{\AA}^{-1}$. The bulk lattice parameters for zero pressure rutile structure obtained by variable cell relaxation using DFT, a = b = 4.615 Å and c = 2.961 Å, were found to be in good agreement with experiments [19] and other theoretical calculations [20].

Appreciable underestimation of band gap and delocalization of d and f electrons are well known limitations of DFT. Therefore, we used DFT + U formalism in these calculations. Our DFT calculations suggested a band gap value of 1.89 eV, consistent with other theoretical calculations [21]. On the other hand, the DFT + U approach with U applied to Ti 3d electrons, varying from 1 to 11 eV, revealed a band gap of 2.85 eV at U = 8 eV, far closer to the experimental value. Nevertheless, choosing U solely on the basis of band gap may lead to incorrect conclusions regarding the effect of dopants on the electronic properties [22]. It should instead be chosen depending on the property of interest [23], which, in the current study, is the photocatalytic behavior of TiO₂ that, in turn, depends upon the position of band gap states and their effect on the electronic structure. Spectroscopic K K Ghuman and C V Singh

experiments for bulk reduced rutile TiO₂ crystals suggest a broad gap state lying about 0.9 eV below the CB edge [24, 25]. Following the approach of Moller *et al* [26], it was found that U = 4.2 eV yields the correct position of band gap states due to Ti interstitial and O vacancy defects, while opening up the band gap to 2.2 eV for rutile. This value of U is consistent with theoretical investigations by Morgan *et al* [27], who calculated it by fitting the peak positions for surface oxygen vacancies to experimental XPS data. Furthermore, the resulting electronic projected density of states (PDOS) plot for Ti interstitial and the O vacancy shows that these defect states are composed mainly of titanium d states, in good agreement with experiments [28].

3. Results and discussion

Experimentally obtained x-ray diffraction peaks of Rh-doped TiO₂ have revealed that Rh is substituted for Ti⁴⁺ sites [29]. This is expected because Rh³⁺ ions (0.805 Å) are bigger than Ti⁴⁺ ions (0.61 Å) [30]. As the radius of Nb (0.64 Å) is also comparable to the Ti atom, it should also be substituted for Ti atoms. The concentration of Rh and Nb ions in the present study is ~1.4%, commensurate with the concentration of dopants considered in experiments [29].

3.1. Structural distortion

Doping leads to local structural disorder that modifies the electronic environment and therefore affects photocatalytic properties. Here, structural distortion was investigated by analyzing the local coordination environment, the nature of chemical bonding, and dopant-O-dopant distances. Undoped rutile has a symmetric structure where each Ti atom is bonded to four nearest and two second-nearest oxygen neighbors with bond lengths of 1.95 Å and 1.99 Å, respectively. The introduction of an Rh-dopant into rutile leads to the elongation of all six Rh-O distances without breaking symmetry. However, the introduction of the Nb-dopant leads to elongation of four Nb-O distances and shortening of the other two Nb-O bonds, thereby affecting the symmetry around the dopants to an appreciable extent. A comparison of ionic radii of dopants with respect to Ti atoms suggests that a dopant with smaller ionic radius leads to larger structural distortion. The local structure around the Rh and Nb in codoped TiO₂ is strongly distorted as compared to Rh and Nb monodoped TiO₂. For (Rh, Nb)-codoped structure the O-Rh bond lengths are 2.038, 2.063, and 2.029 Å and the O-Nb bond lengths are 2.005, 1.997 and 1.925 Å. Thus, in (Rh, Nb)-codoping four Nb-O distances get elongated, two Nb-O distances get shortened, and all six Rh-O distances get elongated. Overall, Nb⁵⁺ attempts to shorten two cation-O distances and leaves most of the Rh-O distances notably elongated in order to obtain a coordination environment favorable for its ionic radius. This results in a comparatively more distorted structure than in monodoped TiO₂ structures.

3.2. Formation energy

The formation energy is an important criterion to evaluate the relative difficulty for the incorporation of dopants into the host lattice and therefore the relative stability of the doped systems. The formation energies of Rh-doping, Nb-doping and (Rh, Nb)-codoping can be written as

$$E_f(\mathbf{Rh}) = E(\mathrm{Ti}_{24-n_1}\mathbf{Rh}_{n_1}\mathbf{O}_{48}) - (E(\mathrm{Ti}_{24}O_{48}) + n_1\mu_1 - n_0\mu_0),$$
(1)

$$E_f(Nb) = E(Ti_{24-n_2}Nb_{n_2}O_{48}) - (E(Ti_{24}O_{48}) + n_2\mu_2 - n_0\mu_0)$$
(2)

$$E_{f}(\text{RhNb}) = E(\text{Ti}_{24-n_{1}-n_{2}}Rh_{n_{1}}Nb_{n_{2}}O_{48})$$
(2)

$$-(E(\mathrm{Ti}_{24}O_{48}) + n_1\mu_1 + n_2\mu_2 - n_0\mu_0), \qquad (3)$$

where $E(\mathrm{Ti}_{24-n_1}\mathrm{Rh}_{n_1}\mathrm{O}_{48}),$ $E(Ti_{24-n_2}Nb_{n_2}O_{48}),$ $E(\text{Ti}_{24-n_1-n_2}\text{Rh}_{n_1}\text{Nb}_{n_2}\text{O}_{48})$ and $E(\text{Ti}_{24}\text{O}_{48})$ are the total energies of the Rh-doped TiO₂, Nb-doped TiO₂, (Rh, Nb)codoped TiO₂ and pure TiO₂, respectively. μ_0 , μ_1 and μ_2 are the chemical potentials of the Ti, Rh and Nb elements, respectively; n_0 , n_1 and n_2 denote the numbers of the host (Ti) atoms substituted, Rh-dopant atoms and Nb-dopant atoms, respectively. In the present study, hcp bulk metal Ti, fcc bulk metal Rh and bcc bulk metal Nb were used to determine the chemical potentials. Since the focus here is on the relative stabilities, the choice of chemical potential should not influence the conclusions on the stability of the doped TiO₂. The calculated formation energies for Rh-doped and Nb-doped rutile were +0.417 eV and -0.0689 eV, respectively. Positive and negative values of the formation energy for Rh- and Nb-doped TiO₂ respectively, suggest that Nb-doped TiO_2 is more stable as compared to Rh-doped TiO_2 .

Calculation of the formation energy is also useful in determining the most stable configuration of the codoped structure. For this purpose, six nearest neighbor codoping systems, labeled 1-6 in figure 1, were constructed. The calculated formation energies for Rh-Nb distances of 2.95, 3.68, 4.62, 5.56, 5.63 and 7.23 Å were equal to 0.232, 0.241, 0.240, 0.239, 0.240 and 0.233 eV, respectively. A relatively small range of formation energies of structures with different Rh-Nb distances indicates high stability of the codoped TiO₂ structures. For subsequent study of the electronic properties, the most stable (Rh, Nb)-codoped structure with dopant–dopant distance of 2.95 Å and $E_f =$ 0.232 eV was chosen. The chosen Rh and Nb atoms are highlighted in blue and green, respectively, in figure 1. (Rh, Nb)-codoped TiO_2 has a smaller formation energy than that of Rh-doped TiO2. Therefore, choosing Nb as a codopant not only favors charge compensation but also makes it easier to incorporate dopants into the host lattice, thus leading to a more stable codoped system as compared to Rh-doped TiO₂. This finding is consistent with experimental observations [29]. On the whole, structural distortion and formation energy results suggest that the stability of defect formation depends on the ionic radius of the dopant, in agreement with Nolan [31]. The strong distortion due to the small ionic radius of dopant Nb makes (Rh, Nb)-codoped TiO₂ more stable than Rh-doped TiO₂.



Figure 1. The (Rh, Nb)-codoped $2 \times 2 \times 3$ supercell of rutile. Ti, O, Rh and Nb atoms are highlighted in gray, red, blue and green, respectively. The six nearest neighboring positions considered for the Nb atom are shown along with dopant–dopant distances.

3.3. Electronic properties

In order to understand the photocatalytic properties of doped systems, the spin polarized DOS and PDOS [32] were calculated for Rh-doped, Nb-doped and (Rh, Nb)-codoped rutile TiO_2 , as shown in figures 2–4. The corresponding spin density plots are also shown. A conventional Gaussian smearing of 0.1 eV was utilized.

3.3.1. Rh-doped rutile TiO_2 . The total DOS with PDOS for the d electrons of Rh and Ti atoms and p electrons of O atoms of the Rh-doped rutile are summarized in figure 2(a). Rh-doping increases the asymmetry between the neighboring atoms and introduces an unpaired d electron from Rh. As a result an intermediate energy band of 0.3 eV width is found approximately 1.0 eV below the CB minima, along with some states at CB and VB tails. This leads to an overall reduction in the band gap by 0.5 eV. To further understand the nature of defect states, consider the electronic configurations of Rh: $4d^85s^1$ and Ti: $3d^24s^2$. Substitution of Ti with Rh leads to a formal +4 state (Rh^{4+}), i.e. $4d^55s^0$ configuration. Since the stable oxidation state of Rh is +3, an electron gets transferred from neighboring O atoms to Rh^{4+} leading to O^{1-} defects. The band gap states are mainly due to hybridization of Rh 4d and O 2p states. The spin density plot (figure 2(b)) also shows that the spin densities are strongly localized on the dopant atom and O¹⁻ sites in its neighborhood. To further clarify the origin of band gap states, we present in figure 2(c)the five-fold degenerate Rh 4d states. The 2-fold degenerate e_g states split into $d_{x^2-v^2}$ and d_{z^2} states, whereas the 3-fold degenerate t_{2g} states split into doubly degenerate states (d_{xz} , d_{yz}) and a single state (d_{xy}). It is evident from figure 2(c) that only the $d_{x^2-v^2}$ state of the Rh 4d orbital contributes to the band gap state. Rh-doping of rutile has also been investigated by Tan et al [33]. Their calculations suggested band gap states very near the VB maxima, whereas in the present case defect states are almost in the middle of band gap. Nonetheless, in



Figure 2. The density of states and projected density of states on the p and d orbitals (a), spin density (b) and projected density of states for the Rh 4d states (c) in the Rh-doped rutile model. The zero energy value is set at the top of VB and the Fermi energy is represented by the vertical dashed line in (a) and (c).

both studies, the contribution to band gap states comes from the same $d_{x^2-y^2}$ state of the Rh 4d orbital. The difference in position of band gap states can be attributed to a different choice of *U* parameter.

The formation of VB by states associated with other elements, along with O 2p, is indispensable in designing visible-light-driven photocatalysts as it moves to the top of the VB to a more positive potential than the oxidation potential of H_2O to O_2 without affecting the CB level and charge migration [34]. Thus an acceptor state at the VB maxima not associated with O 2p but with the Rh³⁺ ions can increase photoactivity in Rh-doped TiO₂ significantly. Additional states present in the band gap may also contribute to increased photoactivity due to electron excitations under visible light irradiation from the top of the VB to the band gap states and then from band gap states to the bottom of the CB. Choi et al [12] also suggest that Rh-doped TiO₂ shows red shift due to charge transfer between Rh and TiO₂ CB or VB, or a d-d transition in the crystal field. These mid-gap states are not without a downside, however, as they can act as recombination

centers, consequently leading to a significant reduction in the photocatalytic efficiency. According to Niishiro et al [29], this recombination is chiefly due to the formation of Rh⁴⁺. Experimental observations on Rh-doped TiO₂ suggest that the formation of Rh⁴⁺ is dependent on the preparation method. For instance, Kitano et al [14] prepared Rh-modified TiO₂ using the equilibrium adsorption method without thermal activation. In contrast, Niishiro et al [29] prepared the Rh-doped system by impregnating the Rh source followed by high-temperature calcination. Due to this, a part of the Rh ions present in the TiO₂ host can get oxidized to Rh⁴⁺, leading to almost negligible photocatalytic activity. In such cases, charge compensated codoping with pentavalent ions such as Nb5+ might be useful for suppressing the formation of Rh⁴⁺ ions. Therefore, we further investigated codoping rutile with Rh and Nb in subsequent discussion.

3.3.2. *Nb-doped rutile TiO*₂. Before proceeding to charge compensated doping, let us describe observations on Nb monodoped rutile. From the total DOS, PDOS and



Figure 3. The density of states and projected density of states on the p and d orbitals (a) and spin density plot (b) for one Nb atom doped in 72-atoms rutile model. The zero energy value is set at the top of VB and Fermi energy is represented by the vertical dashed line in (a).

accompanying spin density plots shown in figure 3, it can be deduced that the substitution of the Ti⁴⁺ atom with Nb⁵⁺ in TiO₂ results in a narrow peak of 0.3 eV width in the band gap approximately 1.3 eV below the CB edge. It is noted here that our independent calculations using DFT alone did not show a band gap state with excess charge occupying the bottom of the CB. This implies the necessity and significance of the DFT + U approach in reproducing electronic states and band structure commensurate with the experimental observations in an accurate and physically consistent manner. The PDOS plot (figure 3(a)) also suggests that the defect state is mainly due to contribution from Ti atoms. Experimental data have also shown a defect state in the band gap well separated from the CB [35], with a height proportional to the Nb concentration. These observations on Nb-doped TiO_2 with DFT + U agree with previous theoretical investigations by Morgan et al [36]. Considering the electronic configuration of Nb $(4p^{6}4d^{3}5s^{2})$, substitution of Ti by Nb should result in the Nb⁴⁺ state, i.e. 4p⁶4d¹5s⁰ configuration. To obtain a stable oxidation state of +5 the extra electron from Nb⁴⁺ is preferentially transferred to Ti⁴⁺ and therefore the Ti³⁺ state is formed. This is confirmed by a spin density plot (figure 3(b)) which shows that the spin density strongly localized on a single Ti site in a nearest neighbor position relative to the Nb-dopant.

3.3.3. (*Rh*, *Nb*)-codoped rutile TiO₂. The presence of Rh states at VB maxima and intermediate band with considerable bandwidth in Rh-doped rutile indicates the great potential of using the Rh-doped material for visible light photocatalytic applications. This intermediate band offers a stepping stone for the absorption of low energy photons via the excitation of electrons at the VB maximum to the intermediate band gap states can also act as recombination centers, see e.g. experimental observations by Niishiro *et al* [29]. This charge recombination renders Rh-doped TiO₂ as an ineffective photocatalyst. These

recombination centers need to be eliminated by suppressing Rh^{4+} ions. This can be achieved by codoping of TiO₂ by a combination of p-type and n-type dopants, as also suggested in [29, 37]. In this context, further codoping of Rh-doped rutile with Nb was investigated with the goal of eliminating Rh^{4+} ions through charge compensation. To study the codoped system, we constructed six nearest neighbor codoped structures. These structures were relaxed and the structure having a Rh–Nb distance of 2.95 Å showed the lowest configuration energy and is therefore considered for further analysis.

Total spin polarized DOS and PDOS for the d electrons of Rh, Nb and Ti atoms and p electrons of O atoms of the (Rh, Nb)-codoped rutile are shown in figure 4(a). Based on the analyses of Rh and Nb monodoping described earlier in the paper, Rh-dopant requires an extra electron to achieve the stable +3 oxidation state whereas Nb-dopant introduces an extra electron into the system. Thus, when rutile is codoped with Rh and Nb the extra electron on Ti³⁺ due to Nb transfers to the Rh-dopant, such that the Rh species attains a + 3 state $(4d^55s^1)$ while the Nb species attains a $+5 (4p^64d^05s^0)$ state, with both resulting states being more stable. This charge compensation of the (Rh, Nb)-codoped system can also be inferred in the spin density plot (figure 4(b)) by the absence of excess spin density states. This codoping reduces the band gap by 0.5 eV relative to undoped TiO₂, due to the new VB consisting of hybridized Rh and O 2p orbitals which results in decreased band gap energy without affecting the CB level. The Rh $d_{x^2-y^2}$ orbital, which was earlier responsible for band gap states in Rh-doped rutile, now shifts to a fully filled state at the VB minimum, as shown in figure 4(c).

In order to explain this behavior, we compare the DOS curves of monodoped and codoped TiO_2 . Band gap states for the monodoped systems (figure 2(a) and figure 3(a)) are too deep in the forbidden gap and do not overlap sufficiently with the band states of TiO_2 . This leads to localization of photogenerated carriers. On the other hand, in the charge



Figure 4. The density of states and projected density of states on the p and d orbitals (a), spin density (b) and projected density of states for the Rh 4d states (c) in (Rh, Nb)-codoped rutile model. The zero energy value is set at the top of VB and Fermi energy is represented by the vertical dashed line in (a) and (c).

compensated codoped system, the acceptor states shift toward the VB edge while the donor states shift toward the CB edge (figure 4(a)). This enhances coupling between the donor states and O 2p states, and between the acceptor states and the CB, resulting into the formation of delocalized holes and electrons [38]. These shallow acceptor and donor states can significantly accelerate the mobility of the trapped charges causing rapid transportation of the photogenerated carriers in the (Rh, Nb)-codoped TiO2 as compared to Rh-doped and Nb-doped TiO₂. Furthermore, the codoped structure does not require formation of O vacancies to provide an extra electron to Rh. This, in turn, leads to a smaller degree of defectiveness and the elimination of recombination centers. Our analysis thus establishes the beneficial aspects of charge compensated codoping and seems to explain the findings of Niishiro et al [29] for (Rh, Nb)-codoped TiO₂.

3.4. Charge density

To further substantiate the electronic properties and to study the variation of chemical bonding induced by Rh

and Nb codoping, the electron charge density distributions for undoped and charge compensated systems were also analyzed. As depicted in figure 5, the contour plots of the charge density on (1 1 0) and (0 1 0) represent the effect of dopants on nearest neighboring O and Ti atoms, respectively. The charge density around Rh and Nb atoms is nearly spherically distributed with a slight deformation toward their nearest neighboring atoms. Figure 5(e) shows that there are clear covalent bridges between dopants and O atoms, which strengthens the judgment of certain covalent characters of (Rh, Nb)-codoped rutile. Furthermore, it can be seen that the overlap of the Nb 4d orbital with O 2p is greater than that of the Rh 4d orbital with O 2p, which indicates that the degree of covalency between Nb and O is stronger than that between Rh and O. A weaker interaction between Rh and O atoms as compared to that between Ti and O atoms makes the Rh-O bond longer and leads to smaller binding energy. Consequently the O 2p states, which are dominating in the VB edge, move toward high energy levels and shift the VB maximum to increased energy, thereby reducing the band gap. From (0 1 0) plane, on comparing with undoped



Figure 5. Two dimensional 110 (a) and 010 (b) planes indicated in black for which charge density contour plots (electron bohr⁻³, (1 bohr = 0.529 Å) units) are depicted. The charge density plot for undoped rutile in the 110 plane (a), undoped rutile in the 010 plane (b), (Rh, Nb)-codoped rutile in the 110 plane (c) and (Rh, Nb)-codoped rutile in the 010 plane (d). The red regions denote the area with nearly zero electron density and the pink regions denote the highest electron density.

rutile (figure 5(d)), it can be seen that there is a considerable charge accumulation in the bonding regions of Rh and Nb dopants (figure 5(f)). This confirms the sharing (or transfer) of

an electron between the dopants. The accumulation of charge in the region close to the dopants also suggests the formation of a metallic contact. It should be noted that the electron

 Table 1. Average charge states (e) of dopants and their adjacent Ti and O atoms from Bader analysis.

_				
Dopant	Rh	Nb	Ti	0
None			+2.3274	-1.1638
Rh	+1.8055		+2.3589	-1.0917
Nb		+2.7154	+2.2118	-1.1744
(Rh, Nb)	+1.6005	+2.7181	+2.3464	-1.1325

charge density plotted on the plane next to doped elements is almost completely unaffected by the presence of the doping elements.

3.5. Bader charge analysis

In order to understand the nature of interatomic charge distributions quantitatively, Bader analysis based on the atom-in-molecule (AIM) theory was conducted [39]. The charge states of atomic species in monodoped and codoped TiO₂ were calculated using a grid based decomposition algorithm [40]. The oxidation states of Rh in Rh-doped TiO_2 and Nb in Nb-doped TiO_2 (table 1) reveal that the Rh valence shell 4d⁸5s¹ loses 1.8055e charge while the Nb valence shell $4p^{6}4d^{3}5s^{2}$ loses 2.7154e to form bonds with adjacent oxygen atoms. As a comparison, Ti in pure TiO₂ loses 2.3274e to form bonds with adjacent oxygen atoms. Thus the charge accumulation around the Rh center (=7.1945e) is smaller by 2.4781e than that of Ti, leading to a weaker coupling between O and Rh. On the other hand, the charge accumulation around the Nb center (=10.2846e) is larger by 0.61198e than that of Ti, leading to stronger coupling between O and Nb as compared to Ti and O. In Rh-doped TiO₂, as Rh tries to attain a stable oxidation state of +3, the charge gets transferred from neighboring O atoms to Rh, leading to oxygen defects. This is in contrast to the Nb-doped system, as in this case Nb attains a stable oxidation state of +5 causing charge transfer from Nb to Ti and thereby leading to Ti defects. Finally, when the (Rh, Nb)-codoped TiO₂ system is considered, it is observed that Rh is less oxidized in this configuration as compared to that in Rh-doped TiO₂, whereas Nb is more oxidized as compared to that in Nb-doped TiO₂. Consequently, the stoichiometric charge states of Ti and O are almost restored to oxidation states present in an undoped TiO₂ configuration.

4. Conclusions

In this work, *ab initio* calculations were conducted to understand conflicting experimental results for photocatalytic behavior of Rh-doped TiO₂ and to explore the design of a more efficient photocatalyst by codoping it with Nb. DFT + U methodology was utilized to remove the excessive delocalization of Ti d orbitals present in standard DFT calculations. Doping rutile with an Rh atom induces states at VB minima and an intermediate band that leads to a red shift in the optical absorption edge, which is also observed in previous experimental investigations. But since these states may also act as recombination centers due to the presence of Rh⁴⁺ ions, codoping with Nb was investigated. The following conclusions can be derived from the present study:

- (i) The formation energy of the Rh-doped system reduces appreciably on codoping it with Nb, suggesting a spontaneous formation of (Rh, Nb)-codoped rutile TiO_2 at room temperature.
- (ii) Codoping affects the symmetry, leading to a weaker interaction and longer bond between Rh and O as compared to Nb and O. This structural distortion reduces the binding energy and the O 2p states tend to move from the VB edge toward high energy levels, reducing the overall band gap. The hybridized O 2p and Rh 4d states at the top of VB in codoped rutile are thought to be responsible for the red shift of the optical absorption edge, confirming previous experimental studies [29, 12, 14].
- (iii) Rh-dopant requires an extra electron to achieve the stable +3 oxidation state whereas Nb-dopant introduces an extra electron into the system. Thus, when the system is codoped with Rh and Nb, both dopants attain their stable oxidation states. It means that the creation of the oxygen vacancy is not required in a codoped structure. This leads to a significant reduction in the level of defectiveness and thus an enhanced photocatalytic activity.
- (iv) Unlike Rh-doped rutile that has an isolated band gap state which may act as a recombination center and can reduce charge migration, charge compensated (Rh, Nb)-codoping does not show such band gap states which commensurate with the experimental findings of Niishiro *et al* [29]. This elimination of recombination centers in combination with a band gap reduction by 0.5 eV makes codoped rutile a better photocatalyst.

Overall, the present study reinforces the usefulness of charge compensated codoping for reducing the band gap in photocatalysts, without creation of unwanted recombination centers. In the near future, we plan to apply this technique further to amorphous TiO_2 in the hope of developing more efficient and cost-effective visible light photocatalysts.

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