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Electronic Conductivity and Stability of Doped Titania ($\text{Ti}_{1-x}\text{M}_x\text{O}_2$, $\text{M} = \text{Nb}$, Ru , and Ta)—A Density Functional Theory-Based Comparison

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The structure, electrical conductivity, and stability of Nb-, Ru-, and Ta-doped titania were compared by density functional theory. Both anatase and rutile structures were investigated. Doping causes lattice expansion in all cases. The mechanism by which Ru-doping induces electrical conductivity in titania differs from those by Ta- and Nb-doping. Ru-doping fills the titania band gap primarily with its own d-electrons. On the other hand, Ta- and Nb-doping shift the Fermi level to the originally unfilled conduction states. Substitution free energy calculations indicate that a uniform $\text{Ti}_{0.75}\text{M}_{0.25}\text{O}_2$ solution is favorable for Nb- and Ta-doping but unfavorable for Ru-doping. In addition, we also considered the effect of dopant concentration on the electrical conductivity of doped titania in the rutile phase. For Nb- and Ta-doping, increasing dopant concentration above mole fractions of 0.0625 and 0.125, respectively, gives diminished increment in Fermi level electron density. On the other hand, electron density at the Fermi level of Ru-doped rutile is more linearly dependent on Ru mole fraction.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising power sources for the future because they do not emit greenhouse gases and are more efficient than internal combustion engines. At present, PEMFCs are approaching energy density levels sufficient for commercial viability. With that accomplishment, the focus of PEMFC research is moving toward long-term durability and development of key components to cope with the high-performance environment. For example, when modern fuel cells operate at higher current densities, they produce water at a faster rate and, consequently, require better water management to prevent flooding. A promising approach is to operate PEMFCs at a higher temperature ($\geq 120^\circ\text{C}$). In addition, higher-temperature operation has advantages that include less vulnerability to CO poisoning, faster reaction kinetics, and recoverable heat.¹ Unfortunately, carbon materials that support Pt catalysts in PEMFCs today (operating at around 80°C) corrode easily under elevated-temperature and high-potential conditions. Ceramics provide an alternative to carbon-based catalyst support material for PEMFCs operating at 120 – 200°C . Antolini and Gonzalez² have recently reviewed studies in this area.

Doped titania ($\text{Ti}_{1-x}\text{M}_x\text{O}_2$, where M is dopant metal and X is dopant mole fraction) is the most viable candidate for ceramic catalyst support materials. $\text{Ti}_{1-x}\text{M}_x\text{O}_2$ can have reasonable specific surface area and acceptable electrical conductivity. Furthermore, it can hold catalyst particles dispersed in good sizes. Studies so far have shown that doped titania is stable in fuel cell conditions. Park and Seol³ demonstrated that Pt supported on Nb-doped TiO_2 has higher oxygen reduction activity than those supported on Vulcan XC carbon. The conductivity of the prepared Nb-doped TiO_2 was reported to be $\sim 0.1 \Omega^{-1} \text{cm}^{-1}$. Garcia et al.⁴ prepared a PtRu catalyst supported on $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$. Tests in a direct methanol fuel cell

showed higher current (A/mgPt) for PtRu supported on $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$ than one supported on E-TEK carbon. Haas et al.⁵ prepared $\text{Ti}_{1-x}\text{Ru}_x\text{O}_2$ support for Pt electrode and showed significant increase in electric conductivity for $X \geq 0.27$; however, they were unable to get a uniform solution at $X < 0.5$. Wang et al.⁶ synthesized a $\text{Pt}/\text{Ti}_{0.9}\text{Ru}_{0.1}\text{O}_2$ electrode that showed high electrocatalytic activity for oxygen reduction with much better stability than that of Pt/C in an antipolarization experiment. This result is quite different from that of Haas et al. who could not obtain a uniform solution at such a low dopant ($X = 0.1$) mole fraction.

Aside from high-temperature PEMFC applications, titania (TiO_2) has been the subject of many studies in both doped and undoped forms. The rutile and anatase polymorphic phases of TiO_2 have particularly received much attention in recent years due to their stability and high surface area. Their applications include photocatalysts,^{13–16} heterogeneous catalyst support,¹⁷ and gas sensors.^{18,19} Transition electron microscopy, scanning electron microscopy, atomic force microscopy, and X-ray diffraction studies have shown that transition metal-doped TiO_2 can form uniform solution with no sign of phase separation.^{7–12} Crystal structures of the polymorphic rutile²⁰ and anatase²¹ phases have been determined by X-ray diffraction and are illustrated in Figure 1. Doping TiO_2 with transition metals has been shown to induce lattice expansion^{15,16,22–24} and electrical conductivity. Electrical conductivity has been reported to be in the range of $\sim 10^3 \Omega^{-1} \text{cm}^{-1}$ for $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$,²⁵ $\sim 10^3 \Omega^{-1} \text{cm}^{-1}$ for $\text{Ti}_{0.85}\text{Ta}_{0.15}\text{O}_2$,²⁶ and $0.78 \Omega^{-1} \text{cm}^{-1}$ for $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$.²⁷ (Note that these values are rough guides since sample preparation and morphology were quite different among authors.) In comparison, pure TiO_2 is a semiconductor with a conductivity of $\sim 10^{-6} \Omega^{-1} \text{cm}^{-1}$.^{28,29}

Recently, our group compared the stability and oxygen reduction reactivity of Pt on several support materials: undoped TiO_2 , Nb-doped TiO_2 , H_2 -reduced TiO_2 , and a commercial carbon.³⁰ Our experiments showed that Pt on Nb-doped TiO_2 retained 60% of the electrochemically active surface area after

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Figure 1. Supercell models for anatase and rutile phases: (a) $1 \times 2 \times 1$ anatase model; (b) $1 \times 1 \times 2$ rutile model. The larger spheres represent oxygen ions, while the smaller spheres represent titanium or dopant ions. In the cases of undoped titania (TiO_2), all small spheres (dark and lighter ones marked M) represent Ti ions. In the cases of $\text{Ti}_{0.75}\text{M}_{0.25}\text{O}_2$, M is the location of the dopant (Nb or Ta or Ru).

1000 cycles. In comparison, Pt on H_2 -reduced TiO_2 retained 42% surface area, while Pt on undoped TiO_2 retained only 32%. The Pt/C catalyst was the least stable and retained only 20% active surface area. On the other hand, the Pt/C had the highest initial oxygen reduction activity due to its larger specific area ($17.1 \text{ m}^2 \text{ g}^{-1}$ vs $5.0 \text{ m}^2 \text{ g}^{-1}$ for Pt/Nb-doped TiO_2) and higher conductivity. The Pt supported on both Nb-doped and reduced TiO_2 was more active than the one supported on undoped TiO_2 . Clearly, $\text{Ti}_{1-x}\text{M}_x\text{O}_2$ is a promising catalyst support for high-temperature PEMFCs; however, more research is required to understand and improve their electrical conductivity and stability.

With our promising experimental results, we now turn to density functional theory (DFT) computations on $\text{Ti}_{1-x}\text{M}_x\text{O}_2$ to gain atomic-level understanding essential for the design of more stable and electrically conductive catalyst supports. Specifically, the objective of this paper is to compare undoped (TiO_2) and doped titania from the theoretical perspectives of conducting electron density and substitution reaction energy to gain insight into their electrical conductivity and stability with doping. Niobium (Nb)^{3,4} and ruthenium (Ru)^{5,6} were chosen as dopants (M) because experimental studies have shown that titania doped with these metals can be deposited with Pt nanoparticles to produce a usable electrode. Tantalum (Ta) was also considered because this metal is stable in harsh electrochemical environments and doping with this metal also improves titania's conductivity.^{26,31} Both anatase and rutile phases of titania were studied. Nb-, Ru-, and Ta-doped titania were compared to undoped titania and to each other in the aspects of structure, partial and total density of states (DOS), and free energy of substitution. In addition, Ru-, Nb-, and Ta-doped rutile at mole fractions of 0.0625 and 0.125 were also studied in order to know the optimal mole fraction with respect to electric conductivity. To our best knowledge, although there are several DFT studies on TiO_2 ,^{32–36} the study and discussions presented in this paper are not available in literature.

Computational Models and Methods

Spin-polarized ab initio calculations based on DFT^{37,38} were performed using projector-augmented waves^{39,40} as implemented in the Vienna Ab-initio Simulation Package version 4.6.^{41–43} Generalized gradient approximation PW91^{44,45} was used for the exchange-correlation functionals. The cutoff energy was set at 520 eV. The three-dimensional Brillouin zone was automatically sampled with the Monkhorst–Pack method using $7 \times 7 \times 7$ k -points; at that point, energy converged to less than 0.01 eV. Geometry optimizations were accomplished with the conjugate-gradient algorithm. The cell structures presented in this paper were plotted with VESTA.⁴⁶ Densities of states were plotted with Xmgrace⁴⁷ and P4VASP.⁴⁸

TABLE 1: Experimental and Theoretical Structural Data for TiO_2

	our work	exptl	other calcd	
		Rutile		
a (Å)	4.641	4.5936 ²⁰	4.545 ³⁴	4.653 ³⁵
c (Å)	2.971	2.9587 ²⁰	2.919 ³⁴	2.965 ³⁵
		Anatase		
a (Å)	3.810	3.7842 ²¹		
c (Å)	9.671	9.5146 ²¹		

Structure, Electronic Density of States, and Free Energy of Substitution. TiO_2 was modeled by supercells that contain $1 \times 2 \times 1$ unit cells of anatase (Figure 1a) and $1 \times 1 \times 2$ unit cells of rutile (Figure 1b). Both rutile and anatase supercells have four titanium ions and eight oxygen ions. All structures were optimized and compared to previous studies^{20,21,34,35} where available as shown in Table 1. $\text{Ti}_{1-x}\text{M}_x\text{O}_2$ were modeled by replacing one out of four Ti ions with Nb, Ta, and Ru as described in Figures 1a and 1b. This corresponds to a 0.25 mol fraction (X) doping, i.e., $\text{Ti}_{0.75}\text{M}_{0.25}\text{O}_2$, where $M = \text{Nb}$, Ta , and Ru . Note that in Figure 1 the larger spheres represent oxygen ions while the smaller spheres represent titanium or dopant ions. In the cases of undoped titania (TiO_2), all small spheres (dark and lighter ones marked M) represent Ti ions. In the cases of $\text{Ti}_{0.75}\text{M}_{0.25}\text{O}_2$, locations where dopants (Nb, Ta, and Ru) replace titanium are represented by lighter spheres marked M.

Effect of Dopant Concentration. The supercell was subsequently expanded to contain $2 \times 2 \times 2$ unit cells of rutile in order to study the effects of lowering dopant concentration. One (Figure 2a), two (Figure 2b), and four (Figure 2c) Ti ions were replaced with M to correspond to $\text{Ti}_{1-x}\text{M}_x\text{O}_2$, where $X = 0.0625$, 0.125, and 0.25, respectively. In Figure 2, metal ions ($M = \text{Nb}$, Ru , and Ta) are represented by light-colored spheres marked M. Unmarked small spheres represent Ti ions while large spheres represent O.

Calculations for $M = \text{Nb}$, Ru , and Ta were performed and compared. Only the rutile phase was chosen for this part because results obtained from the first set of calculations (using $1 \times 2 \times 1$ for rutile and $1 \times 1 \times 2$ anatase as described in the previous paragraph and Figure 1) show that metal doping yields similar electronic effects on the anatase and rutile phases. Furthermore, anatase supercells have higher volumes and are computationally too expensive.

Results and Discussion

Structure. We explored the structures of TiO_2 systems. This also serves as a validation tool for our computational methodology. Table 1 shows experimental X-ray diffraction data and our calculation results for rutile and anatase structures. Results are reported as crystallographic data for direct comparison. Our calculations fall well within the expected range of accuracy for DFT-type calculations.

Experiments have shown that Nb-doping causes the titania lattice expansion.^{22,23} From X-ray diffraction data, Ghicov et al.²² calculated that lattice constants a and c increased by 0.038 and 0.04 Å, respectively, for a Nb-doped anatase annealed from amorphous $\text{Ti}_{0.26}\text{Nb}_{0.13}\text{O}_{0.61}$. Table 2 shows the optimized lattice parameters of TiO_2 versus $\text{Ti}_{1-x}\text{M}_x\text{O}_2$, which demonstrates lattice expansion with doping. Our results indicate that the lattice expansion can partly be attributed to the increase in ionic radii (r) of Ti ions as electrons move toward vacant Ti d-orbitals in the presence of dopants—see detailed discussion in the following section. Lattice expansion can also be caused by a longer M–O

Figure 2. Rutile phase supercell models with different dopant mole fractions: (a) $\text{Ti}_{0.9375}\text{M}_{0.0625}\text{O}_2$, (b) $\text{Ti}_{0.875}\text{M}_{0.125}\text{O}_2$, (c) and $\text{Ti}_{0.75}\text{M}_{0.25}\text{O}_2$. Metal ions ($\text{M} = \text{Nb}$, Ru , and Ta) are represented by light-colored spheres marked M . Unmarked small spheres represent Ti ions, while large spheres represent O ions.

TABLE 2: Optimized Structure of TiO_2 and $\text{Ti}_{0.75}\text{M}_{0.25}\text{O}_2$

	TiO_2	$\text{Ti}_{0.75}\text{Nb}_{0.25}\text{O}_2$	$\text{Ti}_{0.75}\text{Ru}_{0.25}\text{O}_2$	$\text{Ti}_{0.75}\text{Ta}_{0.25}\text{O}_2$
		Rutile		
a (Å)	4.641	4.703	4.702	4.661
c (Å)	2.971	2.996	3.005	2.981
volume (Å ³)	64.00	66.26	66.43	64.76
		Anatase		
a (Å)	3.810	3.874	3.879	3.828
c (Å)	9.671	9.832	9.698	9.847
volume (Å ³)	140.4	147.6	145.9	144.3

bond length compared to the $\text{Ti}-\text{O}$ bond in pure titania; this is the case for Ru -doped titania where changes in $\text{Ti}-\text{O}$ bond length and Ti d-orbital occupancy were not significant, and the lattice expanded due to a longer $\text{M}-\text{O}$ distance.

Electronic Density of States. Semiconductivity, as that found in undoped titania, lies in the inability of valence electrons to cross the Fermi level due to the presence of a band gap. Doping can modify the electronic band structure and improve electrical conductivity by either narrowing or bridging the band gap at the Fermi level, or by shifting the Fermi level.

Figures 3a and b show the total DOS (density of states, up-spin plus down-spin electrons) of undoped and doped rutile and anatase. On the top of each figure is the total density of states of undoped rutile and anatase, respectively. As can be seen, the electron density (y -axis) at the Fermi level ($E - E_f = 0$) is practically zero for undoped rutile and anatase, which is expected as titania is a semiconductor.

The total density of states of Ru -, Nb -, and Ta -doped rutile and anatase are displayed below undoped titania in Figures 3a

Figure 3. Computed total density of states of pure and doped titania (TiO_2 , $\text{Ti}_{0.75}\text{Ru}_{0.25}\text{O}_2$, $\text{Ti}_{0.75}\text{Nb}_{0.25}\text{O}_2$, and $\text{Ti}_{0.75}\text{Ta}_{0.25}\text{O}_2$): (a) anatase phase, (b) rutile phase. As can be seen in the top portion of (a) and (b), the electron density (y -axis) at the Fermi level ($E - E_f = 0$) is practically zero for pure rutile and anatase, which is expected as titania is a semiconductor. The total densities of states of Ru -, Nb -, and Ta -doped titania (second-from-top to bottom, respectively) are displayed below pure TiO_2 . For doped TiO_2 , the electron densities (y -axis) at the Fermi level ($E - E_f = 0$) are significant, confirming the fact that doping induces electrical conductivity in TiO_2 .

and b, respectively. The theoretical DOS of rutile $\text{Ti}_{0.75}\text{Ru}_{0.25}\text{O}_2$ has been previously reported by Glassford and Chelikowsky,³⁶ which yields essentially similar results and agrees reasonably with experiment. However, we did not find any comparison of DOS for Ru - versus Ta - or Nb -doped titania in literature.

Doping perturbs the electronic structure, yielding good amounts of electrons at the Fermi level. Compared with the total DOS of titania, Ta - and Nb -doping shifted bands significantly to the left side. The DOSs of Ta - and Nb -doped titania are hardly distinguishable near the Fermi level, but there is an interesting difference between the DOS profile of Ru -doped versus Ta - and Nb -doped titania. The difference in the DOS profile implies a difference in the origin of electrical conductivity. Our investigations into the local density of states reveal that Ru fills electrons into the band gap with its own d-electrons and perturbs some Ti d-electrons into the same region as shown in Figures 4a and b. On the other hand, Ta and Nb induce electronic conductivity by shifting the Fermi level to the originally unfilled bands of TiO_2 as shown in Figure 4c–f. In contrast to $\text{Ti}_{1-x}\text{Ru}_x\text{O}_2$, the electrons at the Fermi level in

Figure 4. Computed partial density of states of doped anatase and rutile phases: (a) anatase $\text{Ti}_{0.75}\text{Ru}_{0.25}\text{O}_2$, (b) rutile $\text{Ti}_{0.75}\text{Ru}_{0.25}\text{O}_2$, (c) anatase $\text{Ti}_{0.75}\text{Nb}_{0.25}\text{O}_2$, (d) rutile $\text{Ti}_{0.75}\text{Nb}_{0.25}\text{O}_2$, (e) anatase $\text{Ti}_{0.75}\text{Ta}_{0.25}\text{O}_2$, and (f) rutile $\text{Ti}_{0.75}\text{Ta}_{0.25}\text{O}_2$. Lines with triangles represent partial Ti d-electron contribution, lines with squares represent partial dopant (Ru, Nb or Ta) d-electron contribution, and lines with diamonds represent partial oxygen p-electron contribution to the total density of states (simple lines).

$\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$ and $\text{Ti}_{1-x}\text{Ta}_x\text{O}_2$ correspond primarily to Ti d-orbitals (with Nb/Ta d-orbitals and O p-orbitals as minor contributors) as shown in Figures 4c–f. Note that Ru-doping also shifts the Fermi level of $\text{Ti}_{1-x}\text{Ru}_x\text{O}_2$ versus undoped TiO_2 but not enough to fill the conduction bands of titania.

Both mechanisms are known to induce electrical conductivity in semiconductors. This is in agreement with the fact that Ta-, Nb-, and Ru-doped TiO_2 are electrically conductive. Electrical conductivity has been reported to be in the range of $\sim 10^3 \Omega^{-1} \text{cm}^{-1}$ for $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$,²⁵ $\sim 10^3 \Omega^{-1} \text{cm}^{-1}$ for $\text{Ti}_{0.85}\text{Ta}_{0.15}\text{O}_2$,²⁶ and $0.78 \Omega^{-1} \text{cm}^{-1}$ for $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$.²⁷ (Note that these values are rough guides since sample preparation and morphology were quite different among authors.)

Free Energy of Substitution. To investigate the stability of doped titania, we calculated the energies of substituting a Ti ion by a dopant metal ion in the TiO_2 lattice. The free energy for the substitution reaction is defined as

$$E_S = E_{\text{Ti}_3\text{M}_1\text{O}_8} + E_{\text{Ti}} - E_{\text{Ti}_4\text{O}_8} - E_{\text{M}}$$

i.e., energy of products minus reactants. Negative substitution energy would mean that the dopant stabilizes the TiO_2 lattice; on the other hand, positive substitution energy would mean that the dopant destabilizes the TiO_2 lattice. The results are summarized in Table 3. The positive energy value for Ru doping is

TABLE 3: Calculated Free Energy (eV) for the Substitution of Ti with M in TiO₂

	Ti _{0.75} Nb _{0.25} O ₂	Ti _{0.75} Ru _{0.25} O ₂	Ti _{0.75} Ta _{0.25} O ₂
anatase	−0.27	5.57	−2.11
rutile	−0.46	5.04	−2.34

consistent with the observations of Haas et al.,⁵ Kameyama et al.,⁴⁹ and Colomer and Jurado²⁷ who did not see the formation of a uniform Ti_{1−x}Ru_xO₂ solution at $X \sim 0.25$ and below. This is contrary to the study of Wang⁶ et al. who claimed that they synthesized Ti_{0.9}Ru_{0.1}O₂ catalyst support. There are two possible explanations for this: first, the product obtained by Wang could be metastable, or second, doping at $X = 0.1$ is favorable but not at $X = 0.25$. The second case is unlikely because lowering the Ru concentration does not change the fact that Ru will still have to fit into the TiO₂ rutile lattice. Note that increasing X to 0.5, i.e., Ru_{0.5}Ti_{0.5}O₂, would yield the RuO₂ rutile lattice. Ta and Nb, on the other hand, gave favorable (negative) substitution energies at $X = 0.25$ mol fraction. The group of Chambers⁵⁰ reported that Nb can occupy rutile (110) surface and form a uniform solution with molar fraction up to $X = 0.3$ as a thin film. The lower substitution energy of Ta-doped titania is consistent with the work of Traversa et al.⁵¹ who showed that, when prepared by the same method, Ta is more soluble than Nb in the titania lattice.

The stability of doped titania can be rationalized by the perturbation of dopants on the electronic states of TiO₂, as clearly demonstrated in the DOS plots (Figures 3 and 4). Nb- and Ta-doping shift the DOS profile to the left side and lower the energy of the filled TiO₂ electronic states. Ru-doping, on the other hand, does not lower the eigenstates' energy as much while forming more high-energy states.

Effect of Dopant Concentration. We expected the conductivity of Ru-doping to be more linearly dependent on Ru mole fraction (X) due to its prevailing contribution of electrons at the Fermi level. To study the effects of lowering dopant concentration on electric conductivity, our supercell was expanded to contain $2 \times 2 \times 2$ unit cells of rutile. One, two, and four Ti ions in rutile were replaced with M ($M = \text{Ru, Nb, or Ta}$) to model Ti_xM_{1−x}O₂ with $X = 0.0625, 0.125$, and 0.25 , respectively. The models for Ti_{0.9375}M_{0.0625}O₂, Ti_{0.875}M_{0.125}O₂, and Ti_{0.75}M_{0.25}O₂ are shown in Figures 2a,b, and c, respectively. The rutile phase was chosen for this section because anatase supercells have higher volumes and are computationally too expensive. Moreover, the results from the previous section show that metal doping yields similar electronic effects on anatase and rutile.

Based on the plotted results in Figure 5, we can conclude that increasing Nb-dopant concentration to above $X = 0.0625$ gives diminished increment in Fermi level electron density, i.e., diminished improvements in conductivity. This value is very close to the solid solubility limit of Nb in TiO₂ where the conductivity maximum was observed experimentally by Sato et al.²⁵ In the case of Ta, increasing dopant concentration above $X = 0.125$ does not increase Fermi level electron density. As expected, Fermi level electron density in Ti_{1−x}Ru_xO₂ has the strongest dependence on concentration as compared to those of Ti_{1−x}Nb_xO₂ and Ti_{1−x}Ta_xO₂.

Summary

There is a fundamental difference in the mechanism by which Ru-doping induces electrical conductivity in titania when compared with those of Ta- and Nb-doping. Our investigations

Figure 5. Computed electron density at the Fermi level as a function of dopant mole fraction for Ru-, Ta-, and Nb-doped rutile. Increasing Nb-dopant concentration to above $X = 0.0625$ gives diminished increment in Fermi level electron density, i.e., diminished improvements in conductivity. Increasing Ta-dopant concentration above $X = 0.125$ does not increase Fermi level electron density. Fermi level electron density in Ti_{1−x}Ru_xO₂ is the most linearly dependent on dopant concentration.

reveal that Ru fills the titania band gap region with its own d-electrons and perturbs some Ti d-electrons into the same region. On the other hand, Ta and Nb induce electrical conductivity primarily by shifting the Fermi level to the originally unfilled bands of titania. In contrast to Ti_{1−x}Ru_xO₂, the electrons at the Fermi level in Ti_{1−x}Nb_xO₂ and Ti_{1−x}Ta_xO₂ correspond mainly to Ti d-orbitals. Both mechanisms are known to induce electrical conductivity in semiconductors. Due to the differences in origin, the electrical conductivity of Ru-doped titania is more linearly dependent on dopant concentration while the Nb- and Ta-doped show diminished improvements with increased doping beyond $X = 0.0625$ and 0.125 , respectively.

The formation of a uniform Ti_{0.75}Ru_{0.25}O₂ phase is energetically unfavored by ~ 5 eV based on our calculations. Our calculations support the observations of Haas et al.,⁵ Kameyama et al.,⁴⁹ and Colomer and Jurado,²⁷ who did not see the formation of a uniform Ti_{1−x}Ru_xO₂ solution at $X \sim 0.25$ and below. On the contrary, the Nb- and Ta-doped TiO₂ yield favorable energies at $X = 0.25$.

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