Unraveling the impact of Ta doping on the electronic and structural properties of titania: A combined theoretical and experimental approach

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Abstract:
The introduction of new energy levels in the forbidden band through the doping of metal ions is an effective strategy to improve the thermal stability of TiO\textsubscript{2}. In the present study, the impact of Ta doping on the anatase to rutile transition (ART), structural characteristics, anion and cation vacancy formation were investigated in detail using Density Functional Theory (DFT) and experimental characterisation including, X-ray diffraction (XRD), Raman, and X-ray photoelectron spectroscopy (XPS). The average crystallite size of TiO\textsubscript{2} decreases with an increase in the Ta concentration. At high temperatures, more oxygen atoms entered the crystal lattice and occupy the vacancies, leading to lattice expansion. Importantly, we find that Ta doping preserved the anatase content of TiO\textsubscript{2} up to annealing temperatures of 850 °C which allows anatase stability to be maintained at typical ceramic processing temperatures. The substitution of Ti\textsuperscript{4+} by the Ta\textsuperscript{5+} ions increased the electron concentration in the crystal lattice through formation of Ti\textsuperscript{3+} defect states. Raman studies revealed the formation of new Ta bonds via disturbing the Ti-O-Ti bonds in the crystal lattice. It is concluded that under the oxidising conditions, Ta\textsuperscript{5+} ions could be enhanced on Ta-TiO\textsubscript{2} surface due to the slow diffusion kinetics.

Keywords: Anatase; Defects; Dopant; Titanium dioxide; Oxygen vacancy

1. Introduction:
Titanium dioxide (TiO\textsubscript{2}) nanoparticles have been widely used for energy production, wastewater treatment, cosmetics, optics, self-cleaning and bio-medical applications \(^1\). Among its significant crystalline features, the anatase phase of TiO\textsubscript{2} is preferred for use in antimicrobial coatings and hydrogen production due to its higher activity compared to rutile \(^2, 3\). The rutile phase of TiO\textsubscript{2} is preferred for optoelectronic applications \(^2, 4\). Anatase has a simple tetragonal Bravais lattice, whereas that of the rutile has a body centred lattice \(^5\). The degree of octahedra distortion of anatase with D\textsubscript{2d} local symmetry is greater than that of the rutile with inversion C\textsubscript{2h} symmetry \(^5\). The lifetime of electrons in the anatase phase is nearly 100 times higher than that of rutile phase. In particular, the electron diffusion length of anatase is around 100 times larger than rutile \(^6, 7\). The electron diffusion length of anatase is more than 10 μm whereas that of rutile is only 100 nm \(^6\).

The activity of TiO\textsubscript{2} in its applications is determined by its surface and interface characteristics \(^8\). Materials composed of a mixture of both crystalline phases, but with a high anatase content can promote the activity of TiO\textsubscript{2} through enhanced charge carrier separation at the catalyst surface. The performance of materials with heterophase junctions (engineering of a perfect phase interface within the semiconductor) are superior to conventional heterojunction catalysts (fabrication of a heterojunction catalyst from two different semiconductors with respect to their band alignment) \(^9\), which facilitates electron transfer \(^10\). In addition, the existence of a mixed phase can introduce a high abundance of defect sites such as oxygen vacancies, Ti interstitials, and Ti\textsuperscript{3+} in the TiO\textsubscript{2} crystal lattice \(^10\). TiO\textsubscript{2}, with these intrinsic defects, is catalytically more active, compared to pristine TiO\textsubscript{2} \(^10\).

Reports on the interfaces and Fermi levels reveal that the presence of band offsets in the anatase-rutile heterophase, where a built-in electric field was experienced by the photo-generated electrons/holes that could effectively separate the charges \(^11\). In a recent study, TiO\textsubscript{2} heterophase (with 79 % anatase and 21 % rutile) coated cotton fabrics showed excellent performance for the inactivation of bacteriophage MS2, influenza virus and murine norovirus in a shorter duration of time compared to single phase TiO\textsubscript{2} \(^12\).

Degussa P25 is one of the most widely studied TiO\textsubscript{2} heterophase materials and is widely used for various commercial applications \(^11\). Various techniques and additives have been used with Degussa P25 to improve charge transfer in TiO\textsubscript{2} heterophase catalysts, to enrich the performance under all light/dark conditions and expand the thermal stability of anatase crystals at high processing temperatures. One of the competent strategies is the incorporation of impurity energy levels into the forbidden band of TiO\textsubscript{2} via doping of metal ions at Ti\textsuperscript{4+} sites \(^13\). The dopants usually have different ionic radius compared to Ti\textsuperscript{4+}, and therefore can influence...
the geometry, Ti oxidation state, and the formation of oxygen or Ti vacancies. Ta is a bioactive element and it is commonly used with titanium (Ti) alloys/implants to improve the stability, corrosion resistance and electronic properties. The solubility of Ta dopant in TiO₂ matrix is higher, compared to other dopants with +5 oxidation states, for example niobium (Nb) as a result of low energy is required to substitute Ta in the TiO₂ anatase framework. The maximum solid solubility of Ta would be favourable for its uniform distribution in the TiO₂ crystal lattice without deteriorating the crystallization features at low doping concentrations. In addition to that, the energy needed to substitute one Ta atom on a Ti site in the TiO₂ framework is lower than other dopants. The electronic conductivity of Ta doped TiO₂ (Ta-TiO₂) samples arises primarily from the itinerant Ti d electrons. Owing to the electronic structure of V_B elements, a donor energy level can be created in the the forbidden band of TiO₂ to enhance the charge carrier separation.

In recent years, Ta-TiO₂ has been investigated for solar cells, water splitting, corrosion resistance, photovoltaics, wastewater treatment, oxygen reduction reaction, and lithium ion batteries. These reports have shown that Ta could be utilised as an effective additive or dopant to increase the catalytic performance of TiO₂. Nevertheless, most of these studies only disclose the extrinsic features of the Ta dopant on improving the catalytic performance of TiO₂. There have been to date no detailed investigations on theoretical calculations of Ta-TiO₂ and on the role of Ta doping on the stability of TiO₂ phases.

With this in mind, the present study, focuses on the impact of Ta doping on the anatase to rutile transition (ART), structural characteristics, and oxygen and Ti vacancies using density Functional Theory (DFT) which are verified with the help of X-ray diffraction (XRD), Raman, and X-ray photoelectron spectroscopy (XPS) techniques. These results show the incorporation of Ta into the anatase phase can retard the anatase to rutile phase transition up to 850°C, making this material interesting for high temperature applications. Introduction of Ta can produce Ti vacancies to charge compensate the different oxidation states, while formation of O vacancies is enhanced.

2. Experimental:

Synthesis of Ta-TiO₂:

Ta-TiO₂ was synthesized by the sol-gel method with various mol % of Ta (such as 0, 2, 4, 8 and 16 mol %) 12. For example, 0.5 ml of tantalum ethoxide was dissolved in 100 ml of isopropanol to synthesis 2 % Ta-TiO₂. Ta precursor solution was added, dropwise, to the titanium isopropoxide (27.75 ml) and isopropanol mixture (200 ml), under constant stirring.
After that, 200 ml of double distilled water was added dropwise to the above Ta-Ti sol mixture. The resulting white precipitates were dried in an oven at 100 °C for 24 h and then the powders were calcined in a muffle furnace at various temperatures (from 500-900 °C) for 2 h with a ramp rate of 10 °C min.

**Characterization:**

The anatase to rutile transition (ART), crystallinity, and the average crystallite size of Ta-TiO$_2$ were investigated by X-Ray Diffraction (XRD, Siemens D500) with Cu Kα radiation ($\lambda= 0.15418$ nm). The Spurr equation ($F_R = \frac{1}{1+0.8[I_{A(101)}]/I_{R(110)}}$) was used to analyse the anatase and rutile phase compositions of doped TiO$_2$. The average crystallite size was estimated from the Scherrer equation. A grating of 300 gr/mm was employed to obtain the Raman spectra at an acquisition time of 3 sec. The bonding interactions, oxygen vacancies and oxidation states of Ta-TiO$_2$ were examined through X-Ray Photoelectron Spectroscopy (XPS, Thermo-Fisher Scientific Instruments (East Grinstead, UK)) with K-Alpha+ spectrometer.

**DFT calculations:**

First principles calculations have been performed within DFT as implemented in the Vienna Ab Initio Software Package (VASP.5.4.1)$^{23,24}$ using projector augmented wave (PAW) potentials to describe the core-valence interaction and the Perdew, Burke, Ernzerhof (PBE) generalised gradient approximation to the exchange correlation functional$^{25,26}$. The potentials for titanium (Ti), oxygen (O) and tantalum (Ta) explicitly account for 4 ($d^2s^2$), 6 ($s^2p^4$) and 11($p^6s^2d^3$) valence electrons, respectively. The calculations were executed using an energy cut-off for the plane wave basis set at 420 eV and the convergence criteria for electronic relaxations at $10^{-4}$ eV and for ionic relaxations at 0.02 eV/Å.

The computed bulk lattice parameters are $a = b = 3.861$ Å and $c = 9.781$ Å for the anatase phase (I4$_1$/amd) and we used supercells containing $2 \times 2 \times 2$ unit cells (32 atoms). Ti$_{1-x}$Ta$_x$O$_2$ was modelled by replacing Ti ions with one, two, three and four Ta ions; these correspond to a 0.03, 0.06, 0.09 and 0.12 mol fraction (x) doping. The TiO$_2$ supercell is relaxed at each Ta content and no symmetry is imposed. Moreover, in response to this substitution of Ti$^{4+}$ with Ta$^{5+}$ (one extra electron per dopant) the mechanism of charge compensation has been studied through the Ti vacancy formation with four Ta dopants; here each neutral Ti vacancy leaves four holes.
The Brillouin zone was sampled with \((2 \times 2 \times 1)\) Monkhorst-Pack k-point grids\(^{27}\). The calculations were spin-polarised, and no symmetry constraints were imposed. Due to the presence of the extra electron on Ta, we implemented an on-site Hubbard correction \((\text{DFT+U})\)^{28} to describe the partially filled Ti 3d states using \(U = 4.5\) eV\(^{29-32}\). To identify the most stable site for vacancy formation, which is implicated in the transition from the anatase to the rutile phase, different oxygen sites of the Ta-doped structure were considered, taking into account the symmetry of the system. For each oxygen site the vacancy formation energy was computed from the following equation:

\[
E_{\text{vac}} = E(Ta_xTi_{1-x}O_{2-y}) + \frac{1}{2}E(O_2) - E(Ta_xTi_{1-x}O_2) \quad (1)
\]

Where \(E(Ta_xTi_{1-x}O_{2-y})\) denotes the total energy of Ta-\ TiO\(_2\) with a single oxygen vacancy, \(E(Ta_xTi_{1-x}O_2)\) represents the total energy of Ta-TiO\(_2\) without an oxygen vacancy and the oxygen vacancy formation energy is referenced to half the total energy of gas-phase O\(_2\). In addition, the oxidation states were analysed through Bader charge analysis\(^{33}\) and computed spin magnetisations.

3. Results and Discussion:

The effects of Ta dopant in the bulk crystal lattice of anatase TiO\(_2\) on the atomic structure, oxygen vacancy, Ti oxidation state, and lattice parameters were investigated from the DFT calculations. These are validated comprehensively through XRD, and Raman spectroscopic techniques. The introduction of defects, bonding interactions, and other structural changes of TiO\(_2\) were studied by XPS. ART of Ta–TiO\(_2\) was examined in the range of 500-900 °C through determining the anatase and rutile crystalline phase percentages. The distortions of TiO\(_2\) lattice were explored by the Raman analysis. The bare TiO\(_2\) sample (0 % Ta-TiO\(_2\)) calcined at 500 and 700 °C was considered as references for pure anatase and rutile, respectively.

3.1. DFT Studies:

**Tantalum doped Anatase:**

The relaxed structures of Ta- TiO\(_2\) in the most favourable dopant configurations are shown in Figure 1. The doped structure is slightly distorted in the vicinity of the Ta dopant. The Ta–O distances are 2.18 Å for the apical oxygen (O\(_{ap}\)) and 2.09 Å for the equatorial oxygen (O\(_{eq}\)) sites. The Ta-O\(_{ap}\) distance is increased by around 0.20 Å, while the Ta-O\(_{eq}\) distance vary by 0.10 Å when compared to the equivalent Ti–O distances in undoped anatase TiO\(_2\). This is consistent with the larger ionic radius of Ta (0.75 Å) compared to Ti (0.61 Å). The lattice
constants with one Ta dopant are $a = b = 7.620 \, \text{Å}$ and $c = 19.283 \, \text{Å}$. Table 1 shows the computed lattice constant for each Ta doping concentration. In general, substituting a higher concentration of Ta species for Ti results in an increase in the lattice constants.

Figure 1. Atomic structures of $\text{Ti}_{1-x}\text{Ta}_x\text{O}_2$ in the most stable configurations for (a) one, (b) two, (c) three and (d) four Ta dopant atoms.

In pure anatase the computed Bader charges on Ti and oxygen are $q = 1.45$ (giving a net charge of +2.55 electrons) and $q = -7.27$ electrons (giving a net charge of -1.27 electrons), respectively. Ta can take a variety of oxidation states, from -1 to +5. When one Ta is incorporated into the anatase lattice, the computed Bader charge is $q = 8.04$ electrons, showing oxidation of Ta, with a net charge of +2.96 electrons and a computed spin magnetisation of $0.02 \, \mu_B$. Oxygen apical sites in the vicinity of Ta shows a modest decrease in the Bader charge to ca. 7.25 electrons, with a negligible spin magnetization.

At the same time, the nearest adjacent Ti atom shows an increase in the Bader charges of 0.31 electrons, while the Bader charges of the other six neighboring Ti atoms increases by 0.10 electrons. This analysis suggests that the Ta dopant is fully oxidized, with localization of the electron on the adjacent Ti atom and partial localization of the electron over six Ti sites.
Upon increasing the Ta concentration, the Bader charge of Ta and Ti atoms show oxidation of Ta (change in charge of 0.75 electrons) and reduction of Ti (change in charge of ca. 0.40 electrons). The magnetization of the Ti<sub>1-x</sub>Ta<sub>x</sub>O<sub>2</sub> is mainly attributed to the magnetization of each Ti atom that is nearest neighbor to Ta, with computed magnetizations of ca. 1.0 μB.

**Table 1** Summary of computed lattice constants, computed Bader charges and spin magnetizations for Ta-TiO<sub>2</sub> anatase with different Ta contents.

| Ta concentration | 3%  | 6%  | 9%  | 12% |
|------------------|-----|-----|-----|-----|
| **Lattice Constants (Å)** | a = b = 7.757 | a = b = 7.766 | a = 7.795 | a = 7.779 |
|                  | c = 19.150  | c = 19.194  | b = 7.803  | b = 7.781  |
|                  |             |             | c = 19.193  | c = 19.286  |
| **Bader Charge Ta (e<sup>-</sup>)** | Ta<sup>1</sup> = 8.04 | Ta<sup>1</sup> = Ta<sup>2</sup> = 8.12 | Ta<sup>1</sup> = 8.01 | Ta<sup>1</sup> = 8.69 |
|                  | Ti<sup>1</sup> = 1.75 | Ti<sup>1</sup> = Ti<sup>2</sup> = 1.82 | Ti<sup>1</sup> = 1.82 | Ti<sup>1</sup> = 1.95 |
| **Magnetization - Ti – NN (μB)** | Ti<sup>1</sup> = 0.96 | Ti<sup>1</sup> = Ti<sup>2</sup> = 0.96 | Ti<sup>1</sup> = 0.97 | Ti<sup>1</sup> = 0.99 |
|                  | 1.45 – 1.55 | 1.46 – 1.62 | 1.54 – 1.72 | 1.50 – 1.88 |
| **Bader Charge Ti – N (e<sup>-</sup>)** | 7.23 – 7.30 | 7.18 – 7.27 | 7.13 – 7.30 | 7.05 – 7.15 |
| **Bader Charge O (e<sup>-</sup>)** | 7.23 – 7.30 | 7.18 – 7.27 | 7.13 – 7.30 | 7.05 – 7.15 |

**Oxygen Vacancy Formation in Ta-doped TiO<sub>2</sub>**

Figure 2 shows the structures with the lowest computed formation energies for an oxygen vacancy in Ti<sub>1-x</sub>Ta<sub>x</sub>O<sub>2</sub> (Ta concentration = 3 % Figure 2(a), 6 % 2(b), 9 % 2(c) and 12 % 2(d)).
Figure 2. Position of Oxygen vacancy (Ov) in Ta- TiO$_2$ anatase structure at different dopant concentrations and respective energy formation. The bonds formed before the O was removed are dashed.

The positive computed oxygen vacancy formation energy means that the creation of the oxygen vacancy is in principle not spontaneous. It is nonetheless sufficiently small that an oxygen vacancy can form at high calcination temperatures. In addition, this vacancy formation energy is, apart from the 9 % Ta concentration, reduced with respect to the formation energy of an oxygen vacancy in the undoped anatase supercell, for which we compute an oxygen vacancy formation energy of 3.83 eV.

After vacancy formation, the lattice of Ti$_{1-x}$Ta$_x$O$_2$ shows some structural distortions. In the most favourable oxygen vacancy structure, Ta, Ti, and neighboring oxygen ions distort from their initial positions. For Ti$_{1-x}$Ta$_x$O$_2$ with 3 % of Ta concentration, the most favourable oxygen vacancy structure is the configuration in which vacancy was an O in apical position. In this configuration, both Ta and the two Ti atoms moves away from the vacancy, in particular, the Ta – O$_{eq}$ and Ta – O$_{ap}$ distances are decreased by 0.06 Å and 0.11 Å, respectively. The Ti neighboring oxygen atoms in the apical positions tilt towards the vacancy, Ti – O$_{ap}$ distances are increased by 0.08 Å, while the remaining Ti – O$_{eq}$ distances are not distorted.

After the formation of oxygen vacancy for 3 % Ta doping, the computed Bader charge for Ta shows a small change, from q = 8.04 to q = 8.10 electrons, and the change in the spin
magnetisation in the d-orbital is negligible. The two nearest neighbour Ti ions to which the removed O was bound now have computed spin magnetisations of 0.96 $\mu_B$ and a computed Bader charge of 1.90 electrons, while the Bader charge of Ti adjacent Ta increases by 0.02 electrons and the magnetization to 1.0 $\mu_B$, so the total magnetization is ca. 3 $\mu_B$.

In Ti$_{1-x}$Ta$_x$O$_2$ structures at higher Ta concentration, the computed Bader charge of Ta is increased from $q = 8.20$ to $q = 8.88$ electrons as the Ta concentration is increased from 6 to 12%. After formation of oxygen vacancy, the total magnetization on Ta is not negligible, in particular we see values of 0.15 $\mu_B$ at 6 %, 0.10 $\mu_B$ at 9 % and 0.14 $\mu_B$ at 12% Ta. The Bader charge of the Ti ions surrounding Ta increases from $q = 2.09$ to $q = 2.36$ electrons, while the total magnetization of Ti increases, with a value of 3.2 $\mu_B$ over three Ti atoms at 6 % and over five Ti atoms at 9 % and a value of 3.5 $\mu_B$ over five Ti atoms at 12 %.

Titanium Vacancy Formation in Ta-doped Anatase

To analyse the compensation of the different Ti and Ta oxidation states in Ti$_{1-x}$Ta$_x$O$_2$ at 12 % Ta, we have considered the formation of one Ti vacancy. Here each neutral Ti vacancy leaves four holes which compensate the four electrons introduced by the Ta dopants (one electron per dopant). The computed formation energy, relative to the energy of a single Ti atom in the bulk metal ($E_{Ti \text{ vac}} = E(TaTi_{1-x}O_2) + E(Ti) - E(TaTiO_2)$, where $E(Ti)$ is the energy of one Ti atom from bulk Ti metal) is -2.57 eV, confirming that Ti vacancies will form to compensate higher Ta dopant concentrations.

**Figure 3.** The position of titanium vacancy (Ti$_{\text{vac}}$) in Ti$_{1-x}$Ta$_x$O$_2$ at 12 % of Ta concentration
After the formation of Ti vacancy, Ta atoms move close to the vacancy especially the Ta ions indicated as Ta$^1$ and Ta$^4$ in Figure 3; these ions also have Bader charge lower by 0.13 electrons than Ta$^2$ and Ta$^3$. In this configuration Bader charge of Ta ions is lower by ca. 0.75 electrons with respect to Ti$_{1-x}$Ta$_{x}$O$_2$ at 12 % Ta without the Ti vacancy. In addition, Ti atoms have Bader charge lower than the prior system with values between 1.48 and 1.78 electrons and no magnetization is present. This confirms the compensation of the difference in Ti and Ta oxidation states.

**Electronic Structure of Tantalum-Doped TiO$_2$**

The computed projected electronic density of states (PEDOS) for bulk TiO$_2$ in anatase phase, compared with the total density of states (TDOS) of Ta-doped and with oxygen vacancy at different Ta concentration, are shown in **Figure 4** and **Figure S1**, respectively.

![PEDOS](image)

**Figure 4.** The calculated total and partial density of states of pure TiO$_2$ in the anatase phase. Only the total DOS is shown for the spin down electrons.

After Ta doping, states emerge in the band gap region of bulk TiO$_2$ above the valence band maximum (VBM). These correspond principally to Ti 3$d$-orbitals as shown in the left panel of **Figure S.I.** In particular, these states are localized at 0.95, 0.96, 0.48 and 0.64 eV above the VBM in Ta-doped TiO$_2$.

In these configurations, after formation of the oxygen vacancy results in the formation of further occupied Ti 3$d$ states in the band gap, as shown in right panel of **Figure 5**. The
bandgap is reduced by 1.26, 1.42, 1.59 and 1.74 eV for Ta doping at the concentration of 3, 6, 9 and 12 % respectively.

The consequence of charge compensation in the case of Ti vacancy in TiO$_2$ doped with four Ta atoms, was reinforced by analysing the DOS, from which no localized states are found in the VB – CB energy gap, as shown in Figure 6.
Figure 5. The calculated partial density of states (left panels) and bandgap region (right panels) of Ti$_{1-x}$Ta$_x$O$_2$ with oxygen vacancy at different concentrations. Fermi level is set at zero.
3.2. XRD:

The diffraction peaks of Ta-TiO₂ samples calcined at various temperatures are shown in Figure 7. The effect of Ta doping is evidenced through the variations in peak position, width, and intensity. The anatase and rutile phase percentages of TiO₂ are displayed in Table 2. Ta doping can preserve the anatase up to 850 °C. The crystalline phases of orthorhombic tantalum oxide (Ta₂O₅) are observed at high Ta concentration (8 and 16 mol %). For samples calcined at 800, 850 and 900 °C, the 2θ peaks at 22.5, 28.35, 36.96, 49.83, and 50.97 are attributed to the presence of (001), (1110), (1111), (0220), and (2151) orthorhombic phases of Ta₂O₅. Ta₂O₅ formation is increased with respect to the temperature and Ta content, demonstrating the robust reduction reaction at high temperatures. The crystallization of amorphous to orthorhombic Ta₂O₅ occurs at temperatures above 800 °C.

The broadening of XRD peaks signifies the decrease of average crystallite size of TiO₂ with respect to the Ta concentration. A slight peak shift is also observed at high dopant concentration, indicating the incorporation of Ta⁵⁺ in the crystal lattice of TiO₂. The atomic radius of Ta⁵⁺ is slightly bigger than that of Ti⁴⁺, and therefore the substitution of Ta could lead to an enlargement of TiO₂ unit cell.

The average crystallite size of anatase, rutile and Ta-TiO₂ samples are given Table 3. With respect to the calcination temperature, the size of nanoparticles is increased. Conversely, the average crystallite size of the samples is decreased with respect to Ta concentration.
is attributed to the impact of Ta\textsuperscript{5+} dopant to inhibit the grain boundary mobility \textsuperscript{37}. The effect of doping on the crystal growth of TiO\textsubscript{2} is dominant at low Ta concentration.

The decrease of crystallite size with respect to the concentration of Ta is ascribed to the solute drag mechanism \textsuperscript{36}. According to this mechanism, the difference in size between the dopant and Ti ions will induce lattice strain energy ($\Delta G_{\text{strain}}$) in the TiO\textsubscript{2} crystal. $\Delta G_{\text{strain}}$ with electrostatic potential energy could increase the interaction between the grain boundary and the dopant. Consequently, the grain growth of Ta-TiO\textsubscript{2} samples is significantly suppressed due to the size mismatch. The crystal lattice parameters are influenced by the band length difference between the covalent Ti-O (2.01 Å) and Ta-O (2.17 Å) bands \textsuperscript{15}. The decrease of average crystallite size is also attributed to the quantum size effects resulting from the small sized anatase nanoparticles at high Ta content \textsuperscript{38}. 
Figure 7. XRD patterns of Ta-TiO$_2$ at various calcination temperatures

Table 2. Anatase and Rutile percentages of Ta-TiO$_2$ samples at various calcination temperatures

| Samples  |  500 °C | 600 °C | 700 °C | 800 °C | 850 °C | 900 °C |
|----------|---------|---------|---------|---------|---------|---------|
|          | A | R | A | R | A | R | A | R | A | R | A | R |
| 0 % Ta-TiO$_2$ | 100 | - | 8 | 92 | - | 100 | - | 100 | - | 100 | - | 100 |
| 2 % Ta-TiO$_2$ | 100 | - | 100 | - | 82 | 18 | 53 | 47 | 12 | 88 | - | 100 |
| 4 % Ta-TiO$_2$ | 100 | - | 100 | - | 100 | - | 72 | 28 | 19 | 81 | - | 100 |
| 8 % Ta-TiO$_2$ | 100 | - | 100 | - | 100 | - | 100 | - | 25 | 75 | - | 100 |
| 16 % Ta-TiO$_2$ | 100 | - | 100 | - | 100 | - | 100 | - | 54 | 46 | 11 | 89 |
Table 3. Average crystallite size of Ta-TiO\textsubscript{2} samples at various calcination temperatures

| Samples  | 500 °C | 600 °C | 700 °C | 800 °C | 850 °C |
|----------|--------|--------|--------|--------|--------|
|          | A (nm) | A (nm) | R (nm) | A (nm) | R (nm) | A (nm) | R (nm) | A (nm) | R (nm) |
| 0 % Ta-TiO\textsubscript{2} | 13.61  | 20.17  | 35.92  | -      | 38.10  | -      | 39.16  | -      | 41.21  |
| 2 % Ta-TiO\textsubscript{2} | 6.74   | 11.23  | -      | 14.67  | 25.74  | 24.73  | 34.42  | 28.79  | 30.08  |
| 4 % Ta-TiO\textsubscript{2} | 5.71   | 6.51   | -      | 12.86  | -      | 23.16  | 35.54  | 28.26  | 37.59  |
| 8 % Ta-TiO\textsubscript{2} | 5.10   | 6.75   | -      | 9.72   | -      | 18.92  | -      | 19.84  | 36.37  |
| 16 % Ta-TiO\textsubscript{2} | 5.48   | 5.16   | -      | 7.81   | -      | 14.63  | -      | 19.27  | 34.57  |

3.3. Raman:

There are no significant changes in the Raman peak positions for Ta-TiO\textsubscript{2} calcined at 800 °C. However, a slight red shift in peak position is noted for the samples calcined at 850 °C (Figure 8). This is ascribed to the expansion of unit cell and lattice parameter variations with respect to Ta doping and calcination temperature\textsuperscript{36}. B\textsubscript{1g} peak responsible for the Ti-O stretching mode (~390 cm\textsuperscript{-1}) is blue shifted with respect to the Ta concentration, suggesting the substitutional doping of Ta ions in the TiO\textsubscript{2} crystal lattice\textsuperscript{35}. A slight red shift of E\textsubscript{g} peak is noted for the samples calcined at 850 °C. The widening and shifting of E\textsubscript{g} peaks are attributed to the formation of new Ta bonds \textit{via} disturbing the Ti-O-Ti bonds in the crystal lattice. E\textsubscript{g} peak typically depicts the symmetric stretching vibration of O-Ti-O in TiO\textsubscript{2}. Ta-O-Ti or Ta-O-Ta bonds are formed as the Ta\textsuperscript{5+} is substitutionally doped on Ti\textsuperscript{4+} sites\textsuperscript{39}. Raman peak shapes could be influenced by the non-stoichiometry. The incorporation of Ta\textsuperscript{5+} ions could create intrinsic defects to retain the charge neutrality, which could cause local lattice distortion\textsuperscript{40}. The decrease in crystallite size could also lead to the Raman peak shift and broadening\textsuperscript{40}. Phonon confinement effect could also be considered for the doped samples with low particle size compared to the pure TiO\textsubscript{2}\textsuperscript{40}. 
Figure. 8. Raman spectra of Ta-TiO$_2$ at 800 °C and 850 °C
3.4. XPS:

XPS results of TiO$_2$ anatase and Ta-TiO$_2$ samples are shown in Figure 9 and 10. The characteristic peaks of Ti$^{4+}$ appear as doublet around 458.78 eV and 464.48 eV for 2p$_{3/2}$ and 2p$_{1/2}$ states, respectively $^{35}$ (Figure. 9 (a)). Ti 2p and O 1s peaks are slightly red shifted after doping with Ta. An additional peak in the Ti 2p spectrum of Ta-TiO$_2$ is attributed to the existence of Ti$^{3+}$. Ta doping generates Ti$^{3+}$ defect states in the crystal lattice (Figure. 9 (c)). An extra positive charge might be introduced into the TiO$_2$ system by the doping of Ta$^{5+}$ ions. This charge imbalance in the crystal lattice can be compensated through the formation of reduced Ti$^{3+}$ $^{17}$. The atomic radius of Ti$^{3+}$ (0.67 Å) is larger than that of Ta$^{5+}$ (0.64 Å).

In the case of the Ta spectrum, the peaks at 26.36 and 28.25 eV are attributed to the Ta 4f$^{7/2}$ and Ta 4f$^{5/2}$ states, respectively. These peaks are assigned to Ta$^{5+}$. A small peak observed at 22.45 eV is ascribed to O 2s $^{21}$.

The peaks at 531.85 and 532.67 eV are attributed to the existence of Ti-O and Ti-OH groups, respectively. The increase in binding energy of O 1s peaks could be attributed to the existence of Ta-O bonds in the doped samples $^{41}$. The ratio of oxygen vacancies depends on the concentration of Ta. Moreover, at high temperatures, more oxygen atoms could enter into the crystal lattice and occupy the vacancies, leading to lattice expansion $^{13}$. This is also validated by the changes in XRD peak intensity, width, and position.

The formation of oxygen vacancies and Ti$^{3+}$ ions are described as follows $^{36}$:

$$2\text{TiO}_2 + \text{Ta}_2\text{O}_5 \rightleftharpoons 2\text{Ti}^{4+} + 2\text{Ta}^{5+} + 8\text{O}_2 + \text{O}_2 \uparrow$$

$$\text{O}_o \rightleftharpoons 2e^- + \text{V}_o^- + \frac{1}{2} \text{O}_2 \uparrow$$

$$\text{Ti}^{4+} + e^- \rightleftharpoons \text{Ti}^{3+}$$

Here, “’”, “’”, and $\text{V}_o^-$ represent an extra negative charge, extra positive charge, and oxygen vacancies with positive charge, respectively. At low dopant concentration, the substitution of Ta$^{5+}$ and the formation of $\text{V}_o^-$ instigate the reduction of Ti$^{4+}$ to Ti$^{3+}$. The concentration of Ti$^{3+}$ is increased with respect to the concentration of Ta. Nevertheless, the excessive electrons at high Ta contents can be captured by $\text{V}_o^-$ to further convert into $\text{O}_o$, leading to a decrease in concentration of oxygen vacancies. This reverse reaction would decrease the concentration of electrons and restrain the Ti$^{3+}$ content at very high Ta doping levels.
**Figure. 9.** XPS of TiO$_2$ anatase ((a) Ti 2p and (b) O 1s) and 4 % Ta-TiO$_2$ at 800 °C ((c) Ti 2p, (d) O 1s, and (e) Ta 4f)

**Figure. 10.** XPS scans of 4 % Ta-TiO$_2$ at 800 °C
The substitution of Ti$^{4+}$ by the Ta$^{5+}$ ions could increase the electron concentration in the crystal lattice along with the formation of Ti$^{3+}$ defect states. These defect states could introduce new energy levels below the conduction of TiO$_2$ to enhance charge transfer and the light absorption. The defects at low Ta concentration could increase the photocatalytic activity of TiO$_2$ but the defects could also act as charge-carrier recombination centres at higher concentrations. The charge carrier mobility would be decreased at high Ta concentrations due to the distortion of TiO$_2$ crystal lattice. Sing et al. suggested that the an optimum Ta content in TiO$_2$ was responsible for the surface enhanced Raman scattering (SERS) to enrich the charge transfer mechanism on the catalyst surface.

The changes in lattice parameters might be attributed to the introduction of Ta$^{5+}$ and the transition of Ti$^{4+}$. The size of Ta$^{5+}$ and Ti$^{3+}$ ions is slightly larger than that of Ti$^{4+}$ ions, and therefore the Ta-TiO$_2$ crystal lattice is slightly distorted. Mott-Schottky results of a recent study proved that the charge carrier density of Ta-TiO$_2$ is 3.2 times higher than that of pure TiO$_2$. Consequently, Ta-TiO$_2$ could be utilised as a promising material for hydrogen production through photocatalytic or photoelectrocatalytic water splitting owing to the high photocurrent density and charge transfer.

It was suggested that the increase of calcination temperature and Ta content could favour the grain boundary facets. According to the Krogar-Vink notation, the incorporation of Ta in TiO$_2$ under different conditions can be described as follows:

\( \text{At oxidising condition:} \)
\[
2Ta_2O_5(s) \leftrightarrow 4Ta\cdot_{Ti} + 4V_{Ti}''' + 10O_x^0
\]
\[
[Ta\cdot_{Ti}] = 4[V_{Ti}'''']
\]

\( \text{At reducing condition:} \)
\[
2Ta_2O_5(s) \leftrightarrow 4Ta\cdot_{Ti} + 4e' + 8O_x^0 + O_2(g)
\]
\[
[Ta\cdot_{Ti}] = n
\]

Here, \( Ta\cdot_{Ti}, V_{Ti}'''', \) and \( O_x^0 \) signify a substitutional Ta$^{5+}$ ion in a regular Ti lattice site, quadruply charged Ti vacancy, and a regular neutral oxygen species on an oxygen site, respectively.

Under oxidising conditions, the incorporation of Ta is charge compensated through Ti vacancies and ionic species. Here, the diffusion of Ta is accompanied by the diffusion of Ti vacancies, which is a particularly slow process. Under oxidising conditions, the incorporation of Ta is charge compensated by electrons. In contrast, the diffusion of Ta is accompanied by electrons with high mobility under reducing conditions. It was suggested that, under
oxidising conditions, Ta$^{5+}$ ions could be enriched on the surface of Ta-TiO$_2$ due to the slow diffusion kinetics$^{42}$.

4. Conclusions:

The influence of Ta doping on the structural and electronic properties of TiO$_2$ has been successfully investigated. To retain the charge neutrality Ti$^{3+}$ defect states were generated during the substitution of Ta$^{5+}$ in the TiO$_2$ crystal lattice, while at high Ta content Ti vacancies can form to charge compensate the dopant. The formation of intrinsic defects could cause local lattice distortion. The average crystallite size of TiO$_2$ decreased with respect to Ta content and at the same time, it increased as the temperature increases. The crystallite size measurements also revealed the impact of Ta$^{5+}$ dopant on the grain boundary mobility. The ratio of oxygen vacancies was also influenced by the Ta dopant concentration and calcination temperature. Ta dopant preserved the anatase content at high calcination temperatures and the 4 % Ta-TiO$_2$ calcined at 800 °C exhibited 72 % anatase and 28 % of rutile. The incorporation of Ta in TiO$_2$ under oxidising and reducing conditions has been discussed. The incorporation of Ta is charge compensated through Ti vacancies and ionic species under the oxidising conditions. The diffusion of Ta is accompanied by electrons with high mobility under the reducing conditions.

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