Dopant Stability in Multifunctional Doped TiO_2's under Environmental UVA Exposure.

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Abstract

We present a UV irradiation study of three nanomaterials which have been investigated and published by peer review previously, specifically tantalum, tungsten and phosphorus doped TiO_2. These nanomaterials have been previously synthesised, characterised and designed with specific applications in mind, from photo-catalysts to transparent conducting oxides (TCO's) for use in solar cells and touchscreens. We show in this work, using X-ray Photoelectron Spectroscopy (XPS) that under sustained levels of environmental UVA Irradiation (0.42 mW/ cm^2) Ta^{5+} and W^{6+} substitutional doped TiO_2 exhibits little to no variation in dopant concentration and distribution as a function of irradiation time. Interestingly P^{5+} and P^{3-} co-doped TiO_2 experiences a pronounced and nuanced change in dopant distribution and concentration across the surface through to the bulk as a function of irradiation time. Combined with our previous work with nitrogen doped TiO_2, whereby 28 days of environmental UVA irradiation causes interstitial dopant loss and the attrition of functional properties, these results demonstrate that much is still to be understood regarding dopant stability in metal oxides such as TiO_2 under environmental conditions.

Introduction

Doped TiO_2 materials feature heavily within the photo-catalysis community and there has been much exploration over recent decades as to possible variations using both anionic and cationic dopants.[1–5] Many of these materials have potential in environmental photocatalytic remediation strategies or use in advanced electronics as transparent conducting oxides (TCO's).[6–8] These are applications where frequent and sustained exposure to environmental UVA light is likely to feature in the operational lifetime of the devices or applications these materials are used for.[9]

Previous work within our group has focussed on another doped TiO_2, where we demonstrated that interstitially nitrogen (N_i) doped TiO_2 suffers from environmental UVA irradiation induced dopant surface segregation. The dopants are then irreversibly lost through subsequent photo-induced reaction pathways.[10] This correlates with a loss in photo-activity, loss of trap states as seen in transient absorption spectroscopy and a 10.8 % loss in visible light absorption at 450 nm. Thus the specific functional properties that this material exhibits show significant attrition when subjected to conditions not dissimilar to those it would encounter when used in a commercial or environmental setting. This may prohibit it from being considered seriously for such a role as a photo-catalyst for the remediation of environmental pollutants. If this effect can be replicated and understood in other doped TiO_2 materials this would allow the community to identify dopants which are suitable to use in specific applications and move the study of doped TiO_2 into the realm of actual application as well as academic investigation.

Three specific doped anatase TiO_2 materials were chosen for investigation. They were chosen for specific reasons to allow contrast from the physical characteristics found in nitrogen doped TiO_2 we have published previously. The first two are transition metal cation doped TiO_2 samples reported by Sathasivam *et al*, specifically tungsten and tantalum doped TiO_2. Both exhibit substitutional doping with Ta^{5+} and W^{6+} sitting in Ti^{4+} lattice sites respectively.[4,11] Tantalum doped TiO_2 has been shown to be a promising TCO material and exhibits good UVA photo-activity whilst tungsten doped TiO_2 exhibits similar functional properties. The last is a phosphorus doped TiO_2 sample previously characterised by Sotelo-Vasquez *et al*. It exhibits both P^{5+} and P^{3-} dopants which occupy Ti^{4+} and O^{2-} sites respectively.[12] Whilst being a p-block element, like nitrogen, it acts as a substitutional dopant, compared to nitrogen which was found to be majority interstitial.[10]

This report provides an important perspective regarding dopant stability in TiO_2 under levels of UVA irradiation experienced in the natural environment.

Each doped TiO_2 material was cut into small coupons and irradiated for a period of up to 28 days. The intensity of the UVA irradiation was 0.42 mW/ cm^2 which is lower than expected daytime UVA intensities in the UK (0.5-5 mW/ cm^2).[9] X-ray photoelectron spectroscopy measurements (XPS) were undertaken for all coupons so that changes in elemental composition could be quantified over a months' worth of UVA (365 nm) irradiation. Specific experimental conditions can be found in the experimental section. Modelled and fitted XPS graphs for all elemental environments can be found in the supplementary information. The authors think it important to stress that the samples used in this study were synthesised many months before the irradiation study, detailed in this report, and were stored in the dark for periods longer the period of irradiation used in this study. If any process occurs in the dark that affects dopant stability it will have happened to all samples in the dark, thus any changes that occur as a result of irradiation can be thought to occur purely as a result of irradiation.

This is important because materials that display variable dopant stability as a function of irradiation could be considered unfit for purpose for use in photocatalytic, solar cell or touchscreen applications where the lifetime of a device may greatly exceed the UVA exposure used in this report.

Tungsten and Tantalum Doped TiO_2

The physical characterisation of the tantalum and tungsten doped TiO_2 thin films used in this study has been conducted and previously published.[4,11] Both exhibit an anatase crystal structure and the standard Ti^{4+} and O^{2-} environments expected were observed in XPS. Additionally in XPS, tantalum doped TiO_2 exhibits Ta^{5+} occupying Ti^{4+} sites. The same can be said for tungsten doped TiO_2 with W^{6+}

(Figure 1). Tantalum is observed in the 5+ oxidation state in XPS at ~27.0 and ~29.0 eV for the $4f_{7/2}$ and $4f_{5/2}$ states respectively. Tungsten is observed in the 6+ oxidation state in XPS at ~35.0 and ~37.5 eV for the $4f_{7/2}$ and $4f_{5/2}$ states respectively.

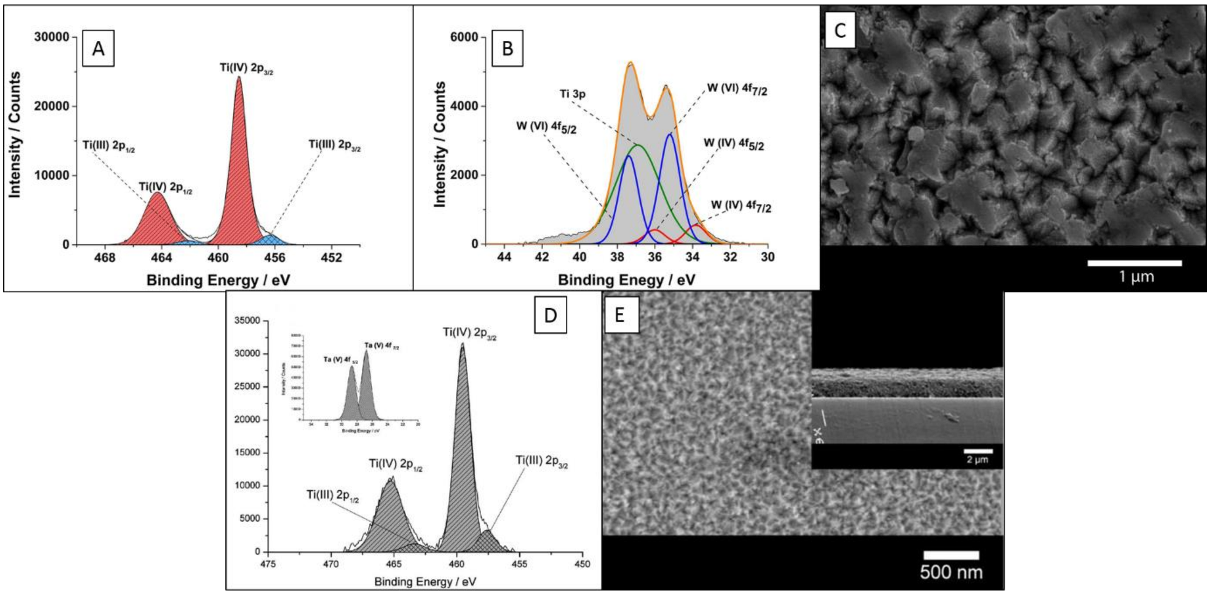

Figure 1: Characterisation of tungsten and tantalum doped TiO_2 thin films synthesised by AACVD. A. XPS graph demonstrating $Ti^{4+/3+}$ environments. B. XPS graph demonstrating $W^{4+/6+}$ environments. C. SEM for tungsten doped TiO_2 demonstrating a high surface area morphology. D. XPS graph showing both $Ti^{3+/4+}$ and Ta^{5+} environments. E. SEM for tantalum doped TiO_2 demonstrating a high surface area morphology. Reused with permission Sathasivam et al[4,11]

Both doped TiO_2's exhibit a blue hue, quantified in UV/Vis spectroscopy, which is attributed to absorption of visible light by Ti^{3+} sites caused by charge compensation from the inclusion of Ta^{5+} and W^{6+} in Ti^{4+} sites.[13,14] Both materials exhibit electrical resistivity values which qualify them as transparent conducting oxides (TCO's) (14 and 0.034 Ω.cm for tantalum and tungsten dopants respectively). They are therefore important materials for use in future technological applications. They also exhibit favourable photocatalytic properties which makes them multifunctional materials.

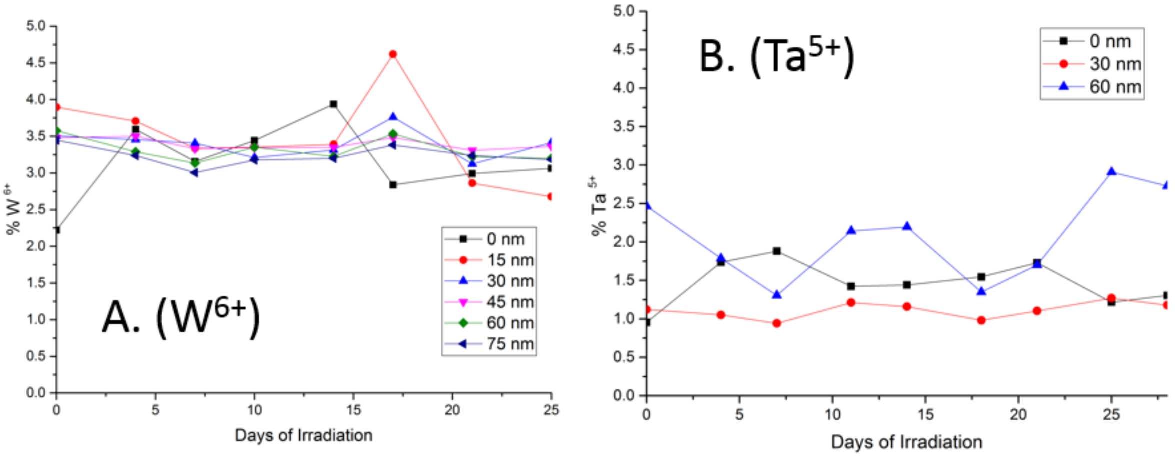

Figure 2: Graphs demonstrating variances in dopant concentration across the depth of the film and across varying days of irradiation. A. Tungsten doped TiO_2 dopant concentration is seem to remain fairly constant across 25 days of irradiation and the film starts homogenously doped and retains this level of homogeneity. B. Tantalum doped TiO_2 exhibits dopant stability across the depth of the film and 28 days of irradiation for all levels.

Both tantalum and tungsten doped TiO_2 exhibit stability in both dopant concentration and distribution from the surface across the bulk for over 25 (W^{6+}) and 28 (Ta^{5+}) days (Figure 2). Specifically, tungsten exhibits a maximum of 2% variation in dopant concentration across 25 days of UVA irradiation and dopant distribution from the surface across the bulk is seen to be constant. This shows the material is homogeneously doped to start with and does not show any attrition or movement of dopants as a result of irradiation. Tantalum doped TiO_2 exhibits a maximum dopant concentration distribution of 1.5%. The spread of data points across 25 days of irradiation, seen in Figure 2 B, shows no overall clear pattern and there is no overall effect across all depths, thus irradiation has little effect on dopant stability. In nitrogen doped TiO_2 clear patterns of dopant movement were present at all material depths. Thus tantalum doped TiO_2 can be considered stable under prolonged exposure to UVA irradiation. Both samples are thus is in stark contrast to what we have reported earlier for an interstitially nitrogen doped TiO_2 thin film.[10] We postulate that the reason for this stability is that the cationic dopants in both materials occupy substitutional Ti^{4+} sites rather than interstitial sites as seen in the nitrogen (NO*) doped sample previously reported. As a result they are covalently bonded to the crystal lattice. The authors hypothesised the reason for interstitial nitrogen (NO*) movement in our previous work was proposed to be via electrostatic diffusion towards the surface and the lability of interstitial nitrogen under other external stimuli is highlighted by the work of Palgrave *et al.*[15] It is therefore logical that covalently bonded atoms would not be subject to electrostatic migration as they are inherently bound in the crystal lattice and typically show low mobility.

This suggests that for environmental applications substitutional dopants are more suitable for long term usage than interstitial, which may exhibit the same problems as the nitrogen doped sample reported previously. Further work however is required to quantify this assertion. Whether cationic dopants can be considered suitable depends on the intended usage of the material. For photocatalytic applications other dopant systems may be considered better. Donor systems such as cationic dopants are known to confer better electrical conductivity by donating electrons to the fermi level, thus moving it closer to the conduction band, but this is generally observed to herald a decrease in photocatalytic activity.[16]

Phosphorus Doped TiO_2

The phosphorus doped TiO_2 sample investigated herein has also been published and characterised previously.[12] XPS and scanning electron microscopy (SEM) can be seen in Figure 3. Both P^{5+} and P^{3-} states were evident with P^{5+} present throughout the material from the bulk through to the surface. P^{3-} was however found only within the bulk. Phosphorus P^{5+} and P^{3-} states were observed at binding energies of 129.0 and 133.5 eV respectively for the 2p states. SEM highlights the high surface area morphology the thin film demonstrated. The interplay of P^{5+} and P^{3-} was thought to result in a material that exhibits a competitive rate of photo-catalysis whilst conferring favourable TCO properties. In this case the material can truly be considered a multifunctional material as the inclusion of substitutional donor dopants (P^{5+}), which heralds a shift in the Fermi energy closer to the conduction band therefore allowing electrical conduction, is usually found to be detrimental to photocatalytic activity. This material is therefore part of a growing class of multifunctional materials as well as cation-anion co-doped systems which are of significant interest in technological applications.[17–19]

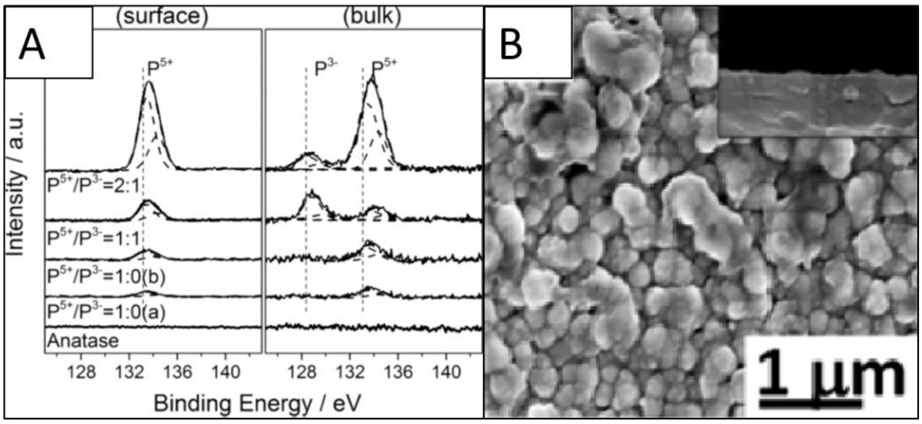

Figure 3: XPS graphs demonstrating the presence of both P^{5+} and P^{3-} states in P doped TiO_2. B SEM demonstrating the surface morphology of P doped TiO_2. Reused with permission from Sotelo-Vaquez et al.[12]

Questions as to its stability under UVA light of intensity it is likely to experience under solar conditions (0.42 mW / cm^2) are therefore of significant interest. The P doped TiO_2 was exposed to sustained UVA irradiation for 25 days as before with the Ta and W doped TiO_2 samples and the concentration of P^{5+} and P^{3-} charted and a function of irradiation time by XPS.

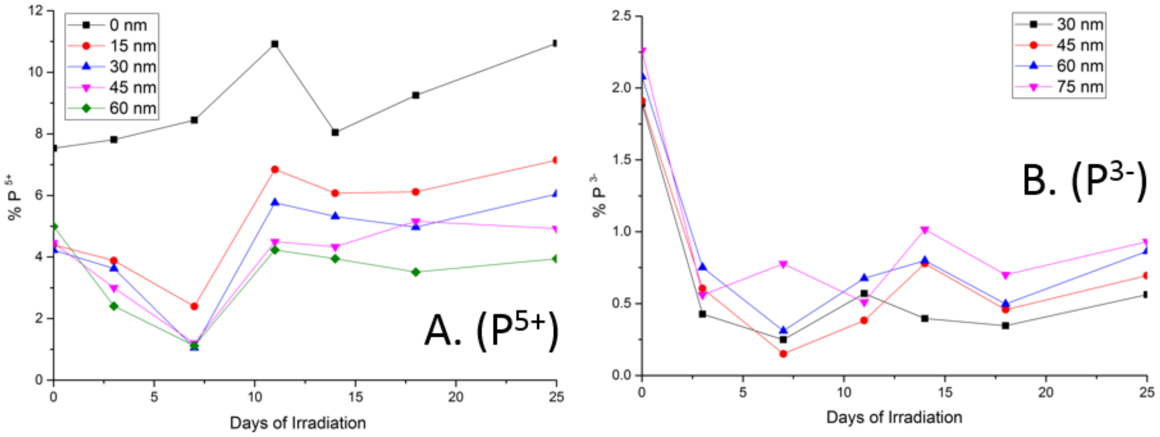

Figure 4: A. The concentration of P^{5+} from the surface through to the bulk, across 25 days' worth of UVA irradiation (0.42 mW / cm^2). Significant variation was observed B. P^{3-} was observed only as a bulk state and is seen to be roughly constant and homogenous within the bulk. This dopant state also exhibits significant concentration variation within the bulk as a result of UVA irradiation (0.42 mW / cm^2).

It is observed in Figure 4 that phosphorus doped TiO_2 exhibits a distinct variation in P^{5+} and P^{3-} from the surface through to the bulk across 25 days of UVA irradiation (0.42 mW / cm^2). From the surface through to the bulk P^{5+} is observed to exhibit significant variation in its concentration. This is unexpected as based on previous experiments in this report on Ta^{5+} and W^{6+} dopants, which are substitutional, P^{5+} and P^{3-} should exhibit dopant stability due to their substitutional nature.

Specifically P^{5+} is observed to exhibit an increase in surface concentration (0-11 days) concurrent with a sustained decrease in P^{5+} levels within the bulk (0-7 days) down to 60 nm. Surface concentration of P^{5+} is then seen to decrease from 11-14 days before increasing again up to 28 days' worth of UVA irradiation. Bulk levels recover and then bulk levels are seen to recover and increase in concentration past 0 days' worth of irradiation. Overall bulk levels of P^{5+} from 15-60 nm were observed to display little variance before irradiation (1%) and after 25 days exhibit a distinct degree of concentration variation (4%) thus a four-fold increase in dopant distribution, showing dopants have moved within the material as a result of UVA irradiation. Interestingly P^{3-} states, which are bulk confined only, exhibit a small spread in concentration before irradiation and after only 4 days of UVA irradiation exhibit a significant decrease in concentration from 30-75 nm within the bulk but retain the small distribution in concentration seen before irradiation (~0.5%). Thus significant dopant variation as a function of UVA irradiation was observed after timescales as little as 4 days. Compared to the expected operational lifetimes of devices which might utilise materials such as those discussed in this work (1-10 years) 4 days is a very small amount of time. Both W and Ta doped TiO_2 show no change in dopant distribution and concentration variation compared to P doped TiO_2.

That P-doped TiO_2 was observed to exhibit dopant mobility even within a substitutional dopant regime indicates that there is much to be understood about the roles and physical characteristics of dopants within TiO_2. We do not claim to know the exact mechanism responsible for this disparity in the expected behaviour of what is observed to be a substitutional dopant, which based on previous reports clearly changes the functional properties of its host matrix, TiO_2, therefore there can be no question that substitutional dopants are present. It could be that dopant and ionic PO_4^{3-} species, which may occupy pores and act as an interstitial dopant could be observed at similar binding energy values in XPS to substitutional P^{5+}.[20,21] Whilst the authors would not expect the substitutional dopant seen in XPS to undergo surface segregation independent PO_4^{3-} units may exhibit this effect. Another possibility is that substitutional P^{5+} centres upon irradiation use electrons and holes to remove themselves from the lattice and form independent PO_4^{3-} units which then surface migrate. It is well established that oxygen can be exchanged and lost between the TiO_2 and air boundary.[22,23] Further investigation is however required to provide authoritative insight into the mechanics of the observed variance in phosphorus concentration as a function of irradiation time.

Conclusion

In this work it has been demonstrated that transition metal cationic substitutional dopants (Ta^{5+} and W^{6+}) exhibit long term stability under UVA irradiation when incorporated in TiO_2. However a non-metal substitutional anionic and cationic dopant pair (P^{5+} and P^{3-}) exhibit UVA irradiation induced concentration variances. The authors would argue, that given this set of experiments in conjunction with our previous work on interstitially nitrogen doped TiO_2 that doped TiO_2's as a class of materials exhibit previously uncharacterised physical phenomena regarding dopant stability that requires further investigation. Given that a wide range of dopants are seen to give roughly similar physical phenomena in TiO_2 such as visible light absorption or enhanced conductivity this study allows us to give a first rough idea of what dopants systems are better for use in long term environmental applications. The authors recognise that this is by no means an exhaustive list of dopants and the authors therefore suggest that dopant stability testing should be considered an important part of research in TiO_2 in the future.

Experimental

Thin film synthesis

All films tested in this work were synthesised using aerosol assisted chemical vapour deposition (AACVD) the specific experimental protocols for each material can be found in published reports.[4,11,12] Generally, a precursor solution containing the necessary chemicals for the host material (TiO_2) and the dopant (Ta^{5+}, W^{6+}, P^{3-} and P^{5+}) are dissolved in a solvent and the resulting solution aerosolised before it is delivered to the deposition chamber under inert gas flow at a specific flow rate. The depositions are carried out at an atmospheric pressure and high temperature regime (~500 °C).

UV Irradiation and X-ray Photoelectron Spectroscopy Study

All samples were cut into small coupons and irradiated with UVA light of an intensity lower or comparable to environmental levels in the UK (0.42 mW/cm^2 compared to 0.5-5 mW/ cm^2 respectively) for periods of time ranging from 0-28 days. In this manner samples representing the same material were created that varied only as a function of irradiation time. X-ray Photoelectron Spectroscopy (XPS) was then undertaken for all samples to chart the change in dopant concentration firstly from the surface to the bulk and secondly as a function of irradiation time. Measurements were taken with a Thermo Scientific K-Alpha instrument with monochromatic Al-Kα source to identify the oxidation state and chemical constituents. High resolution scans were done for Ti (3d), Ta (4f), W (4f), P (2p), O (1s) and C (1s) at a pass energy of 40 eV. The peaks were modelled using Casa XPS software with binding energies adjusted to adventitious carbon (284.8 eV).

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