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Communication: Effect of Oxidation on Excited State Dynamics of Neutral $\text{Ti}_n\text{O}_{2n-x}$ ($n < 10$, $x < 4$) Clusters

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Excited state lifetimes of neutral titanium oxide clusters ($\text{Ti}_n\text{O}_{2n-x}$, $n < 10$, $x < 4$) were measured using a sequence of 400 nm pump and 800 nm probe femtosecond laser pulses. Despite large differences in electronic properties between the closed shell stoichiometric Ti_nO_{2n} clusters and the suboxide $\text{Ti}_n\text{O}_{2n-x}$ ($x = 1-3$) clusters, the transient responses for all clusters contain a fast response of 35 fs followed by a sub-picosecond excited state lifetime. In this non-scalable size regime, subtle changes in the sub-ps lifetimes are attributed to variations in the coordination of Ti atoms and localization of charge carriers following UV photoexcitation. In general, clusters exhibit longer lifetimes with increased size and also with addition of O atoms. This suggests that removal of O atoms develops stronger Ti-Ti interactions as the system transitions from a semiconducting character into a fast metallic electronic relaxation mechanism.

1. INTRODUCTION

Bulk titania (TiO_2) materials are the subject of numerous experimental and theoretical investigations^{1,2} due to their wide application in water splitting,³⁻⁵ white pigments,⁶ and photocatalysis.⁷ The most important aspect of photoactivity is the production of charge carriers with sufficient lifetimes to participate in chemical reactions. Absorption of a photon exceeding the optical gap results in the creation of an exciton, or electron-hole pair, that can recombine through non-radiative processes such as internal conversion or relax through electron scattering. In strongly correlated materials, such as titania, the charge carriers are coupled to lattice vibrations to form polarons, which serve to trap mobile carriers by reducing their mobility and photoconversion yields. Polaron formation is affected by the local geometry of the material, where despite identical chemical compositions, recombination is two orders of magnitude faster in the rutile phase than the anatase phase of TiO_2 .^{8,9} TiO_2 nanoparticles follow two relaxation channels,¹⁰ with holes and electrons relaxing separately over ns to μ s dependent upon the particle size and structure.¹¹⁻¹³ However, the factors affecting these separate lifetimes and how to control these mechanisms remains poorly understood.

A major limitation for bulk titania is the large bandgap which limits electron transport. Defect engineering has become a major focus for titanium oxides, where oxygen deficient materials contain a smaller bandgap, increasingly delocalized density of states (DoS)^{14,15} and therefore can utilize more of the sun's visible spectrum. Suboxides of titania, referred to as $\text{Ti}_n\text{O}_{2n-x}$ ($x > 0$), are easily produced from bulk TiO_2 materials,¹⁶⁻¹⁸ are non-toxic,¹⁹ possess unique optical properties,^{18,20} and may have increased catalytic activity over their stoichiometric counterpart.^{17,21} In particular, Magnéli phase titanium oxides ($\text{Ti}_n\text{O}_{2n-1}$, $n = 4-9$) display enhanced electrical conductivity²² and increased stability over

stoichiometric titania.²³ The overall reactivity of bulk titanium oxides is thought to be heavily dependent on O vacancies and associated Ti^{3+} sites,^{24,25} yet a precise understanding of their influence on the behavior of excitons, polarons, and free charge carriers in titania is needed.

Clusters serve as atomically precise models that enable fundamental studies on the factors that affect charge carrier recombination in bulk materials. Similar to the band structure and photoabsorption in bulk titania, stoichiometric (Ti_nO_{2n}) clusters are closed shell systems with low energy photoexcitation, described as an electron transfer from the O 2p-orbitals to the Ti 3d-orbitals or ligand to metal charge transfer (LMCT). Our measurements on the excited state lifetimes of sub-nanometer Ti_nO_{2n} ($n < 10$) clusters found their large optical gap acts as a relaxation bottleneck, making the properties of the S_1 state strongly correlated with the measured lifetimes.²⁶ The variation in sub-picosecond relaxation dynamics revealed the local cluster geometry and charge carrier separation to be important in adjusting excited state lifetimes.²⁶ Similarly, suboxide clusters act as models for the distortions caused by O vacancies on the surfaces of titania materials. However, the electronic properties of suboxide clusters are quite different due to the presence of partially filled 3d-orbitals, dramatically changing the DoS below the photoexcitation energy and are therefore expected to possess different excited state dynamics. Here, fs pump-probe spectroscopy is employed to measure the excited state lifetimes of suboxide $\text{Ti}_n\text{O}_{2n-x}$ clusters ($n < 10$, $x < 4$). This study supplies a foundation for understanding molecular-scale titania, which will ultimately lead to the production of materials with improved reactivity.

2. EXPERIMENTAL METHODS

The experimental methods and instrumental setup were described previously.^{26,27} Briefly, neutral clusters were

produced through ablation of a pure 0.25" diameter Ti rod by the second harmonic of a pulsed Nd:YAG laser in the presence of a seeded He gas pulse (1% O₂). The ablation plume was confined to a 1 x 60 mm collision region and reduced to a molecular beam diameter of 2 mm by a charged skimmer, deflecting all but the neutral clusters. Neutral clusters were ionized by a sequence of 35 fs laser pulses from a Ti:Sapphire laser and analyzed using a home-built Wiley-McLaren²⁸ type time-of-flight mass spectrometer. The ionized clusters separated in arrival time due to their *m/z* ratio within a field-free region and were subsequently recorded using a microchannel plate (MCP) detector. The 400 nm (3.1 eV) pulse was used to excite (pump) the clusters to an intermediate state and the 800 nm (1.55 eV) probe pulse was sent through a programmed delay-stage before recombining with the 400 nm beam for ionization. A delay to the 800 nm laser pulse was scanned by 10 fs steps and the change of intensity with delay was recorded. An average of 200 shots per time step as the probe was delayed from -1.6 – 6.8 ps. The pump-probe instrumental response function (IRF) of 35 fs was measured using non-resonant excitation of Ar gas. Mass spectra were recorded using 400 nm pump and 800 nm probe pulses of 9.9×10^{14} W/cm² and 3.1×10^{15} W/cm² intensity, respectively. All transient signals were fit using a combination of two Gaussian functions convoluted with an exponential decay to account for the relaxation lifetimes.^{27,29}

3. RESULTS AND DISCUSSION

3.1 TITANIUM OXIDE CLUSTER DISTRIBUTION

Ionization of the neutral titanium oxide molecular beam by the 400 nm pump and 800 nm probe lasers at temporal overlap produced a mass spectrum of Ti₂O to (TiO₂)₁₁ (Fig. 1). The primary clusters recorded follow the series of Ti_nO_{2n-x} (*x* = 0-3) and grow through addition of TiO₂ units.

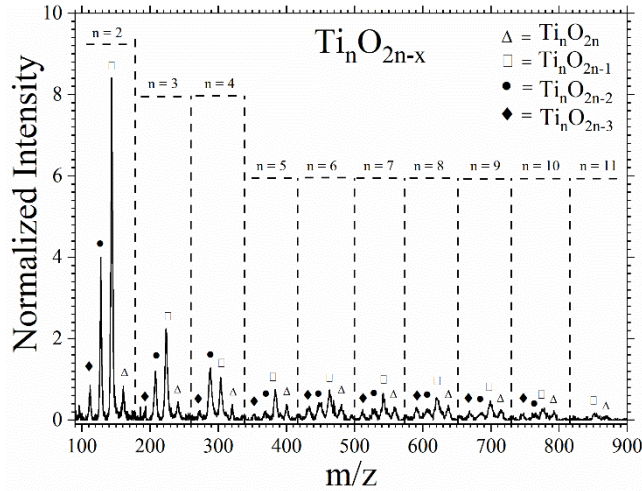


Figure 1: Truncated mass spectrum highlighting neutral Ti_nO_{2n-x} clusters (*n* = 2-11, *x* < 4).

The cluster distribution is consistent with previous studies,³⁰ with the highest intensity peaks generally composed of Ti_nO_{2n-1} or Ti_nO_{2n-2}, and is in agreement with their stabilities.^{15,31} Neutral stoichiometric (Ti_nO_{2n}) clusters have previously only been recorded experimentally using single photon (VUV) ionization thought to be void of fragmentation,³² supporting that fragmentation is not significant in our experiment. Thus, the

formation of O deficient clusters is due to kinetic limitations during the growth of clusters in the ablation plasma.

Sub-nm titanium oxide clusters form hollow cage-like geometries^{33,34} that are different from the bulk lattice structure. The cluster geometries and electronic structures were calculated using time-dependent density functional theory and CAM-B3LYP functional as described in detail in other publications.^{26,31} The two terminal O atoms in Ti_nO_{2n-1} clusters have the lowest binding energy, making the geometry of Ti_nO_{2n-1} clusters similar to Ti_nO_{2n} but lacking one dangling O atom. The lack of one dangling O atom causes the HOMO to shift from an O 2p-orbital onto a Ti 3d-orbital making both the HOMO and LUMO primarily localized on Ti atoms.^{31,35} Therefore, photoexcitation in suboxides is a d-d transition and occurs with a much smaller optical gap.³⁵ The Ti_nO_{2n-2} clusters are similar to Ti_nO_{2n-1} clusters, but do not contain dangling O atoms. Removal of a third O atom leads to an increased number of Ti-Ti bonds and tighter bonding configuration. The reduction of Ti-O bonds increases the d-orbital occupancy and generally decreases bond lengths close to the O vacancy.³¹ The d-electrons are delocalized across the Ti atoms of suboxide clusters, exhibiting metallic characteristics.

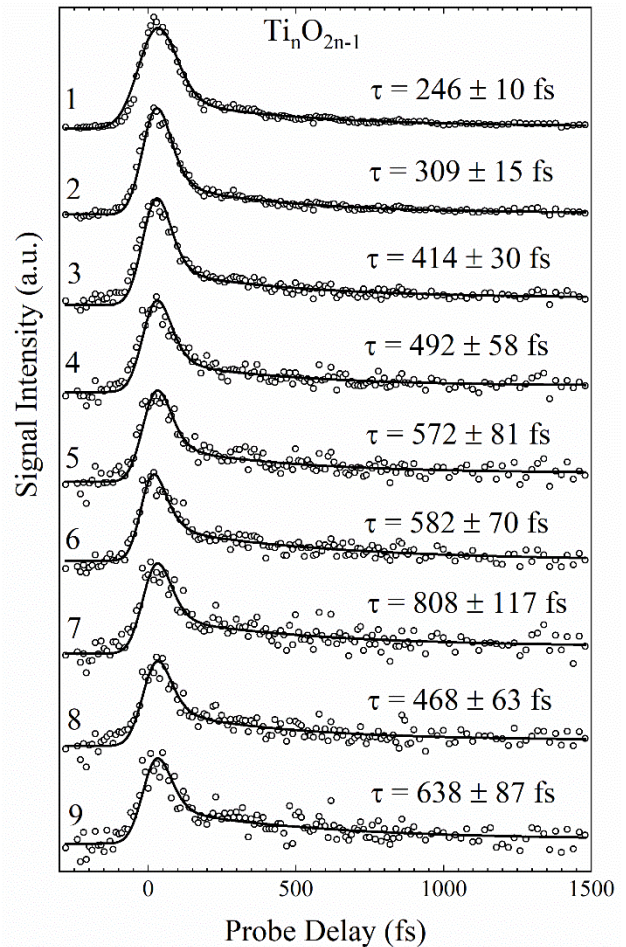


Figure 2: Pump-probe transients of the Ti_nO_{2n-1} series (*n* = 1-9) with the lifetime shown on right and cluster number on left.

3.2 SIZE EFFECT ON SUBOXIDE CLUSTER LIFETIMES

Surprisingly, despite the large changes to the electronic and structural characteristics of the clusters as they gain and lose O atoms,^{26,31} their excited state dynamics remain roughly

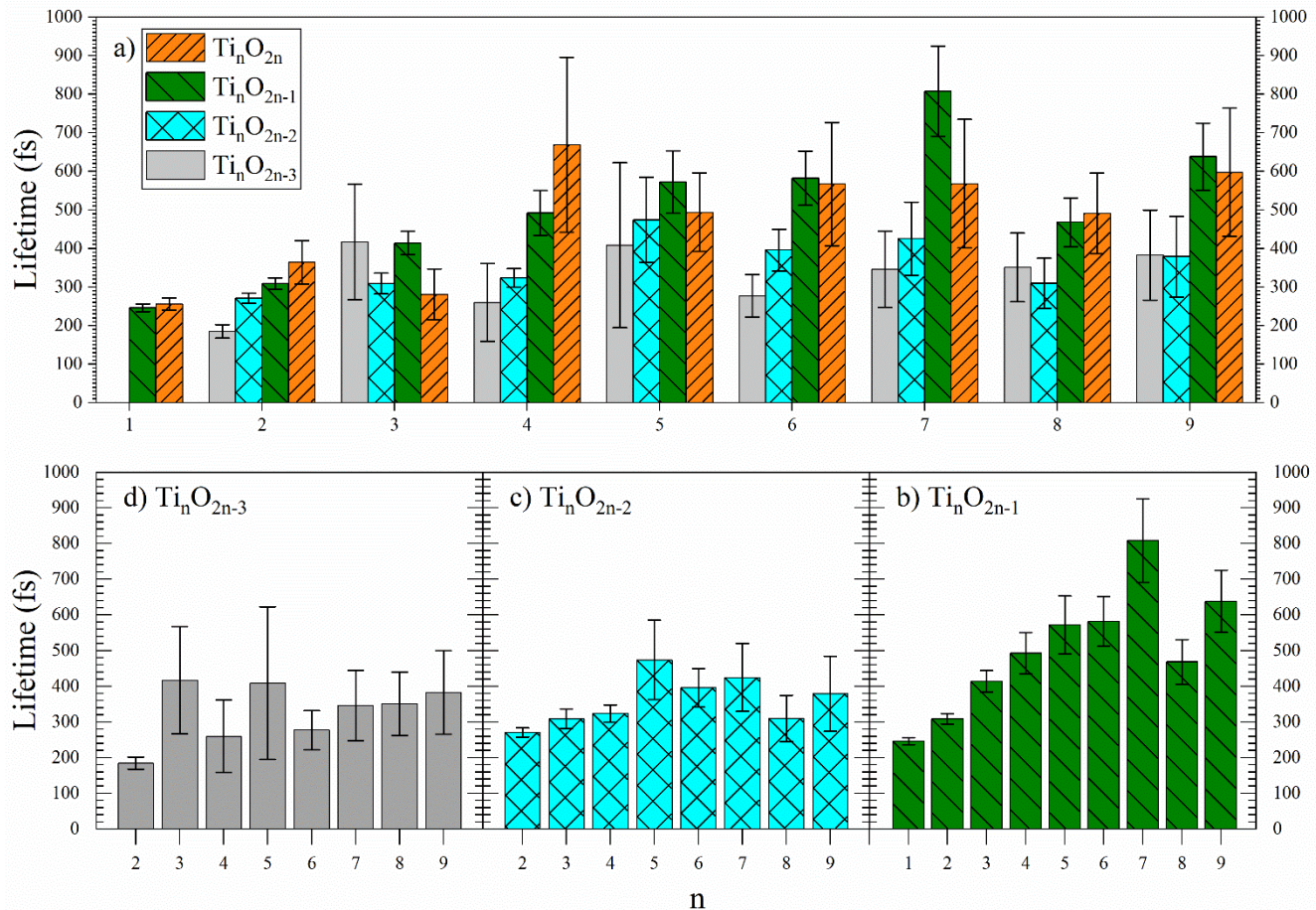


Figure 3: The lifetimes of all $\text{Ti}_n\text{O}_{2n-x}$ clusters (a) showing the Ti_nO_{2n} (orange close slashed lines), $\text{Ti}_n\text{O}_{2n-1}$ (green sparse slashed lines), $\text{Ti}_n\text{O}_{2n-2}$ (cyan crossed lines), and $\text{Ti}_n\text{O}_{2n-3}$ (solid grey) series. Separate plots are shown for b) $\text{Ti}_n\text{O}_{2n-1}$, c) $\text{Ti}_n\text{O}_{2n-2}$, and d) $\text{Ti}_n\text{O}_{2n-3}$ series.

consistent. The transient signals for all clusters contain a fast (35 fs) response and a sub-ps relaxation lifetime (τ). No long-lived states are recorded, and the ratios (κ) of fast/sub-ps fitting coefficients are similar (Table 1). These similarities suggest that the sub-nm scale is perhaps the most important feature, and that relaxation is efficient in these sub-nm clusters due to the restricted proximity of their diameter. The fast component of the transient signal is attributed to a rapid relaxation of a nonresonant excited state. The remaining sub-ps transient ion signal is proportional to the neutral cluster's intermediate excited state population as it relaxes to lower energy. Pump-probe transients of the $\text{Ti}_n\text{O}_{2n-1}$ ($n < 10$) cluster series is presented in Figure 2. Transient signals of the remaining suboxide clusters are presented in the Supplemental Information (Fig. S1 and Fig. S2).

Clusters represent a size regime of non-scalable properties, where every atom impacts the collective electronic and structural properties. Therefore, subtle differences in the excited state lifetimes highlight the variation of cluster geometries and electronic structures on dynamics and excited state lifetimes. Although there is variation in the lifetimes of all cluster series, each $\text{Ti}_n\text{O}_{2n-x}$ series ($x = 0-3$) exhibits a gradual increase in excited state lifetime with the addition of TiO_2 units (Table 1), due to a combination of increased charge carrier separation and overall increase in bonding coordination.

Despite the similarities, each cluster series exhibits a unique trend as they grow in size. A near linear increase in lifetime occurs with size in $\text{Ti}_n\text{O}_{2n-1}$ clusters up to $n = 7$, with the

exception of Ti_6O_{11} (Fig. 3b). All clusters in this series (except Ti_6O_{11}) contain a mirror plane to stabilize the reduced Ti atoms.³¹ Thus, due to a lack of symmetry, the tri-coordinated Ti site of Ti_6O_{11} may retain additional d-electrons that facilitate a faster decay, deviating from the trend. The $\text{Ti}_n\text{O}_{2n-2}$ clusters are more compact, given the absence of any terminal O atoms, and universally have shorter lifetimes. The $\text{Ti}_n\text{O}_{2n-2}$ cluster series of $n \geq 4$ shows an oscillatory nature (Fig. 3c), where odd-numbered clusters have a longer lifetime over even-numbered clusters due to a higher localization of charge carriers. The lifetimes of the $\text{Ti}_n\text{O}_{2n-3}$ series also alternate with increasing cluster size and is most pronounced for the smallest cluster sizes (Fig. 3d). Both oxygen-deficient series exhibit the opposite behavior from the Ti_nO_{2n} series, where even-numbered clusters exhibited longer lifetimes than odd-numbered clusters.²⁶

3.3 OXIDATION EFFECT ON SUBOXIDE CLUSTER LIFETIME

The oxidation states of the Ti atoms are commonly assumed to involve complete electron transfer, where each O atom removes 2 electrons from the Ti atoms. Removal of each O atom from the stoichiometric cluster returns two d-electrons to the Ti atoms. Therefore, the suboxides contain many delocalized d-electrons that should influence the metallicity and consequently the relaxation dynamics of the cluster. Unfortunately, measurements of metallic behavior, such as conductivity, are not possible for clusters of just a few atoms. Another indicator for metallicity is short excited state lifetimes³⁶⁻³⁸ and has been well established for small metal

clusters.^{39–43} Metallic and nonmetallic properties can be identified by the different relaxation behaviors of optically excited states. Strong interactions between delocalized valence d-electrons causes relaxation in metallic species on the fs timescale via Auger-like electron–electron scattering, whereas a weak coupling between electronic excitation and nuclear motion facilitates long (picosecond or longer) lifetimes of electron-hole characteristics in non-metallic semiconductors. Metallic scattering processes dominate if there are many delocalized electrons and a sufficiently high DoS, such as is the case even in small clusters. Thus, the relaxation by electron scattering processes results in many electrons occupying low-lying excited states, similar to the bulk.

However, internal conversion is an alternative possible pathway of relaxation and cannot be ruled out as contributing here. Small molecules can exhibit excited state lifetimes on the order of 10s of fs, particularly when there is passage through a conical intersection between two potential energy surfaces. Despite the well-known role of dangling O atoms in facilitating energy relaxation through conical intersections,⁴⁴ clusters void of terminal O atoms exhibit similar lifetimes to those with them. This suggests that internal conversion is not driving the relaxation. Further, the clusters are sufficiently small such that electrostatic interactions between the hole and electron are efficient for relaxation.

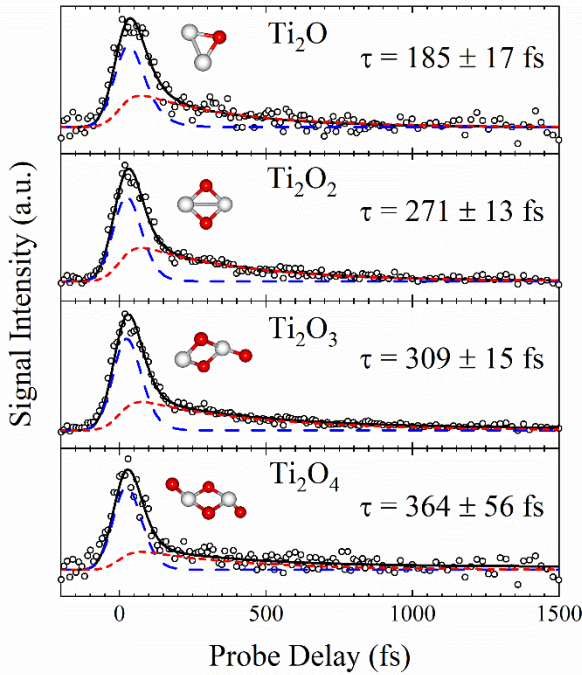


Figure 4: $\text{Ti}_2\text{O}_{4-x}$ ($x < 4$) cluster transients with total fit (black), fast (35 fs) decay (blue long dash) and sub-ps (red short dash) component shown. The sub-ps lifetime is shown for each transient.

The transient signals of neutral $\text{Ti}_2\text{O}_{4-x}$ ($x < 4$) clusters reveal an increase in excited state lifetimes with oxidation (Fig. 4). Here, each O atom changes the oxidation state of the Ti atoms linearly, from a formal oxidation state of +3 (Ti_2O_3) and +2 (Ti_2O_2) which decreases the lifetime by 15% and 26% from the stoichiometric cluster, respectively. Geometries of $\text{Ti}_2\text{O}_{4-x}$ ($x < 4$) clusters are well established^{31,45} (Fig. 4). Ti_2O_4 is the least rigid cluster (containing two terminal O) and therefore should be the easiest to traverse a conical intersection since internal

Table 1: The observed lifetimes of the $\text{Ti}_n\text{O}_{2n-x}$ ($x < 4$) series from $n = 1-9$ and ratio (κ) of fast (35 fs)/sub-ps fitting function amplitudes.

x	n	Lifetime (fs)	κ
1	1	246 ± 10	3.4
	2	309 ± 15	4.6
	3	414 ± 30	5.7
	4	492 ± 58	6.0
	5	572 ± 81	5.5
	6	582 ± 70	5.8
	7	808 ± 117	5.7
	8	468 ± 63	4.4
	9	638 ± 87	4.6
2	2	271 ± 13	3.3
	3	309 ± 27	4.3
	4	324 ± 24	3.9
	5	474 ± 111	5.7
	6	396 ± 54	5.3
	7	425 ± 95	5.4
	8	310 ± 65	3.3
	9	379 ± 105	3.9
3	2	185 ± 17	1.4
	3	417 ± 150	14.8
	4	260 ± 101	5.3
	5	409 ± 214	9.0
	6	277 ± 55	4.0
	7	346 ± 98	5.1
	8	351 ± 89	6.4
	9	383 ± 117	5.8

conversion is less effective in rigid clusters. Yet, it contains the longest lifetime of the series. In contrast, the more rigid ring structure of Ti_2O_2 contains no dangling O atoms and has a faster relaxation, suggesting that internal conversion is not the dominant relaxation mechanism occurring here. Although the number of relaxation pathways decrease with the removal of O atoms, the bond distances shorten³¹ and d-orbital occupancy increases, resulting in a faster relaxation. This influence of O content on lifetime aligns with a metallic to insulator transition occurring with oxidation. Thus, our data supports that relaxation in clusters occurs via Auger-like electron scattering processes similar to bulk metals.

The transient response in O deficient $\text{Ti}_3\text{O}_{6-x}$ ($x < 4$) clusters is different than the other cluster series (Fig. 5). The fully oxidized cluster, Ti_3O_6 , has the shortest excited state lifetime in the Ti_3O_n series, while Ti_3O_3 shows a longer lifetime. However, the Ti_3O_3 transient contains an unreliable sub-ps component with high experimental noise. Therefore, the high variation in κ is not expected to indicate any valuable scientific trend. Ti_3O_6 is unique among the stoichiometric clusters in that it contains a tri-coordinated Ti atom and tri-coordinated O atom, which are not present in other stoichiometric ($n < 6$) structures.^{15,26,35} The tri-coordinated Ti atom sites are common in clusters exhibiting suppressed lifetimes. Ti_3O_5 exhibits a slightly longer lifetime, even though it is further undercoordinated, due to presence of partially filled d orbitals which are delocalized across two Ti atoms. In general, the delocalization of the d orbitals is correlated with extended lifetimes in suboxides.

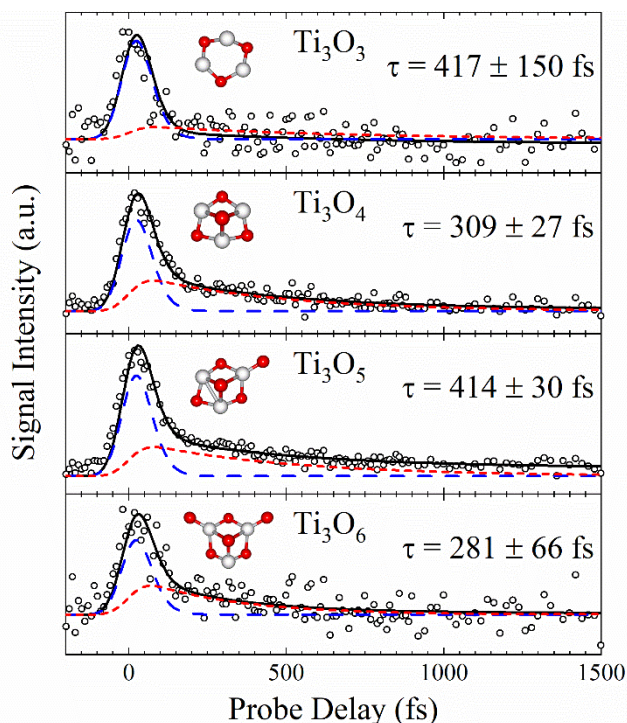


Figure 5: Transients of the $\text{Ti}_3\text{O}_{6-x}$ ($x < 4$) cluster series with fast (35 fs) lifetime (blue long dash), sub-ps lifetime (red short dash) and total fit (solid black). The sub-ps lifetime is shown in each frame.

Similar to the $\text{Ti}_2\text{O}_{4-x}$ clusters, $\text{Ti}_4\text{O}_{8-x}$ ($x < 4$) clusters also highlight an increased lifetime with oxidation (Fig. 3a), supporting a metallic to semiconducting transition. $\text{Ti}_4\text{O}_{8-x}$ ($x < 4$) clusters have 3D structures with the Ti atoms forming a tetrahedron core and O atoms bridging the Ti atoms or as terminal groups for Ti_4O_7 and Ti_4O_8 . The T_d symmetry of Ti_4O_6 lacks terminal O atoms and also contains an increased number of d-electrons which manifest in a large decrease in lifetime. Ti_4O_5 is similar to Ti_4O_6 but contains one less bridging O atom that reduces the Ti-O coordination and decreases the Ti-Ti bond length, resulting in a slightly shorter lifetime. Although there is minimal change in geometry in $\text{Ti}_4\text{O}_{8-x}$ ($x < 4$) clusters, a higher d-orbital occupancy occurs with decreased O atoms from Ti_4O_8 ,³⁵ resulting in a linear decrease in the excited state lifetime.

Lifetimes of $\text{Ti}_5\text{O}_{10-x}$ ($x < 4$) clusters do not change significantly with O (Fig. 3a). The similar lifetimes are due to a similar C_s symmetry and align with the size transition between local and global excitations, where charge carrier delocalization no longer fills the cluster diameter. Further, Ti_5O_{10} exhibits a slightly reduced lifetime in the stoichiometric series, bringing the dynamics closer to Ti_5O_9 . Interestingly, several stoichiometric clusters exhibit shortened lifetimes that deviate from the proposed metallic trend. The Ti_nO_{2n} clusters, where $n = (3, 5, 6)$, contain a tri-coordinated Ti atom instead of the fully tetra-coordinated Ti atoms of the other clusters, and therefore may retain d-electrons that reduce their lifetimes. Such incomplete electron transfer leading to an atypical 3^+ oxidation state is proposed for clusters as small as TiO_2 .⁴⁶

Larger clusters ($\text{Ti}_n\text{O}_{2n-x}$, $n = 6-9$) follow similar trends in excited state behavior (Fig. 3a). Generally, the $\text{Ti}_n\text{O}_{2n-1}$ and Ti_nO_{2n} clusters show longer lifetimes, and exhibit similar lifetimes due to related structures and possibly incomplete

electron transfer, leading to retention of d-electrons on the stoichiometric cluster.¹⁵ Further, in Ti_nO_{2n} clusters, the excited state avoids localization on the Ti atoms with terminal Ti-O bonds,²⁶ which ensures that the excited states behave similarly in the various O deficient clusters and accounts for the minimum influence of lifetime with oxidation. Clusters without terminal O atoms ($\text{Ti}_n\text{O}_{2n-2}$ and $\text{Ti}_n\text{O}_{2n-3}$) show shorter lifetimes and increased d-electron occupancy, indicating that the d-electron scattering is a dominant mechanism affecting dynamics and that bridging O atoms have a minor effect on excited state lifetimes.

A particular outlier to the described trends is Ti_7O_{13} , which exhibits a significantly longer lifetime than Ti_7O_{14} (Fig. 3a). This switched behavior is attributed to its unique structural features, where removal of an O atom from Ti_7O_{14} drives a significant compression of the local Ti-O bonds and creates a new bond forming a tetra-coordinated Ti site adjacent to a tetra-coordinated O atom. This high coordination site may account for its exceptionally long lifetime, in opposition to tri-coordinated Ti sites facilitating fast relaxation. Further, Ti_7O_{13} exhibits the largest separation of charge carriers and electron delocalization, supporting that this delocalization of is correlated with lifetime.

Clusters generally exhibit longer lifetimes with higher oxidation and shorter lifetimes upon removal of O atoms. Although the optical gap of suboxides decreases by ~ 3 eV from the stoichiometric cluster,¹⁵ it does not have a significant influence on the excited state lifetime. This suggests that removal of O atoms develops metallic Ti-Ti bonds of lower coordination, causing the system to transition into a fast scattering-type electronic relaxation mechanism. This is consistent with the idea that as the clusters become more metallic, the lifetimes decrease. Excited state lifetimes are modified by electron-hole interactions which are influenced by Ti bond coordination and cluster size. These results suggest that enhanced excited state lifetimes in bulk titania materials may be achieved through manufacturing structures similar to the Ti_7O_{13} cluster that contain delocalized d-electrons and higher Ti coordination.

4. CONCLUSION

The low-lying excited state lifetimes of neutral $\text{Ti}_n\text{O}_{2n-x}$ ($n = 1-9$ and $x < 4$) clusters were measured using fs pump-probe spectroscopy, and trends in their transient signals related to the size and oxidation are presented. An oscillation in lifetimes as clusters grow in size is attributed to structural differences between the clusters that control charge localization and polaron-like formation. The signal returns to baseline for all clusters, suggesting that relaxation is efficient for these sub-nm materials. We show that the level of coordination increases with cluster size, related to a longer lifetime. The excited state lifetimes of titanium oxide clusters change with oxidation, which affect the Ti coordination and charge carrier localization. The lifetimes show a behavior consistent with a metallic to semiconducting transition with oxidation and related removal of d-electrons from the system. The fundamental information provided herein leads to a deeper understanding of the factors affecting O vacancies in bulk-scale titania materials and will assist in the production of future catalysts of increased reactivity.

Supporting Information

See supplemental material for experimental measurements and fitting of larger $\text{Ti}_n\text{O}_{2n-x}$ ($n = 4-9$, $x < 4$) clusters.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- 1) M.A. Henderson, *Surf. Sci. Rep.* **66**, 185 (2011).
- 2) T.L. Thompson and J.T. Yates, *Chem. Rev.* **106**, 4428 (2006).
- 3) H.G. Xu, X.N. Li, X.Y. Kong, S.G. He, and W.J. Zheng, *Phys. Chem. Chem. Phys.* **15**, 17126 (2013).
- 4) D. Çakir and O. Gülseren, *J. Phys. Condens. Matter* **24**, 13 (2012).
- 5) A. Fujishima and K. Honda, *Nature* **238**, 37 (1972).
- 6) K. Siwińska-Stefańska, M. Nowacka, A. Kołodziejczak-Radzimska, and T. Jesionowski, *Dye. Pigment.* **94**, 338 (2012).
- 7) L. Fernandes Fraceto, A. Espirito Santo Pereira, J. Lischka Sampaio Mayer, A. Rastogi, M. Brestic, M. Zivcak, O. Sytar, H.M. Kalaji, X. He, and S. Mbarki, *Impact Met. Met. Oxide Nanoparticles Plant A Crit. Rev. Front. Chem* **5**, 78 (2017).
- 8) P. Maity, O.F. Mohammed, K. Katsiev, and H. Idriss, *J. Phys. Chem. C* **122**, 8925 (2018).
- 9) A.R. Elmaslmane, M.B. Watkins, and K.P. McKenna, *J. Chem. Theory Comput.* **14**, 3740 (2018).
- 10) B. Li, H. Li, C. Yang, B. Ji, J. Lin, and T. Tomie, *Catalysts* **10**, 1 (2020).
- 11) H.G. Baldoví, B. Ferrer, M. Álvaro, and H. García, *J. Phys. Chem. C* **118**, 9275 (2014).
- 12) Y. Yamada and Y. Kanemitsu, *Appl. Phys. Lett.* **101**, 133907 (2012).
- 13) B. Li, H. Li, C. Yang, B. Ji, J. Lin, and T. Tomie, *AIP Adv.* **9**, (2019).
- 14) L. Li, W. Li, A. Ji, Z. Wang, C. Zhu, L. Zhang, J. Yang, and L.F. Mao, *Phys. Status Solidi Basic Res.* **252**, 2735 (2015).
- 15) H. Du, Y. Jia, C. Niu, K. Hu, H. Li, and L. Yu, *Chem. Phys. Lett.* **731**, (2019).
- 16) B. Xu, H.Y. Sohn, Y. Mohassab, and Y. Lan, *RSC Adv.* **6**, 79706 (2016).
- 17) M. Nagao, S. Misu, J. Hirayama, R. Otomo, and Y. Kamiya, *ACS Appl. Mater. Interfaces* **12**, 2539 (2020).
- 18) Y. Wang, Y. Qin, G. Li, Z. Cui, and Z. Zhang, *J. Cryst. Growth* **282**, 402 (2005).
- 19) A. Jemec Kokalj, S. Novak, I. Talaber, V. Kononenko, L. Bizjak Mali, M. Vodovnik, B. Žegura, T. Eleršek, G. Kalčíkova, A. Žgajnar Gotvajn, S. Kralj, D. Makovec, H. Caloudova, and D. Drobne, *Environ. Sci. Nano* **6**, 1131 (2019).
- 20) J.H. Lee, S. Cho, A. Roy, H.T. Jung, and A.J. Heeger, *Appl. Phys. Lett.* **96**, 163303 (2010).
- 21) X. Pei, T. Zhang, J. Zhong, Z. Chen, C. Jiang, and W. Chen, *Sci. Total Environ.* 145705 (2021).
- 22) M. Yu, T. Saunders, S. Grasso, A. Mahajan, H. Zhang, and M.J. Reece, *Scr. Mater.* **146**, 241 (2018).
- 23) C.N. Bell, D.C. Lee, M.N. Drexler, C.M. Rouleau, K. Sasaki, S.D. Senanayake, M.D. Williams, and F.M. Alamgir, *Thin Solid Films* **717**, 138437 (2021).
- 24) M.L. Weichman, S. Debnath, J.T. Kelly, S. Gewinner, W. Schöllkopf, D.M. Neumark, and K.R. Asmis, *Top. Catal.* **61**, 92 (2018).
- 25) A. Argondizzo, X. Cui, C. Wang, H. Sun, H. Shang, J. Zhao, and H. Petek, *Phys. Rev. B - Condens. Matter Mater. Phys.* **91**, 155429 (2015).
- 26) J.M. Garcia, L.F. Heald, R.E. Shaffer, and S.G. Sayres, *J. Phys. Chem. Lett.* **12**, 4098 (2021).
- 27) J.M. Garcia, R.E. Shaffer, and S.G. Sayres, *Phys. Chem. Chem. Phys.* **22**, 24624 (2020).
- 28) W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* **26**, 1150 (1955).
- 29) T.E. Dermota, D.P. Hydustry, N.J. Bianco, and A.W. Castleman, *J. Phys. Chem. A* **109**, 8259 (2005).
- 30) M. Foltin, G.J. Stueber, and E.R. Bernstein, *J. Chem. Phys.* **111**, 9577 (1999).
- 31) L.F. Heald, J.M. Garcia, and S.G. Sayres, *ChemRxiv* <https://doi.org/10.33774/chemrxiv-2021-rj9cs> (2021).
- 32) Y. Matsuda and E.R. Bernstein, *J. Phys. Chem. A* **109**, 314 (2005).
- 33) S. Hamad, C.R.A. Catlow, S.M. Woodley, S. Lago, and J.A. Mejías, *J. Phys. Chem. B* **109**, 15741 (2005).
- 34) R.J. Hudson, A. Falcinella, and G.F. Metha, *Chem. Phys.* **477**, 8 (2016).
- 35) Y. Guo, J.F. Li, X. Niu, A. Markovits, and R.Q. Zhang, *Phys. Chem. Chem. Phys.* **18**, 10594 (2016).
- 36) M. Wolf, *Surf. Sci.* **377-379**, 343 (1997).
- 37) C. Frischorn and M. Wolf, *Chem. Rev.* **106**, 4207 (2006).
- 38) M. Aeschlimann, M. Bauer, and S. Pawlik, *Chem. Phys.* **205**, 127 (1996).
- 39) N. Pontius, P.S. Bechthold, M. Neeb, and W. Eberhardt, *Phys. Rev. Lett.* **84**, 1132 (2000).
- 40) N. Pontius, G. Lüttgens, P.S. Bechthold, M. Neeb, and W. Eberhardt, *J. Chem. Phys.* **115**, 10479 (2001).
- 41) N. Pontius, M. Neeb, W. Eberhardt, G. Lüttgens, and P.S. Bechthold, *Phys. Rev. B - Condens. Matter Mater. Phys.* **67**, (2003).
- 42) K. Koyasu, C. Braun, S. Proch, and G. Ganteför, *Appl. Phys. A Mater. Sci. Process.* **100**, 431 (2010).
- 43) J. Heinzelmann, P. Kruppa, S. Proch, Y.D. Kim, and G. Ganteför, *Chem. Phys. Lett.* **603**, 1 (2014).
- 44) W.T. Peng, B.S. Fales, Y. Shu, and B.G. Levine, *Chem. Sci.* **9**, 681 (2018).
- 45) Y. Xiao, P. Jin, G. Wang, and L. Zhang, *Phys. Chem. Chem. Phys.* **23**, 4796 (2021).
- 46) D. Koch and S. Manzhos, *J. Phys. Chem. Lett.* **8**, 1593 (2017).