

# Crystal properties without crystallinity? Influence of surface hydroxylation on the structure and properties of small TiO<sub>2</sub> nanoparticles

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## Abstract

TiO<sub>2</sub> nanoparticles (NPs) are widely employed in applications that take advantage of their photochemical properties (e.g. pollutant degradation, photocatalysis). Surface hydroxylation and crystallinity are two of the main factors determining the photoactivity of TiO<sub>2</sub> NPs. Here, we study the interrelation between crystallinity, surface hydroxylation and electronic structure in small titania nanoparticles (NPs) with 1.4 - 2.3 nm diameters using accurate density functional theory calculations. We systematically vary the degree of hydroxylation of a crystalline anatase NP and a series of thermally annealed NPs, where in both cases the NPs follow the corresponding (TiO<sub>2</sub>)<sub>35</sub>(H<sub>2</sub>O)<sub>m</sub> composition. Generally, the effect of thermal annealing tends to form NPs with quasi-spherical morphologies and low crystallinity, which, for the NP sizes considered, are more energetically stable than the corresponding crystalline anatase NPs. With increasing hydroxylation, however, we find that the difference in energetic stability between the two classes of NP significantly diminishes to a point where they are almost degenerate at the highest OH coverages. We find that higher degrees of hydroxylation mainly induce the local coordination environments of the atoms in the thermally annealed NPs to become almost identical to those in the corresponding hydroxylated crystalline anatase NPs. Moreover, the highly hydroxylated annealed NPs also possess electronic band gaps and band edges with very similar energies and orbital characters to those found in the hydroxylated crystalline anatase NPs. Our study thus suggests that one can mimic the gap-local electronic structure of faceted crystalline NPs in non-faceted non-crystalline NPs of the same chemical composition with atoms having local coordination environments in line with crystalline NPs. We refer to these crystallite-mimicking non-crystalline NPs as “crystalikes”. Small crystallike NPs could allow for photochemical applications of titania in the size range where crystalline anatase NPs tend to become

thermodynamically unfavoured (<3-5 nm). Our work implies the anatase crystal structure may not be as essential as previously assumed for TiO<sub>2</sub> NP applications and generally suggests that crystallikes could be possible in other nanomaterials.

## Introduction

Over five decades have passed since the breakthrough discovery that the anatase crystal polymorph of titania (TiO<sub>2</sub>) is able to split water into hydrogen and oxygen under ultraviolet light.<sup>1</sup> Since then, the anatase TiO<sub>2</sub> + water system has become a benchmark for studying the fundamental physiochemical principles underlying a range of photocatalytic processes<sup>2,3</sup> with relevance to numerous practical applications<sup>4</sup> (e.g. production of H<sub>2</sub> as green fuel,<sup>5,6</sup> polluted water remediation<sup>7</sup>). As an extended solid, titania is thermodynamically most stable in the rutile crystal phase, which shows a significantly lower photocatalytic activity than anatase. This polymorphic difference in performance has been discussed with respect to numerous possible factors but is often ascribed to the relative ease in which photo-generated excitons in anatase can reach the surface.<sup>8</sup> Experiments on thin films show that up to a thickness of about 2.5 nm the photoactivity of anatase and rutile are comparable, but that further thickness increase (up to 15 nm) only improves the performance of the anatase films<sup>9</sup>. This result demonstrates: i) that the surface-accessible excitons in anatase can be formed further from the reactive surface than in rutile, and ii) this difference only starts to be measurable for systems with surface-to-interior dimensions greater than 2.5 nm. This implies that the surface accessibility of excitons should not play a role in distinguishing the photoactivity of anatase and rutile nanoparticles (NPs) with diameters ≤5nm. We note that titania NPs close to this size are often employed in photocatalytic experiments where the variation in observed photoactivity is thus most likely dependent on other factors. Herein, we study titania NPs with <2.5 nm diameters and focus on two alternative properties of that are likely to significantly affect their photocatalytic performance: 1) surface hydroxyl (-OH) coverage and 2) crystallinity.

Nanoscale titania has a high surface to bulk ratio and possesses surface atoms with low coordination which readily react with water vapour under ambient conditions resulting in surface hydroxylation.<sup>10</sup> Recently, combined computational and experimental efforts have been used to identify types and locations of the hydroxyl groups on anatase NPs.<sup>11</sup> Generally, the degree of surface hydroxylation can vary depending on TiO<sub>2</sub> system size and the environment (e.g. humidity, temperature).<sup>12</sup> For many years it has been known that the density of surface hydroxyls plays an important role in affecting the photoactivity of titania NPs<sup>13</sup>. This effect is linked to the exciton-induced conversion of surface hydroxyls to hydroxyl radicals (·OH) which

subsequently play a role in photocatalytic oxidation reactions.<sup>3,14,15</sup> The observation that hydroxylated anatase NPs generate more mobile OH species than rutile NP has even been proposed as a key factor to explain the relatively higher activity of anatase NPs for many photooxidative reactions<sup>16</sup>. We note that surface hydroxyl groups can facilitate the interaction of titania NPs with biosystems<sup>17</sup> where the photocatalytic production of hydroxyl radicals can also lead to bio-toxicity<sup>18</sup>.

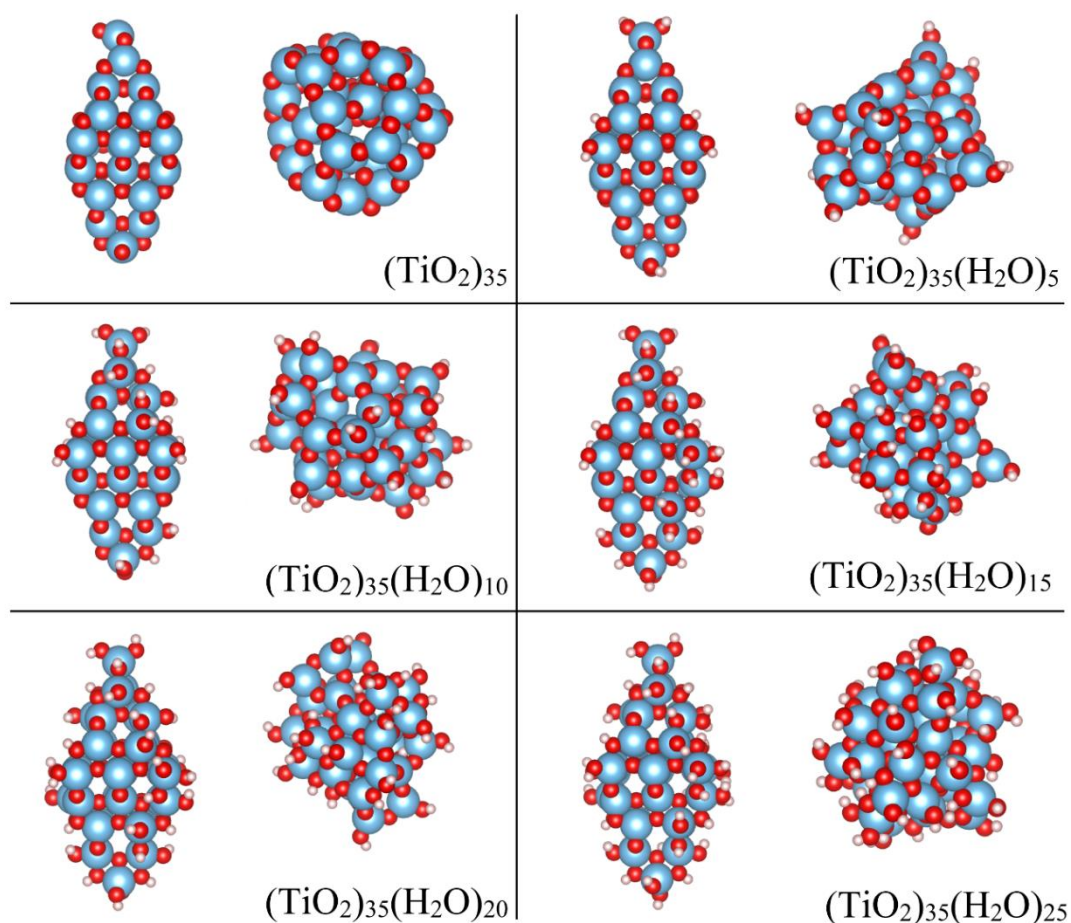
Starting from the stable extended rutile crystal phase, decreasing the system size to the nanoscale decreases the relative thermodynamic stability of rutile with respect to anatase until a crossover is reached for NPs of approximately 14 nm diameter<sup>19</sup>. The exact size at which the more photoactive anatase crystal phase becomes the most stable in NPs is largely determined by surface contributions to the free energy<sup>20</sup> and can thus be significantly affected by adsorbed species<sup>21,22</sup>. Generally, it is known that strongly bound water (e.g. surface hydroxyl groups) plays an essential role in determining the stability of TiO<sub>2</sub> NPs<sup>23</sup>. In the bare case, the anatase crystal phase persists in NPs down to a diameter ~2-3nm, whereupon titania NPs are predicted to energetically favour non-crystalline structures due to the extended influence surface reconstruction from the high proportion of undercoordinated surface atoms.<sup>24,25</sup> In such small amorphous NPs for other materials, the effect of water strongly interacting with the surface has been shown to induce crystallinity by lowering the interfacial energy.<sup>26</sup> For TiO<sub>2</sub> NPs, water adsorption is more exothermic on rutile crystal surfaces than on anatase surfaces.<sup>23</sup> For small crystalline TiO<sub>2</sub> NPs it has been predicted that a high surface coverage of strongly bound water could make rutile NPs thermodynamically competitive with anatase NPs.<sup>27</sup>

For experimental studies on NPs, it is difficult to disentangle the intimate interrelation between the type and degree of crystallinity, the nature of their surfaces and their resulting physicochemical properties. Here we employ accurate and detailed computational models to understand how these interacting factors play out for two types of TiO<sub>2</sub> NPs. We focus on titania NPs with diameters ranging between 1.4-2.3 nm which is close to the non-crystalline/crystalline anatase crossover size for bare NPs<sup>24</sup>. The structure of NPs in this size regime is thus likely to be highly sensitive to surface adsorption. We thus consider both faceted crystalline anatase NPs, and thermally annealed NPs which can explore potentially lower energy non-crystalline structures. Simultaneously, we probe the effect of systematically increasing the degree of surface hydroxylation from the bare case to high -OH coverages for both types of NP. For the resulting two sets of NPs, we then compare the energetic, structural, and electronic properties. To enable a rigorous comparison, we employ the same NP size and degrees of hydroxylation for both NP types. The unique perspective provided by our controlled study allows

us to discern numerous differences and similarities between crystalline and non-crystalline titania NPs with corresponding varying degrees of hydroxylation. For low and intermediate degrees of hydroxylation the two types of NP have distinct atomistic structures and electronic gaps which respond in different ways to varying hydroxylation. For higher degrees of hydroxylation, we find that the electronic gap of both types of NP converges to a very similar value. We also find that the local atomic coordination environments of both types of NP become very similar at high hydroxyl coverages. However, this hydroxylation-induced electronic and local structural convergence does not appear to coincide with an increase in crystallinity in the thermally annealed NPs. Our results show that degree of surface hydroxylation can determine the electronic gap in nanotitania via induced modifications of local structural (i.e. coordination environments). At high -OH coverages, our results also suggest that effect leads to a convergence in the electronic structure, regardless of the degree of crystallinity of the NP. This surprising result indicates that it may be possible to employ hydroxylation to induce electronic properties associated with crystalline anatase NPs in non-crystalline nanotitania. Our concrete example of crystallite-mimicking non-crystalline NPs (or “crystalike” NPs) in small hydroxylated titania NPs could have important implications for photochemical applications. Synthesis of small crystalline anatase NPs is hampered by their low thermodynamic stability.<sup>28</sup> As crystallinity may no longer a requirement to access the characteristic electronic structure of crystalline anatase NPs, small hydroxylated crystallike NPs may offer new opportunities for photochemical applications arising from: higher surface areas, higher energy excitons from quantum confinement, lower radiationless photon transfer from quantization.<sup>29</sup> Overall, our study highlights the possibility of crystallike nanomaterials as a potential means to obtain the desirable properties of crystalline systems without the requirement of long-range crystalline order.

## Models and computational methodology

Our study models the progressive and systematic hydroxylation of realistically structured model  $(\text{TiO}_2)_{35}$  NPs. We assume that hydroxylation occurs from the interaction of this initially anhydrous species with water molecules up to highly hydroxylated NPs with a  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_{25}$  chemical composition. We consider two types of NPs during this process: i) crystalline anatase NPs with a faceted bipyramidal morphology, ii) thermally annealed NP with no fixed morphology (see Fig. 1).



**Fig. 1** DFT-optimized structures of the faceted (left) and annealed (right) (TiO<sub>2</sub>)<sub>35</sub>(H<sub>2</sub>O)<sub>m</sub> NPs for  $m = 0, 5, 10, 15, 20, 25$ . Atom colour key: Ti – blue, O - Red, H - white.

### **Crystalline anatase NP models**

The initial anhydrous faceted (TiO<sub>2</sub>)<sub>35</sub> NP was derived from a top-down cut from the bulk anatase crystal structure following the Wulff construction, as described in previous works.<sup>24,30,31</sup> This procedure results in bipyramidal NPs which exhibit thermodynamically stable (101) surface on all facets in line with experimental observations.<sup>32</sup> From collaborative experimental and computational work, it is known that water molecules interact in a dissociative way with the surfaces of bipyramidal anatase NPs.<sup>11</sup> The resultant -H and -OH species are bound to O and Ti atoms, respectively where the energetic stability of hydroxylation depends on the coordination environment of the surface atoms (*i.e.* apical > equatorial > edge > facet).<sup>11,27</sup> Here we followed this energetically-determined order to progressively hydroxylate the initial faceted anatase (TiO<sub>2</sub>)<sub>35</sub> NP and produce a set of NPs with the composition (TiO<sub>2</sub>)<sub>35</sub>(H<sub>2</sub>O)<sub>m</sub> with  $m = 0 - 25$  (see selected NPs in Fig. 1). Initial faceted NP structures were pre-optimised using the Nano-TiO interatomic potential which has been shown to accurately describe the structures and relative

energetics of nano-titania systems with high computational efficiency.<sup>12,30,31</sup> The final DFT-optimised anatase NPs have maximum diameters ranging between 2.1 - 2.3 nm depending on the degree of hydroxylation.

### ***Thermally annealed NP models***

To compare with the hydroxylation of an anhydrous faceted crystalline NP, we also started from a non-crystalline anhydrous  $(\text{TiO}_2)_{35}$  NP. This initial NP was generated by using a molecular dynamics (MD) based method to thermally anneal the internal structure and morphology of a spherical cut  $(\text{TiO}_2)_{35}$  NP from the anatase crystal structure (see details below). From previous work we have shown that thermally annealed anhydrous NPs of this size lose their crystalline structure and adopt a quasi-spherical morphology. The purpose of the annealing is to search for low energy NP structures. Indeed, bare annealed  $(\text{TiO}_2)_{35}$  NPs are significantly more energetically more stable than bare faceted crystalline anatase NPs of the same size. To this initial NP structure, we first added a dissociated water molecule by binding one H and one -OH species to low coordinated surface O and Ti atoms, respectively. The interaction of NPs with water can strongly affect surface energies and overall NP stability<sup>21,22</sup> and even induce internal crystallisation<sup>26</sup>. As such, for every step of hydroxylation by a single water the NP was again thermally annealed to search for low energy  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NP structures with  $m = 1 - 25$ . This implies that every NP in the series of progressively hydroxylated thermally annealed NPs is structurally independent of each other, unlike in the case of the crystalline anatase NPs. The final DFT-optimised thermally annealed NPs have maximum diameters ranging between 1.4 – 1.8 nm depending on the degree of hydroxylation. Structures of selected annealed NPs are shown in Fig. 1.

### ***MD-based thermal annealing***

Global optimisation searches have been previously employed to search for the lowest energy structure (global minimum) for relatively small, hydroxylated NPs<sup>12,33,34</sup>. As NPs get larger and more chemically complex the corresponding energy landscapes tend to have a very rapidly increasing number of low energy minima. In such cases the global minimum structure is likely to be one of many characteristic minima inhabited by the system. For our chemically complex  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  systems with three atom type and up to 180 atoms we use a physically motivated simulated annealing (SA)<sup>35</sup> approach to guide us to characteristic low energy structures.

Generally, SA involves controlled cycles of heating and cooling to guide the system into regions of energetic stability. Here, we use classical MD in the canonical NVT ensemble to control the temperature of our NPs. Specifically, we use MD runs starting at 300 K with an equilibration of 600 ps. The temperature is then increased gradually for 3500 ps with a step of  $0.5 \text{ K}\cdot\text{ps}^{-1}$ , thus reaching  $\sim 1750 \text{ K}$ . This latter temperature is then maintained for 800 ps, after which the system is then cooled down by 300 K over a period of 1250 ps and, again, maintained for 800 ps. This stepwise cooling process is repeated till the initial temperature of 300 K is reached again, in which the system remains for the final 8000 ps. Five  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  structures were selected from each MD-SA run for each NP composition (i.e. degree of hydroxylation) for further DFT-based refinement (see below). Fig. S1 in the Electronic Supplementary Information (ESI) illustrates the stepwise MD-SA procedure.

The interactions between atoms in the NPs during the MD-SA calculations were modelling using the NanoTiO (IP)<sup>12,30,31</sup>. We note that the internal structure of the NP (including the locations and interactions between -OH groups) and its overall morphology can freely adapt to the degree of hydroxylation during our MD-SA runs while exploring progressively lower energy states. The General Utility Lattice Program (GULP)<sup>36</sup> was used for all IP-based MD-SA calculations. Classical MD simulations have also been employed for studying how the size of spherically cut crystalline anatase NPs affects their surface reactive response to water solvation<sup>37</sup>. In this latter study the anatase crystalline structure and spherical morphology of the studied NPs was relatively unperturbed and the degree of hydroxylation was determined by the solvation. In contrast, here we focus on the interplay of NP crystallinity/morphology and hydroxylation by systematically comparing and varying both aspects.

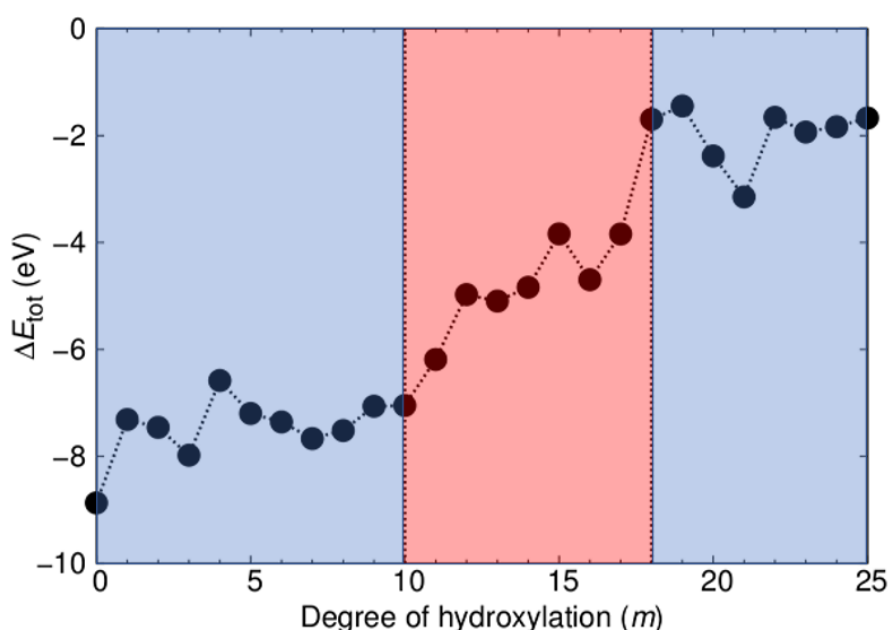
### ***DFT calculations***

To obtain the electronic structure for all  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  compositions the selected low energy annealed NPs and all faceted NPs were further optimised using relativistic all-electron DFT-based calculations as implemented in the FHI-aims code.<sup>38</sup> Structural optimisations were performed using Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional<sup>39</sup> and electronic energy gaps were calculated using a hybrid PBE<sub>h</sub> (12.5% Fock exchange) which has been tailored to well reproduce the electronic structure of various titania systems.<sup>40,41</sup> All calculations employed a light tier-1 numerical atom-centred orbital basis set, which has an accuracy comparable to a TZVP Gaussian-type orbital basis set for  $\text{TiO}_2$ .<sup>42</sup> The convergence thresholds for atomic forces and total energy during the relaxation of the structure of the NPs

were set to  $10^{-5}$  eV·Å<sup>-1</sup> and  $10^{-6}$  eV, respectively. Relativistic effects were included using the Zero Order Regular Approximation (ZORA).<sup>43</sup>

## Results and discussion

Below, we report the calculated energetic, structural and electronic properties of our  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NPs. In particular, we compare how these characteristics are affected by the degree of hydroxylation and by the underlying crystallinity of the respective NP.

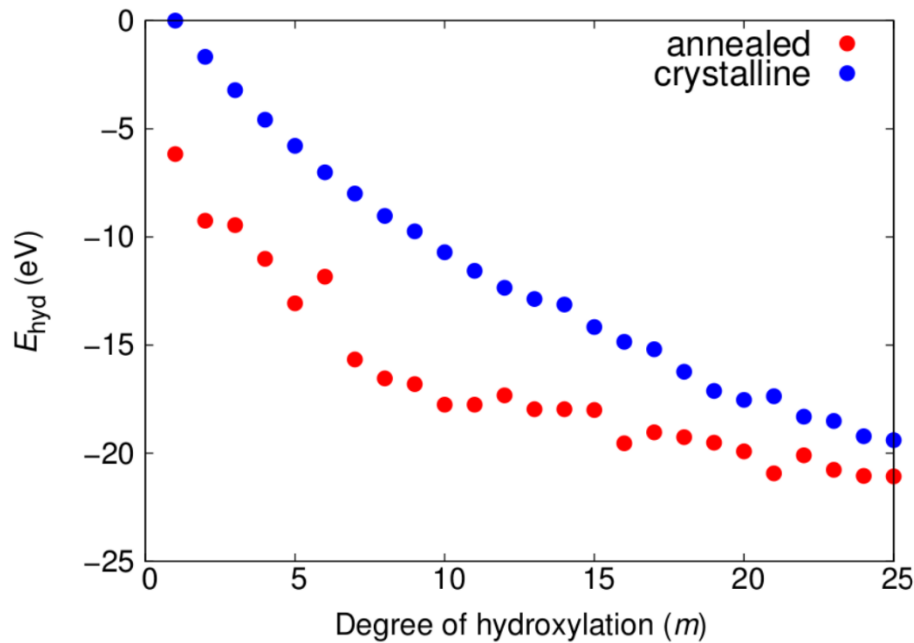


**Fig. 2** Total energy difference ( $\Delta E_{\text{tot}}$ ) between the faceted and annealed  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NPs with respect to degree of hydroxylation induced by the number of dissociatively adsorbed water molecules ( $m$ ). The coloured regions indicate two regions of relatively constant energetic stability (blue) and a transitional region (red).

### *NP energetics with respect to hydroxylation*

As our two types of NP have exactly the same range of compositions, we can directly compare their respective energetic stabilities for all degrees of hydroxylation. In Fig. 2 we show how the difference in total energy between faceted and annealed  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NPs ( $\Delta E_{\text{tot}}(m)$ ) varies





**Fig. 3** Variation of  $E_{hyd}(m)$  with the number of water molecules ( $m$ ) for increasingly hydroxylated faceted and annealed  $(TiO_2)_{35}(H_2O)_m$  NPs. The energy of the anhydrous annealed NP has been adjusted with respect to the anhydrous crystalline NP to reflect the respective difference in  $E_{tot}$ .

with  $m$ . The plot shows that  $\Delta E_{tot}$  is always negative, showing that annealed  $(TiO_2)_{35}(H_2O)_m$  NPs are more energetically stable than faceted NPs for the full range of hydroxylation considered. The largest magnitude of  $\Delta E_{tot}$  occurs for the anhydrous case. Upon increasing hydroxylation, the magnitude of  $\Delta E_{tot}$  remains fairly constant and high ( $|\Delta E_{tot}| = 7.5 \pm 1.4$  eV) for  $m \leq 10$ . When increasing hydroxylation beyond this point in the range  $11 \leq m \leq 17$ , the annealed NPs are progressively destabilized with respect to the faceted anatase NPs by approximately 5 eV. For the highest considered hydroxylation ( $17 < m \leq 25$ ) the magnitude of  $\Delta E_{tot}$  is relatively low and again fairly constant ( $|\Delta E_{tot}| = 2.0 \pm 1.1$  eV). The convergence of the energetic stability of faceted anatase NPs and thermally annealed NPs with increasing  $m$  suggests that hydroxylation could be inducing a structural homogenisation.

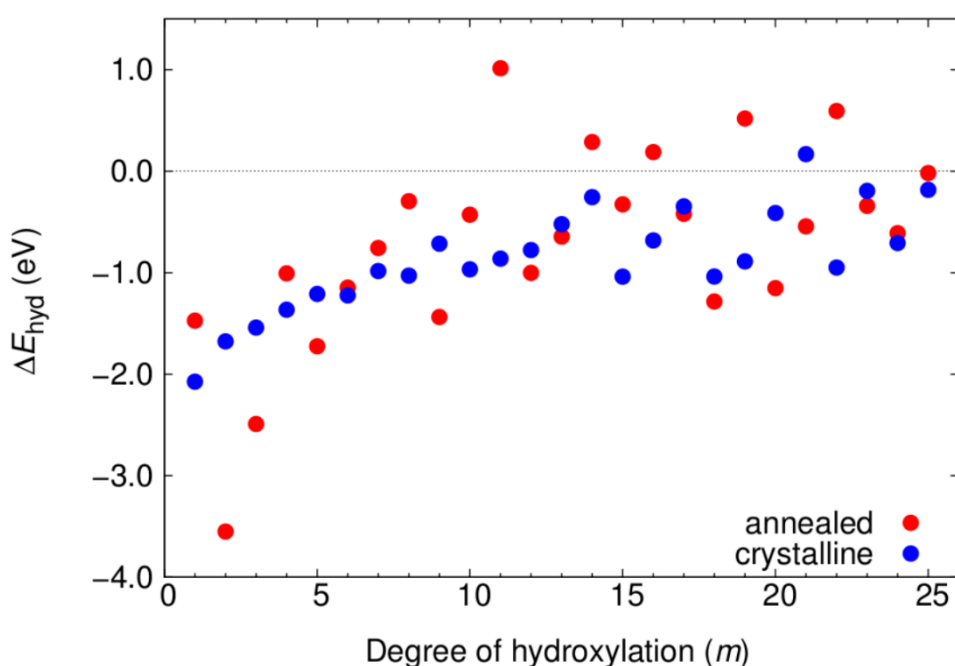
To follow the induced energetic changes due to gradually increasing the degree of hydroxylation for each of our two types of  $(TiO_2)_{35}(H_2O)_m$  NP, we use two quantities:

- 1) the total hydration energy:  $E_{hyd}(m) = E_{tot}(m) - (E_{tot}(0) + m \cdot E_{H_2O})$

and

- 2) the incremental hydration energy:  $\Delta E_{hyd}(m) = E_{tot}(m) - (E_{tot}(m-1) + E_{H_2O})$

where  $E_{\text{tot}}(m)$  is the total energy of a NP with  $m$  dissociatively adsorbed water molecules and  $E_{\text{H}_2\text{O}}$  is the total energy of a water molecule. On the other hand, the  $E_{\text{tot}}(0)$  term stands for total energy of titania NP in its bare configuration. In Fig. 3 the plot of  $E_{\text{hyd}}(m)$  versus  $m$  shows a tendency to become progressively more negative for both NP types with increasing hydroxylation. This implies that dissociative reaction with water molecules is energetically stabilising for all -OH coverages considered for both crystalline and annealed NPs. We note that the stabilising effect of water addition is slightly less effective for the annealed NPs than for the crystalline NPs for higher degrees of hydroxylation. This tendency is in line with the energetics of hydroxylation for smaller globally optimised titania nanoclusters.<sup>12</sup>



**Fig. 4** Variation of  $\Delta E_{\text{hyd}}(m)$  with the number of water molecules ( $m$ ) for increasingly hydroxylated faceted and annealed  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NPs.

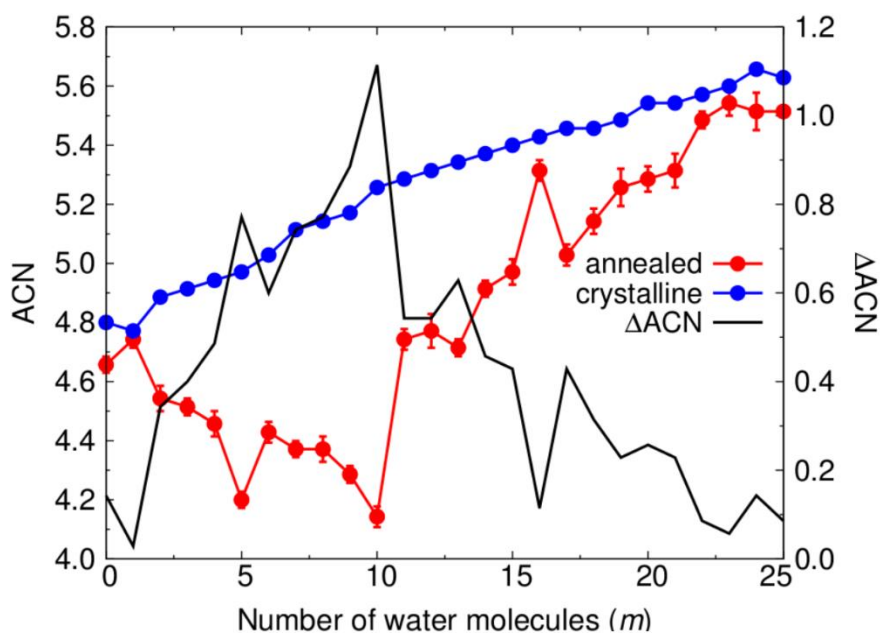
In Fig. 4 we show the evolution of  $\Delta E_{\text{hyd}}(m)$  with respect to the degree of hydroxylation for both NP types. For the structurally unchanging anatase NP core the resulting series of energies indicates how the dissociative reaction energy of adding each successive  $\text{H}_2\text{O}$  water molecule varies with -OH coverage. Here, we see that our chosen sequence of anatase NP hydration, depending on increasing surface coordination of adsorption sites (*i.e.* apical > equatorial > edge > facet), results in nearly every individual  $\text{H}_2\text{O}$  addition reaction being exothermic. Only for  $m = 21$  do we see a small endothermic adsorption energy for incremental

hydroxylation. This is likely to be simply due to the specific adsorption sequence chosen, of which there are a huge number, and does not imply that there is anything unusual for this degree of hydroxylation. Overall, the magnitude of  $\Delta E_{\text{hyd}}(m)$  is highest for lowest hydroxylation (approx. -2.0 eV) and then steadily decreases until about  $m = 14$ . This reflects the progressive adsorption of surface sites with increasing coordination. For the highest hydroxylation  $\Delta E_{\text{hyd}}(m)$  fluctuates around a value of about -0.5 eV.

For the annealed NPs,  $\Delta E_{\text{hyd}}(m)$  is not open to such a simple interpretation (i.e. sequential H<sub>2</sub>O adsorption reaction energy) as for the anatase NPs. For each degree of hydroxylation annealed NPs are produced from a new MD-based stochastic search and are thus structurally independent from each other. Going from  $m$  to  $m+1$ , for example, typically involves a change in the both underlying (TiO<sub>2</sub>)<sub>35</sub> NP structure and the locations of the  $m$  -OH groups. In general, the trend of  $\Delta E_{\text{hyd}}(m)$  for the annealed NPs with increasing  $m$ , is quite similar to that for the anatase NP, but with significantly larger fluctuations. These large changes in  $\Delta E_{\text{hyd}}(m)$  for small changes in  $m$  reflects the corresponding larger structural changes for the annealed NPs. The positive values of  $\Delta E_{\text{hyd}}(m)$  for some values of  $m$  could indicate the difficulty of finding low energy NPs for these degrees of hydroxylation using our MD approach. We note that these positive incremental changes do not affect the fact that the corresponding degrees of hydroxylation are energetically stabilising overall, as shown in Fig. 3. Such behaviour could indicate that energetically costly changes in NP structure are necessary to dissociatively adsorb water in the most energetically favourable way with increasing hydroxylation. Below we analyse the change in NP structure with increasing hydroxylation.

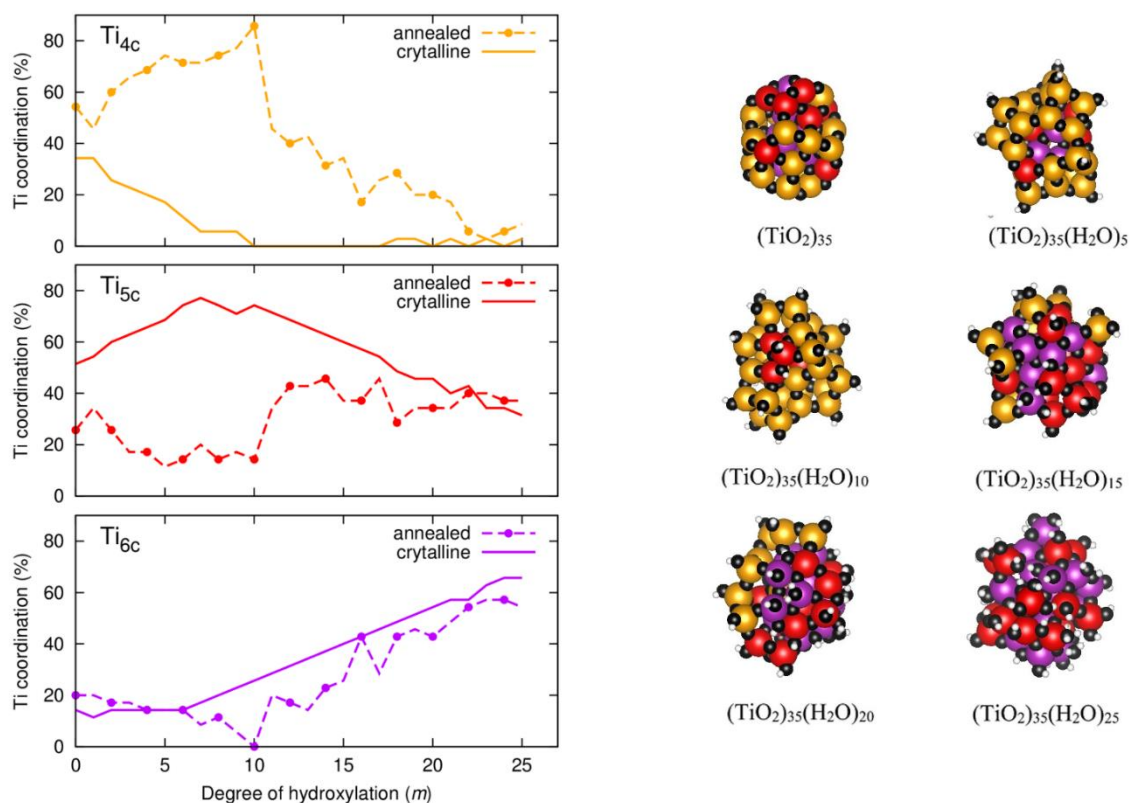
### ***Structure of hydroxylated (TiO<sub>2</sub>)<sub>35</sub> NPs***

To compare the local structure of each type of NP throughout the considered hydroxylation range we follow the change in the local bonding coordination of Ti atoms. To do so we count the number of O atoms around each Ti centre in each NP within a maximum Ti-O cut-off distance of 2.4 Å. Summing the coordination values of each Ti centre within a given NP and then dividing by the total number of Ti centres gives the average coordination number (ACN). Fig. 5 shows the variation in the ACN for crystalline anatase NPs and thermally annealed NPs with respect to hydroxylation, and the respective difference in ACN between both NP types ( $\Delta\text{ACN}$ ). We note that the ACN values for the annealed NPs are averages from values obtained for five low energy NPs from the thermal annealing runs.



**Fig. 5** Average coordination number (ACN) of Ti centres for the annealed and crystalline anatase NPs with respect to hydroxylation (left hand axis). The “error bars” for the annealed NP data indicate the maximum and minimum ACN values found in a sample of five low energy NPs from the annealing runs. The black line follows the difference between the ACN values of the annealed and crystalline NPs ( $\Delta$ ACN) with respect to  $m$ .

For the crystalline anatase NPs, the ACN tends to steadily increase with increasing hydroxylation from 4.8 for the bare case to 5.6 for the highest hydroxylation considered. This increasing tendency is due to new Ti-OH bonds being formed the surface. The small observed fluctuations in the ACN are the result of surface relaxation upon hydroxylation which can sometimes lead to a localised reduction in Ti coordination. In the case of the annealed NPs the bare NP has a relatively lower ACN value of 4.6. Unlike for the anatase NPs, increasing the degree of hydroxylation of the annealed NPs from this point initially tends decrease the ACN until a minimum of 4.2 is reached at  $m = 8$ . Afterwards, for  $m \geq 9$ , the ACN tends to increase and approach the ACN of the respective hydroxylated anatase NPs. This rate of ACN increase with respect to  $m$  is fastest in the range  $11 \leq m \leq 17$ . This range of hydroxylation coincides with that in which rapid energetic destabilisation of the annealed NPs occurs with respect to the anatase crystalline NPs (see Fig. 2). In the range  $17 < m \leq 25$ , the ACN values are very similar for both annealed and crystalline NPs. This is also the hydroxylation regime for which the energetic stabilities of annealed and crystalline NPs are found to be most similar (see Fig. 2). The



**Fig. 6** Left: Evolution of the distribution of 4-, 5- and 6-fold local atomic coordination environments of Ti centres (Ti<sub>4c</sub>, Ti<sub>5c</sub>, and Ti<sub>6c</sub>) with respect to the degree of hydroxylation ( $m$ ) of both crystalline and annealed (TiO<sub>2</sub>)<sub>35</sub> NPs. Right: Location of Ti<sub>4c</sub>, Ti<sub>5c</sub>, and Ti<sub>6c</sub> centres depicted by dark yellow, red, and purple spheres in the thermally annealed NPs for  $m = 0, 5, 10, 15, 20$  and  $25$ .

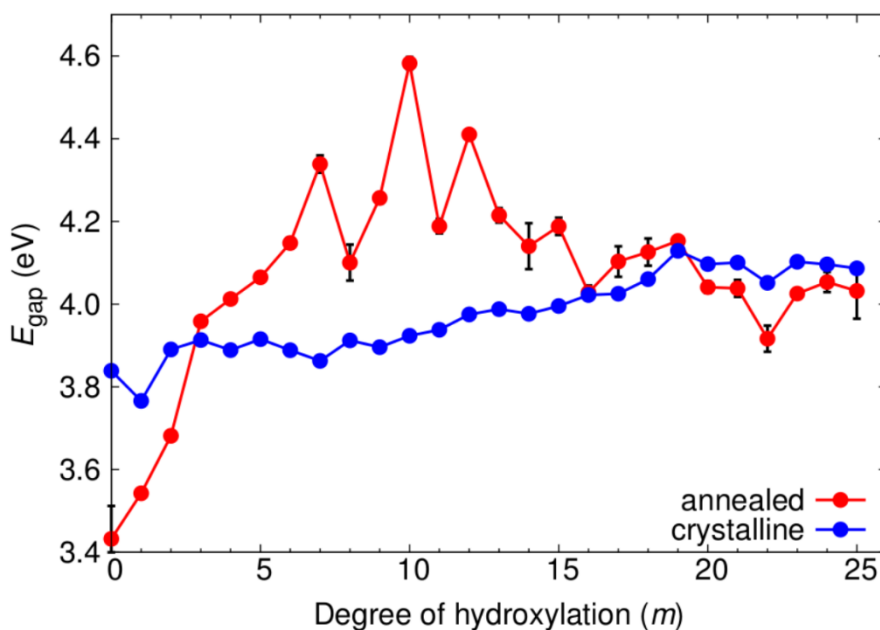
correspondence between the hydroxylation dependence of both ACN and  $\Delta E_{\text{tot}}$  values suggests that annealed NPs become structurally more anatase-like with increasing hydroxylation.

To better understand the  $m$ -dependent ACN trends and differences we follow a more detailed analysis whereby we breakdown the ACN values into contributing proportions of 4-, 5-, and 6-coordinated Ti atoms (denoted as Ti<sub>4c</sub>, Ti<sub>5c</sub>, and Ti<sub>6c</sub>). Fig. 6 (left) displays the evolution of the proportion of Ti<sub>4c</sub>, Ti<sub>5c</sub>, and Ti<sub>6c</sub> centres with respect to hydroxylation. Starting with the Ti<sub>6c</sub> centres, we see that they follow a very similar  $m$ -dependence for both annealed and crystalline anatase NPs. In the hydroxylation range  $0 \leq m \leq 6$  for both NP types, Ti<sub>6c</sub> centres make up 15-20% of the total number of Ti centres. In the anatase NP, for  $m > 6$  the number of these centres increases at steady rate with further hydroxylation until they constitute  $\sim 65\%$  of the total number of Ti centres for  $m = 25$ . For this progressively OH-covered crystalline NP this two-stage  $m$ -dependence can be understood by: i) the initial energetic preference to hydroxylate low

coordinated  $Ti_{4c}$  centres for small  $m$  (reducing the number of  $Ti_{4c}$  centres and increasing the number of  $Ti_{5c}$  centres), and ii) after the exhaustion of  $Ti_{4c}$  centres, the gradual hydroxylation of  $Ti_{5c}$  centres for larger  $m$  producing  $Ti_{6c}$  centres. This explanation is corroborated by following the corresponding tendencies in the proportions of  $Ti_{4c}$  and  $Ti_{5c}$  centres in the anatase NP in Fig. 6 (left).

For the annealed NPs, after initially possessing a similarly constant proportion of  $Ti_{6c}$  centres as for the anatase NP, this value then drops to 0% going from  $m = 7 - 10$ . Thereafter, for  $m = 11 - 25$ , the proportion of  $Ti_{6c}$  centres progressively increases in a very similar way as for the crystalline anatase NP towards a maximum of ~60% at the highest hydroxylation. In this later range of hydroxylation the proportions of  $Ti_{4c}$  and  $Ti_{5c}$  centres in the annealed NPs also gradually approach those found in the anatase NPs in line with the corresponding change in ACN. Although we see a convergence for the ACN and its individual components for both types of NP we find no evidence of significant increases in crystallinity or faceting in the annealed NP with increasing hydroxylation. In the case of highest hydroxylation we extract the pair distribution function for Ti-O distances for each type of NP (see Fig. S2 in the ESI). This shows that the local Ti-O distance distribution is similarly sharp in both types of highly hydroxylated NPs, but for larger Ti-O distances the distributions are broader for the annealed NPs. Generally, the highly hydroxylated annealed NPs tend to structurally mimic the highly hydroxylated anatase NPs on a local scale, but both have distinct overall NP structures and morphologies.

For the initial stages of hydroxylation from  $m = 0 - 10$ , where we see distinct tendencies in the ACN for both NP types, the proportions of  $Ti_{4c}$  and  $Ti_{5c}$  centres are correspondingly also very different. Overall, the proportion of  $Ti_{5c}$  centres in the annealed NPs is fairly constant and relatively low (approx. 10-30 %) in this initial range of hydroxylation low. This is in contrast to the high and increasing proportions of  $Ti_{5c}$  centres in the crystalline anatase NPs. In the same hydroxylation range, we also find a high (approx. 50-90%) and increasing proportion of  $Ti_{4c}$  centres. Considering that the  $m = 0 - 10$  range is where the annealed NPs are most energetically stable with respect to the anatase NPs, it thus appears that  $Ti_{4c}$  centres are helping to stabilise the annealed NPs for low/moderate hydroxylation. NPs have a high proportion of surface atoms and, as noted above, their energetic stability is highly sensitive to changes in surface stress<sup>20,21</sup>.  $Ti_{4c}$  centres have a tetrahedral structure which tend to lead to more open lower density networks with respect to the octahedral  $Ti_{6c}$  centres. We suggest that the density-lowering effect of  $Ti_{4c}$  centres helps to lower the surface stress in the annealed NPs. Inspecting the structure of a low energy annealed  $(TiO_2)_{35}(H_2O)_{10}$  NP, we indeed see that the  $Ti_{4c}$  centres are associated with surface hydroxyls (i.e.  $\equiv Ti-OH$ ). With the increasing number of oxygen atoms in the system due

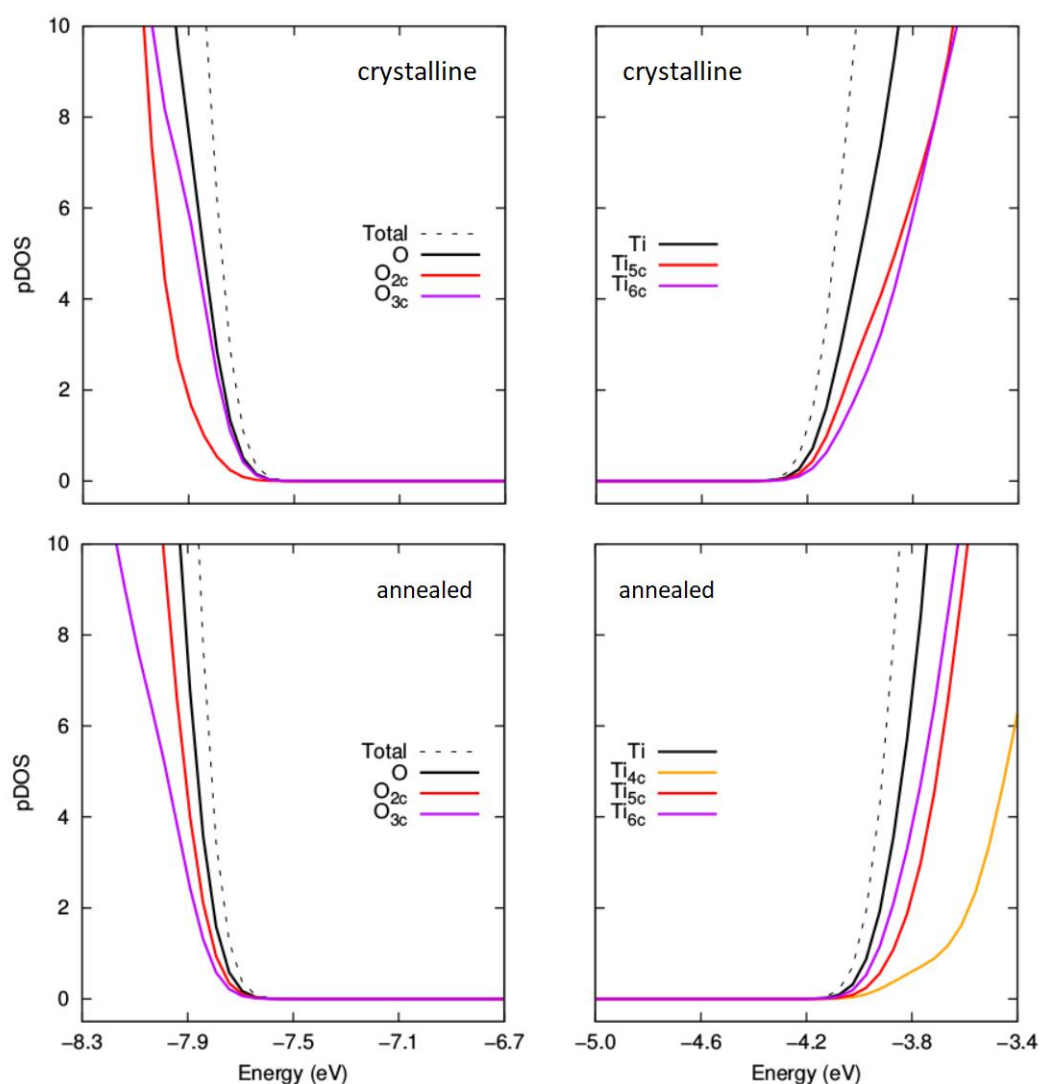


**Fig. 7** Evolution of  $E_{\text{gap}}$  with respect to degree of hydroxylation for crystalline and annealed  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NPs. For the annealed NPs, the data points indicate a mean value of  $E_{\text{gap}}$  from considering five low energy NPs. The “error bars” indicate the range of  $E_{\text{gap}}$  values for each point.

to hydroxylation it appears that the stabilising effect of these surface  $\text{Ti}_{4c}$  species reaches a limit at around  $m = 10$ . After this degree of hydroxylation, we see a sudden significant decrease in the proportion of  $\text{Ti}_{4c}$  centres. We note that  $\text{Ti}_{4c}$  species have also been found near the surface of relatively large anhydrous  $\text{TiO}_2$  NPs after simulated annealing. Here, the centres were not hydroxylated, and their main observed effect was to reduce the band gap of the NP.<sup>30</sup> Below, we examine the effect of hydroxylation and the associated structural changes on the electronic structure of both annealed and crystalline NPs.

### Energy gap and band edges of hydroxylated $(\text{TiO}_2)_{35}$ NPs

In Fig. 7 we show the evolution of the electronic energy gap ( $E_{\text{gap}}$ ), as estimated by the difference of Kohn-Sham orbital energies, of both annealed and crystalline NPs with respect to hydroxylation. The hybrid PBE density functional that contains a 12.5% Fock exchange and accurately reproduces the band gap of stoichiometric and reduced anatase and rutile,<sup>40</sup> has been selected for providing a more accurate estimate of the energy gap and band edges. We

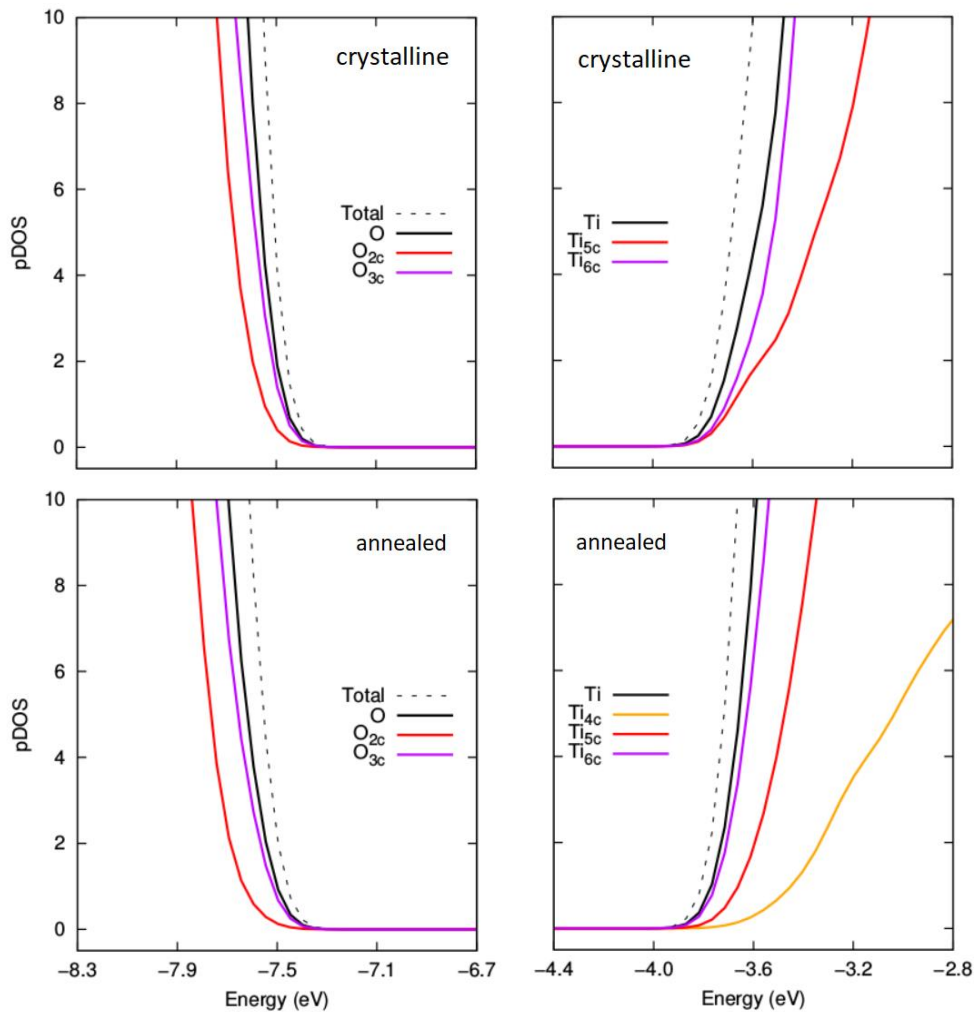


**Fig. 8.** Comparison of projected density of states (pDOS) for the VBM and CBM for crystalline anatase NPs (upper) and thermally annealed NPs (lower) with composition  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_{11}$ .

note that the  $E_{\text{gap}}$  in both systems is higher than for the bulk anatase phase due to the effect quantum confinement in our small NPs<sup>42,44</sup>. From previous work on smaller titania nanoclusters,<sup>12</sup> it is expected that increasing hydroxylation would tend to only slightly and gradually increase the magnitude of the  $E_{\text{gap}}$ . This tendency is in line with the overall effect of hydroxylation to stabilise low coordinated surface sites.

For the crystalline anatase NPs we indeed see this type of behaviour, whereby increasing hydroxylation from the anhydrous state to the highest hydroxylation tends to progressively raise the  $E_{\text{gap}}$  value by  $\sim 0.25$  eV from 3.84 eV to 4.11 eV. However, for the annealed NPs we observe a stark contrast in the hydroxylation dependent  $E_{\text{gap}}$  behaviour. Initially, the anhydrous annealed NP has a  $E_{\text{gap}}$  of 3.45 eV, which is  $\sim 0.4$  eV lower than that of the corresponding anatase NP. With





**Fig. 9.** Comparison of projected density of states (pDOS) for the VBM and CBM for crystalline anatase NPs (upper) and thermally annealed NPs (lower) with composition  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_{20}$ .

increasing hydroxylation up to  $m = 10$  the value of  $E_{\text{gap}}$  rises by 1 eV to a maximum of 4.6 eV. Thereafter, for further increases in  $m$ , the value of  $E_{\text{gap}}$  falls towards that of the highly hydroxylated anatase NPs. For the highest degrees of hydroxylation considered the  $E_{\text{gap}}$  values for the crystalline anatase and annealed NPs are almost identical.

To help understand these  $E_{\text{gap}}$  trends we have extracted the projected density of states (pDOS) with respect to the coordination of the atoms making up the NPs. Generally, valence band maximum (VBM) is dominated by contributions from O centres, while the conduction band minimum (CBM) is dominated by contributions from Ti centres, as expected from the corresponding bulk systems. For anhydrous NPs and very low degrees of hydroxylation the relatively smaller  $E_{\text{gap}}$  values found for the annealed NPs is due to  $\text{O}_{2c}$  2p contributions to the VBM, as found in previous work<sup>30</sup>. For higher degrees of hydroxylation this  $\text{O}_{2c}$ -induced

narrowing of the  $E_{\text{gap}}$  is dominated by gap widening. In Fig. 8, we compare the pDOS for both types of NP for  $m = 11$ , where the  $E_{\text{gap}}$  value for the annealed NP is larger than the corresponding anatase NP. Here we see that both NPs have a VBM with main contributions from  $O_{2c}$  and  $O_{3c}$  centres and a CBM made up from contributions from  $Ti_{5c}$  and  $Ti_{6c}$  centres. We note that the  $Ti_{4c}$  centres in the annealed NP contribute to the pDOS only at higher energies.

We note that the anatase NP for  $m = 11$  has no  $Ti_{4c}$  centres. The VBM in both these cases is found at a similar energy. However, the CBM for the crystalline anatase NP is found at a lower energy than in the annealed NP indicating an electronic destabilisation of the Ti 3d states in its  $Ti_{5c}$  and  $Ti_{6c}$  centres. This destabilisation could be due to the relatively high proportion of  $Ti_{4c}$  centres which tend to disrupt high density structures made from highly coordinated centres. The relative difference in the energy of the CBM seems to be the main contributing factor for the observed difference in the  $E_{\text{gap}}$  value for annealed and crystalline anatase NPs. We note that this link between  $E_{\text{gap}}$  differences and the stability of Ti 3d states in  $Ti_{5c}/Ti_{6c}$  centres is reflected in the difference in the proportion of  $Ti_{6c}$  centres in each type of NP (see Fig. S3 in the ESI).

In Fig. 9 we show the pDOS for for both types of NP for  $m = 20$ . Here, it seems that the unoccupied 3d states associated with the increasing number of  $Ti_{5c}$  and  $Ti_{6c}$  centres tend to become energetically stabilised in the annealed NPs with increasing  $m$ . In particular, we see that both the character and energies of the VBM and CBM are very similar for both annealed and anatase NPs. For higher degrees of hydroxylation, the convergence in  $E_{\text{gap}}$  values between annealed and crystalline NPs is also found to follow a convergence of the VBM and CBM. This implies that annealed and crystalline NPs should become electronically very similar with higher degrees of hydroxylation, in spite of the evident differences in atomic structure.

In summary, the above results show that the gap/edge electronic structure of small hydroxylated anatase NPs can be accurately mimicked by NPs of the same chemical composition and the same distribution of local atomic coordination environments but with a different overall (non-crystalline) structure and morphology. Such crystal-like NPs could be electronically indistinguishable from anatase NPs with respect to photoabsorption. Considering that surface accessibility of photogenerated excitons is unlikely to vary significantly in small NPs (i.e.  $\leq 5$  nm diameter),<sup>9</sup> small hydroxylated titania crystal-like NPs could offer a novel route to photocatalytic applications. In particular, smaller NPs offer potential photochemical performance improvements over larger NPs due to their higher surface areas, higher energy photo-generated carriers due to quantum confinement and lower radiationless photon transfer due to increased quantization of electronic levels.<sup>29</sup> The highly sensitive response of such non-crystalline NPs to

hydroxylation could offer more tunability with respect to crystalline titania NP applications. Generally, our results suggest that the anatase crystal structure may not be as important as previously thought for NP-based photocatalytic applications.

## Conclusions

We have employed DFT-based calculations to analyse and compare the effect of hydroxylation by dissociative water addition on the on the properties of thermally annealed and crystalline  $(\text{TiO}_2)_{35}$  NPs with diameters between 1.4-2.3 nm. In both cases the hydroxylation is energetically favourable for  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NPs up to the considered upper limit with  $m = 25$ . For lower values of  $m$  in this range, the thermally annealed NPs are significantly more energetically stable than the crystalline NPs. With increasing  $m$  there is a rapid convergence in the stability of both types of NP resulting in annealed and crystalline NPs having very similar energies for high hydroxylation. This hydroxylation-induced convergence in stability is not reflected in a convergence of NP morphology or crystallinity. However, for high hydroxylation both quasi-spherical non-crystalline NPs and faceted crystalline anatase NPs are found to converge with respect to their local structure. Specifically, the distributions of local atom coordination environments are found to become almost the same in both types of NP for high hydroxylation. This local structural similarity for high hydroxylation is found to also be accompanied with a convergence in the electronic properties of both NP types. Here we find that both the magnitude of the electronic band gap and the energies and orbital character of the band edges become almost the same in both types of highly hydroxylated NP.

Overall, we show that, for small NPs, one can use hydroxylation to induce the characteristic band gaps and band edge energies of faceted crystalline NPs in compositionally equivalent but non-faceted non-crystalline NPs (i.e. crystallike NPs). The key to this effect is the surface-induced change in the distribution of local atom coordination environments throughout the annealed hydroxylated crystallike NP structures. Our study thus suggests that the anatase crystal structure may not be as essential as previously assumed for applications of photoactive  $\text{TiO}_2$  NPs. In turn this opens the possibility to employ crystallike NPs in a size range where obtaining anatase crystalline samples becomes thermodynamically disfavoured (i.e. diameters  $< 3$ -5 nm). As the realisation of crystallike NPs in titania appears to rely only on mimicking the local coordination environment distribution of a correspondingly crystalline NP, we speculate that it may also be possible to form crystallike NPs of other materials.

## Supplementary Information

MD-SA temperature profile, difference in proportion of  $Ti_{6c}$  centres and  $E_{gap}$  for crystalline and annealed NPs, comparison of the pair distribution function for Ti-O distances in highly hydroxylated crystalline and annealed NPs.

## Conflict of interest

There are no conflicts to declare.

## Acknowledgements

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## References

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- (1) A. Fujishima, K. Honda, *Nature*, 1972, **238**, 37-38.
- (2) J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, *Chem. Rev.*, 2014, **114**, 9919-9986.
- (3) A. Fujishima, X. Zhang, D. A. Tryk, *Surf. Sci. Rep.*, 2008, **63**, 515-582.
- (4) X. Chen, S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891-2959.
- (5) A. Kudo, Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253-278.
- (6) H. Idriss, *Current Opinion Chem. Engineering*, 2020, **29**, 74-82.
- (7) J. Ryu, W. Choi, *Environ. Sci. Technol.*, 2008, **42**, 294-300.
- (8) B. Samanta, Á. Morales-García, F. Illas, N. Goga, J. A. Anta, S. Calero, A. Bieberle-Hütter, F. Libisch, A. B. Muñoz-García, M. Pavone, M. C. Toroker, *Chem. Soc. Rev.*, 2022, **51**, 3794-3818.
- (9) T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, M. Batzill, *Sci. Rep.*, 2014, **4**, 4043.
- (10) C. Deiana, E. Fois, S. Coluccia, G. Martra, *J. Phys. Chem.*, 2010, **114**, 21531-21538.
- (11) L. Mino, Á. Morales-García, S. T. Bromley, F. Illas, *Nanoscale*, 2021, **13**, 6577-6585.
- (12) A. Cuko, A. M. Escatllar, M. Calatayud, S. T. Bromley, *Nanoscale*, 2018, **10**, 21518-21532.
- (13) K. Kobayakawa, Y. Nakazawa, M. Ikeda, Y. Sato, Akira Fujishima, *Ber. Bunsenges. Phys. Chem.*, 1990, **94**, 1439-1443.
- (14) A. Di Paola, M. Bellardita, L. Palmisano, Z. Barbieriková, V. Brezová, *J. Photochem. Photobiology A: Chem.*, 2014, **273**, 59-67.
- (15) J. Wang, X. Liu, R. Li, P. Qiao, L. Xiao, J. Fan, *Catal. Commun.*, 2012, **19**, 96-99.
- (16) W. Kim, T. Tachikawa, G-H. Moon, T. Majima, W. Choi, *Angew. Chem. Int. Ed.*, 2014, **53**, 14036-14041.
- (17) M. J. Limo, A. Sola-Rababa, E. Boix, V. Thota, Z. C. Westcott, V. Puddu, C. C. Perry, *Chem. Rev.*, 2018, **118**, 11118-11193.
- (18) Y. Tanga, R. Caia, D. Caob, X. Konga, Y. Luc, *Toxicology*, 2018, **406-407**, 1-8.
- (19) H. Zhang, J. F. Banfield, *Chem. Rev.*, 2014, **114**, 9613-9644.
- (20) H. Zhang, J. F. Banfield, *J. Mater. Chem.*, 1998, **8**, 2073-2076.
- (21) A. S. Barnard, P. Zapol, *Phys. Rev. B*, 2004, **70**, 235403.
- (22) M. P. Finnegan, H. Zhang, J. F. Banfield, *J. Phys. Chem. C*, 2007, **111**, 5, 1962-1968
- (23) A. A. Levchenko, G. Li, J. Boerio-Goates, B. F. Woodfield, A. Navrotsky TiO<sub>2</sub>, *Chem. Mater.*, 2006, **18**, 6324-6332.
- (24) O. Lamiel-García, A. Cuko, M. Calatayud, F. Illas, S. T. Bromley, *Nanoscale*, 2017, **9**, 1049-1058.

- 
- (25) H. Zhang, B. Chen, J. F. Banfield, G. A. Waychunas, *Phys. Rev. B*, 2008, **78**, 214106-214101.
- (26) H. Zhang, B. Gilbert, F. Huang, J. F. Banfield, *Nature*, 2003, **424**, 1025-1029.
- (27) D. R. Hummer, J. D. Kubicki, P. R. C. Kent, P. J. Heaney, *J. Phys. Chem. C*, 2013, **117**, 26084–26090
- (28) E. Scolan, C. Sanchez, *Chem. Mater.* 1998, **10**, 3217-3223
- (29) M. Anpo, T. Shima, S. Kodama, Y. Kubokawa, *J. Phys. Chem.* 1987, **91**, 4305-4310.
- (30) A. Morales, A. Macia-Escatllar, F. Illas, S. T. Bromley, *Nanoscale*, 2019, **11**, 9032.
- (31) A. M. Escatllar, Á. Morales-García, F. Illas, S. T. Bromley, *J. Chem. Phys.*, 2019, **150**, 214305.
- (32) S. Pigeot-Rémy, F. Dufour, A. Herissan, V. Ruaux, F. Maugé, R. Hazime, C. Foronato, C. Guillard, C. Chaneac, O. Durupthy, C. Colbeau-Justin, S. Cassaignon, *Appl. Catal. B: Environ.*, 2017, **203**, 324-334
- (33) K. E. Jelfs, E. Flikkema, S. T. Bromley, *Phys. Chem. Chem. Phys.*, 2013, **15**, 20438.
- (34) A. Cuko, A. Macià M. Calatayud, S. T. Bromley, *Comp. Theo. Chem.*, 2017, **1102**, 38-43.
- (35) S. Kirkpatrick, C. D. Gelatt, M. P. Vecchi, *Science*, 1983, **220**, 671– 680
- (36) J. D. Gale, A. L. Rohl, *Mol. Simul.*, 2003, **29**, 291-341.
- (37) F. A. Soria, C. Di Valentin, *Nanoscale*, 2021, **13**, 4151-4166.
- (38) V. Blum, R. Gehre, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, *Comput. Phys. Commun.*, 2009, **180**, 2175-2196.
- (39) J. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- (40) K. C. Ko, O. Lamiel-García, J. Y. Lee , F. Illas, *Phys. Chem. Chem. Phys.*, 2016, **18**, 12357-12367.
- (41) A. Morales-García, R. Valero, F. Illas, *Phys. Chem. Chem. Phys.*, 2018, **20**, 18907
- (42) O. Lamiel-García, K. C. Ko, J. Y. Lee, S. T. Bromley, F. Illas, *J. Chem. Theory Comput.*, 2017, **13**, 1785-1793.
- (43) E. van Lenthe, E. J. Baerends, J. G. Snijders. Relativistic Regular Two-component Hamiltonians *J. Chem. Phys.* 1993, **99**, 4597.
- (44) K. C. Ko, S. T. Bromley, J. Y. Lee, F. Illas, *J. Phys. Chem. Lett.*, 2017, **8**, 5593.

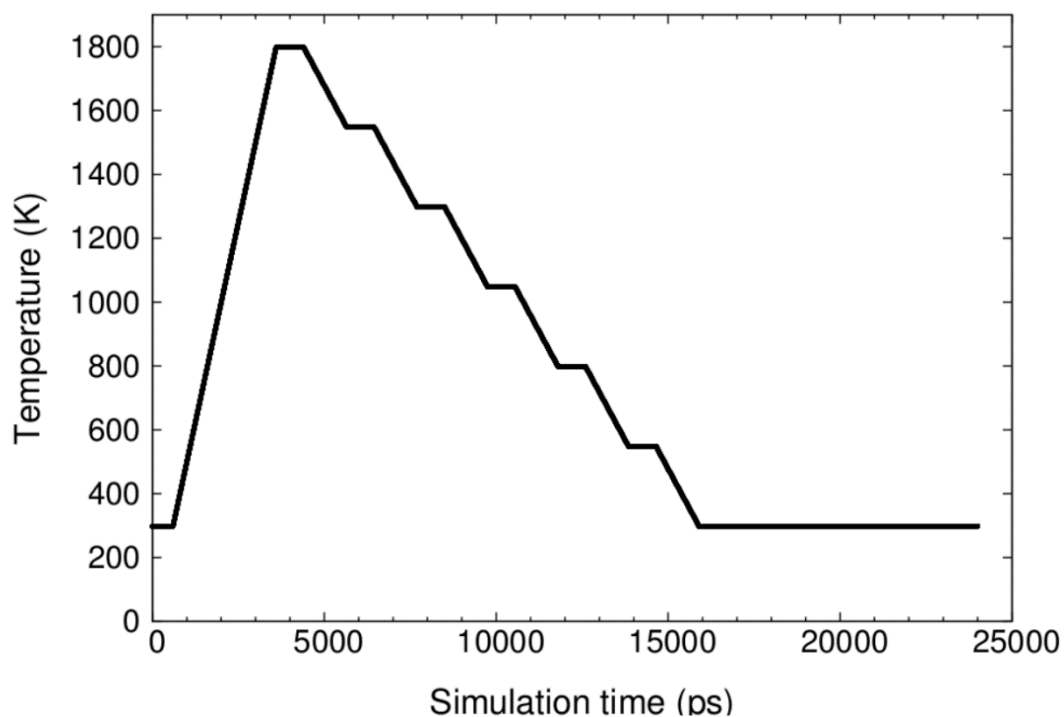
## Electronic Supplementary Information

### Crystal properties without crystallinity? How surface hydroxylation affects the structure and properties of TiO<sub>2</sub> nanoparticles

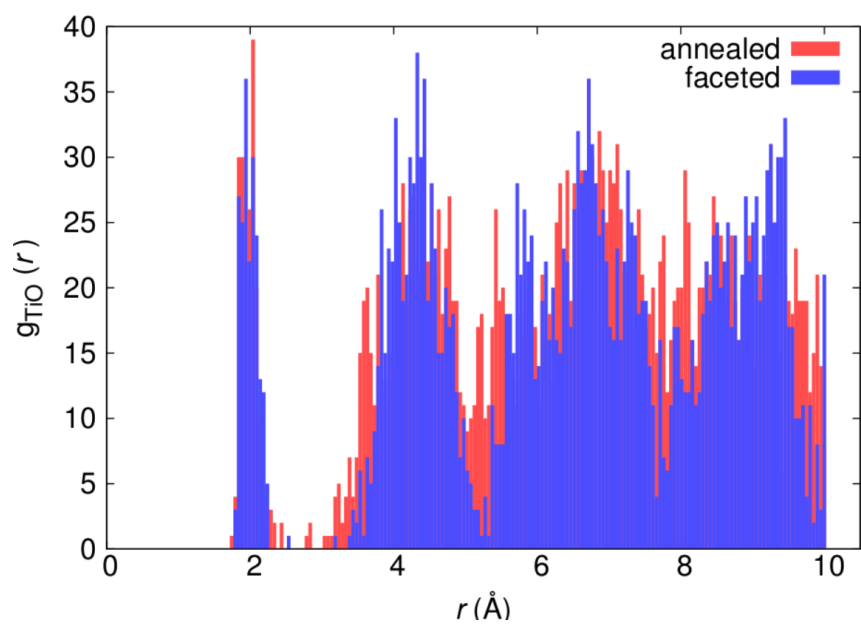
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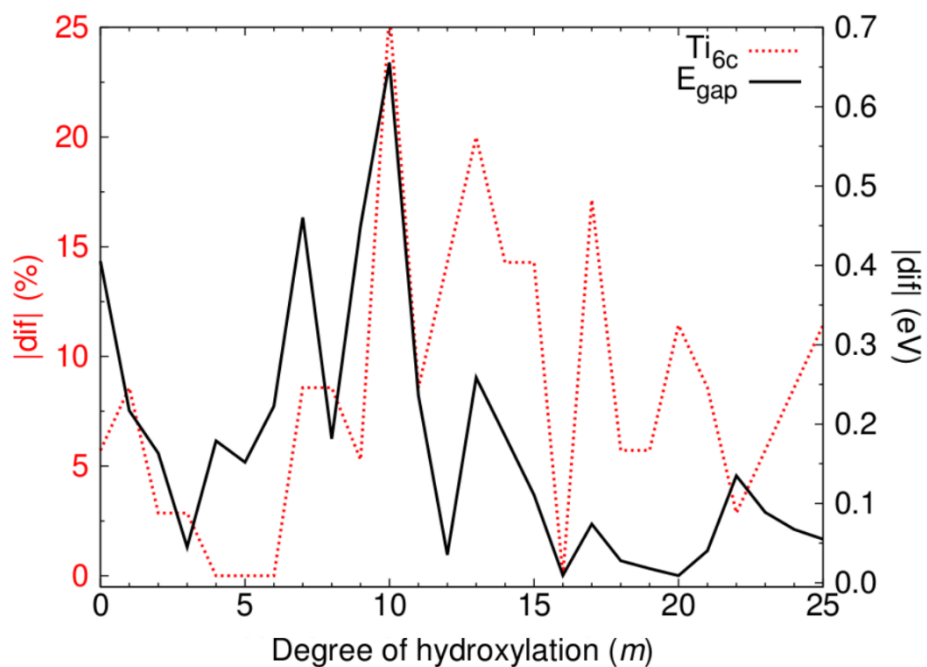
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**Fig. S1** Temperature evolution profile followed during the stepwise molecular dynamics simulated annealing (MD-SA) procedure.



**Fig. S2** Pair distribution function,  $g(r)$ , for Ti-O distances in a faceted crystalline anatase NP (blue) and thermally annealed NP (red) with a  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_{25}$  composition. The bin size for the histogram is 0.05 Å.



**Fig. S3** Difference in the proportion of  $\text{Ti}_{6c}$  centres (left) and  $E_{\text{gap}}$  (right) between the crystalline anatase and annealed  $(\text{TiO}_2)_{35}(\text{H}_2\text{O})_m$  NPs.