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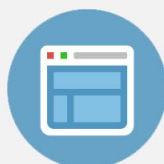
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Quantum chemical elucidation of the mechanism for hydrogenation of TiO₂ anatase crystals

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Hydrogenation of TiO₂ is relevant to hydrogen storage and water splitting. We have carried out a detailed mechanistic study on TiO₂ hydrogenation through H and/or H₂ diffusion from the surface into subsurface layers of anatase TiO₂ (101) by periodic density functional theory calculations implementing on-site Coulomb interactions (DFT + U). Both H atoms and H₂ molecules can migrate from the crystal surface into TiO₂ near subsurface layer with 27.8 and 46.2 kcal/mol energy barriers, respectively. The controlling step for the former process is the dissociative adsorption of H₂ on the surface which requires 47.8 kcal/mol of energy barrier. Both hydrogen incorporation processes are expected to be equally favorable. The barrier energy for H₂ migration from the first layer of the subsurface O_{sub1} to the 2nd layer of the subsurface oxygen O_{sub2} requires only 6.6 kcal. The presence of H atoms on the surface and inside the subsurface layer tends to promote both H and H₂ penetration into the subsurface layer by reducing their energy barriers, as well as to prevent the escape of the H₂ from the cage by increasing its escaping barrier energy. The H₂ molecule inside a cage can readily dissociate and form 2HO-species exothermically ($\Delta H = -31.0$ kcal/mol) with only 26.2 kcal/mol barrier. The 2HO-species within the cage may further transform into H₂O with a 22.0 kcal/mol barrier and 19.3 kcal/mol exothermicity relative to the caged H₂ molecule. H₂O formation following the breaking of Ti–O bonds within the cage may result in the formation of O-vacancies and surface disordering as observed experimentally under a high pressure and moderately high temperature condition. According to density of states analysis, the projected density of states of the interstitial H, H₂, and H₂O appear prominently within the TiO₂ band gap; in addition, the former induces a shift of the band gap position notably towards the conduction band. The thermochemistry for formation of the most stable sub-surface species (2HO and H₂O) has been predicted. These results satisfactorily account for the photo-catalytic activity enhancement observed experimentally by hydrogenation at high temperatures and high pressures. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4799800>]

I. INTRODUCTION

Titania is one of the most versatile metal oxides with a wide range of technological applications, such as catalyst support, photo-catalyst, photo-electrode for solar cell and water splitting and the absorbent for hydrogen storage, just cite a few. There are voluminous references in the literature on these and other applications which can be readily searched via the internet. The subject of this study lies in the elucidation of the mechanism involved in the hydrogenation of TiO₂ nano-crystals for H₂ storage as well as for the enhanced photo-catalytic activity in water splitting,^{1–6} two very important aspects of relevance to hydrogen industry.

The reversible sorption of molecular hydrogen in multi-layer TiO₂ nanotubes (NTs) was studied by Bavykin *et al.*¹ in the temperature range of 78–473 K at 0–6 atm H₂ pressure with as much as 3.8 wt. % of hydrogen uptake at 78 K under 6 atm pressure. The incorporation of H₂ into the layered TiO₂ NTs was concluded to occur by intercalation along

the axial direction between layers forming TiO₂ · xH₂ intercalate compound. The enthalpy change for this molecular intercalation process was estimated to be 7.2 kcal/mol with 10.5 kcal/mol activation energy. Lim and co-workers² reported in a concurrent study at room temperature under 6.3 atm H₂ pressure with up to ~2 wt. % hydrogen uptake by TiO₂ NTs. The result of their temperature-programmed desorption experiment indicated that 75% of H₂ incorporation occurred by physisorption with about 13% weak chemisorption and 12% strong chemisorption, depending on the temperature each desorption peak appeared. Hu *et al.*³ investigated the effect of the Ti-center reduction in mesoporous TiO₂ on the incorporation of H₂ using organometallic reducing agents such as Li naphthalene. They estimated that up to 5.4–5.6 wt. % of H₂ could be stored with the reduced mesoporous TiO₂ at 77 K and 100 atm pressure.

More recently, Chen *et al.*⁴ carried out an interesting and important study demonstrating that hydrogenation of TiO₂ white powder at 473 K under 20 atm of H₂ for 5 days could blacken the powder due to surface disordering with about 0.3 wt. % H₂ incorporation, which resulted in a pronouncedly enhanced water splitting efficiency with a high durability

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using methanol as a sacrificial agent. They also studied the effect of hydrogenation theoretically by analyzing the density of states (DOS) of TiO_2 crystals containing H atoms; the predicted result indicated a significant band-gap narrowing from 3.3 eV to about 1.5 eV, reflecting the experimentally observed spectral change with optical absorption extended up to 1100 nm. An analogous study^{5(a)} on the hydrogenation of TiO_2 rutile nanowires and anatase nanotubes at 350 °C under hydrogen atmosphere was found to improve the performance of photo-electrochemical water splitting with twofold photocurrent enhancement and improvement of electrical conductivity and charge transportation, attributable to the formation of oxygen vacancies (donor density) in TiO_2 with enhanced UV as well as visible and IR absorptions. Similar surface modifications have been achieved by Zheng *et al.*^{5(b)} with the hydrogenation of protonated titania NTs (H-TiNTs) in a 5% H_2 diluted in N_2 using a quartz flow tube at 773 K to convert them into surface-hydrogenated anatase TiO_2 ($\text{TiO}_2\text{-H}$) consisting of nanowire-microspheres with enhanced photocatalytic activities. Sun and co-workers⁶ recently studied the hydrogenation of well-defined nanocrystals of anatase TiO_2 at 723 K under 7 atm hydrogen pressure; they achieved as much as 1.4 wt. % of hydrogen incorporation at a rather high temperature under a mild hydrogen pressure condition. The result of their XRD, TEM, and Raman spectral measurements revealed no morphological and crystallographic changes by hydrogenation, contrary to the finding of Chen *et al.*,⁴ who attributed the enhanced photo-catalytic effect to surface disordering.

Computationally, the capability of hydrogen storage and the enhanced photo-catalytic activity of anatase TiO_2 have been attributed to the diffusion of H atoms into the subsurface layer/bulk and/or to the disordering of crystal surfaces as aforementioned.^{4–8} Islam *et al.*⁷ have calculated the adsorption and migration of H on the anatase TiO_2 (101) surface and diffusion into subsurface oxygen sites, and the desorption of H_2 molecules. On a related study, Aschauer and Selloni⁸ very recently investigated the adsorption and diffusion of H atoms on the anatase (101) surface by first-principles calculations; their result shows that H-migration from the surface to subsurface sites has kinetic barriers which are generally smaller than those of H_2 desorption. Other theoretical calculations have also revealed that the presence of H atoms in the bulk TiO_2 induces the formation of Ti^{3+} centers.^{9(a)} Pan *et al.*^{9(b)} also have calculated the effect of H, N, and the codoping of both atoms on the electronic properties of TiO_2 based on first-principles calculations. They found that interstitial hydrogen leads to the narrowing of the band gaps of all of the TiO_2 polymorphs. Theoretical study on the adsorption behavior and the induced effects of molecular and atomic hydrogen on anatase TiO_2 nanotubes has been calculated by Lin *et al.*^{9(c)}

The results cited above clearly indicate that hydrogen storage may result from two types of physico-chemical processes: weak physisorption and intercalation in the interfaces of nano-structures at low temperatures ($T < 473$ K) and strong chemisorptions and incorporation of hydrogen species (H and/or H_2) into TiO_2 subsurface layer/bulk at $T > 473$ K carried out experimentally. To our knowledge, the direct migration of H_2 into the subsurface layer has not been considered to

date. For hydrogen species to survive the redox reaction in the photo-catalytic water splitting process, only those within TiO_2 subsurface layers are expected to be stable and responsible for the observed efficiency enhancement. Detailed mechanistic studies on TiO_2 hydrogenation and H and/or H_2 diffusion from the surface into subsurface layers of nano-crystals as well as their kinetic behaviors are still lacking. In the present work, an anatase TiO_2 (101) surface model is applied to study these processes by the state-of-the-art quantum chemical calculations.

II. COMPUTATIONAL METHODS

All of our calculations were performed using the Vienna *ab initio* simulation package (VASP)¹⁰ on the basis of the periodic density functional theory (DFT). The projector augmented wave (PAW) method¹¹ with 500 eV cut-off energy was applied to represent electron-ion interactions. The exchange-correlation function treated by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof formulation (PBE) is applied for the total energy calculations.¹² Spin-polarized calculations are carried out throughout the system. In our calculations, we used the surface of anatase (101) model consisting of 24 $[\text{TiO}_2]$ units with $11.097 \times 7.655 \text{ \AA}^2$ surface area extended along the $\langle 111 \rangle$ and $\langle 010 \rangle$ direction, separated perpendicularly by a 15.0 Å vacuum space. The validity of the surface model was tested in our previous studies of H_2O_2 and H_2BO_3 on TiO_2 through predictions of lattice parameters which are in good agreement with experimental data.¹³ The detailed model structure of the anatase (101) surface is shown in Fig. 1. Brillouin zone integrals were evaluated over regular Monkhorst-Pack grids with $2 \times 3 \times 1$ and $2 \times 3 \times 2$ k -points for the surface and bulk, respectively. The surface of anatase (101) is characterized by the presence of acidic-basic pairs of coordinative unsaturated ions, that is, five-fold-coordinated Ti_4^+ ions (Ti_{5c}) and two-fold-coordinated bridging oxygen O_2 ions (O_{2c}) including coordinated ions on the surface (O_{3c} , Ti_{6c}) (see Fig. 1). The climbing-image nudged-elastic band (CINEB) method was applied to locate the transition states for the dissociative adsorption of H_2 and migration processes.¹⁴ All transition states were verified by the number of imaginary frequencies (NIMG) with $\text{NIMG} = 1$. To analyze the electron correlations in transition metal oxides, the conventional DFT calculations based on the local density approximation and GGA failed to predict correctly the values of band gaps. In view of this, the DFT + U method¹⁵ with spin-polarization

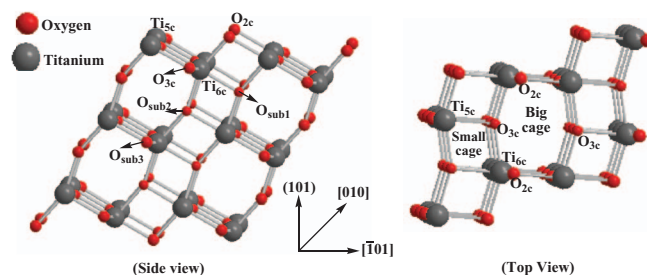


FIG. 1. Perspective view of the TiO_2 anatase (101) surface slab model used in the present study.

calculations was applied in order to more accurately correct the strong on-site Coulomb repulsion of Ti 3d states, where the value of U employed, 4 eV, is consistent with that reported by Finazzi *et al.*¹⁶

For the migration of H₂ and H atoms from the anatase (101) surface into the various subsurface layers are given various names O_{sub1}, O_{sub2}, O_{sub3} (see Fig. 1). The diffusion mechanisms of H₂ and H atoms from the surface into subsurface layer with and without the presence of H atoms on the surface or inside the TiO₂ bulk have been investigated. Our discussions will be based on the results from DFT + U calculations.

III. RESULTS AND DISCUSSION

A. H₂ dissociation on TiO₂ (101) and H atom migration into the subsurface layers

We initially studied molecular and dissociative adsorption of H₂ on the TiO₂ (101) surface. The interaction of the hydrogen molecule with a pair of the two-fold-coordinated bridging oxygen atoms (O_{2c}) with the O_{2c}···O_{2c} separation of 3.828 Å is a van der Waals type attraction leading to H₂···TiO₂, with approximate physisorption energies of 0.7 and 0.3 kcal/mol predicted with the DFT and DFT + U methods, respectively, while the dissociative adsorption results of H₂ on the TiO₂ (101) surface calculated by DFT are shown in Fig. S1 in the supplementary material.¹⁷ It is well known that the DFT method is unable to describe the van der Waals interactions correctly.¹⁸ In the recent version of the VASP code (which is not yet available in our laboratory), the van der Waals interaction correction was introduced by using the Grimme theory with a simple pair-wise force field to estimate the magnitude of these interactions.¹⁹ Experimentally, the adsorption behaviors of hydrogen on anatase and rutile TiO₂ surfaces are measured by using temperature programmed desorption method.^{20,21} On the basis of the results of Göpel *et al.*,²⁰ in the absence of surface defects, no adsorption was observed at 300 K and the activation energy to dissociate the H₂ molecule is too high to be measured. Iwaki²¹ observed that hydrogen was able to reduce titanium dioxide at 673 K through dissociative adsorption, resulting in the production of surface hydroxyl groups. Based on the above experimental results, the van der Waals complex H₂···TiO₂ with a negligibly small binding energy plays no role in H₂ migration and dissociation on TiO₂ surfaces. In the optimized H₂···TiO₂ complex, the H–H distance is 0.751 Å, and the H–O surface distance is 2.787 Å according to DFT + U method. These values may be compared with 0.751 and 2.839 Å obtained by the DFT method. To undergo a dissociative adsorption reaction, the resulting complex has to overcome a 47.8 kcal/mol (49.5 kcal/mol by the DFT method) activation barrier via TS1, to produce two H atoms at the two neighboring O_{2c} sites, 2H–O_{2c}(a), with two equivalent O–H bonds of 0.965 Å. At TS1, the breaking H–H bond is 1.149 Å (see Fig. S2 in the supplementary material).¹⁷ The process is predicted to be exothermic by 18.3 kcal/mol, which corresponds to the reverse barrier of 66.1 kcal/mol for the associative desorption of 2H–O_{2c}(a) (see Fig. 2(a)). This value may be compared with

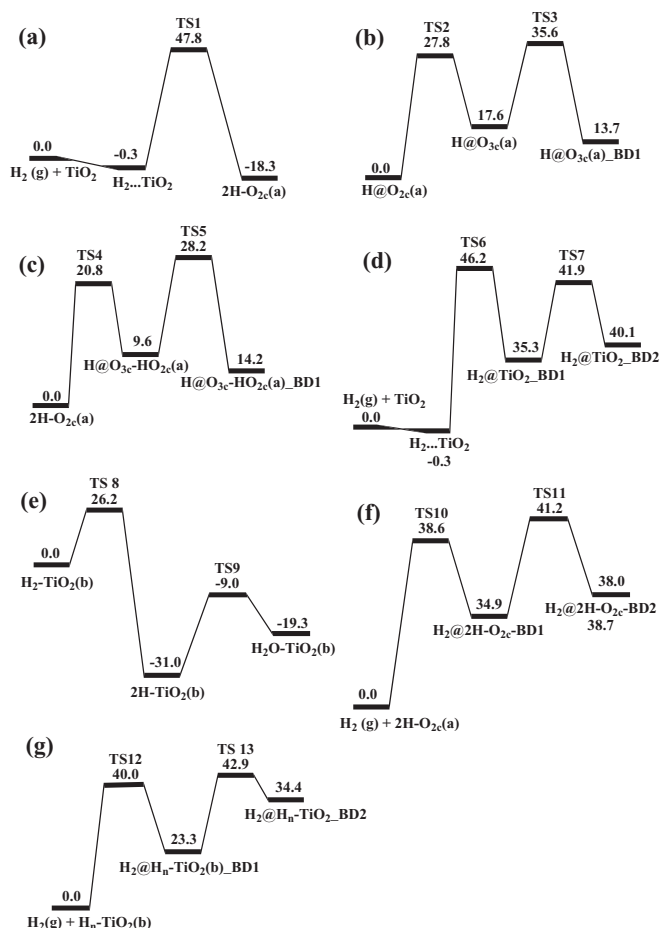


FIG. 2. Calculated potential energy diagram for the (a) H₂ dissociated on the surface, (b) one H atom migration from surface to subsurface layer, (c) after H₂ dissociation on the surface, one of hydrogen atom migration to subsurface layer, (d) H₂ migration from surface to subsurface layer, (e) H₂ dissociation inside the subsurface layer, (f) H₂ migration from surface to subsurface layer with H-effect on top, (g) H₂ migration from surface to subsurface layer with H-effect inside bulk. All the calculations were performed with the DFT + U method (using U = 4.0 eV).

the barrier for the associative desorption of 2H–O_{2c}(a) on a surface layer covering with a 1/3 ML H atoms, 46.4 kcal/mol, predicted at the PBE level.⁸ The bond length of the Ti–OH group in 2H–O_{2c}(a) is lengthened to 2.041 Å when compared to Ti–O_{2c} length in TiO₂, 1.909 Å. Figure 3 illustrates the partial geometries of optimized intermediates and products related to H and H₂ migrations in TiO₂ anatase (101) and their transition states are shown in Fig. S2 in the supplementary material.¹⁷

The H atom has to overcome a 27.8 kcal/mol barrier at TS2 for the diffusion from a most stable O_{2c} site to a neighboring O_{3c} site, with 17.6 kcal/mol of endothermicity (Fig. 2(b)), which is consistent with the predicted barrier of 20.3 kcal/mol and 16.6 kcal/mol by Sun *et al.*⁶ and Aschauer and Selloni,⁸ respectively. A previous study on H-atom migration from a hydroxylated TiO₂ (110) rutile surface to its bulk/subsurface layer reported a barrier energy of 23.8 kcal/mol by a TDS measurement and 25.6 kcal/mol from a DFT method (the PW91 functional was used without DFT + U corrections).²² Our DFT result also gives 22.2 kcal/mol for the same migration process (see Fig. 2). The H atom at an

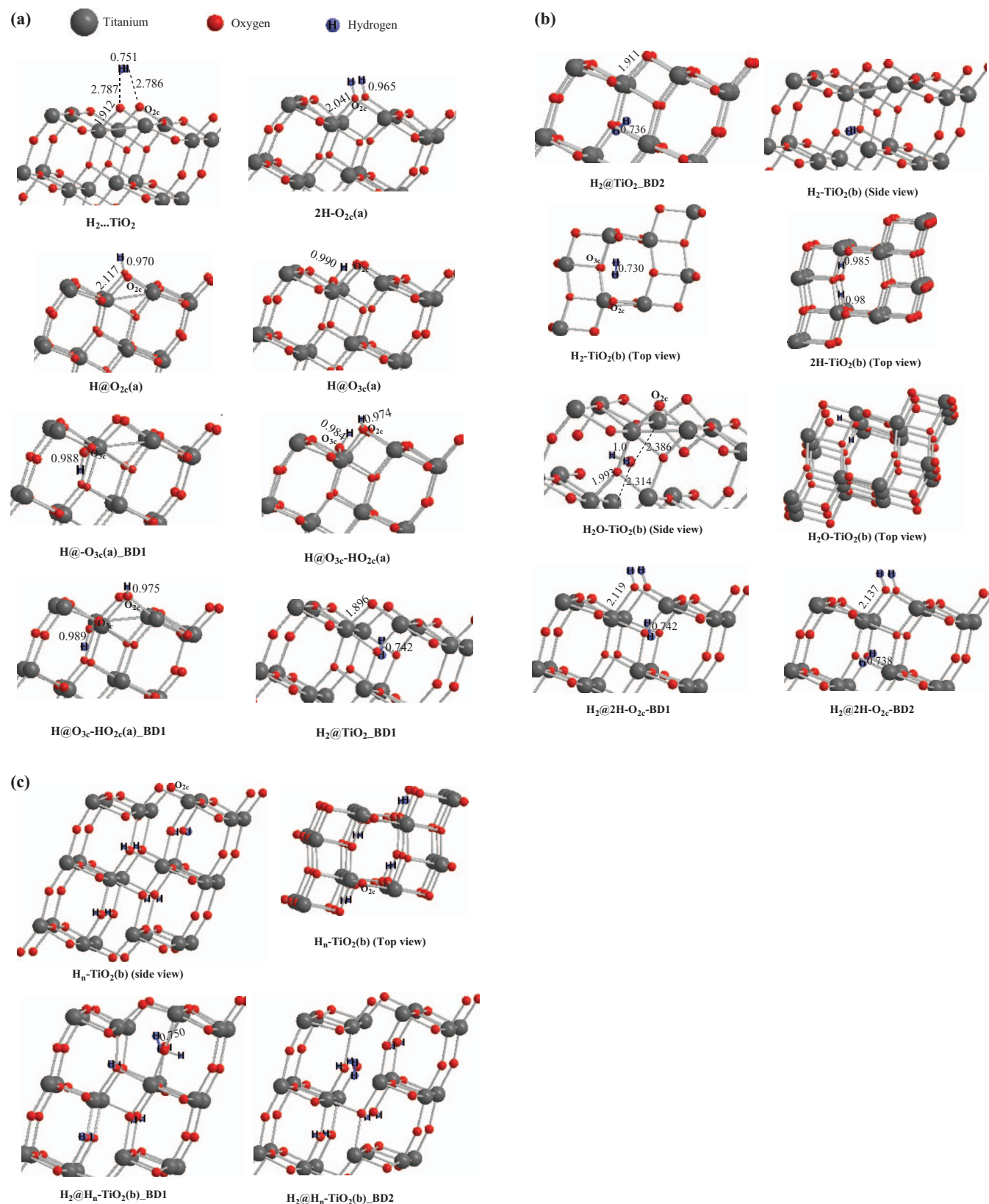


FIG. 3. (a)–(c) Calculated optimized configurations of H and H₂ dissociation and migration intermediates from surface to subsurface layer on the TiO₂ anatase (110) presented in Figure 2.

O_{3c} site pointing towards vacuum can rotate towards the subsurface with an 18.0 kcal/mol barrier giving H@O_{3c}(a)_BD1 (here BD1 denotes bulk diffusion 1) (see TS3). As shown in Fig. S3 in the supplementary material,¹⁷ after the H atom

rotates towards the subsurface layer (H@O_{3c}(a)_BD1), migration from the subsurface into the bulk requires a much less energy. The calculated barrier energy for H-atom migration from H@TiO₂_BD1 to O_{sub 2} (H@TiO₂_BD2), and

H@TiO₂_BD1 to O_{sub3} (H@TiO₂_BD3) requires only 6.7 and 13.7 kcal/mol, respectively, by the DFT method.¹⁷ Similarly, we have also found the mechanism for one of the two H atoms of 2H-O_{2c}(a), formed by H₂ dissociative adsorption on the surface, migrates into the subsurface layer as shown in Fig. 2(c). Similar to the one H atom case, after HO-rotation its migration inside the subsurface layer also requires much less energies (5.8–11.4 kcal/mol by DFT, see Fig. S4 in the supplementary material¹⁷). It is worth mentioning that the barrier for the migration of a single H(a) into the subsurface layer requires a slightly higher energy than that for the H-atom migration described above for a pair of H(a). Previous DFT calculations showed that for H atoms occupying the interstitial sites between titanium oxygen octahedral, the energy barrier for H-incorporation through the anatase (101) surface was lower than that through (001).⁶ We have also found that the H-atom migration on an O_{2c} site to its neighboring O_{2c} site on the surface requires as high as 50.5 kcal/mol of barrier energy, which is only slightly lower than that for the associative desorption of 2H(a) mentioned above and is much higher than that for the migration into the subsurface oxygen layer. A similar conclusion was reported by Aschauer and Selloni on H-migration into the subsurface layer of TiO₂.⁸ We have also performed all the potential energy surfaces (PESs) of H and H₂ migration on TiO₂ anatase (101) with the DFT method as shown in Fig. S1 in the supplementary material.¹⁷

B. H₂ migration into bulk and dissociation inside the subsurface layers

The migration of H₂ from the surface into the subsurface layer of anatase (101) has not been considered before; our computed potential energy surface at the DFT + U level is shown in Fig. 2(d) and that by DFT is shown in Fig. S1(d) in the supplementary material.¹⁷ The bond length of the optimized structure of H₂(g) is 0.754 Å, which is only slightly longer than that of an isolated hydrogen molecule, 0.750 Å. The migration from the surface (big cage) to O_{sub1} (subsurface oxygen layer 1) via TS6 has a barrier of 46.2 kcal/mol, which is 1.6 kcal/mol lower than that for the dissociative adsorption process described above. As shown in the top view of TiO₂ Fig. 1(b), the bond distances between the two O_{2c} sites and two O_{3c} sites on the top layer of the surface are 3.828 Å and 3.797 Å, respectively. The H₂ molecule can migrate easier into the subsurface layer via a big cage, because the size of H₂ is relatively small comparing with that of the big cage in the top layer. As described in the Introduction, various experimental studies show that hydrogen can be incorporated into the subsurface layer/bulk from the surface of anatase TiO₂ in the 200–450 °C temperature range under various pressures up to 20 atm.^{1–9} Bavykin *et al.*¹ found that the molecular hydrogen can intercalate between layers in the walls of TiO₂ nanotubes forming host-guest compounds at temperatures 80–125 °C. In our calculations, we found the high barrier for H₂ migration from the surface to the subsurface layers via a big cage, to occupy interstitial sites between oxygen layers. We further predicted that the barrier energy for H₂ migration from the first layer of the subsurface O_{sub1} to the 2nd layer inside the subsurface layer O_{sub2} (H₂@TiO₂_BD2; here

BD2 denotes bulk diffusion 2) requires only 6.6 kcal. These calculations show that the DFT + U effect is small compared with the DFT results. Significantly, we also found that the H₂ molecules inside the subsurface layer could readily decompose to give a pair of H-TiO₂(b) with a 26.2 kcal/mol intrinsic barrier (TS8). This process is 31.0 kcal/mol exothermic from H₂-TiO₂(b) (see Figs. 2(e) and 3). Thus, the H₂ dissociation inside the subsurface layer needs a significantly less energy than that on the surface and is much more exothermic. As shown in Fig. 2(e), the neighboring two OH groups inside the TiO₂ is more stable, when compared to H₂-TiO₂(b). The migration of the H atom from one of the OH-Ti_{5c} moieties to the neighboring O atom to form H₂O-TiO₂(b) can occur with a 22.0 kcal/mol barrier at TS9 (see Figs. 2(e) and 3) and 19.3 kcal/mol exothermicity related to H₂-TiO₂(b). The bond length of Ti-OH₂ is 2.314 Å. The formation of H₂O following the breaking of Ti-O bonds may result in the creation of O-vacancies and surface disordering observed by Chen *et al.*⁴ under a high pressure and moderately high temperature condition. The H-atom pair 2H-TiO₂(b) thus formed may also migrate to neighboring cages with 10.9–26.7 kcal/mol barriers calculated at the DFT level, depending on the diffusion paths (see Fig. S5 in the supplementary material).¹⁷

C. Effects of H atoms on H₂ migration

Under operational conditions, both H₂ and H atoms are expected to co-exist; here, we study the potential effect of H(a) on the surface and H-TiO₂(b) inside the subsurface layer on H₂ molecular diffusion in both phases. The activation barrier for H₂ to migrate from the top layer of TiO₂ via 2H(a) to O_{sub1} (first sublayer of TiO₂) is found to be 38.6 kcal/mol energy (Fig. 2(f), TS10), which is 7.6 kcal/mol lower than that without the presence of the 2H(a) (Fig. 2(d)). The same TS for this reaction at the DFT level is 2.9 kcal/mol higher. Further migration of the H₂ inside the subsurface 1st layer (denoted by H₂@2H-O_{2c}-BD1) to the 2nd layer of O_{2c} inside the subsurface layer (H₂@2H-O_{2c}-BD2) requires only 6.3 kcal/mol activation energy. We also studied the effect of H₂ migration inside the subsurface layer with more H atoms inside a cage. The barrier for H₂ migration from the surface into the subsurface (through the first sublayer, O_{sub1}) with *n* H-TiO₂(b) via TS12 producing H₂@H_{*n*}-TiO₂(b)_BD1 was found to have a 40.0 kcal/mol activation barrier, which is slightly lower than that without the pre-existing H atoms inside the cage, 46.2 kcal/mol. In the above process, *n* = 8 H atoms and the H atoms bind with each sublayer of O inside the subsurface TiO₂ and each layer has 2 H atoms pointing in the same direction. This process is predicted to be endothermic by 23.3 kcal/mol for the migrated H₂ at first sublayer, O_{sub1} (H₂@H_{*n*}-TiO₂(b)_BD1). The reverse barrier of this reaction is 16.7 kcal/mol which is significantly higher than 10.9 kcal/mol without the presence of the *n* H atoms inside the cage; this suggests that the H atoms inside the cage can significantly enhance the storage of H₂ in the cage. The high temperature experimental study of Sun *et al.*⁶ shows that 1.4 wt. % H₂ can be stored in the anatase (101) TiO₂ at 723 K with no detectable morphological changes; our TiO₂ supercell model containing 24 TiO₂ units with 17 cages can

accommodate equivalently about 13 H_2 molecules with approximately 1 H_2 molecule/cage or, more likely, 2H/cage which can be exothermically formed by dissociation of H_2 within the cage. The lattice constants predicted for 1 H_2 molecule or 2H atoms in the bulk remain essentially the same as those of the pure anatase TiO_2 , consistent with the observation of Sun *et al.*⁶

D. DOS of hydrogenated TiO_2

To further understand the effect of interstitial H and H_2 molecules, we calculated the various adsorption structures of both molecules inside the bulk TiO_2 optimized by the DFT + U method as shown in Fig. S6 in the supplementary material.¹⁷ The DOS and projected DOS (PDOS) of H and H_2 are calculated by using the DFT + U with the value of $U = 4$ eV as mentioned before. The results are presented in Fig. 4. Here for all the DOS plots, the Fermi level is set to be 0 eV on the energy axis as in a previous work.^{9(b)} The DFT + U method can correct the energy level of Ti 3d states by adding the Hubbard-U to Ti d states, and the band gap can be improved to 2.9 eV (from 2.2 eV by DFT method).^{16,23,24} Figure 4(a) shows the band structure of the pure anatase TiO_2 . We can see from the figure that the top of the valence band (VB) of pure TiO_2 mainly consisting of the O 2p states is predominantly found between 4.5 and 0 eV and the lower part of the conduction band (CB) is dominated by Ti 3d states. In our results, the Fermi level of the pure TiO_2 is just above the top of valence band and its conduction band is empty without any electron. Our results are in good agreement with previous results.^{7,9(b)} The detailed structures of all the DOS and PDOS information related to H and H_2 adsorption inside the bulk TiO_2 are given in Fig. S7 in the supplementary material.¹⁷ For the 2H- TiO_2 in Fig. 4(b), the two H atoms get incorporated interstitially forming two OH groups pointing in the same direction and perpendicular to the plane formed by Ti1-Ti2-Ti3 (see geometry in Fig. S6 in the supplementary material¹⁷). The Ti-OH equatorial distance is 2.12 Å (cf. the bulk anatase Ti-O_{eq} distance, 1.99 Å). The bond length of OH is 0.983 Å. The calculated DOS shown in Fig. 4(b) indicates that the band gap is reduced to 2.70 eV (cf. anatase gap 2.90 eV). In the DOS plot of doped 2H- TiO_2 , the Fermi level appeared at 1.5 eV above the valence band. Here, we observed that in the two DOS curves of 2H- TiO_2 and TiO_2 , the CB edge of the former moves about 1.2 eV towards the Fermi level at 0 eV. The new localized states appear at the edge of conduction band and 1.2 eV below the CB. These new peaks in the band gap of 2H- TiO_2 mainly formed by the H and Ti 3d, and the major contribution comes from the latter. Due to the presence of interstitial H atoms which act as extra electron donors, the Fermi level is shifted towards the CB. The extra electron introduced by H is completely delocalized. For TiO_2 reduction or n-doping, hydrogen acts as a reducing agent due to the formation of the two H-O bonds and the reduction of two $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ within the cage. We have substantiated the result by studying the effect on the Fermi level change in $(\text{TiO}_2)^-$ using the same pure anatase TiO_2 supercell and performed the density of states calculation; the Fermi level is

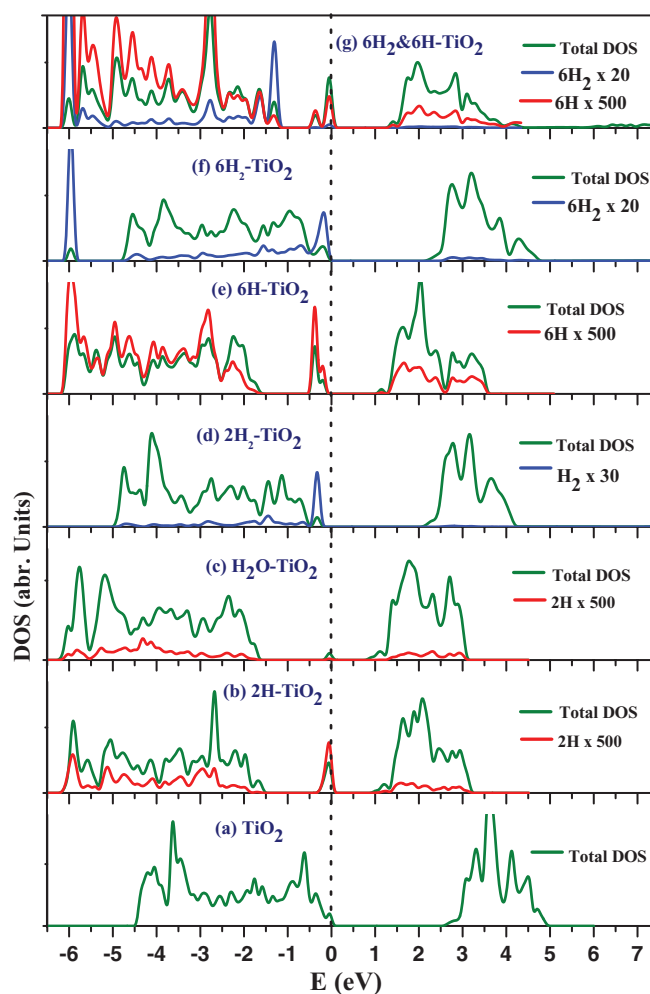


FIG. 4. Density of states (DOS) for the TiO_2 and various H and H_2 molecules adsorbed inside the bulk TiO_2 : (a) pure anatase TiO_2 supercell, (b) 2H atoms, (c) H_2O molecule, (d) 2H_2 molecules, (e) 6H atoms, (f) 6H_2 molecules, (g) 6H and 6H_2 inside TiO_2 calculated at the DFT + U level ($U = 4.0$ eV) (for clarity, H_2 and H PDOS peaks are magnified). Their optimized geometries are shown in Fig. S6 in the supplementary material.¹⁷ The dotted vertical line indicates the adjusted Fermi level placed at 0 eV.

seen to be shifted near to the conduction band as in the 2H- TiO_2 case in Fig. 4(b). Our results are consistent with previous experimental and theoretical results, such as the new energy states appeared at 0.8–1.18 eV below the conduction band attributed to the reduced Ti^{3+} ions and the Fermi level shifting observed.^{7,9(b),16,25,26} These studies account for the enhancement in the visible and near infrared region by the hydrogenation of TiO_2 nanocrystals. We have also calculated the DOS for the H_2O formed in the subsurface of the reduced TiO_2 as shown in Fig. 4(c). The Fermi level and band gap changes are similar to the 2H- TiO_2 case.

In order to understand the Ti-reduction process within the cage, we have carried out Bader charge analysis²⁷ using the DFT + U method for the calculation of the charges of the adsorbed H, H_2 and their neighboring oxygen, titanium atoms inside the TiO_2 anatase as shown in Figure 5. According to the analysis, the charge of O and Ti atoms in the TiO_2 are $-1.02 e$ and $2.05 e$, where e is the magnitude of the charge on an electron (see Fig. 5(a)). Figures 5(b) and 5(c) reveal the significant atomic charge changes in the neighboring

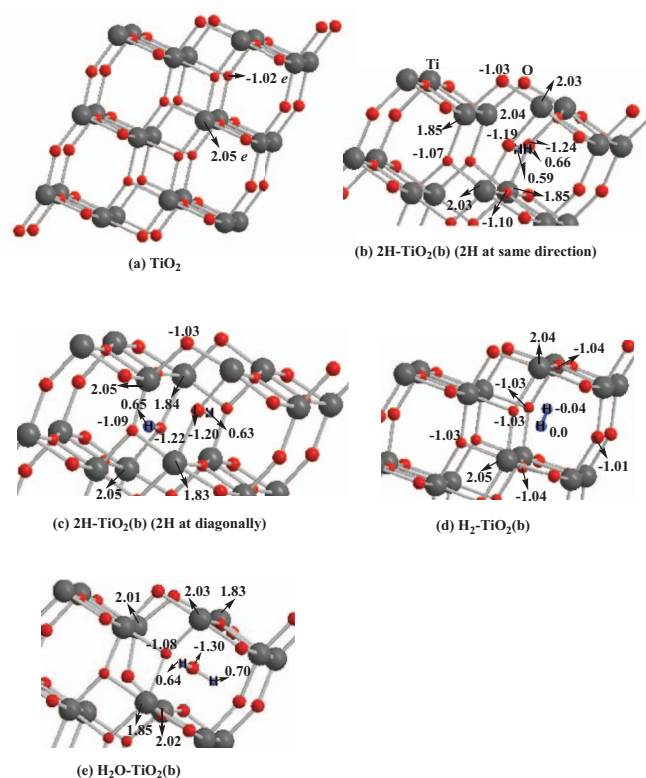


FIG. 5. Bader atomic charges (e) on H and H_2 molecules adsorbed inside the bulk TiO_2 .

oxygen and titanium atoms with $2H_2O(b)$ pairing side by side and pairing diagonally after $H_2(b)$ dissociation. The charge of the bulk oxygen is $-1.02 e$, whereas the charge of the oxygen with H is around $-1.19 e$ (on oxygen) and $0.59 e$ (on hydrogen). Most significantly, the charge on neighboring Ti atom is around $1.85 e$ noticeably deviated from that in the bulk TiO_2 , $2.05 e$. We have also calculated Bader charge distribution for oxygen reduction to H_2O in TiO_2 (Fig. 5(e)), the result clearly shows that the charge of the O in H_2O is $-1.30 e$, whereas the charge of the H is around $0.7 e$. The charge of the neighboring Ti is around $1.83 e$ which are similar to the $2H-TiO_2(b)$ case. However, there are no significant changes in the charges of Ti and O atoms which are close to the undissociated H_2 molecule inside the bulk TiO_2 (see Fig. 5(d)). Thus, both experimental and theoretical studies of atomic hydrogen doping in TiO_2 suggest the formation of a Ti-O(H)-Ti species and one electron is transferred to the empty Ti $3d$ states,^{7,28} resulting in the reduction of Ti in the bulk TiO_2 by H atoms. These results clearly show that the $Ti^{3+} 3d^1$ state is formed below the conduction band of TiO_2 . Atomic hydrogen dopants thus yield donor states near the conduction band, which may be photocatalytically active in the visible region. The formation of Ti^{3+} states in TiO_2 are believed to be responsible for the electronic conductivity and important in various aspects of photocatalysis,²⁹ photochemical water splitting,³⁰ and dye-sensitized solar cells.³¹ Figure 4(d) shows the DOS of two H_2 molecules inside a TiO_2 cage. The two H_2 molecules get incorporated into the interstitial sites between oxygen layers in the bulk TiO_2 via hydrogen bonding with about $1.9 \text{ \AA}$ lengths between H and oxygen (the

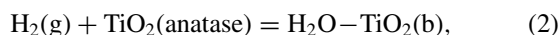
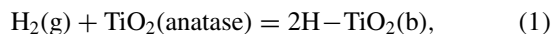
structure of $2H_2-TiO_2$ is shown in Fig. S6 in the supplementary material¹⁷). The Fermi level is located at the $0.5 eV$ above the VB. The DOS indicates that the impurity states are formed about $0.2 eV$ above the top edge of the VB. The PDOS of the H_2 shows that the gap states are composed mostly of H_2 and the O $2p$ orbital. The $2.7 eV$ band gap does not change noticeably. As shown in Figs. 4(b) and 4(d), the PDOS of the H_2 has new localized peaks in between the band gap of TiO_2 which are broad and strong when compared to the H atom peaks.

We also calculated the DOS on the effect of 6H atoms and $6H_2$ molecules within the anatase TiO_2 and their optimized structures are shown in Fig. S6 in the supplementary material.¹⁷ At the higher doping level of 6H, new localized peaks appeared at around $1.2 eV$ below the Ti $3d$ CB, resulting in a decreasing of gap energy by about $2.6 eV$ (anatase TiO_2 is $2.9 eV$), as well as similar to $2H-TiO_2$, the Fermi level located at $1.1 eV$ below the lower edge of CB (see Figs. 4(e) and 4(b)). In the case of $6H_2$ molecules in the TiO_2 bulk, new broad peaks located at around in the $0.2 eV$ above the top of the O $2p$ VB as shown in Fig. 4(f). Here also Fermi level is located $0.4 eV$ above VB, similar to $2H-TiO_2$. As the numbers of H_2 and H atoms increase inside the cage, the new localized peaks in between the band gap of TiO_2 become broad and strong. Finally, the concurrent presence of $6H_2$ and 6H in the supercell as revealed by the DOS is depicted in Fig. 4(g), two new impurity or localized peaks are located -1.2 to $1.7 eV$ range at the top of the VB and completely mix with O $2p$ states to form the valence band maximum and also another new localized peak formed at $1.4 eV$ below the conduction band; main contribution comes from Ti $3d$. The band gap is narrowed to $1.5 eV$. Here, we observed that H_2 has broad and strong peak near the top of the VB, when compared to the H peak near the CB. The appearance of these new broad localized peaks between the VB and CB due to the presence of H_2 and H atoms inside the TiO_2 supercell, may account for the enhanced visible absorption and photo-catalytic activity of titania nanocrystals through hydrogenation at temperatures above $473 K$. As shown in Fig. 4(f), the band gap of both H_2 and H atoms inside the TiO_2 has been reduced up to around $1.6 eV$ (with the shifting of the CB and VB positions); the results are in good agreement with hydrogenated TiO_2 nanoparticles reported by Chen *et al.*⁴ who attributed the narrow optical gap of $1.54 eV$ to the substantially narrowing of intraband transitions due to the surface disorder which could be attributed to the formation of H_2O and the breaking of Ti-O bonds within the subsurface under the high H_2 pressure employed at $473 K$ for a prolonged period of time. The activation energies predicted by our calculations explain why the hydrogenation of TiO_2 nanocrystals (NPs, NTs, or nanowires) giving rise to the enhancement of their photo-catalytic activities requires a high temperature and high pressure conditions.

E. Thermochemistry for H-incorporation

Based on the predicted energetics and potential energy surfaces for the hydrogenation processes presented above, the most stable species formed at high temperatures are $2H-TiO_2(b)$ and $H_2O(b)$ in the subsurface. We have computed

the vibrational frequencies of those species and calculated the equilibrium constants of these reactions based on the energies given in Fig. 2



for the temperature range 300–1000 K, yielding

$$K_1 = 6.21 \times 10^{-27} \exp[-3320/RT] \text{cm}^3/\text{molecule}, \quad (3)$$

$$K_2 = 3.45 \times 10^{-26} \exp[-15300/RT] \text{cm}^3/\text{molecule}, \quad (4)$$

where R is in units of cal/mole K. As the enthalpies for formation of these two subsurface species are only slightly endothermic, 4.3 and 16 kcal/mol, respectively, the $T^{-5/2}$ temperature coefficients of the translational and rotational partition functions of H_2 make the overall enthalpies given above for the two processes to be slightly lower than the predicted values at 0 K. The concentrations of both species are of course proportional to the pressure of hydrogen gas present. Experimentally, high H_2 pressure was typically employed to achieve higher hydrogen incorporation.^{4–6}

IV. CONCLUSIONS

The diffusion and dissociation mechanisms of H_2 and H atoms from the surface into subsurface layers with and without the presence of H atoms on the surface or inside the subsurface layers of anatase TiO_2 (101) have been investigated using periodic DFT calculations. Both standard DFT and DFT + U calculations are used to examine the effect of the Coulomb repulsion of Ti $3d$ states, where the value of U used was 4 eV. The binding energies of H_2 physisorbed species on TiO_2 surface optimized using the DFT and DFT + U methods are very weak. In the H atom migration case, the DFT + U effect is more. For the H_2 migration energies from the surface into the subsurface layer, the DFT + U effect is small when compared to the results without the correction. To summarize, our DFT + U calculations for the hydrogenation of titania (anatase) nanocrystals at medium high temperatures performed experimentally, 473 K–723 K, reveal:

1. Both H atoms and H_2 molecules can migrate from the crystal surface into TiO_2 subsurface layers with 27.8 and 46.2 kcal/mol energy barriers, respectively. The controlling step for the former process is the dissociative adsorption of H_2 on the surface which requires 47.8 kcal/mol of energy barrier. Both hydrogen incorporation processes are expected to be equally favorable.
2. The presence of H atoms on the surface and inside the cage of subsurface layers tend to promote both H and H_2 penetration into the bulk by reducing their energy barriers, as well as to prevent the escape of the H_2 from the cage by increasing its escaping barrier energy.
3. The H_2 molecules inside a cage can readily dissociate and form $2\text{HO}(\text{b})$ species exothermically ($\Delta H = -31.0$ kcal/mol) with only a 26.2 kcal/mol barrier. The hydroxyl species within the cage can undergo further transformation by breaking Ti–O bonds producing

H_2O , whose formation under a high pressure and moderately high temperature condition may result in the collapse of the crystal structure and surface disorders. The thermochemistry for formation of the two most stable subsurface species, $2\text{HO}(\text{b})$ and $\text{H}_2\text{O}(\text{b})$, has been predicted based on the computed potential energy surfaces and the vibrational frequencies of the species involved.

4. The computed densities of states of TiO_2 with interstitial H and H_2 appear to narrow the band gap and the former was noted to shift the band-gap position towards the CB. The results show that three new localized peaks appear in the range of 0.5–1.5 eV above the VB. In the case of 6H_2 and 6H atoms in the subsurface of TiO_2 , H_2 has broad and strong peak near the top of the VB and the H peak near the CB; the main contribution comes from Ti $3d$ and O $2p$, respectively, or probably from both Ti $3d$ and O $2p$ peaks. The predicted energetics for H and H_2 migration and the result of DOS analysis can, respectively, account for hydrogen incorporation capability observed at high temperatures (>473 K) and photo-catalytic activity enhancement observed experimentally.

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