Self-hydrogenated shell promoting photocatalytic H₂ evolution on anatase TiO₂

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As one of the most important photocatalysts, TiO₂ has triggered broad interest and intensive studies for decades. Observation of the interfacial reactions between water and TiO₂ at microscopic scale can provide key insight into the mechanisms of photocatalytic processes. Currently, experimental methodologies for characterizing photocatalytic reactions of anatase TiO₂ are mostly confined to water vapor or single molecule chemistry. Here, we investigate the photocatalytic reaction of anatase TiO₂ nanoparticles in water using liquid environmental transmission electron microscopy. A self-hydrogenated shell is observed on the TiO₂ surface before the generation of hydrogen bubbles. First-principles calculations suggest that this shell is formed through subsurface diffusion of photo-reduced water protons generated at the aqueous TiO₂ interface, which promotes photocatalytic hydrogen evolution by reducing the activation barrier for H₂ (H–H bond) formation. Experiments confirm that the self-hydrogenated shell contains reduced titanium ions, and its thickness can increase to several nanometers with increasing UV illuminance.
Understanding the reaction pathways of photocatalytic hydrogen evolution at the water/TiO$_2$ interface is of crucial importance for developing clean renewable energy technologies. This understanding can be greatly enhanced by direct observation of the interfacial reactions on TiO$_2$ at the nanometer or even atomic scale. Scanning tunneling microscopy (STM) and environmental transmission electron microscopy (ETEM) have proven to be powerful tools for this purpose. For example, previous STM studies have shown that submonolayer water and individual water molecules dissociate at oxygen vacancies on TiO$_2$ surfaces. Recent STM and surface X-ray diffraction measurements have revealed that the structure of water-dipped rutile TiO$_2$ consists of a (2 × 1) ordered array of hydroxyl molecules with molecular water in the second layer. Using an ETEM equipped with water vapor flow and UV illumination system, Zhang et al. found that a heavily hydroxylated amorphous layer of one or two atomic plane thickness covered the anatase TiO$_2$ surface during UV light irradiation in water vapor. However, only a limited amount of water is allowed to operate in STM and ETEM, and it is thus difficult to uncover the photocatalytic reaction pathways at the liquid H$_2$O/TiO$_2$ interface, especially those occurring in real aqueous environment.

Here, we employ a liquid environmental transmission electron microscopy (LETEM) to investigate the photocatalytic reactions occurring on the surface of anatase TiO$_2$ nanoparticles (NPs) immersed in water under ultraviolet (UV) illumination. The photocatalytic reactions found in this research are very different from those observed under vapor conditions in the ETEM. In water environment, we observe the natural growth of a nanoscale shell on the surface of the anatase NPs, followed by the generation of hydrogen nanobubbles. Using electron energy loss spectroscopy (EELS), we find that this shell contains reduced Ti ions and transforms to crystalline reduced titanium oxide (Ti$_2$O$_3$ or TiO) after drying in air. First-principle calculations allow us to rationalize these findings by showing that hydrogen atoms resulting from reaction of water protons with photoexcited electrons on the TiO$_2$ surface can easily migrate subsurface. This leads to formation of a metastable hydrogenated shell containing reduced Ti$_{3+}$ ions, which reduces the activation energy of H$_2$ evolution. The nanoscale hydrogenated TiO$_2$ shell is also observed during photocatalytic reaction on TiO$_2$ NPs loaded with Pt co-catalyst, even though the kinetics of photocatalysis in the presence of co-catalyst is much faster than in the case of neat TiO$_2$ NPs. Our work reveals that the formation of a nanoscale hydrogenated TiO$_2$ shell is vital for the generation of hydrogen bubbles during the photocatalytic process, thus providing important insight into the fundamental mechanism of photocatalytic hydrogen generation on anatase TiO$_2$.

**Results**

**Low dose TEM observation of photocatalytic water splitting on TiO$_2$**. Anatase TiO$_2$ NPs were immersed in water as 0.1 mol L$^{-1}$ aqueous suspension and injected into the LETEM through a homemade liquid flow holder (Fig. 1a). An UV light fiber is introduced in between the pole pieces inside the LETEM, which releases a UV source (characteristic wavelength of 254, 297, 315, 335, 365, 404, and 425 nm) with a flux of 100 mW cm$^{-2}$ at room temperature (Fig. 1a and Methods). The anatase TiO$_2$ samples can be then illuminated in situ by the UV light to investigate the photocatalytic reaction on aqueous TiO$_2$. In order to minimize the radiolytic effect of the electron beam on liquid water and metal oxide NPs, we refreshed the TiO$_2$ NPs solution for each UV exposure experiment via the fluidic holder, e.g., we repeated the photocatalytic reaction for different lengths of UV illumination using a new TiO$_2$ NPs solution. Furthermore, we turned off the electron beam during the UV light illumination process and each TEM frame was recorded at low electron dose rate of about 3 e$^{-}$ Å$^{-2}$ s$^{-1}$ for 1 s. The TEM images in Fig. 1b, c show the gradual growth of bubbles (red arrow in Fig. 1b) around the TiO$_2$ NPs and the formation of surface shells (green arrows in Fig. 1c) on the TiO$_2$ NPs. The bubbles were not visible around the NPs until 18 h of UV illumination. It is important to emphasize that, no matter whether TiO$_2$ NPs are present or not, the bubbles observed here do not come from the radiolytic dissociation of water molecules by electron beam irradiation during the ETEM observations (see detailed discussion in Supplementary Notes 1 and 2). For longer times, the size of the bubble increases steadily: the projection area is 2.6 μm$^2$ at 18 h and becomes 4.7 μm$^2$ at 24 h. The data presented as black squares in Fig. 1d show the thickness of the shell on the TiO$_2$ NPs vs. UV illumination time. These data are fitted (blue curve in Fig. 1d) with a KJMA equation $f = 1 - \exp(-kt)$, where $f$ is the thickness normalized to the maximum thickness of the shell. The $k$ value is ~3.4, which suggests that the growth mode of the surface shell is a 2D growth toward the water/TiO$_2$ interface. The derivative of the curve in Fig. 1d shows that the growth rate of the shell increases up to ~0.7 nm/h in the initial stage, but abruptly drops to less than 0.1 nm/h when the bubbles start to appear ($t \sim 18$ h). Finally, the thickness of the shell reaches a maximum of about 8.8 ± 2.0 nm.

The long incubation time of 16–19 h for the photocatalytic generation of hydrogen at the macrosopic scale has also been confirmed by the detection of the amount of gas evolution in the pure anatase TiO$_2$ aqueous solution in an independent experiment carried out outside the electron microscope (Supplementary Fig. 3a).

**Analysis of hydrogenated TiO$_2$ shell**. In order to understand the formation mechanism of the surface shell on TiO$_2$, the generation of nanobubbles, we analyzed the chemical composition of the bubbles and surface shell after each stage of the photocatalytic process with EELS (see Methods). In the spectrum acquired from the area of the bubbles (black curve in Fig. 1e), a peak presents at ~13 eV, which confirms that the bubbles are composed of hydrogen. On the other hand, neither apparent hydrogen signal (dashed blue curve in Fig. 1e) nor bubbles (Supplementary Fig. 1b) were detected for pure water under electron beam irradiation. Fig. 1f shows EELS spectra for anatase TiO$_2$ (red curve), water (blue curve) and the surface shell (black curve), respectively. The spectrum from the surface shell shows a shift (~2.7 eV) to lower energies and a drop of the integrated intensity ratio of the Ti-$L_2/L_3$ peaks as compared to the spectrum from anatase TiO$_2$. This indicates a valence state reduction of titanium in the surface shell. It is noteworthy that the O K edge of the surface shell has a pre-edge at ~527 eV (between the purple vertical lines in Fig. 1f), which is different from the regular K-edge of oxygen in H$_2$O and TiO$_2$. The same pre-edge of oxygen has been detected in studies of Al(OH)$_3$ and has been attributed to unpaired O originating from the loss of hydrogen in the hydroxyl layer of Al(OH)$_3$ induced by electron radiolysis. This provides implicit evidence that the surface shell around TiO$_2$ NPs also contains hydroxyl species due to diffusion of H atoms into the anatase TiO$_2$ NPs.

**Formation mechanism of hydrogenated TiO$_2$ shell**. During photocatalytic water splitting, H atoms are formed through the reaction of the photoexcited electrons with the protons that are produced in the proton coupled electron transfer steps of water oxidation in agreement with previous studies of photocatalytic water splitting on anatase. O$_2$ evolution is however not observed.
in our experiment, suggesting that the photoexcited holes are probably consumed to form free OH radicals\textsuperscript{12,27–29}. Generally, there are three possible destinations for these H atoms\textsuperscript{15}, namely: migration on the TiO\textsubscript{2} surface, diffusion into the bulk TiO\textsubscript{2}, and desorption from the surface to form molecular H\textsubscript{2}. Previous computational studies reported that H\textsubscript{2} recombinative desorption in vacuum environment is thermodynamically favorable but with a large energy barrier (~ 2 eV), making diffusion of hydrogen atoms into the bulk kinetically favored\textsuperscript{13–15}. To explore the effect of the water environment on this process, we determined the energy barriers of surface-to-subsurface H diffusion on the clean surface and in the presence of adsorbed water by first-principles calculations. In agreement with previous studies\textsuperscript{14,15}, we found that the diffusion process occurs via a surface three-fold oxygen (O\textsubscript{3c}) and can be divided into three steps (Fig. 2a, b). In step 1, the hydrogen atom, initially adsorbed at a bridging oxygen site, is...
transferred to $O_{3c}$ and points away from the surface (state 'sur3-1'); in step 2, H rotates around the $O_{3c}$ so as to point toward the bulk (state 'sur3-2'); finally, in step 3 H diffuses to a subsurface (sub) site. The potential energy profiles of H diffusion without and with adsorbed water are presented in Fig. 2b. We can see that the relative energies of the various intermediates as well as the energy barriers change significantly when the surface is covered with water molecules. In particular, the overall barrier is reduced from 1.13 to 0.77 eV, which makes the diffusion of hydrogen to the subsurface much easier in the presence of adsorbed water. These first-principle calculations thus support the idea that the water environment can effectively facilitate the diffusion of hydrogen to the subsurface of anatase, which ultimately will lead to the formation of a hydrogenated shell (Fig. 2c, d and Supplementary Fig. 4). This is consistent with our experimental finding of a hydrogenated surface shell around the anatase TiO$_2$ NPs.
Reactivity of the hydrogenated TiO$_2$ shell. We next investigated the role of the hydrogenated shell in promoting H$_2$ evolution by performing first-principle calculations of the energetics and kinetics of H$_2$ formation on hydrogenated anatase (101) slabs$^{26,30-32}$ with different H/O atomic ratios ($\sigma$) (Supplementary Movie 1). Our results are summarized in Fig. 2c, f, which show the energy barrier for H$_2$ formation and desorption energies, respectively, both in the case where H$_2$ is formed above and below the TiO$_2$ surface (note that these results do not include entropic contributions, which tend to stabilize the H$_2$ desorbed state at finite temperature), while the corresponding structures are shown in Supplementary Fig. 5. We can see that H$_2$ formation has a prohibitive activation energy of over 2 eV on the non-hydrogenated surface, as already reported in previous studies$^{12}$. However, the barrier is drastically reduced with increasing $\sigma$, becoming $\sim$1 eV for H$_2$ formation in the subsurface region of a hydrogenated slab with $\sigma = 2/3$. At the same time, the H$_2$ diffusion barrier from the subsurface to the surface is obtained as only 0.24 eV. These results reveal that the critical role of the hydrogenated shell is to make hydrogen evolution kinetically viable by reducing the barrier of H$_2$ (H–H bond) formation. Additional DFT results on the stability of the hydrogenated shell and its influence on water adsorption are reported in Supplementary Notes 3-5, Supplementary Figs. 6-9 (Supplementary Movie 2).

Stability of the hydrogenated TiO$_2$ shell. To further explore the stability of the hydrogenated shell on the TiO$_2$ surface, we took the TiO$_2$ NPs out from the aqueous solution after photocatalytic reaction and performed ex situ TEM analyses. High-resolution TEM (HRTEM) images in Fig. 3 show that the dried
hydrogenated TiO$_2$ shell transforms back to a crystalline structure with lower oxygen content and reduced Ti valence, evolving from Ti$_2$O$_3$ to TiO$_2$ as the illumination time is prolonged. The EELS recorded from the surface shell changes in shape and onset position, shifting to lower energies in comparison to the EELS recorded in the bulk (Fig. 3e, f). The thickness of the reduced crystalline shell on dried TiO$_2$ NPs increases with the duration of UV illumination (Fig. 3b–d), which is consistent with the behavior of the hydrogenated shell in the wet state (Fig. 1c).

**Effect of Pt on the formation of hydrogenated TiO$_2$ shell.** The role of co-catalysts in photocatalytic water splitting on TiO$_2$ has been intensively studied during the past few decades$^{11,12,23}$. It has been recognized that the photoexcited electrons can be transferred from the conduction band to a Pt co-catalyst deposited on the surface of TiO$_2$, which greatly reduces the possibility of electron–hole recombination and enhances the hydrogen evolution$^{11}$. To explore the effect of Pt co-catalyst on the formation of the self-hydrogenated shell under UV illumination, we loaded 0.05 wt% Pt co-catalyst on the anatase TiO$_2$ NPs surface by using H$_2$PtCl$_6$ solution under UV light illumination for 4 h, as schematically shown in Fig. 4a. After the loading of Pt, in situ observation of photocatalytic water splitting for The TiO$_2$/Pt NPs was carried out into a LETEM. Fig. 4b shows bubble generation under UV illumination within 15 min and growth with increasing illumination time. The bubble was identified to be H$_2$ by EELS with evidence of a peak at ~13 eV (red curve in Fig. 4e). Clearly, the loaded Pt on TiO$_2$ surface effectively improves the efficiency of water dissociation and accelerates the hydrogen generation process, as shown in Supplementary Fig. 3b. At the same time, the hydrogenated TiO$_2$ surface shell was also observed on the TiO$_2$/Pt NPs (Fig. 4c). The thickening rate of surface shell with illumination time (Fig. 4d) was much faster in the first couple of hours, as compared with that for the neat TiO$_2$ NPs without co-catalyst. As in Fig. 1f, a comparison of the EELS spectra in Fig. 4e between the Ti–L$_2$/L$_3$ peaks for anatase TiO$_2$ (black curve) and the surface shell (blue curve) indicates a reduction of valence state of titanium in the surface shell. The fast formation of the surface shell is mostly induced by the enhancement of hydrogen atom generation after Pt co-catalyst deposition, which inversely shortens the incubation time of hydrogen generation (Supplementary Fig. 3).

After illuminating the water-immersed TiO$_2$/Pt using UV light for different lengths of time, the TiO$_2$/Pt sample was dried out and the morphologic evolution of the surface shell on Pt loaded TiO$_2$ NPs was further studied by ex situ TEM analysis. The high angle annular dark field (HAADF) images (Fig. 4f, j) and the corresponding energy dispersive spectroscopy (EDX) maps (Fig. 4g, k) clearly show that the co-catalyst Pt nano-dots are dispersed on the surface of TiO$_2$ NPs. Two kinds of surface regions, with/without Pt loading, were observed in HRTEM images after about 6 h photocatalytic reaction. In the region (square A1 in Fig. 4g) far from the Pt nano-dots, the dried hydrogenated surface shell was noticeable with a thickness of ~2.5 nm (Fig. 4h) and the shell phase was identified as the cubic TiO$_2$ structure based on the corresponding Fourier Transform (FT) pattern (inset in Fig. 4h). In contrast, no low-valence titanium oxide surface shell was observed in the region (square A2 in Fig. 4g) near the Pt nano-dots and the surface structure remains in the TiO$_2$ phase (Fig. 4i). Again, for the TiO$_2$/Pt sample after longer UV light illumination time of about 12 h, a TiO$_2$ surface shell ~4.5 nm thick (Fig. 4l and inset) was observed in the area (square A3 in Fig. 4k) far from the loaded Pt nano-dots, whereas no low-valence titanium oxides were yet observed on the surface area nearby the Pt co-catalyst (A4, Fig. 4m).

All these results reveal that the hydrogenated TiO$_2$ shell formed on the surface of the anatase TiO$_2$ NPs both with and without Pt co-catalysts during photocatalytic reaction. The Pt co-catalysts enhanced both the formation of the hydrogenated TiO$_2$ shell and the hydrogen evolution. However, the evolution of the hydrogenated TiO$_2$ surface shell near the Pt co-catalyst is quite different from that of the areas far from the Pt nano-dots during the dehydration process. Instead of transforming to a low-valence titanium oxide layer as on the surface of TiO$_2$ NPs without Pt loading (Fig. 3) or the local areas free of Pt nano-dots (Fig. 4h, l), the hydrogenated TiO$_2$ surface shell nearby the Pt nano-dots just converted back to the original TiO$_2$ structure by dehydrogenation (Fig. 4i, m). The main reason should be that H$_2$ formation on Pt is easier than on TiO$_2$, due to the smaller energy barrier of 0.85 eV$^{36}$, which can effectively avoid H accumulation around the Pt.

We have developed a liquid environmental TEM for in situ visualization of the photocatalytic reaction at the interface between bulk water and anatase TiO$_2$. We discovered the formation of a hydrogenated TiO$_2$ surface shell many hours before the generation of hydrogen bubbles on anatase TiO$_2$ without aid of co-catalyst Pt particles. The hydrogenated TiO$_2$ shell was observed also on the surface of anatase TiO$_2$ with Pt co-catalysts, along with hydrogen bubble generation. The shell thickness can be up to about 10 nm. This hydrogenated surface shell is formed via subsurface diffusion of H atoms generated by reaction of water protons with photoexcited electrons and promotes hydrogen generation by reducing the activation energy of H$_2$ (H–H bond) formation. This discovery provides insight into the mechanism of hydrogen evolution on TiO$_2$ that challenges the current understanding of photocatalytic surface chemical reactions without the aid of metal co-catalyst. It also enables a more effective exploration of novel highly efficient photocatalysts for water dissociation.

**Methods**

**In situ TEM imaging for photocatalytic reaction on interface of water/TiO$_2$ NP.** A homemade liquid flow holder was used in this experiment for observation of the photocatalytic reactions in water, the tip of the liquid flow holder was assembled with the self-aligned wet (SAW) cells$^{35}$ to seal the liquid. The SAW cell was covered by two 20 nm thick silicon nitride membranes, which is used to confine the liquid hermetically by O-ring for TEM observations. The gap between the two silicon nitride membranes can be controlled in a range from 5 nm to 1 µm for holding the liquid with a required thickness. A mercury light CEL-M500 (with characteristic UV wavelength of 254, 297, 315, 355, 365, 404, and 425 nm) was used in all the experiment. For the Pt co-catalyst TiO$_2$, 0.1 g of TiO$_2$ particles were suspended in water by sonication for one minute, then H$_2$PtCl$_6$ solution was directly injected to the solution for adjustment to 0.05 wt% Pt loading on the catalyst. After UV illumination the TiO$_2$-H$_2$PtCl$_6$ solution for 4 h, the NP was centrifuged and dried at 313 K in vacuum. The TiO$_2$ or Pt co-catalyst TiO$_2$ aqueous suspensions with 0.1 mol L$^{-1}$ is prepared by adding TiO$_2$ NPs into the de-ionized water (DI water). The suspensions are injected into the liquid flow holder by a liquid pump outside. UV illumination is introduced into the LETEM by using an optical fiber, which can launch the UV light from the CEL-M500 mercury lamp with a wavelength range from 254 to 450 nm (100 mW cm$^{-2}$ at the position of TEM observation area). A JEOL-2100F TEM equipped with a Gatan Enfina EEL S system (energy resolution of 1.2 eV) is used at an operating voltage of 200 kV. The EDS mapping is operated on a Titan G2 60-300 Cs-corrected TEM with accelerating voltage of 300 kV, which is also equipped with a Gatan Dual EELS$^\text{TM}$ system.

**Theoretical models.** First-principles calculations were carried out within the framework of density functional theory (DFT) as implemented in the CP2K/Quick step package$^{32}$. CP2K/Quick step employs a hybrid Gaussian and plane wave basis set and norm conserving Goedecker-Teter-Hutter (GTH) pseudopotentials$^{36–38}$. Gaussian functions consisting of a double-$\zeta$ plus polarization (DZP) basis set were employed to optimize the structures$^{39,40}$. For the calculations of H$_2$ formation above and below TiO$_2$, the triple-$\zeta$ plus polarization (TZP) basis sets were used. The energy cutoff for the real space grid used to represent the electron density was 500 Ry, which yields total energies converged to at least 0.001 eV per atom. We used the gradient-corrected Perdew–Burke–Ernzerhof exchange–correlation functional$^{39,40}$ augmented with on-site Hubbard U term (equal to 4.2 eV) on the 3d orbitals of the Ti atoms and D3 dispersion corrections to account for van der Waals interactions$^{31–43}$. 
Fig. 4 In situ LETEM observation of the photocatalytic water splitting process on TiO$_2$/Pt and ex situ observation of the surface shell on TiO$_2$/Pt NPs. 

- **a** Schematic diagrams showing the deposition process of Pt on the TiO$_2$ NP under UV light illumination for 4 h.
- **b** In situ LETEM observation of bubble evolution near the TiO$_2$/Pt NPs in water under UV illumination for different period of times. The recording time of each TEM image was controlled within 1 s with an electron dose rate of about 3 e$^{-}$·Å$^{-2}$·s$^{-1}$. A surface layer was observed on the TiO$_2$/Pt NPs during the photocatalytic water splitting process.
- **c** Evolution of surface layer thickness on Pt-loaded TiO$_2$ with increasing UV illumination time.
- **d** EELS of the bubble (red curve) at ~13 eV shows that the bubble contains hydrogen. Comparison between the EELS of pristine TiO$_2$ (black curve) and surface layer on TiO$_2$/Pt (blue curve) shows that the valence state of titanium in the surface layer has been reduced, same as the ones in Fig. 1f.
- **e** HAADF image and EDS map of a TiO$_2$/Pt NP, after UV photocatalytic reaction in water for 6 h.
- **f** HRTEM image of surface area far from Pt (A1 in g) and the corresponding FT pattern (inset) from the surface shell, which is identified as cubic TiO.
- **g** HAADF image and EDS map of a TiO$_2$/Pt NP, after UV light illumination in water for 12 h.
- **h** HRTEM image of the TiO$_2$/Pt NP in surface area near the Pt co-catalyst (A4 in k) and the FT pattern for Pt nanodot (inset), showing that the structure of the surface shell on TiO$_2$ is cubic TiO with thickness up to 4.5 nm.
- **i** HRTEM image of the TiO$_2$/Pt NP in surface area near the Pt co-catalyst (A3 in k) and the corresponding FT pattern identified as TiO (inset).
Our models typically consist of periodically repeated anatase (101) slabs with a (3 x 2) surface cell and three TiO₂ tri-layers. K-space sampling was restricted to the Γ point. To avoid the interaction between adjacent slabs, a vacuum space of 15 Å was employed. Hydrogen diffusion was modeled using a (1x3) surface supercell with one extra hydrogen, corresponding to 1/6 ML coverage. Four adsorbed water molecules (2/3 ML) were added to study the effect of the water environment on hydrogen diffusion.

Born–Oppenheimer first-principles molecular dynamic (FPMD) simulations were performed within the canonical (NVT) ensemble at temperature of 300 K. The ionics equations of motion were integrated using the velocity Verlet algorithm with a time step of 0.5 fs. All the FPMD simulations were run for at least 10 ps.

Data availability. The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information. Further information is also available from the corresponding authors upon reasonable request.

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**Additional information**

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