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Low-Energy Hydrogen Ions Enable Efficient Room-Temperature and Rapid Plasma Hydrogenation of TiO₂ Nanorods for Enhanced Photoelectrochemical Activity

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Hydrogenation is a promising technique to prepare black TiO₂ (H-TiO₂) for solar water splitting, however, there remain limitations such as severe preparation conditions and underexplored hydrogenation mechanisms to inefficient hydrogenation and poor photoelectrochemical (PEC) performance to be overcome for practical applications. Here, a room-temperature and rapid plasma hydrogenation (RRPH) strategy that realizes low-energy hydrogen ions of below 250 eV to fabricate H-TiO₂ nanorods with controllable disordered shell, outperforming incumbent hydrogenations, is reported. The mechanisms of efficient RRPH and enhanced PEC activity are experimentally and theoretically unraveled. It is discovered that low-energy hydrogen ions with fast subsurface transport kinetics and shallow penetration depth features, enable them to directly penetrate TiO₂ via unique multiple penetration pathways to form controllable disordered shell and suppress bulk defects, ultimately leading to improved PEC performance. Furthermore, the hydrogenation-property experiments reveal that the enhanced PEC activity is mainly ascribed to increasing band bending and bulk defect suppression, compared to reported H-TiO₂, a superior photocurrent density of 2.55 mA cm⁻² at 1.23 V_RHE is achieved. These findings demonstrate a sustainable strategy which offers great promise of TiO₂ and other oxides to achieve further-improved material properties for broad practical applications.

1. Introduction

Hydrogenation has emerged as an attractive approach for the synthesis of H-TiO₂ with remarkable material properties for clean hydrogen production by solar-driven water splitting.[1–12] However, the widespread application of H-TiO₂ is limited by the harsh conditions of conventional hydrogenation processes: thermal molecular or atomic hydrogenations are widely used,[4–6] but suffer from high temperatures and prolonged treatment times due to energetically and kinetically unfavorable processes at the microscopic level, which requires thermal activation to overcome energy barriers to diffuse sluggishly into the TiO₂ subsurface. More specifically, we demonstrated using density functional theory (DFT) calculations, that in the case of molecular hydrogenation, the hydrogen chemisorption and formation of oxygen vacancies to inefficient hydrogenation and poor photoelectrochemical (PEC) performance to be overcome for practical applications. Here, a room-temperature and rapid plasma hydrogenation (RRPH) strategy that realizes low-energy hydrogen ions of below 250 eV to fabricate H-TiO₂ nanorods with controllable disordered shell, outperforming incumbent hydrogenations, is reported. The mechanisms of efficient RRPH and enhanced PEC activity are experimentally and theoretically unraveled. It is discovered that low-energy hydrogen ions with fast subsurface transport kinetics and shallow penetration depth features, enable them to directly penetrate TiO₂ via unique multiple penetration pathways to form controllable disordered shell and suppress bulk defects, ultimately leading to improved PEC performance. Furthermore, the hydrogenation-property experiments reveal that the enhanced PEC activity is mainly ascribed to increasing band bending and bulk defect suppression, compared to reported H-TiO₂, a superior photocurrent density of 2.55 mA cm⁻² at 1.23 V_RHE is achieved. These findings demonstrate a sustainable strategy which offers great promise of TiO₂ and other oxides to achieve further-improved material properties for broad practical applications.
via the $\text{O}_\text{sc} \rightarrow \text{O}_\text{sub}$ low-energy-barrier pathway requires thermal activation.\cite{6} Therefore, high temperatures are required in case of both atomic and molecular hydrogenation approaches which are thus incompatible with practical applications.

Using kinetic rather than thermal hydrogen species, plasma hydrogenation has attracted recent attention because it does not rely on thermal activation. But conventional plasma hydrogenation again suffers from high temperature or from the high power set by the plasma equipment producing the high-energy hydrogen ions, causing inefficient and uncontrollable hydrogenation.\cite{12-16} Additionally, the highest photocurrent density of 0.9 mA cm$^{-2}$ at 1.23 $V_{\text{RHE}}$ reported to date for plasma-based H-TiO$_2$ is relatively low.\cite{14} Simultaneously, the underlying mechanism of plasma hydrogenation has not yet been reported due to the complexity of the hydrogen species involved in the process.

We develop a room-temperature and rapid plasma hydrogenation (RRPH) strategy to enable hydrogen ions with relatively low kinetic energies using a circular electromagnetic coil to synthesize H-TiO$_2$ nanorods with a controllable disordered shell. We systematically investigate the mechanisms of RRPH and enhanced photoelectrochemical (PEC) activity by combining experimental measurements with DFT calculations. We study the influence of RRPH on the structural, optical, electrical, and PEC properties of H-TiO$_2$ and reveal that the kinetic low-energy hydrogen ions trigger a narrower bandgap and larger band bending, along with the suppression of bulk defects to improve electron–hole pair generation, charge transport, and charge injection. In this way, we achieve improved PEC activity, yielding a higher photocurrent density of 2.55 mA cm$^{-2}$ at 1.23 $V_{\text{RHE}}$ than previously reported H-TiO$_2$. The findings observed experimentally are consistent with our theoretical studies: the efficient RRPH and enhanced PEC performance are ascribed to kinetic low-energy hydrogen ions exhibiting fast subsurface transport kinetics and shallow penetration depth. This allows direct hydrogen ion penetration of the TiO$_2$ surface, the formation of a controllable disordered shell and finally the suppression of the formation of bulk defects. In summary, we demonstrate an efficient RRPH strategy to fabricate H-TiO$_2$ nanorods with enhanced PEC performance owing to kinetic low-energy hydrogen ions.

2. Results and Discussion

2.1. The RRPH Strategy

The novel RRPH strategy we have developed as a highly efficient hydrogenation method for practical applications is schematically shown in Figure 1a. Unlike conventional plasma hydrogenation, the RRPH is realized by integrating a circular electromagnetic coil in the substrate electrode of a radio frequency (RF) plasma physical vapor deposition (PVD) set-up to produce a magnetic field, which can increase the density of hydrogen ions, decrease RF power and self-bias voltage, resulting in controllable kinetic low-energy hydrogen ions (Figures S1 and S2, Supporting Information). Experimentally, a low self-bias voltage ($V_{\text{bias}}$) of $-250$ V was obtained by applying a RF powering of the substrate of 20 W during the RRPH process. Correspondingly, this leads to an upper limit of 250 eV for the kinetic energy of the plasma hydrogen ions (Table S1, Supporting Information). In the control plasma process without using the circular electromagnetic coil, we found that hydrogen plasma cannot be created by applying a RF power of 20 W under the same process conditions, indicating the important role of the circular electromagnetic coil that leads to controllable low-energy hydrogen ions while maintaining the hydrogen plasma. In contrast with conventional plasma hydrogenation, our RRPH enables low-energy hydrogen ions to successfully prepare H-TiO$_2$ nanorods with the best photocurrent density without the need of high power or high temperature (Table S2, Supporting Information).

2.2. Hydrogenation-Property Experiments

To study the influence of RRPH on the structural, optical, electrical, and PEC properties of H-TiO$_2$ nanorods, we fabricated H-TiO$_2$ nanorods samples using treatment times of 2.5, 5, 10, 20, and 40 min, respectively (Table S1, Supporting Information).

To measure the morphological and phase changes of TiO$_2$ before and after RRPH treatment, we performed scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements. The SEM images of pristine TiO$_2$ and H-TiO$_2$ at 5 min show no morphological change (Figure S3a,b, Supporting Information), and no appreciable difference in morphology of H-TiO$_2$ samples was observed. The XRD patterns of pristine TiO$_2$ and H-TiO$_2$ samples show only rutile phase with (110) and (002) peaks (JCPDS No. 89-0920), no additional phases were identified (Figure S4, Supporting Information), indicating no phase change of TiO$_2$ before and after RRPH treatment.

To further quantify the microstructural change of pristine TiO$_2$ and H-TiO$_2$, we conducted transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) experiments. Figure 1b–i shows the TEM and high-resolution transmission electron microscopy (HR-TEM) images of pristine TiO$_2$ and H-TiO$_2$ samples, and Figure 1d shows the fast Fourier transformation (FFT) converted from Figure 1c. It indicates the single-crystalline feature of pristine TiO$_2$ nanorods with [001] growth direction and {110} sidewalls. Compared to the pristine TiO$_2$, H-TiO$_2$ samples are composed of a crystalline core and a disordered shell structure, and the FFT image indicates that the core structure of H-TiO$_2$ remains single-crystalline (Figure 1g), whereas the shell thickness is $\approx 2$ nm for H-TiO$_2$ treated at 5 min (Figure 1f) and increases to $5$ nm for H-TiO$_2$ treated at 40 min (Figure 1i). Figure 2a–f shows the line-scan EELS which provides the change of $[\text{O}]/[\text{Ti}]$ ratio of pristine TiO$_2$ and H-TiO$_2$ samples across the crystalline core and disordered shell interface. The $[\text{O}]/[\text{Ti}]$ ratio of H-TiO$_2$ at both 5 and 40 min gradually decreases in the shell range (Figure 2e,f), indicating the formation of oxygen vacancies in the shell. Moreover, the $[\text{O}]/[\text{Ti}]$ ratio in the core range of H-TiO$_2$ at 5 min is $\approx 2.25$ (Figure 2e) identical to pristine TiO$_2$ (Figure 2d). Hence, it is evident that no oxygen vacancies are formed in the bulk, whereas the $[\text{O}]/[\text{Ti}]$ ratio decreases to 1.7 for H-TiO$_2$ at 40 min (Figure 2f), indicating that more oxygen vacancies are formed in the bulk region.

To determine the composition of the disordered shell, we conducted X-ray photoelectron spectroscopy (XPS) analysis.
Figure 2g shows that the O 1s spectra of pristine TiO$_2$ and H-TiO$_2$ at 5 and 40 min, respectively. The O 1s peak at 530 eV is attributed to Ti-O, whereas the peak at 531.5 eV is assigned to Ti-OH, indicating the formation of Ti-OH in the shell of H-TiO$_2$. Figure 2h shows the Ti 2p spectra of pristine TiO$_2$ and H-TiO$_2$ at 5 and 40 min, respectively. It is noted that Ti$^{3+}$ is formed in the H-TiO$_2$ at 5 min, and strong reduction (Ti$^{4+}$ $\rightarrow$ Ti$^{3+}$ $\rightarrow$ Ti$^{2+}$) has occurred in the H-TiO$_2$ at 40 min, revealing that the higher concentration of Ti$^{3+}$ is obtained in the disordered shell of H-TiO$_2$ at 5 min.

To understand the optical properties of pristine TiO$_2$ and H-TiO$_2$, we measured UV–vis absorption spectra. Figure S5a (Supporting Information) shows that the absorption band edges of H-TiO$_2$ are redshifted, and the absorption in the visible to
infrared range gradually increases with increased treatment time. The Tauc plot demonstrates the bandgap narrowing from 3.0 eV of pristine TiO₂ to 2.91 eV of H-TiO₂ at 5 min (Table 1; and Figure S5b, Supporting Information).

To evaluate the influence of RRPH treatment time on the PEC properties of H-TiO₂, we performed the measurements of the photocurrent density versus potential (J–V) and incident photon-to-current efficiency (IPCE). Figure 3a,b indicates the enhancement of photocurrent density of H-TiO₂ as the treatment time increases up to 5 min, but decreasing when the treatment time is longer than 5 min. At 5 min, the photocurrent density of 2.55 mA cm⁻² at 1.23 V_RHE is achieved, which is the best value among the reported H-TiO₂ studies (Table S3, Supporting Information). The trend of IPCE (Figure S6, Supporting Information) is consistent with that observed in the J–V curves. In comparison to pristine TiO₂, the IPCE of H-TiO₂ is enhanced in the range of 300–420 nm. It is evident that H-TiO₂ at 5 min achieves the highest IPCE whereas the IPCE of H-TiO₂ decrease with increasing the treatment time over 5 min.

To clarify the impact of RRPH treatment on the donor density (N_d), depletion region width (W), and flat band potential (V_fb) of H-TiO₂, we recorded the Mott–Schottky (M–S) plots (Figure 3c) with following Equations (1)–(3)

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon_r N_d} \left( V - V_{fb} - \frac{kT}{e} \right)$$  \hspace{1cm} (1)
$$N_d = \left( \frac{2\varepsilon_0\varepsilon_r}{e_0} \right) \left( \frac{d(1/C^2)}{dV} \right)^{-1}$$  \tag{2}$$

$$W = \sqrt{\frac{2\varepsilon_0\varepsilon_r (V - V_f)}{eN_d}}$$  \tag{3}$$

where $C$ is the capacitance, $\varepsilon_0$ is the electron charge, $\varepsilon_r$ is the permittivity of vacuum, $\varepsilon_r$ is the dielectric constant of TiO$_2$, $N_d$ is the donor density, $V$ is the applied potential, $V_{fb}$ is the flat band potential, $k$ is the Boltzmann constant, $T$ is the temperature, and $W$ is the depletion region width. It is evident that increasing the treatment time leads to an increase in $N_d$ but a decrease in $W$ (Figure 3d), the corresponding values of $N_d$ and $W$ are identified at different treatment time (Table 1). Additionally, the $V_{fb}$ of pristine TiO$_2$ and H-TiO$_2$ were identified by M–S plots (Inset, Figure 3c). Compared with pristine TiO$_2$, the negative shift of $V_{fb}$ of H-TiO$_2$ at 2.5 and 5 min, respectively, is attributed to the substantially increased donor density (Table 1), which consequently shifts the Fermi level ($E_F$) toward the conduction band ($E_c$). The $V_{fb}$ of H-TiO$_2$ increases from $-0.30$ V$_{RHE}$ at 5 min to $-0.10$, $-0.05$, and $-0.02$ V$_{RHE}$ at 10, 20, and 40 min, respectively. This shift is ascribed to oxygen vacancies in the bulk of H-TiO$_2$ when the treatment time is longer than 5 min.

The hydrogenation-property experiments reveal that the best photocurrent density of H-TiO$_2$ at 5 min is primarily attributed to the following factors: i) XPS shows the higher concentration of

<table>
<thead>
<tr>
<th>Treatment time [min]</th>
<th>0</th>
<th>2.5</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
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<tbody>
<tr>
<td>Disordered shell thickness [nm]</td>
<td>0</td>
<td>–</td>
<td>2</td>
<td>2</td>
<td>–</td>
<td>5</td>
</tr>
<tr>
<td>[O]/[Ti] ratio in the core range</td>
<td>2.25</td>
<td>–</td>
<td>2.25</td>
<td>–</td>
<td>–</td>
<td>1.7</td>
</tr>
<tr>
<td>Bandgap [eV]</td>
<td>3.0</td>
<td>2.91</td>
<td>2.91</td>
<td>2.91</td>
<td>2.908</td>
<td>2.908</td>
</tr>
<tr>
<td>$J$ [mA cm$^{-2}$] at 1.23 $V_{RHE}$</td>
<td>0.63</td>
<td>2.01</td>
<td>2.55</td>
<td>2.05</td>
<td>1.68</td>
<td>1.19</td>
</tr>
<tr>
<td>$N_d$ [cm$^{-2}$]</td>
<td>$1.50 \times 10^{17}$</td>
<td>$1.36 \times 10^{19}$</td>
<td>$3.02 \times 10^{19}$</td>
<td>$5.48 \times 10^{19}$</td>
<td>$4.01 \times 10^{20}$</td>
<td>$6.45 \times 10^{20}$</td>
</tr>
<tr>
<td>$W$ [nm] at 1.23 $V_{RHE}$</td>
<td>312</td>
<td>34</td>
<td>23</td>
<td>16</td>
<td>5.9</td>
<td>4.7</td>
</tr>
<tr>
<td>$V_{fb}$ [V$_{RHE}$]</td>
<td>$-0.09$</td>
<td>$-0.15$</td>
<td>$-0.30$</td>
<td>$-0.10$</td>
<td>$-0.05$</td>
<td>$-0.02$</td>
</tr>
<tr>
<td>$V_{SC}$ [V]</td>
<td>0.89</td>
<td>0.95</td>
<td>1.10</td>
<td>0.90</td>
<td>0.85</td>
<td>0.82</td>
</tr>
</tbody>
</table>

The hydrogenation-property experiments reveal that the best photocurrent density of H-TiO$_2$ at 5 min is primarily attributed to the following factors: i) XPS shows the higher concentration of

**Figure 3.** a) $J$–$V$ curves of pristine TiO$_2$ and H-TiO$_2$ at different treatment times in 1 M KOH solution in the dark and under solar illumination. b) Treatment time-dependent photocurrent density of H-TiO$_2$. c) M–S plots of pristine TiO$_2$ and H-TiO$_2$ at different treatment times. d) Treatment time-dependent donor density and depletion region width of H-TiO$_2$. 

**Table 1.** Summary of hydrogenation-property experiments.
Ti\textsuperscript{3+} in the disordered shell which is responsible for the bandgap narrowing (Figure 2h),\textsuperscript{[1,6]} in agreement with the bandgap value of 2.91 eV from UV–vis spectra (Figure S5, Supporting Information; Table 1), leading to efficient electron–hole pair generation; ii) EELS observes that oxygen vacancies are only formed in the disordered shell (Figure 2e), not only indicating the bulk defect suppression to increase charge transport, but also achieving the largest band bending: photoelectrons from the shell prefer to be transferred into the electrolyte rather than the core when H-TiO\textsubscript{2} nanorods are in contact with the electrolyte because there are no localized states (LS)\textsuperscript{[8]} formed in the core, resulting in a maximum potential difference to further promote charge transport and injection. This finding is consistent with a maximum band bending of 1.1 V, which is determined by the highest negative shift in \(V_{fb}\) of –0.30 V RHE from M–S plots (Figure 3c; and Figures S7 and S8, Supporting Information). We conclude that the enhanced PEC activity is mainly ascribed to the narrower bandgap, larger band bending, as well as bulk defect suppression.

We experimentally showed that the efficient RRPH enables the synthesis of H-TiO\textsubscript{2} to attain the highest photocurrent density at 5 min, but the mechanism of RRPH remains unclear, which motivates us to study the interaction between kinetic low-energy hydrogen ions and TiO\textsubscript{2} leading to the improved PEC activity.

### 2.3. DFT Calculations

We employed DFT calculations to evaluate the penetration behavior of kinetic low-energy hydrogen ions into the TiO\textsubscript{2}(110) surface to reveal the mechanisms of RRPH and enhanced PEC performance. In our previous work,\textsuperscript{[6]} we have shown that the main bottleneck for a molecular hydrogen treatment from a microscopic point of view, is the large energy barrier for dissociative H\textsubscript{2} surface adsorption. For atomic hydrogen, the overall reaction barriers for surface adsorption and subsurface diffusion are considerably reduced, resulting in strongly enhanced kinetics of the hydrogen uptake by TiO\textsubscript{2}. Still, in the case of rutile TiO\textsubscript{2}, our previous DFT results indicate an overall barrier of 0.87 eV for the subsurface diffusion of atomic hydrogen such that thermal activation of this process is required and the hydrogenation speed will in general depend on the substrate temperature.\textsuperscript{[6]} As demonstrated experimentally in this work, kinetic low-energy hydrogen ions produced by RRPH are highly efficient in penetrating the TiO\textsubscript{2} surface even at room temperature (Table S1, Supporting Information) indicating that thermal activation is not needed.

To investigate the efficiency of H species from RRPH to directly penetrate the TiO\textsubscript{2}(110) surface from a theoretical point of view, we performed ab initio molecular dynamics (AIMD) simulations using DFT. The technical details of the employed DFT approach are given in the Experimental Section. Impinging H radicals with 8 different initial kinetic energies and 15 different initial lateral positions were placed 3 Å above a periodically repeated rutile TiO\textsubscript{2}(110) surface slab that has been equilibrated at a temperature of 500 K in a separate AIMD run prior to the actual impingement simulations. The TiO\textsubscript{2} slabs were generated from a 2×4 surface supercell and comprised 4 Ti-O layers corresponding to a thickness of 1.1 nm, white, red, and gray, blue spheres represent H, O, Ti atoms, and H radical, respectively, see Figure 4a,b. AIMD simulations where the impinging H radical shot through the slab were repeated with slabs consisting of 8 Ti-O layers to investigate the penetration depth as a function of initial kinetic energy (Figure S9, Supporting Information). Within the limits of adiabatic standard DFT calculations, the impinging H radicals will be charge neutral particles in the starting configuration.
in a typical hydrogen plasma process, the hydrogen species are composed of energetic H$_3^+$ ions (x = 1–3) and thermal [H] radicals,[8] for details see the Supporting Information. It is evident that the modeling of plasma hydrogenation is more complex than that of molecular and atomic hydrogenation. However, the modeling of charge neutral H species can be justified by the fact that the energetic H$_3^+$ ions will decay into energetic charge neutral H radicals upon dissociative recombination close to the surface.[19] Therefore, the restriction of charge neutrality does not pose a severe limitation.[19] Experimentally, in our study a self-bias voltage of ~250 V was achieved during the RRPH treatment such that the maximum energy of singly charged ions is limited to ~250 eV, although the energy distribution is quite broad.[20] Among the charged species, H$_3^+$ ions dominate by far.[20] Because of the fragmentation of H$_3^+$ into H radicals close to the surface and taking into account the bonding energy of H$_3$, we show in the Supporting Information that maximum energies of the relevant H radicals reaching the surface will be around 80.33 eV.[21] In order to sample the full kinetic energy range in our AIMD simulations, we initialized the velocities of the H radicals along the surface normal to obtain initial kinetic particle energies $E_{\text{kin},0}$ of 0.1, 1, 3, 5, 10, 20, 40, and 80 eV. Additionally, random velocity components perpendicular to the surface normal corresponding to a thermal energy of 500 K were applied for the incoming H radicals. For each of the 8 different kinetic energy values $E_{\text{kin},0}$, a lateral spatial 3 x 5 grid was used to sample 15 different initial positions of the impinging H radical as shown in Figure 4a,b; and Figure S10 (Supporting Information). For further details concerning the selection of the 15 inequivalent sampling points, see the Supporting Information.

We explored the penetration ratio of the vertically impinging H radicals as a function of $E_{\text{kin},0}$ (Figure 4c; and Figures S11–S18, Supporting Information). For the lowest investigated initial kinetic energy $E_{\text{kin},0} = 0.1$ eV, all 15 H radicals were reflected (Figure S11, Supporting Information) in agreement with our previous study that predicted a minimal energy barrier of 0.87 eV for the subsurface diffusion.[6] In case of $E_{\text{kin},0} = 1$ eV (Figure S12, Supporting Information), one out of fifteen H radicals could penetrate the TiO$_2$ surface and finally bonded to one of the three-fold coordinated surface O ions (O$_3$c). Increasing the initial kinetic energy to $E_{\text{kin},0} = 10$ eV (Figure S15, Supporting Information), 7 out of 15 H radicals were reflected and 8 out of 15 H radicals penetrated the TiO$_2$ surface. It is noted that for low initial kinetic energies of 1, 3, and 5 eV in addition to penetration and reflection also the adsorption of H radicals on the TiO$_2$(110) surface was observed, for details see Figures S12–S14, Supporting Information. We counted an H radical as penetrating when it either was stopped within the modeled TiO$_2$ slab or shot through and left the slab on the opposite surface. We note that it does not exclude the scenario where some of the H radicals that penetrated the surface and shot through the slab would have left the surface on the upper side again due to a reversion of the direction of velocity within the TiO$_2$ system, if thicker slab models had been considered. Therefore, the actual penetration ratios might be somewhat smaller than found in the simulations. At the highest investigated velocity corresponding to $E_{\text{kin},0} = 80$ eV, 10 out of 15 H radicals penetrated the TiO$_2$ surface corresponding to a penetration ratio of 67% (Figure S18, Supporting Information).

In the other 5 simulations, the impinging H radicals were reflected due to collision with an O or Ti ion of the TiO$_2$ lattice (Video S1 and Figure S18, Supporting Information). In general, we find that with increasing initial velocity, the ratio of penetrating H radicals tends to increase. Figure 4c shows that H radicals with initial kinetic energies $E_{\text{kin},0} \geq 1$ eV can indeed directly penetrate the TiO$_2$ surface without thermal activation, and the penetration ratio of H radicals with $E_{\text{kin},0} \geq 10$ eV can reach a value of around 0.5. At this point, it is interesting from a fundamental point of view to contrast the interaction of energetic H particles with TiO$_2$ surfaces with the thermal H species which dominate atomic and molecular hydrogenation processes.[4,6] In the case of impinging thermal hydrogen species, a direct hydrogen penetration is not possible. Rather the uptake of hydrogen in the subsurface region requires the two subsequent elementary steps: i) chemisorption and ii) subsurface diffusion. As shown in our previous work,[6] molecular hydrogen not only has to overcome a considerable energy barrier for dissociative chemisorption but also suitable unoccupied surface sites are required. In principle, free surface sites for the chemisorption of thermal hydrogen only become available when thermally activated and hence sluggish subsurface H diffusion O$_{3c}$ → O$_{3c}$ → O$_{sub}$ or recombinitative dissociation of H$_2$ molecules occur. The latter process further reduces the hydrogenation efficiency. Atomic hydrogen has more favorable kinetics for the subsurface diffusion O$_{3c}$ → O$_{sub}$ compared to molecular hydrogen. Due to the possibility of adsorption at energetically higher lying surface sites, the energy barrier is somewhat lower but still efficient hydrogenation becomes only possible at elevated substrate temperatures.[6]

In our previous work,[6] we had shown that the minimal energy barrier for diffusion of a chemisorbed H into the subsurface region is 0.87 eV and proceeds via a path in the vicinity of an O$_{3c}$ surface oxygen ion. For the definition of O$_{3c}$ ions, see Figure S10 (Supporting Information). At the same time the barrier for the chemisorption of an H radical at an O$_{3c}$ surface oxygen ion is small with a value of 0.08 eV.[6] From this we conclude that the minimal energy path for direct penetration into the subsurface region will also proceed via a path that is closely related to the O$_{3c}$ → O$_{sub}$ route. This is also consistent with the only trajectory #8 with $E_{\text{kin},0} = 1$ eV (Figure 5; and Figure S12, Supporting Information) that penetrated the rutile surface, which follows a path in the direct vicinity of an O$_{3c}$ surface ion. With increasing initial kinetic energy also multiple penetration pathways with higher energy barriers around O$_{3c}$ → O$_{sub}$ in RRPH become available. This rapidly increases the penetration probability with increasing initial kinetic energy (Figure 5), leading to the highly efficient RRPH. In case of the vertically impinging H radicals shown in Figure 5, the only initial lateral positions where penetration was never observed are those that are directly on top of surface O or Ti ions. Here, direct collisions of the impinging H radical with the surface ions lead to very high energy barriers that even cannot be overcome in the case of the highest investigated initial kinetic energies of 80 eV.

A comparison of the molecular and atomic hydrogenations, along with RRPH from an atomistic point of view is summarized in Table 2, indicating the fast subsurface transport kinetics feature of kinetic low-energy hydrogen ions. Taken together, these results show that the fast subsurface transport
Figure 5. The lateral positions of H radicals with initial kinetic energy of 0.1, 1, 3, 5, 10, 20, 40, and 80 eV that were penetrated the rutile slab. Penetration was never observed for the initial positions of #1, #3, and #13 that are directly on top of surface O or Ti ions.

Table 2. Factors influence the efficiency and kinetics of the different hydrogenation methods based on thermal molecular hydrogen H₂, thermal atomic hydrogen [H], and energetic hydrogen ions H⁺ from RRPH.

<table>
<thead>
<tr>
<th>Hydrogenation species</th>
<th>H₂</th>
<th>[H]</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface adsorption kinetics</td>
<td>Slow</td>
<td>Fast</td>
<td>Not relevant</td>
</tr>
<tr>
<td>(Energy barrier [eV])</td>
<td>(1.86)</td>
<td>(0.08)</td>
<td></td>
</tr>
<tr>
<td>Surface adsorption sites</td>
<td>O₂c</td>
<td>O₃c</td>
<td>Not relevant</td>
</tr>
<tr>
<td>Subsurface transport pathway</td>
<td>O₂c → O₃c → O_sub</td>
<td>O₃c → O_sub</td>
<td>Multiple penetration pathways</td>
</tr>
<tr>
<td>Subsurface transport kinetics</td>
<td>Slow</td>
<td>Intermediate</td>
<td>Fast</td>
</tr>
<tr>
<td>(Energy barrier [eV])</td>
<td>(1.66)</td>
<td>(0.87)</td>
<td>No thermal activation needed for subsurface diffusion</td>
</tr>
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</table>
enables kinetic low-energy hydrogen ions to directly penetrate into TiO$_2$ subsurface via multiple penetration pathways without the need of thermal activation, leading to efficient RRPH.

Moreover, we analyzed the penetration depth of those H radicals that were not reflected or adsorbed, as a function of $E_{\text{kin,0}}$. Typical trajectories from AIMD simulations of H radicals impinging with energies 0.1, 1, 10, 20, 40, and 80 eV are presented in Figure 6a–f, and Videos S2–S7, Supporting Information. The penetration depth was determined as the distance from the TiO$_2$ surface after the H radical came to a halt. An impinging H radical was considered as being trapped when its kinetic energy reached values constantly below 0.5 eV (see the Experimental Section). The structure of the TiO$_2$ surface slab containing 8 Ti-O layers is shown in Figure 6g. All simulations where the impinging H radicals shot through the slab with 8 Ti-O layers, i.e., where the H radical was not stopped within the slab model, are indicated by open circles and arrows at the bottom of the plot. Simulation results where the impinging H radicals were reflected and adsorbed are shown in Figures S11–S18, Supporting Information. Due to the sampling of different initial lateral positions, more than one data point is usually shown for each kinetic energy value, details see Figures S11–S18, Supporting Information. The penetration depths as a function of $E_{\text{kin,0}}$ of the various simulations are shown in Figure 6g. Up to initial kinetic energies of 10 eV, the maximally obtained penetration depths did not exceed 1.0 nm corresponding to the fourth Ti-O layer from the surface as shown in Figure 6a–c. At these lower kinetic energies, indeed most of the H radicals penetrating the surface were stopped at the first or second Ti-O layer by bonding to an O ion. As the example simulation shown in Figure 6d demonstrates, at $E_{\text{kin,0}} = 20$ eV generally larger penetration depths were observed compared to the simulations with lower initial kinetic energies and both stopping of the H radicals within the TiO$_2$ slabs, and through-shot events were detected (Figure 6g). At high initial kinetic energies of 40 and 80 eV, for example trajectories see Figure 6e,f, all H radicals which were not reflected shot through the TiO$_2$ slab even if the thicker slab with 8 Ti-O layers and a dimension of 2.3 nm in the direction along the surface normal was used in the AIMD simulations. It is concluded that when the kinetic energy of H radical is lower than 10 eV, the penetration depths are less than 1 nm; when the kinetic energy is increased to 20 eV, the penetration depths increase to 1–2 nm, some are larger than 2.3 nm; when the kinetic energy further increases to 40 or 80 eV, all penetration depths are larger than 2.3 nm. Our experimental results and our previous ab initio study[6] clearly demonstrate that the surface hydrogenation induces disorder in the rutile phase such that the straight channel structures in which the highly energetic hydrogen species can travel with low energy losses will disappear during the hydrogenation process. This means that also vertically impinging hydrogen radicals with higher kinetic energies of up to 80 eV which penetrate the TiO$_2$ surface will be quickly stopped or reflected upon collision with Ti and O ions of the TiO$_2$ disordered structure. Moreover, we expect that H radicals impinging with an angle of incidence significantly different from 0° will be more prone to strong ion-ion collisions and hence will have a much weaker tendency to channel even in the fully crystalline rutile lattice. Therefore, we assume that the penetration depth of hydrogen radicals larger than 2.3 nm with higher kinetic energies > 20 eV is severely overestimated in our DFT calculations.

In order to investigate whether penetration of the rutile TiO$_2$ surface requires vertically impinging H species at angle of incidence of 0° or is also feasible at angles deviating from 0°, additional DFT MD simulations with angle of incidence of 5°, 15°, 30°, 45°, 60°, and 75° were performed (Figures S19–S25, Supporting Information) for H radicals with $E_{\text{kin,0}} = 10$ eV. It is shown that penetration can be even observed at an angle of incidence of 60° (Figures S19 and S24, Supporting Information), demonstrating that a vertical impingement is not a precondition to have an efficient uptake of kinetic H radicals.

To explore the subsurface transport of H radicals finally resulting in the formation of OH bonds, the kinetic energy along the trajectories of the impinging H radicals was analyzed (Figures S26 and S27, Supporting Information). It is shown that the trajectories of the impinging H radicals before trapping are in general characterized by frequent collisions with the Ti and O ions of the rutile lattice in the subsurface region leading to rapid dissipation of the kinetic energy and finally to the formation of OH bonds which contribute to the formation of a controllable disordered shell. In total we find that impinging H radicals with sufficient initial kinetic energy $E_{\text{kin,0}} \geq 1$ eV have a high probability of directly penetrating the TiO$_2$ rutile surface and that the kinetic energy is efficiently dissipated within the subsurface region. This can explain the efficient hydrogenation of our RRPH close to the surface.

The shallow penetration depth feature of low-energy hydrogen ions revealed by our DFT is confirmed by a reported work where Ohashi et al. used low-energy hydrogen ions of 500 eV to treat the TiO$_2$$(110)$ surface and found that the H depth profile showed a shallow peak at about 1 nm penetration depth.[52] It indicates that low-energy hydrogen ions of up to 80.33 eV generated in our RRPH process likewise lead to shallow penetration depth, a feature that allows them to controllably interact with TiO$_2$ to attain the controllable disordered shell and bulk defect suppression, ultimately contributing to the enhanced performance, in agreement with the hydrogenation-property experiments.

2.4. Efficient RRPH versus State-of-the-Art Hydrogenations

The RRPH shows the following unique features:

i. Efficient hydrogenation via fast subsurface transport kinetics

Chen et al. fabricated H-TiO$_2$ nanoparticle in 20 bar of H$_2$ at 200 °C for 5 days,[4] and Wang et al. synthesized the H-TiO$_2$ nanorods in 1 bar of H$_2$ at 400 °C for 1 h,[3] but high temperature and prolonged treatment time are needed for the molecular hydrogenation. Alternatively, Xu et al. used Pd to dissociate molecular hydrogen into atomic hydrogen to prepare H-TiO$_2$ at 250 °C for 10 min, but noble metal particles and high temperature are required for the atomic hydrogenation.[9] The inefficient molecular and atomic hydrogenations are due to their intrinsic reaction mechanism with TiO$_2$ thermal activation via high temperature is required to overcome the energy barriers of
chemisorption and subsurface diffusion to penetrate the TiO$_2$ surface. Simultaneously, Wang et al. reported for the first time the application of hydrogen plasma at a RF power of 200 W to treat TiO$_2$ nanoparticles at 500 °C for 4 h\cite{12}, and Lepcha et al. prepared H-TiO$_2$ nanofibers by applying a high temperature of 500 °C and RF power of 15 W\cite{13}, which shows that conventional plasma hydrogenations operate at high power or high temperature set by the plasma equipment to provide high-energy hydrogen ions to deeply penetrate the TiO$_2$, causing uncontrollable plasma hydrogenation. In our work, the RRPH strategy achieves kinetic low-energy hydrogen ions, which can directly penetrate into the TiO$_2$ subsurface to efficiently prepare H-TiO$_2$ at room temperature due to the fast subsurface transport kinetics.

ii. **Controllable hydrogenation via shallow penetration depth**

The feature of shallow penetration depth is difficult to be realized by conventional plasma hydrogenations, to the best of our knowledge, it is reported for the first time in this work. Liang et al. fabricated H-TiO$_2$ films by high power of 380 W to gain low photocurrent density of 0.67 mA cm$^{-2}$ at 1.23 $V_{RHE}$\cite{15} and Tian et al. applied RF power of 200 W and high temperature of 425 °C to hydrogenate TiO$_2$ nanorods obtaining the

![Figure 6.](https://onlinelibrary.wiley.com/doi/10.1002/smll.202204136)
characteristics contribute to narrower bandgap and larger band bending, along with a beneficial suppression of bulk defects. Overall, this work showcases a promising strategy to hydrogenate TiO$_2$ and other oxides for a wide variety of applications and provides valuable insight into understanding the underlying hydrogenation mechanisms and improved properties.

4. Experimental Section

**Growth of TiO$_2$ Nanorod Arrays on FTO (F:SnO$_2$) Substrate:** TiO$_2$ nanorods were grown on a FTO substrate by hydrothermal method.$^{[26]}$ Typically, 0.35 mL of tetra-tert-butoxy titanate (Ti(O'Bu)$_4$) was dissolved in 30 mL of 6 M HCl, and the solution was transferred into a steel-lined Teflon autoclave, where a cleaned FTO substrate was placed. The autoclave was maintained at 160 °C for 18 h, then the coated FTO substrate was washed several times with deionized water and ethanol, and dried in air. To remove the chemical residues and improve the crystallinity of TiO$_2$ nanorods and their electric contacts with FTO glass, the samples were annealed at 550 °C for 3 h in air.

**Hydrogenation of TiO$_2$ Nanorods by RRPH:** Figure 1a and Figure S1 (Supporting Information) show the RRPH set-up including an integrated circular electromagnetic coil. The RRPH processing parameters such as RF power, pressure, treatment time, and hydrogen gas flow were controlled precisely by a programmable recipe. Therefore, reproducible hydrogenation of TiO$_2$ nanorods at different treatment times can be achieved (Table S1, Supporting Information).

**Characterizations of the Samples:** The Ti-H$_2$O nanorods were investigated by using SEM Zeiss Supra 35, Empyrean XRD (Cu K$_\alpha$), CARY-500 UV–VIS spectrometer, and HR-TEM Jeol J2010F FEG operating at 200 kV and coupled to a Gatan imaging filter (GIF) spectrometer, and Thermo Scientific K-Alpha XPS system (Al K$_\alpha$).

**PEC Studies:** A Newport solar simulator 150 W Xe lamp with AM 1.5 G filter acted as a light source for the PEC investigation. All photocurrent density versus potential (J–V) curves were recorded with a Princeton Applied Research 2273 potentiostat using 1 M KOH as electrolyte in a three-electrode configuration, in which Ag/AgCl in 3 M KCl was the reference electrode, and platinum wire was the counter electrode. The IPCE was performed based on Newport Oriel QE-PV-S1 and CHI660E electrochemical workstations. The M–S measurements were performed on the Gamry electrochemical workstation.

The conversion from Ag/AgCl to RHE potential is given as follows:

$$\Delta E(\text{RHE}) = \Delta E(\text{Ag/AgCl}) + 0.0591 V + E_0(\text{Ag/AgCl})$$

where $E_0(\text{Ag/AgCl}) = 0.1976 V$ versus normal hydrogen electrode (NHE) at 25 °C and $E(\text{Ag/AgCl})$ is our used working potential.

**DFT Calculations:** We used the Vienna ab initio simulations package (VASP)$^{[27]}$ VASP uses a plane wave basis set in order to describe the valence electrons. The Kohn–Sham wavefunctions of the valence electrons were expanded in a plane wave basis set using a cut-off energy of 400 eV for the ab initio molecular dynamics (AIMD) simulations and of 550 eV for structural relaxations. The projector-augmented wave method (PAW) was employed to take into account the effect of core electrons.$^{[28,29]}$ Standard semilocal DFT functionals tend to underestimate correlation effects due to the localized 3d electrons. To partially correct these deficiencies, a Hubbard term was applied according to the DFT + U scheme of Dudarev et al.$^{[30]}$ Here, we combined the Hubbard correction with the semilocal PBE functional.$^{[31]}$ As Hubbard U parameter we used 4.0 eV following previous studies of defective rutile TiO$_2$ surfaces.$^{[23,24]}$ In all simulations spin polarized DFT calculations were performed except for the AIMD simulations of the 8 Ti-O layer thick slabs where spin-paired calculations had to be made for convergence reasons.

Ab initio molecular dynamics simulations were performed by combining the VASP calculations of the atomic forces with the integration of Newton’s equation of motion using the velocity Verlet...
algorithm as implemented in the Atomic Simulation Environment.\textsuperscript{[34]} Due to the small-time scales of the AIMD simulations, no thermostat was employed, i.e., the NVE ensemble was used. Prior to the simulation of the impingement of H radicals on the rutile surface, the slab systems were equilibrated at a temperature of 500 K. For this purpose, the atom velocities in the fully relaxed slabs were initialized according to the Maxwell–Boltzmann distribution with a temperature of 1000 K. In accordance with the equipartition theorem this resulted after a short AIMD run of 1 ps in an equilibrium temperature of 500 K.

Due to the high speed of the impinging energetic H radicals, small time steps \( \Delta t \) had to be used in the initial phase of the AIMD simulations, whereas longer time steps could be used once the H radical had been slowed down within the rutile structure. In detail, the initial time step \( \Delta t \) was chosen such that the maximum displacement of the impinging H radicals was equal to \( dx_{\max} = 0.02 \text{Å} \). Hence \( \Delta t = dx_{\max} / v_{\max} \), where \( v_{\max} \) is the initial velocity of the impinging H radical. The time step in the AIMD simulations was then adapted after every 1000 simulation steps according to \( \Delta t = dx_{\max} / v_{\max, s} \), where \( v_{\max, s} \) is the maximum atomic velocity encountered in the last third of the previous simulation period. The simulations were continued until either i) \( v_{\max, s} \) was below 9780 m s\(^{-1} \) corresponding to a kinetic energy of the impinging H radical of less than 0.5 eV or ii) the impinging H radical shot through the rutile slab, i.e., left the slab at the bottom surface. We note that \( v_{\max, s} \) means that in the AIMD simulations the kinetic energy of the impinging H radical is less than 0.5 eV for at least 68 fs. For comparison, OH stretching modes in TiO\(_2\) typically have a frequency of 3300 cm\(^{-1}\), corresponding to a period of 10 fs.\textsuperscript{[10]}

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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

Keywords
black titania, low-energy hydrogen ions, multiple penetration pathways, rapid plasma hydrogenation, room-temperature hydrogenation, solar water splitting

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