Achieving overall water splitting using titanium dioxide-based photocatalysts of different phases†

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Titanium dioxide (TiO2) is regarded as the benchmark semiconductor in photocatalysis, which possesses a suitable band structure and makes the overall water splitting reaction thermodynamically possible. However, photocatalytic overall water splitting (POWS) (2H2O → 2H2 + O2) can only take place on rutile but hardly on anatase and brookite TiO2. So obtaining the POWS on TiO2-based photocatalysts has remained a long-standing challenge for over 40 years. In this work, we found that the POWS on anatase and brookite TiO2 becomes feasible under prolonged UV light irradiation. Further investigation by means of electron spin resonance spectroscopy (EPR) and transient infrared absorption–excitation energy scanning spectroscopy (TRIRA-ESS) reveals that both kinetics and thermodynamics factors contributed to unique POWS activity for different phases of TiO2. Kinetically the process of photocatalysis differs on different phases of TiO2 due to the intermediates (°OH radical for anatase and brookite TiO2, peroxy species for rutile TiO2) that are formed. Thermodynamically there are many trapped states lying near the valence band of anatase and brookite but not for rutile TiO2, which reduce the overpotential for water oxidation. These findings develop our understanding of why some semiconductors are inactive as POWS photocatalysts despite having thermodynamically suitable band structures for the proton reduction and water oxidation reactions.

Solar hydrogen production using photocatalytic water splitting is regarded as a promising strategy for harnessing solar energy to supply hydrogen energy.1–2 Titanium dioxide (TiO2) is a popular and standard semiconductor used in photocatalysis, and exists in three common crystalline structures, anatase, rutile and brookite, which have been extensively investigated. Generally, anatase TiO2 is recognized as the most active phase in photocatalysts for environmental applications, while rutile and brookite TiO2 are seldom considered.3–6 In the past few decades, almost all research studies on TiO2 only showed H2 but no O2 was detected during photocatalytic overall water splitting although it has a thermodynamically feasible band structure. In the photocatalytic overall water splitting reaction (POWS, 2H2O → 2H2 + O2), H2 and O2 should be produced simultaneously with a H2/O2 stoichiometric ratio of 2.0, which has been achieved in the photoelectrochemical (PEC) system using a TiO2 photoanode as early as 1972.7 However, it has seldom been achieved on a TiO2-based nanoparticle photocatalyst. This challenge persists despite the fact that TiO2 has a suitable band structure for both proton reduction and water oxidation under UV light irradiation. Besides, a similar phenomenon has been observed for other popular photocatalysts (e.g., Ta2N5, TaON). That is, some photocatalysts have suitable band structures that are thermodynamically feasible for POWS, yet they fail to catalyze the POWS reaction.

Immense efforts have been made to achieve POWS on TiO2 previously. The introduction of some inorganic ions (e.g., Cl−, CO32−) has been reported to somewhat improve the stoichiometric production of H2 and O2, which might be attributed to

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Broader context
Photocatalytic overall water splitting to produce H2 is recognized as a promising strategy for utilization of solar energy. Titanium dioxide (TiO2) has been widely used as the benchmark semiconductor in photocatalysis, which possesses a suitable band structure and makes the overall water splitting reaction thermodynamically possible. However, achieving overall water splitting on TiO2-based photocatalysts has remained a long-standing challenge for over 40 years. In this work, we found that the overall water splitting can take place on all three phases of TiO2 (anatase, rutile and brookite) after a prolonged UV light irradiation. Systematical investigations indicate that both kinetics and thermodynamics factors contributed to unique the photocatalytic overall water splitting activity for different phases of TiO2. This finding will be helpful for understanding why many semiconductors are inactive as overall water splitting photocatalysts despite having thermodynamically suitable band structures for the proton reduction and water oxidation reactions.

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the intermediates involving the ions (e.g., \( \text{C}_2\text{O}_4^{2-}, \text{ClO}^- \)) that are formed in these systems.\(^6,^9\) Recently, it was reported that the POWS can only take place on rutile but not on anatase \( \text{TiO}_2 \).\(^{10}\) Nevertheless, the intrinsic reason for this observation remains unknown. In addition, the water splitting mechanism, especially the mechanism of water oxidation on \( \text{TiO}_2 \)-based photocatalysts are quite controversial in the literature.\(^5,^{11-18}\)

Herein, we report our results that the photocatalytic overall water splitting (POWS) reaction can take place on \( \text{TiO}_2 \)-based photocatalysts with different phases (anatase, rutile and brookite) under prolonged UV light irradiation. We found that the stable overall water splitting with stoichiometric \( \text{H}_2/\text{O}_2 \) ratio can be achieved on rutile \( \text{TiO}_2 \). However, anatase and brookite \( \text{TiO}_2 \) can only produce \( \text{H}_2 \) at the initial stage, but \( \text{H}_2 \) and \( \text{O}_2 \) are obtained simultaneously after long time irradiation. Further investigations using electron spin resonance spectroscopy (EPR), transient infrared absorption–excitation energy scanning spectroscopy (TRIRA-ESS) and DFT calculations reveal that both \( \text{EPR} \), transient infrared absorption–excitation energy scanning investigations using electron spin resonance spectroscopy obtained simultaneously after long time irradiation. Further overall water splitting with stoichiometric \( \text{H}_2/\text{O}_2 \) ratio can be achieved on rutile \( \text{TiO}_2 \). However, anatase and brookite \( \text{TiO}_2 \) can only produce \( \text{H}_2 \) at the initial stage, but \( \text{H}_2 \) and \( \text{O}_2 \) are obtained simultaneously after long time irradiation.

Theoretical calculation has demonstrated that the most stable surfaces of anatase and rutile \( \text{TiO}_2 \) are (101) and (110) facets.\(^{19,20}\) A similar calculation method was also introduced for brookite \( \text{TiO}_2 \), which shows that the (210) facet is the most stable facet (Fig. S1 and Table S1, ESI†). Firstly, anatase, rutile and brookite \( \text{TiO}_2 \) samples exposed with (101), (110) and (210) facets were prepared according to the references.\(^{21,22}\) The as-prepared \( \text{TiO}_2 \) samples were demonstrated to be pure phases and well-crystallized by XRD and Raman characterization (Fig. 1a and b, Fig. S2, ESI†). HRTEM images revealed that the most exposed crystal facets for anatase, rutile and brookite \( \text{TiO}_2 \) samples are (101), (110) and (210), respectively, indicating that their stable surface structures are synthesized successfully (Fig. 1c–n).

Table 1 lists the POWS performance of the prepared different phases of \( \text{TiO}_2 \) samples under irradiation of a Xe lamp (the emission spectrum is shown in Fig. S3, ESI†). Only \( \text{H}_2 \), but no \( \text{O}_2 \), is detected for anatase \( \text{TiO}_2 \) indicating that the POWS reaction does not take place on the anatase \( \text{TiO}_2 \) (entries 1 and 2). However, both \( \text{H}_2 \) and \( \text{O}_2 \) are produced simultaneously on rutile \( \text{TiO}_2 \) with a \( \text{H}_2/\text{O}_2 \) ratio close to 2.0, indicating that the POWS can only take place on rutile but not on anatase \( \text{TiO}_2 \).\(^{10}\) The above results clearly indicate that the POWS performance on the \( \text{TiO}_2 \)-based photocatalyst is closely related to its crystal-line phases.

The photocatalytic \( \text{H}_2 \) or \( \text{O}_2 \) production reaction in the presence of \( \text{CH}_3\text{OH} \) (holes acceptor) or \( \text{AgNO}_3 \) (electrons acceptor) was also performed to further evaluate the performances for \( \text{TiO}_2 \) samples (Fig. S4, ESI†). Anatase and brookite \( \text{TiO}_2 \) show comparable \( \text{H}_2 \) production performances, which is better than rutile \( \text{TiO}_2 \) in the presence of \( \text{CH}_3\text{OH} \). However, rutile \( \text{TiO}_2 \) shows much better \( \text{O}_2 \) evolution performance than anatase and brookite \( \text{TiO}_2 \)
when Ag⁺ was used as an electron acceptor. The result shows the different reduction and oxidation ability for anatase, rutile and brookite TiO₂, which led us to the conclusion that the POWS on TiO₂ is highly dependent on the crystalline phase of the TiO₂, especially for the water oxidation reaction. This result also indicates that anatase and brookite TiO₂ exhibit similar performance both for H₂ production and O₂ production half reactions.

To investigate the photogenerated holes for anatase or brookite TiO₂ during the proton reduction for H₂ production, a photocatalytic experiment under prolonged UV light irradiation (light intensity, 1000 mW cm⁻²) was carried out. As shown in Fig. 2a, only H₂ without O₂ is produced in the initial stage for anatase TiO₂. In a subsequent experiment, the reaction system was then vacuumed and no O₂ was detected, but the H₂ production rate decreased. In the second cycle, the H₂ production rate decreased and O₂ was still not detected. In the third cycle after the whole reaction time of more than 5 hours, small amount of oxygen was detected and maintained in the following cycles. The appearance of O₂ evolution after sufficient light irradiation is a surprising result. Fig. 2b shows the results of rutile TiO₂ throughout several cycles of the reaction test. H₂ and O₂ production with a H₂/O₂ ratio close to 2.0 was always maintained. Interestingly, brookite TiO₂ shows a similar phenomenon to anatase TiO₂ (Fig. 2c), namely, H₂ was only produced at the initial stage but O₂ was generated simultaneously after prolonged UV light irradiation. The phenomenon that anatase and brookite TiO₂ show similar performances for the POWS reaction could be ascribed to the similar atomic structure between brookite(210) and anatase(101) facets. It should be pointed out that all the samples in Table 1 were used in this experiment and the samples with the same phases show similar performance. These results clearly indicate that the POWS to produce both H₂ and O₂ can be achieved not only for rutile TiO₂ but also for anatase and brookite TiO₂. Notably, we found that O₂ can be produced on anatase and brookite TiO₂ after prolonged UV irradiation during the photocatalytic reaction.

To understand why the different phases of TiO₂ perform differently as photocatalysts in the POWS reaction, we characterized major aspects of the issue, including carrier dynamics, kinetics and thermodynamics. Particularly, we focused on the differences in water oxidation for the different phases of TiO₂.

The transient dynamics of the two commonly-used phases, anatase and rutile TiO₂ were studied to probe the lifetimes of photoexcited holes. The lifetimes of the holes excited in rutile TiO₂ were found to be longer than those in anatase TiO₂. However, in the presence of a Pt cocatalyst, the lifetimes were almost the same for both anatase and rutile TiO₂ (shown in Fig. S5a, ESI†). It should be noted that the Pt was deposited as a cocatalyst in all the POWS reactions for both anatase and rutile TiO₂ (without the Pt cocatalyst, no H₂ evolution is detected for either the anatase or rutile TiO₂). Thus, the dynamics of the photogenerated holes in the anatase and rutile TiO₂ are quite similar. To further clarify this point, Ag⁺ (AgNO₃) was introduced as an electron acceptor to investigate the behavior of the photoexcited holes, and again the lifetimes of the photoexcited holes were almost the same, indicating that the dynamics of the photogenerated holes for anatase and rutile TiO₂ are similar. Therefore, we can conclude that the initial dynamics of photoexcited holes are not responsible for the behaviors of the different phases of TiO₂ in POWS.

To further explore the different oxygen-containing intermediates on different phases of TiO₂ we employed the EPR spin-trap technique to probe the reactive oxygen species derived on the surface of TiO₂ under UV light irradiation. Firstly, we performed the EPR experiment for all three TiO₂ samples with DMPO (dimethyl pyridine N-oxide) as an electron trapping agent under an atmosphere of Ar (Fig. 3). No signal was detected in the dark but totally different signals for three TiO₂ samples were obtained under light irradiation. For anatase TiO₂, four characteristic peaks are obviously observed and the standard ratios of intensities are 1:2:2:1, which can be ascribed to *DMPO-OH. In addition, brookite TiO₂ shows
almost the same EPR signal with anatase TiO$_2$, which is in good agreement with their similar photocatalytic performances. However, for rutile TiO$_2$, a typical seven-line paramagnetic signal is detected, which can be ascribed to *DMPO-X as reported. We can infer that it is generated from the oxidation of DMPO by peroxide. It was also reported that peroxy species may serve as the reaction intermediates for the water oxidation on rutile TiO$_2$. Valdes et al. reported that peroxy species can be easily decomposed to O$_2$ by DFT and concluded that this reaction step is the most favored step on rutile in the water oxidation reaction. So we can speculate that the peroxy species can be easily decomposed to produce O$_2$ on rutile. However, for anatase and brookite TiO$_2$, the formed *OH radical may be strongly absorbed on the surface and coupled to evolve O$_2$ after saturation of absorption. The different oxygen-containing intermediates formed on anatase and rutile TiO$_2$ can also be demonstrated by the diversity of surface hydroxyl oxygen of TiO$_2$ before and after the reaction (Fig. S6 and S7, ESI†). It was found that the proportion of hydroxyl oxygen for anatase TiO$_2$ is obviously increased after UV light irradiation (from 5.0% to 9.7%) but remained almost unchanged for rutile TiO$_2$. Thus, the peroxy species are the most likely oxygen-containing intermediate derived from water oxidation on rutile TiO$_2$ while *OH radical species prefer to prevail from water oxidation on anatase TiO$_2$. Our EPR results suggest that different intermediates are really formed during the photocatalytic water splitting for three kinds of TiO$_2$ samples (peroxy species for rutile TiO$_2$, *OH radical for anatase and brookite TiO$_2$). The different intermediates resulted in different surface reaction processes, which mainly contribute to the kinetics for POWS on TiO$_2$-based photocatalysts.

EPR experiments without electron trapping agents were also conducted under an Ar atmosphere. Fig. 4 shows the EPR results with and without UV light irradiation. The red-line signals were collected after 20 min UV light irradiation and then the sample tubes were quickly transferred for detection. No signals were detected for rutile TiO$_2$ regardless of dark conditions or light irradiation. However, anatase TiO$_2$ shows an obvious EPR signal at $g = 1.9998$, which could be ascribed to O$^-$.$^{31,32}$ A weak signal at $g = 1.9890$ could be ascribed to the unsaturated Ti$^{3+}$. The signal of O$^-$ became stronger after UV light irradiation, indicating that part of O$_2^-$ in the lattice could be oxidized to O$^-$ by photoexcited holes during the photocatalytic reaction. For brookite TiO$_2$, no signal was detected under dark conditions while a strong EPR signal at $g = 1.9998$, which is ascribed to O$^-$ similar to anatase TiO$_2$. Interestingly, the signals at $g = 1.9890$ and $g = 1.9621$ were only achieved on brookite TiO$_2$, which are ascribed to the unsaturated Ti$^{3+}$. The presence of Ti$^{3+}$ under light irradiation most possibly contributes to the non-stoichiometric ratio of H$_2$/O$_2$ for anatase and brookite TiO$_2$ because partial photoexcited holes participate in the oxidation of the lattice oxygen to the observed O$^-$. To further investigate the thermodynamics for different POWS performances on TiO$_2$-based photocatalysts, different phases of TiO$_2$ were also characterized by the recently reported transient infrared absorption-excitation energy scanning spectroscopy (TRIRA-ESS), which can identify deep trapped electron energy levels above the valence band (VB) but below the Fermi level of the trapped electrons, the corresponding integrated density of the states, and the shallow trapping energy level below the conduction band.$^{33,36}$ The TRIRA-ESS results shown in Fig. 5a can be divided into two regions: one below the Fermi-level of the trapped electrons (i.e., from 0 to 1.79 eV) arising from the trapping states above the VB, and another region above the Fermi-level of the trapped electrons but below the conduction band (CB) originating from the shallow trapping states. There are remarkable differences between anatase and rutile TiO$_2$ in the region below the Fermi-level of the trapped electrons (denoted as $E_{ps}$, which is different from the Fermi level of free electrons in the...
CB denoted as $E_{\text{CB}}^{37}$, namely, there are deep trapped states obviously observed in the anatase TiO$_2$ that are not present in the rutile TiO$_2$. The TRIRA-ESS for brookite TiO$_2$ was also performed, which shows similar deep trapped states with anatase TiO$_2$ (Fig. S8, ESI†). It can be speculated that the lack of O$_2$ evolution for anatase and brookite TiO$_2$ in the initial stage of the reaction is possibly due to the trapped states that are present in the bulk and surface regions. These states could reduce the overpotential for water oxidation.

Because the photocatalytic performance of anatase TiO$_2$ changed after long exposure to UV light irradiation, the anatase TiO$_2$ film was pre-treated under different conditions for TRIRA-ESS characterization. As shown in Fig. 5b, the trapped states with their energy levels close to the VB are nearly unchanged after saturated with water vapor, only the integrated densities of states are slightly increased. However, when anatase TiO$_2$ was treated with UV-laser irradiation, the trapped states were completely removed within the scanning excitation laser wavelength indicating that light irradiation can indeed change the deep trapped states near the VB of anatase TiO$_2$. Furthermore, we also conducted the Mott–Schottky analysis for all three kinds of TiO$_2$ before and after the UV light irradiation, indicating that the conduction band (CB) positions were not changed after light treatment (Fig. S9, ESI†). From the TRIRA-ESS study, we can conclude that the deep trapped states can only be detected for anatase TiO$_2$ and UV-laser irradiation can remove the deep trapped states, which corresponds to the unique photocatalytic performance for anatase TiO$_2$.

To confirm the above results, we conducted photocatalytic water oxidation with anatase and rutile TiO$_2$ pre-treated under UV light irradiation. Anatase and rutile TiO$_2$ were first irradiated for different times and then used for water oxidation reactions using AgNO$_3$ as the electron acceptor. As listed in Table S2 (ESI†), anatase TiO$_2$ shows a remarkable enhancement in O$_2$ evolution with increasing irradiation time. In fact, the photocatalytic O$_2$ evolution activity of anatase TiO$_2$ pre-irradiated for 8 hours is 4 times that of the untreated sample (entries 1–3). However, rutile TiO$_2$ shows nearly no difference regardless of the irradiation time (entries 4–6). It indicates that the trapped states in anatase TiO$_2$ can be quenched by light irradiation, consequently resulting in the different performances for water oxidation, which is in good agreement with the TRIRA-ESS result.

Based on the above results, we can conclude that the existence of deep trapped states near the VB level of TiO$_2$ is directly responsible for the POWS behaviors for different phases of TiO$_2$. A schematic description of deep trapped states for anatase and rutile TiO$_2$ is shown in Fig. 5c. A plausible explanation is that the deep trapped states located above the VB of anatase TiO$_2$ can reduce the potential of photogenerated holes that are produced during the photocatalytic reaction. When these trapped states are gradually removed by UV light irradiation, the overpotential for water oxidation is increased and O$_2$ is produced subsequently. However, the rutile TiO$_2$ sample does not have trapped states above the VB level, so that it has enough potential to drive the proton reduction and water oxidation reactions even without light treatment. It should be pointed out that the photocatalytic water oxidation on TiO$_2$ can be ascribed to thermodynamics and kinetics, both of which are closely related but not separated to each other. The presence of deep trapped states near the valence band of anatase and brookite TiO$_2$ reduce the overpotential for water oxidation, so that the photogenerated holes are more preferable to oxidizing the H$_2$O molecule to produce the *OH radical. This process is a 2-electron-process, which requires less potential than a 4-electron-process to produce O$_2$ directly. The UV light irradiation with high intensity can gradually reduce the deep trapped states near the valance band of anatase and brookite TiO$_2$, so that the overpotential for water oxidation is increased, and simultaneously leads to the result that H$_2$O can be oxidized by the 4-electron-process to produce O$_2$.

A DFT calculation was also done to simulate the water oxidation process on anatase, rutile and brookite TiO$_2$ (Fig. S10, ESI†). The adsorption energy of H$_2$O onto the anatase(101) surface is calculated to be 0.55 eV, and the first O–H dissociation energy is endothermic by 0.34 eV with a barrier of 0.73 eV. As for the product of this step, the H atom is adsorbed onto the O$_{2c}$ atom, and the OH group is left to attach to the Ti$_{5c}$ atom to form a surface-adsorbed hydroxyl radical. The second O–H dissociation step to produce an O atom is predicted to be endothermic by 0.43 eV, with a barrier of 0.62 eV. For the molecular adsorption of water onto the rutile(110) surface, the calculated adsorption energy for H$_2$O is exothermic by 0.73 eV, and the first O–H dissociation energy is 0.14 eV with a low barrier of 0.23 eV. The second O–H dissociation step is computed to be exothermic by 0.36 eV, with a barrier of 0.45 eV. The calculated adsorption energy for H$_2$O onto the brookite(210) surface is exothermic by 0.36 eV, and the first O–H dissociation energy is 0.25 eV. All the energies on brookite(210) are larger than that of the rutile(110).
surface, which may be attributed to their different photocatalytic performances. The theoretical calculation results suggest that the water decomposition reaction on the rutile(110) surface is more favorable than that on the anatase(101) and brookite(210) surfaces both thermodynamically and kinetically.

It is worth noting that the surface structures of photocatalysts may be reconstructed under light irradiation. It was reported that anatase TiO\(_2\) will form a disordered layer with two monolayer thickness upon irradiation of high intensity UV light.\(^3\) Therefore, it is possible that the surfaces of anatase and brookite TiO\(_2\) may be reconstructed to a quasi-rutile phase surface after prolonged irradiation, which would not only make less trapping states and improve the capability of water oxidation, but also produce more stable and favorable intermediates for the activation of H\(_2\)O molecule.

In conclusion, we report that the POWS reaction can take place on rutile but hardly on anatase and brookite TiO\(_2\). However, the POWS on anatase and brookite TiO\(_2\) become feasible under prolonged UV light irradiation. The POWS performances for different phases of TiO\(_2\) are determined by both kinetics and thermodynamics. Kinetically the process of photocatalysis differs on different phases of TiO\(_2\) due to the intermediates (\(\cdot OH\) radical for anatase and brookite TiO\(_2\), peroxy species for rutile TiO\(_2\)) that are formed. Thermodynamically there are many trapped states lying near the VB of anatase and brookite TiO\(_2\), which reduce the overpotential for water oxidation. These trapped states can be gradually removed by the irradiation of high intensity UV light, such that the POWS reaction can take place finally. Our work will be instructive for understanding the mechanisms for photocatalytic water splitting and shed light on why many semiconductors cannot achieve the POWS despite having thermodynamically suitable band structures for proton reduction and water oxidation reactions.

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