Photocatalysis Hot Paper

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The Nature of Photocatalytic "Water Splitting" on Silicon Nanowires**

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Abstract: *Silicon should be an ideal semiconductor material if it can be proven usable for photocatalytic water splitting, given its high natural abundance. Thus it is imperative to explore the possibility of water splitting by running photocatalysis on a silicon surface and to decode the mechanism behind it. It is reported that hydrogen gas can indeed be produced from Si nanowires when illuminated in water, but the reactions are not a real water-splitting process. Instead, the production of hydrogen gas on the Si nanowires occurs through the cleavage of Si–H bonds and the formation of Si–OH bonds, resulting in the low probability of generating oxygen. On the other hand, these two types of surface dangling bonds both extract photoexcited electrons, whose competition greatly impacts on carrier lifetime and reaction efficiency. Thus surface chemistry holds the key to achieving high efficiency in such a photocatalytic system.*

Utilizing solar energy to split water and produce hydrogen is an ultimate goal for the supply of clean and sustainable energy. The high natural abundance of silicon together with its high fabrication processability and excellent efficiency in photoelectrical conversion are reasons for its promising role in the utilization of solar energy. For this reason, Si nanowires have been employed as the semiconductor material toward hydrogen fuel production such as photoelectrochemical (PEC) water splitting.[1,2] In comparison with the PEC process, direct photocatalysis is a simpler and less expensive approach to hydrogen production as it eliminates the need for a conducting substrate and applied bias despite its lower efficiency of charge separation.[3] In terms of direct photocatalysis, Si nanowires have extensively demonstrated their use in dye degradation[4–8] and palladium-catalyzed organic reactions including Heck coupling, hydrogenolysis, hydrosilylation, and C–H bond functionalization.[9] Theoretical simulations have also indicated that Si nanowires should be a promising photocatalyst for direct water splitting,[10] yet its feasibility needs experimental validation. Like the TiO_2 system that has been intensively investigated,[11–13] it is imperative to closely examine the mechanisms for surface charge behavior and reactions and to understand the nature of water splitting on the Si nanowires before the research community may move forward to realistic applications.

Herein, we report the exploration of water splitting on Si nanowires by performing measurements in pure water under light illumination. The Si nanowires (Supporting Information, Figure S1) are fabricated from Si wafers by metal-assisted etching,[14–16] and thus are supported on the wafers so that they can be facilely separated from solution after photocatalysis enabling the recycling use of photocatalysts. In the fabrication of Si nanowires, hydrofluoric acid (HF) is the most frequently used chemical which can efficiently remove oxide layer to ensure clean Si surface as well as form the SiF_6^{2-} complex to facilitate the Si etching.[14,15] The involvement of HF in Si nanowire fabrication inevitably leaves Si–H bonds on surface, which has been shown to advantage the photocatalysis on Si nanowires.[4,6,17] There is a simple prevailing assumption that the H atoms on Si surface are electron-deficient and may serve as an electron sink to improve charge separation.[4] While agreeing on this plausible explanation, we still need to look into the mechanisms behind at the levels of carrier kinetics and molecular interactions. Photocatalysis is a dynamic process involving formation and cleavage of chemical bonds, so the dependence of photocatalytic activity on surface bonds (not limited to Si–H) may be the dynamic interplay of charge distribution and surface reactions.

We demonstrate by systematic characterizations and simulations that the Si–H traps photoexcited electrons from bulk Si, and meanwhile, the Si–OH formed during photocatalysis competes with the Si–H on the electron extraction, greatly impacting on the efficiency of hydrogen production. More importantly, it turns out that the production of hydrogen gas on Si nanowires occurs through the cleavage of Si–H bonds and the formation of Si–OH bonds, resulting in the low probability of generating oxygen. In other words, the water reactions on Si nanowires are not a real water splitting process.

In our studies, we first carry out photocatalysis by immersing Si nanowires in pure water under full-spectrum irradiation. The reactions indeed produce H_2 gas from the system with apparent quantum efficiency (AQE) of 1.2–1.7% at incident light wavelengths of 350–550 nm (Supporting Information, Table S1); however, the ratio of produced H_2 to O_2 is far above 2, the number anticipated for water splitting (Figure 1a). Given that the amount of O_2 gas is double

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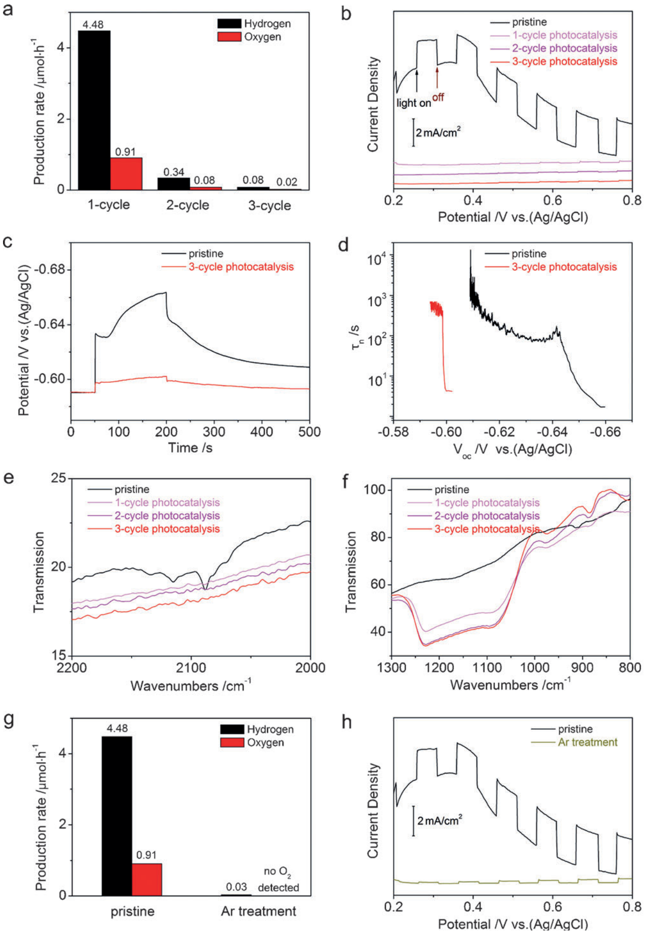

Figure 1. a) Photocatalytic H_2 and O_2 production from pure water under full-spectrum irradiation for 4 h using Si nanowires in different cycles. b) Photocurrent vs. potential responses of photoelectrodes made of the Si nanowires after different photocatalysis cycles. c) Transient OCVD from pristine Si nanowires and those after the third photocatalysis cycle. d) Average lifetime of the photogenerated carriers (τ_n) obtained from the OCVD. IR spectra of the Si nanowires after different photocatalysis cycles at e) 2200–2000 cm^{-1} and f) 1300–800 cm^{-1}. g) Photocatalytic H_2 and O_2 production and h) photocurrent vs. potential responses by the Si nanowires treated with Ar, with respect to the pristine Si nanowires. The "pristine Si nanowires" refer to those obtained directly after metal-assisted HF etching that contain Si–H bonds.

confirmed by gas chromatography (GC) thermal conductivity detector (TCD) and oxygen sensor, this reliable result indicates that the production of H_2 may not take place along a conventional water-splitting process. Moreover, the measurements clearly show that the photocatalytic activity dramatically decays as the reactions proceed to the third cycle. As light absorption has not been altered in different cycles, the activity reduction is most likely related to efficiency of charge separation or surface reactions. We thus have collected photocurrents from the Si nanowires after different photocatalytic cycles that are believed to offer an informative evaluation for the efficiency of electron–hole separation. As shown in Figure 1 b, the photocurrents of Si nanowires are reduced by one order of magnitude after the first cycle of photocatalysis and continue decreasing as the photocatalysis proceeds (see the Supporting Information, Figure S2 for resolving the small photocurrents for 1–3 cycle samples), suggesting the sustantial reduction of charge separation efficiency. To support this argument, we measure transient open-circuit voltage decay (OCVD, Figure 1 c) on the Si nanowires that has been demonstrated as a way to resolve charge kinetics.[18–20] As revealed by the OCVD characterizations (Figure 1 d), the average lifetime of photogenerated carriers has been dramatically shortened by about one order of magnitude.

We are now in a position to address a fundamental question: what change occurring at the Si nanowires results in this performance decay? As X-ray diffraction does not indicate any phase or composition change in bulk Si, we then look into the surface chemistry by employing Fourier-transform infrared (IR) spectroscopy. The pristine Si nanowires that are obtained directly after metal-assisted HF etching contain Si–H on the surface, according to the Si–H stretching band at 2115–2088 cm^{-1} (Figure 1 e)[21–25] and its feature band at 908 cm^{-1} under scissors mode (Figure 1 f).[22] As the photocatalysis proceeds (Supporting Information, Figure S3), the Si–H vibrational peaks vanish while the bands at 978 cm^{-1},[23,26] 800 cm^{-1}[24] and 875 cm^{-1}[22,27] responsible for Si–OH stretching gradually arise. Meanwhile, a broad band at 1225–1080 cm^{-1} that can be assigned to Si–O vibrations[22–27] has also been observed along with the emergence of Si–OH. To further confirm the relevance of charge separation and photocatalytic activity to Si–H and Si–OH, we have employed Ar cleaning to treat the pristine Si nanowires in reactive ion etching (RIE) which can selectively remove Si–H but does not produce Si–OH (as indicated by IR spectroscopy; Supporting Information, Figure S4). Thus such a treatment can generate bare Si surface in the absence of dangling bonds. As shown in Figure 1 g, the bare Si surface almost does not undergo photocatalytic reactions, although the bare Si nanowires exhibit detectable photocurrents (Figure 1 h; Supporting Information, Figure S5). Interestingly, the carriers photogenerated on the Si–OH surface (after photocatalysis; Figure 1 d) have a longer lifetime than those on bare Si nanowires (Supporting Information, Figure S6) despite their lower photocurrents. Taken together, this set of results indicate three key points which provide clues for investigating mechanisms: 1) the Si–H surface not only facilitates charge separation to ensure long carrier lifetime, but offers high activity of producing H_2 and O_2 at a ratio of over 4; 2) the Si–OH helps separate photogenerated charges to some extent but does not yield photocurrents or produce H_2/O_2; and 3) the bare Si surface almost cannot produce H_2/O_2.

To elucidate why the dangling bonds on the Si surface have so complicated implications in photocatalysis, we have employed first-principles investigations on various Si surfaces.[28–30] As indicated by the differential charge density for Si surfaces with or without dangling bonds, both Si–H (Figure 2 a and b) and Si–OH (Figure 2 c and d) can extract electrons from the bare Si surface, facilitating the separation of photoexcited electrons from holes. For this reason, the nanowires with Si–H or Si–OH on the surface exhibit longer carrier lifetimes than the bare Si. On the other hand, Si–H and Si–OH would constitute a competition on the electron

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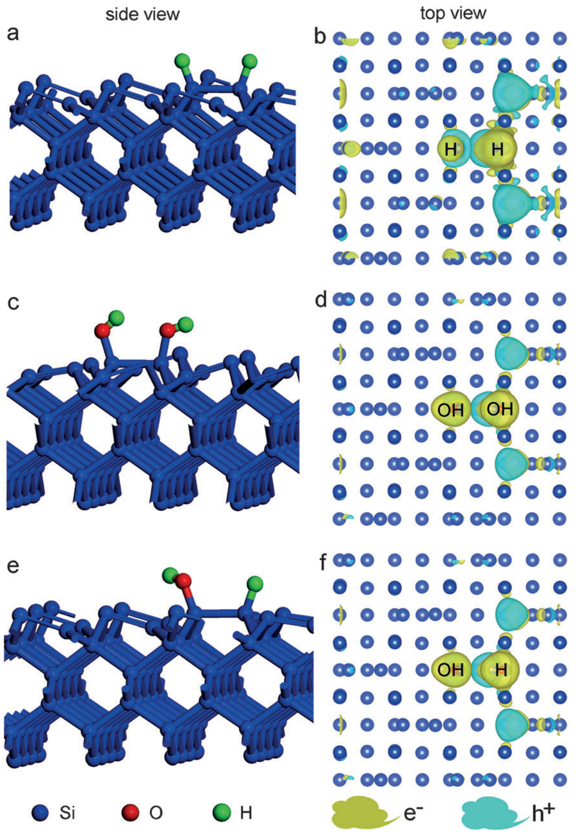

Figure 2. Theoretically optimized models (left column) and differential charge density by first-principles simulations (right column): Si surface with a,b) Si–H only; c,d) Si–OH only; and e,f) both Si–H and Si–OH.

extraction when both are present on the nanowire surface (Figure 2e and f).

Upon recognizing the function of surface bonds in electron trapping, we looked into possible reaction mechanisms occurring on various Si surfaces. We first simulated the adsorption and dissociation of water molecules on Si–H, Si–OH, and a bare Si surface (Supporting Information, Figure S7). According to the obtained adsorption energies (Supporting Information, Table S2), we determine that the dissociation of water prefers to taking place on the bare Si (Figure 3a). The Bader charge analysis based on first-principles simulations suggests that each bare Si atom can accommodate about 0.03 h^+ photogenerated charge, which greatly improves the adsorption of H_2O onto Si. Upon receiving holes, the Reaction (a) would generate Si–OH surface and release H^+ via oxidation. This explains well why the Si–OH bonds gradually form as the photocatalytic reactions proceed. The released H^+ cations are supposed to pick up photoexcited electrons for the reduction. Depending on the locations, Si–H or Si–OH, where the H^+ cations receive the electrons, they undergo Reaction (b) or Reaction (c), respectively. In the case of Reaction (b) (Figure 3b), the reduced H^+ would take H atoms off of the Si surface to produce H_2. However, if Reaction (c) occurs (Figure 3c), the H^+ would form a new H_2O molecule with the OH group on the Si surface during the reduction. Thus Reaction (c) would suppress the production of H_2, and together with the Reaction (a), behaves like electron–hole recombination on surface. As a result, the Si–OH surface does not produce H_2 or yield photocurrents, although the lifetime of photogenerated carriers in bulk can be prolonged by the electron extraction of surface Si–OH. From the reaction mechanism, it can also be easily recognized that bare Si surface should be incapable of producing H_2, as the surface will directly turn into the system of Si–OH once the Reaction (a) starts. Given that both the Si–H and Si–OH extract electrons, Reaction (c) actually forms a competition with Reaction (b) and reduces the efficiency of producing H_2. For this reason, the hydrogen production activity decays as Si–H is gradually replaced by Si–OH during photocatalysis. From the photocurrent test on pristine Si nanowires (Figure 1b), it can be seen that distinct background current at low-potential region that may originate from hydrogen production by Reaction (b), which indicates that hydrogen production can easily occur on pristine Si nanowires. Along with photocatalysis, Si–H dangling bonds are gradually replaced by Si–OH, which makes the hydrogen production more difficult so that this background current disappears.

Then the next question would be: how is the oxygen gas generated in the system of Si nanowires? The answer to this fundamental question may explain why the ratio of produced H_2 to O_2 is above 2, the stoichiometric ratio of conventional water splitting. It was proposed that the production of oxygen gas from water splitting works through the following reactions:[31]

$$h^+ + H_2O \rightarrow OH + H^+ \tag{1}$$

$$h^+ + OH \rightarrow O + H^+ \tag{2}$$

$$h^+ + O + H_2O \rightarrow OOH + H^+ \tag{3}$$

$$h^+ + OOH \rightarrow O_2 + H^+ \tag{4}$$

We thus simulate the Reaction (2) on Si surface (Reaction (d), Figure 3d). It shows that the transition energy barrier of Reaction (d) ($E_a = 9.47$ eV) is significantly higher than others, demonstrating the difficulty of producing O_2. This feature essentially makes the obtained H_2/O_2 ratio far beyond 2. Nevertheless, the Bader charge analysis reveals that the Si atom of a Si–OH dangling bond on the surface (mainly coming from Reaction (a)) can hold about 0.02 h^+ photogenerated charge, which facilitates the process of Reaction (d) (see Note I in the Supporting Information for details). In particular, the reduction Reaction (b) effectively consumes protons from the oxidation reactions above and therefore suppresses any reverse reactions for water splitting, such as Reaction (c). As a result, many Si–OH dangling bonds can be preserved for the generation of oxygen, working through Reaction (d) despite its relatively high reaction barrier. On the other hand, the OH groups in Si–OH can compete with Si–H in extracting photogenerated e^- charges (see Figure 2c and d). Thus although the Si–OH dangling bonds are needed for the oxidation reaction to produce O_2, excessive Si–OH may cause reverse reaction for water splitting (that is, Reaction (c)), lowering the resulted O_2/H_2 ratio.

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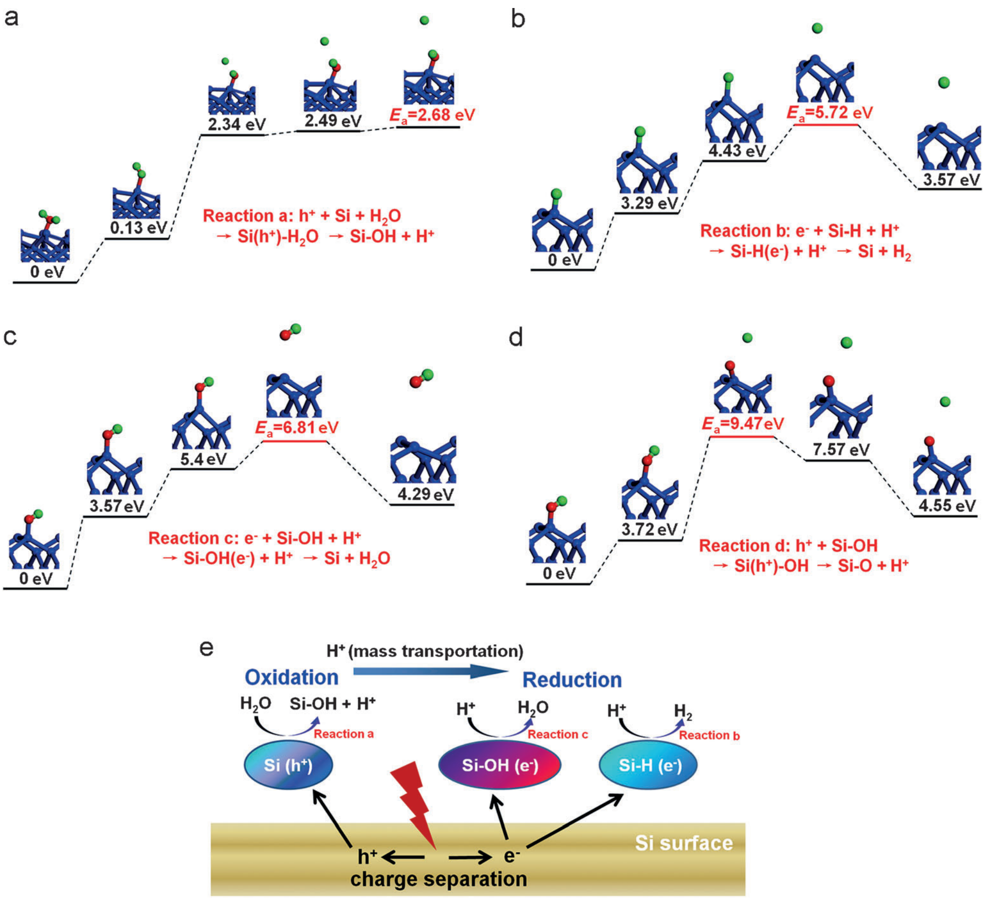

Figure 3. a–d) Energy profiles of each elementary step in 4 key half redox reactions that may occur at various Si surfaces, depicted by first-principles simulations. e) The overall reaction mechanisms that are mainly responsible for photocatalytic hydrogen production on Si surface.

Taken together, we can conclude that the pristine Si nanowires mainly undergo the following reactions owing to the presence of Si–H:

$$\text{Oxidation: } h^+ + Si + H_2O \rightarrow \text{Si-OH} + H^+ \qquad (a)$$

$$\text{Reduction: } e^- + Si{-}H + H^+ \rightarrow Si + H_2 \qquad (b)$$

The production of O_2 takes place along a way of:

$$\text{Oxidation: } h^+ + \text{Si-OH} \rightarrow \text{Si-O} + H^+ \qquad (d)$$

Once the Reaction (a) proceeds to a certain extent, the resulted Si–OH would prefer to hosting the Reaction (c) and suppressing the production of H_2:

$$\text{Reduction: } e^- + Si{-}OH + H^+ \rightarrow Si + H_2O \qquad (c)$$

Given the competition between Si–H and Si–OH (Figure 3e), surface engineering should serve as a versatile tool to maneuver the photocatalytic activity in H_2 production. To test this capability, we have used Ar-treated bare Si nanowires as a model to perform surface engineering. As expected,[6,17] HF treatment can effectively recover Si–H bonds on surface (Supporting Information, Figure S8). The newly formed Si–H backs up the activity of H_2 production (Figure 4a) and the efficiency of charge separation (Figure 4b; Supporting Information, Figure S9), further confirming the functions of Si–H in our system. Certainly along with further photocatalytic reactions, Si–H would still be replaced by Si–OH, resulting in performance decay (Figure 4a–d; Supporting Information, Figure S10). To explore the possibility of recovering the performance, we have also attempted to treat the sample after photocatalysis with HF. It turns out that the H_2 production activity (Figure 4e) and charge separation (Figure 4f; Supporting Information, Figure S11) can indeed be improved. As indicated by IR spectroscopy (Figure 4g,h; Supporting Information, Figure S12), the HF treatment recovers Si–H bonds as well as removes Si–OH from the surface, responsible for the performance improvement. It is worth pointing out that HF is a well-known chemical effective for etching silicon dioxide[6,17] whereas HCl nearly cannot work (Supporting Information, Figure S13 and S14). Although HF can promote photocatalytic activities in both cases (that is, Figure 4a and e), H_2/O_2 ratio varies a lot on the Si nanowires with different treatments. The Ar cleaning creates bare Si surface, followed by the recovery of Si-H by HF treatment. It has been demonstrated that the existence of Si–H helps H_2 production while the generation of O_2 needs Si–OH. For this reason, the absence of Si–OH dangling bonds results in the difficulty of producing O_2 in photocatalysis whereas the capability of H_2 production can be resumed (Figure 4a). In contrast, photocatalysis produces tremendous amounts of Si–OH on surface through Reaction (a). Although the HF treatment may replace most Si–OH dangling bonds by Si–H, some of the Si–OH bonds would be inevitably left on Si nanowires. As a result, the treated Si nanowires exhibit good activity in generating O_2; however, the H_2 production rate cannot be completely recovered (Figure 4e). This comparison also informs us that Ar and HF treatments should be a better approach to recovering the H_2 production activity of Si nanowires.

In summary, we have decoded the nature of photocatalytic hydrogen production on Si nanowires. The majority of this process does not undergo the pathway of conventional water

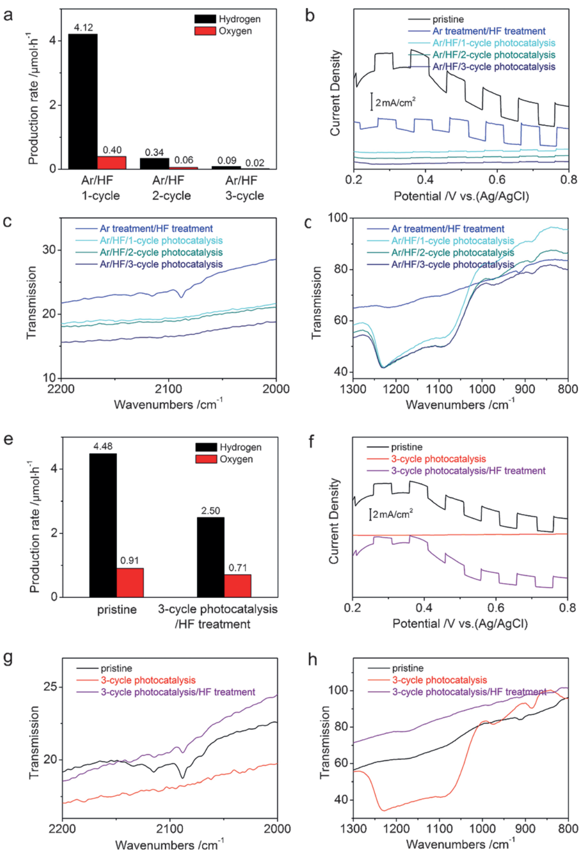

Figure 4. a) Photocatalytic H_2 and O_2 production from pure water under full-spectrum irradiation for 4 h in different cycles, using the Si nanowires that were pre-cleaned with Ar and then treated with HF. b) Photocurrent versus potential responses of photoelectrodes made of the Si nanowires in (a), in reference to pristine Si nanowires. IR spectra of the Si nanowires in (a) at c) 2200–2000 cm^{-1} and d) 1300–800 cm^{-1}. e) Photocatalytic H_2 and O_2 production from pure water under full-spectrum irradiation for 4 h, using the Si nanowires that first underwent three-cycle photocatalysis and then were treated with HF, in reference to pristine Si nanowires. f) Photocurrent versus potential responses of photoelectrodes made of the Si nanowires in (e). IR spectra of the Si nanowires in (e) at g) 2200–2000 cm^{-1} and h) 1300–800 cm^{-1}.

splitting, and instead occurs through cleavage of Si–H and formation of Si–OH bonds. As such, this work demonstrates that surface chemistry matters to photocatalysis, in terms of both charge behavior and surface reactions that mostly interact with each other. More insights are thus needed to put into surface engineering for synergizing charge migration with species activation. As elucidated here, the highlighted system behaves like the reactions mediated by Si–H along the pathway of $Si(h^+) + Si{-}H(e^-) + H_2O \rightarrow Si{-}OH + Si + H_2$. To suppress the side reaction of Si–OH substantially consuming photoexcited electrons, the Si surface has to be recovered with effective etchants such as HF. Si is the most naturally abundant and processable semiconductor thus far, so it holds promise for photocatalytic applications. In particular, Si is a typical material full of surface chemistry,[32] providing us the opportunities of engineering its surface toward efficient photocatalytic hydrogen production. From the AQE measurements, one can see that the solar-to-chemical conversion efficiency of silicon nanowires is comparable to those of many other visible-light photocatalysts; however, we have to point out that the performance decay along with the surface bonding changes would be an issue to limit their realistic applications. To recover their activities, Ar and HF co-treatments would be a promising solution. It is anticipated that the impact of surface chemistry on solar energy conversion is not limited to photocatalytic water splitting and can be applied to other applications including PEC and pollution remedy. It is known that the photocatalytic degradation of dye molecules works through the generation of hydroxyl and superoxide radicals,[33] and thus the oxygen species should also have interactions with catalyst surface. This work thus opens a new window to rationally designing photoactive materials for various reaction systems.

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