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Highly mobile and reactive state of hydrogen in metal oxide semiconductors at room temperature

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Hydrogen in metal oxides usually strongly associates with a neighboring oxygen ion through an O-H bond and thus displays a high stability. Here we report a novel state of hydrogen with unusually high mobility and reactivity in metal oxides at room temperature. We show that freshly doped hydrogen in Nb₂O₅ and WO₃ polycrystals via electrochemical hydrogenation can reduce Cu²⁺ ions into Cu⁰ if the polycrystals are immersed in a CuSO₄ solution, while this would not happen if the hydrogenated polycrystals have been placed in air for several hours before the immersion. Time-dependent studies of electrochemically hydrogenated rutile single crystals reveal two distinct states of hydrogen: one as protons covalently bonded to oxygen ions, while the other one is highly unstable with a lifetime of just a few hours. Observation of this mobile and reactive state of hydrogen will provide new insight into numerous moderate and low temperature interactions between metal oxides and hydrogen.

Hydrogen has been attracting extensive research interests aiming at exploring its versatile behaviors in crystalline solids^{1,2}. Usually being introduced into metal oxides via annealing in H₂ or H₂O-containing atmospheres at elevated temperatures, many interesting, yet sometimes quite complicated features of hydrogen in metal oxides have been revealed^{3–5}. They are meaningful for understanding hydrogen incorporated into metal oxides at high temperatures. However, metal oxide semiconductors usually interact with hydrogen at lower or even room temperature in their hydrogen-related applications, such as hydrogenation catalysis⁶, hydrogen storage^{7,8}, and low-temperature hydrogen sensing⁹. It is well known that the interaction between metal oxides and hydrogen strongly depends on the reaction temperature. For instance, the reaction of MO₃ (M = W or Re) with molecular hydrogen at 500 °C leads to the formation of MO₂, while that with dissociated hydrogen at room temperature forms hydrogen bronze H_xMO₃¹⁰. It is thus doubtful that the properties of hydrogen obtained from high-temperature hydrogen-doped metal oxides are adequate for understanding low-temperature hydrogen-related applications of metal oxide semiconductors. As a matter of fact, some investigations have indicated some very puzzling behaviors of hydrogen incorporated into metal oxides at moderate and low temperatures^{8,11,12}, and some unusually unstable behaviors have also been observed for hydrogen in those low-temperature hydrogen-related applications of metal oxide semiconductors, yet so far our understanding of these behaviors is very limited¹³.

It is thus highly desirable to study metal oxides with hydrogen introduced at low, and if possible, room temperature. Electrochemical hydrogenation through electrolysis of water has been found to be a facile method to dope hydrogen at room temperature into a number of metal oxides, such as TiO₂, Nb₂O₅, WO₃, BaTiO₃ and Pb(Zr,Ti)O₃^{14–18}. In this article, we will present some novel findings with regards to the behaviors of hydrogen in metal oxides obtained through this room temperature hydrogen doping method. In “freshly” hydrogenated Nb₂O₅ and WO₃ polycrystals, a portion of the doped hydrogen apparently exists in a highly mobile and reactive state: a copper layer was deposited on the hydrogenated sample when it was immersed in CuSO₄ solution immediately after hydrogenation, while the copper layer would not form if the hydrogenated sample had been aged for ten hours before the immersion. By electrochemically doping hydrogen into TiO₂ (001) rutile single crystals, we found a wide step appeared at the low angle side of the (002) peak in X-ray diffraction (XRD); the step quickly narrowed and disappeared in a few hours while the distorted (002) peak (due to hydrogen insertion) would slowly recover over hundreds of hours, and the stretch mode of O-H bond was observed by infrared spectroscopy. These contrasts demonstrate two distinct states of hydrogen: one as protons covalently bonded to



oxygen ions, while the other one being highly mobile and reactive, probably as isolated protons “free” to move in the oxide lattices.

Results

As illustrated in Fig. 1a, we electrochemically hydrogenated an Nb_2O_5 ceramic pellet for 24 h; the white color turned into deep blue due to the incorporation of hydrogen in the oxide lattices¹⁵. After that, we immediately immersed the pellet in a 0.5 M CuSO_4 solution for 10 min at room temperature. Surprisingly, we observed a reddish layer appeared on the pellet surface, as shown in Fig. 1b. In contrast, if the hydrogenated pellet (another sample) was placed in air for 10 h at room temperature and then immersed in the CuSO_4 solution, no such layer was deposited though it was still deep blue after 10 h of aging. XRD analysis reveals that the reddish layer is copper as shown in Fig. 1c, and the diffraction peaks of the Cu are much stronger than those of the Nb_2O_5 ceramics. Since Nb_2O_5 by itself could not reduce Cu^{2+} ions as shown in Fig. 1b, the only possible route of the formation of Cu is the reduction of Cu^{2+} by hydrogen from the hydrogenated Nb_2O_5 . What should be emphasized is that in just 10 min the

pellet surface was covered by a thick copper layer, indicating that a relatively large amount of doped hydrogen exists in a highly mobile and reactive state, which could diffuse out of the Nb_2O_5 and react with Cu^{2+} at the surface. The high mobility and reactivity also imply a short lifetime of such hydrogen, and after 10 h of aging they almost disappeared from the oxide lattices so no copper was deposited on the aged pellet during the immersion.

Nb_2O_5 is not the only oxide that can accommodate such highly mobile and reactive hydrogen. Indeed copper was also found to be deposited on a 24 h electrochemically hydrogenated WO_3 pellet when it was immersed in 0.5 M CuSO_4 solution for 10 min immediately after the hydrogenation, but the amount was much less than that formed on similarly hydrogenated Nb_2O_5 (see the XRD pattern in Fig. 1c). As a large amount of hydrogen can be electrochemically inserted into WO_3 , it is strange that only a little portion of inserted hydrogen seems to exist in the mobile and reactive state so the amount of deposited copper was very small. These results suggest that this special state of hydrogen may be not rare among metal oxides, while its concentration can be dramatically different among different metal oxides.

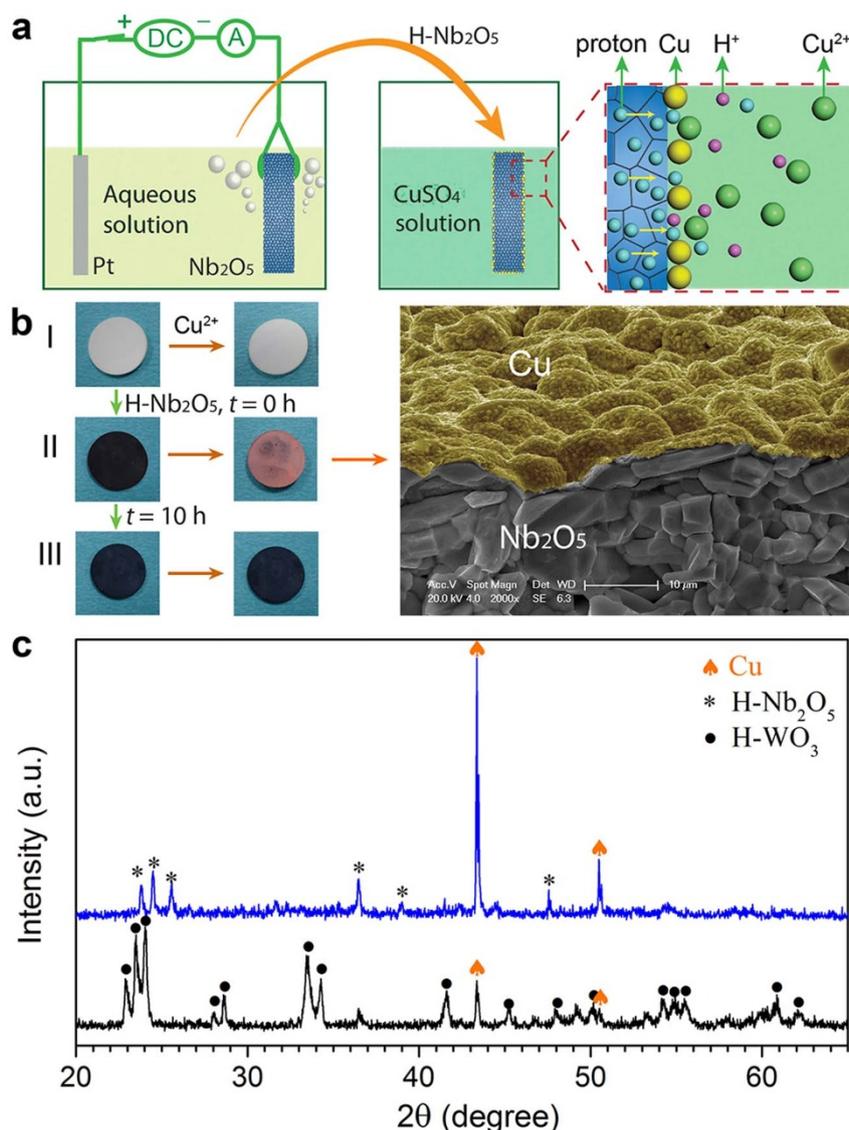


Figure 1 | Highly reactive hydrogen in hydrogenated oxides. (a), Schematic of electrochemically hydrogenating an Nb_2O_5 ceramic pellet and then immersing it into a 0.5 M CuSO_4 solution at room temperature. (b), Optical images of Nb_2O_5 pellets before and after being immersed in 0.5 M CuSO_4 solution for 10 min: I. an as-sintered sample, II. a hydrogenated sample, III. a hydrogenated and 10 h-aged sample. The right side is a scanning electron microscopy image taken over the cross-section of an immersed sample. The Cu layer is shown with a false color. c, XRD pattern taken on the surface of the hydrogenated Nb_2O_5 pellet after 10 min immersion. A pattern taken on the surface of a hydrogenated WO_3 pellet after 10 min immersion is also shown.



We expect that it should be possible to reveal a more detailed evolution of this unstable hydrogen in metal oxide single crystals. As Nb_2O_5 and WO_3 single crystals are not available, we turned to TiO_2 rutile single crystals to conduct time-dependent study. These single crystals have nearly perfect crystal lattices that can eliminate the influence of crystal defects to doped hydrogen. For some metal oxides, phase transformation or crystal reformation occurs upon the hydrogen doping¹⁶. In this study, although we have tried to insert as much hydrogen as possible into the rutile single crystals, no new phases could be detected through XRD. Instead, the lattice of the rutile single crystals was found to be distorted to an extent beyond expectation when much hydrogen was inserted. Figure 2a shows XRD patterns of a hydrogenated rutile single crystal measured at different aging times, t , after 200 h of electrochemical hydrogen insertion. The (002) peak of as-received single crystals is sharp and

highly symmetric (see the inset). In contrast, the (002) diffraction peak of the hydrogenated crystal becomes broad and is distorted to a very irregular shape, indicating non-uniform plane spacing or hydrogen distribution. An important observation is that there exists a wide step at the low angle side of the peak for short aging times, e.g., at 62.42° as indicated by the triangle for $t = 0.3$ h. We note that while the specific shape of the (002) peak could vary depending on the hydrogen insertion time, the broadening of the peak and the arising of a wide step always occur (see Supplementary Information, Fig. S1). Chester and Bradhurst have electrochemically inserted hydrogen into vacuum-reduced rutile single crystals and found that the hydrogen concentration gradient was much higher in the first few microns of the surface layer than in the bulk region (~ 100 μm deep)¹⁹. The wide step revealed in our study can be well explained in term of this layered structure: the concentration of hydrogen is particularly high at the surface, where the plane spacing is expanded by 0.54% at $t = 0.3$ h compared to that of the undoped (002) plane, while at the same time the expansion of the inner layer in the bulk region is only 0.16% as indicated by the distorted peak.

The XRD patterns further reveal that the distortion evolved with the aging time by placing the hydrogenated crystals in air at room temperature, indicating that the distorted crystal lattice as well as the layered structure subsequently experiences a spontaneous and systematic restoration as shown in Fig. 2b. The lattice expansion, Δd , of the hydrogenated crystal decreases exponentially by

$$\Delta d = \Delta d_0 \exp(-t/\tau), \quad (1)$$

where Δd_0 is the initial lattice expansion and τ is a decay constant. For the case of the wide step, $\Delta d_0 = 0.58\%$ and $\tau = 3$ h, indicating that the layered structure exists only for a few hours in our sample after the hydrogen insertion, and thus the hydrogen in the layer is highly mobile. In contrast, it takes longer aging time for the distorted peak to restore to the original state. The distorted (002) peak in Fig. 2a gradually decreases in width, and increases in height and symmetry following the eq. 1 with $\Delta d_0 = 0.17\%$ and $\tau = 39$ h. After an aging time of $t = 150$ h, the peak has almost restored to its original highly sharp and symmetric shape. Spontaneous recovery was also observed for other initial distortions (Supplementary Information, Fig. S2). These two dramatically different decay constants exactly reflect the obvious difference in mobility observed for the step and the peak. The difference suggests that hydrogen in the surface layer is not only of a higher concentration but also much more mobile than that in the bulk region, so there exist two distinct states of hydrogen with different mobilities in these electrochemically hydrogenated rutile single crystals. This is consistent with the observations that only the “freshly” hydrogenated Nb_2O_5 and WO_3 polycrystals could reduce Cu^{2+} ions but those aged samples could not. In other words, highly unstable hydrogen has been observed in all these three metal oxides that were investigated in this study, although its concentration is dramatically different in different metal oxides.

Figure 3 shows infrared absorption spectra measured at 300 K for a rutile single crystal that has been electrochemically hydrogenated for 120 h and an as-received rutile single crystal. The as-received rutile single crystals are colorless and almost transparent without clear absorption peak in the range of $3100\text{--}3400$ cm^{-1} that is common for as-grown rutile single crystals. In contrast, the hydrogenated sample was deep-blue in color and its transparency was greatly decreased. A strong and broad absorption peak centered at 3279 cm^{-1} can be clearly observed. This peak is continuously weakened with increasing aging time and meanwhile the transmittance of the hydrogen-inserted rutile single crystal is increased. It is well known that the infrared absorption peak at 3279 cm^{-1} is due to the stretch mode of O-H bond at room temperature in rutile. So this peak can be assigned to the stretch mode of O-H bond²⁰. As a matter of fact, electrochemically doped hydrogen has been found to greatly

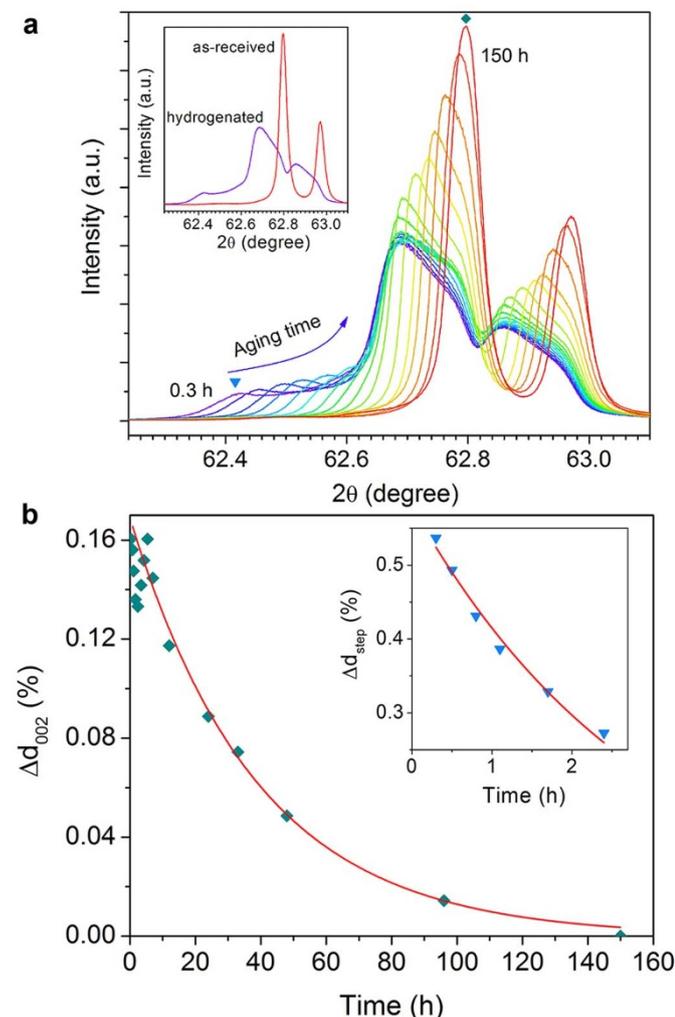


Figure 2 | Crystal structure evolution of electrochemically hydrogenated TiO_2 . (a), XRD patterns of an electrochemically hydrogenated (001) rutile single crystal taken after a series of aging time. The hydrogenation time is 200 h, and the aging times are 0.3, 0.5, 0.8, 1.1, 1.7, 2.4, 3.4, 4.3, 5.4, 7, 12, 24, 33, 48, 96, and 150 h for the patterns from left to right. Inset: XRD patterns of an as-received (001) rutile single crystal and the electrochemically hydrogenated (001) rutile single crystal measured at an aging time of 0.3 h. (b), Lattice expansion of the (002) plane of the hydrogenated crystal compared to that of the undoped one as a function of aging time. The red curve is an exponential fit of the data: $\Delta d = 0.0017\exp(-t/39)$. Inset: the lattice expansion of the wide step indicated by a triangle in panel a. The red curve is also an exponential fit: $\Delta d = 0.0058\exp(-t/3)$.

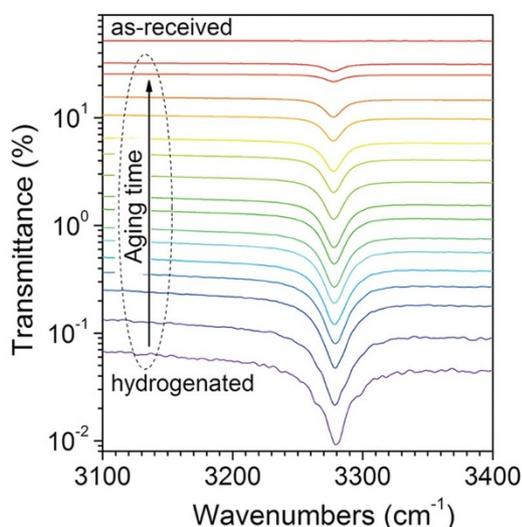


Figure 3 | Infrared absorption spectra of an as-received rutile single crystal and a hydrogenated one measured after a series of aging times. The hydrogenation time is 120 h, and the aging times are 2, 9, 24, 34, 48, 72, 144, 192, 310, 500, 750, 1150, 1550, 2400, and 3000 h for the spectra from bottom to top.

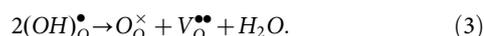
increase the conductivity and act as a shallow donor in rutile single crystals²¹. No other hydrogen-related structures can be observed over a wide frequency range of 500–4000 cm^{-1} (Supplementary Information, Fig. S3), and it is necessary to point out that hydrogen can exist in metal oxides in some forms that are not seen by IR spectroscopy^{22,23}. Obviously, for the two distinct states of hydrogen revealed by XRD, the one with a bigger decay constant can be identified as protons covalently bound to oxygen ions according to the infrared absorption spectra analysis, which can be expressed as $(\text{OH})_O^\bullet$ ²⁴, while the highly mobile one is still largely unknown, e.g., its charge state that can be either positive, neutral or negative²⁵. For simplicity, we tentatively assume a positive charge state for it and term it as H_{im}^\bullet (*i* for interstitial and *m* for mobile) hereinafter.

Discussion

Hydrogen existing as $(\text{OH})_O^\bullet$ is well-known for metal oxides and is found in many applications of metal oxides. For example, for electrochromic metal oxide WO_3 , $(\text{OH})_O^\bullet$ is charged/discharged reversibly through controlling applied voltage¹⁰, which can be expressed using the notation of Kröger and Vink in the following way:



where W'_W represents a W^{5+} at the lattice site of W^{6+} in WO_3 and $H^+(a)$ a proton in a solution. The electrochromic effect is directly related to the formation of W'_W , namely W^{5+} in the lattice. It should be pointed out that the formation of O-H bond tends to weaken the ferroelectric distortion in WO_3 ¹⁰ and with increasing content of $(\text{OH})_O^\bullet$, the crystal structure is modified from monoclinic (WO_3) to tetragonal ($\text{H}_{0.1}\text{WO}_3$ and $\text{H}_{0.33}\text{WO}_3$), and to cubic ($\text{H}_{0.5}\text{WO}_3$)¹⁶. Through thermal treatment, it leaves from the lattice of WO_3 as water²⁶:

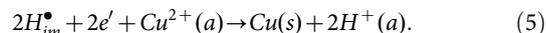


In contrast, as a different state, hydrogen existing as H_{im}^\bullet is expected to leave the oxide lattice in a different form rather than H_2O . A mass spectroscopy analysis of the gas released from electrochemically hydrogenated Nb_2O_5 upon thermal treatment included a large portion of H_2 besides H_2O ^{8,26}. Considering that H_2O is formed from

$(\text{OH})_O^\bullet$, H_2 should be formed from H_{im}^\bullet , which exists in electrochemically hydrogenated Nb_2O_5 , upon thermal treatment in the following way:



where the electron is weakly-bonded or free in the metal oxide and the out-diffusion of hydrogen decreases the concentration of charge carriers and thus the conductivity of metal oxides. As for the deposition of copper on “freshly” hydrogenated Nb_2O_5 and WO_3 pellets when being immersed in the CuSO_4 solution, it reveals the following reaction between H_{im}^\bullet and Cu^{2+} at room temperature:



As H_{im}^\bullet can be of a high concentration in hydrogenated Nb_2O_5 , a large portion of H_2 is formed besides H_2O upon thermal treatment, and a large amount of copper is formed when immersed in CuSO_4 solution at room temperature. On the other hand, since the content of H_{im}^\bullet is very small in electrochemically hydrogenated WO_3 , it is difficult to collect H_2 upon heat-treatment and only H_2O can be detected, and the amount of copper deposition is very small when immersed in CuSO_4 solution.

It is clear that with such surprisingly high mobility and reactivity at room temperature, this special state of hydrogen will not be observed or studied in samples treated through hydrogen-doping at elevated temperatures. Our finding of the highly mobile and reactive state of hydrogen, and this room-temperature hydrogen doping method as well, are thus especially valuable for studying those interactions between metal oxides and hydrogen at moderate and low temperatures. For example, the peculiar aging behavior of electrochemically hydrogenated TiO_2 rutile single crystals^{14,21}, and some other metal oxides as well^{12,18,27}, can now be better understood: the mobile hydrogen H_{im}^\bullet should play an important role in the initial stage of aging, while $(\text{OH})_O^\bullet$ should be mainly responsible for the subsequent aging²⁸. For hydrogen-sensing of metal oxide semiconductors, it is generally considered that the change of electrical resistance with hydrogen exposure is only related to the spilt hydrogen atoms on the surface^{9,29,30}, in this way electron transfer from hydrogen to metal oxides occurs while hydrogen is still highly mobile. According to our present results, however, ionized hydrogen, or proton, can actually exist inside metal oxides while being highly mobile. So it is necessary to examine whether hydrogen will enter into the lattice of metal oxides in the course of hydrogen-sensing. Similarly, hydrogen entrance into the lattice of metal oxides should also be considered for other chemisorption of atomic hydrogen on the surface of metal oxides^{31,32}. Nb_2O_5 is so far the most effective oxide promoter for accelerating adsorption/desorption of hydrogen in magnesium hydride storage materials. It has been assumed that Nb_2O_5 may play the role as a reservoir loading a certain amount of split hydrogen in its lattice in the course of catalysis^{8,11,26}. Obviously, our results provide a direct support for this assumption and more attention should be paid to it when the catalysis mechanism of Nb_2O_5 is studied.

In summary, by studying electrochemically hydrogenated Nb_2O_5 and WO_3 polycrystals, and TiO_2 rutile (001) single crystals, we found the coexistence of hydrogen in two distinct states inside the lattice of these metal oxides: one is as protons attached to oxygen ions by strong O-H bonds while the other one is highly mobile and reactive, but exists only for several hours in the lattice. The properties of this mobile and reactive hydrogen are still largely unknown, and further investigations need to be conducted on this special state of hydrogen, such as what its actual charge state is, how H_{im}^\bullet interacts with metal oxide lattices, how H_{im}^\bullet interacts with other crystal defects like $V_O^{\bullet\bullet}$, and how, if possible, H_{im}^\bullet and $(\text{OH})_O^\bullet$ are transformed into each other. Our results are therefore important for deepening our understanding of hydrogen in metal oxides and for promoting numerous hydrogen-related applications of metal oxides.



Methods

Nb₂O₅ samples were prepared through 2 h sintering at 1250 °C in air of pellets (15 mm in diameter and 2 mm thick) pressed from analytical grade (99%) Nb₂O₅ powders. Analytical grade (99%) WO₃ powder was first ball milled with de-ionized water for 24 h. After drying, the milled powder was pressed into pellets of 15 mm in diameter and 2 mm thick and the pellets were sintered at 1150 °C for 2 h in air. The TiO₂ rutile single crystals used in this work were (001)-oriented 10 × 10 × 0.5 mm³ commercial wafers purchased from HEFEI KEJING (China). Two 2 mm diameter silver electrodes were fired on the two sides of a corner of the single crystals. Electrochemical hydrogen insertion was conducted by immersing a sample in a 0.01 M NaOH solution. The Nb₂O₅ or the WO₃ pellets or the silver electrodes of the rutile single crystals were connected to dc voltages (6 V) to act as the cathode to electrolyze water. Infrared absorption spectra were recorded with a Nicolet iS-10 Fourier transform spectrometer by measuring the transmittance of as-received and hydrogenated rutile single crystals at 300 K. The spectral resolution was 0.5 cm⁻¹. X-ray diffraction patterns were taken through an X-ray diffractometer (Philips PW 3719) with Cu K α radiation.

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Author contributions

W.P.C. designed the research and conducted the experiments. W.P.C. and Z.Y. wrote the manuscript. K.F.H. contributed to the measurements. Z.Y., Y.W. and H.L.W.C. contributed to the project design and data analysis. All authors discussed the results and commented on the paper.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

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