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Authors
Hou, Bingya
Shen, Lang
Shi, Haotian
et al.

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Resonant and Selective Excitation of Photocatalytically Active Defect Sites in TiO_2

Bingya Hou[1], Lang Shen[2], Haotian Shi[3], Jihan Chen[1], Bofan Zhao[1], Kun Li[5], Yi Wang[3], Guozhen Shen[6], Mai-Anh Ha[7], Fanxi, Liu[8], Anastassia N. Alexandrova[7,9], Wei Hsuan Hung[10], Jahan Dawlaty[3], Phillip Christopher[5], and Stephen Cronin[1,3,4]

[1]Ming Hsieh Department of Electrical Engineering, [2]Mork Family Department of Chemical Engineering and Materials Science, [3]Department of Chemistry, [4]Department of Physics and Astronomy, University of Southern California, Los Angeles, CA 90089, USA

[5]Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106-5080, USA

[6]State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Science, Beijing, 100083, P.R. China

[7]Department of Chemistry and Biochemistry, California NanoSystems Institute, University of California, Los Angeles, Los Angeles, CA 90025, USA

[8]Collaborative Innovation Center for Information Technology in Biological and Medical Physics, and College of Science, Zhejiang University of Technology, Hangzhou, 310023, P.R. China

[9]Materials Sciencens Division, Lawrence National Laboratory, Berkeley, CA 94720, USA

[10]Department of Materials Science and Engineering, Feng Chia University, Taichung 407, Taiwan, 40724

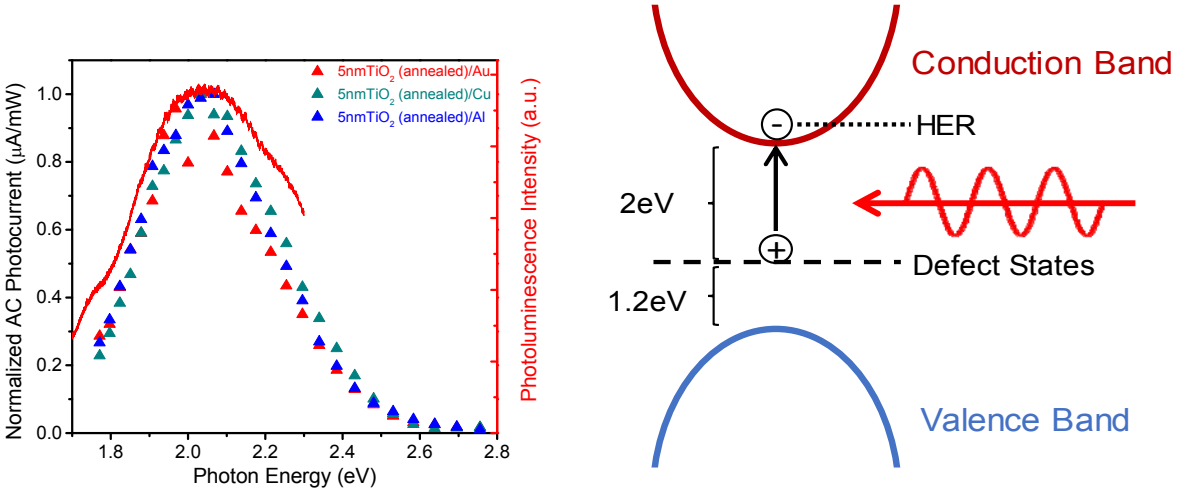
Abstract

It has been known for several decades that defects are largely responsible for the catalytically active sites on metal and semiconductor surfaces. However, it is difficult to directly probe these active sites because the defects associated with them are often relatively rare with respect to the stoichiometric crystalline surface. In the work presented here, we demonstrate a method to selectively probe defect-mediated photocatalysis, through differential AC photocurrent (PC) measurements. In this approach, electrons are photoexcited from the valence band to a relatively narrow distribution of sub-bandgap states in the TiO_2, and then subsequently to the ions in solution. Because of their limited number, these defect states fill up quickly resulting in Pauli blocking, and are thereby undetectable under DC or CW excitation. In the method demonstrated here, the incident light is modulated with an optical chopper while the photocurrent is measured with a lock-in amplifier. Thin (5nm) films of TiO_2 deposited by atomic layer deposition (ALD) on various metal films, including Au, Cu, and Al, exhibit the same wavelength-dependent photocurrent spectra, with a broad peak centered around 2.0eV corresponding to the band-to-defect transition associated with the hydrogen evolution reaction (HER). While the UV-vis absorption spectra of these films show no features at 2.0eV, photoluminescence (PL) spectra of these photoelectrodes show a similar wavelength dependence with a peak around 2.0eV, corresponding to the sub-band gap emission associated with these defect sites. As a control, alumina (Al_2O_3) films exhibit no PL or PC over the visible wavelength range. The AC photocurrent plotted as a function of electrode potential, shows a peak around -0.4 to -0.1V vs. NHE, as the monoenergetic defect states are tuned through a resonance with the HER potential. This approach enables the direct photo-excitation of catalytically active defect sites to be studied selectively without the interference of the continuum interband transitions or

the effects of Pauli blocking, which is limited by the slow turnover time of the catalytically active sites, typically on the order of 1 μsec. We believe this general approach provides an important new way to study the role of defects in catalysis in an area where selective spectroscopic studies of these are few.

Keywords: titania, titanium dioxide, resonate, photocatalysis, active site, catalysis

TOC Figure


5nmTiO2 (annealed)/Au
5nmTiO2 (annealed)/Cu
5nmTiO2 (annealed)/Al
Normalized AC Photocurrent (μA/mW)
Photoluminescence Intensity (a.u.)
Photon Energy (eV)
1.0
0.8
0.6
0.4
0.2
0.0
1.8
2.0
2.2
2.4
2.6
2.8
Conduction Band
HER
2eV
Defect States
1.2eV
Valence Band

Introduction

Defects in TiO_2 have been studied extensively, providing an important mechanism in photocatalytic energy conversion. In particular, oxygen vacancies (i.e., Ti^{3+} states) have been linked to catalytically active sites, particular in the water splitting and CO_2 reduction reactions systems.[1] TiO_2 films deposited by atomic layer deposition (ALD) are also known to have a high concentration of defects and, hence, show enhanced water splitting and CO_2 reduction efficiencies.[2-5] Qiu et al. have quantified these O-vacancies (i.e., Ti^{3+} states) in ALD-deposited TiO_2 films using X-ray photoemission spectroscopy (XPS), and they have correlated these vacancies with the photocatalytic activity of TiO_2 films for both water splitting and CO_2 reduction reactions.[2, 4] Density functional theory calculations performed by Alexandrova's group have provided an atomistic picture of this enhancement mechanism, which show that both H_2O and CO_2 molecules bind stably to these non-stoichiometric Ti^{3+} states.[3, 6] Furthermore, when they allow their calculations to relax to their quantum mechanical ground state, they observe a spontaneous transfer of one electron creating CO_2^-. In these DFT calculations, this CO_2^- species is bent and represents a high barrier intermediate species in this difficult reaction system.

In addition to oxygen vacancies, nitrogen defects can be created in TiO_2 by annealing in NH_3 gas, resulting in substantial sub-band gap absorption.[7-9] This is a well-studied system in which the N-defect concentration can be controlled up to several percent by varying the annealing temperature. Extensive surface science studies of N-doping have been performed in the research groups of Rodriguez[10] and Yates.[11-13] Doping of metal oxides by ion implantation, followed by calcinations in oxygen, has also been studied extensively as a means of dramatically increasing in the photocatalytic activity in the visible wavelength range.[14-23] Among the elements

studied, V, Cr, Mn, Fe, and Ni were found to increase the photocatalytic activity of TiO_2 in the visible range substantially.[24]

In the work presented here, an AC lock-in measurement technique is employed to study photocatalysis, revealing the behavior of sub-band gap states, that are resonant in both wavelength and electrode potential, and give rise to a substantial increase in photocurrent in the hydrogen evolution reaction (HER) process. In order to further characterize these sub-band gap states, we collect photoluminescence (PL) spectra, which provide an independent measure of the energetics of these important sub-band gap states. UV-Vis spectra are also obtained in order to provide a complete picture of the band edge and sub-band gap absorption in the TiO_2 thin film with and without annealing.

Photoelectrodes were fabricated by depositing 100 nm thick films of Au, Cu and Al on glass substrates using electron beam deposition. A 5 nm TiO_2 film was then deposited by ALD at 250°C using TDMAT as the Ti source and water vapor as the O source. The base flow rate during deposition was 20 sccm. The TiO_2 thickness was established by ellipsometry for a 5 nm film, which corresponds to 100 ALD cycles. The TiO_2/Au films were annealed in a quartz tube furnace at 450°C for 30 min while O_2 gas was flowing. The TiO_2/Cu and TiO_2/Al films were annealed in a quartz tube furnace at 450°C for 30 min while argon gas was flowing. UV-vis absorption spectra of a 10nm thick TiO_2 film taken before and after annealing are plotted in Figure S1 of the supplemental information. Figure 1(a) shows an illustration of the sample geometry, in which an insulated copper wire was attached to the TiO_2/metal electrode using silver paint and the whole sample, excluding the top surface, was encased in epoxy to insulate it from the electrolytic solution. Photoelectrochemical measurements were performed using a three terminal potentiostat (Gamry, Inc.), as illustrated in Figure 1(b). For the HER, a Ag/AgCl reference electrode was used and a Pt wire was used as the counter electrode. The electrodes were immersed in a pH=7, Na_2SO_4 solution. We used an AC lock-in technique, which enables us

to detect the relatively small photocurrents (μA) produced by just 5nm of wide-band gap semiconductor material. In order to vary the wavelength of the incident light, a 1000W xenon lamp was used in conjunction with a monochromator to produce monochromatic light throughout the visible wavelength range. The power reaching the sample surface was 2-3mW. Here, the light was filling the entire sample area. The incident light was chopped at frequency $\omega_{chopper}$, which was 200 Hz in our case. The chopper controller (Stanford Research Systems, Inc., Model SR540) was connected to the ''REF IN'' terminal of the lock-in amplifier (Standard Research Systems, Model SRS830 DSP), in order to synchronize the lock-in amplifier with the light modulation. The AC voltage signal from the auxiliary current monitor terminal of the potentiostat was used as the input signal of the lock-in amplifier in order to collect the AC photocurrent generated by the TiO_2/metal films.

Figure 2 shows the AC and DC photocurrents plotted as a function of the reference potential for the HER for 5nm TiO_2 deposited on Au and Cu. Here, we observe a peak in the AC photocurrent around -0.13V vs. NHE corresponding to the conditions under which we tune the potential of the charge associated with the resonantly-excited defect states through the redox potential of the HER half-reaction. This is considerably shifted from the DC onset potential of -0.3V vs. NHE. For the TiO_2/Cu electrode, the peak in AC photocurrent is observed at -0.4V vs. NHE, which is also substantially shifted with respect to the DC onset potential of -0.6V vs. NHE.

Figure S4 shows the light intensity dependence of the AC photocurrent from a TiO_2/Au sample obtained for both reduction and oxidation reactions under 532nm illumination. Here, we observe a linear response to the light intensity, as expected. This result indicates that we are successfully converting photons to hot carriers under optical excitation.[25]

Figure 3(a) shows the normalized AC photocurrent spectra of 5nm TiO_2 deposited on Au, Cu, and Al. Here, a clear peak can be seen around 2eV, which is well below the 3.2eV bandgap of this material. This feature at 2eV corresponds to the photo-excitation of the sub-band gap defect states that serve as catalytically-active sites for the HER, as illustrated in Figure 3(b). Further evidence for this defect state is provided by the PL spectrum, also plotted in Figure 3(a), which also exhibits a peak centered around 2.0eV. Interestingly, no such feature can be seen in the UV-vis absorption spectra at 2.0eV. Figure S1 of the supplemental information shows the UV-vis absorption spectra of both annealed and unannealed TiO_2 films. Here, both spectra show moderate sub-band gap absorption that is monotonically decreasing with wavelength. However, no specific feature is present in these UV-vis spectra at 2.0eV. This indicates that, while there are likely many different types of defect states throughout the band gap, there is a specific defect located at 1.2eV above the valence band edge that is catalytically active for the hydrogen evolution reaction.

Ultraviolet photoemission spectroscopy (UPS) is a common tool to study conduction and valence band structure of materials.[26, 27] The valence band spectrum of an oxygen-annealed 5nm TiO_2 film was obtained by UPS at 21.2eV photon energy. The linear plot, Figure 4(a), shows the position of valence band edge. The valence band edge is 3.2eV below the Fermi energy, which is pinned at the conduction band edge. After annealing, a peak at approximately 2eV below the conduction band edge was observed in the log plot, as shown in Figure 4(b), which agrees with the peak position of photocurrent spectra.

Figure S3 shows an X-ray photoemission spectroscopy (XPS) spectrum of a 5nm TiO_2 film deposited on a Au film by atomic layer deposition. In addition to the main Ti^{4+} peaks, which

correspond to stoichiometric TiO_2, we observe a small shoulder peak corresponding to Ti^{3+} states (i.e., oxygen-vacancies), as reported previously by Qiu et al.[28]

High resolution cross-sectional transmission electron microscope (TEM) images were taken of 5nm and 25nm thick TiO_2 films deposited on Au films. Figure S2(c) shows amorphous TiO_2 material, as expected. This material is non-stoichiometric and contains a high density of oxygen vacancies, as evidenced by the UPS and XPS spectra described above. In contrast, Figure S2(d) shows crystalline material. Qiu et al. have also demonstrated that above 10nm, TiO_2 films become crystalline.[29] These thicker TiO_2 films are crystalline and have poor charge transfer characteristics due to their insulating nature. Thus, we are more interested in thin and amorphous TiO_2 films.

Plane-wave density functional theory (PW-DFT) calculations were performed on defective (101) anatase in order to extract formation energies and spectral analyses of oxygen vacancies. A single oxygen vacancy results in the presence of 2 excess electrons that may localize on neighboring Ti atoms. Experimentally, spectral signatures were found ~2eV from the Fermi energy. Due to the over-delocalization of electrons in DFT, we introduced a strong Hubbard U parameter of 4.0eV into our calculations in order to recover a theoretical band gap is ~2.2eV. Utilizing Bader charge analysis, we were able to determine the localization of electrons on surface Ti sites. For surface oxygen vacancies V_{O1} and V_{O2}, electrons localized on neighboring Ti atoms ~1.9Å from the vacancy site. For surface oxygen vacancy V_{O3}, the two electrons localized on Ti atoms farther away from the vacancy site, one on a Ti atom ~1.9Å and the other on a Ti atom ~3.7Å from the vacancy site. The ramifications of this may be found in the theoretical density of states shown in Figure S7(b). In comparison to $V_{O1\text{-}O2}$, V_{O3}'s spectral signatures of the localized electrons are shifted farther away from the Fermi energy. We

hypothesize that at the deeper oxygen vacancy sites, the spectral signatures of the localized electrons also shift farther away from the Fermi energy. However, the small theoretical band gap of ~2.2eV may obscure these spectral signatures and so, we focus only on $V_{O1\text{-}O3}$. Based on these DFT calculations, it seems that the specific catalytically active defect sites that we observe in our photoelectrochemical measurements actually correspond to sub-surface defects. While these results provide qualitative agreement with our experimental results (i.e., sub-band gap states giving rise to visible light absorption, it is not possible to assign a specific atomic defect to our observation, and it is likely that a large collective ensemble of these defects contribute to the broad spectral distribution observed experimentally.

In our previous work, similar structures consisting of Au films with and without TiO_2 coatings were investigated.[30] For the bare metal electrodes, the mechanism of photocatalysis was attributed to hot electrons photoexcited in the metal. The mechanism of photocurrent generation in TiO_2-coated Au electrodes was attributed to hot electron injected by the metal film because of our inability to detect these defect states in the UV-vis absorption process. However, these defect states are somewhat elusive because of the Pauli blocking associated with their finite density and slow turnover time, and we now have a better understanding of this system. It should be noted that the photoexcited charge generated at these O-vacancy defect sites is bound to the defect site and is not free to propagate throughout the TiO_2 crystal.

In conclusion, we have demonstrated a method to selectively probe defect-mediated photocatalysis through differential AC photocurrent measurements. Here, we drive the photoexcitation of electrons (or holes) from the valence band to relatively narrow distribution of sub-band gap states, and then to the ions in solution. Because of their limited number, these defect states fill up quickly resulting in Pauli blocking and are undetectable under DC or CW

conditions. In the method demonstrated here, the incident light is modulated with an optical chopper and the photocurrent is measured with a lock-in amplifier. Thin (5nm) films of TiO_2 deposited on different metals (Au, Cu, and Al) using ALD exhibit the same wavelength-dependent photocurrent spectra, with a broad peak centered around 2.0eV. PL spectra also show a peak at 2.0eV, corresponding to the sub-band gap emission associated with these defect sites. In addition, the AC photocurrent shows a peak around -0.4 to -0.1V vs. NHE, as the monoenergetic defect states are tuned through a resonance with the HER potential. This approach enables the photoexcitation of catalytically active defect sites to be studied selectively without the interference from the continuum of interband transitions or the effects of Pauli blocking, which is quite pronounced because of the slow turnover time (~1μsec) of the catalytically active sites.

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Figures

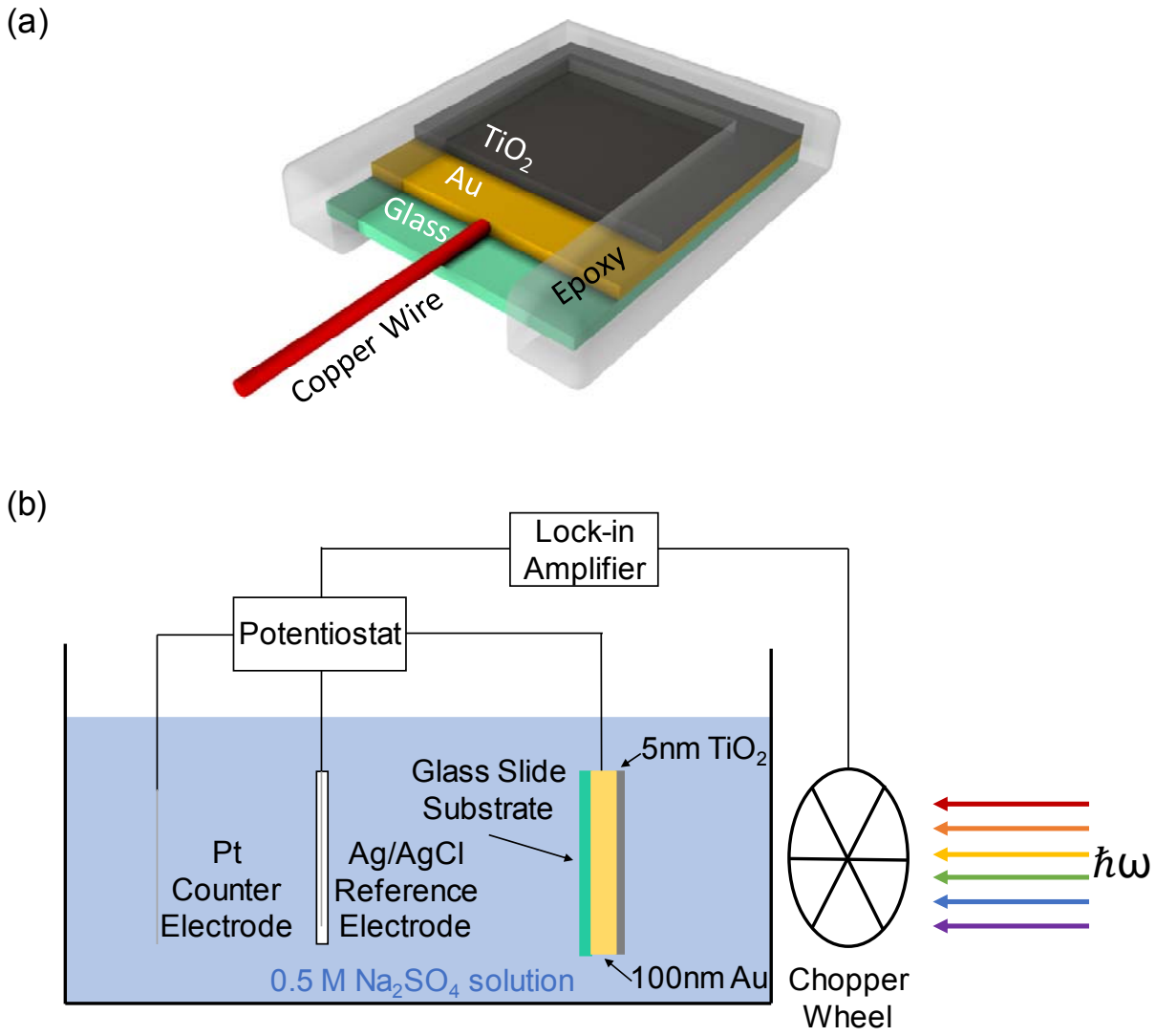


Figure 1. (a) Diagram illustrating the sample configuration. (b) Schematic diagram of the three-terminal photoelectrochemical setup with the modulated light and AC lock-in amplifier.

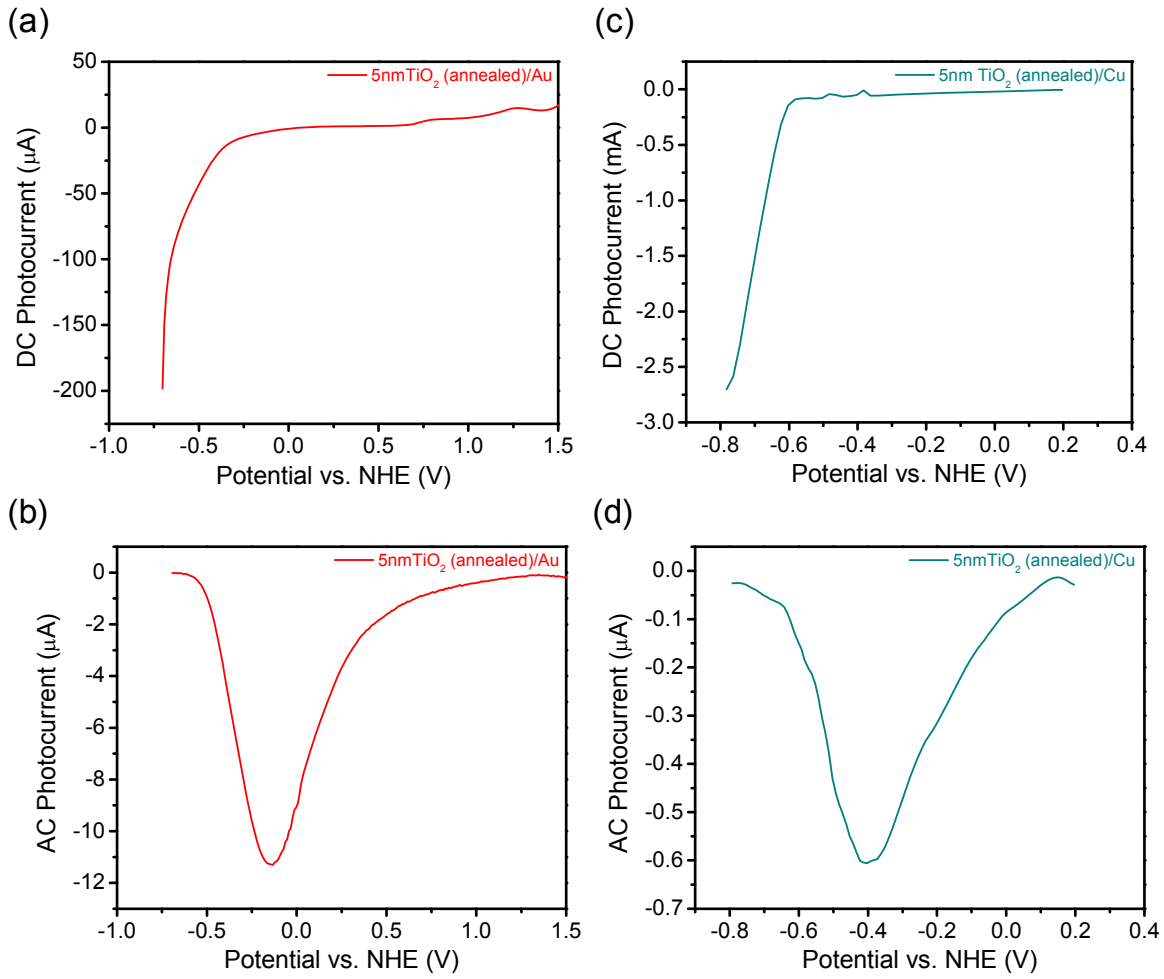
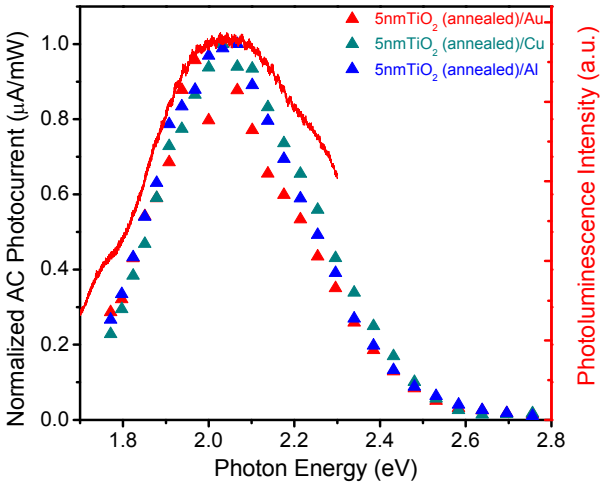


Figure 2. DC (a, c) and AC (b, d) photocurrent plotted as a function of the reference potential for the hydrogen evolution reaction (HER) for (a, b) 5nm annealed TiO_2 deposited on Au under 532nm illumination. (c, d) 5nm annealed TiO_2 deposited on Cu under 532nm illumination.

(a)



(b)

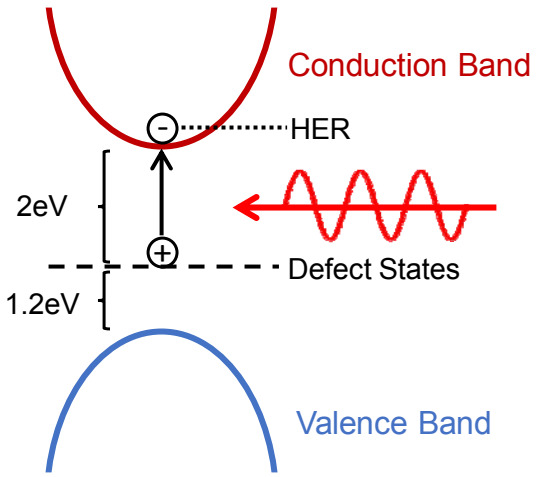


Figure 3. (a) Normalized AC photocurrent spectra of 5nm TiO_2 deposited on Au, Cu, and Al films and corresponding photoluminescence spectrum of 5nm thick annealed TiO_2 deposited on a Au film. (b) Energy band diagram of the photoexcitation mechanism of defect-mediated photocatalysis.

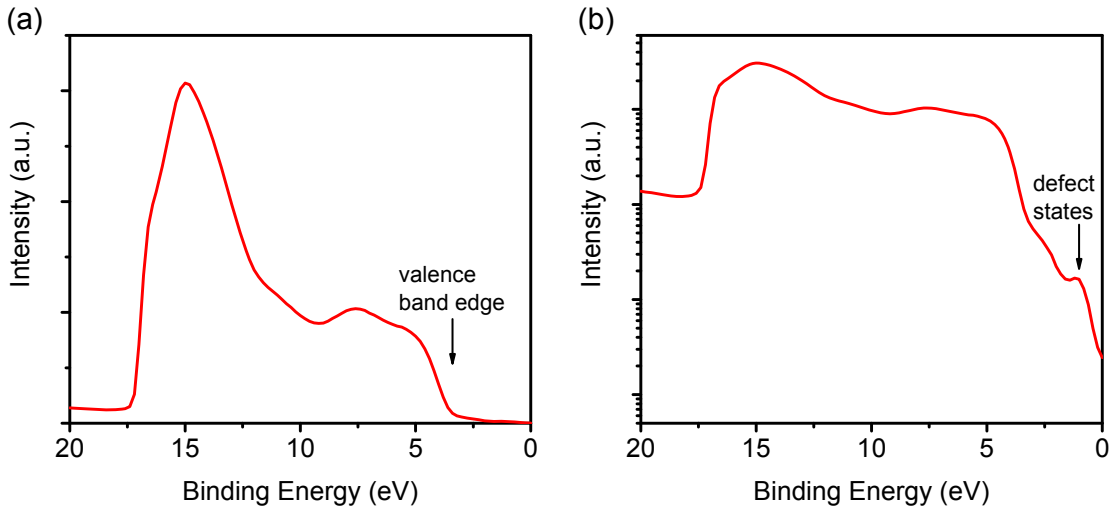


Figure 4. Valence band spectra of a 5nm TiO_2 film obtained by UPS at 21.2eV photon energy plotted on (a) linear and (b) log scales.

ASSOCIATE CONTENT

Supporting Information available:

UV-Vis absorption spectra, High resolution TEM images, XPS spectrum, Frequency dependence of AC photocurrent, Light intensity dependence of AC photocurrent, PL spectra, Transient absorption spectra, Density functional theory calculation, AC photocurrent for 5nm and 25nm annealed TiO_2.

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