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Excitation Wavelength Dependence of Photocatalyzed Oxidation of Methanol on TiO$_2$(110)†

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Post-irradiation temperature-programmed desorption (TPD) has been used to study the photocatalyzed oxidation of methanol on TiO$_2$(110) surface under the irradiation of 360, 380 and 400 nm light. The photocatalytic process initiated by ultraviolet light of different wavelength are similar. Methanol has been photocatalytically converted into formaldehyde, and the released hydrogen atoms transfer to the neighboring twofold coordinated oxygen to form bridging hydroxyls. The reaction rate, however, is strongly wavelength dependent. The reaction rate under 360 nm light irradiation is 4.8 times of that in the case of 400 nm exposure, consistent with a previous femtosecond time-resolved absorption measurement on TiO$_2$ which shows the faster charge carrier recombination in the near-band-gap than the over-band-gap excitation. So far, the underlying factors which govern the excitation wavelength dependence of photocatalytic activity of TiO$_2$ and other photocatalysts remain unclear, and future studies are needed to address this important issue.

Key words: Titanium dioxide, Photocatalysis, Excitation wavelength dependence, Temperature-programmed desorption

I. INTRODUCTION

Solar to chemical energy conversion, a promising strategy dealing with the energy crisis and the energy structure adjustment, is initiated by the seminal discovery of photocatalyzed splitting of water over TiO$_2$ electrode [1]. Being a popular material, TiO$_2$ has shown its potential applications in many energy and environment related field [2−6]. In scientific field, more and more efforts have been devoted to the fundamental research on TiO$_2$, aiming at revealing the underlying mechanism of the applications and improvement of the performance [7−15].

Conventionally, the principle of photocatalysis can be understood as follows [4]: a semiconductor absorbs photons whose energy exceeds the band gap to generate charge carriers; the photogenerated hot electons and holes cool rapidly to the edge of conduction band (CB) and valence band (VB) respectively; after transportation, trapping and detrapping, the charge carriers transfer to the adsorbates to initiate redox chemistry. This scheme suggests the excess energies of the photogenerated charge carriers are lost before charge transfer, a process which limits the photoconversion efficiency.

Therefore, the photocatalytic efficiency is only related to the fluence of photoabsorption while independent of the photon energy which is inverse proportion to the wavelength. This conclusion prevails in the current photocatalysis field since many results show the photon flux rather than photon energy dependence [16−18].

On the other hand, excitation wavelength dependence of photodesorption and potolysis yield have been detected on TiO$_2$(110) surface [19−26]. Instead of investigating the photon energy dependent effect, the authors only took this observation as a criteria of confirming a substrate mediated process. Most recently, Xu and coworkers reported the strong photon energy dependence of the photocatalyzed oxidation rate of methanol on TiO$_2$(110) initiated by 266 and 355 nm light [27]. In contrast to the widely accepted hole mediated oxidation of methanol on TiO$_2$ [4], they proposed an electron mediated process or a dissociation through vibrationally excited adsorbate at the electronically ground state potential energy surface.

Motivated by Xu *et al*'s work, we also studied the photocatalyzed oxidation of methanol on TiO$_2$ as a function of excitation wavelength (360, 380 and 400 nm). The photochemical reaction under these ultraviolet (UV) irradiation cases are similar to those reported previously [28, 29]: methanol is photo-converted into formaldehyde, and the released hydrogen atoms are transferred to basic oxygen sites to form bridging hydroxyls. In agreement with a previous femtosecond time-resolved absorption measurement on TiO$_2$ which

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shows the faster charge carrier recombination in the near-band-gap than the over-band-gap excitation, the reaction rate of photocatalyzed oxidation of methanol on $TiO_2(110)$ under 360 nm light irradiation is 3.8 times higher than that in the case of 400 nm light exposure. However, the underlying factors affect the wavelength dependence of the photocatalytic activity of TiO_2 and other photocatalysts are complicated, and further studies on the photoabsorption, charge carrier dynamics and interfacial charge transfer dynamics are needed to reveal the physical origin of this important issue.

II. EXPERIMENTS

All TPD measurements were carried out in a UHV apparatus (base pressure$<5\times10^{-11}$ mbar) which was equipped with an ion gun (IQE 11/35, SPECS), an electron gun (PU-EQ 22, SPECS), a low electron energy diffraction instrument (ErLEED 150, SPECS), a hemispherical electron energy analyzer (PHOIBOS 100, SPECS) and a differentially pumped mass spectrometer (RGA 200, Stanford Research System) [30−32]. The $TiO_2(110)$ crystal (Princeton scientific Corp, 10 mm$\times$10 mm$\times$1 mm) was fixed onto a Ta plate which was mounted at the end of a manipulator with four-dimensional movement (X, Y, Z and rotation around z axis). Heating (to 1000 K) and cooling (to 100 K) were realized through resistive heating and liquid nitrogen respectively. A K type thermocouple was directly glued (Ceramabond 503, AREMCO) onto the TiO_2 surface to ensure accurate temperature reading. TiO_2 sample was cleaned by cycles of Ar^+ sputtering and UHV annealing at 850 K. After preparation, no contamination was detected in the Auger electron spectroscopy (AES) and a sharp (1$\times$1) LEED pattern was shown. This preparation treatment led to $\sim$4.5% monolayer (ML, 1 ML=5.2×10^{14} molecules/cm^2) bridging oxygen vacancy (O_v) characterized by H_2O TPD method [33, 34]. HPLC grade CH_3OH (Sigma-Aldrich) was purified by freeze-pump-thaw cycles and was dosed onto the TiO_2 surface via a home-made, calibrated effusive molecular beam doser at 120 K. In the present study, the coverage of initially dosed methanol was 0.5 ML. The irradiation light (360−400 nm) from the second harmonic generation (SHG) of an oscillator (80 MHz, MaiTai eHP, Spectra-Physics) has a repetition rate of 80 MHz, an average power of 280 mW and a diameter of 6 mm. It should be noted the absorption of TiO_2 is dependent of the wavelength. However, the measured absorption of TiO_2 varies significantly. Thus we fixed the power of irradiation with distinct wavelength. The effect of the absorption on the photocatalytic reaction rate will be discussed in the end of the third section. The substrate temperature was maintained between 110 and 120 K during the irradiation. All the TPD data were acquired using a heating rate of 2 K/s.

III. RESULTS AND DISCUSSION

The photochemistry of methanol on $TiO_2(110)$ in this work is similar to that reported previously [28]. Therefore in the following we will take the photocatalytic chemistry of methanol on this surface initiated by 360 nm light irradiation as an example to briefly describe the photocatalytic oxidation of methanol. To identify the possible chemical species in the photoinduced process, masses below 100 have been monitored and no products with $m/z>60$ have been detected. Figure 1 shows the TPD spectra of the representative fragment of the main products (methanol, formaldehyde and water) during the photochemistry of 0.5 ML methanol on $TiO_2(110)$ under 360, 380, and 400 nm light irradiation, respectively.

Figure 1(a1) displays the irradiation time dependent desorption of mass 31. The desorption profile of this fragment is identical with that of mass 32, suggesting it is from the electron impact cracking of methanol. Although after prolonged irradiation time there is detectable methyl formate which has a fragment of mass 31 at the lower temperature edge, the amount of methyl formate is near the detection limit of our mass spectrometer. Therefore the fragmentation of methyl formate can be neglected and the mass 31 signal can be attributed to methanol desorption. It is well known that the desorption feature around 300 K corresponds to molecular methanol binding to the Ti_{5c} sites of $TiO_2(110)$ [35], consistent with the slight lower adsorption energy of molecular with respect to dissociative adsorption [36]. As the irradiation time increases, the higher temperature portion of methanol depletes continuously, suggesting the presence of photoinduced process. The depletion of the high temperature portion is attributed to the interaction between bridging hydroxyls which are produced in the photoinduced process and the molecularly adsorbed methanol molecules in a previous study [28].

Figure 1(a2) displays the irradiation time dependent desorption of mass 30. The desorption profile of the 300 K peak is identical with that of mass 31, thus it is assigned to the fragmentation of methanol. Concomitant to the depletion of methanol with irradiation time, a new desorption feature develops at 266 K. The identical desorption profiles of the corrected mass 30, 29 and 28 point to the desorption of formaldehyde at this temperature. Assignment of this desorption feature of mass 30 to formaldehyde is further confirmed by comparing the TPD of formaldehyde from $TiO_2(110)$ [37, 38]. These results unambiguously show that methanol is photocatalytically oxidized into formaldehyde.

To produce formaldehyde, a methanol molecule has to break both a C−H and an O−H bond. As basic sites, the bridging oxygen atoms (O_b's) are likely acceptance of the released atomic hydrogen. We thus have measured the TPD of hydrogen contained species, *i.e.*, H_2 and H_2O. Despite the detection of small amount of
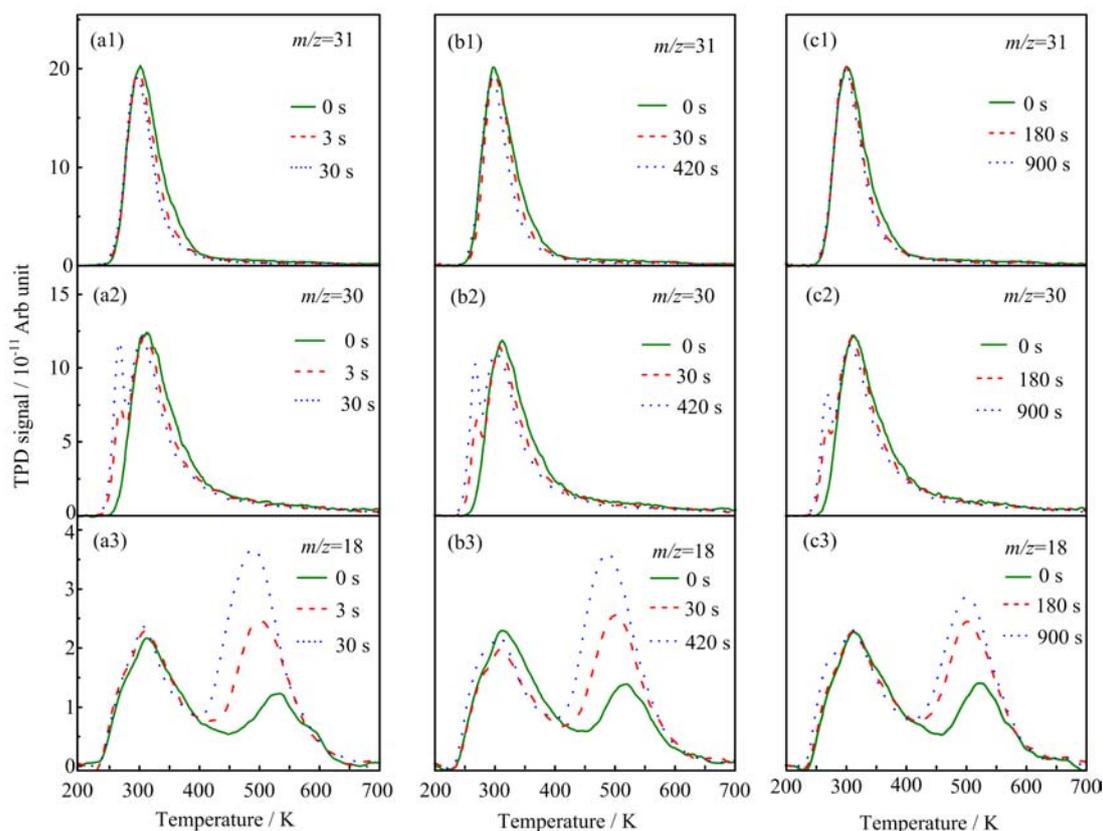
FIG. 1 TPD spectra collected at m/z=31 (CH$_2$OH$^+$), 30 (HCHO$^+$) and 18 (H$_2$O$^+$) after the 0.5 ML CH$_3$OH covered TiO$_2$(110) interface was exposed to (a) 360 nm, (b) 380 nm, and (c) 400 nm light for a series of time durations, respectively.

molecular hydrogen from hydroxylated TiO$_2$ surfaces using a mass spectrometer with extremely low H$_2$ background in the ionization area [39, 40], we don't observe molecular hydrogen desorption signal due to the high hydrogen background of our mass spectrometer. Whether surface hydrogen will diffuse into the bulk of TiO$_2$ is controversial [41−43]. And we can't identify the presence of this process using the experimental techniques in the present study. However, we do observe the desorption of water.

Figure 1(a3) shows the TPD spectra of mass 18 as a function of 360 nm light irradiation. Before exposure to the ultraviolet (UV) light, there are two water desorption featured peaks at 528 and 305 K, respectively. By comparing the TPD of water from TiO$_2$(110) [44], the 305 K signal is ascribed to molecular water adsorb at Ti$_{5c}$ sites. These molecularly adsorbed water is most likely from the hydration of the methanol agent since the desorption signal hardly changes with the UV irradiation time. The desorption at high temperature, however, increases dramatically and shifts downward with irradiation. These properties are characteristics of the recombination of bridging hydroxyls by abstracting lattice oxygen on this surface [43], indicating the transfer of atomic hydrogen to the O$_b$ sites during the photocatalyzed oxidation of methanol. It should be noticed that

methanol will dissociate spontaneously at O$_v$ sites, producing bridging methoxy and hydroxyl pairs [45]. The water signal at 528 K before UV light irradiation is from the recombination of the bridging hydroxyls result from dissociation of methanol.

We have also detected weak signal for methyl formate at prolonged UV irradiation times, suggesting the occurrence of cross coupling between methoxy and formaldehyde on this surface, which has been reported previously [46−48]. As can be seen from Fig.1, the photochemistry of methanol on TiO$_2$(110) under UV irradiation of different wavelengthes is similar. The main phenomena are the depletion of parent methanol and production of formaldehyde and bridging hydroxyls.

Despite the above similarities, the time scale of the photochemistry of methanol on TiO$_2$(110) under distinct irradiation condition in Fig.1 is much different. For example, it costs 3, 30, and 180 s for the recombinative water desorption signal to increase to 2.5×10^{-11} under the irradiation of 360, 380, and 400 nm light of the same average power, respectively. To quantitatively analyze the kinetics of the photochemistry of methanol on TiO$_2$(110) under irradiation of different wavelength, we have plotted the coverage of methanol and water rather than formaldehyde as a function of irradiation time (Fig.2) given the large cross section of photoinduc-
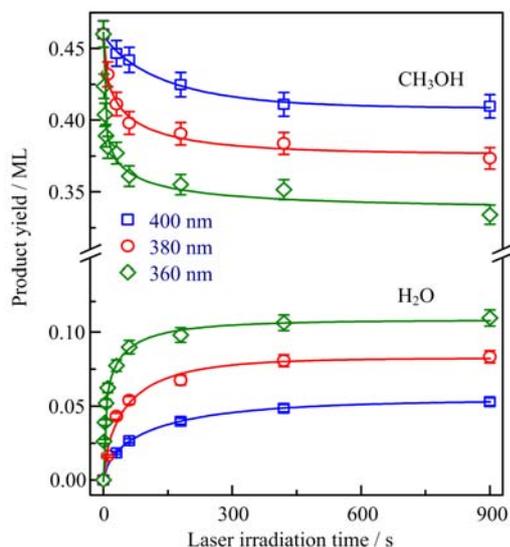
FIG. 2 Depletion of methanol (upper) and production of water (lower) as a function of 360, 380, and 400 nm UV light irradiation time respectively during the photochemistry of 0.5 ML methanol on $TiO_2(110)$. The solid lines are the fractal fitting to the experimental data.

ed desorption of formaldehyde from TiO_2 surface [40]. The experimental data are fitted using a fractal-like kinetics model which is characterized by a time-dependent rate coefficient [49, 50]:

$$k = k_0 t^{-h} \qquad (1)$$

$$h = 1 - \frac{d_s}{2} \qquad (2)$$

where k_0 is the rate coefficient at $t=1$ s, d_s represents the spectral dimension. Although the physical meaning of the fractal-like kinetics model in photocatalysis is not that direct, it is generally accepted this model reflects the trapping and detrapping of charge carriers [51].

As can be seen in Fig.2, the amount of methanol depletion and water production decrease with the wavelength of the excitation light. After 900 s irradiation, the coverage of consumed methanol are 0.17, 0.13 and 0.09 ML, and the produced bridging hydroxyls (which is twice of that of water) are 0.22, 0.16 and 0.10 ML, for the irradiation with 360, 380 and 400 nm light respectively. Dissociation of a methanol molecule into a formaldehyde will generate two bridging hydroxyls. The above experimental data suggest the conversion efficiency is not that high. This is likely caused by the photoinduced desorption of methanol after long time irradiation. Given the high photoinduced desorption yield of methanol and formaldehyde from TiO_2 surface and the inertness of bridging hydroxyls on TiO_2 to the UV exposure [40], we have taken the evolution of water, which is from the recombination of bridging hydroxlys, to analyze the kinetics of photocatalyzed oxidation of methanol on this surface.
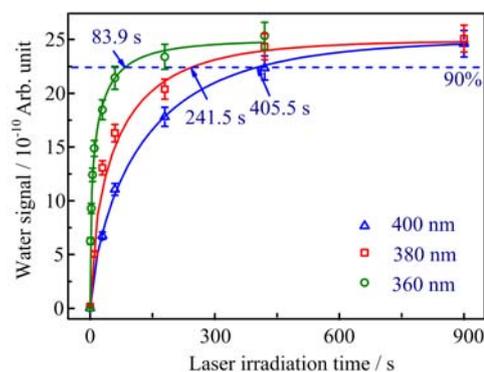

FIG. 3 Time dependent normalized water TPD signal (from recombination of bridging hydroxyls) from 0.5 ML methanol covered $TiO_2(110)$ as a function of excitation wavelength. The solid lines are the fractal fitting to the experimental data.

Figure 3 shows the normalized water TPD signal as a function of irradiation of different wavelength. As shown in the figure, the photocatalytic oxidation of methanol proceeds faster under the irradiation of shorter wavelength. It takes 83.9, 241.5, and 405.5 s for the photoreaction initiated by 360, 380, and 400 nm light respectively to reach 90% of its equilibrium value. This result shows that the reaction rate under 360 nm light irradiation is 4.8 times of that in the case of 400 nm exposure.

Since photoabsorption is the prerequisite in photocatalysis, determination of the wavelength dependence of the absorption coefficient is the first step to understand the wavelength dependent photocatalytic oxidation of methanol on $TiO_2(110)$. Transmitted ultraviolet-visible (UV-Vis) spectroscopy is the most often used method for measuring the absorption of thin films. As we know, the band gap of rutile is 3.05 eV, which leads to a sharp decrease of the UV-Vis absorption between 320 and 400 nm [52]. Due to the variation of the TiO_2 thin film preparation and the data analysis methods, there are great discrepancies between the measured photoabsorption coefficient. For example, the ratios of the absorption coefficient of 360 nm to 400 nm are 2.2, 8.6 and 14.1 according to Tracy Thompson [53], Ren *et al.* [54], and Filmetrics company's [55] measurements, respectively. Such a huge variance in this wavelength range prevents the quantitative analysis of the photoabsorption related process. In order to provide an accurate measurement of the photoabsorption of rutile, one needs to prepare high quality TiO_2 single crystal thin films using reliable methods such as molecular beam epitaxy (MBE). In addition, owing to the reflection of the two surfaces of the thin film, the complex component of the refractive index, instead of the beer law, should be used to calculate the absorption coefficient.

How and how much is the photon energy transferred to the adsorbates is the key question in photocatalysis.

Conventionally, the efficiency of photocatalysis is recognized to be associated with the fluence while independent of the photon energy. In this model, photogenerated charge carriers cool rapidly (in the femtosecond to picosecond time scale) to the band edge before transfer to adsorbates to initiate redox chemistry, indicating the lost of excess energy [4]. However, femtosecond time-resolved diffuse reflectance measurements on TiO$_2$ sample show that the transient absorption decays in a few picosecond in the near-band-gap excitation while remains almost constant after 48 ps in the over-band-gap excitation [55], unambiguously suggestting when excited by irradiation of higher photon energy, the photogenerated carriers survive much longer. This result is consistent with the wavelength dependence of the photocatalyzed oxidation of methanol on TiO$_2$(110) surface in the present work and in a previous study [27].

However, the underlying factors which govern the excitation wavelength dependence of photocatalytic activity of TiO$_2$ and other photocatalysts remain unclear, and future studies on the penetration depth, charge relaxation, transportation, trapping, detrapping and transfer, effect of vibrational excitation of the adsorbates, together with nonadiatatic energy transfer in the substrate-adsorbate system and so on are needed.

IV. CONCLUSION

Photocatalyzed oxidation of methanol on TiO$_2$(110) surface under the irradiation of 360, 380, and 400 nm light have been studied using post-irradiation temperature-programmed desorption (TPD) method. Under these three UV irradiation cases, the main photocatalytic process is the cleavage of O−H and C−H bonds to produce formaldehyde, transferring the released hydrogen atoms to the basic oxygen sites to generate bridging hydroxyls. Nevertheless, the reaction rate is strongly wavelength dependent. The reaction rate under 360 nm light irradiation is 4.8 times of that in the case of 400 nm exposure. This result is consistent with a previous femtosecond time-resolved absorption measurement on TiO$_2$ which shows the faster charge carrier recombination in the near-band-gap than the over-band-gap excitation. The excitation wavelength dependence of photocatalytic activity on TiO$_2$ and other photocatalysts is still an open question, and further research is required to reveal the underlying mechanism.

V. ACKNOWLEDGMENTS

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