# ARTICLE

# Characterization of the Excited State on Methanol/TiO$_2$(110) Interface

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The electronic structure of methanol/TiO$_2$(110) interface has been studied by photoemission spectroscopy. The pronounced resonance which appears at 5.5 eV above the Fermi level in two-photon photoemission spectroscopy (2PPE) is associated with the photocatalyzed dissociation of methanol at fivefold coordinated Ti sites (Ti$_{5c}$) on TiO$_2$(110) surface [Chemical Science 1, 575 (2010)]. To check whether this resonance signal arises from initial or intermediate states, photon energy dependent 2PPE and comparison between one-photon photoemission spectroscopy and 2PPE have been performed. Both results consistently suggest the resonance signal originates from the initially unoccupied intermediate states, *i.e.*, excited states. Dispersion measurements suggest the excited state is localized. Time-resolved studies show the lifetime of the excited state is 24 fs. This work presents comprehensive characterization of the excited states on methanol/TiO$_2$(110) interface, and provides elaborate experimental data for the development of theoretical methods in reproducing the excited states on TiO$_2$ surfaces and interfaces.

**Key words:** Titanium dioxide, Excited states, Two-photon photoemission, Time-resolved

## I. INTRODUCTION

TiO$_2$ is a versatile material which has been applied in many technical fields, such as in heterogeneous catalysis, electronic devices, ceramic, biocompatible bone implants and pigment, as a photocatalyst, coating and gas sensor [1]. The photocatalytic property of TiO$_2$ has attracted tremendous attention since the first report of photocatalyzed splitting of water using UV light in the early 1970's [2]. A lot of work targeted at the discovery of practical application and improvement of the performance of TiO$_2$ based photocatalysts has been reviewed [3−10]. Despite great effort made in the synthesis and modification of TiO$_2$ based photocatalysts, much less is known about the microscopic mechanism of the photocatalytic processes. For example, the excited electronic structure of TiO$_2$ plays a crucial role in dictating the optical excitation and charge transfer, however, there is still very limited information of these unoccupied states.

So far, only a few X-ray absorption spectroscopy (XAS) [11], electron energy loss spectroscopy (EELS) [12], inverse photoemission spectroscopy (IPS) [13−15] and total current spectroscopy (TCS) [16] studies of

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excited states of TiO$_2$ have been reported. The XAS, EELS, IPS and TCS studies which focus on the unoccupied density of states (DOS) of TiO$_2$ in the energy range of 0−10 eV above the Fermi level ($E_F$), together with computational methods, have identified the t$_{2g}$ and e$_g$ components which are the hybridization between Ti3d and O2p from a molecular orbital point of view.

Two-photon photoemission spectroscopy (2PPE), a mature experimental technique in the investigation of the image potential states on metal surfaces [17, 18], has been used to study the electronic structure of TiO$_2$ interface by Petek *et al.* about 10 years ago [19]. 2PPE is a 1+1 pump-probe technique. The first photon excitation is followed by the absorption of a second photon, and the electrons below $E_F$ are excited to a final state beyond the vacuum level. Figure 1 illustrates the direct (B) and indirect (A) pathway of the two-photon excitation. In a direct 2PPE, the electrons in the initial states $|i\rangle$ are excited directly to the final states $|f\rangle$, which is similar to the one-photon photoemission (1PPE, C of Fig.1). While in the indirect 2PPE, the intermediate states $|k\rangle$ are populated before the second excitation to the final states. As a result, 2PPE is sensitive to both the initial and intermediate states and can measure the ultrafast electron dynamics of the excited states by accurate tuning of the delay between pump and probe pulses.

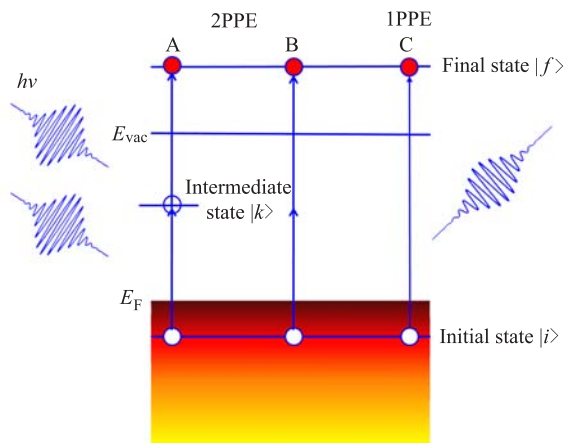Methanol/TiO$_2$ is a photocatalytic system of both

FIG. 1 Schematic of the two-photon excitation process with (A) or without (B) a real intermediate state and one-photon photoemission (C).

practical and fundamental importance [5]. Methanol adsorbs molecularly on the fivefold coordinated Ti sites ($Ti_{5c}$) of $TiO_2(110)$ surface and becomes dissociated under ultraviolet (UV) illumination [20]. The $O-H$ bond and $C-H$ bond break, generating formaldehyde and hydrogen atoms at the bridging oxygen sites ($H_b$) [21]. The dissociation of methanol leads to dramatic change of the electronic structure of methanol/$TiO_2(110)$ interface [20]. A resonance signal at 5.50 eV above $E_F$ has been detected by 2PPE on the methanol/$TiO_2(110)$ interface using 400 nm laser (Fig.2). This signal is present when probed with p-polarized light and absent with s-polarized light. It was once proposed that this resonance signal is from a wet electron state [22], and later studies show it is associated with the photocatalyzed dissociation of methanol at $Ti_{5c}$ sites [20].

Since 2PPE is sensitive to both the initial and intermediate states, experiments have been designed to determine the origin of the resonance signal in 2PPE. Photon energy dependent 2PPE and comparison between 1PPE and 2PPE consistently suggest this resonance signal is from an excited state which is located at 2.45 eV above $E_F$. Dispersion and time-resolved measurements show the excited state is localized and the lifetime is 24 fs. This work presents a comprehensive characterization of the excited state on methanol/$TiO_2(110)$ interface, which provides a model system for the development of theoretical methods in reproducing the excited states on $TiO_2$ surfaces and interfaces.

## II. EXPERIMENTS

The ultrahigh vacuum system (base pressure $5 \times 10^{-14}$ bar) which consists of a sample preparation & characterization chamber and a main probing chamber have been described in detail elsewhere [23]. A hemispherical electron energy analyzer (PHOIBOS 100,

SPECS) has been used to analyze the photoelectrons. Imaging method has been applied to record the energy and angular distribution of the photoelectrons within the energy range of interest simultaneously via a CCD camera (Sensicam, PCO). Two-photon excitation is realized by the second harmonic generation (SHG, 390−410 nm, 28 fs) of a Ti:Sapphire femtosecond oscillator (Synergy, 75 MHz, Femtolasers Produktions GmbH). Tuning of the SHG was realized via slight change of the matching angle of nonlinear crystal BBO. Accurate delay in the time-resolved 2PPE was generated by a Mach-Zehnder interferometer (MZI) [24]. In the 1PPE experiment, the fourth harmonic generation (205 nm) of the Ti:Sapphire oscillator was used.

In this work, both reduced and oxidized $TiO_2(110)$ (Princeton Scientific Corp., 10 mm×10 mm×1 mm) samples were used. The reduced $TiO_2(110)$ was cleaned by cycles of $Ar^+$ sputtering (1 keV, 15 min) and UHV annealing at 850 K (30 min). While the oxidized one was prepared by repeated $Ar^+$ sputtering and annealing at 850 K in the oxygen background ($1 \times 10^{-10}$ bar) cycles. The cleanness and long range order were confirmed by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) respectively.

Before introduced onto $TiO_2(110)$, methanol (Sigma-Aldrich, HPLC grade) was purified by liquid nitrogen freeze-pump-thaw cycles. Dose of multilayers of methanol onto $TiO_2(110)$ through a variable leak valve was followed by a flash to 190 K to get rid of the extra layers, leaving only saturated first layer, which is about 0.77 ML (1 ML=$5.2 \times 10^{14}$ $cm^{-2}$) [25]. The substrate was then recooled down to 110 K for the 2PPE experiments.

## III. RESULTS AND DISCUSSION

Figure 2 shows the 2PPE spectra of 0.77 ML $CH_3OH$ covered oxidized $TiO_2(110)$ after the interface were exposed to the p-polarized probe laser pulse (64.2 mW) for more than 15 min. Compared with s-2PPE, a pronounced resonance signal appears at 5.50 eV above the $E_F$. An intrinsic wet electron state was once reported to be responsible for this feature [22], however, we have proven later that this resonance signal is associated with the photocatalyzed dissociation of methanol at $Ti_{5c}$ sites of $TiO_2(110)$ [20]. As 2PPE carries the information of both initial and intermediate states (Fig.1), further experiments are needed to reveal the origin of the resonance signal in 2PPE spectra. To tell whether the resonance signal is from occupied initial state $|i\rangle$ or unoccupied intermediate state $|k\rangle$, two experiments, *i.e.*, photon energy dependent 2PPE and comparison between 2PPE and 1PPE, have been carried out.

### A. Origin of the resonance signal

According to Fig.1, if 2PPE is indirect, the intermediate states $|k\rangle$ will be populated firstly, and the cor-
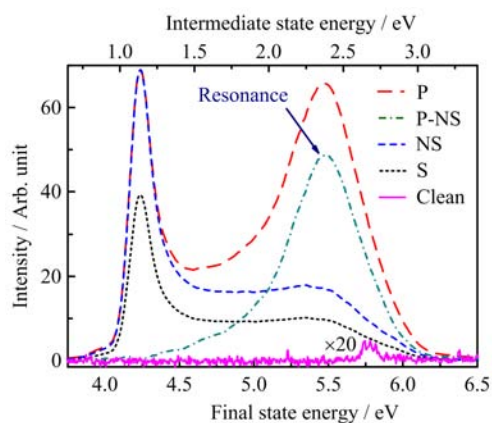
FIG. 2 p-polarized (P) and s-polarized (S) 2PPE spectra of 0.77 ML CH₃OH covered oxidized TiO₂(110) after the interface was exposed to the p-polarized probe laser pulse (64.2 mW) for more than 15 min. Clean means the 2PPE spectrum of the clean TiO₂(110) surface. The net resonance signal was obtained by subtracting the normalized S data (NS) from P. The lower $x$-axis indicates the final energy of the electron emitted to the vacuum. The upper $x$-axis shows the energy of any intermediate excited electronic state present after absorption of the first photon. Each spectrum is acquired with a CCD exposure time of 1 s. The signal in these spectra is integrated from $-5°$ to $+5°$. All the energies were measured relative to $E_F$.
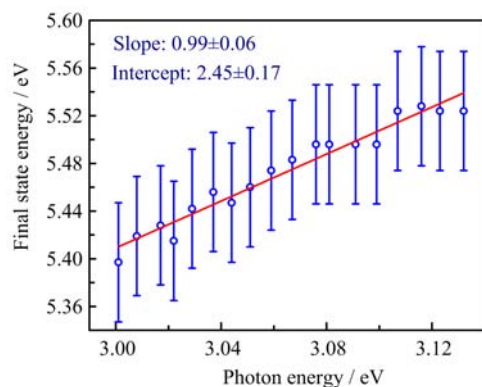


FIG. 3 Peak position of the resonance signal in 2PPE of 0.77 ML methanol/TiO₂(110) as a function of excitation photon energy.

responding kinetic energy of the photoelectrons in the final states is:

$$E_f = E_k + h\nu \qquad (1)$$

Otherwise, in a direct 2PPE process, the final state energy is:

$$E_f = E_i + 2h\nu \qquad (2)$$

where $E_i$, $E_k$, $E_f$, and $h\nu$ stand for the energy of the initial state, intermediate state, final state, and excitation photon, respectively.
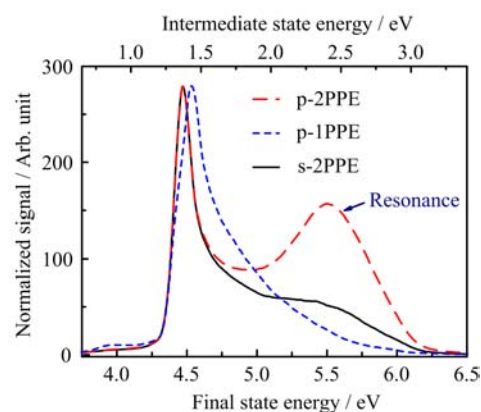


FIG. 4 Comparison between 2PPE and 1PPE of methanol/TiO₂(110) after UV illumination. The signal in these spectra is integrated from $-5°$ to $+5°$. All the energies are measured relative to $E_F$. s and p in the legend denote the polarization of the probe laser. p-1PPE and s-1PPE are identical except the intensity, thus only p-1PPE is shown.

By measuring 2PPE of 0.77 ML methanol/TiO₂(110) as a function of $h\nu$, excitation photon energy dependence of the peak position of the resonance signal has been obtained (Fig.3). A linear fitting gives rise to the slope of 0.99±0.06, which is very close to 1, suggesting the resonance signal in 2PPE of methanol/TiO₂(110) interface comes from an initially unoccupied state, *i.e.*, excited state. The intercept of the fitting line reflects the position of the excited states, which is 2.45±0.17 eV above $E_F$.

Comparison between 2PPE and 1PPE of methanol/TiO₂(110) has also been carried out to further confirm the resonance signal is from initially unoccupied intermediate states. 1PPE is a direct photoemission from initial states $|i\rangle$ to final states $|f\rangle$ (C of Fig.1). It is "blind" to any intermediate states. Whereas 2PPE contains the information of intermediate states if the photon energy is suitable. In the comparison between 2PPE and 1PPE (Fig.4), the wavelength of the excitation source is 410 and 205 nm, respectively, which guarantees similar initial and final state in these two measurements. Therefore, any additional feature in the 2PPE rather than 1PPE spectra results from unoccupied intermediate states. In the p-2PPE spectra, the resonance signal around 5.5 eV is obviously present, however, this feature is totally absent in 1PPE. This result unambiguously suggests the resonance signal in 2PPE arises from the initially unoccupied state, *i.e.*, excited state.

### B. Dispersion of the excited states

Dispersion of the electronic states, which means the lateral momentum (emission angle) dependence of the peak position, is a very important property of the electronic structure. Figure 5 shows the dispersion of the
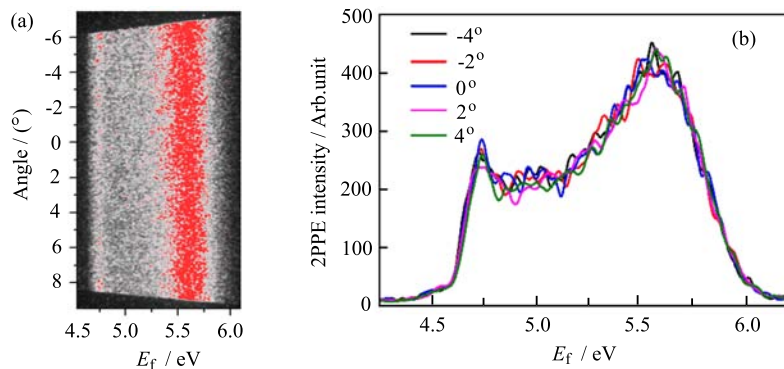
FIG. 5 (a) Two-dimensional 2PPE spectra for methanol/TiO$_2$(110) interface. The horizontal axis represents the final state energy relative to $E_F$, while the vertical one stands for the emission angle of the photoelectrons with respect to the surface normal. (b) 2PPE spectra for methanol/TiO$_2$(110) interface at different emission angles.
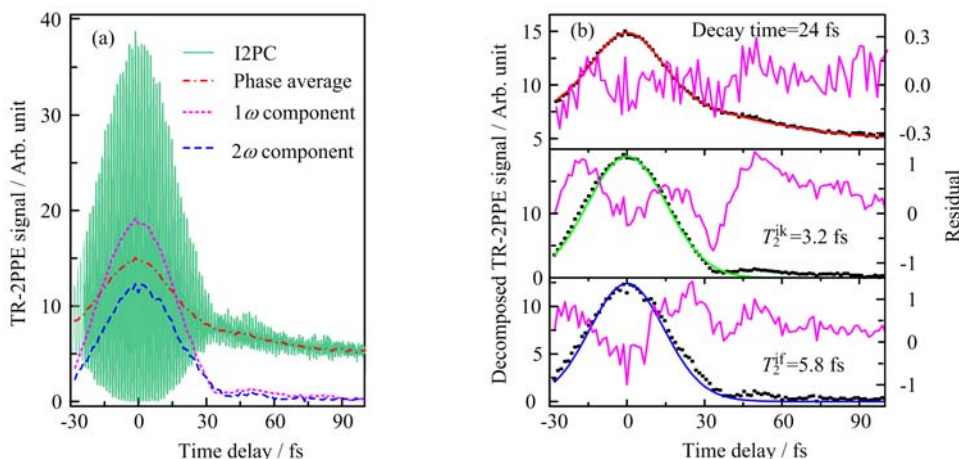


FIG. 6 Time-resolved two-photon photoemission (TR-2PPE) measurement of the excited states on methanol/TiO$_2$(110). (a) Pump-probe delay dependent 2PPE signal and its decomposition. (b) Numeric simulation of the decomposed components. The black dots are the decomposed data points from the left graph. The red, green and blues lines represent the fitting results of phase average, 1$\omega$ and 2$\omega$ components respectively. The magenta lines are the residuals. Where $T_2^{ik}$, $T_2^{if}$ and decay time represent the dephasing time between initial states $|i\rangle$ and intermediate state $|k\rangle$, dephasing time between initial states $|i\rangle$ and final state $|f\rangle$, and the lifetime of the intermediate states, respectively.

excited states on methanol/TiO$_2$(110) interface. Figure 5(a) is a two-dimension imaging of the photoelectrons emitted from methanol/TiO$_2$(110). Figure 5(b) displays a series of 2PPE spectra integrated at different emission angle from Fig.5(a). The peak position of the resonance signal which is associated with the excited states on this interface, remains unchanged when the emission angle varied from $-6°$ to $+8°$ (relative to the surface normal), suggesting the excited states are localized [18].

### C. Ultrafast dynamics of the excited states

Lifetime of the excited states on methanol/TiO$_2$(110) has been measured by time-resolved 2PPE (Fig.6). The phase averaged component of the interferometric two-

pulse correlation has been extracted using the Fourier transformation procedure described before [26]. The 0.77 ML methanol covered TiO$_2$(110) surface has been illuminated by the probe light for an adequate time to saturate the excited resonance signal. The lifetime of the excited state is analyzed by a three-energy-level model [27] to be 24 fs, which is close to previous studies [22] and that on ethanol/TiO$_2$(110) interface with similar adsorbate coverage [28].

### IV. CONCLUSION

The excited states on the light illuminated methanol/TiO$_2$(110) interface have been characterized by photoemission spectroscopy. Photon energy dependent 2PPE and comparison between 1PPE and 2PPE

consistently demonstrate the resonance signal in 2PPE of UV illuminated methanol/TiO$_2$(110) interface comes from the excited state which is located at 2.45 eV above $E_{\mathrm{F}}$. Dispersion and time-resolved measurements show the excited state is localized and the lifetime is 24 fs. This work presents a comprehensive characterization of the excited state on methanol/TiO$_2$(110) interface, which provides elaborate experimental data for the development of theoretical methods in reproducing the excited states on TiO$_2$ surfaces and interfaces.

## V. ACKNOWLEDGMENTS

[1] U. Diebold, Surf. Sci. Rep. **48**, 53 (2003).
[2] A. Fujishima and K. Honda, Nature **238**, 37 (1972).
[3] A. Mills, R. H. Davies, and D. Worsley, Chem. Soc. Rev. **22**, 417 (1993).
[4] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, Chem. Rev. **95**, 69 (1995).
[5] A. L. Linsebigler, G. Q. Lu, and J. T. Yates, Chem. Rev. **95**, 735 (1995).
[6] A. Fujishima, T. N. Rao, and D. A. Tryk, J. Photochem. Photobiol. C **1**, 1 (2000).
[7] X. Chen and S. S. Mao, Chem. Rev. **107**, 2891 (2007).
[8] A. Fujishima, X. Zhang, and D. A. Tryk, Surf. Sci. Rep. **63**, 515 (2008).
[9] X. Chen, S. Shen, L. Guo, and S. S. Mao, Chem. Rev. **110**, 6503 (2010).
[10] N. Serpone and A. V. Emeline, J. Phys. Chem. Lett. **3**, 673 (2012).
[11] D. W. Fischer, Phys. Rev. B **5**, 4219 (1972).
[12] Y. W. Chung, W. J. Lo, and G. A. Somorjai, Surf. Sci. **64**, 588 (1977).
[13] A. K. See and R. A. Bartynski, J. Vac. Sci. Technol. A **10**, 2591 (1992).
[14] A. K. See, M. Thayer, and R. A. Bartynski, Phys. Rev. B **47**, 13722 (1993).
[15] D. Purdie, B. Reihl, A. Thomas, P. J. Hardman, C. A. Muryn, and G. Thornton, J. Phys. IV **4**, 163 (1994).
[16] P. J. Moller, S. A. Komolov, and E. F. Lazneva, J. Phys: Condens. Matter **12**, 7705 (2000).
[17] J. Gudde and U. Hofer, Prog Surf. Sci. **80**, 49 (2005).
[18] P. Szymanski, S. Garrett-Roe, and C. B. Harris, Prog. Surf. Sci. **78**, 1 (2005).
[19] K. Onda, B. Li, and H. Petek, Phys. Rev. B **70**, 045415 (2004).
[20] C. Y. Zhou, Z. F. Ren, S. J. Tan, Z. B. Ma, X. C. Mao, D. X. Dai, H. J. Fan, X. M. Yang, J. LaRue, R. Cooper, A. M. Wodtke, Z. Wang, Z. Y. Li, B. Wang, J. L. Yang, and J. G. Hou, Chem. Sci. **1**, 575 (2010).
[21] Q. Guo, C. Xu, Z. Ren, W. Yang, Z. Ma, D. Dai, H. Fan, T. K. Minton, and X. Yang, J. Am. Chem. Soc. **134**, 13366 (2012).
[22] B. Li, J. Zhao, K. Onda, K. D. Jordan, J. L. Yang, and H. Petek, Science **311**, 1436 (2006).
[23] Z. F. Ren, C. Y. Zhou, Z. B. Ma, C. L. Xiao, X. C. Mao, D. X. Dai, J. LaRue, R. Cooper, A. M. Wodtke, and X. M. Yang, Chin. J. Chem. Phys. **23**, 255 (2010).
[24] H. Petek and S. Ogawa, Prog. Surf. Sci. **56**, 239 (1997).
[25] Z. Li, R. S. Smith, B. D. Kay, and Z. Dohnlek, J. Phys. Chem. C **115**, 22534 (2011).
[26] W. Nessler, S. Ogawa, H. Nagano, H. Petek, J. Shimoyama, Y. Nakayama, and K. Kishio, J. Electron. Spectrosc. **88**, 495 (1998).
[27] B. Li, *Ph. D. Dissertation*, Pittsburgh: University of Pittsburgh, (2006).
[28] Z. B. Ma, C. Y. Zhou, X. C. Mao, Z. F. Ren, D. X. Dai, and X. M. Yang, Chin. J. Chem. Phys. **26**, 1 (2013).