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Photoelectron Spectroscopic Study of Methanol Adsorbed Rutile TiO₂(110) Surface[†]

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Methanol/TiO₂(110) is a model system in the surface science study of photocatalysis where methanol is taken as a hole capture. However, the highest occupied molecular orbital of adsorbed methanol lies below the valence band maximum of TiO₂, preventing the hole transfer. To study the level alignment of this system, electronic structure of methanol covered TiO₂(110) surface has been measured by ultraviolet photoelectron spectroscopy and the molecular orbitals of adsorbed methanol have been clearly identified. The results indicate the weak interaction between methanol and TiO₂ substrate. The static electronic structure also suggests the mismatch of the energy levels. These static experiments have been performed without band gap excitation which is the prerequisite of a photocatalytic process. Future study of the transient electronic structure using time-resolved UPS has also been discussed.

Key words: Methanol, TiO₂, Ultraviolet photoelectron spectroscopy, Level alignment

I. INTRODUCTION

Photocatalysis holds the hope to solve the energy and environment problems we encountered today. Among the countless developed photocatalysts, titanium dioxide has become a prototype due to the excellent characters such as abundance, stability, nontoxicity and relative high photocatalytic efficiency since the seminal work by Honda and Fujishima in 1972 [1]. Adding methanol has been discovered to considerably improve the efficiency of photocatalytic water splitting over TiO₂ based photocatalysts [2] and methanol is regarded to act as a hole scavenger [3–5]. As a result, the chemical properties of methanol on TiO₂ surface have been extensively investigated [6–9].

Surface science studies combining ultraviolet vacuum (UHV), well ordered single crystals and advanced surface analysis techniques have provide microscopic insights such as reaction sites, elementary reaction steps and reaction kinetics into the photochemistry of methanol on TiO₂(110). Methanol prefers molecular adsorption on the five-coordinated Ti sites (Ti_{5c}) on TiO₂(110) and dissociates spontaneously at the bridging bonded oxygen vacancies (O_v) [10, 11]. Upon band gap excitation, methanol on Ti_{5c} sites become dissoci-

ated, producing formaldehyde and bridging hydroxyls [12–16].

As we know, a photocatalytic process include band gap excitation, charge separation, charge transportation, interfacial charge transfer, and finally surface redox reactions. These steps are greatly related to the electronic structure of the system under investigation. Therefore, studies on the occupied and unoccupied electronic structure near the Fermi level (E_F) are of vital importance in understanding the level alignment which is one of the key issues in photocatalysis. The valence band structure of methanol adsorbed TiO₂(110) has been measured by ultraviolet photoelectron spectroscopy (UPS) [17]. Though the molecular orbitals of methanol are not well resolved, one can clearly judge that the highest occupied molecular orbitals (HOMO) of adsorbates is right below the valence band maximum (VBM). The excited states on this interface have also been studied by two-photon photoemission spectroscopy (2PPE). Li *et al.* detected an excited state at ~ 2.4 eV above E_F and attributed it to the lowest unoccupied molecular orbitals (LUMO) of the adsorbates [18]. However, a later study suggests this excited state was associated with the photodissociation of methanol on this surface and the LUMO of adsorbates lie much higher than this state [12]. A most recent investigation reveals the excited state at ~ 2.4 eV above E_F is an intrinsic character of the TiO₂ substrate and it arises from the John-Teller induced splitting of the 3d orbitals of reduced Ti ions, *i.e.*, Ti³⁺ [19]. Theoretical calculations are also used to simulate the levels at methanol/TiO₂ interface [20–23]. Accurate experimental data of elec-

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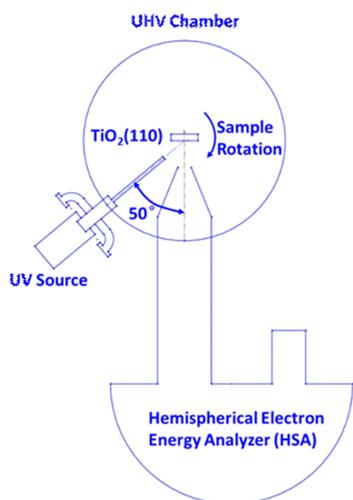


FIG. 1 Schematic overview of the experimental arrangement of the UV source and the hemispherical electron energy analyzer (HSA). The angle between the axes of the UV source and the HSA is fixed to 50°.

tronic structure are needed to verify the validity of the calculations.

As mentioned above, methanol is regarded as a hole capture in TiO₂ based photocatalysis. However, electronic structure measurement suggest the mismatch of the energy levels. Motivated by such contradiction and the lack of accurate molecular orbital data of adsorbed methanol on TiO₂(110), we re-investigate the valence band structure of the interface by UPS. By comparing with gas phase data, molecular orbitals of adsorbed methanol have been clearly identified. The results suggest relative weak interaction between methanol and TiO₂ substrate. The mismatch between the methanol HOMO and the TiO₂ VBM still exists in this static electronic structure measurement. Future time-resolved UPS studies on the transient electronic structure and ultrafast electron dynamics have been proposed.

II. EXPERIMENTS

All the experiments were carried out in the UHV (base pressure $< 1 \times 10^{-10}$ mbar) system [24] which contains two chambers. One is for sample preparation and characterization and the other is for photoelectron spectroscopy measurement. Argon ion source (IQE 11/35, SPECS), home-made resistive heating, X-ray photoelectron spectroscopy (XPS; XR 50, SPECS) and low energy electron diffraction (LEED) are equipped for preparation and characterization of the sample. μ -metal is installed in the whole chamber to shield the earth magnetism. A hemispherical electron energy analyzer (HSA; PHOIBOS 100, SPECS) is used to collect and analyze the photoelectrons which are amplified by two micro-channel plates (MCP) and then imaged by

a two-dimension charge coupled device (2D-CCD) camera (Sensicam, PCO). This imaging method facilitates the simultaneous recording of the energy and angular distribution of the photoelectrons of interest. The ultimate resolution of the HSA is less than 5 meV.

The TiO₂(110) sample (Princeton Scientific Corp, 10 mm \times 10 mm \times 1 mm) used in the present study was prepared by circles of Ar⁺ sputtering (10 min) and UHV annealing at 850 K (30 min). The cleanliness and the long range order were confirmed by XPS and LEED. After purification, HPLC grade CH₃OH (Sigma-Aldrich) was introduced onto the TiO₂(110) via a calibrated effusive beam doser at 120 K. The amount of CH₃OH was determined by temperature-programmed desorption spectroscopy (TPD) which was recorded by a modified quadrupole mass spectrometer (RGA 200, Stanford Research System). The coverage was calculated relative to the density of Ti ions (1 monolayer (ML) = 5.2×10^{14} molecules/cm²) on the (110) surface of TiO₂. The valence band structure of bare TiO₂(110) and CH₃OH/TiO₂(110) were measured by ultraviolet photoelectron spectroscopy (UPS) at about 100 K. Extremely ultraviolet (EUV) source He I (21.2 eV) was generated via discharging of He (UVS 10/35, SPECS). The linewidth of the He I light source is less than 2 meV. Two-photon photoemission spectroscopy (2PPE), which was excited by the second harmonic generation (405 nm) of an 80 MHz oscillator (MaiTai eHP, Spectra-Physics), was chosen to measure the work function of the TiO₂ interfaces.

III. RESULTS AND DISCUSSION

FIG. 2 shows the valence electron spectroscopy of clean and 0.5 ML methanol adsorbed rutile TiO₂(110) surface measured by UPS. The UPS spectra for the clean surface resemble those reported previously [25–27] and can be divided into three regions: (i) the secondary electron (SE) signal which centers at a binding energy of 12.74 eV. The interception of the linear fitting of the rising edge of SE can be used to measure the work function of the surface. (ii) O 2p signal of TiO₂ surface between 10 and 3 eV. The two peaks with binding energies of 5.15 and 7.25 eV are ascribed to the O 2p-Ti 4sp π bond and O 2p-Ti 3d σ bond [28], respectively. (iii) The band gap states signal below 3 eV. Although rutile TiO₂ is a wide band gap (3.05 eV) semiconductor, it can be easily reduced to introduce Ti³⁺, which can be reflected by the presence of a gap state (Ti³⁺ 3d) with a binding energy of ~ 1.00 eV [29–31].

Upon 0.5 ML methanol adsorption, significant changes can be observed: (i) though the peak position remains unchanged, the rising edge of the SE moves towards the higher binding energy direction, suggesting the decrease of the work function which is due to the adsorption of electron donating molecules such as water and methanol [32]. (ii) An obvious shoulder de-

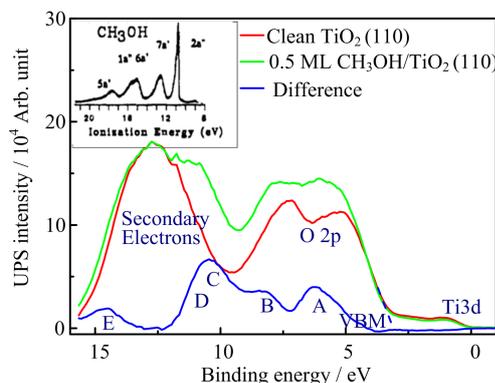


FIG. 2 UPS spectra ($h\nu=21.22$ eV) collected at 100 K on the clean rutile $\text{TiO}_2(110)$ surface (red), the $\text{TiO}_2(110)$ surface after adsorption of 0.5 ML methanol (green) and the difference spectrum by subtracting the spectrum of clean surface from that of the methanol covered $\text{TiO}_2(110)$ surface (blue). The emission angle is 50° and the incidence angle is 0° . The photoemission spectrum of CH_3OH in the gas phase [34] is shown as a inset at the left-top.

velops by the side of the SE peak at 10.95 eV and the overall intensity of the O 2p signal increases by $\sim 10\%$. We will show later that these features contain the contribution from the molecular orbitals of methanol. (iii) The VBM (labeled by dashed line in FIG. 2) increases by ~ 0.05 eV, indicating the downward band bending of the surface band structure, which is consistent with the electron donation of the methanol to the surface [33]. (iv) the signals in the band gap shrink by $\sim 20\%$, which is likely due to the scattering of the photoelectrons by the adsorbates.

In view of investigating the electronic structure of adsorbed methanol on $\text{TiO}_2(110)$ surface, UPS of clean TiO_2 was subtracted from that of 0.5 ML methanol covered rutile. Although such a simple subtraction can't get the exact electronic structure of the pure adsorbed methanol molecules on $\text{TiO}_2(110)$ because of the adsorbate-substrate interaction, the difference spectra can still reflect the rough results since the methanol- TiO_2 interaction is relatively weak, as can be seen in the following analysis. The difference spectrum is shown as blue line in FIG. 2 and the assignments are summarized in Table I. There are four broad peaks with the binding energies of 6.25, 8.25, 10.45, and 14.55 eV respectively. To simplify the description, they are labeled as A, B, C and E. For comparison, the photoelectron spectroscopy of the gas phase methanol [34] is also displayed as an inset in FIG. 2. The five peaks at 10.8, 12.8, 15.0, 16.0, and 17.5 eV are assigned to the molecular orbitals $2a''$, $7a'$, $6a'$, $1a''$ and $5a'$ respectively. The two orbitals $6a'$ and $1a''$ overlap but one can still see the shoulder. It should be noted the relative energies of the photoemission spectra in gas phase and on surface are different. In gas phase, the vertical ionization energy ε_i is measured relative to the vacuum level (E_v), while on surfaces the

TABLE I Assignment of the molecular orbitals of gas phase and adsorbed (on $\text{TiO}_2(110)$) methanol. The unit of the energy is eV. E_v , E_F and SE stand for the vacuum level, Fermi level and secondary electrons respectively. The capital letters in the adsorbed methanol column are the labels of the difference spectra in FIG. 2. The gas phase data are adapted from Ref.[34].

| Molecular orbitals | Gas (relative to E_v) | Gas (relative to E_F) | Adsorbed (relative to E_F) |
|--------------------|--------------------------|--------------------------|-------------------------------|
| $2a''$ | 10.8 | 6.3 | 6.25 (A) |
| $7a'$ | 12.8 | 8.3 | 8.25 (B) |
| $6a'$ | 15.0 | 10.5 | 10.45(C,D) |
| $1a''$ | 16.0 | 11.5 | |
| $5a'$ | 17.5 | 13 | Buried in SE |

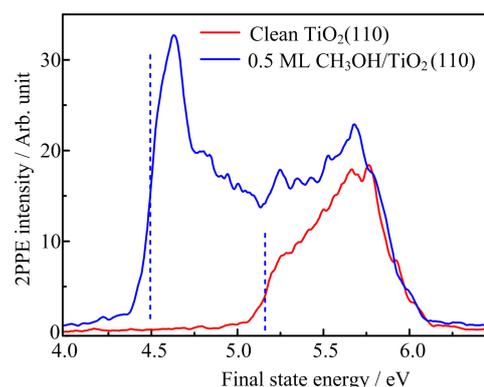


FIG. 3 The 2PPE spectra ($h\nu=3.06$ eV) of the clean and 0.5 ML methanol covered rutile $\text{TiO}_2(110)$ surface. The signal in these spectra is integrated from -5° to $+5^\circ$. All the energies are measured relative to E_F .

binding energy E_b is referred to the Fermi level (E_F). The energies of these two systems can be linked by the following expression [34]:

$$E_b = \varepsilon_i - \phi_{\text{ads}} \quad (1)$$

Where ϕ_{ads} is the work function of the surface after adsorption. In order to establish the relation between the methanol photoelectron spectra in gas phase and on rutile $\text{TiO}_2(110)$, we need to measure the work function of the methanol covered surface first. As mentioned above, the work function in UPS spectra can be obtained by linear fitting the rising edge of the SE peak. However, the regions you choose to carry out the fitting can considerably affect the results, due to the curvature of the rising edge. We therefore measured the work function by 2PPE (FIG. 3) in which the lower and upper cut off are determined by the work function and the two-photon energy ($2h\nu$). Usually, the final state energy at the half height of the SE edge (vertical dash lines) is taken as the work function [32]. According to this criteria, the work function of the clean and 0.5 ML CH_3OH

adsorbed TiO₂(110) surface are measured to be 5.17 and 4.50 eV respectively. Such results are consistent with the decrease of work function after methanol adsorption measured by UPS (FIG. 2).

By subtracting the 4.50 eV work function of the 0.5 ML methanol covered TiO₂(110) from the gas phase methanol photoelectron spectra, we can now compare the electronic structure of gas phase and adsorbed methanol (Table I). Obviously the molecular orbitals of methanol molecules become much broader once they are adsorbed onto the TiO₂(110) surface. The peak position of 2a''(A) and 7a'(B) molecular orbitals of the adsorbed methanol agree well with those in the gas phase. However, the 2a'' orbitals becomes significantly asymmetric with a long tail towards the VBM, suggesting the interaction between the methanol molecules and the substrate. The 6a' and 1a'' orbitals, which are very close and overlap severely even in the gas phase, finally converge into one broad peak (C/D) at 10.50 eV on TiO₂(110) surface. The energies are also consistent with those in the gas phase. The 5a' orbital of the adsorbed methanol is completely buried in the intense SE signal. Peak E is an artifact from the subtraction because of the different cut off in the two UPS spectra.

The comparison of the molecular orbitals of gas phase and adsorbed methanol tell us the following information: (i) the peak position of the five molecular orbitals of the adsorbed methanol agree well with those in the gas phase, indicating methanol remains molecular adsorption on TiO₂(110) and their interaction with the substrate is relatively weak. In fact in a control experiment to check whether the He I light source can affect the adsorption state of methanol on TiO₂(110), all the possible chemical reaction products were measured by TPD when the 0.5 ML methanol/TiO₂(110) interface has been exposed to the light source for adequately long time, and no detectable products have been observed. Therefore, in our experiments the effect of the He I light source on methanol can be neglected. This control study also suggests methanol prefers molecular adsorption in the current experimental conditions, which is consistent with previous experimental and theoretical investigations [11, 12]. (ii) Although the peak position of the highest occupied molecular orbital (HOMO) of the adsorbed methanol, *i.e.*, 2a'', remains the same as that in the gas phase, it develops a long tail towards the VBM. Feature 2a'' is from the ionization of electrons in an out-of-plane (C-O-H plane), non-bonding orbital on oxygen [34]. As we know, the adsorption of methanol on TiO₂ is realized by the donation of the lone pair electrons to the empty Ti 3d orbitals of the substrate. Such a configuration leads to the changes of the oxygen related orbitals of adsorbed methanol compared to those in the gas phase. TiO₂ is an n-type semiconductor, we simply take the conduction band minimum (CBM) as the Fermi level. The HOMO peak of adsorbed methanol and the VBM are located at 6.25 and 3.05 eV respectively. Even when the interaction of methanol with

TiO₂ extends the HOMO upper edge to 4.20 eV, there is a big mismatch of the energy level, preventing the hole transferring from VBM to adsorbate HOMO since in most cases the hot photogenerated charge carriers cool to the relative band edges in ultrafast time scale [5].

The above level alignment are measured without band gap excitation which is the prerequisite of photocatalysis. To investigate the effect of band gap excitation on the interfacial electronic structure, we repeated the above experiments and added a continuous ultraviolet (UV) light source (360 nm) simultaneously during the measurements. However, we did not observe any change which is probably due to the low flux of the UV light source. The development of ultrafast laser techniques in the EUV and soft X-ray range, for example, free electron laser (FEL) and high order harmonic generation (HHG), provides unprecedented opportunities for the investigation of the transient electronic structure. An HHG based time-resolved UPS spectrometer is under construction in our lab. Such a method has been used to study the ultrafast electronic structure [35] and chemical reactions [36, 37] on surfaces. We are going to measure the transient level alignment and ultrafast valence electronic structure of the prototypical TiO₂ based photocatalytic systems with the newly built spectrometer.

IV. CONCLUSION

Valence band structure of methanol covered rutile TiO₂(110) surface has been studied by UPS. Several molecular orbitals of the adsorbed methanol have been identified by comparing with those in the gas phase. The results indicate methanol interacts weakly with the TiO₂ substrate. Static UPS measurements also suggest the mismatch of the adsorbate HOMO and the substrate VBM, contradicting with the generally accepted fact that methanol acts as a hole scavenger in TiO₂ based photocatalysis. Transient level alignment of the photocatalytic systems will be studied with time-resolved UPS in the future.

V. ACKNOWLEDGMENTS

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