

## Surface photochemistry probed by two-photon photoemission spectroscopy

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Two-photon photoemission (2PPE) has been widely used in the study of electronic structure and dynamics of unoccupied electronic states on different types of surfaces and interfaces. Since 2PPE probes electronically excited states, it should be sensitive to surface excited electronic structure changes that accompany surface chemical reactions. Therefore, this method could potentially be used to study the kinetics and dynamics of surface chemical reactions as well as surface photocatalysis. In this article, we briefly review recent progress made in the study of surface photochemistry and photocatalysis using the time-dependent 2PPE (TD-2PPE) method. A few examples are given to demonstrate the application of this method in probing surface photochemistry and photocatalysis, particularly photocatalysis of methanol on TiO<sub>2</sub> surfaces. Since many problems associated with surface photochemistry and surface photocatalysis are related to energy and environmental issues, the 2PPE technique could have important applications in the study of the fundamental problems in energy and environmental sciences.

### 1 Introduction

In gas phase chemical reactions, newly formed reaction products can be routinely probed *via* both vibrational and electronic spectroscopy. Very detailed kinetic and dynamic information about the chemical reactions can be obtained.<sup>1–4</sup> In the study of surface chemical reactions, the kinetics and dynamics are also very important to the understanding of the mechanism of the chemical changes. Various spectroscopic techniques have been

used to probe chemical reactions at interfaces. Since surface chemical reactions involve structural changes, many spectroscopic techniques, such as electron energy loss spectroscopy (EELS),<sup>5–8</sup> infrared (IR) spectroscopy,<sup>9,10</sup> Raman spectroscopy<sup>9,11,12</sup> and sum frequency generation (SFG) spectroscopy<sup>12–14</sup> have been widely used to probe vibrational structures and their changes in surface chemical reactions. In addition, scanning tunnelling microscopy (STM) has also been utilized to study surface chemical reactions by exploiting its ability to probe changes in electronic structure and large geometric changes of species reacting at a surface.<sup>15–19</sup> These techniques have played key roles in the development of surface chemistry and catalysis research. In addition to the structural changes in surface chemical reactions, electronic structures near the reaction sites also change significantly, so electronic spectroscopic techniques such as ultraviolet photoelectron spectroscopy (UPS) and X-ray

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### Broader context

Developing efficient photocatalysts for energy and environmental processes, such as water splitting and photodegradation of environmental contaminants, is an important area of research. Much of the works in this area have been focused on synthesizing and developing new catalysts, while the fundamental study of surface photocatalysis has received much less attention. Developing new and powerful experimental methods to probe the kinetics of surface photocatalytic processes is crucial to understanding these processes at the most fundamental level. This paper provides a brief review on the development of the two-photon photoemission (2PPE) spectroscopy method as a probe for surface photochemistry and photocatalysis. Since 2PPE probes electronically excited states, it is sensitive to surface excited electronic structure changes that accompany surface chemical reactions. We have shown a few examples of photochemistry and photocatalysis studied using the 2PPE method. One particularly interesting example is the kinetic study of photocatalysis of methanol on the TiO<sub>2</sub>(110) surface. The results of these studies show that methanol photocatalysis on TiO<sub>2</sub>(110) occurs mainly on the Ti<sub>5c</sub> sites and that defects have a significant effect on the photocatalytic kinetics. These works demonstrate that 2PPE technique can be applied to the study of fundamental mechanisms in many energy and environment related processes.

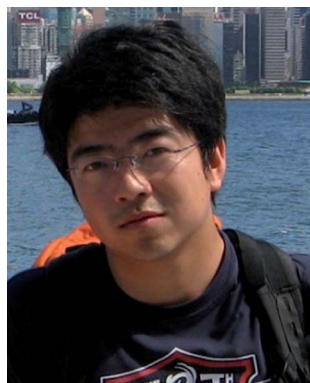
photoelectron photoemission (XPS) have been widely used in experimental studies of surface chemistry and catalysis. However, these conventional photoelectron spectroscopy techniques used in surface chemistry studies only probe the occupied electronic states.



**Chuanyao Zhou**

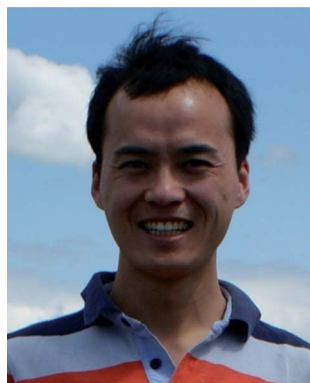
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2PPE has been extensively applied in the study of excited electronic structure and dynamics on metal surfaces.<sup>20–26</sup> Recently, the application of the 2PPE technique has also been extended to the study of excited electronic structure and dynamics of adsorbates on metal oxide surfaces,<sup>27–29</sup> which serve as models for practical catalytic or photocatalytic systems. The application of 2PPE in the study of metal oxide systems provides us with some hope that this method could be used to study photocatalytic processes at surfaces.

The 2PPE method is a variant of (1 + 1) pump-probe technique, in which a one- or two-color experiments can be carried out. In a typical 2PPE experiment, electrons below the Fermi level are excited to states above the Fermi level by one photon ( $h\nu_1$ ) and subsequently a second photon ( $h\nu_2$ ) excites them to an even higher energy above the vacuum level, generating free electrons. The energy and angular distributions of the photoelectrons are then measured. Using polarized light, the 2PPE technique can be used to distinguish surface electronic states from bulk electronic states. Varying the time delay between the



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two photons in a 2PPE experiment could also allow us to probe the ultrafast electron dynamics of excited states, which provide detailed information on the ultrafast electron relaxation and transfer processes. The most attractive feature of the 2PPE technique is its ability to probe the unoccupied states. In comparison to inverse photoemission spectroscopy (IPS) and STM, which can also be used to probe empty surface states, 2PPE is unique because it can be used to measure the lifetimes of unoccupied states with femtosecond time resolution. STM can be used to detect local excited states, while IPS and 2PPE can measure the angular distributions of them. In addition, 2PPE can be used to study the surface photochemical kinetics by probing the real-time change in the excited states due to photochemical reactions. Theoretically, STM and IPS can be used to study photochemical kinetics by monitoring the change in the excited states due to photocatalysis. However, in practice, STM needs to avoid the tip-shadowing problem in photoexcitation, while IPS needs observable photoluminescence from surface excited states. Neither STM nor IPS have been applied to study surface photochemical kinetics. Since photoemitted electrons can be detected with high sensitivity, 2PPE is a more sensitive technique to probe surface electronic states.

When surface excited electronic states change during the course of a surface reaction, the TD-2PPE technique can be used to monitor the kinetics of the surface chemical change. Such experiments have been performed previously, for example, 2PPE has been used to study the photoinduced desorption of Ar from a Cu surface.<sup>30</sup> In an analogous work, 2PPE has been applied to study photoinduced isomerization processes of tetra-tert-butyl-azobenzene (TBA) on Au surfaces.<sup>31–35</sup> In those experiments, surface excited electronic states are clearly changed during the chemical reaction. More recently, we have successfully shown that the femtosecond 2PPE technique can also be applied to the study of photocatalytic processes on metal oxides. Specifically, the kinetics and dynamics of the photocatalytic dissociation of methanol and other alcohols can be probed with the 2PPE technique.

In this mini-review, we describe some of the progress that has been made in surface photochemistry using the 2PPE technique. In the next two sections, we will review the results of the photoinduced desorption of Ar from Cu(110), and those of the photoinduced isomerization of TBA on the Au(111) surface. Then in the following section, we will review in detail recent results obtained mainly in our laboratory on the photocatalysis of methanol and other alcohols on TiO<sub>2</sub> surfaces using a newly built 2PPE apparatus. Finally, in the concluding remarks, we will discuss possible directions for future studies on photochemistry and photocatalysis using 2PPE, in combination with other emerging new surface science techniques.

## 2 Photodesorption of Ar from Cu(100)

Photodesorption of atomic and molecular adsorbates is a common surface chemical process that can be studied with the 2PPE technique because adsorption and desorption can alter the electronic structure of the surface. A very nice example has been given on the photodesorption of Ar from Cu(100) induced by 4.43 eV photons.<sup>30</sup> Fig. 1 shows the 2PPE spectra for bare Cu(100), 1 Ar-covered Cu(100) and 1 ML (monolayer)

Ar-covered Cu(100) after a 4.43 eV photon exposure of  $9.4 \times 10^{22}$  photons cm<sup>-2</sup> (from bottom to top), respectively. The photoelectron kinetic energy distributions from the  $n = 1$  image potential state peaked at 1.64 eV for the bare Cu(100) and 1.48 eV for the 1 ML Ar-covered Cu(100) surfaces, respectively. Clearly this shows that 2PPE can distinguish bare and Ar-covered Cu(100) surfaces based on changes in their excited state electronic structure. By taking into account the cross-section of the 2PPE processes, the amount of desorbed Ar (0.12 ML) was derived.

The kinetics of Ar photodesorption was measured by acquiring the 2PPE signal from the  $n = 1$  image potential state over time (Fig. 2). The photodesorption cross-section was determined and found to be extremely small ( $1.3 \times 10^{-24}$  cm<sup>2</sup>). The linear dependence of the desorbed amount of Ar on the laser exposure time indicates zero-order kinetics. The zero order kinetics is related to the fact that sub-ML Ar adlayers consist of densely packed islands in equilibrium with a 2D Ar “gas phase”. The authors suggest that the desorption of Ar atoms is not thermally induced and proceeds through the formation of a transient negative ion involving occupation of the Ar 4s affinity level by photoelectrons from Cu. This is certainly one possibility. It is also possible that the desorption of Ar atoms could be caused by the local substrate temperature rise generated by electron-hole pair recombination near the adsorption sites. Further study of this process is needed to clarify the desorption mechanism.

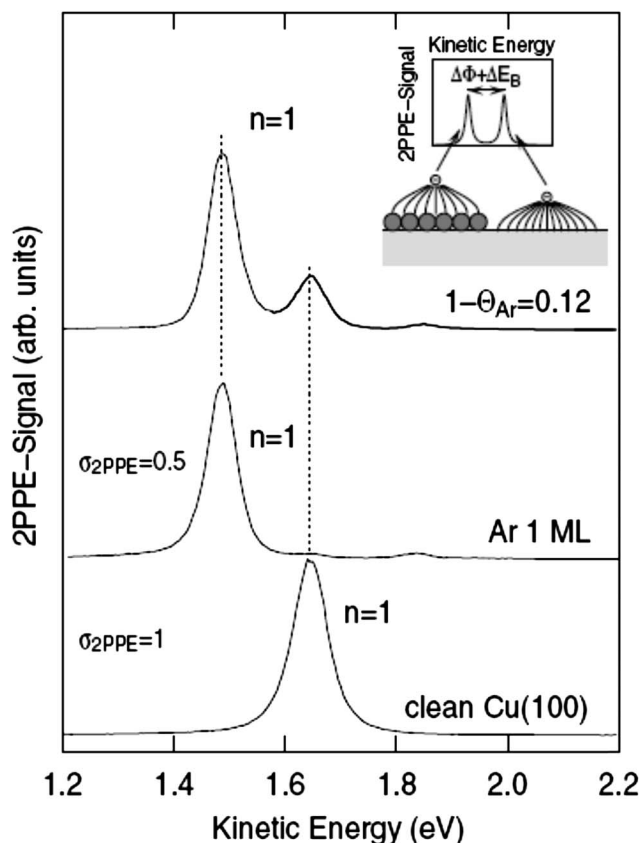
## 3 Photoisomerization of TBA on Au(111)

The photoisomerization of molecules adsorbed on surfaces can also be studied by 2PPE. Azobenzene and its derivatives are examples of the most thoroughly studied molecular switches.<sup>36–38</sup> One of the most intriguing properties of azobenzene (and some of its derivatives) is the reversible photoisomerization between the *trans* and *cis* isomers. The *trans*-isomer is more stable and is planar, whereas the *cis*-isomer is non-planar due to steric repulsion. The UV-induced *trans*–*cis* isomerization and the reverse *cis*–*trans* reaction, which can be driven by visible light or heat, are well studied in both liquid and gas phases.<sup>36–38</sup> In addition, the switching properties of these molecules on surfaces have also been demonstrated.<sup>34,39</sup>

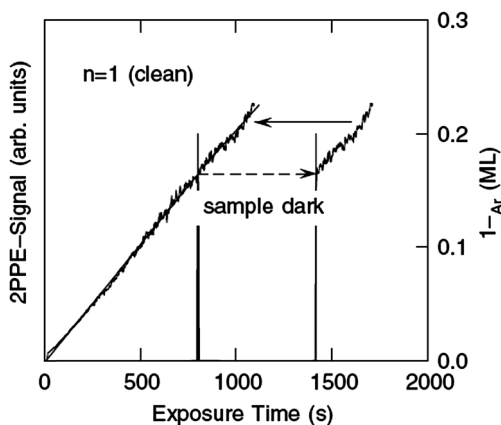
For *trans* TBA, the bulky tert-butyl groups displace the  $\pi$ -electronic system of the molecule from the substrate. In contrast, the *cis*-form with its three dimensional structure is capable of de-planarizing the  $\pi$ -electronic system and the N=N moiety is allowed to much more closely approach the surface. This leads to major isomerization-induced changes in the electronic structure of the excited states of the TBA adsorbates.

The reversible isomerization of this molecule on the Au(111) surface (Fig. 3<sup>40</sup>) has been studied with the femtosecond 2PPE method.<sup>31–34,41</sup> Specifically, *trans*–*cis* isomerization was achieved through UV light exposure. Two-color 2PPE spectra of a 0.9 ML of the TBA-covered Au(111) surface were recorded before and after significant isomerization had taken place, as shown in Fig. 4.<sup>32</sup> After illumination, the work function decreased by 0.05 eV, the peak at the work function edge (letter C in Fig. 4) became much more intense, a new peak at about 5.92 eV (letter B in Fig. 4) appeared and the intensity of the peak at around





**Fig. 1** 2PPE spectra for bare Cu(100), 1 ML Ar-covered Cu(100), and 1 ML Ar-covered Cu(100) after a 4.43 eV photon exposure of  $9.4 \times 10^{22}$  photons  $\text{cm}^{-2}$  (from bottom to top), respectively. Reproduced with permission from ref. 30. Copyright 2004 Elsevier.

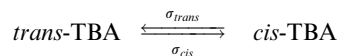


**Fig. 2** The evolution of 2PPE signal of the  $n = 1$  image potential states (characteristic of the bare Cu(100) surface) and also the desorbed Ar coverage as a function of the laser exposure time. Reproduced with permission from ref. 30. Copyright 2004 Elsevier.

6.25 eV (letter A in Fig. 4) dropped dramatically. According to the photon energy dependent results,<sup>32</sup> peaks A, B and C were assumed to originate from the LUMO of *trans*-TBA, the LUMO of *cis*-TBA and the (LUMO+ $n$ ) of *cis*-TBA, respectively. As 2PPE can resolve the LUMO of *trans*- and *cis*-TBA, and can also probe the (LUMO+ $n$ ) of *cis*-TBA, one is able to measure the

amount of the two isomers on the surface as a function of time, recording the kinetics of the photoinduced isomerization process.

The reaction rate of the reversible photoisomerization of TBA on Au(111) was described by a simple kinetic model:



which follows a simple integrated kinetic rate equation:<sup>33</sup>

$$[\text{cis}] = [\text{cis}]_{\infty} (1 - e^{-(\sigma_{\text{trans}} + \sigma_{\text{cis}}) \cdot F \cdot t}) \quad (1)$$

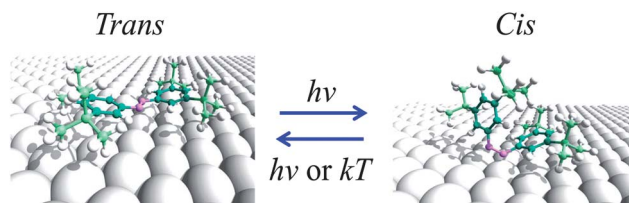
where  $\sigma_{\text{trans}}$  and  $\sigma_{\text{cis}}$  are the cross-section for the *cis*  $\rightarrow$  *trans* and *trans*  $\rightarrow$  *cis* isomerization respectively, and  $F$  is the laser fluence. The 2PPE signal originating from the (LUMO+ $n$ ) of the *cis*-TBA was used as a measure of the switching process (Fig. 5). Given that the intensity of the 2PPE signal is proportional to the square of the laser intensity, the total signal change during the *cis*-TBA formation could be written as:

$$\Delta I_{\text{total}} = \sum F_i^2 \Delta I_{\infty} (1 - e^{-(\sigma_{\text{trans}} + \sigma_{\text{cis}}) \cdot F_i \cdot t}) \quad (2)$$

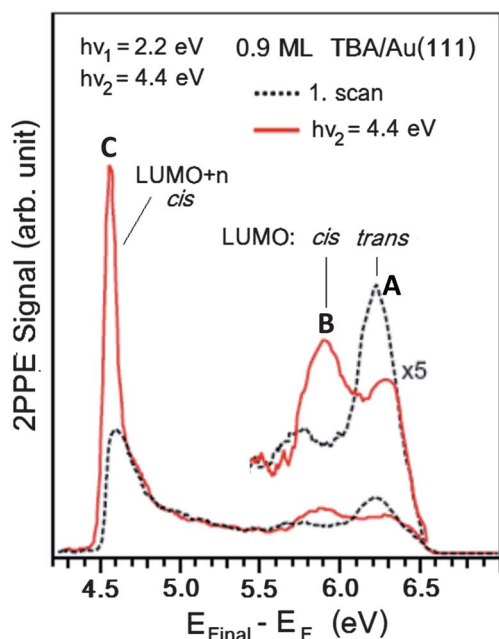
where  $F_i$  represents the fluence for each pixel  $i$  of the CCD camera detector.  $I_{\text{total}}$  stands for the intensity of the 2PPE signal, and  $I_{\infty}$  means the 2PPE intensity at infinite laser irradiation time. A total cross-section of  $6 \times 10^{-22} \text{ cm}^2$  was obtained by fitting the experimental data in Fig. 5 using the above equation.

When the photochemical equilibrium between the *trans*- and *cis*-TBA was reached (also referred to as the photostationary state), The equilibrium constant,  $K$ , could be derived  $-[\text{cis}]_{\infty}/[\text{trans}]_{\infty} = \sigma_{\text{cis}}/\sigma_{\text{trans}} = K$ . Assuming the same detection probability for the LUMO of *trans*- and *cis*-TBA on Au(111), the relative intensity reflects the ratio of the two isomers. The equilibrium constant ( $K = 1.2$ ) as well as the photoisomerization cross-sections ( $\sigma_{\text{trans}} = 2.7 \pm 0.5 \times 10^{-22} \text{ cm}^2$  and  $\sigma_{\text{cis}} = 3.3 \pm 0.5 \times 10^{-22} \text{ cm}^2$ ) were determined.

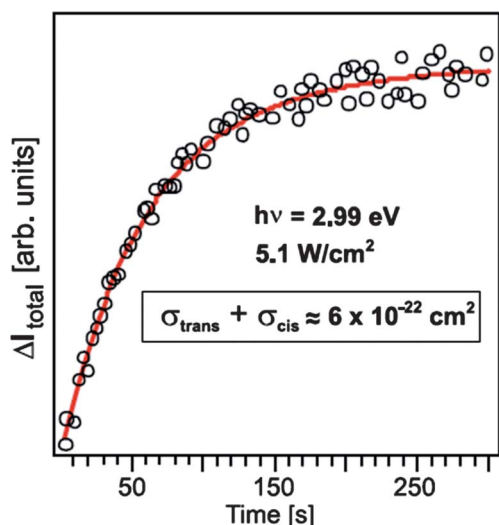
Exposure of the TBA-covered Au(111) surface to light with a photon energy between 2.2 eV and 4.4 eV leads to a constant cross-section for the *trans*-to-*cis* transformation of TBA, whereas below 2.2 eV (above 4.4 eV), the effective *trans*-to-*cis* cross-section decreases (increases) exponentially with energy. As there is no resonance at the photon energy of 3.65 eV (LUMO-HOMO gap), direct electronic excitation as in the liquid phase should not be responsible for the photoisomerization on this surface, and a surface-mediated indirect excitation has been proposed according to the photon energy dependence of the cross-section.<sup>32</sup> Light exposure ( $>2.2$  eV) generates holes in the d-band of Au(111), which subsequently relax to the top of the d-band via Auger decay, then the holes transfer to the HOMO of TBA, which results in the conformational change. The lower threshold



**Fig. 3** Geometric structure of *trans*- and *cis*-TBA adsorption on the Au(111) surface. Reproduced with permission from ref. 40.



**Fig. 4** 2PPE spectra for 0.9 ML of the TBA-covered Au(111) surface at the very beginning and after 4.4 eV photon exposure ( $3 \times 10^{21} \text{ cm}^{-2}$ ). Reproduced with permission from ref. 32. Copyright 2008 American Institute of Physics.



**Fig. 5** 2PPE signal from the LUMO+n state of *cis*-TBA as a function of the laser irradiation time. Reproduced with permission from ref. 33. Copyright 2008 Springer.

is consistent with the gap between the Fermi level and the d-band edge of Au(111). Above 4.4 eV, the relaxation of the photoexcited hole *via* Auger decay will result in the generation of a second hole, which leads to the enhanced switching rate. Such a switching process is also clearly relevant to the study of molecular switches.

#### 4 Photocatalysis of methanol on TiO<sub>2</sub>(110)

One of the greatest challenges in the field of energy and environmental sciences is the development of clean energy sources.

Hydrogen is certainly a potential energy carrier due to its high energy capacity and environmental friendliness.<sup>42</sup> However, clean hydrogen production still remains a big challenge.<sup>43,44</sup> One possible way to produce clean hydrogen is *via* photocatalytic splitting of water on oxide surfaces using sunlight.<sup>45</sup> However, the low efficiency of such processes has hindered developments in this direction. Despite the difficulties, photocatalyzed splitting of water on TiO<sub>2</sub> surface has been extensively investigated, and many strategies have been proposed to increase the hydrogen production, *e.g.*, loading TiO<sub>2</sub> with a noble metal or other semiconductor, doping, sensitizing and adding sacrificial species.<sup>44</sup> It has been reported that methanol is an effective sacrificial agent for hydrogen production.<sup>46,47</sup> Clearly, the photochemistry of methanol on TiO<sub>2</sub> plays a significant role in this process. However, the mechanism of photocatalytic chemistry of methanol and water on TiO<sub>2</sub> surfaces remains unclear.

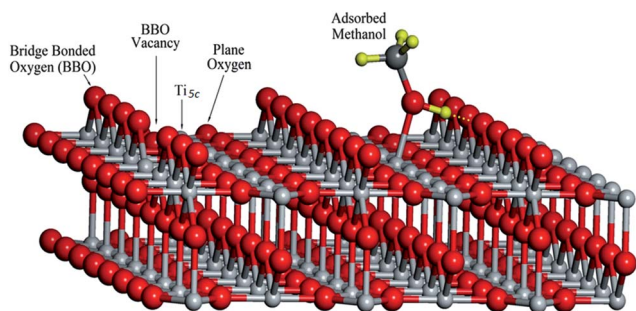
TiO<sub>2</sub> is a wide band gap (rutile 3.05 eV, anatase 3.2 eV) semiconductor. It has a wide range of applications in catalysis, photocatalysis and other energy and environmental application areas.<sup>48,49</sup> The rutile TiO<sub>2</sub> crystal structure is the most stable form at high temperatures, and hence the most easily studied with surface science methods. Among the low index surfaces of rutile TiO<sub>2</sub>, the surface energy of the (110) surface is the lowest.<sup>48</sup> Methods for the preparation of TiO<sub>2</sub>(110) surfaces in ultrahigh vacuum (UHV) conditions are also well established<sup>48,50,51</sup> and this surface has become a prototype for metal oxides.<sup>48,49,51,52–56</sup>

Fig. 6 shows a model of the structure of the TiO<sub>2</sub>(110)-(1 × 1) surface. It is composed of alternating rows of divalent bridge-bonded oxygen (BBO) atoms and pentavalent titanium atoms (Ti<sub>5c</sub>). These rows run in the [001] direction and are separated by in-plane oxygen-atom rows. The model also shows BBO rows exhibiting frequent vacancies, *i.e.*, bridge-bonded oxygen vacancies (BBOv's), which are often preferential adsorption sites on this surface. BBOv's can be easily introduced by thermal annealing,<sup>48,50–52,57</sup> ion sputtering<sup>27,58,59</sup> or electron bombardment.<sup>50,60,61</sup> Besides BBOv's, "near surface defects" such as Ti interstitials and subsurface oxygen vacancies also exist. These defects are, however, more difficult to characterize.<sup>62</sup> It has been shown that both surface BBOv's<sup>47–49,51,52,56,63,64</sup> and subsurface defects<sup>63–72</sup> are capable of affecting the chemistry on the TiO<sub>2</sub>(110) surface.

Because of its important role as a sacrificial agent in photocatalytic water splitting on TiO<sub>2</sub>, scientists in this field consider methanol photochemistry on TiO<sub>2</sub>(110) to be an important model system for metal oxide chemistry and photochemistry. Therefore, the physical and chemical properties of methanol on TiO<sub>2</sub>(110) have been examined in detail both experimentally<sup>29,53,62,73–79</sup> and theoretically<sup>80–84</sup> to probe the active sites and relevant reactive structures. Despite this extraordinary effort, central questions remain unresolved, for example, how methanol enhances the photocatalysis of water or how it is eventually photodegraded on TiO<sub>2</sub>. This is largely due to the difficulties involved in probing the microscopic photocatalysis process *in-situ* using the experimental techniques currently available.

##### 4.1 Adsorption of methanol on TiO<sub>2</sub>(110)

Henderson and coworkers studied the thermal chemistry of methanol on reduced (~8% BBOv's) TiO<sub>2</sub>(110).<sup>73,74</sup> In the



**Fig. 6** The structure of the rutile-TiO<sub>2</sub>(110) surface on which there are rows of bridging oxygen sites, in-plane oxygen sites and Ti<sub>5c</sub> sites.

temperature programmed desorption (TPD) spectra, the peaks positioned at 145 K, 165 K and 295 K corresponded to the desorption of the multilayer, the second layer and the first layer, respectively. As for water, the first layer adsorption of methanol is on the Ti<sub>5c</sub> sites (see Fig. 6). Their results indicated that the majority of the methanol molecules adsorbed on the Ti<sub>5c</sub> sites are not dissociated. The authors suggest that small amounts of methanol might be dissociated at the Ti<sub>5c</sub> sites, based on high resolution electron energy loss spectroscopy (HREELS) and static secondary ion mass spectroscopy (SSIMS).<sup>74</sup> However, these results are not conclusive because the dissociation of methanol could be induced by the high energy electrons used in HREELS or ions used in SSIMS detection.

The conclusion that the majority of the methanol molecules are adsorbed on the TiO<sub>2</sub> surface in molecular form is also consistent with a recent STM study.<sup>75</sup> In this work, molecular methanol diffusion along the Ti<sub>5c</sub> rows was observed, indicating that methanol is not dissociated at the Ti<sub>5c</sub> sites. The 2PPE technique was also used to investigate the electronic structure of the methanol covered TiO<sub>2</sub>(110) surface.<sup>29,53</sup> An excited electronic state was observed at about 2.3 eV above the Fermi level. This was attributed to a “wet electron state” that intrinsically exists on the methanol–TiO<sub>2</sub>(110) surface. (A “wet electron” means an electron solvated in water or other liquids.<sup>85</sup> It has been shown that electrons can be stabilized by water clusters *via* dangling hydrogen atoms, *i.e.*, hydrogen atoms that do not participate in the hydrogen bond.<sup>86–88</sup> And then this concept was applied to explain the electronic structure at interfaces.)

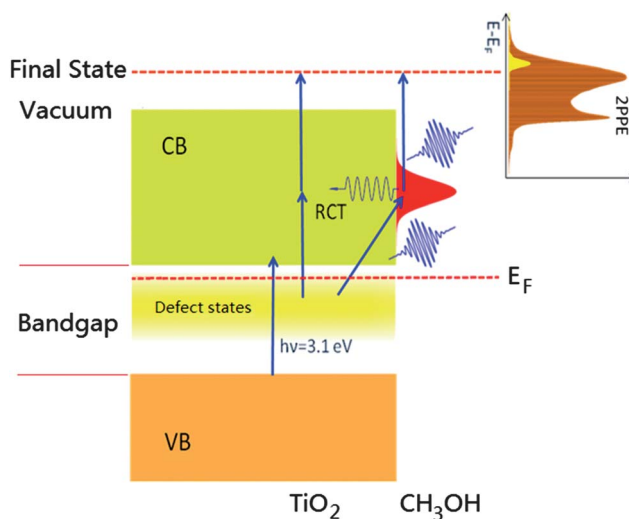
The adsorption of methanol on TiO<sub>2</sub>(110) was also studied using first-principle calculations.<sup>80,81,83</sup> Most DFT calculations show that the transfer of the hydroxyl protons from methanol to the neighboring bridge oxygen sites has a small barrier and the dissociated state of methanol is nearly iso-energetic to the molecular adsorbed state, with the dissociated state being at a slightly higher energy. This suggests that the methanol molecules should be adsorbed on the TiO<sub>2</sub>(110) surface in a molecular form at low temperatures, which is consistent with STM experiments at both room temperature and liquid nitrogen temperature. It is also shown that the dissociation of methanol at BBOv's is energetically favored by about 0.5 eV in comparison to molecular adsorption,<sup>81</sup> suggesting that methanol should be dissociated at the BBOv sites. This result is also consistent with all TPD and STM experimental results so far. Therefore, the adsorption picture of methanol on TiO<sub>2</sub>(110) is quite clear: while

methanol adsorbs on Ti<sub>5c</sub> in the molecular form, it adsorbs on BBOv's in the dissociated form.

## 4.2 Photocatalytic dissociation of methanol on TiO<sub>2</sub>(110)

The methanol–TiO<sub>2</sub>(110) system was recently re-investigated using a 2PPE apparatus in our laboratory. An energy diagram for this experiment is shown in Fig. 7. On this apparatus, a 2D multi-channel plate-CCD camera detector is used to record the energy and angular distribution of the photoelectrons simultaneously.<sup>89</sup> The data are acquired by imaging all the photoelectrons at once, which is more efficient than analyzers used in previous experiments that need energy scanning. This turns out to be a crucial advantage for studying methanol photochemistry on TiO<sub>2</sub>.

The stoichiometric TiO<sub>2</sub>(110) surface was prepared by cycles of Ar<sup>+</sup> sputtering (1 kV, 1.5  $\mu$ A, 20 min) and annealing at 850 K in the presence of oxygen ( $1 \times 10^{-7}$  mbar, 40 min). A 2PPE spectrum of 1 ML of the CH<sub>3</sub>OH-covered stoichiometric TiO<sub>2</sub>(110) surface was measured after the surface had been irradiated by a femtosecond laser pulse (400 nm, 64.0 mW) for about 15 minutes. Here, the 400 nm light serves as the light source for both the band gap excitation of TiO<sub>2</sub>(110) and the 2PPE probe. It is clear that the work function (half the maximum of the lowest energy edge<sup>27</sup>) was lowered by 1.6 eV with 1 ML methanol coverage in comparison with a bare TiO<sub>2</sub>(110) surface. The most significant feature in the spectrum is the appearance of the extra feature at around 5.5 eV in the 2PPE spectra taken using *p*-polarized light. This feature is not present when the spectrum is taken using *s*-polarized light. This suggests that the transition moment of the excited electronic state is along the surface normal,<sup>27</sup> implying that the new feature is a surface electronic resonance state. This feature was not observed in the one-photon photoemission spectra, indicating that it arises from an initially unoccupied excited electronic state. It is necessary to point out that the spectra shown in Fig. 8 are very similar to the results of the previous 2PPE measurements on this surface,<sup>29</sup>



**Fig. 7** Schematic diagram of the electronic structure of TiO<sub>2</sub>(110) and the two-photon photoemission process on this surface. Reproduced with permission from ref. 77.

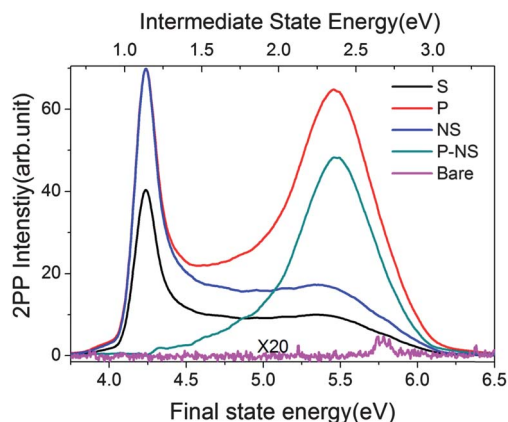


where the unoccupied excited state was interpreted to be an intrinsic “wet electronic state” on the methanol-covered  $\text{TiO}_2(110)$  surface. If the “wet electronic state” exists on the fresh  $\text{CH}_3\text{OH-TiO}_2(110)$  surface, the excited resonance peak around 5.5 eV should appear immediately when the probe laser starts to shine on the freshly prepared 1 ML methanol-covered stoichiometric  $\text{TiO}_2(110)$  surface. However, the resonance peak observed does not appear immediately after the laser irradiation, which suggests that the excited resonance peak is not due to an excited state that intrinsically exists on the freshly prepared methanol- $\text{TiO}_2(110)$  surface.

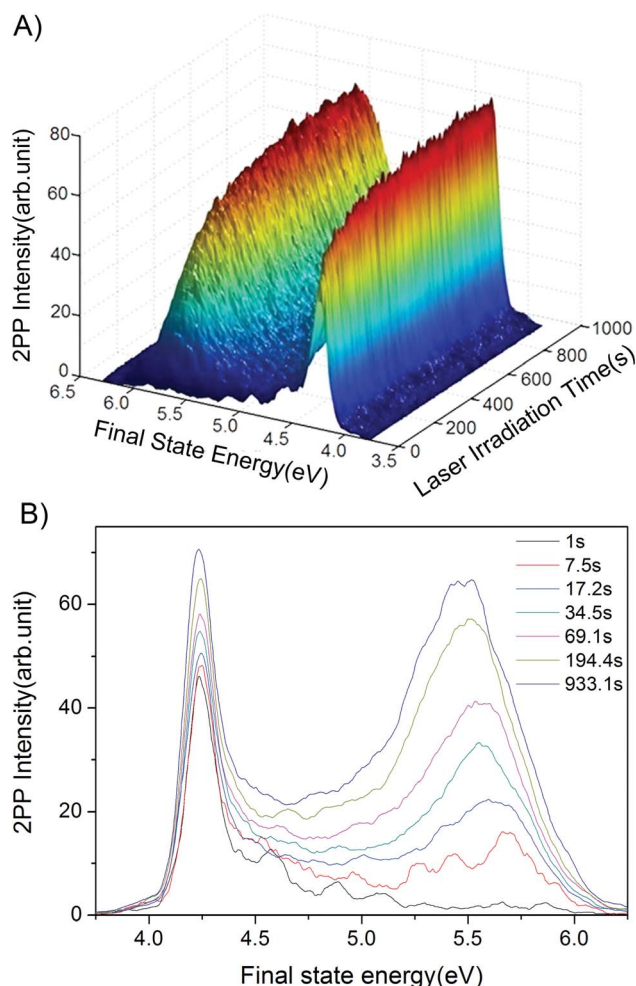
The TD-2PPE spectra were recorded to understand the origin of the excited state on the methanol- $\text{TiO}_2(110)$  surface (see Fig. 9). Here we show TD-2PPE spectra on the freshly prepared 1 ML methanol adsorbed  $\text{TiO}_2(110)$  surface obtained with *p*-polarized laser light recorded repetitively every second for over 900 s. The most intriguing observation is the total absence of the excited resonance signal around 5.5 eV in the spectra when laser illumination is initiated. The excited resonance feature appears to increase with the laser irradiation time, and the peak also shifts towards lower energy. The exact reason for the energy shift is not yet clear. In addition, the excited resonance signal reaches a plateau when the 1 ML  $\text{CH}_3\text{OH}$ -covered stoichiometric  $\text{TiO}_2(110)$  surface was irradiated by the laser for about 20 minutes. This interesting result unambiguously shows that the excited resonance state, which lies at 2.4 eV above the Fermi level, is a photoinduced excited surface state rather than an excited state that is intrinsically present on this interface.

Since a large change in electronic structure is normally associated with chemical structural changes, it is clear that the 400 nm light irradiation induces a chemical change in the methanol- $\text{TiO}_2(110)$  surface. The appearance of the new excited state after laser irradiation implies that the methanol molecules adsorbed on the  $\text{TiO}_2$  surface might be dissociated. In order to understand this process, STM experiments were performed on the methanol- $\text{TiO}_2(110)$  system using UV illumination to help reveal the nature

of the photochemical changes detected by 2PPE.<sup>77</sup> The STM experiments were performed at a surface temperature of 80 K. The  $\text{TiO}_2(110)$  sample in the STM experiment was prepared by cycles of  $\text{Ar}^+$  sputtering and UHV annealing at 900 K. Fig. 10A shows STM images of the bare  $\text{TiO}_2(110)$  surface (4% BBO's). The bright and dark lines correspond to the  $\text{Ti}_{5c}$  and BBO rows, respectively, while the bright spots on the dark lines correspond to the BBO's. Upon adsorption, more than 90% of the methanol (0.02 ML) molecules bind to the  $\text{Ti}_{5c}$  sites and appear as clear bright round spots (Fig. 10B). These molecules can be moved along the  $\text{Ti}_{5c}$  row as a whole or even desorbed by the STM tip, implying that the methanol molecules are adsorbed on the  $\text{Ti}_{5c}$  sites as a whole molecule, not dissociated molecules, which is consistent with previous STM studies at room temperature.<sup>75</sup> The majority of the uniform bright spots became elongated (marked by black arrows in Fig. 10C) after 10 min UV (<400 nm) irradiation from a UV lamp. This is seen more clearly by comparing the STM line scans before (Fig. 10F) and after (Fig. 10G) UV light illumination. The width of the methanol



**Fig. 8** 2PPE spectra for the bare and 1 ML  $\text{CH}_3\text{OH}$ -covered stoichiometric  $\text{TiO}_2(110)$  surface. P and S stand for the spectra acquired by *p* and *s*-polarized light, respectively, and P-NS means the net excited resonance signal obtained by subtracting the normalized S-polarized signal from the P polarized signal. The spectra were integrated from  $-5^\circ$  to  $+5^\circ$  with the  $\text{TiO}_2(110)$  surface normal to the analyzer. The reference energy is the Fermi level. Reproduced with permission from ref. 77.



**Fig. 9** The 2PPE spectra were measured for the freshly  $\text{CH}_3\text{OH}$ -adsorbed stoichiometric  $\text{TiO}_2(110)$  surface after the surface had been exposed for different time durations. (A) This plot shows the time evolution of the 2PPE spectra after the surface was exposed for certain time durations. (B) This panel shows typical 2PPE spectra at seven different surface illumination times.

feature in the line scan has nearly doubled after UV irradiation. This implies that the methanol molecule is likely to be dissociated on the surface. STM manipulation on the elongated methanol molecule was also performed. Clearly, the elongated spots after UV irradiation can be separated into two components by the STM tip, while the molecularly adsorbed methanol species before UV irradiation can only be moved as a whole. One of the components left on the BBO site was confirmed to be an H atom.<sup>90</sup> This clearly indicates that the methanol molecule after UV irradiation is photocatalytically dissociated.

Similar STM experiments using light with wavelengths longer than 400 nm have also been carried out. In this case, no evidence of methanol dissociation was found. This suggests that the photocatalyzed dissociation of methanol on  $\text{TiO}_2(110)$  by UV light with wavelength  $<400$  nm is due to the band gap excitation, indicating that electron–hole pair excitation is responsible for the photocatalytic dissociation of methanol on the  $\text{Ti}_{5c}$  sites of the  $\text{TiO}_2(110)$  surface.

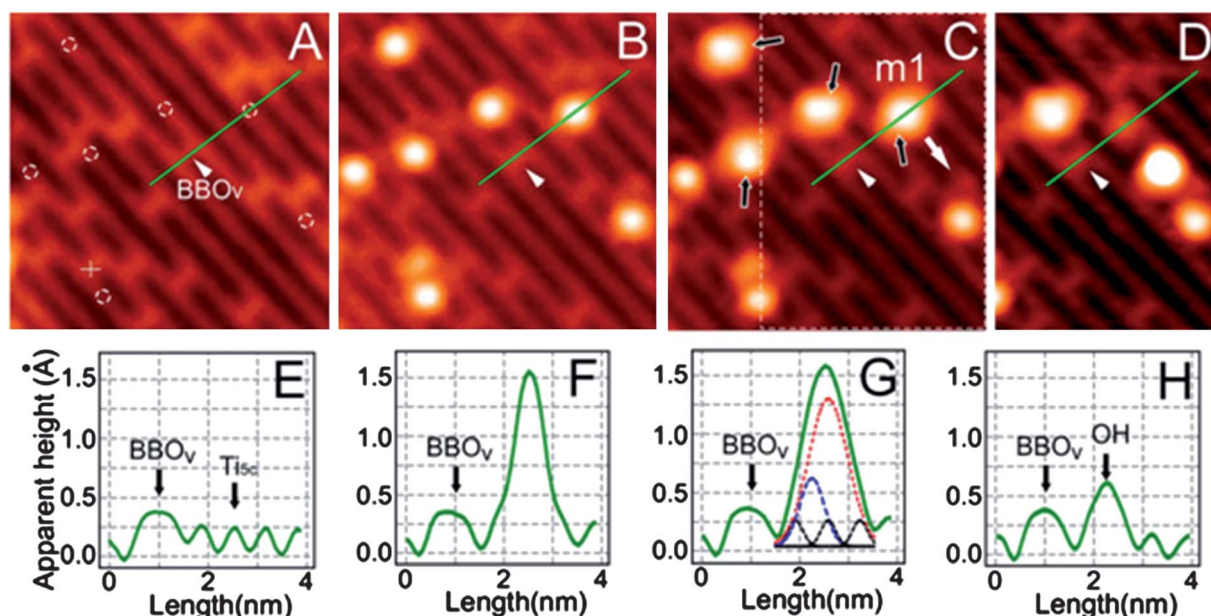
Since 2PPE and STM cannot easily identify the photochemical products of the photocatalytic dissociation of methanol on  $\text{TiO}_2(110)$ , additional analysis of the photochemical products are needed. Henderson and coworkers have studied the photochemistry of methanol on  $\text{TiO}_2(110)$  using the TPD method<sup>79</sup> and found that formaldehyde is the main photochemical product from methanol photochemistry on  $\text{TiO}_2(110)$  with UV light irradiation. Recently, we have also carried out a series of experiments on methanol photochemistry on  $\text{TiO}_2(110)$  by UV light using the highly sensitive TPD technique. Our experimental results confirm that formaldehyde is the main photochemical product from the photocatalytic dissociation of methanol at low methanol coverage. Furthermore, a more detailed experimental study shows that the methanol photocatalytic dissociation on

$\text{TiO}_2(110)$  to form formaldehyde occurs in a step-wise manner. As has been reported, the transfer of hydrogen atoms to bridging oxygen sites is much more stable than to the surface in-plane oxygen sites.<sup>81</sup> Therefore, the photochemical changes of methanol on the  $\text{Ti}_{5c}$  sites induced by UV irradiation is the photocatalyzed splitting of methanol to formaldehyde with the dissociated hydrogen atoms transferred to the neighboring BBO sites.

We have also varied the methanol coverage and the extent of the reduction of the  $\text{TiO}_2(110)$  sample, and observed similar results in the 2PPE spectra to those just presented on the 1 ML methanol covered stoichiometric  $\text{TiO}_2(110)$  surface. These results suggest that the photoinduced chemical changes seen here are independent of both the adsorbate coverage and the extent of the substrate reduction. Therefore, the results in the 2PPE and STM/TPD experiments could be directly related. Thus we are sure that the excited state probed by 2PPE on the methanol– $\text{TiO}_2(110)$  interface is associated with the photocatalyzed splitting of methanol on the  $\text{Ti}_{5c}$  sites.

In addition, we have investigated the dynamics of the excited state on the 1 ML methanol-covered  $\text{TiO}_2(110)$  surface with femtosecond time-resolved two-photon photoemission (TR-2PPE). The measured lifetimes (Fig. 11) are consistent with those reported previously with similar coverage,<sup>29</sup> and no isotope effect was observed. It is necessary to point out that since the excited state is photoinduced, one should not perform ultrafast time-resolved measurements until the density of the excited state reaches its maximum by light illumination.

The excited state about 2.4 eV above the Fermi level on the methanol-covered  $\text{TiO}_2(110)$  surface has been detected and was attributed to the dissociated methanol on the surface. Our DFT calculations provide a possible explanation for the excited



**Fig. 10** Imaging photocatalyzed dissociation of methanol. STM images (acquired at a bias of 1.0 V and set point current of 10 pA, size of  $7.3 \times 7.3$  nm<sup>2</sup>) of (A) bare  $\text{TiO}_2(110) - 1 \times 1$  surface, (B)  $\text{TiO}_2(110)$  surface with adsorbed  $\text{CH}_3\text{OH}$  (0.02 ML), and (C) after 10 min irradiation by 400 nm light. The dashed circles in (A) show the sites for  $\text{CH}_3\text{OH}$  adsorption on the  $\text{Ti}_{5c}$  row, and the cross shows the site for  $\text{CH}_3\text{OH}$  adsorption on the BBOv. The black arrows in (C) indicate the four dissociated molecules after UV irradiation. (D) STM image after manipulation (0.4 V, 700 pA) of the dissociated molecule m1 in the marked area of (C). (E–H) Cut profiles along the green lines in (A–D), respectively. Reproduced with permission from ref. 77.



electronic state. It was assigned to the perturbed Ti 3d orbitals caused by the strong interaction of titanium ions with the methoxy species.<sup>77</sup> Since methoxy radicals on Ti<sub>5c</sub> are intermediate species in the photocatalytic dissociation of methanol to form formaldehyde, this assignment is quite reasonable. Further experimental studies, however, are needed in order to confirm this assignment and to understand if such an excited electronic state also exists in other photocatalytic systems on the TiO<sub>2</sub>(110) surface.

### 4.3 Photocatalytic dissociation kinetics and effect of defects

From the above discussion, it is clear that the photocatalytic dissociation of methanol on TiO<sub>2</sub>(110) can be probed by the 2PPE technique. The development of the TD-2PPE method also allowed us to probe the kinetics of methanol photocatalytic dissociation on TiO<sub>2</sub>(110). Since the excited state in 2PPE is associated with the photocatalyzed splitting of methanol on TiO<sub>2</sub>(110), the evolution of the excited resonance should illustrate the kinetics of methanol dissociation on this surface. By integrating the TD-2PPE signal in Fig. 9A from 4.9 to 6.1 eV, the time-dependent excited resonance signal was obtained and is shown in Fig. 12. It is interesting to point out that it is not possible to fit the kinetic data of methanol photocatalytic dissociation in Fig. 12 with a single exponential function. In fact, the kinetic data can be simulated using a multiple exponential model or a fractal-like kinetic model.

In contrast to the classic kinetics, the rate coefficient is time-dependent in fractal-like kinetics. Assuming the excited resonance signal is proportional to the fraction of dissociated methanol, the time-dependent signal can be simulated by the following formula:<sup>91,92</sup>

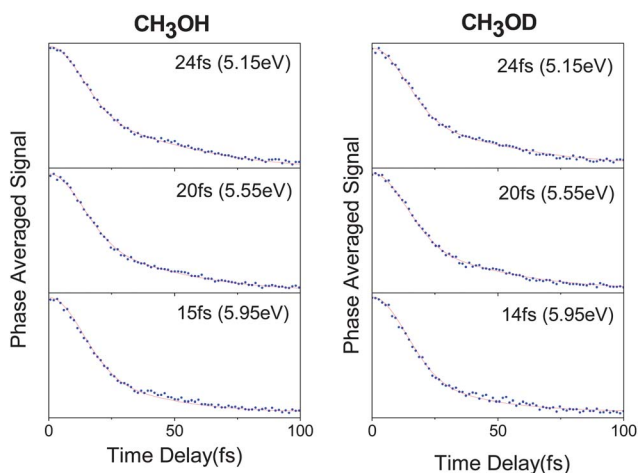
$$I = I_0 \left( 1 - \exp \left( - \frac{k_0}{1-h} t^{1-h} \right) \right) \quad (3)$$

where  $k_0$  is the rate at  $t = 1$ , and  $h$  is equal to  $1 - d_s/2$ , where  $d_s$  is the spectral dimension of the heterogeneous reaction media. The fitting gives rise to  $k_0 = 0.039 \text{ s}^{-1}$  and  $h = 0.362$ . The physical origin of the fractal-like kinetics for photocatalytic dissociation is

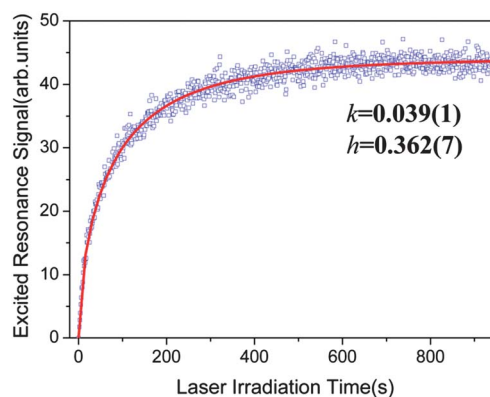
not immediately clear. Nevertheless, the fractal kinetics for the photocatalytic dissociation of methanol on TiO<sub>2</sub>(110) suggests that the methanol photocatalysis process is likely to be a heterogeneous reaction process with multiple steps. There are a few possibilities. Firstly, the heterogeneous catalytic process itself could result in fractal-like kinetics in surface photocatalytic processes; secondly, trapping and detrapping of the charge carriers (electrons and holes) created by photon excitation might also be responsible for the fractal kinetics behavior.<sup>93</sup> In any case, the observation of fractal-like kinetics in photocatalysis is quite interesting, and certainly needs further experimental investigation as well as theoretical modelling.

Surface BBOv's are normally regarded as active reaction sites for catalysis and photocatalysis, but both the 2PPE and STM results have shown the photocatalytic dissociation of methanol occurs mainly on the Ti<sub>5c</sub> sites on this surface.<sup>77</sup> In addition, subsurface defects such as Ti interstitials and subsurface oxygen vacancies have also been reported to have an effect on the surface chemistry of TiO<sub>2</sub>(110).<sup>64,71,72</sup> The effect of these defects on the photocatalytic dissociation process, however, has not been investigated carefully. We have recently carried out a comparative study of the photochemistry of 1 ML CD<sub>3</sub>OD on both stoichiometric and reduced TiO<sub>2</sub>(110) surfaces to study the specific role of defects in the photocatalyzed dissociation of methanol.<sup>62</sup>

TD-2PPE spectra have been measured on both stoichiometric and reduced TiO<sub>2</sub>(110) surfaces with 1 ML deuterated methanol coverage. The appearance of the excited resonance at around 5.5 eV seems to be similar on both surfaces, but the rise times of these excited resonances are dramatically different (see Fig. 13). It took only 37 s for the excited resonance signal to rise to 90% of its maximum level on the reduced surface, whereas on the stoichiometric TiO<sub>2</sub>(110) surface, it took 640 s. There is a difference of about 17 times in the dissociation rate. Interestingly, time-dependent signals of the rising excited resonance on both systems can be simulated with the fractal-like kinetics model, suggesting that methanol photocatalytic chemistry on stoichiometric and reduced TiO<sub>2</sub>(110) surfaces are similar and most likely to occur on the Ti<sub>5c</sub> sites. However, it appears that reducing the TiO<sub>2</sub>(110) surface could considerably accelerate the photocatalytic dissociation of methanol.



**Fig. 11** Time-resolved measurement of the dynamics of the excited state on the 1 ML methanol-covered stoichiometric TiO<sub>2</sub>(110) surface.



**Fig. 12** Time-dependent signal of the excited resonance feature in Fig. 9A and its fractal-like kinetics model fitting. Reproduced with permission from ref. 77.

The large enhancement of the photocatalytic dissociation rate on the reduced  $\text{TiO}_2(110)$  surface is very likely to be caused by the large number of defects on this substrate. Since the main difference between the reduced and stoichiometric surfaces is the density of defects, this could have a remarkable effect on the chemical reactivity of this surface. The amount of both surface and subsurface defects on the reduced  $\text{TiO}_2(110)$  surface is significantly larger than those on the stoichiometric surface. These results clearly suggest that the surface and/or subsurface defects could accelerate the photocatalytic dissociation of methanol on the  $\text{TiO}_2(110)$  surface. Unfortunately, it is difficult to characterize whether the surface defects or subsurface defects are having a more important role in the acceleration of the photocatalytic dissociation of methanol on  $\text{TiO}_2$  because these two types of defects are known to affect the surface chemistry of  $\text{TiO}_2(110)$  in a similar way,<sup>64,70</sup> and it is not possible to quantitatively measure the density of the subsurface defects.

The remarkable enhanced rate of the photocatalytic dissociation of methanol on the reduced  $\text{TiO}_2(110)$  surface is quite intriguing. It is clear that the methanol photocatalytic dissociation mainly occurs at the  $\text{Ti}_{5c}$  sites, as directly revealed by the STM experiments,<sup>77</sup> not at the BBO vacancy sites. It seems that defects on the  $\text{TiO}_2$  substrate reduce the reaction barrier for the photocatalytic dissociation of methanol. This is possible because structural distortions due to defects on the  $\text{TiO}_2$  surface could change the energetics of surface chemical reactions. Another possible origin for the enhanced photocatalytic activity on the  $\text{TiO}_2(110)$  surface is the presence of the defect states lying in the band gap. These defect states are occupied electronic states and can be photoexcited to form electron-hole pairs at the defect sites. Experimental results from our laboratory indicate that excitation of these defect states by photon energy lower than the band gap energy could also induce photocatalytic chemical changes on  $\text{TiO}_2(110)$ . Therefore, with a much higher density of defects on the reduced surface, it is quite possible that the excited electron-hole pairs around the defect sites can enhance photocatalytic activity efficiently. Further experiments are needed to confirm whether this picture is reasonable or not.

In addition to the interesting photocatalytic chemistry of methanol on  $\text{TiO}_2(110)$  probed using the TD-2PPE technique,

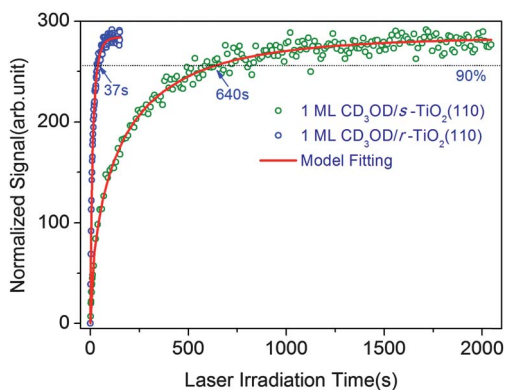
which also allows us to probe the kinetic process of the photocatalytic dissociation, we have also observed similar photocatalytic dissociation of ethanol, propanol and butanol on  $\text{TiO}_2(110)$ . This implies that the 2PPE technique could be quite a general method to probe photochemistry on metal oxide surfaces. Further studies in this direction are now being pursued in our laboratory.

## 5 Concluding remarks

In this article, we have briefly reviewed the application of the 2PPE technique to the study of the kinetics of surface photochemistry and photocatalysis. Two clear examples were given in photochemical studies on metal surfaces: laser-induced desorption of Ar from Cu(100) and photoisomerization of TBA on the Au(111) surface. This research shows that the 2PPE technique could be a powerful tool for examining surface photochemical kinetics. In addition, we have also reviewed the application of the 2PPE technique in the study of the photocatalytic chemistry of methanol on  $\text{TiO}_2(110)$ , which was recently carried out in our laboratory. A photoinduced excited state was clearly observed at about 2.4 eV above the Fermi level and was attributed to the photocatalytic dissociated methanol on the  $\text{Ti}_{5c}$  sites of  $\text{TiO}_2(110)$ , which was supported by a low temperature STM experiment and DFT calculations. A TD-2PPE study shows that the kinetics of the methanol photocatalytic dissociation process is fractal, suggesting that the methanol photocatalytic dissociation process on  $\text{TiO}_2$  is of a heterogeneous nature. Experimental results also show that defects on  $\text{TiO}_2(110)$  could considerably accelerate the photocatalytic dissociation of methanol. One possible reason for this enhanced photocatalytic activity on the reduced  $\text{TiO}_2$  surface is the excitation of occupied defect states.

These three experiments all indicate that the 2PPE probing laser light, even though it has a photon energy as low as 3.1 eV, could itself induce photochemistry on the surface quite efficiently. These results suggest that when surface photocatalysis is studied by many conventional surface related techniques, such as XPS, UPS, HREELS, LEED *etc.*, in which high energy photons or electrons are normally used, one has to be extremely careful. These probing high energy photons and electrons could very likely induce surface chemical reactions,<sup>94,95</sup> as we have demonstrated in the 2PPE experiment. If the effects of the probe itself are ignored in the investigation of photocatalytic systems, one could easily draw incorrect conclusions from these experimental results. Therefore, if we want to use high energy photons and electrons to probe surface photochemical reactions, we need to check if the surface reactions are induced by the probing sources. More ideally, of course, low energy photons or electrons should be used to probe surface chemical reactions in photocatalysis. Therefore, we believe that sensitive infrared (IR), second harmonic generation (SHG), as well as sum frequency generation (SFG) techniques using low energy photons should be applied more in the study of photocatalysis processes on surfaces.

In the present review, we have shown that 2PPE can be a powerful technique to probe the kinetics and dynamics of surface photochemistry on both metal and metal oxide surfaces. Even though the application of the 2PPE technique in the study of surface photocatalysis has just begun, it has already shown great potential for investigating important photocatalytic



**Fig. 13** Normalized time-dependent signal of the excited resonance of 1 ML of  $\text{CD}_3\text{OD}$ -covered stoichiometric (green circle) and reduced (blue circle)  $\text{TiO}_2(110)$  surfaces and the fractal-like kinetics model fitting (red line). Reproduced with permission from ref. 62.

chemistry problems on metal oxides. Since metal oxide catalytic or photocatalytic processes are related to many important energy and environmental problems, the application of 2PPE in the study of metal oxide catalysis and photocatalysis could make a significant impact in this area of research.

As we have shown, 2PPE is a technique to probe surface excited electronic structures and their changes in photocatalytic processes. It is important to emphasize that the combination of the 2PPE technique with other sophisticated methods for photocatalytic studies such as TPD mass spectrometry and STM could be an even more powerful approach to unravelling the mechanism of complex surface photocatalytic processes. Applying ultrafast IR light sources in the study of surface photocatalysis could help us to understand important aspects of surface photocatalytic processes, such as the influence of vibrational excitation of adsorbates in photocatalytic reactions. Furthermore, new ultrafast pump-probe methods using 2PPE as a probe are also desirable in looking at photocatalytic processes in real time. All these developments could further help us to better probe the complex photocatalytic processes on metal and metal oxide surfaces. In addition, high level theoretical calculations, in collaboration with well defined experimental studies could greatly help us to clarify the physical nature of surface photochemistry and photocatalysis.

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