Supplementary Information

1. Experimental Details

The 2PPE experimental apparatus described in detail previously [1] consists of an ultrahigh vacuum system (base pressure $5x10^{-11}$ mbar), which includes a sample preparation and characterization chamber and a main probing chamber, as well as a Ti:Sapphire femtosecond laser system (Synergy, Femtolasers Produktions GmbH) with a repetition rate of 75 MHz (Fig. S1). The whole probing chamber is shielded from the earth magnetism by a μ-metal shield inside the chamber. The key element of this apparatus is the hemispherical electron energy analyzer (PHOIBOS 100, SPECS) for photoelectron detection. The adoption of CCD imaging detection method here facilitates the measurement of the whole electrons within the energy range of interest simultaneously, which makes the study of the kinetics of the surface reaction feasible. The fundamental output of the Ti:Sapphire oscillator is centered at about 790 nm with a pulse width of about 10 fs. It is converted to the second harmonic (typically 401 nm, FWHM 16 nm) before dispersion compensation by a pair of chirped mirrors, and then focused onto the sample. Polarization of the excitation light is rotated through a λ/2 plate before the lens.

The $TiO_2(110)$ sample was mounted on a manipulator with five freedoms. It was heated through electron bombardment method and cooled by liquid nitrogen. K type thermocouple are glued directly to the $TiO_2(110)$ surface using a ceramic adhesive (Ceramabond 503, Aremco Products, INC) to provide accurate temperature reading.

The $TiO_2(110)$ sample (Princeton Scientific Corp., 10x10x1 mm) was polished on both sides to ensure maximum thermal contact. The sample was cleaned by cycles of Ar^+ sputtering (1 KeV, 15 mins) and UHV annealing at 850 K (30 mins). After this preparation procedure, no contamination could be detected in the Auger electron spectroscopy (AES), and a sharp (1x1) LEED pattern was observed. With more cycles of Ar^+ sputtering and UHV annealing at 850 K, the $TiO_2(110)$ became reduced with the work function (WF) to be about 5.2 eV, while by repeated Ar^+ sputtering and annealing at 850 K in the oxygen background ($1x10^{-7}$mbar, 60 mins) followed by cooling in the same oxygen atmosphere to 450 K cycles, the sample became oxidized and the WF increased to 5.5~5.8 eV. There were few bridge-bonded oxygen vacancies (BBOv's) on this oxidized $TiO_2(110)$ surface, thus it could be regarded as nearly stoichiometric.[2] While the density of BBOv's on the reduced surface was 6% as measured by the water TPD (temperature programmed desorption) method.[3] The amount of subsurface Ti interstitial on the reduced surface is also larger.[4]

CD_3OD (Cambridge Isotope Laboratories, Inc, 99.8%) was further purified by several freeze-pump-thaw cycles. Before the experiment, the gas lines and the UHV chamber were filled with D_2O (Acros Organics, 99.8%) vapor for deuterium replacement for two days. The gas lines were heated to 100 ^oC to accelerate the replacement. At the beginning of the replacement process, used D_2O was pumped out and fresh D_2O was injected every 2 hours. The extent of the replacement was examined by measuring the ratio between the amount of mass 17 (OH) and mass 20 (D_2O) with quadrupole mass spectrometer. Finally the gas lines and UHV chamber were washed with purified CD_3OD vapor.

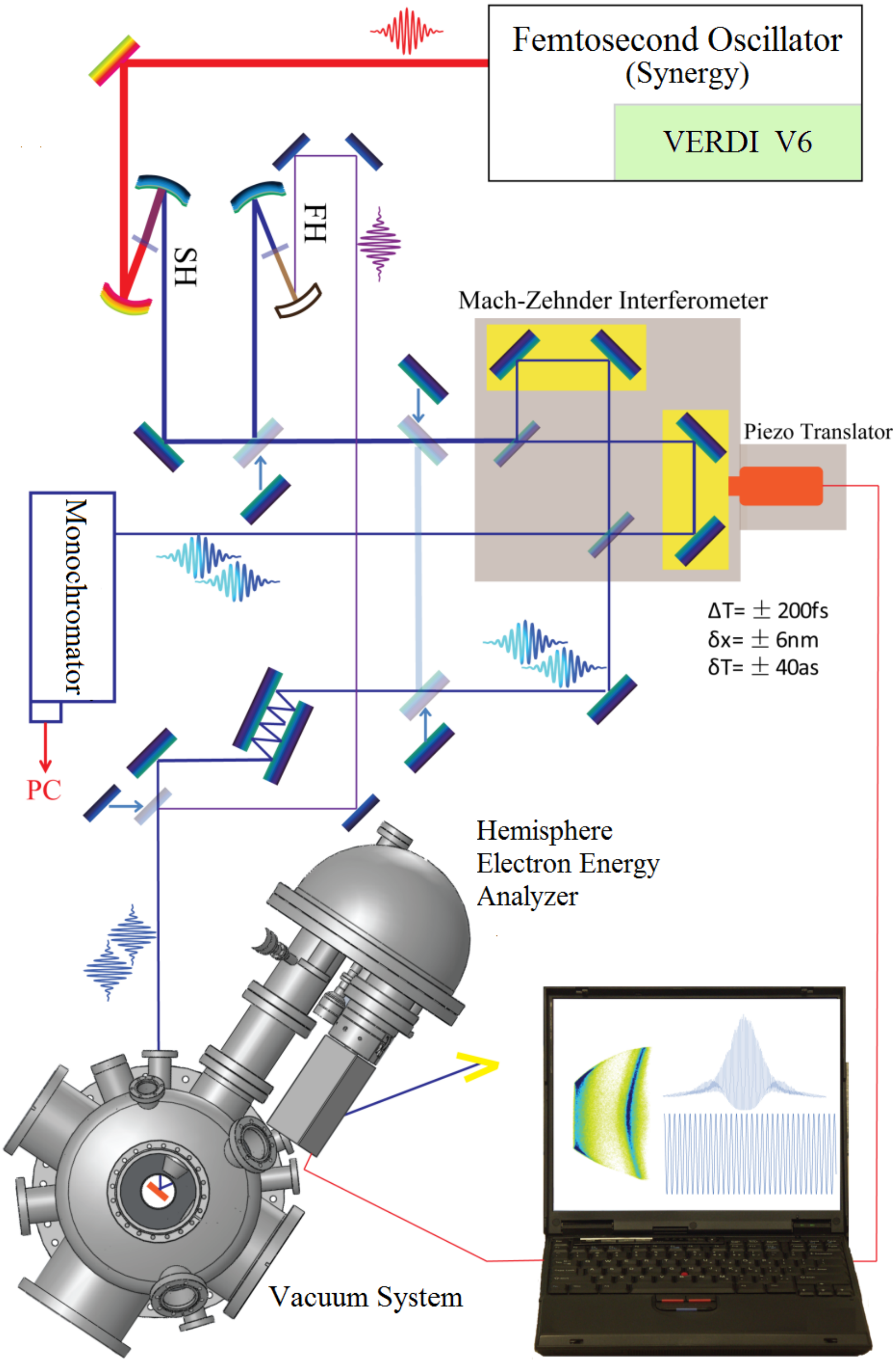

Fig. S1 The schematic diagram of the femtosecond two-photon surface photoemission spectrometer.

The 2PPE signal was recorded continuously with the CCD camera (exposure time 1 s) as soon as the laser was irradiated on the CD_3OD covered $TiO_2(110)$ surface. This allows us to measure the time-dependent 2PPE signal and study the photocatalytic process. The 2PPE measurement scheme for the methanol covered $TiO_2(110)$ surface is shown in Fig. S2.

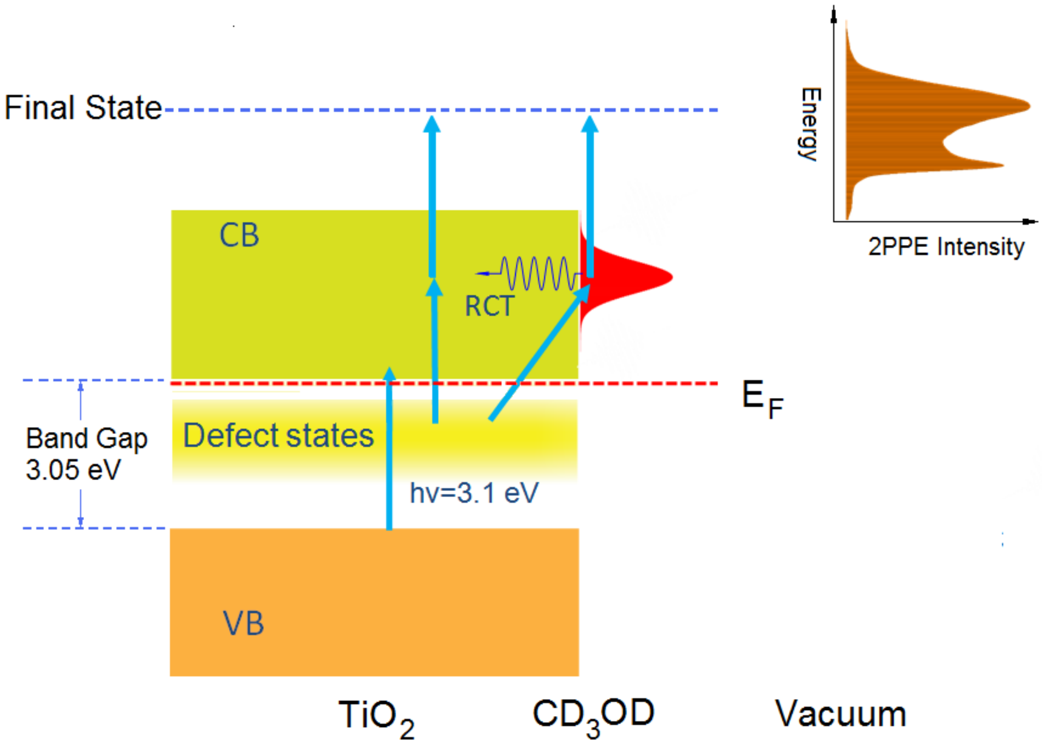

Fig. S2 Experimental scheme of the 2PPE study on the $CD_3OD/TiO_2(110)$ surface.

2. Model of Methanol/TiO_2(110)

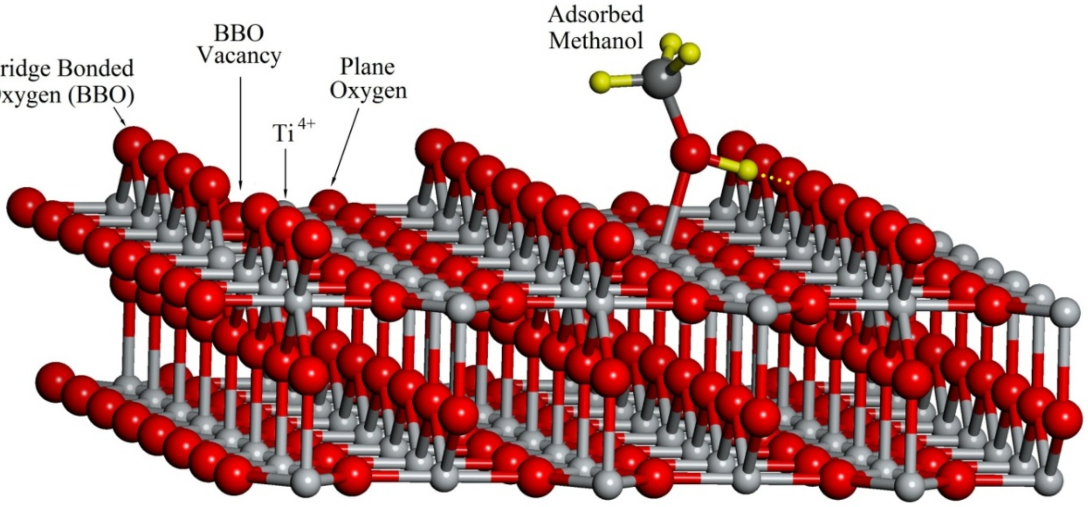

Fig. S3 Schematic model of the adsorption of methanol on Ti_{5c} sites of TiO_2(110).

3. Effect of Surface Roughness on the Photochemistry of Methanol on TiO_2(110)

As we know, annealing the TiO_2(110) sample in the oxygen background will lead to the restructuring of the surface,[5] which will significantly affect the surface chemistry on TiO_2(110).[6-7] In order to examine the effect of surface roughness on the photochemistry of methanol, we have prepared a TiO_2(110) surface with only a few BBOv's and TiOx islands according to the method proposed by Besenbacher et al.[8] The reduced TiO_2(110) with about 6% of BBOv's was first exposed to 5 L (1 L=1.33 mabr×s) oxygen at 120 K and then annealed in UHV at 550 K for 120 s. According to this work,[8] there were only a few BBOv's and TiOx islands on this surface. This surface was regarded nearly perfect. And then we performed the identical TD-2PPE measurements of the photocatalyzed dissociation rate of CH_3OH on this nearly perfect and reduced TiO_2(110) surface to those described in the manuscript. The time dependent excited resonance signal and their fractal fitting results were shown in Figure S4 and Table S1.

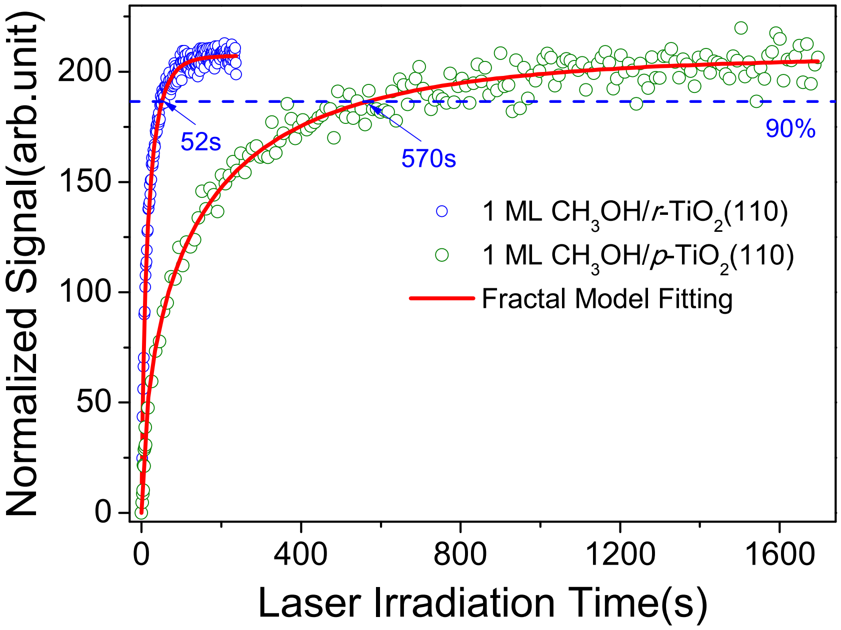

Fig. S4 Normalized time dependent signal of the excited resonance of 1 ML CH_3OH covered nearly perfect (olive circles) and reduced (blue circle) $TiO_2(110)$ surface and the fractal kinetics model fittings (red lines). Laser parameters: 401.0 nm, 60.0 mW.

Table S1 Photocatalyzed Dissociation Rate of CH_3OH on $TiO_2(110)$

TiO_2 Surface	*k_0*	*h*
Perfect	0.032(0)	0.41(1)
Reduced	0.091(2)	0.26(1)

The excited resonance signal on the nearly perfect surface reaches 90% of its maximum in 570 s while on the reduce surface, it took only 52 s. That is to say, the photocatalyzed dissociation of methanol on the reduced $TiO_2(110)$ is about 11 times faster than on the nearly perfect surface. The difference is still significant, though less than that between the stoichiometric and reduced surface (17.3). One may have noticed that the excitation laser power in these two sets of experiments is different, however, the excitation laser power does not change the difference between the photocatalyzed dissociation rate of methanol on stoichiometric and reduced TiO_2(110) surface (data not shown). Therefore the difference in these two sets of experiments is partly due to the measurement errors. The surface roughness seems to have small effect on the photocatalyzed dissociation of methanol on TiO_2(110), however, this effect is minor in comparison with the effect of the defects.

References:

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