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Supplementary Information Methodology and procedure

Experiments were conducted in an UHV chamber equipped with XPS (Perkin-Elmer), sputter gun, SRS200 quadrupole mass spectrometer enclosed in a Pyrex tube with a small aperture, dosing line and other equipment needed to heat the sample. The catalyst, in the form of a thin pellet, was placed on top of a 1 cm² TiO₂ (110) rutile single crystal placed on a tantalum plate (10 x 10 mm). The weight of the catalyst was 21.7mg and 28.9 mg for TiO₂ and 3 wt. % Ag/TiO₂ (anatase-88% + rutile-12%), respectively. A type K thermocouple was attached to TiO₂ anatase single crystal (2×2×1 mm) to measure Contribution from the single crystal is the temperature. negligible when compared to that from the powder catalyst. The surface area of the single crystal is 1 cm² which is ca. 10⁴ times smaller than the surface area of the powder catalyst used (20 mg = 1 m²; BET surface area of the TiO₂ used is about 50 m²/g). The sample was cleaned by successive sputtering and annealing cycles. XPS analysis was performed using an Al anode source. Ethanol was cleaned using freeze-pump-thaw cycles and dosed the dosing 1/16 inc. tube very close to the surface of the catalyst as per the design shown below. XPS C (1s) spectrum was collected at a pass energy (PE) of 50 eV while those of XPS Ti (2p) and XPS O (1s) were at a PE of 25 eV. UV-vis absorbance spectra of the photocatalysts were collected over the wavelength range of 200-900 nm on a Thermo Fisher Scientific UV-Vis spectrophotometer equipped with praying mantis diffuse reflectance accessory. XRD spectra were recorded using a Bruker D8 Advance X-ray diffractometer. A 20 interval between 20 and 90° was used with a step size of 0.010° and a step time of 0.2 sec/step. Transmission electron microscopy (TEM) studies were performed using Titan ST microscope operated at an accelerating voltage of 300 kV equipped with a field emission source. The microscope was operated in high angle annular dark field (HAADF)-STEM mode (Z-contrast).

Temperature programmed desorption study (TPD) was performed adopting the method described in detail elsewhere.¹² Photothermal experiments were conducted in the same chamber. In a typical photothermal experiments the catalyst was saturated with ethanol (64 L exposure) at 300 K followed by an increase in temperature to 628 K for five minutes to ensure similar amounts of irreversibly adsorbed ethanol left on the catalysts surface. Then the temperature was adjusted to the desired one while the chamber was left pumping for 2h to remove desorbed gasses during heating. The photo-thermal reaction was started by exposing UV radiations from a Xenon lamp (320-450 nm; ca. 10 mW cm⁻²) once the background signal of all mass fragments of interest has stabilized.



Figure S1. H_2 production from ethanol pre-dosed TiO₂ and Ag/TiO₂ catalysts upon UV radiations as a function of time at the indicated temperatures. The ethanol-dosed catalyst was flashed to 628 K before the photo-thermal reactions.



Figure S2. Acetaldehyde and H_2 production from ethanol predosed Ag/TiO₂ catalysts upon UV radiations as a function of time at the indicated temperatures. The ethanol-dosed catalyst was flashed to 628 K before the photo-thermal reactions.



Figure S3. CO_2 production from ethanol pre-dosed TiO₂ and Ag/TiO₂ catalysts upon UV radiations as a function of time at the indicated temperatures. The ethanol-dosed catalyst was flashed to 628 K before the photo-thermal reactions.

 $k = 1/\tau$; $t_{1,2}$ = beginning of time intervals

There are two processes for the production of acetaldehyde during photoreaction, a fast and a slow one. Both have been seen over single crystal surfaces and are thought to be linked to the life time of charge carriers¹. We have very recently measured the life time of excited electrons for both anatase and rutile single crystals and found them also to be fitted with two time constants². Other researchers have seen a similar trend over TiO₂ surfaces^{3,4}.

Table S1. Exponential fitting data for acetaldehyde production from TiO_2 and Ag/TiO_2 under photo-thermal conditions at 628K

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Catalyst	TiO ₂	Ag/TiO ₂
Equation	$y = A_1 exp^{(-t_1)} \tau_1^{+} +$	$y = A_1 exp^{(-t_1)} \tau_1 +$
	$A_2 exp^{(-t_2^{\prime})} \tau_2^{(-t_2^{\prime})} + y_0$	$A_2 exp^{(-t_2/\tau_2)} + y_0$
y o	1.46 x 10 ⁻¹⁰	2.34 x 10 ⁻¹⁰
A ₁	1.30 x 10 ⁻⁵	8.8 x 10 ⁻⁹
A ₂	1.75 x 10⁻ ⁹	1.28 x 10 ⁻⁹
τ ₁	7.23s	45.5s
τ ₂	74.5s	388s
k ₁	0.138s ⁻¹	0.022s ⁻¹
k ₂	0.013s ⁻¹	0.0026s ⁻¹
t ₁	5.0s	31.6s
t ₂	51.7s	269s

Yang, J. LaRue, R. Cooper, A. M. Wodtke, Z. Wang, Z. Li, B. Wang, J. Yang and J. Hou. *Chem. Sci.* 2010, **1**, 575-580. ⁴ T. L. Thompson and J. T. Yates, Jr. *J. Phys. Chem. B* 2006, **110**, 7431-7435.

Experimental set up schematic



Fig. 1. a) Image of UHV chamber, b) Schematic of the set up in (a); c) Schematic of the sample holder.

a) Image of the UHV chamber used for the study, b) Schematic of the set up in (a); c) Schematic of the sample holder.

¹ G. Harrison, K. Katsiev, Y. AlSalik, G. Thornton, and H. Idriss. *J. Catalysis, in press.*

² P. Maity, K. Katsiev, O. F. Mohammed and H. Idriss, *J. Phys. Chem. C*, 10.1021/acs.jpcc.8b00256

³ C. Zhou, Z. Ren, S. Tan, Z. Ma, X. Mao, D. Dai, H. Fan, X.