

Site-holding Effect of TiO₂ Surface Hydroxyl in the Photocatalytic Direct Synthesis of 1,1-Diethoxyethane from Ethanol

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Supporting Information:

Catalyst preparation and characterization

All chemicals were analytical grade reagents and used without further purification. The TiO₂-P25 photocatalyst was purchased from Degussa Company. Anatase (A-TiO₂) and brookite (B-TiO₂) photocatalysts were prepared by a hydrothermal process. A-TiO₂: diethylene glycol (5 mL), tetrabutyl titanate (5 mL), and 10% tetrabutyl ammonium hydroxide (20 mL) were mixed under magnetic stirring for 30 min at RT. Then, the mixed solution was transferred to a Teflon-lined autoclave, kept at 200 °C for 24 h, and then allowed to cool down to room temperature. The resulting precipitate was separated in a centrifuge, washed with deionized water, and then dried at 60 °C to obtain A-TiO₂ as white precipitates. B-TiO₂: tetrabutyl titanate (7.8 mL) was directly hydrolyzed in a solution of sodium chloride (1.10 g) and aqueous ammonia (NH₃·H₂O, 68 mL). After stirring for a short time, the resulting suspension was transferred to a Teflon-lined stainless-steel autoclave and heated to 180°C for 24 h. The resulting precipitate was separated in a centrifuge, washed with deionized water, and then dried at 60 °C to obtain B-TiO₂ as white precipitates. R-TiO₂: prepared by calcination of commercial P25-TiO₂ in a muffle furnace in air at 800°C for 8 h.

The F-modified P25-TiO₂ was prepared by soaking commercial P25-TiO₂ in 60 mM NaF aqueous solution (pH = 3.5, by HCl regulation) for 3 h, and then dried at 80°C. The sample was denoted as F-P25-TiO₂. XPS spectra exhibited the characteristic peak of F located at approximately 684.2 eV, indicating the substitution of OH groups by F.

Phase structure was characterized by X-ray diffraction on a D8 Advance power X-ray diffractometer with Cu K α (λ = 0.15406 nm) radiation. The morphology and

microstructure of samples were examined using a transmission electron microscope (JEM-2010).

The determination of amount of surface hydroxyls of photocatalysts

Both XPS method and probe molecule method were used to determine the amount of surface hydroxyls of photocatalysts. XPS was performed on a Thermo Escalab 250 XPS spectrometer with $Al_{K\alpha}$ ($h\nu=1486.6$ eV) radiation. To eliminate the effect of sample surface charging on the shift of XPS peak of carbon, the C1s reference of 284.5 eV was chosen for the calibration of binding energy. High-resolution XPS spectra of the O1s of different phase TiO_2 are shown in Figure S5 and Figure S7b, and the analysis results listed in Table S1.

Table S1. Summary of the amount of bulk O^{2-} species and -OH groups on different TiO_2 catalysts

Sample	O1s(Ti-O) at%	O1s(-OH) at%
P25- TiO_2	67.5	32.5
A- TiO_2	76.7	23.3
B- TiO_2	82.5	17.5
R- TiO_2	88.4	11.6
F-P25-	79.2	20.8

The $\cdot OH$ radicals formed over P25- TiO_2 , A- TiO_2 , B- TiO_2 , R- TiO_2 , and F-P25- TiO_2 were also measured by using terephthalic acid (TA) as the trapping agent. Typically, 0.1 g TiO_2 powder samples with 1% Pt were dispersed in 100 mL of 5×10^{-4} M TA aqueous solution with a concentration of 2×10^{-3} M NaOH. Then the measurements were performed under UV light irradiation using a 300W high-pressure Hg lamp. PL spectra of luminescent 2-hydroxyterephthalic acid (HTA) produced in the reaction between TA and $\cdot OH$ were obtained on a Hitachi F-7000 fluorescence spectrophotometer excited by 315 nm light. $\cdot OH$ is preferentially formed through interfacial reactions between photogenerated holes and surface OH groups.^{1,2,3} The results displayed that the amount of $\cdot OH$ formed per minute per gram of TiO_2 increases in the order of R- TiO_2 < B- TiO_2 < A- TiO_2 < P25- TiO_2 (see Figure S6 and S7). The results from both XPS method and probe molecule method are consistent.

Radical trapping experiments

The EPR studies were carried out in a flat quartz cell, and the spectra recorded on a Bruker EMXPlus-10/12 EPR spectrometer. Ethanol or ethanol- H_2O solution containing 0.05 M 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2.5 mg/ml TiO_2 with 1 wt%

platinum were prepared for EPR experiments. The samples were firstly sonicated for 5 min in an ultrasonic bath, and then were carefully deoxygenated by a stream of argon, subsequently filled in the quartz flat cell. During the EPR photochemical experiments the samples were irradiated at 298 K directly in the EPR resonator, and the EPR spectra were recorded in situ during a continuous photoexcitation. The operating condition was as follows: microwave frequency $\nu = 9.86$ GHz, power of microwave $W = 10.02$ mW, scanning range 3416–3616 G. The irradiation of the sample in EPR cavity was carried out using a 100W UV lamp. The g -values (± 0.0001) were determined using a built-in magnetometer. The EPR spectra obtained were analyzed and simulated using the Easyspin software.

In neat ethanol system, $\cdot\text{OH}$ radicals were measured by the coumarin fluorescence probe method. 0.1 g TiO_2 powder samples with 1% Pt were dispersed in 20 mL of 10^{-3} M coumarin ethanol solution. Then the measurements were performed under UV light irradiation using a 300W high-pressure Hg lamp. PL spectra of luminescent were performed on a Hitachi F-7000 fluorescence spectrophotometer excited by 332 nm light.

Photocatalytic experiments and analysis

All experiments were performed in a tubular quartz photoreactor containing 20 ml of ethanol and 0.1 g photocatalyst, with pure Ar continuously bubbling. Pt co-catalysts were loaded onto the catalyst by in situ photodeposition. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was used as precursor. A 300 W high-pressure Hg lamp was used as light source and was cooled by 20 °C water circulation. The reaction course was monitored by periodically sampling the liquid from a sampling valve, and the catalyst was immediately separated from the solution by centrifugation. Liquid products were analyzed using a gas-chromatograph (GC-950 equipped with a flame ionization detector (FID) and Rtx-5 column from Alltech) and a gas chromatograph–mass spectrometer (Shimadzu GCMS-QP2010 with a mass spectrometer and DB-5 ms column from Alltech). Sample analysis was confirmed by comparing the mass spectrum and retention time of relative pure compound. Quantitative analyses were performed with a GC system using cyclohexane as internal standard. A GC-9790 system (equipped with a thermal conductivity detector and FID) was used to detect CH_4 , CO , CO_2 , and H_2 .

The possible formation mechanism of over-oxidation products in ethanol- H_2O

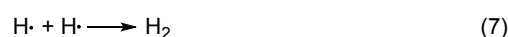
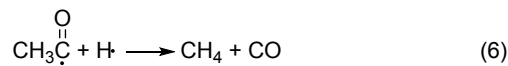
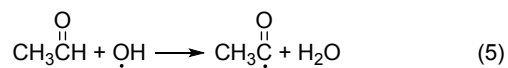
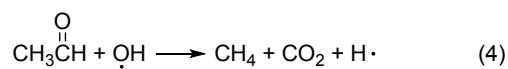
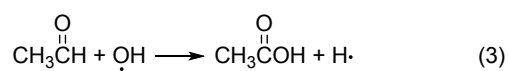
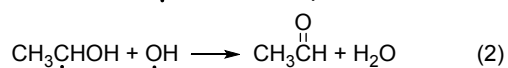
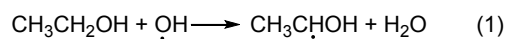


Table S2. Summary of photocatalytic performances in ethanol-H₂O.

Catalyst	Conv.%	Select.%					
		2,3-BD	Aldehyde	Acetic acid	CO ₂	CO	CH ₄
Pt/P25-TiO ₂	19.8	2.6	18.3	24.3	32.9	5.5	16.4
Pt/A-TiO ₂	13.5	20.3	47.6	11.2	11.8	3.3	5.8
Pt/B-TiO ₂	17.4	70.5	10.1	11.1	4.2	1.3	2.8
Pt/R-TiO ₂	5.3	84.7	2.9	6.3	3.0	1.2	1.9
F-P25-TiO ₂	17.6	64.6	19.1	12.2	2.0	1.1	1.0

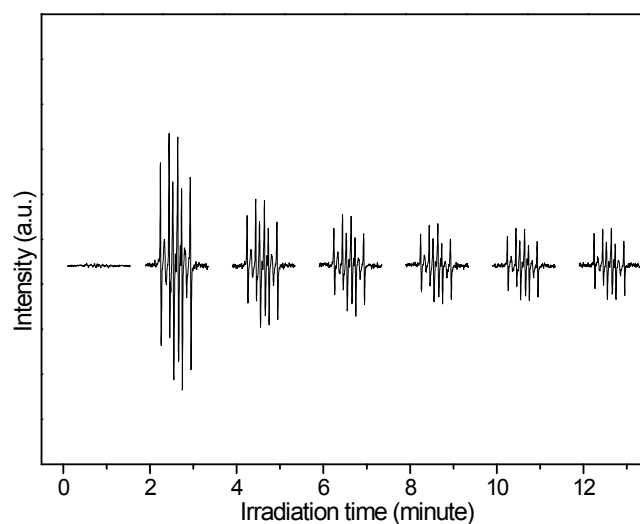


Figure S1. The sets of individual EPR spectra with time obtained upon irradiation of Pt/P25-TiO₂ ethanol suspensions in the presence of spin trapping agent DMPO (2.5 mg·mL⁻¹ TiO₂ with 1 wt% platinum, 0.05 M DMPO).

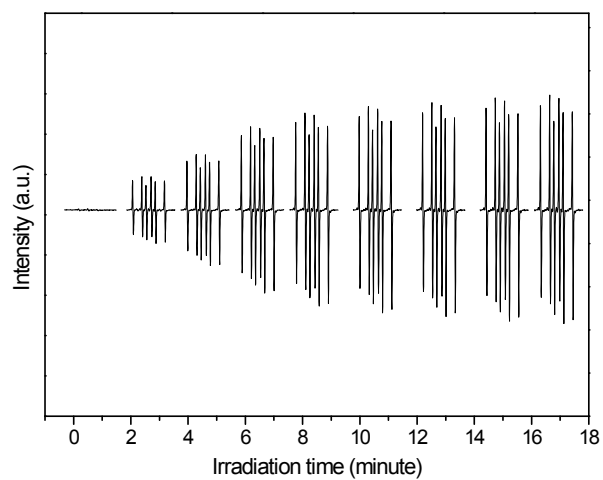


Figure S2. The sets of individual EPR spectra with time obtained upon irradiation of Pt/P25-TiO₂ ethanol-H₂O (20 Vol%) suspensions in the presence of spin trapping agent DMPO (2.5 mg·mL⁻¹ TiO₂ with 1 wt% platinum, 0.05 M DMPO).

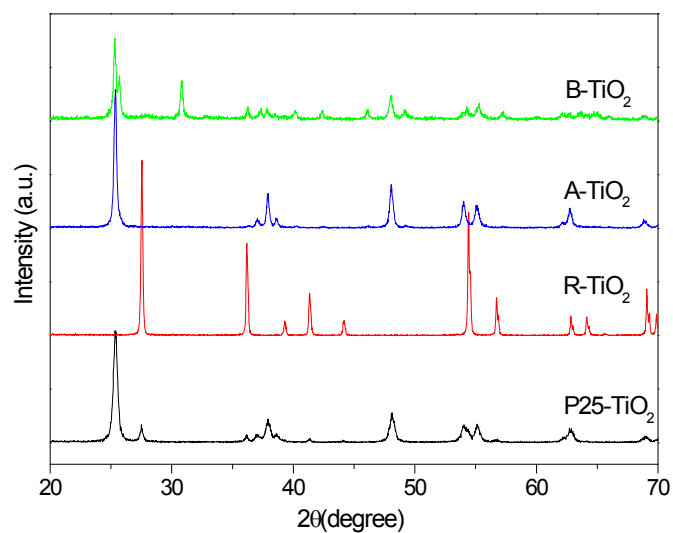


Figure S3. XRD spectra of P25-TiO₂, A-TiO₂, B-TiO₂, and R-TiO₂.

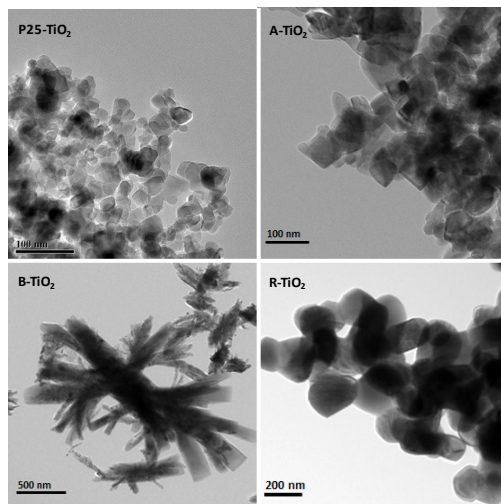


Figure S4. TEM images of P25-TiO₂, A-TiO₂, B-TiO₂, and R-TiO₂.

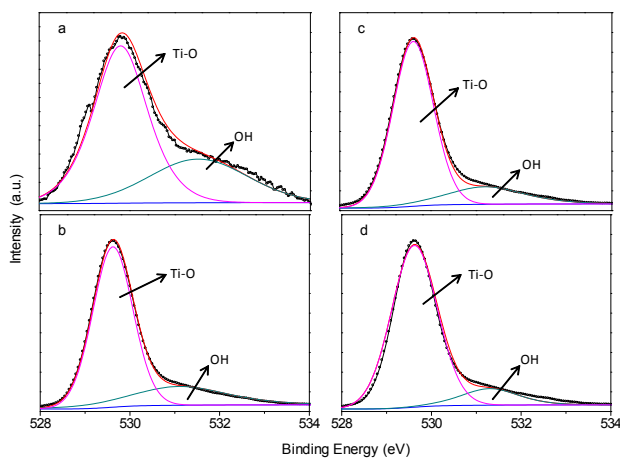


Figure S5. High-resolution XPS spectra of the O1s of P25-TiO₂ (a), A-TiO₂ (b), B-TiO₂ (c), R-TiO₂ (d).

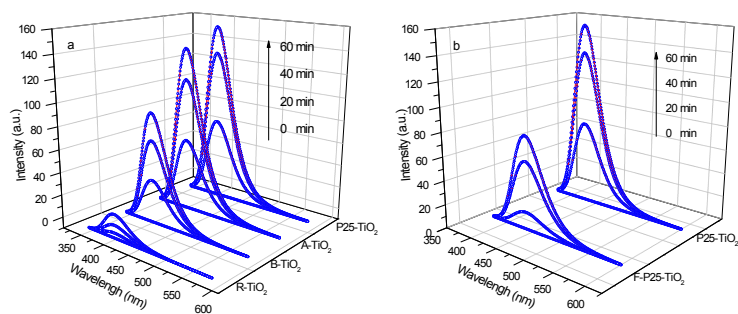


Figure S6. Photoluminescence emission spectra of fluorescent 2-hydroxyterephthalic acid (HTA) *in situ* formed over different phase TiO₂ (a) and F-P25-TiO₂ (b).

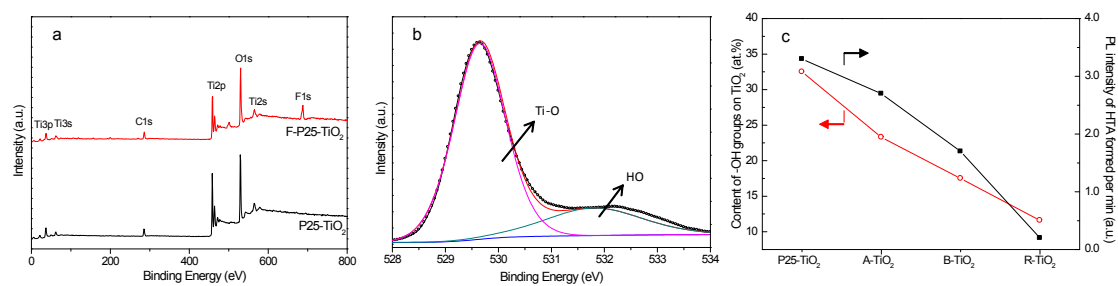


Figure S7. a) XPS spectra of F-P25-TiO₂ and P25-TiO₂; b) O1s XPS spectra of F-P25-TiO₂; c) PL intensity of HTA formed per minute through the reaction of TA and ·OH and content of -OH groups versus the crystalline phases of TiO₂.

References

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