pH-Depending Enhancement of Electron Transfer by {001} Facet-Dominating TiO$_2$ Nanoparticles for Photocatalytic H$_2$ Evolution under Visible Irradiation

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S1. Characterization of TiO$_2$

S1-1 Powder X-ray Diffraction of TiO$_2$

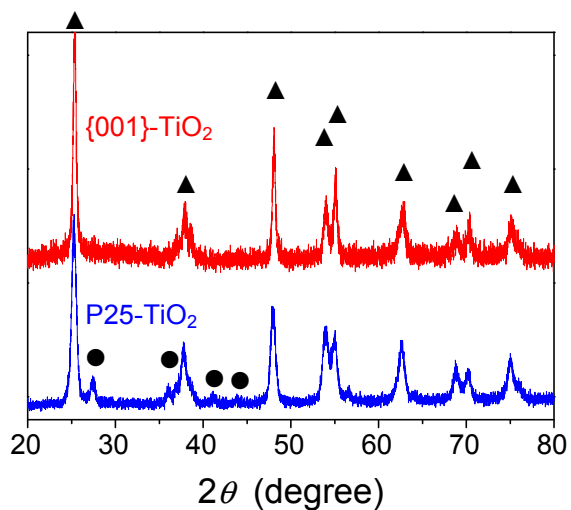The powder x-ray diffraction (MiniFlex, Rigaku, Japan) was measured with the synthesized {001}-TiO$_2$ and P25-TiO$_2$.

Figure S1-1   The powder X-ray diffraction patterns of the synthesized {001}-TiO$_2$ and P25-TiO$_2$ nanoparticles; peaks attributed to anatase (triangle) and rutil (circle) phase of TiO$_2$ are marked .

S1-2 Morphology of TiO$_2$

The {001}-TiO$_2$ and P25-TiO$_2$ nano-particles dispersed in ethanol by sonication were dropped onto carbon-coated copper grids and dried in vacuum for over night. The morphologies were observed by field emission scanning electron microscopy (FE-SEM S-5500, Hitachi, Japan) under an acceleration voltage of 2kV. Since the images indicate random orientation of particles, mostly the particles in the samples were well dispersed in colloidal suspensions in the experimental conditions instead of an aggregation form. The number density of particles in the suspension were determined from the observed diameter with the model of anatase sheet for {001}-TiO$_2$ and anisotropic spire for P25-TiO$_2$ as summarized in Table S1-1.
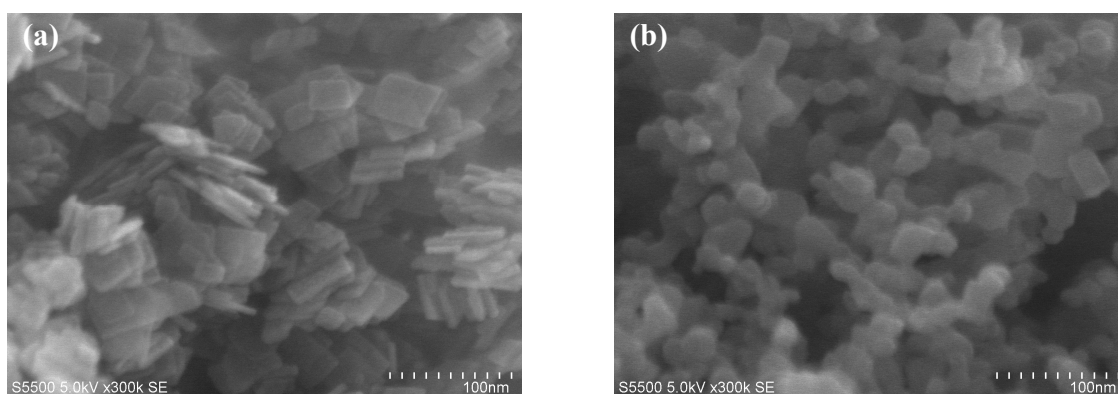

Figure S1-2 SEM images of each (a){001}-TiO$_2$ and (b) P25-TiO$_2$ nanoparticles.

S1-3 Brunauer-Emmett-Teller (BET) Surface Area of TiO$_2$

Brunauer-Emmett-Teller (BET) surface area was determined by a multipoint BET method using the nitrogen adsorption-desorption isotherms (Autosorb-1,Yuasa ionics inc., Japan) in the range of relative pressure, P/P_0 = 0.05~0.20, at 77K and measured values are summarized in Table S1-1. Prior to nitrogen isotherms, all samples were degassed at 150 $^\circ$C for 3h.

S1-4 Adsorption of TCPP on TiO$_2$

The adsorption amount of TCPP was measured by the following procedures. After adsorption reached equilibrium over 12h, the TiO$_2$ nano-particles in the supposition was separated by centrifugation. Absorption spectra of the clear supernatant liquids were obtained by UV-vis spectrometer (V-570-DS, JASCO Inc., Japan) to determine the concentration TCPP remained in the solution, and therefore the amount of adsorbed TCPP on each TiO$_2$ particles was determined by comparison between the concentration of TCPP solution before and after TiO$_2$ particle immersion as summarized in Table S1-1.

Table S1-1 Characteristics of TiO$_2$ nano-particles.

TiO$_2$	{001}-TiO$_2$	P25-TiO$_2$
BET Surface Area (m^2/g)	80	55^a
Diameter (nm)	$d = 41.6$ $t = 7.7$	$d=23$
Number density (#/g)^b	4.1×10^{16}	4.0×10^{16}
Amount of TCPP (μmol/g) (molecules/nm^2)	10.57 (0.08)	9.93 (0.11)

^{a}The value is referred to [1, 2]. ^{b}The number density of particle is calculated for geometry of particles with ideal structures indicated in equation S1 and S2 with a specific weight of anatase TiO$_2$ of 3.9 g/cm^3.

Volume of single nanoparticle of {001}-TiO$_2$

$$V_{\{001\}} = \frac{d^3 \tan(68.3^\circ)}{6} - \frac{\left(d \tan(68.3^\circ) - t\right)^3}{6\tan^2(68.3^\circ)} \tag{S1}$$

Volume of single nanoparticle of P25-TiO$_2$

$$V_{P25} = \frac{\pi d^3}{6} \tag{S1}$$

S1-5 Surface Analysis of TiO$_2$

   X-ray photoelectron spectroscopy (XPS) was applied to characterize the surface of {001}-TiO$_2$ nanoparticles to verify the clean TiO$_2$ surface without the fluorinated residual compounds. Spectra of F (1s) was obtained with scanning XPS microprobe (PHI 5000 Versa Probe, Physical Electronics, Chanhassen, MN) utilized with a monochromatic Al K$_\alpha$ source operated at an X-ray power of 25 watts with a beam diameter of 100 μm, a take-off angle of 45 degrees with respect to the sample plane, a pass energy of 117.4 and 23.5 eV, and an energy step of 0.2 eV for elemental analysis, respectively under vacuum ($< \sim 1.5 \times 10^{-5}$ Pa) as shown in Figure S1-6. The peak of F (1s) disappeared after nanoparitlces were washed by steering in NaOH aqueous solution (0.1M) at room temperature for more than 3days for the purpose of defluorination [3]. Other residual contamination, other than irremovable carbon contaminations, was not observed in survey spectra; not shown.   Therefore the observed results are clearly attributed to the difference in properties of {001}-TiO$_2$ and P25-TiO$_2$ but not to the residual fluorine contamination on the surface.
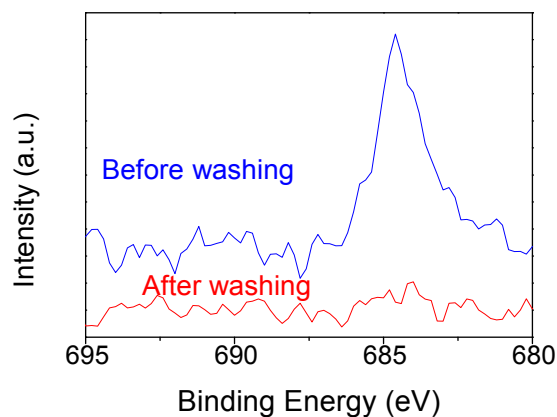

Figure S1-3   XPS spectra of each TiO$_2$ nano-particles for elemental analysis of fluorine, F(1s), region with reference spectra of {001}-TiO$_2$ without defluorination.

S1-6 Dynamic Light Scattering of TiO₂ Suspension

As applied for a TiO$_2$ stock suspension in the photo luminescence experiment in the main section, the colloidal suspension was prepared by sonication of TiO$_2$ nano-particles (4g/L) dispersed in deionized water for more than 30 minutes. The stock suspension was added into MeOH (6.2M) aqueous solutions to prepare the condition of H$_2$ evolution. The diameter of dispersed particles was determined by a method of dynamic light scattering (nano Partica SZ-100, HORIBA, Japan) in each acidic and basic condition by adding HCl and NH$_4$OH, respectively (Figure S1-4).
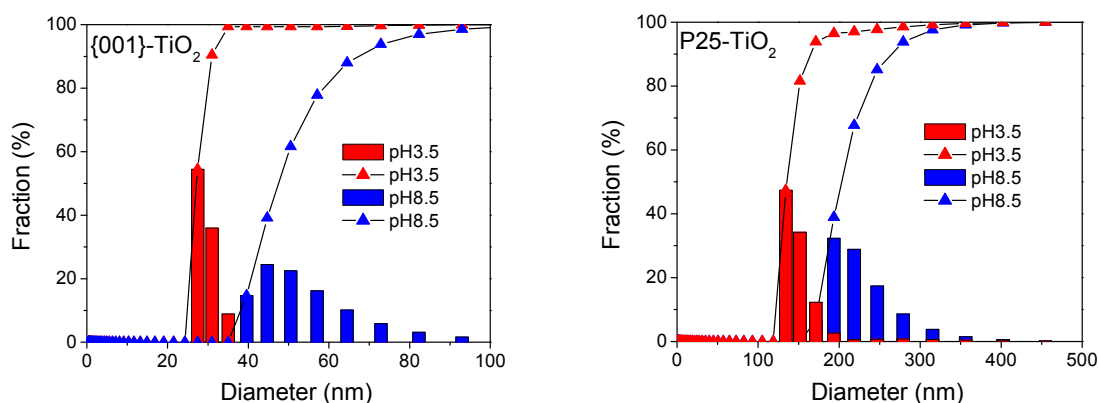

Figure S1-4   The distribution of diameter of each {001}-TiO$_2$ (red) and P25-TiO$_2$ (blue) suspension in aqueous MeOH solution (1g/L).

S2. H$_2$ Evolution with TCPP-sensitized TiO$_2$

H$_2$ evolution of TCPP-sensitized {001}- TiO$_2$ and P25-TiO$_2$ as the reference under a visible irradiation up to 3h in surrounding aqueous MeOH and TEOA solutions were plotted. The trend of H$_2$ evolution by addition of either TEOA or MeOH into initial aqueous donor solution revealed quite similar trend as observed in previous work [4, 5].
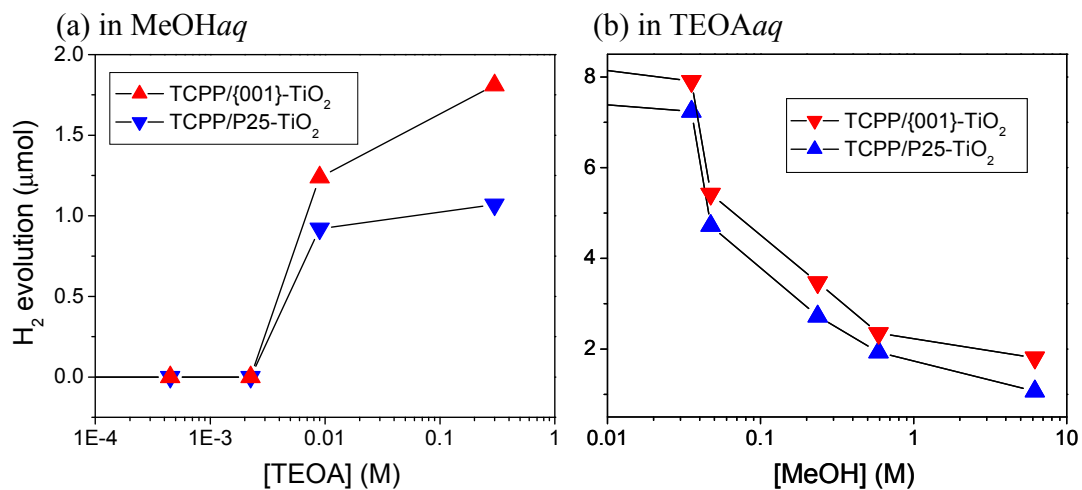

Figure S2-1 H$_2$ evolutions of {001}-TiO$_2$ (red) and P25-TiO$_2$ (blue) in (a) MeOH and (b) TEOA by addition of TEOA and MeOH, respectively. H$_2$ amount was determined after 180min reaction under visible irradiation.

S3. Photochemical Analysis of TCPP-sensitized TiO$_2$

Photochemical analysis based on reciprocal Stern-Volmer relations of TCPP-sensitized {001}- TiO$_2$ and P25-TiO$_2$ in surrounding aqueous MeOH and TEOA solutions were plotted. The values of I_{surf} / I_0 and K_{app} calculated from the reciprocal Stern-Volmer plots by addition of either TEOA or MeOH into initial aqueous donor solution revealed quite similar trends as observed in previous work [3, 4].
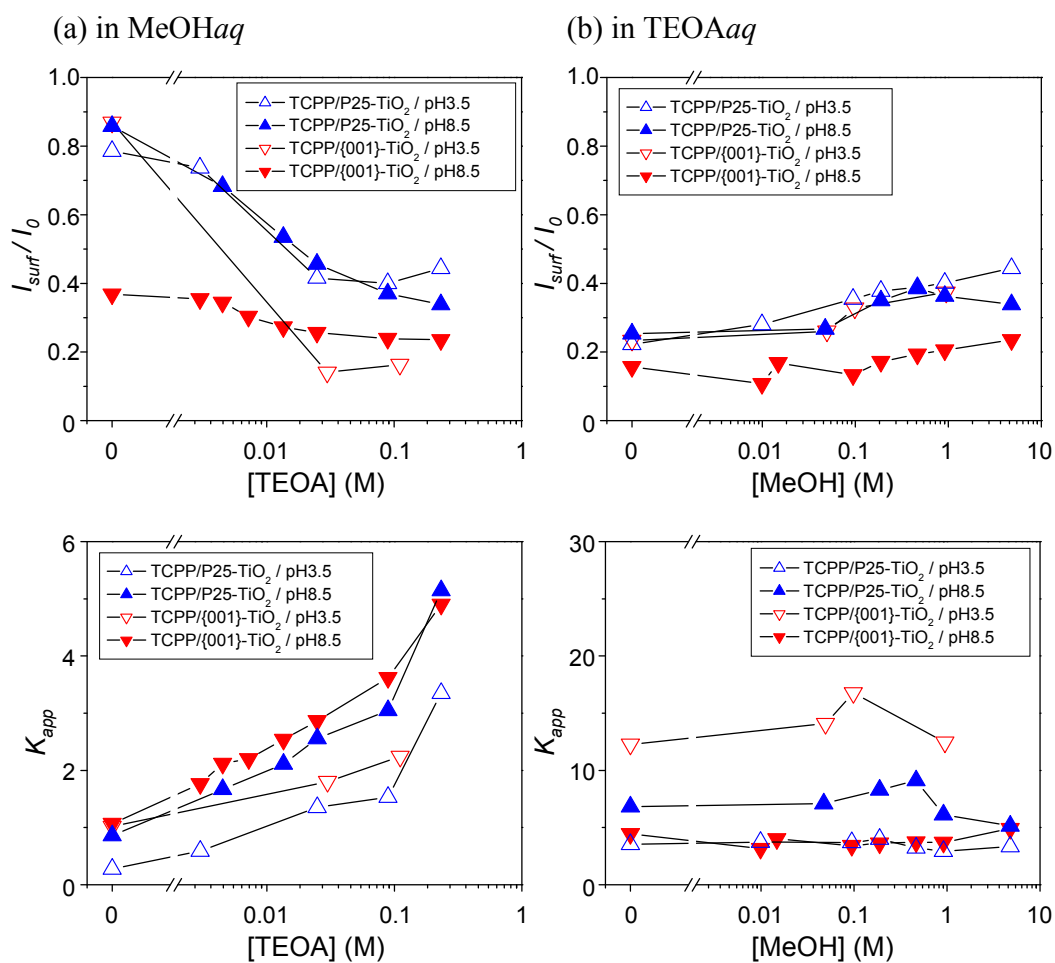

Figure S3-1 I_{surf} / I_0 and K_{app} calculated from the reciprocal Stern-Volmer plots of TCPP-sensitized {001}-TiO$_2$ (Red) and P25-TiO$_2$ (blue) in (a) MeOH and (b) TEOA by addition of TEOA and MeOH, respectively.

S4. Adsorption of TCPP-sensitized TiO$_2$

Since dye-sensitizer can be desorbed from the TiO$_2$ surface after the dye-sensitized TiO$_2$ nanoparticles are dispersed in the electron donor aqueous solution, the amounts of dye adsorbed on TiO$_2$ surface and desorbed into the solution were evaluated by measuring the UV-vis spectra of donor aqueous solution after reaching an equilibrium, 30min. The dispersed TiO$_2$ particles in a donor solution were centrifuged and filtered to obtain the clear supernatant. And then the amount of dye desorbed into the donor solution was calculated from its absorbance. The amount of dye on TiO$_2$ nanoparticles was calculated by subtracting the measured amount of desorbed dye from the initial amount of adsorbed dye on TiO$_2$ as summarized in Table S4-1.

Table S4-1 Adsorption of TCPP on TiO$_2$

TiO$_2$	TCPP on TiO$_2$ (*Initial*) (μmol/g)	pH	TCPP on TiO$_2$ (*after immersion*) (μmol/g)/(%)	TCPP desorbed into solution (*after immersion*) (μmol/g)/(%)
{001}	10.57	3.5	1.69 (16)	8.88 (84)
		5.5	1.58 (15)	8.99 (85)
		8.5	1.19 (11)	9.38 (89)
P25	9.93	3.5	1.42 (14)	8.51 (86)
		5.5	1.49 (15)	8.44 (85)
		8.5	0.87 (9)	9.06 (91)

S5. Absorption Spectra of TCPP in Aqueous Solution

Absorption spectra of TCPP in aqueous solutions were measured by varying pH of solutions. Although the absorbance fluctuates a little in different pH, the spectral features of TCPP solution do not reveal any difference.
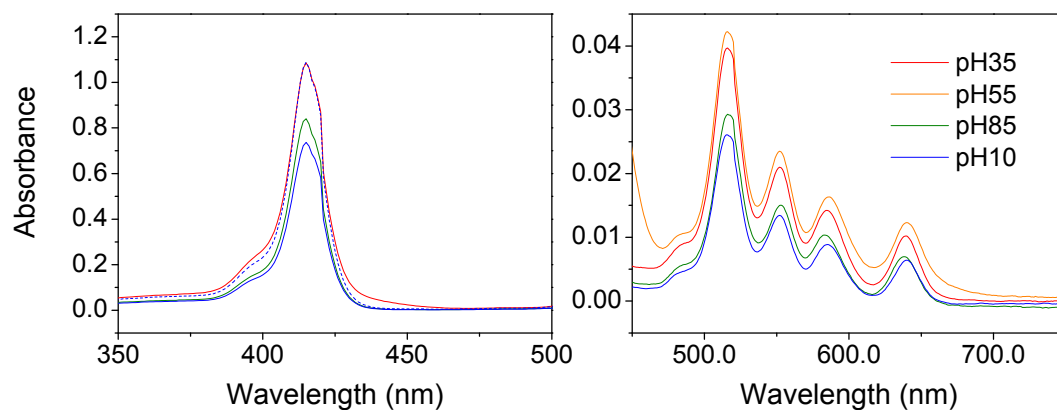
Figure S5-1 Absorption spectra of TCPP in aqueous MeOH solutions with adjusting pH by addition of aqueous HCl and NH$_4$OH solutions.

References

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