Supporting Information for

\textbf{F$^-$ Served as Surface Trapping Sites to Promote the Charge Separation and Transfer of TiO$_2$}

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**Experimental**

**Preparation of F– modified TiO2**

F– modified TiO2 nanoparticles (Degussa p25 TiO2, denoted as TO) were synthesized by adding 0.5 g of TO powder into 30 ml deionized water containing different volume of hydrofluoric acid (HF, 40 wt%) with continuous stirring for 6 h under room temperature. Then, the resulting colloidal suspension was centrifuge with 8000 rpm and washed with distilled water with several times and dried at 60 °C for 12 hours to obtain the target sample. According to the volume of HF (denoted as x, x=0, 0.1, 0.4 and 1.6 ml) added in the solution, the samples of TO-xF were denoted as TO, TO-0.1F, TO-0.4F, TO-1.6F, respectively.

**Characterizations**

The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM; JSM-6701F, JEOL) operated at an accelerating voltage of 3.00 kV. Transmission electron microscopy (TEM) analyses were conducted with a JEM-1200EX electron microscope using a 200 kV accelerating voltage. X-ray diffraction (XRD) were performed on an X' pert PRO diffractometer using Cu Kα radiation at 40 KeV and 40 mA. The XRD patterns were recorded from 20° to 70° with a scanning rate of 0.067°/s. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB250Xi photoelectron spectrometer with an Al Kα X-ray excitation source to analyze the elemental composition of the samples. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded using a Shimadzu UV-2550
spectrophotometer at room temperature. The steady PL spectra was examined under room temperature by fluorescence spectrophotometer (Hitachi, F7000) recorded at the wavelength range of 330-550 nm with an excitation wavelength of 320 nm. The fluorescence lifetimes of as-prepared samples were recorded at room temperature by using a steady/transient fluorescence spectrometer (FLS-1000, Edinburgh Instruments) with excitation wavelength of 365 nm.

All of the samples were degassed at 80°C prior to Brunauer–Emmett–Teller (BET) measurements. The BET specific surface area (SBET) was determined by a multipoint BET method by using the adsorption data within the relative pressure \( \frac{P}{P_0} \) range 0.05–0.3. The desorption branches data were used to determine the pore-size distribution by using the Barret–Joyner-Halender (BJH) method. The nitrogen-adsorption volume at \( \frac{P}{P_0}=0.97 \) was used to determine the pore volume and average pore size.

**Photocatalytic generation experiment of·OH radicals**

Terephthalic acid (TA) was used to detect the generated ·OH radicals under UV-Visible light irradiation. TA formed the highly fluorescent 2-hydroxyterephthalic acid with a specific fluorescence emission maximum at wavelength of 455 nm when reacting with •OH radicals. The generated •OH radicals were examined by measuring the fluorescence intensity (F-7000, Hitachi) at 423 nm with the excitation wavelength of 315 nm.

**Photocatalytic degradation of methyl orange (MO) and phenol**
Typically, 0.1 g of catalyst was dispersed into 100 mL MO aqueous solution (20 mg/L) under vigorous stirring. Upon light irradiation, the suspension was stirred in the dark and kept for 30 min to ensure adsorption-desorption equilibrium. A 300 W Xe arc lamp was used to provide UV-Visible light. The concentration of MO was recorded using a UV-vis spectrometer at 464 nm. The stability of the photocatalyst is performed by testing the performance after four cycles of degradation of MO. After each cycle, the photocatalyst was filtered and dried thoroughly, and then the fresh MO solution was added for further analysis.

A pseudo-first-order kinetic model is used and fitted to quantitatively study the degradation kinetics of MO in photocatalysis (Eq. (1)):

\[ \ln \frac{C_t}{C_0} = -kt \]  

(1)

Where \( C_0 \) (mg/L) is the concentration of MO after adsorption in dark, \( C_t \) is the concentration at time \( t \) (min) and \( k \) (min\(^{-1}\)) is the pseudo first-order rate constant

Recyclability of the composites is evaluated by replicating the degradation experiment of MO under the same process. Typically, the used TO or TO-0.4F catalysts after degrading of MO were filtered thoroughly, washed and dehydrated prior to the next degradation test.

The photocatalytic degradation of phenol was the same as that of MO, except that the concentration of concentration of phenol was \( 10^{-4} \) mol/L. The concentration of phenol was measured by uV-vis spectrophotometer with a maximum absorption wavelength of 270 nm.
Photoelectrochemical measurements

The photoelectrochemical performance was measured using an electrochemical workstation (CHI660E, Chenhua Instruments Co. Shanghai, China) and a standard three-electrode system (Ag/AgCl electrode utilized as reference electrode, platinum gauze electrode as counter electrode, electrolyte solution: 0.5 M NaSO\textsubscript{4} aqueous solution). The working electrode were the samples coated on Fluorine-doped Tin Oxide (FTO) conducting glass. Specifically, 10 mg of sample was dispersed into a mixed solution containing 0.25 ml distilled water, 0.25 ml of isopropanol and 10.0 μl 5% Nafion (ethanol solution) by fully grinding for 10 min. Then the suspension was drop-casted onto FTO conductive glass, which was carefully beforehand washed by ultrasonic concussion in acetone, ethanol, isopropanol and deionized water, respectively. After drying at 80 °C for 2 h, the prepared electrode was used as the working electrode for photoelectronchemical measurement. Electrochemical impedance spectroscopy (EIS) spectra was recorded at bias of 0.2 V (vs. Ag/AgCl) with AC voltage amplitude of 10 mV in the frequency range of 0.01 to 100000 Hz both in the dark and under UV-Visible light irradiation. Mott-Schottky (MS) spectra were recorded in the voltage range of -0.6-0.6 V vs. Ag/AgCl. Carrier density (N\textsubscript{d}) of the samples were calculated based on the slope of Mott-Schottky plot and applied in this Equation (Eq. (2)):

\[
N_d = \frac{2}{q \varepsilon \varepsilon_0} \left[ \frac{d}{(1/C^2)/dV} \right]^{-1}
\]  

(2)

Where \(q\), \(\varepsilon\) and \(\varepsilon_0\) represent the electron charge \((1.60 \times 10^{-19})\), the dielectric constant of semiconductor\((48\) for TiO\textsubscript{2}) and the permittivity of vacuum \((8.85 \times 10^{-12})\),
respectively. \( C \) is the capacitance of the depletion region and \( V \) is the applied voltage, and \( d(1/C^2)/dV \) is the slope of Mott-Schottky plot.
Additional figures and tables

Figure S1. SEM images of (a) TO, (b) TO-0.1F, (c) TO-0.4F and (d) TO-1.6F catalysts.

Figure S2. EDX patterns of as-prepared TO-0.4F
Table S1. Surface composition and atomic ratio of as-prepared TO and TO-xF catalysts calculated from XPS.

| Catalysts  | Atomic concentration (at.% ) | Atomic ratio  |
|------------|-------------------------------|---------------|
|            | Ti   | O     | F   | O\textsubscript{OH}/(O\textsubscript{OH} + O\textsubscript{lattice}) |
| TO         | 23.78 | 76.22 | /   | 28.36 |
| TO-0.1F    | 22.67 | 72.12 | 5.21 | 21.26 |
| TO-0.4F    | 22.16 | 71.46 | 6.38 | 20.53 |
| TO-1.6F    | 22.49 | 71.26 | 6.25 | 19.89 |

Figure S3. FTIR of as-prepared TO and TO-xF catalysts.
Figure S4. N\textsubscript{2} adsorption-desorption isotherms of TO (a), TO-0.1F (b), TO-0.4F (c) and TO-1.6F (d) (inset: average pore diameter according to Barrett-Joyner-Halenda (BJH) method).

Table S2. Textural properties of TO and TO-xF.

| Catalyst   | S\textsubscript{BET}\textsuperscript{a} \((\text{m}^2/\text{g})\) | V\textsubscript{p}\textsuperscript{b} \((\text{cm}^3/\text{g})\) | D\textsubscript{p}\textsuperscript{c} \((\text{nm})\) |
|------------|-----------------------------|-----------------|-----------------|
| TO         | 54.00                       | 0.514           | 12.06           |
| TO-0.1F    | 54.02                       | 0.474           | 12.75           |
| TO-0.4F    | 50.86                       | 0.426           | 14.78           |
| TO-1.6F    | 55.24                       | 0.349           | 14.17           |

\textsuperscript{a}: specific surface area (SBET); \textsuperscript{b}: pore volume (Vp); \textsuperscript{c}: average pore size (Dp).
Figure S5. Photocatalytic degradation of phenol over TO, TO-0.1F, TO-0.4F and TO-1.6F catalysts under ultraviolet-light irradiation.

Figure S6. The stability test of degradation of MO over TO and TO-0.4F catalyst.
**Table S3.** The fitting results of EIS curves for TO, TO-0.1F, TO-0.1F and TO-1.6F. Rs and Rct represents the solution resistance and the charge transfer resistance across the electrode-solution interface.

| Sample   | Rs (Ω) | Rct (Ω) |
|----------|--------|---------|
| TO       | 3.167  | 913.1   |
| TO-0.1F  | 4.948  | 294.9   |
| TO-0.4F  | 3.313  | 289     |
| TO-1.6F  | 7.995  | 1053    |

**Figure S7.** As obtained Mott-Schottky plots of TO (a), TO-0.1F (b), TO-0.4F (c), TO-1.6F (d).

For converting the obtained potential (vs. Ag/AgCl) to RHE (NHE), the following equation (3) was used:
\[ V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \text{PH} + V^0_{\text{Ag/AgCl}} \]  

(3)

where \( V_{\text{Ag/AgCl}} \) vs NHE is 0.209 V at 25 \(^\circ\)C. Therefore, the calculated Fermi level (vs NHE) of TO, TO-0.1F, TO-0.4F and TO-1.6F were 0.502 V, 0.522 V, 0.542 V, and 0.522 V, respectively.

**Figure S8.** Carrier density of TO, TO-0.1F, TO-0.4F and TO-1.6F.

**Table S3.** The fitted transient PL decay results of as prepared TO and TO-xF catalyst.

| Catalyst   | \( \tau_1 \) \[^{[a]}\] | \( A_1 \) \[^{[b]}\] | \( \tau_2 \) | \( A_2 \) | \( \tau_{\text{avg}} \) \[^{[c]}\] |
|------------|----------------|----------------|------------|--------|--------------|
| TO         | 1.45           | 1              | -          | -      | 1.45         |
| TO-0.1F    | 1.02           | 0.312          | 2.63       | 0.688  | 2.08         |
| TO-0.4F    | 1.08           | 0.322          | 2.55       | 0.678  | 2.55         |
| TO-1.6F    | 0.98           | 0.252          | 1.70       | 0.748  | 1.43         |

\[^{[a]}\] \( \tau \) is referred as decay lifetime; \[^{[b]}\] \( A \) represents amplitude of decay; \[^{[c]}\] \( \tau_{\text{avg}} \) is referred as average decay lifetime.

The fluorescence decay curves( Figure 9) of as-prepared TO and TO-xF samples can be fitted using bi-exponential function \( I(t) \) based on a nonlinear least squares analysis using the following equation ( Eq.(4) ) \[^{[1-2]}\]:

\[ I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \]  

(4)
Where $\tau_1$, $\tau_2$ represented the decay time constants, $A_1$ and $A_2$ are the fractional contributions of time-resolved decay time of $\tau_1$ and $\tau_2$ respectively. The average lifetime ($\tau_{av}$) of as prepared samples was calculated using the following equation (Eq. (5)):

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$  \hspace{1cm} (5)

Figure S9. Schematic diagram representing the electronic structure of as prepared TO and TO-0.4F catalyst.

References

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