Electronic Supplementary Information (ESI) available for:

New understanding of fluorinated TiO_2 (brookite, anatase and rutile) nanoparticles as efficient photocatalytic redox catalysts

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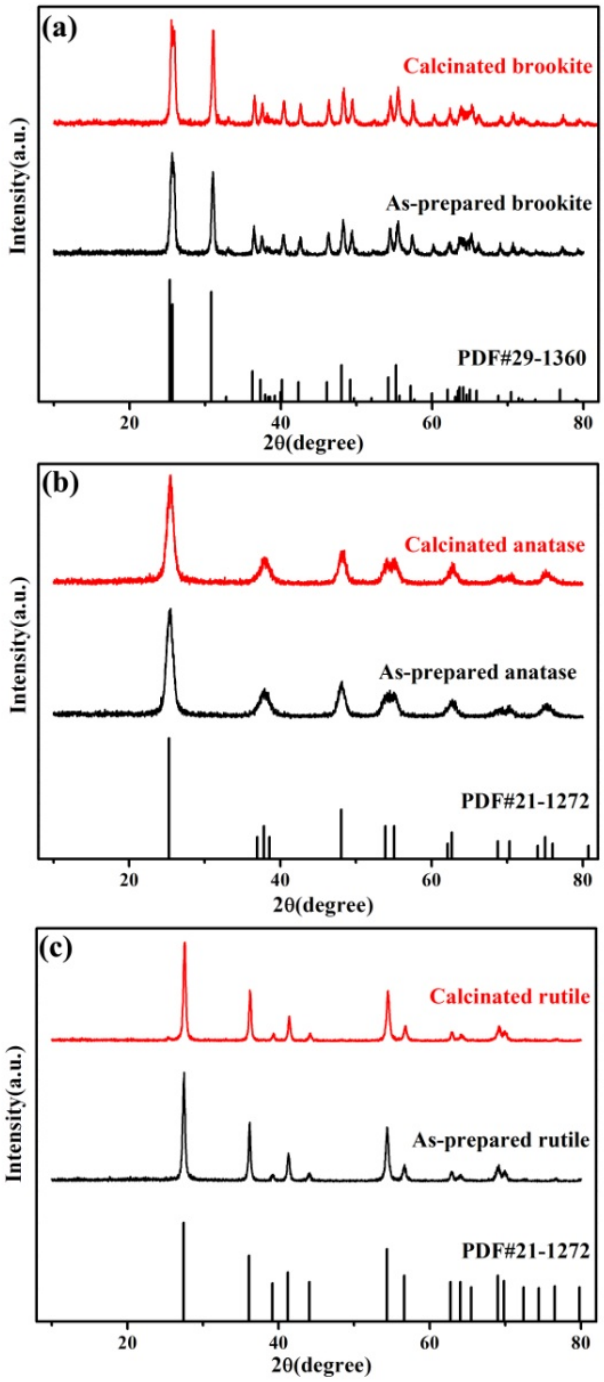

Fig.S1 XRD patterns of as-prepared and calcinated TiO_2 at 400℃ nanoparticles: (a) brookite, (b) anatase and (c) rutile.

The wide angle XRD analysis in Fig.S1a revealed the peaks are consistent with the standard XRD data of the brookite TiO_2 phase (PDF no. 39-1360). In addition, the pattern of as-prepared and calcinated brookite TiO_2 weren't obviously different, which confirmed that the pure phase brookite TiO_2 was prepared in this work and the calcinations didn't cause changes in the phase structure of brookite TiO_2. Similarly, in Fig.S1b and c, these XRD patterns were consistent with the standard XRD data of the anatase and rutile TiO_2 phase (PDF no. 21-1272 and PDF no. 21-1276), respectively, indicating that pure anatase and rutile were also successfully prepared, and after being calcinated, the phase structures were maintained.

Table S1 The calculated lattice parameters, unit cell volume, crystalline size and specific surface area

samples	2 θ (degree)	Lattice parameter			Unit cell Volume($Å^3$)	Crystalline Size$_{(120)}$ (nm)	BET (m^2/g)
		a(Å)	b(Å)	c(Å)			
B-T	25.45	9.1844(5)	5.4542(3)	5.1458(3)	257.77(3)	21.8	31
B-FT400	25.45	9.1982(2)	5.4649(1)	5.1536(1)	259.1 (1)	27.5	17
B-FT500	25.45	9.1690(3)	5.4480(2)	5.1385 (1)	256.68(3)	29.3	17
B-FT600	25.48	9.1666(3)	5.4469(2)	5.1390(2)	256.59(2)	32.2	13
B-FT700	25.51	9.1275(6)	5.4234(4)	5.1146(3)	253.18(2)	37.5	6

The calculated crystallite size by Scherrer formula in equation (1)[1] increased with increasing the temperature of fluorination with the size was about 22-38 nm.

$$D=k\lambda/\beta\cos\theta \qquad (1)$$

In this equation 1, k is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154 nm, β is the full width at half maximum, and θ is the half diffraction angle. In the S-Table 1, the calculated crystallite size for as prepared brookite TiO_2 and fluorinated brookite TiO_2 increased with increasing temperature while the specific surface area was decreased, showing that the fluorination could remarkable promote the crystal growth. Besides, all XRD data were refined by GSAS program. For the as-prepared brookite TiO_2, the refined lattice parameters were a=9.1844(5), b=5.4542(3) and c=5.1458(3) Å, slightly larger than those of the standard values a=9.18, b=5.45 (3) and c=5.16 Å. With fluorinated at different temperature, the lattice parameters and unit cell volume increased or decreased obviously. The lattice parameters of fluorinated brookite TiO_2 at 400℃ were increased to a=9.1982(2), b=5.4649(1) and c=5.1536(1)Å, respectively. However, for the fluorinated brookite TiO_2 at 500,600 and 700℃, the lattice parameters and unit cell volume decreased gradually. The lattice expansion of brookite TiO_2 with calcinated and fluorinated should be closely related to the presence of defects.[2]

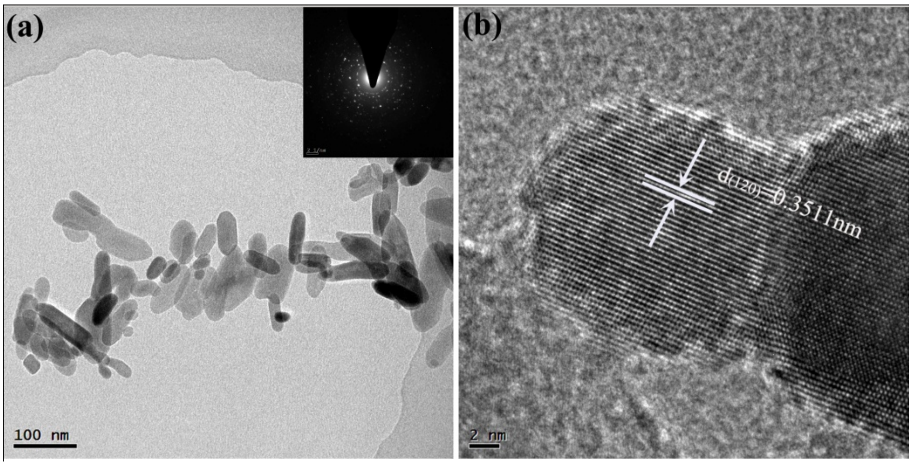

Fig.S2 TEM (a) and HRTEM (b) images of the as-prepared brookite TiO_2, respectively. The insets of (a) show the corresponding selected area electron diffraction.

The morphology of as-prepared brookite TiO_2 was nearly nanorods particles with a width around of 20-40 nm corresponding well with calculated crystalline size from Sherrer equation and XRD data. (S-Table 1) The square-like particles (Fig.S2b) is tiny single crystals, exhibiting a clear lattice fringe of 0.3511 nm correspond to the (120) crystal plane of orthorhombic phase brookite TiO_2.

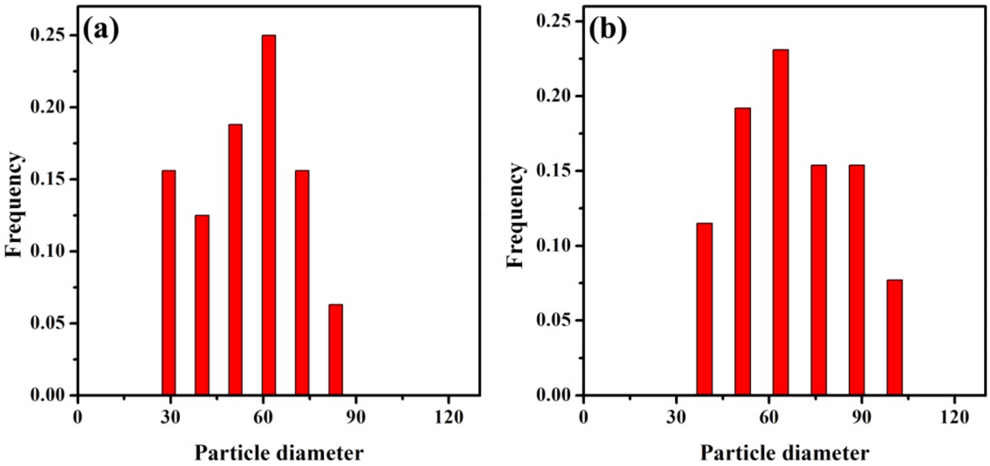

Fig.S3 The particle length distributions of (a) the as-prepared brookite TiO_2 and (b) the fluorinated brookite TiO_2.

Besides, in Fig.S3, particle length distribution for samples is presented, estimated by measuring dimensions across a large number of TEM micrographs. It can be seen that the as-prepared brookite TiO_2 have a narrow length ranging from 30 to 80 nm, with a mean length of 60nm, while for the fluorinated brookite TiO_2 at 400℃, average length is larger, and the length varied from 40 to 100 nm, showing an average length of ca. 60nm.

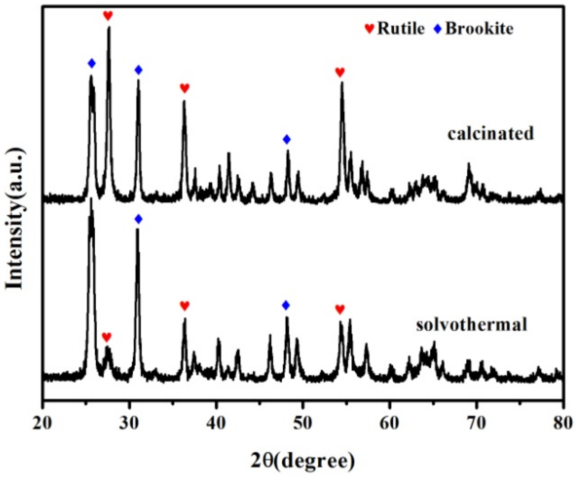

Fig.S4 The XRD patterns of fluorinated brookite and rutile mixed TiO_2 prepared by solvothermal-calcinated methods.

5 ml of TBOT was added into 25 ml absolute ethyl alcohol, after sufficient stirring, this mixed solution was added dropwise into 30 ml deionized water under vigorous stirring. Subsequently, 5g of urea was mixed and dissolved in this solution with agitation. Finally, 5 ml of sodium lactate liquor (60%) and some NH_4F were add to the mixed solution while stirring for about 30 min. The autoclave was sealed and heated in an oven at 200°C for 20h. After reactions, a white product was separated, washed respectively with ethanol and deionized water for 3 times, and dried in an oven at 60°C. In the following, the samples were calcined in an N_2 atmosphere at 500℃ for 4h. The XRD patterns for these samples were shown in Fig.S4. Compared with the method shown in Scheme 1, when the fluorine source (NH_4F) was added in the process of solvothermal methods, the product were brookite and rutile mixed TiO_2, namely, pure brookite TiO_2 cannot be prepared with the above method. Besides, after calcinated at 500℃, the phase content of rutile TiO_2 was increased.

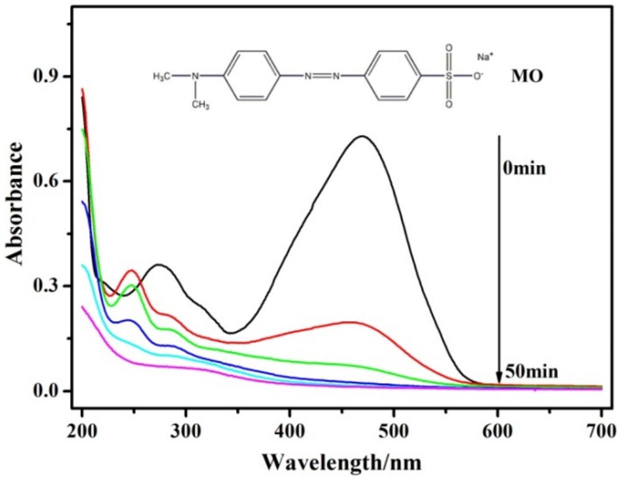

Fig.S5 The degradation of MO under UV-visible light irradiation with time (sampling every 10 min) of the sample that fluorinated brookite TiO_2 at 400℃(inset shows dye structures).

Fig. S5 illustrates the time-dependent degradation spectra of MO aqueous solutions during the UV-vis light irradiation in the presence of fluorinated brookite TiO_2 at 400℃. The maximum absorption of MO solution gradually decreased with prolonging the irradiation time, and MO solution was completely degraded after irradiation for 30 min. In addition, the characteristic absorption band of the dye around 274 nm decreased rapidly with obvious hypsochromic shifts (248 nm), but no new absorption bands appeared, which indicated that a series of N-de-methylated intermediates may have been formed and the whole conjugated chromophore structure of the MO dye may have been cleaved.[3]

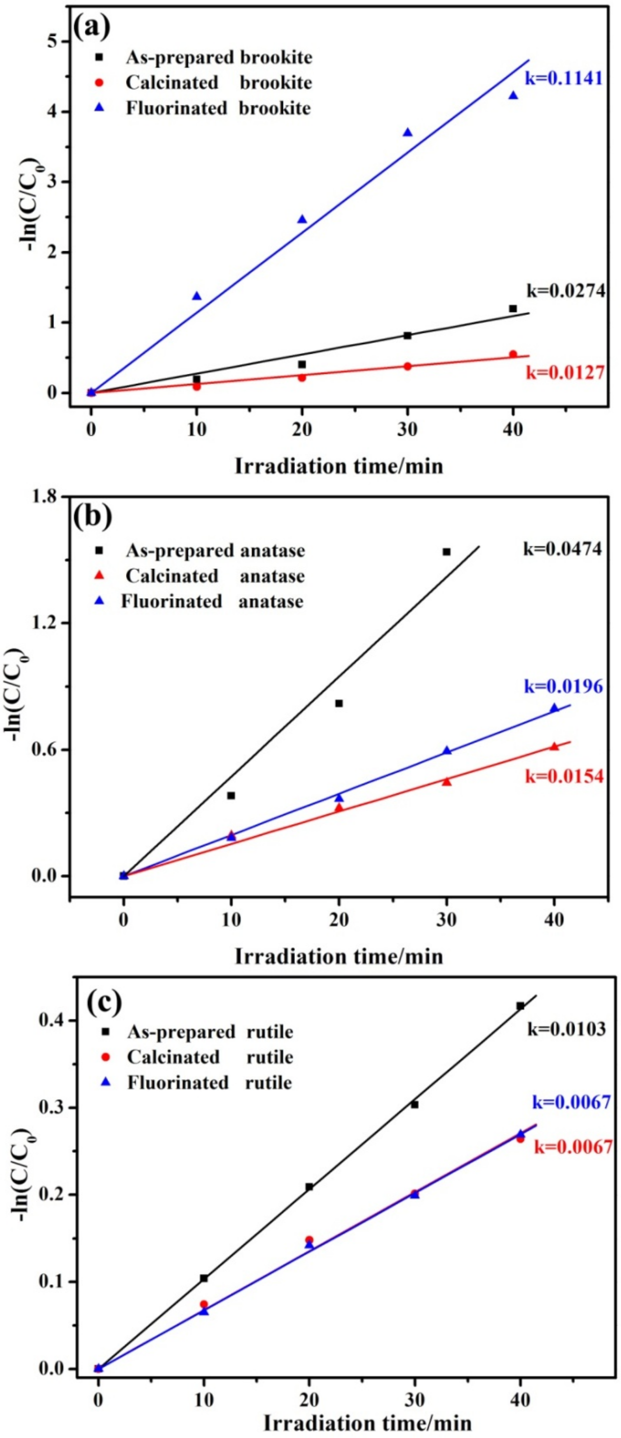

Fig.S6 The kinetics plots for pseudo first order reaction of MO degradation of as-prepared, calcinated and fluorinated TiO_2 at 400℃: (a) brookite, (b) anatase and (c) rutile.

The kinetics of MO degradation of as-prepared, calcinated and fluorinated TiO_2(brookite, anatase and rutile.) at 400℃ are presented in Fig. S6, and are found to follow pseudo-first order reaction as shown in equation (2).[4]

$$-\ln(C/C_0) = kt \qquad (2)$$

where k is the apparent rate constant (min^{-1}), C_0 is the initial concentration of dye and C is the concentration of dye at time (t). As the dye concentration in these experiments remains in the regime where the Beer-Lambert law holds, the concentration can be substituted by the dye absorbance at a given wavelength (typically the peak absorption).

In Fig.S6a, the apparent rate constants of fluorinated, calcinated and as-prepared brookite TiO_2 are 0.1141, 0.0274 and 0.0127 min^{-1}, respectively. The fluorinated brookite TiO_2 clearly presented superior photocatalytic activity towards the degradation of MO compared to calcinated and as-prepared brookite TiO_2. However, in Fig.S6b and S6c, the as-prepared anatase or rutile showed the best photocatalytic activity than the calcinated and fluorinated anatase or rutile. These results showed that surface fluorination enhanced the photocatalytic performance of brookite TiO_2 while reduced the photocatalytic performance of anatase and rutile TiO_2.

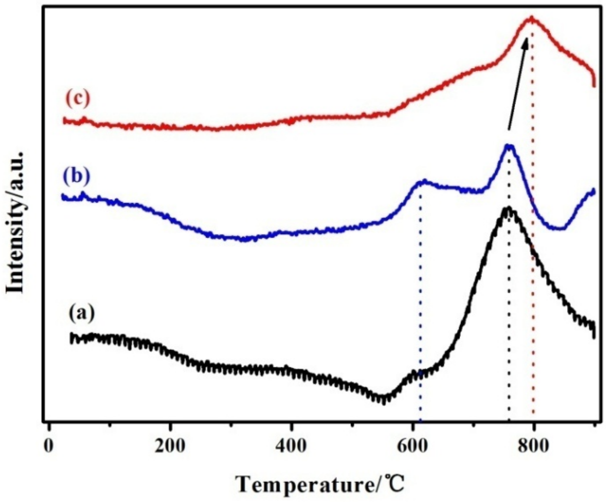

Fig.S7 H_2-TPR of (a) the as-prepared brookite TiO_2, (b) calcinated brookite TiO_2 and (c) fluorinated brookite TiO_2 at 400℃

The species of oxygen for the as-prepared, calcinated and fluorinated brookite TiO_2 were comparatively studied by H_2-TPR. As shown in Fig. S6, two obvious peaks were observed for the as-prepared and calcinated brookite TiO_2 at 610℃ and 760℃, which were due to the reduction of surface adsorbed oxygen and bulk oxygen, respectively. However, for the fluorinated brookite TiO_2, only one obvious peak at 800℃ assigned to bulk oxygen was observed. Besides, a shift of this peak to a higher temperature was also detected, which indicates that the reduction of bulk oxygen was more difficult after fluorination. This is due to the strong electronegativity of fluorine, leading to the formation of ≡Ti-F group and thus the bond of Ti-O became stronger.

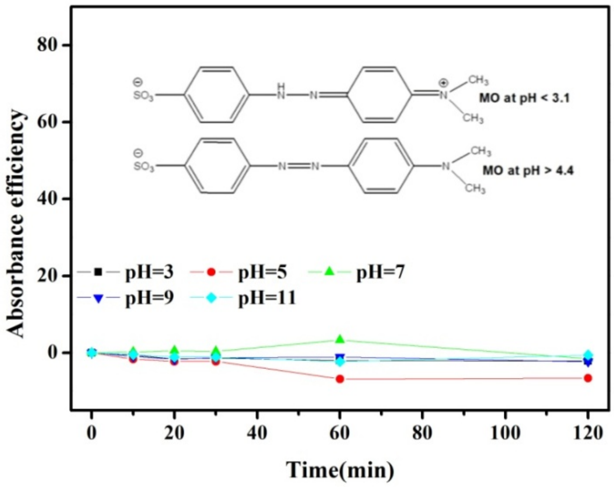

Fig.S8 The adsorption efficiency of MO in dark and at different pH values of the samples that fluorinated brookite TiO_2 at 400℃ (inset shows dye structures at different pH values).

The fluorinated brookite TiO_2 at 400℃ was employed to study the effect of pH on MO adsorption efficiency in the absence of light, based on the decrease in absorption of the solution in which the sample was placed. The variation of color at different pH value could be explained by the changed structure of MO at different pH values.[5] No significant dye degradation takes place during this process but rather equilibrium is formed for dye adsorption-desorption from the semiconductor surface. This is to avoid testing effect caused by dye adsorption during photocatalytic testing (which may be mistakenly attributed to degradation). The results of the dark experiments reveal that MO adsorption is very few and does not show a clear change under different condition of pH values.

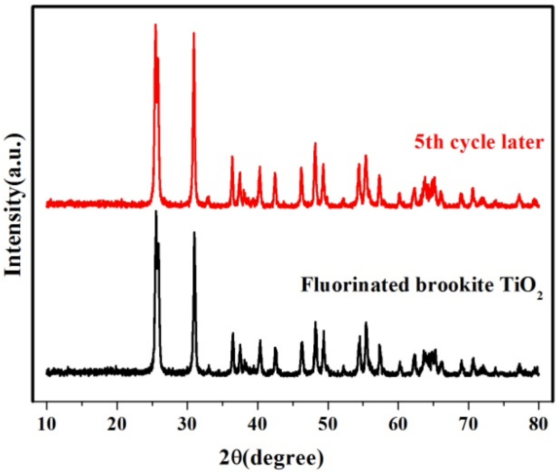

Fig.S9 The XRD pattern of fluorinated brookite TiO_2 before and after 5th photocatalytic cycles toward the photodegradation of MO.

After 5th photocatalytic cycle toward the photodegradation of MO, fluorinated brookite TiO_2 is almost unchanged, indicating the brookite prepared in this work has steady phase structure, which is evident by XRD analyses (Fig. S9).

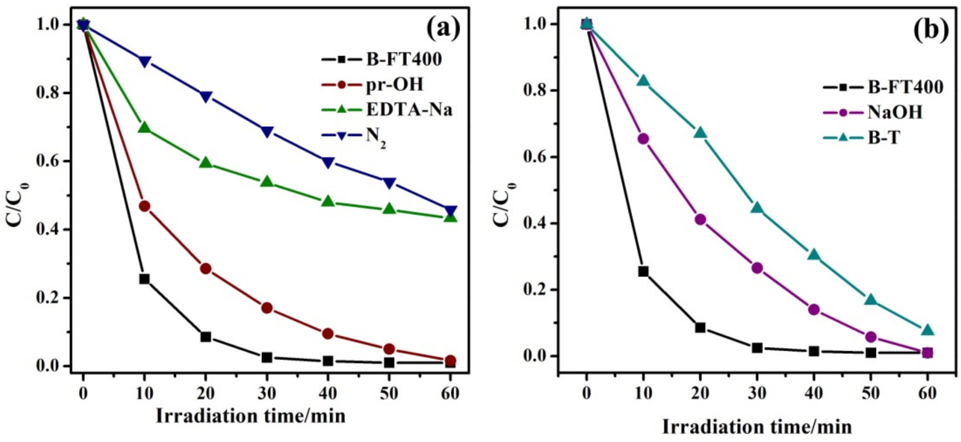

Fig.S10 Plots of (a) photogenerated carrier trapped and (b) with or without NaOH solution washing during the photocatalytic degradation of MO over fluorinated brookite TiO_2 at 400℃ under UV-visible light irradiation

The role of dissolved O_2 in the solution has been examined by a N_2 purging experiment , when N_2 was bubbled into the reaction system, a 50% decline was found in the degradation of MO compared with air-equilibrated conditions, which confirms that dissolved O_2 is favorable for the photodegradation process. Additionally, the photogenerated carrier trapping experiments identified the main oxidant. By adding disodium ethylenediamine tetraacetate (EDTA) to capture the holes, the degradation rate declines by approximately 50%, whereas the addition of 5.0 mL iPrOH as a hydroxyl radical scavenger decreases the degradation rate by 18%, which means that •OH also is one of the active species in the degradation of MO. •OH is generated by a two-electron oxygen reduction route ($\bullet O^{2-}+2H^{+}+2e^{-}\rightarrow H_2O_2+2\bullet OH$),[6] which means that the pH of the solution would increase with the production of •OH. However, there is no obvious change in the pH of the MO solution. This phenomenon is possibly due to CO_2 was produced during the photodegradation, which can lead to the decrease of the pH of the solution. As mentioned above, both $\bullet O^{2-}$ and •OH are the oxidative species in the MO degradation, and indicates that the holes, •O^{2-} and •OH synactic play important roles in the photoreaction.

The NaOH solution can be used to remove F^- on the surface of photocatalyst, when the fluorinated brookite TiO_2 at 400℃ was washed by NaOH solution (0.1M), a 25% decline was found in the degradation of MO compared with that was exempt from washing, which can prove that the F^- was consist in surface of TiO_2 undoubted.

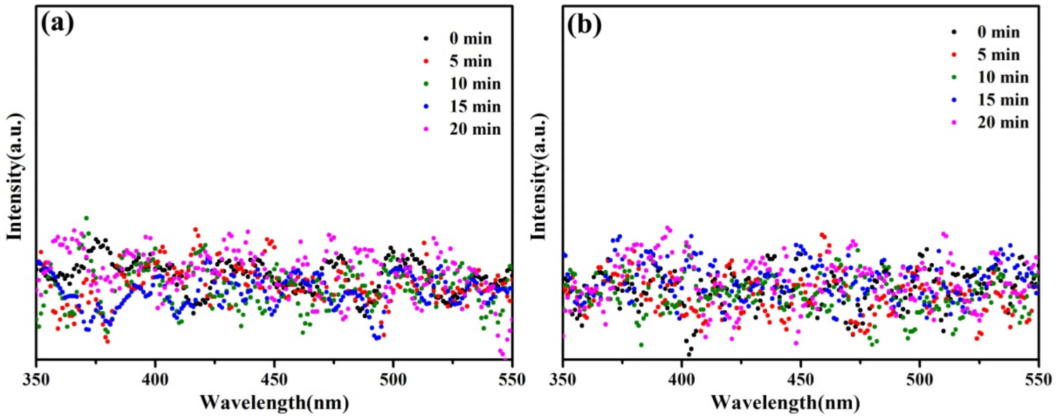

Fig.S11 Fluorescence spectra of a TA–OH solution generated by fluorinated (a) anatase and (b) rutile TiO_2 after calcinations at 400 °C under UV-visible light irradiation.

The fluorinated anatase and rutile TiO_2 at 400 °C were employed to detect the generated •OH on the surface. The PL spectral changes observed during the irradiation of anatase or rutile in terephthalic acid (TA) solution (excitation 315 nm) are exhibited in Fig. S11. As shown in Fig. S11, PL signal at 425 nm is not observed for fluorinated anatase or rutile TiO_2 at room temperature under UV-light irradiation. It clearly indicates that •OH is not formed in the photocatalytic reaction. Therefore, the photocatalytic oxidation activity for fluorinated anatase and rutile TiO_2 were decreased.

References and Notes

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