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Supporting information

Cooperative Photocatalytic Selective Aerobic Oxidation of Alcohols on Anatase TiO_2

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Instrumentations and conditions

XRD

The X-ray diffraction (XRD) was performed to identify the phase nature of the 5(6)-FAM-sensitized TiO_2 photocatalyst and the anatase TiO_2 samples using a Rigaku Miniflex 600 diffractometer with Cu Kα radiation scanned from 10-80^o .

UV-vis

The UV–visible absorption spectra of all 5(6)-FAM-sensitized TiO_2 and TiO_2 samples in this paper were collected on a UV–visible spectrophotometer (Shimadzu UV 3600) equipped with a diffuse reflectance measurement accessory.

HR-TEM

The TEM images of TiO_2 and 5(6)-FAM-sensitized TiO_2 samples were recorded on a JEOL JEM2012—FEF high resolution transmission electron microscope (HR-TEM) operating at 200 kV to obtain the detailed structure information.

BET

The specific surface areas were determined by N_2 physisorption by using an ASAP automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum($<1\times10^{-5}$ bar) in the Micromertics system at

120°C for 12 h prior to N_2 physisorption.

EPR

The EPR experiments were carried out on an electron spin resonance (EPR) spectrometer (JEOL, JES-FA200). 0.2 mmol of benzyl alcohol, 50.5 mg of 5(6)-FAM-sensitized TiO_2 were dispersed in the 5 mL of acetonitrile to get the mixture solution. Subsequently, the EPR signal of DMPO-·OOH, collected at 0 min, 2 min and 4 min respectively, were texted under room temperature after the certain amount of mixture and equal quantity of DMPO was added to the EPR tube. The light irradiation source was a high-pressure Hg lamp with a filter to select the band of 520 nm which is the same as the photo-catalytic reaction. And then 0.004 mmol of CH_3O-TEMPO were mixed to the same EPR tube and collected the EPR signals in situ at 0 min, 2 min and 4 min under the same light irradiation. Finally, the signal was collected after the light irradiation was removed. The EPR signal of conduction band electron was texted by the spectrometer equipped with the same light source at 520 nm.

GC

To measure the conversions of substrates and selectivities of products quantitatively at the same time, gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID) was applied in this research which used high pure N_2 as the carrier gas. The standard analysis conditions of GC-FID: injector temperature 250 °C; detector temperature 280 °C; column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 20 °C/min. The samples were injected into GC-FID with an autoinjector which can warrant the accuracy of the analysis by excluding the uncontrollable factors during manual injection. The results were all obtained using a split mode with a split ratio of 30:1. An Agilent J&W DB-5 capillary column (30 m × 0.32 mm × 0.25 μm, 19,091 J-413) was selected as the column unless otherwise stated; an Agilent J&W DB-17 capillary column (30 m × 0.32 mm × 0.25 μm, 123–1732) was used for the quantitatively analysis of the products for some other substrates, including entries 4 and 8 of Table 5.

Gas chromatography–mass spectrometry (GC–MS) analysis was performed on a Shimadzu GC 2010 gas chromatograph equipped with a Shimadzu GCMS-QP2010 Ultra electron ionization mass spectrometer using a Restek (Rxi®-5Sil MS) capillary column (30 m × 0.25 mm × 0.25 μm) with high pure He as the carrier gas.

Light source

The reaction was generally irradiated with green LEDs, which were obtained from Shenzhen Qilai Optoelectronics Science and Technology Co., LTD., China. In detail, four LED lamps were fastened around a magnetic stirrer in a circle in which the light irradiation was centered on the 10 mL Pyrex vessel. For green LEDs, the irradiating wavelength range is 520 ± 10 nm. Thus, the possible heating of the reaction medium by infrared light and possible leaking of UV light are completely excluded.

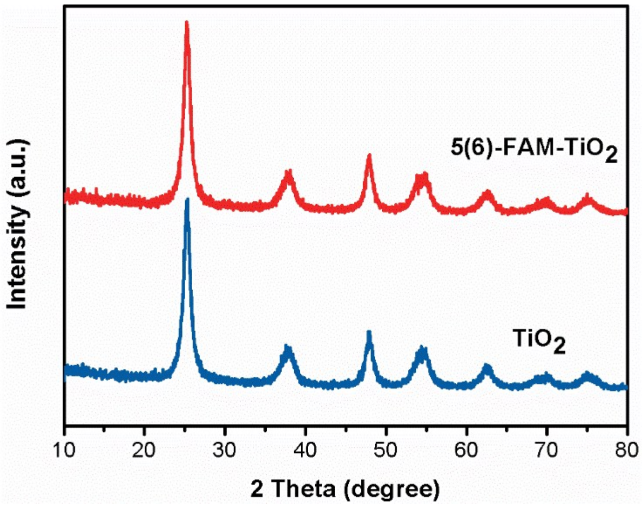
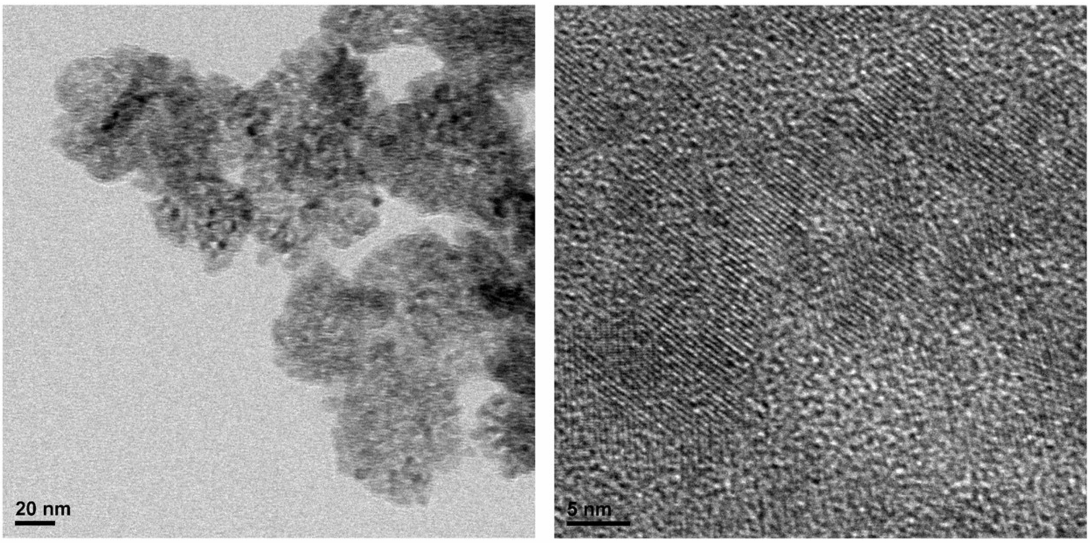
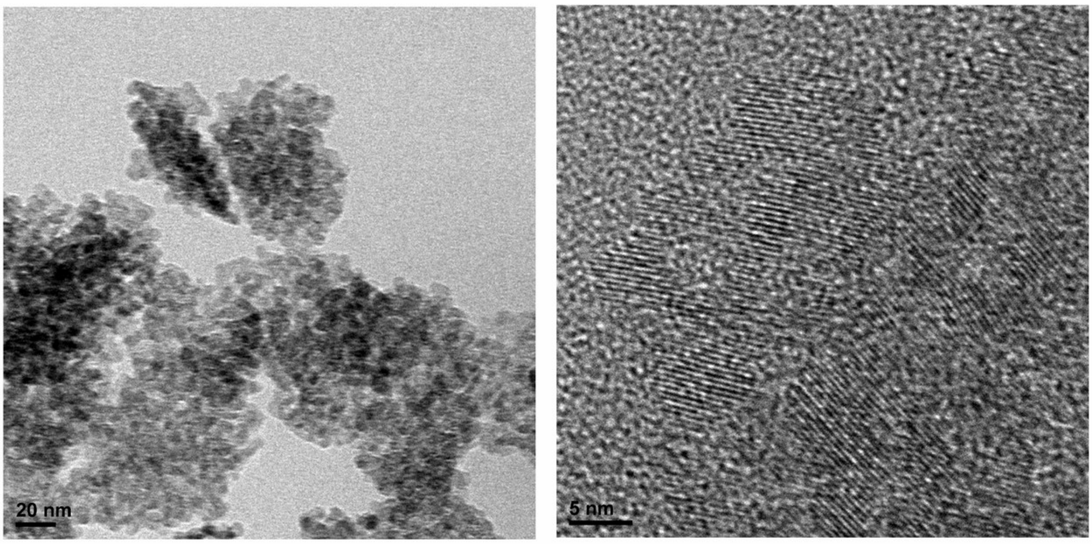


Figure S1. The XRD patterns of anatase TiO_2 and 5(6)-FAM-sensitized TiO_2



(a) **(b)**



(c) (d)

Figure S2. The TEM and HR-TEM images of anatase TiO_2 [(a), (b)] and 5(6)-FAM-sensitized TiO_2 [(c), (d)]

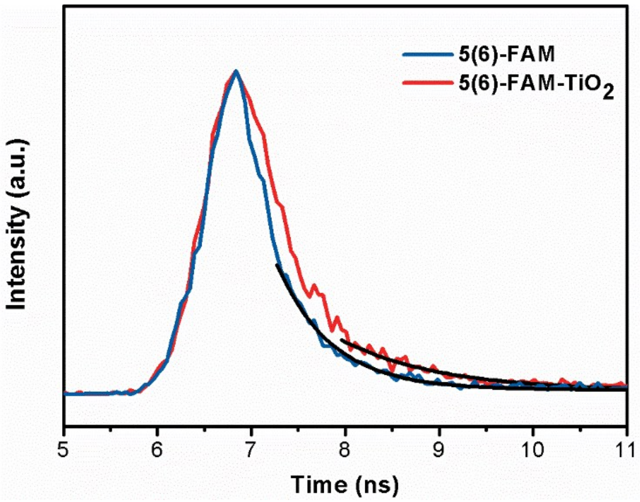


Figure S3. Fluorescence decay of the 5(6)-FAM and 5(6)-FAM-sensitized TiO_2.

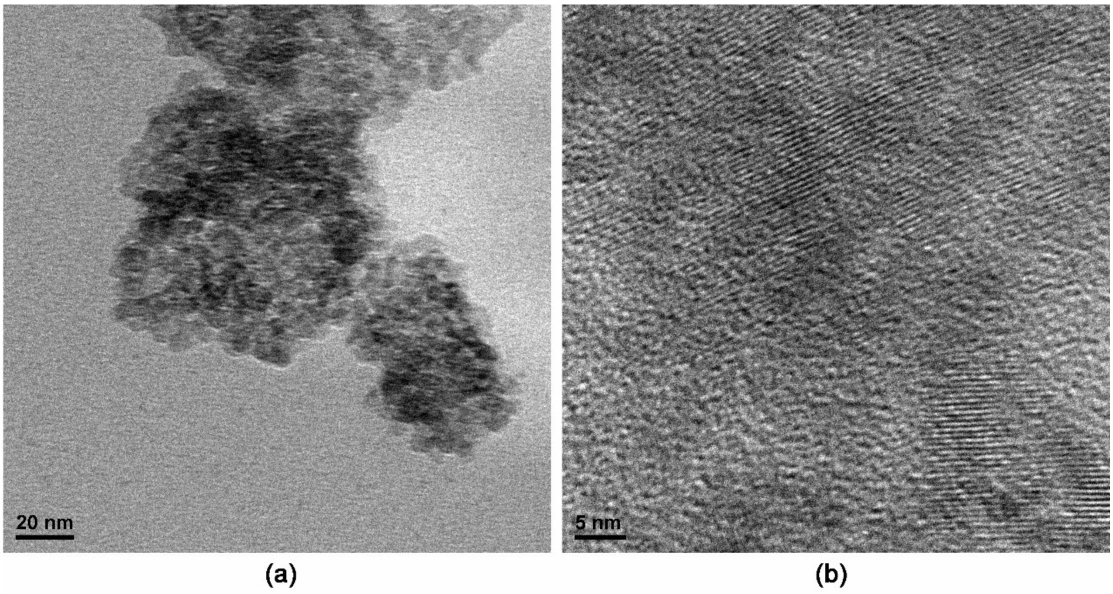


Figure S4. The TEM images of the recycled 5(6)-FAM-sensitized TiO_2 [(a), (b)]

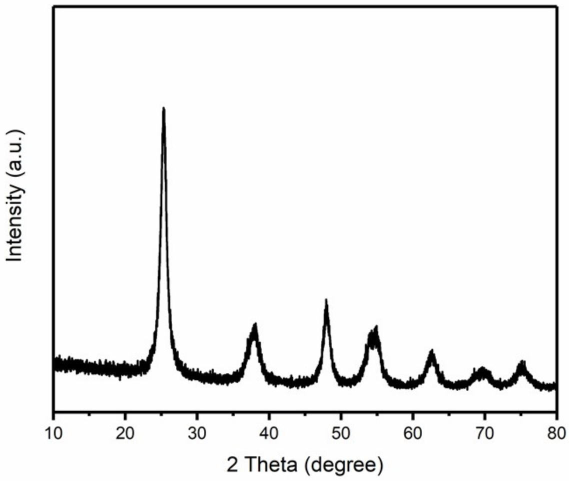


Figure S5. The XRD of the recycled 5(6)-FAM-sensitized TiO_2

Table S1. The influence of different LEDs on the selective aerobic oxidation benzyl alcohol under visible light irradiation [a]

Entry	LED	λ_{max} (nm)	Conv.(%)[b]	Sel.(%)[b]
1	Red	630	6	98
2	Yellow	590	41	98

3	Green	520	81	98
4	Blue	460	80	98
5	Violet	400	78	98
6	White	Continuous	54	98

[a] Reaction conditions: benzyl alcohol (0.2 mmol), 5(6)-FAM-sensitized TiO_2 (50.5 mg, including 1.33×10^{-3} mmol of 5(6)-FAM), CH_3O-TEMPO (0.004 mmol), O_2 (0.1 MPa), green LED irradiation (3 W × 4), CH_3CN (5 mL), 40 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzyl alcohol, and selectivity of benzaldehyde.

Table S2. The influence of the solvent on the selective aerobic oxidation of benzyl alcohol by the visible light photocatalysis of 5(6)-FAM-sensitized TiO_2 and CH_3O-TEMPO [a]

Entry	Solvent	Conv.(%)[b]	Sel.(%)[b]
1	CH_3CN	86	98
2	BTF[c]	41	98
3	EtOAc	37	98
4	PhMe	45	98
5	DCM	39	98
6	DMF	26	98

[a] Reaction conditions: benzyl alcohol (0.2 mmol), 5(6)-FAM-sensitized TiO_2 (50.5 mg, including 1.33×10^{-3} mmol of 5(6)-FAM), CH_3O-TEMPO (0.004 mmol), O_2 (0.1 MPa), green LED irradiation (3 W × 4), solvent (5 mL), 1 h. [b] Determined by GC-FID using

chlorobenzene as the internal standard, conversion of benzyl alcohol, and selectivity of benzaldehyde. [c] Using biphenyl as the internal standard. BTF, benzotrifluoride; EtOAc, ethyl acetate; PhMe, toluene; DCM, dichloromethane; DMF, *N,N'*-dimethylformamide.

Table S3. The influence of the amount of CH_3CN on the selective aerobic oxidation of benzyl alcohol by the visible light photocatalysis of 5(6)-FAM-sensitized TiO_2 and CH_3O-TEMPO [a]

Entry	CH_3CN (mL)	C_0 (M)	Conv.(%)[b]	Sel.(%)[b]
1	1	0.200	68	98
2	2	0.100	69	98
3	3	0.067	77	98
4	4	0.050	79	98
5	5	0.020	86	98

[a] Reaction conditions: benzyl alcohol (0.2 mmol), 5(6)-FAM-sensitized TiO_2 (50.5 mg, including 1.33×10^{-3} mmol of 5(6)-FAM), CH_3O-TEMPO (0.004 mmol), O_2 (0.1 MPa), green LED irradiation (3 W × 4), CH_3CN, 1 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzyl alcohol, and selectivity of benzaldehyde.