

## Supplementary Information for

# Photocatalytic reductive coupling of furfural into deoxyfuroin on mesoporous TiO<sub>2</sub>

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## Experimental

### General Information

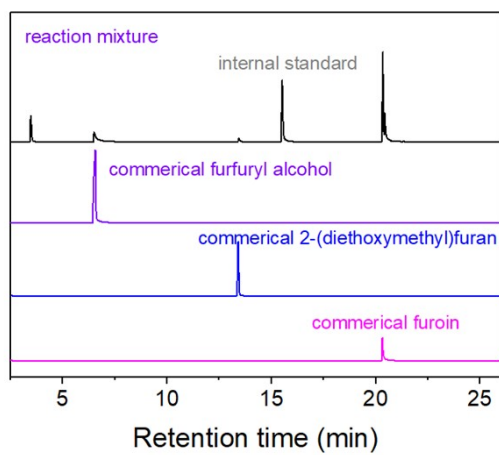
All chemicals were purchased from Aladdin Reagent and Macklin Reagent and used without further purification. The  $^1\text{H}$ - and  $^{13}\text{C}$ - NMR spectra of deoxyfuroin were measured on a Bruker AVIII 400 spectrometer ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 101 MHz). Powder XRD patterns were recorded using a Bruker D8 Advance system. Samples were scanned at  $2\theta$  angles of  $10\text{--}85^\circ$ . Transmission electron microscopy (TEM) was carried out using a Jem-2100F electron microscope. The scanning electron microscope (SEM) was performed on Thermo Scientific Quattro S. UV-Vis-NIR spectra were measured on UV-2400PC (Shimadzu). X-ray photoelectron spectroscopy (XPS) was collected on Thermofisher escalab 250xi. The photocurrent density measurement was performed on a CHI660E electrochemical workstation (Chenhua Instrument). The three-electrode cell was composed of a working electrode (catalyst coated FTO), a reference electrode (saturated calomel electrode, SCE) and a counter electrode (Pt wire). The light source was a Kessil LED ( $\lambda_{\text{max}} = 370 \text{ nm}$ ) lamp and the test was run in  $0.1 \text{ M Na}_2\text{SO}_4$  solution.

**The preparation of mesoporous  $\text{TiO}_2$ .** A 100 mL flask was loaded with a certain amount ( $x$ , 0-1.6 g) of Pluronic F127 and 20 mL ethanol. After stirring for half hour, the 2.1 g tetrabutyl titanate and 0.7 g titanium tetrachloride were added dropwise to obtain the yellow solution. After stirring for another hour, this solution was transferred into a Petri dish and the solvent was evaporated for 36 h at room temperature. The obtained membrane was calcined at  $380^\circ\text{C}$  in argon for 3 h and then calcined at  $y^\circ\text{C}$  in air for 24 h. Then the white powder was collected as the mesoporous  $\text{TiO}_2$  ( $\text{F127}_x\text{-y-mTiO}_2$ ). The preparation procedures of  $\text{CTAB}_{0.4}\text{-400-TiO}_2$  and  $\text{P123}_{0.4}\text{-400-TiO}_2$  were similar to  $\text{F127}_{0.4}\text{-400-TiO}_2$  except of changing the template type.

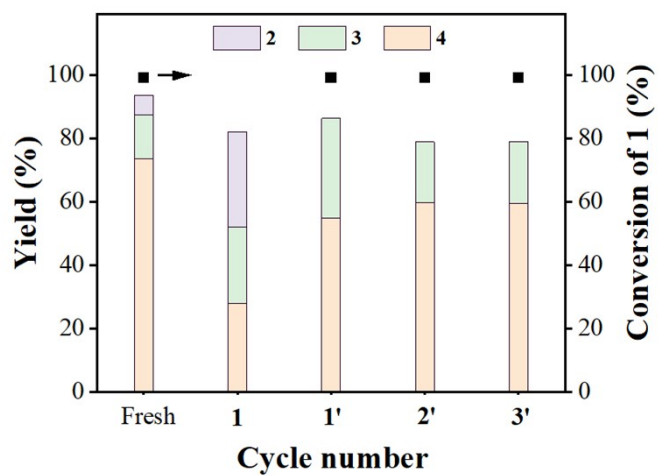
### The preparation of copper loaded mesoporous $\text{TiO}_2$ .

A 150 mL home-made quartz photoreactor was loaded with  $\text{F127}_{0.4}\text{-400-mTiO}_2$  (100 mg) and  $\text{CuCl}_2$  (3 mg). Then ethanol (50 mL) as solvent was added, and the inner atmosphere was switched to argon before sealing. After stirring under dark conditions for 15 minutes, the reactor was irradiated using a Kessil LED lamp (370 nm) under magnetic stirring for 2 hours. The photocatalyst was collected by filtration under vacuum, then washed with excess ethanol.

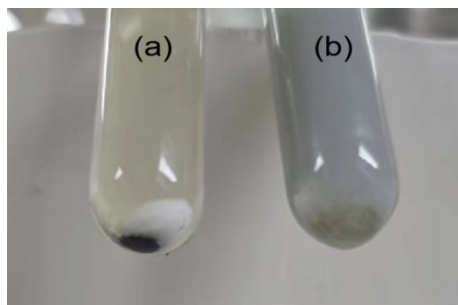
**Photocatalytic test.** In a typical procedure, a 6 mL quartz reactor equipped with a stir bar was loaded with substrate (furfural 30mg or furoin 10 mg), catalyst (5-10 mg), solvent (1-2 mL). Then the atmosphere was switched to argon before sealing the reactor. This mixture was irradiated at room temperature (fan cooling) with homemade LED lamps ( $\lambda_{\text{max}} = 365 \text{ nm}$ , 18 W) for a certain time. After the reaction, the standard solution (1,3,5-trimethoxybenzene in isopropanol) was added. After filtration using a Nylon syringe filter, the solution was analyzed by gas chromatography (Shimadzu GC-2014C).



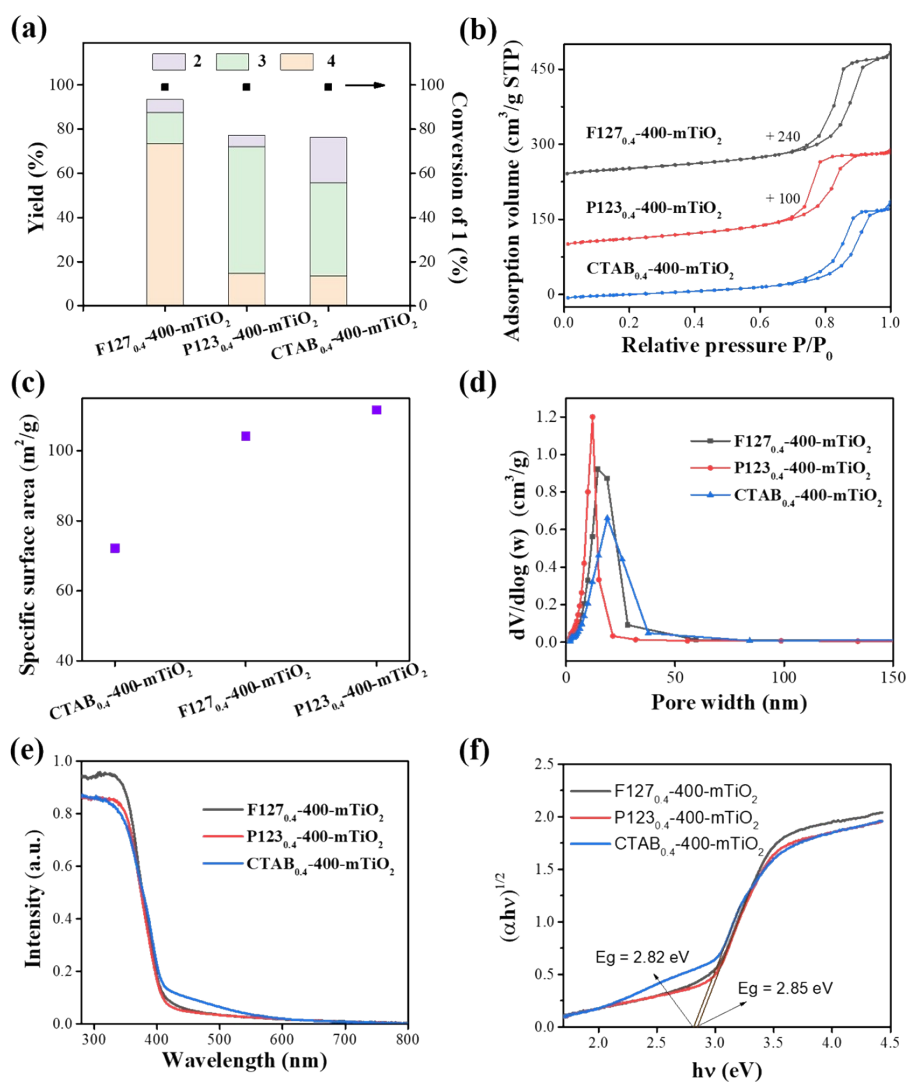
**Figure S1.** The GC analysis of reaction mixture from photocatalytic coupling of furfural using F127<sub>0.4</sub>-400-mTiO<sub>2</sub> and commercial furfuryl alcohol, 2-(diethoxymethyl)furan and furoin.



**Figure S2.** The catalyst cycling experiments. Conditions: F127<sub>0.4</sub>-400-mTiO<sub>2</sub> (5 mg), furfural (30 mg), ethanol (2 mL), 365 nm LEDs, room temperature, argon, 8 h, GC yields. The number of first cycle without catalyst calcination was denoted as **1**. The numbers of cycles with catalyst calcination at 400 °C for 3 hours after each reaction were denoted as **1'**, **2'** and **3'**.

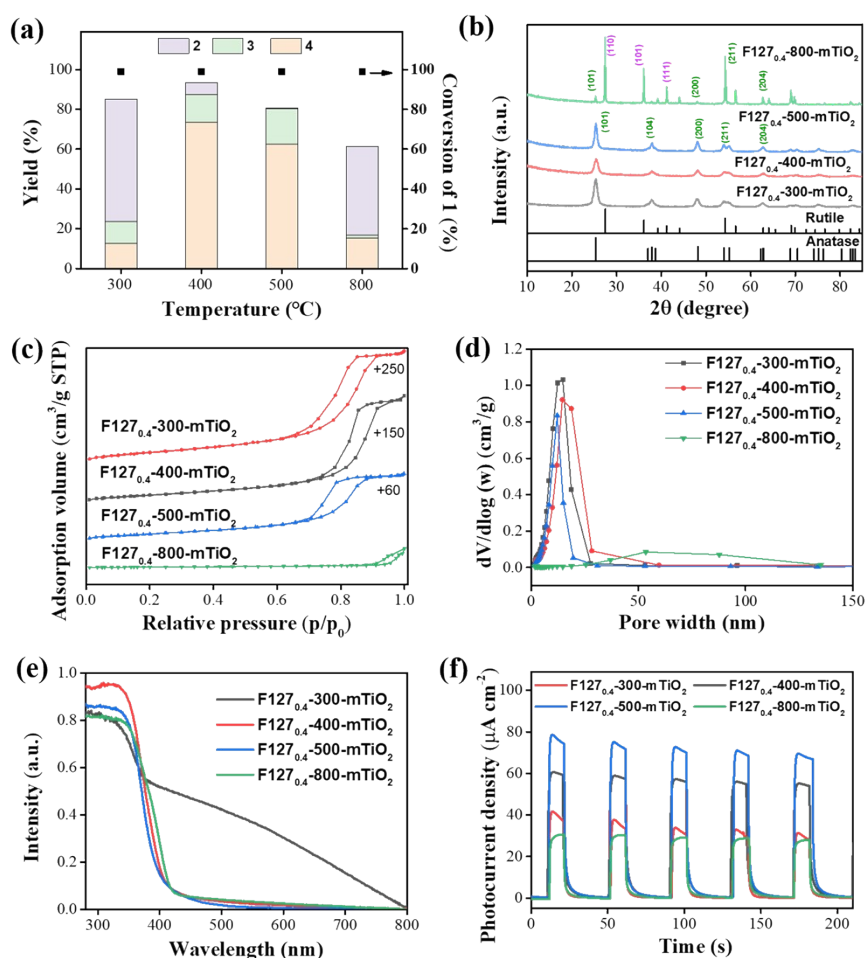


**Figure S3.** The photos of two photocatalysts during the coupling of furfural. (a)  $F127_0-400\text{-mTiO}_2$ , (b)  $F127_{0.4}-400\text{-mTiO}_2$ .



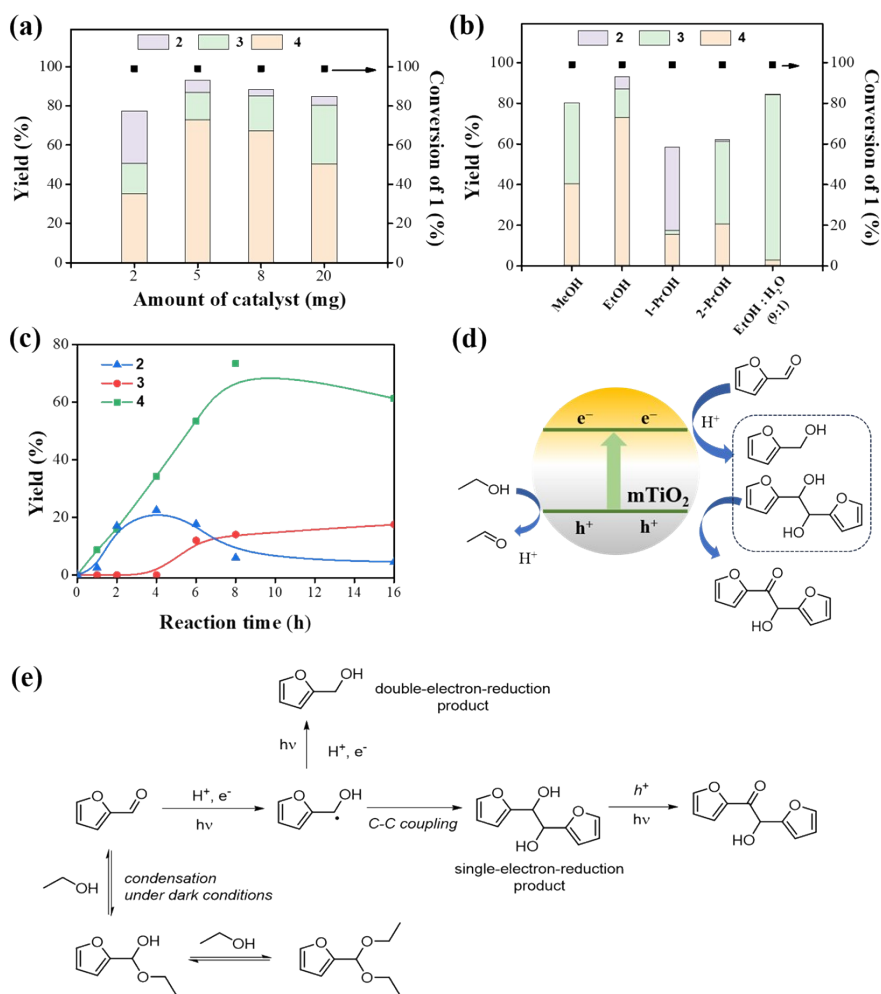
**Figure S4.** The photocatalytic performance, structural characterizations, and absorption property of  $m\text{TiO}_2$  prepared using different templates. (a) Photocatalytic performance in homocoupling of furfural. (b) The nitrogen adsorption-desorption isotherms. (c) The specific surface area. (d) The distribution of pore size. (e) UV-vis absorption. (f) Kubelka-Munk function from the UV-vis absorption.

Apart from F127, the P123 and hexadecyltrimethylammonium bromide (CTAB) were also used as templates in the preparation of  $m\text{TiO}_2$  (Figure S1). Under the similar preparation conditions, the  $m\text{TiO}_2$  using CTAB (CTAB<sub>0.4</sub>-400- $m\text{TiO}_2$ ) had mesopores with a smaller size than F127<sub>0.4</sub>-400- $m\text{TiO}_2$ , while the  $m\text{TiO}_2$  using P123 (P123<sub>0.4</sub>-400- $m\text{TiO}_2$ ) had mesopores with a larger pore size. Among these catalysts, the F127<sub>0.4</sub>-400- $m\text{TiO}_2$  still showed moderate surface area and light absorption. The photocatalytic tests indicated that F127<sub>0.4</sub>-400- $m\text{TiO}_2$  was the optimal catalyst for furfural synthesis. This phenomenon was in accordance with that of changing F127 template amount.



**Figure S5.** The photocatalytic performance, structural characterizations, and absorption property of F127<sub>0.4</sub>- $\gamma$ -mTiO<sub>2</sub> ( $\gamma$  = 300, 400, 500, 800) calcinated at different temperatures. (a) Photocatalytic performance in homocoupling of furfural. (b) XRD patterns. (c) The nitrogen adsorption-desorption isotherms. (d) The distribution of pore size. (e) UV-vis absorption. (f) Transient photocurrent tests.

The calcination temperature also had a remarkable effect on the structure and properties of mTiO<sub>2</sub> when the same amount of F127 was used as template (Figure S2). The mTiO<sub>2</sub> samples prepared under lower calcination temperature (F127<sub>0.4</sub>-300-mTiO<sub>2</sub>) and higher calcination temperature (F127<sub>0.4</sub>-800-mTiO<sub>2</sub>) showed poor photoactivity and delivered more product 2. The template could not be totally removed under lower calcination temperature (300 °C) which induced a poor charge carriers separation efficiency (Figure S2e, f). The crystalline phase of sample under high calcination temperature (800 °C) was rutile and the mesopore disappeared, both of which induced the poor photocatalytic activity.



**Figure S6.** The controlled experiments and mechanism study. (a) The effect of photocatalyst amount on the product distribution. Conditions: F127<sub>0.4</sub>-400-TiO<sub>2</sub> (2-20 mg), furfural (30 mg), ethanol (2 mL), 365 nm LEDs, room temperature, argon, 8 h, GC yields. (b) The effect of solvent on the product distribution. Conditions: F127<sub>0.4</sub>-400-TiO<sub>2</sub> (5 mg), furfural (30 mg), solvent (2 mL), 365 nm LEDs, room temperature, argon, 8 h, GC yields. (c) The time course of photocatalytic coupling of furfural into furoin. Conditions: F127<sub>0.4</sub>-400-TiO<sub>2</sub> (5 mg), furfural (30 mg), ethanol (2 mL), 365 nm LEDs, room temperature, argon, GC yields. (d) The proposed photocatalytic reaction mechanism. (e) The proposed reaction routes of furfural.



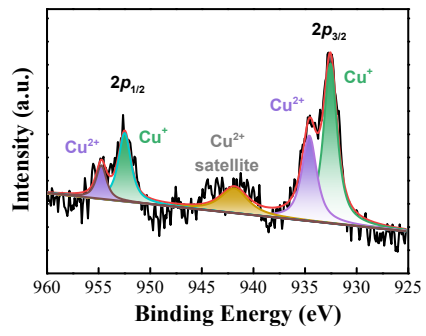


Figure S7. Cu 2p XPS of Cu/mTiO<sub>2</sub> prepared via photodeposition.

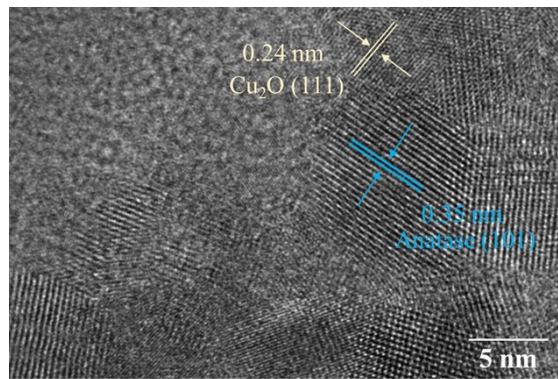
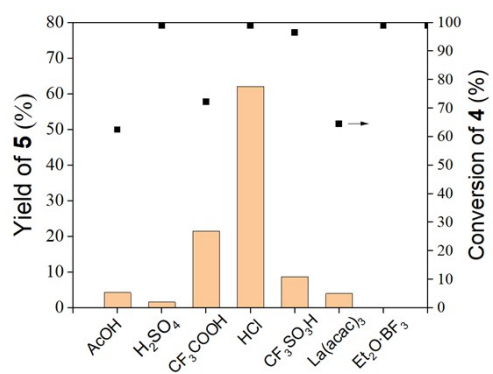
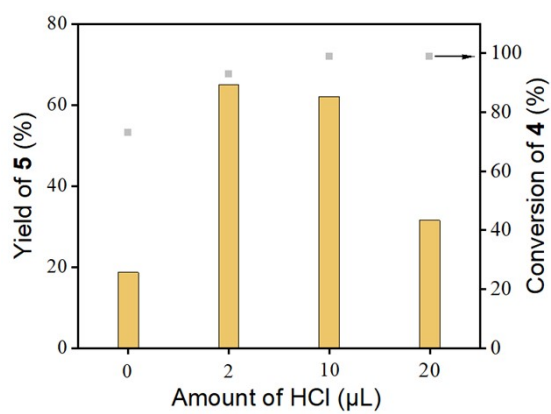


Figure S8. The HRTEM image of Cu/mTiO<sub>2</sub> prepared via photodeposition.

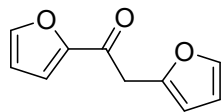


**Figure S9.** The effect of acid additives on the Cu/m-TiO<sub>2</sub> catalyzed deoxygenation of furoin. Cu/F127<sub>0.4</sub>-400-mTiO<sub>2</sub> (10 mg), furoin (10 mg), acid additive (10 μL or 10 mg), i-PrOH/DCE (3:1, 1 mL), 365 nm LEDs, room temperature, argon, 14 h, GC yields.



**Figure S10.** The effect of HCl amount on the photocatalyzed deoxygenation of furoin using Cu/F127<sub>0.4</sub>-400-mTiO<sub>2</sub> as catalyst. Conditions: Cu/F127<sub>0.4</sub>-400-mTiO<sub>2</sub> (10 mg), furoin (10 mg), HCl (37 wt%, 0-20 μL), i-PrOH/DCE (3:1, 1 mL), 365 nm LEDs, room temperature, argon, 14 h, GC yields.

## NMR data of product



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (dd,  $J = 1.6, 0.7$  Hz, 1H), 7.37 (dd,  $J = 1.8, 0.7$  Hz, 1H), 7.24 (dd,  $J = 3.6, 0.6$  Hz, 1H), 6.55 (dd,  $J = 3.6, 1.7$  Hz, 1H), 6.34 (dd,  $J = 3.2, 1.9$  Hz, 1H), 6.26 (dd,  $J = 3.2, 0.7$  Hz, 1H), 4.16 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  183.83, 152.01, 147.75, 146.83, 142.14, 118.25, 112.48, 110.70, 108.39, 38.20.

