### **Supplementary Materials**

S1 Materials characterizations

S2 The testing methods for TOC and COD

**Fig. S1**. The effect of different metal iron salts on the degradation ratio and k of TC,[TC]=50 mg/L; [Catalyst]=0.4 g/L;

Fig. S2. The effect of molar ratio of Fe<sup>3+</sup>to H<sub>2</sub>BDC for the degradation ratio and *k* of TC, [TC]=50 mg/L; [Catalyst]=0.4 g/L;

**Fig. S3.** The effect of solvent thermal temperature on the degradation ratio and k of TC,[TC]=50 mg/L; [Catalyst]=0.4 g/L;

Fig. S4. The k value of TC degradation under different microwave powers.[TC]=50 mg/L; [Catalyst]=0.4 g/L;

Fig. S5. SEM image of the used  $FBV_{0.4}$ 

Fig. S6. N<sub>2</sub> adsorption/desorption isotherm and pore size distribution graph of the used FBV<sub>0.4</sub>

Table S1. List of experimental chemicals.

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Table S5 Specifications of Microwave chemical reactor

### S1 Materials characterizations

The N<sub>2</sub> adsorption/desorption isotherms were measured using a Bruna Emmett Taylor (BET Autosorb-1, USA), and the S<sub>BET</sub> and pore size distribution of the catalysts were calculated. The chemical phase, composition, crystallinity and other characteristics of the samples were analyzed by X-ray diffraction (XRD, Empyrean, Netherlands). Scanning electron microscopy (SEM, Gemini Sigma, Germany) was used to observe the surface morphology and microstructure of the samples. X-ray photoelectron spectroscopy (XPS, K-Alpha, USA) was used to determine the composition, content and chemical valence states of the surface elements. Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet Is5, USA) was utilized to analyze the surface functional groups and chemical bonds. Electron paramagnetic resonance spectroscopy (EPR, A300, Germany) was conducted to confirm the existence of oxygen vacancy defects. The Bruker A300 spectrometer was used to record the electrons spin resonance (ESR, Germany) with 5, 5-dimethyl-1-pyrroline N-oxide (DMPO), 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO) as spin-trapped reagent under microwave irradiation. The UV-Vis diffuse reflectance spectra of the samples were measured using a UV-Vis-NIR spectrophotometer (3600 plus, Japan) to reveal the energy level structure of the catalyst.

# S2 The testing methods for TOC and COD

#### S2.1 Analysis of TOC

The determination of TOC content was carried out using the TOC-L analyzer from Shimadzu, Japan. The sample was filtered through a 0.45  $\mu$ m membrane filter before analysis. The combustion temperature is maintained at 680°C, and platinum catalytic oxidation occurs. Calibration was carried out using potassium hydrogen phthalate standard (0-100 mg/L). The detection limit of the system is 4  $\mu$ g/L, and the relative standard deviation is less than 2%.

# **S2.2 Determination of COD**

According to the different substrates of the wastewater, two methods are adopted: Actual wastewater: COD was determined by the permanganate index method in accordance with GB 11892-89 standard. Simply put, 100 mL of the sample was boiled with 10 mL of KMnO<sub>4</sub> and 5 mL of  $H_2SO_4$  at 100°C for 10 min. Then titrate with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and perform blank correction.

Simulated wastewater: Quantitative analysis of COD was conducted using the Lianhua COD-580 portable rapid analyzer. The pre-calibrated instrument adopts sealed tube digestion, 165°C for 15 min, and spectrophotometric detection at 620 nm (range: 5-2000 mg/L COD).



Fig. S1.The effect of different metal iron salts on the degradation rate and k of TC



Fig. S2. The effect of molar ratio of Fe<sup>3+</sup>to H<sub>2</sub>BDC for the degradation rate and k of TC



Fig. S3. The effect of solvent thermal temperature on the degradation rate and k of TC



Fig. S4. The k value of TC degradation under different microwave powers



Fig. S5. SEM image of the used  $FBV_{0.4}$ 



Fig. S6.  $N_2$  adsorption/desorption isotherm and pore size distribution graph of the used  $FBV_{0.4}$ 

| Experimental                    | Source                                  | category |  |
|---------------------------------|---|----------|--|
| chemical                        | Boulee                                  | category |  |
| ethanol (EtOH)                  | Tioniin Domoo Chomical Poogont Footory  | ۸D       |  |
| (99.7%)                         | Tanjin Damao Chemical Reagent Factory   | AK       |  |
| isopropanol                     | Tioniin Euchen Chemical Descent Fostery | ۸D       |  |
| (IPA) (99.7%)                   | Tanjin Fuchen Chemical Reagent Factory  | AK       |  |
| р-                              |   |          |  |
| benzoquinone (BQ)               | Tianjin Fuchen Chemical Reagent Factory | AR       |  |
| (99.7%)                         |   |          |  |
| silver nitrate                  | Tianjin Weichen Chemical Reagent Co.,   | ٨D       |  |
| (AgNO <sub>3</sub> ) (99.8%)    | Ltd                                     | AK       |  |
| NaCl                            |   | AR       |  |
| Na <sub>2</sub> CO <sub>3</sub> |   | AR       |  |
| NaHCO <sub>3</sub>              | Tioniin Iromia Chamical Descent Co. Itd | AR       |  |
| $Na_2SO_4$                      | Tanjin kemio Chennear Keagent Co., Lid  | AR       |  |
| NaNO <sub>3</sub>               |   | AR       |  |
| NaOH                            |   | AR       |  |
| HNO <sub>3</sub>                | Tianjin Damao Chemical Reagent Factory  | AR       |  |

Table S1. List of experimental chemicals.

|   |                | Reaction Conditions      |                               |                          |             |                              |              |
|---|----------------|--------------------------|-------------------------------|--------------------------|-------------|------------------------------|--------------|
| Catalyst  | Technology     | Catalyst<br>dosage (g/L) | Concentration of<br>TC (mg/L) | Degradation<br>Ratio (%) | 时间<br>(min) | Others                       | es           |
| FBV <sub>0.4</sub>  | MW             | 0.4                      | 50                            | 98.32                    | 10          | P=480 W                      | This<br>work |
| $\alpha$ -Bi <sub>2</sub> O <sub>3</sub> /CoFe <sub>2</sub> O <sub>4</sub> (BO/CFO)                       | MW             | 1                        | 1                             | 97.55                    | 5           | P=450 W                      | 1            |
| ZnO/CoFe <sub>2</sub> O <sub>4</sub> (ZO/CFO)   | MW             | 1                        | 1                             | 88.23                    | 5           | P=450 W                      | 1            |
| Co@NCNTs-5  | MW             | 1.5                      | 20                            | 99.5                     | 6           | P=520 W                      | 2            |
| CeNCN   | Photocatalysis | 0.4                      | 10                            | 80.09                    | 60          | $\lambda \ge 420 \text{ nm}$ | 3            |
| MIL-MIL101Fe (NH <sub>2</sub> )<br>@g-C <sub>3</sub> N <sub>4</sub> @CoFe <sub>2</sub> O <sub>4</sub> /GO | Photocatalysis | 0.4                      | 20                            | 90                       | 65          | $\lambda > 420 \text{ nm}$   | 4            |
| W-Zr-MOF-NH <sub>2</sub> @TpTt-<br>COF  | Photocatalysis | 0.3                      | 20                            | 90.14                    | 40          | $\lambda$ < 420 nm           | 5            |
| Fe-MIL-101  | Photocatalysis | 0.5                      | 50                            | 96.6                     | 180         | $\lambda > 420 \text{ nm}$   | 6            |
| MIL-53(Fe, Al)  | Photocatalysis | 0.1                      | 20                            | 94.33                    | 50          | $\lambda = 365 \text{ nm}$   | 7            |

 Table S2. Comparative study of metal-based catalysts in different literatures.

| ZnO/ Bi <sub>2</sub> MoO <sub>6</sub> /ZIF-67              | photocatalysis | 0.4  | 40 | 90.3 | 90 | $\lambda = 420 \text{ nm}$ | 8  |
|--|----------------|------|----|------|----|----------------------------|----|
| Bi <sub>3</sub> O <sub>4</sub> Br/NH <sub>2</sub> -MIL-125 |                |      |    |      |    |                            |    |
| (Ti)   | photocatalysis | 0.15 | 25 | 88.5 | 90 | $\lambda = 357 \text{ nm}$ | 9  |
| BOB/NMILT  |                |      |    |      |    |                            |    |
| CuBTC/g-C <sub>3</sub> N <sub>4</sub>                      | photocatalysis | 0.1  | 20 | 97.4 | 60 | UV                         | 10 |

Table S3. The intermediate products of microwave catalytic degradation of TC

| Number | m/z   | Chemical  | Name   | Proposed structure   |         |  |
|--------|-------|---|--|--|---------|--|
|        | III/Z | Formula   | Ivanic   | T toposed structure  |         |  |
| тс     | 445   | $C_{22}H_{24}N_2O_8$  | Tetracycline   | H <sub>3</sub> C<br>OH<br>OH<br>OH<br>OH<br>OH<br>OH<br>OH<br>OH<br>OH |         |  |
| Τ1     | 396   | C <sub>20</sub> H <sub>25</sub> NO <sub>7</sub>   | Acetylated nitrous oxide of senecrafinine                | OH CH2 NH2<br>OH OH OH   |         |  |
| T2     | 318   | Benzoic acid,4-[(methoxycarbonyl)oxy]-, 4-ethoxyphenyl ester,<br>318 $C_{17}H_{16}O_6$ Carbonicacid, methyl ester, ester with p-ethoxyphenyl p- | OH CH <sub>2</sub>                                       |  |         |  |
|        |       |   | Carbonicacid, methyl ester, ester with p-ethoxyphenyl p- | ОН   |         |  |
|        |       |   |  | hydroxybenzoate (8CI)  | ~ ∬ ∫ ∬ |  |

Methyl4-(4-ethoxyphenoxycarbonyl)phenyl carbonate

| Т3 | 274 | $C_{16}H_{16}O_4$                               | Benzaldehyde,4,5-dimethoxy-2-(phenylmethoxy)-;<br>Benzaldehyde,2-(benzyloxy)-4,5           |   |
|----|-----|---|--|---|
| T4 | 283 | $C_{13}H_{18}N_2O_5$                            | Hydantoic acid;(S)-2-(Aminocarbonyl)-amino-3-  | H <sub>3</sub> C CH <sub>3</sub><br>OH OH NH <sub>2</sub> |
| Т5 | 230 | C <sub>10</sub> H <sub>15</sub> NO <sub>4</sub> | (R)-N-BOC-Propargylglycine;(R)-N-tert-Butoxycarbonyl-2-am                                  |   |
| Т6 | 432 | $C_{21}H_{22}N_2O_8$                            | b-D-Glucopyranoside, 4-nitrophenyl2-(acetylamino)-2-deoxy-4,6-O-<br>(phenylmethylene)-     |   |
| T7 | 387 | C <sub>20</sub> H <sub>19</sub> NO <sub>7</sub> | Butanoic acid,2,3-bis(benzoyloxy)-4-(dimethylamino)-4-oxo-,<br>(2S,3S)-                    | OH<br>OH O OH O O   |
| T8 | 330 | $C_{18}H_{16}O_{6}$                             | Benzoic acid,2,3-dihydroxy-, 3-(1,3-dihydro-3-oxo-1-<br>isobenzofuranyl)propyl ester (9CI) | ОН О ОН О   |

| Т9  | 461 | C <sub>22</sub> H <sub>25</sub> N <sub>2</sub> O <sub>9</sub> | (4S,6S,12aS)-4-(dimethylamino)-3,6,10,11a,12,12a-hexahydroxy-6-<br>methyl1,11-dioxo-1,4,4a,5,5a,6,11,11a,12,12a-decahydrotetracene-2-<br>carboxamide |  |
|-----|-----|---|--|--|
| T10 | 415 | $C_{21}H_{22}N_2O_7$  | Sancycline;(4S,4aS,5aR,12aS)-4-(Dimethyla)   | H <sub>3</sub> C OH<br>H <sub>3</sub> C OH<br>OH<br>OH<br>OH<br>OH<br>OH |
| T11 | 183 | C <sub>8</sub> H <sub>9</sub> NO <sub>4</sub>                 | 3,4-Dimethoxynitrobenzene;1,2-Dimethoxy-4-nitrobenzene   | O O O NH2  |
| T12 | 145 | C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>                  | Methyl acetoacetate;3-Oxobutanoic acid methyl este   | но   |
| T13 | 79  | $C_6H_6$  | Benzene;1,3,5-Cyclohexatriene;Benzol   |  |
| T14 | 60  | C <sub>3</sub> H <sub>8</sub> O                               | Isopropanol;2-Propanol;Isopropyl alcohol   | ОН   |

|                          | $\mathbf{S}_{\mathrm{BET}}$            | Pore Volume           | Average pore size |
|--------------------------|--|-----------------------|-------------------|
| Catalyst                 | $(\mathbf{m}^2 \cdot \mathbf{g}^{-1})$ | $(cm^3 \cdot g^{-1})$ | ( <b>nm</b> )     |
| Fresh FBV <sub>0.4</sub> | 918.214                                | 0.5329                | 2.3214            |
| Used FBV <sub>0.4</sub>  | 26.066                                 | 0.0516                | 7.5823            |

Table S4 The specific surface area and pore parameters of  $\mathrm{FBV}_{0.4}$  before and after use

|                                     | Parameters  |
|-------------------------------------|-------------|
| Rated input power (W)               | 1350        |
| Rated output power (W)              | 800         |
| Microwave operating frequency (MHz) | 2450        |
| External dimensions (mm)            | 500×420×300 |
| Inner cavity size (mm)              | 320×300×200 |
| Fuselage weight (kg)                | 16.5        |

 $Table \ S5 \ {\rm Specifications} \ of \ {\rm Microwave \ chemical \ reactor}$ 

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