## **Supporting Information**

## Efficient photo-degradation of BPA in textile wastewater assisted by primitive carbonate: The exceptional contribution of PMS in magnetic

## Cu<sup>0</sup>-CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa COFs S-scheme heterojunction

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Text S1. Chemicals and Reagents

Copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O), iron chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), sodium acetate (NaAc), bisphenol A (BPA), methanol (MeOH), ethanol (EtOH), furfuryl alcohol (FFA), phenol (PhOH), sodium nitrate (NaNO<sub>3</sub>), dimethyl sulfoxide (DMSO), N, N-dimethylacetamide (DMA) and benzoquinone (BQ) were purchased from Aladdin Biochemical Technology Co., Ltd. (China). Pyrazine-2,5-diamine (PzDa) and 2,4,6-Triformylphloroglucinol (Tp) were proffered by Bidepharm Co. Ltd. (Shanghai). Hydrochloric acid (HCl), acetic acid, sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sulfadiazine (SDZ), dimethyl phthalate (DMP), carbamazepine (CBZ) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) were purchased from J&K (Beijing, China). All aqueous solutions were prepared using Milli-Q water (18.2MΩ cm), and none of the reagents were further purified.

Text S2. Characterization of materials and DFT calculations.

The morphologies of the catalysts were characterized by scanning electron microscope (SEM, Zeiss Sigma 300, Germany) and transmission electron microscope (TEM, FEI Tecnai G2 F20, America). The crystallinity was evaluated by X-ray diffractometer (XRD, Smart Lab SE, Rigaku, Japan). The chemical composition of the catalyst was analyzed by Fourier transform infrared spectroscopy (FT-IR, Nexus 670, America) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, America). The magnetic properties of the prepared samples were analyzed at room temperature using a vibrating sample magnetometer (VSM, LakeShore 7404, America,  $\pm$  2T). Total organic carbon (TOC) was measured on a multi N/C 3100 TOC analyzer. The concentration of metal ions was measured by atomic absorption spectrometer (AAS, ContrAA700, Germany).

Ultraviolet-visible diffuse reflectance spectrum (UV-vis DRS) was recorded on a Shimadzu UV-3600i Plus. Temperature-dependent PL spectra from 80 to 330 K were measured on an Edinburgh Instruments FLS1000 spectrophotometer with an excitation wavelength of 300 nm. The photoelectrochemical (PEC) performance of the catalysts was analyzed on a CHI-660E (Chenhua, Shanghai) electrochemical workstation. A traditional three electrode system was used to record electrochemical impedance spectroscopy (EIS) and photocurrent (I-t). In detail, the indium-tin oxide (ITO) glass with the catalyst deposited on was served as the working electrode, the Ag/AgCl electrode served as the reference electrode, and Pt wire was used as the counter electrode. 2.5 mM K4Fe(CN)<sub>6</sub> or 0.5 M Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte solution. The work function was determined by ultraviolet photoelectron spectroscopy (UPS, Thermo ESCALAB XI+, America).

This calculation was based on ORCA 5.0.4.<sup>1</sup> To consider the influence of water, the CPCM implicit solvation model was used for optimization and single point energy calculation;<sup>2</sup> In order to reflect the weak interactions in the system, Grimme's DFT-D3<sup>3</sup> modified PBE0-D3 functional was used for optimization,<sup>4</sup> and the 2 zeta Karlsruhe basis set def2-SVP was used for optimization.<sup>5</sup> On the basis of optimized structure, the td-DFT method was used to calculate the excited states,<sup>6</sup> and the RSX-QIDH<sup>7</sup> hybrid functional and def2-TZVPP<sup>5</sup> basis set were used to ensure the accuracy of subsequent results.

Text S3. Experimental Procedure and Analyses.

A 300 W Xe light source (CEL-HXF300, Ceaulight) equipped with a 420 nm cutoff filter was used as the visible light source, and an additional circulating cooling water system was equipped. In a typical experiment, 2 mg catalyst was dispersed in a quartz glass tube containing 20 mL of BPA solution (20 mg/L) and oscillated for 30 minutes under dark conditions. Subsequently, 0.6 mM PMS was added, and the reaction tube was immediately placed under the Xe light source (about 5 cm away from the lamp in the circle) for irradiation, and the samples were collected at a given time for analysis. The specific operation was to take out 1 mL of the above solution with a syringe, passed through a 0.22 µM filter, and then injected it into a chromatographic bottle containing methanol for quenching. The effects of catalyst dosage, PMS dosage, different pH and salt on the degradation performance were studied. The pH of the solution was adjusted using 0.1 M HCl or NaOH solution. In addition, the degradation of other pollutants, such as SDZ, phenol, CBZ and DMP, was also investigated. The concentration of the contaminants was determined by high performance liquid chromatography (HPLC, Shimazu, Japan) equipped with a GIST C18 column (5  $\mu$ m, 4.6  $\times$ 250 mm), and the detection conditions were detailed in Table S1. The degradation products of BPA were determined by a QTRAP 5500 MS/MS system (Applied Biosystems, Foster City, CA) equipped with the ACQUITY UPLC H-Class Plus system (Waters, Milford, USA), and the specific conditions of the gradient elution system were shown in Table S2. The degradation kinetics of BPA was fitted by the pseudo-first-order model ln  $(C_t/C_0) = -kt$ , where k is the apparent rate constant, t is the reaction time, C<sub>t</sub> is the BPA concentration at a certain reaction time (t), and C<sub>0</sub> is the initial concentration of BPA. In order to determine the active substances

produced in the system, quenching experiments were performed using EtOH, TBA, FFA, BQ, (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. In addition, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperidone (TEMP) and 2,2,6,6-tetramethylpiperidine oxide (TEMPO) were selected as spin trapping reagents to explore electron paramagnetic resonance (EPR, Bruker EMXplus-6/1, Germany).

Contaminants	Mobile phase composition (%)	Flow rate (mL·min <sup>-1</sup> )	Wavelength (nm)	Temperature (°C)	
BPA	70% methanol + 30% water	0.80	280	$35\pm1$	
PhOH	70% methanol + 30% water	0.80	270	$35\pm 1$	
CBZ	80% methanol + 20% water	0.70	283	$35\pm1$	
SDZ	60% methanol + 40% water	0.60	278	$35\pm 1$	
DMP	70% methanol + 30% water	0.80	228	$35\pm1$	

**Table S1.** The detection conditions of different pollutants by HPLC.

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 Table S2. Details of the UPLC-MS/MS gradient elution program.

Note: A is 0.1% formic acid acetonitrile. B is 0.1% formic acid solution.

Parameters	textile wastewater			
рН	12			
TOC (mg/L)	166.40			
NO <sub>3</sub> <sup>-</sup> -N (mg/L)	7.93 (0.12 mM)			
$Cl^{-}(mg/L)$	31.62 (0.89 mM)			
SO4 <sup>2-</sup> (mg/L)	48.54 (0.51 mM)			
$CO_3^{2-}$ (mg/L)	355.66 (5.93 mM)			

 Table S3. The physicochemical characteristics of textile wastewater.



Fig. S1. SEM image (a) and TEM image (b) of  $Cu^0$ - $CuFe_2O_4$ .



Fig. S2. SEM images of TpPzDa (a) and Cu<sup>0</sup>-CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa (b).



Fig. S3. BET spectra of TpPzDa, Cu<sup>0</sup>-CuFe<sub>2</sub>O<sub>4</sub> and Cu<sup>0</sup>-CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa.



Fig. S4. The kinetic curve of TpPzDa in visible light system.



**Fig. S5.** The UV-vis DRS spectra (a), the Tauc plots (b), the XPS valence band spectra (c) and the band structures (d) of TpPzDa and TpPzDa-Cu; The band structures, HOMO and LUMO diagrams (e) and electron-hole distribution diagram (f) of the TpPzDa and TpPzDa-Cu cutting models calculated by DFT (green and blue regions represent hole and electron distribution, and orange region represents overlap function of the electron-hole distribution).

The decrease in the CB to -0.64 eV and the VB to 1.36 eV was found for TpPzDa with the addition of Cu<sup>2+</sup>, correspondingly, a reduced band gap of 2.00 eV was obtained.



Fig. S6. The effect of  $Cu^{2+}$  on the UV-vis spectra of TpPzDa.



Fig. S7. The kinetic curves of  $Cu^0$ - $CuFe_2O_4@TpPzDa$  in different systems (a) and  $CuFe_2O_4@TpPzDa$  in vis/PMS system (b).



Fig. S8. The XRD patterns CuFe<sub>2</sub>O<sub>4</sub> and CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa.



Fig. S9. TEM images (a), HRTEM image (b) and the elemental mapping analysis of CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa (c).



Fig. S10. The BPA degradation of CuFe<sub>2</sub>O<sub>4</sub> and CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa in PMS system.



**Fig. S11.** The effects of different scavengers on the degradation of BPA in TpPzDa/vis/PMS system.



**Fig. S12.** The UV-vis DRS spectra (a), the Tauc plots (b), the XPS valence band spectra (c) and the band structures (d) of TpPzDa-Cu and TpPzDa-Cu-PMS.

Compared with TpPzDa-Cu (Fig. S5), the subsequent addition of PMS increased the CB and VB of TpPzDa-Cu-PMS to -0.58 eV and 1.46 eV (Fig. S12 a–d), respectively. The band gap slightly increased to 2.04 eV, correspondingly. This result implied the negative effect of Cu<sup>2+</sup> on band energy of TpPzDa may be restored by PMS to a certain extent.



**Fig. S13.** The comparison of the band structure, HOMO and LUMO diagrams of the TpPzDa-Cu-PMS and TpPzDa-Cu-PMS (a), TpPzDa and TpPzDa-PMS (c); The comparison of the electron-hole distribution diagram of TpPzDa-Cu-PMS and TpPzDa-Cu-PMS (b), TpPzDa and TpPzDa-PMS (d) (green and blue regions represent hole and electron distribution, and orange region represents overlap function).



**Fig. S14.** The effects of different concentrations of  $SO_4^{2-}$  (a),  $NO_3^{-}$  (b),  $Cl^{-}$  (c), as well as the effects of  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $Cl^{-}$ ,  $CO_3^{2-}$  at basal concentrations in actual textile wastewater (d) on BPA degradation in  $Cu^0$ - $CuFe_2O_4@$ TpPzDa/vis/PMS system.



Fig. S15. The pH changes during BPA degradation in  $Cu^0$ - $CuFe_2O_4@TpPzDa/vis/PMS$  system with 5 mM  $CO_3^{2-}$  (a) and the leaching of metal ions in  $Cu^0$ - $CuFe_2O_4@TpPzDa/vis/PMS$  system with/without 5 mM  $CO_3^{2-}$  (b).

The leaching concentration of Cu ions was detected as low as 0.2 mg/L, while no Fe ions leaching was detected (below the detection limit of AAS).



**Fig. S16.** The effects of 5 mM  $CO_3^{2-}$  on the degradation of BPA by TpPzDa (a) and CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa (b) under vis/PMS conditions.



Fig. S17. The high resolution XPS spectra of Cu 2p of the used Cu<sup>0</sup>-CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa with and without  $CO_3^{2^-}$ .



**Fig. S18.** TEM images (a, b) and TEM-mapping (c) of the  $Cu^0$ - $CuFe_2O_4@TpPzDa$  used in the presence of  $CO_3^{2^-}$ .



**Fig. S19.** The EPR spectra of TEMPO-h<sup>+</sup> (a), DMPO-O<sub>2</sub><sup>•-</sup> (b), TEMP-<sup>1</sup>O<sub>2</sub> (c), DMPO-•OH and DMPO-SO<sub>4</sub><sup>•-</sup> (d) in Cu<sup>0</sup>-CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa/vis/PMS system with and without CO<sub>3</sub><sup>2-</sup>. ([Photocatalysts] = 0.1 g/L, [PMS] = 0.6 mM, [TEMPO] = [DMPO] = [TEMP] =100  $\mu$ M).



**Fig. S20.** The degradation of other pollutants in Cu<sup>0</sup>-CuFe<sub>2</sub>O<sub>4</sub>@TpPzDa/vis/PMS/CO<sub>3</sub><sup>2-</sup> system.

The results clearly revealed the preference of this system for the electron-rich pollutants BPA (100%), PhOH (51%) and SDZ (43%), rather than electron-deficient pollutants CBZ (16%) and DMP (16%).



Fig. S21. UPLC-MS analysis conditions of the organic contaminants.



Fig. S22. XRD patterns of the fresh and the used  $Cu^0$ - $CuFe_2O_4@TpPzDa$ .

Compound	Daphnia megna	Bioconcentration	Developmental	Mutagenicity	
Compound	LC <sub>50</sub> (48hr) (mg/L)	factor	Toxicity	(value)	
BPA(A)	1.58	117.27	0.71	Negative (0.09)	
В	1.59	82.39	0.65	Negative (0.07)	
С	0.99	21.05	0.58	Negative (0.10)	
D	10.17	14.66	0.88	Positive (0.52)	
Ε	6.84	0.75	0.83	Negative (0.28)	
F	15.32	7.05	0.74	Negative (0.15)	
G	6.51	47.57	0.57	Negative (0.37)	
Н	12.58	4.43	0.43	Negative (0.11)	
Ι	55.72	1.54	0.32	Negative (0.27)	
J	7.44	7.61	0.58	Negative (0.25)	
K	13.51	13.43	0.52	Negative (0.09)	
L	63.64	7.91	0.61	Negative (0.16)	

**Table S4.** Predicted Acute toxicity, developmental toxicity, mutagenicity of BPA and its transformation products.

Catalyst	BPA concentration (mg/L)	Light source (Xe Lamp)	Catalyst dosage (g/L)	PMS dosage (mM)	Equilib rium time	Degradation performance	k (min <sup>-1</sup> )	Cycles	Refer ence
PI-g-C <sub>3</sub> N <sub>4</sub> membranes	10	300 W	/	2	10 min	100% (30 min)	0.1317	3 (98%)	8
ZIF-CN/g- C <sub>3</sub> N <sub>4</sub>	20	300 W	/	0.1–2	60 min	97% (60 min)	0.05134	5 (~92%)	9
ECN60	20	300 W	0.33	0.1	30 min	100% (20 min)	0.136	5 (94%)	10
PCNC-2	20	300 W	0.33	0.07	30 min	95% (30 min)	0.098	4 (90%)	11
MoS <sub>2</sub> /BiVO <sub>4</sub>	30	300 W	0.2	0.23	30 min	97.5% (20 min)	0.1747	4 (68%)	12
ZnFe <sub>2</sub> O <sub>4</sub> /g- C <sub>3</sub> N <sub>4</sub>	22.8	300 W	0.3	0.5	/	97.7% (60 min)	0.070	3 (52%)	13
(TiOCs)-g- C <sub>3</sub> N <sub>4</sub>	10	300 W	0.2	2	20 min	100% (40 min)	0.09724	5 (94%)	14
CTF-SD <sub>2</sub>	22.8	300 W	0.3	0.3	/	~100% (90 min)	0.043	/	15
PTEB-F <sub>15</sub>	10	300 W	0.1	0.3	/	99% (60 min)	0.0621	5 (82%)	16
COF-TD1	/	/	/	/	30 min	> 97% (120 min)	/	/	17
Cu <sub>SA</sub> /Ace- COF	10	300 W	0.1	0.5	30 min	95.5% (12 min)	/	/	18
H-CTF-Na	22.8	300 W	0.1	0.65	/	/	0.0359	/	19
Cu <sup>0</sup> -CuFe <sub>2</sub> O <sub>4</sub> @TpPzDa (magnetism)	20	300 W	0.1	0.6	30 min	~100% (30 min)	0.1672	/	This study
(magnetism)	20	300 W	0.1	0.6	30 min	~100% (20 min)	0.2189	5 (95%)	This study

**Table S5.** Performance comparison of photocatalysts for PMS activation toward BPA degradation in the previous literatures.

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