## **Supporting Information**

# Metal ion endogenous cycles of CoFe<sub>2</sub>O<sub>4-x</sub> induced boosted photocatalytic/PMS degradation toward polycyclic aromatic

### hydrocarbons

Xiaojuan Bai<sup>a,b\*</sup>, Wei Song<sup>a</sup>, Xuan Ling<sup>a</sup>, Linlong Guo<sup>a</sup>, Derek Hao<sup>c</sup>, Xiao Zhang<sup>d\*</sup> <sup>a</sup>Centre for Urban Environmental Remediation, Beijing University of Civil Engineering and Architecture, Beijing, 100044, China.

<sup>b</sup>Beijing Energy Conservation & Sustainable Urban and Rural Development Provincial and Ministry Co-construction Collaboration Innovation Center, Beijing University of Civil Engineering and Architecture, Beijing, 100044, China. <sup>c</sup>School of Science, RMIT University, Melbourne, VIC 3000, Australia <sup>d</sup>China Univ Petr, State Key Lab Heavy Oil Proc, Beijing 102249, Peoples R China

Corresponding author: Xiaojuan Bai, Xiao Zhang e-mail: baixiaojuan@bucea.edu.cn, heixia.1986@163.com zhangxiao@cup.edu.cn

#### 2.2. Preparation of Ferrite Catalysts

 $ZnFe_2O_4$ : Dissolve 0.01 mol zinc nitrate tetrahydrate and 0.02 mol iron nitrate in distilled water. The following steps are the same as for cobalt ferrite.

 $CuFe_2O_4$ : Dissolve 0.01 mol of copper nitrate trihydrate and 0.02 mol of iron nitrate in distilled water to form a salt solution. The subsequent operation is the same as for the cobalt ferrite.



Fig. S1. Flow chart of synthetic photocatalyst materials.

#### 2.3. Preparation of Modified Ferrite Catalysts

H-MFe<sub>2</sub>O<sub>4-x</sub> (M=Cu, Zn): To eliminate moisture and surface adsorbed gases from the sample, the temperature is increased to 100 °C at a rate of 10 °C/min and held at that temperature for 30 minutes. The temperature was then increased at a rate of 10 °C/min for 90 minutes from 100 °C to the optimum modification temperature (Table S1). Fig. S2 confirm that the material starts to activate at the optimum temperature for exploration, with the potential for oxygen vacancies to arise during the activation phase due to the combination of high temperature and reducing atmosphere.

 $N-MFe_2O_{4-x}$  (M=Cu, Zn): To demonstrate the importance of the reducing atmosphere. Throughout the trials, a dry  $N_2$  gas stream was used. The rest of the experiment followed the same procedures as the H<sub>2</sub>-TPR modification.

V-MFe<sub>2</sub>O<sub>4-x</sub> (M=Cu, Zn): To investigate the effect of N<sub>2</sub>, a vacuum atmosphere was used. CoFe<sub>2</sub>O<sub>4</sub> was placed in a tube furnace. The vacuum environment was pumped for 30 min before the start of the ramp-up phase. the vacuum was ramped up to 400 °C,



450 °C, and 500 °C during the ramp-up phase and maintained for 90 min. the rest of

Fig. S2. (a) CuFe<sub>2</sub>O<sub>4</sub> TPR spectrum, (b) TPR spectrum of CuFe<sub>2</sub>O<sub>4</sub> treated at 400 °C, (c) ZnFe<sub>2</sub>O<sub>4</sub>

#### TPR spectrum.

Table SI	Cobalt	Ierrite	modific	ation 1	temperature	

Materials		Actual handling temperature (°C)			
	Optimum temperature (°C)	H <sub>2</sub> -TPR	N <sub>2</sub> -TPD	Vacuum	
				calcination	
CuFe <sub>2</sub> O <sub>4</sub>	380	400	400/450	400/450/500	
CoFe <sub>2</sub> O <sub>4</sub>	520	520	400/450	400/450/520	
ZnFe <sub>2</sub> O <sub>4</sub>	485		400/450	400/450/500	

#### 2.4. Characterization

Scanning electron microscope (SEM, SU-8000) images were taken using a field-emission SEM operated at an accelerating voltage of 100 kV, and the observation scale was 1  $\mu$ m ~ 500 nm. Transmission electron microscope (TEM, HT7700) from Hitachi was used, and the acceleration voltage was 100 kV. The binding energies of Co, Fe, and O were measured at room temperature using an X-ray photoelectron spectroscope (XPS, ESCALA Xi+, Thermo Fisher) to verify the defective structures and valence state of the photocatalyst. The peak positions of each element were corrected by using C 1s (284.6 eV). Fourier Transform Infrared Spectroscopy (FTIR, Bruker VERTEX 70) was recorded ranging from 500 to 4000 cm<sup>-1</sup>. A diffuse reflectance UV-vis spectrophotometer (DRS, Lambda 650S) was used

to obtain the absorption spectra of samples. Photoluminescence (PL, FP-6500) measurements were performed, and a 420 W Xe lamp was used as the excitation source. Ultra Performance Liquid Chromatography (UPLC, LC-20A) for polycyclic aromatic hydrocarbon content detection.

Photocurrent, linear sweep voltammetry (LSV), Cyclic Voltammetry (CV), Electrochemical impedance spectroscopy (EIS), and Mott-Schottky testing were investigated by the electrochemical station (CHI600E, Shanghai Chenhua Instrument Co., Ltd.) with a three-electrode system. The electrolyte used in this study is 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> salt solution. A three-electrode system was used, with a platinum foil electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a working electrode for the prepared samples. The working electrode is prepared as follows: Catalyst samples were placed in ethanol, dispersed by ultrasonic treatment, and evenly coated on the resistance surface of ITO glass plate.

#### 3. Results and discussion

#### **3.1. Optimal Temperature Exploration**



**Fig. S3.** Linear fit plot of degradation efficiency. (a)  $N_2$ -TPD modified materials at different temperatures, (b) Bulk, vacuum calcination, and  $H_2$ -TPR modified material.

#### 3.2. Surface morphology analyses



**Fig. S4.** (a) XPS spectrum of  $CoFe_2O_4$  and Modified materials, Fe 2p chart of (b)  $CoFe_2O_4$ , (c) N-CoFe\_2O\_{4-x}, (d) V-CoFe\_2O\_{4-x}, (e) H-CoFe\_2O\_{4-x}, Co 2p chart of (f)  $CoFe_2O_4$ , (g) N-CoFe\_2O\_{4-x}, (h) V-CoFe\_2O\_{4-x}, (i) H-CoFe\_2O\_{4-x}.

#### 3.3. Optical and electrochemical characterization



Fig. S5. Band gap of CoFe<sub>2</sub>O<sub>4</sub>, N-CoFe<sub>2</sub>O<sub>4-x</sub>, V-CoFe<sub>2</sub>O<sub>4-x</sub> and H-CoFe<sub>2</sub>O<sub>4-x</sub>.



Fig. S6. Linear fitting plot of degradation efficiency in aqueous phase (a) Degradation of naphthalene

(1ppm), (b) activated PMS to degrade naphthalene (1ppm).



Fig. S7.  $k_{app}$  values for cyclic degradation of 1ppm naphthalene by H-CoFe<sub>2</sub>O<sub>4-x</sub> in aqueous phase.



Fig. S8. Comparison of materials adsorbed by magnets before and after.