Self-assembled monolithic β-FeOOH/copper foam catalysts for enhanced catalytic reduction of nitrogen-containing contaminants in continuous-flow systems

Shan Tai,[a] Yan Wu,[a] Renliang Wang,[b,*] Kun Liu,[b,*] Guofeng Zhao[a,*]

[a] Key Laboratory of Functional Molecular Solids Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China

[b] Institute of Optical Functional Materials for Biomedical Imaging, School of Chemistry and Pharmaceutical Engineering, Shandong First Medical University & Shandong Academy of Medical Sciences, Taian 271016, China

* Corresponding authors: renliangw@163.com (R. Wang), liukun2436@126.com (K. Liu), gfzhao@ahnu.edu.cn (Guofeng Zhao)

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1 Materials and reagents

Ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), Rhodamine B ($C_{28}H_{31}ClN_2O_3$), Methylene blue ($C_{16}H_{18}ClN_3S$), Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$), Methyl Orange ($C_{14}H_{14}N_3NaO_3S$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Urea (CH_4N_2O), Ammonium Fluoride (NH_4F), 4-nitrophenol (4-NP), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP) and sodium borohydride ($NaBH_4$) were purchased from Shanghai McLean Biochemical Technology Co., Ltd. and used directly without further purification. Copper foam (CF) was purchased from Kunshan Zuanyan Metal Technology Co., Ltd.

2 Characterization

Nitrogen adsorption/desorption isotherms were obtained at 77 K on an accelerated surface area and porosimetry system (ASAP2460-4MP, USA) to measure the surface area of the material using the Brunauer-Emmett-Teller (BET) method. Before analysis, the samples were outgassed under dynamic vacuum at 80°C for 5 h. Raman spectra were collected on an in Via instrument with a λ = 532 nm excitation laser. All the reaction solutions were diluted with deionized water and their UV-visible absorption spectra were measured by UV-1000. X-ray diffraction (XRD) was performed using a SmartLab 9KW Advance diffractometer. XRD patterns were recorded with Cu Kα radiation (λ = 0.154 nm, 40 kV, 30 mA) in the 10-80° 2θ range with a 0.02° of 2θ step. Phase identification was made by comparison with the ICDD database. Scanning electronic microscopy (SEM) images were obtained using Regulus 8100. Micrographs from Transmission Electron Microscopy (TEM) were conducted on a HT-7700. X-ray photoelectron spectroscopy (XPS) was performed with an Krayos AXIS Ultra DLD (UK), using Al Kα radiation (1486.6 eV) at a pressure of 9.8×10^{-10} Torr. The peak positions were internally referenced to the C 1s peak at 284.8 eV. The Casa XPS software package was used for data analysis.

3 Preparation of the β-FeOOH@CF catalyst

β-FeOOH@CF foam catalysts were prepared by growing β-FeOOH on monolithic copper foam substrates via hydrothermal synthesis. First, commercial foam copper CF was cut into circular discs (60 PPI, diameter 3.5 cm, thickness 0.5 cm) and immersed in a 1 M hydrochloric acid solution for 10 minutes of ultrasonic treatment to remove the surface oxide layer. Subsequently, the samples were repeatedly rinsed with deionized water until the filtrate became neutral (pH = 7). They were then placed in acetone and sonicated for 10 minutes to remove organic contaminants and grease. Finally, after thorough rinsing with deionized water, excess surface moisture was blotted with filter paper, and the samples were placed in an 80 °C vacuum drying oven until completely dry.

Place the pretreated foam copper at an angle inside a 200 mL high-pressure reactor lined with polytetrafluoroethylene. Separately, dissolve Fe $(NO_3)_3 \cdot 9H_2O$ (1.2 g), urea, NH_4F and in a molar ratio of 3:25:8 using 80 mL of deionized water. Transfer this precursor solution into the reactor, ensuring the foam copper is fully submerged. Heat-treat the reactor at 100°C for 8-14 hours. After reaction completion and natural cooling to room temperature, carefully remove the copper foam coated with the product. Repeatedly rinse with deionized water to remove loosely adsorbed ions and impurities, then dry in an 80°C vacuum oven for 12 hours to obtain the final β-FeOOH@CF product.

4 Catalytic reduction of nitrogen-containing contaminant

In experiments on the catalytic reduction of nitrogen-containing contaminants, we selected 4-nitrophenol (4-NP), 3-nitrophenol (3-NP), 2-nitrophenol (2-NP), methyl orange (MO), Congo red (CR), Rhodamine B (RhB) and methylene blue (MB) as representative nitrogen-containing organic compound models to evaluate the catalytic performance of the continuous-flow system. Flow rate was controlled by adjusting external pressure to optimize conversion rates and

reaction times for nitrogen-containing contaminants. All substrates (4-NP, 3-NP, 2-NP, MO, CR, RhB and MB) were maintained at a concentration of 5.0 $mmol \cdot L^{-1}$ in aqueous solution, with a total volume of 20 mL. For the reduction of nitroaromatics and azo dyes, the $NaBH_4$ dosage was uniformly set at 200 equivalents. The reduction of nitroaromatics and azo dyes to corresponding aniline products was monitored using UV-visible spectrophotometry. Additionally, the fading of the reaction solution served as an intuitive indicator of reaction completion. Typically, the conversion rate was calculated based on the intensity change of the characteristic absorption peak of the 4-nitrophenol anion, using the formula $(C_0 - C_t)/C_0$, where C_0 and C_t represent the concentrations of 4-NP measured by UV-visible spectroscopy at the initial time and at reaction time t, respectively.

5 Catalyst characterization

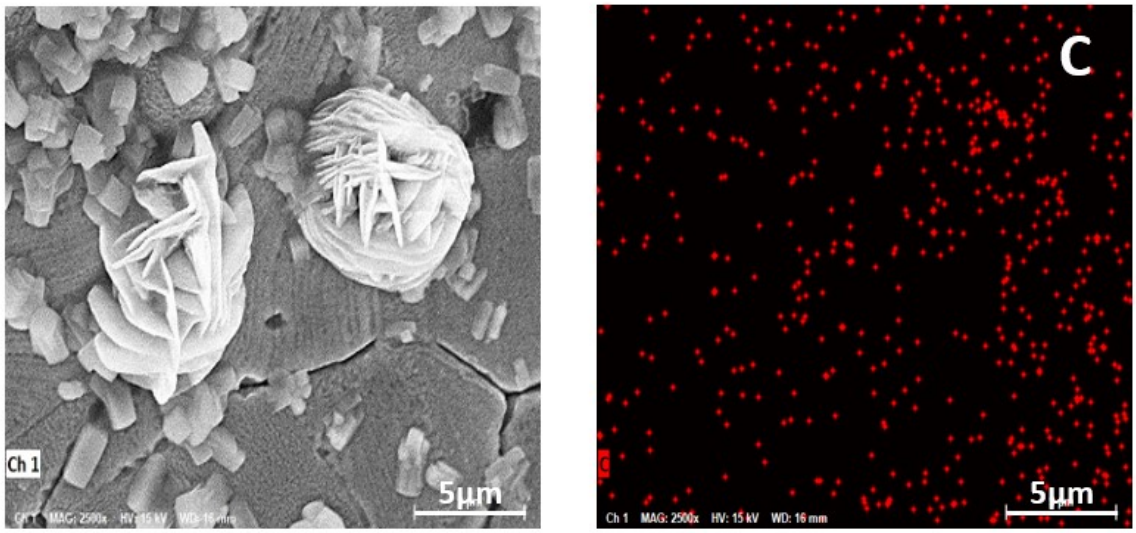

Fig. S1 Element mapping diagram for β-FeOOH@CF (11h).

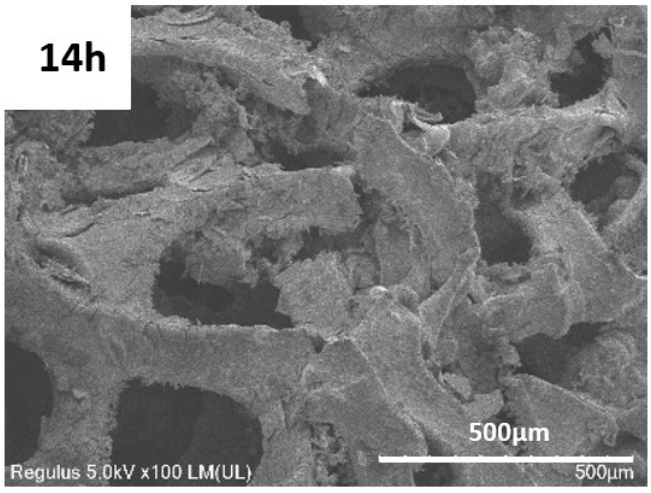

Fig. S2 SEM image of β-FeOOH@CF (14h).

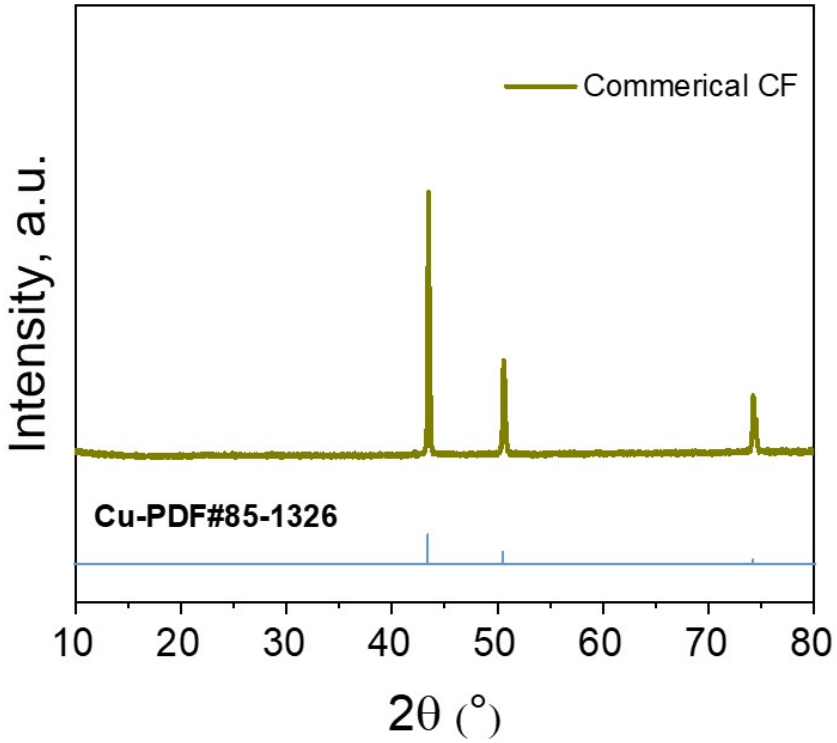

Fig. S3 XRD patterns of the commercial CF catalyst.

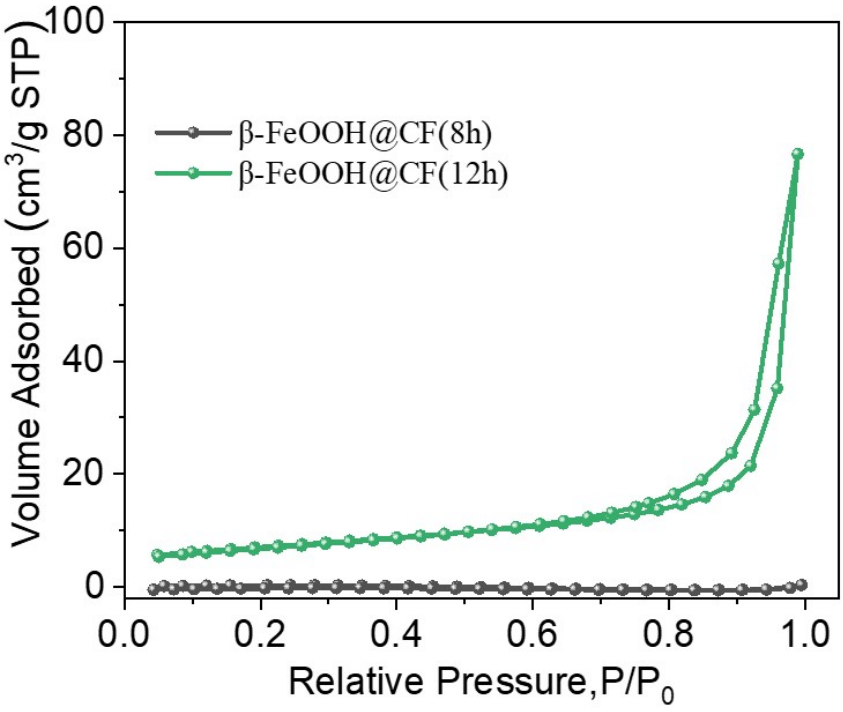

Fig. S4 N_2-physisorption isotherms obtained for β-FeOOH@CF (8h) and β-FeOOH@CF (12h).

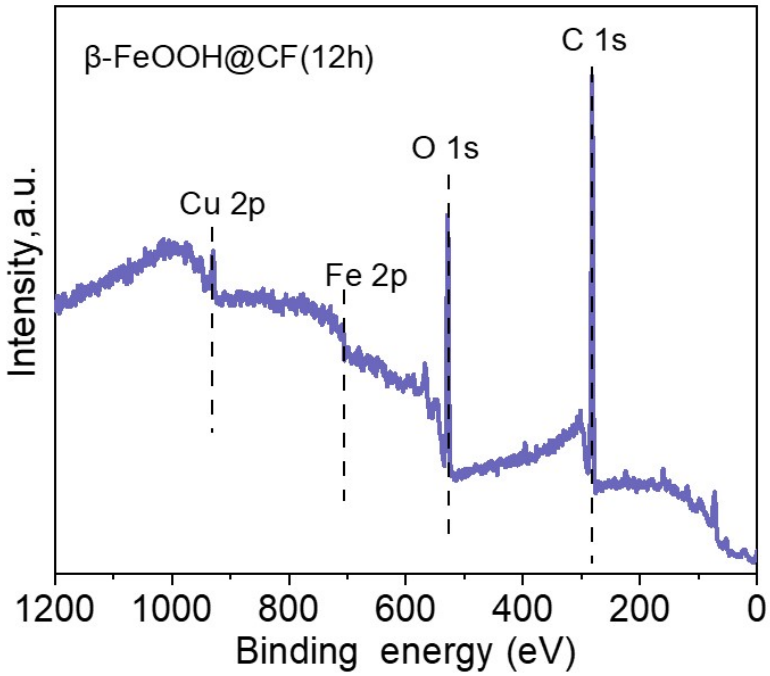

Fig. S5 XPS survey spectrum for β-FeOOH@CF (12h).

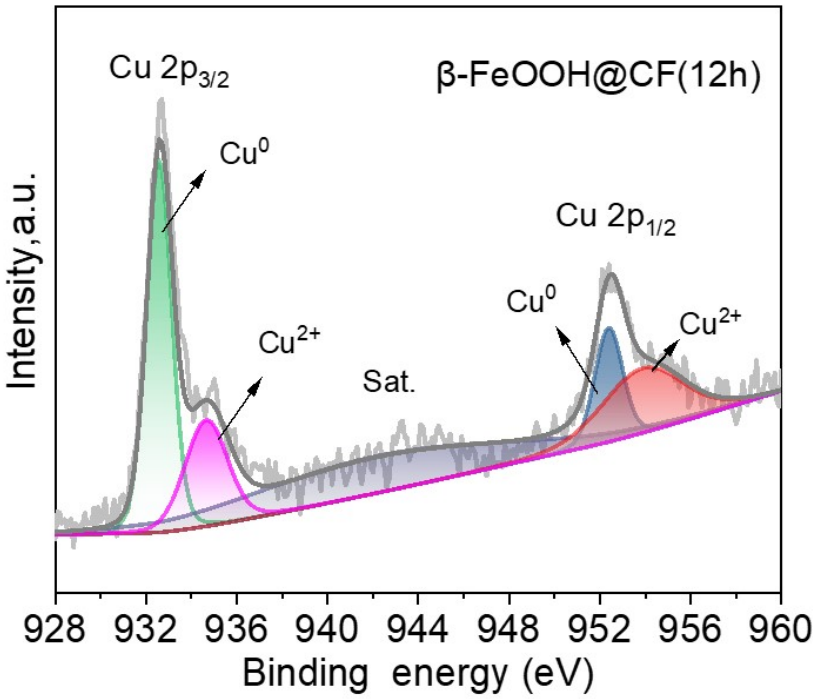

Fig. S6 Cu 2p XPS spectra for β-FeOOH@CF (12h).

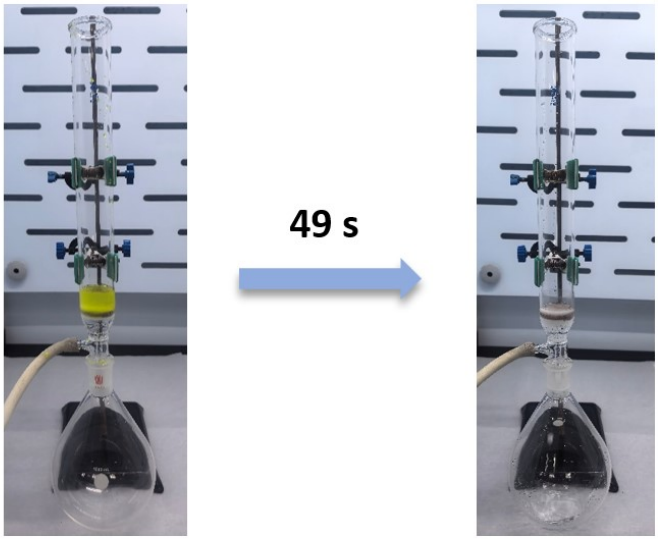

Fig. S7 Schematic diagram of the continuous-flow reactor system for the reduction of 4-Nitrophenol.

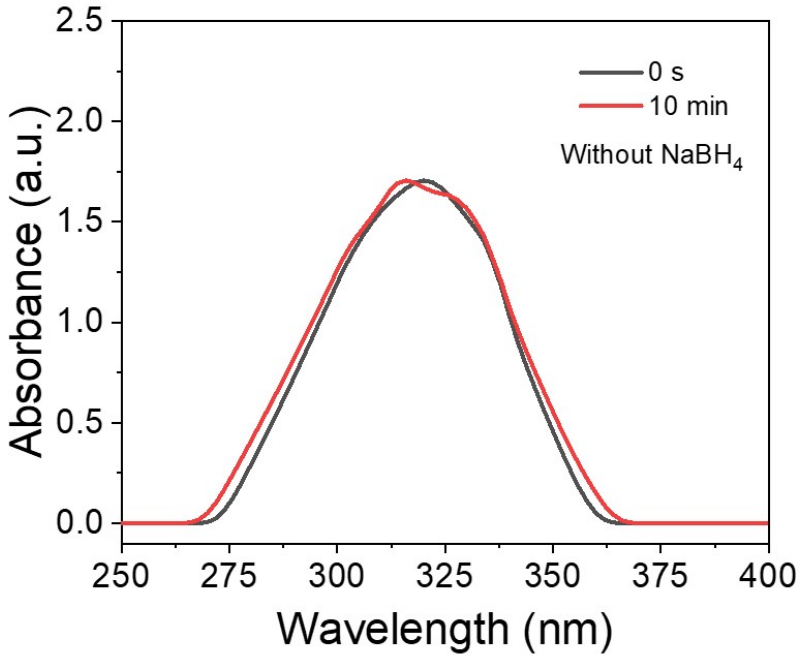

Fig. S8 UV-Vis spectra for the reduction reaction of 4-NP without $NaBH_4$.

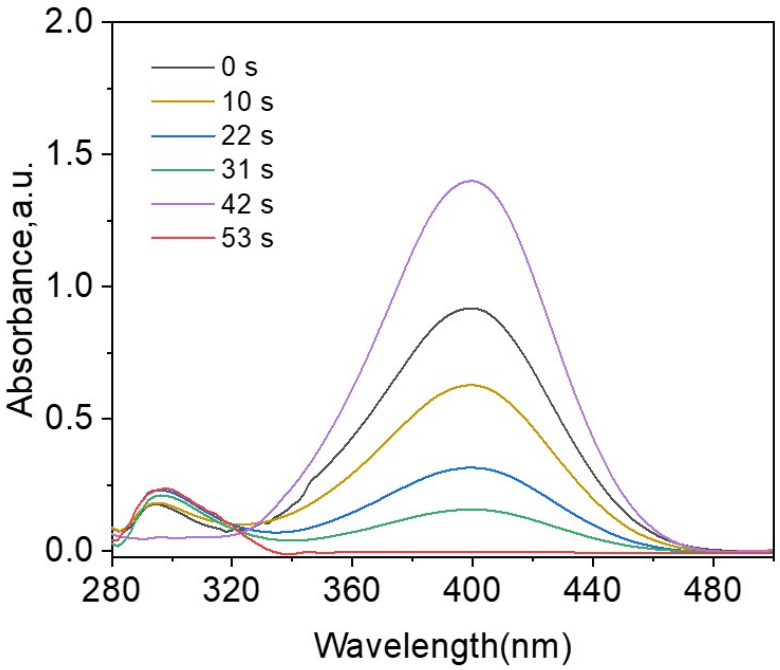

Fig. S9 UV-Vis spectra for the reduction reaction of 4-NP in the batch reaction.

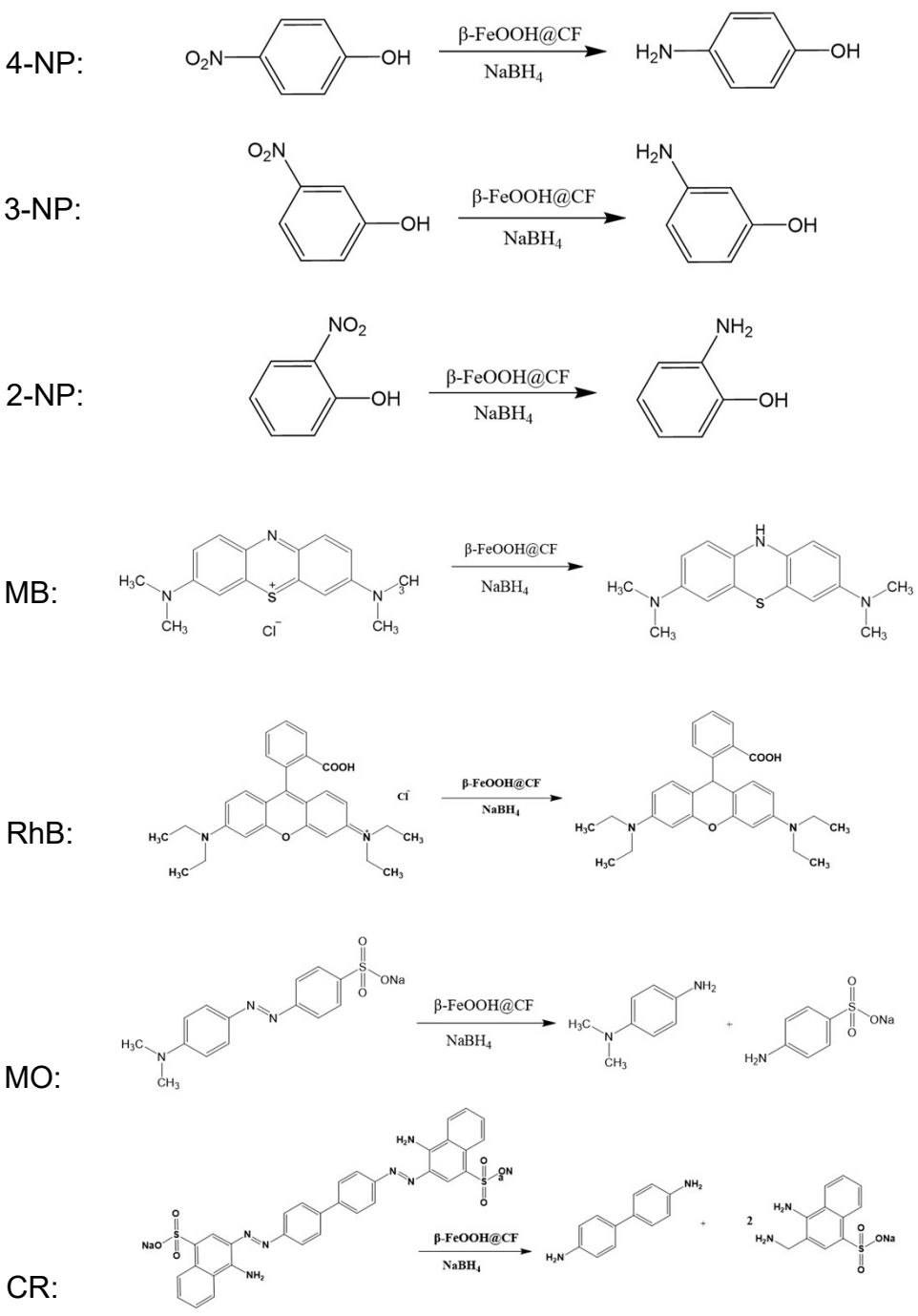

Fig. S10 Catalytic reduction reaction equations of 4-NP, 3-NP, 2-NP, MB, RhB, MO and CR by $NaBH_4$ in the presence of β-FeOOH@CF (12h) catalyst.

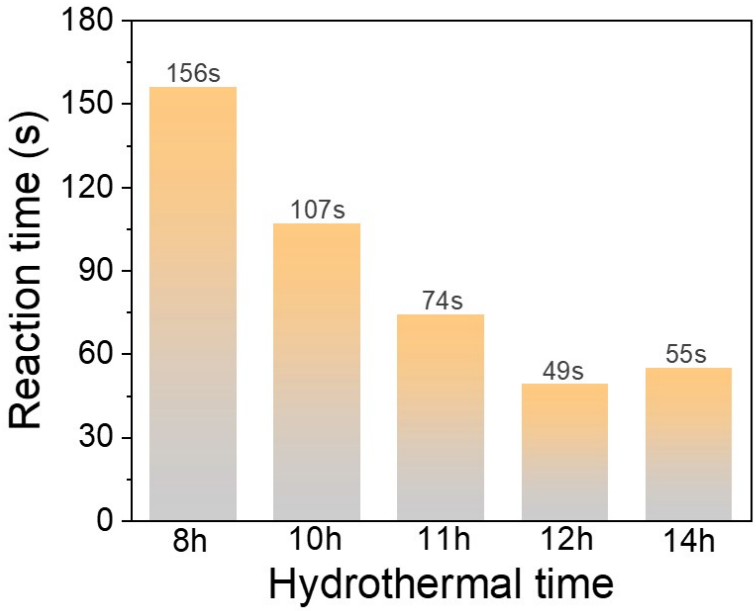

Fig. S11 Performance Comparison of β-FeOOH@CF catays ts at different hydrothermal reaction time.

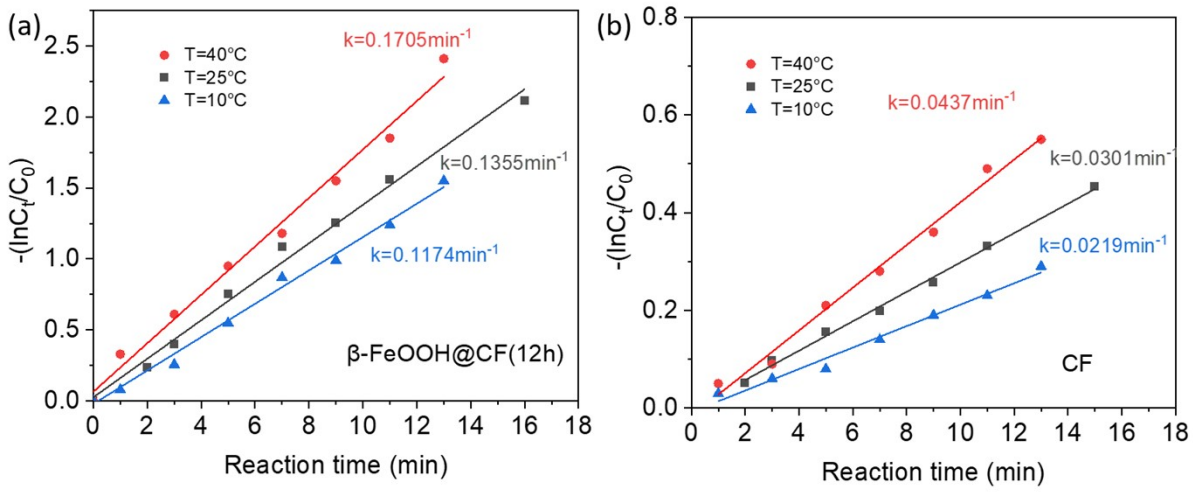

Fig. S12 Plot of $-\ln(C_t/C_0)$ versus reaction time for the reduction of 4-NP by β-FeOOH@CF (12h) and CF at different temperatures.

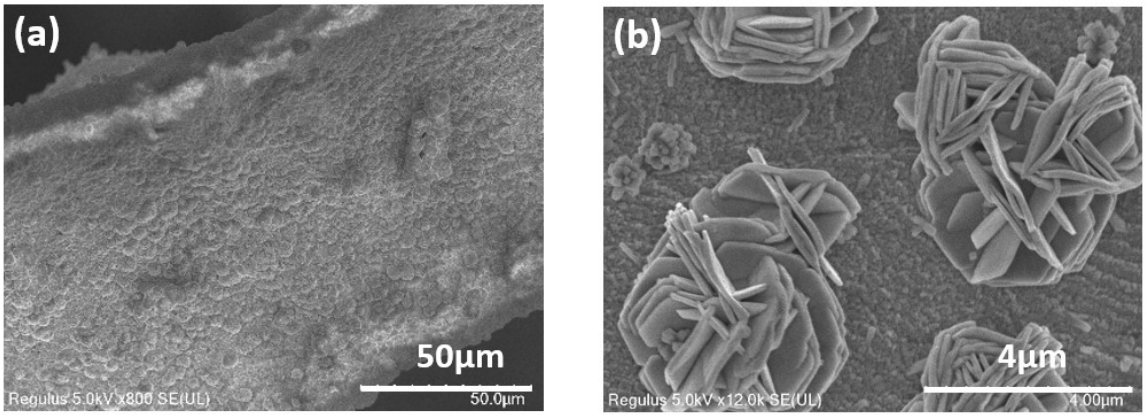

Fig. S13 SEM images of spent catalyst.

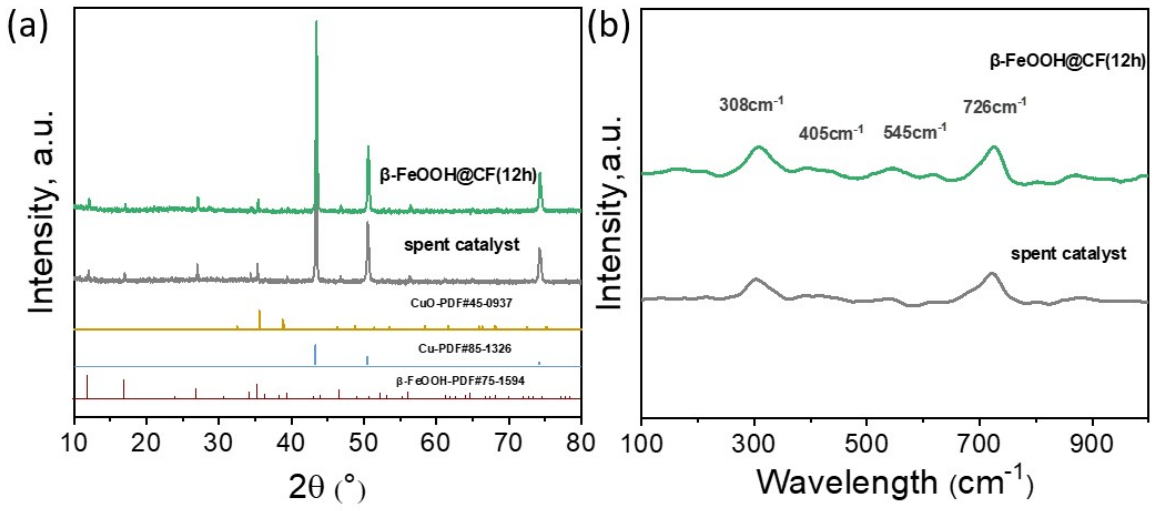

Fig. S14 (a) XRD patterns and (b) Raman spectra of the β-FeOOH@CF (12h) and spent catalyst.

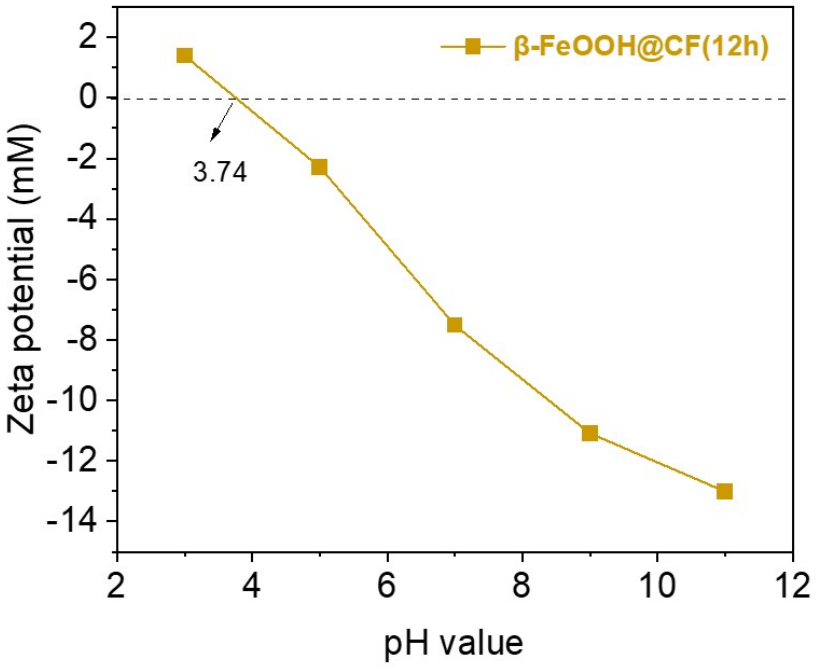

Fig. S15 Zeta potentials of β-FeOOH@CF (12h) at different pH conditions.

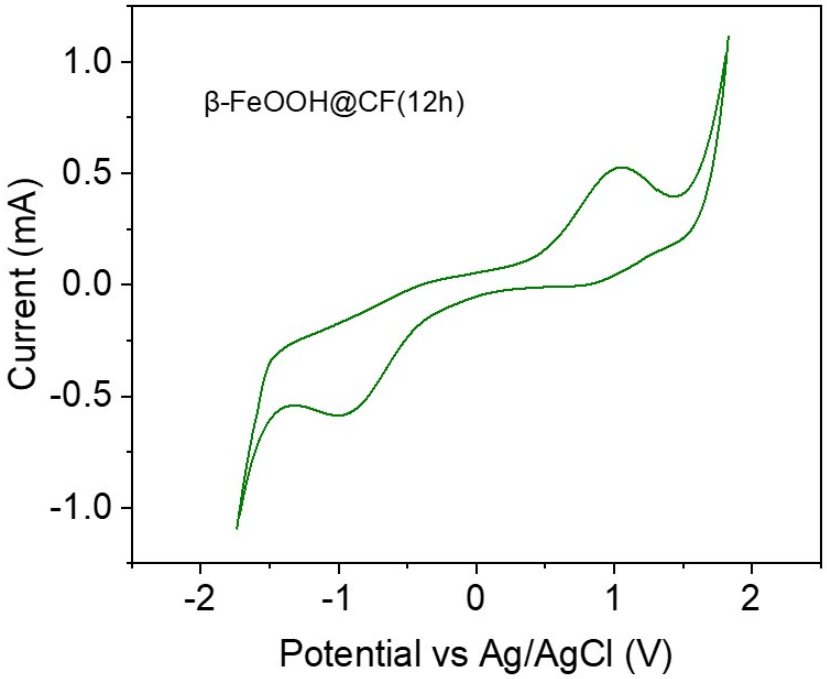

Fig. S16 Cyclic voltammetry of β-FeOOH@CF (12h).

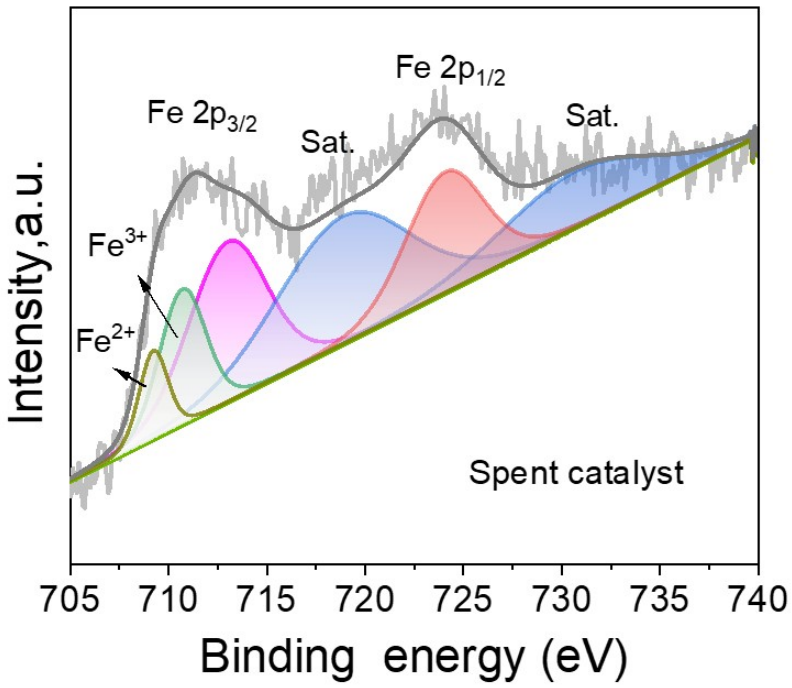

Fig. S17 Fe 2p XPS spectra for spent catalyst.