Supporting Information

Copper-decorated iron oxide nanoparticles highly dispersed on coal-based activated carbons: a recoverable catalyst for the reduction of 4-nitrophenol, Congo Red, and Rhodamine B

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Materials and methods

Materials. Coal-based activated carbons (AC) were prepared according to our previously reported methods.[1] Copper (II) acetate monohydrate [$Cu(CH_3COO)_2 \cdot H_2O$, 99%], Iron (III) nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$, 98.5%], trisodium citrate dihydrate [$C_6H_5Na_3O_7 \cdot 2H_2O$, 99%], hexamethylenetetramine [$C_6H_{12}N_4$, 99%] were purchased from Sichuan Kelong Reagent Company. All reagents were of analytical grade and used without further purification.

Characterization. X-ray diffraction (XRD; Bruker D8) was conducted using filtered Cu Ka radiation. Microstructure analysis was observed by field-emission scanning electron microscopy (FESEM; Hitachi S-4800), transmission electron microscope (TEM), and high-resolution transmission electron microscope (HRTEM FEI Talos F200x). Thermogravimetric analysis (TGA; Netzsch STA 449C) was recorded from room temperature to 700 ^oC at a heating rate of 10 $^oC\ min^{-1}$ in air atmosphere. UV-Vision absorption spectra were monitored by using a Hitachi UV-3900 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was collected using a Thermo ESCALAB 250 instrument with a monochromated Al X-ray resource at

1486.6 eV. Nitrogen adsorption/desorption isotherms were obtained using an ASAP 2020 Xtended Pressure Sorption Analyzer at 77 K. The structure of carbon material in the prepared samples was characterized by the Raman spectrophotometer (Horiba HR Evolution) at 532 nm.

Catalytic reduction of 4-nitrophenol (4-NP). Aqueous 4-NP solution (3.0 mL, 0.1 mM) was mixed with $NaBH_4$ (250 ul, 50 mM), resulting in the formation of a deep yellow solution. Then, 1 mg of the sample was added to the solution. The progress of the reaction was determined by UV-Vis absorption spectroscopy over a scanning range from 250 to 500 nm every 1 min. During the reaction, it could be observed that the color of the solution become colorless from light yellow.

As $NaBH_4$ was in large excess compared to 4-NP, it was reasonable to assume that its concentration remained constant throughout the reaction. The reaction could be considered as a pseudo-first-order kinetics for the 4-NP. The equation is $-dC_t/dt = K_{app}C$, where C_t refers to the concentration of 4-NP at time t, C refers to the initial concentration, and K_{app} is the apparent rate constant (min^{-1}).

As a heterogeneous catalyst, one important factor is the reusability. To evaluate this, the catalyst was carried out for five consecutive reaction cycles. In these experiments, the samples for the catalytic reaction were separated magnetically, washed with distilled water, and dried in a vacuum oven at 60 ℃ for 12 h.

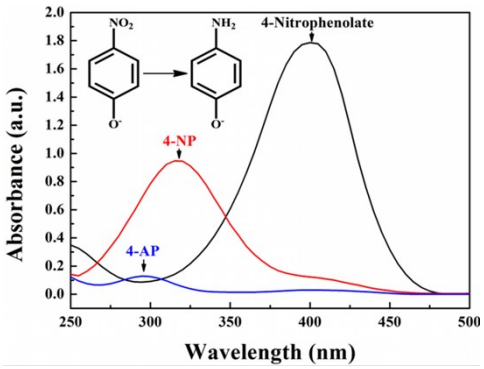

Figure S1 UV-vis spectra of 4-NP, 4-nitrophenolate, 4-AP.

Figure S1 showed the successive reduction of 4-NP to 4-AP in aqueous medium using $NaBH_4$. The maximum absorption peak of 4-NP appeared at 317 nm in an acidic or neutral environment. After adding $NaBH_4$, the absorption peak was shifted to

400 nm due to the formation of the corresponding nitrophenolate anion. Moreover, the color of the solution changed from light yellow to bright yellow.

Catalytic reduction of congo red (CR). CFO/AC nanocomposite (1.0 mg) and 250 ul newly prepared $NaBH_4$ (50 mM) were added into the CR solution (3.63×10^{-5} M, 2 ml) at room temperature. The UV-visible spectra showed no CR absorbance peak at 493 nm after 2 min. The reaction rate was monitored by recording the UV-vis spectra at certain intervals.

Catalytic reduction of rhodamine B (RhB). CFO/AC nanocomposite (1.0 mg) and 250 ul newly prepared $NaBH_4$ (50 mM) were added into the RhB solution (4.03×10^{-5} M, 2 ml) at room temperature. The UV-visible spectra showed no CR absorbance peak at 559 nm after 2 min. The reaction rate was monitored by recording the UV-vis spectra at certain intervals.

Table. S1 Conditions for preparing samples.

CFO: AC / T (°C)	t (h)		
	2.5	3.5	4.5
300		1: 1(CFO/AC-1)	
		1: 0.75(CFO/AC-6)	
400	1: 1(CFO/AC-4)	1: 1(CFO/AC-2)	1: 1(CFO/AC-5)
		1: 1.5(CFO/AC-7)	
500		1: 1(CFO/AC-3)	

Note: the calcination temperature (T), calcination time (t), and mass ratio of copper-decorated iron oxide: AC.

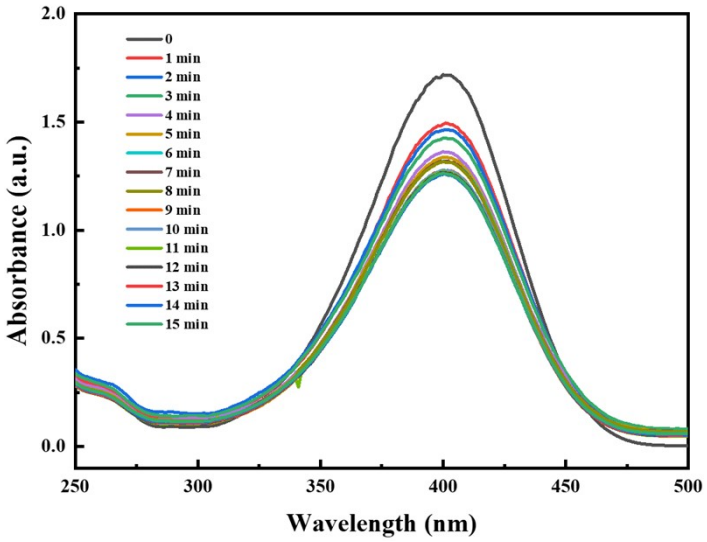

Figure S2 UV-Vis spectra of the catalytic performances of AC.

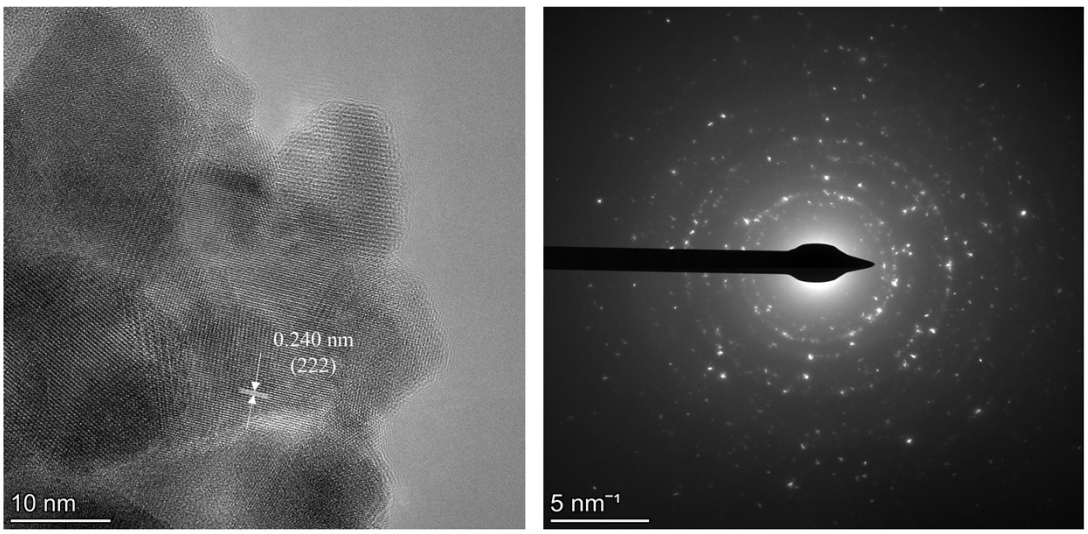

Figure S3 HRTEM image and SAED pattern of CFO/AC-2.

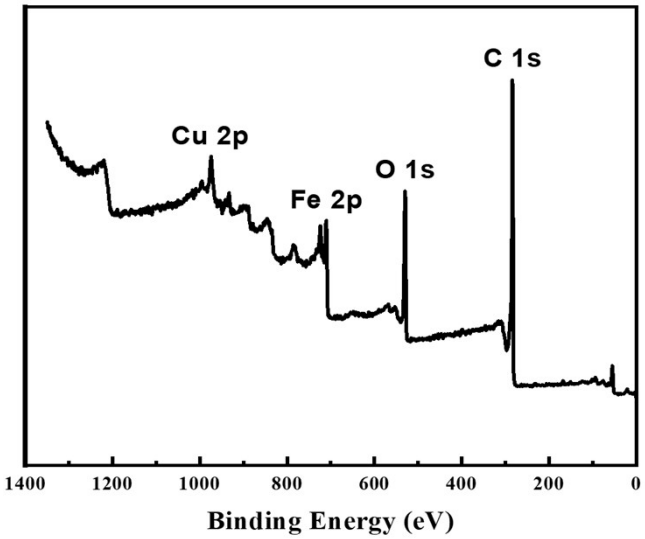

Figure S4 XPS full spectrum of CFO/AC-2.

Table S2 DFT surface area, total volume of samples.

Parameter	CFO/AC-6	CFO/AC-2	CFO/AC-7	AC
$S_{DFT}/m^2 \cdot g^{-1}$	936.39	1002.19	1057.09	1346.73
$V_t/cm^3 \cdot g^{-1}$	0.48	0.52	0.54	0.63

Table S3 The composition of buffer solutions with different pH values.

pH value	composition of buffer solution
pH=3, 4, 5	citric acid – sodium citrate (0.1 mol/L)
pH=6.5, 7	KH_2PO_4 (0.05mol/L)-NaOH
pH=7.8	KH_2PO_4 (0.032 mol/L)-K_2HPO_4 (0.003 mol/L)
pH=9	$NaCO_3$-$NaHCO_3$ (0.1 mol/L)
pH=10, 11	$NaHCO_3$ (0.05mol/L)-NaOH

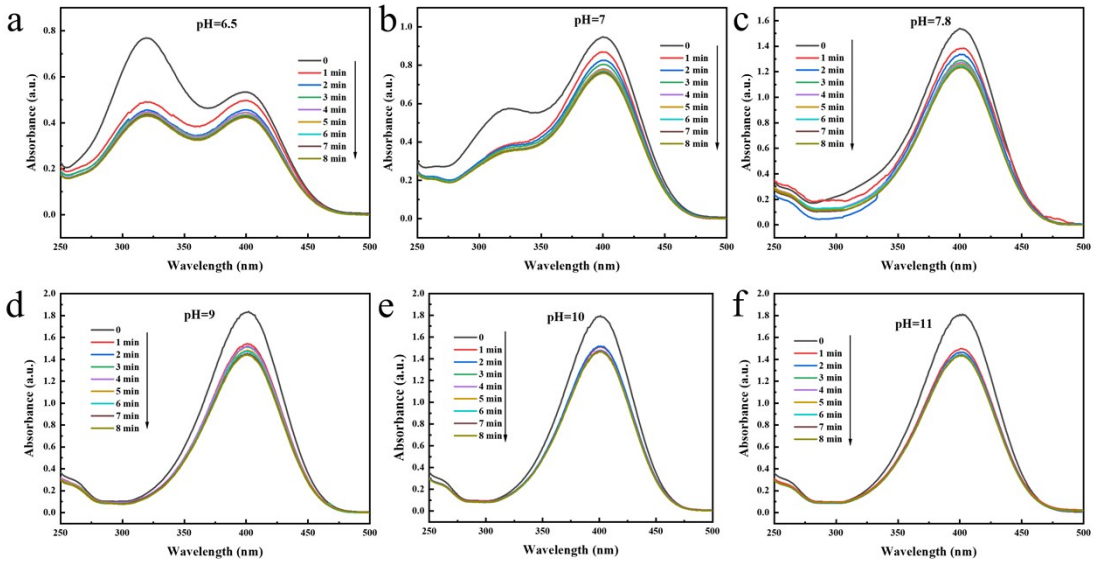

Figure S5 UV-Vis spectra of 4-NP degradation at different pH in the presence of CFO/AC-2 (1:1).

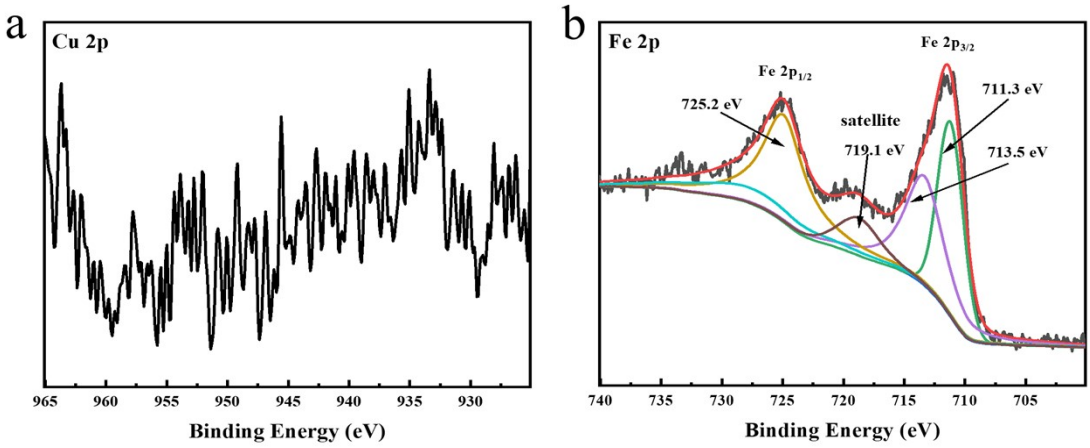

Figure S6 high-resolution XPS spectra of the recycled catalyst's Cu 2p (b) and Fe 2p (c).

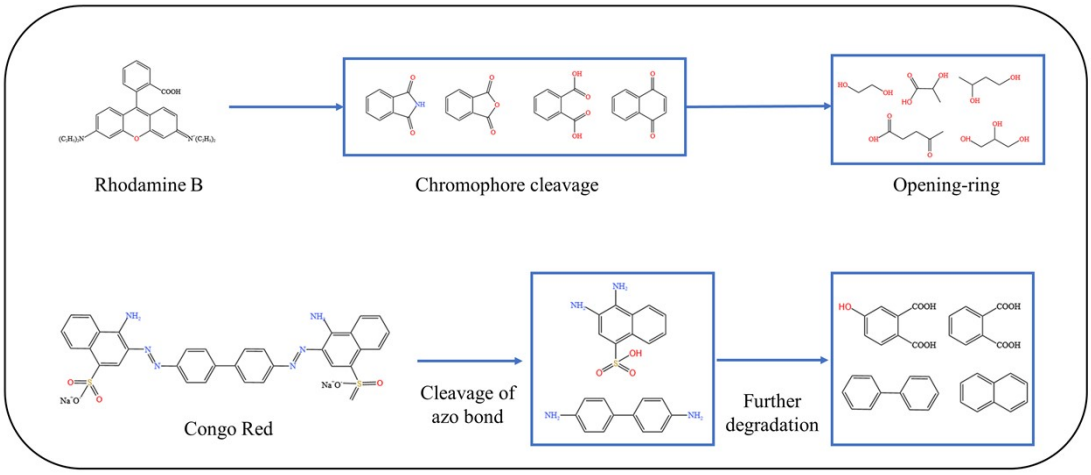

Figure S7 Probable mechanism for degradation of Rhodamine B and Congo Red.

Table S4 Comparison of copper-decorated iron oxide/AC nano-catalysts for the reduction of CR and RhB.

Dyes	Catalyst	Time	Ref.
CR	Copper nanocrystals	500s	2
	Co_3O_4 nanoparticles	5min	3
	Cu nanoparticles /GO/MnO_2	22min	4
	Cu/eggshell	30min	5
	Fe_3O_4/eggshell	20min	
	CFO/AC-2	**2min**	**This work**
RhB	SiNWAs-Cu	14min	6
	Au-PANI nanocomposite	15min	7
	$CoFe_2O_4$–P4VP@Ag nanoparticles	20min	8
	PVA-PDA@Au beads	5min	9
	CFO/AC-2	**2min**	**This works**

References

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