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Electronic Supplementary Information

Covalently linked Single Cobalt Atoms on Polypropylene Membrane for Singlet Oxygen Dominated Advanced Oxidation Processes

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1. Experimental section

1.1. Chemicals

Polypropylene (PP) membrane was purchased from Haining Laisheng equipment Co., Ltd. Cobalt nitrate hexahydrate, ($Co(NO_3)_2 \cdot 6H_2O$), ammonia solution ($NH_3 \cdot H_2O$, 25−28%), sodium hydroxide (NaOH), ethanol, sodium pentacyanoaminoferrate, 4-vinyl pyridine, peroxymonosulfate ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5KSO_4$, PMS), methyl alcohol (MeOH), tert-butyl alcohol (TBA), L-histidine, potassium iodide (KI), disodium dihydrogen phosphate (NaH_2PO_4), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), rhodamine B (RhB), methylene blue (MB), congo red (CR), methyl orange (MO), acid orange (AO), benzoic acid (BA), tetracycline (TC), ofloxacin (OFX) metronidazole (MN), and sulfathiazole (STZ) were obtained from Sinopharm Chemical Reagent Co., Ltd. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperidone (TEMP) were purchased from Sigma-Aldrich. All chemical reagents were used without further purification.

1.2. Preparation of P-P4VP

PP membranes were immersed in a flask containing a methanol solution (100 mL) with a 20 vol% monomer (4-VP) concentration and then added into the irradiation tube. Before irradiation, dissolved oxygen in the solution was eliminated by bubbling N_2 for 15 min. The irradiation tube was sealed and irradiated with a ^{60}Co γ-ray source for 17 h at room temperature. After irradiation, the grafted PP membranes were extracted with boiling acetone in a Soxhlet apparatus for 24 h to eliminate organic impurities. The degree of grafting (D_g) was determined according to equation (1):

$$D_g \, (\%) = (W_1 - W_0) / W_0 \times 100 \, \% \qquad (1)$$

where W_0, W_1, are the weights of PP, and P-P4VP, respectively. The D_g of PP-P4VP the membranes used in this study was 27%.

1.3. Preparation of P-PFe

Sodium pentacyanoaminoferrate was prepared from $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ (sodium nitroferricyanide) according to the procedure reported in the literature with slight modifications.[1] Briefly, a total of 10 g of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ was dissolved in 100 mL of water in ice-bath, subsequently, 4 g NaOH was added quickly to the solution under constant stirring. The solution temperature remained below 0 °C. A 25% (v/v) $NH_3 \bullet H_2O$ solution was added drop until a brownish solution was observed. Afterwards, the mixture was aged overnight, and then the solid product of was sodium pentacyanoaminoferrate precipitated by a NH_4OH/CH_3OH solution and recrystallization three times. Excess sodium pentacyanoaminoferrate (0.5g) dissolved into water, P-P4VP (4×4 cm^2) was immersed in this solution for 72 h at 40 °C. The obtained P-PFe was cleaned by water and dried under vacuum overnight at 40 °C.

1.4. Preparation of P-PFeCo

Briefly, the as-prepared P-PFe was immersed in 100 mL of 1g/L $Co(NO_3)_2$ solution for 12 h at room temperature. Then, the product was taken out, washed with water, and dried in a vacuum overnight at 40 °C. The load of cobalt ion measured by ICP-OES is 0.18 mmol/g (10.62 mg/g).

1.5. Characterization

The morphology of corresponding samples was done by a field emission scanning

electron microscope (SEM, Merlin Compact, Zeiss) with an energy dispersive spectrometer (EDS). The water contacts were measured on a contact angle meter (KSV Instruments Ltd., Finland). A Bruker Tensor 207 Fourier-transform infrared (FT–IR) spectrometer with an attenuated total reflectance (ATR) attachment (diamond crystal) was used from a range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The elemental composition was investigated by X-ray photoelectron spectroscopy (XPS) (PHI-5702 electron spectrometer) using an Al Kα line excitation source with the C 1s at 285.0 eV as a reference. An inductively coupled plasma-atomic emission spectrometry (ICP-OES, Optima 8000, PerkinElmer) was utilized to quantify the metal ions. An X-ray diffraction spectrum (RIGAKU D/MAX2200) using Cu Ka radiation (k = 1.54 Å) was employed to analyze amorphous structures of materials. The TOC of the solution was monitored by a TOC analyzer (Analytik Jena AG). For electron paramagnetic resonance (EPR) analyses, 5, 5-Dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6,-tetramethyl-4-piperidone (TEMP) was used as a spin-trapping agent for the reactive oxygen species. An EPR analyzer (Bruker A320, USA) was used to record the EPR spectra. Reaction condition: DMPO or TEMP = 4 μL, H2O= 200 μL, [Co ions dosage] = 0.02 g/L, [PMS] = 0.1 g/L, T = 25 ℃.

1.6. XAFS measurements and data processing

Co K-edge XAFS measurements were performed at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF).[2] The electron storage ring of SSRF was operated at 3.5 GeV, with a maximum current of 250 mA. XAFS data were collected using a fixed-exit Si (111) double-crystal monochromator, and the energy was

calibrated using metals foil.

Utilizing the ATHENA module of the IFEFFIT software packages, the obtained EXAFS data were performed according to the standard procedures.[3] The EXAFS contributions were separated from different coordination shells by using a hanning windows (dk=1.0 $Å^{-1}$). Subsequently, the quantitative curve-fittings were carried out in the R-space with a Fourier transform k-space range of 2.5-11.8 $Å^{-1}$ using the module ARTEMIS of IFEFFIT. During the curve-fitting, the overall amplitude reduction factor S02 was fixed to the best-fit value of 0.75 determined from fitting the data of Co foil.

1.7. Catalytic activity measurements

The adsorption, degradation, and reusability experiment were carried out in a 200 mL beaker with 100 mL RhB solution (20 mg/L) at a constant temperature of 25 ℃. The P-PFeCo (Co ions dosage = 0.02 g/L) were added with constant stirring for 30 min to establish the adsorption–desorption equilibrium of the organic dyes on the surfaces of P-PFeCo. Then, appropriate amounts of PMS (0.15–1.5 g/L) were added to start the catalytic process. At a given interval, 2 mL of the reaction solution was taken out and quickly injected pure methanol (1 mL) to terminate the oxidation. The concentrations of RhB were determined by the UV–vis spectrophotometer (Hitachi U-3010 spectrophotometer, Japan).

1.8. Models and methods

Quantum chemical calculations based on DFT were carried out using Gaussian 09 program (Revision A.01).[4] A part of the P-PFeCo molecule is intercepted as a model, namely $C_{20}N_{24}H_8Fe_4Co$. In order to maintain the structural characteristics of P-PFeCo

molecule observed by experiments, the atoms of $C_{20}N_{24}H_8Fe_4Co$ were fixed, excepting for the two groups (-CN) near the SO_3O-OH molecule. The geometry optimization were performed using B3LYP exchange–correlation functional, the LANL2DZ basis set for the transition metal (Co, and Fe) atom, and the 6-31G(d) basis set for all other atoms. The adsorption energies of the complexes, E_{ads}, are calculated as follows:

$$\text{Eads} = E_{Total} - E_{P\text{-}PFeCo} - E_{SO_3O\text{-}OH} \qquad (1)$$

where E_{Total}, $E_{P\text{-}PFeCo}$, and $E_{SO_3O\text{-}OH}$ denote the total energies of the complexes, the $C_{20}N_{24}H_8Fe_4Co$ and the SO_3O-OH molecule, respectively.
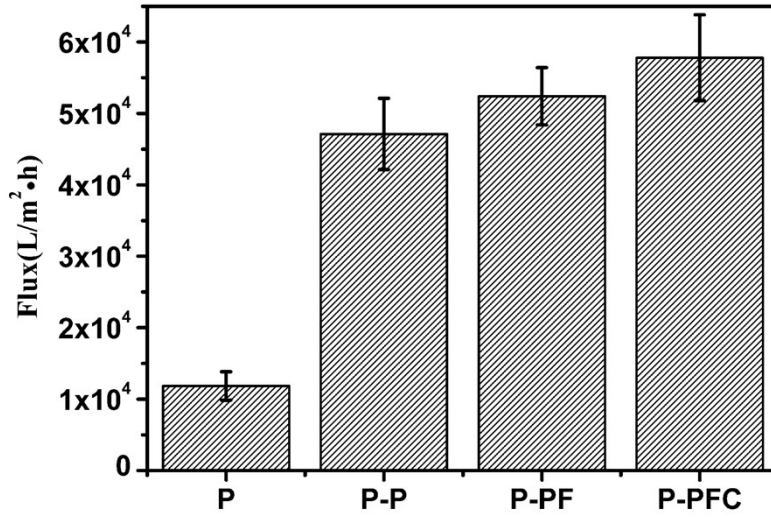
Fig. S1. Permeation flux of the original and resultant PP membranes under the driving external pressure of 0.8 bar.
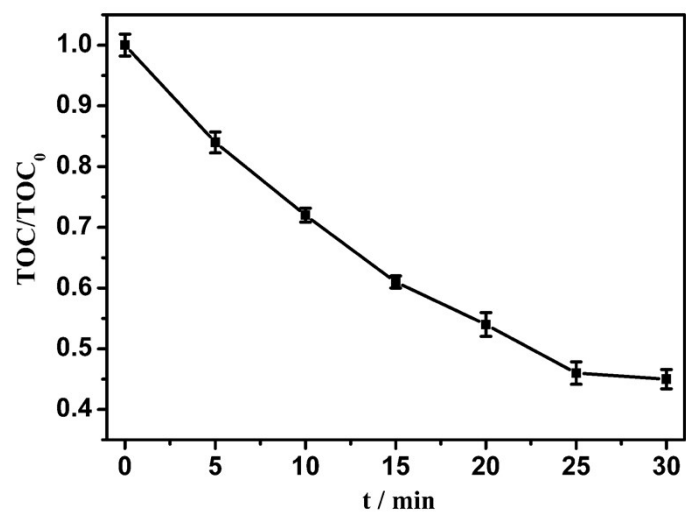
Fig. S2. TOC removal efficiency of P-PFeCo for RhB during 30 min. TOC_0 and TOC

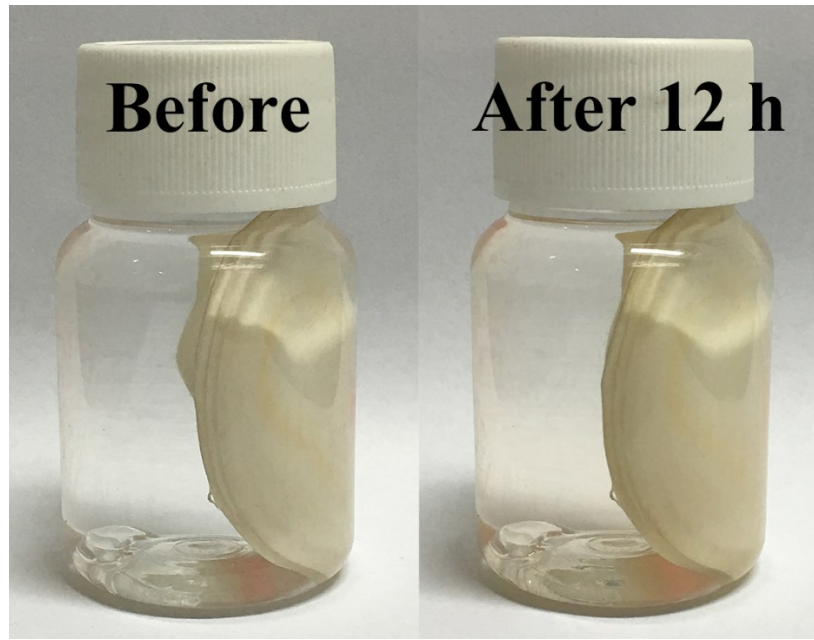represent the initial total organic carbon and total organic carbon at time t.
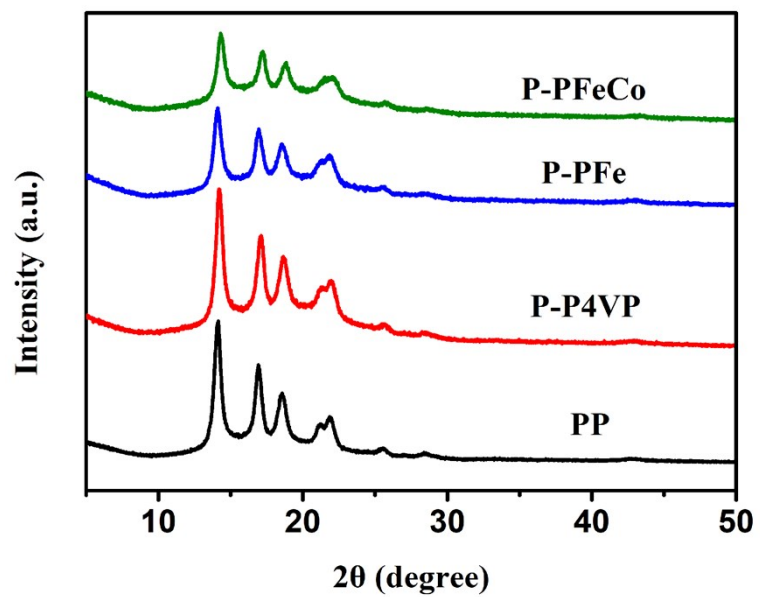
Fig. S3. XRD pattern of PP, P-P4VP, P-PFe, and P-PFeCo.
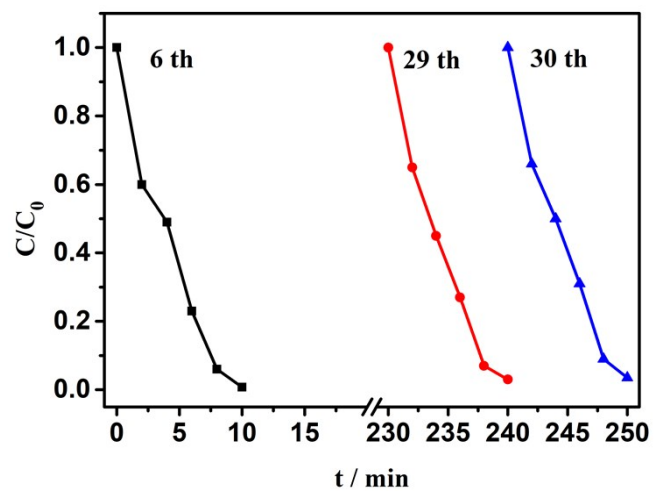
Fig. S4. Reusability test for 30 times on P-PFeCo in terms of RhB removal.

Fig. S5. Photographthe of the collected sample that the P-PFeCo after the device test was immersed in alkaline solution (pH=12) for 12 hours. The color of the solution is transparent.
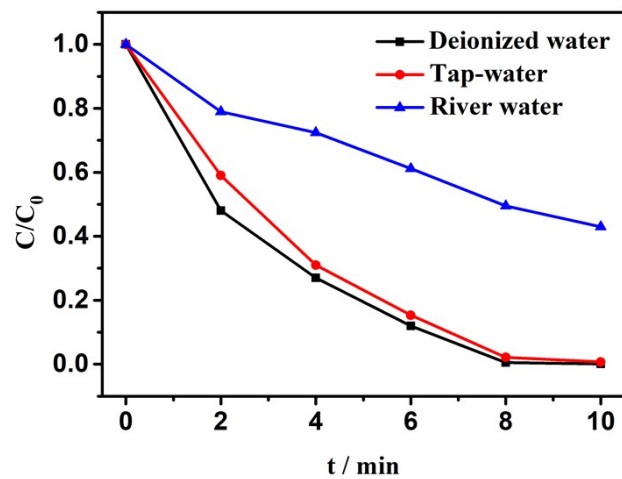
Fig. S6. Removal efficiency of RhB in various water environment

Table 1. Co K-edge fitting parameters.

Sample	shell	N	R (Å)	ΔE_0 (eV)	$\sigma^2(10^{-3}\text{Å}^2)$	R-factor
Water	Co-O	2.0	2.01	5.0	2.0	0.007
	Co-N	4.0	2.18	-5.2	4.4	
After 5 cycles	Co-O	1.8	2.01	4.8	2.0	0.008
	Co-N	4.1	2.18	-4.6	4.4	

N, coordination numbers; R, the internal atomic distance; σ^2, Debye-Waller factor; ΔE_0, the edge-energy shift.

Table S2. The catalytic performance comparison of recently reported different catalysts

for PMS activation.

Catalyst (mg /L)	Pollutant (mg /L)	PMS (mg/L)	Removal efficiency	Leached Co (mg /L)	Ref.
$Fe_{0.8}Co_{2.2}O_4$ (0.1)	BPA (20)	200	95% (60 min)	-	5
Co_3O_4 (0.6)	2,4-DCP (20)	800	85% (120 min)	0.7	6
Co_3O_4@MOFs (0.5)	4-CP (100)	250	100% (60 min)	1.25	7
FeCo-NC-2 (0.1)	BPA (20)	200	100% (4 min)	0.23	8
Co/AC (0.2)	Phenol (25)	2000	100% (60 min)	1.6	9
Fe_3Co_7@C (0.1)	BPA (20)	200	95% (30 min)	3.3	10
CoOx-C (0.1)	Phenol (20)	300	100% (60 min)	-	11
$FeCo_2$@APCFs (0.1)	MeB (100)	100	100% (30 min)	0.96	12
Co@N-C (0.1)	BPA (10)	100	100% (10 min)	0.11	13
Co_3O_4-Bi_2O_3 (0.3)	BPA (20)	100	98.6% (30 min)	0.5	14
MCG (0.5)	Acid Yellow 17 (100)	90	97.6% (20 min)	0.7	15
$CoFe_2O_4$ (0.2)	Orange G (100)	500	99% (20 min)	0.69	16
$CoFe_2O_4$ (0.2)	RhB (100)	3000	97% (60 min)	0.66	17
P-PFeCo (Co^{2+} dosage = 0.02	RhB (20)	100	**100% (8 min)**	**0.2**	**This work**

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