

Intentionally Incorporated Fe Cations in Silverton Polyoxometalates Forming Fenton-like Photocatalysts for Enhanced Degradation

Synthesis of $\text{Co}_4\text{W}_6\text{O}_{21}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

$\text{Co}_4\text{W}_6\text{O}_{21}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (denoted as CoWOH) microcrystals were prepared using a facile hydrothermal route. Firstly, 2 mmol each of sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) and cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were added into 20 mL deionized (DI) water with vigorous stirring to form a transparent solution at room temperature. After that, 2 mmol of 5-sulfosalicylic acid dihydrate (SSA, $\text{C}_7\text{H}_6\text{O}_6\text{S} \cdot 2\text{H}_2\text{O}$) was added to the above mixture with continuous stirring to dissolve SSA completely. Then, the homogeneous brick-red solution was poured into a stainless autoclave and heated at 150°C for 6 h. Afterwards, the resulting Murrey precipitates were washed with deionized water and anhydrous ethanol alternately several times, and then dried at 70°C under a vacuumed condition for 5 h.

Table S1. Metal content quantification by ICP-AES (wt.-%).

	Fe	Co	W
Calcd.	6.29%	6.64%	62.16%
Found	6.41%	7.27%	64.6%

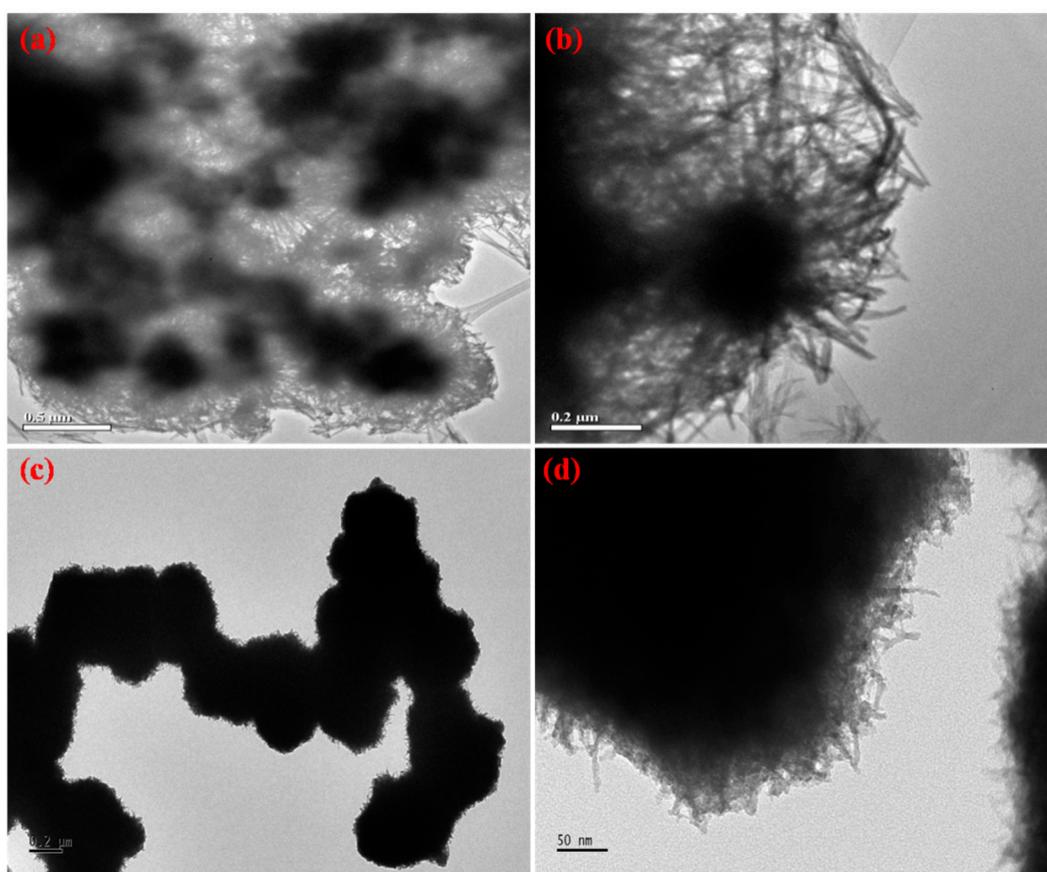


Figure S1. (a-b) TEM images of CoWOH samples; (c-d) TEM images of FeCoWOH-3 samples.

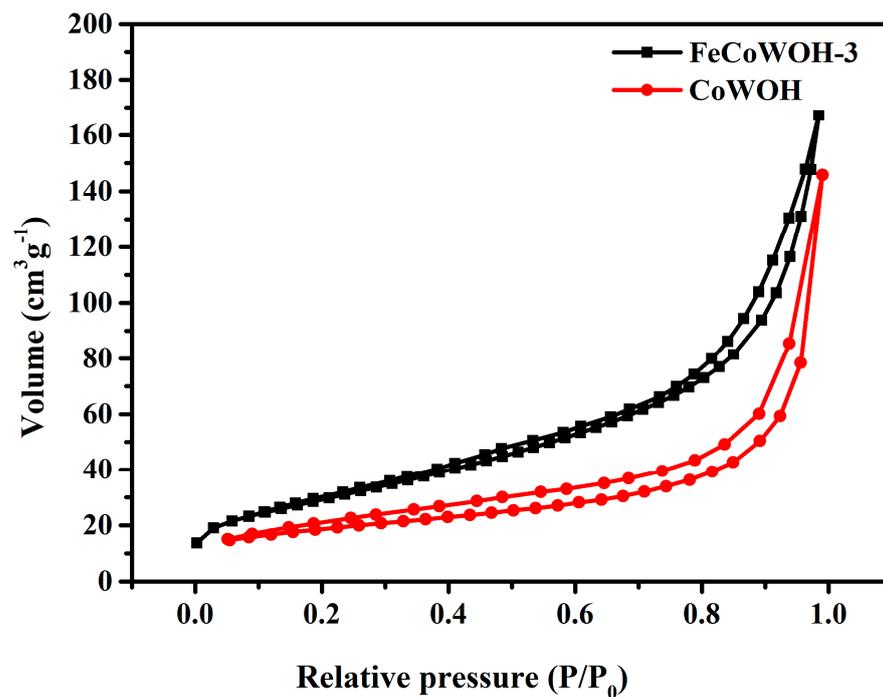


Figure S2. Nitrogen adsorption-desorption isotherms for the as-obtained CoWOH and FeCoWOH-3 samples.

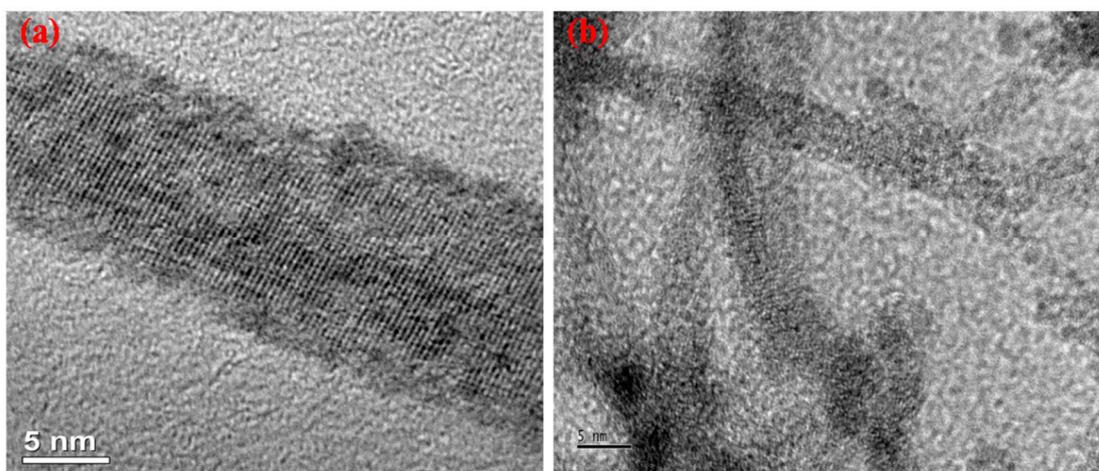


Figure S3. (a) HRTEM images of CoWOH samples; (b) HRTEM images of FeCoWOH-3 samples.

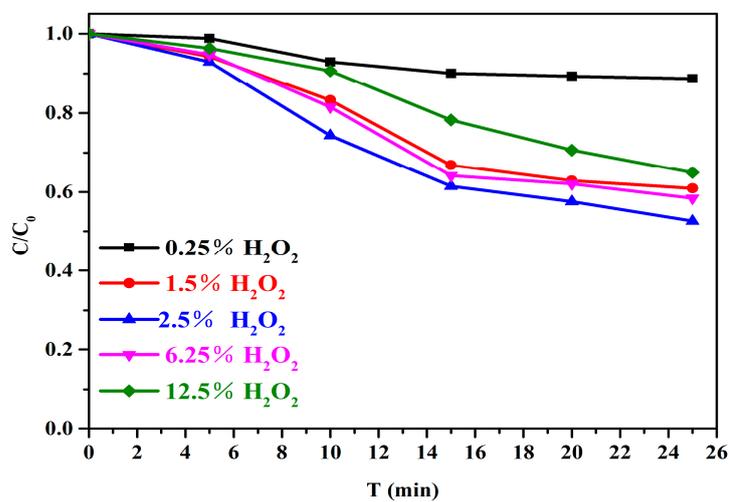


Figure S4. Comparison of different volume ratios of hydrogen peroxide for degradation of RhB dyes without catalyst under visible-light irradiation.

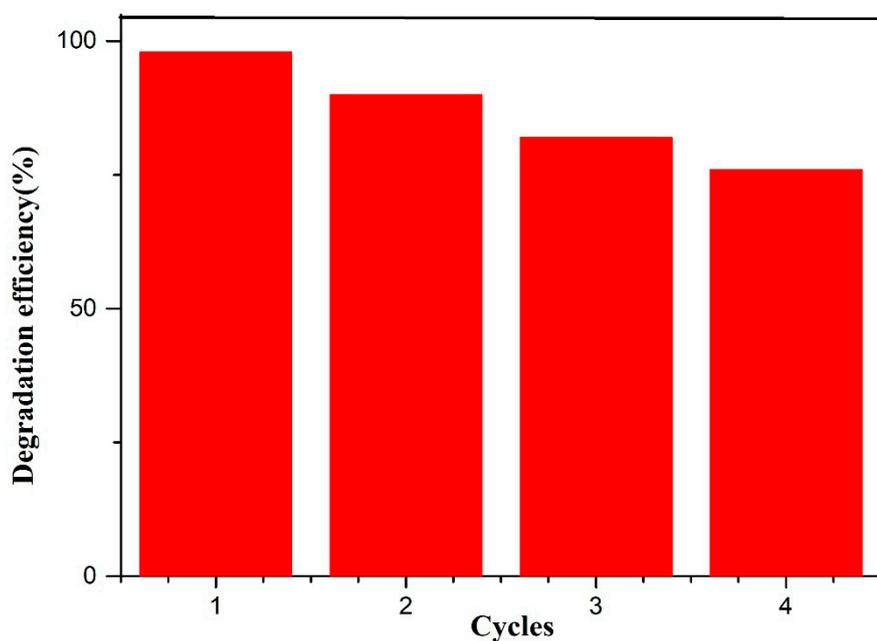


Figure S5. Cycling experiments for the degradation of RhB over FeCoWOH.

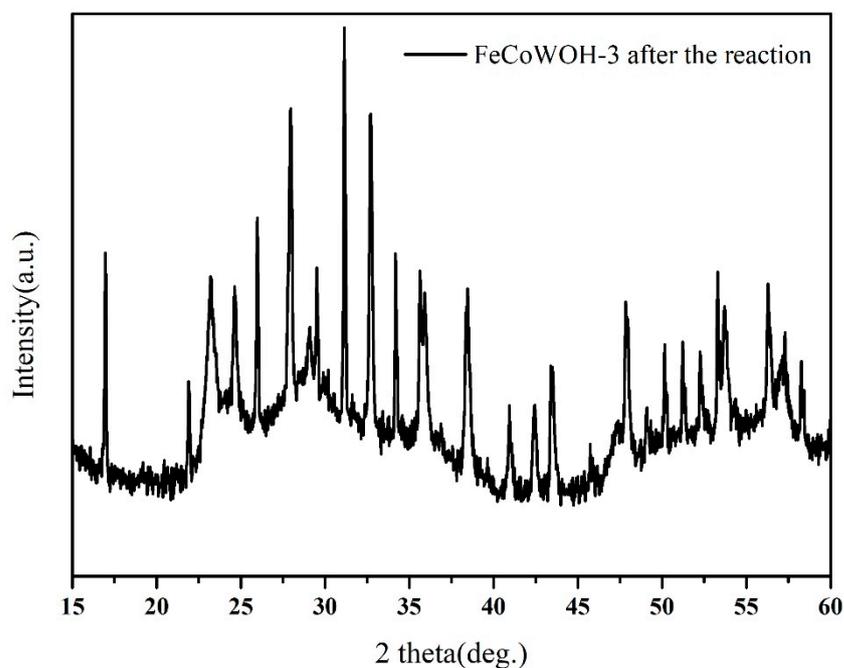


Figure S6. XRD patterns of FeCoWOH-3 samples after the reaction.

Table S2. Comparison of photocatalytic properties of different similar materials.

Catalyst used and amount	Conc. and volume of XO	UV light source	Degradation time (min)	Degradation %	Reference
Polyoxometalate/TiO ₂ /Ag composite nanofibers (20mg)	20mgL ⁻¹ 20 mL	300W Xe	120	100	Applied Catalysis B: Environmental 221

	MO				(2018) 280–289
Ag _x H _{3-x} PMo ₁₂ O ₄₀ /Ag nano-rods/g-C ₃ N ₄ 1D/2D Z-scheme heterojunction 20 mg	20mgL ⁻¹ 20 mL MO	300W Xe	25	100	Dalton Trans., 2019, 48, 6484–6491
POMs@g-C ₃ N ₄ 100 mg	10mgL ⁻¹ 200 mL MB	MSR 575/2, 575 W, Philips	180	15	Journal of Colloid and Interface Science 456 (2015) 15–21
Polyoxometalate-intercalated ZnAlFe-layered double hydroxides 20mg	40 mL MB	25W Xe			Applied Clay Science 157 (2018) 86–91
copper(II) semicarbazone complex and the PMo ₁₂ O ₄₀ ³⁻ polyanion 25mg	25mgL ⁻¹ 50 mL RhB	400W mercury lamp	240	84	Polyhedron 122 (2017) 247–256
POM-based inorganic–organic hybrid Compounds 80mg	20mgL ⁻¹ 100 mL MB/MB	300W Xe	24*60	91 MB 92.1 MV 12.5 RhB 0.6 MO	Dalton Trans., 2015, 44, 9496–9505
FeCoWOH-3 20mg	20mgL ⁻¹ 40 mL RhB	300W Xe	25min	98 RhB	Our work