

# Unleashing the Power of Cobalt Pyroborate: Superior Performance in Sulfate Radical Advanced Oxidation Processes

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**Table 1** Comparative analysis of  $\text{Co}_3\text{O}_4$  heterostructures in previous studies relative to the current work. Abbreviations for organic pollutants: 4-NP signifies 4-nitrophenol; BPA stands for bisphenol-A; PNT represents phenacetin; SDZ denotes sulfadiazine; RhB refers to Rhodamine-B; SMZ is for sulfamethoxazole; SSZ indicates sulfasalazine; CBZ is an abbreviation for carbamazepine; and TC designates tetracycline.

Catalyst	Pollutant	Reaction conditions	Performance	Referenc e
$\text{Co}_3\text{O}_4$ nanoparticles and N-functionalized carbon nanosheet frameworks ( $\text{Co}_3\text{O}_4$ -NCNF)	4-NP	[PMS] = 3 mM; catalyst = 0.14 g/L; [4-NP] = 20 ppm; time = 60 mins	100.0% $k = 0.137 \text{ min}^{-1}$	[1]
Ultrafine $\text{Co}_3\text{O}_4$ incorporated carbon composites ( $\text{Co}_3\text{O}_4/\text{CC}$ )	BPA	[PMS] = 0.66 mM; catalyst = 0.1 g/L; [BPA] = 10 ppm; time = 10 mins	97% $k = 0.45 \text{ min}^{-1}$	[2]
Two-dimensional (2D) ultrathin perforated $\text{Co}_3\text{O}_4$ nanosheet	BPA	[PMS] = 0.25 mM; catalyst = 0.05 g/L; [SMZ] = 10 ppm; time = 30 mins	98.0% $k = 0.112 \text{ min}^{-1}$	[3]

Co <sub>3</sub> O <sub>4</sub> anchored on biochar derived from chitosan (Co <sub>3</sub> O <sub>4</sub> @BCC)	PNT	[PMS] = 1.0 mM; catalyst = 0.05 g/L; [PNT] = 10 ppm; time = 15 mins	100.0% k = 0.32 min <sup>-1</sup>	[4]
Co <sub>3</sub> O <sub>4</sub> -MnO <sub>2</sub> nanoparticles moored on biochar (Co <sub>3</sub> O <sub>4</sub> -MnO <sub>2</sub> /BC)	SDZ	[PMS] = 1.0 mM; catalyst = 0.1 g/L; [SDZ] = 25 ppm; time = 10 mins	100.0% k = 0.482 min <sup>-1</sup>	[5]
Cobalt@porous carbon nanosheets	4-NP	[PMS] = 3.9 mM; catalyst = 0.16 g/L; [4-NP] = 20 ppm; time = 12 mins	99.5% k = 0.618 min <sup>-1</sup>	[6]
Co-doped g-C <sub>3</sub> N <sub>4</sub>	RhB	[PMS] = 0.12 mM; catalyst = 0.4 g/L; [RhB] = 10 ppm; time = 25 mins	99% k = 0.2208 min <sup>-1</sup>	[7]
C <sub>3</sub> N <sub>5</sub> -Co <sub>0.59</sub>	SMX	[PMS] = 1.0 mM; catalyst = 0.5 g/L; [SMX] = 10 ppm; time = 20 mins	99.57% k = 0.3515 min <sup>-1</sup>	[8]
In situ N-doped carbon-coated mulberry-like cobalt manganese oxide (HCoMnOx@NC)	SMZ, SSZ, CBZ, etc.	[PMS] = 0.3 mM; catalyst = 0.1 g/L; [pollutant] = 30 μM; time = 30 mins	100% : SSZ, CBZ 95.4% SMZ k <sub>SMZ</sub> = 0.0867 min <sup>-1</sup> k <sub>SSZ</sub> = 0.1769 min <sup>-1</sup> k <sub>CBZ</sub> = 0.5069 min <sup>-1</sup>	[5]
cobalt sulfide-reduced graphene oxide nanocomposite (CoS-rGO)	RhB	[PMS] = 0.05 mM; catalyst = 0.25 g/L; [RhB] = 30 μM; time = 8 mins	100% k = 0.6714 min <sup>-1</sup>	[9]
Our work Co <sub>2</sub> B <sub>2</sub> O <sub>5</sub>	TC, 4-NP, SMX	[PMS] = 1 mM; catalyst = 0.12 g/L [SMX] = 10 ppm [TC] = 50 ppm [4-NP] = 40 ppm	95.2% SMX k <sub>SMX</sub> = 0.092 min <sup>-1</sup> 97.9% TC k <sub>TC</sub> = 0.16 min <sup>-1</sup> 96.8% 4-NP k <sub>4NP</sub> = 0.12 min <sup>-1</sup>	Our work

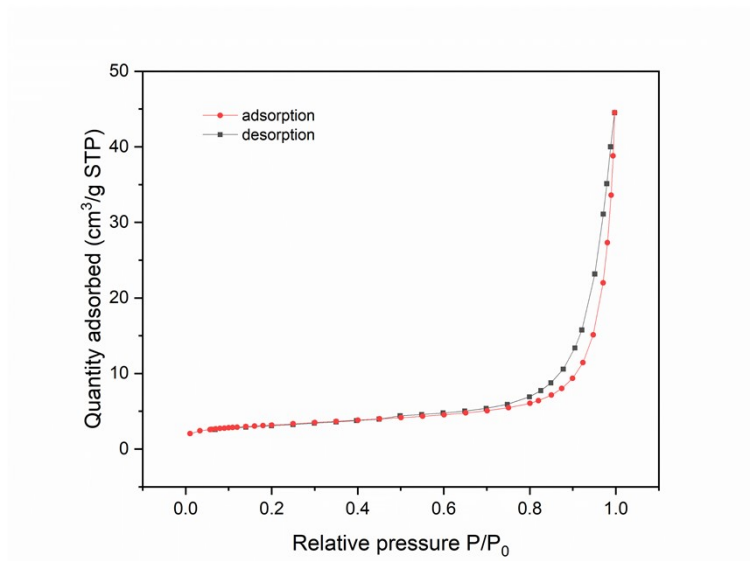
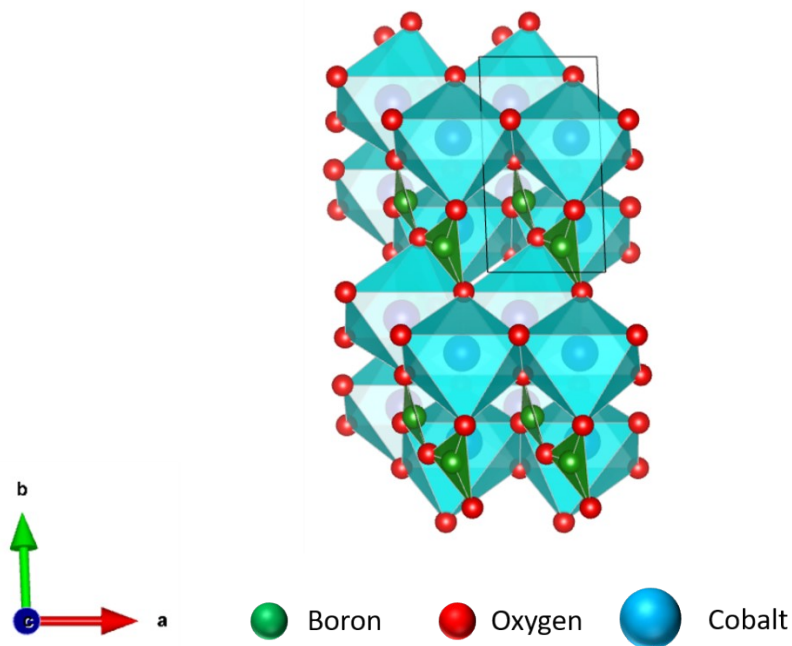


Figure S1. Crystal structure of cobalt pyroborate

Figure S2: BET isotherms using N<sub>2</sub> at 77 K of Co<sub>2</sub>B<sub>2</sub>O<sub>5</sub>

The Fourier Transform Infrared (FTIR) spectrum of Co<sub>2</sub>B<sub>2</sub>O<sub>5</sub> is presented (Fig. 4), revealing several characteristic absorption bands associated with cobalt, boron and oxygen. Notably, several peaks have been identified, including the O-H vibration at 3425.88 cm<sup>-1</sup>, as well as the asymmetric

B-O stretching peaks of the three-coordinate boron at  $1465.58\text{ cm}^{-1}$  and  $1273.52\text{ cm}^{-1}$ , and of four-coordinate boron at  $1170.05\text{ cm}^{-1}$  and  $1012.5\text{ cm}^{-1}$ . [10,11] The symmetric B-O stretching vibration of the four-coordinate boron is evident at  $906\text{ cm}^{-1}$  and  $820.88\text{ cm}^{-1}$ , while the symmetric stretching vibrations of the four-coordinate boron group emerged at  $872\text{ cm}^{-1}$ . [10,11] Additionally, the absorbance band at  $768\text{ cm}^{-1}$  can be assigned to the oxygen bridge of one tetrahedral and one tetragonal boron group. [10,11] The Co-O bond is represented by the absorption peaks at  $595.50\text{ cm}^{-1}$  and  $662.50\text{ cm}^{-1}$ , and the absorbance band at  $697.03\text{ cm}^{-1}$  is due to the O-B-O bonding. [12–15] Our FTIR results is commensurate with the XPS and XRD analyses, which confirms the structural characteristic of  $\text{Co}_2\text{B}_2\text{O}_5$ .

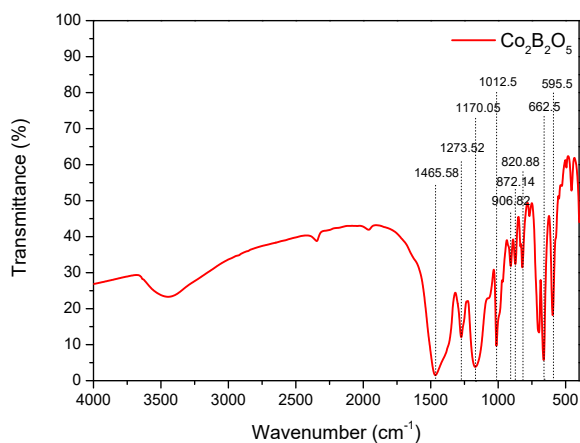
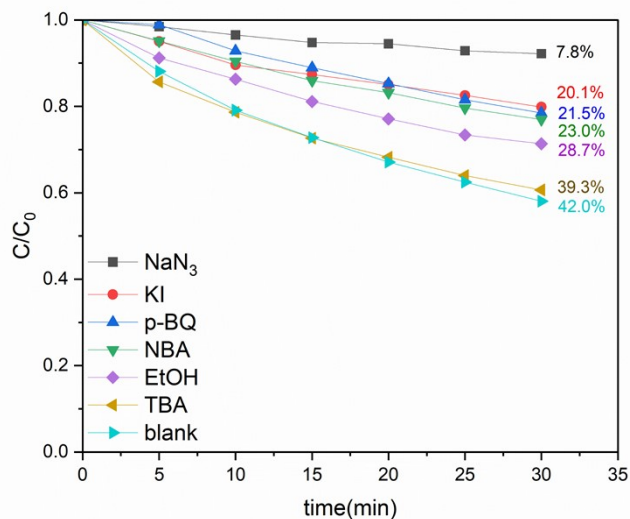


Figure S3: FTIR spectrum of  $\text{Co}_2\text{B}_2\text{O}_5$  nanoparticle

## ICP-MS

The ICP-MS analysis of the  $\text{Co}_2\text{B}_2\text{O}_5$  revealed the elemental composition of Co:B weight ratio to 0.529:0.151, which is commensurate with the theoretical value of 0.536:0.1 (Table S1). The higher proportion of boron than the ideal value may be due to the residual portion of boric



acid during synthesis.

Figure S3: Kinetic plot of trapping experiment using  $\text{CoO}$  as a catalyst in SR-AOPs. Reaction conditions:  $[\text{4-NP}]_0 = 40$  ppm;  $[\text{catalyst}] = 125$  mg/L;  $[\text{PMS}] = 1$  mM;  $[\text{trapping agent}] = 1$  mM.

**Table S2** ICP-MS result of the pristine  $\text{Co}_2\text{B}_2\text{O}_5$  nanoparticles and the solution after a standard SR-AOPs degradation reaction using  $\text{Co}_2\text{B}_2\text{O}_5$  as catalyst

Sample	Element/Concentration	Co	B
	$\text{Co}_2\text{B}_2\text{O}_5$ (ppm)	71.50	20.71
	Weight percent in catalyst (%)	52.9	15.1
	Co and B leached in the solution (ppm)	21.22	7.715

**Table S3** Relative atomic percentage of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  in pristine versus spent  $\text{Co}_2\text{B}_2\text{O}_5$

Elements in different chemical states	Relative contents (at. %)	
	Pristine	Spent
$\text{Co}^{2+}$	39.8	61.3
$\text{Co}^{3+}$	60.2	38.7

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