

Supporting Information

Oxygen vacant Co_3O_4 *in situ* embedded on carbon spheres: cooperatively tuning electron transfer for boosted peroxymonosulfate activation

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Text S1. The synthesis process of different catalysts in the control experiment.

For the Co@CS (without calcination), CS (without calcination) and CS@600, the synthesis procedures were similar to Co₃O₄@CS-600 excluding the following specific processes. Co@CS (without calcination) materials were obtained after the hydrothermal treatment with Co(NO₃)₂·6H₂O as the metal source but without the calcination process. CS (without calcination) was achieved with neither addition of Co(NO₃)₂·6H₂O before the hydrothermal reaction nor calcination treatment for the final step. CS@600 materials were prepared without the addition of cobalt metal source but after the hydrothermal process, the organic materials were calcined in Ar at 600 °C for 2 h. Co₃O₄@600 was obtained by calcinating the final materials in the Air rather than Ar.

Text S2. Spectrophotometric method to measure the PMS concentration

Typically, 0.5 M potassium iodide (KI) solution and 0.05 M sodium bicarbonate (NaHCO₃) solution were prepared firstly. 0.1 mL filtered reaction solution was added into 4.9 mL above-mentioned solution with shaking for 20 min to equilibrate the reaction. Then the sample was analysed at $\lambda = 352$ nm (UV-2600 UV-vis Spectrophotometer, Shimadzu, Japan).

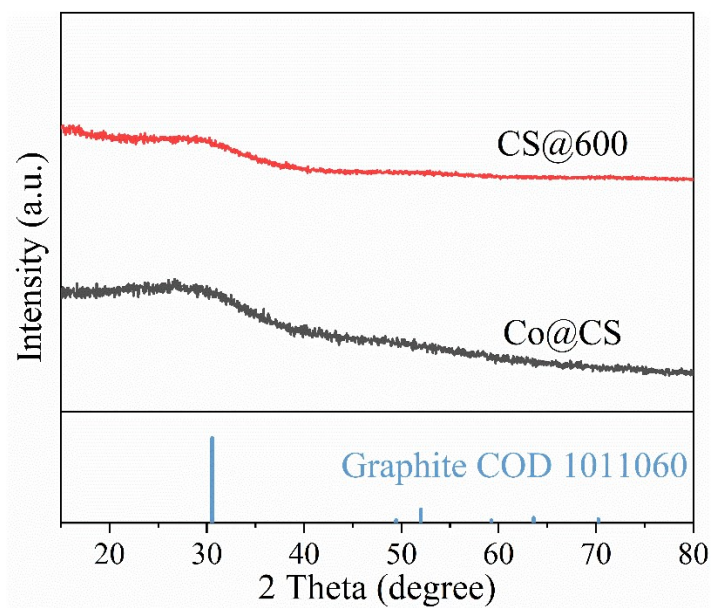


Figure. S1. XRD patterns of CS-600 and Co@CS. Note that all the XRD analysis were conducted with 1000W Co-anode X-ray source with Fe $K\beta$ filters.

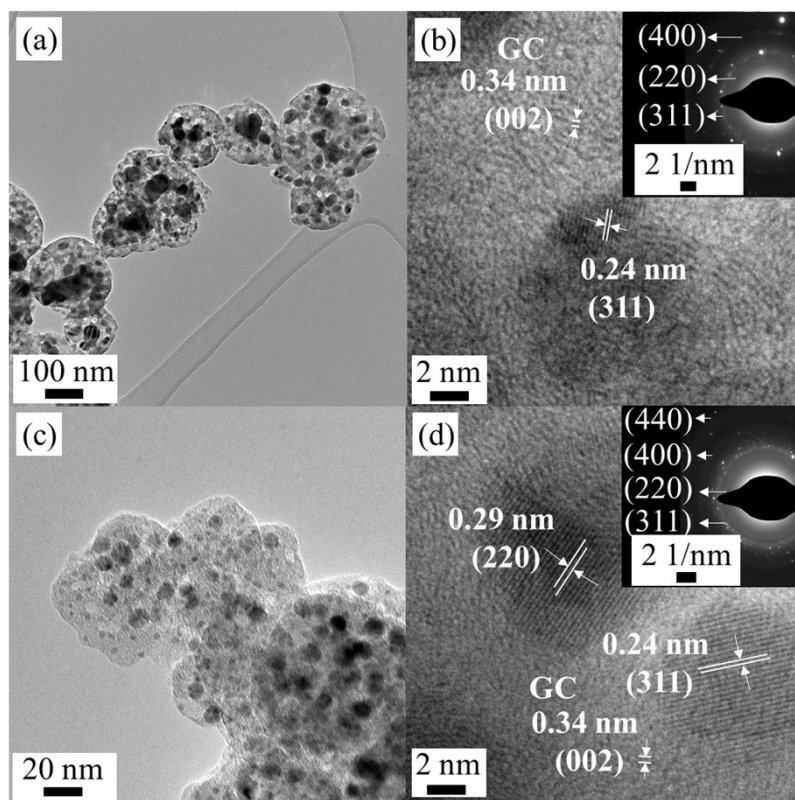


Figure. S2. TEM images of (a) $\text{Co}_3\text{O}_4@\text{CS-500}$ and (c) $\text{Co}_3\text{O}_4@\text{CS-700}$. HRTEM images of (b) $\text{Co}_3\text{O}_4@\text{CS-500}$ and (d) $\text{Co}_3\text{O}_4@\text{CS-700}$.

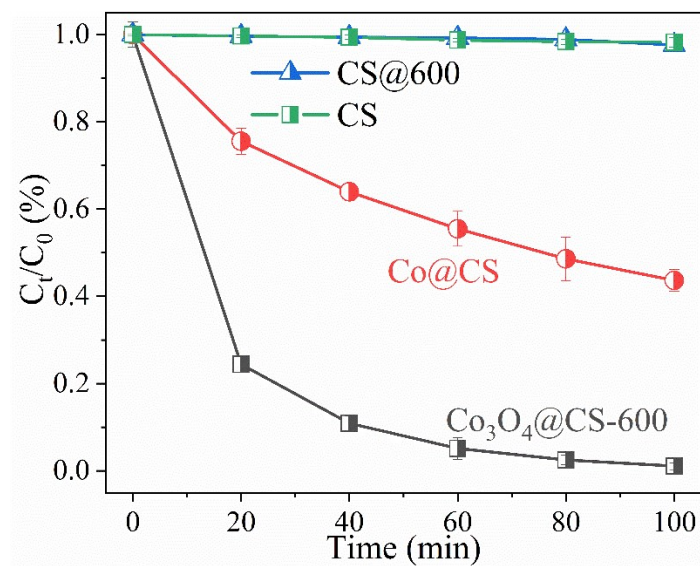


Figure. S3. BPA removal efficiency with Co₃O₄@CS-600, Co@CS, CS@600 and CS@600. BPA: 40 mg/L, catalysts: 0.1 g/L, PMS: 0.2 g/L, initial pH = 6.2, $T = 293$ K.

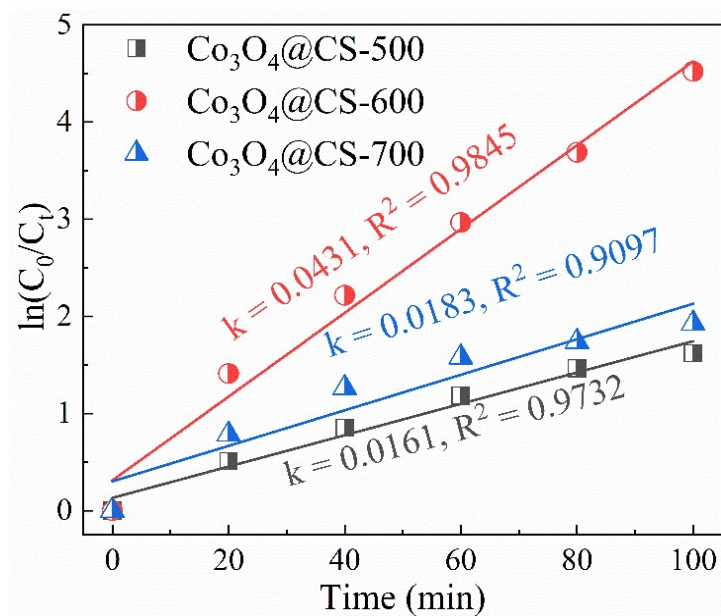


Figure. S4. Pseudo first-order kinetic curves of BPA removal with different catalysts.

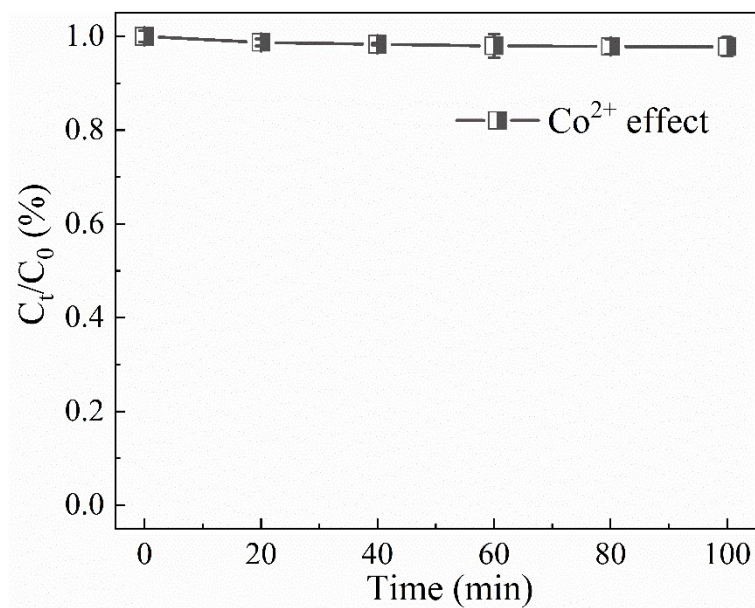


Figure. S5. Effect of the same amount of leached Co^{2+} (0.29 mg/L Co^{2+}) on BPA degradation. Reactions conditions: BPA: 40 mg/L, catalysts: 0.1 g/L, PMS: 0.2 g/L, initial pH = 6.2, $T = 293$ K.

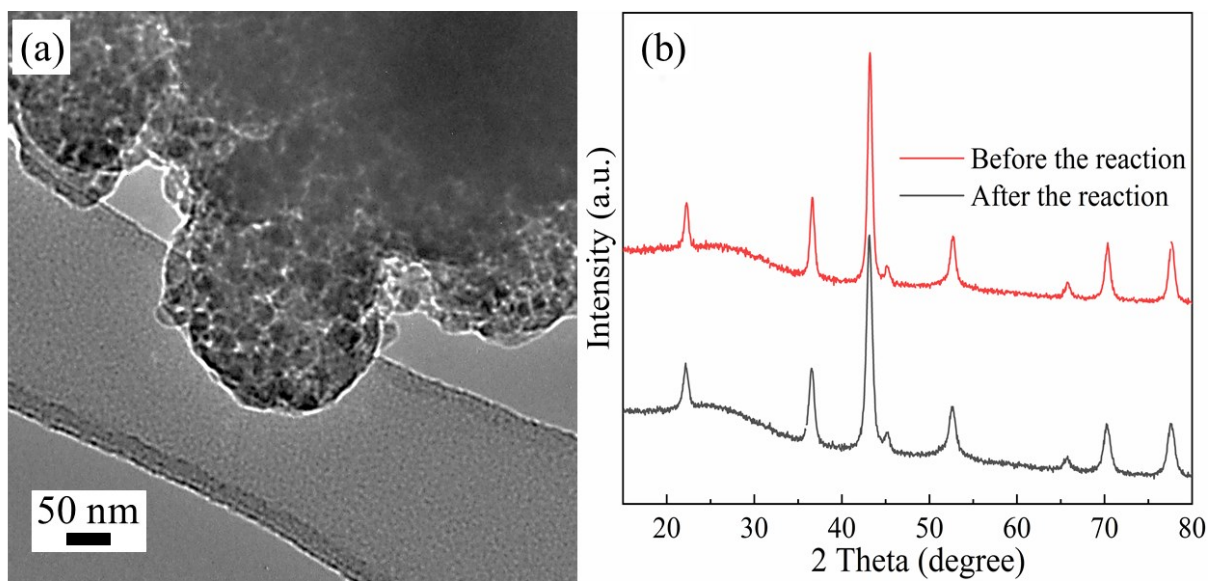


Figure. S6. (a) TEM images of $\text{Co}_3\text{O}_4@CS-600$ after the reaction. (b) XRD patterns of $\text{Co}_3\text{O}_4@CS-600$ before and after the reaction.

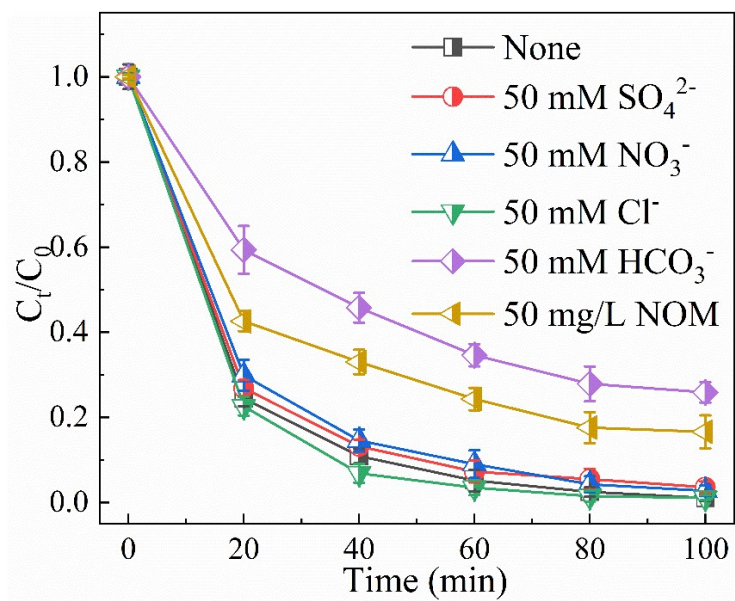


Figure. S7. Effects of inorganic anions SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- and NOM on the degradation of BPA. Reactions conditions: BPA: 40 mg/L, catalysts: 0.1 g/L, PMS: 0.2 g/L, initial pH = 6.2, $T = 293$ K.

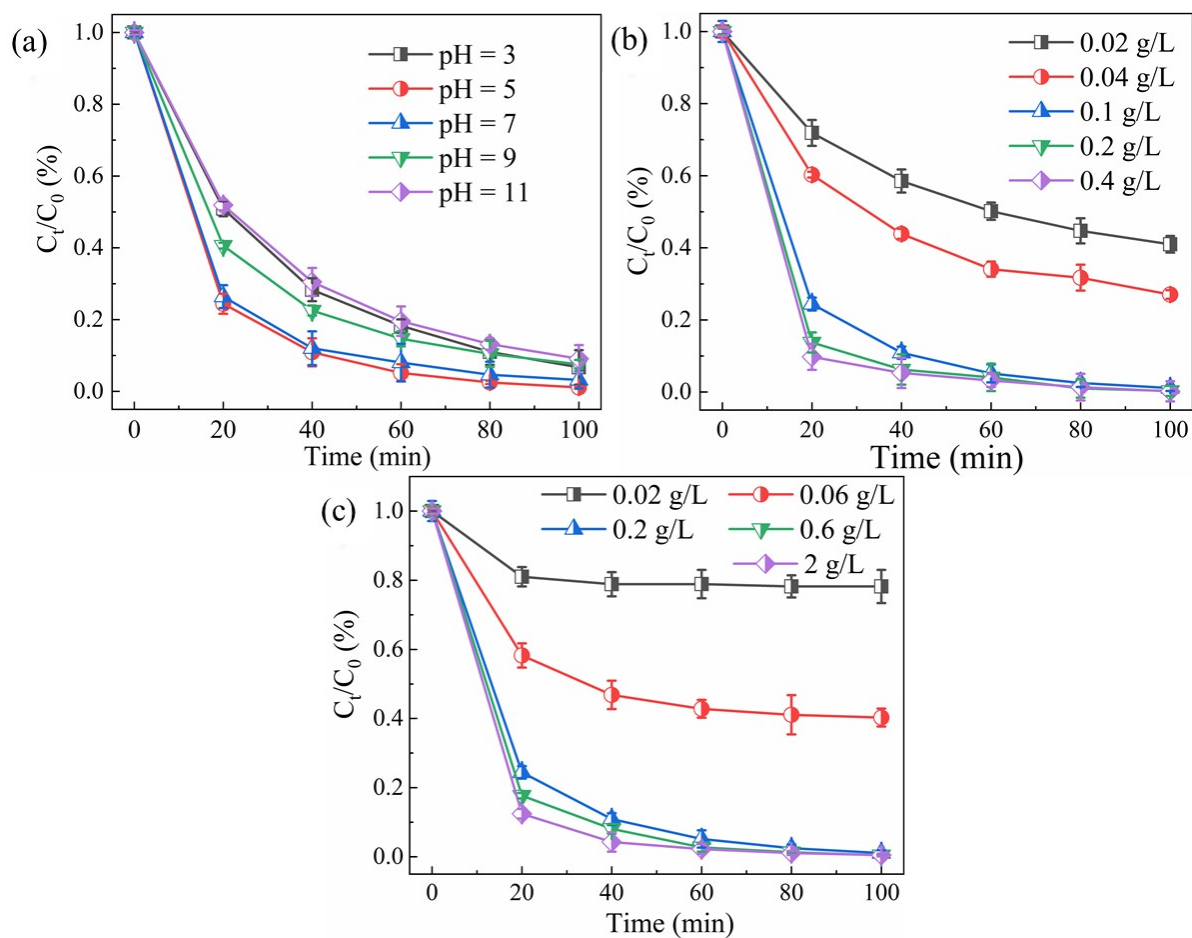


Figure. S8. Effects of (a) initial pH values, (b) catalysts dosage and (c) PMS dosage. Basic reactions conditions: BPA: 40 mg/L, catalysts: 0.1 g/L, PMS: 0.2 g/L, initial pH = 6.2, $T = 293$ K.

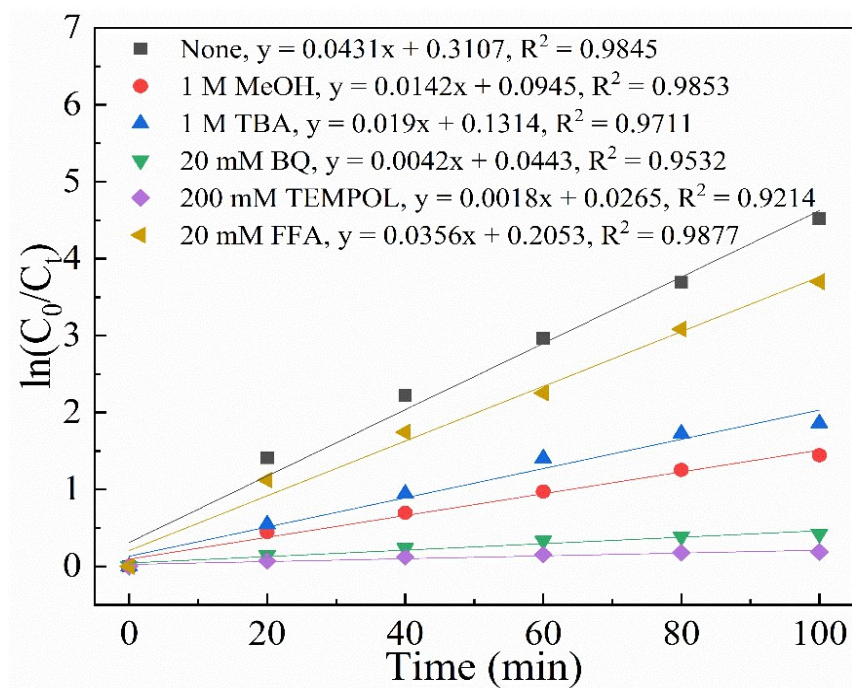


Figure. S9. Pseudo first-order kinetic curves of each quenching test. Reactions conditions:

BPA: 40 mg/L, PMS: 0.2 g/L, initial pH = 6.2, $T = 293$ K.

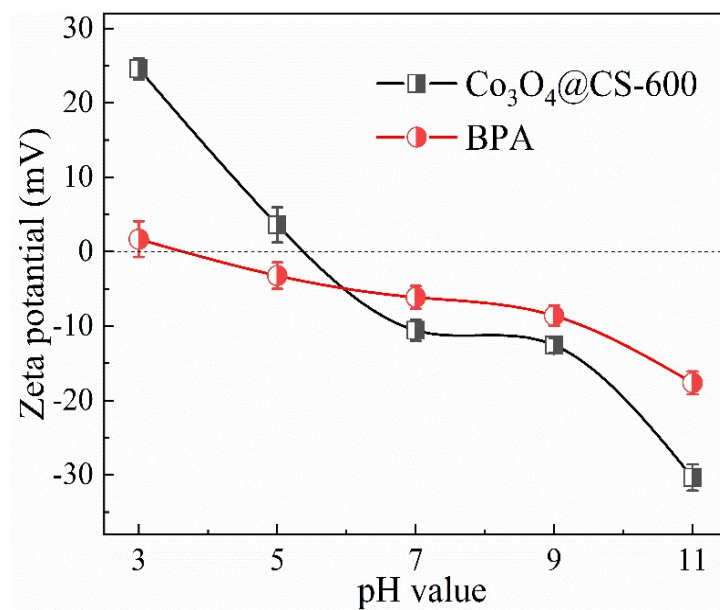


Figure. S10. Zeta potential of Co₃O₄@CS-600 and BPA at different pH conditions.

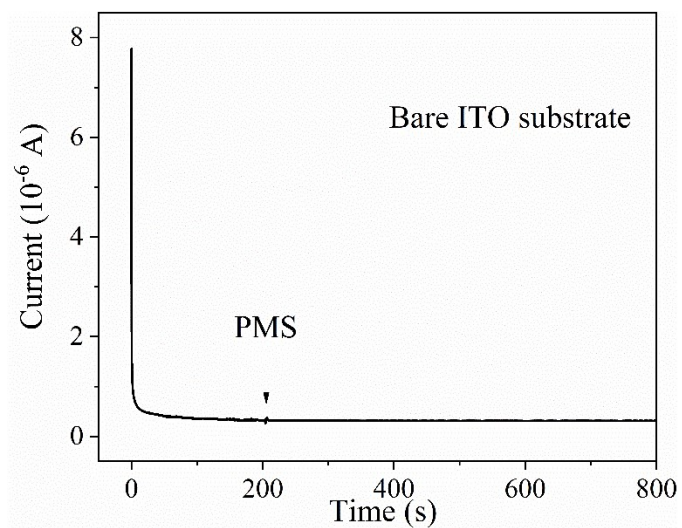


Figure. S11. Current-time (i-t) curves of bare ITO substrate.

Table S1. The concentration of leached cobalt ions with different catalysts

Sample	Leached Co ions concentration (mg/L)
Co@CS	7.85
Co ₃ O ₄ @CS-500	0.58
Co ₃ O ₄ @CS-600	0.29
Co ₃ O ₄ @CS-700	0.16

Table S2. Comparison of different catalysts for base activation of persulfate.

Catalyst	Pollutants (mM)	Persulfate dosage (mM)	Catalyst dosage (g/L)	pH values	Time used for removal	First-order kinetic constants (min ⁻¹)	Main reactive species	References
Co ₃ O ₄ @CNT	norfloxacin, 0.03	PMS, 0.5	0.12	7	60 min, 94.8%	0.0436	¹ O ₂	1
Co ₃ O ₄ -rice husk ash	Rhodamine B, 1	PMS, 1.63 (0.5 g/L)	0.02	6	60 min, 96.3%	0.17	¹ O ₂ , O ₂ ^{·-}	2
Co ₃ O ₄ @NCs	sulfamethoxazole , 0.1	PMS, 0.65 (0.2 g/L)	0.01	9.0	6.67	0.0062	¹ O ₂	3
Co ₃ O ₄ @NSC	paracetamol, 0.07	PMS, 0.5	0.1	5.0	-	0.162 min ⁻¹	¹ O ₂ , O ₂ ^{·-}	4
rGO-Co ₃ O ₄	tetracycline, 0.01	PDS, 0.3	0.1	6	60 min, 96%	0.023	·OH, SO ₄ ^{·-}	5
Co doped Al ₂ O ₃	tartrazine, 0.05	PMS, 0.32	3 mM	3.6	240 min, 98%	-	-	6
Co ₃ O ₄ @CS-600	BPA, 0.16 (40 mg/L)	PMS, 0.65 (0.2 g/L)	0.1	6.2	100 min, 99.0 %	0.0431	O ₂ ^{·-}	This work

Table S3. Crystal lattice parameters of $\text{Co}_3\text{O}_4@\text{CS-600}$ before and after the reaction.

Sample	a=b=c (Å)	Volume (Å ³)
Before the reaction	8.09790	531.03
After the reaction	8.09790	531.03

Table S4. Comparison of catalysts and catalytic performance with our previous work

Sample	BPA degradation rate			Ref.
	(min ⁻¹ , 100 min ⁻¹)	V _O concentration	Carbon content	
Co ₃ O ₄ @CS-500	0.0161	22.3%	85.3%	This work
Co ₃ O ₄ @CS-600	0.0431	42.7%	84.2%	
Co ₃ O ₄ @CS-700	0.0183	27.6%	82.6%	
400-1	0.0116	24.4%	<4%	7
400-2	0.0232	32.4%	<4%	
500-6	0.0050	21.2%	<4%	

Note:

In our previous study, 400-1 was obtained by calcination Co@CS under 400°C with 1 h in the air. 400-2 was obtained by calcination Co@CS under 400°C with 2 h in the air. 500-6 was obtained by calcination Co@CS under 500°C with 6 h in the air.

References:

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