

Supporting information

Coupling electrochemical H₂O₂ production and *in-situ* selective oxidation of organics over a bifunctional TS-1@Co-N-C

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Material Synthesis

Synthesis of TS-1@PDA: 200 mg of TS-1 were added into 100 mL conical flask with 50 mL of HCl-Tris (pH=8.5, 50 mM) solution. The mixture was stirred ultrasonically at 6°C for 20 min, and then 200 mg of dopamine were added. The reaction solution was continuously stirred for 48 h. The obtained nanomaterials TS-1@PDA was collected by centrifugation at a low speed of 6000 rpm and washed three times with ethanol and deionized water, respectively and then vacuum-dried at 60°C overnight.

Synthesis of TS-1@Co-N-C catalyst: 200 mg of prepared TS-1@PDA and 25 mg of cobalt acetate were mixture in a mortar and grinded for 30 min. The obtained mixture power was pyrolyzed in a tube furnace at a heating rate of 5°C min⁻¹ to 200°C under N₂ atmosphere, heated at 200°C for 2h, then heated to 800°C at 2°C min⁻¹ and held for 2 h. After cooling to room temperature, the samples were taken out and ground for 20 min and washed with 0.5 M H₂SO₄ for 12 h in an oil bath at 80°C. The TS-1@Co-N-C bifunctional catalyst was finally obtained by suction filtered and washing with deionized water until neutral, vacuum drying at 60°C overnight and then ground for 20 min.

The catalysts with target temperature of 500, 600, 700, 800, 900°C, or with varying mass ratios of TS-1 and dopamine, different mass ratios of TS-1@PDA and cobalt acetate, or varying DA polymerization time (unit h) were all synthesized through the same process.

Synthesis of Co-N-C+TS-1: Zn(NO₃)₂·6H₂O and 2-methylimidazole with a molar ratio of 1:4 were dissolved in a certain amount of methanol. The mixture solution was stirred vigorously at room temperature for 1 h, then allowed to stand for 24 h. ZIF-8 precursor were obtained after centrifugation and vacuum drying overnight. After that, ZIF-8, 1,10-phenanthroline, Co(CH₃COO)₂·4H₂O with a mass ratio of 4:2:1 were mixed and ground evenly. For pyrolysis, the obtained homogeneous powders were heated at a rate of 1°C min⁻¹ to 400°C under N₂ atmosphere, heated at 400°C for 2 h, then the temperature was heated to 900°C at 2°C min⁻¹ and held 3 h. After cooling to room temperature under nitrogen atmosphere, the sample was washed with 200 mL of 0.5 M H₂SO₄ and 30 mL of H₂O₂ (30 wt%) solution at 90°C for 12 h. After cooling to room temperature, a Co-N-C catalyst was obtained by suction filtration and washing to neutrality, drying at 60°C, and then grinding. The obtained Co-N-C and TS-1 with a mass ratio of 1:1 were mixed by ball milling for 1 h to obtain a mechanically mixed catalyst, denoted as Co-N-C+TS-1.

Structural Characterization

Crystal structure was characterized by X-ray diffraction (XRD, Shimadzu 6000) with a scan rate of 10°C min⁻¹. The morphologies were carried out using a scanning electron microscope (SEM, Nova NanoSEM 450) at a voltage of 5 kV. The pore structure was characterized by a N₂ adsorption-desorption analyzer (X1000 analyzer, Kubo Beijing), and the specific surface area was determined by the Brunauer-Emmet-Teller (BET) method. Transmission electron microscopy (TEM) measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. The energy dispersive X-ray (EDX) mapping was carried out to

reveal the element composition and distribution in the samples. Thermal gravimetric analysis (TGA) was performed by using a TGA4000 (Perkin Elmer) in nitrogen flow.

Electrochemical Test

An electrochemical workstation (VersaSTAT 3) was used to evaluate the electrochemical ORR performance of as-prepared catalysts. A three-electrodes system was assembled with a working electrode of rotating ring-disk electrode (RRDE), an Ag/AgCl (3 M KCl) reference electrode and a Graphite rod counter electrode. The catalyst ink was prepared by ultrasound a mixture of 2 mg of prepared catalyst, 1 ml ethanol and 5 μ L Nafion solution (5wt%, Dupont) for 30 min. Then, 10 μ L of this ink was dropped on the RRDE with geometrical surface area of 0.196 cm², then dried at room temperature. After drying, the working electrode was successfully prepared, and catalyst loading is 0.1 mg cm⁻². Firstly, LSV curves was recorded in N₂ saturated 0.1 M HClO₄ solution. The rotating speed and potential sweep rate were set to 1600 rpm and 5 mV s⁻¹, respectively. The applied potential on the disk electrode was 0 to +1.1 V vs RHE, and the ring electrode was set to 1.2 V vs RHE. Then, with these parameters unchanged, the LSV was performed in O₂ saturated 0.1 M HClO₄. The difference between the current density in the O₂ saturated solution and N₂ saturated solution was used to evaluate the ORR activity of the catalyst.

All the potential was converted into the ones relative to the reversible hydrogen electrode (RHE) with the following formula:

$$E_{\text{RHE}} = E(\text{Ag/AgCl}) + 0.197\text{V} + 0.0591 \cdot \text{pH}$$

The H₂O₂ selectivity and the number of electrons transferred were calculated based on the following equations:

$$H_2O_2\% = 200 \times \frac{I_r}{N \times |I_d| + I_r}$$

$$n = 4 \times \frac{|I_d|}{|I_d| + \frac{I_r}{N_C}}$$

An H-type electrolyzer equipped with three-electrode system was used to continuously evaluate the performance of H₂O₂ production from ORR and its coupling with the selective oxidation of organic substrates at +0.1 V (vs. RHE). The working electrode was prepared by dropping the corresponding catalysts ink onto a 4 cm² carbon paper, and catalyst loading was 0.5 mg cm⁻². The experiment was performed at 40°C O₂ saturated 0.1 M H₂SO₄ solution, and the O₂ flow rate was 60 sccm. After reaction, the amount of H₂O₂ in the aqueous solution was measured by titration with 0.01 M potassium permanganate. With the reaction conditions unchanged, a certain amount of phenol was added to conduct a long-time constant voltage electrolysis to explore the performance of H₂O₂ production coupled with organic oxidation. For pair coupled furfural oxidation, TS-1@Co-N-C and nickel foam (NF) were employed as cathode and anode, respectively. The electrolyte in cathode is 0.5 M H₂SO₄ and that in the anode is 1 M KOH solution. Finally, reaction liquid was collected and analyzed by a high-

performance liquid chromatography (HPLC, Shimadzu LC20AD) equipped with a Hypersil BDS-C18 column (5 μm , 4.6 mm \times 150 mm).

The conversion, selectivity, Faradic efficient (FE) were calculated according to the following equations:

$$\text{Conversion} = \frac{n_{CAT} + n_{HQ} + n_B}{n_{phenol}^0} \times 100\%$$

$$S_{CAT} = \frac{n_{CAT}}{n_{CAT} + n_{HQ} + n_{BQ}} \times 100\%$$

$$S_{HQ} = \frac{n_{HQ}}{n_{CAT} + n_{HQ} + n_{BQ}} \times 100\%$$

$$S_{BQ} = \frac{n_{BQ}}{n_{CAT} + n_{HQ} + n_{BQ}} \times 100\%$$

$$FE = \frac{2F(n_{CAT} + n_{HQ})}{Q} \times 100\%$$

where catechol (CAT) and hydroquinone (HQ) are the target products and benzoquinone (BQ) is the byproduct; n_{phenol}^0 denotes the initial amount of phenol and n_{CAT} , n_{HQ} and n_{BQ} are the detected amounts of corresponding compounds after reaction. FE is the Faradic efficiency for target products, F is the Faradic constant (96485 C mol⁻¹) and Q is the amount of total consumed charge.

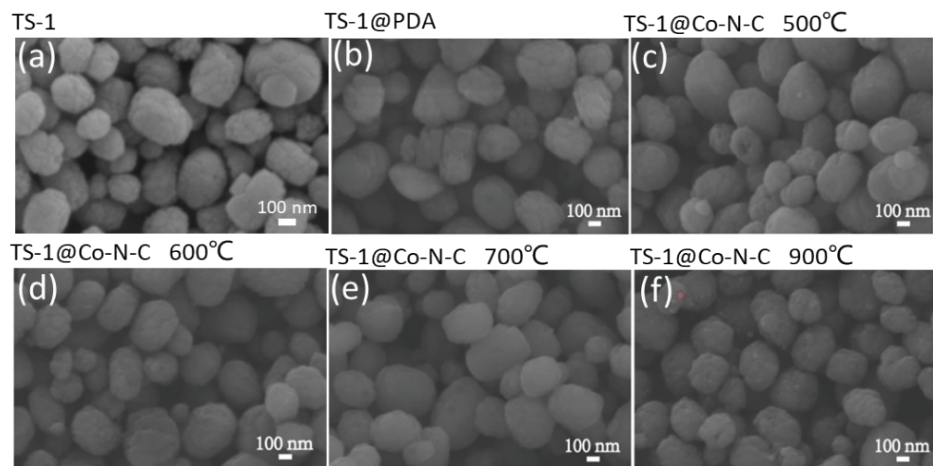


Figure S1. SEM images of TS-1, TS-1@PDA and TS-1@Co-N-C pyrolyzed at different temperature.

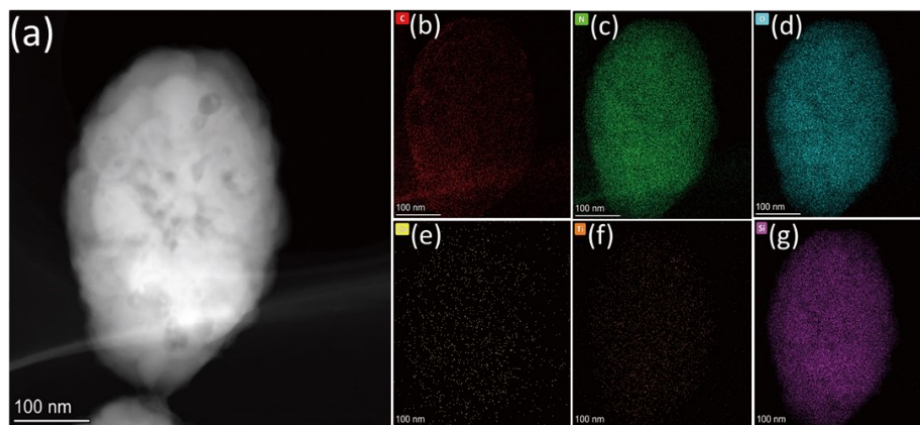


Figure S2. The HAADF-STEM image and corresponding EDX mapping of TS-1@Co-N-C.

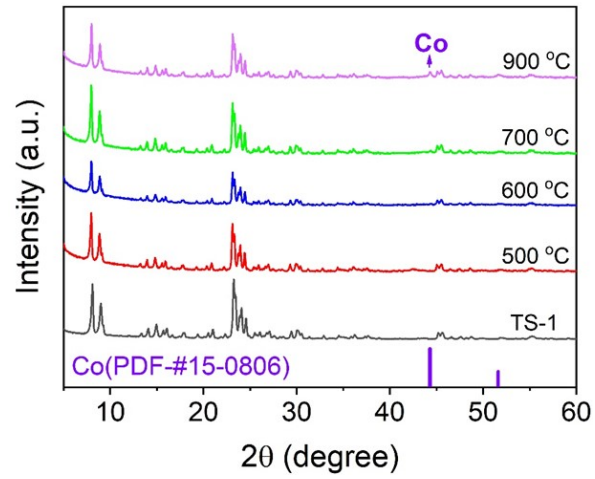


Figure S3. The XRD patterns of prepared TS-1@Co-N-C catalysts pyrolyzed at different temperature.

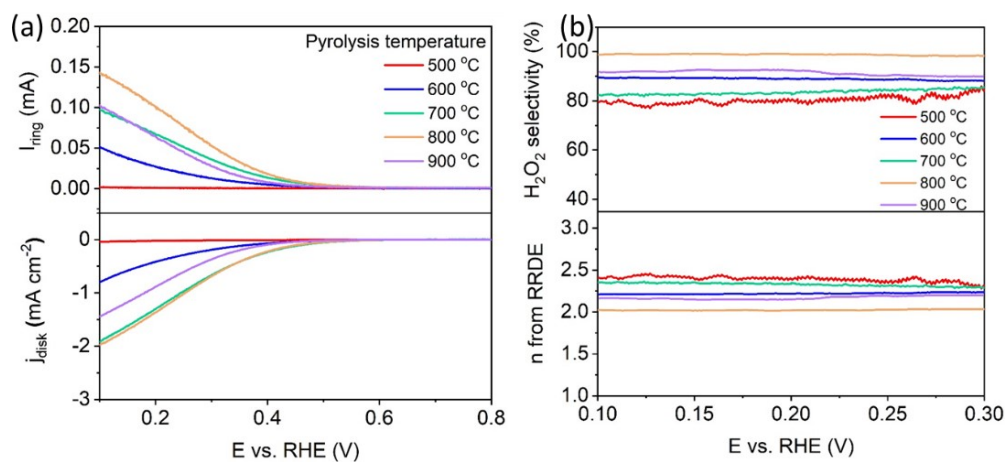


Figure S4. ORR performance of TS-1@Co-N-C catalysts pyrolyzed at different temperature. (a) RRDE polarization curves at 1600 rpm in O₂ saturated 0.1 M HClO₄ solution at 10 mV s⁻¹ and (b) The calculated H₂O₂ selectivity and number of transferred electrons.

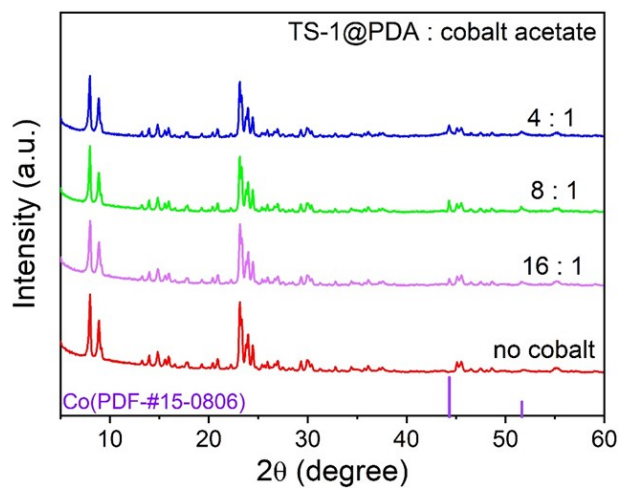


Figure S5. The XRD patterns of prepared TS-1@Co-N-C catalysts with varying cobalt content.

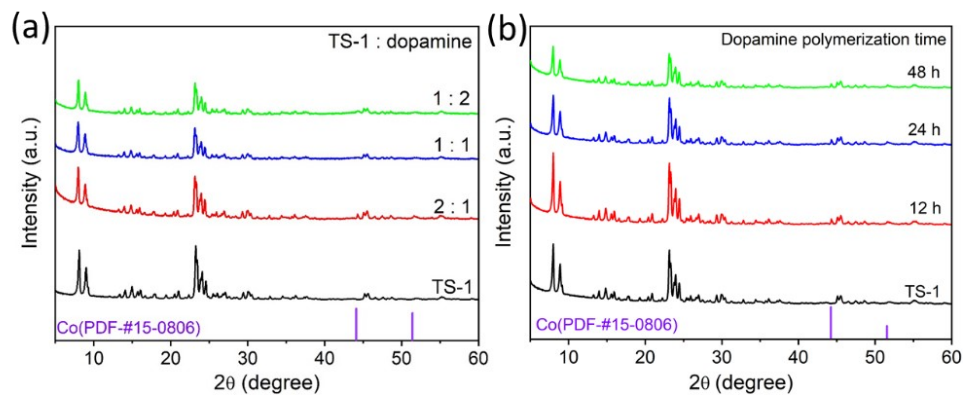


Figure S6. The XRD patterns of prepared TS-1@Co-N-C (a) with varying mass ratio of TS-1 and DP and (b) different polymerization time.

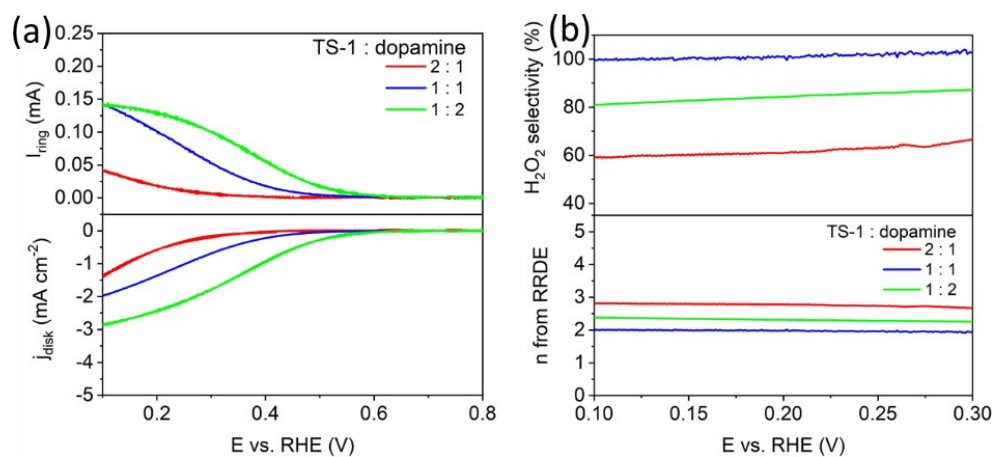


Figure S7. ORR performance of TS-1@Co-N-C catalysts with varying addition of DP and types of nitrogen sources. (a) RRDE polarization curves at 1600 rpm in O₂ saturated 0.1 M HClO₄ at 10 mV s⁻¹. (b) The calculated H₂O₂ selectivity and number of transferred electrons.

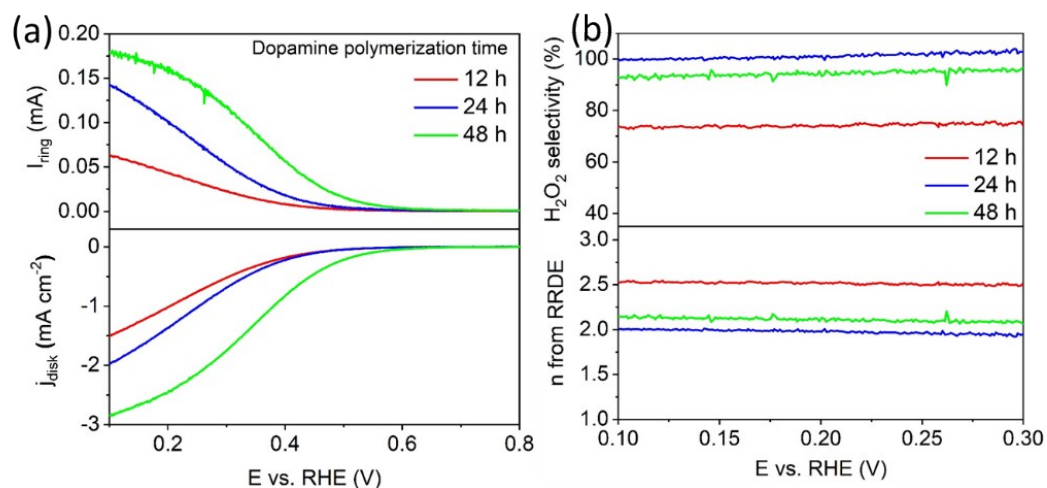


Figure S8. ORR performance of TS-1@Co-N-C catalysts with different polymerization time. (a) RRDE polarization curves at 1600 rpm in O_2 saturated 0.1 M HClO_4 at 10 mV s^{-1} . (b) The calculated H_2O_2 selectivity and number of transferred electrons.

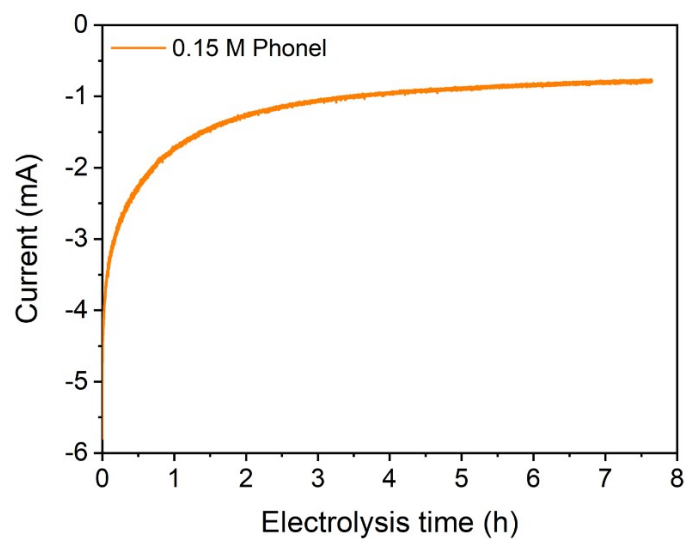


Figure S9. Constant voltage electrolysis for TS-1@Co-N-C at 0.1 V vs. RHE in O₂ saturated 0.1 M H₂SO₄ with 0.15 M phenol.

Table S1. Results of phenol oxidation catalyzed by different catalysts

Catalyst	Phenol Conversion /%	Selectivity /%		
		Catechol	hydroquinone	Benzoquinone
No catalyst	0.08	100	0	0
TS-1	2.82	37.75	62.25	0
Co-N-C	0.01	5	0	95
Co-N-C+TS-1	0.56	10.20	25.37	64.43
TS-1@ Co-N-C-800	1.81	45.04	40.74	14.22

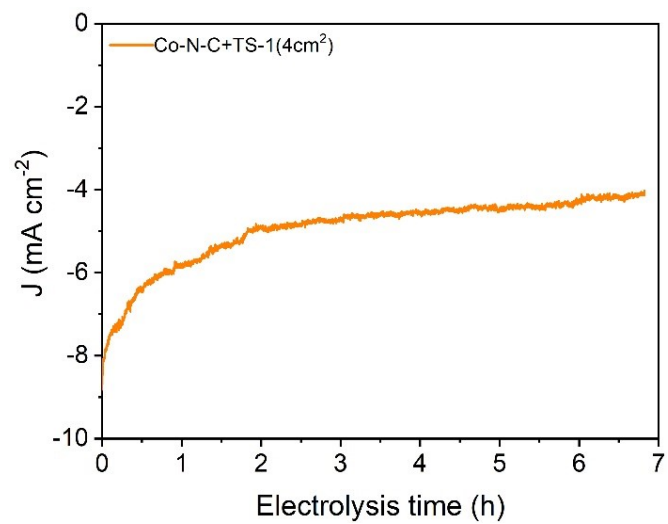


Figure S10. Constant voltage electrolysis for Co-N-C+TS-1 at 0.1 V vs. RHE in O₂ saturated 0.1 M H₂SO₄ with 0.15 M phenol.

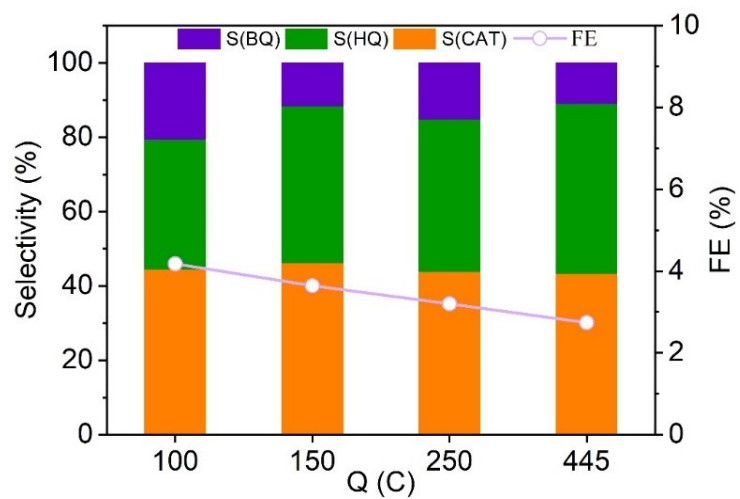


Figure S11. Selectivity and FE over passing charge during the preparative electrolysis of phenol on Co-N-C+TS-1.