

Titanium Carbide Composite Hollow Cobalt Sulfide Heterojunction with Function of Promoting Electron Migration for Efficiency Photo-Assisted Electro-Fenton Cathode

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Text S1

The ORR performance was evaluated on a standard three electrode system on CHI760E (CH instruments, USA). All tests were performed in 0.1 M KOH and 0.1 M Na₂SO₄. The working electrodes were prepared as following steps: the catalyst ink was first prepared by dispersing 5 mg catalyst and 50 μ L Nafion in 200 μ L ethanol solution

and 200 μL deionized water with sonication. Then 15.5 μL of the catalyst ink was drop cast onto the rotating disk electrode (Pine, USA). Cyclic voltammetry (CV) was performed separately on the disk and the ring between -1.6 V and 0.5 V vs SCE at 50 mV/s and 0 rpm in O_2 -saturated electrolyte. RRDE voltammograms of Fig. 5 were recorded by performing LSV on the disk from -1 V to 0.2 V vs. SCE at 50 mV/s and different rotation rates (400, 625, 900, 1225, and 1600 rpm). To record RRDE voltammograms in O_2 -saturated electrolyte, LSV of the catalyst -casted disk was swept in positive direction from -1 V to 0.2 V vs. SCE. meanwhile the Pt ring was held at 1.48 V vs. RHE.

The Koutecki-Levich (K-L) equation (Eq. 1-2) was used to calculate electron transfer number (n) based on the LSVs at various rotation speed of RDE.

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = nFkc_0 + \frac{1}{B\omega^{\frac{1}{2}}} \quad (1)$$

$$B = 0.62nFC_o(D_o)^{\frac{2}{3}}\nu^{-\frac{1}{6}} \quad (2)$$

where J is the measured current density of the working electrode, ω is the angular velocity of the rotating electrode, J_K and J_L are the kinetic and diffusion limiting current densities, F is the Faraday constant (96485 C/mol), n is the electron transfer number during ORR process, ω (s^{-1}) is rotation rate, ν ($1.0 \times 10^{-2} \text{ cm}^2/\text{s}$) is the kinematic viscosity of the 0.1 M KOH solution, D_o and C_o are the diffusivity and solubility of oxygen in 0.1 M KOH solution, respectively. The ORR activity and selectivity were investigated by polarization curves and rotating ring-disk electrode measurements in O_2 saturated electrolyte at a scan rate of 50 mV/s.

The H_2O_2 selectivity (p) and the electron transfer number (n) is calculated using the following equations:

$$p = 2 \times \frac{\frac{i_{ring}}{N}}{i_{disk} + \frac{i_{ring}}{N}} \quad (3)$$

$$n = 4 \times \frac{i_{disk}}{i_{disk} + \frac{i_{ring}}{N}} \quad (4)$$

where i_{disk} and i_{ring} are the disk and the ring current, respectively, and N is the collection efficiency determined.

Text S2

Characterizations: Scanning electron microscopy (SEM, Hitachi, SU8010), Transmission electron microscope and energy dispersive spectroscopy (TEM, FEI, Tecnai G2 F20), X-ray diffraction (XRD) were performed by the Bruker D8 Advance diffractometer with Cu K α radiation source. X-ray photoelectron spectroscopy (XPS) was measured with the Thermo ESCALAB 250XI. The electrochemical property of electrochemical impedance spectroscopy (EIS), Linear-sweep voltammetry (LSV) and chronoamperometry was performed with CHI 760D electrochemical workstation (CH Instruments, Inc., Shanghai) integrated with a three-electrode system. Electron paramagnetic resonance (EPR, Bruker, A300) tests for reactive species detection were performed by employing DMPO as the spin trapping agents.

Preparation of CoS₂/CoS/Ti₃C₂ cathode: A catalyst ink was prepared by mixing 25 mg CoS₂/CoS/Ti₃C₂ with 200 μ L ethanol, 200 μ L deionized water and 50 μ L PTEF after ultrasonic treatment for 30 min. Then, the ink was dipcoated onto carbon cloth (CC) (working area of 5 cm²) and dried at 60°C to prepare CoS₂/CoS/Ti₃C₂ cathode. Similarly, CoS, CoS₂, CoS₂/CoS cathode were obtained in the same way.

Experimental procedure: All typical experiments were carried out in a cylindrical single electrolytic cell. The 500 W Xe lamp was introduced as light source, and SMT

in 0.1 M Na₂SO₄ solution was served as the pollutants. Oxygen was kept flowing into the solution throughout the degradation process at a flow rate of 60 mL/min. The CoS₂/CoS/Ti₃C₂/CC worked as the cathode. 1 mL sample solution were taken at set intervals using an organic filter. The micro-pollutants concentration during the degradation was measured by High Performance Liquid Chromatography (HPLC) (LC-10ADVP, Shimadzu) equipped with a C18 column (2.1×150 mm, particles size 1.9μm). The mobile phase of SMT was a mixture of 0.1% formic acid solution (A) and acetonitrile (B) and the ratio was 4:1. The injection volume of the sample was 10 μL and the flow rate was 0.5 mL/min. The degradation intermediates of sulfadiazine were identified by the QTOF LC/MS (UPLC-M-QTOF).

Table S1 the percentages of various atoms in CoS₂/CoS/Ti₃C₂

| Name | Start BE | Peak BE | End BE | Height CPS | FWHM eV | Area (N) TPP-2M | Atomic % |
|------|----------|---------|--------|------------|---------|-----------------|----------|
| C1s | 297.98 | 284.48 | 279.18 | 26923.25 | 2.92 | 1224.48 | 51.73 |
| Co2p | 811.98 | 778.25 | 771.18 | 37442.33 | 2.39 | 320.47 | 13.54 |

| | | | | | | | |
|------|--------|--------|--------|----------|------|--------|-------|
| S2p | 174.98 | 161.66 | 157.18 | 21450.12 | 2.89 | 762.81 | 32.23 |
| Ti2p | 474.98 | 458.45 | 448.18 | 7407.63 | 1.27 | 59.22 | 2.5 |

Table S2 the percentages of various bonds in CoS₂/CoS/Ti₃C₂

| name | Ti 2p | | | S 2p | | | | Co 2p | | | | |
|-------------|-------|-------|-------|-------|------------------------------|-----------------|-----------------|------------------------------|------------------|-------|------------------|------------------|
| bonds | Ti-C | Ti-O | Ti-O | Ti-F | S ₂ ²⁻ | S ²⁻ | S ⁶⁺ | S ₂ ²⁻ | Co ²⁺ | Sat. | Co ³⁺ | Co ²⁺ |
| | | 2p3/2 | 2p1/2 | | 2p3/2 | 2p3/2 | | 2p1/2 | 2p3/2 | | 2p1/2 | 2p1/2 |
| percentages | 21.8% | 29.2% | 35.6% | 13.4% | 39.2% | 15.7% | 34.0% | 11.1% | 37.0% | 41.5% | 11.0% | 10.5% |

Table S3 performance comparisons of similar research

| catalyst/cathode | electrode area | initial pH | Potential/ current | Target pollutant | reaction speed | Catalyst loading | Ref. |
|---|--------------------|---------------|------------------------|-----------------------|-------------------|----------------------|------|
| CFP@PANI@ MIL-101 | 2 cm ² | 3 | 5 mA/cm ² | dimethyl phthalate | 0.031 | --- | [12] |
| CFP@CoFe ₂ O ₄ | 2 cm ² | 3 | 5 mA/cm ² | p-nitrophenol | 0.035 | --- | [13] |
| B@Ni-F/Fe ²⁺ | 2 cm ² | 3 | 10 mA/cm ² | sulfamerazin e | 0.002 | --- | [47] |
| Fe ₃ O ₄ /N-rGO | 7 cm ² | 3 | 9 mA/cm ² | Bisphenol A | 0.029 | --- | [48] |
| F-BPC | 40 cm ² | 5 | 7.5 mA/cm ² | sulfathiazole | 0.02 | 1 g/L | [49] |
| CMIL- NH ₂ @PCMs | 5 cm ² | 7 | -0.14 V | napropamide | 0.028 | --- | [50] |
| FeS ₂ NWs/Ti ₃ C ₂ | 5 cm ² | 3 | 200 mA | sulfamerazin e | 0.046 | 7 mg/cm ² | [28] |

| | | | | | | | |
|--|-------------------|---|-----------------------|-------------------|-------|----------------------|-----------|
| Pd-Ti/TiO ₂ NTs | --- | 7 | 20 mA | Trichloroethylene | 0.019 | --- | [51] |
| CoS ₂ /CoS/Ti ₃ C ₂ | 5 cm ² | 3 | 20 mA/cm ² | sulfamerazine | 0.031 | 5 mg/cm ² | This work |

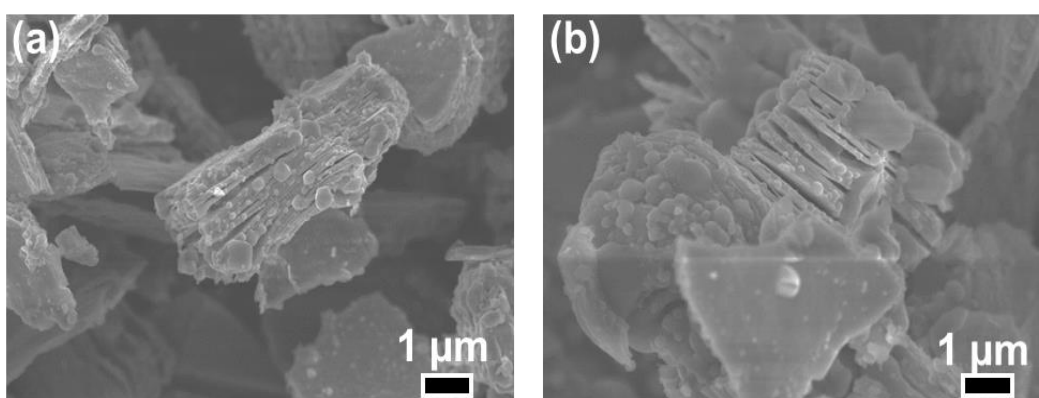


Figure S1. Morphology of Ti₃C₂ sample before etching with hydrofluoric acid.

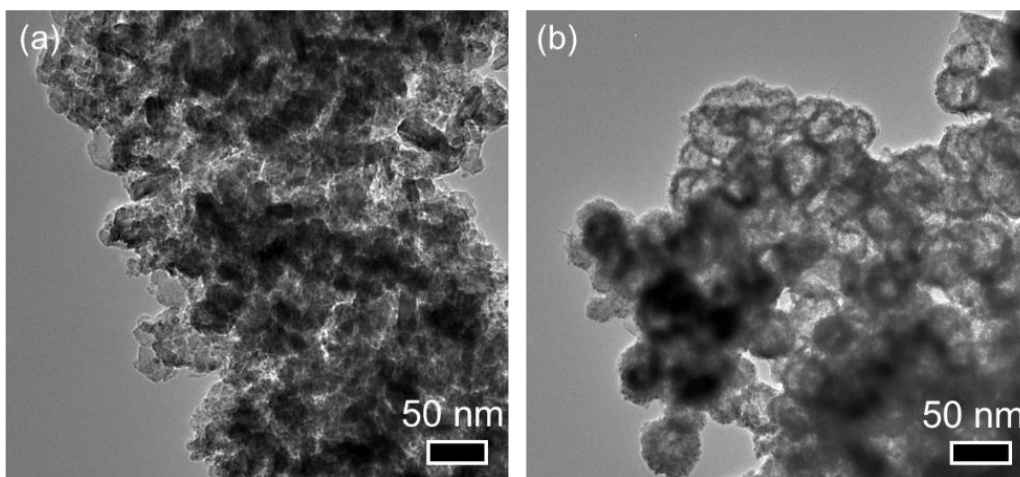


Figure S2. TEM of (a) CoS_2/CoS (b) $\text{CoS}_2/\text{CoS}/\text{Ti}_3\text{C}_2$.

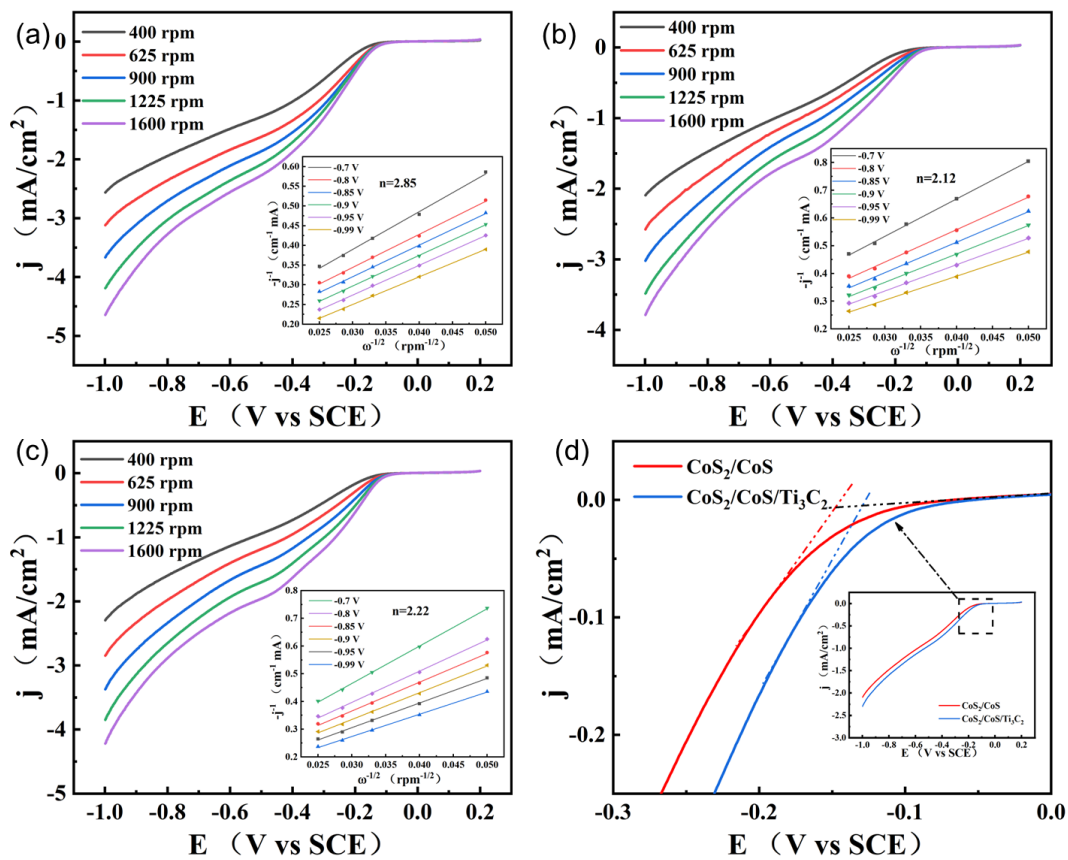


Figure S3. LSVs of (a) CoS_2 , (b) CoS_2/CoS , (c) $CoS_2/CoS/Ti_3C_2$ performed with RDE test in O_2 -saturated ($697 \mu g/cm^2$) and the corresponding K-L curves (inset), (d) LSVs of CoS_2/CoS and $CoS_2/CoS/Ti_3C_2$.

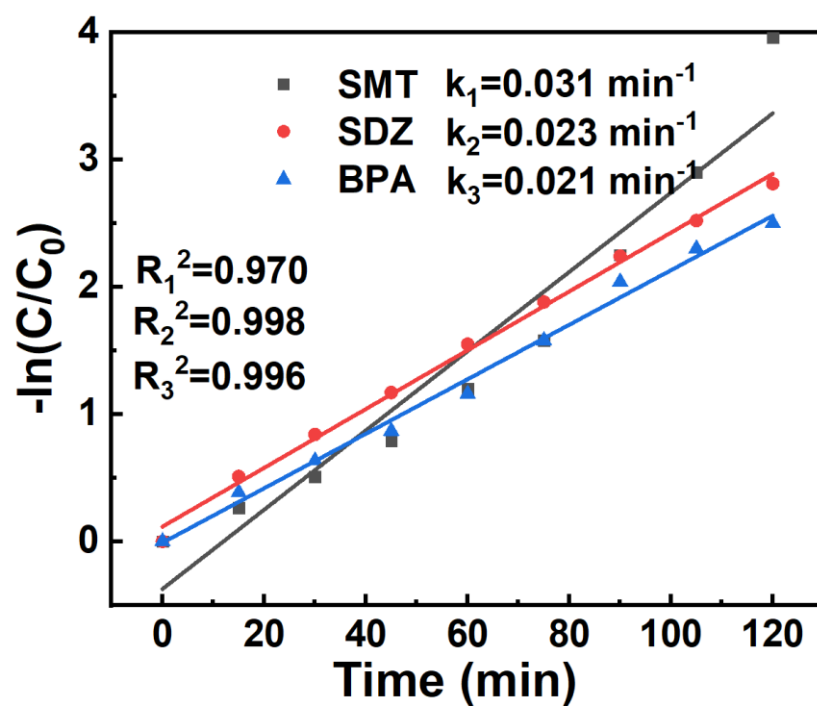


Figure S4. Pseudo first order reaction rate of different substrates in CoS₂/CoS/Ti₃C₂ cathode system.

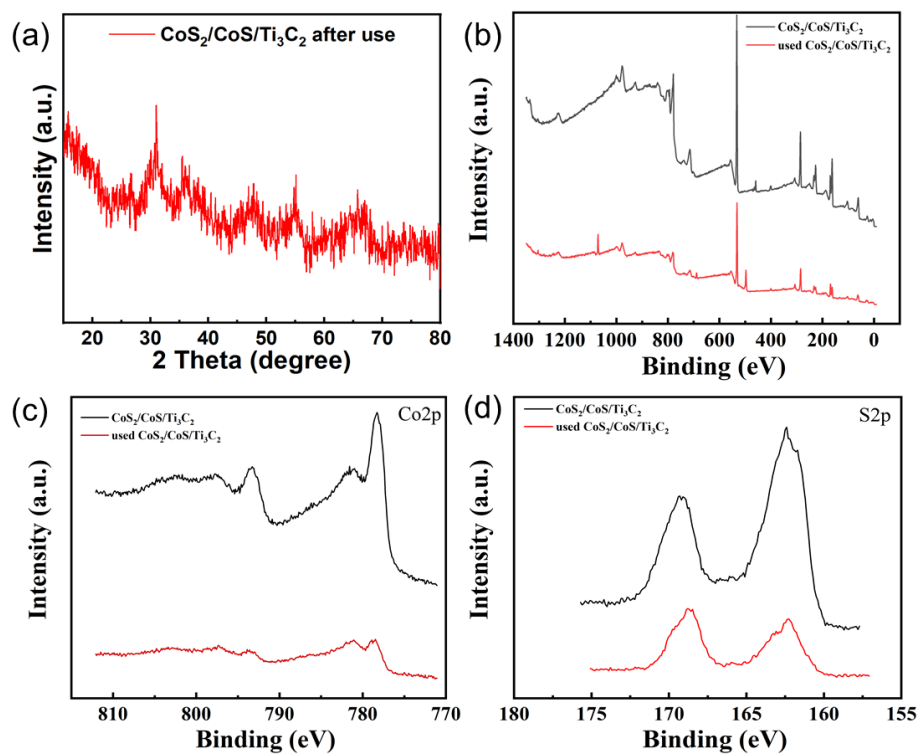


Figure S5. (a) XRD pattern and (b-d) XPS of used $\text{CoS}_2/\text{CoS}/\text{Ti}_3\text{C}_2$ catalyst.

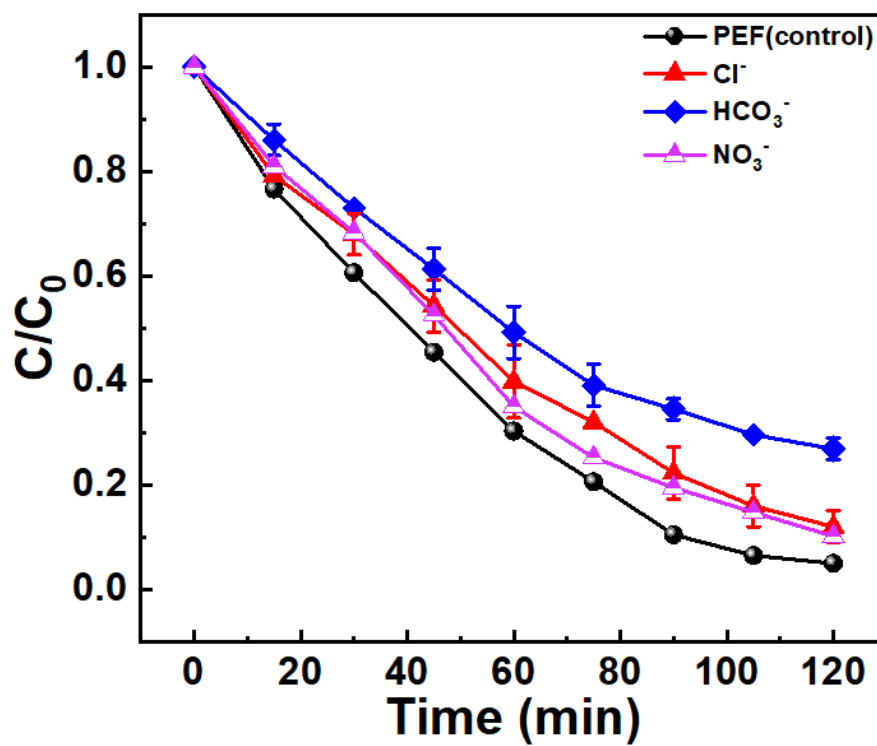


Figure S6. Resistance to ion interference of $\text{CoS}_2/\text{CoS}/\text{Ti}_3\text{C}_2$ cathode

