Supporting Information

Bromine-mediated Strategy Endows Efficient Electrochemical Oxidation of Amine to Nitrile

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Experimental Section

Materials and Methods

No further purification was performed on the reagents and materials obtained from suppliers unless otherwise specified. The following chemicals were procured from Sinopharm Chemical Reagent Co., Ltd with a purity of 99%: NaBr, $CoSO_4 \cdot 7H_2O$, $CO(NH_2)_2$ (urea), *N*,*N*-dimethylformamide (DMF), ethylene glycol (EG), CH_3OH and C_2H_5OH. Sigma Aldrich supplied the amine substrates. GaossUnion Optoelectronics Technology Co., Ltd provided the electrodes (Pt sheet, glassy carbon, reference electrode). Graphite felt (GF) was acquired from Beijing Jinglong Special Carbon Graphite Factory.

FEI Nova NanoSEM NPE218 was employed for the SEM images. The conversion and selectivity of the substrates (Figure S9-S15) and product were analyzed by GC-MS-QP 2010 SE (SHIMADZU). Electrochemical testing was conducted using an electrochemical workstation CHI760E from Shanghai Chenhua Instrument Co., Ltd.

Metal sulfide synthesis and characterization

A one-step solvothermal method was used to synthesize CoS_2/CoS, heterojunction nanoparticles[29]. 2 mmol $CoSO_4 \cdot 7H_2O$, 10 mmol urea, and 25 mmol sublimated sulfur were dissolved in a 70 mL mixture of 30 mL ethylene glycol (EG) and 40 mL DMF. The precursor solution was stirred for 1 h and then poured into a 100 mL Teflon-lined autoclave. The autoclave was heated to 180 °C, kept for 12 h, and cooled to room temperature followed by centrifuging at 7000 rpm for 5 minutes. The samples were rinsed several times with ethanol and deionized water (DI) before being dried under vacuum at 60 °C for 12 h.

In situ generated metal sulfide catalysts on GF and electrode preparation

The precursor solution of CoS_2/CoS was prepared as described above. The modified GF was obtained by immersing the purchased GF (1 cm ×1 cm × 3 mm) in 6 M H_2SO_4 for 12 h, then washing it with DI until the pH was neutral. The modified GF was then transferred into precursor solutions of different metal sulfides for 12 h at 180 °C. After cooling, the GF loaded with metal sulfides was cleaned several times in an ultrasonic cleaner with water until no particles were observed in the washing solution, and then they were dried under vacuum for 12 h at 60 °C to get the final CoS_2/CoS@GF electrode. The mass loading of CoS_2/CoS on the GF was 1.05 mg cm^{-2}.

Br^-/Br_2 redox reaction evaluated by Linear Sweep Voltammetry (LSV)

The catalyst ink was prepared by dispersing 10 mg of CoS_2/CoS in a mixed solution containing 750 μL of H_2O, 200 μL of C_2H_5OH, and 50 μL of Nafion. The ink was then uniformly dropped onto a glassy carbon electrode and allowed to dry naturally to prepare the working electrode. Platinum and saturated calomel electrodes were used as the counter and reference electrodes, respectively. 0.1 M $NaNO_3$ was used as the supporting electrolyte to enhance the solution's conductivity. The electrolyte composition for the Br^-/Br_2 redox reaction was 5 mM NaBr + 0.1 M $NaNO_3$. The scan rate was 50 mV s^{-1}.

Electrochemical synthesis of nitrile from the amine

A typical procedure was as follows: A methanol (25 mL) solution of octylamine (259 mg, 2 mmol) and NaBr (206 mg, 2 mmol) was put in a conventional single cell with CoS_2/CoS@GF (1 cm ×1 cm) as the anode and GF as the cathode (1 cm ×1 cm). A constant current of 60 mA was applied to the cell for 4 h. GC-MS was used to examine the conversion and selectivity of the product using dodecane as internal standard. Before the recycling test, the working electrode was rinsed several times with ethanol and DI water.

The analysis of the product

A sample (500 μL) of the reaction solution was mixed with dichloromethane (500 μL), DI (500 μL), and dodecane (0.2 μL) for extraction, and then dehydrated with anhydrous magnesium sulfate. The extract was subjected to GC-MS to identify the products and quantify the conversion and selectivity.

The conversion (%) of amines and selectivity (%) of nitriles were calculated using the equations below.

$$\textbf{Conversion (\%)} = \frac{Mole\ of\ amine\ consumed}{Mole\ of\ initial\ amine} \times 100\%$$

$$\textbf{Selectivity (\%)} = \frac{Mole\ of\ formed\ nitrile}{Mole\ of\ consumed\ amine} \times 100\%$$

The Faradaic efficiency (*FE*) was computed as follows:

$$\textbf{FE (\%)} = \frac{N_i \times n \times F}{Q} \times 100\%$$

where N_i is the number of moles for the specific product (mole); n is the number of electrons exchanged for product formation, which is $4e^-$ in this reaction; F is the Faradaic constant of 96487 C mol^{-1}, Q is the passed charge.

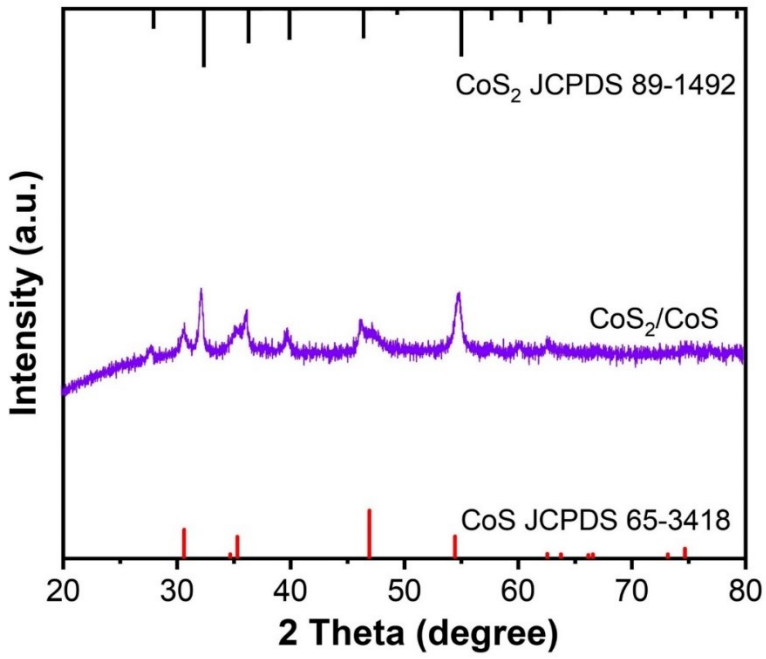


Figure S1 PXRD patterns of the prepared CoS_2/CoS heterojunction.

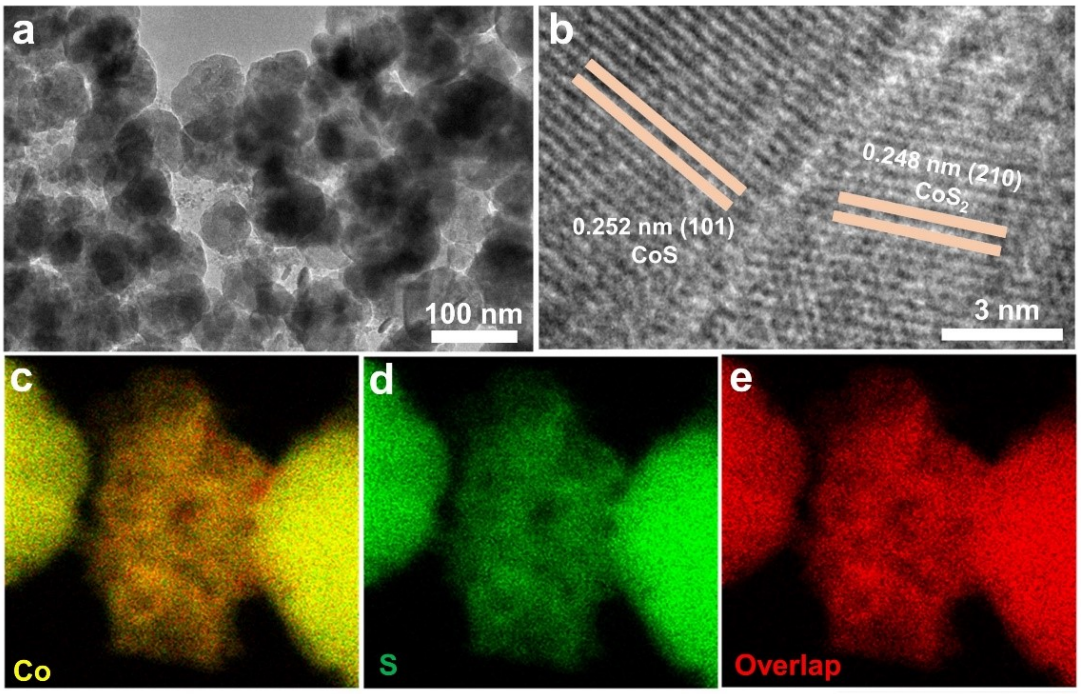


Figure S2 (a) TEM image and (b) High-resolution TEM image of CoS_2/CoS heterojunction, (c-e) elemental mappings of Co and S.

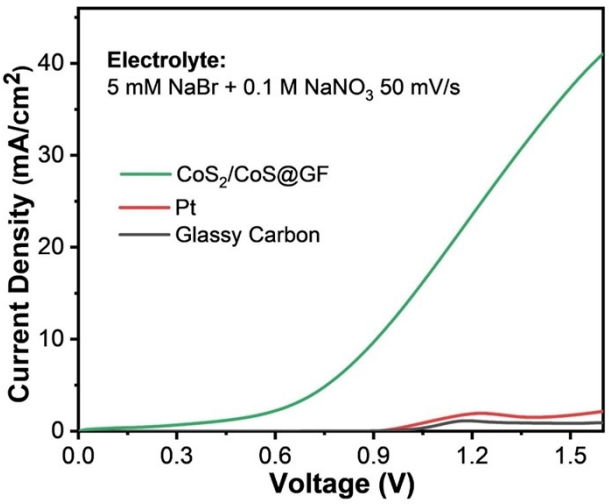


Figure S3 LSV curves of Br^- oxidation ability of the working electrodes: CoS_2/CoS heterojunction, glassy carbon, and platinum.

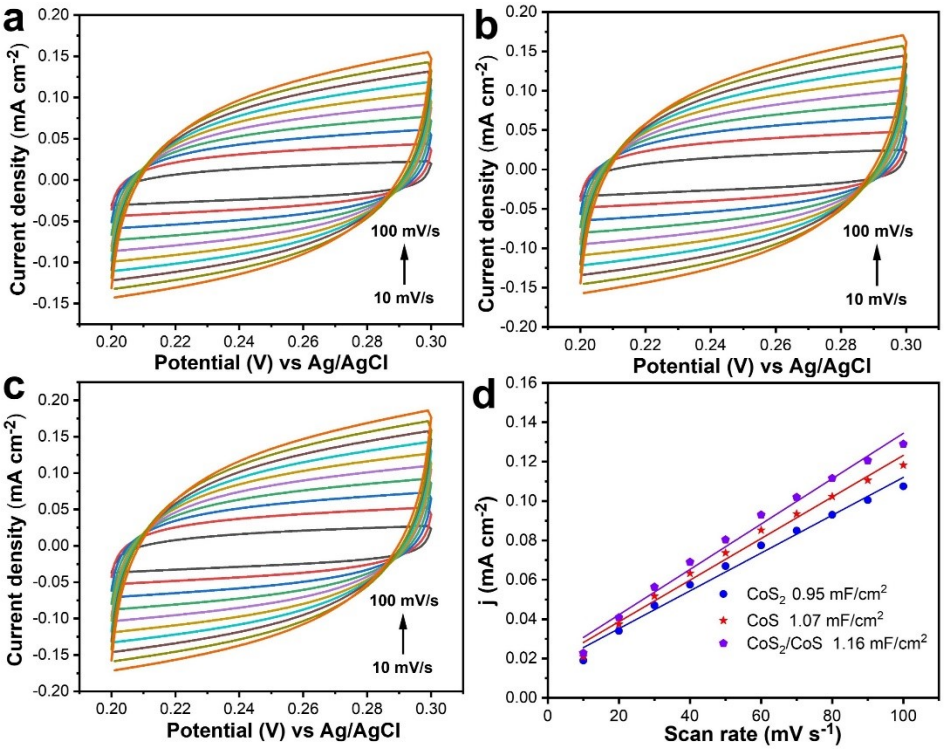


Figure S4 The cyclic voltammetry spectra for (a) CoS_2 (b) CoS, (c) CoS_2/CoS in 0.5 M NaBr aqueous solution in the potential range of 0.2 -0.3 V. (d) Capacitive currents at 0.25 V (vs. Ag/AgCl) of CoS_2, CoS, CoS_2/CoS in 0.5 M NaBr buffer solution. Counter electrode: Platinum. Reference electrode: Ag/AgCl. Scan rate: 10-100 mV/s.

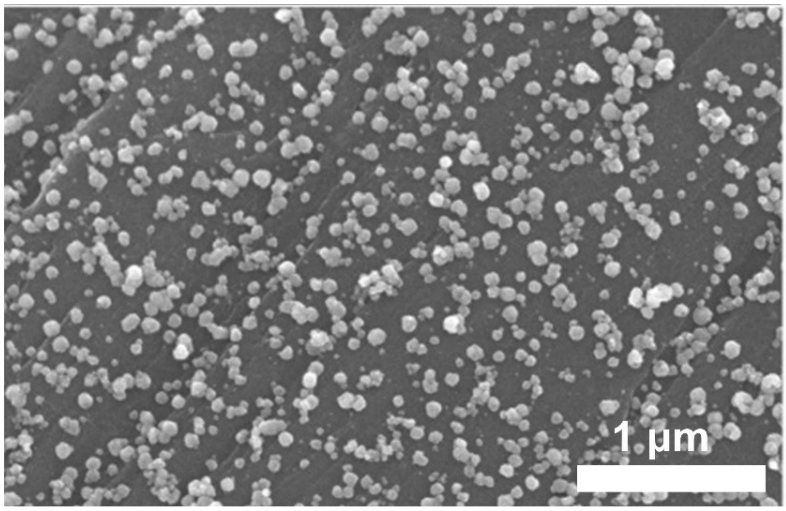


Figure S5 (a) High-resolution SEM image of CoS_2/CoS@GF electrode.

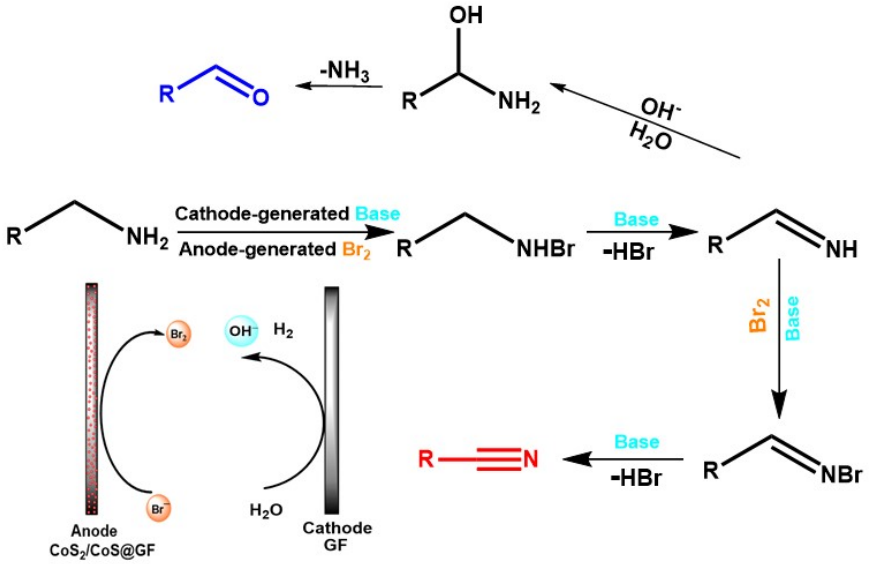


Figure S6 Reaction pathways of electrochemical conversion of amines to nitriles mediated by Br^-/Br_2 redox mediator.

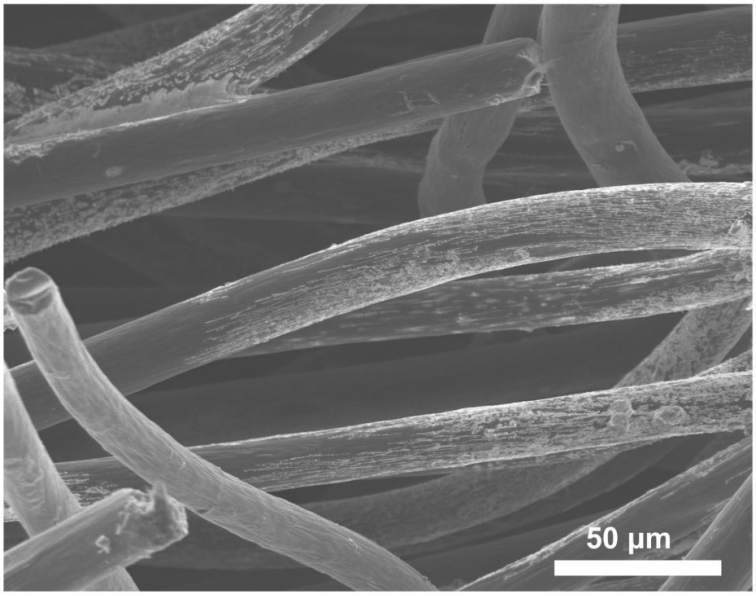


Figure S7 SEM images of the prepared CoS_2/CoS@GF heterojunction electrode after 5 cycles of the electrochemical reaction.

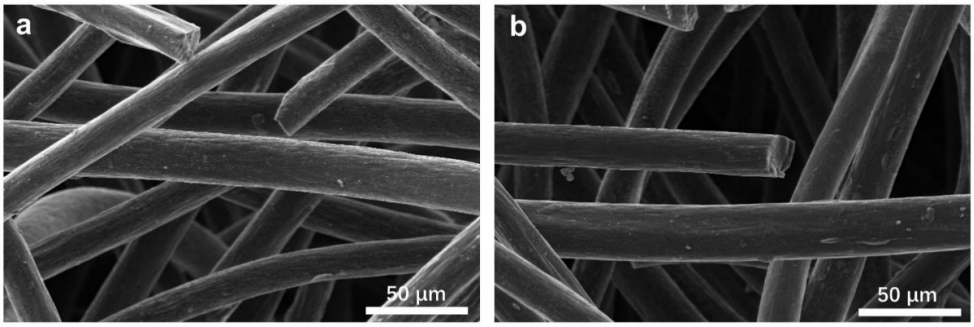


Figure S8 SEM images of the GF cathode (a) before the experiment; (b) after 5 cycles of the electrochemical reaction.

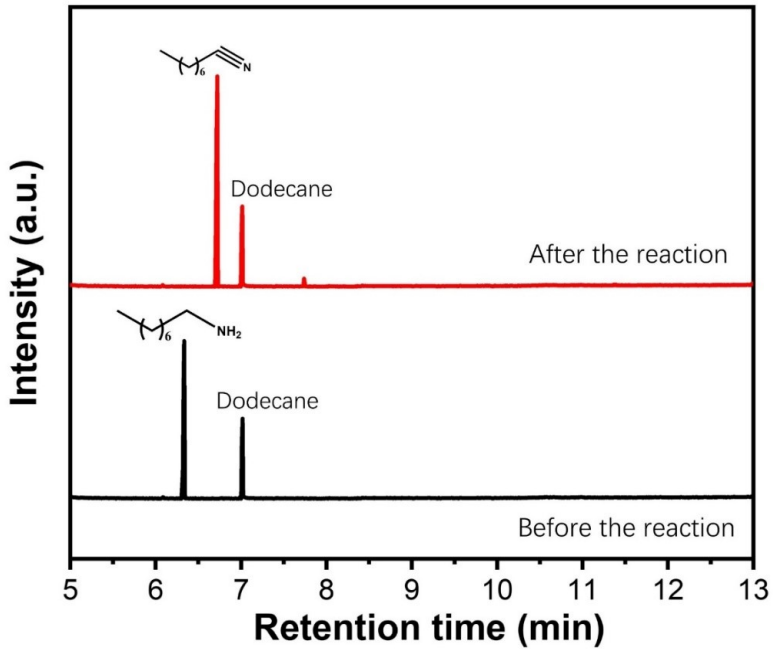


Figure S9 Gas chromatography-mass spectrometry (GC-MS) spectrum of electrochemical oxidation of octylamine to octanenitrile under 60 mA for 4 h using CoS_2/CoS@GF as the anode and GF as the cathode. Dodecane was used as the internal standard for quantification.

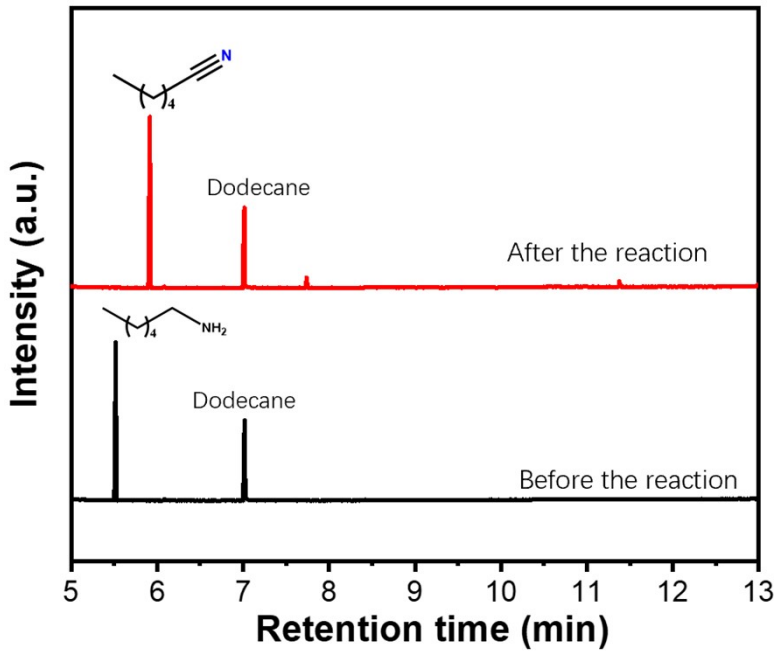


Figure S10 Gas chromatography-mass spectrometry (GC-MS) spectrum of electrochemical oxidation of hexanamine to hexanenitrile under 60 mA for 4 h using CoS_2/CoS@GF as the anode and GF as the cathode. Dodecane was used as the internal standard for quantification.

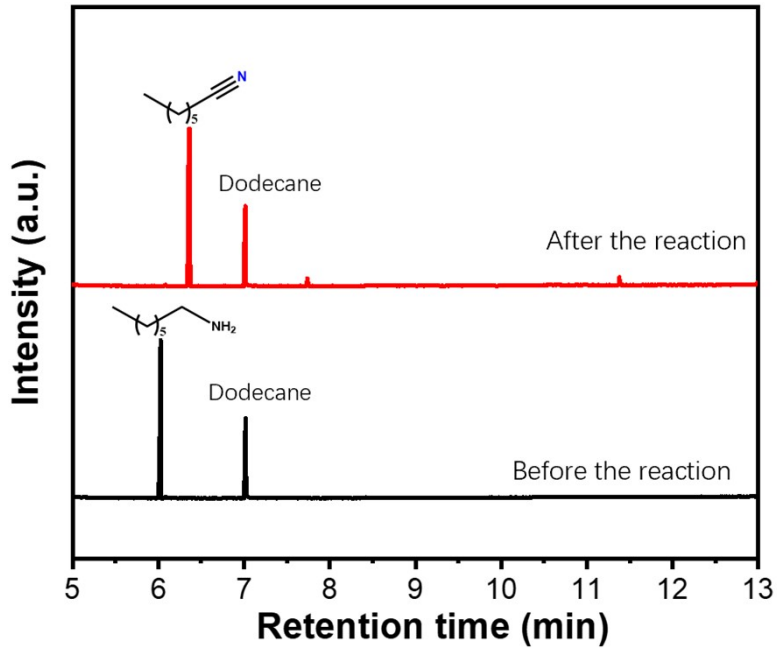


Figure S11 Gas chromatography-mass spectrometry (GC-MS) spectrum of electrochemical oxidation of heptanamine to heptanonitrile under 60 mA for 4 h using CoS_2/CoS@GF as the anode and GF as the cathode. Dodecane was used as the internal standard for quantification.

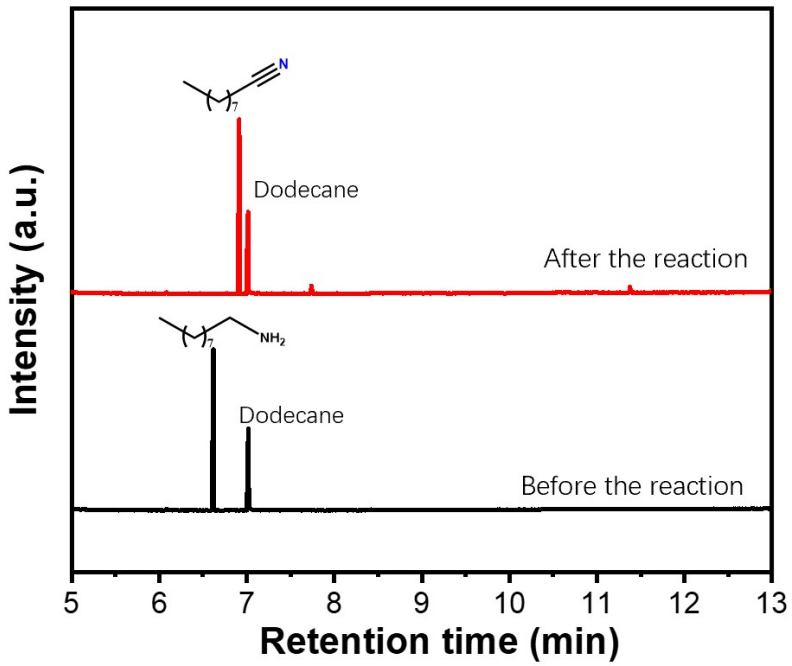


Figure S12 Gas chromatography-mass spectrometry (GC-MS) spectrum of electrochemical oxidation of nonylamine to nonanenitrile under 60 mA for 4 h using CoS_2/CoS@GF as the anode and GF as the cathode. Dodecane was used as the internal standard for quantification.

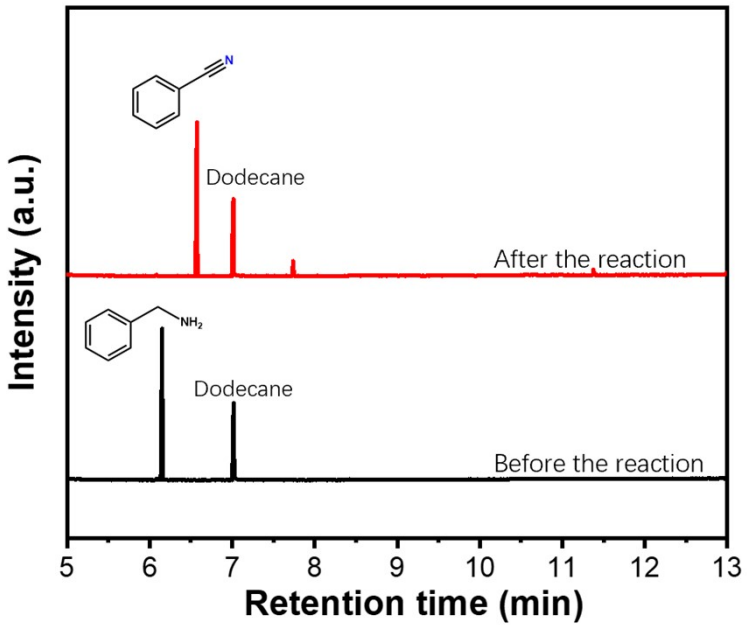


Figure S13 Gas chromatography-mass spectrometry (GC-MS) spectrum of electrochemical oxidation of benzylamine to benzonitrile under 60 mA for 4 h using CoS_2/CoS@GF as the anode and GF as the cathode. Dodecane was used as the internal standard for quantification.

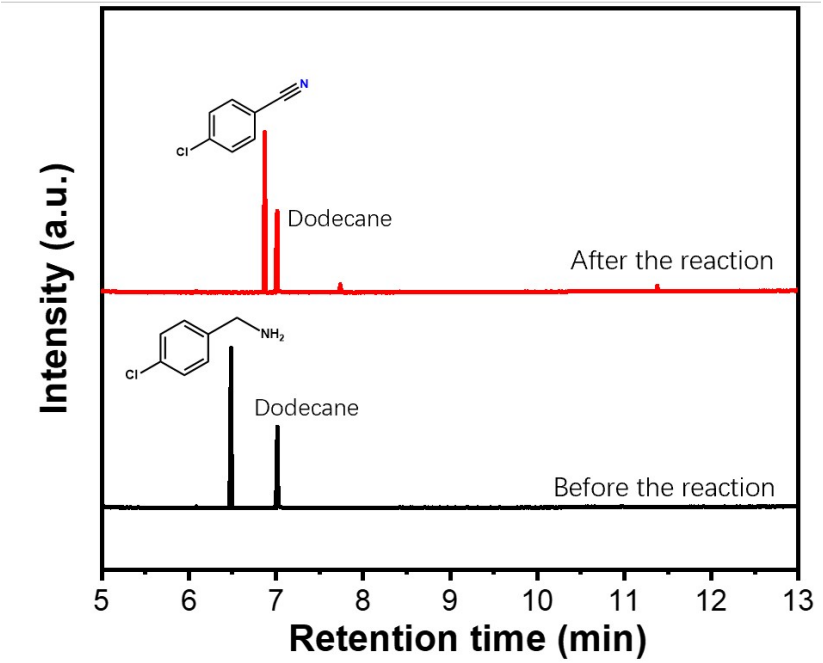


Figure S14 Gas chromatography-mass spectrometry (GC-MS) spectrum of electrochemical oxidation of 4-chlorobenzylamine to 4-chlorobenzonitrile under 60 mA for 4 h using CoS_2/CoS@GF as the anode and GF as the cathode. Dodecane was used as the internal standard for quantification.

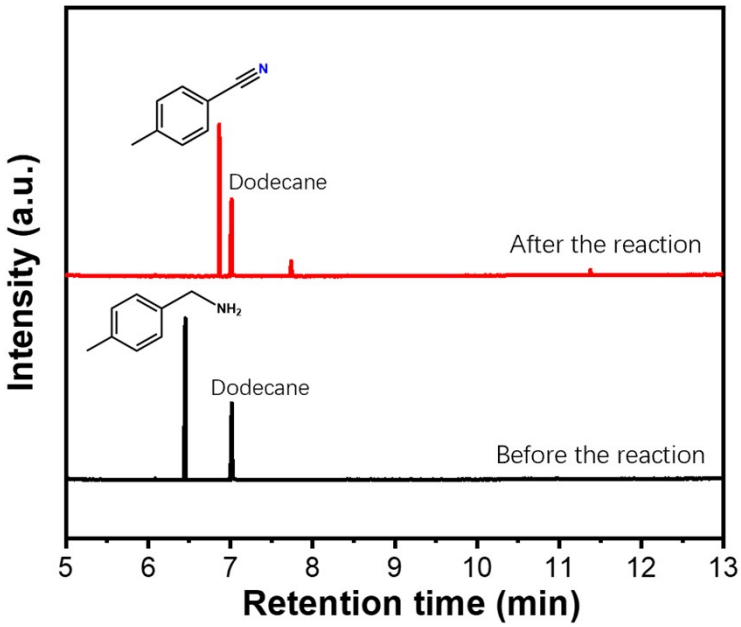


Figure S15 Gas chromatography-mass spectrometry (GC-MS) spectrum of electrochemical oxidation of 4-methylbenzylamine to p-tolunitrile under 60 mA for 4 h using CoS_2/CoS@GF as the anode and GF as the cathode. Dodecane was used as the internal standard for quantification.

Table S1 The effect of temperature on the yield of the nitrile[a]

Temperature (℃)	Conversion[b] (%)	Selectivity[b] (%)	FE (%)
10	100	97(4)	86
20	100	98(3)	87
30	100	98(3)	87
40	100	91(2)	81

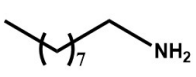
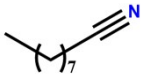
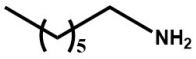
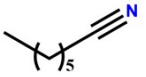
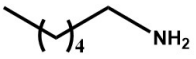
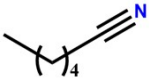
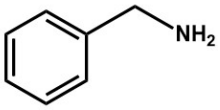
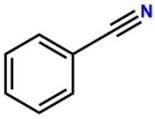
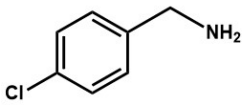
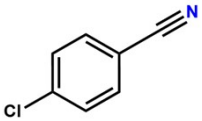
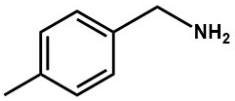
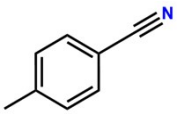
[a]Undivided cell: octylamine: 2 mmol, a constant current of 60 mA at 10, 20, 30, 40 °C for 4 h, anode: CoS_2/CoS@GF, cathode: GF. [b]Determined by GC-MS integrals. Errors are in parentheses.

Table S2 Yield of nitrile and FE using CoS_2/CoS@GF electrode after five consecutive cycles [a].

Current Densities (mA cm^{-2})/Time (h)	**Cycle**	**Conversion[b] (%)**	**Selectivity[b] (%)**	**FE (%)**
60/4	1	100	98	87
60/4	2	100	97	87
60/4	3	100	97	87
60/4	4	100	97	86
60/4	5	100	95	85

[a]Undivided cell: octylamine: 2 mmol, NaBr: 2 mmol, constant current of 60 mA for 4 h at RT, anode: CoS_2/CoS@GF, cathode: GF. [b]Determined by GC-MS integrals.

Table S3 Broaden the substrate's scope for Br^-/Br_2 mediated electrochemical oxidation of amines to nitriles.

Entry	Substrate	Conv.[b] (%)	Select.[b] (%)	Yield (%)	FE (%)
1		100		95	85
	1a		**2a** (95)		
2		97		92	82
	1b		**2b** (95)		
3		99		90	81
	1c		**2c** (89)		
4		100		83	74
	1d		**2d** (83)		
5		94		83	74
	1e		**2e** (92)		
6		97		89	80
	1f		**2f** (88)		

[a]Undivided cell: amine substrate: 2 mmol, NaBr: 2 mmol, a constant current of 60 mA at RT for 4 h, anode: CoS_2/CoS@GF, cathode: GF. [b]Determined by GC-MS integrals.