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Sulfamate synthesis via aqueous electrocatalytic N–S coupling through interfacial microenvironment optimization

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Abstract

Converting hazardous S²⁻ industrial pollutant into valuable chemicals provides a sustainable method for waste upgrading and resource recovery. Here we develop an aqueous electrochemical N–S coupling route to promote anodic S²⁻ oxidation and subsequent coupling with NH₃ to synthesize sulfamate (H₂N–SO₃⁻) under ambient conditions. By optimizing the interfacial microenvironment for efficient enrichment of reactants and facile desorption of products, carbon surface decorated with 40% PTFE exhibits the highest sulfamate Faradaic efficiency (FE) of 24.9% and a yield

rate of $5.1 \text{ mg h}^{-1} \text{ cm}^{-2}$. Mechanistic studies reveal that on-surface N–S bond formation via adsorbed high-valent sulfur species (*SO_3) is more favorable than in-solution coupling between bulk sulfite (SO_3^{2-}) and ammonia. This work provides a practical and environmentally friendly strategy for waste S^{2-} upgrading and value-added sulfamate formation, opening new avenues for electrochemical N–S coupling and broader S-rich waste-to-chemical transformations.

Main

Realizing efficient upcycling of toxic waste to high-value-added fine chemicals represents a crucial research direction to achieve a sustainable society in the future.¹⁻
⁴ Sulfide ions (S^{2-}), a highly hazardous and corrosive pollutant, is primarily found in industrial wastewater (ranging from few to few hundreds of ppm) from packinghouse, papermaking, petrochemical plants, and tanneries.^{5,6} H_2S is prone to interact with the respiratory system and has strong toxicity and asphyxiating properties to humans.⁷ Aqueous S^{2-} could easily form metal sulfides with metals, causing corrosion and deposition of pipelines and equipment.⁸⁻¹⁰ Also, excess sulfide will affect aquatic organisms and shift the redox balance and sulfur cycling. Hence, developing technologies to remove and treat hazardous S^{2-} pollutant is urgently needed to prevent public health concerns and avoid serious environmental consequences.

Traditional methods are widely used for the elimination of sulfides, but they often encounter drawbacks. Chemical oxidation often uses strong oxidants such as chlorine or ozone, which is hard to control, while continuous consumption of oxidants leads to high costs. Biological treatment requires special operation conditions and long cycle. Chemical precipitation could produce hazardous waste sludge and fail to recover metal resources.^{7,11,12} Due to these limitations, the development of more cost-effective, and environmental-friendly techniques for sulfide conversion at mild conditions is needed.

Electrochemical oxidation offers a compelling alternative due to its cost effectiveness, environmental compatibility, mild operation conditions and good energetic efficiency.¹²⁻¹⁵ Though many researchers to date have made efforts on electrochemical oxidation from sulfide (SOR) to low-toxic or value-added products, challenges remain. For example, Nagaiah¹⁶ group successfully oxidizes H₂S to sulfur with a yield of 79.9%, but lacks of sustainable solutions to remove the sulfur precipitate on anode surface. Jin¹⁷ group designs a sulfide-oxidation-assisted electrochemical water splitting system, oxidizing sulfide ions to a mixture of polysulfides (varying chain lengths) with a high Na₂S concentration of 1 M, which is of low economic efficiency. As earth-abundant sulfur is low in value and could readily deposit on electrode surfaces, blocking active sites, and selective synthesis of specific polysulfides is challenging, there is a need to develop more valuable sulfur-containing products from S²⁻/HS⁻ electrochemical oxidation.

Sulfamic acid (NH₂SO₃H) and sulfamate (NH₂SO₃⁻) are important S, N-containing fine chemicals that are directly used in electroplating, descaling, herbicides, and fire retardants as well as widely used for synthesis of sweeteners.^{18,19} Global consumption of sulfamic acid rose steadily from approximately 149,000 tons in 2015 to over 760,000 tons by the end of 2025, indicating rapid growth in its demand across industrial applications. Sulfamic acid is mainly produced through two industrial processes. One is a liquid phase method, where urea reacts with fuming sulfuric acid at 40-70°C to undergo a sulfonation reaction, which requires strict temperature control and long reaction cycle (>16 h).^{20,21} Another is a gas phase method, where gaseous ammonia reacts directly with the gaseous sulfur trioxide.²² However, the operating conditions are extremely demanding, and the production cost is high. Thus, electro-oxidation of S²⁻/HS⁻ to NH₂SO₃H/NH₂SO₃⁻ provides a facile and green N-S coupling pathway to upcycle hazard pollutants into value-added products (**Fig. 1**).

Herein, we develop an innovative electrochemical approach for constructing N–S bonds and synthesize sulfamates by driving the oxidation reaction of hazardous S^{2-} in an NH_3 -containing aqueous solution. Although electrochemical catalysis for N–S bonds formation have been reported previously, those reactions were carried out in organic solvents.^{23,24} In contrast, our work conducts the electrocatalytic N–S coupling process in a greener, more sustainable aqueous medium. Commercially available carbon papers with fluorinated polymers modified are used to optimize the interfacial microenvironment for efficient sulfamate production. The N–S coupling process and mechanism are further investigated through spectroscopic, voltametric, and simulated calculations.

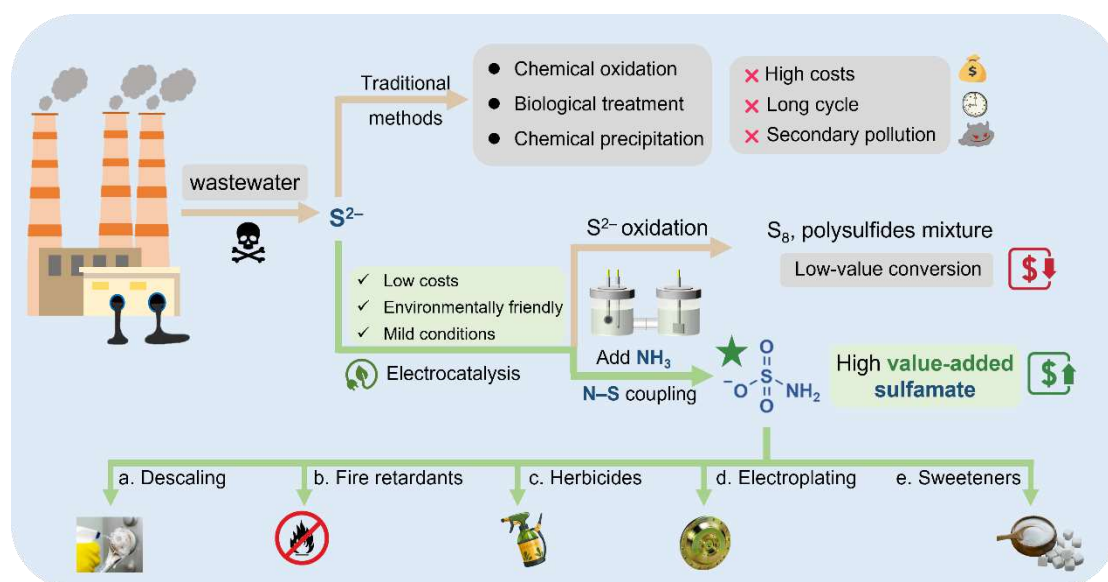


Fig. 1. Schematic representation of the synthesis and applications of sulfamic acids and sulfamates.

Result and Discussion

Screening of types of fluorinated polymer decorated carbon surface

First, we investigated to identify the most suitable reaction conditions for N–S bond coupling between sulfide ions and ammonia. Carbon paper (CP), a stable, inexpensive, and conductive self-supporting electrode, is widely used in electrocatalysis. The local wetting state and microenvironment at the CP surface could affect the mass transport during the electro-oxidation and N–S coupling process.²⁵ Therefore, fluorinated polymers were employed as interfacial modifiers on CPs because their electrochemically stable fluorinated backbones provide tunable hydrophobicity and good compatibility with carbon substrates, enabling control of electrolyte penetration and local aqueous structure. In this work we screened five fluorinated polymers (PTFE, FEP, ETFE, PVDF, and PFA) on CPs, and experimentally found that PTFE-modified CP delivered the highest sulfamate Faradaic efficiency, outperforming both unmodified CP and electrodes modified with other F-containing additives (**Fig. S1**). Thus, we focus on PTFE-modified CP in the subsequent study.

Interfacial engineering of PTFE-modified carbon papers

Next, we systematically characterized CPs containing varying PTFE loadings (0, 20%, 40% and 60%) to investigate the influence of hydrophobicity on electrochemical activity. **Fig. 2a** shows the X-ray diffraction (XRD) patterns of PTFE-modified CPs. The characteristic peak for carbon is observed at around 26°, corresponding well to PDF#75-2078.²⁶ Stronger signals at around 18° are found as the PTFE content increases, attributed to polytetrafluoroethylene (PTFE, PDF#47-2217).²⁷ Scanning electron microscope (SEM) images are shown in **Figs. 2b** and **S2**. PTFE-modified CPs

exhibit regular and interlaced one-dimensional linear structures. Energy-dispersive X-ray spectroscopy (EDS) images are obtained in **Fig. S3** to determine their chemical compositions. The non-conductive hydrophobic PTFE is found to be evenly distributed across the CPs. The elemental distribution displayed in **Table S1** shows that the PTFE contents are consistent with the CP types.

To evaluate the surface wettability, contact angles of the electrolyte (5 μ L drop) on the designed CPs were measured using a contact angle meter (CAM). As shown in **Fig. 2c**, the measured contact angles are 109° for CP, 117° for 20% PTFE, 131° for 40% PTFE, and 143° for 60% PTFE, respectively, verifying the progressive increase in surface hydrophobicity with increasing PTFE loading. Thermogravimetric analysis (TGA) was used to measure the mass loss of the CPs as the temperature changes for PTFE loading determination. As shown in **Fig. 2d**, CP maintains a stable mass up to 800 °C, while pronounced mass loss beginning at around 500 °C for hydrophobic CPs. The total mass losses measured are 18% (20% PTFE CP), 38% (40% PTFE CP), and 53% (60% PTFE CP), consistent with the PTFE loading amounts. The result indicates that the mass-loss step is attributed primarily to PTFE decomposition,^{28,29} which is in good agreement with elemental analysis by EDS.

X-ray photoelectron spectroscopy (XPS) was further carried out to investigate the surface chemistry of interface microenvironment-optimized electrodes. In **Fig. 2e**, XPS survey spectra reveals the presence of F and C elements.³⁰⁻³² F 1s signals at 689.2 eV are ascribed to C-F bond of $-(CF_2-CF_2)_n-$ (**Fig. S4**). Upon deconvolution of high-resolution C 1s spectra in **Fig. 2f**, signals at 284.8 and 292.3 eV are observed in PTFE-

modified CPs, corresponding to C–C and C–F bonds, respectively, indicating the presence of fluoropolymers, while only C–C signal from carbon substrate and a weak signal of surface C–O bond are detected in CP without PTFE.³³ The Brunauer-Emmett-Teller (BET) surface areas measured by N₂ adsorption-desorption are 1.9, 2.7, 2.9, and 3.3 m² g⁻¹ for 0%, 20%, 40%, and 60% PTFE-modified CPs, respectively (**Fig. S5**). The overall increase in BET surface area with PTFE loading can be attributed to PTFE coatings changing the fiber inter-fiber spacing, producing additional accessible surface and mesoporous voids, thus, accelerating mass transport and reactants adsorption.

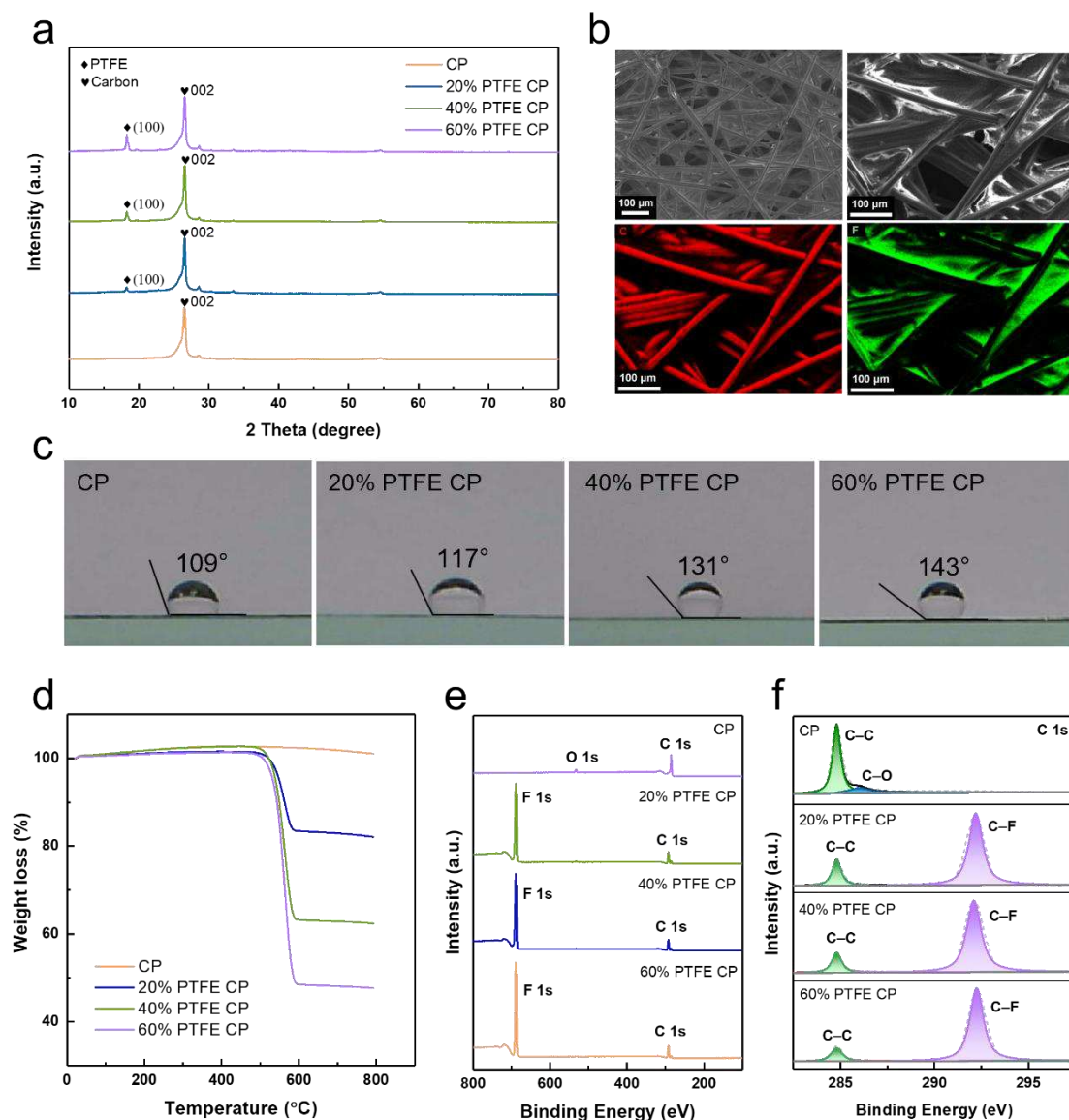


Fig. 2. a) XRD spectra of designed CPs. b) SEM images and corresponding EDS mappings of 40% PTFE CP. c) CAM images of contact angle test, d) TGA tests, e) XPS survey spectra, and f) high-resolution C 1s spectra of designed CPs.

Aqueous electrocatalytic N–S coupling performance

Electrochemical analysis was conducted in a divided electrolytic cell (**Fig. 3a**). At the anode, S^{2-} and NH_3 serve as S source and N source, respectively, with 0.1 M KOH as substrates. To further optimize the interface microenvironment of CP, electrolysis

was initially performed on CPs with different hydrophobicity (20% PTFE CP, 40% PTFE CP, and 60% PTFE CP). Open-circuit potential (OCP) was recorded in 0.1 M KOH on CP electrode. As shown in **Fig. 3b**, upon injecting 10 mM S^{2-} , a more significant OCP decrease is observed on 40% PTFE CP (131.0 mV) than that on 20% PTFE CP (94.6 mV), and 60% PTFE CP (85.0 mV), suggesting strong adsorption of S^{2-} and subsequently steering toward interfacial S^{2-} oxidation.³⁴⁻³⁶ The co-addition of S^{2-} and NH_3 shows a trend similar to that of adding Na_2S only (**Fig. S6a**). In **Fig. S6b**, 0.5 M NH_3 is added at 300 s, all CPs show small OCP changes. This near-zero shift likely indicates that N-only side oxidation is being suppressed on the surface of CPs, thus allowing NH_3 and S-adducts to interact on the surface and undergo downstream electrochemical coupling. When product $\text{NH}_2\text{SO}_3\text{H}$ is injected into the electrolyte (**Fig. 3c**), 40% PTFE carbon paper exhibits the smallest OCP increase of 3.0 mV than that of 20% PTFE CP (22.7 mV), and 60% PTFE CP (26.1 mV). The minimal OCP variation indicates that the reaction products are readily desorbed into the solution without impeding the transfer of reactants. The OCP results demonstrate that carbon paper with moderate hydrophobicity (40% PTFE CP) provides a favorable balance between the adsorption of reactants and desorption of products, which may effectively facilitate the target N–S coupling electrochemical reaction.

Electrolyte solution containing 0.1 M KOH with 10 mM S^{2-} and 0.5 M NH_3 was used for N–S coupling performance evaluation. FE and yield rate were obtained after the 0.5-hour continuous reaction. As shown in **Fig. 3d**, 40% PTFE CP exhibits a highest sulfamate FE of 22.4% at 2.5 V vs. RHE with a yield rate of $3.3 \text{ mg h}^{-1} \text{ cm}^{-2}$ (**Fig. S7**).

Sulfate as the main by-product produced by over-oxidation of S^{2-} is detected in **Fig. S8**.

The promising electrochemical N–S coupling performance of 40% PTFE CP is mainly attributed to its optimal interfacial microenvironment. With well-balanced hydrophobic-hydrophilic attributes, this 40% PTFE surface remains sufficiently wet to ensure an adequate ionic conductivity and a continuous supply of sulfide and ammonia, while limiting excessive flooding of the porous structure to inhibit completing reactions.

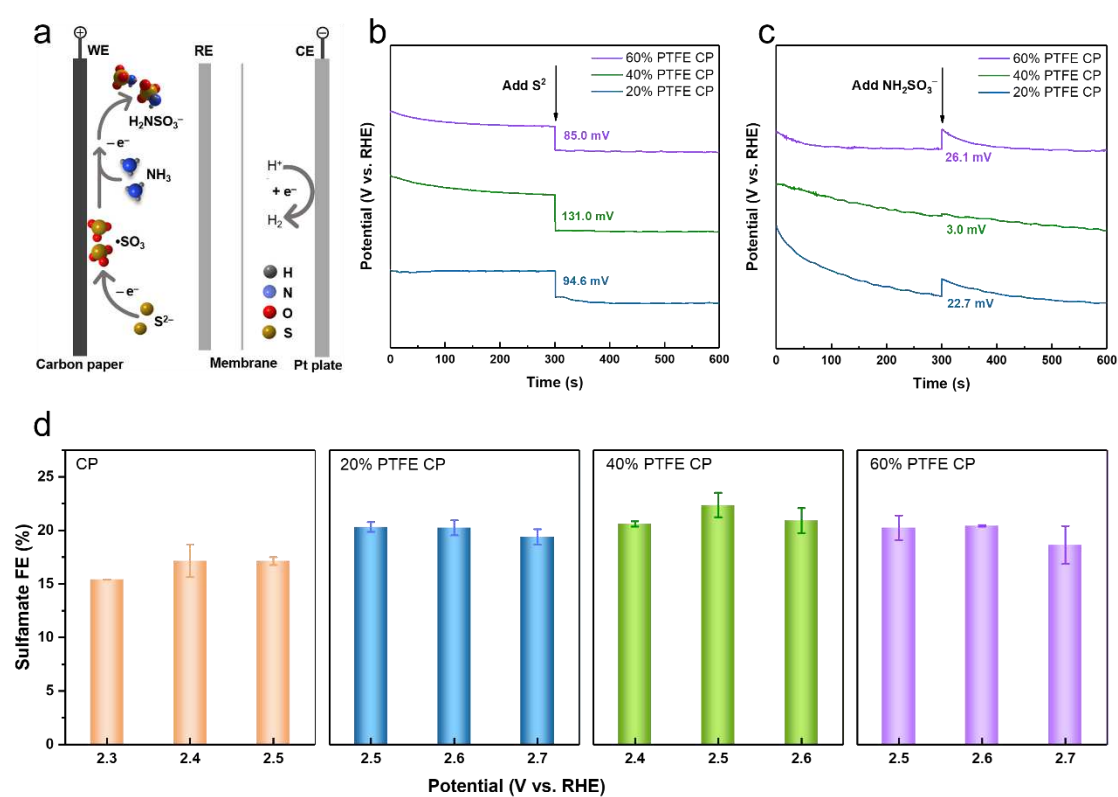


Fig. 3. a) Schematic diagram for electrochemical N–S coupling. OCP response of b) S^{2-} and c) $NH_2SO_3^-$. d) Sulfamate FE of CPs with different hydrophobicity.

Next, 40% PTFE CP was used for the optimization of reactant concentrations. As shown in **Fig. 4a**, linear sweep voltammetry (LSV) curves are recorded in electrolyte with and without S^{2-} . A more negative onset potential and a larger current density are

observed after the addition of S^{2-} , indicating the occurrence of S^{2-} oxidation. While promising performance is achieved at a low S^{2-} concentration of 10 mM (**Fig. S9a**), evaluations on higher concentrations are conducted. In **Fig. 4b**, 40% PTFE CP exhibits a highest sulfamate FE of 24.9% at 2.6 V vs. RHE with a yield rate of $5.1 \text{ mg h}^{-1} \text{ cm}^{-2}$ in electrolyte containing 30 mM S^{2-} , higher than that in 10 mM S^{2-} and 50 mM S^{2-} (**Fig. S9b**). When a more positive potential of 2.7 V vs. RHE is applied, a lower sulfamate FE of 21.1% is observed, while sulfate by-product is also decreased (**Fig. S10**), mainly because of the stronger competitive oxygen evolution reaction (OER). Besides, the concentration of N-source is also optimized. In **Fig. 4c** and **S11**, sulfamate FE and yield rate in electrolyte containing 0.25 M NH_3 , 0.5 M NH_3 and 0.75 M NH_3 are obtained. Results show that the best N–S coupling performance is observed in 0.5 M NH_3 , while low NH_3 concentration leads to a lack of nucleophilic reagents to catch active S-containing intermediates, high NH_3 concentration results in competitive adsorption.

We further investigated the cation effect by replacing K^+ with Li^+ , Na^+ and Cs^+ . As shown in **Fig. 4d**, FE and yield rate for sulfamate followed the order $\text{K}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$. In **Fig. S12**, the highest FE for by-product sulfate is also observed in K^+ , followed by Cs^+ . The highest overall sulfide oxidation activity of K^+ is mainly attributed to its intermediate hydration strength and size, which appear to provide a more favorable double-layer structure and mass transport for stabilizing reactive sulfur intermediates³⁷⁻³⁹, while the strongly hydrated Li^+/Na^+ and weakly hydrated Cs^+ show low S^{2-} oxidation activity.

Stability test was conducted in a flow-cell to investigate the feasibility of our system in practical applications. As shown in **Fig. 4e**, long-term N–S coupling reaction is conducted over 40% PTFE CP, where no visible current decay is observed. Sulfamate is produced in spent 500 mL (1 mL min^{-1}) electrolysis solution after 24-hour continuous electrolysis with a yield rate of 72 mg cm^{-2} . SEM images in **Fig. S13** shows that the morphology remains intact after long-term reaction. EDS mapping observes the occurrence of S element, indicating the strong adsorption of S species on CP surface. The results highlight the promising durability of our system under extended operation. To further demonstrate the scalability and versatility of this electrochemical N–S coupling platform, we replaced ammonia with cyclohexylamine as the N source. Under otherwise identical conditions, the anodic oxidation of sulfide in the presence of cyclohexylamine afforded cyclamate (30 mg cm^{-2}), which are widely used as artificial sweeteners, highlighting that the system can be extended from inorganic ammonia to organic amines to produce value-added N–S products in aqueous solutions.

X-ray photoelectron spectroscopy (XPS) was conducted on electrolyte before and after electrochemical N–S coupling reaction. Ammonia is removed by heating and drying before the XPS analysis to avoid interference with the detection of N–H bonds in sulfamate. In **Fig. S14a**, signals at 162.5 eV and 168.3 eV in high-resolution S 2p spectra are assigned to S^{2-} and oxidized sulfur species, respectively.⁴⁰⁻⁴² High-resolution N 1s spectra in **Fig. S14b** shows that no signals are observed in electrolyte before electrochemical reaction, indicating the evaporation of ammonia during the sample preparation process. For the sample after reaction, the peak located at 399.7 eV

is attributed to the signal of -NH binding for sulfamate, which is consistent with the standard sulfamate sample.⁴³⁻⁴⁶ The XPS results further verify the formation of N-S bond for sulfamate products. Besides, the N-S coupling products are obtained from electrolyte after long-term reaction (See details in SI). ^1H nuclear magnetic resonance (^1H -NMR) is used for structural analysis. As shown in **Fig. 4f**, N-S coupling product exhibits a triplet at ~ 7 ppm for -NH_2 , which is identical to that of the standard sulfamic acid, further validating the presence of sulfamate species in products.

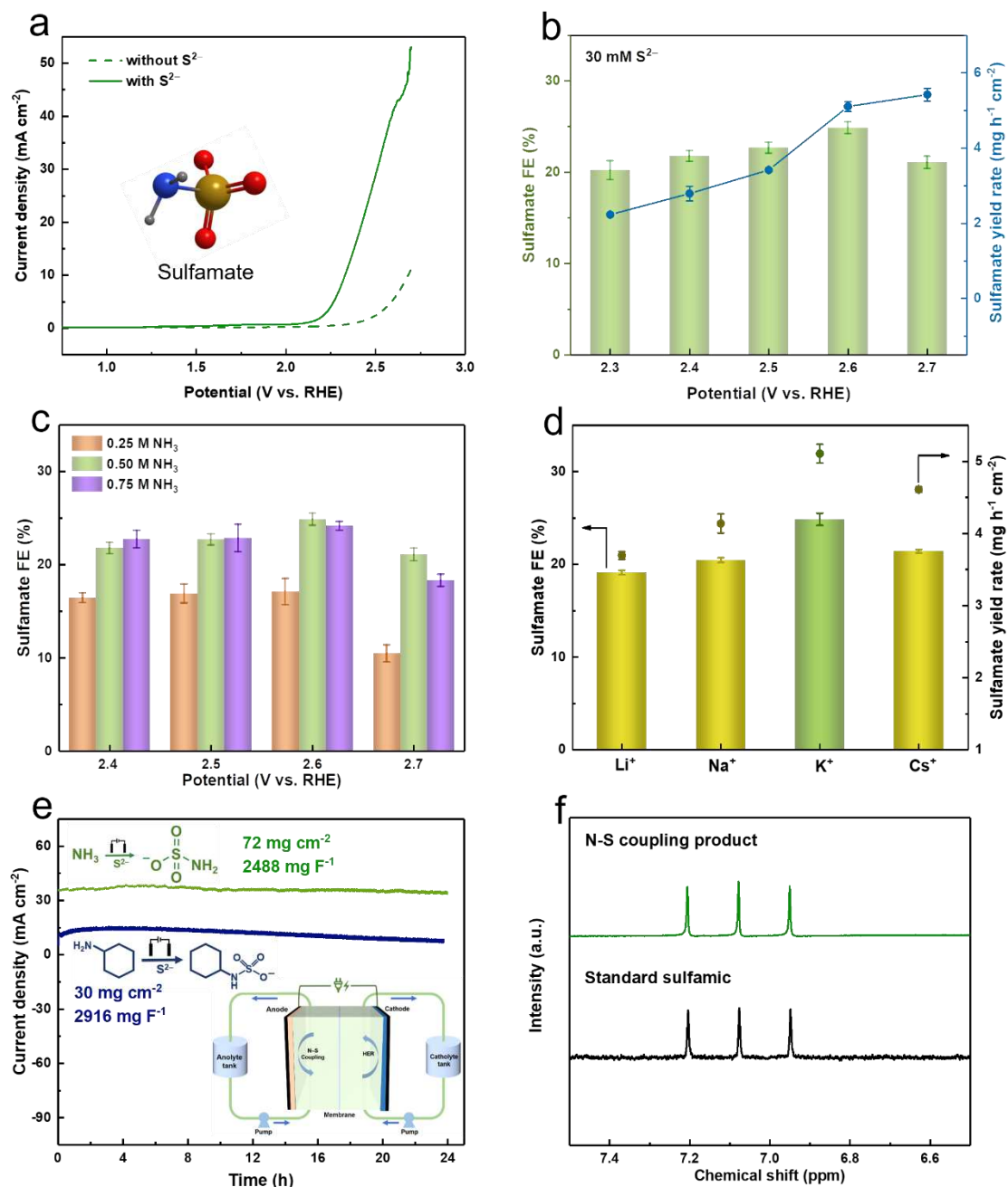


Fig. 4. a) LSV curves of 40% PTFE CP with and without S²⁻ (inset: structure of sulfamate). b) Sulfamate FEs and yield rates in 30 mM S²⁻. c) Sulfamate FEs in 30 mM S²⁻ with designed NH₃ concentrations. d) Sulfamate FEs and yield rates under designed cations (Li⁺, Na⁺, K⁺, and Cs⁺). e) Long-term stability test over 40% PTFE CP with flow electrolytes for 24 hours in 30 mM S²⁻ (inset: schematic diagrams of reactions and flow-cell). f) ¹H NMR spectra of standard sulfamic salt and N–S coupling product.

Mechanistic study for interfacial N–S bond formation

To elucidate reaction intermediates involved in the anodic N–S coupling, experiments combined with simulated calculations are conducted. Density functional theory (DFT) calculations show that the reaction of SO_3^{2-} with NH_3 to form sulfamate has the lowest reaction free energy (ΔG) among the tested bulk sulfur species, indicating that SO_3^{2-} is thermodynamically the most favorable intermediate (**Fig. 5a**). We then varied the effective dielectric constant (ϵ) in the homogeneous implicit-solvent model to qualitatively mimic the interfacial microenvironments of CPs with different hydrophobicity.⁴⁷ As shown in **Fig. 5b**, the reaction exhibits a minimum free energy of -4.35 eV at an intermediate ϵ of 30, whereas both higher and lower ϵ values are less favorable. Although ϵ in this model is not intended to map one-to-one onto a specific PTFE loading, the results suggests that neither a fully hydrated environment nor a strong hydrophobic surface condition is optimal for N–S coupling. An optimized interface microenvironment is therefore vital to strike a balance between reactants co-adsorption and product desorption, thus accelerating N–S bond formation.

A series of control experiments in bulk solution and under electrolysis conditions on 40% PTFE CP electrode were conducted to further investigate the active intermediates for N–S coupling. As shown in **Table 1**, mixing various S oxyanions ($\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_5^{2-}$, $\text{S}_2\text{O}_8^{2-}$, and SO_4^{2-}) with NH_3 in 0.1 M KOH does not produce detectable sulfamate, and only the reaction between SO_3^{2-} and NH_3 yields 7.9 ppm and 5.9 ppm sulfamate with and without electrolysis. However, starting from sulfide S^{2-}

oxidation on anodic surface leads to a high sulfamate production of 113.9 ppm after 0.5-hour electrolysis. The results show that simply having sulfite in bulk solution is insufficient, and efficient N–S bond formation requires the involvement of electrochemically generated S-containing surface species derived from S^{2-} . Thus, a graphene-like cluster model (**Fig. S16 and S17**)^{48,49} is constructed to represent a local carbon site on CP surface to adsorb high-valent sulfur intermediates and evaluate N–S bond formation with NH_3 . Similar DFT protocols have been widely employed to describe local chemistry on carbon materials in computational studies.⁵⁰⁻⁵² As shown in **Fig. 5c**, the free energy of the reaction between $*SO_3$ and NH_3 is -6.89 eV, much lower than that of bulk SO_3^{2-} . The results demonstrate that N–S bond formation is thermodynamically more favorable on an adsorbed high-valent sulfur center ($*SO_3^{2-}$) than from bulk SO_3^{2-} .

Table 1. List of control experiments.

S source (10 mM)	N source (0.5 M)	Electrolyte (0.1 M)	Electricity (Yes/No)	Time (0.5 h)	Sulfamate (Yes/No)	Yield (ppm)	FE (%)
S^{2-}	NH_3	KOH	Yes	0.5	Yes	113.9	22.4%
S^{2-}	NH_3	KOH	No	0.5	No	/	/
S^{2-}	/	KOH	Yes	0.5	No	/	/
/	NH_3	KOH	Yes	0.5	No	/	/
$S_2O_3^{2-}$	NH_3	KOH	No	0.5	No	/	/
$S_2O_5^{2-}$	NH_3	KOH	No	0.5	No	/	/
$S_2O_8^{2-}$	NH_3	KOH	No	0.5	No	/	/
SO_4^{2-}	NH_3	KOH	No	0.5	No	/	/
SO_3^{2-}	NH_3	KOH	No	0.5	Yes	7.9	/
SO_3^{2-}	NH_3	KOH	Yes	0.5	Yes	5.9	1.9%

Frontier orbital analysis was conducted to further testify why adsorbed high-valent sulfur intermediates are more effective for N–S coupling than bulk sulfites. In **Fig. 5d**, the highest occupied molecular orbital (HOMO) of NH_3 serves as the electron donor, while the relevant acceptor orbitals are the lowest unoccupied molecular orbitals (LUMOs) of bulk SO_3^{2-} and $^*\text{SO}_3$. The energy gap between the HOMO of NH_3 and the LUMO of $^*\text{SO}_3$ is significantly smaller than that between the HOMO of NH_3 and the LUMO of SO_3^{2-} , indicating a more electrophilic sulfur center and a better energetic match with the electron-donating NH_3 . Overall, these results demonstrate that the adsorbed high-valent sulfur species ($^*\text{SO}_3$) from S^{2-} oxidation on anode surface are efficient N–S coupling centers, accelerating the formation of sulfamates.

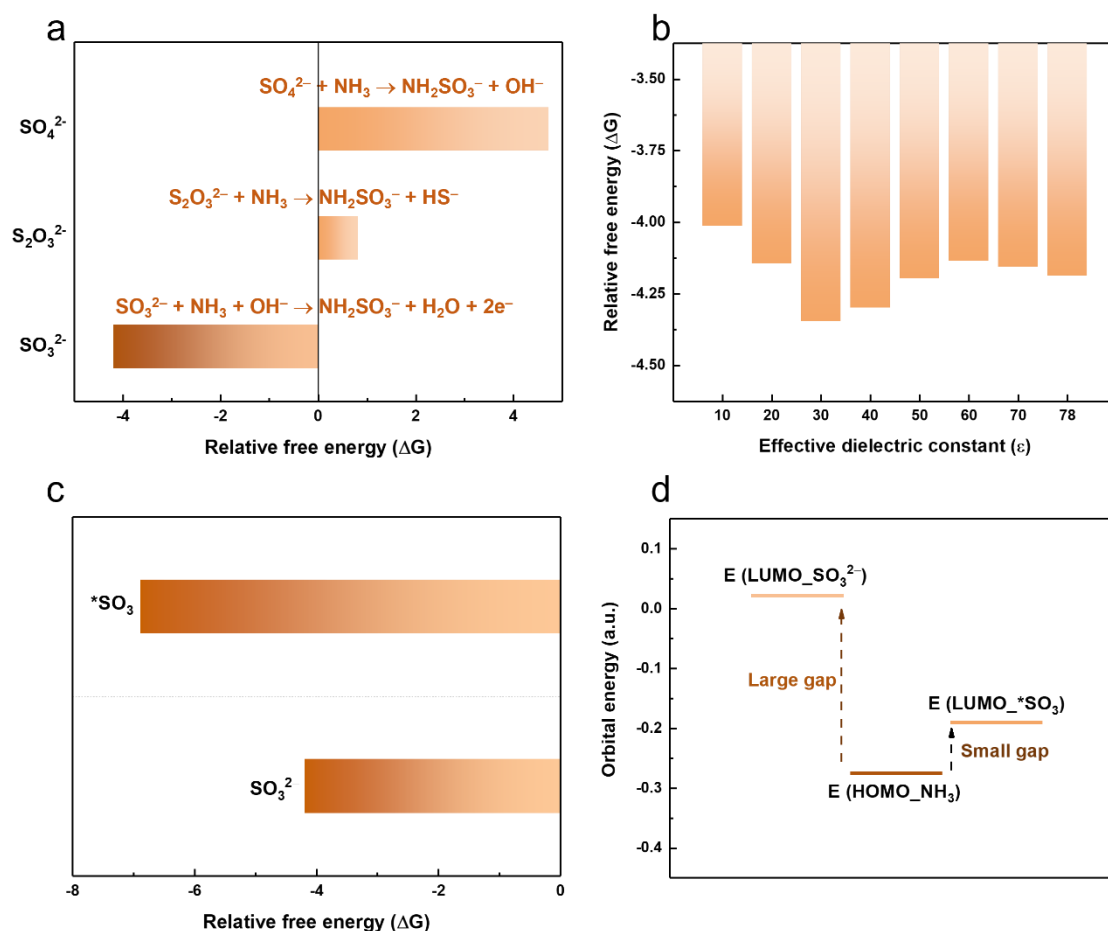


Fig. 5. Relative Gibbs free energy diagrams for the synthesis of sulfamates from a) S-containing intermediates in bulk solution, b) SO₃²⁻ in bulk solution with a range of effective dielectric constant, c) SO₃²⁻ in bulk solution and *SO₃ adsorbed on electrode surface.

Conclusion

In summary, we developed a green and facile electrocatalysis method for both hazardous S²⁻ waste upgrading and value-added sulfamate synthesis via N–S coupling. 40% PTFE CP exhibits the highest sulfamate FE of 24.9% with a yield rate of 5.1 mg h⁻¹ cm⁻² in electrolyte solution containing 30 mM Na₂S, which is mainly attributed to the optimized interfacial microenvironment of the PTFE-decorated carbon surface.

Stability test was also conducted using a flow-cell to evaluate the potential of industrial applications. No visible current decay was observed during the 24-hour continuous reaction, indicating its promising durability. Besides, cyclohexylamine as the N source successfully yield cyclamate, illustrating that the electrochemical N–S coupling strategy is not limited to NH_3 but can be extended to organic amines to generate value-added N–S functional molecules. The N–S coupling mechanism was explored through a complementary experimental-computational study. Adsorbed $\ast\text{SO}_3$ on the electrode surface is identified to be the high-valent active sulfur intermediate to capture NH_3 to form N–S bond, rather than bulk SO_3^{2-} in solution. Our work provides a feasible platform for designing new electrocatalytic N–S coupling transformations, for exploring other N sources and S-rich wastes, and for guiding future theoretical and practical studies on electro-coupling reactions.

Methods

Chemicals and reagents

All chemicals and reagents were described in **Note S1**.

Physicochemical characterizations

Additional information pertaining to the characterization techniques employed for the materials were supplied in **Note S2**.

Electrochemical measurements

Sulfides electro-oxidation studies were conducted using a CHI 660E electrochemical workstation with a three-electrode configuration (Chenhua, Shanghai). Carbon papers with different hydrophobicity, a Hg/HgO electrode (1 M KOH), and a platinum plate were used as the working electrode, reference electrode, and counter electrode, respectively. 0.1 M KOH with Na₂S and NH₃ was used as the anodic electrolyte solution, while 0.1 M KOH in the cathodic chamber of an H-type electrolytic cell. A pretreated ion membrane was used to separate the anodic and cathodic electrolyte solutions. All potentials measured in this work were converted to the reversible hydrogen electrode (RHE) scale based on the Nernst equation below (Eq. 1):

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \text{ pH} + 0.098 \text{ (Eq. 1)}$$

Linear sweep voltammetry (LSV) experiments were performed at a scan rate of 10 mV s⁻¹. The potentiostatic test was carried out at designated potentials for 0.5 h. Electrochemical data is presented from three independent experiments. The stability test was conducted for 24 hours using peristaltic pumps, with 250 mL electrolyte flows continuously at a flow rate of 1.0 mL min⁻¹.

Product analysis

To calculate the sulfide conversion and product selectivity, products after the electrocatalytic reaction were collected and analyzed using an ion chromatograph system (Thermo Scientific, ICS-1100). Standard calibration curve was shown in **Fig. S15**. The yield rate and FE were calculated by equations in **Note S3**.

Data availability

The data supporting the findings of this study are available in the article, the

Supplementary Information is provided with this paper.

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Author contributions

Z.H.Y. and E.C.M.T. proposed the research idea and designed the experiments. Z.H.Y. conducted the electrochemical measurements. Z.H.Y., D.S.C., and J.S. performed the characterizations. T.Z. performed the theoretical calculations. Z.H.Y. and E.C.M.T.

analyzed the data. Z.H.Y. and E.C.M.T. wrote the paper. All authors interpreted the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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