



RESEARCH ARTICLE

Synthesis of 2D Nanosheet FePS₃ Electrocatalyst via Salt-Template Method for Electrochemical Green Ammonia Production

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ABSTRACT

Electrochemical nitrogen reduction reaction (eNRR) offers a sustainable alternative for ammonia (NH₃) synthesis under ambient conditions, addressing the energy-intensive drawbacks of the traditional high-pressure, high-temperature Haber-Bosch process. Although eNRR offers a promising alternative for ammonia synthesis, significant challenges remain in achieving efficient performance. To address these, nanosized 2D layered transition metal phosphorus-sulfide materials, especially those incorporating cost-effective elements like Fe, are being investigated as potential electrocatalysts. In this study, FePS₃ was synthesized using a simple and environmentally friendly NaCl-template method. The eNRR performance of FePS₃ catalyst resulted in an NH₃ yield of 164.4 μg h⁻¹ mg_{cat}⁻¹ with a Faradaic efficiency (FE) of 47% at an applied potential of -0.6 V vs. RHE under neutral pH condition (0.1 M Na₂SO₄). Notably, the electrolyte pH played a crucial role in influencing eNRR activity by modulating proton availability, which in turn affected both eNRR and the hydrogen evolution reaction (HER). This work demonstrates the successful synthesis of a low-cost, eco-friendly eNRR catalyst, emphasizing the potential of FePS₃ for efficient ammonia production.

KEYWORDS

Ammonia, Electrochemical nitrogen reduction reaction, Non-noble electrocatalyst, Ambient pressure synthesis

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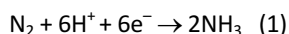


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INTRODUCTION

Nitrogen is essential for agriculture, as it is a key element in fertilizers. Although nitrogen (N_2) is the most abundant gas by volume in the atmosphere (78%), it is chemically inert and unusable by plants. Hence, nitrogen fertilizers are typically in the form of ammonia (NH_3). Most NH_3 production is via the Haber–Bosch process, which produces approximately 170 million metric tons annually [1]. The process requires high temperatures (400–500°C) and high pressures (100–200 bar); thus, it consumes around 1–2% of global annual energy generation [2]. Other applications of NH_3 include the production of synthetic fibers, plastics, resins [3], and as an industrial refrigerant [4]. Additionally, NH_3 is being researched as a green hydrogen carrier [5], to increase the use of variable renewable energy, due to the mild liquefaction conditions of NH_3 and the existing infrastructure for liquid NH_3 transport and storage [6].

To improve the sustainability of NH_3 production, lower energy and ambient condition methods are being developed. One facile and energy-efficient route for NH_3 synthesis is the electrochemical nitrogen reduction reaction (eNRR) at the cathode:



In eNRR, N_2 is adsorbed on the cathode surface, where it is simultaneously reduced by electrons and bonded to protons to produce NH_3 . The advantages of eNRR include mild operating conditions, potential for modularity, compatibility with renewable energy [7], and the use of water as the hydrogen source instead of fossil fuels (natural gas and coal). However, a key drawback of eNRR is the high activation barrier caused by the strong $N \equiv N$ triple bond, which necessitates the use of electrocatalysts to facilitate N_2 reduction. Current research focuses on developing new electrocatalyst materials to improve eNRR efficiency. In aqueous electrolytes, reported catalysts include noble metals, non-noble transition metals, as well as alloys, nitrides, oxides, phosphides, and sulfides [6]. The main challenge for eNRR catalysts is to increase the activity and enhance the selectivity of the reaction. The undesirable hydrogen evolution reaction (HER) is a dominant competing process in aqueous electrolytes, requiring only a two-electron and two-proton transfer at a similar onset potential value as the eNRR, resulting in low Faradaic efficiencies (FEs) [8–11]. The research on electrocatalysts has focused on the development of high-performing and low-cost materials. Particularly, there is growing interest in metal phosphorus-sulfides (MPS_3 , $M=Fe, Co, Ni, Mn$, etc.) due to their 2D layered structure, high specific area, and conductivity caused by interlayer ionic bonding [12]. This work investigates $FePS_3$, with a 2D nanosheet morphology, as an electrocatalyst for eNRR. Theoretical calculations indicate that Fe is among the most active transition metals for eNRR [13]. Additionally, Fe-based catalysts are potentially cost-effective and have been synthesized to have various compositions. A $Fe_3C/Fe_2O_3/Fe/C$ multi-composite catalyst achieved a reasonable performance of $0.6 \mu g h^{-1} cm^{-2}$ NH_3 yield rate and a 0.348% FE [14]. Fe-transition metal sulfides, such as FeS_2 [15], and Fe_3S_4 [16], have also been explored as eNRR catalysts, while adding P to Fe–S nanomaterials was reported to enhance the eNRR activity [17]. In nature, nitrogenase enzymes are two-component systems that convert N_2 and H^+ to NH_3 at ambient temperature and pressure [18]. One component of the enzyme is an Fe-protein containing Fe_4S_4 clusters, which are strong reducing agents that transfer electrons to the Fe_4S_3 or MFe_3S_3 ($M=Mo$ or V) catalytic component where $N \equiv N$ bond breaking, and $N-H$ bond formation occur [18,19]. Additionally, P clusters in the enzymes facilitate electron transfer from the Fe–S centers to the substrate [18]. Aside from composition, the morphology of the catalyst significantly impacts its performance. For instance, high-surface-area structures offer more reaction sites, leading to improved yield [9,11]. Two-dimensional nanomaterials exhibit physical and chemical properties different from other morphologies and that of the bulk due to their larger surface area. MPS_3 compounds are usually synthesized as crystals via chemical vapor transport (CVT) or chemical vapor deposition (CVD) reaction routes [12]. To obtain 2D nanosheets, the bulk material is exfoliated [20,21] yielding low quantities and high defect content [17]. A more efficient synthesis method to obtain 2D nanosheets includes using inorganic salts as templates to direct the growth of layered structures [17,22]. Salt-template synthesis of $FePS_3$ has been explored for electrocatalysts for HER [22] and eNRR [17].

In this work, a single-step NaCl-template method was used to synthesize 2D nanosheet $FePS_3$. The introduction of P and S into cost-effective Fe-based catalysts was observed to achieve eNRR activity. The catalyst performance showed an inverse relationship between the NH_3 yield rate and FE. This study advances the

understanding of the electrocatalytic activity of Fe–P–S based catalysts and highlights FePS₃ as an active electrocatalyst for nitrogen reduction, paving the way for further research in sustainable NH₃ synthesis.

EXPERIMENTAL

NaCl template preparation

The FePS₃ catalyst powder was synthesized via the NaCl-templated method, inspired by salt-templated construction [17,22]. The NaCl template was prepared by mixing 10 mL of 4 M NaCl aqueous solution with 200 mL of ethanol. The resulting mixture was filtered and washed with ethanol to isolate the NaCl precipitates.

Synthesis of the FePS₃ electrocatalyst and electrode

The NaCl precipitate (6.0 g) was combined with 10 mL of 0.1 g iron chloride ethanol solution. The mixture was stirred and heated at 50°C to remove the solvent by evaporation. Subsequently, all precursors, including the iron chloride–NaCl mixture, 0.35 g of elemental sulfur (99.7%, Sigma Aldrich), and 0.1 g of phosphorus, were ground together using a mortar and pestle. Finally, the ground powder was subjected to a two-step heat treatment in a furnace under an N₂ atmosphere. In the first stage, the temperature was raised to 310°C at a rate of 120°C h^{−1} and maintained for 5 h. Then, the temperature was further increased to 500°C and held for 3 h. After heating, the powder was cooled naturally and was subsequently washed in ethanol and then water (see Fig. 1). The electrodes for the FePS₃ catalyst were fabricated using a spray-coating method. The ink for spray coating was prepared by mixing FePS₃ powder with isopropyl alcohol (IPA; 99.7 wt%, Junsei) and Nafion resin solution (5 wt%, Chemorus). Then, the ink solution was ultrasonicated for 0.5 h to ensure that the catalyst was well dispersed in the solution. The GDL for the electrode was 1 cm² carbon paper (22BB, Sigracet, SGL Carbon), with a catalyst loading of 1 mg cm^{−2}.

Physiochemical characterization

X-ray diffraction (XRD, Miniflex II, Rigaku) analysis with Cu Kα radiation at a scan rate of 2 deg min^{−1} was performed to confirm the crystal structure of the bulk catalyst powder. X-ray photoelectron spectroscopy (XPS, Axis Supra, Kratos) and field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) were performed at Korea Basic Science Institute (Daedeok HQ, Daejeon). The XPS data were collected with a monochromatized Al Kα X-ray source (1486.6 eV). The wide scan spectrum was collected at 160 eV pass energy, 1 eV step size, and 0.1 s dwell time, and the narrow scan spectra were collected at 20 eV pass energy, 0.1 eV step size, and 0.2 s dwell time. The number of scans was 20 for Fe 2p, 10 for O 1s, 20 for C 1s, 20 for S 2p, and 30 for P 2p. The charge neutralizer was off for the wide scan and on for the narrow XPS scans. For the SEM image acquisition, the powder samples were attached to carbon tape and the sample surface was not sputter-coated with Pt. The acceleration voltage for the imaging was 15 kV.

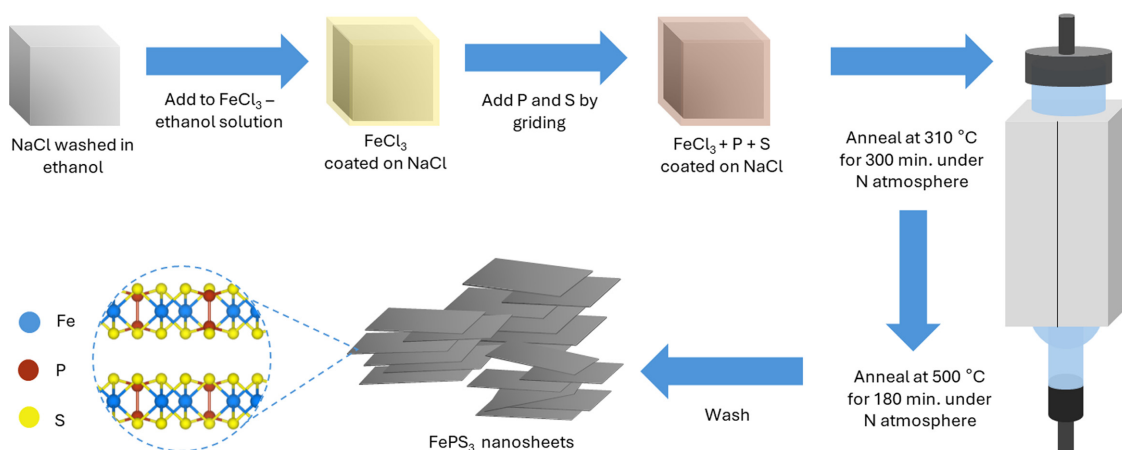


Fig. 1. Schematic diagram of the NaCl salt-template method for the preparation of FePS₃ nanosheets.

Electrochemical measurement

Electrochemical N_2 reduction tests were performed using a potentiostat/galvanostat (PGSTAT-302N, Autolab). The tests were carried out in a three-electrode system, comprising of the catalyst-loaded carbon paper (WE), a Pt wire (CE), and Ag/AgCl (3 M KCl, AMEL) (RE). A neutral electrolyte, 0.1 M Na_2SO_4 (99 wt%, Sigma Aldrich), was used here. Ultrahigh purity N_2 (99.999%, Daedeok) and Ar (99.999%, Daedeok) gas served as the feed gas for the eNRR tests. Prior to eNRR tests, the electrolyte was purged with gas for 0.5 h to saturate the electrolyte. Linear sweep voltammetry (LSV) was conducted at a potential range from 0 to -1.0 V in Ar- and N_2 -saturated electrolytes. Chronoamperometry (CA) tests were carried out using an H-cell set up in N_2 -saturated electrolyte, with catholyte and anolyte volumes set at 65 mL and 25 mL, respectively. The Nafion 115 membrane (Ion Power) used for cell separation underwent pretreatment with a solution of H_2O_2 (30 wt%, Deoksan), H_2SO_4 (95 wt%, Deoksan), and DI water to ensure complete removal of impurities. Each component was purified and prepared using an ultrapure deionized water system (18.2 M Ω cm, Milli-Q). The following equation was used to convert electrochemical potentials to the RHE scale: E (V vs. RHE) = E (V vs. Ag/AgCl) + $(0.059 \text{ V} \times \text{pH}) + 0.197 \text{ V}$. The potential range for the CA tests in eNRR was from -0.4 to -0.8 V vs. RHE at intervals of 0.2 V. The eNRR tests were conducted for 1 h under ambient temperature ($\sim 20^\circ\text{C}$) and pressure conditions. Gases produced at the cathode were collected using an acidic cold trap (3 mM H_2SO_4).

Quantification of NH_3

The salicylic acid method was used to quantify the amount of NH_3 generated by the FePS_3 catalyst. First, to prepare the standard solution with known concentrations (0, 1, 2, 4, 6 and 8 $\mu\text{g mL}^{-1}$), NH_4Cl was dissolved in 0.1 M Na_2SO_4 and diluted. From the as-prepared NH_4Cl solution, 2 mL was mixed with 2 mL of 1 M NaOH (98%, Sigma Aldrich) solution with 5 wt% salicylic acid (99 wt%, Sigma Aldrich) and 5 wt% sodium citrate tribasic dehydrate (Sigma Aldrich). Subsequently, 1 mL of 0.05 M NaClO (Sigma Aldrich) was added as an oxidizing agent, followed by the addition of 0.2 mL of 1 wt% sodium nitroprusside (Sigma Aldrich) as the catalyst. The mixed solutions were stored in a dark room for 2 h to ensure sufficient reaction. The absorbance of each sample was measured by UV-vis spectroscopy (UV-1800, Shimadzu). The wavelength range was from 800 to 550 nm and the absorbance peak at 660 nm was used for fitting the calibration curve. The catholyte solutions after the CA tests were prepared similarly by mixing 2 mL of the catholyte with 2 mL of 1 M NaOH with 5 wt% salicylic acid and 5 wt% sodium citrate tribasic dehydrate, 1 mL of 0.05 M NaClO, and 0.2 mL of 1 wt% sodium nitroprusside in a dark room. The NH_3 concentration of the prepared solutions were measured by UV-vis spectroscopy.

RESULTS AND DISCUSSION

Physical and chemical characterization of eNRR electrocatalyst

FePS_3 was synthesized using a facile single-step NaCl-template reaction. In other FePS_3 synthesis routes, the obtained material has a bulk morphology that needs to undergo exfoliation to obtain nanosheets [20,21]. In this work, NaCl was used to guide the growth of the FePS_3 into 2D nanosheets (see Fig. 2a). The FePS_3 formed in stacked structures composed of sheets with a thickness of about 20 nm. The layered sheet morphology benefit the exposure of active sites and facilitate mass transfer [23]. In Fig. 2b, the XRD pattern of the synthesized material confirms the successful formation of the crystalline FePS_3 material (PDF #01-078-0496) with a $C2/m$ space group and a 002-crystal orientation. The MPS_3 crystal structure consists of 2D layers built from M^{2+} cations and $\text{P}_2\text{S}_6^{4-}$ anions, with the anions forming PS_3 pyramidal units above and below the M center, near the interlayer region.

To further investigate the chemical composition and electronic structure of FePS_3 , XPS measurements were performed, as shown in Fig. 3. MPS_3 may be composed of either divalent homogenous metal ($\text{M}_2^{II}\text{P}_2\text{S}_6$) or multi-component heterogenous transition metals ($\text{M}_1^{II}\text{M}_2^{III}\text{P}_2\text{S}_6$ or $\text{M}^I\text{M}^{III}\text{P}_2\text{S}_6$) [24]. The XPS spectra confirm the composition of divalent Fe in the synthesized FePS_3 . For Fe 2p spectra, the three main peaks at 706.2/719.6, 709.2/722.8 and 712.6/726.3 eV correspond to the Fe(II) $2p_{3/2}$ and $2p_{1/2}$ binding energies, indicating that Fe- S_2 , Fe-P and Fe-S has been placed, respectively [25–27] (see Fig. 3b). For S 2p, the peaks at 159.1, 160.3 and 161.1 eV correspond to the bonding of Fe-S, monosulfide and disulfide, respectively (see Fig. 3c) [26–28]. For P 2p,

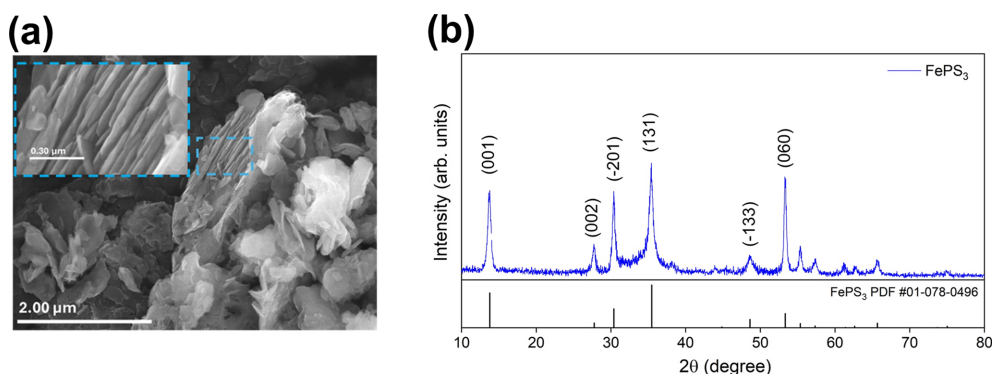


Fig. 2. (a) SEM image of the synthesized layered FePS_3 . Inset shows a magnification of the nanosheets from the outlined area. (b) The XRD diffraction pattern of the synthesized FePS_3 .

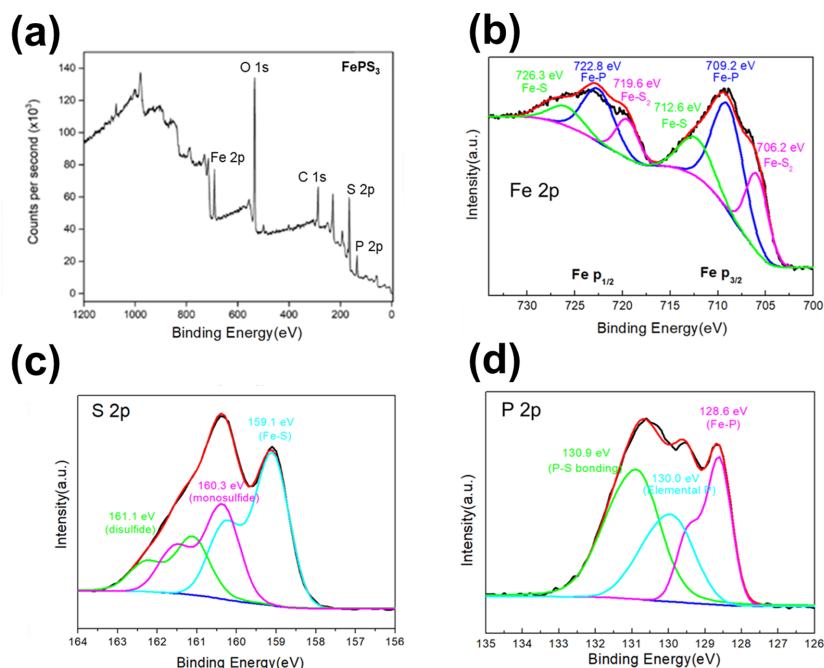


Fig. 3. (a) The XPS wide scan spectra of FePS_3 and the narrow scan spectra for (b) Fe, (c) S, and (d) P.

the peaks at 128.6, 130.0 and 130.9 eV correspond to the binding energies which are caused by Fe–P, elemental P and P–S bonding [29] (see Fig. 3d).

The electrocatalytic performance of FePS_3 is evaluated based on the NH_3 yield rate and FE, both of which are derived from the concentration of electrochemically produced NH_3 . As NH_4^+ ions are soluble in aqueous solvents, their concentrations in both the catholyte and the acidic cold trap were determined using the salicylic acid method. The concentrations of the resulting-colored solutions were then measured via UV-vis spectroscopy. A calibration curve using known concentrations of dissolved NH_3 (1, 2, 4, 6, and 8 $\mu\text{g mL}^{-1}$) was obtained to measure the concentration of the NH_3 synthesized using the FePS_3 catalyst (see Fig. 4a). The equation derived was $\text{Absorbance} = 0.00597 \times c(\text{NH}_4^+) + 1.02191 \times 10^{-4}$, with an $R^2 = 0.998$. The high linearity of this calibration curve confirms its suitability for calculating the NH_3 concentrations of the solutions reacted at different applied potentials. The resulting absorbance spectra indicate that there is a greater concentration of NH_3 synthesized when a more negative potential is applied from -0.4 V to -0.8 V (see Fig. 4b).

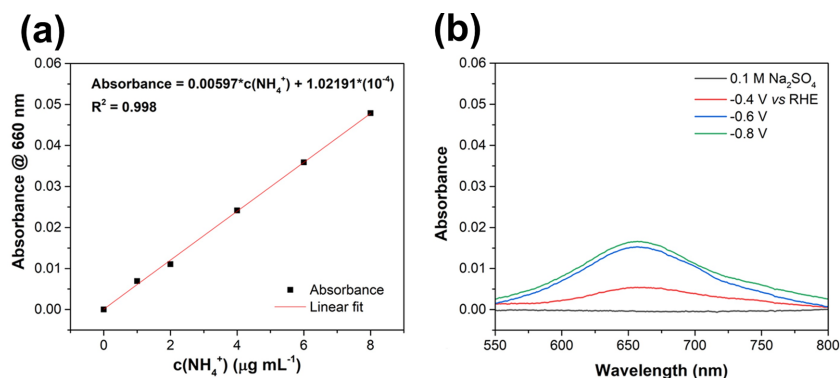


Fig. 4. (a) The calibration curve of the UV-Vis absorbance data for known NH_3 concentrations fitted by absorbance value at 660 nm. (b) The UV-Vis absorbance spectra of the catholyte solution obtained after eNRR at -0.4, -0.6, and -0.8 V.

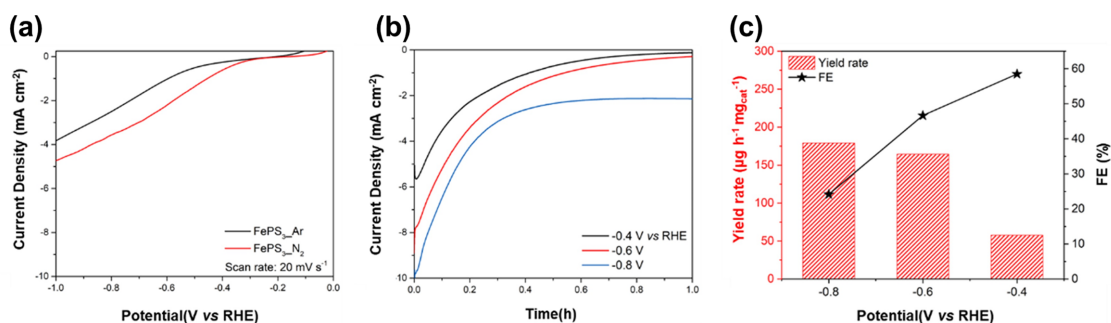


Fig. 5. (a) The LSV curves of FePS_3 electrocatalyst under Ar- and N_2 -saturated electrolyte at a scan rate of 20 mV s^{-1} in $0.1 \text{ M Na}_2\text{SO}_4$ electrolyte. (b) Chronoamperometry curves for potentiostatic measurements at the corresponding potentials using the FePS_3 for 1 h. (c) Normalized NH_3 yield rate (red dashed column) and FE (black symbol line).

Electrochemical activity of NH_3

The electrochemical activity of the FePS_3 catalyst was investigated using LSV and CA. The electrochemical tests used a neutral $0.1 \text{ M Na}_2\text{SO}_4$ electrolyte under ambient temperature ($\sim 20^\circ\text{C}$) and pressure conditions. LSV tests were performed under Ar- and N_2 -saturation conditions using a potential range 0 to -1.0 V vs. RHE to determine the HER and eNRR activity of the catalyst (see Fig. 5a). The eNRR electrocatalytic behavior under N_2 was initiated at about -0.25 V vs. RHE and the difference in the corresponding current densities between the Ar- and N_2 -saturated conditions increased along with decreasing potential. The difference in the corresponding current densities reached a maximum of 1.25 mA cm^{-2} at approximately -0.68 V vs. RHE. The corresponding current density was more negative under N_2 than under Ar-saturation during the LSV tests, indicating eNRR activity for the FePS_3 catalyst in a neutral pH electrolyte within the potential range of 0 to -0.1 V vs. RHE. CA measurements were conducted using potentials of -0.4 , -0.6 , and -0.8 V vs. RHE for 1 h (see Fig. 5b) to determine the optimal potential within the range obtained from LSV. The rate of change in the current densities decreased after approximately 0.3 h of CA. At the potential of -0.4 , -0.6 , and -0.8 V vs. RHE, the corresponding current density approached -0.12 , -0.29 , and -2.1 mA cm^{-2} at the end of the CA test, respectively. A larger magnitude of the current density was obtained at more negative potential values, signifying increased electrocatalytic activity. The NH_3 yield rate and FE were calculated to assess the electrocatalytic behavior of the FePS_3 catalyst (see Fig. 5c). The NH_3 yield rates increased as more negative potentials were applied, corresponding to the higher current densities observed in the CA tests. At -0.8 V , the yield rate reached $179.1 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ with an FE of 24%. At -0.6 V vs. RHE, the yield rate was $164.4 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ with an FE of 47%. At -0.4 V vs. RHE, the yield rate was the lowest at $57.6 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$, but the efficiency was the highest at 58% FE. The results suggest that the optimal potential for eNRR is at about -0.6 V vs. RHE, near the potential value for the

maximum difference between the Ar- and N₂-saturated LSV curves. Similar to this work, FePS₃ as an eNRR catalyst synthesized using the salt-template method was also reported by Huang et al. [17]. Using the same amount of template loading to synthesize FePS₃, they achieved an NH₃ yield rate of 30.1 μg h⁻¹ mg_{cat}⁻¹ at 0.98% FE using a KOH (pH = 13) electrolyte and a potential of -0.40 V vs. RHE. Differences in the crystallinity and testing conditions may account for the performance variations between the reported FePS₃ and the material in this work.

The XRD patterns of both materials had similar peak angles, but with varying intensities. The FePS₃ synthesized by Huang et al. [17] featured a main peak at 13.78° corresponding to the (001) plane. This work produced crystals with a (002) orientation with a peak at 27.76° and higher peaks for (001), and the high-index (131) and (060) planes at 13.78°, 35.45°, and 53.32°, respectively, indicating greater formation of different planes. High-index planes, characterized by high surface free energy and abundant low-coordinated atoms, result in sites with higher catalytic activity due to a stronger affinity for binding reactants and intermediates [30,31]. For instance, Au nanocrystals with high-index facets outperformed lower-index particles in eNRR. DFT calculations revealed that higher index facets have a larger barrier for H⁺ to H* reduction, suppressing HER, and a lower energy barrier for N₂H₂* formation while having a higher energy barrier for N₂H₂* decomposition to N₂ and 2H* [31]. A similar mechanism as a function of the higher concentration of high-index planes may have also occurred in this work.

The variation in performance may also be due to experimental conditions, aside from material properties. Huang et al. [17] performed tests in an alkaline KOH electrolyte (pH = 13), while the experimental material was examined in a neutral 0.1 M Na₂SO₄ electrolyte (pH = ca. 7). The pH of the electrolyte influences eNRR activity by affecting the availability of protons, which are also consumed in the HER that occurs at similar applied potentials. In aqueous systems, HER is kinetically favored over eNRR, making H₂ being the predominant gas produced [32]. Under acidic conditions, the higher H⁺ concentration can promote both eNRR and HER, leading to increased NH₃ yield but lower efficiency [33]. In contrast, alkaline conditions may limit proton transfer, effectively suppressing HER [32]. Adjusting proton concentrations can also enhance N₂ coverage on the catalyst surface, improving the formation and consumption rates of eNRR intermediates [34]. The literature reports that the optimal performance of eNRR catalysts varies with pH, with some performing better under neutral, acidic, or alkaline conditions depending on the specific catalyst and reaction environment [32–37]. In here, 0.1 M Na₂SO₄ neutral electrolyte was used to mitigate HER near the electrode surface by reducing proton availability. These discrepancies highlight the need for further research into the effects of crystal planes and electrolyte pH on the eNRR performance of FePS₃.

CONCLUSIONS

FePS₃, a transition metal-phosphorus-sulfur compound, was successfully synthesized using a facile single-step NaCl-template method, forming particles made of stacked 2D nanosheets. The material was applied as a catalyst for eNRR under mild operating conditions. The optimal potential value in this work was -0.6 V vs. RHE, achieving an NH₃ yield rate of 164.4 μg h⁻¹ mg_{cat}⁻¹ with a high FE of 47%. The results demonstrate the enhanced performance of eNRR using an Fe-based catalyst, attributed to the introduction of P and S. This study enhances the understanding of Fe–P–S-based electrocatalysts and underscores their potential as cost-effective solutions for sustainable NH₃ production. Future work should focus on optimizing crystal plane orientations and investigating the influence of different electrolytes to further improve efficiency.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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