

RESEARCH ARTICLE OPEN ACCESS

Magnetic-Field Control of Surface States in CoFe_2O_4 Thin Films for Nitrate Electroreduction to Ammonia

Touraj Karimpour¹ | Younes Mousazade² | Simon Diel¹ | Shilendra Kumar Sharma³ | Tisita Das³ |
 Nathália C. Verissimo⁴ | Thomas Fischer¹ | Ziyaad Aytuna¹ | Andreas Lichtenberg¹ | Sudip Chakraborty³ |
 Marcel Risch²  | Sanjay Mathur¹

¹Department of Chemistry, Institute of Inorganic and Materials Chemistry, University of Cologne, Cologne, Germany | ²Nachwuchsgruppe Gestaltung des Sauerstoffentwicklungsmechanismus, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany | ³Materials Theory for Energy Scavenging (MATES) Lab, Department of Physics, Harish-Chandra Research Institute (HRI) Allahabad, A C.I of Homi Bhabha National Institute (HBNI), Prayagraj, India | ⁴Department of Circular Metallurgy and Alloy Design (MA), Max Planck Institute for Sustainable Materials, Düsseldorf, Germany

Correspondence: Marcel Risch (marcel.risch@helmholtz-berlin.de) | Sanjay Mathur (Sanjay.mathur@uni-koeln.de)

Received: 4 February 2026 | **Revised:** 13 May 2026 | **Accepted:** 19 May 2026

Keywords: cobalt ferrite spinel | DFT calculations | electrochemical nitrate reduction reaction | magnetite | mf-CVD

ABSTRACT

Magnetic-field-assisted material synthesis enables more control over spin polarization and electronic structure in electrocatalysts, offering new opportunities for complex electrochemical reactions such as nitrate reduction, which underpins sustainable ammonia synthesis and nitrate remediation. Here, we report a magnetic-field-assisted chemical vapor deposition approach to engineer CoFe_2O_4 electrocatalysts, where cobalt serves as the active and selective site while an external magnetic field modulates cation-redistribution and surface morphology. Field-induced structural modification under 1 T delivers a nitrate-to-ammonia production rate of $133 \pm 38 \mu\text{mol cm}^{-2} \text{h}^{-1}$ with a Faradaic efficiency of $96 \pm 3\%$ at -0.5 V vs RHE. This corresponds to a 288% enhancement relative to field-free synthesis and a 2078% increase compared with Fe_3O_4 , yielding an overall performance improvement of 5989%. Density functional theory calculations reveal that the $\text{CoFe}_2\text{O}_4(311)$ facet preferentially stabilizes nitrate adsorption while suppressing hydrogen evolution, enabled by a higher work function (6.98 eV) and stronger thermodynamic affinity for NO_3^- (-5.58 eV) relative to isostructural Fe_3O_4 .

1 | Introduction

Catalysts are central to critical energy processes, from large-scale chemical manufacturing to next-generation renewable energy technologies. Heterogeneous catalysis drives the efficient conversion of small molecules such as water, nitrogen, carbon dioxide, and nitrate into fuels and platform chemicals, cementing catalytic technologies as cornerstones of sustainable development [1–3]. Among these transformations, ammonia synthesis consumes 1%–2% of global energy and accounts for nearly 1% of annual

greenhouse gas emissions, making its decarbonization urgent [4, 5]. One promising pathway involves leveraging nitrate (NO_3^-), a major pollutant from intensive agriculture (e.g., fertilizers, manure) that drives eutrophication of water bodies and damages ecosystems globally, thus providing a highly soluble feedstock for producing value-added ammonia (NH_3) via electrocatalytic conversion [6–9]. To achieve industrial-scale performance via electrochemical nitrate reduction reaction (NO_3RR) at low overpotential, catalysts must break through slow charge transfer barriers to nitrate π -orbitals, accelerate the demanding

Touraj Karimpour and Younes Mousazade contributed equally to this work.

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2026 The Author(s). *Advanced Functional Materials* published by Wiley-VCH GmbH

eight-electron reduction, and suppress competing hydrogen evolution and unwanted nitrogenous by-products [10–12].

Spinel first-row transition-metal oxides (TMOs) exhibit a strong interplay among spin, charge, and orbital degrees of freedom, giving rise to electronic and magnetic states intrinsically coupled to catalytic activity [13]. When redox-active octahedral metal centers are preferentially exposed at the surface, site heterogeneity is minimized, reactant accessibility is enhanced, and short metal–metal distances promote multi-electron transfer and charge transport [14, 15]. Such structural and electronic characteristics accelerate kinetics and improve selectivity. In particular, cobalt-containing octahedral sites offer favorable *d*-band–Fermi-level alignment, lowering kinetic barriers for nitrate reduction and nitric oxide dissociation while reducing reliance on scarce noble metals [16–18]. Moreover, ferri- or ferromagnetic ordering in spinel TMOs, coupled with low crystallographic anisotropy, enables dynamic modulation of surface states under external fields, strain, or temperature, offering a unique opportunity to modulate surface reactivity and electronic structure during operation. By influencing atomic alignment, spin states, and reaction kinetics, applied fields direct nucleation, crystallization, and defect formation, enabling structures and functionalities beyond conventional thermal processing [19]. In materials containing open-shell *d*-elements, an external magnetic field (**B**) introduces a Zeeman energy term ($-\boldsymbol{\mu} \cdot \mathbf{B}$) that selectively stabilizes spin- or orbital-aligned regions. This stabilization increases the driving force for crystallization, lowers nucleation barrier (ΔG^*), and directs preferential nucleation, enabling controlled atomic ordering in structural evolution and facet formation [20]. Our previous work has explored how magnetic fields during CVD influence grain growth (Fe, Fe₂O₃) [21, 22], crystallographic phase modifications (Fe₂O₃ vs Fe₃O₄) [23], magnetically-induced degree of inversion in MgFe₂O₄ spinel [24], stabilization of metastable compounds (UO₂ vs U₃O₈) [25], and surface state, texture, and phase-purity control (TiO₂) [26].

The application of external magnetic fields in electrocatalysis has recently emerged as a promising route to enhance the activity of ferromagnetic spin catalysts for nitrate reduction to ammonia. However, systematic studies remain scarce, with only a single ferromagnetic spin catalyst examined under such conditions [27]. A critical limitation of this strategy is its transience: catalytic enhancement persists only under continuous field application and vanishes once the field is removed. Magnetic-field-assisted synthesis, by contrast, offers an unexplored opportunity to permanently modulate spin configurations and surface states, enabling durable improvements in activity and kinetics for sustainable nitrate-to-ammonia conversion. Here, we leverage magnetic-field-assisted chemical vapor deposition (mf-CVD) to engineer surface states and cation distribution of CoFe₂O₄ thin films. The applied magnetic field preferentially stabilizes Co²⁺ ions in octahedral sites, which constitute the most surface-exposed active sites in spinel structures, enhancing local electron density and facilitating charge transport. This structural modulation strengthens electronic–adsorbate interactions and lowers kinetic barriers for nitrate reduction. Beyond static structural control, field-assisted synthesis also directs dynamic surface reconstruction under electroreduction. CoFe₂O₄ films synthesized under a 1 T field (CoFe₂O₄-1T) exhibit more than 22-fold higher ammonia production rate compared with isostructural Fe₃O₄-

1T, highlighting cobalt critical role in nitrate reduction, and an almost threefold enhancement relative to CoFe₂O₄-0T, demonstrating the efficacy of magnetic-field-driven spinel engineering. Complementary DFT calculations corroborate these findings, identifying cobalt as the primary active site that suppresses competing hydrogen evolution while selectively promoting nitrate conversion.

2 | Results and Discussion

2.1 | Material Synthesis and Characterization

Crystalline thin films of cobalt ferrite and magnetite were deposited using [Co{Fe(OⁱBu)₄}]₂ and [Fe{Fe(OⁱBu)₄}]₂ as novel molecular precursors in a customized magnetic field-assisted cold-wall CVD (mf-CVD) assembly (Note S1, Schemes S1–S4, Figure S1, Table S1). These precursors exhibit precise Co^{II}:Fe^{III} and Fe^{II}:Fe^{III} ratios, ensuring the stoichiometric control necessary for the targeted metal oxide compositions. The deposition process at 550°C and 10^{−5} mbar yielded high-quality films on FTO substrate (Figure 1a). During magnetic-field-assisted chemical vapor deposition, external magnetic fields exert multifaceted influences on nucleation, growth, and structural evolution of magnetically active materials. Thermally activated surface processes are highly sensitive to even modest magnetic fields, as the Zeeman interaction and associated magnetic free energy contributions lower the nucleation barrier and stabilize spin-aligned configurations in nascent clusters, promoting energetically favorable crystallographic orientations [28–30]. In ferrimagnetic nanostructures, externally applied fields induce long-range dipolar interactions between domains, directing cluster assembly into anisotropic two- and three-dimensional superstructures and influencing growth kinetics [31, 32]. The spatial distribution of magnetic flux lines further modulates adatom mobility and adsorption geometries, impacting surface diffusion, precursor decomposition, and phase selection during deposition [33]. Field-enhanced chemical vapor deposition studies confirm that these effects manifest in controlled grain orientation, morphology, and defect density, evidencing a direct link between applied field and microstructural tuning [19]. Magnetic-field-induced structural phase transitions reported in various ferromagnetic compounds demonstrate that even moderate fields can drive metastable configurations and preferential lattice distortions [34–36]. In our system, the proximity of the deposition temperature to the Curie point further amplifies these effects by increasing magnetic susceptibility and spin fluctuations, enhancing field-driven ordering.

The crystallinity and phase purity of thin films deposited under 0, 0.5, and 1 T were evaluated using XRD (Figure 1b, c, and Figure S2). The diffraction peaks at $2\theta = 18.4^\circ$ (111), 30.1° (220), 35.4° (311), 37.1° (222), 43.1° (400), 57.0° (511), and 62.6° (440), match the cubic spinel structure of CoFe₂O₄ (JCPDS card number 00-022-1086; Fd-3m), and Fe₃O₄ (JCPDS card number 03-065-3107; Fm-3m) [37]. Magnetic measurements at 300 K confirm ferromagnetism in CoFe₂O₄ films, with higher coercivities for CoFe₂O₄-1T (2555 Oe) compared to CoFe₂O₄-0T (2442 Oe) and CoFe₂O₄-0.5T (2389 Oe) (Figure 1d,e). The M_r/M_s ratio indicates a pseudo-single-domain regime, reflecting strong uniaxial anisotropy and domain wall pinning in these magnetically hard materials (Table S2, and Figure S1c) [38]. Magnetic-field-assisted synthesis modulates

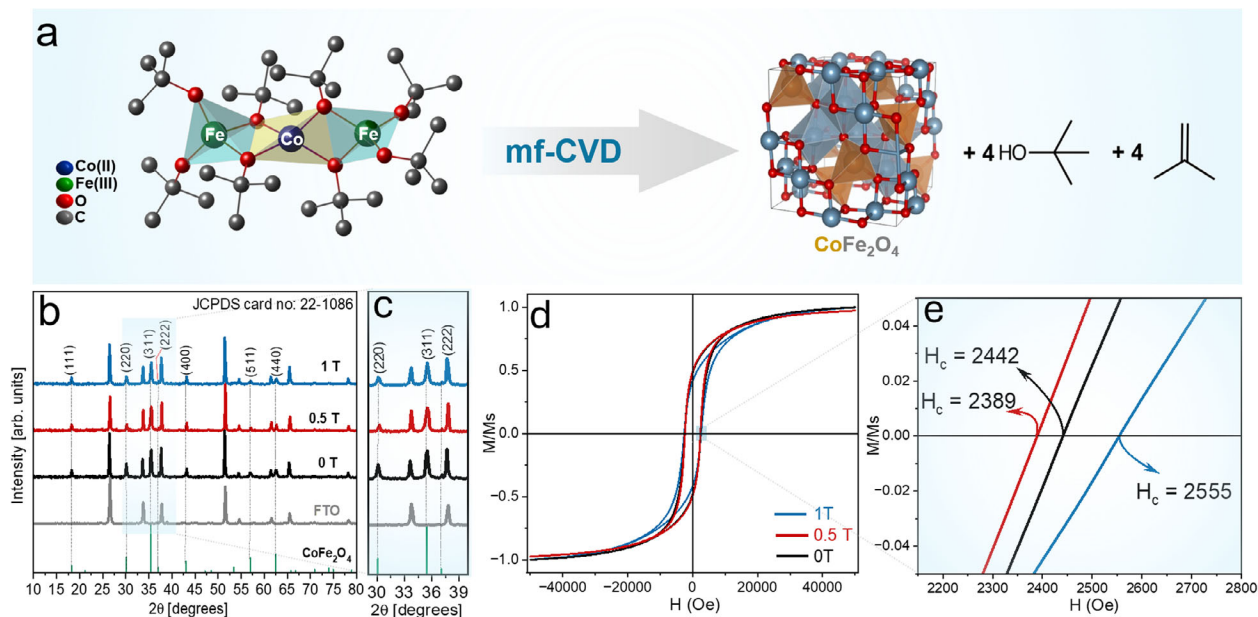


FIGURE 1 | (a) Molecular structure of the $[\text{Co}\{\text{Fe}(\text{O}^t\text{Bu})_4\}_2]$ precursor and its decomposition pathway via mf-CVD leading to the formation of CoFe_2O_4 . (b,c) XRD patterns of CoFe_2O_4 -0T, 0.5, and 1T thin films deposited by mf-CVD. (d,e) Room-temperature magnetic hysteresis loops of CoFe_2O_4 -0, 0.5, and 1T.

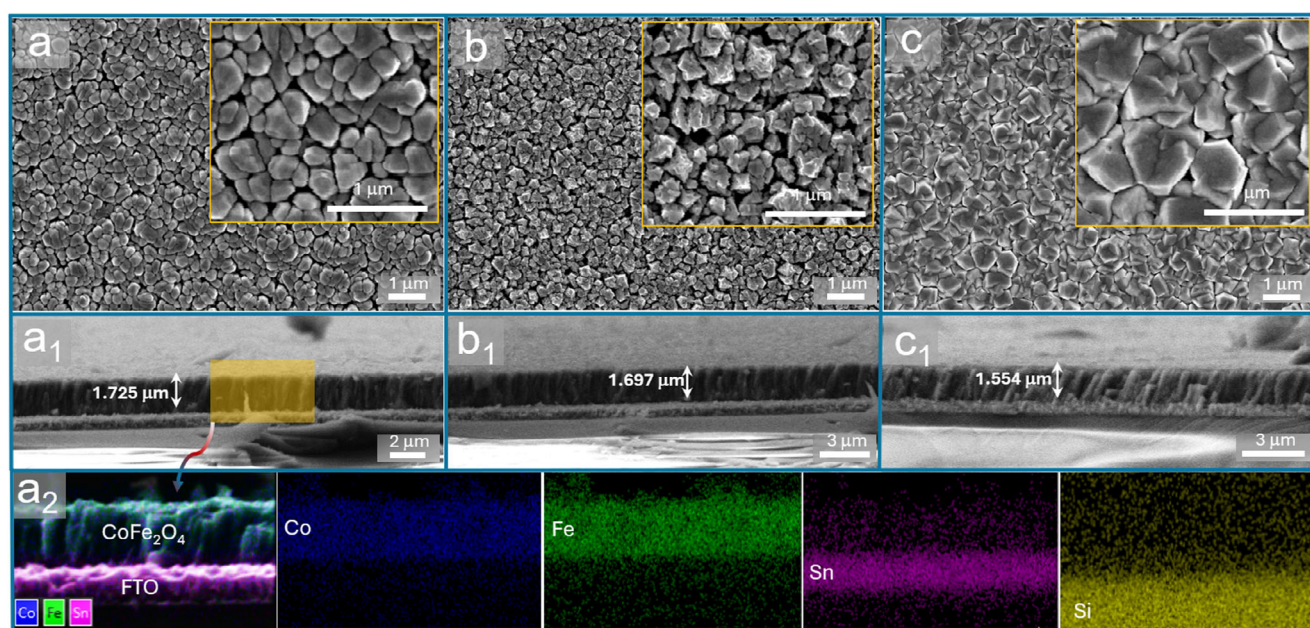


FIGURE 2 | (a–c) Top-view scanning electron microscopy (SEM) images, and (a₁, b₁, c₁) cross-sectional SEM images of CoFe_2O_4 thin films prepared via mf-CVD under different magnetic fields: a: 0T, b: 0.5 T, and c: 1 T. (a₂) Represent energy-dispersive X-ray spectroscopy (EDX) elemental mapping of cross-section morphology for CoFe_2O_4 -0T thin film.

domain architecture and grain boundaries, yielding CoFe_2O_4 -1T films with reduced boundary density, improved crystallographic alignment, and stabilized pseudo-single-domain walls, enhancing spin coherence and catalytic stability [39, 40].

Scanning electron microscopy (SEM) confirmed the uniform deposition of CoFe_2O_4 and Fe_3O_4 thin film on the FTO substrate (Figure 2 and Figures S3–S8). The average thickness of the

CoFe_2O_4 films, prepared under different magnetic fields, was in the range of 1.5–1.7 μm . SEM analyses revealed distinct morphology changes, indicating the influence of the external magnetic field on film growth dynamics. Energy dispersive X-ray (EDX) mapping confirmed homogeneous Co, Fe, and O distribution.

To probe potential non-crystalline secondary phases undetectable by XRD, Raman spectroscopy was employed (Figure 3a–d, and

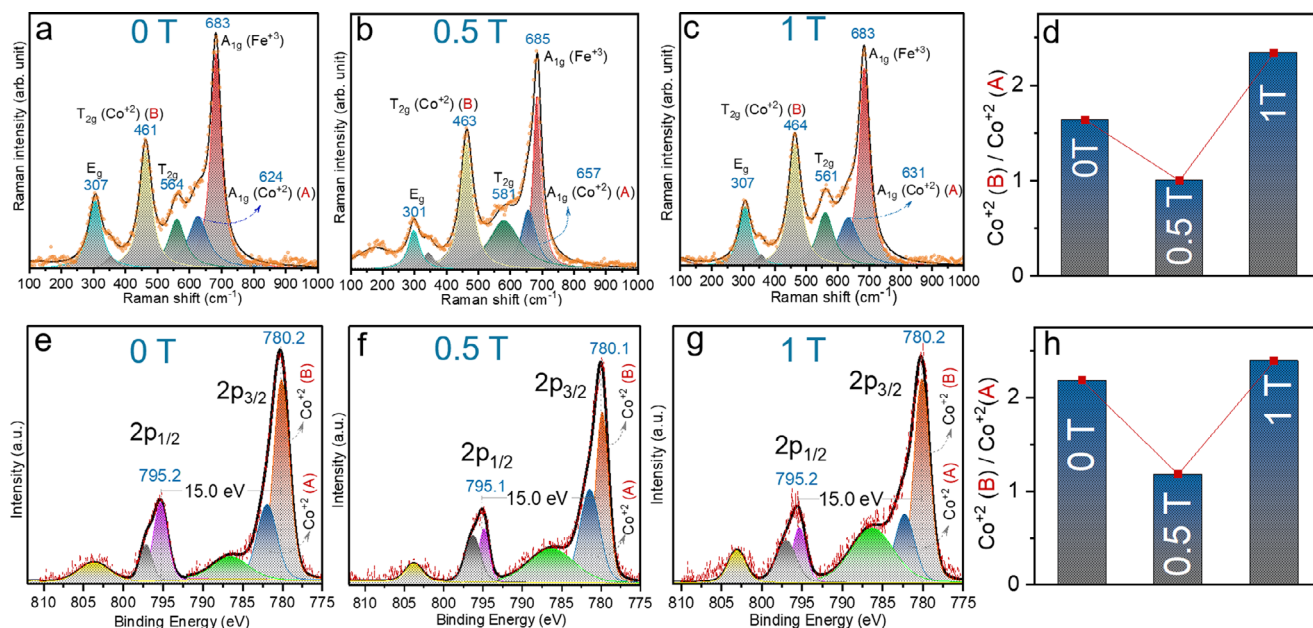


FIGURE 3 | (a–d) Raman spectra of CoFe₂O₄-0T, 0.5, and 1T, with (d) the corresponding Co²⁺ site occupancy ratio derived from Raman analysis. (e–h) High-resolution Co 2p XPS spectra of CoFe₂O₄-0T, 0.5, and 1T, with (h) the extracted Co²⁺ occupancy ratio in octahedral versus tetrahedral coordination.

Figure S1d). Five Raman-active phonon modes, characteristic of spinel CoFe₂O₄ (Fd3m), confirmed highly crystalline films free from amorphous phases [41]. The A_{1g} modes at ~683 and 624–657 cm⁻¹ arise from symmetric stretching of Fe³⁺–O and Co²⁺–O bonds in tetrahedral (A) sites of the spinel lattice, respectively. Below 600 cm⁻¹, T_{2g} symmetry modes at 561–581, and ~464 cm⁻¹, as well as an E_g mode at ~307 cm⁻¹, correspond to bending of metal-oxygen bonds in octahedral (B) sites. The sharp peak at ~464 cm⁻¹, absent in Fe₃O₄ (Figure S9a–c), is assigned to the T_{2g} mode of Co²⁺ in the octahedral cavities. Tailoring Co²⁺ occupancy in octahedral sites modulates the local electronic environment and facilitates more favorable redox transitions at the catalyst surface [14, 15, 42]. Prior study on magnesium ferrite demonstrated that applied magnetic fields modulate inversion degree by altering cation occupancy [24]. Consistently, Raman intensities at 631 and 464 cm⁻¹ indicate higher octahedral Co²⁺ occupancy in CoFe₂O₄-1T relative to CoFe₂O₄-0T, and 0.5T (Figure 3d).

In spinel CoFe₂O₄, the electronic structure of Co²⁺ is strongly governed by its local coordination environment through ligand field effects. Specifically, Co²⁺ in octahedral sites adopts a high-spin d⁷ configuration (t_{2g}⁵eg²) with a larger crystal-field splitting (Δ_o), whereas tetrahedral (T_d) coordination results in a reduced and inverted splitting (Δ_t ≈ 4/9 Δ_o), leading to distinct orbital occupancies and exchange interactions. Consequently, variations in the Co²⁺(B)/Co²⁺(A) ratio directly modulate metal-oxygen covalency and Co–O–Fe superexchange pathways, thereby influencing the electronic structure relevant to catalytic activity.

The chemical states and site-specific coordination of cobalt and iron in ferrite thin films were examined by high-resolution X-ray photoelectron spectroscopy (XPS) (Figure 3e–h, and Figures S1e,f, S9, and S10). The Co 2p spectra exhibit characteristic features of Co²⁺ in an oxide environment, including intense shake-up satellite peaks located ~5–7 eV above the main Co

2p_{3/2} and Co 2p_{1/2} signals, consistent with a high-spin electronic configuration [14, 43]. Deconvolution of the Co 2p_{3/2} region (~780 eV) reveals contributions that can be assigned to Co²⁺ in tetrahedral (A-site) and octahedral (B-site) coordination environments, in agreement with previous reports on spinel CoFe₂O₄ (Figure 3e–g) [14, 44]. The relative positions and intensities of these components are consistent with literature-established binding energy differences between A- and B-site Co²⁺ species. Quantitative analysis indicates an increased Co²⁺(B)/Co²⁺(A) ratio for the CoFe₂O₄-1T sample compared to CoFe₂O₄-0T and 0.5T (Figure 3h), suggesting magnetic-field-induced stabilization of Co²⁺ in octahedral coordination. Enhanced B-site occupancy strengthens electronic coupling with lattice oxygen, accelerating electron transfer during electrocatalysis. The satellite intensity and consistent spin-orbit splitting of ~15.0 eV across all samples corroborate the uniform +2 oxidation state of cobalt. The Fe 2p spectra exhibit characteristic Fe 2p_{3/2} and Fe 2p_{1/2} peaks accompanied by well-defined satellite features, consistent with stoichiometric CoFe₂O₄. The spin-orbit splitting between the Fe 2p_{3/2} and Fe 2p_{1/2} components is maintained at ~13.8 eV, in good agreement with reported values for Fe³⁺ in spinel oxides. The binding energies and satellite structure collectively confirm that iron is predominantly present in the Fe³⁺ oxidation state (Figure S11f) [14, 44]. The combined evidence from Raman and XPS provides a consistent and physically meaningful picture: magnetic-field-assisted synthesis alters cation distribution, which in turn modifies the local electronic structure and spin state of catalytically active Co sites, which are intrinsically linked to catalytic functionality.

2.2 | Electrocatalytic Performance of Catalysts

The electrocatalytic NO₃RR performance of the catalysts was compared as a function of the applied magnetic field during their

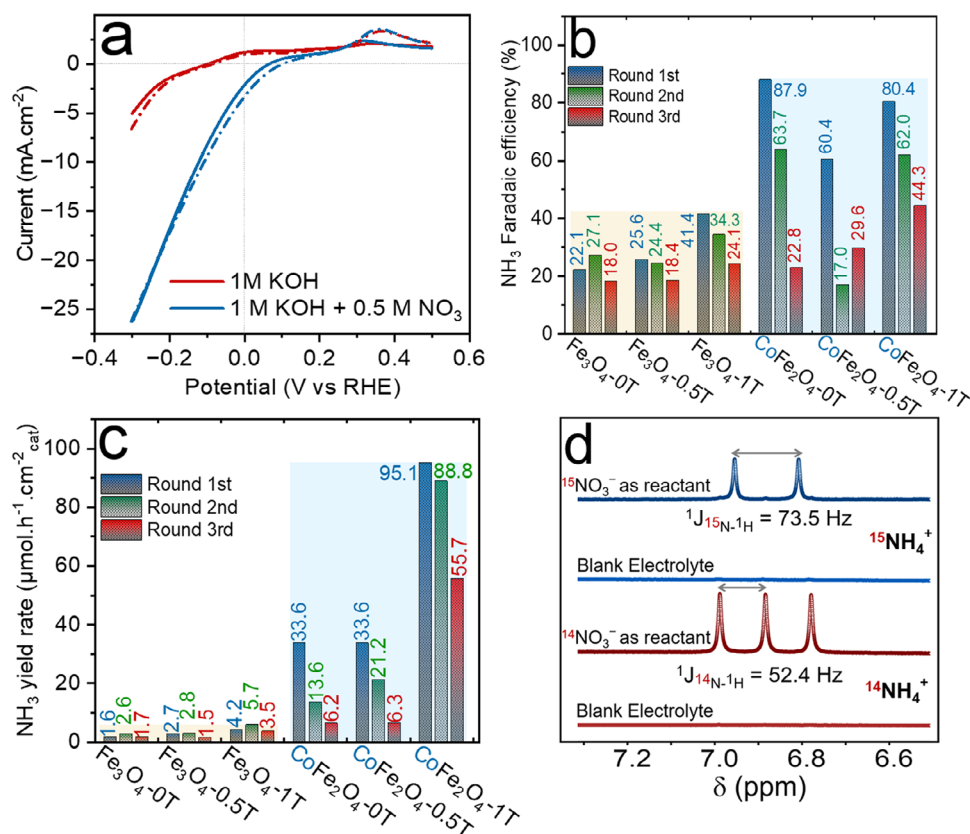


FIGURE 4 | (a) Linear sweep voltammetry (LSV) curves of the as-prepared CoFe₂O₄-1T sample recorded before (solid lines) and after testing (dash-dot lines). (b) Faradaic efficiencies for ammonia production using different catalysts, and (c) ammonia yield rates after 3 h of operation at an applied potential of -0.3 V vs. RHE over three consecutive cycles in 1 M KOH containing 0.5 M NaNO₃ for all thin films. (d) ^1H -NMR spectra of NH₄⁺ produced via electrochemical reduction of $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$ at -0.3 V vs RHE and using CoFe₂O₄-1T thin film.

synthesis. Linear sweep voltammetry (LSV) in anodic direction on CoFe₂O₄-1T, in the presence and absence of nitrate, revealed a clear increase in magnitude of the current density below 0.1 V vs RHE upon NO₃⁻ addition (Figure 4a). This behavior was similarly observed across all electrocatalysts (Figure S12) and persisted following iR correction (Figures S13 and S14). The change in current density upon NO₃⁻ addition provides direct electrochemical evidence of active NO₃RR, which was subsequently quantified by chronoamperometry coupled with ammonia determination using the indophenol method (Experimental section and Figure S15) [45, 46].

A discussion of sample resistance is needed to assess the observed trends in ammonia yield rate and Faradaic efficiency (FE) (Figure 4b,c). Both Fe₃O₄ and CoFe₂O₄ are semiconducting metal oxides with bulk resistances exceeding that of the used electrochemical cell with conductive metal electrodes. Thus, the uncompensated resistance extracted from electrochemical impedance spectroscopy (EIS) includes contributions from the films themselves, with Fe₃O₄ exhibiting lower conductivity than CoFe₂O₄ (Figure S16), consistent with a prior report [47]. Furthermore, resistance increased after three electrochemical cycles (Figure S16), likely due to redox-driven structural changes and redistribution of metal cations among crystallographic sites during electrochemical operation [48, 49]. Additionally, the LSV was clearly overcompensated when corrected for iR_u with R_u from EIS before the LSV (Figures S13 and S14). Consequently,

all electrochemical data are presented without iR_u compensation, and sample resistance may influence the surface potential and thus absolute yield rates and FE values. Notably, iR_u compensation is rarely applied in the NO₃RR literature, including all studies summarized in Table S3. We therefore conclude that the observed performance trends remain meaningful for our systematic comparison of electrocatalyst performance within this study.

Figure 4b,c, and Figure S17 compare FE and ammonia yield rate at an applied potential of -0.3 V vs. RHE for Fe₃O₄ and CoFe₂O₄ films synthesized under magnetic fields of 0, 0.5, and 1 T (Table S4). During the first round of nitrate reduction, the FE increased from 22% for Fe₃O₄ to 88% for CoFe₂O₄. The yield rate increased from 1.6 μmol·h⁻¹·cm⁻² for Fe₃O₄-0T to 33.6 μmol·h⁻¹·cm⁻² for CoFe₂O₄-0T (+2177%), which highlights the role of Co in promoting NO₃RR. Magnetic-field-assisted synthesis further improved the ammonia yield rate to 95 μmol·h⁻¹·cm⁻² (+283% relative to CoFe₂O₄-0T) and enhanced FE for CoFe₂O₄-1T (Figure 4b,c). The same magnetic-field-dependent enhancement was consistently observed for the Fe₃O₄ samples. Specifically, Fe₃O₄-0T exhibited a nitrate-to-ammonia yield rate of 1.6 μmol h⁻¹·cm⁻² with a Faradaic efficiency of 22.1%, whereas Fe₃O₄-1T delivered a substantially improved yield rate of 4.2 μmol h⁻¹·cm⁻² (+262.5%) and a Faradaic efficiency of 41.4% (+187%). The observation of a comparable enhancement in two independent material systems supports that the improved NO₃RR performance originates

from the magnetic-field-assisted synthesis itself, rather than from uncontrolled batch-to-batch or environmental variations. Threefold repetition of the measurements using a streamlined protocol B (Table S5), yielded an average ammonia rate of $69 \pm 42 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and a FE of $78 \pm 7\%$ for CoFe_2O_4 -1T, supporting the representativeness of the selected sample. At a more cathodic potential of -0.5 V vs RHE, the yield rate and FE with standard errors increased to $133 \pm 38 \mu\text{mol}\cdot\text{cm}^{-2} \text{ h}^{-1}$ and $96\% \pm 3\%$, respectively, indicating that higher overpotentials favor product formation and reproducibility (Table S6). Yield rate and FE of the optimized sample are clearly, and for -0.5 V significantly, above the threshold value of $36 \mu\text{mol}\cdot\text{cm}^{-2} \text{ h}^{-1}$ proposed by Choi et al. for “promising” ammonia production [50]. While the yield rate lies in the lower third of recent reports (Table S3), direct comparison is limited by drastic differences in surface area, protocols, and lack of iR_u compensation. The average potential reduction after iR_u compensation was $223 \pm 80 \text{ mV}$ for CoFe_2O_4 -1T at -0.5 V (Table S6), suggesting that the intrinsic overpotential of CoFe_2O_4 -1T was much lower compared to the applied potential.

Experimental protocol A (Table S4) was repeated three times on each of the representative samples (Figure 4b,c, and Figure S17). In the third round, trends in FE and yield rate persisted when comparing magnetic-field-assisted synthesis and Cobalt incorporation. Importantly, CoFe_2O_4 -1T, which exhibited the highest initial activity, showed the least relative degradation of yield rate and FE with repetition testing. At -0.3 V vs. RHE, the yield rate decreased from 95.1 to $55.7 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and FE from 80% to 44% , outperforming CoFe_2O_4 -0T (33.6 to $5.2 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and 88% to 23%). This represents a rare case where synthesis optimization enhanced both intrinsic activity and stability. After three cycles, the yield rate remained above the benchmark proposed by Choi et al. [50]. In a complementary longer experiment, CoFe_2O_4 -1T was assessed by 24 h chronoamperometry at -0.3 V (Figure S18), during which the current density gradually increased from -23 to approximately $-30 \text{ mA}\cdot\text{cm}^{-2}$. These results highlight the promise of magnetic-field-assisted synthesis of CoFe_2O_4 electrocatalyst, while underscoring the potential for further stability optimization. The origin of the changes in FE and yield rate during each catalytic round will be investigated further in future work.

To verify the origin of the produced ammonia, isotopically labeled $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$ were employed as the nitrogen sources under Protocol A (Table S4). Electrolyte samples (5 mL) were collected after 90 min of electrolysis, acidified to $\text{pH } 5$ using 10% sulfuric acid, and analyzed by NMR spectroscopy (Figure 4d). A blank electrolyte (0 min , before reaction) was analyzed under the same conditions to rigorously exclude background contamination. The NMR spectra exhibit a distinct doublet resonance for ammonia produced from $^{15}\text{NO}_3^-$, arising from ^1H - ^{15}N spin coupling, whereas electrolysis with $^{14}\text{NO}_3^-$ yields the expected triplet signal associated with $^{14}\text{NH}_4^+$ [51, 52]. Furthermore, no ammonia-related signals are detected in the blank electrolyte, confirming the absence of adventitious nitrogen sources. To further exclude false-positive contributions, a control experiment was conducted under open-circuit conditions (i.e., without applied potential) following Protocol A. As shown in Figure S19, no indophenol formation was detected within the sensitivity limits of the method. The isotope-dependent spectral signatures

provide direct evidence that the generated ammonia originates exclusively from nitrate reduction. This validation eliminates the possibility of contamination or parasitic nitrogen contributions and firmly establishes the intrinsic NO_3RR activity of the CoFe_2O_4 electrocatalyst.

Differential electrochemical mass spectrometry (DEMS) was employed to qualitatively probe gaseous and volatile intermediates formed during the NO_3RR on CoFe_2O_4 -1T and Fe_3O_4 -1T catalysts (Figure S20). A multistep chronoamperometry protocol was applied in the DEMS cell while continuously monitoring mass signals associated with possible reaction products. The measurements reveal the evolution of signals assignable to NH_2 species and H_2 at the relatively high current of NO_3RR , indicating concurrent nitrate reduction and hydrogen evolution processes. For Fe_3O_4 -1T, these signal changes are observed at 0 V vs RHE, indicating H_2 evolution as well as the formation of highly active NH_2 intermediates shown in Figure S20a (highlighted in cyan). Similar changes are observed for CoFe_2O_4 -1T, but they occur at a higher overpotential (-0.2 V) and higher current (-15 mA) (Figure S20b, indicated by cyan highlighting). This suggests that CoFe_2O_4 -1T promotes the reduction pathway toward NH_3 formation, while the detection of other possible byproducts requires higher current densities. As DEMS is inherently insensitive to dissolved ionic species, the post-reaction electrolyte was subsequently analyzed using the Griess assay to quantify NO_2^- . Following the multistep protocol, chronoamperometry was performed at a constant potential of -0.3 V vs RHE for 5 min before analysis. For both catalysts, measurable concentrations of NO_2^- were detected (Figure S21), confirming nitrite as a key intermediate in the reduction pathway. Notably, despite exhibiting a lower current density at -0.3 V vs RHE (Figure S21b), Fe_3O_4 -1T generates a higher NO_2^- concentration compared to CoFe_2O_4 -1T. This observation is consistent with the Faradaic efficiency trends presented in Figure 4b and suggests that Fe_3O_4 favors partial nitrate reduction to NO_2^- , whereas CoFe_2O_4 more effectively promotes further reduction toward NH_3 .

EIS was employed to elucidate interfacial charge-transfer dynamics during NO_3RR (Note S2, Figures S22–S24, and Tables S7 and S8). Magnetic-field-assisted CoFe_2O_4 films exhibited accelerated charge-transfer kinetics and reduced interfacial resistance, consistent with their enhanced catalytic activity. CoFe_2O_4 -1T demonstrated the most efficient interfacial transport, characterized by minimal surface passivation and markedly reduced charge-transfer resistance.

From CPE_{dl} and R_{ct} in Table S7 and Note S2, we estimated effective capacitances of 1.85 , 0.25 , and 0.03 mF for 0 , 0.5 , and 1 T applied during the synthesis of CoFe_2O_4 , respectively. This matches the size of the trends in grain size in Figure 2a–c reasonably well. The yield in Figure 4c has the opposite trend, where 0 T has the smallest yield rate of $33.6 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and 1 T has the highest yield rate of $95.1 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$. We conclude that the trend in initial surface area cannot explain the trend in activity and attribute it to a change in electronic structure. This demonstrates that magnetic-field-directed synthesis modulates the interfacial electronic structure and energetics, improving NO_3RR performance. Furthermore, systematic thickness-controlled studies confirm that the enhancement

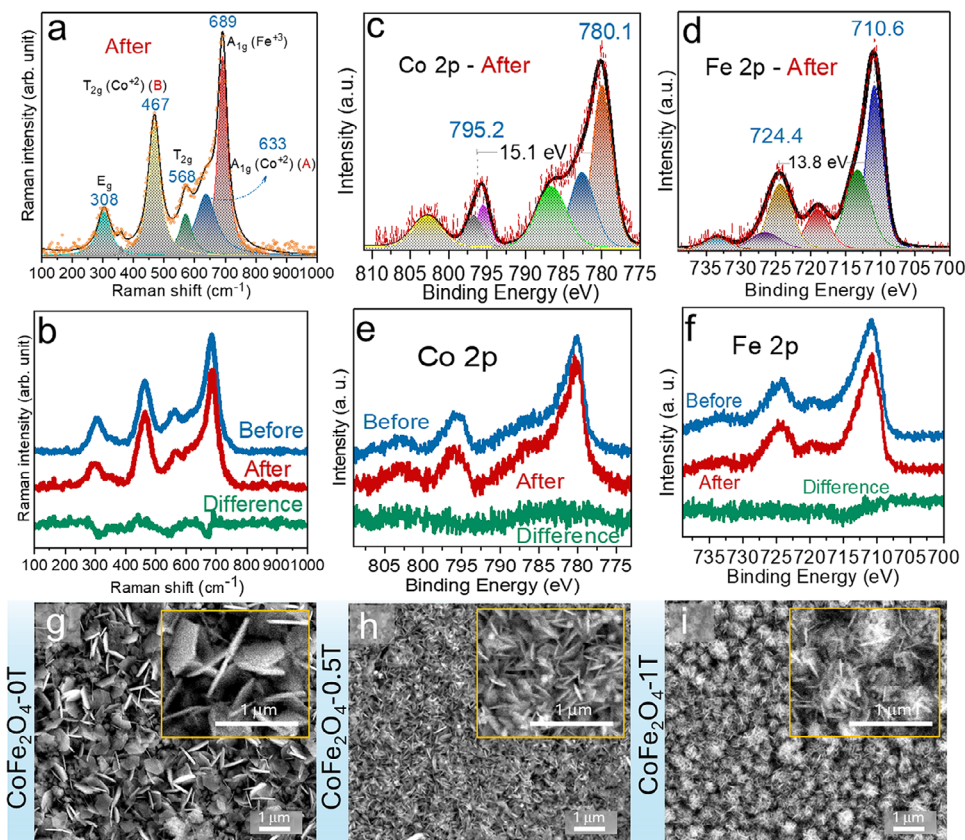


FIGURE 5 | (a) Room-temperature Raman spectra of CoFe_2O_4 -1T recorded after NO_3RR . (b) Comparative Raman spectra of CoFe_2O_4 -1T before (blue) and after (red) NO_3RR , along with the corresponding difference spectrum (after–before, green). High-resolution XPS spectra of CoFe_2O_4 -1T: (c) Co 2p and (d) Fe 2p recorded after NO_3RR ; (e,f) comparative Co 2p and Fe 2p spectra collected before (blue), after (red), and their corresponding difference spectra (after–before, green). Top-view scanning electron microscopy (SEM) images of CoFe_2O_4 thin films after electrochemical nitrate reduction to ammonia (g) CoFe_2O_4 -0T, (h) CoFe_2O_4 -0.5T, and (i) CoFe_2O_4 -1T.

originates from magnetic-field-induced structural modulation rather than variations in film thickness or resistance (Note S3, Figures S25 and S26). The absence of new redox features in LSV for CoFe_2O_4 -1T (Figure 4a) further supports magnetic imprinting of catalytic properties during synthesis, motivating future in-depth physical characterization. However, there is a slight shift toward a lower NO_3RR onset potential for CoFe_2O_4 -1T (Figure 4a), this may be due to minor changes in surface roughness and electronic structure during the experiment.

We performed extensive multimodal post-mortem analyses to understand the role of Co and the magnetic field during synthesis for the formation of the active state after conducting the NO_3RR . Raman spectra (Figure 5a,b) show that the characteristic A_{1g} and T_{2g} modes of the spinel lattice remain unchanged in position and relative intensity, confirming preservation of crystallinity and cation framework under electrochemical conditions. A slight broadening of the $\sim 464\text{ cm}^{-1}$ mode is observed, which is attributed to localized perturbations of Co^{2+} in octahedral sites, likely arising from surface reconstruction and the formation of defect states under electrochemical conditions. XRD patterns showed no alteration in crystallinity (Figure S2), and XPS confirmed invariant Co (2p) and Fe (2p) binding energies, underscoring bulk stability under operating conditions (Figure 5c–f, and Figure S11). Moreover, XPS detected N 1s species ($\sim 400\text{ eV}$) after cycling, absent in pristine samples, evidencing

nitrate adsorption and possible residual surface coverage by nitrogen-containing intermediates (Figure S10). Additional peaks at around 298, 383, and 497 eV correspond to K 2p, K 2s, and Na^+ (KLL) auger transitions, respectively, indicating electrolyte-derived potassium and sodium nitrate [53]. The minor changes for Co 2p and Fe 2p spectral line shapes are attributed to surface-localized interactions with adsorbed nitrogen intermediates and electrolyte ions (K^+/Na^+), rather than modifications of the bulk electronic structure.

In contrast, SEM revealed pronounced surface reconstruction after 9 h of chronoamperometry at -0.3 V . The evolution of morphology correlated with the magnetic field applied during synthesis: CoFe_2O_4 -0T displayed platelet-like features, whereas CoFe_2O_4 -0.5 and 1T formed progressively finer needle-like structures (Figure 5g–i, and Figures S3–S8). The most active catalyst, CoFe_2O_4 -1T, exhibited the finest features, consistent with magnetic-field-directed restructuring. Also, comparable but distinct magnetic-field-dependent trends were observed in Fe_3O_4 films. These results demonstrate that mf-CVD not only controls the initial bulk texture and surface states but also encodes an intrinsic surface responsiveness under electrochemical bias. This can reveal a broader design principle: external magnetic fields imprint persistent electronic and magnetic order that controls both the static architecture and dynamic evolution of spinel oxide catalysts.

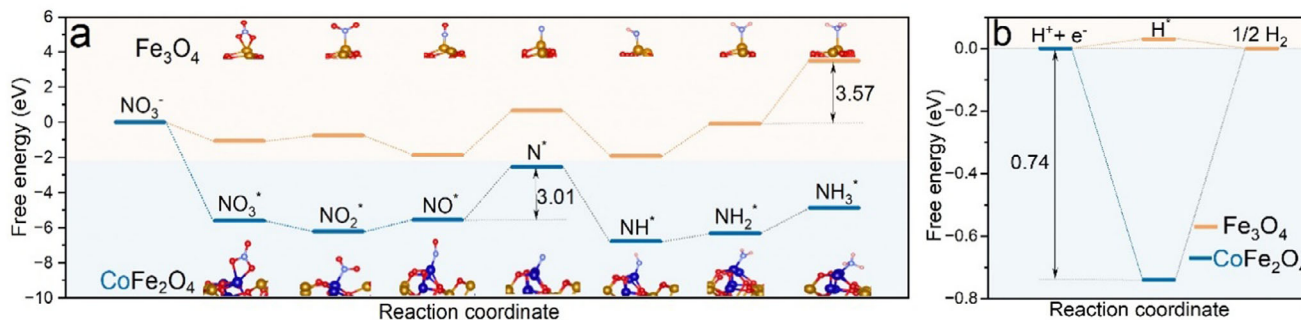


FIGURE 6 | (a) Gibbs free energy profile along the minimum energy pathway for NO₃RR, with representative adsorption configurations of key intermediates. (b) Free energy profile for HER, where the larger ΔG value for H₂ formation on the CoFe₂O₄ surface compared to the Fe₃O₄ surface indicates suppressed HER activity on CoFe₂O₄. Color code: cobalt (blue), iron (brown), oxygen (red), nitrogen (light blue), and hydrogen (light red).

2.3 | DFT-Based Theoretical Insights

Using first-principles density functional theory (DFT) calculations, we modeled ammonia formation on CoFe₂O₄ and Fe₃O₄ surfaces based on experimentally [54–56] and theoretically [57–61] justified facet selection (Figure 6). XRD patterns of CoFe₂O₄ thin films (Figure 1b,c) show the (311) reflection as the most intense peak, indicating that this facet is preferentially expressed under the employed growth conditions and represents the dominant surface orientation. For Fe₃O₄, prior theoretical [57] studies have identified the (111) facet as the most thermodynamically stable low-index surface, consistent with its frequent observation in experimental systems and widespread use in surface reactivity studies. Accordingly, the CoFe₂O₄ (311) and Fe₃O₄ (111) facets were selected as representative models to capture the dominant surface chemistry governing NO₃RR. The calculated work functions were 4.50 eV for Fe₃O₄ (111) and 6.98 eV for CoFe₂O₄ (311). The lower work function of Fe₃O₄ reflects a higher electron-donating capability, consistent with its enhanced HER activity, while the higher work function of CoFe₂O₄ suppresses HER and promotes nitrate reduction. While real catalyst surfaces may exhibit a distribution of facets and dynamic restructuring under operating conditions, these models provide a physically meaningful basis for comparing the intrinsic electronic structure and catalytic behavior of the two systems.

The rate-determining step (RDS) on Fe₃O₄(111) corresponds to the NH₂^{*} → NH₃^{*} transition, with an energy barrier of 3.57 eV, whereas on CoFe₂O₄ (311) the RDS is the NO^{*} → N^{*} step with a lower barrier of 3.01 eV. Competitive HER analysis further supports these trends with Fe₃O₄ (111) showing a lower HER overpotential, consistent with its stronger HER propensity (Figure 6a,b, and Table S9).

For selective nitrate reduction, strong nitrate adsorption combined with intrinsically weaker HER activity is essential [16,17]. CoFe₂O₄ displays much stronger nitrate adsorption energy (−5.58 eV) than Fe₃O₄ (−1.07 eV), providing a stronger thermodynamic driving force for nitrate activation. Simultaneously, its hydrogen adsorption free energy (−0.74 eV) is far from thermoneutral, imposing a substantial kinetic barrier for HER, thereby minimizing competition with nitrate reduction. The upslope from H^{*} to H₂ on CoFe₂O₄ further highlights stronger hydrogen adsorption (H_{ads}) retention, ensuring a

sustained proton reservoir for nitrate reduction. These results show that the exceptional nitrate reduction performance of CoFe₂O₄ originates from a synergistic balance between hydrogen adsorption through water dissociation and its timely consumption by nitrate-derived intermediates. This interplay suppresses competing HER pathways while directing protons toward ammonia formation, maximizing both ammonia yield and FE [62].

3 | Conclusion

This work presents a magnetic-field-assisted synthesis strategy that exploits intrinsic spin and electronic structure control to advance catalyst design for sustainable ammonia production. We show that applying an external magnetic field during the CVD growth of CoFe₂O₄ thin films selectively stabilizes Co²⁺ in octahedral lattice sites, enhances surface morphology, and imprints magnetic and electronic ordering that persists under electrochemical conditions. These field-induced modifications control not only the static structural features of the catalyst but also modulate dynamic surface reconstruction and catalytic selectivity during nitrate electroreduction. Our strategies of incorporating cobalt into the spinel ferrite framework relative to Fe₃O₄ and applying an external magnetic field during synthesis resulted in clear improvements in yield rate for ammonia production and FE that persisted in repeated experiments. Supported by DFT calculations, we identify cobalt as the primary active site that suppresses hydrogen evolution while promoting nitrate reduction. Building on this study, magnetic-field-assisted synthesis emerges as a promising platform for tuning the solid-state properties and catalytic functionality of spinel oxides through controlled modulation of cation distribution and electronic structure. While demonstrated here for CoFe₂O₄, the underlying mechanisms, namely magnetic-field-directed nucleation, spin-dependent energetic stabilization, and field-induced atomic ordering, are expected to apply to a broader class of magnetically responsive materials. At the same time, the extent to which these effects manifest will depend sensitively on composition, electronic structure, and magnetic ordering, underscoring the need for systematic studies across diverse material systems. Advancing this understanding will be critical to defining the scope of magnetic-field-driven synthesis and to establishing it as a versatile approach for the rational design of next-generation electrocatalysts for sustainable chemical transformations.

4 | Experimental Section/Methods

4.1 | Materials Synthesis

4.1.1 | Substrate Preparation

FTO substrates (Sigma–Aldrich) were prepared by cutting into dimensions of 10 mm × 15 mm, followed by a systematic cleaning protocol to ensure optimal surface quality. The substrate underwent sequential ultrasonic treatment for 15 min each in Hellmanex solution, deionized water, *iso*-propanol, and acetone. To avoid cross-contamination, the samples were per-rinsed with the solvent designated for the subsequent cleaning step before immersion in the ultrasonic bath.

4.1.2 | Electrode Preparation

For cathode preparation, in a horizontal cold-wall, chemical vapor deposition reactor equipped with an electromagnet (Mag Mess EM-2), the gas-pass deposition of CoFe_2O_4 , and Fe_3O_4 thin films was conducted utilizing alkoxide complexes as single-source precursors. For each deposition, 50 mg of the precursor was introduced to the system via a glass flange attached to the 10 mL flask, with the precursor temperature maintained at 150°C to ensure consistent and homogeneous gas-phase delivery. Before starting the deposition, the reactor chamber was evacuated to an ultra-high vacuum of 3×10^{-5} mbar to eliminate residual oxygen/moisture and suppress undesired side reactions in the gas phase. The precursor vapor for the desired time (deposition time) was directed toward a DC Joule-heated substrate (without any carrier or reactive gas), maintained at 550°C. For samples synthesized under an external magnetic field, during the deposition, a field strength of 0.5 or 1 T was applied, and field stability was achieved by constant current flow. For all samples, the magnetic field was applied in a vertical orientation relative to both the substrate and the precursor flow. No additional thermal ramping protocol for heating or cooling was implemented, aiming to simplify the process conditions and enhance the reproducibility.

4.2 | Precursor and Materials Characterization

The crystal structure of $[\text{Co}\{\text{Fe}(\text{O}^i\text{Bu})_4\}_2]$ and $[\text{Fe}\{\text{Fe}(\text{O}^i\text{Bu})_4\}_2]$ were determined using single-crystal X-ray diffraction at 100(2)K. Measurements were performed on a Bruker D8 Venture system equipped with a Photon 100 CMOS detector, utilizing Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$; Bruker, Rheinhausen, Germany). The crystal data were managed through APEX3 v2015.5-2. Structural solutions were obtained via dual-space methods implemented in SHELXT (Sheldrick 2015) [63], while refinements were performed with SHELXL 2017 using full-matrix least-squares calculation based on $F_o^2 \geq 2\sigma(F_o^2)$ [64]. Non-hydrogen atoms were refined anisotropically without restraints, and hydrogen atoms were incorporated through riding models. The crystallographic data for $[\text{Co}\{\text{Fe}(\text{O}^i\text{Bu})_4\}_2]$ and $[\text{Fe}\{\text{Fe}(\text{O}^i\text{Bu})_4\}_2]$ are available through the Cambridge Crystallographic Data Center (CCDC) under deposition numbers 2264143, and 2466364, respectively. Elemental analyses were conducted utilizing a HEKAtech CHNS Euro EA 3000 analyzer to ensure precise quantification of carbon and hydrogen in precursors. FT-IR spectra were recorded on a

Platinum ATR Spectrometer, employing a crystal plate as the sampling interface. Spectra data were recorded and analyzed using the PPUS software within the wavenumber range of 400–4000 cm^{-1} .

The crystallinity and phase composition of the synthesized thin films were analyzed through powder X-ray diffraction using a STOE STADI MP diffractometer operating in reflection geometry. The measurements were performed at room temperature under Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), with the instrument operating at 40 kV and 40 mA, ensuring optimal resolution and accuracy in the crystallographic analysis. Raman spectroscopy was conducted using a Lab Ram HR 800 spectrophotometer (Horiba Ltd) equipped with a green line Ar^+ ion laser (514.5 nm) excitation source, and for detailed analysis, the Raman spectra were further deconvoluted into individual Lorentzian peaks. The morphology, elemental distribution, and composition of the synthesized thin films were analyzed using a Zeiss Sigma 300 VP Rise field emission scanning electron microscopy (FESEM) equipped with an EDX spectrometer (Oxford Instruments Xplore 30). The SEM images were obtained at an acceleration voltage of 5 kV, while EDX Elemental mapping was performed at 10 kV to ensure precise compositional analysis. To evaluate the uniformity of film growth across the substrate, SEM survey images were collected from multiple surface locations, all of which demonstrated consistent and representative electrode morphology. For precise thickness measurement, cross-sectional samples were prepared by sectioning the films at their midpoint, followed by SEM imaging of the exposed cross-sectional surface of the films. Magnetic characterizations were performed using a vibrating sample magnetometer (VSM) option integrated into a cryogen-free Quantum Design Physical Property Measurement System (PPMS DynaCool), enabling precise magnetization measurements under controlled temperature and magnetic field conditions. ^1H -NMR spectra were recorded on a Bruker Avance III 500 MHz (^1H : 500 MHz, ^{13}C : 126 MHz). The surface composition was studied using X-ray photoelectron spectroscopy (XPS) with a SPECS Focus 500 monochromator and a Phoibos 100 electron analyzer, utilizing Al $K\alpha$ radiation (Photon energy: 1486.74 eV). The XP spectra were collected at a 90-degree photoelectron take-off angle, with the X-ray source and analyzer oriented at an angle of 54.7 degrees. All spectra were analyzed using CasaXPS software (Casa Software Ltd.) following established fitting protocols for transition-metal oxides. A Shirley background was applied, and the Co 2p region was deconvoluted using mixed Gaussian–Lorentzian line shapes. The spin–orbit splitting between Co $2p_{3/2}$ and Co $2p_{1/2}$ components was constrained to $\sim 15.0 \text{ eV}$, with peak area ratios maintained according to standard photoemission selection rules. Satellite features were fitted consistently across all samples to ensure physically meaningful comparisons. To ensure accuracy, the energy scale calibration was referenced to the adventitious carbon C1s peak at 248.8 eV.

The DEMS cell used in this study follows a design similar to that reported previously [65], incorporating a PTFE membrane (Cobetter Filtration, PF-B002H). The working electrode consisted of a polished titanium plate ($10 \times 5 \times 1 \text{ mm}$) coated with a catalyst thin film, of which an area of $5 \times 5 \text{ mm}$ was exposed to the electrolyte within the flow channel. A titanium substrate was employed because the cell design requires a conductive material on both sides. A leakless Ag/AgCl electrode (1.08 V vs RHE) was

used as the reference electrode. The vacuum system comprised a pre-chamber connected to the membrane, which was evacuated using a scroll pump to a pressure of approximately 0.06 mbar. The pre-chamber was connected to the analysis chamber of the quadrupole mass spectrometer (MKS) via a transfer line equipped with an orifice, a shutter, and a pressure gauge. The electrolyte was passed through the cell in a single-pass (non-circulating) configuration at a flow rate of 2 mL min⁻¹.

4.3 | Electrochemical Measurements

To evaluate the catalytic activity of the synthesized materials, electrochemical measurements were conducted using a Gamry 600 potentiostat in the presence and absence of 0.5 M NO₃⁻ ions in a 1 M KOH electrolyte at 25°C. The experiments were carried out in an H-type two-compartment cell equipped with a Nafion 117 membrane. A Hg/HgO electrode was used as the reference electrode, while a carbon black electrode acted as the counter electrode. Before each electrochemical measurement, the reference electrode was calibrated against a reversible hydrogen electrode (RHE) to ensure the accuracy of the reported potentials (representative measurement in Figure S22a). All potentials in this study are presented relative to the RHE and without iR_u correction due to the sizable potential dependence of the samples on the uncompensated resistance (R_u). Electrochemical impedance spectroscopy (EIS) was conducted to track R_1 , which was determined by extrapolating the Nyquist curve in high frequencies to $-Z_{im} = 0$ and taking Z_{re} as R_1 (representative measurement in Figure S27b). Additional EIS spectra were recorded at -0.3 V with an extended frequency range and fit to various models using the Z_{View} software, version 4, (Figures S22–S24 and Note S2). The quality of the fits between experimental and simulated data was evaluated using chi-square ($\chi^2 = 10^{-5}$). The protocols used and experimental parameters of these methods are documented in supplementary Tables S4 and S6. Standard errors were calculated for three identically prepared samples. The effective capacitance was calculated as $C_{eff} = \{(R_{ct} \text{ CPE}_{dl})^{1/n}\}/R_{ct}$, where R_{ct} is the charge transfer resistance, CPE_{dl} is the constant phase element, and n the ideality factor.

4.4 | Product Quantification and Faradaic Efficiency Calculation

Ammonia quantification was performed using the indophenol method, which provides a reliable correlation between ammonia concentration and colorimetric absorption changes [45, 46]. The indophenol method involved the preparation of three solutions immediately before quantification. Solution A: 5% wt. salicylic acid and 5% wt. sodium citrate dissolved in 1 M KOH. Solution B: 0.05 M NaClO in Milli-Q water. Solution C: 1% nitroprusside in Milli-Q water. These solutions were mixed with the electrolyte samples to initiate the Indophenol formation reaction. Specifically, 1 mL of the sample was combined with 1 mL of solution A, 1 mL of Solution B, and 0.2 mL of Solution C in a plastic vial. The mixture was kept in the dark for 1 h to ensure the reaction reached completion. Depending on the concentration of ammonia, the solution transitioned from light green to dark blue, which was quantified via UV-vis spectroscopy (Shimadzu UV1280). To validate the measurements, a standard

curve was generated using known concentrations of ammonia (Figure S15). By following the same preparation with solutions A to C with these standards, a calibration curve was obtained, providing a direct correlation between absorbance and ammonia concentration. The error from the calibration curve is ± 0.002 .

The FE for ammonia production was calculated using the following formula:

$$FE_{NH_3} = \frac{n_{NH_3} \times z \times F}{\text{total passed charge}} \times 100$$

here, n_{NH_3} represents the moles of ammonia determined from UV-vis spectroscopy, z is the number of electrons involved in ammonia formation from nitrate reduction ($n = 8$), and F is the Faraday constant (96 485 C·mol⁻¹). The error in this calculation comes only from the ammonia calibration curve.

The rate of ammonia production was determined as:

$$\text{Rate yield } (\mu\text{g}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}) = \frac{n_{NH_3} \times M_{NH_3}}{10^{-6} \times A \times t}$$

In this equation, M_{NH_3} is the molar mass of ammonia (g·mol⁻¹), A is the electrode surface area (cm²), and t is the reaction time (h). The error in the rate yield was propagated solely from the ammonia calibration curve.

Nitrite (NO₂⁻) formed after DEMS analysis was quantified using a modified colorimetric method adapted from the National Environmental Methods Index protocol originally developed for nitrate (NO₃⁻) determination [66]. In the standard procedure, VCl₃ is employed to reduce NO₃⁻ to NO₂⁻, followed by reaction with aromatic amines to form a diazo dye, the concentration of which is determined by UV-vis spectroscopy. In the present study, VCl₃ was deliberately omitted to avoid nitrate reduction and to enable selective detection of NO₂⁻. One mL of electrolyte collected from the DEMS cell was transferred to a vial, followed by the addition of 300 μ L of 1 M HCl and 1.5 mL of Griess reagent. The Griess reagent was prepared by dissolving 10 mg of N-(1-naphthyl)ethylenediamine dihydrochloride and 200 mg of sulfanilamide in 200 mL of 0.5 M HCl. The samples were incubated at 25°C for 16 h (overnight) to ensure complete color development. Existence of NO₂⁻ resulted in the formation of a characteristic, fuchsia-colored diazo dye with peak absorption (in our case) at 540 nm.

4.5 | Computational Methodology

Density functional theory (DFT)-based [67, 68] spin-polarized electronic structure calculations were performed to investigate the mechanistic pathways of the nitrate reduction reaction, and hydrogen evolution reaction (HER) on the most thermodynamically stable (311) surface of CoFe₂O₄ and the (111) surface of Fe₃O₄ compound. Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, in conjunction with Projected Augmented Wave (PAW) formalism [69, 70], was employed throughout the electronic structure calculations. Vienna Ab-initio Simulation Package (VASP) [71, 72] was employed to carry out the DFT calculations in order to construct the reaction coordinate

corresponding to NO₃RR and HER mechanisms. The converged plane wave energy cut off 450 eV, and Brillouin zone sampling of $3 \times 3 \times 1$ K-points for CoFe₂O₄ (311) and $7 \times 7 \times 1$ for Fe₃O₄ (111) surface within Monkhorst-pack scheme [73] were used for geometry optimization and adsorption energy calculations. The energy and force convergence criteria for geometry optimization were considered at 10^{−4} eV and −0.01 eV/Å, respectively. The thermodynamic corrections like zero-point energy difference (ΔZPE) and entropic contributions (TΔS), corresponding to the adoption free energy calculation, were considered adequately [74]. All the structural analysis and graphical visualizations were rendered using the VESTA package [75]. The adsorption free energies of all the adsorbed species were calculated using the following equation:

$$\Delta G = E_{\text{ads}} + \Delta ZPE - T\Delta S$$

where E_{ads} is the adsorption energy of the reaction intermediates adsorbed on the CoFe₂O₄ surface, as given by:

$$E_{\text{ads}} = E_{[\text{surface} + \text{adsorbate}]} - E_{[\text{surface}]} - E_{[\text{adsorbate}]}$$

$E_{[\text{surface} + \text{adsorbate}]}$ and $E_{[\text{surface}]}$ denote DFT calculated energies of the surface with and without the adsorbed intermediates, respectively, while $E_{[\text{adsorbate}]}$ is the energy of the adsorbate in the isolated condition.

Acknowledgements

The authors sincerely acknowledge the University of Cologne for providing state-of-the-art research infrastructure and the German Science Foundation (DFG) for financial support. The authors further thank Helmholtz-Zentrum Berlin (HZB) for providing the necessary infrastructure and financial support for conducting electrochemical measurements. S.K.S., T.D., and S. C. would like to acknowledge Harish-Chandra Research Institute (HRI), Allahabad, for the infrastructure and funding. Computational work for this study was carried out at the cluster computing facility at HRI Allahabad. The authors thank Ambrishkumar Devaiya and the Forschungszentrum Jülich for performing the VSM measurements.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. S. Mitchell, A. J. Martín, and J. Pérez-Ramírez, “Transcending Scales in Catalysis for Sustainable Development,” *Nature Chemical Engineering* 1, no. 1 (2024): 13–15, <https://doi.org/10.1038/s44286-023-00005-1>.
2. J. Li, Y. Zhang, K. Kuruvinschetti, and N. Kornienko, “Construction of C–N Bonds from Small-Molecule Precursors Through Heterogeneous Electrocatalysis,” *Nature Reviews Chemistry* 6, no. 5 (2022): 303–319, <https://doi.org/10.1038/s41570-022-00379-5>.
3. H. Chen, L. Liu, X.-H. Ma, et al., “Atomically Precise Silver-based Bimetallic Clusters for Electrocatalytic Urea Synthesis,” *National Science Review* 12, no. 2 (2025): nwae440, <https://doi.org/10.1093/nsr/nwae440>.

4. D. Liu, L. Qiao, S. Peng, et al., “Recent Advances in Electrocatalysts for Efficient Nitrate Reduction to Ammonia,” *Advanced Functional Materials* 33, no. 43 (2023): 2303480, <https://doi.org/10.1002/adfm.202303480>.
5. D. Ye and S. C. E. Tsang, “Prospects and Challenges of Green Ammonia Synthesis,” *Nature Synthesis* 2, no. 7 (2023): 612–623, <https://doi.org/10.1038/s44160-023-00321-7>.
6. J. John, D. R. MacFarlane, and A. N. Simonov, “The Why and How of NO_x Electroreduction to Ammonia,” *Nature Catalysis* 6, no. 12 (2023): 1125–1130, <https://doi.org/10.1038/s41929-023-01060-w>.
7. J. Xu, H. Liu, S. Zhang, et al., “Integrated Cascade Catalysts for Electrochemical Nitrate Reduction to Ammonia,” *Journal of the American Chemical Society* 148, no. 1 (2026): 148–161, <https://doi.org/10.1021/jacs.5c03265>.
8. K. Yang, S.-H. Han, C. Cheng, C. Guo, T. Li, and Y. Yu, “Unveiling the Reaction Mechanism of Nitrate Reduction to Ammonia Over Cobalt-Based Electrocatalysts,” *Journal of the American Chemical Society* 146, no. 19 (2024): 12976–12983, <https://doi.org/10.1021/jacs.3c13517>.
9. Q. Hu, S. Qi, Q. Huo, et al., “Designing Efficient Nitrate Reduction Electrocatalysts by Identifying and Optimizing Active Sites of Co-Based Spinels,” *Journal of the American Chemical Society* 146, no. 5 (2024): 2967–2976, <https://doi.org/10.1021/jacs.3c06904>.
10. Y. Xiong, Y. Wang, J. Zhou, F. Liu, F. Hao, and Z. Fan, “Electrochemical Nitrate Reduction: Ammonia Synthesis and Beyond,” *Advanced Materials* 36, no. 17 (2024): 2304021, <https://doi.org/10.1002/adma.202304021>.
11. J. Li, Y. Wang, X. Xing, Y. Wang, W. Xiong, and H. Li, “Advancing Electrochemical Nitrate Reduction: Overcoming Rate-Limiting Bottlenecks with Copper/Cobalt Catalysts,” *Advanced Functional Materials* 51 (2025): 13717, <https://doi.org/10.1002/adfm.202513717>.
12. H. Chen, K. Qi, X. Dong, et al., “Ligand-Mediated Activity of Cu₄ Clusters Boosts Electrocatalytic Nitrate Reduction,” *Angewandte Chemie International Edition* 34 (2025): 202510429, <https://doi.org/10.1002/anie.202510429>.
13. Y. Sun, G. Chen, S. Xi, and Z. J. Xu, “Catalytically Influential Features in Transition Metal Oxides,” *ACS Catalysis* 11, no. 22 (2021): 13947–13954, <https://doi.org/10.1021/acscatal.1c04393>.
14. S. Jha, P. Jain, R. Palkovits, and P. Popinand Ingole, “Tuning of Cationic Distribution in “Partially Inversed” Cobalt Ferrite Spinel Nanocubes via a Nitrogen-doped Graphene Oxide Support for Enhanced Bifunctional Oxygen Electrocatalysis,” *Journal of Materials Chemistry A* 11, no. 42 (2023): 23034–23047, <https://doi.org/10.1039/D3TA03486K>.
15. S. Sun, Y. Sun, Y. Zhou, et al., “Shifting Oxygen Charge Toward Octahedral Metal: A Way to Promote Water Oxidation on Cobalt Spinel Oxides,” *Angewandte Chemie International Edition* 58, no. 18 (2019): 6042–6047, <https://doi.org/10.1002/anie.201902114>.
16. G.-F. Chen, Y. Yuan, H. Jiang, et al., “Electrochemical Reduction of Nitrate to Ammonia via Direct Eight-electron Transfer Using a Copper-molecular Solid Catalyst,” *Nature Energy* 5, no. 8 (2020): 605–613, <https://doi.org/10.1038/s41560-020-0654-1>.
17. O. Q. Carvalho, R. Marks, H. K. K. Nguyen, et al., “Periodic Journey,” *Journal of the American Chemical Society* 144, no. 32 (2022): 14809–14818, <https://doi.org/10.1021/jacs.2c05673>.
18. X. Meng, X. Tan, Y. Ma, et al., “Recent Progress in Cobalt-Based Electrocatalysts for Efficient Electrochemical Nitrate Reduction Reaction,” *Advanced Functional Materials* 35, no. 14 (2025): 2418492, <https://doi.org/10.1002/adfm.202418492>.
19. B. Singh, T. Fischer, and S. Mathur, “Field-enhanced Chemical Vapor Deposition: New Perspectives for Thin Film Growth,” *Journal of Materials Chemistry A* 13 (2025): 20104–20142, <https://doi.org/10.1039/D5TA01081K>.
20. Y. Ma, K. Watanabe, S. Awaji, and M. Motokawa, “Surface Morphology and Growth Mechanism of YBa₂Cu₃O₇ Films by Chemical Vapor Deposition in a Magnetic Field,” *Journal of Crystal Growth* 233, no. 3 (2001): 483–489, [https://doi.org/10.1016/S0022-0248\(01\)01587-1](https://doi.org/10.1016/S0022-0248(01)01587-1).

21. F. A. Pires, T. Karimpour, D. Patrun, et al., "Field-Directed Growth of Hematite for Advanced Solar Hydrogen Production," *Advanced Energy and Sustainability Research* 7 (2025): 202500313, <https://doi.org/10.1002/aesr.202500313>.
22. D. Stadler, T. Brede, D. Schwarzbach, et al., "Anisotropy Control in Magnetic Nanostructures through Field-assisted Chemical Vapor Deposition," *Nanoscale Advances* 1, no. 11 (2019): 4290–4295, <https://doi.org/10.1039/C9NA00467J>.
23. D. Stadler, D. N. Mueller, T. Brede, et al., "Magnetic Field-Assisted Chemical Vapor Deposition of Iron Oxide Thin Films: Influence of Field–Matter Interactions on Phase Composition and Morphology," *The Journal of Physical Chemistry Letters* 10, no. 20 (2019): 6253–6259, <https://doi.org/10.1021/acs.jpclett.9b02381>.
24. H. Lee, Z. T. Aytuna, A. Bhardwaj, et al., "Controlling Degree of Inversion in MgFe_2O_4 Spinel Films Grown in External Magnetic Fields," *Advanced Engineering Materials* 25, no. 18 (2023): 2300021, <https://doi.org/10.1002/adem.202300021>.
25. A. Raauf, J. Leduc, M. Frank, et al., "Magnetic Field-Assisted Chemical Vapor Deposition of UO_2 Thin Films," *Inorganic Chemistry* 60, no. 3 (2021): 1915–1921, <https://doi.org/10.1021/acs.inorgchem.0c03387>.
26. P. Tutacz, D. Stadler, T. Karimpour, et al., "External Magnetic Field Effects on Shape Anisotropy of TiO_2 Nanostructures Grown from a Paramagnetic Ti(III) Precursor," *Chemistry of Materials* 35, no. 19 (2023): 8050–8056, <https://doi.org/10.1021/acs.chemmater.3c01318>.
27. J. Wang, K. Zhao, Y. Yao, et al., "Ferromagnetic Fe-TiO_2 Spin Catalysts for Enhanced Ammonia Electrosynthesis," *Nature Communications* 16, no. 1 (2025): 1129, <https://doi.org/10.1038/s41467-025-56566-7>.
28. U. Seifert and H. Wagner, "Critical Magnetic Field Dependence of Thermally Activated Surface Processes," *Physical Review Letters* 63, no. 3 (1989): 287–289, <https://doi.org/10.1103/PhysRevLett.63.287>.
29. V. D. Borman, A. N. Pivovarov, A. P. Popov, and V. I. Troyan, "Effect of the Magnetic Field on the Activated Processes at the Surface of a Magnetic Solid in the Vicinity of Its Curie Point," *Surface Science* 232, no. 1–2 (1990): 185–192, [https://doi.org/10.1016/0039-6028\(90\)90597-2](https://doi.org/10.1016/0039-6028(90)90597-2).
30. L. Hu, R. Zhang, and Q. Chen, "Synthesis and Assembly of Nanomaterials under Magnetic Fields," *Nanoscale* 6, no. 23 (2014): 14064–14105, <https://doi.org/10.1039/C4NR05108D>.
31. L. Li, Y. Yang, J. Ding, and J. Xue, "Synthesis of Magnetite Nanooctahedra and Their Magnetic Field-Induced Two-/Three-Dimensional Superstructure," *Chemistry of Materials* 22, no. 10 (2010): 3183–3191, <https://doi.org/10.1021/cm100289d>.
32. R.-P. Ji, J.-S. Jiang, and M. Hu, "How Does the Distribution of External Magnetic Lines of Force Influence the Growth of Ferromagnetic Material?," *The Journal of Physical Chemistry C* 114, no. 28 (2010): 12090–12094, <https://doi.org/10.1021/jp100722s>.
33. P. A. Chernavskii, G. V. Pankina, B. S. Lunin, and N. S. Perov, "Influence of an External Magnetic Field on Gas–Solid Reactions," *Physical Chemistry Chemical Physics* 28, no. 2 (2026): 1026–1036, <https://doi.org/10.1039/D5CP03041B>.
34. L. V. B. Diop, T. Faske, O. Isnard, and W. Donner, "Magnetic-field-induced Structural Phase Transition and Giant Magnetoresistance in $\text{La}_{0.85}\text{Ce}_{0.15}\text{Fe}_{12}\text{B}_6$," *Physical Review Materials* 5, no. 10 (2021): 104401, <https://doi.org/10.1103/PhysRevMaterials.5.104401>.
35. J. Mira, F. Rivadulla, J. Rivas, et al., "Structural Transformation Induced by Magnetic Field and "Colossal-Like" Magnetoresistance Response above 313 K in MnAs ," *Physical Review Letters* 90, no. 9 (2003): 097203, <https://doi.org/10.1103/PhysRevLett.90.097203>.
36. A. F. Gubkin, L. S. Wu, S. E. Nikitin, et al., "Field-induced Magnetic Phase Transitions and Metastable States in Tb_3Ni ," *Physical Review B* 97, no. 13 (2018): 134425, <https://doi.org/10.1103/PhysRevB.97.134425>.
37. M. Hähsler, J. Landers, T. Nowack, et al., "Magnetic Properties and Mössbauer Spectroscopy of Fe_3O_4 / CoFe_2O_4 Nanorods," *Inorganic Chemistry* 59 (2020): 3677–3685, <https://doi.org/10.1021/acs.inorgchem.9b03267>.
38. A. Aftabi, A. Babakhani, and R. Khoshlahni, "Optimized Zn Substituted CoFe_2O_4 Nanoparticles for High Efficiency Magnetic Hyperthermia in Biomedical Applications," *Scientific Reports* 15, no. 1 (2025): 10039, <https://doi.org/10.1038/s41598-025-94535-8>.
39. N. Moumen and M. P. Pileni, "Comparison of the Magnetic Properties of the Nanosized Particles in Dispersed Fluid or in Powder Form," *Chemistry of Materials* 8, no. 5 (1996): 1128–1134, <https://doi.org/10.1021/cm950556z>.
40. H. Sharifi Dehsari and K. Asadi, "Impact of Stoichiometry and Size on the Magnetic Properties of Cobalt Ferrite Nanoparticles," *The Journal of Physical Chemistry C* 122, no. 51 (2018): 29106–29121, <https://doi.org/10.1021/acs.jpcc.8b09276>.
41. S. M. Ansari, K. C. Ghosh, R. S. Devan, et al., "Eco-Friendly Synthesis, Crystal Chemistry, and Magnetic Properties of Manganese-Substituted CoFe_2O_4 Nanoparticles," *ACS Omega* 5, no. 31 (2020): 19315–19330, <https://doi.org/10.1021/acsomega.9b02492>.
42. B. Debnath, S. Parvin, H. Dixit, and S. Bhattacharyya, "Oxygen-Defect-Rich Cobalt Ferrite Nanoparticles for Practical Water Electrolysis with High Activity and Durability," *ChemSuschem* 13, no. 15 (2020): 3875–3886, <https://doi.org/10.1002/cssc.202000932>.
43. E. M. Davis, A. Bergmann, H. Kühlenbeck, and B. Roldan Cuenya, "Facet Dependence of the Oxygen Evolution Reaction on Co_3O_4 , CoFe_2O_4 , and Fe_3O_4 Epitaxial Film Electrocatalysts," *Journal of the American Chemical Society* 146, no. 20 (2024): 13770–13782, <https://doi.org/10.1021/jacs.3c13595>.
44. M. Fantauzzi, F. Secci, M. Sanna Angotzi, et al., "Nanostructured Spinel Cobalt Ferrites: Fe and Co Chemical state, Cation Distribution and Size Effects by X-ray Photoelectron Spectroscopy," *RSC Advances* 9, no. 33 (2019): 19171–19179, <https://doi.org/10.1039/C9RA03488A>.
45. P. J. Rommers and J. Visser, "Spectrophotometric Determination of Micro Amounts of Nitrogen as Indophenol," *The Analyst* 94, no. 1121 (1969): 653, <https://doi.org/10.1039/an9699400653>.
46. D. Scheiner, "Determination of Ammonia and Kjeldahl Nitrogen by Indophenol Method," *Water Research* 10, no. 1 (1976): 31–36, [https://doi.org/10.1016/0043-1354\(76\)90154-8](https://doi.org/10.1016/0043-1354(76)90154-8).
47. S. Saddeler, G. Bendt, S. Salamon, et al., "Influence of the Cobalt Content in Cobalt Iron Oxides on the Electrocatalytic OER Activity," *Journal of Materials Chemistry A* 9, no. 45 (2021): 25381–25390, <https://doi.org/10.1039/D1TA06568H>.
48. S. R. Ede and Z. Luo, "Tuning the Intrinsic Catalytic Activities of Oxygen-Evolution Catalysts by Doping: A Comprehensive Review," *Journal of Materials Chemistry A* 9 (2021): 20131–20163, <https://doi.org/10.1039/D1TA04032D>.
49. P. Xiong, F. Yang, Z. Ding, et al., "Preparation and Electrocatalytic Properties of Spinel $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ Nanoparticles," *International Journal of Hydrogen Energy* 45, no. 27 (2020): 13841–13847, <https://doi.org/10.1016/j.ijhydene.2020.03.098>.
50. J. Choi, B. H. R. Suryanto, D. Wang, et al., "Identification and Elimination of False Positives in Electrochemical Nitrogen Reduction Studies," *Nature Communications* 11, no. 1 (2020): 5546, <https://doi.org/10.1038/s41467-020-19130-z>.
51. J.-H. Huang, H. Zhang, Z.-Y. Wang, et al., "Atomic-Precise Active Site Surgery on Carboranylthiolate-Protected Silver Nanocluster Catalysts," *Journal of the American Chemical Society* 147, no. 19 (2025): 16593–16601, <https://doi.org/10.1021/jacs.5c03721>.
52. S. Zheng, X. Dong, H. Chen, et al., "Unveiling Ionized Interfacial Water-Induced Localized H^+ Enrichment for Electrocatalytic Nitrate Reduction," *Angewandte Chemie International Edition* 64, no. 1 (2025): 202413033, <https://doi.org/10.1002/anie.202413033>.
53. G. Franceschi, P. Kocán, A. Conti, et al., "Resolving the Intrinsic Short-range Ordering of K^+ Ions on Cleaved Muscovite Mica," *Nature*

- Communications* 14, no. 1 (2023): 208, <https://doi.org/10.1038/s41467-023-35872-y>.
54. K. Gandha, K. Elkins, N. Poudyal, and J. Ping Liu, "Synthesis and Characterization of CoFe_2O_4 Nanoparticles with High Coercivity," *Journal of Applied Physics* 117, no. 17 (2015): 17A736, <https://doi.org/10.1063/1.4916544>.
 55. Z. Wang, M. F. Navarro Poupard, R. R. Mohan, et al., "Electrospun CoFe_2O_4 Nanowires Tailored for Magnetoelectrochemistry," *ACS Nano* 19, no. 32 (2025): 29195–29206, <https://doi.org/10.1021/acsnano.5c03628>.
 56. E. Pervaiz, T. Thomas, M. J. Afzal, and M. Yang, "Template Synthesis of CoFe_2O_4 Extended Surface Microspheres for Efficient Water Decontamination and Absorption of Electromagnetic Waves: Twin Behavior," *Materials Research Express* 6, no. 7 (2019): 075506, <https://doi.org/10.1088/2053-1591/abl289>.
 57. X. Yu, C.-F. Huo, Y.-W. Li, J. Wang, and H. Jiao, " Fe_3O_4 Surface Electronic Structures and Stability from GGA+U," *Surface Science* 606, no. 9–10 (2012): 872–879, <https://doi.org/10.1016/j.susc.2012.02.003>.
 58. N. Berdunov, S. Murphy, G. Mariotto, I. V. Shvets, and Y. M. Mykovskiy, "Spin-polarized Tunneling Effects Observed on the Oxygen-terminated Fe_3O_4 (111) Surface," *Journal of Applied Physics* 95, no. 11 (2004): 6891–6893, <https://doi.org/10.1063/1.1688643>.
 59. N. Berdunov, S. Murphy, G. Mariotto, and I. V. Shvets, "Atomically Resolved Spin-Dependent Tunneling on the Oxygen-Terminated Fe_3O_4 (111)," *Physical Review Letters* 93, no. 5 (2004): 057201, <https://doi.org/10.1103/PhysRevLett.93.057201>.
 60. J. Noh, O. I. Osman, S. G. Aziz, P. Winget, and J.-L. Brédas, "Magnetite Fe_3O_4 (111) Surfaces: Impact of Defects on Structure, Stability, and Electronic Properties," *Chemistry of Materials* 27, no. 17 (2015): 5856–5867, <https://doi.org/10.1021/acs.chemmater.5b02885>.
 61. D. Santos-Carballal, A. Roldan, R. Grau-Crespo, and N. H. de Leeuw, "A DFT Study of the Structures, Stabilities and Redox Behavior of the Major Surfaces of Magnetite Fe_3O_4 ," *Physical Chemistry Chemical Physics* 16, no. 39 (2014): 21082–21097, <https://doi.org/10.1039/C4CP00529E>.
 62. K. Fan, W. Xie, J. Li, et al., "Active Hydrogen Boosts Electrochemical Nitrate Reduction to Ammonia," *Nature Communications* 13, no. 1 (2022): 7958, <https://doi.org/10.1038/s41467-022-35664-w>.
 63. G. M. Sheldrick, "Crystal Structure Refinement with SHELXL," *Acta Crystallographica Section C, Structural Chemistry* 71, no. Pt 1 (2015): 3–8, <https://doi.org/10.1107/S2053229614024218>.
 64. G. M. Sheldrick, "A Short History of SHELX," *Acta Crystallographica Section A Foundations of Crystallography* 64, no. Pt 1 (2008): 112–122, <https://doi.org/10.1107/S0108767307043930>.
 65. F. J. Stender and M. Risch, "Different Reactions Define the Electrochemical Window in 1-Butyl-3-Methylimidazolium Triflate on Gold and Platinum Electrodes," *Chemphyschem* 26, no. 23 (2025): 202500096, <https://doi.org/10.1002/cphc.202500096>.
 66. T. A. Doane and W. R. Horváth, "Spectrophotometric Determination of Nitrate with a Single Reagent," *Analytical Letters* 36, no. 12 (2003): 2713–2722, <https://doi.org/10.1081/AL-120024647>.
 67. P. Hohenberg and W. Kohn, "Inhomogeneous Electron Gas," *Physical Review* 136, no. 3B (1964): B864–B871, <https://doi.org/10.1103/PhysRev.136.B864>.
 68. W. Kohn and L. J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects," *Physical Review* 140, no. 4A (1965): A1133–A1138, <https://doi.org/10.1103/PhysRev.140.A1133>.
 69. J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," *Physical Review Letters* 77, no. 18 (1996): 3865–3868, <https://doi.org/10.1103/PhysRevLett.77.3865>.
 70. P. E. Blöchl, "Projector Augmented-wave Method," *Physical Review B* 50, no. 24 (1994): 17953–17979, <https://doi.org/10.1103/PhysRevB.50.17953>.
 71. G. Kresse and J. Furthmüller, "Efficient Iterative Schemes for *Ab Initio* Total-energy Calculations Using a Plane-wave Basis Set," *Physical Review B* 54, no. 16 (1996): 11169–11186, <https://doi.org/10.1103/PhysRevB.54.11169>.
 72. G. Kresse and J. Furthmüller, "Efficiency of *Ab-initio* Total Energy Calculations for Metals and Semiconductors Using a Plane-wave Basis Set," *Computational Materials Science* 6, no. 1 (1996): 15–50, [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
 73. H. J. Monkhorst and J. D. Pack, "Special Points for Brillouin-zone Integrations," *Physical Review B* 13, no. 12 (1976): 5188–5192, <https://doi.org/10.1103/PhysRevB.13.5188>.
 74. F. Ai and J. Wang, "Theoretical Evaluation of Electrochemical Nitrate Reduction Reaction on Graphdiyne-Supported Transition Metal Single-Atom Catalysts," *ACS Omega* 7, no. 35 (2022): 31309–31317, <https://doi.org/10.1021/acsomega.2c03588>.
 75. K. Momma and F. Izumi, "VESTA 3 for Three-dimensional Visualization of Crystal, Volumetric and Morphology Data," *Journal of Applied Crystallography* 44, no. 6 (2011): 1272–1276, <https://doi.org/10.1107/S0021889811038970>.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: adfm76213-sup-0001-SuppMat.docx.