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Metal–organic framework-based catalysts toward the electrosynthesis of urea

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Nitrogen-based fertilizer, primarily urea, production generates 2.1% of global CO_2 emissions through the energy-intensive Bosch–Meiser process. Electrochemical urea synthesis offers a sustainable alternative by significantly reducing greenhouse gas emissions and energy consumption. While numerous review articles have focused on the electrocatalytic synthesis of urea using nanostructures or heterostructures composed of transition metal alloys that leverage the synergistic effects of distinct metal catalytic sites, no comprehensive reviews have explored the application of metal–organic frameworks (MOFs) in this context. Following the publication of the *Nature Synthesis* paper in 2024, which reported a nearly fivefold increase in yield rate compared to existing catalysts, we revisited the electrosynthesis of urea using MOF materials. Over the past two years, a few high-impact papers have been published on MOF-based materials, which have emerged as promising catalysts for electrochemical urea synthesis, demonstrating notable efficiency and stability. This review aims to highlight these MOF-based materials, their catalytic performance, and underlying mechanism in electrocatalytic urea synthesis.

1. Introduction

Urea is an essential nitrogen-based fertilizer that plays a vital role in agriculture. Beyond agriculture, urea serves as a key raw material in the chemical and pharmaceutical industries, contributing to the production of plastics, adhesives, and dermatological products.[1] Industrial urea production typically involves two consecutive processes: the Haber–Bosch method for synthesizing ammonia and the Bosch–Meiser process for converting ammonia into urea.[2,3] The Haber–Bosch process initiates with the conversion of nitrogen (N_2) and hydrogen (H_2) into ammonia (NH_3), facilitated by an iron catalyst under elevated temperatures (400–500 °C) and pressures (10–20 MPa), followed by the Bosch–Meiser process, where NH_3 reacts with carbon dioxide (CO_2) to produce urea, requiring similar harsh

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conditions of 150–200 °C and 15–20 MPa. These conventional methods are highly energy-intensive, operating under extreme conditions of temperature and pressure (Fig. 1). In contrast, electrocatalytic C–N coupling, which utilizes CO_2 and nitrogenous species, offers a promising alternative. This approach enables the direct urea synthesis at ambient conditions *via* a sustainable and energy-efficient pathway.

In recent times, electrocatalysis has emerged as a favorable approach for synthesizing ammonia and urea. Although electrochemical CO_2 reduction and nitrate reduction reactions have shown potential, the electrocatalytic nitrogen reduction reaction (NRR) to synthesize ammonia remains difficult owing to the high bond energy of nitrogen–nitrogen triple bonds. Recent studies have attempted to couple multiple electrocatalytic reactions to synthesize complex chemicals, such as urea, *via* the coupling of CO_2 and N_2. For instance, Chen *et al.* demonstrated the electrocatalytic synthesis of urea through the CO_2 and N_2 coupling process at ambient conditions.[4] This breakthrough has sparked significant interest in urea electrosynthesis, with researchers exploring catalyst design, electrolyte effects, and other factors to improve efficiency as well as selectivity. As the field continues to evolve, a comprehensive overview of the findings and reaction mechanisms is necessary to promote the rational design of efficient catalysts and accelerate industrial applications.

Metal–organic frameworks (MOFs) are crystalline hybrid materials comprising of inorganic metal ions or clusters and organic linkers, renowned for their tunable porosity, large surface area, and diverse structures and applications.[5–7]

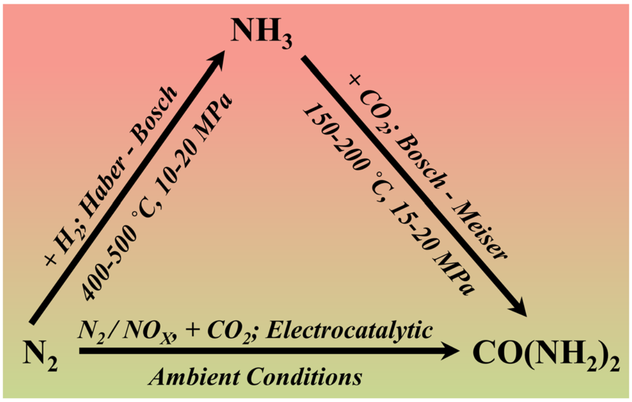

Fig. 1 Comparison of traditional energy-intensive methods with ambient-condition electrocatalytic C–N coupling approaches for urea synthesis.

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These unique properties have enabled MOFs to find applications in numerous electrocatalytic fields, including the oxygen evolution reaction (OER), hydrogen evolution reaction (HER), CO_2 reduction, and ammonia synthesis.[8–12] Moreover, MOFs serve as excellent precursors for producing functional derivatives, such as porous carbon, metal oxides, and metal/carbon composites, through pyrolysis. These MOF derivatives offer enhanced stability, improved electrical conductivity, and diverse active sites due to the incorporation of both metallic as well as non-metallic elements. Despite these advancements, the application of MOF-based materials in electrocatalytic urea synthesis remains in its infancy.

A comprehensive review summarizing the structure–activity relationships of MOFs and/or their derivatives in electrocatalytic urea synthesis could provide valuable insights for developing superior catalysts and advancing the field. Since the publication of Yuan *et al.*'s paper in 2022, which reported the electrosynthesis of urea using the MOF Co–PMDA–2-mbIM, a few high-impact articles (Table 1) have been published. This review focuses on MOF-based materials for electrocatalytic urea synthesis, highlighting their catalytic efficiency, and long-term stability. The aim is to provide valuable insights into their potential and guide future advancements in this rapidly emerging field.

2. Electrochemical urea synthesis through C–N coupling using MOF electrocatalysts

2.1 Using CO_2 and N_2

The high abundance (~77%) of N_2 in the air can be utilized to compensate for the highly demanding urea electrosynthesis process, instead of relying on the energy-intensive industrial method. However, the intrinsically high bond energy of N_2 (940.95 kJ mol^{-1}) and CO_2 (806 kJ mol^{-1}) poses significant challenges for simultaneously activating these inert molecules and coupling numerous reaction intermediates for electrosynthesis of urea under ambient conditions. Therefore, the development of efficient electrocatalysts to enhance C–N coupling performance is highly desirable. In 2020, Wang and colleagues achieved urea electrosynthesis under ambient temperature and pressure by combining N_2 and CO_2 in H_2O using a Pd_1Cu_1–TiO_2 electrocatalyst.[4] They prepared various Pd/Cu alloy ratios loaded on defect-rich TiO_2 supports through the co-reduction of Pd/Cu metal precursors. The optimized catalyst exhibited superior performance for urea formation at −0.4 V *vs.* the reversible hydrogen electrode (RHE), achieving a maximum rate of 3.36 mmol h^{-1} g^{-1} with a Faraday efficiency (FE) of 8.92%. The lower efficiency in electrocatalytic urea synthesis involves primary challenges, such as: (i) the difficulty in chemisorbing the inert N_2 and CO_2 molecules onto the catalyst surface; (ii) the need for a high overpotential to dissociate the highly stable C═O and N≡N bonds; and (iii) the competition between N_2 and CO_2 reduction, which hinders the anticipated C–N bond coupling and results in a complex product distribution.

In 2022, Yuan *et al.* introduced a novel conductive MOF, Co–PMDA–2-mbIM (2-mbIM = 2-methyl benzimidazole; PMDA = pyromellitic dianhydride), which achieved a record-breaking urea yield rate of 14.47 mmol h^{-1} g^{-1} and a FE_{urea} of 48.97% at −0.5 V *vs.* RHE.[13] The high efficiency of this MOF lies in its unique host–guest interactions, which create favorable local electrophilic and nucleophilic regions by transferring electron density for N_2 and CO_2 adsorption. This phenomenon was explained from the calculations of electron density difference (Fig. 2a) which showed that CoO_6 octahedron (cyan region) transfers 0.33 electrons to a 2-mbIM guest molecule (yellow region). From the Bader charge analysis, the Co sites in CoO_6 octahedrons (charge = +1.36) act as local electrophilic sites, while N sites in 2-mbIM guest molecules (charge = −1.24) serve as nucleophilic sites. Therefore, electron-rich N_2 and electron-deficient CO_2 are inclined to chemisorb on electrophilic Co sites of CoO_6 and nucleophilic N sites of 2-mbIM regions in the Co–PMDA–2mbIM catalyst.

The electron transfer facilitates a transition in the CoO_6 octahedral framework from a high-spin Co^{3+} state (HS: $t_{2g}{}^4e_g{}^2$) to an intermediate-spin Co^{4+} state (IS: $t_{2g}{}^4e_g{}^1$) creating an empty e_g orbital. This orbital initially accepts electrons from the σ orbital of an N_2 molecule and subsequently donates electrons to the empty *π orbital of N_2 (Fig. 2b), forming the *N═N* intermediate. Notably, when N_2 binds with a CoO_6 octahedron nearby, the Gibbs free energy (ΔG) for the CO_2 reduction reaction (CO_2RR) drops from 0.60 to 0.52 eV (Fig. 2c), suggesting that N_2 present in the vicinity accelerates CO_2RR, facilitating intermediate *CO production on the N region of the 2-mbIM guest molecule. The empty orbital (e_g) in Co–PMDA–2-mbIM serves as a channel for the

Table 1 Recently MOF-based materials designed for electrosynthesis for urea

MOF	Urea yield rate ($g\ h^{-1}\ g_{cat}{}^{-1}$)	FE_{urea} (%)	Potential (V) *vs.* RHE	Electrolyte	Gas	Stability tasted (hour)	Ref.
Co–PMDA–2mbIM	0.869	48.97	−0.5	0.1 M $KHCO_3$	N_2 + CO_2	20	13
Cu^{III}-HHTP	0.467	23.09	−0.6	0.1 M $KHCO_3$	N_2 + CO_2	18	14
Cu-HATNA	1.46	25	−0.6	0.1 M $KHCO_3$ + 0.1 M KNO_3	CO_2	10	15
Mo-PCN-222(Co)	0.84	33.9	−0.6	0.1 M $KHCO_3$ + 0.05 M KNO_3	CO_2	—	16
PcNi–Fe–O	2.1	54.1 ± 1.3	−0.6	0.1 M KNO_3	CO_2/Ar	20	17
γ-Fe_2O_3@Ni-HITP	20.4	67.2	−0.8	0.1 M $KHCO_3$ + 0.1 M KNO_3	CO_2	150	18
$BiVO_4$@MIL-5	1.335	23.5	−0.9	0.1 M KNO_3	CO_2	—	19

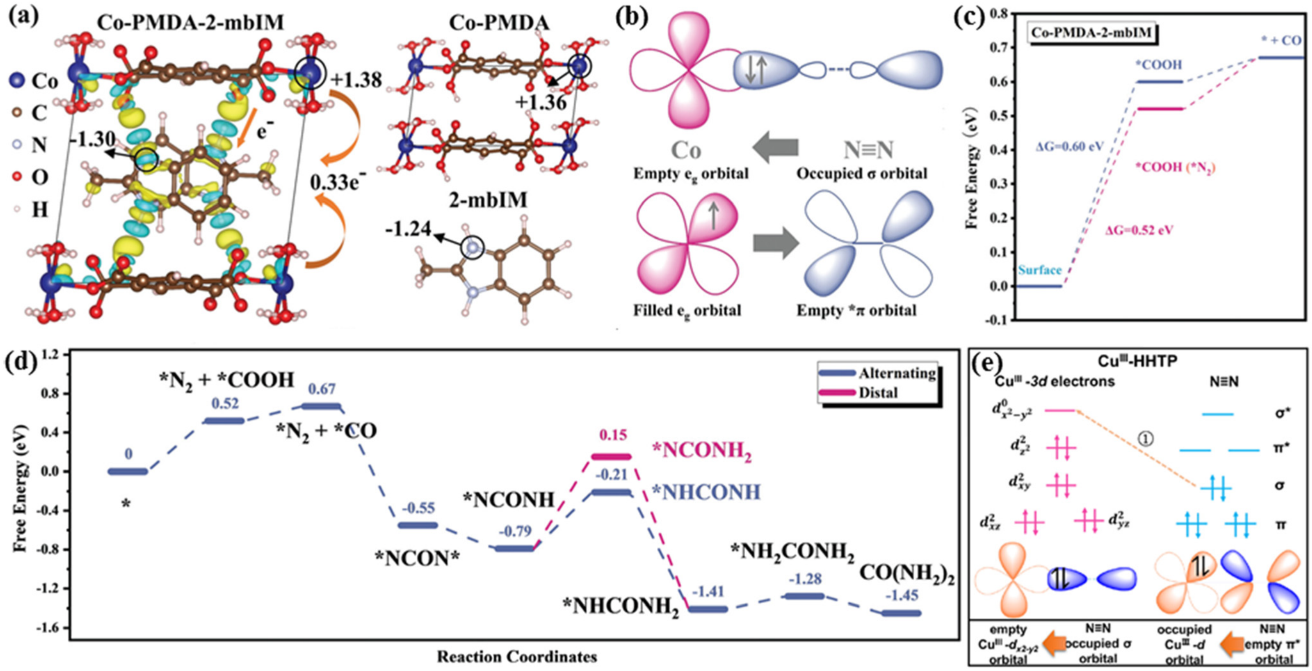

Fig. 2 (a) The charge density and corresponding Bader charge analysis of Co–PMDA–2-mbIM; the yellow and cyan colors indicate electron accumulation and depletion, respectively. (b) Schematic diagram showing N_2 bonding to a Co center. (c) Free energy diagrams comparing CO_2 reduction with and without N_2 adsorption on Co–PMDA–2-mbIM. (d) The plausible mechanism for urea electrosynthesis. Reproduced with permission from ref. 13. Copyright 2022 RSC Publishing. (e) Schematic representation of the single-electron transfer pathway in Cu^{III}-HHTP facilitating C–N coupling. Reproduced with permission from ref. 14. Copyright 2023 Springer Nature.

"σ-orbital carbonylation", initiating the challenging C–N coupling reaction and forming the *NCON* urea precursor. Once the *NCON* intermediate forms, hydrogenation can proceed *via* an alternative or distal mechanism (Fig. 2d), with the distal pathway transitioning from *NCONH to *$NCONH_2$ at a ΔG of 0.94 eV, while the alternating pathway (*NCONH to *NHCONH) has a lower ΔG of 0.58 eV.

Gao *et al.* investigated the impact of spin states on the electrocatalytic properties of MOFs in urea synthesis.[14] They synthesized two MOFs, Cu^{III}-HHTP and Cu^{II}-HHTP, (HHTP: 2,3,6,7,10,11-hexahydroxytriphenylene) and compared their performance. The results showed that Cu^{III}-HHTP exhibited a significantly higher urea production rate (7.78 mmol h^{-1} g^{-1}) and FE (7.78 mmol h^{-1} g^{-1}) at − 0.6 V *vs.* RHE. Further analysis revealed that the isolated Cu^{III} species, with a spin ground state of $S = 0$, acted as the active site in Cu^{III}-HHTP. This differed from Cu^{II}-HHTP, where the Cu^{II} species had a spin ground state of $S = 1/2$. An empty $d^0_{x^2-y^2}$ orbital of Cu^{III}-HHTP facilitated a single-electron transfer pathway, where the σ orbital electron of N_2 migrate into that empty Cu-3d orbital to form Cu–N_2 and *CO, thereby decreasing the energy barrier for C–N coupling (Fig. 2e) and enhancing urea production. In contrast, Cu^{II}-HHTP followed a two-electron transfer pathway, leading to reduced urea formation.

2.2 Using CO_2 and NO_3^-

A significant obstacle in urea electrosynthesis is the efficient utilization of abundant, low-cost CO_2 and nitrogen sources to produce urea with high FE. The nitrate ion, having lower dissociation energy compared to nonpolar N_2, can be a more efficient nitrogen source for the urea electrosynthesis. Zhang *et al.* developed a robust two-dimensional MOF, Cu-HATNA (HATNA–6OH = diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine-2,3,8,9,14,15-hexol), featuring planar CuO_4 centers, which demonstrated exceptional electrocatalytic activity for urea synthesis from CO_2 and NO_3^-.[15] The newly synthesized MOF showcased impressive performance, achieving a urea yield rate of 1.46 g h^{-1} g_{cat}^{-1}, accompanied by a high current density of 44.2 mA cm^{-1} at an applied potential of −0.6 V *vs.* RHE. The flat CuO_4 centers within the MOF's structure proved highly adept at producing the crucial *NH intermediate, thereby facilitating the C–N bond formation that yields urea.

However, this electrocatalyst exhibited a lower faradaic efficiency, achieving only 25% at −0.6 V *vs.* RHE. This may be attributed to the use of a single-site catalyst. The effectiveness of urea synthesis relies heavily on the formation of two C–N linkages. Notably, the formation of the second linkage requires a nitrogen-containing precursor generated at a separate catalytic site, posing a challenge for single-site catalysts. This challenge arises from the difficulty of optimizing the adsorption energy for both intermediates on a single active site. Consequently, materials scientists are driven to explore catalysts with dual active catalytic sites.

Qiu *et al.* developed a novel two-dimensional (2D) MOF, PcNi–Fe–O, featuring square-planar FeO_4 nodes and nickel-phthalocyanine (NiPc) ligands.[17] This MOF demonstrated exceptional performance, yielding urea at a high current density of 10.1 mA cm^{-2} with 54.1% FE in a neutral aqueous medium. Scaling up the electrode area to 25 cm^2 and operating for 8 hours, the as-synthesized electrocatalyst was able to produce 0.164 g of high-purity urea. Mechanistic studies revealed that the improved performance can be attributed to the synergistic interaction between NiPc and FeO_4 sites, *i.e.*, dual-site catalytic mechanism, which proved to be more efficient than single-site catalysis. Operando attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) detected characteristic peaks corresponding to the $*NH_2$ intermediate, *COO and $*NO_2$ species. Density functional theory (DFT) calculations were performed to support the experimental findings and elucidate the reaction pathway. The results indicated that the FeO_4 site facilitates the reduction of NO_3^- to NH_3 with a low energy barrier (ΔG = 0.13 eV) in comparison to the NiPc site (ΔG = 0.56 eV), making the process more energetically favorable. Additionally, NH_3 desorption is easier at the FeO_4 site (ΔE = −0.64 eV for Ni and ΔE = −0.06 eV for Fe), suggesting its role as the primary NH_3-producing center. Conversely, the NiPc site exhibits a lower formation energy for *NHCOO (ΔG = −2.16 eV) compared to the FeO_4 site (ΔG = −1.81 eV), indicating that CO_2 preferentially reacts with the *NH intermediate adsorbed on NiPc. The intermediate *NHCOO is further reduced to produce *NHCOOH at the NiPc site, which subsequently interacts with NH_3 from the FeO_4 site to form the key intermediate $*NHCONH_2$ (Fig. 3a) *via* the preferred thermodynamic pathway (Fig. 3a inset). Subsequent hydrogenation and reduction of $*NHCONH_2$ at the NiPc site ultimately lead to urea formation. Gao *et al.* have developed a tandem catalyst, Mo-PCN-222(Co), which integrates molybdenum and cobalt sites to synergistically facilitate the electrochemical conversion of NO_3^- and CO_2 into urea.[16] The cobalt sites enhance CO_2 reduction to form carbonic oxide (CO), while the molybdenum sites efficiently reduce nitrate to the $*NH_2$ intermediate. This dual-site catalyst enables the seamless coupling of carbon and nitrogen atoms, resulting in a remarkable urea production rate. The Mo-PCN-222(Co) catalyst demonstrated exceptional performance, achieving a urea yield rate of 844.11 mg h^{-1} g^{-1}

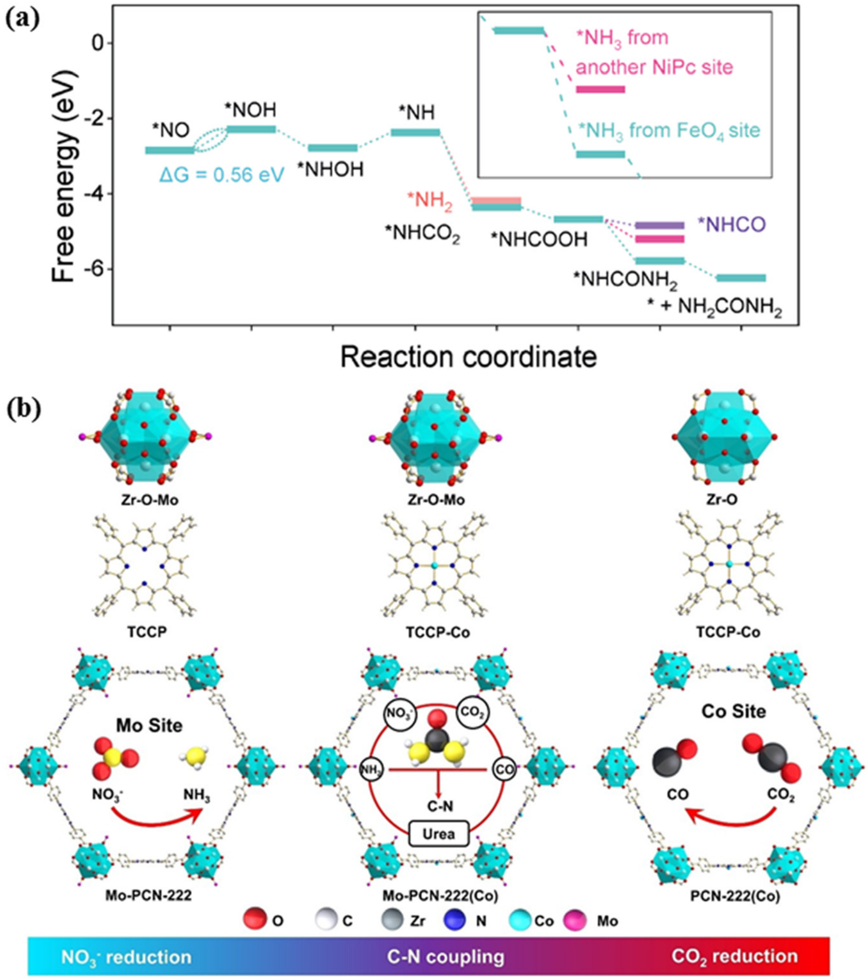

Fig. 3 (a) Free energy diagram for urea electrosynthesis on PcNi–Fe–O, highlighting the key thermodynamic steps (inset: comparison of the pathways for second C–N bond formation with $*NH_3$ produced from another NiPc site and FeO_4 site). Reproduced with permission from ref. 17. Copyright 2024 Wiley. (b) Crystal structure illustration of metal–organic frameworks Mo-PCN-222, PCN-222(Co), and Mo-PCN-222(Co). H atoms are omitted for clarity, and Zr_6 clusters are accentuated for better visualization. Reproduced with permission from ref. 16. Copyright 2024 Wiley.

and a corresponding FE of 33.90% at −0.4 V *vs.* RHE. Mechanistic investigations, combining *in situ* spectroscopy and density functional theory calculations, revealed that the tandem catalyst enables the efficient stabilization of the $*CONH_2$ intermediate. This is achieved through the concerted action of the molybdenum and cobalt sites, which generate the $*NH_2$ and *CO intermediates, respectively (Fig. 3b).

To further enhance current density and faradaic efficiency for urea synthesis, a promising approach is the encapsulation of metal oxide nanoparticles within MOF nanopores, a technique that has gained significant attention with the advancement of nanoscience. This strategy not only improves nanoparticle stability but also offers additional benefits such as uniform size distribution, confined effects, and enhanced conductivity. Huang *et al.* developed a MOF composite, γ-Fe_2O_3@Ni-HITP, by encapsulating ultrasmall γ-Fe_2O_3 nanoparticles within a conductive MOF, Ni-HITP (HITP: 2,3,6,7,10,11-hexaaminotriphenylene) (Fig. 4).[18] This hybrid material exhibited exceptional electrocatalytic properties for urea synthesis, leveraging the co-reduction of CO_2 and nitrate in a neutral aqueous solution. The γ-Fe_2O_3@Ni-HITP catalyst achieved remarkable performance, exhibiting a FE of 67.2(6)% and a current density of −90 mA cm^{-2}. Notably, the material sustained an impressive yield rate of 20.4(2) g h^{-1} g_{cat}^{-1} over 150 hours of continuous operation. Mechanistic investigations revealed that Fe(III) ions of the γ-Fe_2O_3 nanoparticles played a pivotal role, generating crucial intermediates ($*NH_2$ and *COOH) and facilitating the C–N coupling reaction. Specifically, paired Fe(III) ions acted as highly active catalytic sites, driving the generation of the key intermediate $*CONH_2$ and leading to the exceptional performance of γ-Fe_2O_3@Ni-HITP.

Catalysts for CO_2 and NO_3^- reduction typically perform well in inert environments, but they tend to have poor tolerance to oxygen, leading to a decline in activity even with minimal O_2 exposure.[20–22] This reduction in efficiency is primarily attributed to competitive oxygen reduction or catalyst degradation during the CO_2 and NO_3^- reduction process. In industrial applications, flue gas comprising approximately 15% CO_2 and 85% N_2 serves as a cost-effective feed gas for such reactions.[23,24] However, in addition to its lower CO_2 concentration, flue gas often contains trace amounts of oxygen, which can significantly affect reduction reactions.[25,26] Therefore, there is an urgent need to develop highly efficient catalysts capable of simultaneously reducing NO_3^- and low-concentration CO_2 while demonstrating strong resistance to oxygen. Such advancements are crucial for the practical and efficient production of urea. A recent study by Yao *et al.* employed a polyoxometalate-confinement strategy to synthesize ultrafine $BiVO_4$ nanoclusters by integrating $[V_{10}O_{28}]^{6-}$ (V_{10}) into an NH_2-MIL-101-Al (MIL) MOF.[19] The V_{10}@MIL-*n* composites (where n = 3, 5, 7, or 10, indicating the mass of V_{10} in milligrams) served as precursors for the controlled formation of $BiVO_4$ nanoclusters within the MIL framework. These $BiVO_4$@MIL-*n* composites exhibited a synergistic effect, enhancing both nitrate electroreduction (NO_3ER) and carbon dioxide electroreduction (CO_2ER), which facilitated C–N coupling for urea synthesis. The optimized $BiVO_4$@MIL-5 catalyst achieved an exceptionally high urea yield of 47.7 mmol g_{cat}^{-1} h^{-1} with a FE of 23.5%, significantly surpassing the yields of pristine MIL (4.8 mmol g_{cat}^{-1} h^{-1}) and pure $BiVO_4$ (2.4 mmol g_{cat}^{-1} h^{-1}). Under CO_2 airflow in the cathode chamber, the urea yield and FE further increased to 88.5 mmol g_{cat}^{-1} h^{-1}and 32.8%, respectively. Notably, a record urea yield of 63.4 mmol g_{cat}^{-1} h^{-1} was attained when exposed to a CO_2/O_2 gas mixture containing 33% O_2, and similar performance was observed when using flue gas, underscoring its remarkable tolerance to O_2 and N_2. The introduction of O_2 or N_2 helped modulate the competitive adsorption of NO_3^- and CO_2 on active sites, thereby enhancing the efficiency of urea electrosynthesis. Mechanistic investigations further revealed that the MIL framework, functionalized with $-NH_2$ groups, played a role in enriching CO_2 and activating NO_3^-, while the $BiVO_4$ nanoclusters effectively reduced NO_3^- and CO_2 to generate the *NCON intermediate, a crucial step in urea formation.

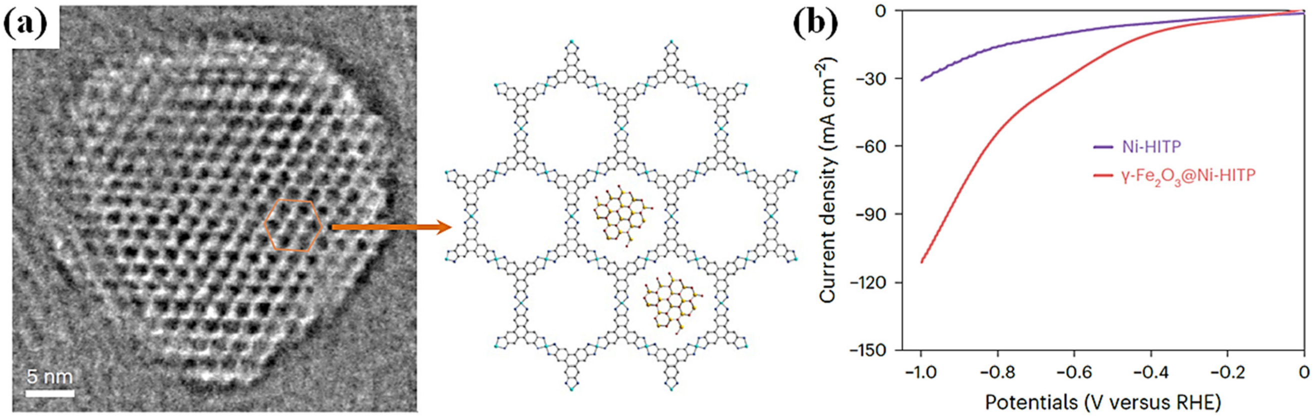

Fig. 4 (a) STEM image of γ-Fe_2O_3@Ni-HITP along [001] direction (left), the bright spots in the orange hexagon indicating γ-Fe_2O_3 nanoparticles in Ni-HITP, showed also in structure-diagram (right). (b) LSV curves of γ-Fe_2O_3@Ni-HITP. Reproduced with permission from ref. 18. Copyright 2024 Springer Nature.

3. Conclusions and future research directions

The traditional industrial process accounts for 1–2% of the global annual energy consumption and contributes to 1% of world's CO_2 emissions.[27] Therefore; the development of efficient electrocatalysts for urea synthesis under ambient conditions has shown significant progress in recent years. This review article highlights the potential of metal-based catalysts and MOFs in improving C–N coupling efficiency, leading to enhanced urea yield and faradaic efficiency. Despite these advancements, several challenges remain, including the low adsorption efficiency of inert N_2 and CO_2, the high overpotentials required for bond cleavage, and competing side reactions that reduce selectivity. Recent breakthroughs in MOF-based catalysts, such as γ-Fe_2O_3@Ni-HITP and PcNi–Fe–O, have demonstrated promising results, achieving high urea yield rates and faradaic efficiencies. The utilization of alternative nitrogen sources, such as NO_3^-, has also emerged as a viable strategy to overcome the limitations associated with N_2 activation. Additionally, the encapsulating metal oxide nanoparticles within MOF structures has proven to be an effective approach for enhancing catalyst stability, conductivity, and overall electrocatalytic performance.

Future works should seek the rational design of electrocatalysts with tuned electronic structures and active sites to optimize these different reaction pathways. Though significant progress has been made in enhancing catalytic activity, utilizing advanced computational modeling and *in situ* spectroscopic techniques can yield more information about the mechanisms involved in these reactions, which can be leveraged into the design principles for more effective catalyst systems. To put those in practice, extending the scalability as well as the economic feasibility of electrocatalytic urea synthesis will become an important task. Overcoming these obstacles will open avenues towards sustainable and energy-efficient urea manufacturing routes, making chemical synthesis greener going forward.

Single-atom and dual-atom catalysts based on copper (Cu) and iron (Fe) have demonstrated exceptional performance in electrocatalytic urea synthesis.[28–32] MOFs are emerging as a promising platform for immobilizing single-atom catalysts, owing to their ability to achieve high metal loadings while maintaining stability.[33,34] Gerke *et al.* explored the potential of molecular copper boron-imidazolate cages, specifically BIF-29(Cu), for urea production and achieved remarkable selectivity of 68.5% and an impressive activity of 424 μA cm^{-2}.[35] Given these advancements, single- or dual-atom catalysts confined within or supported on MOFs may represent the future of high-performance catalysts for efficient urea electrosynthesis.

Another sustainable route for future development in this field of electrocatalyst design can be achieved with the integrated help of artificial intelligence (AI) and machine learning.[36,37] AI-driven models can accelerate the discovery of new catalyst materials by predicting optimal compositions and reaction conditions. Additionally, exploring hybrid catalyst systems that combine different active sites may enhance reaction selectivity and efficiency. Further investigations into electrode design, electrolyte composition, and reaction conditions will also be necessary to improve overall system performance and stability.

Data availability

We declare that our manuscript has no data.

Conflicts of interest

There are no conflicts to declare.

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