Ultrathin Fe2O3 nanoparticles encapsulated in the pores of a metal-organic framework for highly efficient electrostatic synthesis of urea

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Ultrafine Fe$_2$O$_3$ nanoparticles encapsulated in the pores of a metal-organic framework for highly efficient electrosynthesis of urea

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ABSTRACT: Electrochemical co-reduction of CO$_2$ and nitrate to synthesize urea is a crucial and challenging task. So far, the reported catalysts have suffered from either low Faradaic efficiency (FE) or inadequate current density, leading to a restricted yield rate of urea. In this work, by a “ship-in-a-bottle” strategy, the ultrafine γ-Fe$_2$O$_3$ nanoparticles (NPs) (< 2 nm) were introduced into the pores of a conductive (40 S cm$^{-1}$) metal-organic framework Ni-HITP, resulting in a new composite material, namely γ-Fe$_2$O$_3$@Ni-HITP. Under neutral conditions, γ-Fe$_2$O$_3$@Ni-HITP exhibited a state-of-art electrocatalytic performance for urea synthesis through the co-reduction of CO$_2$ and nitrate in CO$_2$-saturated 0.1 M KHCO$_3$ and 0.1 M KNO$_3$ aqueous solution, achieving an FE$_{\text{urea}}$ of 65.8(6)%, a current density of ~90 mA cm$^{-2}$ and an ultrahigh yield rate of 20.4 g h$^{-1}$ g$_{\text{cat.}}^{-1}$ (7.7 mg h$^{-1}$ cm$^{-2}$), which is about 5 times higher than those of reported catalysts. No obvious degradation was observed over 150 hours of continuous operation at such ultrahigh yield rate. Enlarging the electrode area by 125 times and working for 8 hours, about 1.05 g of high-purity urea was obtained, highlighting the potential industrial application. Mechanistic study revealed that the Fe(III) ions of γ-Fe$_2$O$_3$ NPs exhibit high activity to generate the key intermediates $^{*}$NH$_2$ and $^{*}$COOH. Furthermore, the synergistic effect between a pair of adjacent Fe(III) ions of γ-Fe$_2$O$_3$ NPs promotes the C=N coupling between $^{*}$NH$_2$ and $^{*}$COOH, resulting in the formation of the subsequent key intermediate $^{*}$CONH$_2$, thereby contributing to the exceptional high-performance for urea production. This work significantly expands the applicability of NPs by combining them with conductive porous matrices, and paves the way for innovative design of high-performance catalysts.

Urea, as the most widely used nitrogen fertilizer globally, plays a pivotal role in agriculture, accounting for ca. 40% of global food production$^1$. Besides, urea also serves as a crucial raw material in pharmaceuticals and various fine chemical processes$^2$. Traditional industrial production of urea has heavily relied on the Bosch-Meiser process, involving the reaction of CO$_2$ and ammonia under extreme conditions (temperatures of 150 – 200 °C and pressures of 150 – 250 bar)$^3$. However, this process is characterized by substantial energy consumption and emissions, responsible for 80% of the ammonia produced by the global Haber-Bosch process and emitting a large amount of CO$_2$.$^4$. In light of these environmental concerns, using environment-friendly and low energy consumption methods to yield urea are of great significance. Compared with conventional fossil-fuel-based refineries, emerging electrochemical synthesis offers a sustainable and carbon-neutral alternative. Moreover, it provides decentralization and modularization benefits, facilitating system integration and innovation while enabling on-site and on-demand production$^1$. Therefore, electrochemical urea synthesis has gained significant attention as a viable and sustainable candidate.

Notably, the release of substantial industrial wastewater, characterized by nitrate concentrations of up to 41.6 mM, poses a severe environmental threat$^6$. The wastewater can infiltrate the soil, ultimately contaminating groundwater and surface water, and leading to eutrophication and the disturbance of ecosystem$^7$. Meanwhile, the continuous increase in atmospheric CO$_2$ concentration due to fossil energy consumption and human activities since the industrial revolution era has exacerbated global warming, leading to a series of increasingly severe environmental challenges, such as climate change, melting of bipolar glacier, rising sea-levels and natural disasters$^8$-10. Hence, the electrochemical co-reduction of CO$_2$ and nitrate to synthesize urea emerges as a dual-purpose strategy that addresses the challenges posed by nitrogenous fertilized wastewater and climate-related environmental problems, and has attracted much attention. For instance, in order to
achieve high urea production rates, Wang, Yu, and Zhang et al. developed a series of new catalysts and made significant progress\textsuperscript{11-22}. However, existing catalysts often grapple with the conundrum of achieving high current density and high Faradaic efficiency (FE) simultaneously, thereby resulting in urea production rates typically lower than \(3 \text{ g h}^{-1} \text{ g}_{\text{cat}}^{-1}\). Consequently, there is an imperative need to devise more efficient catalysts while unraveling the underlying mechanisms, ultimately advancing urea production through the co-electroreduction of CO\(_2\) and nitrate.

Metal oxide nanoparticles (NPs) are widely used in energy conversion and catalytic synthesis of high value-added products, but they face problems such as uneven size distribution, structure instability, and a tendency to aggregate at smaller sizes (< 5 nm). With the rapid development of nanoscience, encapsulating metal oxide NPs into nanopores has become one of the most promising strategies to address the stability concerns of NPs. In addition, this encapsulation offers the potential for synergistic effects between NPs and encapsulating materials, simultaneously improving both current density and FE\(_{\text{urea}}\). With well-defined structures, good designability, and uniform pore shapes and sizes, metal-organic frameworks (MOFs) have proven to be a sort of ideally encapsulating materials for metal or metal oxide NPs\textsuperscript{23,24}. Constructed from Ni(II) ions and HATP (2,3,6,7,10,11-hexamaminotriphenylene) ligands, Ni-HITP represents a conductive (40 S cm\(^{-1}\)) two-dimensional (2D) MOF possessing 1D pores with a diameter of ~2 nm\textsuperscript{26}. Therefore, it appears to be a promising material for encapsulating NPs aimed at electrochemical synthesis. Considering the well-known catalytic propensity of iron ions to catalyze nitrate reduction to NH\(_2\)\textsuperscript{27} and activate CO\(_2\) to *COOH\textsuperscript{28,29}, the diiron(III) sites composed of two adjacent iron(III) ions in \(\gamma\)-Fe\(_2\)O\(_3\) NPs (Supplementary Fig. 1) may exhibit high activity for the co-reduction of CO\(_2\) and nitrate to synthesize urea. Based on this premise, we adopted a "ship-in-a-bottle" strategy to encapsulate \(\gamma\)-Fe\(_2\)O\(_3\) NPs into Ni-HITP, and investigated its performance and reaction mechanism in electrochemical synthesis of urea through the co-reduction of CO\(_2\) and nitrate.

Ni-HITP was prepared according to the literature method\textsuperscript{26}, and its purity was confirmed by the powder X-ray diffraction (PXRD) patterns (Supplementary Fig. 2), scanning electron microscopy (SEM) images (Supplementary Fig. 3), thermogravimetric (TG) curves (Supplementary Fig. 4), and N\(_2\) sorption isotherms measured at 77 K (Supplementary Fig. 5). The high-resolution transmission electron microscopy (HR-TEM) images showed that Ni-HITP has a rod-shaped morphology and honeycomb-like 1D pores with pore size of 2 nm (Supplementary Fig. 6a). Immersing activated Ni-HITP in an \(N, N\)-dimethylformamide (DMF) solution of Fe(NO\(_3\))\(_3\) at 60 °C for 3 h to obtain \(\gamma\)-
The PXRD patterns demonstrated that the framework remained intact after the "ship-in-a-bottle" approach (Supplementary Fig. 2). The failure to detect the diffraction peaks of γ-Fe₂O₃ NPs may be attributed to their ultrasmall particle sizes < 5 nm, leading to both broad peaks and low signal-to-noise ratio thereby making them difficult to be observed. Besides, the low content of γ-Fe₂O₃ NPs in the framework, determined to be 4.5 wt% using inductively coupled plasma atomic emission spectrometry (ICP-AES) (Supplementary Table 1), may also lead to no obvious peaks of γ-Fe₂O₃ NPs in the PXRD patterns. The successful encapsulation and uniform distribution of γ-Fe₂O₃ NPs (< 2 nm) within the channels of Ni-HITP is evidenced by scanning transmission electron microscopy (STEM) through comparing with the pristine material (Figs. 1b, c, Supplementary Fig. 6), and further supported by energy-dispersive spectroscopy (EDS) mapping (Supplementary Fig. 7). The high-resolution X-ray photoelectron spectroscopy (XPS) was conducted to further understand the chemical composition and oxidation state of γ-Fe₂O₃@Ni-HITP. Specifically, the wide-scanning XPS spectrum (Supplementary Fig. 8a) of γ-Fe₂O₃@Ni-HITP sample revealed the co-existence of Ni, Fe, C, N, and O elements. The Ni 2p spectrum (Supplementary Fig. 8b) consisting of two spin–orbit doublets of Ni 2p3/2 (855.21 eV), Ni 2p1/2 (872.51 eV) and two satellites at 859.84 eV and 877.14 eV indicated that the oxidation state of Ni is +2. Similarly, the deconvoluted peaks at 710.65 eV and 723.85 eV and two satellites at 720.12 eV and 733.32 eV can be attributed to Fe(III) ions (Supplementary Fig. 8c). To further elucidate the coordination configuration and valence state of iron ions, X-ray absorption spectroscopy (XAS) measurement for Fe K-edge spectra of γ-Fe₂O₃@Ni-HITP was performed. The K-edge X-ray absorption near-edge structure (XANES) spectra also indicated the presence of Fe(III) ions and the absence of metallic iron (Fig. 1d), which is consistent with the XPS results. The extended X-ray absorption fine structure (EXAFS) spectra showed that the coordination environment of γ-Fe₂O₃@Ni-HITP is similar to that of iron oxide, with a main signal at 1.48 Å corresponding to Fe–O bond distance (Supplementary Fig. 9b). Furthermore, the results of fitting the EXAFS spectra indicated that the Fe₂O₃ NPs are γ-Fe₂O₃ NPs (Fig. 1e, Supplementary Fig. 9, Table 2) rather than α-Fe₂O₃ NPs or the Fe ions replacing Ni ions in the Ni-HITP framework (Supplementary Fig. 10, Table 3). The TG curves (Supplementary Fig. 4) of γ-Fe₂O₃@Ni-HITP showed that the first mass loss before 100°C is due to the release of guest water molecules, and the framework remains thermostable before heating to 350°C. The N₂ sorption isotherms (Supplementary Fig. 5) measured at 77 K showed that the adsorption amount decreased slightly after the "ship-in-a-bottle" treatment, indicating the presence of γ-Fe₂O₃ NPs within partial pores of the MOF.

To evaluate the performance of γ-Fe₂O₃@Ni-HITP for electro-synthesis of urea, the microcrystalline powder of the catalyst was coated on a gas diffusion layer modified carbon paper using Nafion binder to prepare the working electrode. As shown in Supplementary Fig. 11, the charge transfer resistance (Rct) of Ni-HITP and γ-Fe₂O₃@Ni-HITP were calculated as 62.4 and 82.1 Ω, respectively, indicating a lower charge transfer resistance during the electrolysis process. By analyzing the cyclic voltammetry (CV) curves obtained at different scanning rates in non-faradaic regions (Supplementary Fig. 12), the electrochemical double-layer capacitances (Cdl) of Ni-HITP and γ-Fe₂O₃@Ni-HITP were estimated to be 2.38 and 7.66 mF cm⁻², respectively, indicating that Ni-HITP and γ-Fe₂O₃@Ni-HITP are suitable as electrocatalysts. The performance tests were carried out in a 3-electrode flow cell using CO₂ saturated 0.1 M KHCO₃ + 0.04 M KNO₃ aqueous solution as electrolyte (see Supporting Information for details). The gaseous products were detected by gas chromatography (GC) (Supplementary Figs. 13, 14). The chronoamperometric method (Supplementary Figs. 15-18) was used for the detection and quantification of liquid phase products, including urea, ammonia, and NO₂⁻. From the LSV curve (Fig. 2a), it can be seen that the platform appeared after −0.4 V vs. reversible hydrogen electrode (RHE), and there was a significant increase in current within the range of −0.6 ~ −1.0 V, which may be due to the acceleration of the formation of urea and hydrogen evolution reaction (HER). Subsequently, we conducted potentiostatic electrolysis at different potentials from −0.6 ~ −1.0 V vs. RHE (Fig. 2b) and analyzed different products. The ultraviolet-visible (UV-vis) spectra (Supplementary Fig. 18) showed that as the potential increases, the FEurea exhibits a volcanic pattern (Fig. 2b) and reaches its maximum value of 62.3(3)% with a current density of −54 mA cm⁻² at −0.8 V vs. RHE, giving a record spatiotemporal yield rate of up to 14.67 g h⁻¹ gcat⁻¹. Importantly, such yield rate is about 5 times higher than those of reported catalysts (Fig. 2e, Supplementary Table 6). At higher overpotentials, more competitive HER occurs, thus inhibiting the formation of urea. In order to determine that the catalytic activity stems from the γ-Fe₂O₃ NPs embedded in the pore of Ni-HITP, we conducted the performance tests on pure γ-Fe₂O₃ NPs with the size of ca. 24 nm (Supplementary Figs. 19, 20) and Ni-HITP for co-reduction of CO₂ and NO₃⁻ under the same conditions, respectively. Interestingly, for pure γ-Fe₂O₃ NPs, it exhibited a good FE(urea) of 41.2%, but a smaller current density of 7 mA cm⁻² that resulted in a smaller urea yield of 0.56 g h gcat⁻¹ (Supplementary Figs. 21, 22), while there is no urea generation for Ni-HITP (Supplementary Figs. 23, 24), indicating that γ-Fe₂O₃ NPs indeed acted as the catalytic sites, while Ni-HITP only acted as a support. In order to further investigate the effect of the particle
size of γ-Fe₂O₃ NPs on the performance for urea electroosynthesis. We conducted a series of control experiments on the catalytic performance of γ-Fe₂O₃ NPs (with different sizes of ca. 24, 7.9, 3.8 and < 2 nm) encapsulated in Ni-HITP. As shown in Supplementary Figs. 25-34, the smaller the size of γ-Fe₂O₃ NPs, the higher the urea yield rate. This result might be ascribed to the ultrafine nanoparticle size making more active sites available and more active. The above results also indicated that the iron ions on γ-Fe₂O₃ NPs are indeed the active sites for urea electroosynthesis.

In order to determine the content of urea more accurately, we also used ¹H nuclear magnetic resonance (¹H NMR) for quantitative detection of urea product. It can be seen from Supplementary Figs. 35 and 36, there is a singlet peak of −NH₂ of urea with a chemical shift of 5.7 ppm. According to the linear relationship between the urea concentration and peak area of −NH₂ in the standard curve, we can conclude that at −0.8 V vs. RHE, the FEs of urea, NH₃, NO₃⁻, and H₂ with γ-Fe₂O₃@Ni-HITP as electrocatalyst. NMR spectra of urea. The above results also indicated that the iron ions on γ-Fe₂O₃ NPs are indeed the active sites for urea electroosynthesis.

Fig. 2 | Co-reduction of CO₂ and NO₃⁻ performance of γ-Fe₂O₃@Ni-HITP. a, LSV curve of γ-Fe₂O₃@Ni-HITP. b, FEs of urea, NH₃, NO₃⁻, and H₂ with γ-Fe₂O₃@Ni-HITP as electrocatalyst. c, NMR spectra of urea. d, Overall performance comparison between γ-Fe₂O₃@Ni-HITP and representative electrocatalysts for co-reduction of CO₂ and NO₃⁻ to urea conversion. e, Comparison of urea yield and FEs for representative electrocatalysts for CO₂ and NO₃⁻ to urea conversion (Table S3). f, 150 h stability test of γ-Fe₂O₃@Ni-HITP in the electrocatalysis at the potential of −0.8 V vs. RHE.
the co-reduction of CO\textsubscript{2} and NO\textsuperscript{3−}. In addition, the \textsuperscript{15}N NMR spectrum (Fig. 2c) clearly shows that the peak at 78 ppm belongs to the \textsuperscript{15}N of \text{-}NH\textsubscript{2} in urea, and the \textsuperscript{13}C NMR spectrum shows that the peak at 163 ppm can be assigned to the \textsuperscript{13}C of -\text{CO-} in urea. Moreover, when only CO\textsubscript{2} or nitrate was used as feedstock, it can be seen that no urea product was detected, further demonstrating that urea indeed comes from the co-reduction of CO\textsubscript{2} and NO\textsuperscript{3−} (Supplementary Fig. 39-42). To evaluate the stability, a continuous co-reduction of CO\textsubscript{2} and NO\textsuperscript{3−} was performed at -0.8 V vs. RHE. The result (Fig. 2f) indicated that \textgreek{γ}-Fe\textsubscript{2}O\textsubscript{3}@Ni-HITP can continuously working for at least 150 hours at such ultrahigh yield rate of 14.67 g h\textsuperscript{−1} g\textsuperscript{−1} cat., representing the state-of-art performance so far (Fig. 2e, Supplementary Table 6). According to the TEM images (Supplementary Fig. 7), XPS spectra (Supplementary Fig. 8), PXRD patterns (Supplementary Fig. 2), XANES and EXAFS spectra (Supplementary Figs. 9, 43, 44 and Tables 2, 4), no obvious changes of \textgreek{γ}-Fe\textsubscript{2}O\textsubscript{3}@Ni-HITP can be observed after electrolysis, suggesting high stability during electrocatalysis.

In order to prepare gram level high-purity urea, a flow cell with a larger window area (5 × 5 cm\textsuperscript{2}) was used with a catalyst mass of 9.01 mg. After 8 hours of electrolysis in CO\textsubscript{2} saturated 0.1 M KHCO\textsubscript{3} + 0.04 M KNO\textsubscript{3} aqueous solution, 1.05 g pure urea (without electrolyte, NO\textsuperscript{2−} and NH\textsubscript{4+}) was extracted from electrolyte using benzene, directly giving a urea yield rate of 14.56 g h\textsuperscript{−1} g\textsuperscript{−1} (Supplementary Fig. 45). The urea yield rate is consistent with that obtained by the diacetyl monoxime and \textsuperscript{1}H NMR methods. Such results not only demonstrate the validity of the results obtained from diacetyl monoxime and \textsuperscript{1}H NMR methods, but also indicate the potential industrial application. Considering the salt concentration in the electrolyte has important effect on the urea yield rate and the concentration of KHCO\textsubscript{3} + KNO\textsubscript{3} of 1 M + 0.1 M was usually used to evaluate the catalytic performance, we also optimized the concentrations of KHCO\textsubscript{3} + KNO\textsubscript{3}. In the electrolyte of CO\textsubscript{2}-saturated 1 M KHCO\textsubscript{3} and 0.1 M KNO\textsubscript{3} mixed solution, the urea yield rate was significantly increased from 14.67 to 20.4 g h\textsuperscript{−1} g\textsuperscript{−1} or 5.5 to 7.7 mg h\textsuperscript{−1} cm\textsuperscript{−2} (Supplementary Figs. 46, 47, Table 6), further demonstrating the ultra-high catalytic performance of \textgreek{γ}-Fe\textsubscript{2}O\textsubscript{3}@Ni-HITP.
To reveal the mechanism of electrosynthesis of urea, the operando attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurement was conducted at different potentials to determine the intermediates. As shown in Fig. 3a, the peak at 1392 cm⁻¹ can be assigned to the important intermediate *COOH in CO₂ reduction process. The peak at 1413 cm⁻¹ can be identified as the v₃n for C–N bond. The peaks of *NO and *NH₂ intermediates can be found at 1160 and 3110 cm⁻¹ (Fig. 3a). To further illustrate how these two intermediates *NO and *NH₂ were generated, we conducted some control experiments. Operando ATR-FTIR tests were conducted under 0.04 M KNO₃ and 0.1 M KHCO₃ conditions (Supplementary Fig. 48), respectively. It was found that under CO₂ reduction conditions, only a peak at 1392 cm⁻¹ assigned to v(COOH) was observed, while no peak around 2100 cm⁻¹ for CO appeared. Under NO⁻ reduction condition, there were peaks at 1392 cm⁻¹ and 1575 cm⁻¹ assigned to v(NO₂) and v(NH), respectively. Under the conditions of co-reduction of CO₂ and NO-, both the peaks of v₃n(CN) + v(COOH) were observed. The above results indicated that the intermediates *COOH and *NH₂ observed during the co-reduction process should come from the reduction of CO₂ and NO⁻, respectively. Since no peak for *CO intermediate was observed, and in order to further determine that the formation of the C–N bond is not originated from the coupling between *NH₂ and *CO, we used CO instead of CO₂ as the feedstock for the synthesis of urea. Interestingly, the results showed that no urea was generated (Supplementary Fig. 49), suggesting the *CO intermediate had not taken part in the co-reduction reaction of CO₂ and NO⁻. Such mechanism is completely different to that proposed in previous reports (*CO is the key intermediate). As we could only observe the two intermediates *COOH and *NH₂, and did not observe the CO intermediate commonly observed in literature, we speculated that C–N coupling may have occurred between these two intermediates, rather than the C–N coupling between *CO and *NH₂ as reported. Based on the operando ATR-FTIR results, periodic density functional theory (PDFT) calculations were conducted to elucidate the reaction path during the co-reduction of CO₂ and NO⁻. In light of the free-energy diagram of the energy pathway as profiled in Fig. 3b, the urea production initiates from thermodynamically spontaneous reduction of NO⁻ to *NH₂ intermediate on γ-Fe₂O₃ with a Gibbs free energy barrier ΔG = -5.76 eV. And the reduction of CO₂ to *COOH intermediate by the Fe(III) ion of γ-Fe₂O₃ NP also gave a lower ΔG = -0.46 eV. Then, due to the synergistic effect of two adjacent Fe(III) ions, the C–N coupling occurs between the preceding two intermediates of *NH₂ and *COOH with ΔG = -1.07 eV (Fig. 3b step 6 and step 7), which is much lower than that of the reduction of *COOH to *CO (ΔG = -0.47 eV). Subsequently, urea product was obtained through further multi-electron hydrogenation reduction and C–N coupling. Fig. 3c provides a schematic diagram of the key intermediates in the reaction pathway. The above calculation results are consistent with the experimental results and indicated that the diiron(III) sites of γ-Fe₂O₃ NPs indeed have high activity for catalyzing the co-reduction of CO₂ and nitrate to synthesize urea. In addition to the catalytic activity of the catalyst, the current density of the catalyst is usually related to its conductivity. To investigate the role of the conductivity of Ni-HHTP as a support in the electrosynthesis of urea, and to validate the applicability of this "ship-in-a-bottle" strategy, an isostructural MOF Ni-HHTP (2,3,6,7,10,11-triphenylenehexol = HHTP) with poorer conductivity was also used as support to encapsulate γ-Fe₂O₃ NPs (Supplementary Fig. 50). The purity of γ-Fe₂O₃@Ni-HHTP was confirmed by the PXRD patterns, SEM images, TEM images, XAS spectra and ICP–AES analyses (Supplementary Figs. 51-54 and Supplementary Tables 1 and 5). Interestingly, the FEₐrea of γ-Fe₂O₃@Ni-HHTP (FEₐrea = 50%) (Supplementary Figs. 55, 56) is somewhat close to that of γ-Fe₂O₃@Ni-HHTP (FEₐrea = 62.3%), but its current density (j = -20.2 mA cm⁻²) is much lower than that of the latter (j = -54 mA cm⁻²) resulting in a much lower yield rate than γ-Fe₂O₃@Ni-HHTP (Supplementary Fig. 57), which might be ascribed to the poor conductivity of Ni-HHTP than that of Ni-HITP. This result indicates that the conductivity of the support greatly affects the performance of electrocatalysis, especially the current density. In words, the ultrahigh yield rate of urea of γ-Fe₂O₃@Ni-HHTP can be ascribed to both high catalytic activity of the ultrafine γ-Fe₂O₃ NPs and conductivity of the support Ni-HITP.

Conclusions

To summarize, by using conductive Ni-HITP as the encapsulating material, the uniform and ultrafine γ-Fe₂O₃ NPs were, for the first time, successfully synthesized through a "ship-in-a-bottle" strategy, resulting in a catalyst γ-Fe₂O₃@Ni-HITP for electrosynthesis of urea. Utilizing both of CO₂ and nitrate as feedstocks, γ-Fe₂O₃@Ni-HITP exhibited an ultrahigh yield rate of urea, setting a new benchmark in terms of performance. Mechanistic study showed the synergistic effect between two adjacent Fe(III) ions of γ-Fe₂O₃ NPs played a pivotal role in promoting the crucial C–N coupling. Furthermore, our experimental results also indicate that conductive mesoporous MOFs are indeed promising supports. The uniform pores of MOFs can provide a confined space that is conducive to the synthesis of uniformly sized and ultrafine metal oxide NPs. Additionally, their excellent conductivity significantly contributes to the current density of electrocatalysis.
This work provides a novel strategy for synthesis of ultrafine and highly dispersed metal or metal oxide NPs, as well as guidance for the preparation of efficient electrocatalysts.

Methods

Chemicals
Nickel(II) acetate tetrahydrate (Ni(OAc)₂·4H₂O), 2,3,6,7,10,11-hexaaminotriphenylene (HATP·6HCl), N,N-dimethylformamide (DMF), N,N-dimethylamine (DMA), sodium acetate (NaOAc), iron(III) nitrate (Fe(NO₃)₃), methanol (MeOH), Nafion (5 wt%), hydrophobic carbon paper (Sigracet 29 BC), potassium nitrate (KNO₃), phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄), diacetylmonoxime (DMAM), thiosemicarbazide (TSC), urea, dimethyl sulfoxide (DMSO), sodium hydroxide (NaOH), salicylic acid, sodium citrate, sodium hypochlorite (NaClO), sodium nitroferricyanide, ammonium chloride (NH₄Cl), N-(1-naphthyl)ethylene-diamine dihydrochloride (SED), acetic acid (HOAc), potassium nitrite (KNO₂), potassium nitrite—¹⁵N (¹⁵KNO₂) were all commercially available from Aladdin Ltd. (Shanghai, China).

Materials and General Methods
All reagents were commercially available and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer (Cu Kα). Scanning electron microscope (SEM) images were obtained by a SU8010 system. High resolution transmission electron microscope (HR-TEM) images were obtained by an FEI Tecnai G² F30. Elemental analyses (EA) were conducted using an Elementar Vario EL analyzer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) tests were performed on an iCAP6500 Duo (Thermo Fisher). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer (Thermo-VG Scientific). Nuclear magnetic resonance (NMR) data were collected on a Bruker AVANCE II/III 600HD with liquid helium ultra-low temperature TCI detection probe. ATR-FTIR tests were performed on a Nicolet 6700 spectrometer.

Ni and Fe K-edge X-ray absorption measurement.

The X-ray absorption spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the samples at Fe and Ni K-edge were collected at the Singapore Synchrotron Light Source (SSLS) center, where a pair of channel-cut Si(111) crystals was used in the monochromator. The Fe and Ni K-edge XANES data were recorded in a transmission and fluorescence mode, respectively. X-ray absorption data reduction and analysis were processed by Athena and Artemis software.

ICP-AES measurement
ICP-AES was performed on an Optima8300 spectrometer (PerkinElmer, USA). Typically, 2 mg of the sample was accurately weighed and placed into a 20 mL glass vial. Following this, 3 mL of H₂O₂ and 2 mL of HNO₃ were added. The mixture was then heated at 200 °C for 10 minutes until the solution turned transparent. Subsequently, distilled water was used to dilute the solution to a final volume of 50 mL, resulting in a colourless, transparent solution. A blank control sample was prepared using the same method, with the only difference being the absence of the sample.

Synthesis of Ni-HITP
Ni(OAc)₂·4H₂O (3.5 mg) was dissolved in DMF/DMA (v/v = 1:1) (6 mL), an aqueous NaOAc solution (4 mL, 2 mol·L⁻¹) was then added, and the mixture was heated with stirring at 65°C for 0.5 hours. An aqueous solution (1.5 mL) containing HATP·6HCl (5 mg) was then added, and the mixture was continually stirred at 65°C for 2 hours in the air. Upon cooling, the black powder was collected by centrifugation and washed with large amount of H₂O and methanol, and dried under vacuum.

Synthesis of Ni-IIHITP
A solid mixture of HHTP (7 mg) and Ni(OAc)₂·4H₂O (10 mg) was dissolved in deionized water (4.0 mL) in a 20-mL glass vial. The reaction mixture was heated in an isothermal oven at 85°C for 12 hours resulting in small dark blue crystals. The reaction mixture was allowed to cool naturally to room temperature and the crystals were washed with deionized water and acetone three times.

Synthesis of γ-Fe₂O₃@Ni-IIHITP
Typically, a mixture of Fe(NO₃)₃ (10 mg), activated Ni-IIHITP (20 mg) and DMF (15 mL) was sonicated at 0°C for 30 minutes to obtain an uniform dispersed solution. Then the mixture was heated in a 20-mL open glass with vigorous stirring at 60°C for 3 hours. After cooling down to room temperature, the resulting black powder was filtered, and washed with large amount of water and methanol, and dried under vacuum. Synthesis of γ-Fe₂O₃@Ni-IIHITP was similar to γ-Fe₂O₃@Ni-IIHITP, by using Ni-IIHITP instead of Ni-IIHITP.

Preparation of working electrode
Preparation of working electrode was performed by a general method. Briefly, Ni-IIHITP or γ-Fe₂O₃@Ni-IIHITP powder (5 mg) was dispersed into a mixed solution of isopropanol (450 μL), H₂O (500 μL) and Nafion (50 μL), followed by sonicated for 30 minutes to obtain a uniform dispersed ink. The aforementioned sample ink (75 μL) was dropped onto a hydrophobic carbon paper (Sigracet 29 BC) of gas diffusion layer electrode (GDE) with an area of 1 cm² to afford high surface area and enable rapid mass transport of gas phase CO₂ and dried under room temperature. The average mass loading was 0.375 mg cm⁻².

Electrochemical measurements
Electrochemical measurements were carried out in a typical three-electrode flow cell, with a platinum foil (1.0 × 1.5 cm²) counter electrode, an Ag/AgCl electrode (in saturated KCl solution) as reference electrode and the prepared gas diffusion electrode (GDE) as the working electrode in a CHI660 electrochemical workstation. Anode chamber and cathode chamber were separated by an anion exchange membrane (FIA-3-PK-130). The cathode and anode were connected with copper tape (current collector), respectively. Before tests, the anion exchange membrane was pretreated by submerging it in 0.1 M KOH aqueous solution at 25°C for 12 hours and then in 0.1 M KHCO₃ aqueous solution at 25°C for another 12 h, followed by rinsing the membrane with deionized water. For electrochemical urea synthesis, potentiostatic tests at
the potentials of \(-0.6, -0.7, -0.8, -0.9\) and \(-1.0\) V vs. RHE were carried out in CO\(_2\)-saturated 0.1 M KHCO\(_3\) and 0.04 M KNO\(_3\) mixed solution (the volume of the electrolyte in the anode and cathode chamber was 40 mL for each) for 20 min, which circulated through the cathode and anode at a rate of 10 mL min\(^{-1}\) under the pressure applied by peristaltic pump (EC200-01, Gauss Union). The constant potential electrolysis experiments were repeated three times, and the results presented were the averaged values. The CO\(_2\) flow was kept constant at 30 sccm using a mass flow controller (KMG3, Alicat Scientific). The effective area of working electrode in the flow cell was 0.2 cm\(^2\). All potentials (without \(iR\) compensated) in this study were converted to the RHE reference scale via the following equation: 
\[E_{\text{RHE}} = E_{\text{VSS}} + 0.196 V + 0.0591 \times \text{pH}.\]
Electrocatalytic CO\(_2\) reduction reaction was carried out at CO\(_2\)-saturated 0.1 M KHCO\(_3\). Electrocatalytic NO\(^{-}\) reduction reaction was performed at Ar-saturated 0.04 M KNO\(_3\).

**Products detection and quantification**

**Gas products**

The electrolyzer outlet gas was introduced directly into the gas-sampling loop of the gas chromatograph (GC; Agilent 8890C). A GC run was initiated every 840 s. Argon (99.999%) was used as the carrier gas. A flame ionization detector (FID) was used to quantify CO, CH\(_4\), and C\(_2\)H\(_6\) while a thermal conductivity detector (TCD) was used to quantify H\(_2\). The FE of a certain gas product was calculated by the equation:
\[
FE = \frac{PV}{T} \times \frac{\nuNF}{I}
\]
in which \(P, V\) and \(T\) represent the pressure (1 atm), gas flow rate (30 mL min\(^{-1}\)) and room temperature, and \(\nu\) (vol\%), \(N, F, I\) and \(I\) represent the volume concentration of gas product, number of the electron transfer in electrocatalysis, Faraday constant (96485 C mol\(^{-1}\)), and current, respectively.

**Liquid products**

The extracted electrolyte was initially subjected to the quantification of urea, NH\(_3\) and NO\(^{-}\) with colorimetric methods with some modifications.

**Determination of urea concentration**

The concentration of urea in the electrolyte was measured by the diacetyl monoxime method\(^{41}\). Typically, FeCl\(_3\) (100 mg) was dissolved in the mixed solution of concentrated phosphoric acid (100 mL), concentrated sulfuric acid (300 mL) and distilled H\(_2\)O (600 mL), denoted as acid-ferric solution. Diacetylmonoxyde (DAMO, 5 g) and thiosemicarbazide (TSC, 100 mg) were dissolved in distilled water (1000 mL), denoted as DAMO-TSC solution. Subsequently, acid-ferric solution (2 mL) and DAMO-TSC solution (1 mL) were added into the mixed solution of urea-containing solution (0.6 mL) and fresh electrolyte (0.4 mL) and mixed vigorously. Finally, the above solution was heated to 90°C and maintained for 20 min, during which the reaction between the diacetyl monoxide and urea in acid generated a pink product. After cooling to room temperature, the absorbance curve with the maximum absorbance at 525.5 nm was collected by Ultraviolet-Visible (UV-vis) spectrophotometer. The concentration-absorbance curves were calibrated by using standard urea solutions for a series of concentrations, which contained the salt solution as same as electrolyte, as shown in Supplementary Fig. 15. There was a linear relationship between the absorbance and the concentration of urea, and the concentration of urea after the electrochemical test was acquired according to the calibration curve. The average urea yield rate \((R_{\text{area}})\) was calculated as follows:
\[
R_{\text{area}} = \frac{C_{\text{area}} \times V}{t \times m}
\]
where \(C_{\text{area}}\) is the measured concentration of urea (\(\mu g\cdot mL^{-1}\)), \(V\) is the total volume of electrolyte (mL), \(t\) is time (h) for electrocatalysis and \(m\) is usage quality of catalyst (mg) on carbon paper. The FE of urea was calculated by using the following formula:
\[
FE_{\text{urea}} = \frac{16 \times F \times C_{\text{area}} \times V}{60.06 \times Q}
\]
where \(F\) is the Faraday constant (96485 C mol\(^{-1}\)), \(Q\) is the total charge passed through the working electrode (C). For the measurement of \(^1\)H NMR spectra of urea, a mixed solution of electrolyte (500 \(\mu\)L) after electrocatalysis in cathode chamber, deuterated water (50 \(\mu\)L) and dimethyl sulfoxide (DMSO, 4 ppm, 50 \(\mu\)L), was quantified by \(^1\)H NMR spectra with solvent (H\(_2\)O) suppression. The concentration of urea exhibits a linear relationship with the integral area of the characteristic peaks (chemical shift: 5.7 ppm), thus the concentration of the products could be calculated via the equation of the calibration curves (Supplementary Fig. 35).

**Determination of NH\(_3\)**

The amount of NH\(_3\) in the solution was determined by colorimetry using the indophenol blue colorimetric method\(^{42}\). Typically, 2 mL of 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, NaClO (0.05 M, 1 mL) and sodium nitroferricyanide (1 wt%, 0.2 mL) were added in turn to the mixed solution of NH\(_3\)-containing solution (0.6 mL) and fresh electrolyte (1.4 mL) and mixed vigorously. After standing at room temperature in dark box at room temperature for 15 min, the absorbance curve with the maximum absorbance at 530.5 nm was collected by UV-vis spectrophotometer. The concentration-absorbance curves were calibrated by using standard ammonium chloride solutions for a series of concentrations, which contained the salt solution as same as electrolyte, as shown in Supplementary Fig. 16. The FE of NH\(_3\) was calculated using the following formula:
\[
FE_{\text{NH}_3} = \frac{8 \times F \times C_{\text{NH}_3} \times V}{17 \times Q}
\]
where \(C_{\text{NH}_3}\) is the measured concentration of NH\(_3\) (\(\mu g\cdot mL^{-1}\)), \(V\) is the total volume of electrolyte (mL), \(F\) is Faraday constant (96485 C mol\(^{-1}\)) and \(Q\) is the quantity charge (C).

**Determination of NO\(^{-}\)**

The concentration of NO\(^{-}\) was quantified by the Griess test\(^{43}\). Typically, sulfanilic acid (SA, 0.5 g) and N-(1-naphthyl)ethylenediamine dihydrochloride (NED, 5 mg) were dissolved in a mixture solution of acetic acid (5 mL) and H\(_2\)O (95 mL), denoted as SA-NED solution. SA-NED solution (4 mL) was added into the mixed solution of NO\(^{-}\)-containing solution (0.4 mL) and fresh electrolyte (0.6 mL), in which the sulfonamide reacts with the NO\(^{-}\) to form a diazonium salt and then further reacts with the amine to form an azo dye (magenta). After kept in dark box at room temperature for 15 min, the absorbance curve with the maximum absorbance at 530.5 nm was collected by UV-vis spectrophotometer.
The concentration-absorbance curves were calibrated by using standard KNO$_2$ solutions for a series of concentrations, which contained the solution as same as the electrolyte, as shown in Supplementary Fig. 17.

The FE of NO$_2^-$ was calculated using the following formula:

$$FE_{NO_2^-} = \frac{2 \times F \times C_{NO_2^-} \times V}{46 \times Q}$$

where $C_{NO_2^-}$ is the measured concentration of NO$_2^-$ ($\mu$g mL$^{-1}$), $V$ is the total volume of electrolyte (mL), $F$ is Faraday constant (96485 C mol$^{-1}$) and $Q$ is the quantity charge (C).

The $N_{\text{total}}$-selectivity were calculated according to the following equations:

$$N_{\text{urea}} \text{- selectivity} = \frac{n_{\text{urea}(N)}}{n_{\text{total}(N)}}$$

where $n_{\text{urea}(N)}$ are the moles of nitrogen in the as-produced urea, while $n_{\text{total}(N)}$ represents the moles of nitrogen in all the products from the reduction of nitrate.

**15NO$_2^-$ isotopic labelling experiment**

The produced urea was quantitatively confirmed by an isotope-labelled experiment with the same conditions of the electrosynthesis of urea only by using 0.04 M K$^{15}$NO$_2$ instead of K$^{14}$NO$_2$ solution as the N source. After 24 hours of electrocatalytic reduction, $^{15}$NH$_2$CO$^{14}$NH$_2$ in the reaction solution was tested by using $^1$H NMR and $^{15}$N NMR spectra.

**Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements**

ATR-FTIR measurements were carried out on a Nicolet iS50 (Thermo Fisher) equipped with a liquid nitrogen cooled MCT detector. Data were collected at the different potentials in the mixed solution of 0.1 M KHCO$_3$ and 0.04 M KNO$_3$ using a home-made ATR-FTIR electrolysis cell. Electrochemical co-reduction of CO$_2$ and NO$_3^-$ was performed on the glassy carbon electrode, with Ag/AgCl electrode as the reference electrode and Pt wire as the counter electrode. The gas inlet and outlet used to purge CO$_2$ was then purged into the cell at a flow rate of 30 sccm for another 30 min.

After that, a background IR spectrum was taken. Then potentiostatic test of different potentials was applied to electrocatalysis of the co-reduction of CO$_2$ and NO$_3^-$.

**Computational Methods**

All periodic density functional theory (PDFT) calculations were performed in the Materials Studio 5.5 package. A single cell was used as the calculation model, the size and the periodicity are according to the cell parameters and space group of the crystal structure of $\gamma$-Fe$_3$O$_4$. The structures of all intermediates in electrocatalysis were firstly optimized by Dmol$^3$ module. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function and TS for DFT-D correction were employed to the calculations. The convergence tolerance of energy, force and displacement convergence were set as $1 \times 10^{-5}$ Ha, $2 \times 10^{-3}$ Ha and $5 \times 10^{-3}$ Å, respectively. The core was treated using the effective core potential (ECP), and the electrons were treated by double numerical plus (DNP) basis set. The adsorption energy of an intermediate on the catalyst surface was calculated as

$$\Delta E = E_{\text{total}} - E_{\text{catal}} - E_{\text{int}}$$

where $E_{\text{total}}$, $E_{\text{catal}}$ and $E_{\text{int}}$ are the total energies of the catalyst structure after the adsorption of the intermediate, the pristine catalyst and the isolated intermediate, respectively. The corresponding Gibbs free energy of adsorption was calculated as

$$\Delta G = \Delta E + \Delta ZPE - T \Delta S$$

where $\Delta ZPE$ and $\Delta S$ are the changes in zero-point energy and entropy, respectively, after the intermediate adsorption. $T$ is the temperature (298.15 K).

**Data availability**

The data supporting the finding of the study are available in the paper and its Supplementary Information. Source data are provided with this paper.

**References**

8. Matthews, M. D. & Wyne, S. Current global efforts are insufficient to limit warming to 1.5°C. *Science* 376, 1404-1409 (2022).
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