

Rational Design of Bimetallic 2D Covalent Organic Frameworks for Interlayer Electrocatalytic Urea Production from N₂ and CO₂

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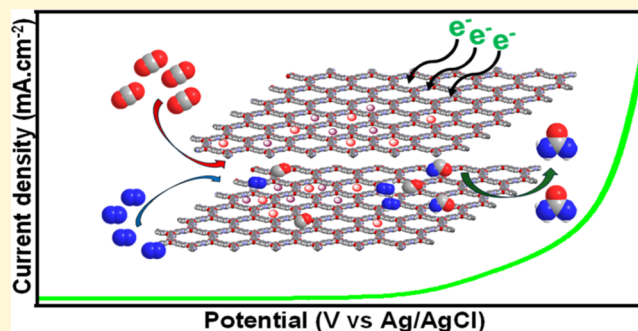
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ABSTRACT: The electrocatalytic synthesis of urea directly from N₂ and CO₂ offers a potential approach for transforming these gases into highly concentrated nitrogen-containing fertilizer in an environmentally friendly way. Developing electrocatalysts for the simultaneous activation of inert N₂ and CO₂ followed by C–N coupling for urea synthesis on specific active sites is challenging. Catalysts with dual metal sites have gained major interest in electrocatalysis for their ability to improve active site accessibility and optimize electronic structures. However, precise and controlled incorporation of dual-metal sites into the materials remains a significant challenge for achieving desired catalytic performance. In this work, we systematically integrate Fe³⁺ and Co²⁺ into chelation sites ((E)-3-(phenylamino) acrylaldehyde and 2,2'-bipyridyl) of porous 2D-covalent organic frameworks (Fe–Co@TpBpy), which demonstrates efficient electrocatalysis for urea production from N₂ and CO₂ in 0.1 M aq. H₂SO₄ solution. At –0.75 V vs Ag/AgCl, the urea yield rate reaches 11.25 mmol g_{cat}^{–1} h^{–1} with a Faradaic efficiency of 22.52%. Density functional theory (DFT) calculation reveals that the bipyridyl attached Co center promotes the adsorption and conversion of CO₂ to CO, whereas the Fe center promotes N₂ activation and facilitates the C–N coupling between *NH₂ and *CO, resulting in the generation of the key intermediate *CONH₂, required for urea formation. Furthermore, DFT studies reveal that the interlayer confinement effect in 2D-Fe–Co@TpBpy promotes an energy-efficient C–N coupling mechanism for urea electrosynthesis. The work presents a unique approach for designing and constructing a bimetallic 2D-COF-based electrocatalyst toward electrochemical urea synthesis.



1. INTRODUCTION

The global need for food is rising rapidly due to the growing population, creating major strain on fertilizer production.¹ Among nitrogen-rich fertilizers, urea (CO(NH₂)₂) is the most frequently utilized, accounting for 40–60% of total food production worldwide in 2023. The global urea market reached 177 million metric tons, with around 90% of this urea being used in agriculture and the remaining 10% for industrial purposes such as the manufacture of pharmaceuticals, resins, animal feeds, and cosmetics. The traditional method of urea production via the Bosch–Meiser process, which involves the reaction between the ammonia (NH₃) and carbon dioxide (CO₂), faces several difficulties.^{2–5} This technology is energy-intensive (150–200 °C, 150–250 bar), with high carbon emissions and an intricate production process. Moreover, urea production consumes ~80% of globally produced NH₃, which primarily comes from the Haber–Bosch process (N₂ + 3H₂ → 2NH₃).⁶ However, it

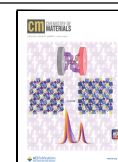
requires extreme conditions to break the inert N≡N triple bond (940.95 kJ mol^{–1}), consuming ~2% of global energy annually.⁷ Overall conventional method of urea production presents a significant barrier to sustainable growth and carbon neutrality, emphasizing the urgent need for greener and more energy-efficient alternatives. To overcome these limitations, simultaneous electrochemical reduction of N₂ and CO₂ followed by C–N coupling is being explored as an alternative method to produce urea, this process includes a several-step proton/electron coupling process (N₂ + CO₂ + 6H⁺ + 6e[–] → CO(NH₂)₂ + H₂O).⁸ This approach provides a potentially

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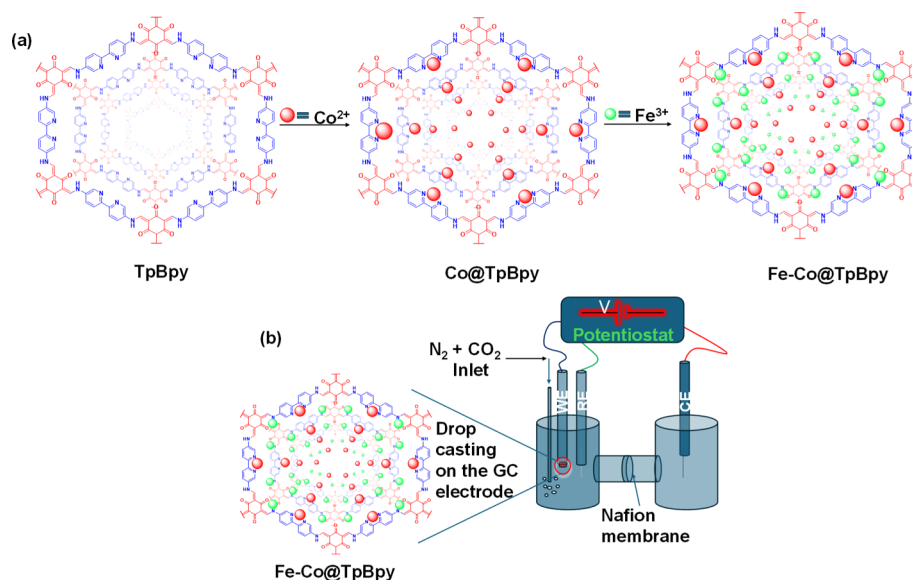
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Scheme 1. (a) Proposed Systematic Installation of Co^{2+} and Fe^{3+} inside the TpBpy COF and (b) Electrochemically Urea Production^b



^aWE = working, RE = reference, CE = counter Electrode. ^bWE = working, RE = reference, CE = counter Electrode.

viable solution to the high energy consumption and environmental impact associated with conventional urea production processes, while simultaneously addressing the challenge of excess carbon emissions. However, the poor intrinsic activity and selectivity resulting from the inertness of N_2 , and the sluggish kinetics of C–N coupling process, and the competing reactions at reduction potentials severely limit the practical realization of this ideal method for urea production. Therefore, extensive theoretical and practical research has been devoted to the design of effective electrocatalysts.⁹

Recent studies have reported a wide variety of electrocatalysts for urea production via the coreduction of N_2 and CO_2 , including metal borides,^{10,11} metal oxides,^{12–14} metal alloys,^{15,16} MXenes,¹⁷ and MBenes.¹⁸ In this context, Ghorai and co-workers developed a series of transition metal-phthalocyanine complexes as molecular electrocatalysts for the simultaneous reduction of N_2 and CO_2 into urea.^{19–21} These systems emphasize the critical importance of well-defined molecular structures in influencing the kinetic barriers of C–N coupling, hence increasing catalytic performance and selectivity. While some of these materials have demonstrated promising results, they still face limitations such as low local concentrations of N_2 and CO_2 due to poor solubility in aqueous electrolytes, as well as weak adsorption on the surface of the catalyst, poor electron transfer, low selectivity toward urea formation, limited long-term stability in aqueous medium, and less efficient C–N coupling reaction. These shortcomings result in reduced catalytic efficiency which significantly hinders their industrial application. Therefore, rational catalyst design is required for improving the selectivity and activity of urea electrosynthesis.

Over the past few decades, porous crystalline materials, such as metal–organic frameworks (MOFs),^{22–26} have been explored as highly efficient heterogeneous electrocatalysts for both urea production and urea oxidation reaction. These porous structures facilitate rapid mass transfer and provide a high density of accessible active sites along with enhanced gas adsorptive capacity. Nevertheless, the electrochemical cor-

duction of N_2 and CO_2 using porous crystalline materials is rare in the literature. Mostly their application in urea synthesis has been limited to CO_2 and NO_3^- feedstocks.^{27,28} In this respect, metal ions integrated two-dimensional covalent organic frameworks (2D COFs) have the potential to address few key challenges in electrocatalyst design and development. COFs are emerging classes of porous material composed of light elements (C, O, N, B, etc.) with outstanding features such as high crystallinity, low framework density, and high specific surface area, as well as tunable porosity, chemical robustness, and excellent structural designability. These properties make COFs an appealing platform for fine structural control and functional design, with potential applications in selective gas adsorption, catalysis, sensing, and energy-related disciplines.^{29–31} It has been reported that cobalt (Co)-based COFs are effective electrocatalysts for CO_2 reduction reaction (CO_2 to CO) due to their optimal binding affinity and efficient activation capacity.³² Similarly, iron (Fe)-based COFs efficiently activate N_2 for ammonia production.³³ Despite these advancements, the design of COFs that promote C–N coupling for urea synthesis has been constrained, limiting their use in this field. This issue can be addressed by employing multiple metal active centers within the substrate framework, enabling the simultaneous activation of N_2 and CO_2 , followed by C–N coupling. The functionalized pores of 2D-COFs can systematically host two catalytic active sites, allowing for metal ion chelation and synergistic effects, as well as facilitating high electron mobility via out-of-plane 1D channels and providing exceptional structural potential for electrocatalytic reactions. Nevertheless, most experimental research on bimetallic COF-based electrocatalysis has primarily focused on H_2O_2 production,³⁴ and the electrochemical oxygen evolution reaction,^{35–37} However, dual-metal site-based 2D-COFs for electrochemical urea synthesis from N_2 and CO_2 remain unexplored, primarily due to limitations in designing and synthesizing efficient electrocatalysts. We present a unique approach to the design, development, and synthesis of a bimetallic 2D COF in which distinct metal centers are

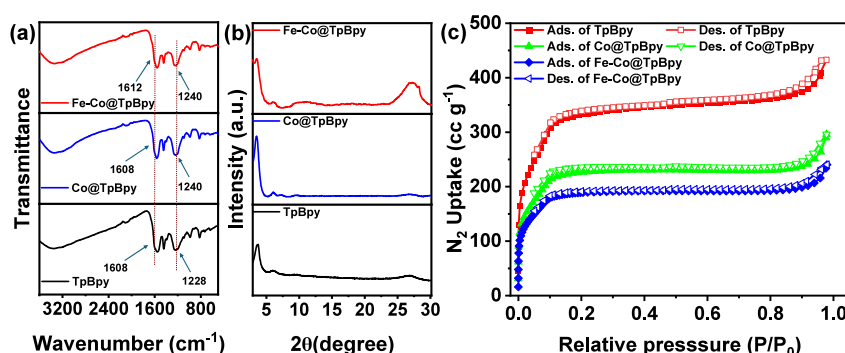


Figure 1. (a) FT-IR, (b) PXRD, and (c) N_2 adsorption–desorption isotherms of TpBpy, Co@TpBpy, and Fe–Co@TpBpy.

selectively integrated into the 2D-porous framework to meet the requirements for electrochemical urea production. Vertically stacked layers are hypothesized to form an interlayer nanoreactor, where a metal site in one layer activates N_2 and a complementary metal site from the neighboring layer reduces CO_2 . Specifically, the close proximity of these dual-layer active sites is anticipated to enable an efficient C–N coupling mechanism, offering a synergistic approach for urea generation that overcomes the constraints of typical monolayers or bulk catalysts.

Herein, we report on a 2D-COF (Fe–Co@TpBpy), in which Fe and Co centers are systematically incorporated into the selective chelating sites of the TpBpy^{38,39} framework (Scheme 1). Fe–Co@TpBpy exhibits efficient electrocatalytic activity for urea synthesis directly from N_2 and CO_2 in 0.1 M aq. H_2SO_4 , achieving a Faradaic efficiency of 22.52% at -0.75 V vs Ag/AgCl. The bimetallic (Fe/Co) sites work in synergy, effectively activating both N_2 and CO_2 followed by C–N coupling, essential for urea synthesis. According to density functional theory (DFT) calculations, the COF-attached Co center facilitates adsorption and activation of CO_2 , whereas the Fe center promotes N_2 activation and facilitates interlayer C–N coupling between $*NH_2$ and $*CO$, leading to the generation of the $*CONH_2$ intermediate for urea production. This strategy aids in developing dual-metal site-integrated 2D COFs as a heterogeneous electrocatalyst, not only for a green and sustainable route of urea production but also opens an avenue for designing catalysts involving various types of organo-metallic coupling reactions.

2. EXPERIMENTAL METHODS

2.1. Synthesis of Co@TpBpy

In a 50 mL round-bottom flask, anhydrous ~ 5 wt % $CoCl_2$ was added to 50 mg of TpBpy in 15 mL of ethanol. The resulting mixture was stirred overnight at $60^\circ C$. After completion of the reaction, the desired deep red powder was collected by filtration, thoroughly washed with ethanol, and subsequently dried at $60^\circ C$ for 24 h.

2.2. Synthesis of Fe–Co@TpBpy

In a 50 mL round-bottom flask, 3 mL of a water–ethanol (1:9, v/v) mixture was stirred for 20 min at -60 to $-70^\circ C$ to generate an ultralow-temperature solvent system appropriate for the reaction. After that, ~ 5 wt % $Fe(OAc)_2$ was added to the solution mixture at ultralow temperatures (-60 to $-70^\circ C$). The resulting mixture was stirred for 30 min before adding 50 mg of Co@TpBpy powder. After 12 h of stirring, 500 μL of NH_4OH (30% in water) and 40 mg KOH powder were added to the solution mixture and stirred for another 2 h at $-60^\circ C$. Finally, the desired Fe–Co@TpBpy was obtained as a red powder after washing the reaction mixture with a copious amount of anhydrous methanol and drying at $60^\circ C$ under vacuum.

2.3. General Instrumentation

Powder X-ray diffraction (PXRD) experiments were carried out at $25^\circ C$ using a Rigaku Smart Lab SE diffractometer with $Cu K\alpha$ source ($\lambda = 1.5406 \text{ \AA}$) between 3° and 30° at a scan speed of 2° min^{-1} and a step size of 0.01° . BET surface area analysis was carried out using Micromeritics ASAP2020Plus surface area and porosity analyzer using N_2 sorption isotherms at 77 K. Scanning electron microscopy (SEM) images were collected using the JEOL JSM-IT200 benchtop electron microscope at a 15 kV accelerating voltage whereby dry samples of COFs were put on carbon tape. FT-IR experiments were conducted using a Nicolet iS50 FT-IR spectrometer. XPS (X-ray photoelectron spectroscopy) analysis of the COF samples was carried out using the PHI 5000 Versaprobe Scanning XPS Microprobe. Shimadzu ICPMS-2030 was used to analyze the concentration of metals in the electrolyte solution and COF materials.

2.4. X-ray Absorption Spectroscopy Method

Co K- and Fe K-edge X-ray absorption spectra were measured at the Stanford Synchrotron Radiation Light source (SSRL) on the 1.3 T bending magnet beamline 2-2 under standard ring conditions (3 GeV, ~ 500 mA) using the fully automated high-throughput XAS setup (2-2HT). The samples were prepared by pressing 20 mg of each sample into a 7 mm diameter pellet. All samples were measured in the transmission mode using nitrogen-filled ion chambers. For each sample, nine scans were collected and averaged. Co or Fe foils were scanned simultaneously in transmission geometry and used as energy calibration standards. X-ray absorption spectroscopy (XAS) data were analyzed with the Demeter software package. Raw data were processed and normalized with Athena. The same set of background identification and normalization parameters were used for all standard and catalyst samples at the same edge (Co K- or Fe K-). The only exception is the Fe K-edge data on the Co–Fe/TpBpy sample, which used a shorter range for both spline formula and normalization to avoid the interference of Co K-edge appearing at $k \approx 10 \text{ \AA}^{-1}$ of Fe K-edge. The energy of all spectra at the same edge was aligned using the edge energy of the reference spectra (corresponding metal foil) collected simultaneously, to ensure accuracy in XANES interpretation. After processing, EXAFS fitting was then conducted using Artemis. The k -range used in Fourier transformation and R -range used in the fit are listed in Tables S2 and S3. Detailed model descriptions are provided in Note S1.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

The TpBpy was synthesized by using the previous reported methods with slight modifications,³² utilizing [2,2'-bipyridine]-5,5'-diamine and 2,4,6-triformylphloroglucinol as secondary building units (SBUs). TpBpy contains two chelating sites ((*E*)-3-(phenylamino) acrylaldehyde and 2,2'-bipyridyl) within its backbone, designed for the selective binding of Co and Fe centers. The Co@TpBpy COF was synthesized by treating TpBpy with the anhydrous $CoCl_2$ in ethanol, stirring at $60^\circ C$

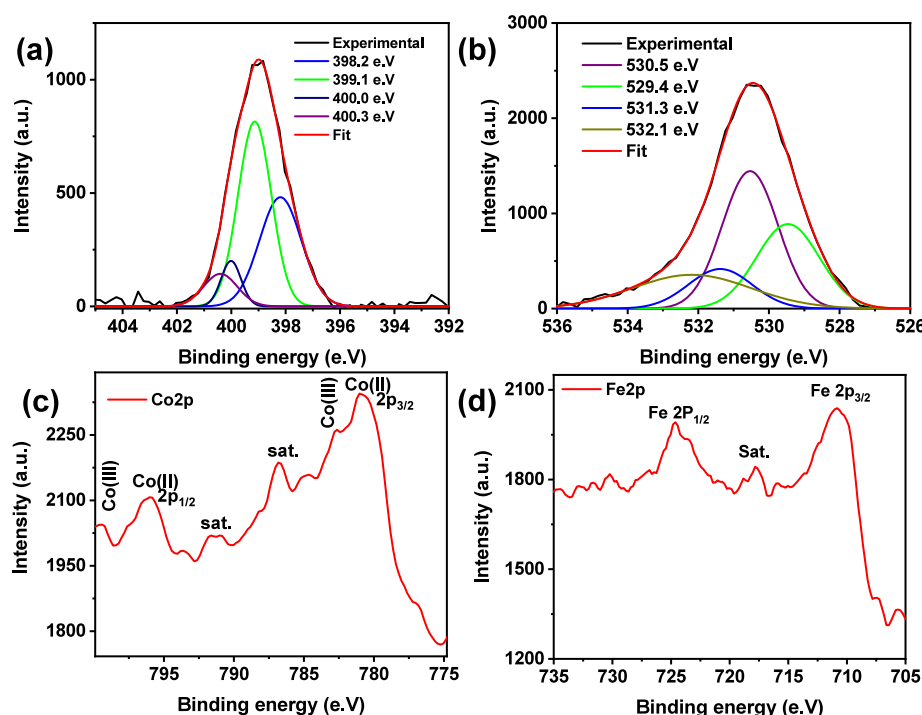


Figure 2. Deconvoluted XPS peaks for the element of (a) N 1s and (b) O 1s on the Fe–Co@TpBpy surface. (c,d) XPS spectra for Co 2p and Fe 2p on the Fe–Co@TpBpy surface.

for overnight. The Co@TpBpy was further treated with Fe(OAc)₂ in ethanol at -60°C to generate active catalyst Fe–Co@TpBpy. The dual metal incorporation into the active Fe–Co@TpBpy catalyst has been verified by a comparative structural analysis of pristine TpBpy, Co@TpBpy, and Fe–Co@TpBpy using several characterization techniques. FT-IR spectrum of TpBpy (Figure 1a) reveals distinct peaks at 1608, 1567, and 1228 cm^{-1} , which correspond to C=O, C=C, and C–N stretching vibrations (of bipyridine groups). After introducing Co²⁺ ions in TpBpy (Co@TpBpy), the C–N band broadens and shifts significantly to 1240 cm^{-1} , whereas the C=O peak at 1608 cm^{-1} remains unaltered.³⁸ This demonstrates that Co²⁺ ions coordinate with the C–N sites preferentially rather than the O atoms of β -ketoenamine groups. In addition, the absence of peaks related to cobalt oxides or hydroxyl groups suggests that cobalt is atomically scattered rather than precipitated. The C=O stretching band is subsequently shifted to 1612 cm^{-1} in the dual-metalated Fe–Co@TpBpy; however, the C–N band remains at 1240 cm^{-1} . Furthermore, the C=O stretching band in Fe@TpBpy shifts to 1611 cm^{-1} (Figure S1), while the C–N bond stretching frequency remains at 1228 cm^{-1} , which is consistent with the pristine TpBpy. This suggests that the Fe³⁺ ions specifically interact with the C=O groups of the β -ketoenamine backbone, whereas Co²⁺ occupies the bipyridine sites. The crystallinity and structural integrity of COFs were further investigated using PXRD (Figure 1b). The primary diffraction peaks correspond to 100 planes of Co@TpBpy and Fe–Co@TpBpy remains at the same $2\theta = 3.45^{\circ}$ as the pristine TpBpy, indicating that AA eclipsed interlayer stacking and the underlying 2D hexagonal lattice are preserved after post-synthetic metalation. Interestingly, the dual-metalated Fe–Co@TpBpy exhibits a significant rise in the intensity of the (001 plane) reflection at $\sim 26^{\circ}$, while the pattern for Co@TpBpy remains mostly identical to the parent TpBpy. This is

most likely due to the COF layers distortion caused by the presence of charged Co²⁺ ions and further Fe³⁺ addition, which increases the repulsive interactions between the COF layers.⁴⁰ ICP–MS (inductively coupled plasma mass spectrometry) of Fe–Co@TpBpy reveals that the contents of Fe and Co in Fe–Co@TpBpy are ~ 3.04 and ~ 3 wt %, respectively.

3.2. Surface Area Measurements and SEM Analysis

The permanent porosity of COFs was analyzed by N₂ sorption isotherm measurements at 77 K (Figure 1C). The calculated BET surface areas for TpBpy, Co@TpBpy, and Fe–Co@TpBpy are found to be 1071, 700, and 605 m^2g^{-1} , respectively. A significant decrease in BET surface area after metalation indicates that the Co²⁺ and Fe³⁺ ions have been effectively integrated into the TpBpy backbone, resulting in partial pore blocking and restricted N₂ accessibility within the COF. Furthermore, the SEM study of Fe–Co@TpBpy reveals a heterogeneous morphology consisting of aggregated sheet-like and rod-shaped formations with rough surface textures (Figure S2). The energy-dispersive X-ray mapping images indicate that the metal ions are uniformly distributed in Fe–Co@TpBpy (Figure S2).

3.3. XPS and XAS Analyses

XPS was conducted to analyze the chemical states of the elements present in Co@TpBpy and Fe–Co@TpBpy. In the O 1s XPS spectra of TpBpy, the binding energies at 530.4 and 531.2 eV correspond to the enol- and keto-forms, respectively (Figure S3). For the N 1s XPS spectra of TpBpy, binding energies at 399.94 and 398.73 eV are observed, corresponding to the –C=N–C– and –C–NH–C– groups, respectively (Figure S3). In the O 1s spectra of CoCl₂–TpBpy, two additional peaks are observed, with binding energies of 532.3 and 534.4 eV (Figure S4 and Table S1). These are likely associated with coordinated H₂O molecules at the Co center and adsorbed H₂O on the COF surface. The N 1s XPS

spectrum also reveals the presence of imine bonds (400.5 eV), pyridinic nitrogen (399.1 eV), and pyridinic nitrogen coordinated with Co (399.8 eV). The Cl 2p XPS spectrum displays binding energies for Cl 2p_{3/2} and Cl 2p_{1/2} at 197.3 and 198.6 eV. The Co(II) 2p_{3/2} and Co(II) 2p_{1/2} photoelectron lines are observed at 780.7 and 796.5 eV with accompanying satellite peaks arising from the shakeup mechanism approximately 5–6 eV higher than the main Co(II) 2p lines. Furthermore, XPS analysis indicates that Fe and Co in Fe–Co@TpBpy exist in the approximate +3 and +2 oxidation states (Figure 2). Notably, XPS spectrum of the Fe 2p of Fe–Co@TpBpy shows two main peaks at 710.8 and 724.9 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}. Interestingly, the O 1s spectra show a significant binding energy shift following the incorporation of Fe. The O=C (keto form) peak is shifted to 530.8 eV from 531.4 eV due to Fe···O=C interaction, while a peak appears at 530.0 eV, attributed to Fe···O–H (enol form), shifted from 531.3 eV. Two additional peaks at 532.5 and 535.1 eV are observed, corresponding to H₂O coordination with the metal centers and residual moisture. According to XPS, the surface atomic concentrations of Fe–Co@TpBpy are found to be ~61.63% for C 1s, ~10.49% for N 1s, ~20% for O 1s, ~4.94% for Fe 2p, and ~2.91% for Co 2p (Table 1). The

Table 1. Surface Atomic Concentration (Atomic %) from XPS of Fe–Co@TpBpy

elements	C	N	O	Cl	Co	Fe
atomic %	61.63	10.49	20	0.03	4.94	2.91

optical properties of Fe–Co@TpBpy are investigated using UV–vis DRS (ultraviolet–visible diffuse reflectance spectroscopy) (Figure S5). UV–vis DRS spectrum shows the charge transfer band (ligand to metal) around 605 nm of Fe–Co@TpBpy.

The coordination environments of Co and Fe sites in Co, Fe, and Fe–Co@TpBpy were further characterized by XAS. In Co K-edge X-ray absorption near-edge spectroscopy (XANES, Figure 3a), the intensity of the pre-edge feature (at ~7710 eV) in both Co@TpBpy (black) and Fe–Co@TpBpy (red) is slightly higher than that in Co(NO₃)₂·6H₂O (blue), in which all Co have octahedral geometry coordinated with 6 H₂O ligands, and significantly lower than that in Co₃O₄ (green), in which one-third of Co have tetrahedral and two-thirds have octahedral geometry. As this pre-edge feature originates from the dipole-forbidden but quadrupole-allowed 1s → 3d transition, its intensity is positively correlated with the deviation of Co from centrosymmetry, and thus the degree of d–p hybridization.^{41,42} Hence, such observation indicates that Co sites in both samples are in slightly distorted octahedral geometry, due to coordination to N/O atoms in TpBpy and hydration under ambient, the latter of which was indicated by XPS. The coordination to N-containing binding sites in TpBpy, which have stronger field strengths than H₂O and lattice O in Co₃O₄, leads to higher energy of the pre-edge feature (7710.0 eV, defined as the crossing point with y = 0 in the first derivatives, Figure S6a) than that in both Co₃O₄ (7709.5 eV) and Co(NO₃)₂·6H₂O (7709.8 eV).⁴³ The close-to-octahedral geometry is supported by the shape of the white-line (Figures 3a and S6a), which originates from dipole-allowed 1s → 4p transition, being a broadened single

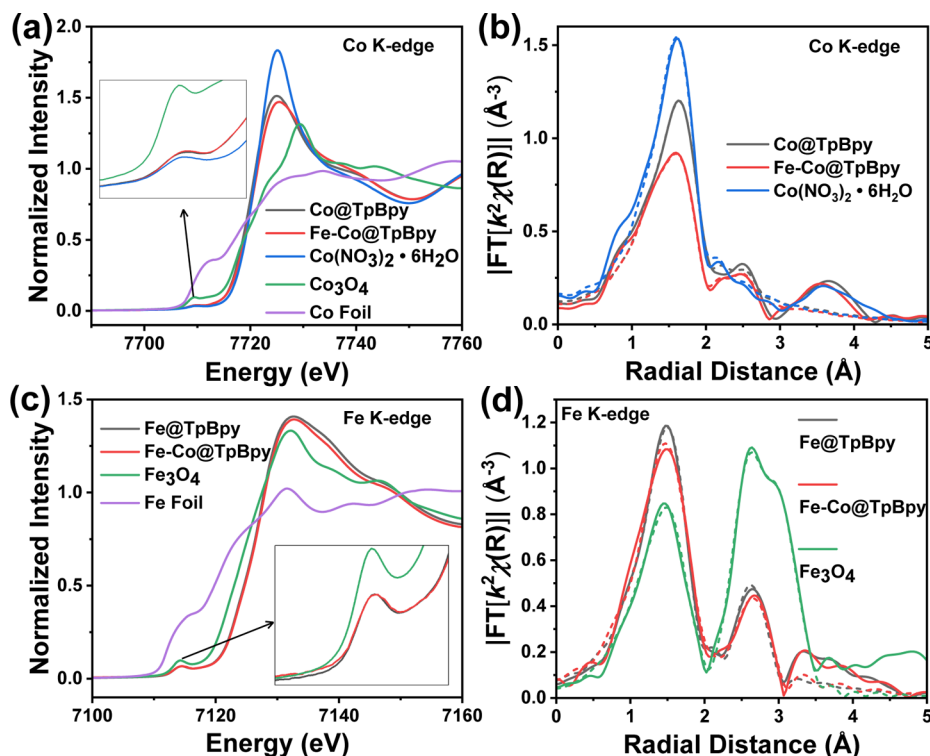


Figure 3. X-ray absorption spectroscopy (XAS) results on Co@TpBpy, Fe@TpBpy, and Fe–Co@TpBpy. (a) Co K-edge XANES, in reference to several standards. (b) Co K-edge EXAFS in R-space magnitude, with the best fit shown as dashed curves. (c,d) Same data with (a,b), respectively, at Fe K-edge. Supplemental spectra (first derivatives of XANES, EXAFS in k-space and R-space imaginary part only) are reported in Figure S6. Complete EXAFS fit parameters are reported in Tables S2 and S3.

component similar to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, rather than the triplet in Co_3O_4 caused by significant p_x – p_y – p_z splitting in tetrahedral geometry. For both samples, the white-line intensity (Figure 3a) and the edge energy (defined as the maximum in the first derivatives, Figure S6a) are slightly lower than those of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the reference standard with similar ligand environments and geometry to them, indicating slight electron enrichment relative to +2 formal oxidation state.

The proposed coordination environment of Co sites (coordinated with bipyridyl or Tp-binding site on TpBpy and H_2O molecules) is consistent with the extended X-ray absorption fine structure (EXAFS, Figure 3b) analysis. The best fit model for both samples shows that the total coordination number (N) of Co with directly bonded O/N atoms is close to 6 (Tables 2 and S2). Two types of O/N

Table 2. Direct (First-Shell) Coordination Environment of Co Single Atoms Extracted from the EXAFS

	Co@TpBpy		$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
$N(\text{Co}-\text{O}_\text{W})$	3.9 ± 0.9	3.3 ± 0.8	6
$R(\text{Co}-\text{O}_\text{W})$ (Å)	2.11 ± 0.02	2.08 ± 0.01	2.07 ± 0.04
$\sigma^2(\text{Co}-\text{O}_\text{W})$	0.008 ± 0.004	0.006 ± 0.002	0.0086 ± 0.0007
$N(\text{Co}-\text{TpBpy})$	2	2	N/A
$R(\text{Co}-\text{TpBpy})$ (Å)	2.00 ± 0.05	1.93 ± 0.02	N/A
$\sigma^2(\text{Co}-\text{O}/\text{N})$	0.013 ± 0.002	0.008 ± 0.002	N/A
$N(\text{Co}-\text{O}/\text{N})_\text{total}$	5.9 ± 0.9	6.1 ± 0.8	6

neighbors are clearly differentiated in the EXAFS models (Table 2): 4 of them have longer Co–O/N bond length (R) of ~ 2.1 Å, similar to the H_2O ligands in $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (denoted as “Co–O_W”), while 2 of them have shorter $R(\text{Co}-\text{O}/\text{N})$ between 1.9 and 2.0 Å, attributed to coordination to N and/or O atoms in TpBpy (denoted as “Co–TpBpy”). The difference in length between the two types of Co–O/N bonds is consistent with the distortion in octahedral geometry shown by XANES. EXAFS cannot differentiate the bipyridyl and Tp-binding sites offered by TpBpy because the coordination numbers are identical (2), and O and N have similar Z -numbers.⁴⁴ The additional scattering intensity in the two samples compared to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, between 2 and 3 Å (Figure 3b), can be fit appropriately with a scattering path from the closest nonbonding C atoms in TpBpy in the proposed structure, with N between 2 and 3, in general agreement with the expected values (3 or 4), and $R \approx 3.0$ Å (Table S2). Attempts to fit the intensity with a nonbonding Co–Co scattering path leads to extremely small N values not beyond the fitting uncertainties (Table S3) even before considering the mandatory Co–C path, indicating that the presence of CoO_x clusters beyond the detection limit of the EXAFS is unlikely,⁴⁵ i.e., most, if not all, Co are single atoms. This is supported by the observation that compared to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ that has all Co as single atoms, neither sample shows preferential enhancement of oscillation in the high- k range (Figure S6b), which would be observed if additional scatterer heavier than C/O/N (Co) exists.⁴⁶

Depositing Fe sites alters XAS characteristics of Co single atoms, indicating coordination environment changes. In the EXAFS, $R(\text{Co}-\text{TpBpy})$ shrinks slightly with Fe, from 2.00 ± 0.05 Å to 1.93 ± 0.02 Å, with the Debye–Waller factor (σ^2) of the path decreasing from 0.013 ± 0.002 to 0.008 ± 0.002 (Table 2). Meanwhile, $N(\text{Co}-\text{O}_\text{W})$ sees a minor decrease from

3.9 ± 0.9 to 3.3 ± 0.8 . Although such difference is not beyond fitting uncertainties, the scattering intensity between 1 and 2 Å is also visually damped after Fe deposition in Figure 3b, despite the decrease in σ^2 that would visually intensify scattering.⁴⁷ In XANES, pre-edge intensity sees a minor increase with Fe deposition, suggesting slightly more distortion in the octahedral geometry, while the white-line intensity slightly decreases and further deviates from that in $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Figure 3a). All these changes caused by Fe deposition are consistent with enhanced coordination of Co single atoms to the binding sites in TpBpy, with a possible loss of H_2O ligands.

In Fe K-edge XANES (Figure 3c), both Fe@TpBpy (black) and Fe–Co@TpBpy (red) show lower intensity of the pre-edge feature than Fe_3O_4 (green), suggesting more centrosymmetric geometry of Fe sites than those in Fe_3O_4 on average. The decrease relative to M_3O_4 is, however, to a less extent than Co samples at Co K-edge ($\sim 40\%$ decrease in Figure 3c compared to $\sim 65\%$ in Figure 3a). The energy of the pre-edge feature in the two samples is both higher than Fe_3O_4 (7114.5 eV compared to 7114.3 eV, Figure S6d showing the first derivatives), indicating coordination with N-containing binding sites in TpBpy, but again, the difference with M_3O_4 is smaller than Co K-edge data in Figure S6a. The higher edge energy and white line intensity than Fe_3O_4 indicate higher average oxidation states of Fe sites on the samples, consistent with XPS showing exclusively Fe(III). The edge shape has a clear doublet in Figure S6d, suggesting 4p-orbital splitting due to broken symmetry, to a higher degree than Co sites that show a single component (Figure S6a) but a lower degree than Fe_3O_4 that shows full triplet. These XANES characteristics suggest that for Fe sites on Fe@TpBpy and Fe–Co@TpBpy, the average degree of deviation from octahedral geometry is between that of Fe_3O_4 (one-third tetrahedral Fe^{2+} and two-third octahedral Fe^{3+}) and Co sites (all slightly distorted octahedral single atoms). In the EXAFS (Figure 3d), the best fit model to describe data from both Fe samples shows directly bonded $N(\text{Fe}-\text{O}/\text{N}) \approx 6$, with the average $R(\text{Fe}-\text{O}/\text{N}) \approx 1.99$ Å (Table S3). H_2O and Tp/bipyridyl ligands from TpBpy are not differentiable as two paths. Different from Co K-edge EXAFS, the intensity between 2 and 3 Å in neither sample can be appropriately fit by only a nonbonding Fe–C path (Figure S6g). Rather, an additional nonbonding Fe–Fe path is required, with the best models showing $N(\text{Fe}-\text{Fe}) = 2.4 \pm 0.5$ and 2.2 ± 0.6 for Fe@TpBpy and Fe–Co@TpBpy, respectively, and $N(\text{Fe}-\text{C}) \approx 2$ for both (Table S3). The presence of Fe–Fe path with extremely low N values relative to bulk Fe_3O_4 (12) indicates that a small fraction of Fe form aggregates in nm- or even subnm size regime during the deposition and processing,⁴⁸ while others exist as TpBpy-coordinated single atoms. This interpretation is consistent with XANES showing that the average geometry of Fe sites has more distortion from octahedral than Co but less than Fe_3O_4 . Neither XANES nor EXAFS shows evidence suggesting that Co single atoms alter the coordination environment of Fe sites.

4. ELECTROCHEMICAL UREA PRODUCTION USING FE–CO@TPBPY

Electrochemical studies were conducted in a two-compartment H-cell separated by a Nafion membrane and equipped with a three-electrode setup.⁴⁹ The catalyst ink-coated glassy carbon electrode served as a working electrode along with Ag/AgCl (sat. KCl) and Pt-mesh reference and counter electrodes, respectively. To investigate the electrocatalytic performance of

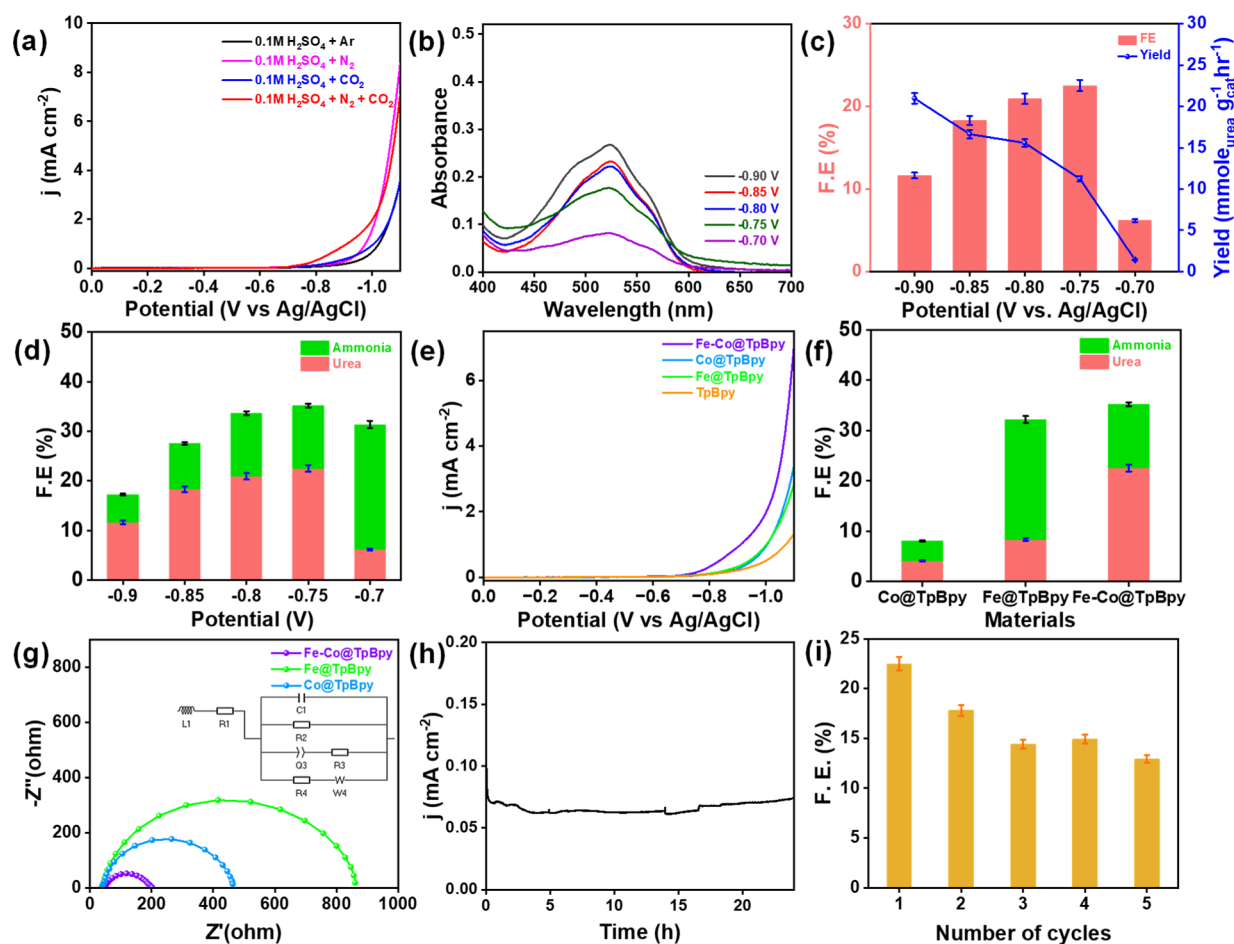


Figure 4. (a) Linear scan voltammograms (LSVs) at various conditions, the LSV curves are shown using the classical/polarographic convention, (b) UV-vis spectra of electrolyte solution for urea detection by the diacetylmonoxime-thiosemicarbazide (DAMO-TSC) method after running chronoamperometry for coreduction of N₂ and CO₂ at different potentials, catalyzed by Fe-Co@TpBpy. (c) Faradaic efficiency and urea formation yield rate at different potentials; (d) corresponding product selectivity bar diagrams. (e) LSVs for different materials at N₂ + CO₂ saturated environment exhibiting their ability toward electrocatalytic coreduction of N₂ and CO₂. (f) Product selectivity bar diagrams of Fe-Co@TpBpy, Fe@TpBpy, and Co@TpBpy at -0.75 V vs Ag/AgCl. (g) Nyquist plots of Fe-Co@TpBpy, Fe@TpBpy, and Co@TpBpy. (h) Chronoamperometric curve of Fe-Co@TpBpy at -0.75 V vs Ag/AgCl for 24 h in N₂ and CO₂ saturated 0.1 (M) H₂SO₄ solution. (i) Cyclic stability of Fe-Co@TpBpy catalyst during urea electrosynthesis.

Fe-Co@TpBpy toward the coreduction of N₂ and CO₂ for urea synthesis, linear sweep voltammetry (LSV) was conducted in 0.1 M aqueous H₂SO₄ solution, saturated with different gases (Ar, N₂, CO₂, and N₂/CO₂ mixture) within a potential range of 0.0 to -1.1 V (vs Ag/AgCl).

Figure 4a shows the current density change pattern with applied potential in different atmospheres. Generally, the recorded current density in an Ar-saturated electrolyte (black line) represents the hydrogen evolution reaction (HER), whereas the resulting current density in a N₂ atmosphere (magenta line) corresponds to both the HER and nitrogen reduction reaction (NRR).

Similarly, the measured current density under CO₂-saturated electrolyte (blue line) stands for HER and carbon dioxide reduction (CO₂RR), while the observed current density in mixed N₂ + CO₂ atmosphere (red line) signifies the combination of HER and coreduction of N₂ and CO₂. LSV curves in different gaseous environments display an enhanced current density compared to Ar-saturated conditions, demonstrating the potentiality of the Fe-Co@TpBpy toward the respective electrochemical applications. The monitored maximum net current density $j_{N_2+CO_2} - j_{Ar}$ indicates the highest

electrocatalytic activity of the Fe-Co@TpBpy toward coreduction of N₂ and CO₂.

The success of the electrochemical N₂-CO₂ coreduction reaction is further validated by analyzing the products via ¹H NMR and UV-vis spectroscopic techniques (diacetylmonoxime-thiosemicarbazide (DAMO-TSC) and indophenol blue methods for colorimetric detection of urea and NH₃).⁵⁰ Following electrolysis under ¹⁴N₂ and ¹²CO₂ purging, the electrolyte's ¹H NMR spectrum displays a broad singlet at ~5.6 ppm, which corresponds to urea (Figure S7). In contrast, a broad doublet centered at ~5.6 ppm ($J \approx 92$ Hz) is observed in the ¹H NMR spectrum obtained under ¹⁵N₂ and ¹²CO₂ purging during the electro-co-reduction process, which is clearly attributed to ¹⁵NH₂CO¹⁵NH₂ (Figure S7).⁵¹ Similarly, the electrolysis product collected with an Ar-gas purged conditions did not show any characteristic peaks corresponding to urea. Therefore, it is confirmed that urea formed during electrocatalytic coreduction of N₂ and CO₂ catalyzed by Fe-Co@TpBpy involves the N-atoms of the purged N₂ gas. Furthermore, the appearance of a unique absorption band in UV-vis spectra at approximately 525 nm provides evidence of considerable urea formation (Figure 4b). In addition, control

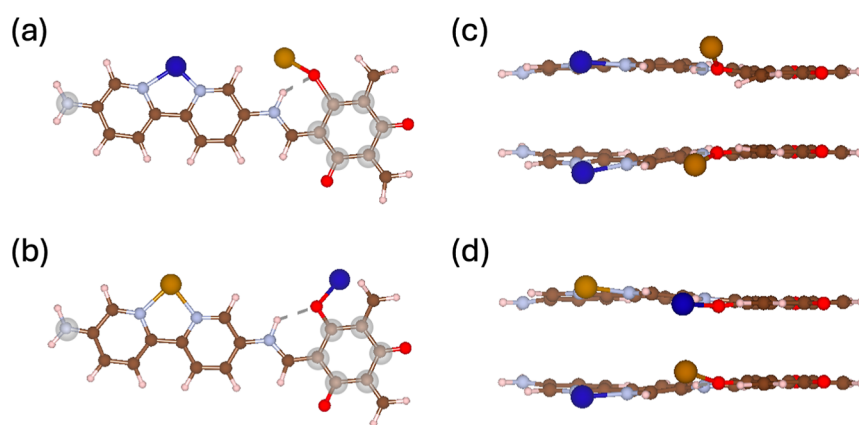


Figure 5. Optimized configurations with metal ions on possible combinations of coordination sites. Metal ions are represented in large spheres color-coded as Co (blue) and Fe (brown). Atoms on the COF framework are represented by small spheres color-coded as C (brown), H (pink), N (blue), O (red); gray shading indicates positional constraint on a COF framework atom to maintain experimental morphology. (a,b) Top views of single-layer structures. (c,d) Side views of bilayer structures, on which consistent positional constraints are enforced with shadings omitted for clarity.

electrolysis was conducted in a fully Ar-saturated electrolyte to ensure that the identified urea was generated by CO_2/N_2 coreduction rather than ambient contamination. The absence of urea signals in UV-vis again suggests that urea synthesis takes place exclusively through the coreduction of externally provided CO_2 and N_2 feed (Figure S8). To identify product selectivity and Faradaic efficiency toward $\text{N}_2\text{-CO}_2$ coreduction, a series of chronoamperometry studies were performed at different applied potentials for a period of 1 h and the electrolysis products were analyzed spectrophotometrically for the probable liquid products (i.e., urea and ammonia). Prior to this, calibration curves were generated for both the products (urea and ammonia) from the standard solution of commercial urea and ammonium chloride salts by following diacetylmoxime-thiosemicarbazide (DAMO-TSC) and indophenol blue methods, respectively (Figures S9). The UV-absorbance spectrum and selectivity trend of the liquid products at various applied potentials are presented in Figures 4b–d and S10. The Fe–Co@TpBpy exhibits the highest Faradaic efficiency of 22.52% toward urea production along with a selectivity of 11% for ammonia production at -0.75 V vs Ag/AgCl. Similarly, the rate of urea formation is found to be $11.25 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ at -0.75 V vs Ag/AgCl.

To better understand the synergistic effects of the dual-metal sites in Fe–Co@TpBpy toward urea production, the electrocatalytic activities of related monometallic COFs (Fe@TpBpy and Co@TpBpy) were also investigated. The LSV curves (Figure 4e), UV-vis absorbance spectrum (Figure S11a,b), and product analysis bar diagram (Figures 4f and S11c) of monometallic Co@TpBpy and Fe@TpBpy show very low electrocatalytic activity toward N_2/CO_2 coreduction. Moreover, their performance is significantly lower than that of the bimetallic Fe–Co@TpBpy, demonstrating the requirement of dual-metal sites inside the framework probably for the efficient C–N coupling. Few gaseous products are also identified qualitatively. The GC chromatogram is recorded during electrolysis by Fe–Co@TpBpy at -0.9 V vs Ag/AgCl (Figure S12), demonstrating the characteristic peaks corresponding to C_2H_4 , CH_4 , CO, and H_2 along with atmospheric N_2 and O_2 inferring the involvement of other side reaction in addition to the urea formation. ATR-FTIR spectroscopy was used to characterize all relevant chemical bonds and intermediates

generated during electrochemical urea production (Figure S13). The formation of NH_x intermediates during urea synthesis is indicated by a broad band in the region of $3200\text{--}3500 \text{ cm}^{-1}$, which corresponds to N–H/O–H stretching. *COO^- intermediates generated by CO_2 activation are shown by bands in the $1380\text{--}1430 \text{ cm}^{-1}$ area, whereas a strong peak around $1650\text{--}1700 \text{ cm}^{-1}$ is due to C=O stretching of *CONH_2 species. In particular, C–N stretching vibrations are given a distinct peak at $\sim 1452 \text{ cm}^{-1}$, demonstrating the critical C–N coupling step toward urea production. The electrochemical surface area (ECSA) and double-layer capacitance (C_{dl}) of Fe–Co@TpBpy, Co@TpBpy, and Fe@TpBpy were calculated to distinguish inherent catalytic activities from surface area effects and provide a precise measure of electrocatalytic efficiency (Figure S14 and Table S4). The Fe–Co@TpBpy exhibited the highest ECSA (0.96 cm^2) among all three materials, describing maximum availability of active sites. Similarly, the electrochemical impedance spectroscopy analysis was also performed to find the charge transfer resistance (R_{ct}) of the catalyst materials (Figure 4g and Table S5). The Fe–Co@TpBpy revealed the lowest charge transfer resistance ($R_{\text{ct}} = 156.7 \Omega$) among all three materials. The highest ECSA and lowest R_{ct} value of the materials indicate the enhanced catalytic activity of the Fe–Co@TpBpy than Fe@TpBpy and Co@TpBpy catalysts. Fe–Co@TpBpy exhibits better catalytic performance for urea electrosynthesis from N_2 and CO_2 when compared with the reported benchmark electrocatalysts (Table S6).

Furthermore, stability is an essential factor in evaluating the electrocatalytic efficiency of the Fe–Co@TpBpy fabricated electrode during the long-term coreduction of CO_2 and N_2 . Figure 4h demonstrates minor attenuation over a 24 h period in the chronopotentiometry curve obtained at -0.75 V vs Ag/AgCl in CO_2 and N_2 saturated 0.1 (M) H_2SO_4 solution. In addition, five consecutive cycles have been conducted (Figure 4i) which suggested that the Fe–Co@TpBpy catalyst is reusable over multiple cycles. We have performed ICP-MS experiments with the electrolytes after bulk electrolysis to evaluate the leaching of Fe–Co@TpBpy catalyst from the electrode surface. It confirms the absence of Co in the solution as no trace was detected. However, it shows very negligible amount of Fe ($\sim 0.2 \text{ ppm}$), which may be originated from the

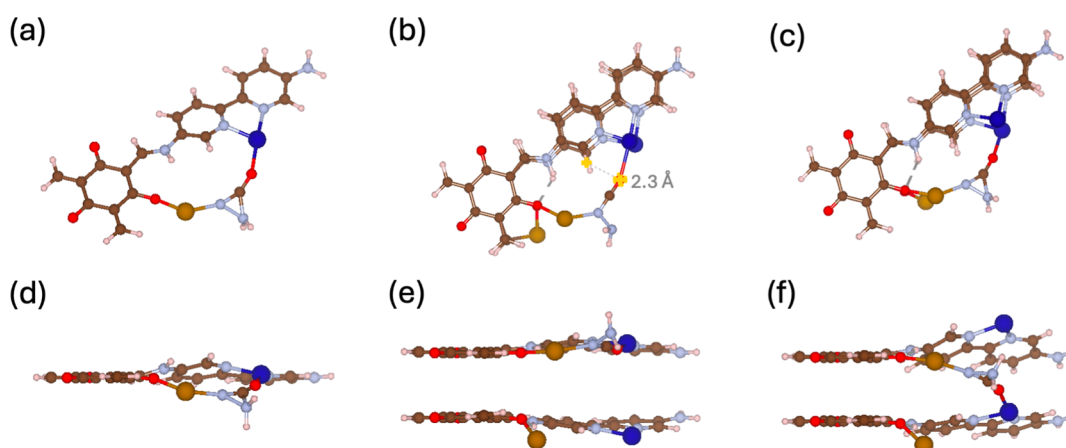


Figure 6. Optimized C–N coupling intermediates for the single layer model in the top (a) and side (d) views; the intralayer coupling in the bilayer model in the top (b) and side (e) views; the interlayer coupling in the bilayer mode in the top (c) and side (f) views.

contamination of H_2SO_4 used in the electrolyte. All these results support the robust embedding of the Fe–Co@TpBpy on the electrode surface, which leads to good stability and durability during urea electrosynthesis.

The structural stability of Fe–Co@TpBpy catalyst using PXRD, FT-IR, SEM, and EDS after bulk electrocatalysis has been examined (Figures S15 and S16). The PXRD and FT-IR results remain consistent with those obtained prior to catalysis, indicating that the structural integrity of the catalyst is well preserved. SEM and EDS analyses of Fe–Co@TpBpy after catalysis show only slight changes in the morphological structure, with the existence of the essential components still clearly visible, similar to the preelectrocatalysis catalyst.

5. DFT CALCULATIONS

To gain insight into the reaction mechanism of urea production over the bimetallic Fe–Co@TpBpy framework, DFT calculations were performed using the ORCA 6.1.0 package.^{52,53} Geometry optimizations were carried out with the PBE0 hybrid functional^{54,55} together with the def2-TZVP basis set⁵⁶ on all atoms. The def2/J auxiliary basis⁵⁷ was used for Coulombic fitting, and RIJCOSX⁵⁸ was employed to accelerate hybrid functional calculations. Grimme's D3(BJ) dispersion correction^{59,60} was included to account for long-range van der Waals interactions. For the construction of the free-energy diagram, we account for the externally applied voltage and experimental pH values via the computational hydrogen electrode method.^{61,62} Solvent effects were included using the CPCM implicit solvation model^{63,64} with water as the dielectric medium. For simplicity, we prepare two molecular models, a single-layer and a bilayer structure-by taking fragments from an experimentally determined crystal structure. To maintain the planar COF morphology in molecular models, we constrain selected framework atoms (shaded in gray in Figure 5) throughout this work. To find out the possible locations of Co^{2+} and Fe^{3+} inside the TpBpy framework, candidate initial configurations were generated by placing the metal ions near chemically heuristic coordination sites within the framework for all possible combinations. Each configuration was optimized using DFT, and the lowest-energy structure (Figure 5a,c) was selected as the working model for subsequent electrocatalysis calculations.

As shown in Figures S17a,b, the reaction pathways for urea formation were investigated based on the mechanism proposed

in previous studies^{65,66} of analogous systems. The overall process involves initial CO_2 reduction on the Co site, followed by N_2 adsorption on the neighboring Fe site and a sequence of hydrogenation and C–N coupling steps leading to urea formation. Key intermediates considered along the pathways include $^*\text{COOH}$, $^*\text{CO}$, $^*\text{N}_2$, partially hydrogenated nitrogen species, and C–N coupled intermediates relevant to urea formation. In both pathways, CO_2 adsorption on the Co site is energetically favorable, and subsequent proton–electron transfer leads to the formation of the $^*\text{COOH}$ intermediate, which is further reduced to $^*\text{CO}$. Meanwhile, N_2 adsorption occurs preferentially at the Fe site. The two pathways differ primarily in the sequence of nitrogen hydrogenation relative to C–N coupling. In pathway A (Figure S17a), C–N coupling between $^*\text{CO}$ and $^*\text{N}_2$ occurs prior to hydrogenation of the nitrogen species. Subsequent hydrogenation steps then proceed on the coupled intermediate to form $^*\text{NCON}$, $^*\text{NCONH}$, $^*\text{NCONH}_2$, $^*\text{NHCONH}_2$, and $^*\text{NH}_2\text{CONH}_2$. This pathway involves relatively high-energy intermediates following C–N coupling, resulting in energetically unfavorable intermediates. In contrast, pathway B (Figure S17b) proceeds via initial hydrogenation of adsorbed $^*\text{N}_2$ at the Fe site to form partially hydrogenated nitrogen species (e.g., $^*\text{N}_2\text{H}$ and $^*\text{NHNH}$) before C–N bond formation. The coupling between $^*\text{CO}$ and hydrogenated nitrogen intermediates occurs at a later stage, leading to more stabilized C–N coupled species and a smoother energy profile along the reaction coordinate.

Overall, the more thermodynamically favorable intermediates observed in pathway B indicate that early-stage nitrogen hydrogenation prior to C–N coupling is energetically preferred on the Fe–Co dual-site catalyst. These results suggest that pathway B is the dominant route for urea formation within our single-layer molecular model. To further elucidate the origin of the catalytic activity from an electronic structure perspective, charge density difference analysis was performed for CO_2 adsorption on the Co site and N_2 adsorption on the Fe site, as shown in Figure S18. The results reveal pronounced charge redistribution upon adsorption, indicating activation of CO_2 at the Co center and polarization of the N_2 molecule at the Fe center (detailed in the Supporting Information, Page S-22). To assess condensed-phase effects arising from COF stacking, we extended our investigation using the bilayer model. Compared with the single-layer model, interlayer confinement in the bilayer structure

significantly restricts framework flexibility and suppresses the ring rotation previously observed in the single-layer model (Figure 6a,d). As a consequence, intralayer C–N coupling in the bilayer model experiences substantial steric hindrance from a C–H groups on the framework, as illustrated in Figure 6b,e. In particular, the O atom of the tower complex approaches a H-atom on the COF backbone with the shortest interatomic distance of approximately 2.3 Å (Figure 6b). This distance is considerably shorter than the sum of their van der Waals radii (≈ 2.7 Å, based on Bondi radii⁶⁷), indicating a strong steric repulsion. As a result, intralayer C–N coupling becomes energetically unfavorable in the bilayer model. Given the layered nature of the experimental COF structure, a similar steric hindrance is also expected, thereby impeding intralayer coupling pathways.

To identify alternative pathways that are less affected by the intralayer steric hindrance, we further examined interlayer C–N coupling mechanisms in the bilayer model. The additional spatial freedom available in the interlayer region allows the C–N coupled intermediate to relax more effectively, alleviating steric repulsion and leading to a significantly lower-energy configuration compared to intralayer coupling. The optimized structures of interlayer C–N coupling in the bilayer model are shown in Figure 6c,f. As shown in Figure 7, the reaction begins

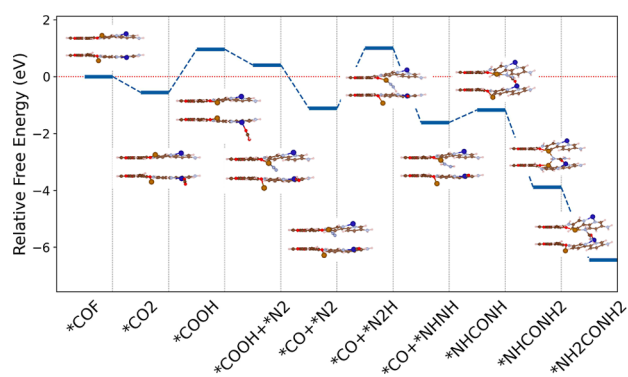


Figure 7. Energy diagram of the interlayer reaction mechanism.

with CO₂ adsorption at the Co site, where the CO₂ molecule interacts with the Co center and becomes activated. The adsorbed CO₂ then undergoes a proton–electron transfer step ($*CO_2 + 1H^+ + 1e^- \rightarrow *COOH$) to form the $*COOH$ intermediate, followed by a second proton–electron transfer ($*COOH + 1H^+ + 1e^- \rightarrow *CO + H_2O$) that generates $*CO$ adsorbed on the Co site. Meanwhile, N₂ adsorption occurs at the neighboring Fe site in the adjacent layer. The adsorbed N₂ is subsequently hydrogenated via sequential proton–electron transfer steps to form partially hydrogenated nitrogen intermediates, such as $*N_2H$ and $*NHNH$. Following the formation of these activated nitrogen species, the key C–N bond formation step occurs through coupling between the $*CO$ intermediate at the Co site and the hydrogenated nitrogen species at the Fe site across the interlayer region. The larger spatial separation between the two layers allows the reacting intermediates to adopt a more favorable orientation during C–N coupling, thereby reducing steric constraints present in the single-layer model and stabilizing the resulting coupled intermediate. After the initial C–N bond formation, the coupled intermediate undergoes successive proton–electron transfer steps to form $*NHCONH_2$ and ultimately $*NH_2CONH_2$ intermediate, which corresponds to adsorbed

urea. Finally, desorption of the urea molecule regenerates the Fe and Co sites, completing the catalytic cycle. The corresponding free–energy diagram (Figure 7) closely resembles that obtained in the single-layer model (Figure S17b), indicating that the fundamental 6-proton-6-electron reaction sequence remains unchanged except that an interlayer pathway without substantial steric hindrance is identified.

These results highlight the synergistic catalytic roles of the two metal centers in the COF framework. The Co site preferentially activates CO₂ through the formation of $*COOH$ and $*CO$ intermediates, while the neighboring Fe site facilitates N₂ adsorption and hydrogenation to form partially hydrogenated nitrogen species. The spatial proximity of these two active centers enables efficient interaction between the activated carbon and nitrogen intermediates, thereby promoting C–N bond formation and subsequent urea synthesis. However, our calculations reveal that the current COF structure experiences significant steric hindrance for the intralayer C–N coupling process. In particular, the presence of hydrogen atoms on the framework generates strong steric repulsion when the $*CO$ and nitrogen-containing intermediates approach each other within the same layer. As a result, the intralayer pathway becomes energetically less favorable, and the reaction preferentially proceeds through the interlayer mechanism where additional spatial freedom allows the intermediates to adopt more favorable orientations for coupling. The intralayer steric hindrance analysis also provides a promising route for future improvement of this COF catalyst. Eliminating the framework hydrogen atoms responsible for the strong intralayer steric repulsion when coupling CO₂ and N₂ will open up the intralayer C–N coupling pathway, which could be more robust due to the more rigid intralayer structure (than noncovalently bound interlayer ones), further enhancing urea formation efficiency.

6. CONCLUSION

This work successfully presents an environmentally friendly approach for electrocatalytic urea synthesis from N₂ and CO₂ under mild conditions. The systematic integration of Fe³⁺ and Co²⁺ dual-atom sites into a 2D-COF (TpBPy) effectively addressed the challenge of simultaneously and selectively activating inert N₂ and CO₂ for electrocatalytic C–N coupling. The resultant catalyst (Fe–Co@TpBpy) generated urea at the rate of 11.25 mmol g_{cat}^{−1} h^{−1} and achieved an FE of 22.52% at −0.75 V vs Ag/AgCl. DFT studies revealed major insights into the synergistic mechanism, suggesting that each type of the metal centers plays a unique role: bipyridyl-coordinated cobalt promotes CO₂ reduction, whereas the iron center drives N₂ activation. Most importantly, the data indicate that the interlayer structure of these dual atoms reduces the energy barriers for the synthesis of the critical $*CONH_2$ intermediate. This research not only proposes a high-performance COF-based electrocatalyst for urea production but also establishes a structural framework for constructing interlayer active sites, providing the groundwork for potential developments in N₂ fixation and carbon utilization technologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.6c00311>.

Additional experimental details, materials, and measurement methods; synthesis of COFs; PXRD and FT-IR of the Fe@TpBpy; SEM and EDS of Fe–Co@TpBpy; XPS of TpBpy and Co@TpBpy; DRS of COFs; XAS analysis; EXAFS fitting parameter; ^1H NMR, UV–vis spectra, and GC chromatogram of electrolysis products; ATR–FTIR of electrolytes; cyclic voltammograms of Fe–Co@TpBpy, Co@TpBpy, and Fe@TpBpy; electrochemical surface area and impedance analysis; energy diagram of the single-layer model; charge density difference maps; and comparison table (PDF)

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Notes

The authors declare no competing financial interest.

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