Electrochemical conversion of abundant carbon- and nitrogen-containing small molecules into high-valued organonitrogen compounds is alluring to reducing current dependence on fossil energy. Here we report a single-cell electrochemical oxidation approach to transform methanol and ammonia into formamide under ambient conditions over Pt electrocatalyst that provides 74.26% selectivity from methanol to formamide and a Faradaic efficiency of 40.39% at 100 mA cm⁻² current density, gaining an economic advantage over conventional manufacturing based on techno-economic analysis. A 46-h continuous test performed in the flow cell shows no performance decay. The combined results of in situ experiments and theoretical simulations unveil the C–N bond formation mechanism via nucleophilic attack of NH₃ on an aldehyde-like intermediate derived from methanol electrooxidation. This work offers a way to synthesize formamide via C–N coupling and can be extended to substantially synthesize other value-added organonitrogen chemicals (e.g., acetamide, propenamide, formyl methylamine).
can contribute to greenhouse gas mitigation for a carbon-neutral future. Notably, direct thermal-catalytic oxidation of aromatic alcohol using over-stoichiometric oxidants to form an aldehyde-like intermediate and react with ammonia under high pressure was proved to prepare aromatic amides by Noritaka Mizuno and co-workers. Therefore, we propose that the utilization of nucleophilic attack of NH₃ on the in situ formed formaldehyde-like intermediate from methanol electrooxidation may afford a greener process to produce formamide under ambient conditions.

Herein, we demonstrate a methanol electrolysis approach to synthesize formamide in an aqueous ammonia medium at ambient temperature and pressure (Fig. 1b). Among all the screened electrocatalysts, Pt shows the highest performance. The optimized selectivity from methanol to formamide and Faradaic efficiency can reach 74.26% and 40.39% at 100 mA cm⁻² current density in a single cell. The key reaction intermediates are recognized by isotope-labeled in situ Attenuated Total Reflection Fourier Transformed Infrared Spectroscopy (ATR-FTIR) and online differential electrochemical mass spectrometry (DEMS). Combining the computational study, the high formamide production efficiency is ascribed to the moderate binding affinity of the reaction intermediates on PtO₂, which is formed on the surface of the Pt electrocatalyst during the reaction. Furthermore, a flow cell is adopted for continuous formamide electrosynthesis without performance decay in a 46-h stability test. Notably, the techno-economic analysis (TEA) proves the cost advantage of formamide electrosynthesis strategy over current industry manufacturing.

**Results**

The conjecture of formamide electrosynthesis from methanol and ammonia oxidation is testified in a membrane-free single cell. The cathode is metal Ni. Ten species of metal anode catalysts, including Pt, Ni, Fe, Cu, Al, Co, Ti, Pb, Mo, and W, were screened using the galvanostatic method. A single cell can greatly reduce the operating cost compared with a membrane-separated two-chamber cell. The mixture of methanol and ammonia with a 2:1 volume ratio in 0.5 M NaHCO₃ aqueous solution was measured at the current density of 10 mA cm⁻². The carbonaceous liquid product was analyzed and quantified by ¹H-nuclear magnetic resonance (¹H-NMR, Supplementary Fig. 1). After 3-h electrolysis, Pt, Ni, and Fe catalysts show the capacity for formamide formation, and their Faradaic efficiencies (FEformamide) are 11.70%, 7.31%, and 1.44% (Supplementary Fig. 2a), respectively. Among them, Pt delivers the main carbonaceous liquid product of formamide while Ni and Fe mainly produce formic acid products (Supplementary Fig. 2b). At different current densities (20, 40, 80, 100, 120, and 150 mA cm⁻²), Pt exhibits higher Faradaic efficiency and yield rate for formamide compared with Ni and Fe (Fig. 1a and Supplementary Figs. 3, 4). The optimized FEformamide over Pt reaches 32.70% at the current density of 100 mA cm⁻². This FEformamide value corresponds to the yield rate of 305.4 μmol cm⁻² h⁻¹, greatly higher than Ni (4.93%, 46.03 μmol cm⁻² h⁻¹) and Fe (1.43%, 13.36 μmol cm⁻² h⁻¹) (Supplementary Fig. 5). To cut the cost of catalyst, Pt-covered Ti foil was synthesized by electrodeposition of Pt on Ti foil for replacing bulk Pt foil (Supplementary Fig. 6). Pt-Ti shows a similar performance to bulk
CH3OH: NH3

obvious change. And slight surface oxidation of used Pt is con-
by oxidation, SEM and XRD of used Pt-Ti samples still show no
mometer (ICP). Although a small amount of Pt dissolution is induced
NaHCO3. The Faradaic ef
reducing the alkalinity, formamide emerges. The Faradaic ef
is only formic acid and formamide is completely suppressed in 0.5 M
(Fig.2c and Supplementary Fig. 8). The carbonaceous liquid product
of formamide reaches the maximum in the electrolyte of 0.5 M
(Fig.11)21. In addition, this approach can be utilized in the
synthesis of acetamide, propenamide, and formyl methylamine,
the volume ratio of CH3OH to NH3 from 1:1 to 11:1. The optimized
content of the catalyst should be con-
tatement Fig. 12).

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Pt for formamide generation at 100 mA cm−2 (Fig. 2b and Supple-
mental Fig. 7).

The performance optimization and stability measurement of
Pt-Ti catalyst
The FEformamide increases firstly and then decreases with increasing
the volume ratio of CH3OH to NH3 from 1:1 to 11:1. The optimized
FEformamide reaches 40.39% at 4:1 at 100 mA cm−2 and the corre-
spending selectivity from methanol to formamide was 74.26% (Fig. 2c and Supplementary Fig. 8). The carbonaceous liquid product
is only formic acid and formamide is completely suppressed in 0.5 M
NaOH aqueous solution (Fig. 2d and Supplementary Fig. 9). After
reducing the alkalinity, formamide emerges. The Faradaic efficiency of formamide reaches the maximum in the electrolyte of 0.5 M
NaHCO3 or 0.25 M H2SO4. The stability of Pt-Ti catalyst for for-
 scaleX5/2 signal peak at 78.1 eV (Supple-
mental Fig. 15). In addition, this approach can be utilized in the
synthesis of acetamide, propenamide, and formyl methylamine, suggesting the expandability of our methodology (Supple-
mental Fig. 12).

Mechanistic studies
To explore the reaction pathway, Density Functional Theory (DFT) is
conducted to determine the reaction pathway. Electrochemical in situ Raman spectroscopy (Supplementary Fig. 13), a
surface-sensitive technique, is adopted to trace the active phases of
those catalysts during the reaction process. As shown in Fig. 3a–c, with
increasing the current density, the peak intensities of α-PtO2, β-NiOOH, and α-FeOOH on Pt, Ni, and Fe can be identified22,23. These results indicate that the active phases of Pt, Ni, and Fe for formamide electro-
synthesis are α-PtO2, β-NiOOH, and α-FeOOH, respectively. There-
fore, α-PtO2, β-NiOOH, and α-FeOOH are used to build the surface
models for DFT simulations. The complete reaction pathway and
energy diagram of the coupling reaction as well as the electronic analysis of the C–N bond formation steps are displayed in Fig. 3d, Supplementary Figs. 14–20 and Supplementary Tables S1–S5. There are three pathways for amide formation using alcohol and ammonia as the feedstocks on α-PtO2 (Path 1) aldehyde from alcohol dehydration reacted with NH3 to form hemiaminal that is subsequently dehydrated to formamide24,25; (Path 2) aldehyde as the intermediate of methanol oxidation reacts with NH3 to form aldimine via a hemiaminal inter-
mediate, and then the aldimine is oxidized to nitrile that can be further
hydrolyzed to formamide26; (Path 3) alcohol-derived CHO* reacts with
NH3-derived NH2* to generate formamide (Supplementary Fig. 14, Supplementary Table 1). For Path 1 the C–N coupling requires two
adjacent active intermediates of CHO* and NH2*, which are both easy
to be solely oxidized into the corresponding carbon–nitrogen-con-
taining byproducts24,25. Thus, the direct nucleophilic attack of NH3 on the in situ formed aldehyde in Paths 1 and 2 seems more possible (Fig. 3d). As for formamide formation on β-NiOOH and α-FeOOH, only Path 1 is possible (Fig. 3d, Supplementary Figs. 15–18, Supplementary Tables 2, 3). The key C–N coupling step is then analyzed from a kinetic
point (Supplementary Fig. 19, Supplementary Table 4). The C–N bond
formation between *CH2O and NH3 is the nucleophilic attack process, i.e., the positively charged C is attacked by the electronegative N atom in NH326,27. Thus, the charged states of C in *CH2O and N in NH3/NH2 qualitatively demonstrate the feasibility of the C–N bond-making process. The charge analysis of the relevant adsorbates is done using
Bader charge analysis. As shown in Supplementary Table 4, C in *CH2O is positively charged in the order of +1.60 e on α-PtO2 > +1.36 e on
β-NiOOH > +0.20 e on α-FeOOH. We, therefore, propose that the barrier energies for the C–N bond coupling process by NH$_3$ nucleophilic attack of *CH$_2$O are very likely to be in the order of α-PtO$_2$ > β-NiOOH > α-FeOOH. For Path 1, the minimum applied potentials demanded to make all elementary reactions exoergic are 1.00, 2.51, and 2.57 V for α-PtO$_2$, β-NiOOH, and α-FeOOH, respectively (Supplementary Table 5).

α-PtO$_2$ performs an obviously stronger catalytic activity toward the coupling of methanol and ammonia, which is rooted in its higher ability of oxidizing methanol and stabilizing *CH$_2$ONH$_2$. It should be noted that α-PtO$_2$ also benefits the suppression of the complete methanol oxidation due to its smallest driving force of the *CH$_2$O-*CHO step (Fig. 3d, Supplementary Table 5). For Path 2, the crucial reaction step of *CH$_2$ONH$_2$ dehydration only thermodynamically takes place on α-PtO$_2$ with Gibbs free energy of -0.19 eV, which excludes the possibility of Path 2 on β-NiOOH and α-FeOOH (Supplementary Table 5). Thus, α-PtO$_2$ facilitates the formamide formation via Path 1 and provides one more possible Path 2.

To confirm the reaction pathway, we first testify the methanol electrolysis without ammonia. The carbonaceous liquid product is only formic acid. Then, no other carbonaceous liquid product is detected when the mixture of formic acid and ammonia is electrolyzed. In addition, an H-type electrolysis experiment proves the cathode reaction does not affect formamide formation (Supplementary Fig. 20). Those results indicate that formamide is formed from the
combination of the intermediate from methanol-to-formic acid conversion (formaldehyde-like intermediate) and ammonia. Formaldehyde intermediate can be quickly converted to formic acid during the electrolysis without ammonia, which makes it undetectable. When methanol feedstock is replaced with formaldehyde, formamide can be detected, further proving the existence of an aldehyde-like intermediate (Supplementary Table 6). These results are consistent with theoretical simulation. To further understand and real-time monitor the catalytic process, the cutting-edge in situ ATR-FTIR is carried out in a transmission mode, suggesting the product signal in the form of the downward peak during the measurement process (Supplementary Fig. 21). Using $^{14}$NH$_4^+$ as the nitrogen source, the signal shows an increasing tendency with the current density (Fig. 3e). The characteristic peaks at around 1220, 1435, 1520, 1680, and 2185 cm$^{-1}$, corresponding to C–O, C–N, CO$_3^{2-}$/NO, H$_2$O, and C≡N, can be identified$^{31-35}$, suggesting the production of multiple intermediates.

For confirming the C–N bond formation, isotope-labeling in situ ATR-FTIR is carried out using $^{15}$NH$_4^+$ (Fig. 3f). By applying the increasing current density, C–N and C≡N shift to the lower wavenumber region (1360 cm$^{-1}$ for C–N, and 2120 cm$^{-1}$ for C≡N) because of the isotope effect$^{33,36}$. NO signal at around 1460 cm$^{-1}$ is also observed$^{37}$. Moreover, a series of control experiments prove the Au substrate and single CH$_3$OH/NH$_3$ electrooxidation do not disturb the detection of C–N and C≡N signals in FTIR spectra (Supplementary Figs. 22, 23). C–N in H$_2$C–NH is traced based on online DEMS (Supplementary Fig. 24)$^{38}$. Accompanied by the on/off switching circuit (Supplementary Fig. 25a), the signal of H$_2$C–NH raises and falls, implying its generation. The 46 molecular weight of formamide product (molecular weight should plus 1 in the positive ion mode) is identified by the liquid chromatography-mass spectrometry (LC-MS) (Supplementary Figs. 25b and 26). The combined results of isotope-labeling in situ ATR-FTIR and online DEMS confirm the existence of Path 2 for formamide generation on $\alpha$-PtO$_2$.

For realizing its continuous production, a flow cell is designed for the electrosynthesis of formamide. CH$_3$OH and NH$_3$ as the feedstocks flow along one side of the Pt-Ti anode, then go through its slit, and are finally attached to the other side of Pt-Ti with H$_2$ evolution from the cathode reaction (Fig. 4a). According to the above-mentioned
optimized condition, 0.5 M NaHCO₃ and 4:1 volume ratio of CH₂OH to NH₃ are adopted. Different flow rates from 0.25 mL min⁻¹ to 5 mL min⁻¹ are carried out. As shown in Fig. 4b, FE for formamide increases with decreasing the flow rate and the maximum value can reach 37.88% at 0.25 mL min⁻¹, corresponding to 353.35 μmol h⁻¹ of yield rate. A technoeconomic analysis (TEA, Supplementary Note 1, Supplementary Fig. 27) indicates the profit per tonne of formamide from this electrolysis reaches $1325.67 (marked as a star in Fig. 4c) and as high as $2158.90 with adding the other dividends such as the benefits of hydrogen, sodium formate, sodium nitrate, and sodium nitrite. After 46 h of continuous operation, the catalyst can maintain its performance (Fig. 4d).

Discussion

A sustainable electrooxidation approach is reported to synthesize formamide using methanol and ammonia as the feedstocks at ambient temperature and pressure. After screening 10 metal catalysts, Pt exhibits the highest activity for formamide synthesis. The maximum Faradaic efficiency reaches 40.39% at the current density of 100 mA cm⁻² in NaHCO₃ solution. The combined results of theoretical simulation and isotope-labeled in situ electrochemical characterizations unveil the reaction pathway for formamide formation and the high activity origin of Pt catalyst. The formamide product is further confirmed by isotope-labeled LC-MS. This work presents a novel synthesis approach to formamide using the CO₂-derived feedstock under mild conditions as a promising alternative to thermal chemical manufacturing with fossil-supported feedstock and energy. Impressively, this facile method is also suitable for the synthesis of acetamide, propenamide, and formyl methyamine, highlighting the promising application potential.

Methods

Materials

All reagents and metal catalysts (Pt, Ni, Fe, Cu, Al, Co, Ti, Pb, Mo, W foils, and Pt powder) were obtained from commerce without further purification. CH₂OH, HCHO, HCN, dimethyl sulfoxide (DMSO), HCOONa, HCONH₂, NaHCO₃, Na₂SO₃, (NH₄)₂SO₄, NaOH, NH₄F, NaAuCl₄·2H₂O, K₂PtCl₄, NH₄Cl, Na₂SO₃, and Na₂S₂O₃·5H₂O are analytical grade. The concentrations of NaHCO₃, H₂SO₄, HNO₃, HCl, H₂O₂, D₂O, and HF are 25 mM, 0.5 M, 0.12 M NaOH, 0.23 g NaAuCl₄·2H₂O, 0.13 g NH₄Cl, 0.95 g Na₂SO₃, 0.62 g Na₂S₂O₃·5H₂O were dissolved in 100 mL H₂O denoted as Solution A; HNO₃ = 1:1 for 20 min and then polished using the Al powder for 10 min. After washing three times with water, the clean monocrystal silicon was obtained; (3) The above monocrystal silicon was immersed in the aqua regia (V(HCl):V(HNO₃) = 1:1) for 20 min and then polished using the Al powder for 10 min. After washing three times with water, the clean monocrystal silicon was obtained. (2) The monocrystal silicon was immersed in the aqua regia (V(HCl):V(HNO₃) = 1:1) for 20 min and then polished using the Al powder for 10 min. After washing three times with water, the clean monocrystal silicon was obtained. The above monocrystal silicon was immersed in the aqua regia (V(HCl):V(HNO₃) = 1:1) for 20 min and then polished using the Al powder for 10 min. After washing three times with water, the clean monocrystal silicon was obtained.

Synthesis of Pt-coated Ti substrate (Pt-Ti)

Pt-Ti was synthesized by the electro-deposition method. First, 1 cm × 3 cm Ti substrate, carbon rod, and Pt powder (50 wt% Pt:50 wt% C) were obtained from commerce without further purification. CH₂OH, HCHO, HCN, dimethyl sulfoxide (DMSO), HCOONa, HCONH₂, NaHCO₃, Na₂SO₃, (NH₄)₂SO₄, NaOH, NH₄F, NaAuCl₄·2H₂O, K₂PtCl₄, NH₄Cl, Na₂SO₃, and Na₂S₂O₃·5H₂O are analytical grade. The concentrations of NaHCO₃, H₂SO₄, HNO₃, HCl, H₂O₂, D₂O, and HF are 25 mM, 0.5 M, 0.12 M NaOH, 0.23 g NaAuCl₄·2H₂O, 0.13 g NH₄Cl, 0.95 g Na₂SO₃, 0.62 g Na₂S₂O₃·5H₂O were dissolved in 100 mL H₂O denoted as Solution A; HNO₃ = 1:1 for 20 min and then polished using the Al powder for 10 min. After washing three times with water, the clean monocrystal silicon was obtained; (3) The above monocrystal silicon was immersed in the aqua regia (V(HCl):V(HNO₃) = 1:1) for 20 min and then polished using the Al powder for 10 min. After washing three times with water, the clean monocrystal silicon was obtained.

Material characterization

Scanning electron micrograph (SEM) image and the corresponding energy dispersive X-ray (EDX) spectrum were performed on a Regulus 8100 field emission scanning electron microscopy. X-ray diffractometry (XRD) pattern was carried out on a Bruker D8-Focus instrument. X-ray photoelectron spectroscopy (XPS) spectrum was collected on a Thermo Fisher Scientific K-Alpha+ instrument.

Electrochemical measurements

CH₂OH and ammonia with different volume ratios were added into a 0.5 M NaHCO₃ aqueous solution. Ni foil, Pt-Ti, and Ag/AgCl were inserted in the solution and as the cathode, the anode, and the reference electrode, respectively. Finally, different current densities from 10 to 150 mA cm⁻² were carried out using the electrochemical workstation (CS150H, Wuhan CorrTest Instruments Co., Ltd) and the reaction time was set as 3 h. The influence of the reactant ratio on the catalytic performance was performed by controlling the total volume of 15 mL, the mixture of CH₂OH and ammonia) and other experimental conditions were kept consistent. The influence of anion on the catalytic performance was performed by changing the different electrolytes and controlling the total molar of the mixture of the anion and the cation in different electrolytes was the same.

Product quantification

The gaseous products were quantified using gas chromatography (Agilent 7890A) equipped with thermal conductivity detection (TCD) and flame ionization detection (FID). High-purity He was employed as the carrier gas. The carbonaceous liquid products were analyzed by 'H nuclear magnetic resonance (1H-NMR) using the DMSO as the internal standard. The preparation of the internal standard for 1H-NMR detection was as follows: 10 μL DMSO was diluted 100 times by water and then mixed with D₂O with a 11 (V/V) ratio. The calibration curves of the carbonaceous liquid products were obtained by plotting the standard sample concentration vs. the 1H-NMR peak area ratio of the standard sample/DMSO (Supplementary Fig. S1). Formamide was further identified by a liquid chromatography-tandem mass spectrometry (LC-MS) ( SCIEX 6500 PLUS) using a Phenomenex NH₂ column. The parameters for LC-MS detection were set as follows: the aqueous solution with acetonitrile/water (40:60, V/V) was used as the mobile phase. The injected quantity, flow rate, and detection wavelength were 10 μL, 0.2 mL min⁻¹ and 195 nm, respectively. The data collection was recorded in the positive ion mode. Nitrate and nitrite were analyzed by ion chromatography (IC). The parameter for IC detection was set as follows: 25 mM KOH was used as the mobile phase. The injected quantity, flow rate, and column temperature were 25 μL, 1 mL min⁻¹, and 30 °C, respectively.

Online differential electrochemical mass spectrometry (DEMS) measurement

Online DEMS was carried out to detect the volatile matters during the real-time electrolysis process (Shanghai Linglu Instrument & Equipment Co.). The signal was collected through a hydrophobic polytetrafluoroethylene (PTFE) membrane, which played a key role in permitting the volatile matter and simultaneously preventing water into the vacuum chamber. The electrolysis reaction occurred on one side of the PTFE membrane and the produced volatile matters were brought to the other side through a pump (Supplementary Fig. S24). Sequentially, those matters were detected by mass spectrometry.

In situ attenuated total reflection flourisher transformed infrared spectroscopy (ATR-FTIR) measurement

In situ ATR-FTIR was carried out to trace the signals of the intermediates using a Nicolet Nexus 670 Spectroscopy equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector. An ECIR-II cell equipped with a Plu Veemax III ATR in a three-electrode system was provided from Shanghai Linglu Instrument & Equipment Co. The data was collected through the Pt-covered monocrystal silicon. To improve the signal intensity, the monocrystal silicon was initially coated with a layer of Au using the chemical plating method as follows: (1) 0.12 g NaOH, 0.23 g NaAuCl₄·2H₂O, 0.13 g NH₄Cl, 0.95 g Na₂SO₃, 0.62 g Na₂S₂O₃·5H₂O were dissolved in 100 mL H₂O (denoted as Solution A); (2) The monocrystal silicon was immersed in the aque regia (V(HCl):V(HNO₃) = 1:1) for 20 min and then polished using the Al powder for 10 min. After washing three times with water, the clean monocrystal silicon was obtained; (3) The above monocrystal silicon was immersed in the mixture of H₂SO₄ and H₂O₂ (V(H₂SO₄):V(H₂O₂) = 1:1) for...
labeled (15NH4)2SO4 was used as the electrolyte. To keep conditions consistent, (14NH4)2SO4 was also performed.

In situ electrochemical Raman spectroscopy measurement

In situ Raman was carried out to trace the surface transformation of the electrocatalysts using a Renishaw inVia reflex Raman microscope equipped with an excitation of 633 nm laser. The configuration was described in our recent works. Different current densities were controlled by an electrochemical workstation.

Data availability

The data that support the plots within this paper are available from the corresponding author upon reasonable request. The source data underlying Figs. 2–4 are provided as a Source Data file. Source data are provided with this paper.

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Acknowledgements
The authors are grateful to the National Natural Science Foundation of China (Nos. 22271213 (B.Z.), 22109115 (N.M.), and 22071173 (Y.Y.)).

Author contributions
B.Z. conceived the idea and directed the project. B.Z., Y.Y., and N.M. designed the experiments. N.M. and J.S. carried out the materials synthesis and characterization. H.L. contributed to the theoretical calculation. Y.W. assisted in electrochemical in situ ATR-FTIR. X.F. contributed to LC-MS. C.L. discussed the mechanism, N.M. and H.L. co-wrote the paper. Y.Y. and B.Z. revised the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-33232-w.

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Peer review information Nature Communications thanks the other anonymous reviewer(s) for their contribution to the peer review of this work. Peer review reports are available.

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