Selective electrocatalytic synthesis of urea with nitrate and carbon dioxide

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Abstract:

Synthetic nitrogen (N) fertilizers, especially urea ($CO(NH_2)_2$) with the highest nitrogen content, nourish crop production to underpin human life. The conventional urea synthesis relies on harsh industrial processes, which consumes approximately 2% of annual global energy. Instead, electrocatalysis is an emerging sustainable technology to produce urea at ambient conditions. Herein, by directly coupling nitrate (NO_3^-) with carbon dioxide (CO_2) on an indium hydroxide catalyst, we realize highly selective urea electro-synthesis at ambient conditions. We derive that CO_2 can suppress adverse hydrogen evolution reaction by transforming the surface semiconducting behaviour of the model catalyst in our work. The key step of C–N coupling initiates at an early stage through the reaction of $^*NO_2$ with $^*CO_2$ intermediates owing to the low energy barrier on {100} facets, hence the subsequent urea is synthesized with high Faradaic efficiency, nitrogen selectivity, and carbon selectivity, which reach 53.4%, 82.9% and ~100%, respectively. This work offers a desirable urea synthesis route and provides deep insights into the fundamental origin of C–N coupling for guiding other sustainable synthesis of indispensable chemicals.

Introduction

Urea ($CO(NH_2)_2$), a vital fertilizer to feed more than half the world's population, is mainly synthesized using ammonia (NH_3) with carbon dioxide (CO_2)[1]. Thereinto, the Haber-Bosch approach still dominates the industrial production of NH_3, of which approximately 80% is consumed to lay the foundation for urea synthesis[2]. Such process involves energy-intensive reactions operating under harsh conditions (100–200 bar and 400–500 °C), accounting for more than 2% of global energy consumption[3]. With the impetus to reduce the dependence on fossil fuels and thus lower environmental pollution, tremendous efforts have been diverted to develop innovative routes enabling NH_3 synthesis under milder conditions[4].

Electrocatalytic dinitrogen reduction reaction (N_2RR), producing NH_3 from atmospheric nitrogen and water at ambient conditions, is an emerging technology[5]. Up till now, many metal-based (Bi, Au, et al.) or metal-free materials (B, P, et al.) represent the state-of-the-art electrocatalysts towards NH_3 synthesis[6–13]. Further synthesizing urea in industry by the reaction of NH_3 with CO_2, nonetheless, also relies on extreme conditions, which results in complexity and impracticality. Recent advances demonstrate that electrocatalytic coupling N_2 with CO_2 provides an intriguing picture for direct urea production under ambient conditions[14,15]. For instance, Wang et al reported that $^*N_2$ could boost the reduction of CO_2 to CO, which was in favour of reacting with $^*N_2$ for the subsequent urea formation with a Faradaic efficiency (FE) of 8.92%.[14] Despite efficient C–N coupling realized by as-employed electrocatalysts, the dilemma still exists in breaking the N≡N bond of dinitrogen.

In this regard, nitrate (NO_3^-) is a highly desirable nitrogen-containing reactant. Given the merits of the lower dissociation energy for the N=O bond (204 kJ mol^{-1}) in stark contrast with that for N≡N bond (941 kJ mol^{-1}), very recently, the NO_3^- reduction reaction (NO_3^-RR) has provoked many attentions from the chemists to circumvent the aforementioned problem[16–20]. Drawing inspiration from recent reports, coupling NO_3^- or NO_2^- with CO_2 might be an alternative path to drive electrocatalytic urea synthesis[21–24]. Key challenges include: seeking active sites for prior C–N coupling to increase the urea selectivity, and suppressing the occurrence of adverse hydrogen evolution reaction (HER) to enhance the FE.

Described herein, we present that high-selectivity urea production is realized on indium hydroxide ($In(OH)_3$) through electrochemically coupling NO_3^- with CO_2 (**Fig. 1a**). On this catalyst, the {100} facets favour the direct C–N coupling by means of the reaction between $*NO_2$ and $*CO_2$ intermediates. Superior to the mechanisms based on $*NH_2$ reacting with $*CO_2$ or *CO, direct C–N coupling at such an early stage renders an obviously increased urea selectivity by reducing the by-product formation possibility towards NH_3, N_2, CO or HCOOH, which generally emerged in previous reports[25,26]. The surface chemistry underpinning the fundamental kinetics is acquired by operando synchrotron-radiation Fourier transform infrared spectroscopy (SR-FTIR).

The CO_2 source in this process is also critical. Other than serving as the reactant to synthesize urea, surface-absorbed CO_2 can reduce the HER competition by capturing the electrons to endow the n-type $In(OH)_3$ with a surface p-type semiconducting behavior, which is revealed by the Mott-Schottky (M-S) measurements. The hole accumulation layer on p-type $In(OH)_3$ will repel protons to inhibit the HER process. Promoted by these features, $In(OH)_3$ with single {100} facets ($In(OH)_3$-S) affords an average urea yield of 533.1 $\mu g\ h^{-1}\ mg^{-1}_{cat.}$ at −0.6 V versus reversible hydrogen electrode (RHE), as well as ultra-high FE of 53.4%, nitrogen selectivity (N_{urea}-selectivity) of 82.9% and carbon selectivity (C_{urea}-selectivity) of ~100%, surpassing most of previous achievements.

Results

Structural characterization. Primarily, we prepared $In(OH)_3$-S with well-defined {100} facets *via* a reported solvothermal approach with some modification[27] (please see details in Methods). Evidenced by X-Ray diffraction (XRD), the obtained sample is cubic indium hydroxide (JCPDS: 76-1463) without any detectable impurity phase (Fig. 1b). To determine the surface chemical status of $In(OH)_3$-S, X-ray photoelectron spectroscopy (XPS) was employed. The In 3d XPS signals can be observed at 452.1 and 444.5 eV (Fig. 1c), which confirms the valence state of In^{3+} [28]. As reflected in the de-convoluted O 1s XPS spectrum (Fig. 1d), the fitting peaks at 531.4 (O_I), 532.4 (O_{II}) and 533.4 eV (O_{III}) are assignable to lattice oxygen, surface hydroxyl/absorbed oxygen and absorbed water, respectively[29,30]. The Fourier transform infrared spectroscopy (FTIR) spectrum of $In(OH)_3$-S displays the peaks at 3,235, 3,121, 1,155, 1,068, 852, 782, and 499 cm^{-1} (Supplementary Fig. 1), elucidating the presence of O–H, –OH and In–O bonds[27,31]. By analysis of Raman spectrum shown in Supplementary Fig. 2, the surface ν_3In–O bond could be probed at 304 cm^{-1} [32]. Characterization of the $In(OH)_3$-S by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) exhibits cube-like nanocrystals with sizes of 100~200 nm (Fig. 1e,f and Supplementary Fig. 3a,b). The high-resolution transmission electron microscopy (HRTEM) collected on the surface of an $In(OH)_3$-S nanocube shows an interfringe of 90° (Supplementary Fig. 3c), which is a typical feature of {100} facets on a crystal with cubic structure. The exposed facets were also investigated by selected-area electron diffraction (SAED) pattern focusing on an individual $In(OH)_3$-S nanocube with a circle in Fig. 1f. The square symmetrical SAED pattern is showcased with clear diffraction spots of (110) and (200) lattice planes of $In(OH)_3$ (Fig. 1g). This can be ascribed to [001] zone axis diffraction of bcc $In(OH)_3$.[33] Based on above, the cube-like $In(OH)_3$-S is enclosed by {100} facets. The relevant atomic configuration of {100} facets is depicted in Supplementary Fig. 4.

Electrocatalytic urea synthesis performance. Evaluation of the electrocatalytic urea synthesis performance of $In(OH)_3$-S was executed in an H-cell reactor using chronoamperometry (CA) method at fixed potentials under ambient condition. The as-employed electrolyte (0.1 M KNO_3) was saturated with bubbling of high-purity CO_2, which was continuously streamed to the cathode during the CA tests (for details, please see the Methods). The amounts of urea produced were quantitatively determined by diacetyl monoxime method (Supplementary Fig. 5, details are presented in Methods). At the first place, the mass loading is optimized on the basis of the obtained FE as displayed in Supplementary Fig. 6. The electrocatalysis tests are conducted at the potentials of −0.5 to −0.8 V *vs.* RHE, of which the UV-Vis and CA results are shown in Supplementary Figs. 7 and 8. The peak value of average urea yield reaches 533.1 μg h^{-1} $mg^{-1}_{cat.}$ for $In(OH)_3$-S at −0.6 V *vs.* RHE (Fig. 2a). Noticeably, at the same potential, $In(OH)_3$-S catalyst delivers a urea-producing FE of 53.4%. Such high urea yield and FE basically stabilizes after successive four runs (Supplementary Figs. 9 and 10). The relatively stable electrocatalytic activity is also reflected in long-term (12 h) CA result (Supplementary Fig. 11). This can be ascribed to the retention of the crystalline phase, the cubic shape, the valence of surface indium, as well as the {100} facets (Supplementary Figs. 12–15).

To highlight the role of {100} facets on $In(OH)_3$-S in boosting the urea production, the comparison tests are also conducted on $In(OH)_3$ with mixed facets of {100} and {110}, which is denoted as $In(OH)_3$-M (for synthesis details, please see the Methods). Except having extra {110} facets, $In(OH)_3$-M exhibits consistent phase, size, surface chemical status and effective surface area as $In(OH)_3$-S (Supplementary Figs. 16–20). In stark contrast, electrocatalytic urea synthesis performance of $In(OH)_3$-S vastly surpasses that of $In(OH)_3$-M, which depicts a lower average urea yield of 392.6 μg h^{-1} $mg^{-1}_{cat.}$ and FE of 34.6% (Fig. 2c and Supplementary Fig. 21). It suggests the standout electrocatalytic performance toward urea synthesis for $In(OH)_3$-S depends on the exposed facets.

The control experiment was conducted in 0.1 M K_2SO_4 without any nitrogen source, which resulted in no urea production as reflected in the UV-Vis spectra (Supplementary Fig. 22). This indicates that the element of N in urea indeed originates from nitrate in 0.1 M KNO_3

electrolyte. To further prove that, the isotope-labelling electrocatalysis experiments were also performed in 0.1 M $K^{15}NO_3$ electrolyte. The peaks of ^{15}N labelled urea are observed in the ^1H NMR spectrum (Supplementary Fig. 23a). In addition, the NH_3 by-product derived from nitrate is also confirmed by NMR (Supplementary Fig. 23b). The as-produced NH_3 was further quantified by indophenol blue method (Supplementary Fig. 24, details were presented in Methods). Unlike the urea production, the average NH_3 yield increases dramatically at more negative potentials (Supplementary Figs. 25a and 26). Supplementary Fig. 25b displays the corresponding FEs. Apart from the conversion to urea and ammonia, no other side reactions arise such as nitrite, hydrazine or dinitrogen production from nitrate as probed by ion chromatogram (IC), colorimetric methods and gas chromatograph with a flame ionization detector (FIDs) and a thermal conductivity detector (TCD) (GC-FID/TCD), respectively (for details, please see the Methods and Supplementary Figs. 27 and 28). Calculations on the urea and ammonia yields, the N_{urea}-selectivity has been obtained as shown in Fig. 2d, where the highest value reaches 82.9% at −0.6 V *vs.* RHE. As for $In(OH)_3$-M, nearly the same activity is realized in average NH_3 yield and FE (Supplementary Fig. 29). Accordingly, the N_{urea}-selectivity of $In(OH)_3$-S is higher than that of $In(OH)_3$-M (Fig. 2e). This manifests that the {100} facets prefer urea production.

Indicated by the urea-dependent UV absorbance which vanishes without CO_2 feeding gas (Supplementary Fig. 30), the carbon in as-produced urea indeed stems from the CO_2. The isotope-labelling electrocatalysis experiments were conducted by using $^{13}CO_2$ as feeding gas to further affirm the above result. The ^{13}C NMR spectra only display the peak assignable to the ^{13}C-labelled urea (Supplementary Fig. 31). This explicitly indicates that the CO_2 feeding gas is the carbon origin to produce urea. The absence of by-products stemmed from CO_2, in terms of CO or HCOOH, is confirmed by GC-FID/TCD and high-performance liquid chromatography (HPLC), respectively (for details, please see the Methods). Based on above results, the full distributions of all detected electrocatalysis products are shown in Supplementary Figs. 32 and 33, together with their Faradaic efficiencies. Remarkably, it demonstrates that $In(OH)_3$-S enables urea synthesis with a C_{urea}-selectivity of ~100% for the applied potential range. Such high electrocatalysis activity outperforms the current state-of-the-art electrocatalysts as summarized in Supplementary Table 1. Without CO_2 feeding, lower ammonia yield and FE are obtained under the exact same conditions (Supplementary Figs. 34–36). Meanwhile, the corresponding CA results exhibit higher current densities relative to that measured in CO_2 (Supplementary Figs. 8 and 37). As the only competing reaction is HER without CO_2 feeding, the facts that CO_2 promotes nitrate reduction with decreased current densities hint a significant suppression of HER by CO_2. In addition, similar phenomena are also reflected in the linear sweep voltammetry (LSV) curves tested in CO_2- and Ar-saturated 0.1 M KNO_3 electrolytes (Fig. 2f). At the potential range from −0.2 to −0.9 V *vs.* RHE, the current density is lowered by CO_2 feeding. Therefore, based on a series of electrochemical tests, it implies the HER process can be inhibited by CO_2 to boost urea synthesis as illustrated in Fig. 1a.

To validate the above deduction, the electrocatalysis tests were also performed in a mixed electrolyte of 0.1 M KNO_3 and 0.05 $KHCO_3$. With the absence of CO_2, the urea yield and corresponding FE at −0.6 V *vs.* RHE dwindle dramatically to 92.6 $\mu g\ h^{-1}\ mg^{-1}_{cat.}$ and 1.9%, respectively, even though HCO_3^- ions participate in urea synthesis (Supplementary Fig. 38). The low FE towards urea synthesis can be ascribed to the adverse HER as reflected in higher current densities from CA results (Supplementary Fig. 39). When using the electrolyte of 0.1 M $KHCO_3$ containing 200 ppm NO_3^- (KNO_3), the CO_2-promoted urea production is also realized as presented in Supplementary Fig. 40. Assisted by feeding CO_2, the CA measurements demonstrate lower current densities, which results in higher FEs (Supplementary Figs. 40 and 41). Similar to LSV tests in 0.1 M KNO_3 electrolyte, lower current densities driven by CO_2 for 0.1 M $KHCO_3$ electrolyte (with or without 200 ppm NO_3^-) are expected in Supplementary Figs. 42 and 43. Thus, above results elucidate that CO_2 not only enables urea synthesis with NO_3^- through electrocatalysis, but also plays a key role in suppressing HER.

Mechanism towards HER suppression. The observed CO_2-induced HER suppression phenomenon differs from recent work that highlighted the inferior HER activity on Au catalyst limited by electrochemical CO_2 reduction reaction (CO_2RR)[34]. In our work, notwithstanding no electrochemical CO_2RR is involved, the HER process is also suppressed. Inspired by the recent demonstration that the type of semiconductor catalysts strongly correlated with their catalytic chemistry[35], as-prepared catalyst might be tailored to a particular type adverse to HER. To uncover the semiconductor type, we employed the Mott-Schottky (M-S) measurements. Known as an n-type semiconductor, $In(OH)_3$-S shows a positive slope in the M-S plot under the protective atmosphere of Ar (Fig. 3a). It indicates an intrinsic n-type semiconducting behavior of $In(OH)_3$ [36]. It is noteworthy that the M-S plot can be divided into two regions after replacing Ar with CO_2 (Fig. 3b). Apart from the positive slope representing the n-type semiconducting behavior, the negative slope arises which is assignable to the p-type semiconducting behavior[37]. Besides, the slope of M-S plot obtained in CO_2 atmosphere is much higher than that in Ar (Fig. 3a,b). Since the slope values from the linear regime of M-S plots are inversely proportional to the carrier concentration[38], the electron concentration in n-type $In(OH)_3$-S decreases in CO_2 atmosphere. In combination with the emergence of p-type semiconducting behaviour on $In(OH)_3$-S, it manifests that CO_2 can capture the electrons to introduce hole accumulation layer on the surface of the catalyst[37]. Owing to the presence of surface hole accumulation layer, the semiconducting nature of the surface on $In(OH)_3$ shifts from n- to p-type as depicted in Fig. 3c. The CO_2-induced hole accumulation layer can repel protons to approach $In(OH)_3$, which plays the determinant role in impeding HER on $In(OH)_3$ catalyst. The capture of surface electrons will be difficult for bicarbonate due to its electronegative nature. This may explain the lower FEs for the electrocatalysis tests in 0.1 M $KHCO_3$ electrolyte without feeding CO_2 (Supplementary Fig. 40).

As for the M-S measurement on $In(OH)_3$-M in Ar, it also shows a positive slope, of which the value is almost the same as that for $In(OH)_3$-S (Supplementary Fig. 44a). Such a CO_2-

induced n-p transformation in semiconductor type is also realized on $In(OH)_3$-M as reflected in the M-S plot (Supplementary Fig. 44b). Moreover, $In(OH)_3$-M presents a higher slope in M-S plot in relative to that of $In(OH)_3$-S. This unveils that the {110} facets can accommodate more CO_2 absorption. However, the HER suppression ability of $In(OH)_3$-M decreases, which has been reflected in its higher FE for HER (Supplementary Fig. 33). Enlightened by the possibility to construct surface junction by the mixed facets[39,40], the electrons transfer between {100} and {110} facets on $In(OH)_3$-M may balance the surface holes induced by CO_2. To decipher above, a combination of theoretical and experimental studies was carried out. The total density of states (TDOS) is calculated on the {100} and {110} facets of $In(OH)_3$ to disclose the band structures. On the basis of the TDOS analysis, the conduction band minimum (CBM) of {100} facets is slightly lower than that of {110} facets, when the valence band maximum (VBM) is located at the same position (Supplementary Fig. 45). The XPS valence band spectra recorded on $In(OH)_3$-S and $In(OH)_3$-M further experimentally verify the above VBM relationship (Supplementary Fig. 46a). The band alignment between {100} and {110} facets in $In(OH)_3$-M is established as illustrated in Supplementary Fig. 46b, where the electrons can transfer from {110} to {100} facets. Thus, the holes at {100} facets of $In(OH)_3$-M are combined with electrons from {110} facets, which weakens the HER suppression ability. This can be evidenced by the decrease in total nitrogen reduction products (urea and ammonia) as well as the corresponding FEs for $In(OH)_3$-M.

Facet-dependent activity analysis. To unravel the fundamental origins of the facet-dependent activity, density functional theory (DFT) calculations are conducted (for details regarding the calculations, please see the Methods). In light of free-energy diagram of the lowest energy pathway as profiled in Fig. 4a, the urea production initiates from thermodynamically spontaneous reduction of NO_3^- (HNO_3) to $*NO_2$ intermediate on the {100} facets of $In(OH)_3$ with an adsorption free energy of −2.48 eV. In contrast with the spontaneous formation of $*NO_2$, the protonation process of CO_2 needs the energy increase of 0.38 eV. This results in high coverage of $*NO_2$ on the surface of catalysts during the electrocatalysis process, which impedes the adsorption and reduction of CO_2 on $In(OH)_3$-S. Fig. 4b exhibits the relevant atomic configurations of each step for the urea synthesis on the {100} facets of $In(OH)_3$. As extracted from further calculations of charge density difference, the electrons on two coordinatively unsaturated In atoms transfer to $^*NO_2$ (Supplementary Fig. 47), which makes it possible to improve its intrinsic activity for C–N coupling. Supported by a local “In–O–C–O–In” configuration for electron transfer to $^*CO_2$ (Supplementary Fig. 48), the C–N coupling is realized with the reaction between above two intermediates. By contrast with the energy barrier for protonation of $^*NO_2$ to $^*HNO_2$ (0.62 eV), the lower energy barrier of 0.35 eV for $^*CO_2NO_2$ formation is beneficial for direct C–N coupling at a very early stage (insert in Fig. 4a). This result infers that the {100} facets facilitate the selective urea synthesis. Referring to the electrocatalysis results, the lower energy increase for C–N coupling and the spontaneous formation of $^*NO_2$ might synergistically determine the extremely high values of C_{urea}-selectivity and N_{urea}-selectivity. To experimentally prove the C–N formation at a very early stage by direct coupling $^*NO_2$ and $^*CO_2$, the contrast electrocatalysis test is performed in 0.1 M K_2SO_4 electrolyte containing 200 ppm NH_4^+. As no urea is synthesized under this condition (Supplementary Fig. 49), above mechanism can be affirmed, which differs from the previous reports in the C–N coupling step[14,15,23,26]. Further protonation processes are inclined to occur on $^*NO_2$ part of $^*CO_2NO_2$ to form $^*CO_2NH_2$ intermediate (Fig. 4a). When facing the protonation of $^*CO_2NH_2$ intermediate into $^*COOHNH_2$, it delivers a free energy increase of 1.58 eV, which is the potential determining step for the overall urea production. The subsequent urea synthesis processes follow thermodynamically spontaneous pathways, including the formation of $^*CONH_2$ intermediate, the generation of $^*CONO_2NH_2$ intermediate by coupling the second $^*NO_2$, and the further protonation of $^*CONO_2NH_2$ to form $^*CO(NH_2)_2$. The $^*CO(NH_2)_2$ might also be obtained by direct coupling $^*CONH_2$ with other nitrogen-contained intermediates derived from nitrate through the NO_3^-RR process (such as $^*NH_2$ shown in Supplementary Fig. 50). However, aside from $^*NO_2$, other nitrogen-containing intermediates adsorb on the catalyst by N–In bonds or the N atoms are passivated by H atoms, which impede their C–N coupling with $^*CONH_2$.

Unlike strong adsorption on {100} facets, the $*NO_2$ on {110} of $In(OH)_3$ is in weak adsorption state with a small adsorption energy of −0.52 eV (Supplementary Fig. 51). Importantly, only limited charge transfer to $*NO_2$ occurs on the {110} facets lacking strong adsorption as reflected in charge density difference analysis (Supplementary Fig. 52). In marked contrast, the grand challenge in C–N coupling at the next step rules out further urea formation (Supplementary Fig. 53), while only NO_3^-RR proceeds to synthesize NH_3 on the {110} facets of $In(OH)_3$. The –OH groups between In sites on {110} facets (Supplementary Figs. 52 and 53) prevents the formation of $*NO_2CO_2$, which is the key intermediate of urea production here. It implies that the {110} facets are not in favour of C–N coupling, which explains the lower urea yield, FE and N_{urea}-selectivity for $In(OH)_3$-M with extra {110} facets. To further capture an in-depth understanding upon the facet-dependent activity, we study the In_2O_3 with {100} and {110} facets derived from $In(OH)_3$-S and $In(OH)_3$-M. In short, the simulations agree with experiments in elucidating that the {100} facets of In_2O_3 are apt to enable urea production likewise (Supplementary Figs. 54–64). In combination with above, it indicates that the facet-dependent activity originates from the atomic structures of different facets. At the first place, the {100} facets conduce to strong $*NO_2$ adsorption, rendering it active for potential C–N coupling. Furthermore, the {100} facets possess relatively adjacent indium atoms to endow catalysts with favourable platforms for architecting "In–O–C–O–In" configuration. Such configuration can stabilize the adsorption of $*CO_2$, which decreases the energy barrier toward C–N coupling.

Operando SR-FTIR measurements. Experimentally, advanced operando SR-FTIR measurements were conducted on $In(OH)_3$-S to validate the C–N coupling mechanism. Supplementary Figs. 65 and 66 show the experimental setup and cell for corresponding measurements. The infrared (IR) signals are collected from 1,000 to 4,000 cm^{-1} during negative scan from −0.4 to −0.9 V *vs.* RHE (Fig. 5a). The operando SR-FTIR results of from 3,000 to 3,600 cm^{-1} confirm the emergence of H–N–H stretching mode, N–H stretching mode, and N–H bending mode at 3,440, 3,368, and 3,187 cm^{-1} [41], respectively, which starts to appear from −0.5 V (Fig. 5b). As for the range from 1100 to 1,800 cm^{-1} (Fig. 5c), IR bands are probed at 1,635 and 1,170 cm^{-1}, which are assignable to the bending mode and rocking mode of $–NH_2$ in urea[42]. The wagging mode of $–NH_2$ is also found at 1,307 cm^{-1} [43]. Apart from the IR bands of $–NH_2$, the stretching mode of C–N can be observed at 1,419 cm^{-1} [42,44]. Evidenced by the operando SR-FTIR results, the C–N coupling is successfully realized for subsequent urea synthesis, correlating well with the electrocatalysis experiments. In contrast with free urea, the stretching frequency shift of C–N implies the urea has coordinated with surface metal atoms (In) through the oxygen atom of C=O group[42,44]. What's more, the OCO vibrational band arises at 1,396 cm^{-1} (Fig. 5c)[45]. These results explicitly justify the presence of CO_2NH_2 intermediate. The rate-determining step is also proved to be the protonation of $*CO_2NH_2$ into $*COOHNH_2$ [46], in line with above theoretical analysis.

Discussion

A sustainable urea production route is developed using nitrate, carbon dioxide, water and electricity. We achieve selective urea production with an average yield of 533.1 μg h^{-1} $mg^{-1}_{cat.}$ at −0.6 V, FE of 53.4%, nitrogen selectivity of 82.9%, and carbon selectivity of ca. 100% on an $In(OH)_3$ electrocatalyst with well-defined {100} facets. As evidenced by theoretical calculation, the $*NO_2$ and $*CO_2$ intermediates prefer to be coupled directly at an early stage on the {100} facets rather than the {110} facets, which leads to the facet-dependent activity of $In(OH)_3$. In sharp contrast with the protonation of $*NO_2$ or $*CO_2$ separately, the lower energy barrier toward direct coupling $*NO_2$ and $*CO_2$ enables abovementioned high selectivity. Taking the advantage of operando synchrotron-radiation Fourier transform infrared spectroscopy, the early C–N coupling mechanism has been verified. Our study also shows that CO_2 can suppress the HER process to boost urea production, by means of inducing n-p transform in surface semiconducting behavior of $In(OH)_3$ catalyst. This report provides new insight into the C–N coupling originating from NO_3^- and CO_2 through room-temperature electrocatalysis technology, paving the way for more sustainable chemistry approaches.

Figure Legends/Captions (for main text figures)

Fig. 1. Structural characterizations of $In(OH)_3$-S. (**a**) Illustration for urea synthesis process on the surface of $In(OH)_3$-S. (**b**) XRD pattern. (**c**) In 3d XPS spectrum. (**d**) O 1s XPS spectrum. (**e**) SEM image. (**f**) TEM image (**g**) Corresponding SAED pattern of the labelled area in (**f**); scale bars in (**e**), (**f**) and (**g**) are 500 nm, 50 nm and 5 1/nm, respectively.

Fig. 2. Electrochemical properties. (**a**) Urea yields, and (**b**) FEs at different potentials for $In(OH)_3$-S in 0.1 M KNO_3 electrolyte with CO_2 feeding gas. (**c**) Urea synthesis performance comparison between $In(OH)_3$-S and $In(OH)_3$-M at −0.6 V *vs.* RHE. (**d**) N_{urea}-selectivity at different potentials for $In(OH)_3$-S in 0.1 M KNO_3 electrolyte with CO_2 feeding gas. (**e**) N_{urea}-selectivity comparison between $In(OH)_3$-S and $In(OH)_3$-M at −0.6 V *vs.* RHE. (**f**) LSV cure for $In(OH)_3$-S 0.1 M KNO_3 electrolyte with Ar or CO_2 feeding gas.

Fig. 3. Semiconductor type analysis on $In(OH)_3$-S. Mott-Schottky plots measured in (**a**) Ar, and (**b**) CO_2. (**c**) Schematic illustration of n-p transformation process in semiconductor type.

Fig. 4. DFT calculations. (**a**) Free-energy diagram for urea production on the {100} facets of $In(OH)_3$ at 0 V *vs*. RHE. (**b**) Corresponding atomic configurations for each step.

Fig. 5. Operando SR-FTIR spectroscopy measurements under various potentials for $In(OH)_3$-S during the electrocatalytic coupling of nitrate and carbon dioxide. (**a**) 3D-FTIR spectra in the range of 1,000–4,000 cm^{-1}. (**b**) Infrared signals in the range of 3,000–3,600 cm^{-1}. (**c**) Infrared signals in the range of 1,100–1,800 cm^{-1}.

Methods

Materials Synthesis. All reagents were received from Sigma-Aldrich, and used without further purification. The $^{13}CO_2$ (99 atom % ^{13}C) and $K^{15}NO_3$ (98 atom % ^{15}N) were used for isotope-labelling experiment.

$In(OH)_3$-S: First, 0.293 g (1.0 mmol) of $InCl_3 \cdot 4H_2O$ was dissolved in 10 mL of ethylene glycol with continuous stirring as solution A. Then, 2 g NaOH was dissolved in 5 mL H_2O as solution B, which was mixed with solution after the dissolution of NaOH. The precursor solution was transferred into 25 mL Teflon-lined stainless steel autoclaves and maintained at 200 °C for 24 h in oven.

$In(OH)_3$-M: For $In(OH)_3$-M, the synthesis procedure was almost the same as that of $In(OH)_3$-M, while the amounts of EG and H_2O were changed to 15 and 2 mL, respectively.

In_2O_3-S and In_2O_3-M: The In_2O_3-S and In_2O_3-M were obtained from $In(OH)_3$-S and $In(OH)_3$-M, repectively, by calcination at 500 °C for 2 h.

Material Characterization. The structure of the obtained samples were confirmed by X-ray diffraction (XRD) on Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). The morphology of the samples were observed by a field-emission SEM (JEOL JSM-7600F). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on JEOL 2100F. X-Ray photoelectron spectroscopy (XPS) was accomplished using a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer with a pass energy of 20.00 eV and an Al Kα excitation source (1486.6 eV). Fourier transform infrared (FTIR) spectra were tested on a FTIR Perkin Elmer Frontier. Raman spectra were recorded on a confocal Raman spectroscopic system (Renishaw, In Via) using a 633 nm laser. The nuclear magnetic resonance (NMR) spectroscopy was collected on Bruker Avance III HD 800 MHz (18.8 T) standard-bore NMR spectrometer, and the dimethylsulfoxide-d_6 was used as an internal standard.

Operando synchrotron-radiation Fourier transform infrared spectroscopy (SR-FTIR) measurements. Operando SR-FTIR measurements were made at the infrared beamline BL01B of the National Synchrotron Radiation Laboratory (NSRL, China) through a homemade top-plate cell reflection infrared set-up with a ZnSe crystal as the infrared transmission window (cut-off energy of ~625 cm^{-1}).This end station was equipped with an FTIR spectrometer (Bruker 70 v/s) with a KBr beam splitter and various detectors (herein a liquid nitrogen cooled mercury cadmium telluride detector was used) coupled with an infrared microscope (Bruker Hyperion 2000) with a ×15 objective. The catalyst electrode was tightly pressed against the ZnSe crystal window with a micrometre-scale gap in order to reduce the loss of infrared light. To ensure the quality of the obtained SR-FTIR spectra, the apparatus adopted a reflection mode with a vertical incidence of infrared light. Each infrared absorption spectrum was acquired by averaging 128 scans at a resolution of 4 cm^{-1}. The background spectrum of the catalyst electrode was acquired at an open-circuit voltage before each systemic measurement, and the measured potential ranges of the electrocoupling reaction were −0.4 to −0.9 V *vs.* RHE with an interval of 0.1 V. The in situ electrochemical set up and cell are shown in Supplementary Figs. 65 and 66.

Mott-Schottky measurements. The Mott-Schottky experiments were conducted on an Autolab PGSTAT204 by using a three-electrode configuration (working electrode, counter electrode of Pt foil, and reference electrode of Ag/AgCl/saturated KCl). The potential range was −2.0~0 V vs. Ag/AgCl. The frequency was 1000 Hz.

Electrochemical urea ($CO(NH_2)_2$) synthesis. Before tests, the Nafion 117 membrane was pretreated by heating it in H_2O_2 (5%) aqueous solution at 80 °C for 1 h and ultrapure water at 80 °C for another 1 h, respectively, followed by treatment in 0.05 M H_2SO_4 for 1 h and ultrapure water for another 3 h. The electrochemical experiments were conducted on a Solartron Electrochemical Analyzer (England) by using a three-electrode configuration with a H-Cell (working electrode, counter electrode of Pt foil, and reference electrode of Ag/AgCl/saturated KCl). All potentials were converted to reversible hydrogen electrode (RHE).

For electrochemical urea synthesis, potentiostatic tests were carried out in CO_2 saturated 0.1 M KNO_3 (the volume of the electrolyte in the anode and cathode chamber is 30 mL for each), which was bubbled with CO_2 for 20 min before the measurement. Then, the purified CO_2 was continuously fed into the cathodic compartment with a constant flow rate of 20 mL min^{-1} during the experiments. The electrolyte in the cathodic compartment was stirred at a rate of 300 rpm during electrolysis.

Electrochemical NO_3^- reduction reaction (NO_3^-RR) measurements. For electrochemical NO_3^-RR tests, potentiostatic tests were carried out in 0.1 M KNO_3 without feeding CO_2. The volume of the electrolyte in the anode and cathode chamber is 30 mL for each. The electrolyte in the cathodic compartment was stirred at a rate of 300 rpm during electrolysis.

Cathode preparation. Typically, approximately 8 mg of catalyst, 2 mg carbon black and 40 μL of Nafion solution (5 wt%) were dispersed in 760 μL of absolute ethanol by sonicating for 1 h to form a homogeneous ink. And then, 10 μL of homogeneous ink was loaded onto a hydrophilic carbon paper electrode (TGP-H-090) with area of 1x1 cm^2 with a graphitic electrode holder (J110, Tianjin Aida Hengsheng Technology Co. Ltd.). The average mass loading is ca. 0.1 mg cm^{-2}. The applied potentials were all converted to the reference hydrogen electrode (RHE) scale using the following relation:

$$E\ (vs.\ \text{RHE}) = E\ (vs.\ \text{Ag/AgCl}) + 0.197\ \text{V} + 0.059\ \text{V} \times \text{pH}\quad (1)$$

Determination of urea. As-produced urea was spectrophotometrically determined by diacetyl monoxime method[47]. First, 1 mL aliquot of the solution was removed from the electrochemical reaction vessel. Then, 2 mL of acid-ferric solution (100 mL concentrated phosphoric acid, 300 mL of concentrated sulfuric acid, 600 mL DI water, and 100 mg ferric chloride) and 1 mL of Diacetylmonoxime (DAMO)-thiosemicarbazide (TSC) solution (5 g of DAMO and 100 mg TSC were dissolved in 1000 mL DI water) were added. Then, the solution was heated to 100 °C and maintained for 20 min. After cooling to room temperature, the absorbance was acquired at 525 nm using an ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu UV-2700). The concentration-absorbance curves were calibrated using standard urea solutions, as shown in Supplementary Fig. 5, which contained the same concentrations of electrolytes as used in the electrocatalysis experiments.

Determination of ammonia (NH_3). As-produced ammonia was spectrophotometrically determined by the indophenol blue method with modification after diluting the post-test electrolytes to appropriate concentration to match the range of calibration curves[48]. First, 2 mL aliquot of the solution was removed from the electrochemical reaction vessel. Then, 2 mL of a 1 M NaOH solution containing 5wt% salicylic acid and 5 wt% sodium citrate, followed by addition of 1 mL of 0.05 M NaClO and 0.2 mL of an aqueous solution of 1 wt % $C_5FeN_6Na_2O$ (sodium nitroferricyanide). After 2 h at room temperature, the absorption spectrum was measured using an ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu UV-2700). The formation of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard ammonia sulfate solutions, as shown in Supplementary Fig. 24, which contained the same concentrations of electrolytes as used in the electrocatalysis experiments.

Determination of hydrazine (N_2H_4). The hydrazine presented in the electrolyte was estimated by the method of Watt and Chrisp[49]. A mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Calibration curve was plotted as follow: First, preparing a series of reference solutions, by pipetting suitable volumes of the hydrazine hydrate-nitrogen 0.1 M HCl solution in colorimetric tubes; Second, making up to 5 mL with diluted 0.1 M Na_2SO_4 electrolyte; Third, adding 5 mL above prepared color reagent and stirring 10 min at room temperature. Fourth, the absorbance of the resulting solution was measured at 457 nm, and the yields of hydrazine were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using hydrazine monohydrate solutions of known concentration as standards, and the fitting curve shows good linear relation of absorbance with $N_2H_4 \cdot H_2O$ concentration by three times independent calibrations (Supplementary Fig. 27).

Determination of nitrite ions (NO_2^-). The amounts of possible NO_2^- were quantified by ion chromatogram instrument (930 compact IC Flex, Metrohm).

Determination of formic acid (HCOOH). The amount of possible formic acid produced from CO_2 reduction was quantified by high-performance liquid chromatography (HPLC, Agilent 1260 Infinity) and ion chromatogram instrument (930 compact IC Flex, Metrohm).

Determination of carbon monoxide (CO), hydrogen (H_2) and dinitrogen (N_2). The amounts of CO, H_2 and N_2 was quantified by in-line gas chromatograph (7890B, Agilent) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FIDs).

Calculations of average urea yield rate and Faradaic efficiency. The average yield rate of urea was calculated as follows:

$$R_{urea} = (c_{urea} \times V)/(t \times m) \qquad (2)$$

where c_{urea} is the measured urea concentration (μg mL^{-1}), V is the total volume of electrolyte (mL), t is time (h) for electrocatalysis and m is the catalyst loadings (mg).

The Faradaic efficiency for urea electrosynthesis can be calculated using the following formula:

$$\text{Faradaic efficiency} = (16F \times c_{urea} \times V) / (60.06 \times Q) \qquad (3)$$

where F is the Faraday constant (96485.3 C mol^{-1}), Q is the total charge passed through the working electrode (C).

Calculations of average ammonia yield rate and Faradaic efficiency. The average yield rate of ammonia was calculated as follows:

$$R_{NH_3} = (c_{NH_3} \times V)/(t \times m) \qquad (4)$$

where c_{NH_3} is the measured NH_3 concentration (μg mL^{-1}), V is the total volume of electrolyte (mL), t is time (h) for NO_3^-RR and m is the catalyst loadings (mg).

The Faradaic efficiency for NO_3^-RR can be calculated using the following formula:

$$\text{Faradaic efficiency} = (8F \times c_{NH_3} \times V) / (17 \times Q) \qquad (5)$$

where F is the Faraday constant (96485.3 C mol^{-1}), Q is the total charge passed through the working electrode (C).

Calculations of N_{urea}-selectivity and C_{urea}-selectivity. The N_{urea}-selectivity was calculated as follows:

$$N_{urea}\text{-selectivity}= n_{urea}(N)/n_{total}(N) \qquad (6)$$

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

The C_{urea}-selectivity was calculated as follows:

$$C_{urea}\text{-selectivity}= n_{urea}(C)/n_{total}(C) \qquad (7)$$

where the $n_{urea}(C)$ represents the moles of carbon in as-produced urea, $n_{total}(C)$ represents the moles of carbon in total products from CO_2.

Computational method.

Spin-polarized density functional theory calculations were performed by using the projected augmented wave potential[50] as implemented in the Vienna *ab initio* simulation package (VASP)[51,52]. The generalized gradient approximation with the Perdew-Burke-Ernzerhof functional[53] was used to model the electronic exchange-correlation energy. A cut-off energy of 400 eV was set for plane-wave expansion. All structures were relaxed by the conjugate gradient method until remaining forces were less than 0.01 eV/Å, and the convergence criteria of total energy in the self-consistent field method was set to 10^{-5} eV. The simulated lattice constants of bulk $In(OH)_3$ and In_2O_3 were 8.05 Å and 10.30 Å, respectively. The slab model was used to simulate the {100} and {110} surfaces. The vacuum layer in the slab model is larger than 15 Å to avoid superficial interaction between periodical slabs. The k-point grids (<0.2 $Å^{-1}$) used for the Brillouin-zone integration were sampled by the Monkhorst-Pack scheme[54]. The adsorption free energies of reaction intermediates were calculated by using the computational hydrogen electrode (CHE) model developed by Nørskov et al[55]. Supplementary Fig. 67 shows the details of the computational models.

Data availability

All data that support the findings in this paper are available within the article and its Supplementary Information. Source data are available from the corresponding author upon reasonable request.

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Author contributions

G.Y. and Q.Y. conceived and directed the project. C.L. carried out key experiments and wrote the manuscript. L.Z. and S.L. performed theoretical calculations. H.L. and L.S. conducted operando SR-FTIR measurements. C.Y. carried out the design of catalysts. M.C., Y.K., J.L., C.L., D.L. conducted part of the characterizations. C.L., L.Z., Z.F., Q.Y., G.Y., G.C., L.S. and S.L. analysed the data. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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