

Boosting Reduction of CO₂ and Dimethylamine for C-N Bonding to Synthesizing DMF Via Modulating the Electronic Structures of Indium Single Atom

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Experimental Procedures

Synthesis of Indium single atom catalysts with different nitrogen coordination

(InN₄ and InN₃): Dissolve 5.6g of zinc nitrate and 0.2g of indium nitrate in 40ml of methanol and stir evenly. And dissolve 12.3g of dimethylimidazole in 40ml of methanol and stir for 3 hours to obtain ZIF-8. Slowly add the salt solution of zinc nitrate and indium nitrate dropwise to the solution of dimethylimidazole, stir for 12 hours, and centrifuge and filter. Take the filtered precipitate, vacuum dry for 12 hours, and grind the dried block shaped white solid into powder to obtain indium doped ZIF-8 powder. By controlling the calcination temperature, these white powders were subjected to high-temperature calcination to obtain indium single atom catalysts with different nitrogen coordination. Place the indium doped ZIF-8 powder sample into a covered crucible and place it flat in a tube furnace. Under the protection of a nitrogen atmosphere, raise the temperature at a rate of 5 °C min⁻¹ to 900 °C and hold for 3 hours, then cool naturally to room temperature to obtain In-N₄; Place indium doped ZIF-8 powder sample in a covered crucible and place it flat in a tube furnace. Under the protection of a nitrogen atmosphere, raise the temperature at a rate of 5 °C min⁻¹ to 1000 °C and hold for 3 hours. Cool naturally to room temperature to obtain an unsaturated coordinated indium nitrogen triple coordinated indium single atom In-N₃ catalyst

Material characterization and product detection

The X-ray diffraction (XRD, D8 Focus X-ray diffractometer, Bruker, Germany) was used to test the crystal structure of the catalyst, and the morphology of the catalyst was observed by high resolution transmission electron microscope (HR-TEM, JEM 2100). The elemental composition and chemical valence states of the InN₄ and InN₃ single atom catalysts were characterized using X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD). The extended X-ray absorption fine structure (EXAFS) of InN₃ and InN₄ was detected on the 14w beam line of the Shanghai Synchrotron Radiation Facility (SSRF). The BL14W1 line station uses 38 pole Wiggler inserts with a maximum magnetic field strength of 1.2T. The optical system of the line

station mainly includes a collimating mirror, a liquid nitrogen cooled bicrystal monochromator, a focusing mirror, and a harmonic suppression mirror. The monochromator we use is Si (311) crystal, which can test indium species. During the sample preparation process, we finely grind the sample with a mortar and evenly apply it onto the conductive tape. We place the prepared sample powder in the light window of the line station and adjust the position of the light window so that the light spot shines in the middle of the sample, which is beneficial for testing of synchrotron radiation. Differential electrochemical mass spectrometry (HPR-40 DEMS, Hiden Analytical Ltd) was used analysis of intermediates about synthesis of N, N-dimethylformamide from CO₂ and dimethylamine.

Electrochemical synthesis of N, N-dimethylformamide from CO₂ and dimethylamine

When preparing the electrochemical cathode, 2 mg of InN₄ or InN₃ single atom catalysts were added to 350 μ L ethanol and 50 μL Nafion (5%) were added to 600 μ L deionized water, and sonicated for 3 hours to mix evenly. Spin coat 100 μ L of the mixed sample onto a 1 cm x 1 cm carbon paper. Dry the prepared working electrode at 60 °C for 3 hours. The prepared electrode is the working electrode, platinum plate is used as the counter electrode, and saturated calomel electrode is used as the reference electrode. The electrocatalytic reduction of carbon dioxide and dimethylamine C-N coupled N-formylation to synthesize N, N-dimethylformamide was performed in a self-made reaction cell (6 mL electrolyte).

Reaction product detection

The product N, N-dimethylformamide (DMF) during the electrocatalytic reduction of CO₂ and dimethylamine was determined via high-performance liquid chromatography (HPLC, Aglient 1260) equipped with a C18 column (4.6 × 100 nm, 3.5 μm). The measurement method uses methanol and water as mobile phases (10:90), with a wavelength of 210 nm and a flow rate of 0.6 ml min⁻¹.

In-situ infrared spectroscopic measurements

The in-situ electrochemical infrared spectrometer (Nicolet 8700, Thermo Fisher Scientific Inc., USA) was used to detect the reaction intermediates of CO₂ and

dimethylamine C-N coupling to form N, N-dimethylformamide under different potential conditions. The voltage is regulated by the Chenhua CHI660 electrochemical workstation. Disperse InN_4 and InN_3 single atom catalyst powders (2 mg) ultrasonically in a mixture of 0.2 mL of water, ethanol, and Nafion in a volume ratio of 60:35:5. Drop the mixed sample (20 μL) onto a glassy carbon electrode and dry it at 60 °C for 3 hours. The electrochemical cathode, saturated calomel electrode (SCE), and 0.1 mm platinum wire were prepared as the working electrode, reference electrode, and counter electrode, respectively. In a saturated CO_2 solution of 0.1 M KHCO_3 + 0.1 M dimethylamine, the scanning potential range is -0.2 to -1.8 V, with a step size of -0.2 V, and real-time in-situ electrochemical infrared spectroscopy is detected.

Computational method

The Vienna Ab Initio Package (VASP)^{1, 2} was used to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation³. The ionic cores were described by the projected augmented wave (PAW) potentials^{4, 5}. We also take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn–Sham orbitals were accepted by the gaussian smearing method and a width of 0.05 eV. when the energy change was smaller than 10^{-5} eV, the electronic energy was considered self-consistent. When the force change was smaller than 0.02 eV \AA^{-1} , the geometry optimization was considered convergent. The dispersion interactions were described by Grimme’s DFT-D3 methodology⁶.

We constructed a graphene monolayer model using it, and optimized the equilibrium lattice constant of a hexagonal graphene unit cell separated by a vacuum layer at a depth of 15 \AA to $a=2.468$ \AA , with p (5 × 5) periodicity in the X and Y directions and a monolayer in the Z direction. This graphene model consists of 50 carbon atoms. Models 1 and 2 were constructed by doping graphene with InN_3 and InN_4 , respectively. The adsorption energy is: $E_{\text{ads}}=E_{\text{A/Surf}} - E_{\text{Surf}} - E_{\text{A (g)}}$, where $E_{\text{A/Surf}}$ is the energy of the adsorption system, E_{Surf} is the energy of the InN_4 or InN_3 indium single atom surface, and $E_{\text{A(g)}}$ is the energy of the free molecules CO_2 and

dimethylamine. If the E value is negative, it indicates that adsorption is an exothermic reaction. The transition state of the elementary reaction is determined by the NEB method, in which the pathway between reactants and products is discretized into five consecutive images, and the structure is optimized to a vertical force of less than 0.02 eV Å⁻¹. The free energy of gaseous molecules and surface adsorbates is calculated using the $G=E+ZPE-TS$ formula, where E is the total energy, ZPE is the zero point energy, T is the Fahrenheit temperature (currently 298.15K), and S is the entropy.

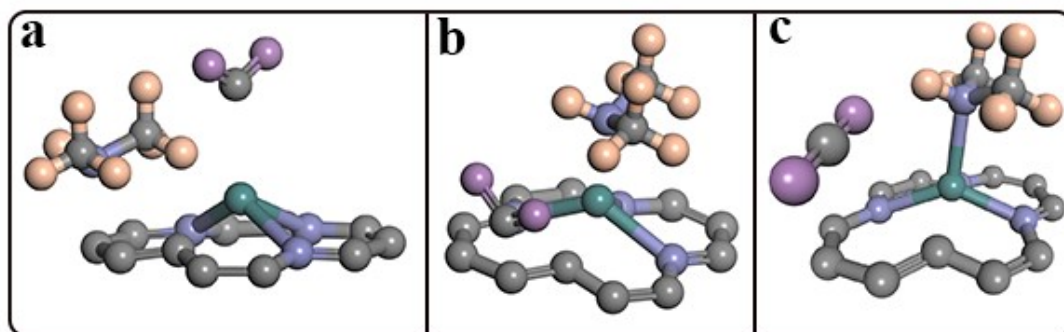


Fig. S1 adsorption configurations for CO₂ and dimethylamine on InN₃ in DFT calculations. (a) the guess configuration of that CO₂ adsorbed at the indium site and dimethylamine adsorbed at the nitrogen vacancy; (b) the guess configuration of CO₂ adsorbed near nitrogen vacancies and dimethylamine adsorbed at indium sites; (c) the optimized structure for CO₂ and dimethylamine on InN₃ in DFT calculations.

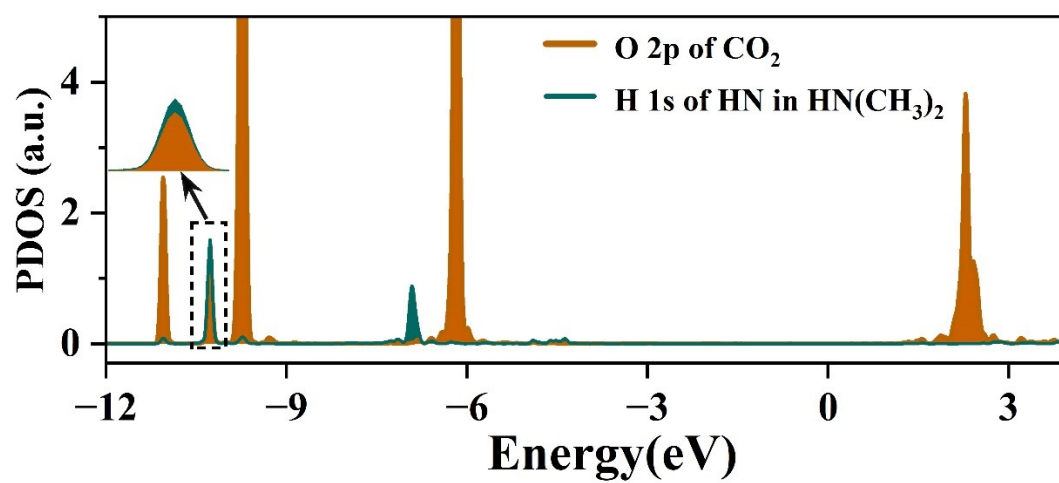


Fig. S2 PDOS for co-adsorption of HN(CH₃)₂ and CO₂ on InN₃ catalyst.

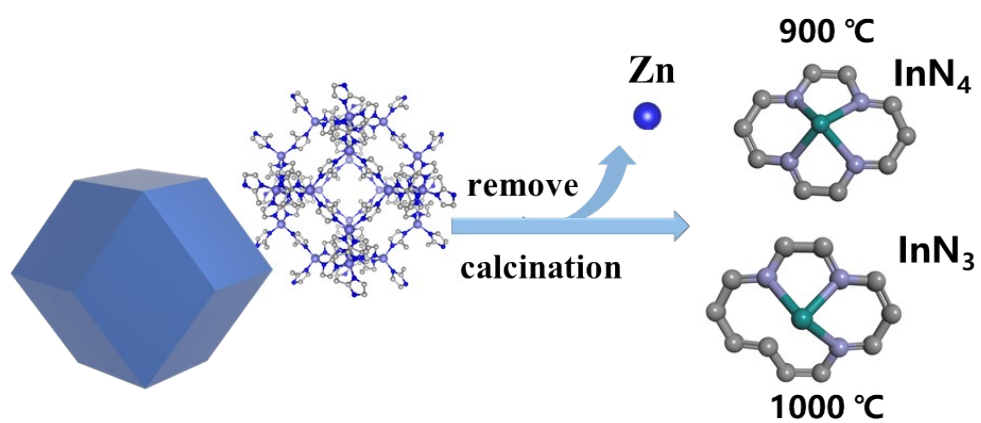


Fig. S3 Synthetic scheme of indium single-atom catalyst (InN_3 , InN_4)

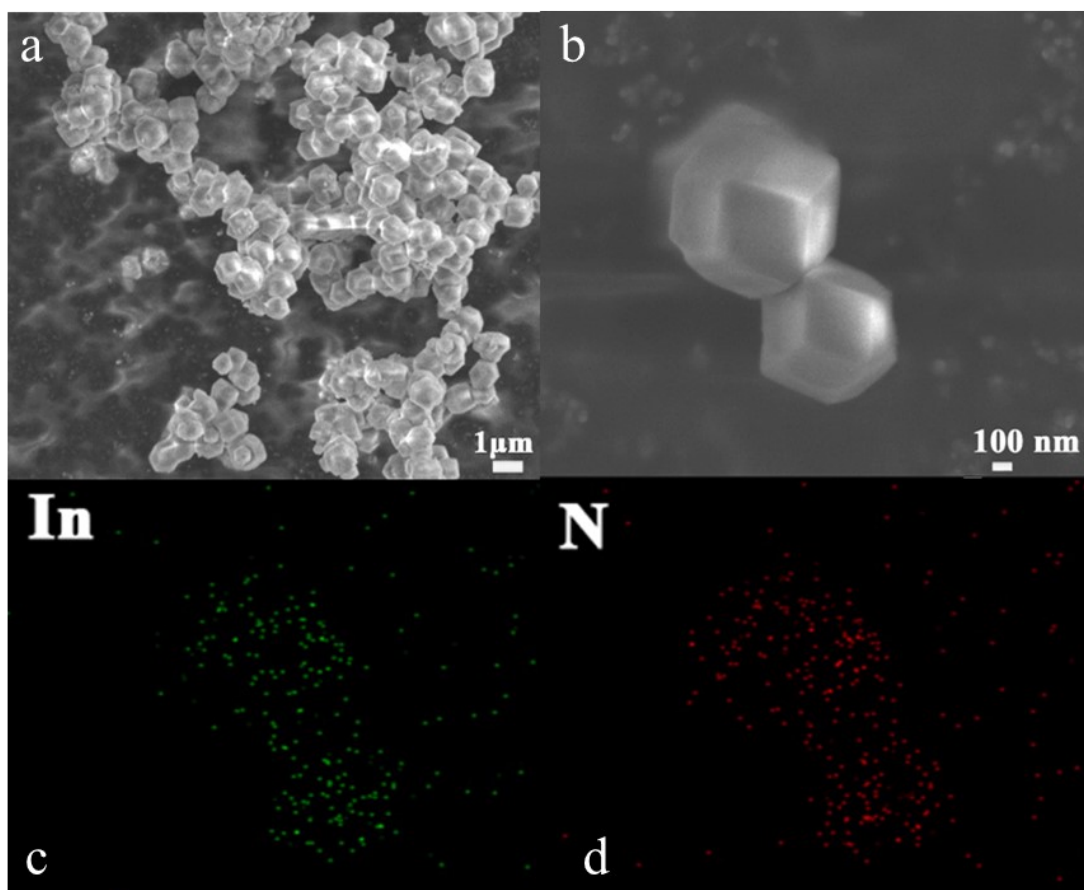


Fig. S4 Scanning electron microscopy images of nitrogen coordinated indium single atom InN_3 catalyst (a), (b); Energy dispersive X-ray spectroscopy (EDS) mapping of In and N elements in nitrogen coordinated indium single atom InN_3 (c), (d).

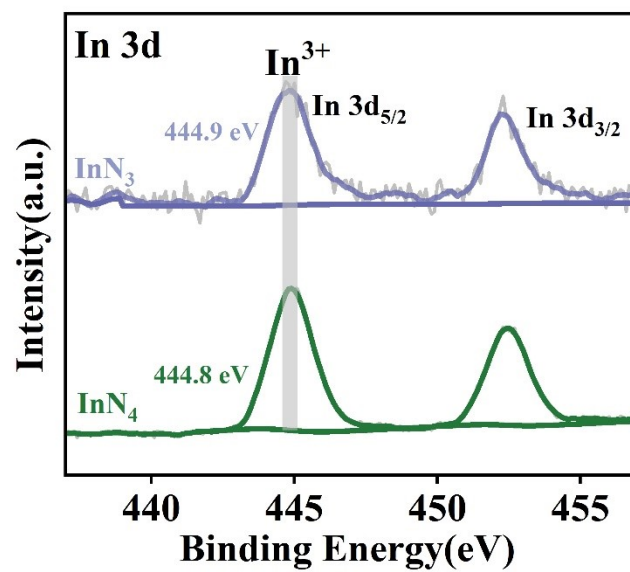


Fig. S5 XPS of In 3d spectra in single atom catalysts InN₃ and InN₄

Table S1 K-edge EXAFS data fitting results of In on InN₃ and InN₄

Calcination temperature (°C)	shell	CN ^a	R (Å) ^b	$\sigma^2(10^{-3}\text{Å}^2)$ ^c	R factor ^d
900	In-N	4	2.16	3.5	0.0064
1000	In-N	3	2.10	3.2	0.0192

a CN: coordination numbers.

b R (Å): bond distance.

c $\sigma^2(10^{-3}\text{Å}^2)$: Debye-Waller factors.

d R factor: goodness of fit.

After calcination of indium doped ZIF-8 material at 900 °C, InN₄ material was obtained. The indium atom is coordinated with four nitrogen atoms, and the bond length of In-N bond was 2.16 Å. The goodness of fit is 0.0064. After calcination of indium doped ZIF-8 material at 1000 °C, the material obtained is InN₃. The indium atom is coordinated with three nitrogen atoms, and the bond length of In-N bond is 2.10 Å. The goodness of fit is 0.0192. Through the R factor of the two materials, it can be found that the quality of our data fitting is good.

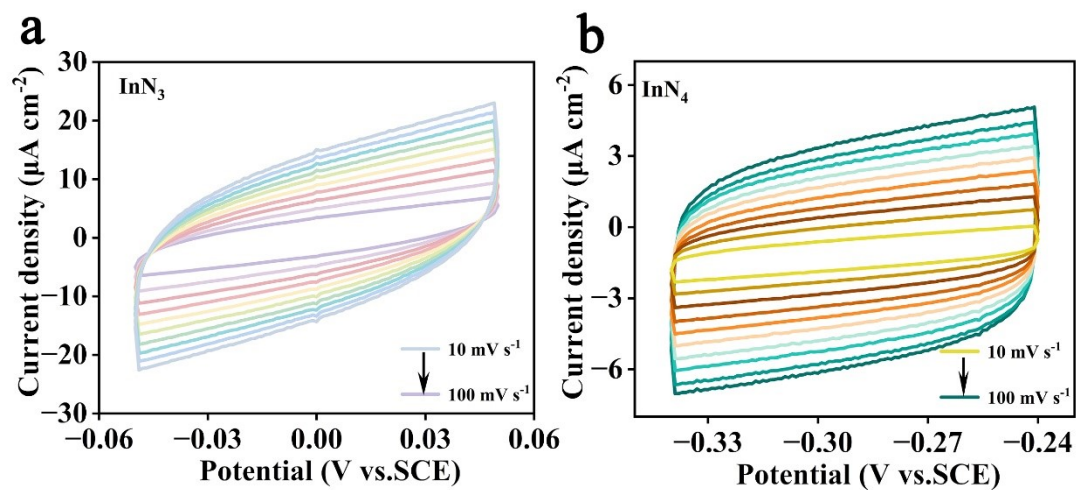


Fig. S6 Cyclic voltammograms of InN_3 and InN_4 electrodes at non Faradaic potentials.

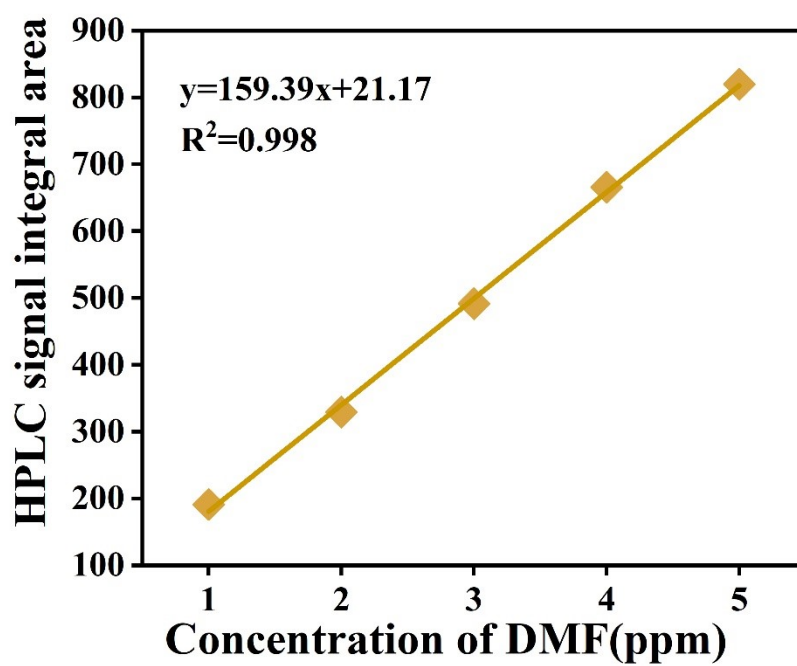


Fig. S7 calibration curves for quantification of N, N-dimethylformamide (DMF) via HPLC.

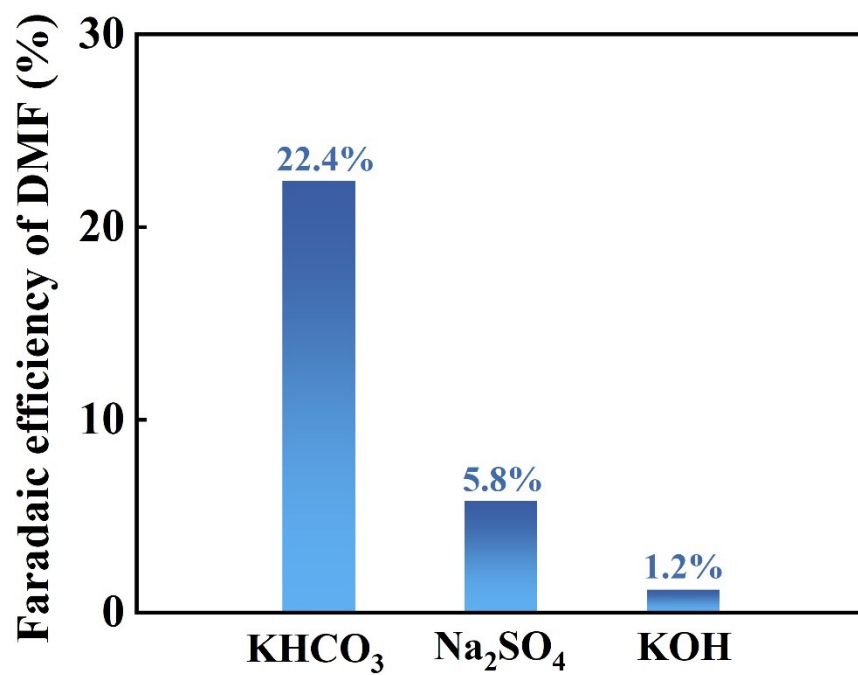


Fig. S8 Faradaic efficiency of different electrolyte solutions for the synthesis of DMF from CO_2 and dimethylamine via InN_3 .

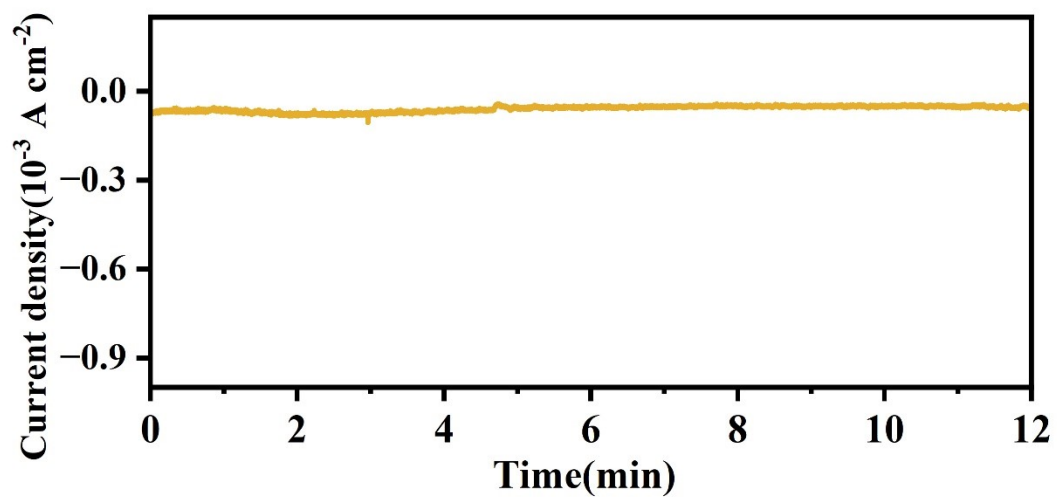


Fig. S9 Chronoamperometric curves for electrocatalytic synthesis of DMF from CO₂ and dimethylamine under -0.8 V over InN₃.

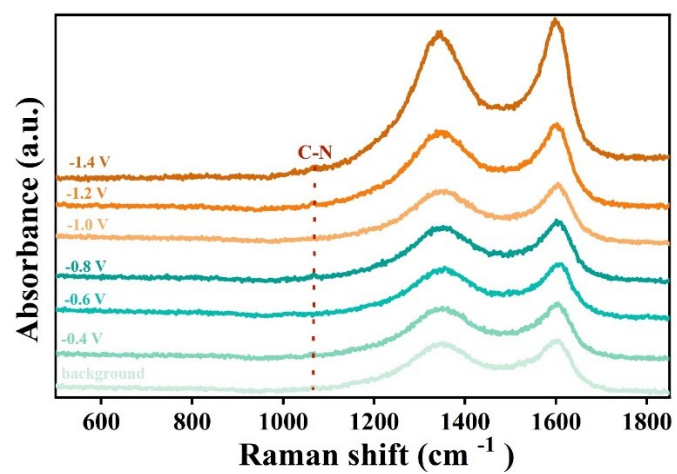


Fig. S10 In situ Raman spectra of InN₄ for electrocatalytic reduction of CO₂ and dimethylamine to synthesize DMF.

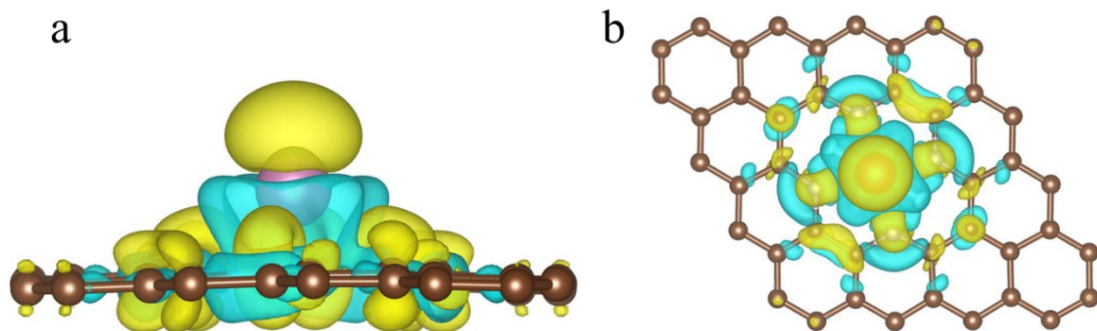


Fig. S11 Charge density difference of InN_3 . Accordingly, electron accumulation and depletion regions are indicated by yellow and cyan, respectively.

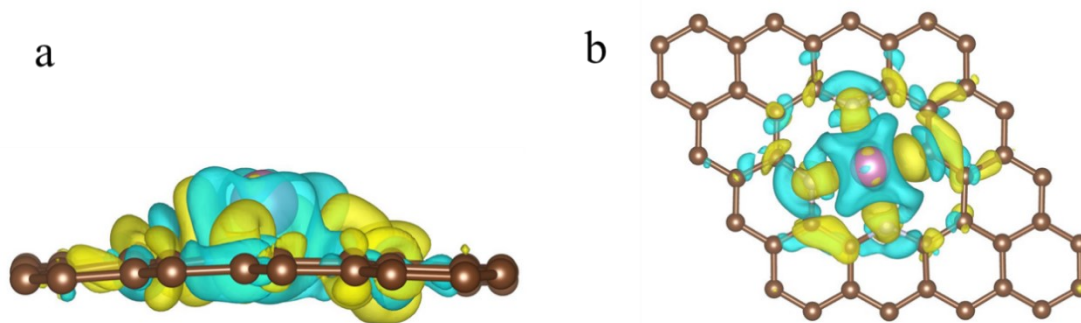


Fig. S12 Charge density difference of InN_3 . Accordingly, electron accumulation and depletion regions are indicated by yellow and cyan, respectively.

Notes and references

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