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Electrochemical C-N coupling with perovskite hybrids toward efficient urea synthesis

In this work, Zhang *et al.* proposed a unique ultrasonic bath method to fabricate perovskite structural $\text{BiFeO}_3/\text{BiVO}_4$ hybrids. The local charge redistribution in $\text{BiFeO}_3/\text{BiVO}_4$ hybrids promotes the targeted adsorption and activation of inert N_2 and CO_2 molecules and further electrochemical C-N coupling reactions to form urea with high efficiency. The authors appreciate the help from Chinese artist, Miss Lina Zhao, for the designing of this cover image.

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Electrochemical C–N coupling with perovskite hybrids toward efficient urea synthesis†

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Electrocatalytic C–N coupling reaction by co-activation of both N₂ and CO₂ molecules under ambient conditions to synthesize valuable urea opens a new avenue for sustainable development, while the actual catalytic activity is limited by poor adsorption and coupling capability of gas molecules on the catalyst surface. Herein, theoretical calculation predicts that the well-developed built-in electric field in perovskite hetero-structured BiFeO₃/BiVO₄ hybrids can accelerate the local charge redistribution and thus promote the targeted adsorption and activation of inert N₂ and CO₂ molecules on the generated local electrophilic and nucleophilic regions. Thus, a BiFeO₃/BiVO₄ heterojunction is designed and synthesized, which delivers a urea yield rate of 4.94 mmol h^{−1} g^{−1} with a faradaic efficiency of 17.18% at −0.4 V vs. RHE in 0.1 M KHCO₃, outperforming the highest values reported as far. The comprehensive analysis further confirms that the local charge redistribution in the heterojunction effectively suppresses CO poisoning and the formation of the endothermic *NNH intermediate, which thus guarantees the exothermic coupling of *N=N* intermediates with the generated CO via C–N coupling reactions to form the urea precursor *NCON* intermediate. This work opens a new avenue for effective electrocatalytic C–N coupling under ambient conditions.

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1 Introduction

Nitrogen (N₂), accounting for 78% of the atmosphere, exists in the gaseous form that can't be directly utilized in biology and chemistry fields.^{1–3} On the other hand, carbon dioxide (CO₂) generated from industries and transportation is the principal greenhouse gas causing serious environmental concerns.^{4–8} Thus, converting N₂ and CO₂ into value-added fuels and chemical products via the C–N coupling reaction is a promising approach for not only mitigating environmental issues and energy crisis but also high-value utilization of N₂ and CO₂.^{9–12}

However, the highly stable double-bond (C=O, 806 kJ mol^{−1}) in CO₂ molecules and the triple-bond (N≡N, 940.95 kJ mol^{−1}) in N₂ molecules make the inert gas molecules difficult to activate mildly.^{13–17} Although conventional industrial processes such as the Haber–Bosch method and carbon capture and sequestration achieve the activation of inert gas molecules, their further utilization is impeded by the large energy consumption and complex synthetic processes.^{18–22} In comparison, energy-saving and environmentally benign electrocatalysis technologies such as the nitrogen reduction reaction (NRR) and the carbon dioxide reduction reaction (CO₂RR) are drawing growing attention.^{23–30} Besides, the emerged electrochemical C–N coupling reaction may provide a new possibility of enhancing the spectrum of products of CO₂ by using CO₂ and amine derivatives/nitrogen sources (nitrate, nitrite, NO, and even N₂) as feedstock.^{9,31,32}

The desired product urea [CO(NH₂)₂] will be produced when the electrochemical C–N bond formation occurs by employing both N₂ and CO₂ as the feeding gas.⁹ Urea is commonly utilized as the general feedstock in industry and the primary fertilizer for agriculture.^{33,34} The industrial urea synthesis proceeds by two consecutive processes, including N₂ + H₂ → NH₃ followed by NH₃ + CO₂ → CO(NH₂)₂, which operate under harsh reaction conditions (350–550 °C, 150–350 bar and 150–200 °C, 150–250 bar, respectively).³⁵ Compared with the complex industrial synthetic process, simultaneous electrocatalytic fixation of N₂ and CO₂ driven by a renewable energy source under ambient

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conditions provides a clean route for urea production.⁹ The main issues in electrochemical synthesis of urea lie in three aspects: (1) extraordinarily weak chemical adsorption of inert CO₂/N₂ on the catalysts surface;^{29,30,36,37} (2) the dissociation of the highly stable C=O bond and N≡N bond requires high overpotential;^{13,15} (3) the parallel reaction of CO₂/N₂ reduction suppresses the efficiency of C–N coupling and strongly competes with the desired urea formation reaction, further resulting in a large distribution of complex products.⁹

Although a few noble metal Pd-based catalysts can achieve urea electrosynthesis, the related catalytic activity showed a maximum urea yield rate of 3.36 mmol h^{−1} g^{−1} with a FE of 8.92%.⁹ Besides, the high price and scarcity of the used noble metals impede their real application on the large scale. Thus, further improvement of the catalytic activity with earth-abundant materials remains a challenge. Inspired by the different electronic structures of N₂ and CO₂ molecules, tuning the electronic state of the electrocatalyst's surface can be a feasible strategy to optimize the adsorption of reactant gas molecules and suppress the competing electro-reduction reactions to promote urea generation. In this regard, fabricating a built-in electronic field to accelerate the local charge redistribution in perovskite heterostructures displays fascinating potential to deliver impressive urea electroproduction activity. On the one hand, perovskite structured transition-metal oxide (ABO₃) semiconductors possess a distinctive electronic structure, which can lead to the alteration of electron density when combining with other domains.^{38,39} On the other hand, the work function difference in perovskite heterostructures drives the local charge redistribution by the band bending at the heterointerface, which is preferred for targeted adsorption and activation of inert small molecules such as N₂, CO₂, H₂O, and so on.⁴⁰ Despite the encouraging merits, inducing the local charge redistribution in perovskite hybrids toward the specific urea electrosynthesis hasn't been explored.

In this work, with the aid of theoretical simulation, we exploited perovskite structured p-type BiFeO₃ and an n-type semiconductor BiVO₄ to fabricate innovative p–n heterojunction electrocatalysts, aiming at enabling spontaneous electron transfer at the heterointerfaces by the desirable built-in electric field. The obtained perovskite structured BiFeO₃/BiVO₄ showed high electrocatalytic activity toward the C–N coupling reaction to synthesize urea, and exhibits a FE of 17.18% in 0.1 M KHCO₃ at −0.4 V vs. RHE. The urea yield rate can reach 4.94 mmol h^{−1} g^{−1} which is much higher than the recently reported best values with Pd-based electrocatalysts. The activity can further be improved by adding an ionic liquid to the electrolyte. The generated local electrophilic and nucleophilic regions enhanced the targeted adsorption and activation of inert N₂ and CO₂ molecules and balanced the competing electro-reduction reactions to further promote the formation of the *NCON* intermediate *via* the C–N bond coupling reaction. Thus, engineering a built-in electric field to facilitate local charge redistribution has been proposed as an appealing strategy to enhance electrocatalytic C–N bond coupling and further urea synthesis.

2 Results and discussion

Conspicuously, the charged surface can give rise to a significant effect on the targeted adsorption of reactant molecules.³⁰ In this regard, constructing built-in fields at the heterointerface to promote a spontaneous electron transfer process will supply more possibilities for generating desirable two opposite charged regions.⁴¹ This design concept has been confirmed by the investigation of various perovskite-based semiconductor catalysts, which can constitute distinct p–n junctions and thus accelerate local charge redistribution at the heterointerface.⁴⁰ The band theory of solids has confirmed that the behavior of electron transfer is strongly correlated to the work function of semiconductors.⁴² As presented in Fig. 1a and b, the theoretical simulation results showed that the work function values of BiVO₄ and BiFeO₃ were 3.23 eV and 6.30 eV, respectively, which allow self-driven electron transfer from BiVO₄ to BiFeO₃. The profile of the planar averaged electrostatic potential along the z-direction for BiFeO₃/BiVO₄ hybrids is depicted in Fig. 1c. Compared with pristine BiVO₄ and BiFeO₃ that possess periodic lattice potential, BiFeO₃/BiVO₄ hybrids showed a big built-in potential at the interfaces. Additionally, electron density difference calculation was further performed to reveal the charge distribution at the interface of BiFeO₃/BiVO₄ hybrids. As described in Fig. 1d, the charge depletion and accumulation are represented by the cyan region and yellow region, respectively. An increase of the charge density was observed at the BiFeO₃ surface and a decrease at the BiVO₄ surface, which confirmed that the spontaneous electron transfer induced the local charge redistribution around the interface and endowed the surfaces of BiFeO₃ and BiVO₄ with local nucleophilic and electrophilic regions. Bader analysis results further demonstrate that BiVO₄ can transfer 2.33 electrons to BiFeO₃. Previous research has proven that the chemisorption of inert CO₂ and N₂ is the initial step for electrocatalytic urea production. As shown in Fig. S1,† the N atom in the N₂ molecule and the C atom in the CO₂ molecule are electron-rich and electron-deficient, respectively. Therefore, it can be deduced that the rationally designed BiFeO₃/BiVO₄ hybrids with local nucleophilic and electrophilic regions would adsorb targeted reactant molecules by electrostatic interaction. To confirm the above hypothesis, density functional theory (DFT) calculations were performed to reveal the gas adsorption behavior on the surface of the electrocatalyst. As expected, the calculated adsorption energies of BiFeO₃/BiVO₄ hybrids for N₂ and CO₂ are −0.17 eV and −0.06 eV, much lower than those of individual architectures of BiFeO₃ and BiVO₄ (Fig. 1e and f), proving that N₂ and CO₂ show a stronger tendency to adsorb on the surface of BiFeO₃/BiVO₄ hybrids than on pristine BiFeO₃ and BiVO₄ due to the interfacial interaction triggered by the well-defined space-charge region, which is favorable for much readily chemisorbing inert gas molecules and thus facilitating the electrocatalytic urea production process.

As a proof-of-concept experiment, perovskite structured BiFeO₃/BiVO₄ hybrids were designed and synthesized by the facile ultrasonic bath method. The field-emission scanning

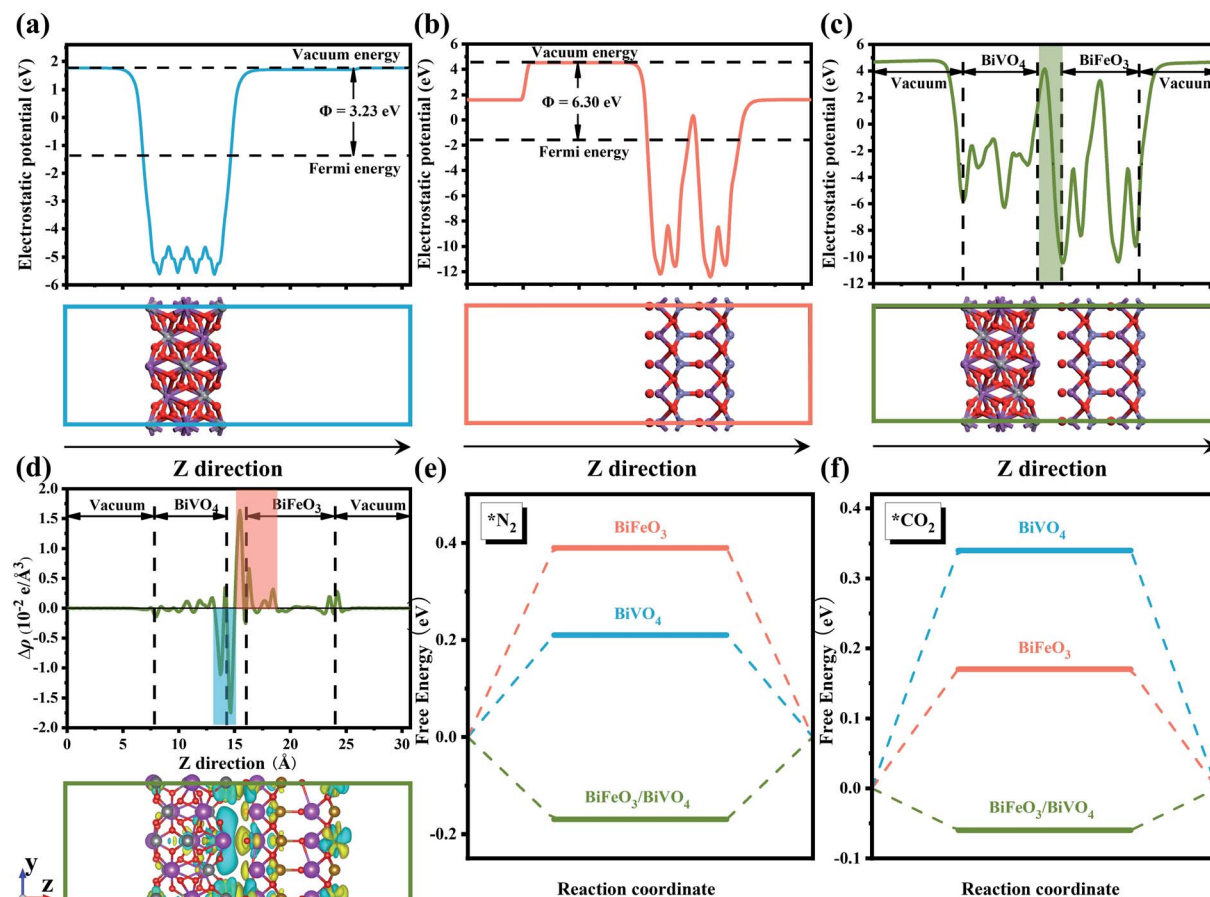


Fig. 1 The calculated electrostatic potentials and work functions for (a) BiVO₄, (b) BiFeO₃ and (c) BiFeO₃/BiVO₄ heterojunction surfaces; (d) planar average charge density difference along the z-direction for the BiFeO₃/BiVO₄ heterojunction, the bottom image shows the charge density difference of the BiFeO₃/BiVO₄ heterojunction, the yellow and cyan color indicate electron accumulation and depletion, respectively, with an isosurface value of 0.013 e Å⁻³; free energy diagrams for (e) N₂ and (f) CO₂ adsorption on BiFeO₃, BiVO₄ and the BiFeO₃/BiVO₄ heterojunction.

electron microscopy (FE-SEM) image in Fig. 2a reveals that BiFeO₃/BiVO₄ heterostructures possess a rice-like morphology with an average length of 1 μm and a diameter of approximately 400 nm, respectively. The relevant elemental mapping demonstrates the evenly distributed Bi, Fe, V, and O elements. In comparison, pristine BiVO₄ still maintains the same morphology as heterostructured hybrids (Fig. 2c), whereas the BiFeO₃ displays an irregular nanoparticle structure (Fig. 2b). As surveyed by high-resolution transmission electron microscopy (HR-TEM), the well-resolved lattice fringes of 0.282 nm and 0.312 nm corresponded to the (104) plane and (130) plane of BiFeO₃ and BiVO₄ crystals (Fig. 2e). Meanwhile, the distinct interface generated by the intimate contact of BiFeO₃ and BiVO₄ confirms the representative establishment of nanoscale heterostructures (Fig. 2d).

In Fig. 3a and b, the XRD spectra show that the hexagonal BiFeO₃ structure (JCPDS: 86-1518) and monoclinic BiVO₄ phase (JCPDS: 83-1700) can be obtained in pristine BiFeO₃ and BiVO₄ samples. Concerning BiFeO₃/BiVO₄ hybrids, both sets of diffraction peaks are consistent with those of pristine samples, except for the slight shift of the characteristic peaks of BiFeO₃ and partial peaks of BiVO₄ to higher diffraction angles (Fig. 3c),

which indicates the possible interaction between the two distinct domains.^{43,44} As further revealed by Mott-Schottky (M-S) curves, BiFeO₃ with a negative slope (Fig. 3d) and BiVO₄ with a positive slope (Fig. 3e) matched well with the apparent characteristics of a p-type and an n-type semiconductor, respectively. In comparison, the as-prepared BiFeO₃/BiVO₄ hybrids exhibited evident p-n heterojunction features (Fig. 3f), which furnish the rational architecture to achieve the desired local charge redistribution by the above theoretical prediction. In Raman spectra (Fig. 4a), the typical vibrational bands at 137 and 171 cm⁻¹ represent the Fe-O-Fe bonds of the BiFeO₃ sample,^{45,46} whereas they exhibit a slightly negative shift accompanied by an intensity decrease when coupled with BiVO₄ domains. Likewise, the detected V-O stretching modes (637, 702, and 826 cm⁻¹) and VO₄³⁻ tetrahedron bending modes (327 and 367 cm⁻¹) also negatively shifted after the establishment of the heterostructure with the space-charge region.⁴⁷⁻⁴⁹ This broadening of vibrational modes and position shifting in BiFeO₃/BiVO₄ hybrids manifest the intense coupling interaction between BiFeO₃ and BiVO₄.^{50,51} Besides, compared to the UV-Vis spectrum of pristine samples, the dominant peak in BiFeO₃/BiVO₄ hybrids exhibited an obvious blue shift, evidencing the

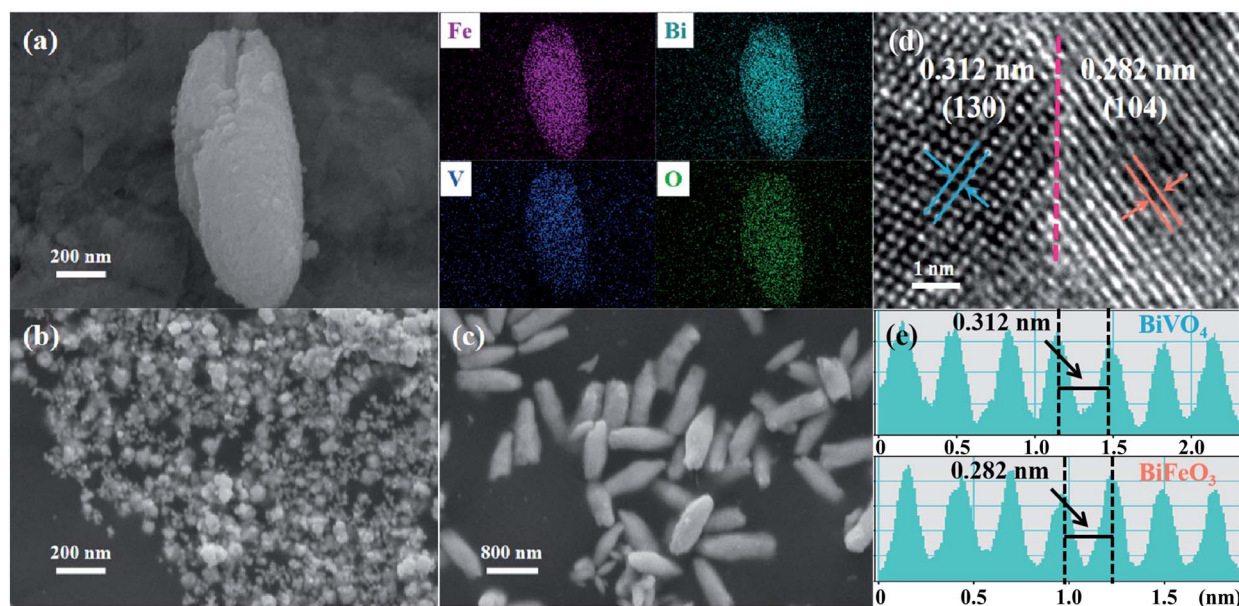


Fig. 2 (a) SEM image and the corresponding elemental mapping of BiFeO₃/BiVO₄ hybrids; SEM images of (b) BiFeO₃ and (c) BiVO₄; (d) high-resolution TEM image of BiFeO₃/BiVO₄ hybrids and the dotted line represents the heterointerfaces; (e) the well-resolved lattice fringe of BiFeO₃/BiVO₄ hybrids in Fig. 2d.

existence of the charge transfer effect (Fig. 4b).⁵² To further reveal the electronic effects between BiFeO₃ and BiVO₄, the chemical components and the alteration of valence states in the formed catalysts were further examined by X-ray photoelectron spectroscopy (XPS). The survey spectra, displayed in Fig. 4c,

illustrate the presence of Bi, Fe, V, and O elements in the obtained electrocatalysts, which is consistent with the above SEM characterization. The high-resolution Bi 4f spectrum displayed two predominant peaks of Bi³⁺ 4f_{7/2} and Bi³⁺ 4f_{5/2} at the binding energies of 159.3 eV and 164.7 eV (Fig. 4d).^{53,54}

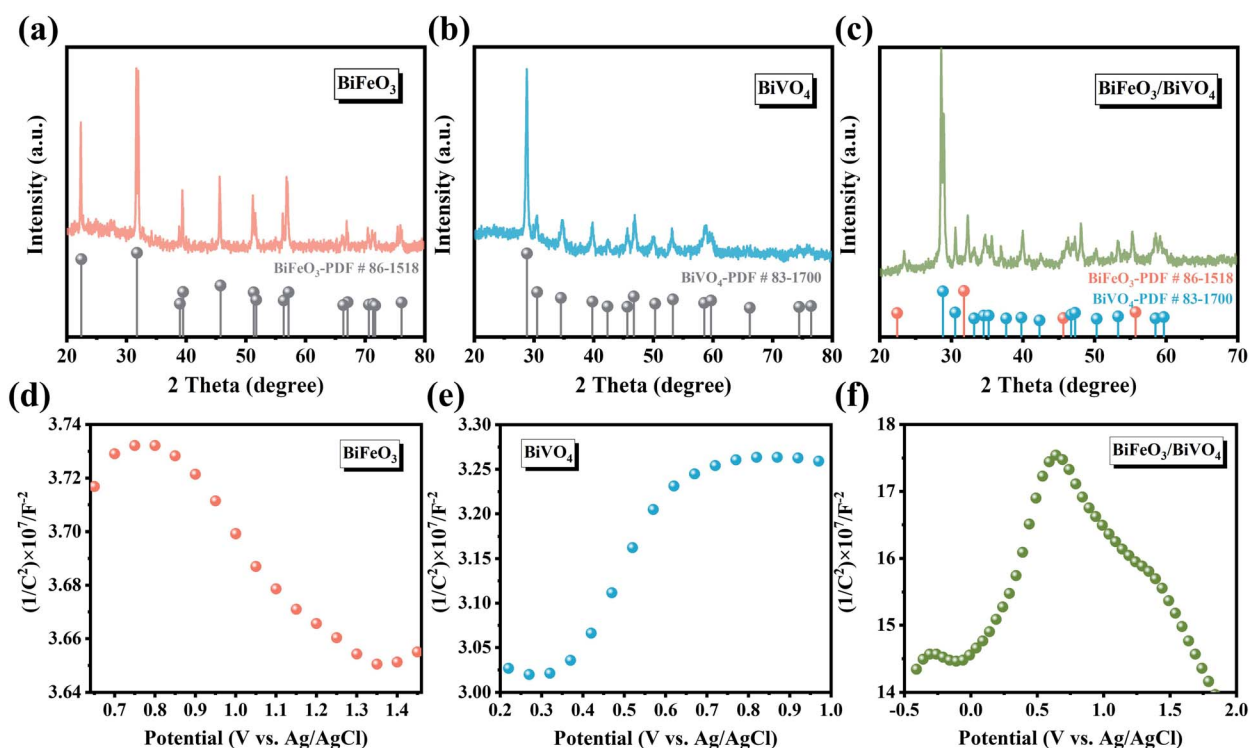


Fig. 3 XRD patterns of (a) BiFeO₃, (b) BiVO₄ and (c) BiFeO₃/BiVO₄; Mott-Schottky plots of (d) BiFeO₃, (e) BiVO₄ and (f) BiFeO₃/BiVO₄.

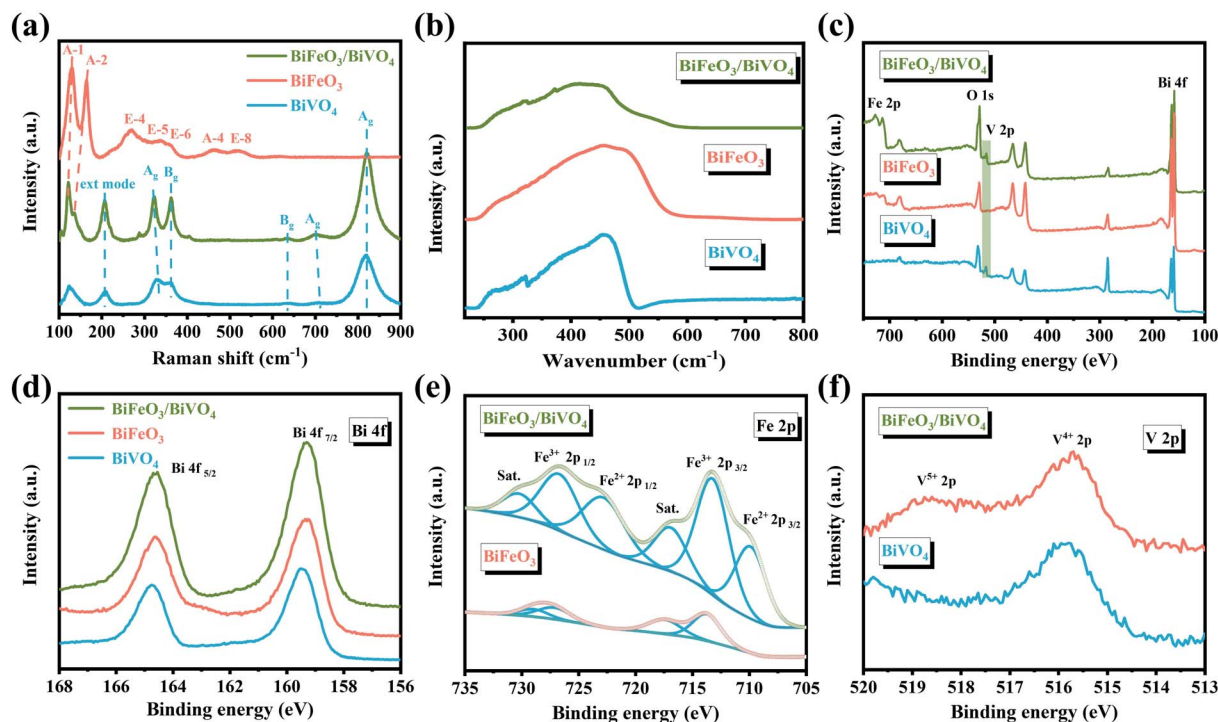


Fig. 4 (a) Raman spectra, (b) UV-Vis spectra, (c) XPS survey spectrum and (d) high-resolution Bi 4f spectrum of BiFeO₃, BiVO₄ and BiFeO₃/BiVO₄; (e) high-resolution Fe 2p spectrum of BiFeO₃ and BiFeO₃/BiVO₄; (f) high-resolution V 2p spectrum of BiVO₄ and BiFeO₃/BiVO₄.

Besides, two distinct peaks centered at 713.4 eV and 726.9 eV in the Fe 2p region can be attributed to the binding energies of Fe³⁺ 2p_{3/2} and Fe³⁺ 2p_{1/2}, respectively (Fig. 4e).^{55,56} And the XPS peak positioned at 515.8 eV in the V 2p spectrum illustrates the presence of V⁴⁺ (Fig. 4f). It is noteworthy that when BiFeO₃ was coupled with BiVO₄, the emerged new peaks in BiFeO₃/BiVO₄ hybrids are assigned to Fe²⁺ 2p and V⁵⁺ 2p peaks in contrast to pristine samples, elucidating that the apparent electronic interactions between BiFeO₃ and BiVO₄ domains are due to the formation of p-n heterojunctions.^{57,58} More importantly, the related changes in the valence state further demonstrate that the charge transferred from BiVO₄ to BiFeO₃. All these results convincingly suggest the successful establishment of unique p-n heterojunctions and the transfer of electrons between BiVO₄ and BiFeO₃. The induced local charge redistribution contributes to the targeted adsorption of reactant molecules and thus enhances the electrocatalytic urea production ability.

The electrocatalytic activity of BiFeO₃/BiVO₄ hybrids for the C-N coupling reaction toward urea production was tested in a 0.1 M KHCO₃ solution utilizing an H-type two-compartment cell separated by a Nafion 211 membrane, which is equipped with a three-electrode configuration (Fig. S2†). Ultrahigh purity CO₂ gas (99.999%) and N₂ gas (99.999%) were continuously purged into the cathodic chamber with the same flow rate of 5 mL min⁻¹ during the electrolysis process. The possibly generated liquid products (urea and NH₃) in the electrolytes were spectrophotometrically measured by the diacetyl monoxime method and indophenol blue method.^{22,59} Meanwhile, the related calibration curves are displayed in Fig. S3.† Besides,

online gas chromatography monitored the possible gas products such as CO and H₂. It has been reported that the electrochemical catalytic activity of the C-N coupling reaction for urea production was dominant as a result of effectively coupling the carbon dioxide reduction reaction (CO₂RR) with the nitrogen reduction reaction (NRR). As displayed in Fig. 5a and b, the BiFeO₃/BiVO₄ hybrids possess a high NH₃ faradaic efficiency (FE) (12.81%) for the NRR and CO FE (20.21%) for the CO₂RR, which establish the baseline of N₂ and CO₂ reduction activity. The linear sweep voltammetry curves (LSV) were initially examined in 0.1 M KHCO₃ saturated with different gas feeds (Ar, CO₂, N₂, or CO₂ + N₂). As depicted in Fig. 5c, the distinctly enhanced current density in CO₂ + N₂ saturated electrolyte relative to that in CO₂ and N₂, respectively, indicates the occurrence of the electrocatalytic C-N coupling reaction for urea production. A potentiostatic experiment was further performed to quantitatively assess the performance of electrocatalytic urea production of BiFeO₃/BiVO₄ hybrids at different working potentials. As shown in Fig. S4,† the corresponding chronoamperometry curves within the potential range of -0.3 V to -0.7 V exhibit stable current density after electrolysis for 2 h. As demonstrated in Fig. 5d, the urea yield rate and the corresponding FE increase with the increase of applied potential. The highest urea yield rate is 4.94 mmol h⁻¹ g⁻¹ with a FE of 17.18% at -0.4 vs. the reversible hydrogen electrode (RHE), outperforming all the reported values for Pd based catalysts (Table S1†). However, at more negative potentials, the electrocatalytic urea production performance decreases, which may result from the occupation of the active sites for N₂ and CO₂

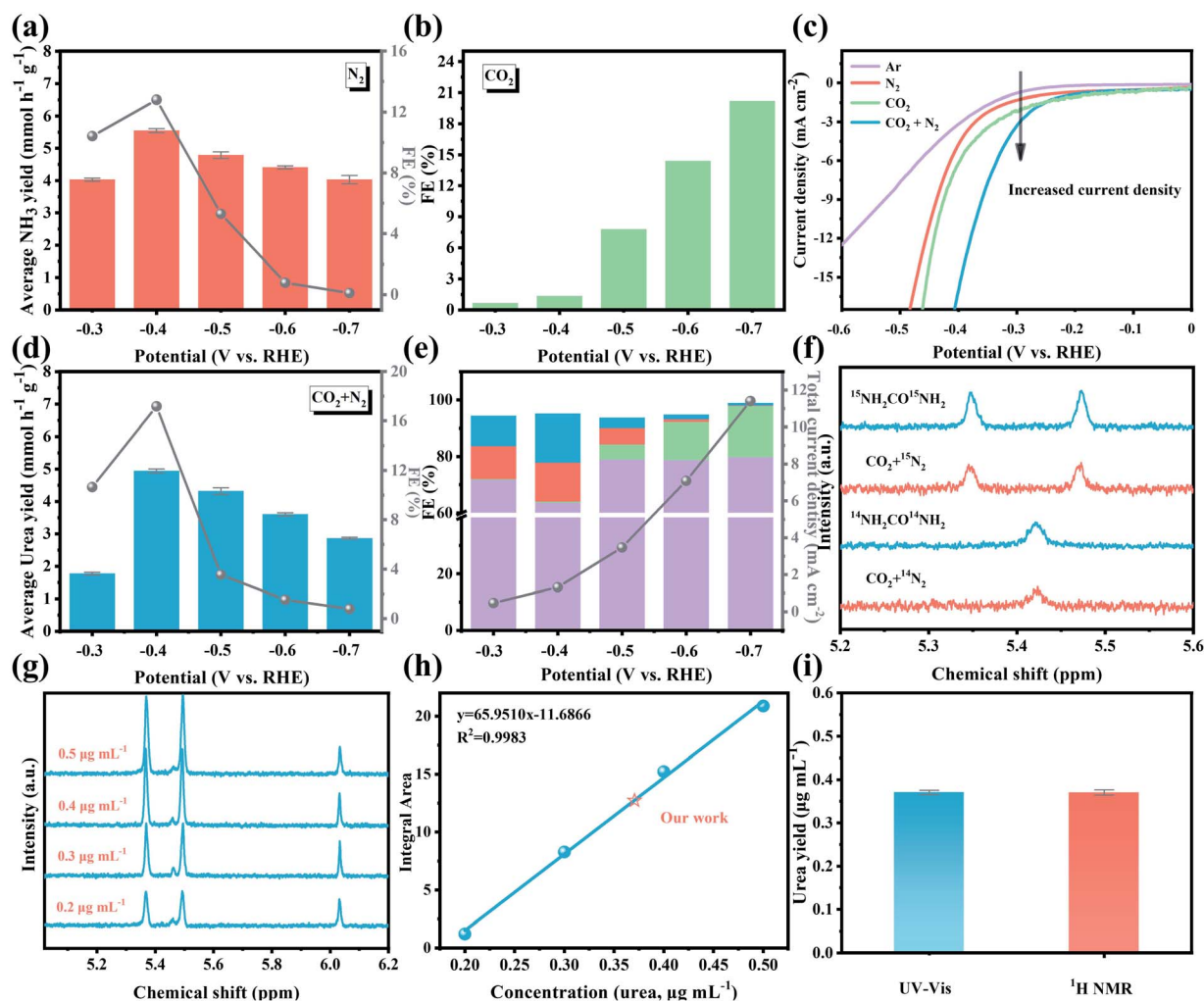


Fig. 5 (a) NH₃ synthesis with N₂ as the feed gas and (b) CO generation with CO₂ as the feed gas at various potentials for BiFeO₃/BiVO₄ hybrids; (c) LSV curves of BiFeO₃/BiVO₄ hybrids in Ar, N₂, CO₂ and N₂ + CO₂ saturated electrolyte; (d) the urea yield rate and faradaic efficiencies and (e) the corresponding product distribution of H₂ (purple color), CO (cyan-blue color), NH₃ (red color) and urea (blue color) for urea production with N₂ and CO₂ as the feed gas at various potentials for BiFeO₃/BiVO₄ hybrids; (f) ¹H NMR spectra of electrolyte saturated with ¹⁵N₂ + CO₂/¹⁴N₂ + CO₂ after 2 h of electrolysis and standard ¹⁵NH₂CO¹⁵NH₂/¹⁴NH₂CO¹⁴NH₂ solution; (g) ¹H NMR spectra of standard ¹⁵NH₂CO¹⁵NH₂ solution at concentrations of 0.2–0.5 μg mL⁻¹; (h) integral area (¹⁵NH₂CO¹⁵NH₂/C₄H₄O₄)–concentration linear relation calibrated using standard ¹⁵NH₂CO¹⁵NH₂ solution; (i) the urea yield of BiFeO₃/BiVO₄ hybrids after 2 h of electrolysis determined using the UV-Vis spectrum and ¹H NMR spectra.

reduction by the excessively released CO (Fig. 5e). Additionally, the as-obtained BiFeO₃/BiVO₄ hybrids retain 96% of the initial current density after a 10 h long-term chronopotentiometry test (Fig. S5†). Likewise, when conducting five cycling tests, negligible change is observed in the electrocatalytic urea production performance (Fig. S6†), attesting to the superior electrocatalytic stability of BiFeO₃/BiVO₄ hybrids. The corresponding characterization studies further reveal that the BiFeO₃/BiVO₄ hybrids were well-matched with their original morphology, crystal phase, and chemical states after 10 h of continuous electrolysis (Fig. S7†), corroborating their robust structural stability. Impressively, with the aid of enhanced CO₂ adsorption capacity of an ionic liquid,⁶⁰ when the 1-butyl-3-methylimidazolium tetrafluoroborate–KHCO₃ ([Bmim]BF₄–KHCO₃) electrolyte was used in the system, a higher electrocatalytic activity for urea production is achieved (FE: 20.75%, urea yield rate: 5.42 mmol

h⁻¹ g⁻¹) than that obtained in pristine KHCO₃ solution at the same potential (Fig. S8†).

To gain solid proof that the produced urea originated from the C–N coupling reaction with CO₂ and N₂, a rigorous protocol was employed to avoid false-positive results caused by the contamination of environmental NO_x (Fig. S9†). Under all the control experiment conditions, negligible urea was detected, which excludes the possible effect of environmental NO_x on the urea electrosynthesis (Fig. S10†). ¹⁵N₂ isotopic labeling experiment was further utilized to corroborate the N source of the generated urea [CO(NH₂)₂]. The standard CO(¹⁵NH₂)₂ sample displays two dominant peaks at approximately 5.35 ppm and 5.47 ppm in ¹H Nuclear Magnetic Resonance (NMR) (Fig. 5f), while the standard CO(¹⁴NH₂)₂ sample possesses one distinct peak at about 5.42 ppm. When utilizing ¹⁵N₂ and CO₂ as the feed gas, the detected ¹H NMR signals of the produced urea

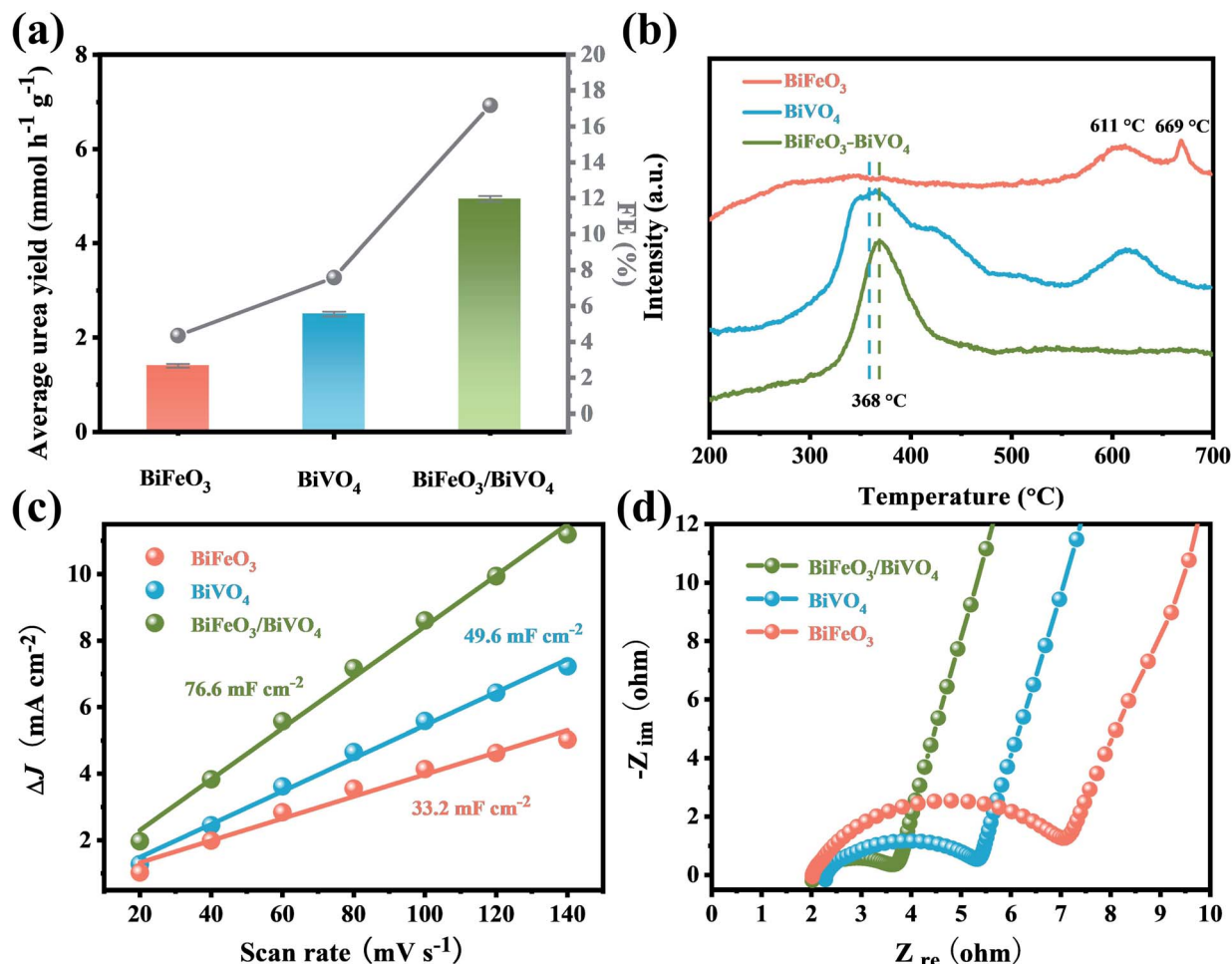


Fig. 6 (a) Average urea yield; (b) carbon dioxide temperature-programmed desorption (CO₂-TPD) spectra; (c) ΔJ of electrocatalysts plotted against scan rate at -0.05 V vs. RHE; (d) Nyquist plots of electrochemical impedance spectra (EIS) of BiFeO₃, BiVO₄ and BiFeO₃/BiVO₄.

matched well with the standard CO(¹⁵NH₂)₂ signals. Additionally, the concentration of CO(¹⁵NH₂)₂ was also quantitatively detected by ¹H NMR, and the related signal integration–concentration linear relation is exhibited in Fig. 5g and h. As expected, the calculated urea concentration is consistent with the quantitative results of the diacetyl monoxime method (Fig. 5i). All these results are convincingly indicative of urea originating from the C–N coupling reaction from N₂ and CO₂ catalyzed by BiFeO₃/BiVO₄ hybrids.

For comparison, the pristine BiFeO₃ and BiVO₄ were also evaluated under identical conditions. At the optimal potential of -0.4 V, the electrocatalytic activities of BiFeO₃ (urea yield rate: $1.41 \text{ mmol h}^{-1} \text{ g}^{-1}$, FE: 4.35%) and BiVO₄ (urea yield rate: $2.50 \text{ mmol h}^{-1} \text{ g}^{-1}$, FE: 7.59%) were much inferior to those of BiFeO₃/BiVO₄ hybrids for urea production (Fig. 6a). This indicates that the local charge redistribution in BiFeO₃/BiVO₄ hybrids plays a critical role in enhancing electrocatalytic urea production. As revealed by temperature-programmed desorption (TPD), compared with pristine BiFeO₃ and BiVO₄, BiFeO₃/BiVO₄ hybrids exhibited stronger binding strength and larger desorption peak in the CO₂- and N₂-TPD spectra (Fig. 6b and S11†), elucidating that the local charge redistribution in BiFeO₃/

BiVO₄ hybrids endows the surfaces of BiFeO₃ and BiVO₄ with local nucleophilic and electrophilic regions and thus promotes the targeted adsorption of CO₂ and N₂ molecules, which is in good agreement with the aforementioned theoretical prediction. The electrochemically active surface area (ECSA) results suggest that the BiFeO₃/BiVO₄ hybrids (76.6 mF cm^{-2}) display a higher electrochemical double-layer capacitance (C_{dl}) than pristine BiFeO₃ (33.2 mF cm^{-2}) and BiVO₄ (49.6 mF cm^{-2}), which signifies that local charge redistribution promotes the exposure of more active sites in BiFeO₃/BiVO₄ hybrids for gas molecule adsorption and activation (Fig. 6c and S12†). Electrochemical impedance spectroscopy (EIS) analysis further reveals that the BiFeO₃/BiVO₄ hybrids possess a smaller semi-circle and higher slope than pristine samples, evincing that the presence of local charge redistribution in BiFeO₃/BiVO₄ hybrids significantly promotes electron/ion transfer kinetics during the electrocatalytic process (Fig. 6d).^{29,43}

To obtain deeper insight into the C–N coupling reaction mechanism toward the electrocatalytic urea production, DFT calculation was further employed to assess the intermediate variation and energy barrier during the reaction process. The corresponding BiFeO₃/BiVO₄ heterostructured architecture is

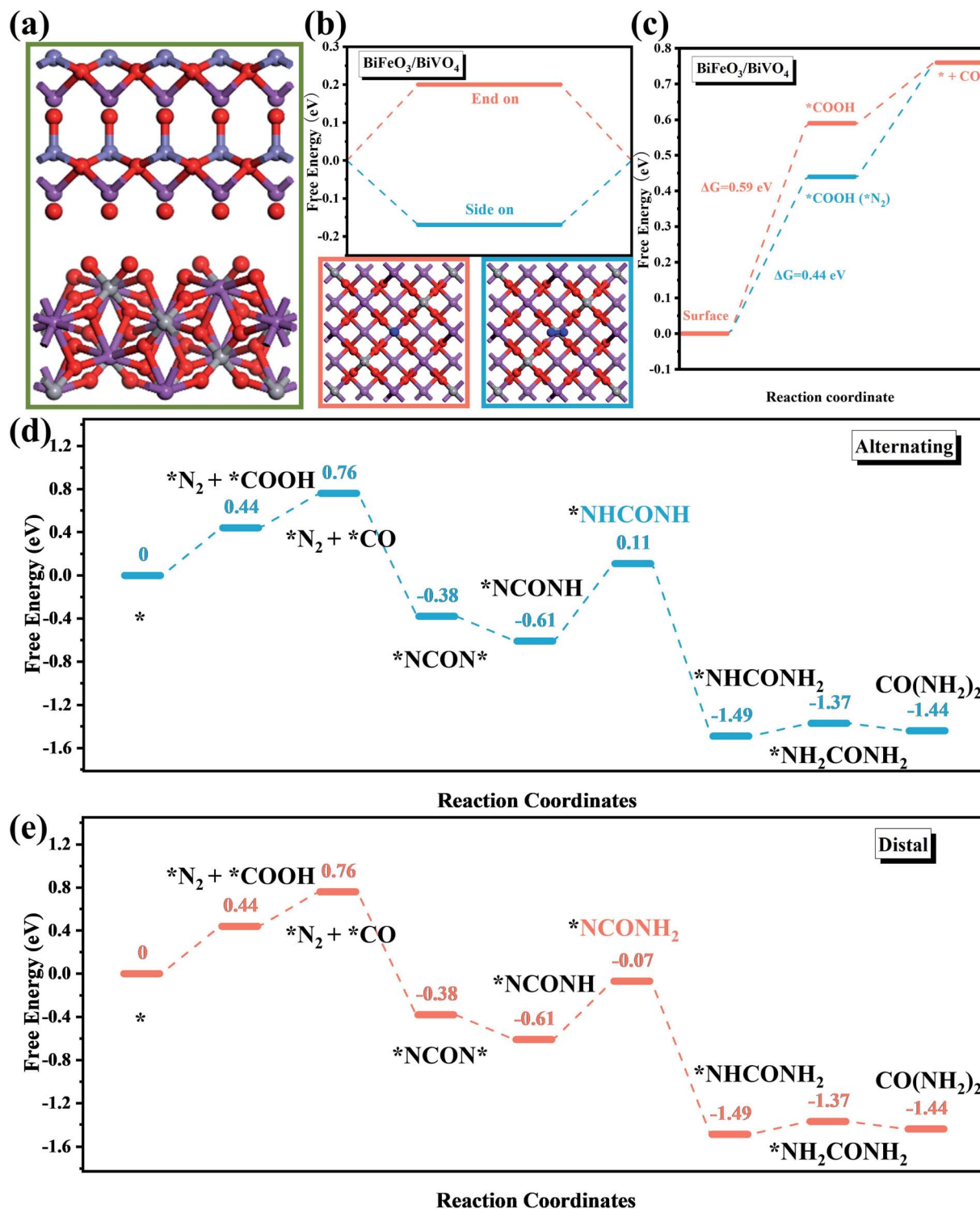


Fig. 7 (a) The calculation model of the $\text{BiFeO}_3/\text{BiVO}_4$ heterostructure; free energy diagrams for (b) N_2 adsorption and (c) CO_2 reduction with and without N_2 adsorption on the $\text{BiFeO}_3/\text{BiVO}_4$ heterostructure; the electrolytic urea production via (d) alternating and (e) distal mechanisms.

displayed in Fig. 7a. Since the chemisorption of inert CO_2 and N_2 molecules is the initial step for electrocatalytic urea production, it is critical to reveal the competitive adsorption between these gas molecules. In comparison with CO_2 -TPD, the peaks in the N_2 -TPD spectrum of the heterostructured hybrids

appeared at a higher temperature and exhibited enhanced intensity, demonstrating that the $\text{BiFeO}_3/\text{BiVO}_4$ hybrids possessed stronger N_2 chemisorption ability than that for CO_2 molecules (Fig. 6c and S11†).⁹ In other words, the C–N coupling reaction was initiated with chemisorption of N_2 molecules on

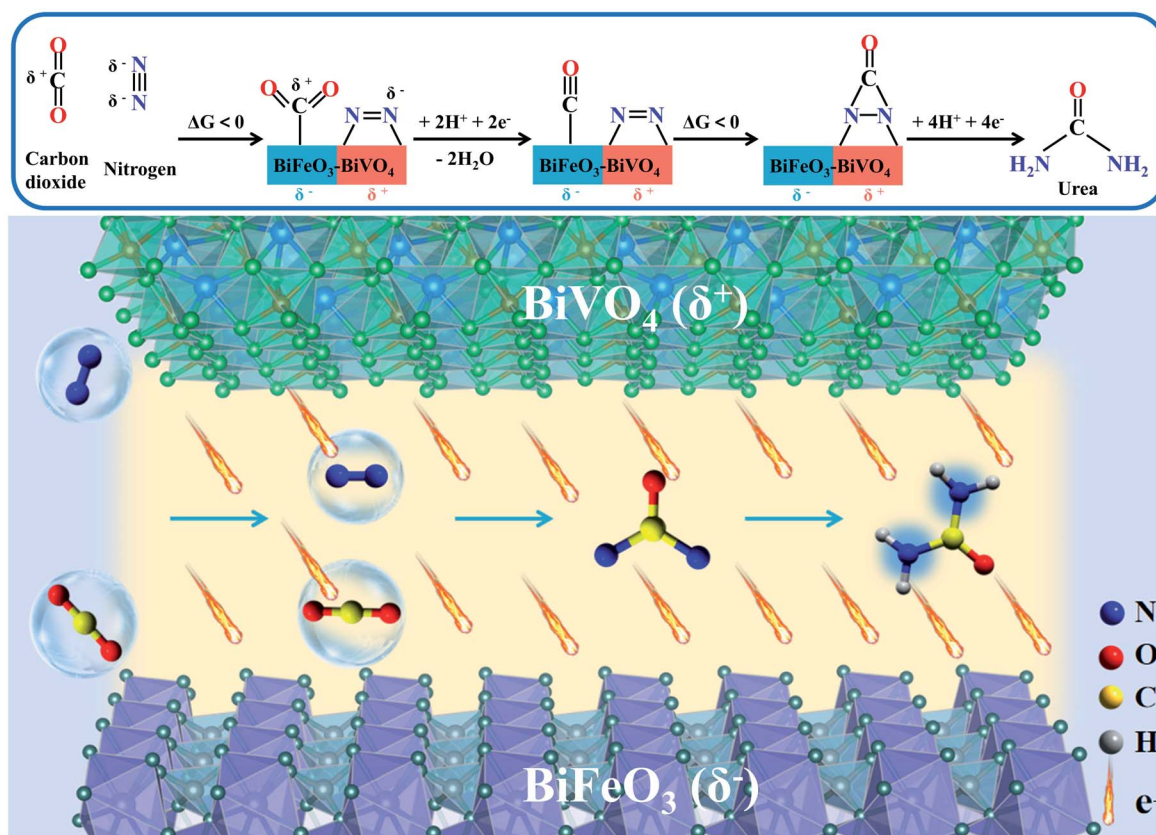


Fig. 8 The schematic electrocatalytic urea production mechanism based on BiFeO₃/BiVO₄ p-n heterostructure synergistic effects.

the BiFeO₃/BiVO₄ hybrids. Besides, the free energy of the N₂ adsorption with a side-on configuration was more negative than that of an end-on configuration, suggesting that N₂ preferably adsorbed on the local electrophilic BiVO₄ regions *via* the more stable side-on configuration (Fig. 7b). Impressively, as identified in Fig. 7c, the BiFeO₃/BiVO₄ hybrids required the highest Gibbs free energy (ΔG) of 0.59 eV to reduce CO₂, while the ΔG decreased to 0.44 eV when the N₂ molecules emerged in neighboring BiVO₄ regions. Therefore, it can be deduced that the adsorbed/activated N₂ molecules would facilitate the reduction of adsorbed CO₂ to CO on local nucleophilic BiFeO₃ regions. Then the C-N coupling reaction spontaneously occurred between the activated N₂ molecules (*N=N*) and *in situ* generated CO to form the *NCON* intermediate, due to the matching molecular orbitals. The corresponding ΔG further corroborates that the formation of the *NCON* intermediate is an exothermic process. Once the *NCON* intermediate is generated, the subsequent hydrogenation of *NCON* would produce two possible reaction pathways involving distal and alternating mechanisms. Concerning the alternating pathway, the (H⁺ + e⁻) alternately reacted with the two N atoms, while the protonation continuously attacked the distal N atoms for the distal mechanism. As displayed in Fig. 7d and e, when the reduction of *NCON* follows the distal pathway, the required ΔG decreased to 0.54 eV compared to that of the alternating pathway (0.72 eV), suggesting that the BiFeO₃/BiVO₄ hybrids

were prone to pursue the distal mechanism until the release of urea molecules rather than the alternating pathway from the thermodynamic perspective.³¹

The selectivity of the electrocatalytic urea production is closely associated with the formation of *NCON* intermediates. The possible N₂ reduction or the excessive release of CO would result in a decrease in the efficiency of the electrocatalytic C-N coupling reaction and further reduce the selectivity. On the one hand, the ΔG for the reductive protonation of *N₂ into *N₂H (N₂ + H⁺ + e⁻ + * → *NNH), which is regarded as the potential-determining step (PDS) toward the NRR, was calculated to be 0.14 eV (Fig. S13†),⁶¹ which was much higher than that for the C-N coupling reaction to form *NCON*. Such a significantly larger energy barrier makes BiFeO₃/BiVO₄ hybrids inactive for the electrocatalytic NRR, let alone generating side product NH₃. On the other hand, the release of the generated *CO intermediate was strongly associated with the selectivity of the electrocatalytic urea production. Thus, the stability of the as-prepared electrocatalysts against CO poisoning was evaluated through an electrochemical CO-stripping experiment. As shown in Fig. S14†, the CO-stripping peak of BiFeO₃/BiVO₄ hybrids (0.251 V *vs.* RHE) exhibits a more negative shift than that of pristine BiFeO₃ (0.261 V *vs.* RHE) and BiVO₄ counterparts (0.265 V *vs.* RHE), indicating that the BiFeO₃/BiVO₄ hybrids possessed higher stability against CO poisoning, which is due to the elimination of some of the strong adsorption sites by the



local charge redistribution.⁶² Notably, the amount of CO should be well controlled. As confirmed by Fig. 5e, when the applied potential exceeded -0.4 V, the excessively released CO occupied the adsorption sites for N_2 and CO_2 and resulted in a remarkable decrease of the FE for urea production.

By combining the aforementioned experimental results and computational simulations, the overall urea electrosynthesis process can be summarized in the following steps: (i) the built-in electric field in $BiFeO_3/BiVO_4$ hybrids accelerates the local charge redistribution, (ii) N_2/CO_2 molecules first adsorbed on the generated electrophilic/nucleophilic regions by electrostatic interaction, (iii) the produced $*N_2$ promotes CO_2 reduction under the electric field, and then the generated CO will further react with $*N_2$ to produce the desirable $*NCON$ intermediate through exothermic electrocatalytic C–N coupling reaction, and (iv) the subsequent protonation process preferentially undergoes the distal mechanism until the formation of urea (Fig. 8).

3 Conclusion

In summary, inspired by the theoretical simulation predictions, a facile ultrasonic bath strategy was proposed to elaborately integrate the perovskite structured $BiFeO_3$ and $BiVO_4$ as a unique p–n heterojunction. The well-developed built-in electric field at the heterointerfaces facilitates the local charge redistribution and thus endows the $BiFeO_3$ and $BiVO_4$ surfaces with local nucleophilic and electrophilic regions, which promote the targeted adsorption and activation of N_2 and CO_2 molecules. Besides, the local charge redistribution also contributed to fully exposing the active sites and accelerated electrocatalytic kinetics, which is beneficial for the formation of the C–N bond and generation of the desired $*NCON$ intermediate. As a result, the $BiFeO_3/BiVO_4$ hybrids exhibit a maximum urea yield rate and FE of $4.94\text{ mmol h}^{-1}\text{ g}^{-1}$ and 17.18% at -0.4 V vs. RHE in 0.1 M $KHCO_3$. Besides, the related urea yield rate and FE can be further improved to $5.42\text{ mmol h}^{-1}\text{ g}^{-1}$ and 20.75% in (Bmim) BF_4 – $KHCO_3$ electrolyte. This work proposed an innovative local charge redistribution concept to design urea production catalysts by promoting electrocatalytic C–N bond coupling.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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