Isolation of Metalloid Boron Atoms in Intermetallic Carbide Boosts the Catalytic Selectivity for Electrocatalytic N₂ Fixation

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The electrochemical N₂ reduction reaction (eNRR) is considered to be an attractive alternative to overcome the short-comings of the Haber-Bosch method, where the electrocatalysts play a vital role in the eNRR efficiency. Herein, isolated single-B sites with electron deficiency in intermetallic carbide are rationally designed to trigger charge density redistribution, achieving excellent selectivity for eNRR. The B-rich VC nanocrystals are in situ synthesized on carbon nanofibers (B-VC/CNFs), and the ordered intermetallic structure of VC can isolate contiguous B atoms into single-B sites with specific electronic structures. In light of density functional theory calculations, the as-designed B–C–V configuration can regulate the adsorption behavior of N₂ and decrease the energy barrier for the proton–electron coupling and transferring process (\(^{6}\)NN \rightarrow \(^{6}\)NNH), endowing the distinguished activity and selectivity, as evidenced by excellent Faradaic efficiency (46.1%) and NH₃ yield of 0.443 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\). The operando Raman spectra reveals the formation of \(=\)NH intermediates on the surfaces of B-VC/CNFs, further confirming the calculated eNRR pathway. This intermetallic carbide host strategy for generating electron-deficient single-B sites offers powerful guidelines for designing advanced eNRR electrocatalysts to achieve effective ammonia production.

1. Introduction

The industrial synthesis of ammonia mainly relies on the Haber-Bosch (H-B) process, which requires high temperature (350–550 °C) and pressure conditions (50–350 atm).\(^{[1–3]}\) Up to date, it has become a new research hotspot to produce ammonia through electrochemical nitrogen reduction reaction (eNRR) technology under ambient conditions due to its environmentally friendly characteristics, flexibility, and low cost.\(^{[4]}\) The extremely stable \(\text{N}_2=\text{N}\) bond, weak \(\text{N}_2\) adsorption, and high energy barrier of key intermediates usually require electrocatalysts to improve the eNRR activity and selectivity in ammonia production.\(^{[5]}\) However, developing advanced electrocatalysts to improve the eNRR performance with high selectivity is challenging work. Boron-based materials such as boron carbide nanosheets, metal boride, boron nitride, and B-doped carbon have been considered as promising eNRR electrocatalysts.\(^{[6–9]}\) Doping engineering and pyrolysis of B-based organic compounds are the two main strategies to generate B active sites.\(^{[10,11]}\) Yan groups have demonstrated that boron-rich covalent–organic frameworks could effectively facilitate the \(\text{N}_2\) accessibility, achieving a high Faradaic efficiency (FE) of 45.43%.\(^{[12]}\) This work shows a sign that increasing the B contents and numbers of B active sites could be an effective approach to improve the eNRR activity and selectivity.

Recently, applying intermetallic compounds to achieve isolated single-atom sites is an important strategy to improve atomic utilization and break the intrinsic activity limit.\(^{[11–17]}\) Extensive efforts mainly focus on the metal sites isolation using intermetallic compounds. Few works have reported the non-metal site isolation in intermetallic compounds and these atomic-scale regulations have become a grand challenge. As a special intermetallic compound, vanadium carbide (VC) has high compositional richness and structural diversity that can make the nonmetal C atoms as well as B and N atoms mutually soluble in the VC crystal matrix.\(^{[18]}\) The ordered intermetallic structure of VC can isolate contiguous B atoms into single-B sites with specific electronic structures. Rational regulation in
electronic structures could effectively favor the N₂ adsorption, activation, and hydrogenation (N₂-AAH) process. The above consideration inspires us to use the VC as a host to generate the high concentration of isolated single B sites and expect superior eNRR performance.

Herein, we demonstrated that boron-rich vanadium carbide with a high concentration of electron-deficient single-B sites could regulate the adsorption behavior of N₂ and decrease the energy barrier for the proton-electron coupling and transferring process (*NN → *NNH), endowing the distinguished activity and selectivity. The boron-rich vanadium carbide (B-VC) were in situ synthesized on carbon nanofibers (CNFs) through the thermodynamic-driven solid-phase diffusion approach by combining the electrospinning technology and high-temperature carbonization. In the B-VC structures, the B and adjacent C bonded with V form the B–C–V bond due to the affinity among the electronegatively weak B, V, and strong C. Both of the B and V atoms donate electrons to C atoms, leading to the redistribution of charge density on V and B sites. The electron-deficient single-B sites with unoccupied p orbitals can enhance the N₂ adsorption and activation. When serving as eNRR electrocatalysts, excellent activity and selectivity with a high ammonia yield of 0.443 μmol h⁻¹ cm⁻² and outstanding FE of 46.1% were realized in 0.5 M K₂SO₄ solution under ambient conditions. In light of density functional theory (DFT) calculations, the as-designed B–C–V configuration can facilitate the electron redistribution that is beneficial for the charge transfer and improve both the activity and selectivity toward eNRR. The operando Raman spectra revealed the formation of −NH intermediates on surfaces of B₁₁–VC/CNFs, further confirming the calculated eNRR pathway.

2. Results and Discussion

To understand the impact of electron-deficient single-B atoms in B–C–V structures with electron redistribution and assess the capability that B-VC catalyzes eNRR, we used DFT calculations to reveal the NRR pathway and corresponding free energy diagrams on B-VC structures. A schematic illustration of the eNRR on B-VC was shown in Figure 1a. The optimized V–C and B–C–V models in VC/CNFs and B-VC/CNFs were proposed based on the VC (200) planes. For the active catalytic surface, the (200) facet terminate with V or C termination atoms (B–C–V bonds). According to the Bader charge analysis, in V–C structures, the Bader charge of C atoms bonded with V atoms was ~1.29 e (Figure 1b). For the B–C–V structures, due to the smaller electronegativity of B (2.04) than that of C (2.55), the B atoms donated electrons to C atoms, making the Bader charge of C atoms nearby B atoms increased from ~1.29 to ~1.57 e. Meanwhile, the V atoms nearby the B and C atoms (B–C–V) exhibited a much lower Bader charge relative to the V atoms of the VC structure (Figure 1b). The results revealed that the bridging C atoms received the electron donation from both the B and V atoms, leading to the charge redistribution at B and V atoms. Therefore, these electron-deficient B sites in B–C–V structures can serve as active centers for simultaneously promoting the N₂-AAH process. In addition, the partial density of states (pDOS) of V–C and B–C–V models were shown in Figures S1 and S2 (Supporting Information). Interestingly, both of the two models displayed high density states across the Fermi level, suggesting that the incorporation of B with VC did not weaken the metallic features of VC. This feature also ensured the electron transfers in the subsequent catalytic process for B–C–V models.

We compared the eNRR pathway on B sites of (200) facet in the B–C–V model and V sites of (200) facet in the VC and B–C–V models (Figure 1c, Figures S3 and S4, Supporting Information). The associative reaction process of eNRR pathway showed that the N₂ absorption, activation, and hydrogenation were the vital steps for determining the eNRR performance. Both of the V sites in the V–C and B–C–V models have stronger N₂ adsorption capability than B sites in the B–C–V model. The adsorption energy of N₂ on V sites (0.096 eV) in the B–V–C model was lower than that one B sites (0.346 eV) in the B–C–V model. The free energies of the eNRR steps were calculated and shown in Figure 1d. The Gibbs free energy diagrams showed that the first N₂ hydrogenation to form *NNH intermediates was the potential determining step (PDS). For V sites in the B–C–V model, the first N₂ hydrogenation to form *NNH needed to overcome an energy barrier (ΔG_PDS) of 1.624 eV, which was much higher than that on B sites in B–C–V (0.984 eV). The results revealed that the B sites in B–C–V became the real active sites for promoting the first N₂ protonation to form *NNH and significantly reducing the energy barrier of PDS for eNRR. Therefore, in the whole eNRR pathway, the B sites in B–C–V achieved the lower energy barrier for N₂-AAH processes (N₂ absorption, activation, and hydrogenation) than those of V sites in B–C–V. These results strongly demonstrated that the designed B–C–V structures with electron-deficient B centers simultaneously promote the activation of N₂ and reduction of ΔG_PDS for eNRR.

To verify the prediction of the DFT calculations, the B-rich vanadium carbide supported on carbon nanofibers with different B contents (Bₓ-VC/CNFs, 0 ≤ x ≤ 15) were synthesized through a thermodynamic-driven solid-phase diffusion approach by combining the electrospinning technology and high-temperature carbonization (see details in Supporting Information). Briefly, as shown in Figure 2a, the boric acid and acetylacetonate vanadium (H₃BO₃ and C₉H₁₈O₅V) were firstly homogeneous dissolved in the polyacrylonitrile/N, N'-dimethylformamide (PAN/DMF) solution. The H₃BO₃, C₉H₁₈O₅V, and PAN were used as B, V, and C sources, respectively. Then, the B and V salt/PAN precursor nanofiber membrane was obtained through the electrospinning process. After the graphitization at 1000 °C, the B-VC/CNFs with unique B–C–V structures were finally produced. The intermetallic compound vanadium carbide exhibits the superior B contents and by adjusting the mass ratios of B and V salts, the B-VC/CNFs with various B contents (B atom ratio = 0, 3, 5, 8, 11, and 15 at%) were prepared. Their chemical formulas were denoted as VC/CNFs, B₀-VC/CNFs, B₃-VC/CNFs, B₅-VC/CNFs, B₀₁-VC/CNFs, and B₁₅-VC/CNFs, respectively. The elemental composition was investigated by the energy-dispersive X-ray spectra (EDS) (Table S1, Supporting Information).

The morphologies of the B₁₁/CNFs, VC/CNFs, and B₁₁/CNFs hybrids were investigated by field emission scanning...
electron microscopy (FESEM) and transmission electron microscopy (TEM). The B_{11}/CNFs (Figure S5a, Supporting Information), VC/CNFs (Figure S5b, Supporting Information), and B_{11}-VC/CNFs (Figure 2b) all displayed distinct nanofiber morphologies with random distributions to form the unique three-dimensional (3D) network architectures. The B_{11}/CNFs exhibited a smooth surface (Figure S5c, Supporting Information) while both of the VC/CNFs (Figure S5d, Supporting Information) and B_{11}-VC/CNFs (Figure 2c) indicated that plenty of small nanocrystals were distributed on the substrate CNFs homogeneously without obvious aggregation. High-angle annular dark field scanning TEM (HADDF-STEM) images of B_{11}-VC/CNFs (Figure 2d) demonstrated that the diameter of B_{11}-VC nanocrystals ranged from 5 to 10 nm while the size of CNFs varied from 150 to 300 nm. The high-resolution TEM image of B_{11}-VC/CNFs (Figure 2e) displayed the nanoparticles were crystallized with the interplanar spacing of 2.1 Å, corresponding to the (200) planes of VC.

The HAADF-STEM image (Figure 2f) and STEM electron energy loss spectrum (STEM-EELS) mapping images (Figure 2g–i) of the B_{11}-VC nanoparticles supported on CNFs revealed the uniform distribution of the C, B, and V elements. STEM-EELS spectrum was recorded on the surface of B_{11}-VC nanocrystal (Figure 2j). The EELS spectrum revealed the presence of the K edges for C and B and L edges for V, respectively. The energy-loss near-edge structure (ELNES) of the C K-edge showed a well-defined graphitic character with a π* peak at 285 eV and a detailed σ* structure above 295 eV. When compared with the π* peak of B elementary substance (188 eV), the π* peak in B K-edge of B_{11}-VC shifted to 192 eV, indicating the presence of B-C bonds. The ELNES of V L_{2,3}-edges showed peaks at 524 and 517 eV, corresponding to the signals from the

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**Figure 1.** a) Schematic illustration of the eNRR on B-VC. b) Charge distribution on VC model and B-VC model. c) DFT-calculated eNRR reaction cycle through distal pathway on the B site in B-VC model. d) Free energy diagrams of distal eNRR pathway on the V site of VC, V site of B-VC, and B site of B-VC.
vanadium valence state of +4.[26] Therefore, the EELS evidence confirmed that B atoms were successfully incorporated into the VC crystal matrix, forming the B–C–V structures.

Typical X-ray diffraction (XRD) patterns of VC/CNFs and B\textsubscript{11}-VC/CNFs were shown in Figure 3a,b. A broad band around 22° was assigned to the amorphous carbon of CNFs. A series of peaks were well indexed to the (111), (200), (220), (311), and (222) planes of cubic VC phase (JCPDS No. 73-0476).[27] Interestingly, the enlarged XRD patterns in Figure 3b indicate the slightly shifts (0.18° of 2θ) in peak positions of the (111) and (200) planes for the VC and B\textsubscript{11}-VC phases, demonstrating that the B incorporation into the VC crystal lattice can lead to enlarged V\textsubscript{C} lattices.

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical states of VC/CNFs and B\textsubscript{11}-VC/CNFs. All the binding energies (BEs) were calibrated by the C 1s peak at 284.6 eV. The B 1s spectra of VC/CNFs without B doping exhibited no B signals (Figure 3c). Meanwhile, the B 1s XPS spectra of B\textsubscript{11}-VC/CNFs can be fitted by four distinct peaks at 189.9, 190.4, 191.2, and 192.3 eV, corresponding to BC\textsubscript{3}, B–C–V, BC\textsubscript{2}O, and BCO\textsubscript{2} species, respectively (Figure 3c).[28] The B XPS spectra strongly demonstrated the successful formation of B–C and B–C–V bonds in B\textsubscript{11}-VC/CNFs. The atomic concentration of B was determined to be 11.2 at% via XPS spectra, which was well matched with the EDS results (Table S1, Supporting Information). Figure 3d revealed the typical C 1s spectra of VC/CNFs and B\textsubscript{11}-VC/CNFs. The VC/CNFs displayed three main peaks at 282.0, 284.6, and 286.3 eV corresponding to the C–V, C–C, and C–O bonds, respectively.[29] Meanwhile, the B\textsubscript{11}-VC/CNFs exhibited four main peaks at 282.2, 284.3, 284.6, and 286.3 eV, which were ascribed to the B–C–V, C–B, C–C, and C–O bonds, respectively. Due to the incorporation of B into V–C, the BE of B–C–V bonds (282.2 eV) in B\textsubscript{11}-VC/CNFs exhibited a positive shift of 0.2 eV when compared with the BE (282.0 eV) of C–V bonds in VC/CNFs, suggesting the electron donation from V and B atoms to C atoms. The V 2p spectra of VC/CNFs can be deconvoluted into six peaks (Figure 2e), which were attributed to the V\textsuperscript{2+} (513.7 and 520.9 eV), V\textsuperscript{3+} (515.3 eV and 525.1 eV), and V\textsuperscript{4+} (516.8 and 523.7 eV), respectively.[30] Furthermore, the BEs of V\textsuperscript{4+} for B\textsubscript{11}-VC/CNFs shifted to the relatively high values of 516.6 and 523.5 eV, also indicating that the V atoms tended to donate electrons to C atoms. The results indicated that the formation of B–C–V bonds leads to the enhanced electron transfer among the V, B, and C atoms.

Temperature-programmed desorption (TPD) was further used to investigate the N\textsubscript{2} adsorption capacity of VC/CNFs and B\textsubscript{11}-VC/CNFs.[31] As shown in Figure 3f, both of the VC/CNFs and B\textsubscript{11}-VC/CNFs showed two obvious peaks in the range of 100–600 °C, which can be attributed to the physical and chemical adsorption of N\textsubscript{2} molecules on the surface of catalysts, respectively. Interestingly, the peak intensity of the chemisorption peak of B\textsubscript{11}-VC/CNFs at about 530 °C was significantly reduced.
stronger than that of VC/CNFs. The N$_2$-TPD results indicate that the formation of B–C–V significantly enhanced the chemical adsorption capacity of N$_2$, which would lead to the enhanced eNRR performance.

The eNRR activity of as-prepared catalysts was performed in an H-type cell with a typical three-electrode system in 0.5 m K$_2$SO$_4$ solution under continuous N$_2$ flow. In the H-type cell, the Ag/AgCl reference electrode was placed in the cathode chamber while the platinum wire counter electrode was placed in the anodic chambers. The cathode chamber and anodic chambers were separated by the commercial Nafion 117 membrane. All the as-prepared samples were employed as cathodes for eNRR. The B$_{11}$-VC/CNFs membrane with an electrode area of 0.25 cm$^2$ (0.5 × 0.5 cm) was fixed on a Teflon motor clip as the working electrode. During the eNRR process, N$_2$ pretreated with an acid solution was continuously provided to the cathode. The H$^+$ in the electrochemical cell transported through the 0.5 m K$_2$SO$_4$ electrolyte and reacted with N$_2$ on the catalyst surface for NH$_3$ production. The possible eNRR products in the 0.5 m K$_2$SO$_4$ electrolyte were NH$_3$ and N$_2$H$_4$, respectively. The NH$_3$ product was determined by the indo-phenol blue method (Figure S6, Supporting Information), and the byproduct N$_2$H$_4$ was detected by the Watt-Christo method (Figure S7, Supporting Information). As shown in Figure S8 (Supporting Information), the UV-vis spectra indicate that no N$_2$H$_4$ byproduct was detected, suggesting that the reaction on B$_{11}$-VC/CNFs gives excellent selectivity for NH$_3$ production. The eNRR activity of B$_{11}$-VC/CNFs was initially evaluated by linear sweep voltammetry (LSV) polarization curves in the N$_2$- and Ar-saturated 0.5 m K$_2$SO$_4$ electrolytes (Figure S9, Supporting Information). The LSV curve in the N$_2$-saturated electrolyte exhibited enhanced current density relative to that in the Ar-saturated electrolyte, suggesting that the B$_{11}$-VC/CNFs was certainly active for the eNRR. Moreover, in the potential window...
from $-0.4$ to $-0.8$ V, a significantly higher current density was achieved in the N$_2$-saturated electrolyte than that in the Ar-saturated electrolyte. Therefore, the potential window from $-0.4$ to $-0.8$ V was selected for the eNRR. The electrochemical active surface area (ECSA) was determined based on the electrochemical double-layer capacitance ($C_{dl}$). The B$_{11}$-VC/CNFs obtained the highest $C_{dl}$ value of 13.2 mF cm$^{-2}$ relative to those of VC/CNFs (8.3 mF cm$^{-2}$) and B$_{11}$/CNFs (1.5 mF cm$^{-2}$), respectively, indicating the high intrinsic activity of B$_{11}$-VC/CNFs (Figure S10, Supporting Information).

A series of control experiments were used to investigate the effect of N$_2$ as the N source and eliminate the interferences of contaminants in the testing system (Figure 4a). Specifically, no ammonia was detected in the initial N$_2$-saturated 0.5 m K$_2$SO$_4$ electrolyte and the electrolyte catalyzed by B$_{11}$-VC/CNFs under open-circuit potential. These experiments can rule out the effect of contamination in the N$_2$ gas flow and the B$_{11}$-VC/CNFs itself. In the Ar atmosphere, the UV–vis spectra show negligible absorption peak while a strong absorption peak can be observed in the N$_2$ atmosphere, suggesting the production of NH$_3$ catalyzed by B$_{11}$-VC/CNFs during the eNRR process. These results demonstrated that the detected ammonia was only produced from the eNRR process. The eNRR activities of B$_{11}$-VC/CNFs were quantified via chronoamperometry measurements at different potentials for 2 h (Figure 4b). The current density increased with the potentials ranged from $-0.4$ to $-0.9$ V. To investigate the contributions of the B–C, VC, and B–C–V structures for the eNRR performance, the B$_{11}$/CNFs with BC$_3$ structures were also prepared at the same condition. We performed a variety of comparative experiments to eliminate the influencing factors on NRR activity. Figure 4c,d shows the corresponding Faradaic efficiencies (FE) and NH$_3$ yields of B$_{11}$/CNFs, VC/CNFs, and B$_{11}$-VC/CNFs catalysts at each potential. The FE and NH$_3$ yield on VC/CNFs exhibit negligible values, and the B$_{11}$/CNFs with BC$_3$ structures display the FE of 8.4% and the NH$_3$ yield of 0.062 µmol h$^{-1}$ cm$^{-2}$ at $-0.7$ V versus RHE. The results indicated that without the B incorporation, the pure VC had little effect on NRR activity. In comparison, the B$_{11}$-VC/CNFs with B–C–V bonds reached a maximum FE of 46.1% and an NH$_3$ yield of 0.443 µmol h$^{-1}$ cm$^{-2}$ at $-0.6$ V versus RHE, which was significantly higher than the reported level in the literature (Table S2, Supporting Information).

We have further explored the influences of B contents on the eNRR performances. As shown in Figure S11a,b (Supporting Information), with the increased B contents, the FEs and NH$_3$ yields of the as-synthesized B$_x$-VC/CNFs electrocatalysts displayed an escalating trend due to the increased numbers of B active sites in B–C–V. However, when the B contents increased to 15%, the B$_{15}$-VC/CNFs exhibited decreased FE of 34.1% and NH$_3$ yield of 0.275 µmol h$^{-1}$ cm$^{-2}$. The results demonstrated that except for the B–C–V active sites, the additionally formed BC$_3$ structures in B$_{15}$-VC/CNFs could not afford the high eNRR activity, further confirming that the eNRR activity was determined by B–C–V structures in B-VC/CNFs. Therefore, the main contribution in B$_{11}$-VC/CNFs for eNRR was attributed to the unique B–C–V structures, which can regulate...
the adsorption behavior of N\textsubscript{2} and reduce the energy barrier of rate-determining steps.

The important stability of the catalyst was investigated by various characterization tests. The time–current curves performed at \(-0.60\) V versus RHE (Figure 5a) exhibited a negligible decrease in current density during the 15 h long-term electrolysis experiment. After long-term stability tests, the B\textsubscript{11}-VC/CNFs still maintained the uniform nanofiber morphology with 3D architecture (Figure S12a,b, Supporting Information), crystal phase (Figure S12c, Supporting Information), and chemical composition and states (Figure S12d, Supporting Information), confirming the excellent stability. In addition, the FE and NH\textsubscript{3} yield before and after 15 h long-term electrolysis was not substantially reduced (Figure S13, Supporting Information). Furthermore, we continuously cycled the NRR test at \(-0.6\) V versus RHE by changing the feeding gas (Ar and N\textsubscript{2}) in 0.5 m K\textsubscript{2}SO\textsubscript{4} (Figure 5b) and the FEs and NH\textsubscript{3} yields were calculated for each experiment. The results demonstrate that FE (46.1\%) and NH\textsubscript{3} yield (0.443 \textmu mol h\textsuperscript{-1} cm\textsuperscript{-2}) of B\textsubscript{11}-VC/CNFs can be well maintained during each cycle in N\textsubscript{2}-saturated electrolyte. We further continuously performed the cycle tests five times in N\textsubscript{2}-saturated 0.5 m K\textsubscript{2}SO\textsubscript{4} (Figure S15, Supporting Information) and the NH\textsubscript{3} yield of 0.443 \textmu mol h\textsuperscript{-1} cm\textsuperscript{-2} after continuously five cycles, confirming that the B\textsubscript{11}-VC/CNFs has superior stability.

The NH\textsubscript{3} production was further verified by nuclear magnetic resonance (NMR) using the isotope labeling method with 14N\textsubscript{2} and 15N\textsubscript{2} as feeding gases. As shown in Figure 5d, when 15N\textsubscript{2} was utilized as a nitrogen source, the \textsuperscript{1}H NMR exhibit distinct doublet with a chemical shift of 72 Hz, which was ascribed to \textsuperscript{15}NH\textsubscript{4}\textsuperscript{+}. For 14N\textsubscript{2} used as the nitrogen source, three signal peaks with a chemical shift of 52 Hz were attributed to 14NH\textsubscript{4}\textsuperscript{+}.\textsuperscript{[33]} In addition, the calculated FEs and NH\textsubscript{3} yields using NMR were almost consistent with the calculation by colorimetry (Figure S14, Supporting Information). When the Ar was introduced as feeding gas, there was no ammonia signal displayed in NMR spectra. The results proved that the detected ammonia was produced during the eNRR process catalyzed by B\textsubscript{11}-VC/CNFs, eliminating the effects of NH\textsubscript{3} or NO\textsubscript{3}\textsuperscript{−} contaminants.

To understand the reasons for achieving the high selectivity for NH\textsubscript{3} by B-VC, the capability of B\textsubscript{C} to suppress the competitive HER was further revealed by the DFT calculations. The differences between the eNRR limiting potential and the competitive HER limiting potential are vital descriptors for eNRR selectivity (Figure 6a).\textsuperscript{[33]} The limiting potential \((U_L)\) can be defined as the lowest negative potential at which all basic steps are exergonic. The catalytic activity for HER at the B site and V site in B\textsubscript{C} models can be assessed by the calculated Gibbs free energy of hydrogen adsorption (Figure S15, Supporting Information). It can be seen that the B\textsubscript{C} sites in B\textsubscript{C} models have the relatively stronger hydrogen adsorption capability (0.19 eV) than V\textsubscript{C} (0.67 eV) models. Compared with V\textsubscript{C} models, although the \(U_L(\text{HER})\) of B\textsubscript{C} sites is slightly smaller, it has more positive \([U_L(\text{NRR}) − U_L(\text{HER})]\) values, suggesting that the B\textsubscript{C} sites in the B\textsubscript{C} model possess distinguished NRR activity and selectivity.

The projected-crystal orbital Hamilton population (pCOHP) was carried to analyze the interaction between the activity center and the nitrogen adatom.\textsuperscript{[34]} The integrated-crystal OHP

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Figure 5. a) Chronoamperometry test of B\textsubscript{11}-VC/CNFs under continuous NRR electrolysis for 15 h. b) FEs and the corresponding NH\textsubscript{3} yields of B\textsubscript{11}-VC/CNFs performed at \(-0.6\) V versus RHE by alternating Ar-saturated and N\textsubscript{2}-saturated 0.5 m K\textsubscript{2}SO\textsubscript{4}. c) NH\textsubscript{3} yields and the corresponding FEs of B\textsubscript{11}-VC/CNFs obtained at \(-0.6\) V versus RHE during five-time cycles for NRR in N\textsubscript{2}-saturated 0.5 m K\textsubscript{2}SO\textsubscript{4}. d) \textsuperscript{1}H NMR spectra of electrolytes after NRR electrolysis on B\textsubscript{11}-VC/CNFs using 14N\textsubscript{2}, 15N\textsubscript{2}, and Ar as feeding gases.
(ICOHP) analysis of the N≡N bond was performed to investigate the activation degree for N₂ molecules (Figure 6b). In general, the activation degree of N₂ molecules was negatively correlated with the values of ICOHP. The ICOHP values followed the order: V–C model (−17.74) < B–C–V model (−16.82), suggesting that the activation degree of the N≡N bond by B–C–V was stronger than that by V–C. To further investigate the influences of the electron-deficient B sites and V sites on regulating the adsorption behavior of *NNH intermediate, the charge density difference of *NNH state configuration at VC and B-VC models were shown in Figure 6c,d. The results demonstrate that the electron transfer from B–C–V to the *NNH intermediate was 11.66 eV, which was higher than that from V–C (11.25 eV) to *NNH intermediate, suggesting the stronger electron interaction between B–C–V and the *NNH intermediate. The designed B–C–V can simultaneously promote the formation of *NNH intermediates and stabilize them on B sites.

In situ Raman spectroscopy was further used to monitor the possible reaction intermediates or products on VC/CNFs (Figure S16, Supporting Information) and B₁₁-VC/CNFs (Figure 6e) during the eNRR operation at different potentials in a N₂-saturated 0.5 mM K₂SO₄ electrolyte. As shown in Figure S13 (Supporting Information), with the increased applied potential from −0.4 to −1.0 V versus RHE, a Raman peak appeared at 981 cm⁻¹, assigned to the sulfate radical species absorbed on the surface of VC/CNFs, suggesting the excellent wettability for the electrolyte.[36] For the B₁₁-VC/CNFs as electrocatalysts (Figure 6e), under applied potential from −0.4 to −0.5 V versus RHE, a new Raman peak emerged at 1525 cm⁻¹, ascribed to the −NH, demonstrating the strong nitrogen reduction on B₁₁-VC/CNFs. Time-resolved in situ Raman spectra of B₁₁-VC/CNFs collected at −0.6 V versus RHE under a N₂ atmosphere for 1 h were shown in Figure 6f. Besides the Raman peaks at 981 cm⁻¹ for sulfate radical species, the Raman peaks at 1525 cm⁻¹ for
−NH gradually emerged and enhanced as the eNRR progressed. No such Raman peak at 1525 cm$^{-1}$ was detected for VC/CNFs, suggesting their unfavored NRR performances.\(^{[37]}\) The Raman results demonstrate the formation of −NH intermediates on surfaces of B\(_{11}\)-VC/CNFs, further confirming the calculated eNRR pathway and the excellent eNRR performance of B\(_{11}\)-VC/CNFs. Thus, we have theoretically and experimentally demonstrated that applying the intermetallic compounds VC as host to create high contents of electron-deficient B sites make the enhanced eNRR selectivity and activity by regulating the adsorption behavior of N\(_2\) and decreasing the energy barrier for the proton–electron coupling and transferring process.

3. Conclusion

In summary, we have designed the electron-deficient single-B sites in B-rich VC nanocrystals supported on CNFs by combining the electrospinning technology and carbonization process. DFT calculations demonstrated the charge redistribution over the B=C−V structures. The B=C−V structures with electron-deficient B sites simultaneously can boost the activation of N\(_2\) and reduce the energy barrier of PDS for eNRR. The B\(_{11}\)-VC/CNFs exhibited an excellent FE of 46.1% and NH\(_3\) yield of 0.443 μmol h$^{-1}$ cm$^{-2}$ at −0.6 V versus RHE. This intermetallic carbide host strategy offers powerful guidelines for achieving effective ammonia production by generating the electron-deficient dual active centers. The operando Raman spectra demonstrated that the B=C−V structures with −NH intermediates in the eNRR progress. This intermetallic carbide host strategy for generating the electron-deficient B active centers offers powerful guidelines for designing advanced eNRR electrocatalysts to achieve effective ammonia production.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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