Regulating the Electronic Configuration of Supported Iron Nanoparticles for Electrochemical Catalytic Nitrogen Fixation

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Electrocatalytic nitrogen reduction reaction (eNRR) is a sustainable alternative to the traditional Haber–Bosch process due to its eco-friendly nature and capability of utilizing renewable energy. However, its low Faradic efficiency (FE), caused by the excessive adsorption and reduction of protons, has been regarded as the main challenge, which leads to low ammonia yield as well. Herein, a carbon-supported iron electrocatalyst is reported, which is fabricated by low-temperature (300 °C) potassium vapor reduction of FeF$_3$-intercalated graphite fluoride, for efficient electrochemical nitrogen reduction. The strategy enables the unique formation of exposed Fe nanoparticles uniformly anchored on graphene and in situ doped with fluorine heteroatoms. These specific features can alter the electronic configuration of the Fe nanoparticles, leading to strong surface polarization that boosts nitrogen absorption capability for eNRR, resulting in high FE (41.6%) and ammonia yield rate (53.3 μg h$^{-1}$ mg$^{-1}$) simultaneously. First-principle calculation attributes this enhanced eNRR capability to more empty orbitals carried by the Fe atoms through the electron transfer with F dopant and substrate. As a versatile strategy for synthesizing various ultrafine and highly dispersed metal nanoparticles on the carbon support, this work might shed light on rational designing essential electrocatalysts with effective electronic structure manipulation.

1. Introduction

Ammonia (NH$_3$), one of the essential chemicals in the world, has been widely exploited in synthetic fertilizers, fabrics, and pharmaceutical industries.$^{[1-4]}$ Currently, the Haber–Bosch (H–B) process ($\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$) is the most mature technology for scalable ammonia synthesis. However, the H–B reaction possesses intrinsic issues in terms of high energy consumption and CO$_2$ emission due to the harsh synthetic conditions (100–300 atm, 300–500 °C) and the requirement of high-purity hydrogen that is mainly derived from natural gas.$^{[5-7]}$ With the rapid development of the economy, the consumption of these ammonia-derived products has been continuously increased, making the ammonia synthesis industry a significant contributor to the energy crisis and environmental deterioration. In response to this issue, ambient nitrogen reduction for ammonia synthesis (e.g., electrocatalysis
and photocatalysis), combing with renewable energy, which is potentially featured with energy-saving and zero-emission characteristics, has attracted increasing attention recently.\[8\textendash}^{12}\]

Especially, the electrocatalytic nitrogen reduction reaction (eNRR) involves a simple process to directly reduce nitrogen (N\(_2\)) molecules and yield ammonia in an aqueous solution and under ambient conditions, which is exceptionally energy-efficient, eco-friendly, and sustainable.\[13\] Similar to the H\(_2\)B process, eNRR inherits the high kinetic barrier for nitrogen activation.\[14\] Besides, eNRR, typically carried out in an aqueous environment, also faces the unique challenge of excessive protons and extremely low solubility of N\(_2\) gas, leading to competitive hydrogen evolution reaction (HER) and low ammonia yield rate. Consequently, to simultaneously achieve a high ammonia yield rate and suppress the undesirable HER (i.e., a high Faradaic efficiency (FE)), eNRR electrocatalysts should not only be capable of effectively adsorbing N\(_2\) molecules rather than protons but also complete the cleavage and hydrogenation of N\(\equiv\)N triple-bonds even in very low concentration of N\(_2\).\[15\textendash}^{17}\]

To date, the Fe-based catalysts, which are widely adopted in the industrial H\(_2\)B process, are still one of the most promising and popular candidates for eNRR catalysts.\[18\textendash}^{20}\] In the H\(_2\)B process, it is believed that the capability of such Fe-based catalysts for N\(_2\) activation originates from the occupation of electron density in N\(\equiv\)N \(\pi\)-antibonding orbits deriving from the iron sites, which can efficiently adsorb N\(_2\) molecules and weaken the N\(\equiv\)N bond to facilitate the reduction of nitrogen.\[21\] As for the electrocatalytic process, however, the excessive protons rather than N\(_2\) molecules are more likely adsorbed on the catalyst surface to generate hydrogen, thus leading to unsatisfactory FE in eNRR.

Considering this, enhancing the N\(_2\) adsorption on the surface of Fe-based catalysts is critical for promoting the eNRR activity and inhibiting the undesirable proton adsorption (i.e., the HER). The strategy of enlarging the surface polarization, that is, redistributing the surface charge state of catalysts, has been proven effective for enhancing the adsorption of a serial of reactants, including N\(_2\). For example, we reported that transition metal single atoms (e.g., Fe, Co, and Ni) are able to modulate the electronic structure of Ru nanoparticles on O-doped graphene, which can optimize the adsorption free energy of H\(^+\) species, resulting in enhanced HER activity.\[22\] Besides, metal oxide nanoplates composed of multi-elements could obtain optimal electronic structures to realize favorable adsorption energies of oxygenated intermediates for oxygen evolution.\[23\]

Moreover, the intrinsic defects on graphene can also regulate its surface electron distribution, delivering appropriate intermediate adsorption energies for the oxygen reduction.\[24\textendash}^{24}\]

However, these strategies seem to have limited effects for enhancing nitrogen adsorption due to the very inert bond environment in N\(_2\) molecules.\[25\] For efficient nitrogen adsorption, the surface electronic state redistribution of the Fe-based electrocatalysts should be even more significantly strengthened in comparison with the aforementioned strategies. To achieve this, fluorine, with the highest electronegativity among all the elements, is an ideal candidate for decorating the Fe-based catalysts due to its extremely strong affinity to electrons that can intensively attract the outer electrons of Fe atoms and result in a significantly positive-charged surface in the surrounding regions for efficient N\(_2\) adsorption. However, due to its strong electronegativity, fluorine usually undergoes an excessively violent reaction with various metal species to form metal fluorides that is incapable of adsorbing nitrogen molecules or catalyzing eNRR. Consequently, mild yet controllable fluorine modification of metal nanoparticles would be more favorable in regulating their electronic structures for eNRR catalysis, which is, however, rarely achieved by far.

Besides, the fabrication of Fe-based catalysts with a sufficiently exposed active surface is another challenge.\[26\] Traditionally, such catalysts usually consist Fe particles incorporated with different types of carbon hosts; and they are almost exclusively fabricated either under high temperature, for example, by annealing carbon precursors with iron salts or with other forms of energy input, for example, by high-energy ball milling graphite in the presence of iron salts.\[27\textendash}^{28}\] Due to the high mobility of iron species in carbon matrix under such conditions, the obtained Fe particles are often large and coated by thick graphitic layers;\[29\] which inevitably compromises the adsorption of N\(_2\) molecules on their surface. Consequently, it would be more favorable that Fe nanoparticles are fabricated under significantly lower temperatures to avoid their sintering and graphite coating.\[30\] Besides, they should also have sufficient affinity with the carbon host to effectively suppress their aggregation, which is especially easy to occur when their sizes are small enough, even at low temperatures. Unfortunately, there are still hardly any studies reporting such technologies.

Based on these considerations, we herein report ultrasmall F-doped Fe particles that are anchored on graphene for eNRR catalysis, obtained by a low-temperature potassium vapor treatment of FeF\(_2\)-intercalated graphite. The doped F atoms on Fe nanoparticles would strongly manipulate the surface charge distribution of Fe nanoparticles, resulting in a significant surface polarization, which can effectively boost their nitrogen absorption capability for enhancing eNRR activity. High FE of 41.6\% and ammonia yield rate of 53.3 \(\mu\)g mg\(^{-1}\) h\(^{-1}\) can be simultaneously acquired with excellent catalytic stability, which achieved significant progress in the yields and FE of non-noble metal catalysts, possessing potentials for high energy efficiency. According to the first principle calculations, this enhanced eNRR capability should be attributed to more empty orbitals from the Fe atoms through the electron transfer with F dopant and substrate.

2. Results and Discussion

The material was obtained through molten-salt intercalation and low-temperature potassium vapor reduction processes, as schematically illustrated in Figure 1a. As demonstrated in
the initial graphite fluoride (denoted (CF)$_n$) precursor, the $sp^2$ hybridization of graphite turns into $sp^3$ hybridization by forming C–F bonds in (CF)$_n$. Using it as the precursor, a molten-salt intercalation treatment was conducted by soaking it in molten FeCl$_3$. In this process, FeCl$_3$ reacted with (CF)$_n$ via a displacement reaction between Cl and F to form FeF$_3$-intercalated graphite (denoted FeF$_3@(CF)_n$). Subsequently, potassium vapor was applied at a relatively low temperature (300 °C) to reduce the FeF$_3@(CF)_n$ and any residual (CF)$_n$, during which ultrasmall F-doped Fe particles were formed anchoring on graphene (denoted as F-Fe@F-G). After removing the fluorine in the graphite fluorides, the excessive potassium may further intercalate into the graphite layers, forming KC$_8$. When KC$_8$ is exposed to water or methanol during the subsequent washing process, hydrogen will be released and exfoliate the graphite layer, forming graphene. For comparison, (CF)$_n$ was also directly treated by potassium vapor reduction without being intercalated by FeF$_3$ (denoted RG).

Scanning electron microscopy (SEM) was first used to observe the structural evolution in the two-step reaction. As shown, (CF)$_n$ exhibits an expanded structure with loosely stacked layers (Figure S1a, Supporting Information). After the molten-salt intercalation, FeF$_3@(CF)_n$ was obtained with a layered morphology that is similar to (CF)$_n$, but decorated by numerous particles on its surface (Figure S1b, Supporting Information). For the final F-Fe@F-G, isolated nanosheets were obtained, similar to typical graphene material (Figure 1b). It is worth noting that F-Fe@F-G shows a very smooth surface under SEM, and no particles can

Figure 1. a) Schematic diagram of the synthesis of the F-Fe@F-G; b) SEM; c) TEM; d) AFM; e) STEM images of F-Fe@F-G and the relevant particle size-distribution histogram; f) the corresponding elemental mapping; and g) the high-resolution STEM image of F-Fe@F-G.
be observed. This suggests the very small sizes of the obtained F-doped Fe particles anchored on graphene by this low-temperature treatment, which is hard to obtain by traditional high-temperature reduction methods. The corresponding structural evolution of the iron species on graphene was investigated with X-ray diffraction (XRD, Figure S1c, Supporting Information). In the XRD pattern of (CF)\textsubscript{n}, (001) plane was identified, with an interlayer spacing of 3.63 Å, similar to the previous reports.[34] It infers that the sp\textsuperscript{2} hybridization in graphene was distorted upon fluorination. Besides, another board absorption peak at 41.1° can be identified to (100) facet, with an in-plane lattice constant \(d_{100}\) of 2.17 Å. It is worth noting that the corresponding (100) peak shifts to a higher degree for RG, corresponding to a smaller \(d_{100}\) value and suggesting the reformation of sp\textsuperscript{2} hybridization after this low-temperature reduction.[31]

Compared with (CF)\textsubscript{n} and RG, the diffraction pattern in FeF\textsubscript{3}@((CF)\textsubscript{n}) becomes more distinct. Apart from the peaks that correspond to FeF\textsubscript{3} (PDF No.850481), the additional ones at 15.1, 26.1, and 35.4° can be indexed to the (001) facet of FeCl\textsubscript{3} (PDF No.770998), (131) plane of CF\textsubscript{2}Cl\textsubscript{2} (PDF No.760420), and (110) facet of FeO\textsubscript{2} (PDF No.791741), respectively. After the potassium vapor reduction, Fe-F@Fe-G manifests a strong diffraction peak at 25.7°, ascribed to the (002) facet of graphene. Compared with RG, the (002) peak of F-F@F-G shifts to a lower degree, indicating the broadened interlayer distance that is possibly caused by intercalated species. Besides, in the enlarged region between 40° and 50°, two peaks can be identified as the (100) facet of graphene and the (110) facet of Fe (PDF No. 897 194), indicating the reduction of the FeF\textsubscript{3} during the potassium vapor reduction.

Under transmission electron microscopy (TEM), a large, flat, and smooth sheet can be observed for F-F@F-G under low magnification (Figure 1c and Figure S1d, Supporting Information). The section analysis under atomic force microscopy indicates that the sheet possesses a layered structure with a thickness of 1.7 nm (Figure 1d), verifying the material is few-layered graphene. Figure 1e demonstrates the scanning transmission electron microscopy (STEM) image of F-Fe@F-G, dotted with abundant bright spots, which should be iron species. The particle size-distribution histogram demonstrates that the iron species possess an average diameter of 5.08 nm. On them, clear lattice fringes with a distance of \(\approx 0.203\) nm can be recognized that corresponds to the (110) facet of iron (Figure S2, Supporting Information).

STEM-based energy dispersive spectroscopy (STEM-EDS) mapping was then carried out to further confirm the chemical composition of the material. The quantitative STEM-EDS results show the existence of C (83.0%), Fe (6.3%), F (1.0%), and O (9.6%) (Figure S3a, Supporting Information). Noticeably, the actual ratio of Fe and F is much higher than the value of FeF\textsubscript{3}, which again confirms that FeF\textsubscript{3} compound on graphene has been reduced by K vapor, consistent with XRD results (Figure S1c, Supporting Information). The STEM-EDS mapping illustrates that the sheet is mostly carbon, and the bright spots overlap with iron. Besides, the F element distribution is mainly consistent with that of the Fe element, with a small portion evenly distributing over the graphene substrate as well (Figure 1f). The O element in the mapping may come from oxidation during sample preparation or environment.[32]

Afterward, high-resolution STEM observation was performed to investigate the fine structure of the material (Figure 1g). Clear lattice fringes can be seen over the entire surface, which can be ascribed to two components. The first component with clear honeycomb structures can be ascribed to the graphene substrate with sp\textsuperscript{2} hybridization, which is absent in the TEM images of FeF\textsubscript{3}@((CF)\textsubscript{n}) and consistent with the XRD results (Figure 3b,c), verifying the formation of graphene. The area enclosed in the yellow dotted rectangle overlaps an ultrasmall particle of 3 nm, determined by the corresponding dark-field STEM image (Figure 1g left inset). Based on these structure characterizations, a simulation model can be generated (Figure 1g right inset): Ultrasmall iron particles with a diameter of several nanometers are bonded on few-layered graphene, with fluorine atoms decorated both on the particle surface and graphene substrate. Apart from F-F@F-G, this low-temperature potassium vapor reduction strategy can also be readily extended to other metal nanoparticles/graphene systems. For example, by using molten PtCl\textsubscript{6} or RuCl\textsubscript{3} to react with (CF)\textsubscript{n}, and followed by the low-temperature potassium vapor reduction process, a high loading of fine Ru and Pt nanoparticles can be formed on the graphene surface as well (Figure S4, Supporting Information), with a highly uniform distribution, suggesting the versatility of this strategy. The Raman spectra of carbon support in F-F@F-G, FeF\textsubscript{3}@((CF)\textsubscript{n}), and (CF)\textsubscript{n} were obtained to illustrate the chemical state of carbon in the catalysts (Figure S5, Supporting Information). The calculated \(I_{2D}/I_{G}\) ratios for ((CF)\textsubscript{n}, FeF\textsubscript{3}@((CF)\textsubscript{n}), and F-Fe@F-G are 1.22, 1.24, and 1.21, respectively. The difference of \(I_{2D}/I_{G}\) ratio is relatively small, indicating the similar defective graphitic structure of the materials. Details about the material’s structure and composition can be found in the following discussion.

The chemistry of the materials was then investigated by X-ray photoelectron spectroscopy (XPS, Figure 2a). The XPS survey spectrum of (CF)\textsubscript{n} shows the existence of F and C elements. After molten FeCl\textsubscript{3} treatment, both Fe and F can be found on FeF\textsubscript{3}@((CF)\textsubscript{n}) while F disappears after the potassium vapor reduction for both RG and F-F@F-G. The fine chemical state of the elements in the samples was then studied by high-resolution XPS. The Fe 2p spectra for F-F@F-G and FeF\textsubscript{3}@((CF)\textsubscript{n}) show different features (Figure 2b). The deconvoluted Fe 2p spectrum of F-F@F-G has four peaks at lower binding energy (703.5/709.8 eV for Fe 2p\textsubscript{3/2} and 722.5/724.4 eV for Fe 2p\textsubscript{1/2}), identified as Fe\textsuperscript{0} and Fe\textsuperscript{2+} species.[33] In comparison, FeF\textsubscript{3}@((CF)\textsubscript{n} only has Fe\textsuperscript{3+} species from FeF\textsubscript{3}.[34] These results demonstrate that FeF\textsubscript{3} is reduced to a lower oxidation state (Fe-C or Fe-Fe), consistent with the observed iron particles in STEM results (Figure 1e). The high-resolution C 1s spectrum of F-F@F-G can be deconvoluted into four peaks at 283.9, 284.6, 285.6, and 286.7 eV, corresponding to C-Fe, C-C (sp\textsuperscript{2} hybridization), C-C (sp\textsuperscript{3} hybridization), and C=O, respectively (Figure 2c).[35] The sp\textsuperscript{2} hybridization C is typical of graphene, while the sp\textsuperscript{3} hybridization C reveals that part of the conjugated \(\pi\) bonds has been opened and connected to other elements such as, fluorine and iron.[36] The C=C (sp\textsuperscript{2} hybridization), C-C (sp\textsuperscript{3} hybridization), and C=O species also exist in FeF\textsubscript{3}@((CF)\textsubscript{n}) and RG, but the latter showed a smaller C-C (sp\textsuperscript{3} hybridization) peak. Similar to the survey spectra results, no F 1s signal could be detected on F-F@F-G and RG, which...
may be ascribed to the low F content on the material surface (Figure 2d).

The local coordination of iron in F-Fe@F-G was further probed by X-ray absorption fine structure and K-edge extended X-ray absorption fine structure (EXAFS) analysis. FeF₃@(CF)ₙ, Fe foil, and Fe₃O₄, with typical Fe–F, Fe–Fe, and Fe–O coordination structures, were used as references. In the K-edge X-ray absorption near edge structure, the absorption edge of FeF₃@(CF)ₙ locates at the highest position, followed by Fe₃O₄, F-Fe@F-G, and Fe foil, which indicates that the oxidation state of Fe in F-Fe@F-G is between the Fe states in FeF₃@(CF)ₙ and Fe foil (Figure 2e), in agreement with the XPS results. The Fourier-transformed Fe k³-weighted EXAFS spectra of Fe in F-Fe@F-G and reference samples featured three peaks at 1, 1.5, and 2.4 Å, corresponding to the nearest Fe–C, second nearest Fe–F, and the Fe–Fe coordination, respectively (Figure 2f).

The wavelet transform (WT) analysis was further conducted to discriminate the backscattering atoms and to resolve the coordination structure of the Fe species in the material. As demonstrated in Figure 2g, the WT contour plot of F-Fe@F-G exhibits three intensity maximums: the intensity maximum nearest to the iron center locates at ≈0.6 Å⁻¹, which is smaller than the maximum in Fe₂O₃ (≈1.0 Å⁻¹), ascribed to the Fe–C coordination; the second closest intensity maximum locates at ≈3.1 Å⁻¹, which is consistent with the intensity maximum nearest to the iron center in FeF₃@(CF)ₙ, ascribed to the Fe–Fe coordination; and the intensity maximum at ≈6.1 Å⁻¹ that can be attributed to the Fe–Fe coordination. The first-shell Fe–C coordination illustrates the strong connection between the graphene and iron species, and the Fe–Fe bond should be attributed to the iron particles. Besides, the intensity maximum of the Fe–F bond indicates the existence of fluorine that is bound with iron after the potassium vapor reduction process, in agreement with the STEM-EDS mapping results.

The catalytic performance of F-Fe@F-G was evaluated and compared with the FeF₃@(CF)ₙ, (CF)ₙ, and RG for eNRR (Figure 3 and Figures S6–S12, Supporting Information), in an H-type cell separated by a Nafion membrane under ambient conditions. An Ag/AgCl electrode and a platinum mesh (1 × 1 cm²) were used as the reference and counter electrode, respectively. Cyclic voltammetry (CV) under different atmospheres was first conducted to investigate the materials’ eNRR activity (Figure S6a–d, Supporting Information). After potassium vapor reduction, the stacked graphite was exfoliated and form few-layered graphene, which can expose more reacting surface, increasing the ammonia yield. The CV results are presented in Figure S7, Supporting Information. The calculated ECS of FeF₃@(CF)ₙ and F-Fe@F-G is 0.013 and 0.063 cm², respectively. The higher electrochemical surface of F-Fe@F-G is derived from the exfoliated graphene layers, which ensures more active sites for eNRR. For F-Fe@F-G, a distinct increase of reducing current can be observed when the atmosphere was changed from Ar to N₂, demonstrating its capability for eNRR catalysis. It also showed a larger current difference than the other samples, which suggests its higher selectivity and/or ammonia yield rate during eNRR.

The ammonia yield rates of F-Fe@F-G and analogs were assessed by chronoamperometry test and quantified by the Nessler-reagent method. To exclude the possible ammonia contamination from the environment or feeding gas, we first...
assessed the ammonia concentration of the electrolytes tested under Ar atmosphere, exposed to air overnight at the open-current voltage (V_{oc}), and purged with nitrogen at V_{oc} for 6 h, and no ammonia was detected in them (Figure 3a). Considering no nitrogen-containing precursors were employed during materials fabrication, and no nitrogen was detected on the material according to the XPS and STEM-EDS results, it is reasonable to deduce that the detected ammonia in the electrolyte should come from the electrochemical reduction of the N2 feeding gas. The amount of N2H4 has been estimated via the method of Watt and Chrisp and no N2H4 was detected in the electrolyte after reaction, indicating the only products are ammonia and hydrogen (Figure S11, Supporting Information).

Among the samples, F-Fe@F-G shows the highest ammonia yield (R_{NH3}) at all potentials (Figure 3b). For F-Fe@F-G, the R_{NH3} increased rapidly from 11.9 μg mg^{-1} h^{-1} at −0.28 V to the maximum value of 53.3 μg mg^{-1} h^{-1} at −0.38 V. In comparison, FeF3@(CF)\textsubscript{n}, (CF)\textsubscript{n}, RG show much lower R_{NH3} in the whole potential range, suggesting their much inferior eNRR catalytic activity (Figure 3b and Figures S7–S9, Supporting Information). The corresponding FE values at these potentials were then calculated (Figure 3c). At -0.28 V, F-Fe@F-G again shows the highest FE of 43.6%. On the contrary, the peak FE values of the other samples are far lower than F-Fe@F-G, indicating the strongest capability of F-Fe@F-G for suppressing the undesired HER, the competing reaction against eNRR.

The stability of F-Fe@F-G was then evaluated by continuously performing eNRR at −0.38 V (Figure S13a–c, Supporting Information). The R_{NH3} and Faradaic efficiencies at all potentials were then calculated. As shown, the R_{NH3} decreases from 50.2 μg mg^{-1} h^{-1} to 44.3 μg mg^{-1} h^{-1} initially and remained fairly stable at ≈44.0 μg mg^{-1} h^{-1} afterward, with the FE values showing a similar trend (Figure S13c, Supporting Information). Compared with the recent literature (Figure 3d), [38–46] F-Fe@F-G simultaneously delivers a high R_{NH3} and FE, which is especially favorable for the practical eNRR applications.

Density functional theory (DFT) calculations were subsequently carried out to clarify the mechanism of the eNRR over F-Fe@F-G. We adopted a model comprising a Fe\textsubscript{65} cluster with a diameter of 1.1 nm supported on graphene monolayer (Fe@G), with either the cluster or substrate decorated by F atoms (F-Fe@G, Fe@F-G, and F-Fe@F-G, respectively) as displayed in Figure 4a and Figure S14, Supporting Information. Freestanding Fe\textsubscript{65} clusters with or without F decoration were also considered for comparison. Models with different concentrations of F atoms that are anchored on either the Fe cluster or the graphene substrate were tested, which generally show a similar trend of activity. Herein, we mainly discuss three representative cases, that is, the Fe\textsubscript{65} cluster on graphene with a single F atom located on top of the Fe\textsubscript{65} cluster or graphene, respectively.

The doping of electronegative F species in either cluster or substrate can induce notable electron redistribution over Fe\textsubscript{65} and graphene, which largely enhances the cluster-substrate interaction. As shown by Figure 4b, the binding energy of F-doped Fe\textsubscript{65} on graphene or Fe\textsubscript{65} on F-doped graphene is strengthened by up to 1.92 eV. Accompanied by the strong interface interaction, the activity of Fe\textsubscript{65} can be significantly enhanced. In these cases, the N\textsubscript{2} molecule is chemisorbed on the Fe\textsubscript{65} cluster in the side-on configuration with adsorption energies of −0.30 to −1.23 eV, and the N=N bond length is elongated to 1.18–1.26 Å, in comparison with 1.11 Å for free N\textsubscript{2} molecules. Consequently, the presence of F element in either cluster or graphene substrate greatly boosts the capability of Fe\textsubscript{65}...
Figure 4. a) Atomic structures and Bader charge analysis of Fe\textsubscript{65} with F decoration supported on graphene fluoride. The positive (negative) charge indicates the electron gain (loss). b) The binding energy (\(E_b\)) between Fe\textsubscript{65} cluster and substrate and the adsorption energy (\(\Delta E_{\text{N}_2}\)) of N\textsubscript{2} molecule over supported Fe\textsubscript{65} cluster with and without F decoration. The insert shows differential charge density of N\textsubscript{2} molecule and supported Fe\textsubscript{65} cluster with F decoration. c) The adsorption energy of N\textsubscript{2} molecules as a function of the net charge of active sites, and the limiting potential (\(U_L\)) of eNRR on various supported Fe\textsubscript{65} particles. The insert is the differential charge density of Fe\textsubscript{65} and graphene substrate. d) The free energy diagram of eNRR on Fe@G and F-Fe@F-G (the intermediate structures of eNRR on F-Fe@F-G. The light blue and pink colors represent the electron accumulation and depletion regions, respectively, with an isosurface value of 0.036 e Å\textsuperscript{-3}. The H, C, N, F, and Fe atoms are shown in white, grey, blue, green, and orange colors, respectively).
for activation of N2 molecule (Figure 4b). Different from some gas molecules as electron acceptors (e.g., CO2), the activation of N2 molecules is realized through the donation and π-back-donation mechanism, which requires the empty orbital of the active species. According to our Bader charge analysis, the Fe65 cluster loses electrons to both F dopants (0.60–0.71 e per F atom) and graphene substrate (1.98–2.32 e per cluster). As the Fe atom loses more electrons, the electron donation from N2 to the Fe site of the supported Fe65 is more favorable, resulting in stronger N2 binding, as manifested by Figure 4c.

Furthermore, N2 reduction to NH3 on the supported Fe65 cluster occurs through the enzymatic pathway (Figure S15, Supporting Information). In this process, protons are alternatively attached to the N atoms of adsorbed N2 molecules, leading to the successive formation and release of two NH3 molecules. For Fe@G without F modification, which has the weak binding capability to N2 and other intermediates, the reaction diagram is uphill for the formation of NH3 species and encounters a large limiting potential of ~0.83 eV. For the counterparts with F decoration (i.e., F−Fe@G, Fe@F−G, and F−Fe@F−G), which have the strong binding capability, the free energy curves are generally downhill, and the limiting potentials are as small as ~0.36 eV (Figure 4d). Therefore, our DFT calculations suggest that F doping in either Fe particles or graphene substrate induces the electron flow out of Fe atoms and endows more empty orbitals for Fe, which is beneficial for the donation and π-back-donation with N2 molecule, hence improving the eNRR performance. At last, we assess the activity of Fe cluster supported on graphene substrate with and without F decoration for HER. Our calculations show H* species is chemisorbed on the Fe65 cluster with absorption energy of 0.19 to ~1.45 eV (Table S2, Supporting Information). Similar to N2 molecule, the presence of F element also enhances H* species adsorption. It’s worth noting that H* species can chemically adsorb on graphene fluoride substrate (Figure S16, Supporting Information), while N2 is not adsorbed on the substrate and is directly attached to Fe65 cluster. This might decrease the competitive of HER with eNRR.

3. Conclusion

In summary, graphene supported ultrasmall and F-doped iron particles were successfully designed and fabricated by a low-temperature potassium vapor reduction process for eNRR catalysis. A high FE of 41.6% and ammonia yield rate of 53.3 g mg−1 h−1 can be simultaneously acquired, accompanied by excellent catalytic stability. The first-principle calculation reveals that enhanced eNRR capability is attributed to more empty orbitals carried by the Fe atoms through the electron transfer with F dopant and substrate. Considering the highly versatile feature of this strategy for various metals (Fe, Ru, and Pt), it should facilitate the development of a series of essential electrocatalysts from the aspect of electronic structure manipulation.

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

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

carbon-based electrocatalyst, electronic configuration, fluorine functionalization, iron nanoparticle, nitrogen fixation

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