Available active sites on ε-Fe₃N nanoparticles synthesized by a facile route for hydrogen evolution reaction

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ABSTRACT
Exploring efficient noble-metal-free water splitting electrocatalysts from earth-abundant elements is of great importance to realize wide applications in the generation of hydrogen fuel for clean energy. Here we reported a facile route to synthesize ε-Fe₃N single-phase nanoparticles by thermal ammonolysis of Fe precursors. The roles of nitrogen atoms in tailoring the hydrogen evolution reaction (HER) activities of ε-Fe₃N have been systematically investigated. HER activity is enhanced by reducing the effective coordination number of nitrogen atoms from 2.61 to 1.67, where the standard coordination number in ε-Fe₃N is 2. Density functional theory (DFT) calculations reveal that the reduction of nitrogen content lowers the energy of the Tafel process on the (1̅100)-FeN exposed and (11̅20) N-exposed surfaces. Both surfaces are thermodynamically favored for the HER. Furthermore, the active sites of the Tafel process changes from the kinetically less favored hollow sites of Fe atoms to the kinetic more favored top site of N atoms and the bridge site of Fe atoms on both (1̅100)-FeN and (11̅20) N-exposed surfaces. Our findings propose a novel strategy to enhance
HER activity by utilizing nitrogen deficiency, which is of great importance for the development of highly active transition metal based electrocatalysts.

1. Introduction

Hydrogen, with the highest gravimetric energy density of any fuel and zero carbon emissions, is considered an ideal renewable energy source to replace traditional fossil fuel energy systems.\cite{1, 2} The hydrogen evolution reaction (HER) is a crucial half reaction of water decomposition (into hydrogen and oxygen) and is been considered as one of the most important methods to produce hydrogen. Electrolysis of water requires a highly efficient and stable catalyst to lower the energy barrier for water decomposition. For the large-scale and sustainable application of electrolytic HER, economic feasibility and catalytic efficiency are considered. High-performance HER catalysts based on earth-abundant materials are intensively studied to replace the Pt based catalytic materials.\cite{3, 4} In recent years, transition metal compounds including transition metal oxides,\cite{5} nitrides,\cite{6} phosphides,\cite{7} carbides,\cite{8} sulfides,\cite{9} etc. are studied as catalysts for HER and oxygen evolution reaction (OER) due to their low cost, high efficiency and good stability. In particularly, transition metal nitrides are promising because of their unique electronic structures, high electrical conductivity, and good corrosion resistance.\cite{1, 10}

A variety of strategies have been attempted to improve the electrocatalytic performance of transition metal nitrides.\cite{1, 11} Doping \cite{3, 12}, alloying \cite{13, 14} and structural modifying \cite{15} of transition metal nitrides can combine the advantages of various elements and play a synergistic effect in improving their electrocatalytic performance. Secondly, tuning the stoichiometry and composition \cite{16} of the transition metal nitrides by changing the ratios of metal to nitrogen. In addition to designing the metal nitrides composition, optimization of support structures \cite{13, 17} provides large surface area, enables efficient fluid diffusion, and promotes the charge transportation and transfer.
to boost the electrocatalytic performance. For example, Y. Hu et al.\cite{12} indicates that improvement of electrocatalytic activity of CoAl-Fe$_2$N/Fe$_3$N nanoparticles can be connected to the reduction of d-band center of Fe$_2$N by doping Co and Al, which neutralizes the electron density of iron and optimize the electronic structure. The result shows that the CoAl-Fe$_2$N/Fe$_3$N nanoparticles achieve a lower HER overpotential of 145 mV at 10 mA cm$^{-2}$ in 1 M KOH solution, while the undoped Fe$_2$N/Fe$_3$N requires 461mV to attained the same current density. Z. Liu et al.\cite{13} grow the Ni$_3$FeN nanostructure on carbon cloth. On one hand, the carbon cloth offers extremely large surface area, promoting charge transportation and transfer in HER and OER. On the other hand, the combination of nickel and iron in the structure tunes their electrical and chemical properties.\cite{13} The Ni$_3$FeN/CC exhibits HER activity with an overpotential of 105 mV at the current density of 10 mA cm$^{-2}$ in 1 M KOH solution, much less than those of Ni$_3$N/CC (178 mV) and Fe$_2$N/CC (172 mV).

Although the above methods have been applied to improve the catalytic performance of metal nitrides, these treatments inevitably make the understanding of catalytic mechanism of metal nitrides complicated and unachievable. It is worth noting that homogeneous single-phase materials are ideal substances for understanding catalytic mechanism, which was successfully proved in MoS$_2$\cite{18-23} and layered double hydroxides (LDH)\cite{24, 25}. B. Hinnemann et al.\cite{18} firstly proposed experimentally and theoretically that single-phase MoS$_2$ is a promising HER electrocatalyst due to the active sites of MoS$_2$ edge structure revealed by DFT calculations. Subsequently, Jaramillo et al.\cite{19} further discovered that HER activity of MoS$_2$ nanoparticles correlate linearly with the number of MoS$_2$ edge sites quantified by scanning tunneling microscopy. This understanding has led to significant attention focused on enhancing HER activity of MoS$_2$ by enhancing the number of active sites\cite{20}, improving electrical conductivity through doping\cite{21}, and crystal-phase engineering\cite{22}, these fundamental studies have been extended to many other transition metal dichalcogenides\cite{23}. Similarly, NiFe-LDH, a unique kind of lamellar ionic crystals with two-dimensional structures\cite{24}, presented attractive OER activities under alkaline conditions. C. Peng et al.\cite{25} discovered that Fe
edge sites surpass Ni edge sites and lattice sites in OER activity according to DFT calculations. Subsequently, they realized in-situ formation of Fe edge sites in single-phase NiFe LDH through a facile acid-etching method. High OER activity with an OER overpotential of 308 mV at 10 mA cm\(^{-2}\) in 1 M KOH was obtained, agreeing well with their theoretical calculations.

From these reports it is clear that the identification of active sites plays a crucial role in the design and development of advanced catalytic materials.\(^{[18-25]}\) However, in the investigation of electrocatalytic mechanism of transition metal compounds, iron nitrides have received inadequate attention, despite the fact that iron is the most abundant transition metal element in the earth’s crust.\(^{[26]}\) The challenge is twofold, 1) precise control of nitrogen content in single-phase iron nitride and 2) achieving a favorable d-band energy for the HER.\(^{[12, 27]}\) In this work, we proposed a facile approach to synthesize single-phase ε-Fe\(_3\)N nanoparticles by thermal ammonolysis of Fe precursors. The nitrogen content in the single-phase ε-Fe\(_3\)N was successfully tuned by controlling the nitridation temperature. Furthermore, we apply density functional theory (DFT) calculations to identify the active site on the surface of ε-Fe\(_3\)N, to correlate HER performance with the roles of nitrogen atoms in ε-Fe\(_3\)N. Eventually, the catalytic mechanism of ε-Fe\(_3\)N was elucidated. Our research on single-phase ε-Fe\(_3\)N is of great significance for uncovering the underlying HER mechanism of iron nitrides, and is conductive to the development of metal nitride based high-performance catalysts for water splitting.

2. Results and Discussion
Figure 1. (a) Schematic illustration showing preparation of $\varepsilon$-$\text{Fe}_3\text{N}$ from $\alpha$-Fe and NH$_3$ gas. (b) SEM images of the samples under different nitridation temperatures of 500°C (I FeN500), 550°C (II FeN550) and 650°C (III FeN650) (below: the corresponding particle size distribution). (c) I Scanning TEM image of FeN500 (inset: electron diffraction patterns with scale bar of 10 nm$^{-1}$); II and III the corresponding Fe and N EDX elemental mappings; IV High-resolution TEM image of a $\varepsilon$-$\text{Fe}_3\text{N}$ (FeN500) nanoparticle.

The $\varepsilon$-$\text{Fe}_3\text{N}$ single-phase nanoparticles were synthesized by a thermal nitridation process of Fe precursors as illustrated in Figure 1a. We prepared samples with different nitridation temperatures, to investigate the effect of temperature on electrocatalytic activity. Figure 1b shows nanoparticle morphologies and corresponding particle size distribution of $\varepsilon$-$\text{Fe}_3\text{N}$ nanoparticles obtained under
different nitridation temperatures of 500 °C (marked as FeN500), 550°C (marked as FeN550) and 650°C (marked as FeN650). All samples show similar size distributions with a center at 40~60 nm, although the FeN500’s size distribution profile seems sharper than those of the FeN550 and the FeN650.

*Figure 1c* shows a scanning transmission electron microscope (STEM) image of FeN500. The inset diffraction pattern shows concentric ring indexed to (1121) and (3030) reflections of the ε-Fe$_3$N. The spatial distribution of Fe and N elements was given by energy dispersive X-ray (EDX) elemental mapping technology. As displayed in *Figure 1c II* and *III* the Fe and N elements are distributed uniformly in ε-Fe$_3$N. The high-resolution TEM (HRTEM) image further verifies the phase structure of as-prepared nanoparticles. As shown in *Figure 1c IV* the observed lattice fringes with interplanar distances of 2.35 Å, corresponding to the (1120) lattice planes, respectively. The above results strongly indicate our successful synthesis of ε-Fe$_3$N nanoparticles through thermal ammonolysis of α-Fe precursors.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition and valence information of the iron and nitrogen elements in the ε-Fe$_3$N samples. *Figure 2a-2b* and Table *S1* show the XPS high-resolution spectrum and element atomic ratio of ε-Fe$_3$N prepared at different nitridation temperatures. As expected, due to the lower amount of energy driving the reaction, the nitrogen content decreased with decreasing of the nitridation temperature (Table *S1*). In addition, from *Figure 2a and 2b*, the FeN500, FeN550, FeN650 show similar peaks of Fe 2p and N 1s, indicating that the binding state of the elements in ε-Fe$_3$N has not been significantly changed by the nitridation temperature. *Figure 2a* shows the XPS high-resolution spectrum of Fe 2p. The peaks at 708.5 eV (2p3/2) and 722.0 (2p1/2) corresponds to the Fe metal bond of iron nitride (Fe-N), which proves the existence of iron nitride. The peaks at 710.9 eV and 713.5 eV are assigned to Fe 2p3/2 of Fe$^{2+}$ and Fe$^{3+}$, where the peaks at 724.3 eV and 727.0 eV belong to Fe 2p1/2 of Fe$^{2+}$ and Fe$^{3+}$. 

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The fitting peaks of Fe 2p appear at 707.3 eV (2p3/2) and 720.3 (2p1/2) which can be attributed to the Fe$^0$, suggesting the presence of metallic bonds in samples. As shown in Figure 2b, the peak of N1s at 398.19 eV reconfirms the formation of Fe-N bonds in ε-Fe$_3$N. 

Figure 2. (a and b) High-resolution XPS spectra of Fe 2p and N 1s. In (a), the fitted peaks of FeN500 correspond to Fe$^0$ 2p3/2 (707.3 eV) and Fe$^0$ 2p1/2 (720.3 eV), Fe-N 2p3/2 (708.5 eV) and Fe-N 2p1/2 (722.0), Fe$^{2+}$ 2p3/2 (710.9 eV) and Fe$^{2+}$ 2p1/2 (724.3 eV), Fe$^{3+}$ 2p3/2 (713.5 eV) and Fe$^{3+}$ 2p1/2 (727.0 eV). In (b), the fitted peaks of FeN500 correspond to N-Fe (398.19 eV). (c) Lattice structure of ε-Fe$_3$N. (d) XRD patterns of the Fe precursor and the samples after nitridation at different temperatures. (e) XAFS results of samples after nitridation at different temperatures. (f) Fourier transformed EXAFS curves (solid) and corresponding simulation fitting curves (dashed).

Figure 2d shows X-ray diffraction (XRD) patterns of the FeN500, FeN550 and FeN650 samples. The samples after nitridation exhibit three main peaks centered around 38°, 41° and 43°, corresponding to (11̅20), (0002) and (11̅21) reflections of the ε-Fe$_3$N structure [P6$_3$22, JCPDS No. 49-1663], indicating that the samples after nitridation are single-phase ε-Fe$_3$N. The ε-Fe$_3$N structure is shown in Figure 2c, in which Fe atoms are hexagonally closely packed whereas N atoms partially occupy the octahedral interstices of Fe atoms. The iron atom is surrounded by 2 nitrogen atoms and 12 iron atoms as the first and second nearest shells, respectively. In Figure 2d, we can also observe...
peaks’ shift towards lower angles together with peaks’ sharpening as the nitridation temperature increases from 500 °C to 650 °C. According to Bragg equation, peak shifts towards lower-angle means the expansion of the lattice cell of the ε-Fe₃N. In terms of Scherrer equation, peaks’ sharpening indicates the improvement of crystallinity and the growth of crystalline grains in ε-Fe₃N nanoparticles. In ref. [31], the nitrogen content varied with the changes of nitridation temperature, which led to different interplanar spacings. It indicates us that the increase of lattice cell parameters in ε-Fe₃N is most probably related to a rise of nitrogen content in the ε-Fe₃N structure caused by elevating the nitridation temperature.

To capture and verify the above structural changes, we further conducted X-ray absorption fine-structures (XAFS) measurements at Beijing Synchrotron Radiation Facility. XAFS is a powerful technique for exploring the local atomic arrangements in materials and highly sensitive to the change of local geometrical structure. Figure 2e shows the X-ray absorption fine-structures of Fe K edge for FeN650, FeN550 and FeN500 samples. At the near-edge absorption region, no obvious difference is observed among the samples, indicating no phase change. Figure 2f is the Fourier transformation (FT) of the extended XAFS (EXAFS), which shows useful information of local atomic arrangements around Fe atoms. Two main peaks are presented in the range of 1.5–2 Å and 2.5-3 Å, corresponding the first and the second nearest neighboring shells of Fe atoms. The quantitative results (see Table 1) were extracted through fitting the experimental results. The simulating curves (dashed lines) fit well with the experimental curves (solid lines). In the fits, the crystal structure of ε-Fe₃N in P6₃22 space group (Figure 2c) was used to generate the initial structure for EXAFS.

**Table 1.** Local structure parameters around Fe extracted by EXAFS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R(Å)</th>
<th>S₀²</th>
<th>N·S₀²</th>
<th>∆δ²(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeN650</td>
<td>Fe-N</td>
<td>2</td>
<td>1.95</td>
<td>1.305</td>
<td>2.61</td>
<td>0.00675</td>
</tr>
</tbody>
</table>

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As seen in Table 1, the effective coordination number of the first nearest nitrogen atoms decreases from 2.61 (FeN650) to 1.67 (FeN500), whereas the standard coordination number of nitrogen atoms in the ε-Fe$_3$N is 2. The deviation from the nitrogen coordination number suggests that the nitrogen content is different in the FeN650, FeN550 and FeN500 samples. Lower nitridation temperature results in lower nitrogen content in the ε-Fe$_3$N structure, as previously discussed (Table S1). Moreover, the Fe-Fe distance decreases from 2.73 Å (FeN650) to 2.34 Å (FeN500). The shortening of Fe-Fe distance confirms that the Fe atom is surrounded by less nitrogen atoms in samples prepared at lower nitridation temperature. To well describe the above structural changes, we use the expression of ε-Fe$_x$N$_y$ instead of ε-Fe$_3$N hereafter.
Figure 3. HER electrocatalytic performance measurements: (a) polarization curves, (b) corresponding Tafel plots, (c) electrochemical impedance spectroscopy, and (d) electrochemical active surface area test results, in which slopes are equal to the double-layer capacitance $C_{dl}$.

The electrochemical measurements were conducted via a standard three-electrode system in 1.0 M KOH electrolyte solution to evaluate the electrocatalytic activity of the as-obtained electrocatalysts. We loaded the nano-particle samples onto a glassy carbon electrode as the working electrode. The reference electrode and counter electrode were a Hg/HgO electrode and a graphite electrode, respectively. As seen in Figure 3a, the liner sweep voltammetry (LSV) polarization curves with iR-correction indicate that the commercial Pt/C (20%) powder catalyst used for comparison exhibits the lowest overpotential of 50 mV at the current density of 10 mA cm$^{-2}$. The FeN500 requires a very small overpotential of 171 mV to achieve the current density of 10 mA cm$^{-2}$, which is lower than that of the FeN550 (182 mV) and the FeN650 (425 mV). It can be also found that the Pt/C exhibits higher HER performance than the FeN500 in the low-current-density region, whereas in the high-current-density region the overpotential of FeN500 is almost close to the Pt/C. We have further analyzed the Tafel slopes of the samples to gain a deep insight into the
electrochemical performance. In Figure 3b, the FeN650, FeN550 and FeN500 show Tafel slopes of 136, 105 and 96 mV dec$^{-1}$, respectively. The FeN500 exhibits the smallest Tafel slope among all the samples, suggesting rapid reaction kinetics during the electrocatalytic process.$^{[32]}$

Electrochemical impedance spectroscopy (EIS) was performed to investigate the electrode kinetics under the HER operating conditions. As seen the Nyquist plots in Figure 3c, the FeN500 has smaller charge-transfer resistance than the FeN550 and the FeN650, indicating the electrode loaded with FeN500 has the fastest electron transfer process among all samples, agreeing well with the smallest Tafel slope in Figure 3b. The electron transfer process for HER in the alkaline medium involves three steps: to transfer from the electrode to the catalyst, to transport through the catalyst, and to activate a H$_2$O molecule at an active site to form hydrogen. Fast electron transportation and transfer process requires good electrical contact between the glassy carbon electrode and the catalyst, good conductivity of the catalyst, and sufficient active sites on the catalyst surface exposed to the electrolyte. Due to the intrinsic metallic features of ε-Fe$_3$N, it is reasonable to state that sufficient active sites on the exposed surfaces are key to realize high catalytic activities.

Electrochemical active surface area (ECSA) is considered to reflect the actual active area of the electrocatalyst exposed to the electrolyte, and is usually positively correlated with catalytic activity.$^{[33]}$ The ECSA can be evaluated by measuring the electrochemical effective double-layer capacitance ($C_{dl}$) through a cyclic voltammetry (CV) method with varied scanning rates.$^{[34]}$ The working electrode was swept by a potential ranging from 0 to 0.3 V vs. RHE, where no faradic process occurs. The CV curves recorded at different scan rates for all the above samples are shown in Figure S1. The measured current density ($i_{anode}$-$i_{cathode}$)/2 at 0.15 V vs. RHE are plotted as a function of the scan rate in Figure 3d. According to the slopes of the plots, the FeN500 exhibits a $C_{dl}$ of 207.4 mF cm$^{-2}$, which is much higher than that of the FeN550 (186.8 mF cm$^{-2}$) and the FeN650 (16.8 mF cm$^{-2}$), indicating that the higher catalytic activity of the FeN500. With an electrode area of
0.071 cm$^2$, the HER ECSAs of FeN650, FeN550 and FeN500 are 29.7, 330.1 and 366.5 cm$^2$EC$^2$, respectively, assuming that the specific capacitance ($C_s$) of the electrocatalysts is 0.04 mF cm$^{-2}$. After normalizing the HER LSV curves of these catalysts to ECSA (see Figure S2), the catalytic performance of FeN500 is still better than that of FeN550 and FeN650, which also proves that FeN500 catalyst has better intrinsic catalytic activity.

To provide a fundamental understanding of these results, DFT calculations were utilized to elucidate mechanism between the local structural change and the electrochemical performance. For the transition metals based HER electrocatalysts, the Gibbs free energy of the intermediate adsorption on potential active sites can be used as an index to define the electrochemical performance of the electrocatalysts for HER. In order to obtain the relationship between the various exposed surfaces and the HER activities of the nitridated samples, DFT calculations were thoroughly employed to investigate the Gibbs free energies of the intermediate one hydrogen and two hydrogens adsorbed on the (0001), (11̅10) and (11̅20) surfaces of the $\varepsilon$-Fe$_x$N$_x$ ($x=3, 2$). The exposed surfaces were chosen according to the results of surface energy calculations (see Figure S3-S6). $X$ was defined as 3 or 2 to correlate to the EXAFS result of the effective coordination number of the first nearest nitrogen atoms, which decreases from 2.61 (FeN650) to 1.67 (FeN500).

Theoretically, the reaction pathway of HER in alkaline media can be concluded by the following two steps: (1) electrolyzed water, $H^*$ formed on surface (Volmer step) and (2) $H^*$ forms into molecular $H_2$, the consequent $OH^-$ released to the solution. The second step can be described by two mechanisms: Heyrovsky process or Tafel process. The calculated adsorption Gibbs free energies are shown in Figure 4a and 4b. It is well known that too negative Gibbs free energy indicates that hydrogen intermediate $H^*$ chemisorbed on its surface is too strong to facilitate product desorption. The too positive free energy indicates that $H^*$ adsorption is too weak to facilitate reactant adsorption. Both of these are unfavorable for HER. On the contrary, an appropriate Gibbs free
energy close to zero is more thermodynamically favored by HER from considerations of both reactant adsorption and product desorption. **Figure 4a** shows the Gibbs free energy of the Heyrovsky process for the ε-Fe$_6$N$_3$ (dashed) and the ε-Fe$_6$N$_2$ (solid). It can be seen that the (0001) N-exposed surface exhibits a too negative Gibbs free energy for both ε-Fe$_6$N$_3$ (-1.83 eV) and ε-Fe$_6$N$_2$ (-1.46 eV), which are not thermodynamically favored by HER. The most favored Gibbs free energies appear on the (I100) FeN-exposed surface (-0.45 eV) of ε-Fe$_6$N$_3$ and the (I100) FeN-exposed surface (-0.48 eV) of ε-Fe$_6$N$_2$. As seen the Tafel process in **Figure 4b**, the ε-Fe$_6$N$_3$ has Gibbs free energies on the (I100) FeN-exposed surface and the (1120) N-exposed surface of 0.21 eV and 0.20 eV, respectively. The ε-Fe$_6$N$_2$ has favored Gibbs free energies on the (I100) FeN-exposed surface and the (1120) N-exposed surface of -0.07 eV and -0.08 eV, respectively. The ε-Fe$_6$N$_2$ shows the absolute values of Gibbs free energies much lower than the corresponding ones of the ε-Fe$_6$N$_3$, suggesting that the ε-Fe$_6$N$_2$ has more thermodynamically favored exposed surfaces in the Tafel process.

**Figure 4.** Calculated free energy diagrams of (a) Heyrovsky step and (b) Tafel step for ε-Fe$_x$N$_x$ (x=3, 2) on a series of different exposed surfaces. (c) A schematic diagram of HER process on (0001), (I100) and (1120) exposed surfaces of ε-Fe$_6$N$_3$ and ε-Fe$_6$N$_2$ nanoparticles. Solid green circle represents the...
active sites for Heyrovsky step. Dotted green circle represent the active sites for Tafel step. The Gibbs free energies of the Heyrovsky step (H step) and the Tafel step (T step) on each surface are also shown. The red-marked Gibbs free energies are HER thermodynamically favored, which should be better to be close to zero from both consideration of reactant adsorption and product desorption.

The above DFT calculation results accompanied with the corresponding exposed surfaces are illustrated in Figure 4c. It can be directly seen that the ε-Fe₆N₂ has more thermodynamic favored exposed surfaces (marked as red characters) for HER than the ε-Fe₆N₃, no matter in the Heyrovsky process or in the Tafel process. Furthermore, on the HER thermodynamically favored (1100)-FeN exposed surface and (1120) N-exposed surface, the active site of the Tafel process changes from the hollow site of iron atoms in ε-Fe₆N₃ to the top site of nitrogen atoms and the bridge site of Fe atoms in ε-Fe₆N₂. Active sites on each surface can be also seen in Figure S7. According to the steric hindrance effect on adsorption kinetics, the top and the bridge sites are more kinetic favored for the reactant adsorption and product desorption as comparison with the hollow site. Therefore, the above thermodynamic and kinetic effects enhance the HER activity through decreasing nitrogen content in ε-Fe₆Nₓ. It also suggests us that decreasing the nitrogen content x far below 2 in the ε-Fe₆Nₓ material is probably an approach to further enhance HER activity, which will be investigated in our future work.

3. Conclusion

In summary, we have synthesized ε-Fe₃N single-phase nanoparticles by a thermal nitridation process from Fe precursors. The nitrogen content decreases as the nitridation temperature decreases from 650 °C(FeN650) to 500 °C(FeN500), resulting in the shrinkage of lattice cell and an enhancement in HER performance (e.g., the overpotential to achieve a current density of 10 mA cm⁻² decreases from 425 mV (FeN650) to 171 mV (FeN500)). The EXAFS result reveals that the effective
coordination number of the Fe atom’s first nearest neighboring nitrogen atoms decreases from 2.61 (FeN650) to 1.67 (FeN500), which deviates from the standard nitrogen coordination number of 2 in ε-Fe₃N. The DFT calculation suggests that the number of thermodynamically favored exposed surfaces for HER increases as the x in ε-FeₓNₓ decreases from 3 to 2. Furthermore, the active site of the Tafel process changes from the kinetic less favored hollow site of Fe atoms in ε-Fe₆N₃ to the kinetic more favored top site of N atoms and bridge site of Fe atoms in ε-Fe₆N₂ on the HER thermodynamically favored (1100)-FeN exposed and (1120) N-exposed surfaces. Therefore, the HER activity is enhanced by the decrease of the nitrogen content, agreeing well with the experimental results. Our work reports a facile nitridation approach of the earth-abundant iron to prepare HER active electrocatalyst and uncovers the roles of nitrogen atoms in tailoring the HER activity of iron nitride. It suggests a strategy of nitrogen-deficient design in iron nitrides to enhanced HER activities, which is of importance for the development of highly active transition metal based electrocatalysts.

4. Experimental Section

Chemicals: Iron (II) chloride hydrate (FeCl₂⋅4H₂O), Sodium borohydride (NaBH₄), NaOH, KOH and ethanol were purchased from Beijing Chemical Works. Nafion (5% w/w in water and 1-propanol) was purchased from Alfa Aesar. All the reagents were of analytical grade. Deionized water was used throughout the experiments.

Synthesis of Fe₃N nanoparticle: Fe nanoparticle precursors were synthesized by using a solution reduction method. Briefly, FeCl₂⋅4H₂O was dissolved in deionized water to form 0.5 M Fe²⁺ solution. 1 M NaBH₄ solution was configured in the sodium hydroxide solution with pH=11-13. Then, the NaBH₄ solution was dropwise added into the Fe²⁺ solution under magnetic stirring for 2 h. The mixture solution was filtrated and then dried at 80 °C for 24 h in vacuum. After that, Fe nanoparticle precursors (100 mg) were placed in quartz boat and transferred to a tube furnace for being
pyrolyzed in an atmosphere of flowing NH$_3$ (150 mL min$^{-1}$) at 500-650 °C for 10 h with a heating rate of 10 °C min$^{-1}$. The resulting black powder product was collected for use.

**Characterization:** X-ray diffraction (XRD) were conducted on a diffractometer (Rigaku DMAX-2500) operated at 40 kV and 200 mA with Cu Kα radiation (λ=1.5405 Å). Scanning electron microscope (SEM) observation was performed using a Zeiss Sigma Field Emission SEM with an Oxford INCA PentaFETx3 energy dispersive spectrometer (EDS) system (model 8100). Transmission electron microscope (TEM) observation was conducted on a JEM-2100F electron microscope operating at 200 kV equipped with an EDS accessory. The TEM samples were prepared by dropping the suspension of the nanoparticles dispersed in ethanol onto carbon-coated copper grid and then dried in the air. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCA Lab 250Xi X-ray photoelectron spectrometer operating at 150W monochromatic Al Kα radiation, the binding energies were corrected by referencing C 1s line at 284.8 eV. Fe K-edge X-ray absorption fine structure (XAFS) measurements were performed at the Beijing Synchrotron Radiation Facility.

**Electrochemical tests:** The electrochemical measurements were performed on a CHI650D electrochemical workstation with a standard three-electrode configuration. The electrolyte was 1 M KOH solution. The reference electrode and counter electrode were a Hg/HgO electrode and a graphite electrode, respectively. The working electrode was a glassy carbon electrode coated with the electrocatalysts. For the measurements, 5 mg electrocatalyst (the prepared samples and the Pt/C-20% powder for comparison) and 20 μL 5 wt.% Nafion solution were dispersed in 980 μL ethanol followed by sonication for at least 30 min to form a homogeneous solution. Then, 5 μL of the above catalyst ink was dropped on the glassy carbon electrode (3 mm diameter), resulting in an electrocatalyst loading of ~0.35 mg cm$^{-2}$. The electrochemical impedance spectroscopy (EIS) measurements were conducted with a frequency range from 0.01 to $10^5$ Hz. The linear sweep
voltammetry (LSV) curves were recorded at a scan rate of 5 mV s\(^{-1}\), and were corrected with iR compensation. The overpotential values were calculated according to the following equation

\[
E_{\text{RHE}} = E(Hg/HgO) + 0.098 + 0.05916 \cdot pH - iR_{\text{solution}} \quad (1)
\]

where \(E(Hg/HgO)\) is the measured potential against the Hg/HgO reference electrode, the solution resistance \(R_{\text{solution}}\) is obtained by EIS measurement, and the \(iR_{\text{solution}}\) is used for iR correction.

The electrochemically active surface area (ECSA) was determined by measuring the double-layer capacitance \(C_{dl}\).\(^{34}\) The potential was swept between 0 and 0.3 V vs. RHE at different scan rates (20, 40, 60, 80 and 100 mV s\(^{-1}\)). We measured the capacitive currents at 0.15 V vs. RHE where no faradic process was observed.

**DFT Calculation:** For the periodic structures, DFT calculations were performed using the program VASP (Vienna Ab Initio Simulation Package),\(^{40}\) where the electronic wave functions have been expanded into plane-waves up to an energy cutoff of 500 eV, and a projected-augmented-wave (PAW)\(^{41}\) scheme has been used to describe the interactions between the valence electrons and the nuclei (ions). The exchange–correlation interactions between electrons were treated within the generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE).\(^{42}\) The atomic positions were optimized until all components of the residual forces are smaller than 0.01 eV Å\(^{-1}\). A \(2\times2\times2\) \(\varepsilon\)-Fe\(_x\)N\(_x\) (x=2, 3) supercell was built to create the surfaces along [0001] and [\(\bar{1}100\)] direction. A \(1\times1\times2\) \(\varepsilon\)-Fe\(_x\)N\(_x\) (x=2, 3) supercell was built to create the surface along [1\(\bar{1}20\)] direction. A \(1\times1\times1\) k-space grid was considered. A sufficient 20 Å thickness of the vacuum layer was used to avoid the interaction between repeated slabs in all surface models. The surface energy is determined as follows,

\[
E_{\text{surf}} = (E_{\text{Slab}} - N * E_{\text{Bulk}} - n_i * \mu_i) / 2A \quad (2)
\]
where $E_{\text{slab}}$ is the total energy of the slab, $E_{\text{bulk}}$ is the energy of per unit $\varepsilon$-Fe$_x$N$_y$ (x=2, 3) in the bulk, $N$ is the number of $\varepsilon$-Fe$_x$N$_y$ (x=2, 3) units contained in the slab, $n_i$ is the number of excess atoms of the species $i$ in the slab, $\mu_i$ is the chemical potential of the species $i$, and $A$ represents the surface area. The chemical potential of iron atom and nitrogen atom is a range in this system and such defect formation energy can be defined by $\mu_N$ as

$$E_{\text{surf}}^{Fe,N} = E_{\text{surf}}^{Fe,N} = a \mu_{Fe} + b \mu_{N}$$

$$\Delta \mu_N = \mu_N - \frac{1}{2} E_{N_2}$$

$a$ and $b$ represent the number of Fe and N in a $\varepsilon$-Fe$_x$N$_y$ (x=2, 3) unit cell, respectively. N-rich condition can be defined by a half of the calculated energy of $N_2$ (-14.42 eV).

The first step of HER at the cathode electrode in the alkaline medium usually happens as follows:

$$H_2O + \ast + e^- \rightarrow H^* + OH^-$$

(Volmer process)

The next step can be described as:

$$H^* + H_2O + e^- \rightarrow H_2 + OH^- + \ast$$

(Heyrovsky process)

or

$$2H^* \rightarrow H_2 + 2\ast$$

(Tafel process)

The Gibbs free energies on different surfaces were calculated as

$$\Delta G = \Delta E_{\text{int}}^{\ast} + \Delta ZPE - T \Delta S$$
where $E_{\text{ad}}^H$ is the hydrogen adsorption energy, $\Delta ZPE$ is the zero point vibrational energy, and $T\Delta S$ is the referenced entropy value 0.40 eV.\textsuperscript{[38]} The free energy of H$_2$O, OH was gained by DFT energy of H$_2$O and H$_2$ in the gas phase.

Supporting Information

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

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Conflict of Interest

There are no conflicts of interest to declare.

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