Exposed facet-controlled $\text{N}_2$ electroreduction on distinct Pt$_3$Fe nanostructures of nanocubes, nanorods and nanowires

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ABSTRACT

Understanding the correlation between exposed surfaces and performances of controlled nanocatalysts can aid effective strategies to enhance electrocatalysis, but this is as yet unexplored for the nitrogen reduction reaction (NRR). Here, we first report controlled synthesis of well-defined Pt$_3$Fe nanocrystals with tunable morphologies (nanocube, nanorod and nanowire) as ideal model electrocatalysts for investigating the NRR on different exposed facets. The detailed electrocatalytic studies reveal that the Pt$_3$Fe nanocrystals exhibit shape-dependent NRR electrocatalysis. The optimized Pt$_3$Fe nanowires bounded with high-index facets exhibit excellent selectivity (no $\text{N}_2\text{H}_4$ is detected), high activity with $\text{NH}_3$ yield of $18.3$ $\mu$g $\text{h}^{-1}$ $\text{mg}^{-1}$ cat $\times$ (0.52 $\mu$g $\text{h}^{-1}$ cm$^{-2}$ ECSA; ECSA: electrochemical active surface area) and Faraday efficiency of 7.3% at $-0.05$ V versus reversible hydrogen electrode, outperforming the $\{200\}$ facet-enclosed Pt$_3$Fe nanocubes and $\{111\}$ facet-enclosed Pt$_3$Fe nanorods. They also show good stability with negligible activity change after five cycles. Density functional theory calculations reveal that, with high-indexed facet engineering, the Fe-3d band is an efficient $d$-$d$ coupling correlation center for boosting the Pt 5d-electronic exchange and transfer activities towards the NRR.

Keywords: Pt$_3$Fe, nanowire, high-index, facet-controlled, $\text{N}_2$ reduction

INTRODUCTION

Ammonia ($\text{NH}_3$), an essential composition for fertilizer feedstock, industrial and chemical precursors [1], not only plays a vital role in the development of ammonia fuel cells but is also a promising candidate for the hydrogen economy because of its high energy density and large hydrogen capacity [2]. However, from a thermodynamic point of view, the high bond energy of the triple bond in nitrogen ($\text{N}_2$) makes it an intricate multi-step reaction to convert $\text{N}_2$ to $\text{NH}_3$ [3]. Currently, the Haber-Bosch method is most widely applied because efficient synthesis of $\text{NH}_3$ from $\text{N}_2$ and $\text{H}_2$ has reached industrial-scale yields [4]. However, this method requires conditions of high temperature of 400–500 °C and pressure of 200–250 bar [5]. It also consumes 1–2% of the global annual energy supply and is responsible for >1% of global CO$_2$ emissions [6]. Therefore, a more effective process for $\text{NH}_3$ synthesis under mild conditions is highly desirable.

Recently, tremendous efforts for converting $\text{N}_2$ to $\text{NH}_3$ have been made in pursuit of efficient and sustainable catalysis with use of biocatalytic, photocatalytic and electrocatalytic methods [7–14]. One possible strategy for $\text{NH}_3$ synthesis is electroreduction of $\text{N}_2$ to $\text{NH}_3$ in which the $\text{N}_2$ reduction reaction (NRR) process can be operated by renewable electricity energy, and operated at mild temperature and pressure [15–18]. There have been several investigations on NRR with noble-metal catalysts ($\text{Ru}$ [19], $\text{Au}$ [20], $\text{Pd}$ [21] and $\text{Rh}$ [22]), as summarized in Table S1. More recently, several efforts have been devoted to optimizing electrocatalysts to enhance NRR, including size regulation [23], crystal engineering [24], ion incorporation [25], introduction of defect sites [26,27] and component regulation [28]. However, to the best of our knowledge, surface structure regulation, as one of the most effective strategies to precisely tune catalytic properties, has not yet been demonstrated for NRR.
Previous research revealed that the NRR performance is gravely limited by linear scaling of the two vital intermediate energetics between \( ^*N_2H \) and \( ^*NH_2 \) (\(^*\) indicates the adsorption site). Further theoretical analyses disclose that Fe and Pt atoms can effectively address the energetics of \( ^*N_2H \) and \( ^*NH_2 \), respectively, synergistically providing efficient active sites to enhance NRR activity [29,30]. Herein, we report a facile method for selectively growing Pt3Fe nanowires (NWs), Pt3Fe nanorods (NRs) and Pt3Fe nanowires (NWs) (Supplementary Fig. 1), which give rise to active and stable electrocatalysts for NRR. Optimized Pt3Fe NWs bounded with high-index facets exhibit much enhanced NH3 yield (18.3 \( \mu g \) h\(^{-1}\) mg\(^{-1}\) cat, 0.52 \( \mu g \) h\(^{-1}\) cm\(^{-2}\) (ECSA; ECSA: electrochemical active surface area), Faradaic efficiency (7.3%) and selectivity (no N\(_2H_4\) is detected) at \(-0.05\) V versus reversible hydrogen electrode (RHE), and are much better than those of \{200\} facet-enclosed Pt3Fe NCs and \{111\} facet-enclosed Pt3Fe NRs. The Pt3Fe NWs also show durable stability with negligible activity decay for five cycles. Density functional theory (DFT) calculation reveals that, on the high-indexed surface engineering, strong orbital interaction between Pt and neighboring Fe sites induces an obvious correlation effect for boosting up Pt-5d electronic activities for efficient NRR.

RESULTS AND DISCUSSION

A simple wet-chemical method is adopted to control the synthesis of Pt3Fe nanocrystals. Taking Pt3Fe NWs synthesis as an example, potassium tetachloroplatinate (II) (K2PtCl4) and iron nonacarbonyl (Fe2(CO)9) are chosen as metal precursors, ribose is used as the reducing agent, cetyltrimethyl ammonium chloride (CTAC) and oleylamine (OAm) are applied as the surfactant and solvent, respectively. Uniform Pt3Fe NWs with average diameter of 15 nm and zigzag border along the whole length are obtained (Fig. 1a and Supplementary Fig. 2), characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and TEM. The X-ray diffraction (XRD) pattern (Fig. 1b) of Pt3Fe NWs shows distinct diffraction peaks at 40.32, 46.92, 68.42, 82.52 and 87.2°, which are readily indexed to \{111\}, \{200\}, \{220\}, \{311\} and \{222\} reflections of face-centered cubic (fcc) Pt3Fe (JCPDS number 29–0717), being consistent with those of Pt3Fe NCs and Pt3Fe NRs (Supplementary Fig. 3) [31]. The crystal structure model of the Pt3Fe NWs represents a primitive cubic structure. It is composed of a periodic square matrix of Fe and Pt, which are located at the corner and face center of each unit cell, respectively. The HAADF-STEM image and elemental mappings show the elemental distributions of Pt and Fe (Fig. 1c). The Pt (green), Fe (red) and mixed images indicate that all elements are evenly distributed on the Pt3Fe NWs, confirming the alloyed structure (Supplementary Fig. 4). The selected area electron diffraction (SAED) image (Fig. 1d) further indicates that the Pt3Fe NWs have good crystallinity and fcc structure. Spherical aberration correction HRTEM images reveal the distinct lattice fringes. The measured value of lattice spacing is 0.195 nm. In addition, a high-index facet of \{311\} can be readily observed (Fig. 1e and Supplementary Fig. 5), which is reported to exhibit much higher catalytic performance compared to most common facets (\{200\} and \{111\}) because of the high density of atomic steps and ledges [32–34]. Notably, when ribose is replaced by maltose, while maintaining the other synthetic parameters unchanged, Pt3Fe NCs with average diameter of 5 nm are obtained (Fig. 1f and Supplementary Fig. 6). Meanwhile, Pt3Fe NRs with average diameter of 3 nm are realized by merely changing the precursor of Pt (Fig. 1g; Supplementary Figs 7 and 8). Detailed X-ray photoelectron spectroscopy (XPS) is carried out to determine the electronic properties of surface Pt atoms. Compared with commercial Pt/C, the Pt^0 4f7/2 binding energy of Pt3Fe nanocrystals has a negative shift from 71.2 to 70.6 eV, indicating that the charge is transferred from Fe to Pt, because of the lower electronegativity of Fe (Supplementary Fig. 9a) [35]. We can see that the Pt 4f spectra show two distinct peaks, which are assigned to the Pt 4f7/2 and Pt 4f5/2 orbit levels. Each peak can be further split into two doublets, which are assigned to Pt^6 and Pt^2+ chemical valence states. It is clearly shown that the majority of the Pt of Pt3Fe is in mainly metallic state. The Pt(II)/Pt(0) ratio is summarized in Table S2. The XPS spectra of Fe 2p reveal two distinct peaks at 710.3 and 724.1 eV, which are assigned to the characteristic peaks of Fe 2p3/2 and Fe 2p1/2 orbit levels. Each peak can be further split into two doublets, which are assigned to Fe^3+ and Fe^2+ chemical valence states. It is clearly shown that the majority of the Fe is mainly in an oxidized state (Supplementary Fig. 9b) [36]. The lattice spacings of Pt3Fe NCs and Pt3Fe NRs are measured to be 0.195 and 0.0224 nm, corresponding to the \{200\} and \{111\} facets, respectively (Supplementary Figs 10 and 11). Hence, well-defined Pt3Fe nanocrystals bounded with distinct facets have been successfully created and can be adopted as ideal model electrocatalysts for fundamental understanding of the relationship between surface structure and catalysis.

Pt NCs, Fe3O4 NPs (Supplementary Fig. 12) and Pt3Fe nanocrystals were first loaded onto
carbon (C, Vulcan XC-72) to investigate the NRR properties. The resulting electrocatalysts were called Pt NPs/C, Fe3O4 NPs/C, Pt3Fe NCs/C, Pt3Fe NRs/C and Pt3Fe NWs/C. A schematic for the electrochemical NRR is shown in Supplementary Fig. 13. During each NRR measurement, pure N2 flowed into the cathode electrolyte at a flow rate of 30 standard mL/min, wherein N2 combined with electrons to form N2 reduction product. Using Pt3Fe nanocrystals as the cathodic catalysts, only NH3 without the by-product of N2H4 could be detected, highlighting the good selectivity for NH3 (Supplementary Fig. 14). The standard calibration curves are given in Supplementary Figs 15 and 16. Saturated calomel reference electrode is calibrated on reversible hydrogen electrode (Supplementary Fig. 17). During the NRR progress, the Pt3Fe NWs/C exhibited negligible decay in current density under different applied potential, indicating the good corrosion resistance ability (Fig. 2a). The Pt NPs/C (Supplementary Fig. 18) had very poor NRR activity compared with Pt3Fe NCs/C, indicating that introduction of Fe is essential for the NRR. In addition, the NRR activity of Pt3Fe NRs/C exhibited much improvement compared with Pt3Fe NCs/C. The average NH3 yield and Faraday efficiency (FE) of the Pt3Fe NWs/C under different applied potentials is given in Fig. 2b and c. The NRR was performed at 0 V, the measured yield of NH3 was 10.2 μg h⁻¹ mg⁻¹cat (0.29 μg h⁻¹ cm⁻²ECSA) with the highest FE of 12.3%. The NH3 yield increased to a maximum value of 18.3 μg h⁻¹ mg⁻¹cat (0.52 μg h⁻¹ cm⁻²ECSA) until −0.05 V, indicating that it consumed less energy to effectively convert N2 into NH3. The NRR performance of Pt3Fe NWs/C was much better than that of the Fe3O4 catalysts (Supplementary Fig. 19). The maximum yield of NH3 was further quantitatively determined by an indophenol blue method [37]. As observed, the calculation value of NH3 yield was close to the quantitative result from the Nessler reagent method (Supplementary Figs 20 and 21). The FE linearly decreased when it reached a more negative potential, because of the existence of a competition reaction between NRR and hydrogen evolution reaction (HER) [38]. We compared the NRR activity with different reaction temperatures at −0.05 V to assess the apparent activation energy and investigate the different exposed facets effect of Pt3Fe nanocrystals. As observed, the NH3 yield enhanced with increasing reaction temperature due to faster mass transfer rate of reactants (Supplementary Fig. 22). The estimated apparent activation energies were 11.0, 16.9 and 27.3 kJ mol⁻¹ for Pt3Fe NWs/C, Pt3Fe NRs/C and Pt3Fe NCs/C, respectively (Fig. 2d). That is, the Pt3Fe NWs/C bounded with high-index facets could significantly decrease the apparent activation energy and hence enhance the NRR activity. Significantly, the NH3 yield and FE of Pt3Fe NWs/C were higher than those of Pt3Fe NCs/C and Pt3Fe NRs/C (Fig. 2e), indicating that different surface structures of Pt3Fe nanocrystals indeed have essential influence on the NRR activity and the high-index facets of Pt3Fe nanocrystals play a vital role in the improvement of NRR activity.

We then carefully examined the N source of the produced NH3. There were no distinguishable peaks in the N 1s region, indicating that no nitrogenous species existed on the surface of synthetic
The error bars in (b) indicate the standard deviations of three independent tests in the same conditions.

**Figure 2.** (a) i-t curves, (b) NH\textsubscript{3} yield and (c) FE of Pt\textsubscript{3}Fe NWs/C at different applied potentials. (d) Apparent activation energy for NRR with different Pt\textsubscript{3}Fe electrocatalysts. (e) Histograms of the NH\textsubscript{3} yield and FE of Pt\textsubscript{3}Fe NCs/C, Pt\textsubscript{3}Fe NRs/C and Pt\textsubscript{3}Fe NWs/C. The error bars in (b) indicate the standard deviations of three independent tests in the same conditions.

\textsuperscript{1}H nuclear magnetic resonance spectra show a double coupling peak of \textsuperscript{15}NH\textsubscript{3}\textsuperscript{+} without the triple coupling peak of \textsuperscript{14}NH\textsubscript{3}\textsuperscript{+}. Hence, the result confirmed that the NH\textsubscript{3} was derived from the electroreduction of N\textsubscript{2} in the presence of Pt\textsubscript{3}Fe NWs/C (Supplementary Fig. 30). In addition, by varying the N\textsubscript{2} flow rate, the current density exhibited small change. The tiny fluctuation of FE and NH\textsubscript{3} yield implied that N\textsubscript{2} diffusion was not the rate-determining step (Supplementary Fig. 31) [39].

The intrinsic reason for higher catalytic activity of Pt\textsubscript{3}Fe NWs/C was investigated. The Tafel slope is a vital parameter to evaluate the HER mechanism [40,41]. The higher value of 163.8 mV dec\textsuperscript{-1} gained from Pt\textsubscript{3}Fe NWs/C suggested its sluggish HER kinetics, which may in turn enhance the NRR performance (Supplementary Fig. 32), further confirmed by theoretical calculation (Supplementary Fig. 33).

After that, surface valence spectra was created to investigate the relationship between electronic effect and the binding strength of adsorbates. As observed, the d-band center shifts upwards from Pt NCs/C to Pt\textsubscript{3}Fe NCs/C (Fig. 3a–f). The energetic gain of about 4.86 eV. However, the (111) and (200) surfaces present nearly two-times higher electrons above EF to N\textsubscript{2} 2p orbital (Fig. 3d). The pre-eminent d-electron exchange and transfer activities (d-EXTA) on the high indexed surface have been demonstrated through projected partial density of states (PDOSs) analysis (Fig. 3d–f). The edge of dominant peak of Pt-5d band reflects a direct determination of 5d-EXTA for efficient N\textsubscript{2} fixation.

We used DFT calculations to further interpret the NRR activity differences of Pt\textsubscript{3}Fe (311), (111) and (200). The bonding and antibonding orbitals near the Fermi level (EF) exhibit an electron-rich distribution on the Pt\textsubscript{3}Fe (311) surface (Fig. 3a), while (111) and (200) surfaces present less electron-localizing on the surface (Fig. 3b and c). The preferred d-electron exchange and transfer activities (d-EXTA) on the high indexed surface have been demonstrated through projected partial density of states (PDOSs) analysis (Fig. 3d–f). The edge of dominant peak of Pt-5d band reflects a direct determination of 5d-EXTA for efficient N\textsubscript{2} fixation. Taking this trend, on the (311) surface, the Fe-3d orbital clearly merges at the EF without an evident gap between the \( \epsilon_\text{g} \) and \( \epsilon_\text{t} \) components. The energetic interval between Pt-5d and Fe-3d is nearly 0.95 eV, which cost less energetic barrier for transferring d-electrons above EF to N\textsubscript{2} 2p orbital (Fig. 3d). The (111) and (200) present nearly two-times higher to freely cross EF (Fig. 3e and f). The comparison of energetic trends reveals that the NRR pathway on the (311) is the most energetically beneficial with an energetic barrier of merely 0.16 eV and overall gain of \(-4.86\text{ eV}\). However, the (111) and (200) denote a higher energy gain of about \(-2.0\text{ eV}\).
Figure 3. (a–c) The real spatial contour plots of bonding and anti-bonding orbitals near EF on Pt3Fe (311), (111) and (200) surfaces, respectively. (d–f) PDOS of d-bands for surface Pt-5d and Fe-3d sites on the (311), (111) and (200) are given, respectively. (g) The NRR energetic pathway on the surfaces of (311), (111) and (200), respectively. (h) Direct adsorption comparison for N2+6H and N2 on the surfaces of (311), (111) and (200), respectively.

and the energy barriers are 0.75 and 0.34 eV, respectively (Fig. 3g). In the distal reaction pathway, the N atom furthest away from the catalyst surface preferentially undergoes hydrogenation, to form the first NH3 molecule. The NH3 molecule is released after the N≡N triple bond breaks. The remaining N atom continues under hydrogenation to generate another NH3 molecule. According to the above results, the reaction path of our work could be a distal reaction pathway. We further reason that the better activity of NRR on the (311) is attributed to the excellent energetic preference of N2 fixation, while the underperformance of (200) for NRR is ascribed to overbinding of adsorbing H for efficient N-hydrogenation (Fig. 3h). The energetic trend is consistent with analysis of electronic activities from both experimental and theoretical perspectives.

A chronoamperometric test was first conducted at −0.05 V in N2-saturated KOH electrolyte to evaluate the durability of Pt3Fe NWs/C. The current density (Fig. 4a) exhibited negligible decay after 30 h electrolysis. The stability of Pt3Fe NWs/C was also evaluated by successive cycle electrolysis at −0.05 V. After five successive cycles, the total current density exhibited no evident fluctuation (Supplementary Fig. 35). The NH3 yield and FE of Pt3Fe NWs/C were measured after each cycle, with no obvious changes (Fig. 4b). After stability testing, TEM image, elemental mapping (Supplementary Fig. 36) and SEM-EDS (Supplementary Fig. 37) of the Pt3Fe NWs/C confirmed that its structure and composition were largely maintained, demonstrating that the Pt3Fe NWs/C was stable enough for NRR.

CONCLUSION

In summary, we have demonstrated facile synthesis of Pt3Fe nanocrystals with tunable morphologies (NC, NR and NW) to evaluate the NRR performance on different exposed facets. The detailed studies show that the Pt3Fe nanocrystals exhibit
Figure 4. (a) I-t curve of the Pt3Fe NWs/C in N2-saturated KOH electrolyte at −0.05 V and (b) NH3 yield and FE calculated after each cycle at −0.05 V.

shape-dependent electrocatalytic activity towards NRR. Notably, the Pt3Fe NWs bounded with high-index facets exhibit much improvement in NH3 yield (18.3 μg h⁻¹ mg⁻¹ cat, 0.52 μg h⁻¹ cm⁻² ECSA), FE (7.3%) as well as selectivity (no N2H4 is detected) at −0.05 V under ambient conditions, which are much better than that of those of {200} facet-enclosed Pt3Fe NCs and {111} facet-enclosed Pt3Fe NRs. The Pt3Fe NWs also show durable electrochemical stability with no obvious activity decay after five successive electrolysis cycles. DFT calculation reveals that strong d-d coupling between Pt and Fe sites bridges the electron transfer for prominent NRR. This work provides the first example of the fundamental correlation between exposed surfaces and NRR performances of distinct nanocrystals.

METHODS

Preparation of Pt3Fe NWs

In preparation of monodisperse Pt3Fe NWs, K2PtCl4 (10.4 mg), Fe2(CO)9 (4.6 mg), ribose (45 mg), CTAC (32 mg) and OAm (5 mL) were added to a reaction bottle (volume: 35 mL), which was capped and ultrasonicated for 1 h. The reaction bottle was heated from room temperature to 180°C within 0.5 h and maintained at 180°C for 5 h in an oil bath. After cooling to room temperature, the obtained products were collected by centrifugation and washed three times with a cyclohexane/ethanol mixture.

Preparation of Pt3Fe NRs

The synthesis of monodisperse Pt3Fe NRs was similar to that of Pt3Fe NWs, except Pt(acac)2 (9.8 mg) was used as precursor and the amount of ribose was 90 mg at the beginning.

Preparation of Pt3Fe NCs

The synthesis of monodisperse Pt3Fe NCs was similar to that of Pt3Fe NWs, except maltose (108 mg) was used as reductant at the beginning.

Preparation of Pt NCs

In preparation of monodisperse Pt NCs, Pt(acac)2 (10 mg), PVP (200 mg), formaldehyde solution (40%, 2.5 mL) and benzyl alcohol (10 mL) were added to a reaction bottle. After sonication for 0.5 h, the homogeneous solution was transferred to a 20 mL Teflon-lined stainless autoclave and then heated at 150°C for 10 h. The product was collected via centrifugation and further washed with an ethanol-acetone mixture.

Preparation of Fe3O4 NPs

In preparation of monodisperse Fe3O4 NPs, Fe2(CO)9 (9.2 mg), ribose (45 mg), OAm (4.8 mL) and OAC (0.2 mL) were added to a reaction bottle, which was capped and then ultrasonicated for 1 h. The reaction bottle was heated from room temperature to 200°C within 0.5 h and maintained at 200°C for 5 h in an oil bath. After cooling to room temperature, the obtained products were collected by centrifugation and washed three times with a cyclohexane/ethanol mixture.

Catalytic measurements

Firstly, different morphology of Pt3Fe nanocrystals, Fe3O4 NPs, commercial carbon, cyclohexane (1 mL) and ethanol (8 mL) were added to a reaction bottle. The Pt NCs, commercial carbon, ethanol (1 mL) and acetone (8 mL) were also added to a reaction bottle. After sonication for 1 h, the homogeneous solution was centrifuged and dried naturally to obtain a powder. Then, the powder was annealed at 150°C for 1 h under ambient atmosphere. To prepare catalysts, the above powder (5 mg), Nafion solution (6 μL, 5 wt%) and absolute isopropyl alcohol (500 μL) were mixed and sonicated for 0.5 h to form homogeneous ink, which was then dropped (10 μL) evenly on carbon paper with geometric area of 1 × 1 cm². The carbon paper was dried under ambient conditions.

The electrochemical tests were performed in a gas-tight two-chamber electrolytic cell separated by Nafion 115 membrane. Before electrochemical
NRR measurements, the Nafion 115 membrane was first pretreated in 80°C H₂O₂ (5%) aqueous solution for 1 h and then washed in 80°C ultrapure water for another 1 h. The electrochemical experiments were conducted on a CHI660E electrochemical analyzer (CHI Instruments) using a three-electrode configuration (working electrode of synthetic catalysts, reference electrode of saturated calomel electrode and counter electrode of carbon rod). The mentioned potentials have been converted to RHE. The cyclic voltammetry (CV) tests were carried out in 0.1 M HClO₄ solution with a scan rate of 50 mV s⁻¹ under ambient conditions. The ECSA was obtained by integrating the hydrogen adsorption charge (Q_H₂) between -0.25 V and 0.1 V on the CV curves. The value of adsorbed single-layer hydrogen (q_H₂) on the Pt surface is 210 μC cm⁻² and the formula is ECSA = Q_H₂/(q_H₂ × m) (Supplementary Fig. 38).

Potentiostatic tests were carried out in electrochemical NRR. Before the measurement, highly pure N₂ gas was flowed continuously into the cathode electrolytic cell with a proper position for 0.5 h.

Calculation of NH₃ yield, Faraday efficiency and apparent energy

In NRR tests, FE is defined as the amount of charge for the synthesis of NH₃ divided by the total charge through the electrodes during the electrolysis process. The NH₃ yield was determined by a colorimetric method using Nessler’s reagent. The formation of each NH₃ molecule requires three electrons, hence the FE of NH₃ can be determined by the below formula:

\[
\ln K = -\frac{E_d}{RT} + C.
\]

The NH₃ yield was determined by the below formula:

\[
FE = \frac{3 \times F \times C_{NH_3} \times V}{17 \times Q},
\]

where Q: quantity of electric charge; F: Faraday constant, 96485 C mol⁻¹; V: the KOH electrolyte volume; C_{NH_3}: the calculated NH₃ concentration; t: the reduction time; A: the ECSA of the catalysts.

According to the Arrhenius equation, the apparent energy calculations process is below:

\[
V_{NH_3} = \frac{C_{NH_3} \times V}{t \times A},
\]

where K: NH₃ yield rate at temperature T; R: Molar gas constant (J mol⁻¹ K⁻¹); E_d: Apparent energy (kJ mol⁻¹); T: Absolute reaction temperature (K). We plot lnK against 1000/T, and the slope is k, so E_d = -kR.

Determination of ammonia yield

The yield of NH₃ was determined via a colorimetric method using Nessler’s reagent. The calibration curve was obtained as follows: first, a series of reference solutions was prepared, by pipetting known NH₄Cl solutions and 0.1 M KOH working electrolyte into colorimetric tubes. These were made up to the mark (10 mL) with 0.1 M KOH solution. Next, 1 mL of 0.2 M potassium sodium tartrate (KNaC₄H₄O₆, chelating soluble metal ion) ultrapure water solution was pipetted into each of the tubes and these were mixed thoroughly, followed by pipetting of 1 mL Nessler’s reagent into each of the tubes and further mixing. The mixed solutions were left for 0.5 h. Using a blank solution for background correction, the absorbance of the solutions was measured at 425 nm in a 10 mm glass cuvette. The calibration curve (y = 0.162x-0.005, R² = 0.998) exhibited a good linear relationship between absorbance and NH₄⁺ concentration according to three independent calibration tests.

Determination of hydrazine hydrate

The hydrazine hydrate was determined by a colorimetric method using Watt-Chrisp reagent. Para (dimethylamino) benzaldehyde (5.99 g), concentrated HCl (30 mL) and absolute ethanol (300 mL) were mixed as color reagents. A calibration curve was obtained as follows: first, different reference solutions were prepared, by pipetting hydrazine hydrate-nitrogen 0.1 M HCl solution into colorimetric tubes. These were made up to 5 mL with diluted hydrochloric acid electrolyte (pH = 1), then 5 mL was pipetted above the color reagent and this was left to stand for 0.5 h for color development under ambient conditions. The absorbance of the color solution was measured at 455 nm with a 10 mm glass cuvette, and the yields of hydrazine were determined by the standard calibration curve using a mixture of 5 mL remaining solution and 5 mL color reagent. The calibration curve (y = 1.208x-0.088, R² = 0.977) was obtained with hydrazine monohydrate solutions of different known concentrations, and exhibited a good linear relationship between absorbance and N₂H₄·H₂O concentration according to three independent calibration tests.

Determination of NOₓ

The concentration of NOₓ was measured with a colorimetric method using N-(-1-naphthyl) ethylenediamine dihydrochloride as color reagent. A mixture of 0.5 g sulfanilic acid, 5 mg n-(-1-naphthyl)-ethylenediamine dihydrochloride,
90 mL H$_2$O and 5 mL acetic acid was stirred to form a homogeneous solution. This was transferred to a 100 mL volumetric flask to obtain the color agent. A mixture of 1 mL electrolyte and 4 mL color agent was left for 0.5 h in the dark. The absorbance of the solutions was measured at 540 nm from the UV-vis absorption spectrum. The calibration curve was obtained by using different known concentrations of potassium nitrite solution in 0.1 M KOH.

**15N isotope labeling experiment**

An $^{15}$N isotopic labeling experiment was carried out to verify the source of produced ammonia. After $^{15}$N$_2$ electroreduction at $-0.05$ V in KOH electrolyte for 10 h, the obtained product was qualitatively determined by $^1$H nuclear magnetic resonance (NMR, Agilent 600 MHz). In detail, 30 mL of the electrolytic solution was moved out and then acidized to pH $\sim 3$. The solution was concentrated to 2 mL at 80°C. Afterwards, 0.9 mL of concentrated solution and 0.1 mL D$_2$O containing 100 ppm dimethyl sulphoxide (99.99%) as an internal standard were mixed for $^1$H NMR test.

**DFT calculations**

The DFT+$U$ calculations were carried out with CASTEP code [45]. In this framework, we use rotationally invariant (Anisimov type) functional DFT+$U$ [46]. The Hubbard U parameter is self-consistently determined for the pseudized C-2p, Fe-3d and Pt-5d orbital by the new linear response way [47–53]. The geometry optimization used the Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm in all DFT+$U$ calculations. The PBE functional was chosen for PBE+$U$ calculations with a kinetic cutoff energy of 750 eV, with the valence electron states expressed in a plane-wave basis set. The ensemble DFT (EDFT) method of Marzari et al. [54] was used for convergence on the transition metal contained compounds.

The $2 \times 2 \times 1$ supercell of Pt$_3$Fe (311) surface model was chosen with 112 atoms (i.e. Pt$_{96}$Fe$_{28}$) and seven layers thick. The $2 \times 2 \times 1$ supercell of Pt$_3$Fe (111) surface model was chosen with 128 atoms (i.e. Pt$_{96}$Fe$_{32}$) and eight layers thick. The Pt$_3$Fe (200) surface model was chosen with 144 atoms (i.e. Pt$_{108}$Fe$_{36}$) and eight layers thick. The vacuum thickness was set to be 10 Å. The reciprocal space integration was performed using the mesh of $2 \times 2 \times 1$ [55] with Gamma-center-off, which was self-consistently selected for total energy minimization. With these special k-points, the total energy converged to less than 5.0 × 10$^{-7}$ eV per atom. The Hellmann-Feynman forces on the atom converged to less than 0.001 eV/Å.

The Fe and Pt norm-conserving pseudopotentials were generated using the OPIUM code in the Kleinman-Bylander projector form [56], the non-linear partial core correction [57] and a scalar relativistic averaging scheme [58] are used to treat the spin-orbital coupling effect. For this treatment, we actually similarly chose a non-linear core correction technique for correcting the valence-core charge density overlapping in such heavy fermions elements, the details of this method are given in a previous work [47,48]. In particular, we treated the (3d, 4s, 4p) and (5d, 6s, 6p) states as the valence states of both Fe and Pt atoms. The RRKJ method was chosen for optimization of the pseudopotentials [59].

For all of the electronic state calculations, we used self-consistent determination for the U correction on the localized d orbitals to correct the on-site Coulomb energy of the electron spurious self-energy. By that method, the Hubbard U parameters on the half-filled shell of 3d$^8$ orbitals of Fe are self-consistently determined to be U$_d = 6.03$ eV, and U$_d = 5.26$ eV for Pt-5d$^9$ within the Pt$_3$Fe system.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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**AUTHOR CONTRIBUTIONS**

H.-X.Q. and S.Q. proposed and supervised the project. T.W. and W.-P.T. conceived and designed the experiments. T.W. carried out the material synthesis, characterizations and electrochemical tests. H.-B.L. carried out DFT calculations. T.W., W.-P.T., H.-B.L., S.Q. and H.-X.Q. co-wrote the manuscript. All authors participated in discussing and analyzing the experimental results.

Conflict of interest statement. None declared.
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