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Greatly Improving Electrochemical N₂ Reduction over TiO₂ Nanoparticle by Fe Doping

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Abstract: It is highly needed to develop Ti-based catalysts simultaneously achieving a large NH₃ yield with a high Faradic efficiency (FE) for electrocatalytic N₂ reduction to NH₃. Here, we report that Fe, one of the cheapest and most abundant metals on the earth, acts effectively as a dopant to greatly improve the NRR performances of TiO₂ nanoparticle for ambient N₂-to-NH₃ conversion. In 0.5 M LiClO₄, such Fe-doped TiO₂ catalyst attains a high FE of 25.6 % and a large NH₃ yield of 25.47 µg h⁻¹ mg_{cat.}⁻¹ at –0.40 V vs. reversible hydrogen electrode, comparing favourably to the behaviours of all reported Ti- and Fe-based NRR electrocatalysts in aqueous media. The catalytic mechanism is further discussed by theoretical calculations.

As an essential activated nitrogen source, NH₃ is extensively used to manufacture dyes, polymers, fertilizers, and explosives, and it also serves as carbon-neutral energy carrier with high energy density.^[1–3] To date, the dominant industrial route for NH₃ synthesis is the Haber-Bosch process using N₂ and H₂ as the feeding gases, but this process operating at high temperature and high pressure consumes a large amount of energy and emits CO₂.^[4] Electrochemical N₂ reduction offers an attractive alternative in an environmentally benign and sustainable manner, but the strong N≡N bond makes it inert and thus difficult to take part in a chemical reaction, underlying the need of electrocatalysts with high activity for the N₂ reduction reaction (NRR).^[5–8]

So far, noble metals perform efficiently for the NRR, but the scarcity and high cost limit their application in large-scale production.^[8–11] Research focus has thus been increasingly shifted to develop noble-metal-free alternatives.^[12–24] TiO₂ are highly adaptable as a semiconductor catalyst due to its long-term thermodynamic stability, natural abundance, and nontoxicity.^[25] Recent studies have demonstrated that oxygen-defected TiO₂ has good electrocatalytic activity for the NRR,^[26,27] and heteroatoms (B,^[28] C,^[29] V,^[30] and Zr,^[31]) are effective dopants to enhance the NRR performances of TiO₂ catalysts. However, Ti-based catalysts simultaneously achieving a large NH₃ yield with a high Faradic efficiency (FE) are not available so

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As one of the cheapest and most abundant metals on the earth,^[32] Fe also exists in biological nitrogenases for natural N₂ fixation.^[33] Fe compounds have been widely utilized as catalysts for artificial N_2 fixation in the Haber-Bosch^[4] and electrochemical^[34-39] processes. It is thus natural for us to explore using Fe as a dopant for TiO₂, which however has not been reported before. Herein, we report on our recent experimental results that Fe-doped TiO₂ is superior in performances for electrocatalytic N₂ reduction under ambient conditions. In 0.5 M LiCIO₄, such catalyst achieves a high FE of 25.6 % and a large NH₃ yield of 25.47 μ g h⁻¹ mg_{cat.}⁻¹ at -0.40 V vs. reversible hydrogen electrode (RHE), outperforming pristine TiO₂ as well as all Ti- and Fe-based NRR electrocatalysts reported before. Remarkably, it also shows high electrochemical and structural stability. The NRR mechanism on Fe-doped TiO₂ (101) surface is further discussed using density function theory (DFT) calculations.



Figure 1. (a) XRD patterns of pristine TiO_2 and $Fe-TiO_2$. TEM images of (b) pristine TiO_2 and (c) $Fe-TiO_2$. (d) HRTEM image taken from $Fe-TiO_2$. (e) STEM image and the corresponding EDX elemental mapping images of (f) Fe, (g) Ti, and (h) O for $Fe-TiO_2$.

Figure 1a shows the X-ray diffraction (XRD) patterns for pristine TiO₂ and Fe-TiO₂ (see Experimental Section for preparative details). Clearly, both materials show diffraction peaks characteristic of anatase TiO₂ (JCPDS NO. 97-009-3098) and the peaks of iron oxides are not obtained for Fe-TiO₂. Moreover, Fe-doped TiO₂ exhibits broader diffraction peaks compared to pristine TiO₂, indicating a slightly poor crystal quality due to Fe ions doping.^[40-43] Figure S1 shows the XRD patterns of Fe-TiO2 with various RFe values (RFe is the mass ratio of Fe:Ti). As observed, the peak at 25.3° not only is slightly shifted toward lower diffraction angle (25.2°), but also the peak at 37.8° obviously weaken and broaden with increasing R_{Fe} value to 2.8 % (Figure S1), which is attributed to the increase of TiO₂ lattice constants by Fe doping.^[31,42] Therefore, it can be inferred that the Fe ions incorporate into the TiO₂ lattice, forming an iron-titanium solid solution. Transmission electron microscopy (TEM) images of TiO₂ (Figure 1b) and Fe-TiO₂ (Figure 1c) indicate that they both are nanoparticles and Fe doping has no obvious influence on the particle size. High-resolution TEM (HRTEM) images taken from TiO2 and Fe-TiO2 nanoparticles

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show the lattice fringes with a distance of 0.349 nm and 0.352 nm (Figure S2 and Figure 1d), which corresponds to the (101) plane of anatase TiO₂. This difference is ascribed to that Fedoping has a slight effect on the crystalline structure of TiO₂. Thus, it is reasonable to assume that Ti⁴⁺ can be replaced by Fe ions without significant alteration of the crystal structure.^[41] Scanning TEM (STEM) and corresponding energy dispersive X-ray (EDX) elemental mapping images (Figure 1e-h) further confirm the uniform distribution of Fe, Ti, and O elements in Fe-TiO₂ nanoparticle.



Figure 2. (a) XPS survey spectrum of Fe-TiO₂. XPS spectra in (b) Fe 2p, (c) Ti 2p, and (d) O 1s regions.

The X-ray photoelectron spectroscopy (XPS) survey spectrum. of Fe-TiO₂ confirms the presence of Fe, Ti, and O elements (Figure 2a).^[44] As shown in Figure 2b, the two characteristics peaks centred at binding energies of 711.4 and 724.72 eV are presented in Fe 2p spectrum, which are attributed to Fe 2p_{3/2} and 2p1/2, respectively. After deconvolution, both the peaks can be resolved into two peaks at 711.78 and 725.08 eV, which are assigned to Fe3+, and the peaks at 709.08 and 723.32 eV correspond to Fe2+. XPS spectrum of Ti 2p (Figure 2c) shows that the typical Ti 2p3/2 peak is observed at 458.59 eV, which corresponds to Ti⁴⁺, and other two Ti $2p_{1/2}$ peaks at 463.02 eV and 464.39 eV are assigned to Ti^{3+} and Ti^{4+} , respectively. Compared to pristine TiO₂ (Figure S3), the peaks for Ti 2p_{3/2} and Ti 2p_{1/2} of Fe-TiO₂ exhibit positive shifts of 0.38 and 0.48 eV, respectively, which could be ascribed to lattice distortions.[45] The existence of Ti³⁺ species indicates that Ti⁴⁺ ions obtain electrons from nearby oxygen vacancies.^[44] For O 1s peaks (Figure 2d), it can be seen that three peaks is deconvoluted, and the maximum peak appears at about 529.86 eV, which is attributed to the Ti-O bond; the other two oxygen peaks are obtained at 531.55 eV and 532.98 eV, which are ascribed to the surface chemiadsorbed oxygen (O) and hydroxyl groups (OH), respectively.^[44,46,47]

The electrochemical NRR tests were conducted in a typical Hcell separated by a piece of Nafion membrane in 0.5 M LiClO₄ solution under ambient conditions. Fe-TiO₂ catalyst was deposited on carbon paper (Fe-TiO₂/CP with a Fe-TiO₂ loading of 0.10 mg cm⁻²) as the working electrode. All potentials are recorded with respect to a RHE scale. The concentrations of produced NH₃ were spectrophotometrically determined using the indophenol blue method^[48] and possible by-product N₂H₄ were confirmed through Watt and Chrisp method.^[49] Corresponding calibration curves are shown in Figure S4 and S5. Timedependent current density curves for 2 h from -0.35 to -0.55 V are presented in Figure 3a and corresponding UV-Vis absorption spectra of the electrolytes stained with indophenol indicator are displayed in Figure 3b. Results show that the peak of highest absorbance intensity is located at -0.40 V. Corresponding FEs and NH₃ yields at different potentials are plotted in Figure 3c. Both FEs and NH₃ yields increase as moving negatively applied potential until -0.40 V, and then decrease gradually, which is ascribed to the competitive selectivity toward the hydrogen evolution reaction (HER).^[18,50] The highest FE (25.6%) and maximum NH₃ yield (NH₃ yield: 25.47 μ g h⁻¹ mg_{cat.}⁻¹) are achieved at -0.40 V, outperforming pristine TiO₂ shown in Figure 3d (FE: 3.65 %; NH₃ yield: 5.36 μ g h⁻¹ mg_{cat.}⁻¹). It should be mentioned that this catalyst also compares favourably to the behaviors of all reported Ti- and Fe-based NRR electrocatalysts in aqueous electrolytes (Table S1). The NH₃ yields are also determined through ion chromatography analysis (Figure S6). As observed, both techniques offer comparable values.



Figure 3. (a) Time-dependent current density curves of Fe-TiO₂/CP under various potentials in N₂-saturated 0.5 M LiClO₄ for 7200 s. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator at various potentials. (c) FEs and NH₃ yields over Fe-TiO₂/CP at various potentials. (d) FEs and NH₃ yields over Fe-TiO₂/CP at -0.40 V for 2 h. (e) Amount of NH₃ over different electrodes at -0.40 V after electrolysis for 2 h. (f) Cycling test of Fe-TiO₂/CP for NRR at -0.40 V.

We also compare the amount of NH₃ generated over three electrodes: Fe-TiO₂/CP, TiO₂/CP and bare CP are considered. As shown in Figure 3e, the latter two electrodes yield NH₃ with much smaller amount, implying Fe-TiO₂ has superior NRR activity for NH₃ formation. Moreover, we also employed Fe-TiO₂/CP as the working electrode in Ar-saturated electrolyte at -0.40 V for 2 h and corresponding UV-Vis absorption spectrum is presented in Figure S7. Results show that it is very close to

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the blank electrolyte, indicating almost no NH₃ production. Significantly, no N₂H₄ is detected after 2 h electrolysis (Figure S8), revealing Fe-TiO₂/CP possesses excellent selectivity toward N₂ to NH₃ conversion. Electrochemical impedance spectroscopy (Figure S9) analysis of Fe-TiO₂/CP shows that its charge-transfer resistance is lower than that of TiO₂/CP, suggesting that electron transfer is accelerated as introducing Fe dopant into TiO2.^[51] We also performed NRR electrolysis at -0.40 V in 0.1 M Na₂SO₄. Figure S10 compares the NH₃ yields and FEs in two electrolytes, suggesting Fe-TiO₂/CP is also active but with decreased performance metrics in 0.1 M Na₂SO₄. In addition, consecutive five recycling tests were considered to evaluate stability of Fe-TiO₂/CP at -0.40 V, which is a critical factor in practical applications (Figure 3f). Both FEs and NH₃ yields show a slight variation, indicating the high stability of Fe-TiO₂/CP during N₂ reduction process. XRD analysis after longterm NRR electrolysis (Figure S11) demonstrates that this catalyst is no change in the crystalline phase, implying it is extremely stable during NRR process. TEM image shows that this catalyst still maintains its nanoparticle morphology after long-term NRR electrolysis (Figure S12). ¹⁵N isotopic labeling experiment was also performed to confirm the N source originated from Fe-TiO₂/CP through NRR process. Figure S13 displays ¹H nuclear magnetic resonance (NMR) spectra. As observed, only ¹⁵NH₄⁺ signals are detected when ¹⁵N₂ is bubbled into the cathode.



Figure 4. Free energy diagram of NRR on V₂₋₁ site at U= -0.40 V and corresponding atom configurations. Ti, gray; Ti^{3+} (Ti_{4c}), orange; Ti^{3+} (Ti_{5c}), purple; Fe, brown; O, red; N, blue; H, white.

DFT calculations on the active site and corresponding electronic structure were carried out to gain further insight into NRR mechanism at an atom scale. XRD and HRTEM indicate that (101) surface is mainly exposed in Fe-TiO₂ system and thus is applied to catalyze NRR. In general, Fe atom prefers to substitute five-coordination Ti atom on TiO₂ (101) surface and it is more probable to create oxygen vacancy (V) because of the charge compensation between the metal dopant and lattice defect.^[52] Our calculations show that the V₁ site near the Fe dopant atom is most probable on Fe-TiO₂(101) surface with oxygen vacancy formation energy of 1.42 eV (E_f = 1.42 eV), which is lower than that of V₁-decorated pristine TiO₂ (101) surface with Fe-doped TiO₂ (101) surface has more oxygen vacancies

than that of pristine TiO_2 (101). Figure S15 shows the room temperature electron spin resonance (ESR) spectra of TiO₂ and Fe-TiO₂. The Fe-TiO₂ shows a definite oxygen vacancy signal located at g = 2.003, demonstrating a large number of oxygen vacancies are formed in the wake of ${\rm Ti}^{3+}$ centers. $^{[26,53]}$ The unpaired electrons from V1-decorated Fe-TiO2 present openshell singlet configuration ($\uparrow\downarrow$), indicating the absence of Ti³⁺ (Figure S16a),^[52] Given Ti³⁺ exists in this catalyst, the second oxygen vacancy is further considered and corresponding three possible vacancy sites are selected, including V2-1, V2-2, and V2-3 (Figure S14). Calculation results show that V₂₋₁ site is most preferable with a lower E_f (3.71 eV) and this energy consumption is comparable with that of V1-decorated pristine TiO2 (101). It implies that V_{2-1} site generating is reasonable on V_1 -decorated Fe-doped TiO₂(101) surface [named as V₁+V₂₋₁-decorated Fe-TiO₂ (101)], as shown in Figure 4a. For this case, bi-Ti³⁺ appears around V₂₋₁ site (Figure S16b). Based on above results, it is reasonably concluded that V1 and V2-1 are coexistence on Fedoped TiO₂ (101) surface.

Subsequently, we calculate the whole NRR process on V1and V1+V2-1-decorated Fe-TiO2 (101) surfaces. For V1-decorated Fe-TiO₂ (101) surface, N₂ molecule is adsorbed on Fe site by end-on coordination with a free energy change of 0.07 eV (ΔG = 0.07 eV) and Bader charge analysis indicates that 0.08 e⁻ is transferred into N₂ molecule, suggesting N₂ is effectively activated. Nevertheless, the hydrogenation process of N₂ is terminated at *NH₂NH₂ intermediate, as shown in Figure S17, which suggests that NH₃ formation is difficult on V₁-decorated Fe-TiO₂ (101) surface. Then, N₂ adsorption on V_1+V_{2-1} decorated Fe-TiO₂ (101) surface is calculated and results show that it prefers to adsorb on V2-1 site between four- and fivecoordination Ti atom sites (named as Ti_{4c} and Ti_{5c}) by end-on coordination with $\Delta G = 0.14 \text{ eV}$ (Figure 4b and S16b). Bader charge analysis shows that 0.15 e is transferred into N₂ molecule, which is twice higher than those of V₁-decorated pristine TiO₂ (101) and V₁-decorated Fe-TiO₂ (101) surfaces. The bond length of N_2 is obviously elongated from 1.112 to 1.123 Å, which is higher than those of V_1 -decorated pristine TiO₂ (101) and V₁-decorated Fe-TiO₂ (101) surfaces whose bond lengths change from 1.112 to 1.118 Å. We calculate the work function (WF) on V₁-decorated pristine TiO₂ (101), V₁-decorated Fe-TiO₂ (101) and V₁+V₂₋₁-decorated Fe-TiO₂ (101) surfaces, and results show that corresponding values are 5.01, 5.11 and 4.71 eV, respectively. It can be seen that V₁+V₂₋₁-decorated Fe-TiO₂ (101) has lowest WF value and thus the back-donation electron on this surface is most readily transferred to N₂ molecule. The first hydrogenation of *N₂ to *NNH experiences an uphill pathway with $\Delta G = 0.43 \text{ eV}$ (Figure 4c). Hydrogenation of *NNH has two pathways, including *NNH to *NNH₂ and *NNH to *NHNH processes, respectively. For distal pathway, *NNH to *NNH₂ process consumes energy in 0.55 eV, but the subsequent *NNH₂ is hydrogenated to *NHNH₂ rather than *N and *NH₃, and thus is termed as the mixed pathway. Our calculation results show that the mixed pathway, *NNH₂ to *NHNH₂ process, is a downhill pathway with $\Delta G = -1.27$ eV. And then *NHNH₂ to *NH₂NH₂ process is an uphill pathway with $\Delta G =$ 0.58 eV. Importantly, *NH₂NH₂ is quickly hydrogenated to *NH₂ and *NH₃ with $\Delta G = -2.65$ eV, and NH₃ desorptions in the whole NRR process consume lower energies (0.57~0.59 eV). For the alternating pathway, *NNH to *NHNH process is an uphill pathway with $\Delta G = 0.13$ eV, which is lower than that of distal

pathway (*NNH to *NNH₂) with $\Delta G = 0.55$ eV. Then, the

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hydrogenation process of *NHNH to *NHNH₂ is a downhill pathway with $\Delta G = -0.85 \text{ eV}$. The remaining hydrogenation and NH₃ desorption processes are consistent with the mixed pathway. The hydrogenation of *NH₂NH₂ is a key process for NRR. Our calculation results show that *NH₂NH₂ can be hydrogenated to *NH₂+*NH₃ on V₁+V₂₋₁-decorated Fe-TiO₂ (101) surface with bi-Ti³⁺ (Figure 4), but V₁-decorated Fe-TiO₂ (101) surface without bi-Ti³⁺ is not preferable, suggesting the synergy effect of bi-Ti³⁺ on *NH₂NH₂ intermediate promotes *NH₂NH₂ to *NH₂+*NH₃ conversion. Overall, above calculations reveal that the introduction of Fe into TiO₂ (101) spontaneously increases the number of oxygen vacancy, and thus further promotes N₂ activation. At the moment, the synergistic role of bi-Ti³⁺ arised from oxygen vacancy is responsible for NRR process.

In summary, Fe is proven as an effective dopant to boost the NRR activity of TiO₂ catalyst. In 0.5 M LiClO₄, Fe-doped TiO₂ catalyst attains a high FE of 25.6 % and a large NH₃ yield of 25.47 μ g h⁻¹ mg_{cat.}⁻¹ at -0.40 V, with high electrochemical and structure stability. DFT calculation results reveal that the introduction of Fe into TiO₂ (101) spontaneously increases the number of oxygen vacancy and thus further promotes N₂ activation. The synergistic effect of bi-Ti³⁺ and oxygen vacancy is responsible for the high catalytic performances. This work not only offers an attractive earth-abundant nanocatalyst for NH₃ electrosynthesis, but also would open up an exciting new avenue to the rational design of Fe-doped transition metal oxides for artificial N₂ fixation with enhanced performance.

Keywords: $TiO_2 \cdot Fe$ doping $\cdot N_2$ reduction electrocatalysis $\cdot Ti^{3+} \cdot density$ functional theory

- [1] V. Smil, Nature 1999, 400, 415.
- [2] R. Schlögl, Angew. Chem. Int. Ed. 2003, 42, 2004-2008.
- [3] T. Vegge, R. Z. Sørensen, A. Klerke, J. S. Hummelshøj, T. Johannessen, J. K. Nørskov, C. H. Christensen, *Indirect Hydrogen Storage in Metal Ammines*, British Welding Research Association, **2008**, p. 533–564.
- I. Dybkjaer, Ammonia, Catalysis and Manufacture (Ed.: Nielsen, A.), Springer, Heidelberg, 1995, p. 199–308.
- [5] V. Kyriakou, I. Garagounis, E. Vasileiou, A. Vourros, M. Stoukides, *Catal. Today* 2017, 286, 2–13.
- [6] C. Guo, J. Ran, A. Vasileff, S. Qiao, Energ. Environ. Sci. 2018, 11, 45–56.
- [7] R. Zhao, H. Xie, L. Chang, X. Zhang, X. Zhu, X. Tong, T. Wang, Y. Luo, P. Wei, Z. Wang, X. Sun, *EnergyChem* 2019, 1, 100011.
- [8] M. Shi, D. Bao, B. R. Wulan, Y. Li, Y. Zhang, J. Yan, Q. Jiang, Adv. Mater. 2017, 29, 1606550.
- D. Bao, Q. Zhang, F. Meng, H. Zhong, M. Shi, Y. Zhang, J. Yan, Q. Jiang, X. Zhang, *Adv. Mater.* 2017, 29, 1604799.
- [10] H. Huang, L. Xia, X. Shi, A. M. Asiri, X. Sun, Chem. Commun. 2018, 54, 11427–11430.
- [11] J. Wang, L. Yu, L. Hu, G. Chen, H. Xin, X. Feng, *Nat. Commun.* 2018, 9, 1795.
- Y. Liu, M. Han, Q. Xiong, S. Zhang, C. Zhao, W. Gong, G. Wang, H. Zhang, H. Zhao, *Adv. Energy Mater.* **2019**, *9*, 1803935.
- [13] J. Zhao, J. Yang, L. Ji, H. Wang, H. Chen, Z. Niu, Q. Liu, T. Li, G. Cui, X. Sun, *Chem. Commun.* **2019**, 55, 4266–4269.
- [14] Z. Wang, F. Gong, L. Zhang, R. Wang, L. Ji, Q. Liu, Y. Luo, P. Gao, B. Li, B. Tang, X. Sun, *Adv. Sci.* 2018, *5*, 1801182.
- [15] J. Li, L. He, X. Liu, X. Cheng, G. Li, Angew. Chem. Int. Ed. 2019, 58, 1759–1763.
- [16] X. Zhang, T. Wu, H. Wang, R. Zhao, H. Chen, T. Wang, P. Wei, Y. Luo, Y. Zhang, X. Sun, ACS Catal. 2019, 9, 4609–4615.
- [17] C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou, G. Yu, Angew. Chem. Int. Ed. 2018, 57, 6073–6076.

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- [18] W. Qiu, X. Xie, J. Qiu, W. Fang, R. Liang, X. Ren, X. Ji, G. Cui, A. M. Asiri, G. Cui, B. Tang, X. Sun, *Nat. Commun.* **2018**, *9*, 3485.
- S. Zhang, C. Zhao, Y. Liu, W. Li, G. Wang, Y. Zhang, H. Zhang, H. Zhao, *Chem. Commun.* **2019**, *55*, 2952–2955.
- [20] S. Gao, Y. Zhu, Y. Chen, M. Tian, Y. Yang, T. Jiang, Z. Wang, *Mater. Today* **2019**, *28*, 17–24.
- [21] Y. Wang, M. Shi, D. Bao, F. Meng, Q. Zhang, Y. Zhou, K. Liu, Y. Zhang, J. Wang, Z. Chen, D. Liu, Z. Jiang, M. Luo, L. Gu, Q. Zhang, X. Cao, Y. Yao, M. Shao, Y. Zhang, X. Zhang, J. Chen, J. Yan, Q. Jiang, *Angew. Chem. Int. Ed.* **2019**, *58*, 9464–9469.
- [22] L. Han, X. Liu, J. Chen, R. Lin, H. Liu, F. Lu, S. Bak, Z. Liang, S. Zhao, E. Stavitski, J. Luo, R. R. Adzic, H. Xin, *Angew. Chem. Int. Ed.* **2019**, *58*, 2321–2325.
- [23] L. Li, C. Tang, B. Xia, H. Jin, Y. Zheng, S. Qiao, ACS Catal. 2019, 9, 2902–2908.
- [24] H. Cheng, L. X. Ding, G. F. Chen, L. Zhang, J. Xue, H. Wang, *Adv. Mater.* 2018, *30*, 1803694.
- [25] W. Yin, B. Wen, C. Zhou, A. Selloni, L. Liu. Surf. Sci. Rep. 2018, 73, 58–82.
- [26] L. Yang, T. Wu, R. Zhang, H. Zhou, L. Xia, X. Shi, H. Zheng, Y. Zhang, X. Sun, *Nanoscale* **2019**, *11*, 1555–1562.
- [27] R. Zhang, X. Ren, X. Shi, F. Xie, F. Zheng, X. Guo, X. Sun, ACS Appl. Mater. Interfaces 2018, 10, 28251–28255.
- [28] Y. Wang, K. Jia, Q. Pan, Y. Xu, Q. Liu, G. Cui, X. Guo, X. Sun, ACS Sustainable Chem. Eng. 2019, 7, 117–122.
- [29] Q. Qin, Y. Zhao, M. Schmallegger, T. Heil, J. Schmidt, R. Walczak, G. Demner, H. Jiao, M. Oschatz, *Angew. Chem. Int. Ed.* **2019**, *58*, 13101–13106.
- [30] T. Wu, W. Kong, Y. Zhang, Z. Xing, J. Zhao, T. Wang, X. Shi, Y. Luo, X. Sun, Small methods 2019, 3, 1900356.
- [31] N. Cao, Z. Chen, K. Zang, J. Xu, J. Zhong, J. Luo, X. Xu, G. Zheng, *Nat. Commun.* **2019**, *10*, 2877.
- [32] P. Jiang, Q. Liu, Y. Liang, J. Tian, A. M. Asiri, X. Sun, Angew. Chem. Int. Ed. 2014, 126, 13069–13073.
- [33] T. M. Buscagan, P. H. Oyala, J. C. Peters, Angew. Chem. Int. Ed. 2017, 129, 6921–6926.
- [34] S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su, G. Centi, Angew. Chem. Int. Ed. 2017, 56, 2699–2703.
- [35] J. Kong, A. Lim, C. Yoon, J. H. Jang, H. C. Ham, J. Han, S. Nam, D. Kim, Y. E. Sung, J. Choi, H. S. Park, ACS Sustainable Chem. Eng. 2017, 5, 10986–10995.
- [36] Q. Liu, X. Zhang, B. Zhang, Y. Luo, G. Cui, F. Xie, X. Sun. Nanoscale 2018, 10, 14386–14389.
- [37] L. Hu, A. Khaniya, J. Wang, G. Chen, W. E. Kaden, X. Feng, ACS Catal. 2018, 8, 9312–9319.
- [38] X. Zhu, H. Wang, Z. Liu, R. Zhao, H. Chen, T. Wang, F. Wang, Y. Luo, Y. Wu, X. Sun, Chem. Commun. 2019, 55, 3987–3990.
- [39] X. Zhao, X. Lan, D. Yu, H. Fu, Z. Liu, T. Mu, Chem. Commun. 2018, 54, 13010–13013.
- [40] S. Xu, S. Pan, Y. Xu, Y. Luo, Y. Zhang, G. Li, J. Hazard. Mater. 2015, 283, 7–13.
- [41] M. Zhou, J. Yu, B. Cheng, H. Yu, Mater. Chem. Phys. 2005, 93, 159–163.
- [42] C. Wang, C. Bottcher, D. W. Bahnemann, J. K. Dohrmann, J. Mater. Chem. 2003, 13, 2322–2329.
- [43] J. Zhu, Z. Deng, F. Chen, J. Zhang, H. Chen, M. Anpo, J, Huang,
 L. Zhang, *Appl. Catal. B* 2006, *62*, 329–335.
- [44] H. Khan, I. Swati, Ind. Eng. Chem. Res. 2016, 55, 6619–6633.
- [45] E. M. Neville, M. J. Mattle, D. Loughrey, B. Rajesh, M. Rahman, J. M. D. MacElroy, J. A. Sullivan, K. R. Thampi, *J. Phys. Chem. C* 2012, *116*, 16511–16521.
- [46] C. Yang, X. Zhang, J. Qin, X. Shen, R. Yu, M. Ma, R. Liu, J. Catal. 2017, 347, 36–44.
- [47] B. Li, Z. Zhao, F. Gao, X. Wang, J. Qiu, Appl. Catal. B 2014, 147, 958–964.
- [48] D. Zhu, L. Zhang, R. E. Ruther, R. J. Hamers, Nat. Mater. 2013, 12, 836–841.
- [49] G. W. Watt, J. D. Chrisp, Anal. Chem. 1952, 24, 2006–2008.
- [50] X. Ren, J. Zhao, Q. Wei, Y. Ma, G. Cui, A. M. Asiri, B. Li, B. Tang, X. Sun, ACS Central Sci. 2019, 5, 116–121.

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- [51] P. Chen, N. Zhang, S. Wang, T. Zhou, Y. Tong, C. Ao, W. Yan, L. Zhang, W. Chu, C. Wu, Y. Xie, *Proc. Natl. Acad. Sci. USA* 2019, *116*, 6635–6640.
- [52] J. González-Torres, L. Cipriano, E. Poulain, V. Domínguez-Soria, R. García-Cruz, O. Olvera-Neria, J. Mol. Model. 2018, 24, 276.
- [53] H. Hirakawa, M. Hashimoto, Y. Shiraishi, T. Hirai, J. Am. Chem. Soc. 2017, 139, 10929–10936.

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Fe doping greatly improves electrochemical N₂ reduction over TiO₂ nanoparticle for ambient N₂-to-NH₃ fixation with excellent selectivity. In 0.5 M LiClO₄, this catalyst attains a high Faradic efficiency of 25.6 % and a large NH₃ yield of 25.47 μ g h⁻¹ mg_{cat}⁻¹ at -0.40 V vs. reversible hydrogen electrode. The catalytic mechanism is discussed and the synergistic effect of bi-Ti³⁺ and oxygen vacancy is responsible for the superior activities.

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Greatly Improving Electrochemical N₂ Reduction over TiO₂ Nanoparticle by Fe Doping