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Cr_2O_3 nanofiber: a high-performance electrocatalyst toward artificial N₂ fixation to NH₃ under ambient conditions[†]

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NH₃ synthesis heavily depends on the energy-intensive Haber-Bosch process, which produces serious carbon emission. Electrocatalytic N₂ reduction emerges as an environmentally benign process for sustainable artificial N₂ fixation but requires efficient, stable and selective catalysts for the N₂ reduction reaction (NRR). Here, we report that Cr₂O₃ nanofiber behaves as a superb nonnoble-metal NRR electrocatalyst for artificial N₂ fixation to NH₃, with excellent selectivity under ambient conditions. In 0.1 M HCl, this catalyst achieves a high Faradaic efficiency of 8.56% and a high NH₃ formation rate of 28.13 µg h⁻¹ mg_{cat}.⁻¹, placing it amongst the most active aqueous-based NRR electrocatalysts. Moreover, this catalyst also shows strong electrochemical durability during electrolysis and the recycling test. It opens a new avenue to explore the rational design of Cr-based nanostructures as advanced catalysts for N₂ fixation and other applications.

As an activated nitrogen building block, NH_3 is essential in the manufacture of fertilizers, medicines, dyes, explosives, resins, *etc.*¹⁻³ It is also an attractive carbon-free energy carrier, having 17.6 wt% hydrogen, in the future hydrogen economy.^{4,5} The ever-increasing need for NH_3 has stimulated intensive research on artificial NH_3 production.^{6,7} N_2 fixation, however, is extremely difficult due to the high energy barrier for $N \equiv N$ bond cleavage. In the Haber–Bosch process for industrial NH_3 production from N_2 and H_2 , N_2 reduction is accomplished at high temperature and pressure, and the entire process is rather energy-intensive and highly CO₂-emissive.^{8,9} Therefore, there is a great need to develop an environmentally benign process for sustainable artificial N_2 fixation.

In N_2 -fixing bacteria, the enzymatic reduction of N_2 to NH_3 is catalyzed by nitrogenase enzymes under ambient conditions through multiple proton and electron transfer steps using

chemical energy from adenosine 5'-triphosphate hydrolysis.7,10 Inspired by the natural process, electrochemical NH₃ synthesis using proton from water as the hydrogen source has been proposed as a carbon-free and energy-efficient N2-fixing process under ambient conditions, while the challenge associated with N₂ activation underlines the need for efficient electrocatalysts for the nitrogen reduction reaction (NRR).^{11,12} Precious metal (Au,¹³ Ru,¹⁴ Rh¹⁵)-based catalysts demonstrate favorable NRR activity, but the high cost and scarcity of these catalysts hinder their widespread use. Much attention has thus been focused on designing and developing non-noble-metal alternatives. Several such NRR electrocatalysts are documented, including Fe₂O₃-CNT,¹⁶ Fe₃O₄/Ti,¹⁷ MoO₃,¹⁸ Mo nanofilm,¹⁹ MoS₂,²⁰ Mo₂N,²¹ MoN,²² Li⁺-incorporated poly(N-ethyl-benzene-1,2,4,5-tetracarboxylic diimide),²³ B₄C,²⁴ N-doped carbon,²⁵ etc. More recently, by the marriage of amorphous Bi₄V₂O₁₁ and CeO₂, Lv et al. constructed a hybrid nanofiber for N2 reduction electrocatalysis capable of achieving a high Faradaic efficiency (FE) of 10.16% but with a NH₃ yield $(V_{\rm NH_2})$ of 23.21 µg h⁻¹ mg_{cat.}^{-1.26} Although impressive NRR performance has been achieved, a prime challenge still lies in simultaneously achieving a high NH₃ formation rate and high FE using a crystalline material, which is thermodynamically more stable.27

Herein, we report that Cr_2O_3 nanofiber behaves as a superb electrocatalyst toward ambient N_2 fixation to NH_3 , with excellent selectivity in acids. In 0.1 M HCl, such nanofiber achieves a FE as high as 8.56%, with a high NH_3 formation rate of 28.13 µg h⁻¹ mg_{cat.}⁻¹. Moreover, it is also excellent in electrochemical durability.

 Cr_2O_3 nanofiber was derived from the electrospun nanofiber of polyacrylonitrile/chromium acetate *via* annealing in air (see ESI† for preparation details). The X-ray diffraction (XRD) patterns present diffraction peaks characteristic of a Cr_2O_3 phase (JCPDS No. 38-1479) without any impurities (Fig. 1a). Scanning electron microscopy (SEM) analysis indicates that shorter Cr_2O_3 nanofibers were obtained from the precursor after annealing, with sizes approximately within the range 0.6–5.0 µm (Fig. 1b and c). Transmission electron microscopy (TEM) analysis further reveals

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Fig. 1 (a) XRD pattern of Cr_2O_3 nanofiber. SEM images of the nanofibers of (b) precursor and (c) Cr_2O_3 . (d) TEM image of Cr_2O_3 nanofibers. (e) HRTEM image and (f) SAED pattern taken from one single Cr_2O_3 nanofiber. (g) XPS survey spectrum for Cr_2O_3 nanofiber. XPS spectra of Cr_2O_3 nanofiber in the (h) Cr 2p and (i) O 1s regions.

the rough nature of such Cr_2O_3 nanofibers (Fig. 1d). The highresolution TEM (HRTEM) image (Fig. 1e) taken from one single Cr_2O_3 nanofiber shows lattice fringes with interplanar spacings of 0.248 and 0.266 nm, corresponding to the (110) and (104) planes of the Cr_2O_3 phase, respectively. The corresponding selected area electron diffraction (SAED) pattern (Fig. 1f) shows four diffraction rings indexed to the (012), (104), (116), and (214) planes of the Cr_2O_3 phase. The X-ray photoelectron spectroscopy (XPS) survey spectrum of Cr_2O_3 nanofiber confirms the presence of Cr and O elements (Fig. 1g). In the Cr 2p region, three peaks (at 576.7, 575.3, and 586.5 eV) correspond to Cr $2p_{3/2}$ and Cr $2p_{1/2}$, respectively (Fig. 1h), confirming the existence of Cr^{3+} .^{28,29} The strong peak at 530.2 eV in the O 1s region (Fig. 1i) is attributed to surface lattice oxygen combined with Cr^{3+} , whereas the small peak at 532.1 eV is typical of a hydroxyl group chemisorbed at the surface.^{30,31}

Cr₂O₃ nanofiber was deposited onto a carbon paper electrode (Cr₂O₃/CPE with Cr₂O₃ loading of 0.1 mg) for testing. During electrolysis, N2 gas was bubbled into the cathode, where protons transported through the electrolyte (0.1 M HCl aqueous solution) can react with N2 on the surface of the catalyst to produce NH₃ (Fig. 2a and Fig. S1, ESI[†]). Both NH₃ product and possible by-product N₂H₄ were detected after electrolysis, and the concentration of NH₃ was spectrophotometrically determined by the indophenol blue method,³² while N₂H₄ was estimated by the method of Watt and Chrisp.³³ Fig. S2 and S3 (ESI[†]) show the calibration curves. Fig. 2b presents the UV-Vis absorption spectra of the electrolyte stained with indophenol indicator after 2 h electrolysis at a series of potentials. It is suggested that the electrocatalytic N₂ reduction process operates within the potential range of -0.65 to -1.05 V. Its average $V_{\rm NH_2}$ and corresponding FEs under various potentials are calculated and plotted in Fig. 2c. Hydrogen evolution reaction (HER) becomes the primary process when the applied potential is below -0.75 V, and $V_{\rm NH_2}$ and FE values decrease due to the



Fig. 2 (a) Schematic diagram to illustrate the electrochemical setup. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after electrolysis at a series of potentials for 2 h. (c) $V_{\rm NH_3}$ and FE at each given potential. (d) Production of NH₃ with different electrodes after 2 h electrolysis at potential of -0.75 V under ambient conditions.

competitive HER. The highest FE of 8.56% with a $V_{\rm NH_2}$ of 28.13 μ g h⁻¹ mg_{cat.}⁻¹ is obtained at -0.75 V, outperforming most reported aqueous-based NRR electrocatalysts (Table S1, ESI[†]). Note that both NH₃ yields and FEs at various potentials (Fig. S4, ESI[†]) determined by ion chromatography data (Table S2, ESI[†]) are quite comparable to the values determined by the indophenol blue method. Significantly, N2H4 was not detected (Fig. S5, ESI⁺), indicating that this catalyst possesses excellent selectivity. Of note, inductively coupled plasma-atomic emission spectrometry suggests the absence of Cr³⁺ in the electrolyte after NRR electrolysis, implying that such crystalline Cr₂O₃ is chemically stable and robust enough to withstand the harsh acidic environment.³⁴ In addition, we also investigated the NRR performance of Ru/C under the same reaction conditions. As shown in Fig. S6 (ESI†), Ru/C also presents a superior $V_{\rm NH_2}$ but with a low FE due to its excellent HER catalytic activity. To verify that the product is generated via N2 reduction electrocatalyzed by Cr2O3, we also performed electrolysis in N2-saturated solution at open circuit potential and Ar-saturated solution at -0.75 V. The corresponding UV-Vis absorption spectra and amount of NH₃ are presented in Fig. S7 (ESI⁺), suggesting that almost no NH₃ was detected. Moreover, the time-dependent experiment shows that the production of NH₃ actually is observed to increase with reaction time, further confirming NRR on the Cr₂O₃/CPE (Fig. S8, ESI[†]). Fig. 2d compares the amount of NH₃ formed with different electrodes at -0.75 V after 2 h electrolysis. Obviously, bare CPE has poor electrocatalytic NRR activity. Of note, conventional Cr₂O₃ powder is efficient in electrochemically catalyzing N2 reduction, yielding 2.1 µg NH₃. In sharp contrast, Cr₂O₃ nanofiber shows greatly enhanced NRR activity, with a much larger yield of NH₃. The superior activity of Cr₂O₃ nanofiber can be rationally attributed to the nanofiber nature, which leads to more effective absorption of N₂ on the surface. It is worth mentioning that although Cr_2O_3 is a p-type semiconductor with about 3 eV band gap,³⁵ the highly porous feature of such Cr₂O₃ nanofiber not only

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Fig. 3 (a) Chronoamperometry curves at corresponding potentials in N_2 -saturated 0.1 M HCl. (b) Recycling test at the potential of -0.75 V.

favors the diffusion of N_2 and the reaction product, but also exposes more active sites which effectively contact the CPE surface, offering rich three-phase contact points of N_2 , electrolyte and catalyst,³⁶ and thus allowing for more efficient N_2 reduction.

In addition, durability is another important factor in evaluating the performance of electrocatalysts.^{37–43} The chronoamperometry curves at corresponding potentials in N₂-saturated 0.1 M HCl are presented in Fig. 3a, which indicates that this catalyst possesses stable electrocatalytic N₂ reduction performance. Electrolysis for 20 h at -0.75 V potential leads to a slight decrease in current density, with steady FE throughout the process (Fig. S9, ESI†). As observed in Fig. 3b, Cr₂O₃/CPE shows negligible variation in $V_{\rm NH_3}$ and FE during recycling tests of up to 6 times. The influence of N₂ flow rate on electrocatalytic N₂ reduction was also investigated. The $V_{\rm NH_3}$ and FE values show no significant fluctuation after varying the N₂ flow rate (Fig. S10, ESI†). All these observations suggest its excellent electrochemical durability.

Fig. 4a shows the XRD pattern for Cr_2O_3/CPE after stability testing. Besides the peak at 2θ value of 26.5° originating from the CPE substrate (black line in Fig. 4a), all other peaks can be indexed to Cr_2O_3 , confirming the Cr_2O_3 composition of the catalyst. TEM image (Fig. 4b) further suggests that Cr_2O_3 retains its initial morphology after NRR electrolysis. All these results indicate this catalyst is robust enough to support NRR electrolysis.

Based on the fact that no N_2H_4 was detected in the final product, a possible NRR mechanism over Cr_2O_3 can be proposed according to the previous study.⁴⁴ Firstly, N_2 approaches the surface of Cr_2O_3 , forming chemisorbed * N_2 . Secondly, the activated H proton in the electrolyte is favored to form a more stable N–H bond and break the $N \equiv N$ triple bond. Finally, hydrogenation of N_2 is carried out by adding H atoms one by one from the electrolyte and an electron from the electrode surface. We envisage that both the distal associative and partially alternative routes would be the



Fig. 4 (a) XRD pattern for Cr_2O_3/CPE after the stability test. (b) TEM image for Cr_2O_3 nanofiber after the stability test.

general reaction mechanism in our case, as shown in mode 1 and mode 2:

$${}^{*}N_{2} \rightarrow {}^{*}NNH \rightarrow {}^{*}NHNH \rightarrow {}^{*}NHNH_{2} \rightarrow {}^{*}NH + NH_{3}$$

$$\rightarrow {}^{*}NH_{2} + NH_{3} \rightarrow {}^{*}NH_{3} + NH_{3} \rightarrow {}^{*} + 2NH_{3}$$

$$(1)$$

$${}^{*}N_{2} \rightarrow {}^{*}NNH \rightarrow {}^{*}NNH_{2} \rightarrow {}^{*}NNH_{3} \rightarrow {}^{*}N + NH_{3}$$

$$\rightarrow {}^{*}NH \rightarrow {}^{*}NH_{2} \rightarrow {}^{*} + NH_{3}$$

$$(2)$$

where * is a surface binding site.

In conclusion, Cr₂O₃ nanofiber has been proposed as a highly active and durable electrocatalyst for artificial N2 fixation under ambient conditions. This catalyst is superior in both FE and $V_{\rm NH}$. Our present study not only provides us an attractive earth-abundant catalyst material in electrolysis devices for electrochemical NH₃ production, but opens a new avenue to explore the rational design of Cr-based nanostructures as advanced catalysts for N2 fixation and other applications. Our next research will focus on the structure optimization of the Cr2O3 catalyst toward improved NRR performance by constructing a Cr₂O₃/carbon nanohybrid with enhanced conductivity and engineering surface oxygen vacancy for more efficient molecular N2 adsorption and activation.^{26,45,46} There is also another suggestion to further increase the current efficiency for NH₃ formation by suppressing the competitive HER in organic media using ionic electrolyte enabled by superhydrophobic coating of metal-organic frameworks.47

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Conflicts of interest

There are no conflicts to declare.

References

- 1 R. Schlögl, Angew. Chem., Int. Ed., 2003, 42, 2004-2008.
- 2 T. Murakami, T. Nishikiori, T. Nohira and Y. Ito, J. Am. Chem. Soc., 2003, **125**, 334-335.
- 3 V. Rosca, M. Duca, M. T. de Groot and M. T. Koper, *Chem. Rev.*, 2009, **109**, 2209–2244.
- 4 C. J. Pickett and J. Talarmin, Nature, 1985, 317, 652-653.
- 5 C. H. Christensen, T. Johannessen, R. Z. Sørensen and J. K. Nørskov, *Catal. Today*, 2006, **111**, 140–144.
- 6 R. F. Service, Science, 2014, 345, 610.
- 7 K. A. Brown, D. F. Harris, M. B. Wilker, A. Rasmussen, N. Khadka, H. Hamby, S. Keable, G. Dukovic, J. W. Peters, L. C. Seefeldt and P. W. King, *Science*, 2016, 352, 448–450.
- 8 P. J. Chirik, Nat. Chem., 2009, 1, 520-522.
- 9 X. Zhang, R. Kong, H. Du, L. Xia and F. Qu, *Chem. Commun.*, 2018, 54, 5323–5325.
- 10 B. K. Burgess and D. J. Lowe, Chem. Rev., 1996, 96, 2983-3012.
- 11 Z. Wang, Y. Li, H. Yu, Y. Xu, H. Xue, X. Li, H. Wang and L. Wang, *ChemSusChem*, 2018, **11**, 3480–3485.
- 12 C. Guo, J. Ran, A. Vasileff and S. Qiao, *Energy Environ. Sci.*, 2018, **11**, 45–56.
- 13 M. Shi, D. Bao, B. R. Wulan, Y. Li, Y. Zhang, J. Yan and Q. Jiang, *Adv. Mater.*, 2017, 29, 1606550.
- 14 K. Kugler, M. Luhn, J. A. Schramm, K. Rahimi and M. Wessling, *Phys. Chem. Chem. Phys.*, 2015, **17**, 3768–3782.
- 15 H. Liu, S. Han, Y. Zhao, Y. Zhu, X. L. Tian, J. Zeng, J. Jiang, B. Y. Xia and Y. Chen, *J. Mater. Chem. A*, 2018, **6**, 3211–3217.

- 16 S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su and G. Centi, Angew. Chem., Int. Ed., 2017, 56, 2699–2703.
- 17 Q. Liu, X. Zhang, B. Zhang, Y. Luo, G. Cui, F. Xie and X. Sun, Nanoscale, 2018, 10, 14386-14389.
- 18 J. Han, X. Ji, X. Ren, G. Cui, L. Li, F. Xie, H. Wang, B. Li and X. Sun, J. Mater. Chem. A, 2018, 6, 12974–12977.
- 19 D. Yang, T. Chen and Z. Wang, J. Mater. Chem. A, 2017, 5, 18967–18971.
- 20 L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang and X. Sun, *Adv. Mater.*, 2018, **30**, 1800191.
- 21 X. Ren, G. Cui, L. Chen, F. Xie, Q. Wei, Z. Tian and X. Sun, *Chem. Commun.*, 2018, 54, 8474-8477.
- 22 L. Zhang, X. Ji, X. Ren, Y. Luo, X. Shi, A. M. Asiri, B. Zheng and X. Sun, *ACS Sustainable Chem. Eng.*, 2018, **6**, 9550–9554.
- 23 G. Chen, X. Cao, S. Wu, X. Zeng, L. Ding, M. Zhu and H. Wang, J. Am. Chem. Soc., 2017, 139, 9771–9774.
- 24 W. Qiu, X. Xie, J. Qiu, W. Fang, R. Liang, X. Ren, X. Ji, G. Cui, A. M. Asiri, G. Cui, B. Tang and X. Sun, *Nat. Commun.*, 2018, 9, 3485.
- 25 Y. Liu, Y. Su, X. Quan, X. Fan, S. Chen, H. Yu, H. Zhao, Y. Zhang and J. Zhao, *ACS Catal.*, 2018, **8**, 1186–1191.
- 26 C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou and G. Yu, Angew. Chem., Int. Ed., 2018, 57, 6073–6076.
- 27 A. Bergmann, E. Martinez-Moreno, D. Teschner, P. Chernev, M. Gliech, J. F. Araujo, T. Reier, H. Dau and P. Strasser, *Nat. Commun.*, 2015, 6, 8625.
- 28 T. Yang, Z. Chen, H. Zhang, M. Zhang and T. Wang, *Electrochim. Acta*, 2016, 217, 55–61.
- 29 H. Ma, Y. Xu, Z. Rong, X. Cheng, S. Gao, X. Zhang, H. Zhao and L. Huo, Sens. Actuators, B, 2012, 174, 325-331.
- 30 B. Choudhary, D. Paul, A. Singh and T. Gupta, *Environ. Sci. Pollut. Res.*, 2017, 24, 16786–16797.

- 31 A. M. Glushenkov, D. H. Jurcakova, D. Llewellyn, G. Q. Lu and Y. Chen, *Chem. Mater.*, 2010, 22, 914–921.
- 32 D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, 12, 836–841.
- 33 G. W. Watt and J. D. Chrisp, Anal. Chem., 1952, 24, 2006-2008.
- 34 C. Shi, T. Wang, Z. Pei, J. Gong and C. Sun, J. Mater. Sci. Technol., 2014, 30, 1193.
- 35 M. M. Abdullah, F. M. Rajab and S. M. Al-Abbas, *AIP Adv.*, 2014, 4, 027121.
- 36 Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.*, 2011, **10**, 780–786.
- 37 X. Ren, R. Ge, Y. Zhang, D. Liu, D. Wu, X. Sun, B. Du and Q. Wei, J. Mater. Chem. A, 2017, 5, 7291–7294.
- 38 J. Zhao, X. Ren, H. Ma, X. Sun, Y. Zhang, T. Yan, Q. Wei and D. Wu, ACS Sustainable Chem. Eng., 2017, 5, 10093–10098.
- 39 D. Wu, Y. Wei, X. Ren, X. Ji, Y. Liu, X. Guo, Z. Liu, Q. Wei and X. Sun, *Adv. Mater.*, 2018, **30**, 1705366.
- 40 X. Ren, X. Ji, Y. Wei, D. Wu, Y. Zhang, M. Ma, Z. Liu, Q. Wei and X. Sun, *Chem. Commun.*, 2018, 54, 1425–1428.
- 41 Y. Wei, X. Ren, H. Ma, X. Sun, Y. Zhang, X. Kuang, T. Yan, H. Ju, D. Wu and Q. Wei, *Chem. Commun.*, 2018, 54, 1533–1536.
- 42 H. Du, X. Zhang, Q. Tan, R. Kong and F. Qu, Chem. Commun., 2017, 53, 12012–12015.
- 43 X. Guo, R. Kong, X. Zhang, H. Du and F. Qu, ACS Catal., 2018, 8, 651-655.
- 44 M. A. Shipman and M. D. Symes, Catal. Today, 2017, 286, 57-68.
- 45 C. Li, T. Wang, Z. Zhao, W. Yang, J. Li, A. Li, Z. Yang, G. A. Ozin and J. Gong, Angew. Chem., Int. Ed., 2018, 57, 5278–5284.
- 46 H. Hirakawa, M. Hashimoto, Y. Shiraishi and T. Hirai, J. Am. Chem. Soc., 2017, 139, 10929–10936.
- 47 H. K. Lee, C. S. L. Koh, Y. H. Lee, C. Liu, I. Y. Phang, X. Han, C.-K. Tsung and X. Y. Ling, *Sci. Adv.*, 2018, 4, eaar3208.