

RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2023, 10, 1431High-efficiency electrosynthesis of ammonia with selective reduction of nitrite over an Ag nanoparticle-decorated TiO₂ nanoribbon array†Xiaoya Fan,^{a,b} Xun He,^b Xianchang Ji,^b Longcheng Zhang,^b Jun Li,^b Long Hu,^b XiuHong Li,^b Shengjun Sun,^c Dongdong Zheng,^b Yongsong Luo,^b Yan Wang,^b Lisi Xie,^d Qian Liu,^d Binwu Ying^{b,*a} and Xuping Sun^{b,*c}

Electrochemical nitrite (NO₂[−]) reduction can yield value-added ammonia (NH₃) while removing NO₂[−] as an environmental pollutant in wastewater; however, it involves a six-electron transfer process and requires highly efficient and selective electrocatalysts. In this study, we report high-efficiency electrosynthesis of NH₃ via NO₂[−] reduction enabled by an Ag nanoparticle-decorated TiO₂ nanoribbon array on a titanium plate (Ag@TiO₂/TP). When tested in 0.1 M NaOH containing 0.1 M NO₂[−], such Ag@TiO₂/TP shows a large NH₃ yield of 514.3 μmol h^{−1} cm^{−2} and a high faradaic efficiency of 96.4% at −0.5 V vs. a reversible hydrogen electrode. Significantly, it also demonstrates excellent durability for 12 h electrolysis.

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Ammonia (NH₃) is widely applied to manufacture nitrogen fertilizers, explosives, chemical products, etc., and it is also considered as an attractive hydrogen carrier and zero-carbon fuel.^{1–3} Although the Haber–Bosch method realizes industrial NH₃ synthesis from hydrogen and nitrogen under high temperature and high pressure, this process is highly energy-intensive and emits a mass of greenhouse gases.⁴ Electrochemical nitrogen reduction is thus deemed as a potential alternative to the Haber–Bosch process for ambient NH₃ synthesis, although the competitive hydrogen evolution reaction and unsatisfactory adsorption and cleavage effects of N₂ severely hinder the selectivity and activity of the electrochemical nitrogen reduction reaction.^{5–14}

NH₃ synthesis via electrochemical nitrite (NO₂[−]) reduction, in contrast, needs lower energy to cleave the N=O bond with faster reaction kinetics and achieves higher reaction substrate concentrations, leading to a larger NH₃ yield and higher faradaic efficiency (FE).^{1,15,16} In addition, excess NO₂[−] accumulated in groundwater could destroy the ecological balance and harm human health.¹⁷ Electrochemical conversion of waste NO₂[−] can produce value-added NH₃ under ambient conditions

and simultaneously remove NO₂[−], which provides a solution for restoring the imbalance in the global nitrogen cycle. However, the electrochemical NO₂[−] reduction reaction (NO₂[−]RR) involves a complex six-electron pathway with various possible by-products (N₂H₄, N₂, and H₂), thus requiring highly active catalysts for selective NO₂[−]-to-NH₃ conversion.^{18–27}

Noble metal (Au,²⁸ Pd,^{28,29} Ru,³⁰ Ir,³¹ Pt³²)-based catalysts are active for the NO₂[−]RR, but their scarcity hinders large-scale applications. Compared with the above noble metals, Ag is relatively low in price and high in abundance, and it also performs efficiently in NO₂[−] reduction electrocatalysis.³³ As an Earth-abundant transition metal oxide with high chemical and structural stability, TiO₂ is widely used as a support to load noble metal nanoparticles for catalysis applications.^{34–39} Our recent studies also suggest that it is active for the NO₂[−]RR and its activity can be enhanced by introducing oxygen vacancies⁴⁰ and P doping.⁴¹ We believe that TiO₂ could be an ideal support for Ag nanoparticles for an enhanced NO₂[−]-to-NH₃ conversion performance with much less usage of noble metals, which, however, has not been reported to date.

In this study, we constructed an Ag nanoparticle-decorated TiO₂ nanoribbon array on a titanium plate (Ag@TiO₂/TP) as a highly selective NO₂[−]RR catalyst for NH₃ synthesis. When tested in NO₂[−]-containing solution, Ag@TiO₂/TP is capable of delivering a large NH₃ yield of 514.3 μmol h^{−1} cm^{−2} with a high FE of 96.4% at −0.5 V vs. a reversible hydrogen electrode (RHE). Furthermore, Ag@TiO₂/TP exhibits robust stability for long-term electrolysis.

As shown in Fig. 1a, Ag@TiO₂/TP was synthesized through a hydrothermal method in an alkaline solution, Ag⁺ exchange,

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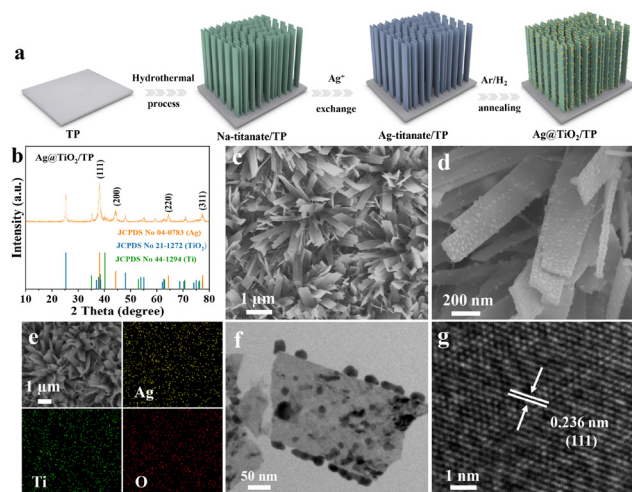


Fig. 1 (a) Schematic illustration of the fabrication process of Ag@TiO₂/TP. (b) XRD pattern and (c) and (d) SEM images of Ag@TiO₂/TP. (e) SEM and corresponding elemental mapping images of Ag@TiO₂/TP. (f) TEM and (g) HRTEM images of Ag@TiO₂.

and an annealing process under an Ar/H₂ atmosphere (see the ESI† for details). Fig. 1b depicts the X-ray diffraction (XRD) pattern of Ag@TiO₂/TP. The diffraction peaks at 38.15°, 44.30°, 64.43°, and 77.50° correspond to the (111), (200), (220), and (311) lattice planes of Ag, respectively (JCPDS No. 04-0783),³³ while the other diffraction peaks can be assigned to metallic Ti (JCPDS No. 44-1294) and TiO₂ (JCPDS No. 21-1272), and these are in accordance with those for TiO₂/TP (Fig. S1†). As depicted in Fig. S2 and S3,† the scanning electron microscopy (SEM) images show that the TiO₂ nanoribbon array was grown on TP. With regard to Ag@TiO₂/TP, plenty of nanoparticles are decorated on the surface of the TiO₂ nanoribbon (Fig. 1c and d). Additionally, the SEM image and corresponding energy-dispersive X-ray (EDX) elemental mapping images of Ag@TiO₂/TP confirm the existence of Ag, Ti, and O elements with a homogeneous distribution (Fig. 1e). Furthermore, the result of the EDX spectrum confirms that the Ag content in Ag@TiO₂/TP is approximately 13.63% (Fig. S4†). The transmission electron microscopy (TEM) image also provides evidence of the formation of a large number of nanoparticles without agglomeration on the nanoribbon, as shown in Fig. 1f. A high-resolution TEM (HRTEM) image taken from one such nanoparticle displays a lattice spacing of 0.236 nm indexed to the (111) plane of Ag (Fig. 1g). All these observations confirm the successful fabrication of an Ag nanoparticle-decorated TiO₂ nanoribbon array.

The X-ray photoelectron spectroscopy (XPS) survey spectrum (Fig. 2a) also shows the presence of Ag, O, and Ti elements. The Ag 3d region spectrum (Fig. 2b) is divided into two peaks at 368.28 and 374.28 eV, which are ascribed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively.^{42,43} In the Ti 2p spectrum, two fitting peaks at 459.38 and 465.08 eV are assigned to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively (Fig. 2c).^{44,45} In addition, two fitting peaks in the O 1s spectrum are attributed to metal–oxygen bonds (M–O,

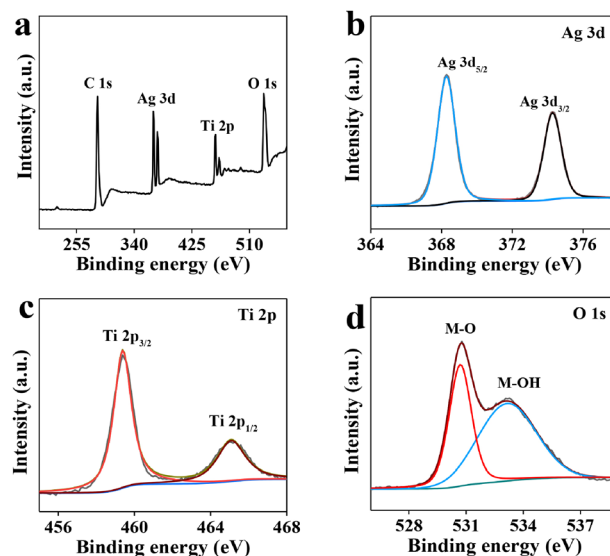


Fig. 2 (a) XPS survey spectrum, and high resolution XPS spectra in the (b) Ag 3d, (c) Ti 2p, and (d) O 1s regions of Ag@TiO₂.

530.78 eV) and adsorbed surface hydroxyl groups (M–OH, 533.18 eV) (Fig. 2d).^{42,45}

The electrochemical experiments of Ag@TiO₂/TP, Ag/TP, and TiO₂/TP toward the NO₂[−]RR were implemented in Ar-saturated NO₂[−]-free and NO₂[−]-containing 0.1 M NaOH electrolytes. UV-vis spectra and related calibration curves are depicted in Fig. S5 and S6.† Linear scanning voltammetry (LSV) of Ag@TiO₂/TP was firstly conducted. Obviously, a markedly enhanced current density (*j*) emerges upon the addition of NO₂[−] (Fig. 3a), verifying that Ag@TiO₂/TP enables efficient NO₂[−] reduction. In comparison, Ag/TP and TiO₂/TP display lower *j* with NO₂[−]-containing electrolytes (Fig. S7†), confirming that the electrocatalytic NO₂[−]RR activity of Ag@TiO₂/TP is superior to those of Ag/TP

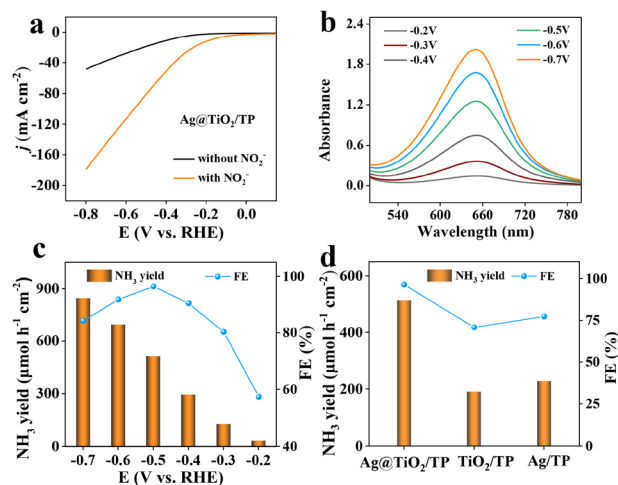


Fig. 3 (a) LSV curves of Ag@TiO₂/TP in 0.1 M NaOH with/without 0.1 M NO₂[−]. (b) UV-vis spectra of Ag@TiO₂/TP at various potentials. (c) NH₃ yields and FEs of Ag@TiO₂/TP at various potentials. (d) Comparison of NH₃ yields and FEs of Ag@TiO₂/TP, TiO₂/TP, and Ag/TP at −0.5 V.

and TiO_2/TP . Chronoamperometry (CA) measurements at given potentials (from -0.2 V to -0.7 V) were then executed to study the NH_3 -generation ability of $\text{Ag}@\text{TiO}_2/\text{TP}$ (Fig. S8†), where the peak intensity of the relevant UV-vis spectra strengthens with an increase in the given potential (Fig. 3b), manifesting that a more negative potential results in more NH_3 . Furthermore, we evaluated NH_3 FEs and yields of $\text{Ag}@\text{TiO}_2/\text{TP}$ in test windows (Fig. 3c). Noticeably, as the cathode potential negatively shifts, the NH_3 yields of $\text{Ag}@\text{TiO}_2/\text{TP}$ progressively increase, and eventually the largest value of $846.3 \mu\text{mol h}^{-1} \text{cm}^{-2}$ ($14\,387.1 \mu\text{g h}^{-1} \text{cm}^{-2}$) at -0.7 V is obtained. Furthermore, the maximum FE of NH_3 production is 96.4% at -0.5 V with an NH_3 yield of $514.3 \mu\text{mol h}^{-1} \text{cm}^{-2}$ ($8743.1 \mu\text{g h}^{-1} \text{cm}^{-2}$), confirming an excellent NO_2^- RR electrocatalyst. The NH_3 yields and FEs of $\text{Ag}@\text{TiO}_2/\text{TP}$ exceed those of most reported NO_2^- RR electrocatalysts (Table S1†). As shown in Fig. 3d, $\text{Ag}@\text{TiO}_2/\text{TP}$ exhibits a much better performance than Ag/TP (77.38%, $228.5 \mu\text{mol h}^{-1} \text{cm}^{-2}$) and TiO_2/TP (70.8%, $190.9 \mu\text{mol h}^{-1} \text{cm}^{-2}$).

The NO_2^- reduction process of $\text{Ag}@\text{TiO}_2/\text{TP}$ was further assessed by quantifying various by-products (N_2H_4 , H_2 , and N_2). As exhibited in Fig. S9,† no N_2H_4 signals were monitored as was proved by identical UV-vis absorption spectral peaks at different potentials. Meanwhile, traces of H_2 and N_2 were detected (Fig. 4a) with the maximal H_2 and N_2 yields being $2.82 \mu\text{mol h}^{-1} \text{cm}^{-2}$ and $1.85 \mu\text{mol h}^{-1} \text{cm}^{-2}$, with FEs of 4.9% and 1.42%, respectively, much lower than that of NH_3 at every

potential, verifying the superb selectivity of such $\text{Ag}@\text{TiO}_2/\text{TP}$ electrocatalysts for NH_3 synthesis. Furthermore, the partial current densities (j_{partial}) of $\text{Ag}@\text{TiO}_2/\text{TP}$ for NH_3 reach $-122.1 \text{ mA cm}^{-2}$ at -0.7 V, clearly higher than that of H_2 (-4.1 mA cm^{-2}) and N_2 (-1.04 mA cm^{-2}) (Fig. 4b), again proving great NO_2^- RR selectivity towards NH_3 electrosynthesis. Control experiments were then performed to determine whether the synthesized NH_3 just comes from the NO_2^- RR on $\text{Ag}@\text{TiO}_2/\text{TP}$. It is clearly seen that the amounts of NH_3 generated after 1 h of electrolysis in a blank solution ($0.29 \mu\text{g}$) and open circuit potential (OCP, $0.66 \mu\text{g}$) are extremely small (Fig. S10†), which excludes possible interference factors from the electrolytic solution and device.

Six alternative-cycle measurements were then carried out in NO_2^- -free/ NO_2^- -containing electrolytes at -0.5 V, and NH_3 only is generated in NO_2^- -containing electrolytes (Fig. 4c), demonstrating that NH_3 just originates from NO_2^- via the NO_2^- RR on $\text{Ag}@\text{TiO}_2/\text{TP}$. Additionally, stability is an extremely important parameter of the NO_2^- RR process for NH_3 synthesis. We thus implemented a 12 h electrolysis test, as displayed in Fig. 4d, and the $\text{Ag}@\text{TiO}_2/\text{TP}$ electrode maintained an initial j of nearly 100% with almost no fluctuation, confirming the excellent tolerance of our catalyst. Furthermore, we carried out 8 consecutive measurements on $\text{Ag}@\text{TiO}_2/\text{TP}$ at -0.5 V, and the volatility of NH_3 yields and FEs was negligible, again proving the durability of $\text{Ag}@\text{TiO}_2/\text{TP}$ (Fig. 4e and S11†), which is also in good accordance with the LSV curve (Fig. S12†), XRD pattern (Fig. S13†), and SEM images (Fig. S14†) of $\text{Ag}@\text{TiO}_2/\text{TP}$ after long-term electrolysis. These results suggest that $\text{Ag}@\text{TiO}_2/\text{TP}$ has excellent stability for the electrocatalytic reduction of NO_2^- to NH_3 .

In summary, a Ag nanoparticle-decorated TiO_2 nanoribbon array is proved to be an efficient and stable NO_2^- RR catalyst for NO_2^- -to- NH_3 conversion in an alkaline electrolyte, producing a remarkable NH_3 yield of $8743.1 \mu\text{g h}^{-1} \text{cm}^{-2}$ with a large FE of 96.4%. This study not only offers a highly selective electrocatalyst for ambient NH_3 synthesis via NO_2^- reduction, but also opens up a new avenue to construct a nanostructured Ag/ TiO_2 hybrid array for applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 J. Liang, Q. Liu, A. A. Alshehri and X. Sun, Recent advances in nanostructured heterogeneous catalysts for N-cycle electrocatalysis, *Nano Res. Energy*, 2022, **1**, e9120010.

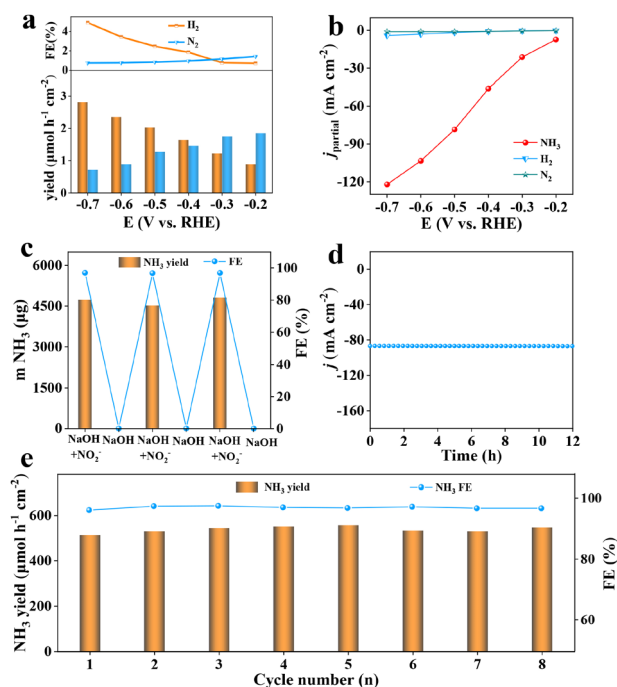


Fig. 4 (a) Yields and FEs of N_2 and H_2 of $\text{Ag}@\text{TiO}_2/\text{TP}$ at different potentials. (b) j_{partial} of NH_3 , N_2 , and H_2 of $\text{Ag}@\text{TiO}_2/\text{TP}$ at different potentials. (c) NH_3 yields and FEs of $\text{Ag}@\text{TiO}_2/\text{TP}$ during the alternating cycling tests. (d) Time-dependent current density curve during 12 h electrolysis of $\text{Ag}@\text{TiO}_2/\text{TP}$ at -0.5 V. (e) Recycling tests of $\text{Ag}@\text{TiO}_2/\text{TP}$ at -0.5 V.

- 2 J. Liang, W. Hu, B. Song, T. Mou, L. Zhang, Y. Luo, Q. Liu, A. A. Alshehri, M. S. Hamdy, L. Yang and X. Sun, Efficient nitric oxide electroreduction toward ambient ammonia synthesis catalyzed by a CoP nanoarray, *Inorg. Chem. Front.*, 2022, **9**, 1366–1372.
- 3 D. Qi, F. Lv, T. Wei, M. Jin, G. Meng, S. Zhang, Q. Liu, W. Liu, D. Ma, M. S. Hamdy, J. Luo and X. Liu, High-efficiency electrocatalytic NO reduction to NH_3 by nanoporous VN, *Nano Res. Energy*, 2022, **1**, e9120022.
- 4 I. Dybkjaer, in *Ammonia, catalysis and manufacture*, ed. A. Nielsen, Springer, Heidelberg, 1995, pp. 199–327.
- 5 Y. Ji, L. Li, W. Cheng, Y. Xiao, C. Li and X. Liu, A CeP nanoparticle-reduced graphene oxide hybrid: an efficient electrocatalyst for the NH_3 synthesis under ambient conditions, *Inorg. Chem. Front.*, 2021, **8**, 2103–2106.
- 6 L. Li, C. Tang, H. Jin, K. Davey and S.-Z. Qiao, Main-group elements boost electrochemical nitrogen fixation, *Chem*, 2021, **7**, 3232–3255.
- 7 N. Cao, Z. Chen, K. Zang, J. Xu, J. Zhong, J. Luo, X. Xu and G. Zheng, Doping strain induced Bi-Ti³⁺ pairs for efficient N_2 activation and electrocatalytic fixation, *Nat. Commun.*, 2019, **10**, 2877.
- 8 C. Guo, J. Ran, A. Vasileff and S. Qiao, Rational design of electrocatalysts and photo(electro)catalysts for nitrogen reduction to ammonia (NH_3) under ambient conditions, *Energy Environ. Sci.*, 2018, **11**, 45–56.
- 9 D. Chanda, R. Xing, T. Xu, Q. Liu, Y. Luo, S. Liu, R. A. Tufa, T. H. Dolla, T. Montini and X. Sun, Electrochemical nitrogen reduction: recent progress and prospects, *Chem. Commun.*, 2021, **57**, 7335–7349.
- 10 Y. Luo, Q. Li, Y. Tian, Y. Liu and K. Chu, Amorphization engineered VSe_{2-x} nanosheets with abundant Se-vacancies for enhanced N_2 electroreduction, *J. Mater. Chem. A*, 2022, **10**, 1742–1749.
- 11 Y. Li, Y. Liu, J. Wang, Y. Guo and K. Chu, Plasma-engineered NiO nanosheets with enriched oxygen vacancies for enhanced electrocatalytic nitrogen fixation, *Inorg. Chem. Front.*, 2020, **7**, 455–463.
- 12 S. Zhang, C. Zhao, Y. Liu, W. Li, J. Wang, G. Wang, Y. Zhang, H. Zhang and H. Zhao, Cu doping in CeO₂ to form multiple oxygen vacancies for dramatically enhanced ambient N_2 reduction performance, *Chem. Commun.*, 2019, **55**, 2952–2955.
- 13 C. Liu, S. Li, Z. Li, L. Zhang, H. Chen, D. Zhao, S. Sun, Y. Luo, A. A. Alshehri, M. S. Hamdy, Q. Liu and X. Sun, Ambient N_2 -to- NH_3 fixation over CeO₂ nanoparticles decorated three-dimensional carbon skeleton, *Sustainable Energy Fuels*, 2022, **6**, 3344–3348.
- 14 Q. Li, P. Shen, Y. Tian, X. Li and K. Chu, Metal-free BN quantum dots/graphitic C₃N₄ heterostructure for nitrogen reduction reaction, *J. Colloid Interface Sci.*, 2022, **606**, 204–212.
- 15 X. He, X. Li, X. Fan, J. Li, D. Zhao, L. Zhang, S. Sun, Y. Luo, D. Zheng, L. Xie, A. M. Asiri, Q. Liu and X. Sun, Ambient electroreduction of nitrite to ammonia over Ni nanoparticle supported on molasses-derived carbon sheets, *ACS Appl. Nano Mater.*, 2022, **5**, 14246–14250.
- 16 S. Li, J. Liang, P. Wei, Q. Liu, L. Xie, Y. Luo and X. Sun, ITO@TiO₂ nanoarray: an efficient and robust NO₂[−] reduction reaction electrocatalyst toward NH_3 production under ambient conditions, *eScience*, 2022, **2**, 382–388.
- 17 X. Zhu, X. Zeng, X. Chen, W. Wu and Y. Wang, Inhibitory effect of nitrate/nitrite on the microbial reductive dissolution of arsenic and iron from soils into pore water, *Ecotoxicology*, 2019, **28**, 528–538.
- 18 Q. Liu, Q. Liu, X. Lisi, L. Yue, T. Li, Y. Luo, N. Li, B. Tang, L. Yu and X. Sun, 3D FeOOH nanotube array: an efficient catalyst for ammonia electrosynthesis by nitrite reduction, *Chem. Commun.*, 2022, **58**, 5160–5163.
- 19 C. Wang, W. Zhou, Z. Sun, Y. Wang, B. Zhang and Y. Yu, Integrated selective nitrite reduction to ammonia with tetrahydroisoquinoline semi-dehydrogenation over a vacancy-rich Ni bifunctional electrode, *J. Mater. Chem. A*, 2021, **9**, 239–243.
- 20 L. Hu, D. Zhao, C. Liu, Y. Liang, D. Zheng, S. Sun, Q. Li, Q. Liu, Y. Luo, Y. Liao, L. Xie and X. Sun, Amorphous CoB nanoarray as a high-efficiency electrocatalyst for nitrite reduction to ammonia, *Inorg. Chem. Front.*, 2022, **9**, 6075–6079.
- 21 X. Zhang, Y. Wang, Y. Wang, Y. Guo, X. Xie, Y. Yu and B. Zhang, Recent advances in electrocatalytic nitrite reduction, *Chem. Commun.*, 2022, **58**, 2777–2787.
- 22 L. Ouyang, L. Yue, Q. Liu, Q. Liu, Z. Li, S. Sun, Y. Luo, A. A. Alshehri, M. S. Hamdy, Q. Kong and X. Sun, Cu nanoparticles decorated juncus-derived carbon for efficient electrocatalytic nitrite-to-ammonia conversion, *J. Colloid Interface Sci.*, 2022, **624**, 394–399.
- 23 J. Wang, T. Feng, J. Chen, V. Ramalingam, Z. Li, D. M. Kabtamu, J. He and X. Fang, Electrocatalytic nitrate/nitrite reduction to ammonia synthesis using metal nanocatalysts and bio-inspired metalloenzymes, *Nano Energy*, 2021, **86**, 106088.
- 24 L. Mattarozzi, S. Cattarina, N. Comisso, P. Guerriero, M. Musiani, L. Vázquez-Gómez and E. Verlatoa, Electrochemical reduction of nitrate and nitrite in alkaline media at CuNi alloy electrodes, *Electrochim. Acta*, 2013, **89**, 488–496.
- 25 R. Zhang, S. Zhang, Y. Guo, C. Li, J. Liu, Z. Huang, Y. Zhao, Y. Li and C. Zhi, A Zn–nitrite battery as an energy-output electrocatalytic system for high-efficiency ammonia synthesis using carbon-doped cobalt oxide nanotubes, *Energy Environ. Sci.*, 2022, **15**, 3024–3032.
- 26 S. E. Braley, J. Xie, Y. Losovyj and J. M. Smith, Graphite conjugation of a macrocyclic cobalt complex enhances nitrite electroreduction to ammonia, *J. Am. Chem. Soc.*, 2021, **143**, 7203–7208.
- 27 Z. Chen, A. Jaworski, J. Chen, T. M. Budnyak, I. Szweczyk, A. Rokicińska, R. Dronskowski, N. Hedin, P. Kuśtrowski and A. Slabon, Graphitic nitrogen in carbon catalysts is important for the reduction of nitrite as revealed by naturally abundant ¹⁵N NMR spectroscopy, *Dalton Trans.*, 2021, **50**, 6857–6866.

- 28 H. Li, S. Guo, K. Shin, M. S. Wong and G. Henkelman, Design of a Pd–Au nitrite reduction catalyst by identifying and optimizing active ensembles, *ACS Catal.*, 2019, **9**, 7957–7966.
- 29 H. Shin, S. Jung, S. Bae, W. Lee and H. Kim, Nitrite reduction mechanism on a Pd surface, *Environ. Sci. Technol.*, 2014, **48**, 12768–12774.
- 30 X. Huo, D. J. Van Hoomissen, J. Liu, S. Vyas and T. J. Strathmann, Hydrogenation of aqueous nitrate and nitrite with ruthenium catalysts, *Appl. Catal., B*, 2017, **211**, 188–198.
- 31 H. Li, C. Yan, H. Guo, K. Shin, S. M. Humphrey, C. J. Werth and G. Henkelman, Cu_xIr_{1-x} nanoalloy catalysts achieve near 100% selectivity for aqueous nitrite reduction to NH₃, *ACS Catal.*, 2020, **10**, 7915–7921.
- 32 M. C. Figueiredo, V. Climent and J. M. Feliu, Nitrite reduction on bismuth modified Pt (111) surfaces in different electrolytic media, *Electrocatalysis*, 2011, **2**, 255–262.
- 33 Q. Liu, G. Wen, D. Zhao, L. Xie, S. Sun, L. Zhang, Y. Luo, A. A. Alshehri, M. S. Hamdy, Q. Kong and X. Sun, Nitrite reduction over Ag nanoarray electrocatalyst for ammonia synthesis, *J. Colloid Interface Sci.*, 2022, **623**, 513–519.
- 34 S. Chang and X. Xu, Au nanocrystals decorated TiO₂ nanotubes for photocatalytic nitrogen fixation into ammonia, *Inorg. Chem. Front.*, 2020, **7**, 620–624.
- 35 W. Shi, A.-H. Park, S. Xu, P. J. Yoo and Y.-U. Kwon, Continuous and conformal thin TiO₂-coating on carbon support makes Pd nanoparticles highly efficient and durable electrocatalyst, *Appl. Catal., B*, 2021, **284**, 119715.
- 36 A. Shoaib, M. Ji, H. Qian, J. Liu, M. Xu and J. Zhang, Noble metal nanoclusters and their in situ calcination to nanocrystals: precise control of their size and interface with TiO₂ nanosheets and their versatile catalysis applications, *Nano Res.*, 2016, **9**, 1763–1774.
- 37 S. Zhang, W. Wang, Y. Gao, S. Deng, L. Ding, H. Zhuo, Z. Bao, W. Ji, C. Qiu and J. Wang, Pd–Co alloy supported on TiO₂ with oxygen vacancies for efficient N₂ and O₂ electrocatalytic reduction, *Appl. Surf. Sci.*, 2021, **567**, 150680.
- 38 L.-N. Chen, S.-H. Wang, P.-Y. Zhang, Z.-X. Chen, L. Xiao, H.-J. Yang, T. Sheng, W.-F. Lin, N. Tian, S.-G. Sun and Z.-Y. Zhou, Ru nanoparticles supported on partially reduced TiO₂ as highly efficient catalyst for hydrogen evolution, *Nano Energy*, 2021, **88**, 106211.
- 39 Z.-W. Wei, H.-J. Wang, C. Zhang, K. Xu, X.-L. Lu and T.-B. Lu, Reversed charge transfer and enhanced hydrogen spillover in platinum nanoclusters anchored on titanium oxide with rich oxygen vacancies boost hydrogen evolution reaction, *Angew. Chem., Int. Ed.*, 2021, **60**, 16622–16627.
- 40 D. Zhao, J. Liang, J. Li, L. Zhang, K. Dong, L. Yue, Y. Luo, Y. Ren, Q. Liu, M. S. Hamdy, Q. Kong, Q. Liu and X. Sun, A TiO_{2-x} nanobelt array with oxygen vacancies: an efficient electrocatalyst toward nitrite conversion to ammonia, *Chem. Commun.*, 2022, **58**, 3669–3672.
- 41 L. Ouyang, X. He, S. Sun, Y. Luo, D. Zheng, J. Chen, Y. Li, Y. Lin, Q. Liu, A. M. Asirif and X. Sun, Enhanced electrocatalytic nitrite reduction to ammonia over P-doped TiO₂ nanobelt array, *J. Mater. Chem. A*, 2022, **10**, 23494–23498.
- 42 Q. Qin, Y. Li, W. Bu, L. Meng, X. Chuai, Z. Zhou and C. Hu, Self-template-derived ZnCo₂O₄ porous microspheres decorated by Ag nanoparticles and their selective detection of formaldehyde, *Inorg. Chem. Front.*, 2021, **8**, 811–820.
- 43 Y. Fang, S. Zhang, Z.-P. Wu, D. Luan and X. W. Lou, A highly stable lithium metal anode enabled by Ag nanoparticle-embedded nitrogen-doped carbon macroporous fibers, *Sci. Adv.*, 2021, **7**, eabg3626.
- 44 Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong and C. Zhi, Pd doping-weakened intermediate adsorption to promote electrocatalytic nitrate reduction on TiO₂ nanoarrays for ammonia production and energy supply with zinc-nitrate batteries, *Energy Environ. Sci.*, 2021, **14**, 3938–3944.
- 45 X. Fan, C. Ma, D. Zhao, Z. Deng, L. Zhang, Y. Wang, Y. Luo, D. Zheng, T. Li, J. Zhang, S. Sun, Q. Liu and X. Sun, Unveiling selective nitrate reduction to ammonia with Co₃O₄ nanosheets/TiO₂ nanobelt heterostructure catalyst, *J. Colloid Interface Sci.*, 2023, **630**, 714–720.