Enabling the electrocatalytic fixation of N$_2$ to NH$_3$ by C-doped TiO$_2$ nanoparticles under ambient conditions$^{†}$

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The conventional Haber−Bosch process for industrial NH$_3$ production from N$_2$ and H$_2$ is highly energy-intensive with a large amount of CO$_2$ emissions and finding a more suitable method for NH$_3$ synthesis under mild conditions is a very attractive topic. The electrocatalytic N$_2$ reduction reaction (NRR) offers an environmentally benign and sustainable route. In this communication, we report that C-doped TiO$_2$ nanoparticles act as an efficient electrocatalyst for the NRR with excellent selectivity. In 0.1 M Na$_2$SO$_4$, it achieves an NH$_3$ yield of 16.22 $\mu$g h$^{-1}$ mg$_{cat}^{-1}$ and a faradaic efficiency of 1.84% at −0.7 V vs. the reversible hydrogen electrode. Furthermore, this catalyst also shows good stability during electrolysis and recycling tests.

NH$_3$ is an essential ingredient in the manufacture of fertilizers, medicaments, resins, dyes, explosives, etc.$^{1−4}$ In 2017, total worldwide NH$_3$ production exceeded 150 million tons, and the demand for NH$_3$ continues to grow.$^5$ Industrially, NH$_3$ is produced almost via the Haber−Bosch process.$^6$ In order to overcome the kinetic limitations of strong N≡N triple bonds, elevated temperature (350–550 °C) and high pressure (150–350 atm) are necessary throughout the whole process.$^7$ Moreover, it not only consumes a large amount of energy, but inevitably leads to significant CO$_2$ emission. So, it is imperative to develop an environmentally friendly process for the sustainable conversion of N$_2$ to NH$_3$.

Electrochemical NH$_3$ synthesis from N$_2$ and H$_2$O is a promising candidate for artificial N$_2$ fixation under ambient conditions due to its environment-friendly, convenient and low-cost characteristics.$^{10−15}$ Although electrochemical reduction is feasible for achieving the conversion of N$_2$ to NH$_3$, it requires electrocatalysts for the N$_2$ reduction reaction (NRR) to meet the challenge associated with N$_2$ activation. Noble-metal catalysts such as Ru,$^16$ Au,$^{17,18}$ Ag,$^{19}$ and Rh$^{20}$ were reported as NRR catalysts with attractive catalytic performances, but the scarcity of these catalysts limits their wide application. Recently, transition metal oxides (TMOs)$^{21−26}$ have attracted much attention as NRR electrocatalysts, as they are inexpensive and can be easily prepared on a large scale. Therefore, it is still highly desirable to develop TMOs for the NRR. TiO$_2$ is nontoxic with a high thermal stability,$^27$ but its low electronic conductivity hinders its electrocatalytic application.$^{28}$ It has been reported that carbon doping can enhance the electronic conductivity of TiO$_2$ and facilitate charge transfer from the bulk to the surface region,$^{29}$ offering us a possible catalyst for the NRR, which, however, has not been explored before.

Herein, we report that C-doped TiO$_2$ nanoparticles (C-TiO$_2$) are effective for electrochemical N$_2$ conversion to NH$_3$ with excellent selectivity under ambient conditions. In 0.1 M Na$_2$SO$_4$, the catalyst achieves an NH$_3$ yield of 16.22 $\mu$g h$^{-1}$ mg$_{cat}^{-1}$ and a faradaic efficiency (FE) of 1.84% at −0.7 V vs. the reversible hydrogen electrode (RHE). Remarkably, it also demonstrates a high electrochemical stability. Compared with pristine TiO$_2$ (NH$_3$ yield: 8.49 $\mu$g h$^{-1}$ mg$_{cat}^{-1}$; FE: 1.28%), C-TiO$_2$ has a superior NRR performance. This result suggests that the introduction of carbon can enhance the electrocatalytic activity of TiO$_2$.

C-TiO$_2$ nanoparticles were prepared by a facile calcination assisted solvothermal method (see the ESI† for preparation details). Fig. 1a presents the X-ray diffraction (XRD) patterns of C-TiO$_2$ and TiO$_2$. The diffraction peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, and 62.7° can be indexed to the (101), (004), (200), (105), (211), and (204) planes of anatase TiO$_2$ (JCPDS no. 21-1272), respectively, which is similar to the pattern of C-TiO$_2$. Thermal gravimetric analysis (Fig. S1†) demonstrated that the content of C was 2.97 wt%. Scanning electron microscopy (SEM) images (Fig. S2†) indicate that the crystallite size of C-TiO$_2$ is smaller than that of TiO$_2$. Fig. 1b shows a transmission electron microscopy (TEM) image which evidences the nanoparticle growth. The electronic supplementary information (ESI) available: Experimental section and supplementary figures. See DOI: 10.1039/c8na00300a

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nature of C-TiO₂. A high-resolution TEM (HRTEM) image (Fig. 1c) reveals a well-resolved lattice fringe with an interplanar distance of 0.35 nm, indexed to the (101) plane of C-TiO₂. The selected area electron diffraction (SAED) pattern of C-TiO₂ (Fig. 1d) exhibited four diffraction rings indexed to the (101), (004), (200) and (211) planes of the TiO₂ phase.

Fig. 2a shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of C-TiO₂, which confirms the presence of Ti, C, and O elements. Fig. 2b presents the Ti 2p spectra for the C-TiO₂ and TiO₂ samples. The binding energies (BEs) of Ti 2p₃/2 and Ti 2p₁/2 for TiO₂ are 458.38 and 464.07 eV, respectively. Compared to the TiO₂ sample, the Ti 2p peaks of C-TiO₂ show a positive shift of 0.3 eV, which could be attributed to lattice distortions. Fig. 2c reveals the O 1s spectra for C-TiO₂ which are in good agreement with those of pure TiO₂. The BEs at 529.92 and 531.33 eV in the O 1s region are ascribed to the Ti–O–Ti (lattice oxygen) and O–H bonds in C–TiO₂. For the C 1s XPS spectra (Fig. 2d), three peaks can be deconvoluted at around 284.76, 286.15, and 289.12 eV for C-TiO₂. The peak at 284.76 eV could be attributed to the surface adventitious carbon. The two peaks at 286.15 and 289.12 eV are characteristic of the oxygen bound species C–O and Ti–O–C, respectively. This result indicates that carbon atoms substitute for some of the lattice titanium atoms and form a Ti–O–C structure. Compared with C-TiO₂, only one C 1s XPS spectrum corresponding to C–C is observed for the TiO₂ sample, further confirming the existence of C in C-TiO₂. In addition, the ultraviolet-visible (UV-vis) absorption spectra and the corresponding Kubelka–Munk plots of C-TiO₂ and TiO₂ are displayed in Fig. S3.† The band gap energies of C-TiO₂ (2.79 eV) and TiO₂ (2.96 eV) were determined by the intercept of the plots of $(aνhν)^{1/2}$ versus photon energy ($hν$), indicating a narrower band gap after C doping. The enhancement of visible light absorption for C-TiO₂ and TiO₂ should be attributed to the carbon doping in the TiO₂ lattice, which would introduce a series of localized occupied states into the band gap of the TiO₂ lattice, leading to a strong visible light absorption. All of the above results strongly support the successful preparation of C-TiO₂ nanoparticles.

The electrocatalytic NRR performance of C-TiO₂ was tested using a typical two-compartment and three-electrode device as the reaction vessel. C-TiO₂ was deposited on carbon paper (C-TiO₂/CP with a C-TiO₂ loading of 0.10 mg) for the test. All of the potentials for the NRR were reported on the RHE scale. The produced NH₃ was detected by spectrophotometry with salicylic acid. The relevant calibration curves are shown in Fig. S4.† The chronoamperometry curves at the corresponding potentials in N₂-saturated 0.1 M Na₂SO₄ are displayed in Fig. 3a, which can directly express the relationship between current density and time during the whole test process. Fig. 3b presents the UV-vis absorption spectra of the electrolyte stained with indophenol indicator after 2 h electrolysis at a series of potentials, and the
values of absorbance at 660 nm were used to calculate the concentrations of the generated NH₃ at different applied potentials according to the calibration curve of NH₃. Combined with the collected data, the final results including the NH₃ yields and FEs under various potentials were calculated and are plotted in Fig. 3c. Both the NH₃ yields and FEs increase as the negative potential rises to –0.7 V, which is the optimum potential point when the NH₃ yield and FE are 16.22 μg h⁻¹ mg⁻¹ and 1.84%, respectively. After that, as the potential continually increases, both the NH₃ yields and FEs decrease significantly which is mainly caused by the competitive hydrogen evolution reaction. For comparison, the pure TiO₂ sample was tested under the same conditions and the corresponding results are presented in Fig. 3d. It is worth noting that the performance of C-TiO₂ is evidently better than that of pure TiO₂. The superior NRR performance of C-TiO₂ can be rationally attributed to the C-TiO₂ nanoparticles having more exposed active sites (Fig. S5†), enabling more effective utilization of them as electrocatalysts. The enhanced conductivity of C-TiO₂ also contributes to its higher catalytic activity. The charge transfer resistance related to the electrocatalytic kinetics can be determined from the diameter of the semicircles in the low frequency zone.¹⁸ Electrochemical impedance spectroscopy data (Fig. S6†) show that C-TiO₂/CP possesses a smaller radius of the semicircle compared to TiO₂/CP, suggesting that the C-TiO₂ sample has a lower charge transfer resistance³⁹ and thus faster NRR kinetics. Meanwhile, C-TiO₂ shows a higher performance than some of the previously reported NRR electrocatalysts.⁴⁰–⁴⁴ More detailed comparisons are listed in Table S1.†

To prove that NH₃ was generated via the N₂ reduction process of C-TiO₂, three sets of control experiments were carried out: (1) immersing the samples in Ar-saturated solution at –0.7 V for 2 h; (2) immersing the samples in N₂-saturated solution at an open circuit potential for 2 h; and (3) immersing the samples at –0.7 V with alternating 2 h cycles between N₂-saturated and Ar-saturated solutions, for a total of 12 h. As shown in Fig. 4a and Fig. S7,† a trace amount of NH₃ production was detected under Ar-saturated solution and an open circuit potential. Combined with Fig. S8,† this result indicates that only N₂ provides the nitrogen source to NH₃. Moreover, controlled trials were carried out to investigate the performance of bare CP. The relevant UV-vis absorption spectra are displayed in Fig. S9.† The results show the poor electrocatalytic activity of bare CP, indicating that C-TiO₂ is an active material for the NRR (Fig. 4b). In addition, stable performance is another important indicator for evaluating catalysts. Recycling tests were performed in N₂-saturated 0.1 M Na₂SO₄ 6 times and the results are shown in Fig. 4c. The NH₃ yield and FE results show no obvious fluctuation over the whole process, suggesting that C-TiO₂ possesses a stable NRR performance. Moreover, only a slight fluctuation of current density is observed at –0.7 V after 24 h electrolysis, further suggesting an excellent electrochemical stability.

Hydrazine (N₂H₄), as a possible by-product in the NRR test, was detected by the method of Watt and Chrisp.⁴⁵ The relevant calibration curves are displayed in Fig. S10.† The UV-vis absorption spectra of N₂H₄ after 2 h electrolysis in a N₂ atmosphere at a series of potentials are shown in Fig. S11.† The concentrations of the possible by-product N₂H₄ are determined according to the values of absorbance at 455 nm. The results demonstrated that no N₂H₄ was detected at all potentials, implying the excellent selectivity of C-TiO₂ as an NRR electrocatalyst.

In summary, C-TiO₂ nanoparticles have been proven as an effective non-noble-metal electrocatalyst for the NRR at moderate temperatures and atmospheric pressure. This electrocatalyst achieves an NH₃ yield of 16.22 μg h⁻¹ mg⁻¹ and a FE of 1.84% at −0.7 V vs. RHE in 0.1 M Na₂SO₄. It also exhibits excellent selectivity and satisfactory electrochemical stability during the process of electrochemical NH₃ synthesis under ambient conditions. This work not only offers us an attractive earth-abundant electrocatalyst for the NRR, but also opens up an exciting new avenue for the design and development of doped Ti-based catalysts⁴⁶–⁴⁷ with enhanced performances toward electrocatalytic N₂ and nitrite⁴⁸ reduction for applications.

Conflicts of interest

There are no conflicts to declare.

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