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Enabling the electrocatalytic fixation of N₂ to NH₃ by C-doped TiO₂ nanoparticles under ambient conditions†

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The conventional Haber–Bosch process for industrial NH₃ production from N₂ and H₂ is highly energy-intensive with a large amount of CO₂ emissions and finding a more suitable method for NH₃ synthesis under mild conditions is a very attractive topic. The electrocatalytic N₂ reduction reaction (NRR) offers us an environmentally benign and sustainable route. In this communication, we report that C-doped TiO₂ nanoparticles act as an efficient electrocatalyst for the NRR with excellent selectivity. In 0.1 M Na₂SO₄, it achieves an NH₃ yield of 16.22 μg 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.

NH₃ is an essential ingredient in the manufacture of fertilizers, medicaments, resins, dyes, explosives, *etc.*^{1–4} In 2017, total worldwide NH₃ production exceeded 150 million tons, and the demand for NH₃ continues to grow.⁵ Industrially, NH₃ 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.^{7–9} Moreover, it not only consumes a large amount of energy, but inevitably leads to significant CO₂ emission. So, it is imperative to develop an environmentally friendly process for the sustainable conversion of N₂ to NH₃.

Electrochemical NH₃ synthesis from N₂ and H₂O is a promising candidate for artificial N₂ 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 N₂ to NH₃, it requires

electrocatalysts for the N₂ reduction reaction (NRR) to meet the challenge associated with N₂ activation. Noble-metal catalysts such as Ru,¹⁶ Au,^{17,18} Ag,¹⁹ and Rh²⁰ 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. TiO₂ 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 TiO₂ 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 TiO₂ nanoparticles (C-TiO₂) are effective for electrochemical N₂ conversion to NH₃ with excellent selectivity under ambient conditions. In 0.1 M Na₂SO₄, the catalyst achieves an NH₃ yield of 16.22 μg 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 TiO₂ (NH₃ yield: 8.49 μg h⁻¹ mg_{cat.}⁻¹; FE: 1.28%), C-TiO₂ has a superior NRR performance. This result suggests that the introduction of carbon can enhance the electrocatalytic activity of TiO₂.

C-TiO₂ 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-TiO₂ and TiO₂. 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 TiO₂ (JCPDS no. 21-1272), respectively, which is similar to the pattern of C-TiO₂. 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-TiO₂ is smaller than that of TiO₂. Fig. 1b shows a transmission electron microscopy (TEM) image which evidences the nanoparticle

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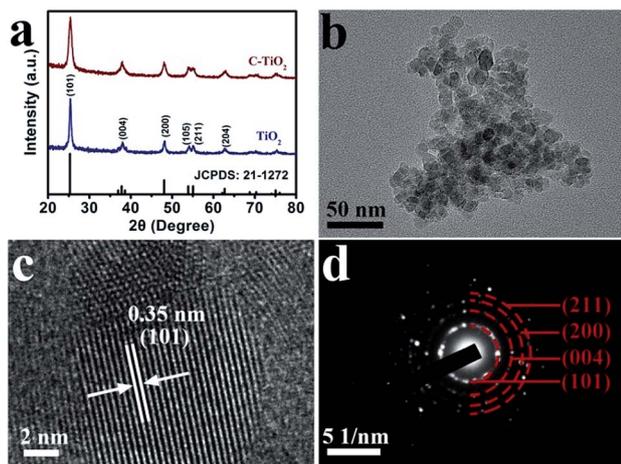


Fig. 1 (a) XRD patterns for C-TiO₂ and TiO₂. (b) TEM and (c) HRTEM images for the C-TiO₂ nanoparticles. (d) SAED pattern for C-TiO₂.

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 2p_{3/2} and Ti 2p_{1/2} for TiO₂ are 458.38 and 464.07 eV, respectively.³⁰ 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.³¹ 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.^{32,33} For the C 1s

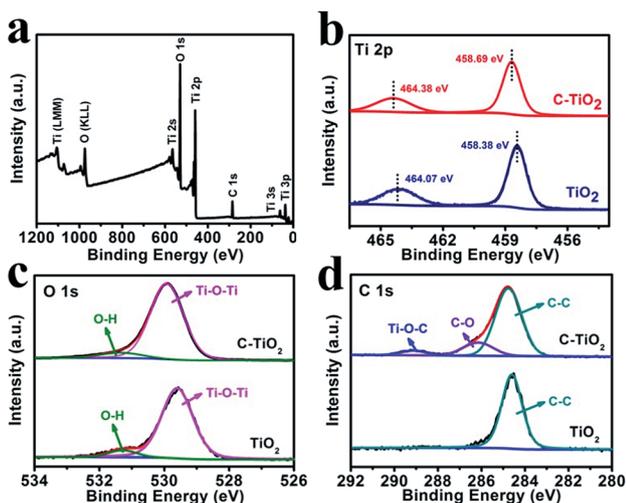


Fig. 2 (a) XPS survey spectrum for C-TiO₂. XPS spectra of C-TiO₂ and TiO₂ in the (b) Ti 2p, (c) O 1s and (d) C 1s regions.

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.³⁰ The two peaks at 286.15 and 289.12 eV are characteristic of the oxygen bound species C-O and Ti-O-C, respectively.³⁴ This result indicates that carbon atoms substitute for some of the lattice titanium atoms and form a Ti-O-C structure.³⁰ 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 $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$),³⁵ 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.³⁶ 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.³⁷ 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

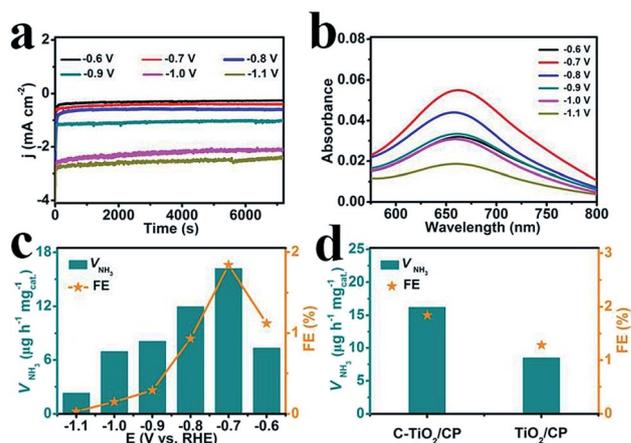


Fig. 3 (a) Chronoamperometry curves at the corresponding potentials in N₂-saturated 0.1 M Na₂SO₄. (b) UV-vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h electrolysis at a series of potentials. (c) The NH₃ yields and FEs of C-TiO₂ for the NRR at a series of potentials. (d) The amount of NH₃ with different electrodes at -0.7 V after 2 h electrolysis under ambient conditions.



values of absorbance at 660 nm were used to calculate the concentrations of the generated NH_3 at different applied potentials according to the calibration curve of NH_3 . Combined with the collected data, the final results including the NH_3 yields and FEs under various potentials were calculated and are plotted in Fig. 3c. Both the NH_3 yields and FEs increase as the negative potential rises to -0.7 V, which is the optimum potential point when the NH_3 yield and FE are $16.22 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ and 1.84%, respectively. After that, as the potential continually increases, both the NH_3 yields and FEs decrease significantly which is mainly caused by the competitive hydrogen evolution reaction. For comparison, the pure TiO_2 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 TiO_2 . 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.³⁸ Electrochemical impedance spectroscopy data (Fig. S6†) show that C-TiO₂/CP possesses a smaller radius of the semicircle compared to TiO_2 /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 NH_3 was generated *via* the N_2 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 N_2 -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 N_2 -

saturated and Ar-saturated solutions, for a total of 12 h. As shown in Fig. 4a and Fig. S7,† a trace amount of NH_3 production was detected under Ar-saturated solution and an open circuit potential. Combined with Fig. S8,† this result indicates that only N_2 provides the nitrogen source to NH_3 . 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 N_2 -saturated 0.1 M Na_2SO_4 6 times and the results are shown in Fig. 4c. The NH_3 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 (N_2H_4), 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 N_2H_4 after 2 h electrolysis in a N_2 atmosphere at a series of potentials are shown in Fig. S11.† The concentrations of the possible by-product N_2H_4 are determined according to the values of absorbance at 455 nm. The results demonstrated that no N_2H_4 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 NH_3 yield of $16.22 \mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ and a FE of 1.84% at -0.7 V vs. RHE in 0.1 M Na_2SO_4 . It also exhibits excellent selectivity and satisfactory electrochemical stability during the process of electrochemical NH_3 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 catalysts^{46,47} with enhanced performances toward electrocatalytic N_2 and nitrite⁴⁸ reduction for applications.

Conflicts of interest

There are no conflicts to declare.

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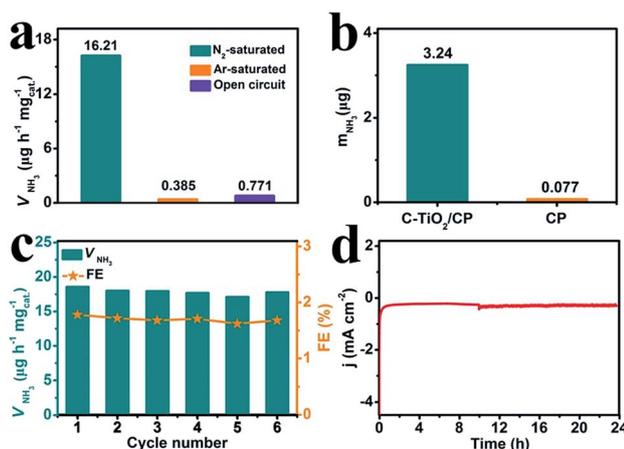


Fig. 4 (a) NH_3 yields for C-TiO₂ under different conditions. (b) The amount of NH_3 with different electrodes at -0.7 V after 2 h electrolysis under ambient conditions. (c) NH_3 yields and FEs at a potential of -0.7 V during 6 recycling tests. (d) Chronoamperometry curve at a potential of -0.7 V using a C-TiO₂/CP catalyst for 24 h.



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