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# 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 us 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<sub>3</sub> is an essential ingredient in the manufacture of fertilizers, medicaments, resins, dyes, explosives,  $etc.^{1-4}$  In 2017, total worldwide NH<sub>3</sub> production exceeded 150 million tons, and the demand for NH<sub>3</sub> continues to grow.<sup>5</sup> Industrially, NH<sub>3</sub> is produced almost via the Haber–Bosch process.<sup>6</sup> In order to overcome the kinetic limitations of strong N $\equiv$ N triple bonds, elevated temperature (350–550 °C) and high pressure (150–350 atm) are necessary throughout the whole process.<sup>7-9</sup> Moreover, it not only consumes a large amount of energy, but inevitably leads to significant CO<sub>2</sub> emission. So, it is imperative to develop an environmentally friendly process for the sustainable conversion of N<sub>2</sub> to NH<sub>3</sub>.

Electrochemical NH<sub>3</sub> synthesis from N<sub>2</sub> and H<sub>2</sub>O is a promising candidate for artificial N<sub>2</sub> fixation under ambient conditions due to its environment-friendly, convenient and low-cost characteristics. <sup>10–15</sup> Although electrochemical reduction is feasible for achieving the conversion of N<sub>2</sub> to NH<sub>3</sub>, it requires

Herein, we report that C-doped  $TiO_2$  nanoparticles (C-TiO<sub>2</sub>) 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  $-0.7 \, V \, \nu s$ . 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<sub>2</sub> 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 $^{\dagger}$  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 $^{\dagger}$ ) demonstrated that the content of C was 2.97 wt%. Scanning electron microscopy (SEM) images (Fig. S2 $^{\dagger}$ ) 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

electrocatalysts for the  $N_2$  reduction reaction (NRR) to meet the challenge associated with  $N_2$  activation. Noble-metal catalysts such as Ru, <sup>16</sup> Au, <sup>17,18</sup> Ag, <sup>19</sup> and Rh<sup>20</sup> were reported as NRR catalysts with attractive catalytic performances, but the scarcity of these catalysts limits their wide application. Recently, transition metal oxides (TMOs)<sup>21–26</sup> 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, <sup>27</sup> but its low electronic conductivity hinders its electrocatalytic application. <sup>28</sup> 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, <sup>29</sup> offering us a possible catalyst for the NRR, which, however, has not been explored before.

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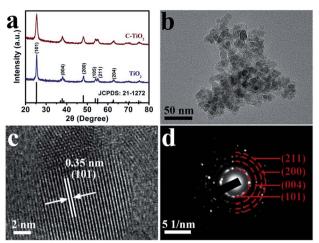


Fig. 1 (a) XRD patterns for  $C-TiO_2$  and  $TiO_2$ . (b) TEM and (c) HRTEM images for the  $C-TiO_2$  nanoparticles. (d) SAED pattern for  $C-TiO_2$ .

nature of C-TiO<sub>2</sub>. 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-TiO<sub>2</sub>. The selected area electron diffraction (SAED) pattern of C-TiO<sub>2</sub> (Fig. 1d) exhibited four diffraction rings indexed to the (101), (004), (200) and (211) planes of the TiO<sub>2</sub> phase.

Fig. 2a shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of C-TiO<sub>2</sub>, which confirms the presence of Ti, C, and O elements. Fig. 2b presents the Ti 2p spectra for the C-TiO<sub>2</sub> and TiO<sub>2</sub> samples. The binding energies (BEs) of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> for TiO<sub>2</sub> are 458.38 and 464.07 eV, respectively.<sup>30</sup> Compared to the TiO<sub>2</sub> sample, the Ti 2p peaks of C-TiO<sub>2</sub> show a positive shift of 0.3 eV, which could be attributed to lattice distortions.<sup>31</sup> Fig. 2c reveals the O 1s spectra for C-TiO<sub>2</sub> which are in good agreement with those of pure TiO<sub>2</sub>. 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-TiO<sub>2</sub>.<sup>32,33</sup> For the C 1s

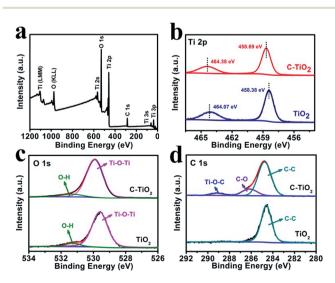


Fig. 2 (a) XPS survey spectrum for C-TiO $_2$ . XPS spectra of C-TiO $_2$  and TiO $_2$  in the (b) Ti 2p, (c) O 1s and (d) C 1s regions.

XPS spectra (Fig. 2d), three peaks can be deconvoluted at around 284.76, 286.15, and 289.12 eV for C-TiO<sub>2</sub>. 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-TiO<sub>2</sub> (2.79 eV) and TiO<sub>2</sub> (2.96 eV) were determined by the intercept of the plots of  $(\alpha h \nu)^{1/2}$ versus photon energy (hv),35 indicating a narrower band gap after C doping. The enhancement of visible light absorption for C-TiO<sub>2</sub> and TiO<sub>2</sub> 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-TiO $_2$  was tested using a typical two-compartment and three-electrode device as the reaction vessel. C-TiO $_2$  was deposited on carbon paper (C-TiO $_2$ /CP with a C-TiO $_2$  loading of 0.10 mg) for the test. All of the potentials for the NRR were reported on the RHE scale. The produced NH $_3$  was detected by spectrophotometry with salicylic acid. The relevant calibration curves are shown in Fig. S4.† The chronoamperometry curves at the corresponding potentials in N $_2$ -saturated 0.1 M Na $_2$ SO $_4$  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

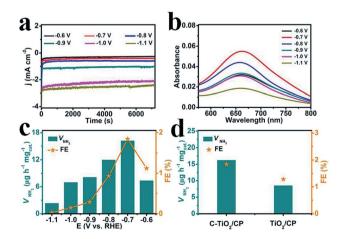


Fig. 3 (a) Chronoamperometry curves at the corresponding potentials in  $N_2$ -saturated 0.1 M  $N_2$ SO<sub>4</sub>. (b) UV-vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h electrolysis at a series of potentials. (c) The  $NH_3$  yields and FEs of C-TiO $_2$  for the NRR at a series of potentials. (d) The amount of  $NH_3$  with different electrodes at -0.7 V after 2 h electrolysis under ambient conditions.

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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 NH<sub>3</sub> yields and FEs under various potentials were calculated and are plotted in Fig. 3c. Both the NH<sub>3</sub> yields and FEs increase as the negative potential rises to -0.7 V, which is the optimum potential point when the NH<sub>3</sub> yield and FE are 16.22 µg h<sup>-1</sup> mg<sub>cat.</sub><sup>-1</sup> 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-TiO<sub>2</sub> is evidently better than that of pure TiO<sub>2</sub>. The superior NRR performance of C-TiO<sub>2</sub> 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-TiO<sub>2</sub> 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 TiO2/CP, suggesting that the C-TiO<sub>2</sub> sample has a lower charge transfer resistance<sup>39</sup> 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-TiO<sub>2</sub>, 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<sub>2</sub>-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<sub>2</sub>-

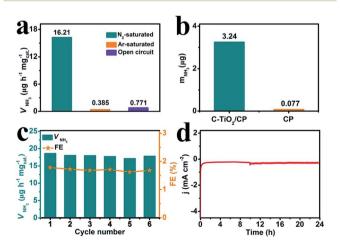


Fig. 4 (a) NH<sub>3</sub> yields for C-TiO<sub>2</sub> under different conditions. (b) The amount of NH₃ with different electrodes at −0.7 V after 2 h electrolysis under ambient conditions. (c) NH<sub>3</sub> yields and FEs at a potential of -0.7 V during 6 recycling tests. (d) Chronoamperometry curve at a potential of -0.7 V using a C-TiO<sub>2</sub>/CP catalyst for 24 h.

saturated and Ar-saturated solutions, for a total of 12 h. As shown in Fig. 4a and Fig. S7,† a trace amount of NH<sub>3</sub> 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 NH<sub>3</sub> 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<sub>2</sub>H<sub>4</sub>), 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<sup>-1</sup> mg<sub>cat.</sub> and a FE of 1.84% at -0.7 V vs. RHE in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. 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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