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## Enabling the electrocatalytic fixation of N<sub>2</sub> to NH<sub>3</sub> by C-doped TiO<sub>2</sub> nanoparticles under ambient conditions†

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The conventional Haber–Bosch process for industrial NH<sub>3</sub> production from N<sub>2</sub> and H<sub>2</sub> is highly energy-intensive with a large amount of CO<sub>2</sub> emissions and finding a more suitable method for NH<sub>3</sub> synthesis under mild conditions is a very attractive topic. The electrocatalytic N<sub>2</sub> reduction reaction (NRR) offers us an environmentally benign and sustainable route. In this communication, we report that C-doped TiO<sub>2</sub> nanoparticles act as an efficient electrocatalyst for the NRR with excellent selectivity. In 0.1 M Na<sub>2</sub>SO<sub>4</sub>, it achieves an NH<sub>3</sub> yield of 16.22 μg h<sup>-1</sup> mg<sub>cat.</sub><sup>-1</sup> 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.*<sup>1–4</sup> 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≡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

electrocatalysts for the N<sub>2</sub> reduction reaction (NRR) to meet the challenge associated with N<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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.

Herein, we report that C-doped TiO<sub>2</sub> nanoparticles (C-TiO<sub>2</sub>) are effective for electrochemical N<sub>2</sub> conversion to NH<sub>3</sub> with excellent selectivity under ambient conditions. In 0.1 M Na<sub>2</sub>SO<sub>4</sub>, the catalyst achieves an NH<sub>3</sub> yield of 16.22 μg h<sup>-1</sup> mg<sub>cat.</sub><sup>-1</sup> 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<sub>2</sub> (NH<sub>3</sub> yield: 8.49 μg h<sup>-1</sup> mg<sub>cat.</sub><sup>-1</sup>; 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<sub>2</sub>.

C-TiO<sub>2</sub> 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<sub>2</sub> and TiO<sub>2</sub>. 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<sub>2</sub> (JCPDS no. 21-1272), respectively, which is similar to the pattern of C-TiO<sub>2</sub>. 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<sub>2</sub> is smaller than that of TiO<sub>2</sub>. Fig. 1b shows a transmission electron microscopy (TEM) image which evidences the nanoparticle

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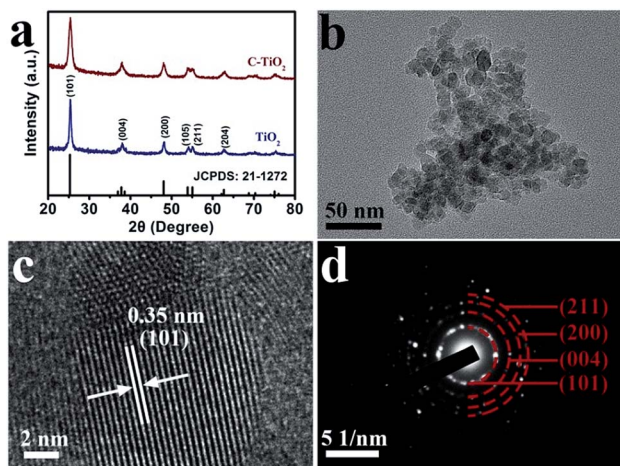


Fig. 1 (a) XRD patterns for C-TiO<sub>2</sub> and TiO<sub>2</sub>. (b) TEM and (c) HRTEM images for the C-TiO<sub>2</sub> nanoparticles. (d) SAED pattern for C-TiO<sub>2</sub>.

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

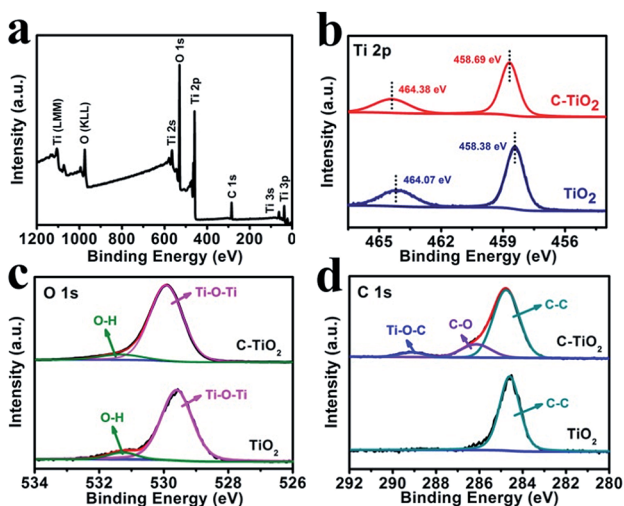


Fig. 2 (a) XPS survey spectrum for C-TiO<sub>2</sub>. XPS spectra of C-TiO<sub>2</sub> and TiO<sub>2</sub> in the (b) Ti 2p, (c) O 1s and (d) C 1s regions.

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.<sup>30</sup> The two peaks at 286.15 and 289.12 eV are characteristic of the oxygen bound species C-O and Ti-O-C, respectively.<sup>34</sup> This result indicates that carbon atoms substitute for some of the lattice titanium atoms and form a Ti-O-C structure.<sup>30</sup> Compared with C-TiO<sub>2</sub>, only one C 1s XPS spectrum corresponding to C-C is observed for the TiO<sub>2</sub> sample, further confirming the existence of C in C-TiO<sub>2</sub>. In addition, the ultraviolet-visible (UV-vis) absorption spectra and the corresponding Kubelka-Munk plots of C-TiO<sub>2</sub> and TiO<sub>2</sub> 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 ( $h\nu$ ),<sup>35</sup> 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 TiO<sub>2</sub> lattice, which would introduce a series of localized occupied states into the band gap of the TiO<sub>2</sub> lattice, leading to a strong visible light absorption.<sup>36</sup> All of the above results strongly support the successful preparation of C-TiO<sub>2</sub> nanoparticles.

The electrocatalytic NRR performance of C-TiO<sub>2</sub> was tested using a typical two-compartment and three-electrode device as the reaction vessel. C-TiO<sub>2</sub> was deposited on carbon paper (C-TiO<sub>2</sub>/CP with a C-TiO<sub>2</sub> loading of 0.10 mg) for the test. All of the potentials for the NRR were reported on the RHE scale. The produced NH<sub>3</sub> was detected by spectrophotometry with salicylic acid.<sup>37</sup> The relevant calibration curves are shown in Fig. S4.† The chronoamperometry curves at the corresponding potentials in N<sub>2</sub>-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> 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

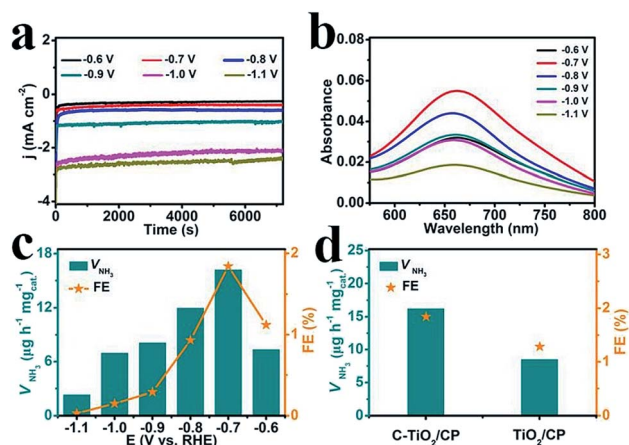


Fig. 3 (a) Chronoamperometry curves at the corresponding potentials in N<sub>2</sub>-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub>. (b) UV-vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h electrolysis at a series of potentials. (c) The NH<sub>3</sub> yields and FEs of C-TiO<sub>2</sub> for the NRR at a series of potentials. (d) The amount of NH<sub>3</sub> 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  $\text{NH}_3$  at different applied potentials according to the calibration curve of  $\text{NH}_3$ . Combined with the collected data, the final results including the  $\text{NH}_3$  yields and FEs under various potentials were calculated and are plotted in Fig. 3c. Both the  $\text{NH}_3$  yields and FEs increase as the negative potential rises to  $-0.7$  V, which is the optimum potential point when the  $\text{NH}_3$  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  $\text{NH}_3$  yields and FEs decrease significantly which is mainly caused by the competitive hydrogen evolution reaction. For comparison, the pure  $\text{TiO}_2$  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-TiO<sub>2</sub> is evidently better than that of pure  $\text{TiO}_2$ . The superior NRR performance of C-TiO<sub>2</sub> can be rationally attributed to the C-TiO<sub>2</sub> nanoparticles having more exposed active sites (Fig. S5<sup>†</sup>), 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.<sup>38</sup> Electrochemical impedance spectroscopy data (Fig. S6<sup>†</sup>) show that C-TiO<sub>2</sub>/CP possesses a smaller radius of the semicircle compared to  $\text{TiO}_2$ /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-TiO<sub>2</sub> shows a higher performance than some of the previously reported NRR electrocatalysts.<sup>40–44</sup> More detailed comparisons are listed in Table S1.<sup>†</sup>

To prove that  $\text{NH}_3$  was generated *via* the  $\text{N}_2$  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  $\text{N}_2$ -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  $\text{N}_2$ -

saturated and Ar-saturated solutions, for a total of 12 h. As shown in Fig. 4a and Fig. S7,<sup>†</sup> a trace amount of  $\text{NH}_3$  production was detected under Ar-saturated solution and an open circuit potential. Combined with Fig. S8,<sup>†</sup> this result indicates that only  $\text{N}_2$  provides the nitrogen source to  $\text{NH}_3$ . Moreover, controlled trials were carried out to investigate the performance of bare CP. The relevant UV-vis absorption spectra are displayed in Fig. S9.<sup>†</sup> The results show the poor electrocatalytic activity of bare CP, indicating that C-TiO<sub>2</sub> 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  $\text{N}_2$ -saturated 0.1 M  $\text{Na}_2\text{SO}_4$  6 times and the results are shown in Fig. 4c. The  $\text{NH}_3$  yield and FE results show no obvious fluctuation over the whole process, suggesting that C-TiO<sub>2</sub> 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 ( $\text{N}_2\text{H}_4$ ), as a possible by-product in the NRR test, was detected by the method of Watt and Chrisp.<sup>45</sup> The relevant calibration curves are displayed in Fig. S10.<sup>†</sup> The UV-vis absorption spectra of  $\text{N}_2\text{H}_4$  after 2 h electrolysis in a  $\text{N}_2$  atmosphere at a series of potentials are shown in Fig. S11.<sup>†</sup> The concentrations of the possible by-product  $\text{N}_2\text{H}_4$  are determined according to the values of absorbance at 455 nm. The results demonstrated that no  $\text{N}_2\text{H}_4$  was detected at all potentials, implying the excellent selectivity of C-TiO<sub>2</sub> as an NRR electrocatalyst.

In summary, C-TiO<sub>2</sub> nanoparticles have been proven as an effective non-noble-metal electrocatalyst for the NRR at moderate temperatures and atmospheric pressure. This electrocatalyst achieves an  $\text{NH}_3$  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  $\text{Na}_2\text{SO}_4$ . It also exhibits excellent selectivity and satisfactory electrochemical stability during the process of electrochemical  $\text{NH}_3$  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<sup>46,47</sup> with enhanced performances toward electrocatalytic  $\text{N}_2$  and nitrite<sup>48</sup> reduction for applications.

## Conflicts of interest

There are no conflicts to declare.

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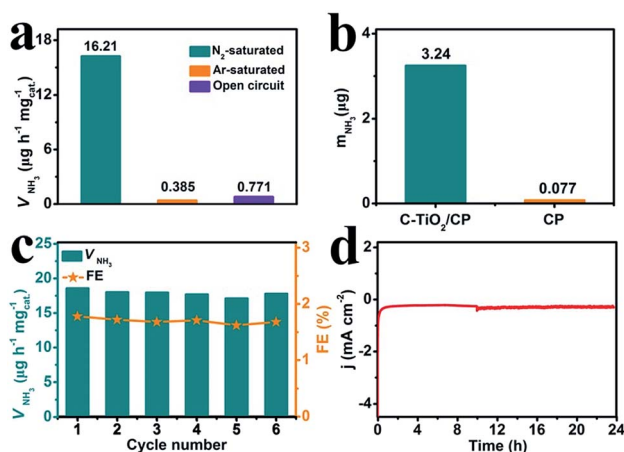


Fig. 4 (a)  $\text{NH}_3$  yields for C-TiO<sub>2</sub> under different conditions. (b) The amount of  $\text{NH}_3$  with different electrodes at  $-0.7$  V after 2 h electrolysis under ambient conditions. (c)  $\text{NH}_3$  yields and FEs at a potential of  $-0.7$  V during 6 recycling tests. (d) Chronoamperometry curve at a potential of  $-0.7$  V using a C-TiO<sub>2</sub>/CP catalyst for 24 h.





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