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# In Situ Hydrothermal Growth of TiO<sub>2</sub> Nanoparticles on a Conductive Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene Nanosheet: A Synergistically Active Ti-Based Nanohybrid Electrocatalyst for Enhanced N<sub>2</sub> Reduction to NH<sub>3</sub> at **Ambient Conditions**

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**S** Supporting Information

ABSTRACT: The traditional power-wasting Haber-Bosch process still dominates industrial NH<sub>3</sub> production. Recent years witnessed the rapid development of an electrochemical N<sub>2</sub> reduction reaction (NRR) because of its environmentally benign and sustainable feature. Here, we demonstrate the first utilization of a  $Ti_3C_2T_r$  MXene nanosheet as both the precursor and conductive substrate toward the in situ hydrothermal growth of TiO<sub>2</sub> nanoparticles. The marriage of  $TiO_2$  and  $Ti_3C_2T_x$  leads to a synergistically active Ti-based nanohybrid catalyst that can strengthen N<sub>2</sub> reduction electrocatalysis. When tested in 0.1 M HCl, such a  $TiO_2/Ti_3C_2T_x$  hybrid is superior in catalytic performance, capable of affording a  $NH_3$  yield of 26.32  $\mu$ g h<sup>-1</sup> mg<sup>-1</sup><sub>cat.</sub> with a 8.42% Faradaic efficiency (FE) at -0.60 V versus reversible hydrogen electrode (RHE), larger than those for  $TiO_2$  and  $Ti_3C_2T_3$ . Notably, this nanohybrid also shows good NH<sub>3</sub> selectivity with high electrochemical durability.

mmonia (NH<sub>3</sub>), a promising chemical, has been widely Aapplied in fertilizers, pharmaceuticals, dyes, explosives, resins, etc.,<sup>1,2</sup> because of its high hydrogen content and carbonfree character.<sup>3</sup> Although dinitrogen  $(N_2)$  is affluent in the atmosphere, its strong bonding energy and low polarizability make it a great challenge for artificial N<sub>2</sub> fixation. Currently, the practical NH<sub>3</sub> industry is mainly dependent on the century-old Haber-Bosch process, which, however, suffers from operation at high temperatures and pressures and emission of carbon dioxide  $(CO_2)$ .<sup>4</sup> As such, it is important to seek a route that is sustainable and can economically produce NH<sub>3</sub>.

Electrocatalysis prevails in the  $N_2$  reduction reaction (NRR) because it is convenient and cost-effective; however, it requires efficient electrocatalysts to activate the inert N2 molecule and break the firm  $N \equiv N$  bond.<sup>5</sup> Noble-metal-based catalysts work efficiently but suffer from high cost.<sup>6–10</sup> Encouragingly, a variety of earth-abundant transition-metal-based NRR catalysts have recently been proven to be efficient for  $N_2$  reduction electrocatalysis.<sup>11–24</sup> Recent studies from Sun's group show that nontoxic titanium dioxide  $(TiO_2)$  is able to electrochemically catalyze the NRR.<sup>25-27</sup> This oxide, however, suffers from

low electronic conductivity, which is not beneficial to electrochemical applications.  $Ti_3C_2T_x$  (T = F, OH) MXene with superior electronic conductivity<sup>28</sup> is also reported to be efficient as a 2D NRR electrocatalyst.<sup>29</sup> We thus expect that TiO<sub>2</sub> and  $Ti_3C_2T_x$  are two good candidates to be married as a synergistically active Ti-based nanohybrid catalyst for enhanced N<sub>2</sub> reduction electrocatalysis.

Here, we first report the use of a  $Ti_3C_2T_r$  MXene nanosheet as both the conductive substrate and Ti source toward the in situ hydrothermal growth of TiO<sub>2</sub> nanoparticles (see the Supporting Information for preparation details). An as-formed  $TiO_2/$  $Ti_3C_2T_r$  nanohybrid is superior in NRR activity to its two components under ambient conditions. The NH<sub>3</sub> yield and Faradaic efficiency (FE) of  $TiO_2/Ti_3C_2T_x$  at -0.6 V versus reversible hydrogen electrode (RHE) achieve 26.32  $\mu {
m g}~{
m h}^{-1}$ mg<sup>-1</sup><sub>cat.</sub> and 8.42% in 0.1 M HCl, respectively, which are much larger than those for TiO<sub>2</sub> (8.36  $\mu$ g h<sup>-1</sup> mg<sup>-1</sup><sub>cat.</sub> and 1.86%) and  $Ti_3C_2T_x$  (10.24  $\mu g h^{-1} mg^{-1}_{cat}$  and 3.14%). Besides, the selectivity and electrochemical stability are also well-behaved in NH<sub>3</sub> formation.

The X-ray diffraction (XRD) patterns for  $Ti_3C_2T_r$  and  $TiO_2/$  $Ti_3C_2T_r$  are displayed in Figure 1a. Two increased peaks at 25.28° and 48.04° in the XRD pattern for  $TiO_2/Ti_3C_2T_x$  arose from the (101) and (200) planes of the tetragonal anatase TiO<sub>2</sub> phase (JCPDS 21-1272),<sup>30</sup> and the intensity of  $Ti_3C_2T_x$ decreases. The scanning electron microscopy (SEM) image for  $Ti_3C_2T_x$  confirms that, with the HF etching,  $Ti_3C_2T_x$ MXenes show a particular exfoliated 2D morphology (Figure S1). After hydrothermal treatment, the resulting  $TiO_2/Ti_3C_2T_4$ still remains a 2D feature of  $Ti_3C_2T_x$  but gets rough (Figure 1b). Figure 1c presents the transmission electron microscopy (TEM) image of a single  $TiO_2/Ti_3C_2T_x$ . The high-resolution TEM (HRTEM) image (Figure 1d) indicating the formation of nanoparticles with an average diameter of about 40 nm reveals clear lattice fringes with an 0.35 nm interplanar distance that are attributed to the (101) plane of anatase  $TiO_2$  on a  $Ti_3C_2T_x$ nanosheet. Both the energy-dispersive X-ray spectroscopy (EDX) elemental mapping images (Figure 1e) and spectrum

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**Figure 1.** (a) XRD patterns for  $Ti_3C_2T_x$  and  $TiO_2/Ti_3C_2T_x$ . (b) SEM image of  $TiO_2/Ti_3C_2T_x$ . (c) TEM and (d) HRTEM images of  $TiO_2/Ti_3C_2T_x$ . (e) EDX elemental mapping images of  $TiO_2/Ti_3C_2T_x$ .

(Figure S2) for  $TiO_2/Ti_3C_2T_x$  suggest the coexistence of Ti, C, O, and F elements.

The X-ray photoelectron spectroscopy (XPS) survey spectra of  $Ti_3C_2T_x$  and  $TiO_2/Ti_3C_2T_x$  are shown in Figure 2a. Figure 2b



**Figure 2.** (a) XPS survey spectra for  $Ti_3C_2T_x$  and  $TiO_2/Ti_3C_2T_x$ . XPS spectra for  $Ti_3C_2T_x$  and  $TiO_2/Ti_3C_2T_x$  in the (b) Ti 2p, (c) C 1s, and (d) O 1s regions.

illustrates that, in the Ti 2p region, eight peaks of binding energies (BEs) at 454.95, 460.91, 455.78, 461.83, 456.61, 462.96, 458.27, and 464.19 eV are assignable to the  $2p_{3/2}$  and  $2p_{1/2}$  orbitals of Ti–C, Ti<sup>2+</sup>, Ti<sup>3+</sup>, and Ti<sup>4+</sup>, respectively.<sup>31,32</sup> Moreover, the increment of the Ti–O peak and the decrement of all of the other peaks in the XPS spectrum of TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>

occurred simultaneously, illuminating that  $Ti_3C_2T_x$  is consumed and transformed to  $TiO_2$  during hydrothermal treatment. In the C 1s region (Figure 2c), three peaks of BEs are at 281.4, 284.7, and 285.2 eV corresponding to Ti-C, C-C, and C-O bonds, respectively.<sup>32-34</sup> Also, the slight reduction of the Ti-C peak for  $TiO_2/Ti_3C_2T_x$  is assigned to consumption of the  $Ti_3C_2T_x$  phase. As for the O 1s region (Figure 2d), the peak of BE at 529.67 eV conspicuously increases for  $TiO_2/Ti_3C_2T_x$  because of the increment of the O-Ti species. Another peak of BE at 531.40 eV can be indexed to  $C-Ti-(OH)_{xy}$  and the last peak of BE at 533.43 eV is ascribed to the H-O-H bonds.<sup>32-34</sup> All of the observations verify that the  $TiO_2$  nanoparticles are successfully prepared on a  $Ti_3C_2T_x$  nanosheet.

The electrochemical process proceeded in a gastight twocompartment cell, and the produced NH<sub>3</sub> was obtained at the cathode with the aid of N<sub>2</sub>. A Nafion 211 membrane was also used for separation of the gastight two-compartment cell to restrict the diffusion of NH<sub>3</sub>. To assess the NRR ability, the working electrode was deposited with TiO<sub>2</sub>, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and TiO<sub>2</sub>/ Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> onto carbon paper (CP; the mass loadings of TiO<sub>2</sub>/CP, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/CP, and TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/CP are all the same at 0.1 mg). The RHE scale is used in all potentials unless specifically stated. We employ the indophenol blue method<sup>35</sup> to determine the amount of product NH<sub>3</sub> and the Watt and Chrisp method<sup>36</sup> to confirm whether the possible byproduct hydrazine (N<sub>2</sub>H<sub>4</sub>) is generated, and the results are presented in Figures S3 and S4.

Figure 3a exhibits 2 h time-dependent current density curves of  $TiO_2/Ti_3C_2T_x/CP$  ranging from -0.55 to -0.75 V in the



**Figure 3.** (a) Time-dependent current density curves at corresponding potentials in 0.1 M HCl. (b) UV–vis absorption spectra of the 0.1 M HCl stained with an indophenol indicator for 2 h. (c) NH<sub>3</sub> yields and FEs of  $TiO_2/Ti_3C_2T_x$  at each potential. (d) Amount of NH<sub>3</sub> with different electrodes at -0.6 V after 2 h of electrolysis under ambient conditions.

electrolyte. The spectrum that mixed the indophenol indicator with the electrolyte of each potential after 2 h is shown in Figure 3b. Figure 3c plots the calculated results in all five potentials. With the negative potential decreased to -0.60 V, both the NH<sub>3</sub> yields and FEs rose, illuminating that there is optimum potential when the NH<sub>3</sub> yield and FE are  $26.32 \,\mu g \, h^{-1} \, mg^{-1}_{cat}$  and 8.42%. Note that the performance achieved by our TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/CP compares favorably to the majority of the other NRR electrocatalysts under comparable reaction conditions like  $V_2O_3/C$  (12.3  $\mu g \, h^{-1} \, mg^{-1}_{cat}$  and 7.28%),<sup>22</sup> and a more

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detailed comparison is listed in Table 1. Accompanied by a continuous lowering of the potential, the NH<sub>3</sub> yield and FE

Table 1. Comparison of the Electrocatalytic N<sub>2</sub> Reduction Performances for  $TiO_2/Ti_3C_2T_x$  and Other Aqueous-Based Electrocatalysts at Ambient Conditions

catalyst	electrol	yte NH <sub>3</sub> yi	eld ( $\mu$ g h <sup>-1</sup> cm <sup>-2</sup> )	FE (%)
Au nanorod	s <sup>7</sup> 0.1 M KC	ЭН	1.6	3.88
$MoS_2/CC^{13}$	0.1 M Na	$_{2}SO_{4}$	4.94	1.17
Fe <sub>2</sub> O <sub>3</sub> /CNT	0.1 M KH	HCO3	0.22	0.15
AuHNCs <sup>39</sup>	0.5 M Li	ClO <sub>4</sub>	3.90	30.2
Mo nanofilm	n <sup>40</sup> 0.01 M H	I <sub>2</sub> SO <sub>4</sub>	1.89	0.72
catalyst	electro	NH <sub>3</sub> lyte	$mg^{-1}_{cat.})$ yield ( $\mu g h^{-1}$	FE (%)
Pd/C <sup>9</sup>	0.1 M PI	35	4.5	8.2
Rh <sup>10</sup>	0.1 M K	ОН	23.88	0.217
$Nb_2O_5^{12}$	0.1 M H	Cl	43.6	9.26
$TiO_2/rGO^{27}$	0.1 M N	a <sub>2</sub> SO <sub>4</sub>	15.13	3.3
$Ti_3C_2T_x^{29}$	0.1 M H	Cl	20.4	9.3
$Cr_2O_3^{41}$	0.1 M N	a <sub>2</sub> SO <sub>4</sub>	25.3	6.78
$MoO_3^{42}$	0.1 M H	Cl	29.43	1.9
$Au/CeO_x/RO$	GO <sup>43</sup> 0.1 M H	Cl	8.31	10.1
catalyst	electrolyte	$\rm NH_3$ yield (10 <sup>-</sup>	$^{-10}$ mo1 s <sup>-1</sup> cm <sup>-2</sup> )	FE (%)
MnO <sup>17</sup>	0.1 M Na <sub>2</sub> SO <sub>4</sub>	1	.11	8.02
$SnO_2^{18}$	0.1 M Na <sub>2</sub> SO <sub>4</sub>	1	.47	2.17
MoN <sup>44</sup>	0.1 M HCl	3	3.01	1.15
VN <sup>45</sup>	0.1 M HCl	(	).84	2.25

decrease because of the existence of the hydrogen evolution reaction (HER).<sup>37,38</sup> Furthermore, Figure S5 displays the H<sub>2</sub> yields and corresponding FEs of the HER. Moreover, no byproduct N<sub>2</sub>H<sub>4</sub> is detected (Figure S6), revealing the benign selectivity of TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/CP in generating NH<sub>3</sub>. In order to make a control experiment, NRR measurements of bare CP, TiO<sub>2</sub>/CP, and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/CP were carried out at -0.60 V. The amount of NH<sub>3</sub> derived from diverse electrodes at -0.6 V is shown on Figure 3d. Bare CP has necessitous NRR activity, while TiO<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> are active for NRR, producing NH<sub>3</sub> of 2.04 and 1.67 µg, respectively. In contrast, the TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> hybrid catalyst yields NH<sub>3</sub> of 5.26 µg, implying that both TiO<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> work synergistically to catalyze the N<sub>2</sub>-to-NH<sub>3</sub> conversion. Results suggested that Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> was efficient for NRR under neutral conditions (Figure S7).

In control experiments, we submerged samples in the electrolyte and then bubbled N<sub>2</sub> with an open circuit and Ar at -0.6 V for 2 h, respectively. The corresponding results are presented in Figure S8, and a negligible amount of NH<sub>3</sub> production can be detected under both of them. The masses of the catalyst loading were also explored, and we reached the conclusion that 0.1 mg of this catalyst was the optimal amount (Figure S9). To further certify that the  $N_2$  reduction process of  $TiO_2/Ti_3C_2T_x$  is the only approach to generating NH<sub>3</sub>, one more control experiment is alternate bubbling of N<sub>2</sub> or Ar every 2 h into electrolyte-submerged samples at -0.6 V for up to 12 h (Figure 4a). Futhermore, the curve of  $NH_3$  yield versus electrolysis time within 4 h is plotted in Figure 4b, which exhibits a good linearity and also reveals a stable NH<sub>3</sub> yield rate of  $TiO_2/Ti_3C_2T_x$ . To evaluate the practical application of electrocatalysts, stability is another important factor. The NH<sub>3</sub> yield rates and FEs manifest no obvious fluctuation over six sequential cycles (Figure 4c), indicating that  $TiO_2/Ti_3C_2T_x$  has a stable NRR ability.  $TiO_2/Ti_3C_2T_x$  still maintains strong



**Figure 4.** (a) NH<sub>3</sub> yields and FEs for TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with alternating 2 h cycles between N<sub>2</sub>- and Ar-saturated electrolytes. (b) Curve of NH<sub>3</sub> production versus time recorded at -0.6 V. (c) Cycling stability test of TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. (d) Time-dependent current density curve for the TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalyst at -0.6 V for 24 h.

electrochemical durability during the 24 h NRR process in Figure 4d, further indicating stability.

In summary, hydrothermal treatment of  $Ti_3C_2T_x$  has been proven as an effective strategy for the in situ development of  $TiO_2$  nanoparticles on its surface. The  $TiO_2/Ti_3C_2T_x$  nanohybrid behaves as a synergistically active NRR electrocatalyst with enhanced activity. In 0.1 M HCl, the NH<sub>3</sub> yield and FE of  $TiO_2/Ti_3C_2T_x$  at -0.6 V versus RHE achieve 26.32  $\mu$ g h<sup>-1</sup> mg<sup>-1</sup><sub>cat</sub>. and 8.42%, respectively. This work not only offers us a fascinating electrocatalyst for NH<sub>3</sub> synthesis but also could open new avenues toward the rational design of hybrid nanocatalysts using MXenes as the starting materials in high-performance artificial N<sub>2</sub> fixation.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00606.

Experimental section, SEM image, EDX spectrum, UV– vis absorption spectra and calibration curves,  $H_2$  yields and FEs, time-dependent current density curves, and  $NH_3$ yields and FEs (PDF)

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#### Notes

The authors declare no competing financial interest.

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