

Cite this: *Nanoscale Adv.*, 2024, 6, 481

# *In situ* growth of copper oxide on MXene by combustion method for electrochemical ammonia production from nitrate†

Sagar Ingavale,<sup>a</sup> Phiralang Marbaniang,<sup>b</sup> Manoj Palabathuni<sup>a</sup> and Nimai Mishra<sup>a,c</sup>

The elimination of the nitrogen pollutant nitrate ions through the electrochemical synthesis of ammonia is an important and environment friendly strategy. Electrochemical nitrate reduction requires highly efficient, selective, and stable catalysts to convert nitrate to ammonia. In this work, a composite of copper oxide and MXene was synthesized using a combustion technique. As reported, nitrate ions are effectively adsorbed by Cu<sub>x</sub>O (CuO & Cu<sub>2</sub>O) nanoparticles. Herein, MXene is an excellent assembly for anchoring Cu<sub>x</sub>O on its layered surface because it has a strong support structure. Powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses show the presence of oxidation states of metal ions and the formation of Cu<sub>x</sub>O nanofoam anchors on the surface of MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>). The optimized Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> composite exhibits an improved nitrate reduction reaction. The electrochemical studies of Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> show an interesting nitrate reduction reaction (NO<sub>3</sub>RR) with a current density of 162 mA cm<sup>-2</sup>. Further, Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> shows an electrocatalytic activity with an ammonia production of 41982 μg h<sup>-1</sup> m<sub>cat</sub><sup>-1</sup> and its faradaic efficiency is 48% at -0.7 V vs. RHE. Thus, such performance by Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> indicates a well-suitable candidate for nitrate ion conversion to ammonia.

Received 7th August 2023  
Accepted 23rd November 2023

DOI: 10.1039/d3na00609c

rsc.li/nanoscale-advances

## 1. Introduction

Ammonia is a basic nitrogen source for industrial applications widely used for manufacturing fertilizers, pharmaceuticals, textiles, and plastics.<sup>1,2</sup> Ammonia is mostly synthesized by the traditional Haber–Bosch process, requiring high temperature and pressure to convert nitrogen and hydrogen gases to ammonia in the presence of a iron-based catalyst.<sup>3</sup> Though the preparation of ammonia is carbon-free, it consumes >1% of the global energy supply (the energy obtained by burning huge amounts of fossil fuels resulting in hundreds of millions of tons of CO<sub>2</sub> release).<sup>4</sup> The electrochemical conversion of nitrogen to

ammonia at ambient conditions is the best approach as an alternative and environmentally friendly method.<sup>5</sup> However, the direct electrochemical reduction of N<sub>2</sub> to ammonia is hindered due to the high energy barrier necessary for breaking the inert N≡N bond, the poor contact between non-polar N<sub>2</sub> and active sites of catalysts, and the low solubility of N<sub>2</sub> in water.<sup>6–8</sup> In contrast, nitrates have special benefits as nitrogen sources for the electro-synthesis of NH<sub>3</sub>, as the polar N–O bond has a bond energy that is four times lower than the non-polar N≡N triple bond (204 kJ mol<sup>-1</sup>), allowing the N–O bond to be easily activated at lower energies.<sup>9</sup> Nitrate is widely distributed in the environment and builds up over time as a result of industrial

<sup>a</sup>Department of Chemistry, SRM University-AP, Andhra Pradesh, Neerukonda, Guntur (Dt), Andhra Pradesh, 522240, India

<sup>b</sup>Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

<sup>c</sup>Institute of Chemical Technology Mumbai, IOC Odisha Campus Bhubaneswar, Bhubaneswar, Odisha, 751013, India. E-mail: n.mishra@iocb.ictmumbai.edu.in

† Electronic supplementary information (ESI) available: The details of materials used for the synthesis of Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, physical characterization, electrochemical measurements and determination of the concentration of ammonia (including the faradaic efficiency and NH<sub>3</sub> yield) are given. XPS survey spectra for Cu<sub>x</sub>O and Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. LSVs curve for Cu<sub>x</sub>O-2/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and Cu<sub>x</sub>O-3/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> at 10 mV s<sup>-1</sup> with nitrate ions in 0.1 M K<sub>2</sub>SO<sub>4</sub> electrolyte. Comparative LSV pattern at 10 mV s<sup>-1</sup> and chronoamperometric curve of Cu<sub>x</sub>O, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with nitrate ions in 0.1 M K<sub>2</sub>SO<sub>4</sub> electrolyte. NH<sub>3</sub> yield and faradaic efficiency for NH<sub>3</sub> production of Cu<sub>x</sub>O, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts at -0.7 V vs. RHE.

UV-Vis spectra for indo-phenol determination of different known concentrations of NH<sub>4</sub><sup>+</sup> standards. Calibration curve obtained from linear fit. Photograph of standard NH<sub>4</sub><sup>+</sup> solution. UV-Vis spectra for Watt and Chrisp determination of different known concentrations of hydrazine standards. Calibration curve obtained from linear fit. Photograph of standard hydrazine solution. Electrochemical *i*-*t* experiments at various applied potentials of Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalyst, UV-Vis spectra for indo-phenol determination of ammonia and Watt and Chrisp determination of hydrazine in electrolytes obtained from electrocatalytic CA experiments at different applied potentials respectively. Photograph of ammonia and hydrazine solution. UV-Vis spectra for Watt and Chrisp determination of hydrazine in electrolytes obtained from electrocatalytic CA experiments at -0.7 V vs. RHE. Chronoamperometric analysis of Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalyst at -0.7 V vs. RHE in 0.5 M KNO<sub>3</sub> + 0.1 M K<sub>2</sub>SO<sub>4</sub> electrolyte. Comparative current vs. scan rate profile; (b) ECSA and roughness factor for Cu<sub>x</sub>O, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and Cu<sub>x</sub>O/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> electrocatalysts. See DOI: <https://doi.org/10.1039/d3na00609c>

and agricultural production activities, mostly having negative impacts on aquatic ecosystems and human health, including methemoglobinemia development, thyroid effects, and cancer.<sup>10–12</sup> Hence, the electroreduction of nitrate for  $\text{NH}_3$  generation not only complies with energy sustainability but also serves as a strategy to reduce pollution.

The adsorption of nitrate ions, deoxygenation of the N-species, hydrogenation of the N-species, and desorption of the reduced species are the steps involved during the conversion of  $\text{NO}_3^-$  ions to  $\text{NH}_3$  on the electrode surface by the electroreduction process.<sup>13</sup> A copper (Cu)-based catalyst was recently developed for nitrate reduction with >90% faradaic efficiency (FE).<sup>14</sup> Cu-based composites with different particle sizes and oxidation states were studied and observed to have multiple active sites for ammonia production from nitrate ions.<sup>15</sup> Generally, copper easily gets oxidized. The effect of the oxidation state of Cu on the activity and selectivity of  $\text{NO}_3^-$  electroreduction to  $\text{NH}_3$  is still unknown.<sup>15</sup> According to Zhao *et al.*, a  $\text{Cu}_2\text{O}$  film formed on Cu foam exhibits catalytic activity for  $\text{NO}_3\text{RR}$ . It is stated that the creation of a strong preferred (111) orientation and a nanopyramid terminated on the surface of the  $\text{Cu}_2\text{O}$  film account for the increased efficiency and selectivity for ammonia production.<sup>16</sup> Gong *et al.* reported that  $\text{Cu}_2\text{O}$ , subjected to plasma treatment, provides a hydroxyl group-rich surface and a high concentration of oxygen vacancies, resulting in greater charge density near the Cu sites and an upshifted d-orbital.<sup>17</sup> The treated  $\text{Cu}_2\text{O}$  enhances electron transport between the surface and chemical intermediates, making  $\text{NO}_3\text{RR}$  more favourable. Furthermore, to enhance electron transport, Zhang *et al.* generated electron-deficient Cu by dispersing Au particles on the surface of Cu (111), allowing electrons to move from Cu to Au atoms.<sup>1</sup> Similarly, CuPd nanocubes favour  $\text{NO}_3^-$  ion adsorption because the Cu sites favour bridge-bidentate  $\text{NO}_3^-$  adsorption and increase ammonia production due to Pauli repulsion between \*N and the d-orbital of Pd, which facilitates protonation of N-bonded species towards  $\text{NH}_3$ .<sup>18</sup> Cu nanowires supported by Ru (Ru-CuNW) also improve the adsorption of  $\text{NO}_3^-$  ions, allowing it to hydrogenate with N atoms better than CuNW.<sup>13</sup> However, it is not preferred to use expensive metals, and Wang's group claims that oxidised Cu metal, *i.e.*, CuO exhibits strong adsorption towards  $\text{NO}_3^-$  ion.<sup>19</sup> Additionally, MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ;  $\text{T}_x = \text{Cl}^-$ ,  $\text{OH}^-$  and  $\text{F}^-$ ) possesses excellent conductivity, hydrophilicity, large specific surface area, and exceptionally rich surface groups thanks to its distinctive structural characteristics. Because of its huge surface area and high concentration of surface groups, it serves as an excellent anchoring and dispersal medium for a wide variety of electrocatalysts.<sup>20,21</sup>

An interesting electrocatalytic activity towards  $\text{NO}_3\text{RR}$  can be expected from a composite of  $\text{Cu}_x\text{O}$  and MXene due to  $\text{Cu}_x\text{O}$  potency at adsorbing nitrate ions and MXene potency at supporting  $\text{Cu}_x\text{O}$  on its surface. Therefore, in this study, we developed an efficient electrocatalyst for  $\text{NH}_3$  generation by *in situ* growing  $\text{Cu}_x\text{O}$  on MXene *via* a combustion approach. The presence of metal ion oxidation states and the creation of a  $\text{Cu}_x\text{O}$  nanofoam anchor on the surface of  $\text{Ti}_3\text{C}_2\text{T}_x$  are evidenced by powdered-XRD, XPS, SEM, and TEM analyses. The

electrochemical reduction of nitrate by  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  was demonstrated in the presence and absence of nitrate ions. The electrochemical studies of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  show interesting  $\text{NO}_3\text{RR}$  with a current density of  $162 \text{ mA cm}^{-2}$ . Further,  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  shows an electrocatalytic activity with ammonia production of  $41\,982 \mu\text{g h}^{-1} \text{ m}_{\text{cat}}^{-1}$  and its faradaic efficiency is 48% at  $-0.7 \text{ V vs. RHE}$ . Thus, such performance by  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  indicates a well-suitable candidate for nitrate ion conversion to ammonia. In the future, similar composites with various synthesis techniques may be highlighted for  $\text{NO}_3^-$  reduction to ammonia.

## 2. Experimental section

### 2.1. Chemicals and materials

All chemicals purchased were of analytical grade (refer ESI†) and used without being tested for purity.

### 2.2. Synthesis of MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) from MAX phase ( $\text{Ti}_3\text{AlC}_2$ )

MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) was synthesized from the MAX phase ( $\text{Ti}_3\text{AlC}_2$ ) using the methods described in the recently published article. In brief, 500 mg of  $\text{Ti}_3\text{AlC}_2$  powder was sonicated and stirred at room temperature for 24 hours in HF (40 wt%) solution. The solution was centrifuged at 5000 rpm and was rinsed in deionized water until the pH was neutral, resulting in nano-sheets of  $\text{Ti}_3\text{C}_2\text{T}_x$ .

### 2.3. Preparation of copper oxide and MXene composite

Copper oxide and MXene composites were synthesized using a simple combustion process. 500 mg of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 20 mg of MXene were mixed together in 1 ml of ethylene glycol for 15 minutes until a homogeneous dispersed solution was achieved. A Petri dish was pre-heated for 15 minutes at  $250^\circ\text{C}$ . The solution is then poured into a Petri dish, where an immediate combustion reaction occurs with the effervescence to generate copper oxide and MXene composite. The product was collected and labelled as  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  after cooling to ambient temperature. Similarly, composites were optimized using the same technique and by altering the weight ratio of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  by 250 mg and 750 mg, respectively, and are indicated as  $\text{Cu}_x\text{O}-1/\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{Cu}_x\text{O}-2/\text{Ti}_3\text{C}_2\text{T}_x$ . Similar steps were taken to synthesise  $\text{Cu}_x\text{O}$ , but in the absence of  $\text{Ti}_3\text{C}_2\text{T}_x$ .

## 3. Results and discussion

MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) was synthesized from the MAX phase ( $\text{Ti}_3\text{AlC}_2$ ) by etching Al in a 40% HF solution. The as-prepared  $\text{Ti}_3\text{C}_2\text{T}_x$  was first homogeneously dispersed in ethylene glycol with  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , followed by a combustion technique in order to self-assemble  $\text{Cu}_x\text{O}$  on  $\text{Ti}_3\text{C}_2\text{T}_x$ . MXene is a well-known material in the current research due to its excellent properties especially electrical conductivity, which is the highest among all synthesized 2D materials, more than ten times the conductivity of reduced graphene oxide (rGO) films. It is also a good supporter because of the consistent negative charge at the surface of  $\text{Ti}_3\text{C}_2\text{T}_x$ , which attracts the positively charged ions



like  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  on its surface. Fig. 1 depicts a schematic illustration of the  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  synthesis.

The crystal structures of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composites were compared to those of  $\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{Cu}_x\text{O}$  using XRD analysis, as shown in Fig. 2(a). The presence of a peak at  $8.4^\circ$  suggests the production of exfoliated layers corresponding to the (002) plane.<sup>22</sup> The peak at  $8.4^\circ$  moved to a broad peak at  $11.6^\circ$  along with the appearance of other  $\text{Cu}_x\text{O}$  peaks after  $\text{Cu}_x\text{O}$  self-assembled on  $\text{Ti}_3\text{C}_2\text{T}_x$ , confirming the composite creation of  $\text{Cu}_x\text{O}$  and  $\text{Ti}_3\text{C}_2\text{T}_x$ .  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composites show diffraction peaks for  $\text{CuO}$  at  $32.5^\circ$ ,  $35.5^\circ$ ,  $38.6^\circ$ ,  $48.7^\circ$ ,  $53.6^\circ$ ,  $58.1^\circ$ ,  $61.5^\circ$ ,  $66.2^\circ$ ,  $68.0^\circ$  and  $73.7^\circ$ , corresponding to Miller indices (110), (002), (111), ( $-202$ ), (020), (202), ( $-113$ ), ( $-311$ ), (220), and (221), respectively (agreed with reference code JCPDS no. 01-089-5898). It is also observed that the peaks of  $\text{Cu}_2\text{O}$  at  $29.5^\circ$ ,  $36.4^\circ$ ,  $42.3^\circ$ , and  $61.5^\circ$  correspond to (110), (111), (200), and (220) planes, respectively (JCPDS no. 01-078-2076). Thus, from XRD analysis, it is observed that  $\text{Cu}_x\text{O}$  in the composite retains the same crystal structure as compared to the as-prepared  $\text{Cu}_x\text{O}$ . The comparative survey spectra of  $\text{Cu}_x\text{O}$  and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  are given in Fig. S1† to provide the relative abundance of elements. Both the catalysts display the presence of Cu 2p metal. XPS analysis was used to determine the chemical state of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$ , and Gaussian fitting was used to deconvolute the C 1s, Ti 2p, Cu 2p, and O 1s core levels. Fig. 2(b) depicts the deconvoluted C 1s core level as four peaks at 283.6 eV, 284.7 eV, 285.9 eV, and 288.7 eV, which correspond to the C–Ti, C=C, C–O, and C=O bonds, respectively.<sup>22</sup> The deconvoluted peaks of Cu(II) and Cu(I) states are shown in Fig. 2(c). Peaks at 934.9 eV and 954.1 eV are assigned to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , respectively, and the gap between these peaks is 19.2 eV, which coincides well with the creation of  $\text{CuO}$  on the composite.<sup>23</sup> The peaks at 933.6 eV and 953.6 eV are attributed to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , respectively, which represented  $\text{Cu}_2\text{O}$ . The main Cu  $2p_{3/2}$  peak at 934.9 eV is accompanied by two satellite peaks on the higher binding energy side at around 944.3 eV and 941.8 eV, indicating the presence of  $\text{CuO}$ .<sup>24,25</sup> Fig. 2(c) clearly depicts the main peak of Cu  $2p_{1/2}$  at 954.1 eV and its satellite peak at 962.5 eV, which also confirms the presence of  $\text{CuO}$ . Because of the presence of the partially filled  $d^9$  shell arrangement in the ground state, the  $\text{CuO}$  ( $\text{Cu(II)}$ ) spectrum shows prominent shake-up satellite features, whereas no shake-up satellite is seen for  $\text{Cu}_2\text{O}$  ( $\text{Cu(I)}$ ) due to its filled  $d^{10}$  arrangement in the ground state. Fig. 2(d) depicts the core level of Ti 2p deconvoluted into two peaks at 458.3 eV and 464.4 eV, which correspond to the Ti–C and Ti–O

bonds, respectively.<sup>22</sup> The appearance of Ti–O bonding could be due to oxidation during the combustion process, which converts unstable Ti–C bonds to Ti–O bonds. Furthermore, as seen in Fig. 2(e), the O 1s core level is deconvoluted into two peaks, 530.0 eV and 532.2 eV, which correspond to the metallic oxygen and O=C bonds, respectively.

Surface morphologies and microstructures of  $\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  samples were examined using SEM and TEM, respectively. Fig. 3(a) displays a typical  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheet layered structure with an accordion-like structure, and the separated layer of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets suggests successful aluminium etching from the MAX phase. The TEM image of  $\text{Ti}_3\text{C}_2\text{T}_x$  revealed exfoliated nanoflakes with distinct edges (Fig. 3(b)), and crystallinity was confirmed by the HRTEM image with interplanar spacing of 0.19 nm (Fig. 3(c)). The nanoflakes distinct edges of  $\text{Ti}_3\text{C}_2\text{T}_x$  may be required for *in situ*  $\text{Cu}_x\text{O}$  development on its surfaces, which may promote nitrate ion adsorption, charge transfer, and electron transport. Fig. 3(d) indicates that  $\text{Cu}_x\text{O}$  is evenly distributed on  $\text{Ti}_3\text{C}_2\text{T}_x$ , owing to the combustion process, which produces a smooth nanofoam of  $\text{Cu}_x\text{O}$  on the surface of MXene (a  $\text{Cu}_x\text{O}$  nanofoam structure is created as a result of nitrate ions escaping from the precursor during the combustion process). As shown in Fig. 3(f), the interplanar spacing values were 0.25 nm, which is in good agreement with the (111) plane of  $\text{Cu}_2\text{O}$ . Consequently, the formation of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  is evident from the morphologies.

## 4. Electrochemical nitrate reduction by $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$ catalysts

Electrochemical ammonia production is an environment friendly process because it converts nitrate waste into a valuable ammonia product. Consequently, electrochemical measurements were conducted on the  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite, and the construction of electrodes is described in ESI.† Initially, we employed 0.1 M  $\text{K}_2\text{SO}_4$  solution with and without nitrate ions (0.5 M  $\text{KNO}_3$ ) to conduct the electrochemical nitrate reduction to ammonia using the linear sweep voltammetry (LSV) technique. As shown in Fig. 4(a), the LSVs show that nitrate reduction occurs when compared to the competent hydrogen evolution reaction. The neutral electrolyte, 0.1 M  $\text{K}_2\text{SO}_4$ , aids in minimizing the HER reaction and improving nitrate reduction. The current density was determined to be around  $162 \text{ mA cm}^{-2}$  in the presence of nitrate solution and around  $43 \text{ mA cm}^{-2}$  in the absence of nitrate solution, demonstrating a successful electrochemical nitrate reduction reaction. After adding nitrate solution, the overpotential was reduced to approximately 310 mV to obtain a current density of  $20 \text{ mA cm}^{-2}$ . Along with the optimized composite, the nitrate reduction of other controlled catalysts was analysed using LSV and shown in Fig. S2.† The significance of synergetic effects between  $\text{Cu}_x\text{O}$  and  $\text{Ti}_3\text{C}_2\text{T}_x$  composite was assessed by comparing the  $\text{NO}_3\text{RR}$  catalytic activity of  $\text{Cu}_x\text{O}$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ , and the optimised  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite, as shown in Fig. S3.† At  $-0.7 \text{ V vs. RHE}$ , the current density for  $\text{Cu}_x\text{O}$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  is determined to be roughly  $45 \text{ mA cm}^{-2}$ ,  $37 \text{ mA cm}^{-2}$ , and  $162 \text{ mA}$

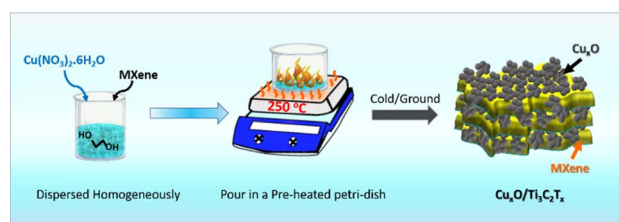


Fig. 1 Schematic illustration of the preparation of the  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite.





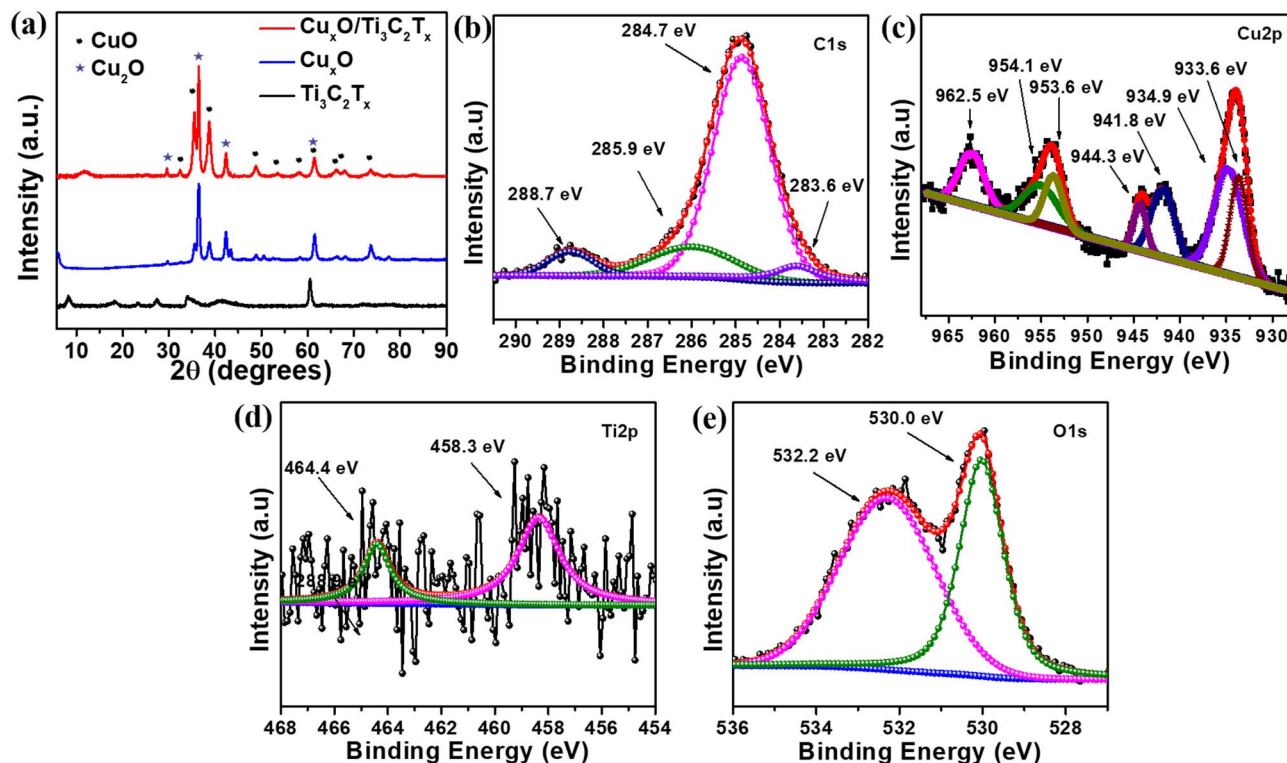


Fig. 2 (a) Comparative XRD patterns of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{Cu}_x\text{O}$  and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$ . Deconvoluted XPS spectrum for (b) C 1s, (c) Cu 2p, (d) Ti 2p and (e) O 1s of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite.

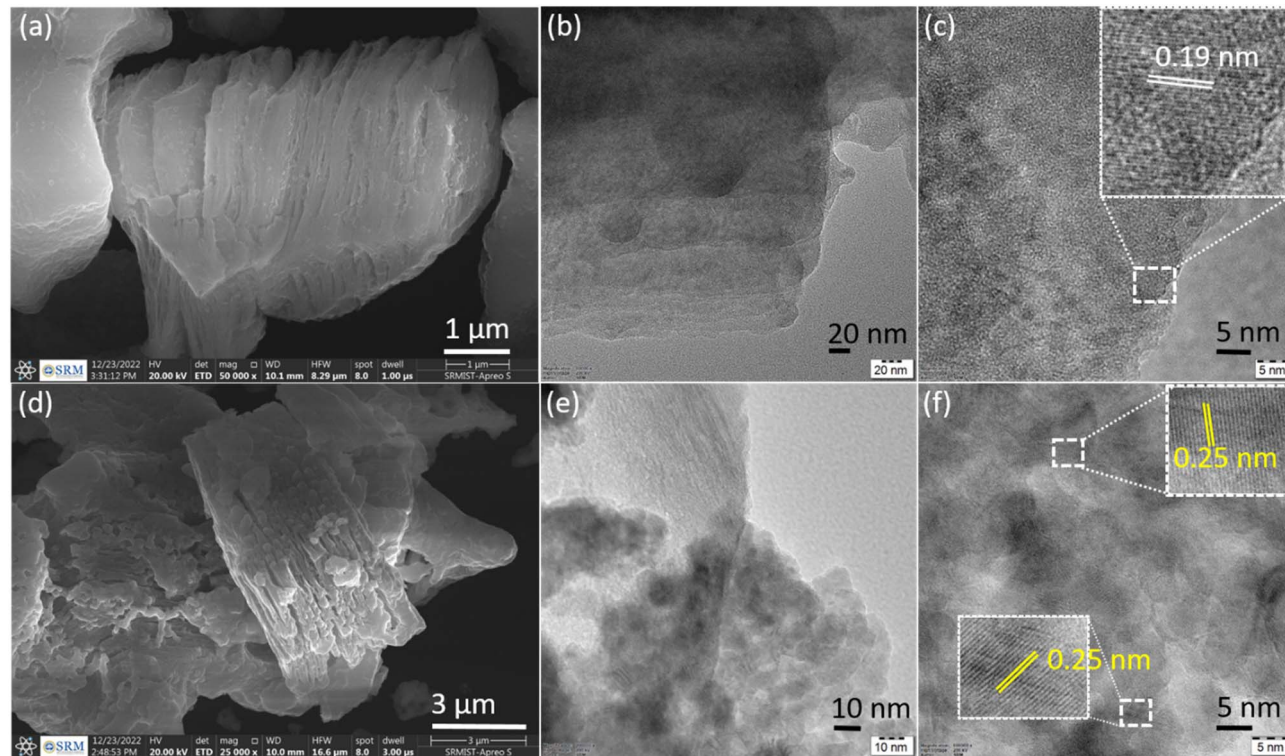


Fig. 3 SEM of (a)  $\text{Ti}_3\text{C}_2\text{T}_x$  and (d)  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite. TEM image of (b and c)  $\text{Ti}_3\text{C}_2\text{T}_x$  and (e and f)  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite.

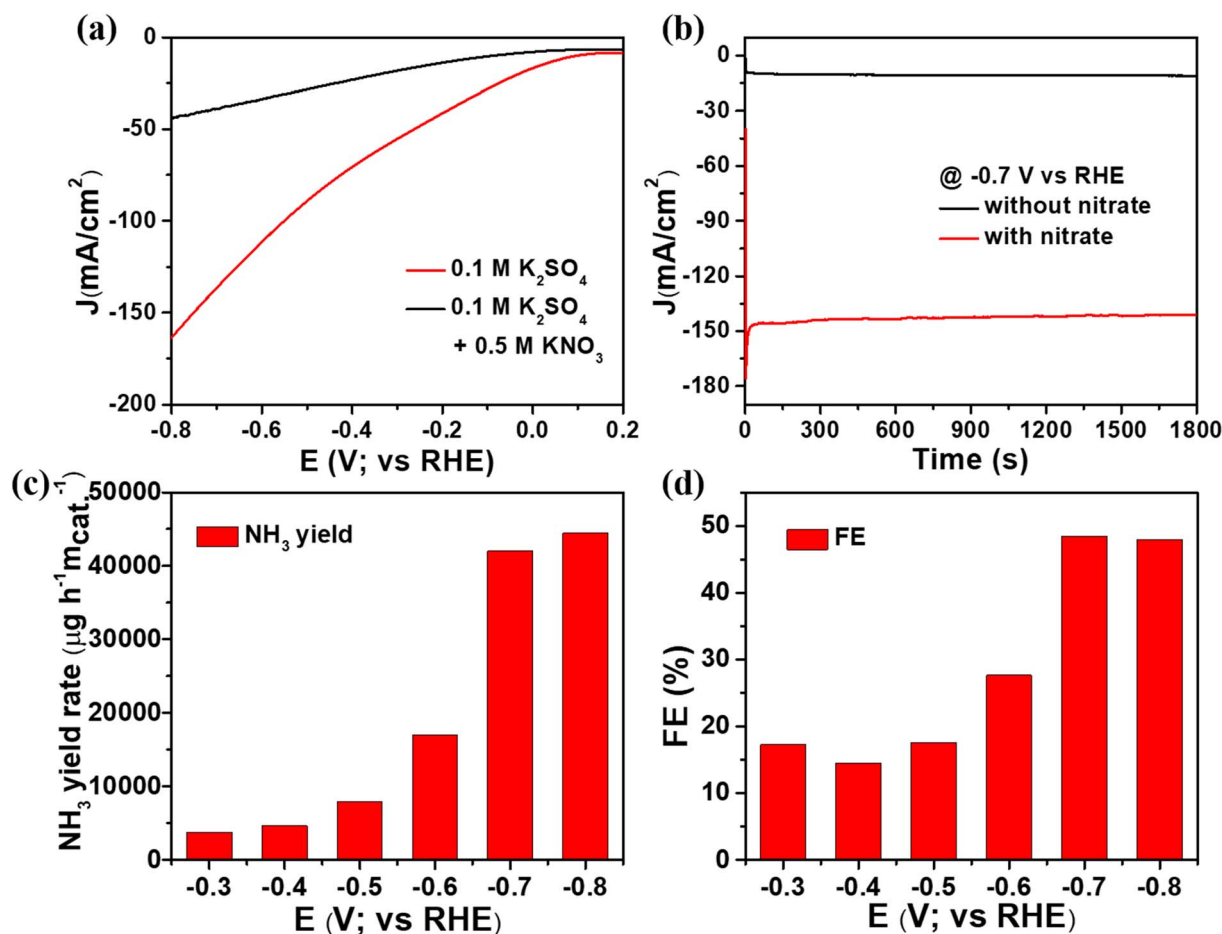


Fig. 4 (a) LSVs curve for  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  at  $10 \text{ mV s}^{-1}$  with and without nitrate ions in  $0.1 \text{ M K}_2\text{SO}_4$  electrolyte, (b) chronoamperometric measurements at  $-0.7 \text{ V vs. RHE}$  with and without nitrate ions (c)  $\text{NH}_3$  yield and (d) faradaic efficiency for  $\text{NH}_3$  production of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  catalyst at various potentials.

$\text{cm}^{-2}$ , respectively (Fig. S3(a)†). According to a chronoamperometry investigation, the current density for  $\text{Cu}_x\text{O}$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  was found to be approximately  $28 \text{ mA cm}^{-2}$ ,  $32 \text{ mA cm}^{-2}$ , and  $150 \text{ mA cm}^{-2}$ , respectively, at  $-0.7 \text{ V}$ , as shown in Fig. S3(b)†. It is obvious that the composite catalyst outperforms the  $\text{Cu}_x\text{O}$  or  $\text{Ti}_3\text{C}_2\text{T}_x$  catalysts by three times due to their synergy effect. This is because  $\text{Ti}_3\text{C}_2\text{T}_x$  solely (consisting of a negatively charged surface) is unfavourable to adsorb the electron-rich nitrate due to electrostatic repulsion. Whereas,  $\text{Cu}_x\text{O}$  is favourable but the poor conductivity properties decrease the electroreduction of nitrate ions. As a result, as compared to either  $\text{Cu}_x\text{O}$  or  $\text{Ti}_3\text{C}_2\text{T}_x$  alone, the combination of  $\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{Cu}_x\text{O}$  provides an excellent activity for the nitrate reduction reaction. Consequently, the  $\text{NH}_3$  yield and FE of the optimized composite were determined using the chronoamperometric method, which consisted of conducting experiments at varying potentials with time. The electrolyte was collected after 30 minutes of analysis, and indophenol blue was used to evaluate  $\text{NH}_3$  production and FE of catalysts (details of the indophenol blue method procedure are included in the ESI†). The confirmation of  $i-t$  measurements in  $0.1 \text{ M K}_2\text{SO}_4$

electrolyte at  $-0.7 \text{ V vs. RHE}$  to identify  $\text{NH}_3$  generated by nitrate ions is shown in Fig. 4(b).

The electrochemical process of converting nitrate ions to ammonia requires eight electron transitions. We initially standardized ammonia and hydrazine so that we would know the precise concentration of ammonia and hydrazine solution, as shown in Fig. S4 and S5,† which is necessary for our final goal of ammonia manufacturing. In order to calculate the amount of nitrate converted by the  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite, half-hour-long chronoamperometric measurements were recorded at several potentials while the solution included nitrate electrolyte. Fig. 4(c) and (d) displays the results of a spectroscopic investigation, which determined that the  $\text{NH}_3$  yield and FE at  $-0.7 \text{ V vs. RHE}$  were approximately  $41982 \mu\text{g h}^{-1} \text{ m}_{\text{cat}}^{-1}$  and 48%, respectively. We found that the  $\text{NH}_3$  production was slightly less at  $-0.7 \text{ V vs. RHE}$  as compared to  $-0.8 \text{ V vs. RHE}$ , but the FE was the highest at  $-0.7 \text{ V vs. RHE}$ ; thus, we consider it as the optimized potential. Additionally, the nitrate reduction reaction comparison study of  $\text{Cu}_x\text{O}$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite was examined at  $-0.7 \text{ V vs. RHE}$ . The spectroscopic examination results for the composites are displayed in Fig. S3(c) and (d)†. In the case of  $\text{Cu}_x\text{O}$ , the  $\text{NH}_3$  yield and FE at



$-0.7$  V vs. RHE were approximately  $3987 \mu\text{g h}^{-1} \text{m}_{\text{cat}}^{-1}$  and 22%, respectively. The bare  $\text{Ti}_3\text{C}_2\text{T}_x$  delivered  $\text{NH}_3$  yield and FE at  $-0.7$  V vs. RHE were approximately  $3175 \mu\text{g h}^{-1} \text{m}_{\text{cat}}^{-1}$  and 21%, respectively. Thus, the optimized  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite delivered better  $\text{NH}_3$  yield and the highest FE compared to  $\text{Cu}_x\text{O}$  and  $\text{Ti}_3\text{C}_2\text{T}_x$ . Generally, another product, hydrazine, which could be generated during nitrate reduction, was investigated. As shown in Fig. S6(c) and (e),† no UV-Vis absorption peak was found at 460 nm, and there was no colour associated with hydrazine. As a result, the selective conversion of nitrate to  $\text{NH}_3$  is confirmed.

The stability of catalysts can be evaluated by comparing the amount of  $\text{NH}_3$  produced to the number of cycles the catalyst has undergone. As a result, ten successive cycles of the  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  catalyst were performed for half an hour at  $-0.7$  V vs. RHE, as shown in Fig. 5(a). The detailed spectroscopic analysis of the  $\text{NH}_3$  production process is depicted in Fig. 5(b) and S5.† The  $\text{NH}_3$  production drops by as much as 60% after 10 cycles as the number of cycles increases. However, after 10 cycles, the average FE dropped by only 3% from the initial FE, as shown in Fig. 5(c) and (d). As shown in Fig. S7,† no UV-Vis absorption peak was found at 460 nm after 10 cycles as there was no colour associated with hydrazine. In addition,  $i$ - $t$

measurements were performed for 8 hours on the  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  catalyst at  $-0.7$  V vs. RHE to get insight into the catalyst's stability (see Fig. S8†). After 8 hours, the current density slightly changed, demonstrating the composite's remarkable stability.

In addition, the electrochemically active surface area (ECSA) was analysed for  $\text{Cu}_x\text{O}$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composites as shown in Fig. S9(a) and (b).† Commonly, double layer capacitance is correlated to the capacitive current and the scan rate by the following equation:<sup>26</sup>

$$I_{\text{dl}} = C_{\text{dl}} \times \text{scan rate}$$

where  $I_{\text{dl}}$  is the capacitive current and  $C_{\text{dl}}$  is the electrochemical double layer capacitance. Thus,  $C_{\text{dl}}$  ( $\text{F cm}^{-2}$ ) can be achieved from the slope of the curve of  $I_{\text{dl}}$  plotted as a function of scan rate. Afterwards, the ECSA of various catalysts was calculated using the following equation,<sup>27</sup>

$$\text{ECSA} = C_{\text{dl}}/C_s$$

where  $C_s$  is the specific capacitance of catalyst material ( $\text{F cm}^{-2}$ ). For the subsequently prepared transition metal-based composite, the specific capacitance value used for the

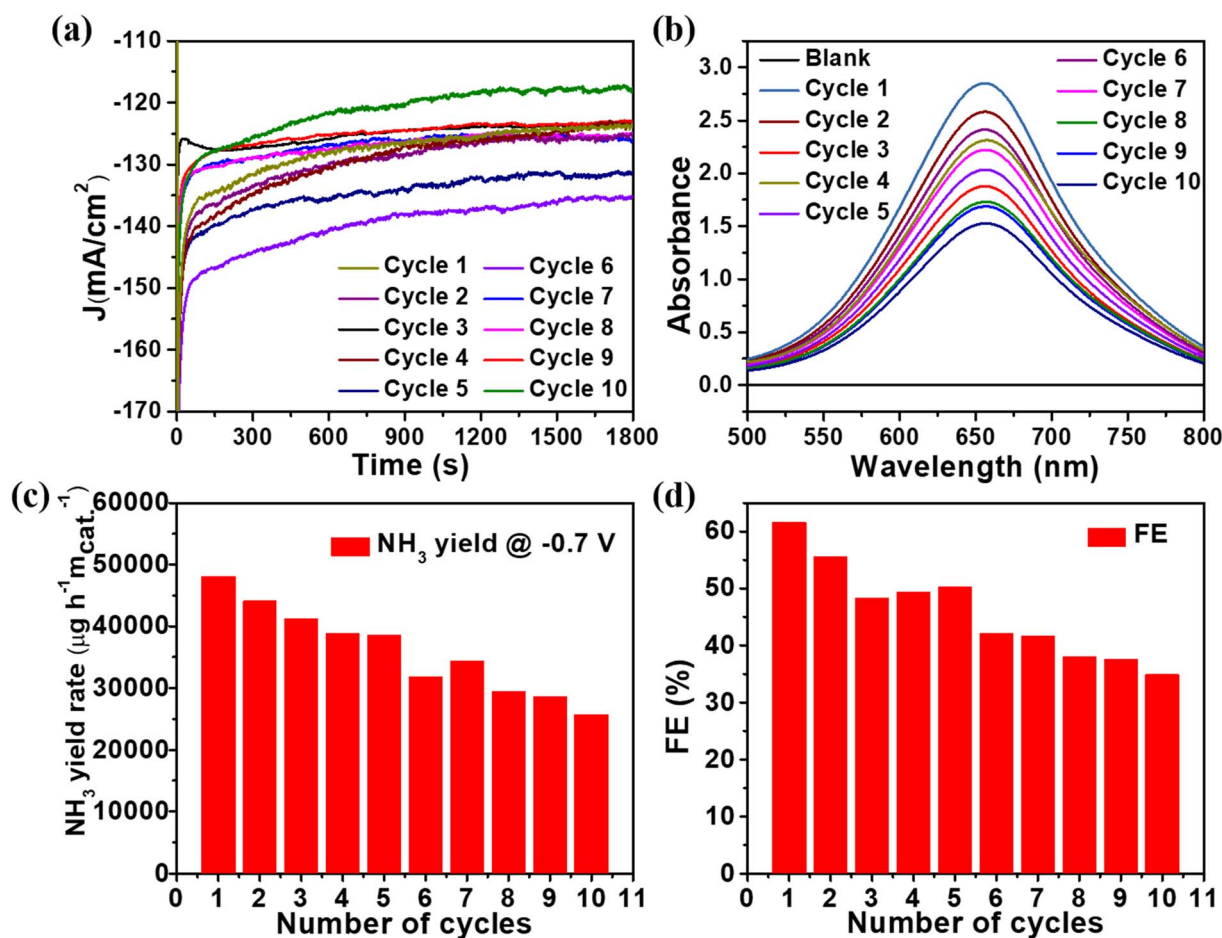


Fig. 5 (a) Chronoamperometric measurements at  $-0.7$  V vs. RHE (b) UV-Vis spectra (c)  $\text{NH}_3$  yield and (d) faradaic efficiency for  $\text{NH}_3$  production of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  catalyst.



calculation is  $0.040 \text{ mF cm}^{-2}$ . In the same way, the roughness factors (RF) of the electrodes for all electrocatalysts were determined by dividing the surface area of the electrode by the obtained ECSA value ( $\text{RF} = \text{ECSA}/0.0707 \text{ cm}^2$ ). In the present work, the CV analyses were carried out in the potential range from 0.1 to 0.3 V vs. RHE at different scan rates (20, 50, 70, and  $100 \text{ mV s}^{-1}$ ). The ECSA values found from the non-faradaic region for  $\text{Cu}_x\text{O}$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  were found to be  $0.0085 \text{ m}^2 \text{ g}^{-1}$ ,  $0.11875 \text{ m}^2 \text{ g}^{-1}$ , and  $0.0114 \text{ m}^2 \text{ g}^{-1}$ , respectively (Fig. S9(a)†), while the roughness factors were obtained as 0.068, 0.945, and 0.091, respectively, as shown in Fig. S9(b)†. Due to capacitive behavior, bare  $\text{Ti}_3\text{C}_2\text{T}_x$  displayed higher ECSA and roughness factor than other composites, it slightly helped to enhance the active surface area and electric conductivity for the composite when compared to  $\text{Cu}_x\text{O}$ . However, because  $\text{NO}_3\text{RR}$  is associated with ammonia production, it depends on faradaic efficiency and product yield, where  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  produces the most relative to the other two. Thus, it is clear that the catalytic performance of  $\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{Cu}_x\text{O}$  is inferior as compared to the optimized  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite. This is because  $\text{Ti}_3\text{C}_2\text{T}_x$  alone (consisting of a negatively charged surface) is unfavourable for adsorbing the electron-rich nitrate due to electrostatic repulsion. Whereas,  $\text{Cu}_x\text{O}$  is favourable but the poor conductivity properties decrease the electroreduction of nitrate ions. As a result, as compared to either  $\text{Cu}_x\text{O}$  or  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  alone, the combination of  $\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{Cu}_x\text{O}$  provides an excellent response for the nitrate reduction reaction.

## 5. Conclusion

In summary, we successfully constructed a  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composite *via* a combustion approach for electrochemical  $\text{NH}_3$  synthesis. The development of  $\text{Cu}_x\text{O}$  nanofoam on the  $\text{Ti}_3\text{C}_2\text{T}_x$  surface improved the catalytic conversion of  $\text{NO}_3^-$  to  $\text{NH}_3$ . This is because  $\text{Cu}_x\text{O}$  is an excellent candidate for adsorbing nitrate ions and reducing it to  $\text{NH}_3$ . The improved nitrate reduction reaction with  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  is considerably superior as compared to  $\text{Cu}_x\text{O}-2/\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{Cu}_x\text{O}-3/\text{Ti}_3\text{C}_2\text{T}_x$ . Electrochemical experiments of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  reveal an interesting  $\text{NO}_3\text{RR}$  with a current density of  $162 \text{ mA cm}^{-2}$ . Furthermore, the  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  exhibits electrocatalytic activity with ammonia production of  $41982 \mu\text{g h}^{-1} \text{ m}_{\text{cat}}^{-1}$  and a faradaic efficiency of 48% at  $-0.7 \text{ V}$  vs. RHE. As a result, the performance of  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  indicates that it is a good candidate for nitrate ion conversion to ammonia. Furthermore,  $\text{Cu}_x\text{O}/\text{Ti}_3\text{C}_2\text{T}_x$  composites may be a promising candidates in the future since they meet the parameters for an electrocatalyst for  $\text{NO}_3^-$  reduction to ammonia.

## Author contributions

Sagar Ingavale: conceptualization, investigation, methodology, writing – original draft, writing – review & editing. Phiralang Marbaniang: conceptualization, methodology, writing – original draft. Manoj Palabathuni: investigation, methodology. Nimai Mishra: funding acquisition, resources, supervision, writing – review & editing.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

We acknowledge the HRTEM facility at SRMIST set up with support from MNRE (project no. 31/03/2014-15/PVSR&D), Government of India. S. I. thanks SRM University, Andhra Pradesh, for financial support.

## References

- 1 Y. Zhang, X. Chen, W. Wang, L. Yin and J. C. Crittenden, *Appl. Catal., B*, 2022, **310**, 121346.
- 2 S. Ingavale, P. Marbaniang, M. Palabathuni, V. N. Kale and N. Mishra, *Nanoscale*, 2023, 11497–11505.
- 3 N. C. Kani, N. H. L. Nguyen, K. Markel, R. R. Bhawnani, B. Shindel, K. Sharma, S. Kim, V. P. Dravid, V. Berry, J. A. Gauthier and M. R. Singh, *Adv. Energy Mater.*, 2023, 2204236, early view.
- 4 F. Jiao and B. Xu, *Adv. Mater.*, 2019, **31**, 1805173.
- 5 J. Wang, S. Chen, Z. Li, G. Li and X. Liu, *ChemElectroChem*, 2020, **7**, 1067–1079.
- 6 Y. Huang, D. D. Babu, Z. Peng and Y. Wang, *Adv. Sci.*, 2020, **7**, 1902390.
- 7 L. Li, C. Tang, H. Jin, K. Davey and S. Z. Qiao, *Chem*, 2021, **7**, 3232–3255.
- 8 H. Shen, C. Choi, J. Masa, X. Li, J. Qiu, Y. Jung and Z. Sun, *Chem*, 2021, **7**, 1708–1754.
- 9 J. Li, Y. Zhang, C. Liu, L. Zheng, E. Petit, K. Qi, Y. Zhang, H. Wu, W. Wang, A. Tiberj, X. Wang, M. Chhowalla, L. Lajaunie, R. Yu and D. Voiry, *Adv. Funct. Mater.*, 2022, **32**, 2108316.
- 10 H. Chen, Y. Pang, Y. Wei, X. He, Y. Zhang and L. Xie, *Environ. Sci. Pollut. Res.*, 2022, **114**, 1–10.
- 11 M. Varsha, P. S. Kumar and B. S. Rath, *Chemosphere*, 2022, **287**, 132270.
- 12 T. R. Kumaraswamy, S. Javeed, M. Javaid and K. Naika, *Fresh Water Pollut. Dyn. Remediat.*, 2020, 1031, pp. 69–81.
- 13 F. Y. Chen, Z. Y. Wu, S. Gupta, D. J. Rivera, S. V. Lambeets, S. Pecaut, J. Y. T. Kim, P. Zhu, Y. Z. Finfrook, D. M. Meira, G. King, G. Gao, W. Xu, D. A. Cullen, H. Zhou, Y. Han, D. E. Perea, C. L. Muhich and H. Wang, *Nat. Nanotechnol.*, 2022, **17**, 759–767.
- 14 W. Jung and Y. J. Hwang, *Mater. Chem. Front.*, 2021, **5**, 6803–6823.
- 15 J. Yuan, Z. Xing, Y. Tang and C. Liu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 52469–52478.
- 16 Q. Zhao, Z. Tang, B. Chen, C. Zhu, H. Tang and G. Meng, *Chem. Commun.*, 2022, **58**, 3613–3616.
- 17 Z. Gong, W. Zhong, Z. He, Q. Liu, H. Chen, D. Zhou, N. Zhang, X. Kang and Y. Chen, *Appl. Catal., B*, 2022, **305**, 121021.
- 18 Q. Gao, H. S. Pillai, Y. Huang, S. Liu, Q. Mu, X. Han, Z. Yan, H. Zhou, Q. He, H. Xin and H. Zhu, *Nat. Commun.*, 2022, **13**, 1–12.



- 19 Y. Wang, W. Zhou, R. Jia, Y. Yu and B. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 5350–5354.
- 20 K. Li, Y. Lei, J. Liao and Y. Zhang, *Inorg. Chem. Front.*, 2021, **8**, 1747–1761.
- 21 L. X. Li, W. J. Sun, H. Y. Zhang, J. L. Wei, S. X. Wang, J. H. He, N. J. Li, Q. F. Xu, D. Y. Chen, H. Li and J. M. Lu, *J. Mater. Chem. A*, 2021, **9**, 21771–21778.
- 22 L. Wang, X. Yao, S. Yuan, Y. Gao, R. Zhang, X. Yu, S. T. Tu and S. Chen, *RSC Adv.*, 2023, **13**, 6264–6273.
- 23 X. Su, G. Feng, L. Yu, Q. Li, H. Zhang, W. Song and G. Hu, *J. Mater. Sci.: Mater. Electron.*, 2019, **30**, 3545–3551.
- 24 W. Lv, L. Li, Q. Meng and X. Zhang, *J. Mater. Sci.*, 2020, **55**, 2492–2502.
- 25 J. Yuan, J. J. Zhang, M. P. Yang, W. J. Meng, H. Wang and J. X. Lu, *Catalysts*, 2018, **8**, 171.
- 26 S. Ingavale, P. Marbaniang, B. Kakade and A. Swami, *Catal. Today*, 2021, **370**, 55–65.
- 27 S. B. Ingavale, I. Patil, H. Parse, D. C. Sesu, P. Marbaniang, N. Ramgir, B. Kakade and A. Swami, *Int. J. Hydrogen Energy*, 2019, **44**, 24922–24933.

