

#### A Journal of the Gesellschaft Deutscher Chemiker A DOCH International Edition Market Chemiker CDCh Chemiker Ch

# **Accepted Article**

**Title:** Built-in Electric Field Triggered Interfacial Accumulation Effect for Efficient Nitrate Removal at Ultra-Low Concentration and Electroreduction to Ammonia

Authors: Wu-Ji Sun, Hao-Qin Ji, Lan-Xin Li, Hao-Yu Zhang, Zhen-Kang Wang, Jing-Hui He, and Jian-Mei Lu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202109785

Link to VoR: https://doi.org/10.1002/anie.202109785

# WILEY-VCH

RESEARCH ARTICLE

### WILEY-VCH

IVIANUSCII

# Built-in Electric Field Triggered Interfacial Accumulation Effect for Efficient Nitrate Removal at Ultra-Low Concentration and Electroreduction to Ammonia

Wu-Ji Sun, Hao-Qin Ji, Lan-Xin Li, Hao-Yu Zhang, Zhen-Kang Wang, and Jing-Hui He,\* Jian-Mei Lu\*

[\*] W.-J. Sun, L.-X. Li, H.-Y. Zhang, Prof. J.-H. He, and Prof. J.-M. Lu

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou Nano Science and Technology, National United Engineering Laboratory of Functionalized Environmental Adsorption Materials, Soochow University, Suzhou 215123, P. R. (China) E-mail: jinghhe@suda.edu.cn; Juim@suda.edu.cn

Prof. H.-Q. J and Z.-K. Wang

College of energy, Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Soochow University, Suzhou 215006, China.

Abstract: Nitrate removal from water with low pollution concentration and its subsequent electroreduction to higher-value ammonia is becoming progressively essential. However, this process still suffers from low selectivity and activity due to slow mass transfer of nitrate and the induced limited reagent supply to reaction interface. Herein, we demonstrate that a built-in electric field in electrocatalyst can significantly accumulate higher concentration of NO3- ions near electrocatalyst surface region, thus facilitating mass transfer for efficient nitrate removal at ultra-low concentration and electroreduction reaction (NO3RR). A model electrocatalyst are created by stacking CuCl (111) and rutile TiO<sub>2</sub> (110) layers together, in which a built-in electric field induced from the electron transfer from TiO<sub>2</sub> to CuCl (CuCl\_BEF) is successfully formed as demonstrated by density functional theory (DFT) calculations and X-ray absorption near edge structure (XANES). Molecular dynamics simulation and finite element analysis suggest that this built-in electric field effectively triggers interfacial accumulation of NO3- ions around the electrocatalyst. The electric field also rises the energy of key reaction intermediate \*NO to lower down energy barrier of the rate determining step. A NH<sub>3</sub> product selectivity of 98.6%, a low NO<sub>2</sub><sup>-</sup> production of <0.6%, and mass-specific ammonia production rate of 64.4 h<sup>-1</sup> is achieved with this proof-of-concept system, which are all the best among studies reported at 100 mg L<sup>-1</sup> of nitrate concentration to date.

#### Introduction

In recent decades, low concentration nitrate in surface and ground water has been increasing as vast amounts of nitrous oxides emitted from fossil fuels combustion, as well as fertilizers and pesticides discharged from industry, agriculture and domestic sewage.<sup>[11]</sup> Nitrite causes acid rain, photochemical smog, methemoglobinemia and cancers. Therefore the Safe Drinking Water Act (SDWA) regulations proposed by United States Environmental Protection Agency stated that public water systems should not have nitrate above 10 milligrams per liter (mg L<sup>-1</sup>).<sup>[21]</sup> Therefore, Nitrate removal from water with low pollution concentration and its subsequent electroreduction to higher-value product is becoming progressively essential.

Ammonia, as one of major fertilizers, is mainly produced through Haber-Bosch process,<sup>[3]</sup> which consumes 1–2% of global energy and releases equal amount of CO<sub>2</sub>.<sup>[4]</sup> As an alternative, utilizing hydrogen from water to electrochemically reduce nitrate

as the nitrogen source receive much attention, as inspired by the low dissociation energy of the N=O bond (204 kJ mol<sup>-1</sup>) and unlimited solubility of polar NO<sub>3</sub><sup>-</sup> ions.<sup>[5]</sup> Therefore electrocatalytic nitrate reduction reaction (NO<sub>3</sub>RR) to ammonia<sup>[6]</sup> are of great interest to reduce energetic consumption as well as water treatment.

To date, various metals, metal oxides and two-dimensional materials displays great potential in electrocatalytic nitrate reduction reaction to ammonia (NO<sub>3</sub>RR).<sup>[7]</sup> However, the present NO<sub>3</sub>RR electrocatalysts still suffers from low ammonia production rate toward nitrate low than 100 mg L<sup>-1</sup> as the mass transfer was too weak due to small concentration gradient near the electrode region. On the other hand, electrocatalytic reduction of nitrate to ammonia involves an eight-electron, nine proton process.<sup>[7c, 8]</sup> Many intermediates such as highly toxic NO<sub>2</sub><sup>-</sup>, hydroxylamine and diamine may leak as byproducts if the adsorption from catalysts is weak.<sup>[8a, 9]</sup> Therefore, the simple metal/support architectures of catalysts will result in low selectivity, low Faradaic efficiency, and in consequence release of toxic byproducts, which are unsatisfactory in practical water treatment.

Herein, we demonstrate that a built-in electric field in electrocatalyst can significantly accumulate higher concentration of NO<sub>3</sub><sup>-</sup> ions near electrocatalyst surface region, thus facilitating mass transfer of reagent for efficient nitrate removal at ultra-low concentration and subsequent electroreduction to higher-value ammonia. A model electrocatalyst CuCl\_BEF was created by stacking CuCl (111) and rutile TiO<sub>2</sub> (110) layers together to form a built-in electric field induced by electrons transfer from TiO2 to CuCl, as demonstrated by density functional theory (DFT) calculations and X-ray absorption near edge structure (XANES). The built-in electric field effectively triggers interfacial accumulation of NO3- ions around the electrocatalyst and also rises the energy of key reaction intermediate \*NO proved by molecular dynamics simulation and finite element analysis. Nitrate was converted to NH3 with a selectivity of 98.6%, a low NO2<sup>-</sup> production of <0.6% and a mass-specific production rate of 64.4 h<sup>-1</sup>, which are both the best among all reported at 100 mg L<sup>-</sup> <sup>1</sup> of nitrate to date (Supporting Information Table S1).

### **RESEARCH ARTICLE**

#### **Results and Discussion**



*Figure 1.* Schematic illustration of CuCl\_BEF electrocatalyst with a build-in electric field. a) Illustration of the CuCl\_BEF in-situ formed on the MXene surface. b) Differential charge density of CuCl\_BEF. The side view of the charge transfer difference between CuCl and TiO<sub>2</sub> layers, where the yellow and cyan areas indicate the charge accumulation and depletion with iso-surfaces at 0.004 e/Å<sup>3</sup>. The green, red, blue, and cyan balls refer to Cl, O, Cu, and Ti atoms, respectively. c) and d) Molecular dynamics simulation of CuCl and CuCl\_BEF in KNO<sub>3</sub> (100 mg L<sup>-1</sup>) solution. Scale bar, 0.5 nm. e) Distribution of NO<sub>3</sub><sup>-</sup> along the *z*-axis electrode distance based on molecular dynamics simulation. f) and g) Finite element analysis of ions distribution difference near CuCl and CuCl\_BEF in KNO<sub>3</sub> solution.

To create a built-in electric field in electrocatalysts, we stacked CuCl and TiO<sub>2</sub> with different work functions as a model catalyst (Figure 1a). Stacking any two dissimilar materials (at least one is semiconductor), charge will cross their interface to produce a built-in electric field until their Fermi levels align. Density functional calculations were first employed to survey crystal lattice match and electron transfer between the CuCl and rutile TiO2. The CuCl is of zincblende-like structure, and its (111) plane considerably corresponded with (110) surfaces of rutile TiO<sub>2</sub> because of the substantial chemical bond formation between O and Cu (Figure 1b). The theoretically calculated differential charge distribution show that 0.57 electrons per super unit cell transfer from the TiO<sub>2</sub> layer, producing a space charge density of approximately 0.5 e<sup>-</sup>/nm<sup>3</sup> to create a CuCl-based catalyst with a built-in electric field (noted as CuCl\_BEF). Our theoretical prediction was consistent with earlier ultraviolet photoelectrons high-resolution spectroscopy and electron energy-loss spectroscopy of the CuCl on rutile TiO<sub>2</sub>(110) in ultra-highvacuum,<sup>[10]</sup> where Cu–O bond is formed and the work functions difference between these two materials,  $\Delta \Phi$ , was approximately 0.8 eV. On the condition of the built-in electric potential  $\Delta U$  (= $\Delta \Phi/e$ , *e* is the electron charge) was mainly confined to the nearest stacking CuCl and TiO<sub>2</sub> layers with a thickness of *d* =1 nm, the built-in electric field strength was roughly estimated to be 8×10<sup>8</sup> V m<sup>-1</sup> using *E*= $\Delta U/d$ , very strong compared to normal p-n junctions with space charge layers generally of several nanometer in thickness.

Compared to a pure CuCl catalyst without this built-in electric field, CuCl\_BEF attracts higher concentration of K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions at the side of interface from the electrolyte, as demonstrated by molecular dynamics simulation (Figures 1c, d). We placed CuCl\_BEF and CuCl in NO<sub>3</sub><sup>-</sup> electrolyte (100 mg L<sup>-1</sup>). After 10 ns, the maximum concentration of NO<sub>3</sub><sup>-</sup> in the diffusion layer as 1–2 nm away from the side of CuCl\_BEF reaches 12.3 ions/nm<sup>3</sup>, which is higher than that of on pure CuCl surface (6.3/nm<sup>3</sup> Figure 1e).

### **RESEARCH ARTICLE**



*Figure 2.* a) and b) DFT calculations of reaction pathways for  $NO_3^-$  reduction to  $NH_3$  on the surface of CuCl\_BEF and pure CuCl. The key intermediates are marked in pink shadow. c) Schematic illustration of in-situ differential electrochemical mass spectrometry measurement. d) The gaseous intermediate/products are collected and analyzed by mass spectroscopy.

To understand such the accumulation effect of the built-in electric field, we further simulate the adsorption using finite element analysis. The CuCl\_BEF was modeled by two stacking layers of same thicknesses as in the DFT calculation, and the interaction between  $NO_3^-$  and heterojunction was described by electrostatics equations solved in a two-dimensional box. After just 0.1 ns, the built-in electric field had already accumulated 140 mg L<sup>-1</sup> of  $NO_3^-$  near the junction, whereas the pure CuCl had no such effect. The accumulative distance extended to approximately 3 nm away from the electrocatalyst surface, this is comparable to the typical thickness of the electric double layer. Under an electrochemical reaction, this promotional migration effect works synergistically

with diffusion caused by the concentration gradient to drive mass transfer, significantly improving the reaction rate.

The built-in electric field also significantly modulates the reaction kinetics by changing the formation barriers of the key intermediates by tuning the oxidation state of Cu(I), as revealed by the DFT calculations. The electroreduction of nitrate to ammonia generally involves an eight electron and nine proton process, as previously reported, which occurs in nine elementary steps (Figure 2a and Supporting Information Figure S1). Nitrate ions are first adsorbed on CuCl\_BEF with a formation free energy change of -2.79 eV (using the initial reactant state as the reference level).

### **RESEARCH ARTICLE**



*Figure 3.* Morphology and structure of the CuCl\_BEF electrocatalyst. a) TEM image of as-synthesized CuCl\_BEF. The inset presents the elemental mapping images of the white dotted box area. b) Representative HRTEM image of CuCl\_BEF. The insets show a representative crystal plane of CuCl (111) and (220). c) XRD pattern of CuCl\_BEF. The asterisk represents the characteristic peaks of MXene. d) Cu K-edge XANES spectra. The inset indicates average Cu oxidation state determination in CuCl\_BEF, using the Cu K-edge energy shift of the reference Cu foil, Cu<sub>2</sub>O and CuO.

After that, \*NO<sub>3</sub><sup>-</sup> reacts with one proton-electron pair to produce \*NO<sub>2</sub> with a free energy of -4.1 eV. Afterward, NO<sub>2</sub> can attack the second proton-electron pair to produce \*ON (-4.36 eV). After the formation of \*ON on the CuCI\_BEF surface, the reaction could occur in two case, the fourth proton-electron pair can attack \*NO either through O side or N side to form \*NOH or \*ONH species, which represent two different mechanisms, i.e. \*NOH pathway, and \*ONH pathway respectively. From \*NO to \*NOH, the calculated free energy change increases sharply ( $\Delta G=0.39 \text{ eV}$ ), which is thus energy unfordable in our experimental condition.<sup>[7f,</sup> <sup>11]</sup> In contrast, the formation of \*ONH species is more favorable with the free energy increases of only 0.18 eV. Thereafter, \*ONH<sub>2</sub> and \*ONH<sub>3</sub> species might be spontaneously formed on the surface of catalyst with negative  $\Delta G$  of -0.48 eV and -0.03 eV, respectively. The \*OH intermediate can be formed by releasing one ammonia to the electrolyte, and the free energy change for this step increases slightly. The eighth electrochemical step is the formation of \*H<sub>2</sub>O species on the CuCl BEF surface with a negligible free energy change ( $\Delta G$ =0.07 eV). In short, the highest free energy change is from  $NO \rightarrow ONH/ONH$  (Intermediate 1), and \*ONH<sub>3</sub>/\*NH<sub>2</sub>OH release NH<sub>3</sub> or H<sub>2</sub>O (Intermediate 2), consequently, these steps are considered as rate-determining steps of the entire reduction pathway.

We compared the reaction barriers on CuCl\_BEF with pure CuCl and pure TiO<sub>2</sub> without a built-in electric field. The  $\Delta G$  for Step 1 on CuCl\_BEF is 0.18 eV, which is significantly reduced compared to theses on pure CuCl ( $\Delta G$  =0.42 eV, Supporting Information Figure S2) and pure TiO<sub>2</sub> ( $\Delta G$  =0.78 eV, Supporting Information Figure S3). This is due to the relatively higher free

energy of \*ON binding configuration on CuCl\_BEF than the pure. As previously calculated for the adsorption of nitric oxide on Cu(I) in zeolite model catalyst, NO can bonds to Cu(I) either through N-Cu or O-Cu bond.<sup>[12]</sup> In both modes, there is an unpaired electron donation from NO  $\pi^*$  orbital to Cu<sub>s, d</sub> and back donation from Cu  $d_{vz}$  to NO  $\pi^*$  orbital, leading to an overall electron donation from NO to Cu(I).<sup>[12a]</sup> Thus, with the built-in electric field, an electron richer Cu(I) suppress the electron donation from NO but facilitate the back donation to NO  $\pi^*$ . While the donation attenuates the binding energy and rises the free energy, the back donation weakens the N=O bond and promotes further hydrogenation. This considerably explains why CuCl BEF has a much lower formation barrier for Intermediates 1. Similarly, for Intermediates 2, pure CuCl has a formation barrier of  $\Delta G = 0.17 \text{ eV}$ , while CuCl BEF has not barrier (-1.97 eV Figure 2a). Conversely, since the release barrier of NO<sub>2</sub><sup>-</sup> is rather high ( $\Delta$ G =2.64 eV) and there is an extra ion accumulation effect from the built-in electric filed, the NO2- will be more difficult to desorb from CuCl BEF than from pure CuCl. Because of the relatively fast hydrogenation of NO<sub>2</sub><sup>-</sup>, there is less chance to release NO<sub>2</sub><sup>-</sup>, explaining the ultralow NO<sub>2</sub><sup>-</sup> vield. Subtly, the energy barrier of H<sub>2</sub> formation on CuCl BEF is 0.73 eV. This high barrier inhibits the hydrogen evolution reaction (HER), and thus, ammonia production over CuCl BEF is efficiently promoted (Supporting Information Figure S4).<sup>[13]</sup>

To prove the above mechanism, in-situ electrochemical online differential electrochemical mass spectrometry (DEMS)<sup>[14]</sup> was used to sample the reaction intermediates (Figure 2c). In DEMS experiments, the electrocatalyst slurry was pasted on the PTFE membrane and conductively connected through Au foil to

### **RESEARCH ARTICLE**

electrochemical work station. The PTFE membrane is porous and its back side is exposed to the mass spectroscopy, allowing penetration of different gaseous products with varied mass-tocharge (*m/z*) ratio to mass spectrograph. When four voltage pulses from -0.1 to -1.4 V were applied in series to the electrocatalyst, the *m/z* signals of 46, 30, 33, 17 that correspond to NO<sub>2</sub>, NO, ONH<sub>3</sub>, and NH<sub>3</sub>, respectively, were detected (Figure 2d). Particularly, the NO<sub>2</sub> signal was considerably weak, confirming its low production rate.

To experimentally prepare the CuCl\_BEF, we employed Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene as both support and Ti source because of its large surface area, rich surface group and reducibility.<sup>[15]</sup> Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene aqueous solution was prepared by etching Ti<sub>3</sub>AlC<sub>2</sub> power using LiF in concentrated HCI and it comprised Ti<sub>3</sub>C<sub>2</sub> monolayers terminated by OH and CI groups.<sup>[16]</sup> The MXene surfaces were negatively charged (Supporting Information Table S2) after release of H<sup>+</sup> groups, and thus, positive Cu<sup>2+</sup> ions were adsorbed, reduced and precipitated. A dark precipitate was produced from Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene dispersion after adding CuSO<sub>4</sub> solution dropwise. Transmission electron microscopy (TEM) and high-angle annular dark field image (HAADF) scanning TEM imaging (Insert in Figure 3a) show that the nanoshuttles comprised the uniform distribution of Ti, Cu, O, and Cl on the MXene layers (Figure 3a and Supporting Information Figure S5). These nanoshuttles are approximately 50 nm in length, 10 nm in width judging from TEM and 13.3 nm in height measured by atomic force microscopy (AFM) (Supporting Information Figure S6). The high-resolution TEM (HRTEM) images reveal that these nanoshuttles are mainly composed by rutile  $TiO_2$  as its characteristics (110) and (101) diffraction fringes, dominating on the entire nanoshuttles. Additionally, there are a few (1-5) of CuCl nanodots in each nanoshuttle, showing lattice fringes of CuCl (111) and CuCl (220) embedded on surfaces. The CuCl nanodots are in the dimension of 1-2 nm, approximately one layer thick considering its most exposed (111) plane from X-ray diffraction (XRD), and CuCl\_BEF is formed on MXene sheets (Figure 3b). XRD patterns detected (111), (220) and (311) planes of CuCl (PDF no. 06-0344), as well as the (110), (101) and (211) planes of rutile TiO<sub>2</sub> (PDF no. 21-1276, Figure 3c).

To explore the valence of Cu in CuCl\_BEF, X-ray absorption near edge structure (XANES) and X-ray photoelectron spectrum (XPS) were conducted (Figure 3d). The oxidation state of Cu in CuCl\_BEF shifts to +0.68 by Cu K-edge EXAFS spectra, using Cu foil, Cu<sub>2</sub>O and CuO as the references (Figure 3d),<sup>[17]</sup> further confirming the electron transferring from TiO<sub>2</sub> to CuCl and the successful creation of the built-in electric field. The Cu 2p peak in XPS is closely corresponded with CuCl (Supporting Information Figure S7). The Cl 2p peak displays two chemical environments, corresponding to formation of Cl–Cu and Cl–Ti bonds (Supporting Information Figure S8). Because of OH<sup>-</sup> species exist on MXene surface, the major Cu (I) is CuCl rather than Cu or Cu<sub>2</sub>O as verified by the Cu LMM Auger spectrum (Supporting Information Figure S9).<sup>[7e, 18]</sup>

While the Cl<sup>-</sup> source for CuCl\_BEF is solely from MXene surface, the formation of CuCl\_BEF relies on Cl<sup>-</sup> diffusion on the MXene surface and this two-dimensional confinement determine the limited size and distribution of CuCl nanoshuttles. When the Cu-to-Ti molar ratio in the reactants increases from 1%, 5%, 10%, 20% to 50%, the obtained nanoshuttles are evenly distributed on

the MXene sheets, and they possess similar morphologies and dimensions (Supporting Information Figures S10, 11). When the Cu-to-Ti molar ratio is 10%, the highest density of nanoshuttles is obtained, as confirmed by both TEM and XRD (Figure 3c and Supporting Information Figure S12). In contrast, a higher ratio of Cu-to-Ti exhaust mostly Ti (0) and collapse the MXene layers, whereas a lower Cu:Ti ratio resulted in the relatively low density of the nanoshuttles with relatively poor crystallinity. While the dimension of the CuCl nanodots is as thin as one monolayer in CuCl\_BEF, the built-in electric field in CuCl\_BEF is strong enough to show its dual roles. This is further proved by that the electrochemical active surface area (ECSA) of CuCI\_BEF is up to 900 cm<sup>-2</sup>, which is considerably larger than that of pure MXene (195 cm<sup>-2</sup>) and other reported electrocatalysts (Supporting Information Figure S13). Therefore, CuCI\_BEF catalysts render an ideal model to survey the CuCl catalyst with built-in electric field effect in nitrate electroreduction.

Inspired by the enhanced mass transfer and reaction kinetics using the built-in electric field, we quantified the NO<sub>3</sub>RR activity of CuCl\_BEF. Linear sweep voltammetry (LSV) demonstrated that starting from -0.4 V (vs. Reversible Hydrogen Electrode, RHE, hereafter), the CuCl BEF catalyst displays significantly larger current density in 100 mg L<sup>-1</sup> of NO<sub>3</sub><sup>-</sup> solution than in NO<sub>3</sub><sup>-</sup> free solution (Figure 4a). To verify the origin of ammonia and eliminate the possible interference from electrocatalyst or external environment, the <sup>1</sup>H NMR spectra of <sup>15</sup>N-NO<sub>3</sub><sup>-</sup> and <sup>14</sup>N-NO<sub>3</sub><sup>-</sup> isotopic labeling were analyzed. The <sup>1</sup>H NMR spectra of commercial (14NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and (15NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> samples were collected as standard spectra.<sup>[19]</sup> The <sup>1</sup>H NMR spectra of <sup>15</sup>N–NH<sub>4</sub><sup>+</sup> showed double peaks at  $\delta$  = 7.11 and 6.92 ppm, while <sup>14</sup>N–NH<sub>4</sub><sup>+</sup> showed triple peaks at  $\delta$  = 7.15, 7.02 and 6.89 ppm (Figure 4b), confirming that the formation of ammonia originated from the electroreduction of nitrate.<sup>[20]</sup> The concentration of ammonium, determined by the peak area of <sup>1</sup>HNMR (Supporting Information Figures S14, 15), was also consistent with the result using Nessler's reagent method (Supporting Information Figures S16-18 and Table S3). Altogether, the results demonstrate the excellent performance and reliability of electrocatalytic reduction of nitrate to ammonia.

By varying the applied potential, the nitrate conversion and ammonia production rate reach maximum at -1.0 V (Supporting Information Figure S19), which is in consequence chosen as the operation voltage. We further test the performances of CuCI\_BEF electrocatalysts with Cu-to-Ti molar ratios varying from 1%, 5%, 10%, 20% to 50%. The CuCl\_BEF with Cu/Ti=10% shows the maximum NH $_3$  yield rate at 2.15 mg h<sup>-1</sup> cm<sup>-2</sup> and NH $_3$  selectivity up to 95.6% within 2 hours, thus, the ratio is chosen (Supporting Information Figure S20). By calculating specific activity based on the unit copper mass (Supporting Information Figure S21), the NH<sub>3</sub> yield rate of CuCl\_BEF electrocatalyst is 64.4 h<sup>-1</sup> (1.82 mg h<sup>-1</sup> <sup>1</sup> cm<sup>-2</sup>). To the best of our knowledge, this is the highest among all reported NO<sub>3</sub>RR activities using NO<sub>3</sub><sup>-</sup> (<100 mg L<sup>-1</sup>) (Supporting Information Table S1). NO<sub>3</sub>RR follow a first-order reaction kinetics towards 100 mg L<sup>-1</sup>, reflect that the CuCl\_BEF has sufficient activity and diffusion is rate-limiting factor. The nitrate conversion is continuously improved to 92.0% and NH<sub>3</sub> selectivity up to 98.6% by prolonging of reaction time after 6 h (Figure 4c, Figure S22).

## **RESEARCH ARTICLE**



*Figure 4.* NO<sub>3</sub>RR activity of the CuCl\_BEF electrocatalyst. a) Linear sweep voltammetry curves of CuCl\_BEF tested in 0.5 M Na<sub>2</sub>SO<sub>4</sub> with and without 100 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>. The "j" is current density (j/A m<sup>-2</sup>) which is the amount of charge per unit time that flows through a unit area of electrode. b) <sup>1</sup>H NMR spectra of the electrolyte after electrocatalytic NO<sub>3</sub>RR using <sup>15</sup>NO<sub>3</sub><sup>-</sup> and <sup>14</sup>NO<sub>3</sub><sup>-</sup> as the nitrogen source. c) Time dependent concentration change of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>3</sub> tested at –1.0 V. d) Seven consecutive recycling tests at –1.0 V. e) Selectivity of ammonia with different initial NO<sub>3</sub><sup>-</sup> concentrations. f) Average NH<sub>3</sub> yield rate within 6 h of using different electrocatalysts.

In addition, The nitrate conversion and ammonia production with 20 mg L<sup>-1</sup> and 50 mg L<sup>-1</sup> initial nitrate are continuously improved by prolonging of reaction time after 6 h (Supporting Information Figure S23). The steady concentrations of nitrate and nitrite then are below 8 and 0.6 mg L<sup>-1</sup> respectively, and both are lower than the concentration stated in the Safe Drinking Water Act (SDWA) regulations (10 and 1 mg L<sup>-1</sup>) proposed by United States Environmental Protection Agency.<sup>[2]</sup> The NO<sub>3</sub>RR performance of the CuCl\_BEF electrocatalyst at different pH and temperature were compared. The results showed that the NO3RR was favorable under pH>7, but unfavorable under pH=3. This attributed to the dominant hydrogen evolution reaction (HER) under acidic atmosphere, which suppressed NO<sub>3</sub>RR. On the other hand, the temperature was favorable for NO<sub>3</sub>RR at 25°C. The activity of CuCI\_BEF electrocatalyst reduce at lower temperatures (0 °C) and the ammonia is easy to escape at higher temperatures (35 °C). (Supporting Information Figures S24, 25).). Additionally, the CuCl\_BEF catalyst exhibits good stability, sustaining an ammonia selectivity of >90% and nitrite selectivity of <1% after seven cycles of running (Figure 4d) with intact nanoshuttles morphologies (Supporting Information Figure S26). When NO<sub>3</sub>-N concentration varies from 20 to 200 mg L<sup>-1</sup>, the selectivity of ammonia remains at high-levels (>80%), and it approximately 100% at 100 and 200 mg L<sup>-1</sup> with negligible nitrite production, displaying a wide concentration tolerance (Figure 4e).

We compare the catalytic performance of CuCl\_BEF to that of a simple blend of CuCl and MXene (denoted by CuCl + MXene), a mixture of TiO<sub>2</sub> nanoparticles and MXene (TiO<sub>2</sub> + MXene), and pure MXene under identical test condition. The NH<sub>3</sub> yield rate of CuCl\_BEF (1.82 mg h<sup>-1</sup> cm<sup>-2</sup>) is significantly higher than that of the latter three (0.85, 0.57 and 0.34 mg h<sup>-1</sup> cm<sup>-2</sup>, respectively, Figure 4f). Additionally, the Faradaic efficiency, NO<sub>3</sub><sup>--</sup> conversion rate and ammonia selectivity of CuCl\_BEF are 44.7%, 92.0%, 98.6%, respectively, which are significantly higher than those of CuCl + MXene (20.1%, 38.8%, 79.3%), TiO<sub>2</sub> + MXene (60.2%, 54.8%, 73.7%) and MXene (20.5%, 27.3%, 81%, Supporting Information Figure S27). The superiorities of CuCl\_BEF over others in NO<sub>3</sub>RR proves that the effective promotion of the NO<sub>3</sub>RR performance is due to the built-in electric field rather than from TiO<sub>2</sub> or MXene.

#### Conclusion

In conclusion, we demonstrate that a built-in electric field in electrocatalyst can significantly accumulate higher concentration of reagent ions near the electrocatalyst surface region to improve mass transfer for the efficient removal of nitrate at ultra-low concentration and conversion to ammonia. A strong built-in electric field in the CuCl\_BEF electrocatalyst, induced by electrons transfer from TiO<sub>2</sub> to CuCl, effectively triggers interfacial accumulation of NO3<sup>-</sup> ions around the electrocatalyst, as revealed by the molecular dynamic simulation and finite element analysis. The electric field also rises the energy of the key reaction intermediate \*NO to reduce energy barrier of the rate-determining step. Taking advantage of the built-in electric field, nitrate at low concentration was efficiently converted with a high ammonia production selectivity (98.6%), low nitrite (0.6 mg L<sup>-1</sup>) and a copper mass-specific ammonia yield rate up to  $64.4 \ h^{-1}$ , which are all the highest among all reported results at 100 mg  $L^{-1}$  to date. Our results will inspire the use of a built-in electric field as an efficient strategy for the further development of NO3RR electrocatalysts, and it may also be effective for other electrocatalytic reactions.

# **RESEARCH ARTICLE**

#### Acknowledgements

We gratefully acknowledge the financial support provided by the National Key R&D Program of China (2020YFC1818401, 2017YFC0210906), National Natural Science Foundation of China (21978185, 21938006, 21776190), Basic Research Project of Leading Technology in Jiangsu Province (BK20202012), Suzhou Science and Technology Bureau Project (SYG201935) and the project supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

**Keywords:** Built-in electric field • Electroreduction of nitrate to ammonia • MXene

#### Reference

- [1] L. Su, D. Han, G. Zhu, H. Xu, W. Luo, L. Wang, W. Jiang, A. Dong, J. Yang, Nano Lett. 2019, 19, 5423-5430.
- a) USEPA, Vol. Volume I: Human Health Evaluation Manual (Part A) EPA/540/1-89/002, http://www. epa. gov/superfund/programs/risk/ragsa/index. htm, Washington, DC, 1989;
  b) USEPA, Risk assessment guidance for superfund, Vol. 1, Office of Emergency and Remedial Response, US Environmental Protection Agency, Washington, D.C., 1989.
- [3] F. Haber, R. Le Rossignol, Zeitschrift für Elektrochemie und angewandte physikalische Chemie 1913, 19, 53-72.
- [4] a) G.-F. Chen, X. Cao, S. Wu, X. Zeng, L.-X. Ding, M. Zhu, H. Wang, J. Am. Chem. Soc. 2017, 139, 9771-9774; b) Z. J. Schiffer, K. Manthiram, Joule 2017, 1, 10-14; c) J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, M. G. Kanatzidis, P. King, K. M. Lancaster, S. V. Lymar, P. Pfromm, W. F. Schneider, R. R. Schrock, Science 2018, 360; d) B. H. R. Suryanto, H.-L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, Nat. Catal. 2019, 2, 290-296.
- [5] A. Stirling, I. Papai, J. Mink, D. R. Salahub, J. Chem. Phys. 1994, 100, 2910-2923.
- [6] S. Giddey, S. P. S. Badwal, A. Kulkarni, Int. J. Hydrogen Energy 2013, 38, 14576-14594.
- [7] a) G.-F. Chen, Y. Yuan, H. Jiang, S.-Y. Ren, L.-X. Ding, L. Ma, T. Wu, J. Lu, H. Wang, Nat. Energy 2020, 5, 605-613; b) L. Mattarozzi, S. Cattarin, N. Comisso, R. Gerbasi, P. Guerriero, M. Musiani, L. Vazquez-Gomez, E. Verlato, J. Electrochem. Soc. 2015, 162, D236-D241; c) Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D.-H. Nam, C.-S. Tan, Y. Ding, J. Wu, Y. Lum, D. Cao-Thang, D. Sinton, G. Zheng, E. H. Sargent, J. Am. Chem. Soc. 2020, 142, 5702-5708; d) J. Li, G. Zhan, J. Yang, F. Quan, C. Mao, Y. Liu, B. Wang, F. Lei, L. Li, A. W. M. Chan, L. Xu, Y. Shi, Y. Du, W. Hao, P. K. Wong, J. Wang, S.-X. Dou, L. Zhang, J. C. Yu, J. Am. Chem. Soc. 2020, 142, 7036-7046; e) Y. Wang, W. Zhou, R. Jia, Y. Yu, B. Zhang, Angew. Chem. Int. Edit. 2020, 59, 5350-5354; f) R. Jia, Y. Wang, C. Wang, Y. Ling, Y. Yu, B. Zhang, ACS. Catal. 2020, 10, 3533-3540; g) Y. Wang, C. Liu, B. Zhang, Y. Yu, Sci. China Mater. 2020, 63, 2530-2538; h) M. Chen, J. Bi, X. Huang, T. Wang, Z. Wang, H. Hao, Chemosphere 2021, 278, 130386-130386; i) C. H. Wang, Z. Y. Liu, T. Hu, J. S. Li, L. Q. Dong, F. Du, C. M. Li, C. X. Guo, Chemsuschem 2021, 14, 1825-1829.
- [8] a) C. A. Clark, C. P. Reddy, H. Xu, K. N. Heck, G. Luo, T. P. Senftle, M. S. Wong, ACS Catal. 2020, 10, 494-509; b) D. P. Butcher, Jr., A. A. Gewirth, Nano Energy 2016, 29, 457-465.
- [9] Y. Lan, J. Chen, H. Zhang, W.-x. Zhang, J. Yang, J. Mater. Chem. A 2020, 8, 15853-15863.
- [10] M. C. Wu, P. J. Moller, Chem. Phys. Lett. 1990, 171, 136-140.
- [11] Y. Yu, C. Wang, Y. Yu, Y. Wang, B. Zhang, Sci. China. Chem. 2020, 63, 1469-1476.

- a) P. Kozyra, M. Radon, J. Datka, E. Broclawik, Struct. Chem. 2012, 23, 1349-1356; b) W. F. Schneider, K. C. Hass, R. Ramprasad, J. B. Adams, J. Phys. Chem. B 1998, 102, 3692-3705.
- [13] a) P. Li, M. Wang, X. Duan, L. Zheng, X. Cheng, Y. Zhang, Y. Kuang, Y. Li, Q. Ma, Z. Feng, W. Liu, X. Sun, Nat. Commun. 2019, 10; b) L. Tan, S.-M. Xu, Z. Wang, Y. Xu, X. Wang, X. Hao, S. Bai, C. Ning, Y. Wang, W. Zhang, Y. K. Jo, S.-J. Hwang, X. Cao, X. Zheng, H. Yan, Y. Zhao, H. Duan, Y.-F. Song, Angew. Chem. Int. Edit. 2019, 58, 11860-11867.
- a) S. Garcia-Segura, M. Lanzarini-Lopes, K. Hristovski, P. Westerhoff, Appl. Catal. B-Environ. 2018, 236, 546-568; b) S. Wasmus, E. J. Vasini, M. Krausa, H. T. Mishima, W. Vielstich, Electrochim. Acta 1994, 39, 23-31.
- [15] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, Adv. Mater. 2011, 23, 4248-4253.
- [16] W.-J. Sun, Y.-Y. Zhao, X.-F. Cheng, J.-H. He, J.-M. Lu, ACS Appl. Mater. Inter. 2020, 12, 9865-9871.
- [17] a) Z. Wang, Z. Xu, H. Huang, X. Chu, Y. Xie, D. Xiong, C. Yan, H. Zhao, H. Zhang, W. Yang, ACS Nano. 2020, 14, 4916-4924; b) J. Becher, D. F. Sanchez, D. E. Doronkin, D. Zengel, D. M. Meira, S. Pascarelli, J.-D. Grunwaldt, T. L. Sheppard, Nat. Catal. 2021, 4, 46-53; c) M. Croft, D. Sills, M. Greenblatt, C. Lee, S. W. Cheong, K. V. Ramanujachary, D. Tran, Phys. Rev. B 1997, 55, 8726-8732.
- [18] A. S. W. Wong, R. G. Krishnan, G. Sarkar, J. Vac. Sci. Technol. 2000, 18, 1619-1631.
- [19] a) H. Cheng, L.-X. Ding, G.-F. Chen, L. Zhang, J. Xue, H. Wang, Adv. Mater. 2018, 30; b) S. Z. Andersen, V. Colic, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Norskov, I. Chorkendorff, Nature 2019, 574, E5-E5.
- [20] H. Cheng, P. Cui, F. Wang, L.-X. Ding, H. Wang, Angew. Chem. Int. Edit. 2019, 58, 15541-15547.

# **RESEARCH ARTICLE**

#### **Entry for the Table of Contents**

Insert graphic for Table of Contents here.



Insert text for Table of Contents here.

A model electrocatalyst are created by stacking CuCl (111) and rutile TiO<sub>2</sub> (110) layers together, in which a built-in electric field induced from the electron transfer from TiO<sub>2</sub> to CuCl (CuCl\_BEF) is successfully formed as demonstrated by density functional theory (DFT) calculations and X-ray absorption near edge structure (XANES). Molecular dynamics simulation and finite element analysis suggest that this built-in electric field effectively triggers interfacial accumulation of NO<sub>3</sub><sup>-</sup> ions around the electrocatalyst. The electric field also rises the energy of key reaction intermediate \*NO to lower down energy barrier of the rate determining step. A NH<sub>3</sub> product selectivity of 98.6%, a low NO<sub>2</sub><sup>-</sup> production of <0.6%, and mass-specific ammonia production rate of 64.4 h<sup>-1</sup> is achieved with this proof-of-concept system, which are all the best among studies reported at 100 mg L<sup>-1</sup> of nitrate concentration to date.