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Ambient electrochemical N₂ reduction to NH₃ under alkaline conditions enabled by layered K₂Ti₄O₉ nanobelt

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To make NH₃, electrocatalytic N₂ reduction is considered as an attractive environmentally-friendly alternative to the Haber-Bosch process that is rather energy-intensive with heavy CO₂ emission, but only limited success has been made in identifying metal oxides as effective electrocatalysts for the N₂ reduction reaction (NRR) under alkaline conditions. In this communication, we report that K₂Ti₄O₉ nanobelt is able to effectively electrocatalyze the ambient NRR for N₂-to-NH₃ fixation at alkaline pH. When tested in 0.1 M KOH, it attains a high NH₃ yield of 22.88 µg h⁻¹ mg⁻¹_{cat.} and a Faradaic efficiency of 5.87%. Moreover, the K₂Ti₄O₉ also shows good selectivity and high electrochemical stability for NH₃ formation.

Nitrogen is a fundamental component of living organisms and plays a key role in controlling primary production in the biosphere.¹ Although N₂ is widely available in the atmosphere , its fixation to NH₃ is a difficult reaction owing to the chemical inertness of N=N triple bond.²⁻⁴ Industrially, the artificial nitrogen fixation is carried out by the Haber-Bosch process (N₂ + $3H_2 \rightarrow 2NH_3$) at harsh conditions, which seriously relies on consumption of fossil fuels and results in a large amount of CO₂ emission.^{5,6} Thus, a sustainable and environmentally-benign approach to produce NH₃ is urgently demanded.

Electrochemical method offers a promising alternative for ambient NH₃ synthesis via the N₂ reduction reaction (NRR), while the challenge associated with N2 activation underlines the requirement of efficient electrocatalysts for NRR.7-9 Noble metals catalysts perform efficiently for the NRR,¹⁰⁻¹³ but the high cost and scarcity limit their wide applications. Much attention has thus focused on developing noble-metal-free NRR electrocatalysts.¹⁴⁻⁴¹ Among such catalysts, metal oxides/hydroxides that can be easily made on a large scale have received more considerable attention for the NRR in acidic and neutral media.²⁶⁻⁴³ Given that oxygen evolution reaction (OER) also simultaneously occurs at the anode during the NRR and a variety of earth-abundant OER electrocatalysts under alkaline reaction conditions are available,^{44,45} it is also highly attractive to identify NRR electrocatalysts operating efficiently in alkaline media while only limited metal oxides have been reported for such applications like Fe_2O_3/TiO_2 (16.52 μg h⁻¹ mg⁻¹cat.; 0.31%),⁴⁶ Fe₂O₃ (0.46 μg h⁻¹ cm⁻²; 6.04%),⁴⁷ and Fe₂O₃-CNT (0.4125 μg h⁻¹ cm⁻²; 0.028).⁴⁸

In this communication, we report our recent experimental finding that $K_2Ti_4O_9$ nanobelt is capable of effectively electrocatalyzing the ambient NRR toward N₂-to-NH₃ fixation with excellent selectivity in alkaline electrolytes. In 0.1 M KOH, this catalyst offers a NH₃ yield of 22.88 µg h⁻¹ mg⁻¹_{cat.} and a Faradaic efficiency (FE) of 5.87% at -0.50 V vs. reversible hydrogen electrode (RHE), superior to TiO₂ (NH₃ yield: 7.46 µg h⁻¹ mg⁻¹_{cat.}; FE: 1.51%) and reported metal oxides at alkaline media. It also shows high electrochemical stability.

Fig. 1a shows the X-ray diffraction (XRD) pattern for $K_2Ti_4O_9$ with diffraction peaks at 10.089°, 14.297°, 28.036°, 30.272°, 31.026°, 32.902°, 33.665° and 41.265° indexed to the (200), (201), (310), (311), (004), (-603), (-313) and (512) planes of $K_2Ti_4O_9$ phase (JCPDS No. 32–0861), respectively.⁴⁹ Fig. 1b presents a typical scanning electron microscopy (SEM) image of $K_2Ti_4O_9$ with the stacks of layered belt-like structure. The transmission electron microscopy (TEM) image of $K_2Ti_4O_9$ further evidences the layered nanobelt structure, as shown in Fig. 1c. High-resolution TEM (HRTEM) image (Fig. 1d) reveals lattice fringes with an interplanar distance of 0.267 nm

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indexed to the (-313) crystal face of $K_2Ti_4O_9$. TEM and corresponding energy-dispersive X-ray (EDX) elemental mapping images reveal uniform distribution of K, Ti and O elements within $K_2Ti_4O_9$ (Fig. 1e).



Fig. 1. (a) XRD pattern for $K_2Ti_4O_9$. (b) SEM image of $K_2Ti_4O_9$. (c) TEM image for $K_2Ti_4O_9$. (d) HRTEM image for $K_2Ti_4O_9$. (e) TEM and corresponding EDX elemental mapping images of K, Ti and O for $K_2Ti_4O_9$.



X-ray photoelectron spectroscopy (XPS) was employed to explore the surface chemical components and corresponding chemical bonds of $K_2Ti_4O_9$. Fig. 2a shows the XPS survey spectrum of $K_2Ti_4O_9$, confirming the presence of K, Ti and O elements. In the K 2p spectrum (Fig. 2b), the binding peaks at 295.2 eV and 292.4 eV can be assigned to K $2p_{1/2}$ and K $2p_{3/2}$, respectively.⁵⁰ The XPS peaks of O 1s for the sample is shown in Fig. 2c. The peaks centered at the binding energies (BEs) of 532.3 eV, 530.9 eV and 529.5 eV were assigned to the adsorbed oxygen, hydroxyl oxygen Dand 0.14 the Coxygen, respectively.⁵¹ The presence of hydroxyl oxygen was indicative of trace amount of water molecules on the surface of sample, while the lattice oxygen peak observed is indicative of the existence of a Ti-O-Ti bond in the layered material. Fig. 2d shows XPS spectrum in the Ti 2p core-level region. The peaks located at the BEs of 463.6 eV and 457.9 eV, which are attributed to spin orbit components of $2p_{1/2}$ and $2p_{3/2}$, respectively. A spin orbit splitting energy between Ti $2p_{1/2}$ and Ti $2p_{3/2}$ is determined as 5.7 eV, which corresponds to Ti⁴⁺ in K₂Ti₄O₉.⁵²



Fig. 3. (a) LSV curves of $K_2Ti_4O_9/CP$ in Ar- and N_2 -saturated 0.1 M KOH. (b) Timedependent current density curves of $K_2Ti_4O_9/CP$ at various potentials for 2 h in N_2 -saturated 0.1 M KOH. (c) UV-V is absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis at a series of potentials for 2h. (d) NH₃ yields and FEs of $K_2Ti_4O_9/CP$ for NRR at a series of potentials.

The NRR catalytic performance was tested using a threeelectrode system comprising of a graphite rod as a counter electrode, Ag/AgCl as a reference electrode and $K_2Ti_4O_9$ deposited on carbon paper (CP) electrode as a working electrode ($K_2Ti_4O_9/CP$; $K_2Ti_4O_9$ loading: 0.1 mg cm⁻²). The potentials for NRR are reported based on an RHE scale. Both produced NH₃ and possible by-product hydrazine (N₂H₄) were spectrophotometrically determined by the indophenol blue method⁵³ and Watt and Chrisp method,⁵⁴ respectively. The corresponding calibration curves of NH₃ and N₂H₄ are shown in Fig. S1 and Fig. S2. Fig. 3a shows the linear sweep voltammetry (LSV) curves under N₂- and Ar-saturated 0.1 M KOH solutions. A distinct current density enhancement under N₂ atmosphere reveals that K₂Ti₄O₉/CP has catalytic activity for the NRR. Fig. S3 shows the cyclic voltammetry curves for K₂Ti₄O₉/CP and CP in Ar- and N2-saturated 0.1 M KOH solution, respectively. It is clearly seen that $K_2Ti_4O_9/CP$ attains higher current density in N2-saturated solution, which is consistent with the results of LSV curves. As shown in Fig. 3b, the currents of chronoamperometry curves at different potentials reveal good stability for 2 h electrolysis under N₂-saturated electrolytes. After electrolysis, the collected electrolytes were colored with indophenol indicator and measured by ultraviolet spectrophotometer. The corresponding UV-Vis absorption spectra are shown in Fig. 3c. Clearly, the electrocatalytic N₂ reduction over K₂Ti₄O₉/CP occurs at potential ranges from – 0.40 V to -0.60 V. The average NH₃ yields and corresponding

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FEs are shown in Fig. 3d. As observed, NH₃ yields and FEs increase with more negative potential until -0.50 V, where the maximum NH₃ yield of 22.88 μ g h⁻¹ mg⁻¹_{cat.} and a FE of 5.87% are achieved. The values are higher than those for most reported NRR electrocatalysts (Table S1). The NH₃ yield and FE of $K_2Ti_4O_9/CP$ increase initially from -0.40 V to -0.50 V. However, they start to decrease as the potential is negatively shifted to -0.60 V, which is ascribed to the competitive adsorption of nitrogen and hydrogen species on the electrode surface.²⁷ Beyond this negative potential, the reduction rate and FE decrease obviously, which is due to the competition of the hydrogen evolution reaction on the electrode surface.55,56 Also note that TiO₂ offers a NH₃ yield of 7.46 μ g h⁻¹ mg⁻¹_{cat.} and a FE of 1.51% at -0.50 V (Fig. S4). NRR on the surface of $K_2Ti_4O_9$ may follow the associative mechanism where the nitrogen molecules are step-by-step reduced with protons and electrons.57 Alkali metal ions, which can bind with N2, have been utilized in electrolyte to enhance the NRR performances because such cations electrostatically enriched in the stern layer interact with the dissolved N2 molecules leading to higher concentrations of N_2 at the electrode surface than in the electrolyte.⁵⁸ The enhanced N_2 adsorption would then boost the N_2 reduction activity and selectivity on $K_2 Ti_4 O_9$ catalyst. That can explain why K₂Ti₄O₉ rich with K⁺ has higher NRR activity compared with TiO₂. It is expected that other K-Ti-0 catalysts with various compositions or Na-Ti-O nanomaterials are also capable of effectively catalyzing the NRR.

To verify that the detected NH₃ was indeed generated from electrocatalytic NRR over K₂Ti₄O₉, control experiments were conducted in Ar-saturated solution at -0.50 V and in N₂saturated solutions at open circuit potential (Fig. S5). Clearly, almost no NH₃ is detected in either case. In addition, we performed experiments with alternating 2 h cycles between N₂- and Ar- saturated solutions at -0.50 V (Fig. 4a). Clearly, NH₃ was only obtained in N₂-saturated solution. There is a tiny amount of NH₃ in Ar-saturated solution that may come from the trace amount of NH_3 in air.59 Moreover, the amount of detected NH₃ increases roughly linearly during a total reaction time of 4 h (Fig. S6). These results declare that the N₂ fixation process takes place by $K_2 Ti_4 O_9$. No by-product $N_2 H_4$ is detected in final electrolytes at all potentials (Fig. S7), indicating that $K_2Ti_4O_9$ has good selectivity for NRR. For comparison, we investigated the NRR performance of CP and TiO2, the precursor of K₂Ti₄O₉, at -0.50 V for 2 h electrolysis at ambient conditions (Fig. 4b). The relevant UV-vis absorption spectra are displayed in Fig. S8. Obviously, CP has almost no catalytic activity for the NRR. TiO₂/CP shows much poorer NRR performance than those of $K_2Ti_4O_9/CP$. Stability is also critical to the catalyst for practice. The corresponding UV-Vis absorption spectra are plotted in Fig. S9 and the NH₃ yield rates as well as the FEs shown in Fig. 4c, NH₃ yields and FEs shows small changes during consecutive tests for 6 times at -0.50 V, indicating the high stability of K₂Ti₄O₉. In addition, the long-term electrochemical stability of K₂Ti₄O₉ was also tested at -0.50 V in N₂-saturated electrolyte, revealing a stable current profile for the testing period of 24 h (Fig. 4d). SEM nComm Accepted Manuscrip

image shows the preservation of nanobelt feature for $K_2 T_{14} \Omega_{0}$ (Fig. S10) after NRR electrolysis. XRD^{O} and SR^{O} (Fig. S12) confirms that $K_2 Ti_4 \Omega_9$ has no obvious change in crystalline phase after stability test. The XPS spectra of $K_2 Ti_4 \Omega_9$ almost remain unchanged after long-term NRR electrolysis, as shown in Fig. S12. Those results imply the high structure stability.





In summary, $K_2Ti_4O_9$ has been experimentally proven as a high-active catalyst for ambient N_2 -to-NH₃ fixation with excellent selectivity. This catalyst achieves a high NH₃ yield of 22.88 µg h⁻¹mg⁻¹_{cat.} with a FE of 5.87% at -0.50 V vs. RHE in 0.1 M KOH. This study not only offers us an attractive earth-abundant catalyst for electrochemical NH₃ synthesis in alkaline media, but it would open up new avenues to the rational design of titanate–based materials for N₂ fixation applications.

Conflicts of interest

There are no conflicts to declare.

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