Doping strain induced bi-Ti$^{3+}$ pairs for efficient N$_2$ activation and electrocatalytic fixation

Na Cao$^{1,4}$, Zheng Chen$^{1,4}$, Ketao Zang$^2$, Jie Xu$^2$, Jun Zhong$^3$, Jun Luo$^2$, Xin Xu$^1$ & Gengfeng Zheng$^1$

The electrochemical N$_2$ fixation to produce ammonia is attractive but significantly challenging with low yield and poor selectivity. Herein, we first used density function theory calculations to reveal adjacent bi-Ti$^{3+}$ pairs formed on anatase TiO$_2$ as the most active electrocatalytic centers for efficient N$_2$ lying-down chemisorption and activation. Then, by doping of anatase TiO$_2$ with Zr$^{4+}$ that has similar d-electron configuration and oxide structure but relatively larger ionic size, the adjacent bi-Ti$^{3+}$ sites were induced and enriched via a strained effect, which in turn enhanced the formation of oxygen vacancies. The Zr$^{4+}$-doped anatase TiO$_2$ exhibited excellent electrocatalytic N$_2$ fixation performances, with an ammonia production rate (8.90 $\mu$g·h$^{-1}$·cm$^{-2}$) and a Faradaic efficiency of 17.3% at $-0.45$ V versus reversible hydrogen electrode under ambient aqueous conditions. Moreover, our work suggests a viewpoint to understand and apply the same-valance dopants in heterogeneous catalysis, which is generally useful but still poorly understood.
The production of ammonia (NH₃) by the well-known Haber–Bosch process from N₂ and H₂ has marked over a century of success for providing >80% nitrogen source for fertilizer and an alternative energy carrier with large energy density. Despite the natural abundance of N₂, the high bond energy of the N≡N triple bond (941 kJ mol⁻¹) prevents it as a reactive form and thus demands a significant amount of the global energy cost annually. In addition, the use of fossil fuels to produce H₂ reactant also leads to a significant level of CO₂ release. The electrochemical N₂ fixation (also known as N₂ reduction reaction, N₂RR) can be processed in ambient conditions and use inexpensive aqueous electrolytes as the proton source, and thus is regarded as a promising alternative approach. The direct electron transfer from electrode surface to N≡N requires overcoming substantially high energy barriers, so the key to achieve efficient N₂ fixation is to develop active catalytic centers that can efficiently reduce the large activation barrier of N≡N and promote its dissociation. As an overwhelming level of water molecules exists than solvated N₂, the other key to achieve this goal is to enrich the electrocatalytic centers that can favorably proceed with the N₂RR over the hydrogen evolution reaction.

Theoretical calculations have suggested that metal sites with low chemical valence are potential to enhance the electron-donating ability to the π* antibonding orbitals of N₂ molecule, which weakens the N≡N bond and drives the eventual cleavage of N₂. Some noble metal-based catalysts such as Ru and Au with stepped surfaces can strongly bind to N₂ and the intermediates, and thus can lower the overpotential and increase the rate of the N₂RR in an aqueous electrolyte. Earth-abundant compounds, including metal oxides, nitrides and carbides, have also been investigated as electrocatalysts with tailorable activities by specific facets, defects, vacancies, or hybrid material interfaces. Nonetheless, to date, the electrocatalytic N₂ fixation is still limited by its low yields and slow kinetics. The critical understanding and rational tuning the active centers of N₂RR electrocatalysts remain as a highly challenging but imperative issue.

Previously, the roles of oxygen vacancies (Vo’s) in transition metal oxides have been extensively discussed, and the low-valence dopants have also been suggested to facilitate the formation of Vo’s, but the knowledge of their contributions to the N₂RR is still limited. For example, Li et al. reported that TiO₂ with Vo’s can chemisorb and activate N₂ molecules, and the formation of each Vo’s is, in turn, related to the formation of a pair of Ti⁵⁺ ions. Hirakawa et al. suggested that two Ti⁵⁺ ions in adjacent positions, which are inherently created on the surface defects of rutile TiO₂ (110) surfaces, behave as active sites for photocatalytic conversion of N₂ to ammonia with water. However, more-recent calculations provide different results and indicate that such rutile TiO₂ (110) surfaces are unlikely to be the relevant surface for the N₂RR. To date, all the theoretical and experimental studies have not been able to reconcile the discrepancies in which types of TiO₂ are the best for the N₂RR, or what is the bonding nature of the active centers. Herein, by means of density function theory (DFT) calculations, we first reveal that two adjacent Ti⁵⁺ sites (designated as a bi-Ti⁵⁺ pair) on anatase TiO₂ (101) can chemically adsorb and activate N₂ molecules in a lying-down manner, whereas single or isolated Ti⁵⁺ sites cannot. On the other hand, similar bi-Ti⁵⁺ pair on rutile (110) surface cannot adsorb and activate N₂, unless the strong repulsion between one of its nearest lattice oxygens at the bridge sites and the negatively charged N₂ upon activation can be eliminated. Thus, the formation of two adjacent Ti⁵⁺ sites on anatase (101) should be the most-effective electrocatalytic centers for N₂ fixation.

Accordingly, we develop an experimental strategy for inducing such adjacent bi-Ti⁵⁺ sites on anatase (101) surfaces as N₂RR active centers, using a dopant-induced Vo formation strategy. Zr⁴⁺ is selected to dope in the TiO₂ framework, owing to its similar d-electron configuration and oxide structure, as well as its suitable size. As shown in Fig. 1, doping of Zr⁴⁺, which has a relatively larger radius of 72 pm (compared with 52 pm of Ti⁴⁺) into anatase TiO₂, can still retain its anatase crystal structure but also exert a tension on the TiO₂ framework, which can enhance the formation of Vo. As the oxidation number of Zr⁴⁺ is fixed, the newly formed Vo must be associated with the formation of two adjacent Ti⁵⁺ sites, which are beneficial to enrich active centers and enhance the N₂RR over the HER. In contrast, Ce⁴⁺ with a much larger ion radius (106 pm) cannot be incorporated into the TiO₂ framework without breaking the original crystal structure, whereas Ce⁵⁺ can also be associated with the newly formed Vo’s, thus not contributing to the formation of the bi-Ti⁵⁺ pairs as active centers. Electrochemical measurements demonstrate that the Zr⁴⁺-doped anatase TiO₂ exhibit significant enhanced N₂RR performances, including an ammonia formation rate of 8.90 ± 0.17 μg h⁻¹ cm⁻² catalyst and a corresponding Faradaic efficiency (FE(NH₃)) of 17.3%, significantly surpassing those of undoped TiO₂ or Ce⁴⁺-doped TiO₂, whose efficiencies were limited by their lower Ti⁵⁺ densities.

Results and discussion

Theoretical calculations. In order to tune Ti⁵⁺-based electrocatalysts for the N₂RR, DFT calculations were first carried out to rationally screen different types of Ti⁵⁺ for a better understanding of bonding structures of these active centers. The calculations for screening an ideal N₂RR electrocatalyst are often based on the following criteria: first, strong chemisorption of N₂ molecules; second, effective stabilization of N₂H⁺; and third, destabilization of NH₂⁺. In the present study, we also investigated the capability of forming Vo’s efficiently, as the fourth criterion.

According to the four criteria above, several types of Ti⁵⁺ sites were screened for the N₂RR, including adjacent bi-Ti⁵⁺ pairs on anatase (101) surfaces (designated as A(101)-Vo), rutile (110) surfaces with 1 or 2Vo’s (designated as R(110)-Vo, R(110)-2Vo,
adjacent bi-Ti$^{3+}$ sites on R(110)-Vo (Supplementary Fig. 1a) and single Ti$^{3+}$ sites on the A(101)-Vo (Fig. 3b) can only adsorb N$_2$ in a standing-up manner, with much less charge transfer and negligible N–N bond length elongation. Furthermore, by comparing the geometry structures between the adsorbed N$_2$ on R(110)-Vo and that on A(101)-Vo, it can be seen that there exists a large repulsion in the former between the adsorbed N$_2$ and one of the adjacent lattice oxygens at the bridge site, owing to a close distance between negatively charged N and the lattice oxygen $O^{2-}$ (Fig. 2 and Supplementary Fig. 1a). Thus, it is only when such lattice $O^{2-}$ is removed and an adjacent bi-Ti$^{3+}$ pair on R(110)-2Vo is formed, the efficient activation of N$_2$ can occur as shown by a significant amount of negative charge on N$_2$ and an elongated N–N bond length (Supplementary Fig. 1b).

Based on the aforementioned Criterion 2, the first hydrogenation step was further investigated. The results show that the initial N$_2$ adsorption has a large impact on the subsequent hydrogenation. As illustrated in Fig. 3a and Supplementary Fig. 1b, the calculated reaction free energies ($\Delta G$) for the first hydrogenation step on A(101)-Vo and R(110)-2Vo are 0.24 and 0.25 eV, respectively, much lower than those on the single Ti$^{3+}$ sites (0.50 eV, Fig. 3b) and the adjacent bi-Ti$^{3+}$ sites on R(110)-Vo (0.75 eV, Supplementary Fig. 1a), whereas N$_2$ is also inactivated in the latter two cases. Our calculation results agree with the previous hypothesis$^{30}$, and show that R(110)-Vo is unlikely to be the relevant surface for the N$_2$RR. Here, we can now rule out the two configurations of single Ti$^{3+}$ sites and the adjacent bi-Ti$^{3+}$ sites on R(110)-Vo, which cannot activate N$_2$ and are unfavorable for the first hydrogenation step.

By examining the Criterion 3, we found that the reaction free energies for the hydrogenation of NH$_2^*$ on A(101)-Vo (Fig. 3a) and R(110)-2Vo (Supplementary Fig. 1b) are 0.18 and 0.23 eV, respectively. These numbers can be favorably compared with those for the first hydrogenation step. Hence, following the first three criteria, both the adjacent bi-Ti$^{3+}$ pair sites on A(101)-Vo and R(110)-2Vo are active for the N$_2$RR. However, as shown in Supplementary Fig. 1a and b, the formation of two adjacent Vo’s on rutile (110) surfaces is 0.36 eV higher than the formation of two separated Vo’s (see more discussion in the Methods section). This downplays the role of the adjacent bi-Ti$^{3+}$ sites on R(110)-2Vo. Hence, the anatase (101) surface is the more suitable support for the development and enrichment of the active bi-Ti$^{3+}$ pair sites. The feasibility of the N$_2$RR on the adjacent bi-Ti$^{3+}$ on A(101)-Vo is also confirmed by the whole free energy pathway calculated at 0 and $-0.24$ V as presented in Supplementary Fig. 2.

Low-valence dopants have often been utilized to facilitate the formation of Vo’s$^{19}$. However, their incorporation into TiO$_2$ does not guarantee the formation and enrichment of the active bi-Ti$^{3+}$ sites. On the other hand, the same-valence dopants are generally useful in heterogeneous catalysis$^{19}$, whereas their roles are less understood. Assuming that the same-valence dopants could introduce strain into the original lattice, we examined how lattice expansion and contraction would change the formation energy of Vo’s. As shown in Supplementary Fig. 3, both the tensile strain and the compressive strain can lower the formation energy of Vo’s in the anatase lattice (see the Methods for more computational details). Considering Ti$^{4+}$ is the smallest cation for the oxidation state of M$^{4+}$ (e.g., 72 pm of Zr$^{4+}$, or 106 pm of Ce$^{4+}$, with compared as 52 pm of Ti$^{4+}$) introducing the tensile strain is practically feasible. Note that Zr$^{4+}$ has a similar d-electron configuration and oxide structure, it is thus an ideal replacement of Ti$^{4+}$. Furthermore, as the oxidation number of Zr$^{4+}$ is fixed, the newly formed Vo’s are expected to be associated with the formation of two adjacent Ti$^{3+}$, which are beneficial to the enrichment of the active sites. In contrast, Ce$^{4+}$ has a much larger ion radius (106 pm), presumably lowering the formation
energy of Vo’s to a larger extent. Nevertheless, it is more likely to break the original crystal structure of TiO2 upon Ce4+ doping. Furthermore, Ce4+ can be reduced to Ce3+ during the formation of Vo’s24, and thus does not contribute to the formation of the bi-Ti3+ active centers upon doping.

**Synthesis and structural characterizations.** TiO2 anatase nanotubes were first synthesized by a hydrothermal method, followed by incubation of Zr4+ or Ce4+ dopants with subsequent annealing (see Methods section). The crystal structures of different samples were investigated by X-ray diffraction (XRD, Fig. 4a). For the undoped and Zr4+-doped TiO2 (designated as Zr-TiO2) nanotubes, all the diffraction peaks correspond to an anatase phase (JCPDS# 21-1272). The TiO2 peak intensity decreases with the Zr4+ doping, suggesting the slight decrease of TiO2 crystallinity, but no peaks associated with ZrO2 are observed. Close examination of the spectra shows that with the increasing Zr4+ content, the XRD peaks gradually shift toward lower diffraction angles (Fig. 4b), indicating the increase of TiO2 lattice constants upon Zr4+ doping. The corresponding interplanar spacing values of the (101) planes change from 0.351 nm for undoped TiO2 to 0.359 nm for Zr-TiO2. This observation of anatase TiO2 expansion upon the Zr4+ doping is supported by the DFT calculations (Supplementary Table 2 and Supplementary Table 3). In contrast, the Ce-doped TiO2 does not exhibit characteristic peaks of TiO2, but presents peaks that are associated with CeO2 (JCPDS# 43-1002), suggesting the loss of TiO2 anatase structure and the formation of CeO2 crystals upon the Ce4+ doping. As a comparison, the Zr4+ doping on rutile TiO2 (designated as Zr-rutile-TiO2) was also conducted to illustrate the effect of different active sites. The XRD peaks (Supplementary Fig. 4) confirm the typical rutile phase (JCPDS# 21-1276).

High-resolution transmission electron microscopy images show that the undoped (pristine) TiO2 anatase nanotubes have
a tubular structure, with the outer and inner diameters of 7–9 and ~4 nm, respectively (Fig. 4c). The resolved lattice fringes are measured as 0.351 nm, consistent with the interplanar distance of (101) planes of anatase TiO₂. After doping with 5% Ce⁴⁺ (i.e., Ce-TiO₂, Fig. 4d), small CeO₂ nanoparticles are observed on the exteriors of original TiO₂ nanotubes, suggesting an inhomogeneous behavior of phase separation. In contrast, for TiO₂ nanotubes doped with 5% Zr⁴⁺ (i.e., Zr-TiO₂, Fig. 4e), no nanoparticles are observed outside the nanotubes. The resolved lattice fringes of 0.359 nm are similar but slightly larger than those of (101) planes of anatase TiO₂, also in good accord with the XRD results. The energy-dispersive X-ray spectroscopy (EDS) and mapping confirm the existence and uniform distribution of Ti, O, and Zr elements in the nanotubes (Fig. 4f and Supplementary Fig. 5).

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was then used to characterize the dopant distribution in different types of TiO₂ nanotubes. Compared with the undoped TiO₂ nanotubes (Fig. 5a), individual Zr⁴⁺ ions are observed to occupy the original positions of Ti⁴⁺, exhibiting a distribution of single atoms (highlighted by red circles in Fig. 5b). The electron energy loss spectroscopy (EELS) analysis of Ti-edge was conducted to probe the phase and chemical states of titanium for the undoped, Zr- and Ce-doped TiO₂ nanotubes, respectively (Fig. 5c). The undoped TiO₂ nanotubes present Ti⁴⁺ features with two peaks at 458.4 (Ti-L₃) and 463.7 eV (Ti-L₂), respectively. For Zr-TiO₂, the centers of these two peaks shift to lower energy near 457.5 and 462.7 eV, respectively, indicating that the cation incorporation elevates the content of the unoccupied Ti 3d state as well as the distorted Ti³⁺ coordination. Furthermore, a shift of 0.6 eV to lower energy is observed for the Ti-L₃ edge in the EELS spectra of Ce-TiO₂, associating with the existence of a distorted structure in Ce-TiO₂ samples. Based on the intensity of L₂ and L₃ from the Zr-TiO₂ sample (Supplementary Fig. 6a), the ratio of Ti³⁺/ΣTi (ΣTi = Ti³⁺ + Ti⁴⁺) is estimated to be 29.1%. Similarly, the Ti³⁺/ΣTi values of undoped TiO₂ and Ce-TiO₂ are calculated as 8.5% and 21.0%, respectively (Supplementary Fig. 6b, c).

X-ray photoelectron spectroscopy (XPS) was further conducted to study the oxidation states of metal ions on the catalyst surfaces.

Fig. 4 Structural and compositional characterizations. a X-ray diffraction (XRD) patterns of ZrO₂, CeO₂, undoped TiO₂, Ce-TiO₂, and Zr-TiO₂. b The enlarged view of XRD pattern at 22°–28° range. c–e High-resolution transmission electron microscopy (HRTEM) images of c undoped TiO₂, d Ce-TiO₂, and e Zr-TiO₂ samples. Insets: Transmission electron microscopy (TEM) images of the corresponding nanotubes. f High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image with corresponding element mappings of Zr-TiO₂, showing the distribution of Ti (green), O (blue), and Zr (red). (Source data are provided as a Source Data file.)
For the undoped TiO2 nanotubes (Fig. 5d, bottom panel), two main peaks centered at 458.9 and 464.6 eV are observed, corresponding to the Ti 2p3/2 and Ti 2p1/2 peaks, respectively. These two peaks can be further deconvoluted into four sub-peaks, assigned to Ti3+ 2p3/2 (457.4 eV), Ti4+ 2p3/2 (458.9 eV), Ti3+ 2p1/2 (463.1 eV), and Ti4+ 2p1/2 (464.6 eV), respectively, confirming the coexistence of Ti3+ and Ti4+ species. The ratio between Ti3+ and Ti4+ for undoped TiO2 is calculated as 10%. The incorporation of Zr4+ into TiO2 frameworks leads to a clear shift to lower binding energy direction and widening both peaks (Fig. 5d, top panel), suggesting the increase of the Ti3+ content. The Ti3+/Ti4+ ratio is calculated as 31% for Zr-TiO2 nanotubes, in which the increase of Ti3+ percentage is a clear indication of oxygen vacancy increase. In comparison, the Ti3+/Ti4+ ratio for Ce-TiO2 nanotubes is measured as 21% (Fig. 5d, middle panel), which can be attributed to the loss of TiO2 anatase structure, in good accord with XRD results. Accordingly, the analyses of both the Zr 3d peaks (Supplementary Fig. 7a) and Ce 3d peaks (Supplementary Fig. 7b) confirm the existence of Zr4+ and Ce4+ in the Zr-TiO2 and Ce-TiO2 nanotubes, respectively. The defects of unpaired electrons in materials were also probed by electron paramagnetic resonance spectra. Among the three samples (Supplementary Fig. 8), the Zr-TiO2 sample presents the largest signal at g = 2.003, further confirming its largest concentration of Ti3+.

To further verify their electronic structures, these samples were characterized by X-ray Absorption Near-edge Fine Structure (XANES) spectroscopy. The XANES spectra of Ti K-edge in Zr- or Ce-doped TiO2 samples are similar to that in undoped TiO2 (Supplementary Fig. 9), confirming similar local structure modification of Ti cations. The main Ti pre-edge peak at 4970.9 eV (indicated by the black arrow) in the three samples (Fig. 6a) is ascribed to the weak symmetry of the surrounding Ti cations in these catalysts. The slight increase of the pre-edge intensity in both Zr-TiO2 and Ce-TiO2 indicates the existence of more distorted structures and defective Ti environment. The main peak of Ti K-edge at 4987.6 eV in Zr- or Ce-doped TiO2 samples (Fig. 6b, indicated by the black arrow) is lower than that in pure TiO2 (4987.3 eV), indicating that the Ti species are partially reduced after doping. The bond length information of different samples was further investigated by the Fourier transformed (FT) k3-weighted of Ti K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectra (Fig. 6c). The undoped TiO2 nanotubes show two peaks at 1.39 and 2.41 Å, corresponding to the Ti-O and Ti-Ti bonds, respectively. Interestingly, the doping of relatively larger Zr4+ in the TiO2 framework results in a contracted Ti-O bond length (1.34 Å) with a larger distribution, suggesting that Zr4+ cations are interstitially incorporated in TiO2 lattice and result in abundant surface defect sites. This observation is consistent with a previous report that the contracted Ti–O bonds associated with coordinately unsaturated Ti cations acted as Lewis acid sites.

The Zr K-edge spectra of Zr4+-doped TiO2 nanotubes were also investigated to probe the local structure surrounding Zr cations (Fig. 6d). The main Zr K-edge in the range of 18,020–18,040 eV is split into two peaks at 18,018.5 eV (Peak A) and 18,030.0 eV (Peak B), indicating six-coordinated Ti4+ cations that are consistent with the coordination of Ti3+ in anatase TiO2 structure. These features are distinctively different from those of pure tetragonal ZrO2 with 7- or 8-coordinated Ti4+ cations. The EXAFS spectra of Zr-TiO2 (Fig. 6e) only present the bond length of Zr–O (1.52 Å) but not Zr–Zr (3.20 Å), in agreement with the HAADF-STEM results that the Zr4+ cations in the TiO2 framework exhibit a single-atomic distribution.

**Electrochemical N2 fixation.** The nitrogen temperature-programmed desorption (N2-TPD) was first carried out to evaluate the capability of N2 adsorption by these samples (Supplementary Fig. 10). The two broad peaks centered at 170 and 500 °C are attributed to physisorption and chemisorption of N2, respectively. Both the undoped TiO2 and Ce-TiO2 show very weak chemisorption peaks. In contrast, the Zr-TiO2 sample presents a strong N2 chemisorption, suggesting that the incorporation of Zr4+ in the anatase TiO2 lattice leads to a significant increase of active sites for N2 adsorption.

The aqueous electrocatalytic N2 reduction was then conducted in an electrochemical cell at room temperature and pressure. N2...
gas was supplied in a feed gas stream to the cathode, while 0.1 M KOH aqueous solution was used as the electrolyte (Methods section). All the voltages reported in this work were converted into values versus reversible hydrogen electrode (vs. RHE), as shown in Supplementary Fig. 11. The linear sweep voltammetric (LSV) curves of the Zr-TiO2 nanotubes were first measured in both N2-saturated and Ar-saturated electrolytes, respectively, in the same voltage range (Fig. 7a). A clear current density increase is observed for the N2-saturated electrolyte, suggesting the occurrence of the N2RR11. The thermodynamic equilibrium potential of N2 to NH3 in 0.1 M KOH is calculated as 0.056 V vs. RHE (detailed calculation shown in the Supplementary Note 1), based on the free energies tabulated in literature45. Here, the onset potential of the overall electrochemical reactions is defined as the total current density gets over 50 µA cm−2. In order to achieve this current density, the onset potentials of the undoped TiO2, Ce-TiO2, Zr-rutile-TiO2, and Zr-TiO2 catalysts are −0.246, −0.178, −0.497, and −0.141 V vs. RHE, respectively (Supplementary Fig. 12 and Fig. 13). For a current density of 1 mA cm−2 achieved, the undoped TiO2, the Ce-TiO2, Zr-rutile-TiO2, and Zr-TiO2 require −0.643, −0.578, −0.715, and −0.538 V vs. RHE, respectively. This comparison suggests that the incorporation of Zr4+ should be the main contributor of active sites for catalyzing N2RR. The partial current densities for ammonia production were calculated by multiplying the total current density with the FENH3 at selected potentials (Supplementary Fig. 14). By defining the current density level toward NH3 production as 25 µA cm−2, the N2RR onset potential for the Zr-TiO2 is calculated as −0.4 V vs. RHE, corresponding to the overpotential of 456 mV.

The average yields of ammonia and the corresponding FENH3 of those electrocatalysts were measured using the sodium salicylate-sodium hypochlorite method13 (Methods section). The corresponding calibration plots were displayed (Supplementary Fig. 15). All samples were measured with over three times to get the average values. The quantification of ammonia was carefully controlled to avoid possible contamination sources46. To rule out the possible contamination of ammonia from the air or the solution, several control experiments were carried out, as specified in Supplementary Fig. 16. Very little ammonia was detected in those controls, and the photographs of their colorimetric assays showed no color difference. In addition, as a control, the electrochemical tests were also conducted for all the electrocatalysts under Ar controls47. The corresponding ultraviolet-visible (UV–Vis) spectra of electrolyte after 3 h electrolysis and chromogenic reaction show the maximum values are comparable to the spectrum backgrounds (Supplementary Fig. 17), suggesting almost no ammonia was produced for all samples in an Ar-saturated electrolyte.

For the electrochemical tests of Zr-TiO2 conducted in N2-saturated electrolytes, the UV–Vis spectra show a significant enhancement of the peak centered around 660 nm, suggesting that the Zr-TiO2 nanotubes catalyze N2 reduction (Supplementary Fig. 18). No N2H4 product is detected in the electrolyte for the Zr-TiO2 catalysts after 3 h N2RR test (Supplementary Fig. 19). For the Zr-TiO2 nanotubes, both the ammonia production rate and the corresponding FENH3 reach their peak values at −0.45 V vs. RHE, which are calculated as 8.90 ± 0.17 µg h−1 cm−2 catalyst and 17.3% (Fig. 7b), respectively. Further increase the negative potential leads to the decrease of the ammonia production rate and FENH3, which can be attributed to the increase of the competitive HER on the electrode surfaces. The quantitative measurement of the ammonia production was further verified by

Fig. 6 X-ray absorption spectroscopy characterizations. a, b Enlarged Ti K-edge X-ray absorption near-edge structure (XANES) spectra, and c Fourir transformed (FT) k3-weighted of Ti K-edge (EXAFS) spectra of the undoped TiO2, Zr-TiO2, and Ce-TiO2 samples. d Zr K-edge XANES spectra and e Fourier-transformed k3-weighted of EXAFS spectra of pure ZrO2 and Zr-TiO2 samples. (Source data are provided as a Source Data file.)
two other methods, including the ion chromatography (IC) and the nuclear magnetic resonance (NMR) \(^4\). The \(^1\)H NMR spectra show a triplet coupling (~ 52 Hz) for \(^{14}\)NH\(_4^+\) and a doublet coupling (~ 72 Hz) for \(^{15}\)NH\(_4^+\) (Fig. 7c). The obtained ammonia production rate and the corresponding FENH\(_3\) for \(^{15}\)N\(_2\) as the feeding gas are comparable to those used \(^{14}\)N\(_2\) (Fig. 7d and Supplementary Fig. 20), confirming that the ammonia detected is attributed to the electroreduction of N\(_2\). The total ammonia produced during the 3 h electrochemical reaction time was calculated as 0.538 \(\mu\)mol (detailed calculation shown in the Supplementary Note 2).

In contrast, all the undoped TiO\(_2\) (Fig. 7e), Zr-rutile-TiO\(_2\) (Supplementary Fig. 21), and Ce-TiO\(_2\) (Supplementary Fig. 22) electrocatalysts exhibit much lower ammonia production rates, with the peak values of 1.48, 3.22, and 5.79 \(\mu\)g h\(^{-1}\) cm\(^{-2}\) catalyst at a higher negative potential of \(-0.65\) V, respectively. Furthermore, the N\(_2\)RR tests were also conducted on ZrO\(_2\) and CeO\(_2\) nanoparticles under the same catalytic potential of \(-0.45\) V vs. RHE to probe the effect of Zr-incorporation (Fig. 7f). Both the pure CeO\(_2\) and ZrO\(_2\) nanoparticles exhibit lower or even negligible NH\(_3\) production rates. This comparison suggests that the bi-Ti\(^{3+}\) pairs induced by Zr\(^{4+}\)-doped TiO\(_2\) function as
excellent electrocatalytic centers for the N₂ fixation at ambient conditions.

Finally, the chronoamperometry tests at selected applied potentials of −0.5 and −0.45 V (where the ammonia yields were the highest) show that the N₂RR performance of the Zr-TiO₂ nanotubes catalyst was stable after several hours of continuous electrolysis (Supplementary Fig. 23). This cycling stability test was further repeated for a total of six runs (Supplementary Fig. 24), showing no obvious change in the NH₃ yield rate and current efficiency. After the electrochemical test, the Zr-TiO₂ catalyst was re-measured with XPS (Supplementary Fig. 25). No obvious difference is observed compared with that before the electrochemical test, further confirming the good stability of the Zr-TiO₂ nanotubes in N₂RR electrocatalysis.

In this work, we have first screened several types of Ti³⁺ sites by means of DFT calculations. The adjacent bi-Ti³⁺ pairs formed on the most-stable surface of anatase TiO₂ (i.e., A(101)-Vo) are identified as the active electrocatalytic centers, which can lead to a lying-down manner as efficient N₂ chemisorption and subsequent activation. However, similar bi-Ti³⁺ pair sites formed on the most stable surface of rutile TiO₂ (i.e., R(110)-Vo), as well as the single Ti³⁺ site, are concluded as the inactive sites. By further removing a second O²⁻ to form R(110)-2Vo, the adjacent bi-Ti³⁺ pairs on rutile TiO₂ can now induce a lying-down chemisorption manner for N₂ (Supplementary Fig. 1b), exhibiting a significant amount of negative charge on N₂ and an elongated N–N bond length. Nevertheless, as shown in Supplementary Fig. 1a and b, the formation of two adjacent Vo’s on rutile (110) surfaces is 0.36 eV higher than the formation of two separated Vo’s, downplaying the role of the adjacent bi-Ti³⁺ pairs on R(110)-2Vo. Hence the anatase (101) surface is the more suitable host for the development and enrichment of the active bi-Ti³⁺ pairs.

The competitive adsorption of H₂O and activation of HER on these bi-Ti³⁺ catalytic sites are also estimated (Supplementary Table 4). For convenience, here we assume the chemical potential of the water in solution is equal to 3.169 kPa as pure liquid water at room temperature. Then, the calculated adsorption free energy changes is only 0.04 eV, when the adsorbed H₂O on the bi-Ti³⁺ pairs is replaced by the N₂ under working condition (the corresponding structures are presented in Supplementary Fig. 26).

For HER, the adsorption free energy of the first hydrogen is calculated to be 0.19 eV on the oxygen vacancy, which is only slightly more advantageous than that of N₂RR of 0.24 eV. Meanwhile, one has to take into account the fact that the high pH of the electrolyte (pH 13) has an inhibiting effect on the HER. Thus, N₂ in our situation is able to compete with H₂O and H for adsorption and activation as shown in our experiments.

In addition, previous literatures show that if the anatase nanoparticles are exposed under reduction condition with hydrogen, it results in reduced nanoparticles comprising a crystalline TiO₂ core and a disordered shell with abundant oxygen vacancies. With respect to the corresponding pristine surface O*, the calculated free energy diagrams for the further reduced surface OH* and H₂O* of pristine A(101) surface, with and without Zr-doping under different potentials, are shown in Supplementary Fig. 27. The result suggests that the surface with O* totally hydrogenated is the most stable under working conditions for U_RH < −0.40 eV, such that the oxygen vacancies should remain thermodynamically stable, which should not be annihilated by the O*⁺ or OH* species.

As Zr⁴⁺ into the anatase TiO₂ framework is a useful strategy to induce and enrich the specific adjacent bi-Ti³⁺ pairs on the anatase surfaces. Owing to its similar d-electron configuration and oxide structure but relatively larger ion size as compared with Ti³⁺, the doped single Zr⁴⁺ ion induces a strained effect without breaking the original TiO₂ structure, which, in turn, enhances the formation of oxygen vacancy and subsequently bi-Ti³⁺ sites on the anatase surfaces. Control experiments reveal that Ce⁴⁺ doping does not have the same role as Zr⁴⁺ doping, for Ce⁴⁺ has a too larger size and a variable oxidation state.

Based on an expanded anatase lattice with lattice constants that are 1.023 times larger than the optimized one by DFT, various anatase A(101) surfaces were built without or with different Zr⁴⁺ concentrations in surfaces or subsurfaces. The calculated results for some representatives of the strained A(101) surfaces are shown in Supplementary Table 3. The Vo formation energy without Zr⁴⁺ doping is calculated to be 0.27 eV lower than the A (101) surface based on the optimized lattice. With various contents of Zr⁴⁺ dopants in surfaces or subsurfaces, the calculated Vo formation energies are within 0.22 and 0.33 eV smaller than that of the optimized lattice. The DFT results support the experiment observation that Zr⁴⁺ enhances the Vo formation on A(101) surface, which is owing to the tensile strain induced by the Zr⁴⁺ doping.

Owing to the efficient chemisorption and activation of the N₂ molecules by the Zr⁴⁺ doping-induced bi-Ti³⁺ pairs on anatase TiO₂, the Zr-TiO₂ exhibits an outstanding ammonia production rate, a high FE_N₂, and excellent electrochemical stability, significantly exceeding those of the undoped TiO₂ or Ce-TiO₂ samples under similar testing conditions. Compared with other N₂RR electrocatalysts in aqueous solutions at ambient conditions reported to date (Supplementary Table 5), our Zr-TiO₂ sample demonstrated one of the highest NH₃ production rates and FE_N₂ values.

In conclusion, our study demonstrates the bonding nature of the active centers and a unique approach of optimizing electrocatalytically active sites by rational design of dopant size and charge, enabling new opportunities for efficient electrochemical N₂ reduction. Our work not only reveals bi-Ti³⁺ pairs on anatase TiO₂ as effective N₂RR active centers, but also suggests an attractive viewpoint to understand and apply the same-valence dopants in heterogeneous catalysis, which is generally useful but still poorly understood. Further development of similar multiple active sites with cooperative binding and activation effects on N₂ may lead to a vast variety of opportunities of enhancing the N₂RR capabilities and potential large-scale utilization toward direct atmospheric N₂ fixation.

Methods

Chemicals and materials. Titanium (IV) oxide (P25, Sinopharm Chemical Reagent Co., Ltd, analytically pure), zirconium nitrate pentahydrate (Aladdin, Z190748, 99.5%), cerium nitrate hexahydrate (Aladdin, C103578, 99.5%), sodium hydroxide (Macklin, S817977, ≥ 98%), salicylic acid (Macklin, S817529, 99.5%), potassium sodium tartrate tetrahydrate (Macklin, P816438, 99.5%), sodium nitroferricyanide (III) hydrate (Macklin, S81341, 99.9% metal basis), sodium hypochlorite solution (Macklin, S828471, available chlorine 4.0%), monochloro-acetic acid (Macklin, A801305, 99.8%), hydrazine monohydrate (Alfa Aesar, A14005, 98%), hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd, 10011018, 36.0~38.0%), potassium hydroxide (Aladdin, A801305, 99.8%), hydrazine monohydrate (Alfa Aesar, A14005, 98%), hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd, 10011018, 36.0~38.0%), sodium perchlorate (Sinopharm Chemical Reagent Co., Ltd, 10009218, ≥ 99.7%), 4-(dimethylamino) benzaldehyde (Sigma-Aldrich, 156477, 99%), Nafion solution (DuPont), 211 Nafion membrane (DuPont), deoxygen (DI) water (Millipore, 18.2 MΩ cm), N₂ gas (99.99%), Ar gas (99.99%), Ammonium sulfate [(NH₄)₂SO₄, 99.9%], (NH₄)₂SO₄, 98 atom% ¹⁵N), and nitrogen-15 N₂ (98 atom% ¹⁵N) were purchased from Sigma-Aldrich. All chemical reagents were used as received without further purification.

Characterization. The XRD data were characterized by Bruker SMART APEX (II)-CCD (Germany). X-ray photoelectron spectroscopy was recorded on a Perkin
Elmer PHI 5000 C ESCA system (Perkin Elmer, USA). The high-resolution transmission electron microscopy images and the EDX spectroscopy spectra were recorded by a JEM 2100 F (JEOL, Japan) and a Tecnai 20 (FEI, USA) transmission electron microscopy. The HAADF-STEM, EELS, and the EDX mapping experiments were performed using Titan Cubed Themis G2 300 (FEI) microscope equipped with Super-X detectors at 200 kV. N2-TPD measurements were performed on a Micrometrics Autochem II 2920 system. Electron-spin resonance signals were recorded on a Bruker ESR A300 spectrometer at room temperature. XANES and EXAFS data were collected on beamline 14 W at the Shanghai Synchrotron Radiation Facility (SSRF). The UV–Vis absorption spectrum was recorded by an ultraviolet-visible spectrometer (U-3900H, Hitachi, Japan). –H-NMR (nuclear magnetic resonance) measurements were performed on a Bruker NM600. IC analysis was performed on an ICS-2000 (Thermo Fisher Scientific) equipped with an isotropic pump.

Synthesis of Zr-TiO2. In a typical synthesis, 2.0 g of TiO2 (P25) was mixed with 60 mL of (10 M) NaOH solution in a Teflon-lined stainless autoclave at 150 °C for 20 h. The slurry was washed with 0.1 M HCl solution for several times until the pH value reached 1.6, and then with DI water until pH was close to 7, to being filtrated to obtain TiO2 nanotubes. The introduction of Zr6+ to TiO2 was conducted by wet impregnating the TiO2 nanotubes with 20 mL of 0.35 M zirconium nitrate solution. The mixture was stirred at room temperature for 4 h. After the reaction, the substrate was washed with DI water and ethanol for several times, followed by drying at 60 °C and then annealed in Ar at 400 °C, with a ramping rate of 2 °C min⁻¹ for 2.5 h.

Electrochemical measurements. A total of 5 mg of catalyst was dispersed in 0.5 M of ethanol followed by the addition of 50 µL of NaCl solution. The mixture was sonicated thoroughly to form a homogeneous ink. The working electrodes were then prepared by drop-casting the catalyst inks onto carbon paper (area 0.2 cm²) to achieve a loading of 1.0 mg cm⁻². All the electrochemical performance measurements were performed with an Autolab electrochemical workstation (Autolab PGSTAT204) at room temperature (25 ± 2 °C). The potential of SCE is the standard potential of SCE at 25 °C. The potential of RHE, E_RHE, is calculated by subtracting the background signal of non-electrochemical formation, thus providing the thermodynamic driving force.

### Determination of hydrazine. The hydrazine presented in the electrolyte was estimated by the method of Wang and Champ25. A mixture of para-(dimethyl amino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent B. In brief, 5 mL of testing electrolyte after the electrocatalytic reaction was taken out from the electrochemical cell, followed by adding 5 mL of color reagent B. After 20 min for color development, the UV-Vis absorbance spectra were measured at 455 nm. The concentration-dependence plot was obtained by using standard hydrazine monohydrate solutions with different concentrations. The fitting curve showed good linear relation of absorbance with NH₃H₂O concentration (y = 0.7624x + 0.0161, R² = 0.9992) by three times independent calibrations.

### Computational details. The Vienna ab initio simulation package was utilized to perform all DFT calculations52. The 2 × 2 × 2 supercell of 12 atomic layers was used to model the 3d, 4s electrons in titanium and the 5s, 4d, 5p electrons in zirconium were treated as valence electrons, whereas the kinetic energy cutoff for the plane wave basis sets was set to be 400 eV. The remaining core electrons were described by the projector augmented-wave method53. The surface Monkhorst-Pack meshes of 2 × 2 × 1 and 5 × 5 × 5 k-point samples in the surface Brillouin zone were employed for slab model and bulk, respectively. For bulk optimization, all atoms as well as lattice constants were allowed to fully relax. For systems involving anatase (101), a 3 × 2 supercell of 12 atomic layers was used, where the bottom five layers of atoms were fixed in their optimized bulk positions, whereas the top seven layers, as well as the adsorbate, were allowed to fully relax. For systems involving (110), a 3 × 2 supercell of 12 atomic layers was used, where the bottom five layers of atoms were fixed in their optimized bulk positions, whereas the top seven layers, as well as the adsorbate, were allowed to fully relax. After the convergence criteria for optimizations were met, the largest remaining force on each atom was less than 0.02 eV Å⁻¹. For all calculations, the spin-polarized generalized gradient approximation of the Perdew–Burke–Ernzerhof functional54 was used. As the standard DFT functionals tended to over-delocalize electrons, DFT + U was employed55 with an effective U value of 3.3 eV for Ti 3d-orbitals, as obtained from linear response56. For the dopants, we used standard DFT on Zr, as there were no issues with spin polarization.

### Oxygen vacancy formation energies were calculated. The 2 × 2 × 2 supercell of 12 atomic layers was used, where the bottom five layers of atoms were fixed in their optimized bulk positions, whereas the top seven layers, as well as the adsorbate, were allowed to fully relax. After the convergence criteria for optimizations were met, the largest remaining force on each atom was less than 0.02 eV Å⁻¹. For all calculations, the spin-polarized generalized gradient approximation of the Perdew–Burke–Ernzerhof functional57 was used. As the standard DFT functionals tended to over-delocalize electrons, DFT + U was employed58 with an effective U value of 3.3 eV for Ti 3d-orbitals, as obtained from linear response59. For the dopants, we used standard DFT on Zr, as there were no issues with spin polarization. For surface reactions, the contributions of dispersive interactions were accounted for by using the DFT + D3 method with Becke-Jonson damping60,61. Bader’s theory of atoms in molecules was used for charge analysis62,63.

### Calculation of ammonia faradaic efficiency. The electrochemical ammonia faradaic efficiency (EF_NH3 (electrochemical)) was calculated by subtracting the background signal of non-electrochemical ammonia47, using Equation (3):
The adsorption free energies of gases on the surfaces were calculated as:
\[ \Delta G_{\text{gas}} = G_{\text{gas/surface}} - G_{\text{gas}} - G_{\text{surface}}, \]
where \( G_{\text{gas/surface}}, G_{\text{gas}}, \) and \( G_{\text{surface}} \) are the total free energy of the adsorption systems of surfaces with or without vacancies, and adsorbate species in the gas phase, respectively. Here, we assumed that in addition to the total electronic energies, only the translation and rotation contributions of the gas phase species are significant and the other parts can be ignored. Assuming the gas phase species as ideal gases, the partition functions of translation \( Q_{\text{trans}}^m \) and rotation \( Q_{\text{rot}}^m \) were calculated as:
\[ Q_{\text{trans}}^m = \left( \frac{2m_m k_B T}{h^2} \right)^\frac{3}{2}, \]
\[ Q_{\text{rot}}^m = \frac{1}{\sigma} \left( \frac{k_B T}{h^2} \right)^{3/2} \sum \frac{n!}{A^{n}B^{m}C^{m}}, \]
where \( P \) (1 atm) and \( m \) are the partial pressure and molecular mass, respectively, \( k_B \) is the Boltzmann constant, \( T \) (298.15 K) is the absolute temperature, \( V = \frac{N}{N_A} \) is the volume of the system, \( \sigma \) is the symmetry factor, \( A^{m}, B^{m}, C^{n} \) are rotational constants, and \( h \) is the Plank's constant.

In our work, the DFT calculations were carried out to rationally screen four types of Ti\(^3+\) for a better understanding of bonding structures of the active centers (Fig. 2): (a) the adjacent bi-Ti\(^3+\) on anatase (101) surfaces with one oxygen vacancy (i.e., A(101)-Vo); (b) the single Ti\(^3+\) with four coordination on anatase (101) surfaces with one oxygen vacancy; (c) the adjacent bi-Ti\(^3+\) on rutile (110) surfaces with one oxygen vacancy, (i.e, R(110)-Vo); (d) the adjacent bi-Ti\(^3+\) on rutile (110) surfaces with a pair of oxygen vacancies together, (i.e., R(110)-2Vo). Cases (a) and (c) were chosen because anatase and rutile are the most common crystal phases for TiO\(_2\), and anatase (101) and rutile (110) surfaces are, respectively, the most exposed surfaces. Case (b) was chosen for its low coordination. Case (d) was formed after the removal of one nearby lattice O\(_2\) in Case (c). This nearby lattice O\(_2\) presents a large repulsion with the chemisorbed N\(_2\) in a lying-down manner, which precludes the bi-Ti\(^3+\) site of R(110)-Vo from effective N\(_2\) activation.

The overall N\(_2\)RR process (N\(_2\) + 6 H\(^+\) + 6 e\(^-\) = 2 N\(_2\)H\(_2\)) involves several proton-coupled electron transfer steps. The Gibbs free energy change (\( \Delta G \)) of each elementary step was calculated by using the standard hydrogen electrode \( \Delta G = \Delta U + T \Delta S + \Delta G_{\text{rot}} + \Delta G_{\text{el}} \)

where \( \Delta H \) and \( \Delta S \) are the enthalpy change and entropy change, respectively, \( \Delta G_{\text{rot}} \) is the free energy contribution related to electrode potential \( \Delta G_{\text{el}} \) is the correction of the \( H^+ \) free energy by the concentration, which can be calculated as:
\[ \Delta G_{\text{el}} = 2.303 \times k_B T \times pH \]

Data availability
All data relevant to this study are available from the corresponding author upon reasonable request. The source data underlying Fig. 3–7 and Supplementary Figs. 4–25 are provided as a Source Data file.

Received: 1 November 2018 Accepted: 6 June 2019
Published online: 28 June 2019

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Acknowledgements

We thank the following funding agencies for supporting this work: the National Key Research and Development Program of China (2017YFA0206901, 2018YFA0209401), the Natural Science Foundation of China (21773036, 21661082, 2176115012), the Science and Technology Commission of Shanghai Municipal Government (17JC1400100, 19XD1420400), the Innovation Program of Shanghai Municipal Education Commission (2019-01-07-00-07-E00045), and the Collaborative Innovation Center of Chemistry for Energy Materials (11-iChem). We thank the support from Shanghai Synchrotron Radiation Facility (SSRF).

Author contributions

G.Z. and X.X. proposed, designed, and supervised the project. G.Z., X.X., J.L., N.C. and Z.C. wrote the manuscript. N.C., K.Z., J.X., J.Z., and J.L. performed the experiments and analyzed the data. Z.C. and X.X. performed the theoretical calculations. All the authors discussed, commented on, and revised the manuscript.

Additional information

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-019-10888-5.

Competing interests: The authors declare no competing interests.

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Peer Review Information: Nature Communications thanks Zhongfang Chen, and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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