

Article

Subscriber access provided by University of Massachusetts Amherst Libraries

Efficient Ammonia Electrosynthesis from Nitrate on Strained Ruthenium Nanoclusters

Jie Li, Guangming Zhan, Jianhua Yang, Fengjiao Quan, Chengliang Mao, Yang Liu, Bo Wang, Fengcai Lei, Lejing Li, Alice W.M. Chan, Liangpang Xu, Yanbiao Shi, Yi Du, Weichang Hao, Po Keung Wong, Jianfang Wang, Shi-xue Dou, Lizhi Zhang, and Jimmy C. Yu J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.0c00418 • Publication Date (Web): 29 Mar 2020

Downloaded from pubs.acs.org on March 31, 2020

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

~	
2	
3	
4	
5	
6	
7	
8	
0	
9 10	
10	
11	
12	
13	
14	
15	
16	
17	
12	
10	
19	
20	
21	
22	
23	
24	
25	
25	
20	
27	
28	
29	
30	
21	
31	
31 32	
31 32 33	
31 32 33 34	
31 32 33 34 25	
31 32 33 34 35 26	
31 32 33 34 35 36	
31 32 33 34 35 36 37	
31 32 33 34 35 36 37 38	
31 32 33 34 35 36 37 38 39	
31 32 33 34 35 36 37 38 39 40	
31 32 33 34 35 36 37 38 39 40 41	
31 32 33 34 35 36 37 38 39 40 41 42	
31 32 33 34 35 36 37 38 39 40 41 42 43	
31 32 33 34 35 36 37 38 39 40 41 42 43 44	
31 32 33 34 35 36 37 38 39 40 41 42 43 44	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 950	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 950 51	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 950 51 52	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 950 51 52	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 950 51 52 37	
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 9 51 52 53 4	
31 32 33 34 35 36 37 38 39 40 42 43 44 45 46 47 48 9 51 52 53 54 55	
31 32 33 34 35 36 37 38 39 41 42 34 45 46 47 48 9 51 52 53 55 56	
31 32 33 34 35 36 37 38 30 41 42 34 45 46 47 48 9 51 52 53 55 57	

60

Efficient Ammonia Electrosynthesis from Nitrate on Strained Ruthenium Nanoclusters

Jie Li,^{†,},[¬] Guangming Zhan,^{‡,},[¬] Jianhua Yang,[§] Fengjiao Quan,[‡] Chengliang Mao,[‡] Yang Liu,[†] Bo Wang,^{†,} Fengcai Lei,[†] Lejing Li,[†] Alice W. M. Chan,[†] Liangpang Xu,[†] Yanbiao Shi,[‡] Yi Du,^{⊥,#} Weichang Hao,[#] Po

Keung Wong,[∥] Jianfang Wang,[§] Shi-Xue Dou,^{⊥,#} Lizhi Zhang,^{*,‡} and Jimmy C. Yu^{*,†}

[†]Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China

[‡] Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, Institute of Environmental & Applied Chemistry, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan 430079, China

[§]Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China [§]School of Life Sciences, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, P. R. China

[⊥]Institute for Superconducting and Electronic Materials (ISEM), Australian Institute for Innovative Materials (AIIM), University of Wollongong, Wollongong, New South Wales 2500, Australia

[#]School of Physics, BUAA-UOW Joint Research Centre, Beihang University, 37 Xueyuan Road, Beijing 100191, China

^vThese authors contributed equally to this work

*Correspondence and requests for materials should be addressed to Jimmy C. Yu (jimyu@cuhk.edu.hk) or Lizhi Zhang (zhanglz@mail.ccnu.edu.cn)

ABSTRACT: The limitations of the Haber-Bosch reaction—particularly high-temperature operation—have ignited new interests in low-temperature ammonia-synthesis scenarios. Ambient N₂ electroreduction is a compelling alternative, but is impeded by a low ammonia production rate (mostly <10 mmol g_{cat}^{-1} h⁻¹), small partial current density (<1 mA cm⁻²), and high-selectivity hydrogen-evolving side-reaction. Herein, we report that roomtemperature nitrate electroreduction catalyzed by strained ruthenium nanoclusters generates ammonia at a higher rate (5.56 mol g_{cat}^{-1} h⁻¹) than the Haber-Bosch process. The primary contributor to such performance is hydrogen radicals, which are generated by suppressing hydrogen-hydrogen dimerization during water splitting enabled by the tensile lattice strains. The radicals expedite nitrate-to-ammonia conversion by hydrogenating intermediates of the rate-limiting steps at lower kinetic barriers. The strained nanostructures can maintain nearly 100% ammoniaevolving selectivity at >120 mA cm⁻² current densities for 100 hours due to the robust subsurface Ru-O coordination. These findings highlight the potential of nitrate electroreduction in real-world, low-temperature ammonia synthesis.

INTRODUCTION

Ammonia is produced in a large scale by the Haber-Bosch process.¹ This industrial N₂ reduction reaction (NRR) has a typical yield below 200 mmol g_{cat} ⁻¹ h⁻¹.^{2,3} The process is energy-intensive because it proceeds at high temperatures of 400-600°C.⁴ A more sustainable approach for ammonia production is aqueous-based electrocatalytic NRR at ambient conditions.⁵⁻⁷ However, these reaction rates and partial current densities are usually less than 10 mmol g_{cat} ⁻¹ h⁻¹ and 1 mA cm⁻², respectively.

In contrast to N₂ requiring 941 kJ/mol to break the N=N bond, nitrate can be disintegrated into deoxygenated species with a much lower energy of 204 kJ/mol.⁸⁻¹⁰ From an energetic viewpoint, it makes perfect sense to explore electrocatalytic nitrate reduction reaction (NITRR) as a promising low-temperature ammonia synthesis tool. NITRR occurs at solid-liquid interfaces with a lower reaction energy barrier than solid-gas-liquid interfaces of NRR. It also has an advantage in selectivity because the kinetics of NITRR can be optimized against the competing hydrogen-evolving reaction (HER).¹¹ Furthermore, nitrate is abundant in natural environments as a consequence of the worldwide use of nitrogen-containing fertilizers and pesticides. Nitrate in drinking water is known to cause diseases such as methemoglobinemia and non-Hodgkin's lymphoma.¹² Converting nitrate to ammonia via electrocatalysis potentially offers a good solution to energy and environmental problems.¹³⁻¹⁸

Electrocatalyzed nitrogen transformation from nitrate to ammonia involves the transfer of 9 protons and 8 electrons (NO₃⁻ + 9H⁺ + 8e⁻ \rightarrow NH₃ + 3H₂O) during which nitrogen oxyanions and dinitrogen are unavoidably generated as undesired byproducts.¹⁹⁻²² With traditional metal-based catalysts, a decent nitrate-to-ammonia selectivity is attainable only under low overpotentials and small current densities, while hydrogen-evolution still dominates at high overpotentials.²³⁻²⁵ Further exploiting the potential of NITRR in ammonia synthesis hinges on the creation of more efficient electrocatalysts.

In this work, we designed Ru/oxygen-doped-Ru core/shell nanoclusters to electrocatalyze NITRR to ammonia. Oxygen dopants expand the Ru unit-cell to trigger tensile strains. The strains suppress HER but favor •H formation by lifting the barrier of hydrogen-hydrogen coupling. The resulting •H promotes the hydrogenation of reaction intermediates to ammonia. Benefiting from the HER prevention and NITRR promotion, our room-temperature electrocatalysis exhibits an ammonia-synthesizing rate (5.56 mol g_{cat}^{-1} h⁻¹ or 1.17 ± 0.04 mmol h⁻¹ cm⁻²) exceeding that of the state-of-the-art NITRR electrocatalysis. Moreover, our strained nanoclusters maintain a high selectivity across a wide range of applied potentials, and they show superior durability against strong currents because of the firm bonding of Ru with subsurface oxygen dopants.



Figure 1. Characterizations of the tensile strain structure of Ru/oxygen-doped-Ru core/shell nanoclusters. (a) Transmission electron microscopy (TEM) image, (b, c) aberration-corrected HAADF-STEM image, (d) EELS elemental map, (e) XPS, (f) Ru K-edge XANES, (g) Ru oxidation state, and (h) Ru K-edge EXAFS of Ru-ST-12.

The inset in panel **a** shows the size distribution of Ru-ST-12. The inset in **g** shows the first-order derivatives of Ru K-edge XANES spectrum shown in **f**. To quantify the Ru oxidation state, we obtained a linear equation by plotting the Ru oxidation state as a function of the positions where the peak values of the first-order derivatives are achieved. We extracted the corresponding oxidation state based on the equation and the position measured for the maximal first-order derivative of our strained samples. Three-dimensional (3D) topographic strain distribution images of Ru-ST-12 (i), Ru-ST-5 (j), and Ru-ST-0.6 (k).

RESULTS AND DISCUSSION

The strained electrocatalysts were prepared by impregnating oxygen into Ru nanocluster subsurface. We first synthesized ruthenium oxychlorides as pre-catalysts with Ru, O, and Cl distributed homogeneously via a sol-gel route (Figure S1).^{26,27} The pre-catalysts were then electrochemically reduced through the cyclic voltammetry (CV) treatment to achieve strained Ru nanoclusters of approximately 2 nm in diameter that maintained oxygen at the sublayers but with chlorine completely removed. The resulting core/shell motif has a pure Ru core and a subsurface shell surrounded by oxygen.

We next characterized the core/shell nanostructures (Figure 1). Elemental mappings from electron energy loss spectroscopy (EELS) show the annulus-shaped distribution of oxygen dopants (Figure 1d). The Ar⁺ sputtering X-ray photoelectron spectroscopy (XPS) reveals oxygen resides at the subsurface with a penetration depth of roughly 0.3 nm, while the ruthenium signals are distributed uniformly throughout the entire nanoclusters (Figure S2). The oxygen dopant concentration was calculated by normal XPS to be 6.3 at.% (Figure 1e). X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the O-doped nanoclusters as well as the linear equation plotting Ru oxidation states *versus* the peak positions of the first-order derivatives of the corresponding XANES,²⁸ reveal that Ru has an average valence state of +0.27 induced by dopant-mediated charge balancing (Figures 1f-h) and is primarily a metallic phase. These characterization results collectively identify metallic Ru as the core and O-doped Ru as the shell, suggesting that the oxygen dopants do not alter the subsurface metallic phase.

The ultra-small size of the pre-catalysts plays an important role in forming the core/shell structure. The force of electroreduction pulls all of the anions out of the core lattice along the short diffusion channels, while the quantum confinement of electrons—together with the higher affinity of Ru toward oxygen than chlorine—detains oxygen at the sub-lattice.²⁹ Meanwhile, the force of electrooxidation promotes coordination between residual oxygen and subsurface Ru. Such highly strained configuration cannot be achieved with a larger pre-catalyst (12 nm; Figure S3).

We then sought experimental evidence for the strained configuration. In principle, strain (%) is defined by $(l_{od} - l_{pr})/l_{pr}$, where l_{pr} and l_{od} represent the Ru-Ru bond lengths in pristine and O-doped Ru metals, respectively.³⁰⁻⁴⁸ We measured l_{od} from aberration-corrected high-angle annular dark-field (HAADF) images and mapped the spatial distribution of the strains by geometrical phase analysis (GPA) on the HAADF images.⁴⁹⁻⁵³ Doping 6.3 at.% oxygen into interstitial sites results in an enlarged l_{od} and, thus, 12% tensile strain (Figure 1i).

The strain degree was varied by tailoring the subsurface oxygen concentration. Exquisite controls over electro-redox potential ranges and CV cycles allow for lessening oxygen concentrations to 2.9 and 0.09 at.% (Figures S4 and S5), which in turn trigger strains of 5% and 0.6% (Figures 1j,k and S6), respectively. This trend verifies that subsurface oxygen is responsible for the generation of tensile strain. We call 0.6%, 5%, and 12% strained Ru as Ru-ST-0.6, Ru-ST-5, and Ru-ST-12, respectively. As a counterexample, further increasing oxygen dopant concentration above 6.3 at.% leads to subsurface phase transition from oxygen-doped Ru to ruthenium oxide (Figure S7). This leads to a reduction in the lattice difference ($l_{od} - l_{pr}$) and consequently diminishes strain. The strain values decrease to 10.3%, 8.7%, and 6.5% when the dopant concentrations increase to 6.5, 6.9, and 7.9 at.% (Figure S8), respectively. Thus, it is reasonable to conclude that the highest tensile strain we could achieve in a Ru nanocluster is 12%.

To further validate the strains, we performed supplementary characterization. X-ray diffraction (XRD) patterns display a dopant-dependent shift of the peaks toward a lower degree (Figure S9a), indicating the dopant-

mediated lattice expansion. To quantify this lattice variation, we parsed the HAADF images by plotting the integrated pixel intensity profiles of the lines along the (100) direction (Figures S9b-e). The averaged (100) spacing of Ru-ST-0.6 was 2.34 Å, which nicely matches with the theoretical value of pure Ru. Oxygen doping led to increased values: 2.46 Å for Ru-ST-5 and 2.63 Å for Ru-ST-12. This affords direct and visual evidence for the existence of the tensile strains. We also simulated the Ru K-edge EXAFS of Ru-ST-0.6, Ru-ST-5, and Ru-ST-12 (Figure S9f). The Ru-Ru length was calculated to be shortest for Ru-ST-0.6, modest for Ru-ST-5, and longest for Ru-ST-12 (Figure S9g). For each of the three samples, the differences among the strain values calculated from the GPA, the intensity profiles, and the fitted EXAFS are within 5% (Figure S9h). All of these results clearly justify the strain values determined above.



Figure 2. Performance of the strained nanoclusters for electrocatalytic NITRR to NH₃. (a) NITRR and HER Faradaic efficiencies (FE_{NH3} and FE_{HER}) and (b) NITRR partial current densities (J_{NH3}) of Ru-ST-12, Ru-ST-5 and Ru-ST-0.6 under the applied potentials of -1.0, -0.9, -0.8, -0.7, -0.6, -0.5, -0.4, -0.3, -0.2, -0.1, 0.0, 0.1, and 0.2 V *versus* RHE. (c) FE_{NH3} and J_{NH3} of Ru-ST-12 under the applied potential of -0.2 V *versus* RHE during 100 times of one-hour electrocatalytic NITRR. (d) Comparison of the electrocatalytic NITRR performance of Ru-ST-12 with other extensively reported electrocatalysts.

Having the strained electrocatalysts in hand, we next sought to evaluate the benefit that the strain could bring to ammonia electrosynthesis from NITRR operating under room temperature and atmospheric pressure. The electrocatalysis was performed using Ag/AgCl as the reference electrode, platinum mesh as the counter electrode, and carbon paper coated by the strained catalysts as the working electrode. All of the electrodes were assembled within a H-type cell, an electrolyzer with mature applications in CO₂ and N₂ electroreduction.⁵⁴ The possible effects of other electrocatalytic reactions are minimized by bubbling high-purity argon into nitratecontaining electrolytes throughout NITRR. The products of H₂ and ammonia were quantified by gas chromatography (GC) and by ion chromatograph (IC) and nuclear magnetic resonance (NMR), respectively. We determined the Faradaic efficiency (FE_{NH3}) for nitrate-to-ammonia as well as the ammonia-evolving rate (ν_{NH3}), and the partial current density (J_{NH3}), respectively, according to FE_{NH3} = ($8F \times C_{NH3} \times V$)/Q, $\nu_{NH3} = (C_{NH3} \times V)/(t \times m)$, and $J_{NH3} = (Q \times FE_{NH3})/t$. Here, F is the Faraday constant, C_{NH3} is the molar concentration of measured ammonia, V is the volume of the electrolyte, Q is the charge passing through the catalyst, t is the reaction time, and m is the catalyst mass.⁵⁵

The electrolyte, in which our NITRR worked best, is a mixture of 1 M KOH and 1 M KNO₃ (Figures S10-12). This electrolyte is beneficial for NO_3^- transfer, adsorption, and activation. In addition, the highly alkaline media can also suppress HER.⁵⁶ Under such optimal conditions, our Ru-based electrocatalysts performed NITRR with H₂ and ammonia as the only two products. Other side products including NO_2^- , NO, N₂O, and N₂ were undetectable (Figure S13). The experimental observations that non-electrocatalysis in KOH/KNO₃ and electrocatalysis in KOH both yielded no ammonia and that ¹⁵NH₄⁺ was tracked when ¹⁵NO₃⁻ was employed confirm that the detected ammonia is derived from the nitrate feedstock (Figures S14 and S15).

The tensile strain inhibits HER, which is the only side-reaction of NITRR over Ru-ST-0.6, Ru-ST-5, and Ru-ST-12. This inhibition was more pronounced with catalysts having higher strain (Figure 2a). As a result, the scope of the potentials, in which >96% FE_{NH3} was accessible, for Ru-ST-12 (0.2 to -0.3 V *versus* reversible

hydrogen electrode (RHE)) was broader than those of Ru-ST-5 (0.2 to -0.2 V *versus* RHE) and Ru-ST-0.6 (0.2 to -0.1 V *versus* RHE).

The tensile strain promotes NITRR (Figures 2a,b). At any potentials from 0.0 to -1.0 V versus RHE, FE_{NH3}, J_{NH3} , and v_{NH3} all followed the trend of Ru-ST-12 > Ru-ST-5 > Ru-ST-0.6 implying a strain-dependent performance. J_{NH3} values (recorded at -0.8 V versus RHE) of Ru-ST-12 and Ru-ST-5 were improved to be 77 and 14 times that of Ru-ST-0.6, respectively. We compared $v_{\rm NH3}$ of the three samples with that of Ru nanoclusters possessing 7.9 at.% oxygen dopants and 6.5% strain. $v_{\rm NH3}$ plotted as a function of oxygen dopant concentration follows a volcano-shaped trend rather than linear (Figure S16) and excludes the dominant role of dopant-mediated ligand effects in our NITRR. To further highlight the role of the strain, we prepared Ru nanoclusters having a diameter of around 2 nm, almost no dopant, and close-to-zero strain (called Ru-2nm) (Figures S17). The NITRR activity is much lower than that of any strained Ru nanoclusters reported herein (Figure S18). When $v_{\rm NH3}$ of these strained nanoclusters was normalized with electrochemically active surface area (ECSA),⁵⁷ their performance differences are marginally narrowed (Figures S18 and S19 and Table S1). These results—along with the observation that Ru-ST-12, Ru-ST-5, and Ru-ST-0.6 have nearly commensurate Brunauer-Emmett-Teller (BET) surface areas (Table S1)—indicate that the tensile strains behave as the performance descriptor and that the main contribution of the strains to the performances does not stem from the improvement in the reactive site quantity.

To evaluate the structural stability, we measured Ru and O K-edge XANES of Ru-ST-12 in situ during NITRR at -0.2, -0.6, and -0.8 V *versus* RHE (Figures S20a-d). We observed nearly unshifted XANES edges and an inappreciable decrease in both Ru oxidation state and subsurface Ru-O signal. When operated at -0.8 V *versus* RHE for 1 hour, Ru-ST-12 shows a red-shift edge in the Ru K-edge XANES compared with Ru foil and Ru-2nm (Figure S21). These observations demonstrate that the subsurface Ru-O coordination is robust enough to resist strong currents and that the dopant-triggered strains indeed affect the electrocatalysis. This structural robustness

could be rationalized by the fact that we synthesized Ru-ST-12 by heavy electro-reduction of the pre-catalyst under -1.2 V *versus* RHE, which is more negative than the working potentials (0.2 to -1 V *versus* RHE). Simulations reveal that such a drastic reductive treatment leads to a subsurface reconstruction and, hence, to a strong bonding between Ru and subsurface oxygen. This leads to a prohibitive energy barrier for the dopant diffusion from the lattice interior to the exterior (Figures S22). We also found that high-temperature H₂ reduction could not curtail the subsurface oxygen (Figures S20e-h). These dopants did not increase after exposing Ru-ST-12 in air for 30 days (Figures S20i-I). When the NITRR was run at J_{NH3} over 120 mA cm⁻² for 100 hours, there was no appreciable decay in activity and selectivity (Figure 2c). Furthermore, the after-reaction catalysts showed negligible changes in the strain degree, the location and proportion of the dopants, and the core/shell structure (Figure S23).

The 12% tensile strain empowers Ru-ST-12 with the highest v_{NH3} among all of the ever-reported ammonia-synthesizing scenarios (Figure 2d). Averaging v_{NH3} of 20 independently-synthesized Ru-ST-12 gave 5.56 ± 0.18 mol g_{cat} ⁻¹ h⁻¹ (or 1.17 ± 0.04 mmol h⁻¹ cm⁻²) (Figure S24) outpacing the state-of-the-art v_{NH3} of NITRR electrocatalysis and of Haber-Bosch-, electrocatalysis-, and photocatalysis-based NRR (Tables S2 and S3). To confirm this performance, we determined v_{NH3} via the following four parallel experiments. In the first experiment we used IC as the ammonia detector and ${}^{14}NO_{3}$ ⁻ as the nitrogen source. A second used IC and ${}^{15}NO_{3}$ ⁻, a third employed NMR and ${}^{14}NO_{3}$ ⁻, and a fourth adopted NMR and ${}^{15}NO_{3}$ ⁻ (Figure S25). The experimental results are very close to each other and validate the values seen here. The observation that the CP coated with Ru-ST-12 is far more active than catalyst-absent CP (Figure S26) demonstrates that the CP support acts essentially as a current collector during our NITRR; the superior performance originates primarily from the strained catalyst. For further comparison, we prepared electrocatalysts including strain-free nanocrystals of Ru, Rh, and Ir, transition metal dichalcogenides, carbon materials, metal-organic frameworks (MOFs), and MOFderived single-atom catalysts. When operated under the same conditions, these systems exhibited v_{NH3} 1–4 orders

of magnitude lower than our strained nanoclusters (Figures S27 and S28). The maximum turnover frequency (TOF) of Ru-ST-12 reaches up to 1.79 s⁻¹, which is 29.3-fold higher than that of Rh metal.

We next sought to understand the origin of the strain-induced extremely efficient ammonia electrosynthesis. Theoretical calculations reveal that the nitrate reduction over the strained and strain-free Ru surfaces both proceed through deoxygenation (N-O₃ \rightarrow N-O₂ \rightarrow N-O) and hydrogenation (N-O \rightarrow H-N-O \rightarrow H₂-N-O \rightarrow N-H₂ \rightarrow N-H₃) steps (Figure S29).⁵⁸ The exothermal nature of the entire process can nicely explain why our NITRR is easier-to-achieve than NRR, which is usually endothermal. The observation that the energy is downhill in N-O₃ \rightarrow N-O₂, N-O₂ \rightarrow N-O, N-O \rightarrow H-N-O and considerably uphill in N-O \rightarrow N₂O₂ as the intermediate steps of generating N₂O and N₂ rationalizes the aforementioned absence in our NITRR process of NO₂⁻, NO, N₂O, and N₂. In contrast, these byproducts are routinely seen in other NITRR cases.

Two very interesting findings were also obtained from the theoretical calculations. First, our tensile strain inconspicuously affects the NITRR thermodynamic barriers. Second, the reaction steps are more endothermic in hydrogenation than in deoxygenation. Besides, *in situ* Fourier-transform infrared spectroscopy (FTIR) measurements indicate that the strains pose negligible improvement in nitrate adsorption (Figure S30).¹⁴ These findings suggest that the leading contribution of the strain to the performance is amelioration in the kinetics of the hydrogenation process.



Figure 3. Origin of the strain-dependent NITRR performances. (a) ESR spectra of the solutions obtained after 10 minutes of NITRR electrocatalyzed by Ru-ST-12, Ru-ST-5, and Ru-ST-0.6 in 1 M KOH under argon using DMPO as the •H-trapping reagent. (b, c) Energy diagram of the reaction steps from HNO to H₂NO and from NH₂ to NH₃ over the strained Ru surface. (d) DMPO-involved ESR spectra of the Ru-ST-12-catalyzed NITRR solution in the presence of KNO₃ with the concentration increased from 0 to 1 M. e, NITRR partial current densities and activation energies of Ru-ST-12, Ru-ST-5, and Ru-ST-0.6 with and without DMPO involvement.

Given the intimate correlation of hydrogenation kinetics with the proton, we shifted our attention to the water-splitting process that supplies protons for the NITRR. The HER performance was evaluated by performing electrochemical linear sweep voltammetry measurements in 1 M KOH without KNO₃ (Figure S31). The overpotential at 10 mA cm⁻² follows the tendency of Ru-ST-12 > Ru-ST-5 > Ru-ST-0.6 again confirming the suppressive role played by the tensile strain in water decomposition. To study the underlying reason, we calculated HER elemental steps. The HER over the strained and strain-free surfaces includes Volmer (H₃O⁺ + e⁻ \rightarrow H_{ads} + H₂O) and Heyrovsky (H_{ads} + H₃O⁺ + e⁻ \rightarrow H₂ + H₂O) reactions (Figure S31a).⁵⁹ The strain has a slight impact on the Volmer step but upraises the Heyrovsky reaction energy by 0.94 eV. This result reveals that the strain-induced HER inhibition stems from the increase in the energy required for dimerizing hydrogen to form dihydrogen. As a result, parts of H_{ads} survive, desorb away from the Ru surface, and ultimately evolve into hydrogen radicals (•H) existing in the reaction medium.⁶⁰

To further verify the existence of hydrogen radicals, we turned to the electron spin resonance (ESR) technique using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as the radical trapping reagent. The electrocatalysis was still run in bare 1 M KOH to exclude possible disturbances. It was done under argon to prevent oxygenmediated quenching and for 10 minutes to enable equilibrium between the •H formation and quenching. Nine ESR peaks were observed when the product from the reaction was added into DMPO (Figure 3a). Their intensity ratio approaches 1:1:2:1:2:1:2:1:1 and is consistent with the hyperfine coupling constant calculated as $\alpha_N = 16.3$ G and $\alpha_H = 22.5$ G. This allows for the assignment of the signal to a spin adduct, that is, DMPO-H.^{61,62} The DMPO-H signals were strongest for Ru-ST-12, modest for Ru-ST-5, and weakest for Ru-ST-0.6. This has the opposite trend as a function of the strain with the HER performance. These observations nicely match the HER simulations and experiments above. They verify the existence of •H and support a strain-induced •H formation mechanism. Moreover, higher tensile strain makes hydrogen dimerization more difficult and consequently enhances •H accessibility.

Considering that radicals expedite catalysis,⁶³ we reasoned that the •H radicals detected and confirmed above could expedite our NITRR kinetics. To theoretically support this speculation, we ascertained the kinetic "black box" through calculations of the transition states (TSs) in the hydrogenation steps with and without •H involvement (Figure S32). Our calculation focused on H-N-O \rightarrow H₂-N-O and N-H₂ \rightarrow N-H₃ steps because they play a rate-limiting role for the entire NITRR. In the •H-absent case, a hydrogen-shuttling model was adopted where hydrogen first adsorbs atop Ru and then migrates and adheres on nitrogen-based intermediates. The •Hengaged case donates hydrogen to intermediate molecules. This was shown by a previous simulation study on hydronium-assisted CO₂ electroreduction with hydronium as the dominant existing state of •H in solution.⁶⁴ Compared with the hydrogen-shuttling pathway, the hydronium-involved mode reduces the TS energies of H-N-O \rightarrow H₂-N-O and N-H₂ \rightarrow N-H₃ over the strained surface by 1.09 and 1.26 eV to 0.53 and 0.51 eV (Figures 3b,c), respectively, suggesting the promotion effect of •H on hydrogenating intermediates.

We finally sought to verify experimentally the beneficial effects of \cdot H on the NITRR kinetics. A prerequisite of realizing this goal is to ensure that the reactions of \cdot H with nitrate or NITRR intermediates indeed occur. The ESR spectra of Ru-ST-12 that underwent electrocatalysis in 1 M KOH containing 0–1 M KNO₃ were recorded (Figure 3d). The variation of the KNO₃ concentration from 0 to 1 M caused the DMPO-H-assigned peaks to be gradually attenuated and provides solid evidence for the participation of \cdot H on our NITRR. We introduced DMPO as the \cdot H scavenger into the reaction to directly investigate the effect of \cdot H on our NITRR intermediates.⁶⁵ Before the addition of DMPO, *J*_{NH3} recorded at -0.2 V *versus* RHE for Ru-ST-12, Ru-ST-5, and Ru-ST-0.6 were 128.1, 51.5, and 6.7 mA cm⁻², respectively. The enhancements of Ru-ST-12 and Ru-ST-5 in comparison with Ru-ST-0.6 were as high as 19- and 8- fold (Figure 3e), respectively. After the addition of DMPO to quench \cdot H, *J*_{NH3} of Ru-ST-12 and Ru-ST-5 dramatically decreased to 10.5 and 8.1 mA cm⁻² with enhancement factors dropping to 1.7 and 1.3, respectively. These comparisons clearly indicate the correlation of the strain-dependent NITRR kinetics with the \cdot H engagement.

To further examine the contribution of •H to the kinetics, we compared the NITRR activation energies (E_a) in the absence and presence of DMPO. The reactions were carried out at different temperatures to determine E_a from Arrhenius plots (Figures 3e and S33).⁶⁶ Ru-ST-12 showed the lowest E_a of 2.7 kJ mol⁻¹ in comparison with Ru-ST-5 (11.6 kJ mol⁻¹) and Ru-ST-0.6 (53.2 kJ mol⁻¹). The addition of DMPO increased E_a of Ru-ST-12, Ru-ST-5, and Ru-ST-0.6, by 46.3, 40, and 1.1 kJ mol⁻¹, respectively. This reveals a positive proportional relationship between the DMPO-mediated E_a increment and the •H formation capacity and strongly supports the ability of •H to lower the kinetic barriers. Collectively, the strong dependences of •H, E_a , and v_{NH3} on the strain point toward a strain-enabled-hydrogenation mechanism. Hydrogen radicals reduce kinetic barriers in hydrogenating intermediates into ammonia. Their formation is favored on tensile strain-rich surfaces that lift the H-H coupling energy.

CONCLUSIONS

Our experiments and simulations demonstrate that electrocatalytic NITRR enables ambient ammoniasynthesis with fast rates, high selectivities, and strong current densities when using catalyst of strained Ru nanoclusters. Such performance originates from the tensile lattice strains, while the strain-endowed •H behaves as the dominating reactive species to accelerate NO₃-to-NH₃ electrocatalysis. This benefit results in an ultrahigh rate for ammonia production at room temperature (5.56 mol g_{cat} -¹ h⁻¹ or 1.17 ± 0.04 mmol h⁻¹ cm⁻²). This surpasses that of reported best NITRR electrocatalysis. Our findings suggest that electrocatalytic NITRR is a promising, low-temperature ammonia-synthesis scenario for industrial applications. Our strain-steered radicalevolving idea will open up new possibilities for enhancing other catalytic reactions.

METHODS

Chemicals and materials. Ruthenium chloride hydrate (RuCl₃·xH₂O, 99.98%), rhodium chloride hydrate (RhCl₃·xH₂O, 99.98%), iridium chloride hydrate (IrCl₃·xH₂O, 99.98%), ammonium molybdate tetrahydrate $((NH_4)_6Mo_7O_{24} \cdot 4H_2O, \geq 99\%)$, ammonium paratungstate $((NH_4)_{10}H_2(W_2O_7)_6 \cdot xH_2O, 99.99\%)$, thiourea ($\geq 99\%$), propylene oxide (\geq 99%), 2-methylimidazole (99%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), benzene-1,3,5-tricarboxylic acid (BTC, 95%), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, \geq 98%), fumaric acid (\geq 99%), potassium hydroxide (KOH, ≥99.95%), potassium nitrate (KNO₃, 99.99%), ¹⁵N labelled potassium nitrate (K¹⁵NO₃, >99.5%), lithium nitrate (LiNO₃, >99%), sodium nitrate (NaNO₃, >99%), rubidium nitrate (RbNO₃, 99.7%), cesium nitrate (CsNO₃, 99%), ethanol (\geq 99.5%), methanol (\geq 99.9%), dimethylformamide (DMF, \geq 99%), Nafion solution (5 wt%) and acetone (≥99.9%) were purchased from Sigma-Aldrich. Sodium borohydride (NaBH₄, ≥98%), graphite powder (≥99.85%), sodium nitrate (NaNO₃, ≥99%), potassium permanganate (KMnO₄, >99.5%), concentrated sulfuric acid (H₂SO₄, 95~98%), hvdrogen peroxide (H₂O₂, 30%), hvdrochloric acid (HCl, 36.0~38.0%), and bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O₁, \geq 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%), iron chloride hexahydrate (FeCl₃·6H₂O, 99%), iron acetylacetonate (98%), cobalt acetylacetonate (98%), nickel acetylacetonate (95%), and cetyltrimethylammonium bromide (CTAB, ≥99%) were purchased from Aladdin (China). Carbon paper used as a substrate was purchased from Fuel Cell Store (USA). All the chemicals were directly utilized without further purification.

Preparation of the amorphous ruthenium oxychloride nanoclusters by a modified sol-gel route.^{26,27} Solution A was prepared by dissolving 1.2 mmol of RuCl₃ in 2 mL of ethanol. Solution B was prepared by mixing 2 mL of ethanol with 0.2 mL of ultrapure water (resistivity of 18.00 M Ω ·cm). The solution A and B were kept in a refrigerator for 5 hours for cooling. The solution B and 1 mL of propylene oxide were added drop by drop into the solution A, which lasted for 20 minutes. The mixture was first incubated at 15°C for 48 hours to yield a black gel (see Figure S1a), then added with acetone, next stirred vigorously for 3-5 days, and subsequently sonicated by an ultrasonic cell disrupter in an ice bath for 12 hours. The resulting mixture solution was centrifuged at 5,000 r.p.m. for 5 minutes to remove the large particles in the sample. The supernatant was collected, washed with ethanol and acetone thoroughly, and centrifuged at 15,000 r.p.m. for 10 minutes. These washing procedures were repeated for several times to obtain amorphous ruthenium oxychloride nanoclusters.

Preparation of the amorphous ruthenium oxychloride with the size larger than 10 nm. Solution A was prepared by dissolving 1.2 mmol of RuCl₃ in 2 mL of ethanol. Solution B was prepared by mixing 2 mL of ethanol with 0.2 mL of ultrapure water (resistivity of 18.00 M Ω ·cm). The solution A and B were kept in a refrigerator for 5 hours for cooling. The solution B and 1 mL of propylene oxide were added quickly into the solution A. The mixture was first incubated at 25°C for 96 hours to yield a black gel, then added with acetone and subsequently stirred vigorously for 3-5 days. The resultant mixture solution was washed with ethanol and acetone thoroughly and centrifuged. These washing procedures were repeated for several times to obtain amorphous ruthenium oxychloride with its size larger than 10 nm.

Synthesis of Ru-ST-12, Ru-ST-5 and Ru-ST-0.6 by electrochemical redox treatment of the amorphous ruthenium oxychloride nanoclusters. 10 mg of the amorphous ruthenium oxychloride nanoclusters were added into the mixture of 0.5 mL of ultrapure water (resistivity of 18.00 M Ω ·cm) and 0.6 mL of ethanol. The mixture was sonicated for 30 minutes and then dropped onto a carbon paper (CP, 1 cm² of area). The catalyst-coated CP was placed within a culture dish with a cover until the water and ethanol were naturally evaporated. Electrochemical redox treatment of the amorphous ruthenium oxychloride nanoclusters was performed in 1 M KOH using a three-electrode system with the resultant CP as the working electrode, Ag/AgCl (with 3 M KCl as the filling solution) as the reference electrode, and platinum mesh as the counter electrode. Scanning cyclic voltammetry (CV) across the working electrode was conducted to reduce and re-oxidize the amorphous ruthenium oxychloride nanoclusters to enable the incorporation of oxygen into the subsurface lattice. Ru-ST-12, Ru-ST-5 and Ru-ST-0.6 were obtained by scanning CV, from 0.3 to -1.2 V *versus* RHE for 30 cycles, from 0.3

to -1.6 V *versus* RHE for 60 cycles, and from 0.0 to -2.0 V *versus* RHE for 100 cycles, respectively. Ru-2nm was synthesized by scanning CV from 0.3 to -2.2 V *versus* RHE for 120 cycles, followed by a thermal reduction under H₂ at 300 °C for 6 hours. The Ru nanoclusters with 10.3%, 8.7%, and 6.5% tensile strains were prepared by scanning CV, from 0.3 to -1.0 V *versus* RHE for 25 cycles, from 0.3 to -0.8 V *versus* RHE for 20 cycles, and from 0.3 to -0.6 V *versus* RHE for 30 cycles, respectively. Amorphous ruthenium oxychloride with the size larger than 10 nm was treated by scanning CV from 0.3 to -1.2 V *versus* RHE for 30 cycles. The catalysts used for NITRR were obtained by peeling off the samples from the CP.

Characterization. The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with monochromatized Cu K α radiation ($\lambda = 0.15418$ nm). The morphology of the samples was observed on a JEOL 6700-F field-emission scanning electron microscope (SEM) and a JEOL JSM-2010 high-resolution transmission electron microscopy (HRTEM). For the TEM sample preparation, the powders were suspended in ethanol, and then a drop of this suspension was deposited onto a holey carbon film supported by a copper grid and then dried in air prior to the TEM examination. Chemical compositions and states were analyzed using XPS (Thermo Scientific ESCLAB 250Xi). All binding energies were referenced to the C 1s peak (284.6 eV) arising from the adventitious carbon. Electron spin resonance (ESR) spectra with 5, 5-dimethyl-1pyrroline-*N*-oxide (DMPO) as the hydrogen radical spin-trapping reagent were acquired on a Bruker ESR 300E spectrometer.

HAADF-STEM and EELS elemental mapping. HAADF-STEM images were acquired on a double-aberrationcorrected JEOL JEM-2200FS operated at 200 keV. STEM was also conducted using detectors including bright field (BF-STEM), medium-angle annular dark field (MAADF-STEM) and high-angle annular dark field (HAADF-STEM), all of which were implemented on JEOL JEM 2200-FS equipped with double aberration correctors and operated at 200 keV as well as on a C₅-corrected Nion UltraSTEM100 operated at 100 keV under UHV conditions (typical pressure $<2 \times 10^{-9}$ Torr). Improvement of image quality and suppression of noise in the resultant images were enabled by a wide range of signal detection methods, including the collection of a plethora of successive images of the sample, which were aligned using the SDSD plugin for Digital Micrograph to correct for image drift. EELS elemental mapping was carried out on Gatan UHV Enfina spectrometer and Nion UltraSTEM100. STEM-EELS was conducted using a 1340 channel detector outfitted with energy resolution of 0.2 eV/channel that was comparable to the energy spread of the cold FEG electron gun. Elemental mapping was conducted by the integration of each point of the EELS spectral images through a window of ca. 50 eV above the Ru, O, and Cl EELS edge onsets, following a background subtraction exploiting a power law model. The EELS data collected was de-noised by adopting Principle Component Analysis.

EXAFS measurements. X-ray absorption fine structure (XAFS) spectra were performed at beamline 1W1B station in Beijing Synchrotron Radiation Facility (BSRF) and at beamline14W1 station in Shanghai Synchrotron Radiation Facility (SSRF). The storage rings of BSRF and SSRF were operated at 2.5 GeV with a maximal current of 250 mA and at 3.5 GeV with the current of 300 mA, respectively. The acquired EXAFS data were processed following the standard procedures based on the ATHENA module that was implemented in the software package of IFEFFIT. The k2-weighted EXAFS spectra were acquired by subtracting the post-edge background from the full absorption and then normalizing with the edge-jump step. Subsequently, k2-weighted $\chi(k)$ data at K-edge were Fourier-transformed to real (R) space using a hanning windows ($dk = 1.0 \text{ Å}^{-1}$) to separate the EXAFS contributions from different coordination shells.

Electrocatalytic NITRR Measurements. 5 mg of the catalyst was ultrasonically dispersed in the mixture of 0.4 mL of ultrapure water (resistivity of 18.00 M Ω ·cm), 0.6 mL of ethanol, and 80 µL of Nafion (5 wt%) solution. 10 µL of the resulting catalyst slurry was dropped onto 0.25 cm² of carbon paper (catalyst loading amount: ca. 0.185 mg cm⁻²), followed by natural drying within a culture dish with a cover. A compact film was formed and used as the working electrode in the following electrolysis process. All NITRR experiments were performed using a three-electrode system connected to an electrochemical workstation with a built-in electrochemical impedance spectroscopy (EIS) analyzer. Ag/AgCl (with 3 M KCl as the filling solution) and platinum mesh were used as the reference and counter electrodes, respectively. Electrode potentials were converted to the reversible hydrogen electrode (RHE) reference scale using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.210 \text{ V} + 0.0591 \times \text{pH}$. The experiments were performed in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion117) at room temperature of 25°C. The mixed KOH/KNO₃ solution was used as the electrolyte. The electrolyte in the cathodic compartment was stirred at a rate of 300 r.p.m. during electrolysis. Argon gas was delivered into the cathodic compartment at a rate of 10 standard cubic centimeters per minute (s.c.c.m.). The outlet was immersed in 0.05 M HCl solution in a gas-scrubbing bottle to collect the ammonia evaporated from the cathodic compartment. The ammonia in the cathodic compartment solution and in the gas-scrubbing bottle solution was respectively detected and quantified. Their ammonia sum was used to calculate the Faradaic efficiency and ammonia-evolving rate. IC was used to detect and analyze the products, such as NH_4^+ and NO_2^- . The dosage of the solution for acquiring

IC spectra ranged from 10 μ L to 1 mL. To quantify the ammonia, we prepared NH₄Cl (analytical standard,

Sigma-Aldrich) with different concentrations and obtained a linear equation correlating the ammonia concentration with the area of NH_4^+ peak. In this study, 20 µL of the solution was taken out of the after-reaction electrolyte for analysis. Based on the equation and the peak area measured, we extracted the concentration of the ammonia generated during our NITRR.

We used NMR as a tool to complement IC. For the NMR measurement, the pH of the after-reaction electrolyte was adjusted to 2 by the addition of HCl. 20% DMSO-d6 and maleic acid with the concentration of 1 mM were employed as the internal standard. The ¹H NMR signal was recorded on a Bruker 400 MHz system.

The Faradaic efficiency for NITRR was defined as the quantity of electric charges used for the synthesis of ammonia divided by the total charge passing through the electrodes during the electrolysis. The total amount of produced NH₃ was measured by IC. Because eight electrons are needed to produce one NH₃ molecule, the Faradaic efficiency (FE_{NH3}), ammonia-evolution rate (v_{NH3}), and partial current density (J_{NH3}) can be calculated as follows: FE_{NH3} = ($8 \times F \times C_{NH3} \times V$)/Q, $v_{NH3} = (C_{NH3} \times V)/(t \times m)$, and $J_{NH3} = (Q \times FE_{NH3})/t$, where *F* is the Faraday constant, C_{NH3} is the molar concentration of measured ammonia, *V* is the volume of the electrolyte, *Q* is the amount of charges passing through the catalyst, *t* is the reaction time and *m* is the catalyst mass. All of the current densities reported in this work were calculated based on the geometric electrode area.

The catalysts' ECSA was calculated from the double-layer capacitance method using the equation of ECSA = C_{dl}/C_s , where C_{dl} is the catalyst's double-layer capacitance and the C_s stands for the catalyst's specific capacitance or the capacitance of an atomic-level ultra-smooth planar surface of the catalyst per unit area under equal electrolyte surroundings. Because our NITRRs were performed in alkaline medium, we adopted $C_s = 0.040 \text{ mF cm}^{-2.57}$ To determine the C_{dl} , CV was scanned within a non-faradaic region (-0.45 to -0.65 V *versus* RHE) at different scan rate (30, 60, 90, 120, and 150 mV s⁻¹). The capacitive current differences, (Ja – J_b)/2, were plotted as a function of the CV scan rates. The slope of the obtained linear equation is the C_{dl}.

TOF was calculated via the equation of TOF (s⁻¹) = (Q × FE_{NH3} × A)/(8 × t × F × N_{Ru}),²⁷ where Q is the amount of charges passing through the catalyst, FE_{NH3} is the Faradaic efficiency for electrocatalytic NITRR to ammonia, A is the geometric area of the electrode, t is the reaction time, F is the Faraday constant, and N_{Ru} is the mole number of Ru atoms in the electrode. The N_{Ru} was calculated via the equation of N_{Ru} = (M_{loading} × A_{BET} × R_{Ru/RuO})/(S_{RuO} × N_A), where M_{loading} is the loading mass of the catalyst, A_{BET} is the specific surface area, R_{Ru/RuO} is the molar percentage of Ru in the catalyst, S_{RuO} is the unit cell's surface area, and N_A is Avogadro's constant. For temperature-dependent measurements, the sealed glass cell was suspended in a thermostatic silicone oil bath.

The electrodes were passed through holes in the lid with an O-ring slightly larger than the electrodes to minimize evaporative loss. As expected, the kinetics of the nitrate reduction increased with temperature, reflecting the

temperature dependence of the chemical rate constant. The temperature dependence is approximately proportional to $\exp(-\Delta H^*/kT)$, where ΔH^* is the apparent enthalpy of activation (hereafter simply termed as the activation energy), and k is the Boltzmann's constant. Specifically, the apparent electrochemical activation energy (*E*a) for NRR can be determined using the Arrhenius relationship

$$\frac{\partial(\log i_k)}{(\partial(1/T)}|_{\nu} = \frac{\Delta H *}{2.3}$$

where i_k is the kinetic current at v = -200 mV, T is the temperature, and R is the universal gas constant.

Computational Details. All computations were performed by means of density functional theory (DFT) methods using the Vienna *Ab initio* Simulation Package (VASP) code except the molecular orbital analysis in external electron field. The exchange-correlation functionals described by Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional, using a plane-wave cut-off energy of 450 eV, and representative 4*4 Ru super-cells were employted to describe strained Ru. The Brillouin zone was sampled by 3*3*1 k-points using the Monkhorst–Pack scheme. The vacuum thickness was larger than 20 Å between two Ru layers to avoid interactions between periodic images. During optimization, the energy and force converged to $10^{-4} \text{ eV}/\text{atom}$ and 0.02 eV/Å. Thermal and zero-point energy (ZPE) corrections were calculated over G points.

The Gibbs free energy change (ΔG) for every elemental step was determined as follows: $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the electronic energy difference directly obtained from DFT calculations, ΔZPE is the change in zero-point energies, *T* is the temperature (T = 298.15 K), and ΔS is the entropy change.

The zero-point energies and entropies of the NITRR species were computed from the vibrational frequencies, in which only the adsorbate vibrational modes were calculated explicitly, while the catalyst sheet was fixed. The entropies and vibrational frequencies of molecules in the gas phase were taken from the NIST database.

ASSOCIATED CONTENT

Supporting Information

Figures S1-S33, Tables S1-S3, and additional references

AUTHOR INFORMATION

Corresponding Authors

*jimyu@cuhk.edu.hk

2 3	
4 5	
6 7	(
, 8 9	
10 11	
12 13	
14 15]
16 17	
18 19	•
20 21]
22 23	
24 25	
26 27	
28 29	,
30 31	
32 33	
34 35 26	,
36 37	
38 39 40	,
40 41 42	
42 43 44	1
45 46	
47 48	
49	
50 51 52	
53 54	
55 56	-
57 58	
59	

*zhanglz@mail.ccnu.edu.cn

ORCID

Yi Du: 0000-0003-1932-6732

Weichang Hao: 0000-0002-1597-7151

Po Keung Wong: 0000-0003-3081-960X

Jianfang Wang: 0000-0002-2467-8751

Lizhi Zhang: 0000-0002-6842-9167

Jimmy C. Yu: 0000-0001-9886-3725

Author Contributions

^v J.L. and G.Z. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by Research Grants Council of the Hong Kong Special Administrative Region (Project No. 14304019), Natural Science Funds for Distinguished Young Scholars (Grant No. 21425728), National Science Foundation of China (Grant No. 51472100), the 111 Project (Grant No. B17019), and Australian Research Council (DP160102627, DP170101467, and FT180100585). This work has benefited from National Synchrotron Radiation Laboratory in Beijing and Shanghai for the characterization. We thank the National Supercomputer Center in Jinan for providing high performance computation.

REFERENCES

(1) Chen, J. G.; Crooks, R. M.; Seefeldt, L. C.; Bren, K. L.; Bullock, R. M.; Darensbourg, M. Y.; Holland, P. L.; Hoffman, B.; Janik, M. J.; Jones, A. K. Inorganic chemistry beyond fossil fuel-driven nitrogen transformations. *Science* **2018**, *360*, eaar6611.

(2) Haber, F.; Rossignol, R. L. Über die technische darstellung von ammoniak aus den elementen. Z. *Elektrochem. Angew. Phys. Chem.* **1913**, *19*, 53–72.

(3) Kandemir, T.; Schuster, M. E.; Senyshyn, A.; Behrens, M.; Schlögl, R. The haber-bosch process revisited: on the real structure and stability of "ammonia iron" under working conditions. *Angew. Chem., Int. Ed.* **2013**, *52*, 12723–12726.

(4) Liu, Y.; Cheng, M.; He, Z.; Gu, B.; Xiao, C.; Zhou, T.; Guo, Z.; Liu, J.; He, H.; Ye, B.; Pan, B.; Xie, Y. Pothole-rich ultrathin WO₃ nanosheets triggering N≡N bond activation of nitrogen for direct nitrate photosynthesis. *Angew. Chem., Int. Ed.* 2019, *58*, 731–735.

(5) Xue, Z. H.; Zhang, S. N.; Lin, Y. X.; Su, H.; Zhai, G. Y.; Han, J. T.; Yu, Q. Y.; Li, X. H.; Antonietti, M.; Chen, J. S. Electrochemical reduction of N₂ into NH₃ by donor-acceptor couples of Ni and Au nanoparticles with a 67.8% faradaic efficiency. *J. Am. Chem. Soc.* **2019**, *141*, 14976–14980.

(6) Liu, X.; Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z. Building up a picture of the electrocatalytic nitrogen reduction activity of transition metal single-atom catalysts. *J. Am. Chem. Soc.* **2019**, *141*, 9664-9672.

(7) Huang, P.; Liu, W.; He, Z.; Xiao, C.; Yao, T.; Zou, Y.; Wang, C.; Qi, Z.; Tong, W.; Pan, B.; Wei, S.; Xie, Y. Single atom accelerates ammonia photosynthesis. *Sci. China: Chem.* 2018, *61*, 1187–1196.

(8) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Norskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: insights into materials design. *Science* **2017**, *355*, eaad4998.

(9) Rosca, V.; Duca, M.; de Groot, M. T.; Koper, M. T. Nitrogen cycle electrocatalysis. *Chem. Rev.* 2009, *109*, 2209–2244.

(10) Hirakawa, H.; Hashimoto, M.; Shiraishi, Y.; Hirai, T. Selective nitrate-to-ammonia transformation on surface defects of titanium dioxide photocatalysts. *ACS Catal.* **2017**, *7*, 3713–3720.

(11) Duca, M.; Koper, M. T. M. Powering denitrification: the perspectives of electrocatalytic nitrate reduction. Energy Environ. Sci. 2012, 5, 9726–9742.

(12) Rogan, W. J.; Brady, M. T. Drinking water from private wells and risks to children. Pediatrics 2009, 123, e1123-e1137.

(13) Dima, G. E.; de Vooys, A. C. A.; Koper, M. T. M. Electrocatalytic reduction of nitrate at low concentration on coinage and transition-metal electrodes in acid solutions. J. Electroanal. Chem. 2003, 554, 15–23.

(14) Pérez-Gallent, E.; Figueiredo, M. C.; Katsounaros, I.; Koper, M. T. M. Electrocatalytic reduction of nitrate on copper single crystals in acidic and alkaline solutions. *Electrochim. Acta* 2017, 227, 77-84.

(15) Wang, Y.; Zhou, W.; Jia, R.; Yu, Y.; Zhang, B. Unveiling the activity origin of a copper-based electrocatalyst for selective nitrate reduction to ammonia. Angew. Chem., Int. Ed. 2020, DOI: 10.1002/anie.201915992.

(16) McEnaney, J. M.; Blair, S. J.; Nielander, A. C.; Schwalbe, J. A.; Koshy, D. M.; Cargnello, M.; Jaramillo, T. F. Electrolyte engineering for efficient electrochemical nitrate reduction to ammonia on a titanium electrode. ACS Sustainable Chem. Eng. 2020, DOI: 10.1021/acssuschemeng.9b05983.

(17) Lu, C.; Lu, S.; Qiu, W.; Liu, Q. Electroreduction of nitrate to ammonia in alkaline solutions using hydrogen storage alloy cathodes. *Electrochim. Acta* 1999, 44, 2193–2197.

(18) Jia, R.; Wang, Y.; Wang, C.; Ling, Y.; Yu, Y.; Zhang, B. Boosting selective nitrate electroreduction to ammonium by constructing oxygen vacancies in TiO₂. ACS Catal. 2020, DOI: 10.1021/acscatal.9b05260.

(19) Butcher, D. P.; Gewirth, A. A. Nitrate reduction pathways on Cu single crystal surfaces: effect of oxide and Cl⁻. Nano Energy 2016, 29, 457–465.

(20) Duca, M.; van der Klugt, B.; Hasnat, M. A.; Machida, M.; Koper, M. T. M. Electrocatalytic reduction of nitrite on a polycrystalline rhodium electrode. J. Catal. 2010, 275, 61-69.

(21) Yang, J.; Sebastian, P.; Duca, M.; Hoogenboom, T.; Koper, M. T. M. pH dependence of the electroreduction of nitrate on Rh and Pt polycrystalline electrodes. Chem. Commun. 2014, 50, 2148–2151.

(22) Siriwatcharapiboon, W.; Kwon, Y.; Yang, J.; Chantry, R. L.; Li, Z.; Horswell, S. L.; Koper, M. T. M. Promotion effects of Sn on the electrocatalytic reduction of nitrate at Rh nanoparticles. *Chem. Electrochem.* **2014**, *1*, 172–179.

(23) Guo, S.; Heck, K.; Kasiraju, S.; Qian, H.; Zhao, Z.; Grabow, L. C.; Miller, J. T.; Wong, M. S. Insights into nitrate reduction over indium-decorated palladium nanoparticle catalysts. *ACS Catal.* **2018**, *8*, 503–515.

(24) Bae, S. E.; Stewart, K. L.; Gewirth, A. A. Nitrate adsorption and reduction on Cu(100) in acidic solution. *J. Am. Chem. Soc.* **2007**, *129*, 10171–10180.

(25) Liu, J. X.; Richards, D.; Singh, N.; Goldsmith, B. R. Activity and selectivity trends in electrocatalytic nitrate reduction on transition metals. *ACS Catal.* **2019**, *9*, 7052–7064.

(26) Augustyn, V.; Come, J.; Lowe, M. A.; Kim, J. W.; Taberna, P. L.; Tolbert, S. H.; Abruña, H. D.; Simon, P.; Dunn, B. High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance. *Nat. Mater.* 2013, *12*, 518–522.

(27) Zhang, B.; Zheng, X.; Voznyy, O.; Comin, R.; Bajdich, M.; Garcia-Melchor, M.; Han, L.; Xu, J.; Liu, M.; Zheng, L.; Garcia de Arquer, F. P.; Dinh, C. T.; Fan, F.; Yuan, M.; Yassitepe, E.; Chen, N.; Regier, T.; Liu, P.; Li, Y.; De Luna, P.; Janmohamed, A.; Xin, H. L.; Yang, H.; Vojvodic, A.; Sargent, E. H. Homogeneously dispersed multimetal oxygen-evolving catalysts. *Science* 2016, *352*, 333–337.

(28) Kim, J.; Shih, P. C.; Tsao, K. C.; Pan, Y. T.; Yin, X.; Sun, C. J.; Yang, H. High-performance pyrochloretype yttrium ruthenate electrocatalyst for oxygen evolution reaction in acidic media. *J. Am. Chem. Soc.* **2017**, *139*, 12076–12083.

(29) Teschner, D.; Novell-Leruth, G.; Farra, R.; Knop-Gericke, A.; Schlögl, R.; Szentmiklosi, L.; Hevia, M. G.;
Soerijanto, H.; Schomäcker, R.; Pérez-Ramírez, J. In situ surface coverage analysis of RuO₂-catalysed HCl oxidation reveals the entropic origin of compensation in heterogeneous catalysis. *Nat. Chem.* 2012, *4*, 739–745.

(30) Luo, M. C.; Guo, S. J. Strain-controlled electrocatalysis on multimetallic nanomaterials. *Nat. Rev. Mater.*2017, 2, 17059.

(31) Xia, Z.; Guo, S. Strain engineering of metal-based nanomaterials for energy electrocatalysis. *Chem. Soc. Rev.* 2019, *48*, 3265–3278.

(32) Bu, L. Z.; Zhang, N.; Guo, S. J.; Zhang, X.; Li, J.; Yao, J. L.; Wu, T.; Lu, G.; Ma, J. Y.; Su, D.; Huang, X. Q. Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis. *Science* **2016**, *354*, 1410–1414.

(33) Zhu, H.; Gao, G.; Du, M.; Zhou, J.; Wang, K.; Wu, W.; Chen, X.; Li, Y.; Ma, P.; Dong, W.; Duan, F.; Chen, M.; Wu, G.; Wu, J.; Yang, H.; Guo, S. Atomic-scale core-shell structure engineering induces precise tensile strain to boost hydrogen evolution catalysis. *Adv. Mater.* 2018, *30*, 1707301.

(34) Wang, H. T.; Xu, S. C.; Tsai, C.; Li, Y. Z.; Liu, C.; Zhao, J.; Liu, Y. Y.; Yuan, H. Y.; Abild-Pedersen, F.; Prinz, F. B.; Nørskov, J. K.; Cui, Y. Direct and continuous strain control of catalysts with tunable battery electrode materials. *Science* **2016**, *354*, 1031–1036.

(35) Tang, C. Y.; Zhang, N.; Ji, Y. J.; Shao, Q.; Li, Y. Y.; Xiao, X. H.; Huang, X. Q. Fully tensile strained Pd₃Pb/Pd tetragonal nanosheets enhance oxygen reduction catalysis. *Nano Lett.* **2019**, *19*, 1336–1342.

(36) Feng, Q.; Zhao, S.; He, D.; Tian, S.; Gu, L.; Wen, X.; Chen, C.; Peng, Q.; Wang, D.; Li, Y. Strain engineering to enhance the electrooxidation performance of atomic-layer Pt on intermetallic Pt₃Ga. *J. Am. Chem. Soc.* **2018**, *140*, 2773–2776.

(37) Yao, Y.; Hu, S.; Chen, W.; Huang, Z. Q.; Wei, W.; Yao, T.; Liu, R.; Zang, K.; Wang, X.; Wu, G.; Yuan, W.; Yuan, T.; Zhu, B.; Liu, W.; Li, Z.; He, D.; Xue, Z.; Wang, Y.; Zheng, X.; Dong, J.; Chang, C. R.; Chen, Y.; Hong, X.; Luo, J.; Wei, S.; Li, W. X.; Strasser, P.; Wu, Y.; Li, Y. Engineering the electronic structure of single atom Ru sites via compressive strain boosts acidic water oxidation electrocatalysis. *Nat. Catal.* 2019, *2*, 304–313.

(38) Zhou, D. J.; Wang, S.; Jia, Y.; Xiong, X.; Yang, H.; Liu, S.; Tang, J.; Zhang, J.; Liu, D.; Zheng, L. R.; Kuang, Y.; Sun, X.; Liu, B. NiFe hydroxide lattice tensile strain: enhancement of adsorption of oxygenated intermediates for efficient water oxidation catalysis. *Angew. Chem., Int. Ed.* 2019, *58*, 736–740.

(39) Hsu, S. H.; Hung, S. F.; Wang, H. Y.; Xiao, F. X.; Zhang, L.; Yang, H.; Chen, H.; Lee, J. M.; Liu, B. Tuning the electronic spin state of catalysts by strain control for highly efficient water electrolysis. *Small Methods* **2018**, *2*, 1800001.

(40) Yan, K.; Maark, T. A.; Khorshidi, A.; Sethuraman, V. A.; Peterson, A. A.; Guduru, P. R. The influence of elastic strain on catalytic activity in the hydrogen evolution reaction. *Angew. Chem., Int. Ed.* **2016**, *55*, 6175–6181.

(41) Kitchin, J. R.; Nørskov, J. K.; Barteau, M. A.; Chen, J. G. Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces. *Phys. Rev. Lett.* **2004**, *93*, 156801.

(42) Sethuraman, V.; Vairavapandian, D.; Lafouresse, M.; Adit Maark, T.; Karan, N.; Sun, S.; Bertocci, U.;
Peterson, A.; Stafford, G.; Guduru, P. Role of elastic strain on electrocatalysis of oxygen reduction reaction on Pt. *J. Phys. Chem. C* 2015, *119*, 19042–19052.

(43) Meng, G.; Sun, W.; Mon, A. A.; Wu, X.; Xia, L.; Han, A.; Wang, Y.; Zhuang, Z.; Liu, J.; Wang D.; Li, Y. Strain regulation to optimize the acidic water oxidation performance of atomic-layer IrO_x. *Adv. Mater.* 2019, *31*, 1903616.

(44) Khorshidi, A.; Violet, J.; Hashemi, J.; Peterson, A. A. How strain can break the scaling relations of catalysis. *Nat. Catal.* **2018**, *1*, 263–268.

(45) Wang, X.; Zhu, Y.; Vasileff, A.; Jiao, Y.; Chen, S.; Song, L.; Zheng, B.; Zheng, Y.; Qiao, S. Z. Strain effect in bimetallic electrocatalysts in the hydrogen evolution reaction. *ACS Energy Lett.* **2018**, *3*, 1198–1204.

(46) Yan, K.; Kim, S. K.; Khorshidi, A.; Guduru, P. R.; Peterson, A. A. High elastic strain directly tunes the hydrogen evolution reaction on tungsten carbide. *J. Phys. Chem. C* **2017**, *121*, 6177–6183.

(47) Humbert, M.; Chen, J. G. Correlating hydrogenation activity with binding energies of hydrogen and cyclohexene on M/Pt(111) (M = Fe, Co, Ni, Cu) bimetallic surfaces. *J. Catal.* **2008**, *257*, 297–306.

(48) Mao, J.; Chen, W.; Sun, W.; Chen, Z.; Pei, J.; He, D.; Lv, C.; Wang, D.; Li, Y. Rational control of the selectivity of a ruthenium catalyst for hydrogenation of 4-nitrostyrene by strain regulation. *Angew. Chem., Int. Ed.* **2017**, *56*, 11971–11975.

(49) Ling, T.; Yan, D.; Wang, H.; Jiao, Y.; Hu, Z.; Zheng, Y.; Zheng, L.; Mao, J.; Liu, H.; Du, X.; Jaroniec, M.;
Qiao, S. Z. Activating cobalt (II) oxide nanorods for efficient electrocatalysis by strain engineering. *Nat. Commun.* 2017, *8*, 1509.

(50) Li, H.; Du, M.; Mleczko, M. J.; Koh, A. L.; Nishi, Y.; Pop, E.; Bard, A. J.; Zheng, X. Kinetic study of hydrogen evolution reaction over strained MoS₂ with sulfur vacancies using scanning electrochemical microscopy. *J. Am. Chem. Soc.* **2016**, *138*, 5123–5129.

1	
2 3	
4	
5	
6 7	
, 8	
9	
10	
11	
13	
14	
15	
17	
18	
19	
20 21	
22	
23	
24	
26	
27	
28	
29 30	
31	
32	
33 34	
35	
36	
37 38	
39	
40	
41 42	
43	
44	
45 46	
40 47	
48	
49 50	
50 51	
52	
53	
54 55	
56	
57	
58	
74	

(51) Li, Z.; Fu, J. Y.; Feng, Y.; Dong, C. K.; Liu, H.; Du, X. W. A silver catalyst activated by stacking faults for the hydrogen evolution reaction. *Nat. Catal.* **2019**, *2*, 1107–1114.

(52) You, B.; Tang, M. T.; Tsai, C.; Abild-Pedersen, F.; Zheng, X.; Li, H. Enhancing electrocatalytic water splitting by strain engineering. *Adv. Mater.* **2019**, *31*, 1807001.

(53) Oh, M. H.; Cho, M. G.; Chung, D. Y.; Park, I.; Kwon, Y. P.; Ophus, C.; Kim, D.; Kim, M. G.; Jeong, B.; Gu, X. W.; Jo, J.; Yoo, J. M.; Hong, J.; McMains, S.; Kang, K.; Sung, Y. E.; Alivisatos, A. P.; Hyeon, T. Design and synthesis of multigrain nanocrystals via geometric misfit strain. *Nature* 2020, *577*, 359–363.

(54) Ross, M. B.; De Luna, P.; Li, Y.; Dinh, C. T.; Kim, D.; Yang, P.; Sargent, E. H. Designing materials for electrochemical carbon dioxide recycling. *Nat. Catal.* **2019**, *2*, 648–658.

(55) Martínez, J.; Ortiz, A.; Ortiz, I. State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates. *Appl. Catal., B* **2017**, *207*, 42–59.

(56) Lu, B.; Guo, L.; Wu, F.; Peng, Y.; Lu, J. E.; Smart, T. J.; Wang, N.; Finfrock, Y. Z.; Morris, D.; Zhang, P.;
Li, N.; Gao, P.; Ping, Y.; Chen, S. Ruthenium atomically dispersed in carbon outperforms platinum toward hydrogen evolution in alkaline media. *Nat. Commun.* 2019, *10*, 631.

(57) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16977–16987.

(58) Huo, X.; Van Hoomissen, D. J.; Liu, J.; Vyas, S.; Strathmann, T. J. Hydrogenation of aqueous nitrate and nitrite with ruthenium catalysts. *Appl. Catal.*, *B* **2017**, *211*, 188–198.

(59) Zheng, Y.; Jiao, Y.; Zhu, Y.; Li, L. H.; Han, Y.; Chen, Y.; Jaroniec, M.; Qiao, S. Z. High electrocatalytic hydrogen evolution activity of an anomalous ruthenium catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 16174–16181.

(60) Zhu, L.; Lin, H.; Li, Y.; Liao, F.; Lifshitz, Y.; Sheng, M.; Lee, S. T.; Shao, M. A rhodium/silicon coelectrocatalyst design concept to surpass platinum hydrogen evolution activity at high overpotentials. *Nat. Commun.* **2016**, *7*, 12272.

(61) Wang, Y. F.; Zhao, D.; Ji, H. W.; Liu, G. L.; Chen, C. C.; Ma, W. H.; Zhu, H. Y.; Zhao, J. C. Sonochemical hydrogen production efficiently catalyzed by Au/TiO₂. *J. Phys. Chem. C* **2010**, *114*, 17728–17733.

(62) Kohno, M.; Mokudai, T.; Ozawa, T.; Niwano, Y. Free radical formation from sonolysis of water in the presence of different gases. *J. Clin. Biochem. Nutr.* **2011**, *49*, 96–101.

(63) Tse, E. C. M.; Barile, C. J.; Kirchschlager, N. A.; Li, Y.; Gewargis, J. P.; Zimmerman, S. C.; Hosseini, A.; Gewirth, A. A. Proton transfer dynamics control the mechanism of O₂ reduction by a non-precious metal electrocatalyst. *Nat. Mater.* **2016**, *15*, 754–759.

(64) Seifitokaldani, A.; Gabardo, C. M.; Burdyny, T.; Dinh, C. T.; Edwards, J. P.; Kibria, M. G.; Bushuyev, O. S.;
Kelley, S. O.; Sinton, D.; Sargent, E. H. Hydronium-induced switching between CO₂ electroreduction pathways. *J. Am. Chem. Soc.* 2018, *140*, 3833–3837.

(65) Makino, K.; Imaishi, H.; Morinishi, S.; Hagiwara, T.; Takeuchi, T.; Murakami, A.; Nishi, M. An artifact in the ESR spectrum obtained by spin trapping with DMPO. *Free Radical Res. Commun.* **1989**, *6*, 19–28.

(66) Liu, M.; Pang, Y.; Zhang, B.; De Luna, P.; Voznyy, O.; Xu, J.; Zheng, X.; Dinh, C. T.; Fan, F.; Cao, C.; de Arquer, F. P. G.; Safaei, T. S.; Mepham, A.; Klinkova, A.; Kumacheva, E.; Filleter, T.; Sinton, D.; Kelley, S. O.; Sargent, E. H. Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration. *Nature* 2016, *537*, 382–386.

