

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Metal-sulfur linkages achieved by organic tethering of Ru nanocrystals for enhanced electrochemical nitrogen reduction

Authors: Muhammad Ibrar Ahmed, Chuangwei Liu, Yong Zhao, Wenhao Ren, Xianjue Chen, Sheng Chen, and Chuan Zhao

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

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202009435

Link to VoR: https://doi.org/10.1002/anie.202009435

WILEY-VCH

COMMUNICATION

WILEY-VCH

Metal-sulfur linkages achieved by organic tethering of Ru nanocrystals for enhanced electrochemical nitrogen reduction

Muhammad Ibrar Ahmed,^{[a]+} Chuangwei Liu,^{[b]+} Yong Zhao,^[a] Wenhao Ren,^[a] Xianjue Chen,^[a] Sheng Chen,^[a] and Chuan Zhao^{*[a]}

[a] M.I. Ahmed ^[+], Dr. Y. Zhao, Dr. W. Ren, Dr. X. Chen, Dr. S. Chen, Prof. C. Zhao* School of Chemistry, University of New South Wales, Sydney, 2052, Australia <u>chuan.zhao@unsw.edu.au</u>
[b] Dr. C. Liu ^[+] Department of Energy Conversion and Storage, Technical University of Denmark, Lyngby, 2800, Denmark

[+] These authors contributed equally to this work.

Abstract: Electrochemical nitrogen reduction (NRR) is a clean, facile, and sustainable approach towards ammonia (NH₃) production at ambient conditions. However, the inert nature of nitrogen and competitive hydrogen evolution reaction (HER) command it towards sluggish kinetics and poor selectivity. Inspired by the metal-sulfur (M-S) linkages in the nitrogenase enzyme, here we show a surface modification strategy to modulate the electronic structure and improve the N₂ availability on the catalytic surface, which suppresses the HER and synergistically improved the rate of NH₃ production. Thus, ruthenium nanocrystals anchored on reduced graphene oxide (Ru/rGO) are modified with different aliphatic thiols to achieve M-S linkages. A high faradaic efficiency (11%) with an improved NH₃ yield (50 µg h⁻¹ mg⁻¹) is achieved at -0.1 V vs RHE in acidic conditions by using dodecanethiol. DFT calculations reveal intermediate N₂ adsorption and desorption of the product is achieved by electronic structure modification along with the suppression of the HER by surface modification. The modified catalyst exerts excellent stability and recyclability for NH₃ production, as confirmed by rigorous control experiments including the ¹⁵N isotope labeling experiments.

Ammonia (NH₃) is an important commodity in the food and chemical industry. Due to its high gravimetric hydrogen content and energy density, it is also considered as a promising hydrogen carrier.^[1,2] Haber-Bosch (HB) process has been producing NH₃ for more than 100 years, which consumes energy and emits carbon dioxide in vast amounts. Therefore, it is highly desirable to develop a clean, facile, and sustainable alternative to this process. Electrochemical nitrogen reduction reaction (NRR) powered by renewable energy sources is potentially a sustainable approach for nitrogen (N₂) fixation. However, the inert nature of N2 and intensive competition from hydrogen evolution reaction (HER) impede its performance with sluggish kinetics and low selectivity.^[3-7] Ru-based transition metal catalysts are active catalysts for NRR at ambient conditions that can activate and polarize the inert N₂ molecule by accepting and donating electronic density.^[8–11] However, they are limited by the low selectivity and faradaic efficiency (FE) towards NH₃ that could be attributed to the high affinity of H-adsorption on the Ru surface.

To overcome this selectivity challenge, Norskov et al. proposed different strategies to limit proton and electron flow to the catalyst surface,^[12] such as (i) decreasing the concentration

of proton, and (*ii*) limiting the proton transfer rate. The activity of proton in bulk electrolytes can generally be controlled by using non-aqueous solvents or aprotic ionic liquid-based electrolytes. However, their use at a large scale with high current densities is limited due to the high viscosity, low conductivity, and mass transport, as well as complex setup requirements for NRR.^[13] In this regard, surface modification by organic tethering is a facile strategy that can induce hydrophobicity to limit the proton transfer on the surface of the catalyst by creating a barrier that resists the flow of proton without interruption to the flow of non-polar moieties like N₂ and CO₂.^[14–16] This results in the enhanced availability of reactant moieties on the surface of the catalyst as compared to the proton.

Nitrogenase in nature has evolved M-S linkages in the enzyme for prebiotic N₂ fixation to help retain low-valence metal localized charge density sites^[17,18] which can facilitate the N₂ adsorption and subsequent activation and polarization.^[19] Moreover, the proton-accepting ability of sulfur is also supporting the hydrogenation steps in the NRR pathway. Inspired by nitrogenase, here we show a Ru-based catalyst with Ru-S linkages for NRR, achieved by facile surface modification of Ru with aliphatic thiols. Thiols are known to form self-assembled monolayers (SAM) on Ru surfaces.[20,21] The organic and hydrophobic nature of the SAM limits proton transfer while allowing N₂ transport to the surface of the catalyst. Importantly, the formation of Ru-S linkage also modifies the electronic structure to facilitate the N2 adsorption, activation, and polarization on the active site (Ru).^[22] This enhanced interaction with N2 improves the overall selectivity of NRR process by suppression of HER. A cumulative effect of HER suppression, electronic structure modulation, and enhanced N₂ availability results in enhanced overall NRR performance. Compared with non-modified Ru nanocrystals anchored on reduced graphene oxide (Ru/rGO), significantly enhanced FE of 11% and improved rate of NH₃ production (50 μ g h⁻¹ mg⁻¹) is achieved at -0.1 V vs RHE on Ru nanocrystals anchored on reduced graphene oxide modified with dodecanethiol (Ru/rGO-C12). Also, control samples of Ru/rGO modified with different alkyl chain lengths including hexanethiol (Ru/rGO-C6), and octadecanethiol (Ru/rGO-C18) are also evaluated for NRR. Rigorous analysis including ¹⁵N isotope labeling experiments is employed for NRR detection following the recently developed protocols.^[23] Due to its facile and versatile nature, this approach can be employed to different other catalysts to ameliorate the NRR selectivity.



Figure 1. a) Schematic illustration of synthesis and modification of Ru/rGO with aliphatic thiols, b) TEM image, c) HR-TEM image, inset c) FT pattern, and TEM-EDS elemental mapping of Ru/rGO-C12.

A solvothermal approach is used for the development of Ru/rGO by employing ethylene glycol and sodium oleate as reducing and structure-directing agent (Figure 1a).^[24] Surface modification of these nanocrystals is done by stirring in 0.05 M ethanolic solution of different aliphatic thiols for 24 h. Transmission electron microscopy (TEM) image of Ru/rGO-C12 reveals a homogenous distribution of Ru nanocrystals on the surface of rGO with a size of around 5-8 nm (Figure 1b). Furthermore, crystalline nature of Ru nanocrystals is also confirmed by high-resolution transmission electron microscopy (HR-TEM) (Figure 1c), and fast Fourier transform analysis indicating lattice fringes of 0.22 nm corresponding to the (101) lattice plane of Ru, which is consistent with the XRD analysis (Figure S5a). In addition, elemental mapping confirms the incorporation of sulfur (S) after surface modification (also see Figure S1 line spectrum). Similarly, Figures S2-S4 reveal the morphological elucidation with the elemental mapping of control samples.

Figure S5a shows the XRD patterns of all prepared samples with broad peaks that reflect the small size of the Ru nanocrystals. A peak at 23° is ascribed to the presence of rGO. suggesting the reduction of graphene oxide during the solvothermal process. Peaks at 38.4°, 42.3°, and 44.0° are the characteristic peaks of the Ru hexagonal phase (JCPDS-006-0663) that can be ascribed to the (100), (002) and (101) planes, respectively. The overall decrease in the intensity of Ru peaks is observed after the modification with different thiols due to the amorphous nature of carbon. Fourier transform infrared spectroscopy (FTIR) is conducted to investigate the interaction of different thiols on the surface of the Ru nanocrystals (Figure S5b). Characteristic peaks of rGO at 1586 and 1730 cm⁻¹ can be ascribed to the C=C and C=O linkages, respectively. The -CH stretching peaks in the region between 2850-3000 cm⁻¹ also confirm the presence of long alkyl tails of thiols on the surface of Ru/rGO as they are absent in the non-modified sample.^[25] These -CH peaks are more prominent in C18 molecules as compared to C6 and C12 due to the long alkyl tail (Figure S5c). Raman spectroscopy (Figure S5d) reveals an increase in the I_D/I_G ratio after the transformation of graphite oxide (GO) to rGO in the solvothermal process. However, the $I_{\text{D}}/I_{\text{G}}$ ratio of the thiolmodified samples is slightly larger which could be attributed to the reduction in C=O moieties after surface coverage with thiols. It is accepted that these defect sites are usually the attachment sites for thiols in the form of thiolates.[26]



Figure 2. a) CA curves in 0.05 M H₂SO₄, b) UV-visible colorimetric spectra at different voltages stained by Indophenol blue method after 2h NRR in N₂, c) FE and rate of NH₃ production and d, e) Control experiments evaluated by ¹H-NMR and Indophenol blue method for Ru/rGO-C12, f) comparison of FE and rate of NH₃ for different catalysts.

Figure S6a reveals the XPS spectrum of Ru3d and C1s for all samples. For Ru/rGO sample, peaks at 280.3 eV and 284.7 eV are characteristic of the split spin-orbit region of Ru3d and can be ascribed to Ru3d_{5/2} and Ru3d_{3/2} component of metallic Ru, respectively.^[27] After modification, there is a clear decrease in the intensity of Ru peaks that validates the surface coverage with thiols and is more prominent with long-tail thiols (Figure S7). Moreover, a peak shift of 0.1 to 0.3 eV to higher binding energy for Ru is also observed in modified samples that could be ascribed to the Ru-S thiolate bond with localized charge density sites.^[20] Such localized charge density sites can potentially act as the adsorption sites for the N₂. Moreover, corresponding C1s peaks are present in all samples that can be attributed to the chemical structure of rGO. However, due to the waxy nature of octadecanethiol, the disappearance of the C-O peak in Ru/rGO-C18 suggests the surface coverage with thiols. Furthermore, Figure S6b shows the S2p region of the XPS spectra of modified samples. An interaction of Ru-S is confirmed by the peak for S2p_{3/2} at 162.6 eV that is assigned to Ru-S linkage.^[26,28] It can be inferred from these results that S atoms are mostly attached to Ru NPs along with residual free thiols distributed on the surface of rGO. Similarly, corresponding O1s and the survey spectrum for all samples are shown in Figure S6c and S6d, respectively. There is no evident peak of S in the survey spectrum of the non-modified samples. Also, there is no N peak at 400 eV that confirms well that our synthesis approach is clean without any N interference. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis shown in Table S1 suggests the amount of Ru and S are approximately 5 and 3 wt% in modified samples, respectively.

The electrocatalytic NRR performance is evaluated in 0.05 H_2SO_4 in a three-electrode, double compartment Μ electrochemical cell where two compartments are separated by a glass frit (Figure S8). Ammonia quantification is established by the Indophenol blue method (IB) and ¹H NMR with respective calibration curves after three independent sets of measurements (Figure S9 and S10). Watt and Chrisp method is opted for the estimation of hydrazine (N2H4) as a possible by-product (Figure S11). Figure S12 reveals the linear sweep voltammograms of modified and non-modified samples in the Ar atmosphere. A clear decrease in current density is observed for the thiolmodified samples, as compared to the non-modified samples, due to the HER suppression as a result of surface modification.^[16] Chronoamperometric experiments (CA) were conducted for 2 h in $N_{\rm 2}$ and the respective electrolytes were analyzed for NH₃ by IB and ¹H NMR methods. A comparative LSV data in Ar and N2 atmosphere is indicative of NRR



Figure 3. a, b) Recyclability of NRR performance and long-term stability of Ru/rGO-C12 after NRR in 0.05 M H₂SO₄, c) FE, and rate of NH₃ in ¹⁴N₂ and ¹⁵N₂ environment, d) NH₃ quantification by ¹H-NMR in ¹⁵N₂ environment.

capability of this catalyst (Figure S13). CA curves for Ru/rGO-C12 are shown in Figure 2a that reflects good stability and durability of the catalyst surface. The initial decrease in the current density is attributed to double-layer capacitance current and the fast depletion of available reactants on the electrode surface.^[5] Figure 2b reveals the stained electrolytes by the IB method after CA experiments on Ru/rGO-C12 surface at different applied potentials. At 655 nm, the highest absorption was achieved at -0.1 V vs RHE. A FE of 11% with a high rate of NH₃ production (50 μ g h⁻¹ mg⁻¹) is achieved and confirmed by three independent measurements (Figure 2c). This rate of NH₃ decreases as expected at higher applied potentials due to the competing HER, which is kinetically faster than NRR.^[29] Control experiments under open circuit potential in N₂, and at -0.1 V in Ar confirmed that there is no interference from the applied gas impurity, environment, and the catalyst system itself. These control experiments results are corroborated well with both approaches as shown in Figures 2d and 2e. From the above results, it can be concluded that the origin of produced NH₃ is from the reduction of applied N₂ gas. There is no detectable Ru leaching is observed after NRR evaluations in the electrolyte at different voltages (Table S3).

The above results show Ru/rGO-C12 outperformed all other control samples in NRR performance (Figure 2f). Importantly, all modified samples produced NH₃ with a higher rate as compared to the non-modified sample except Ru/rGO-C18, suggesting the formation of Ru-S linkage can promote NRR and suppress HER. However, due to the short alkyl tails of hexanethiol, there is an appreciable amount of HER that lowered the NRR as compared to Ru/rGO-C12. Relatively low NRR performance observed on Ru/rGO-C18 is ascribed to the dense coverage of thiol on the catalyst surface that reduced the overall electrode conductivity and available active sites. Modification with dodecanethiol provided an optimum surface coverage of thiols that suppresses HER along with the electronic structure modulation and enhanced availability of reactants on the surface of the catalyst by the selective allowance of N_2 over proton. $^{[30]}$ This is further elaborated by the double-layer capacitance measurements of all by cyclic voltammetry (Figure samples S14). The electrochemical surface area of the modified samples decreased drastically as compared to the non-modified sample but the NRR performance improved more than ten folds. Corresponding NRR performance data for control samples is provided in Figure S15. Also, no N₂H₄ was obtained after the 2h CA electrolysis experiment at -0.1 V vs RHE confirming the excellent selectivity of this catalyst (Figure S16). The NMR analysis of electrolyte was also carried out after the 2h CA experiment in Ar at -0.1 V vs RHE that shows no distinct peak of thiol present in the electrolyte confirming negligible thiol leaching from the catalyst



Figure 4. a) The optimized atomic configuration b) Bader charge distribution of *N_2 on modified samples c) the Gibbs free energy profile of NRR on Ru/rGO-C12. Black, purple, white, red, and yellow spheres represent C, Ru, H, O, and S, respectively.

surface (Figure S17).

A recyclability experiment was conducted for Ru/rGO-C12 by using the same electrode for different cycles. After five cycles of 2h-electrolysis, a stable FE was achieved around 11% (Figure 3a) with a small decrease in the rate of NH₃ production that could be attributed to the consumption of defects sites on the rGO or the adsorption of NH₃ on the catalyst surface.^[9] Moreover, a stable current density was obtained during continuous electrolysis for 12 h, indicating the stability and durability of this catalyst (Figure 3b). The homogenous size distribution of Ru nanocrystals is retained after 12 h electrolysis that validates the role of surface modification in the stability and durability of material (Figure S18). ¹⁵N₂ isotope labeling experiment was conducted similarly as $^{14}\mathrm{N}_2,$ except a bubbling of Ar gas for 30 min before the ¹⁵N₂ NRR experiments to confirm the origin of produced NH₃. Quantification of the produced NH₃ by ¹⁴N₂ and ¹⁵N₂ was done by the respective calibration curves after standardization with $^{14}\mathrm{NH}_3$ and $^{15}\mathrm{NH}_4\mathrm{CI}$ ($^{15}\mathrm{N}$ isotope-labeled ammonium chloride). At -0.1 V vs RHE, a similar amount of NH₃ is produced with 11% FE after NRR for 4h in $^{14}\text{N}_2$ and $^{15}\text{N}_2$ (Figure 3c) that further confirms the applied N₂ gas is the main source for NH₃ formation. Corresponding NMR spectrum for the ¹⁵N₂ isotope labeling experiment is shown in Figure 3d.

DFT calculations were performed to understand the origin and mechanistic insights of the "modification effect" (ESI for computational details). Figure 4a and S19 represent the optimized atomic configuration of Ru/rGO modified with a thiol. Also, S-CH₂-CH₃ (Ru/rGO-C6), S-CH₂-CH₂-CH₃ (Ru/rGO-C12), and S-CH₂-CH₂-CH₂-CH₃ (Ru/rGO-C18) were employed to simplify calculation models. An optimized charge density of N2 with an increase in bond lengths from 1.10 to 1.15 Å is observed in modified samples that can be attributed to the facile adsorption, activation, and polarization of N2 molecule on Ru due to the electronic structure modification by thiols (Figure 4b). A decrease in N₂ adsorption energy value is observed as the carbon chain length of thiol increased which resulted in the deviation of electronic density away from Ru due to attached thiols and a corresponding loss of Bader charges from 0.53 to 0.85 eV is observed. Figure S20 represents optimized structures and HER capability of Ru site directly attached to the carbon chain. Figure 4c, S21, and S22 reveal the free energy NRR profile by distal and alternating pathways for Ru-rGO-C12, RurGO-C6, and Ru-rGO-C18, respectively. Importantly, HER becomes more energy-intensive as the tail length of thiol increased. The 1st hydrogenation step for NRR requires the same amount of energy for both pathways for all samples, but later hydrogenation steps are showing variations. For Ru-rGO-

WILEY-VCH

Manusc

Accepted

COMMUNICATION

C12 and Ru-rGO-C18, the 2nd and 3rd hydrogenations require lower energy for the distal pathway compared with the alternating pathway making the distal pathway as the plausible route for NRR. However, the 2nd hydrogenation in Ru-rGO-C6 for the alternating pathway is more favorable as compared to the distal pathway that can be ascribed to the enhanced N₂ adsorption on the surface of Ru in this structure as evident from the N₂ adsorption energy values. Also, the 3rd hydrogenation step for the alternating pathway is more energy-intensive, which makes it less favorable for NH₃ production. Although the RurGO-C6 has a relatively smaller ΔG_{max} , it also has low energy requirements for HER in comparison with other modified samples. The improved NRR performance on Ru-rGO-C12 can be assigned to intermediate N₂ adsorption and desorption capabilities by electronic modifications along with suppression of the competing HER reaction by surface modification.

In summary, we developed a facile organic tethering strategy to suppress HER with an improved rate of NH₃ production. Ru/rGO-C12 achieved an optimum surface coverage of thiols that induces electronic structure modulation and improved molecular confinement along with HER suppression. A high FE of 11% with an improved NH₃ yield (50 μ g h⁻¹ mg⁻¹) is achieved at -0.1 V vs RHE. Also, this modified catalyst exerts excellent stability and recyclability that are confirmed by different control experiments including ¹⁵N isotope labeling experiments. It can be anticipated that M-S linkages will provide an opportunity towards rational catalyst design strategy for NRR as well as for other energy-related applications. Specifically, inspired by nature's nitrogenase, the development of M-S-C or M-S-M' linkages will pave a pathway to bridge between homogeneous and heterogeneous catalysis for nitrogen fixation.

Acknowledgments

C. Z. acknowledges the award of Future Fellowship from the Australian Research Council (FT170100224). X. C. acknowledges support from ARC (DE180100294). This research used equipment located at the UNSW Mark Wainright Analytical Centre (MWAC). M. I. A. acknowledges Dr. Douglas Lawes from UNSW MWAC for NMR discussions.

Keywords: Nitrogen fixation • Ammonia • Surface modification • Hydrogen evolution reaction • Organic tethering

- S. Zhang, M. Jin, T. Shi, M. Han, Q. Sun, Y. Lin, Z. Ding, L. R.
 Zheng, G. Wang, Y. Zhang, et al., *Angew. Chemie Int. Ed.* 2020, 230026, 2–9.
- G. Qing, R. Ghazfar, S. T. Jackowski, F. Habibzadeh, M. M.
 Ashtiani, C.-P. Chen, M. R. Smith, T. W. Hamann, *Chem. Rev.* 2020, 120, 5437–5516.
- [3] Y. Li, X. Tan, R. K. Hocking, X. Bo, H. Ren, B. Johannessen, S. C. Smith, C. Zhao, *Nat. Commun.* **2020**, *11*, 1–9.
- [4] L. Zhang, L. X. Ding, G. F. Chen, X. Yang, H. Wang, Angew. Chemie - Int. Ed. 2019, 58, 2612–2616.
- [5] M. I. Ahmed, S. Chen, W. Ren, X. Chen, C. Zhao, *Chem. Commun.* 2019, 55, 12184–12187.
- [6] Y. Li, X. Tan, H. Tan, H. Ren, S. Chen, W. Yang, S. C. Smith, C. Zhao, *Energy Environ. Sci.* 2020, 1799–1807.

- [7] L. Yu, J. Qin, W. Zhao, Z. Zhang, J. Ke, B. Liu, *Int. J. Photoenergy* 2020, 2020, 1–11.
- [8] Z. Wang, C. Li, K. Deng, Y. Xu, H. Xue, X. Li, L. Wang, H. Wang, ACS Sustain. Chem. Eng. 2019, 7, 2400–2405.
- S. Cheng, Y. J. Gao, Y. L. Yan, X. Gao, S. H. Zhang, G. L. Zhuang,
 S. W. Deng, Z. Z. Wei, X. Zhong, J. G. Wang, *J. Energy Chem.* 2019, 39, 144–151.
- B. Yu, H. Li, J. White, S. Donne, J. Yi, S. Xi, Y. Fu, G. Henkelman,
 H. Yu, Z. Chen, et al., *Adv. Funct. Mater.* 2019, *1905665*, 1–11.
- [11] B. H. R. Suryanto, D. Wang, L. M. Azofra, M. Harb, L. Cavallo, R. Jalili, D. R. G. Mitchell, M. Chatti, D. R. MacFarlane, ACS Energy Lett. 2019, 4, 430–435.
- [12] A. R. Singh, B. A. Rohr, J. A. Schwalbe, M. Cargnello, K. Chan, T. F. Jaramillo, I. Chorkendorff, J. K. Nørskov, ACS Catal. 2017, 7, 706–709.
- [13] F. Zhou, L. M. Azofra, M. Ali, M. Kar, A. N. Simonov, C. McDonnell-Worth, C. Sun, X. Zhang, D. R. MacFarlane, *Energy Environ. Sci.* 2017, 10, 2516–2520.
- [14] Y. Yang, S. Q. Wang, H. Wen, T. Ye, J. Chen, C. P. Li, M. Du, Angew. Chemie - Int. Ed. 2019, 58, 15362–15366.
- F. Li, A. Thevenon, A. Rosas-Hernández, Z. Wang, Y. Li, C. M.
 Gabardo, A. Ozden, C. T. Dinh, J. Li, Y. Wang, et al., *Nature* 2020, 577, 509–513.
- D. Wakerley, S. Lamaison, F. Ozanam, N. Menguy, D. Mercier, P.
 Marcus, M. Fontecave, V. Mougel, *Nat. Mater.* 2019, *18*, 1222–1227.
- [17] L. Shi, Y. Yin, S. Wang, H. Sun, ACS Catal. 2020, 10, 6870–6899.
- [18] K. Tanifuji, Y. Ohki, *Chem. Rev.* **2020**, *120*, 5194–5251.
- [19] Y. Roux, C. Duboc, M. Gennari, *ChemPhysChem* 2017, 18, 2606– 2617.
- H. Sato, S. Ushiyama, M. Sogo, M. Aoki, K. I. Shudo, T. Sugawara,
 S. Yanagisawa, Y. Morikawa, S. Masuda, *Phys. Chem. Chem. Phys.* 2012, *14*, 15412–15420.
- [21] N. Chakroune, G. Viau, S. Ammar, L. Poul, D. Veautier, M. M. Chehimi, C. Mangeney, F. Villain, F. Fiévet, *Langmuir* 2005, 21, 6788–6796.
- [22] B. H. R. Suryanto, D. Wang, L. M. Azofra, M. Harb, L. Cavallo, R. Jalili, D. R. G. Mitchell, M. Chatti, D. R. MacFarlane, ACS Energy Lett. 2019, 4, 430–435.
- S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, et al., *Nature* 2019, *570*, 504–508.
- [24] K. Kusada, H. Kobayashi, T. Yamamoto, S. Matsumura, N. Sumi, K. Sato, K. Nagaoka, Y. Kubota, H. Kitagawa, J. Am. Chem. Soc. 2013, 135, 5493–5496.
- [25] N. Ramila Devi, M. Sasidharan, A. K. Sundramoorthy, J. Electrochem. Soc. 2018, 165, B3046–B3053.
- [26] E. Pensa, E. Cortés, G. Corthey, P. Carro, C. Vericat, M. H. Fonticelli, G. Benítez, A. A. Rubert, R. C. Salvarezza, *Acc. Chem. Res.* 2012, *45*, 1183–1192.
- [27] H. Wang, Y. Li, D. Yang, X. Qian, Z. Wang, Y. Xu, X. Li, H. Xue, L. Wang, *Nanoscale* **2019**, *11*, 5499–5505.
- [28] M. S. Inkpen, Z. F Liu, H. Li, L. M. Campos, J. B. Neaton, L. Venkataraman, *Nat. Chem.* **2019**, *11*, 351–358.
- [29] R. D. Kumar, Z. Wang, C. Li, A. V. N. Kumar, H. Xue, Y. Xu, X. Li, L. Wang, H. Wang, J. Mater. Chem. A 2019, 33–35.
- [30] Y. Fang, X. Cheng, J. C. Flake, Y. Xu, *Catal. Sci. Technol.* 2019, 9, 2689–2701.

WILEY-VCH

COMMUNICATION

Table of Contents



This work represents a facile organic tethering strategy to suppress HER along with electronic structure modulation on the surface of Ru nanocrystals and a FE of 11% with a high rate of NH₃ (50 μ g h⁻¹ mg⁻¹) is achieved.