

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

## **Accepted Article**

Title: Vacancy-rich Ni(OH)2 Drives the Electrooxidation of Amino C-N Bonds to Nitrile C≡N Bonds

Authors: Wenbin Wang, Yutang Wang, Ruoou Yang, Qunlei Wen, Youwen Liu, Zheng Jiang, Huiqiao Li, and Tianyou Zhai

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.202005574

Link to VoR: https://doi.org/10.1002/anie.202005574

## WILEY-VCH

**RESEARCH ARTICLE** 

#### WILEY-VCH

## Vacancy-rich Ni(OH)₂ Drives the Electrooxidation of Amino C-N Bonds to Nitrile C≡N Bonds

Wenbin Wang<sup>+[a]</sup>, Yutang Wang<sup>+[a]</sup>, Ruoou Yang<sup>+[b]</sup>, Qunlei Wen<sup>[a]</sup>, Youwen Liu<sup>\*[a]</sup>, Zheng Jiang<sup>\*[b]</sup>, Huiqiao Li<sup>[a]</sup>, Tianyou Zhai<sup>\*[a]</sup>

[a]	W. B. Wang, Y. T. Wang, Q. L Wen, Dr. Y. W. Liu, Prof. H. Q. Li, and Prof. T. Y. Zhai
	State Key Laboratory of Material Processing and Die & Mould Technology, and School of Materials Science and Eng
	Huazhong University of Science and Technology
	Wuhan, Hubei, 430074, P. R. China
	E-mail: zhaity@hust.edu.cn; ywliu@hust.edu.cn
[b]	R. O. Yang, and Prof. Z. Jiang
	Shanghai Synchrotron Radiation Facility, Zhangjiang National Lab, Shanghai Advanced Research Institute
	Chinese Academy of Sciences
	Shanghai, 201204, P. R. China
	E-mail: jiangzheng@sinap.ac.cn

[\*] These authors contributed equally to this work.

Abstract: Electrochemical synthesis based on electron as reagents provide a broad prospect for commodity chemical manufacturing. A direct one-step route from amino C-N bonds electrooxidation to nitrile C≡N bonds offer an alternative pathway for nitriles producting. However, this promising topic has not been fully explored whether the chemical bond reforming process or the performance optimization. Here we proposed a model of vacancies-rich Ni(OH)<sub>2</sub> atomic layer to understand performance relationship with structure. By theory calculations, the vacancy-induced local electropositive site chemisorbs the N atom with lone pairs of electrons and then attack the corresponding N(sp3)-H, thus accelerating amino C-N bond activates dehydrogenation directly into nitrile C≡N bond. Vacanciesrich nanosheets exhibit up to 96.5% propionitrile selectivity at a moderately potential of 1.38 V. These findings will initiate a new pathway for triggering stubborn catalytic reaction in the chemicals industry.

#### Introduction

Nitriles with unique reactivity and activating ability occupies a decisive position in organic synthesis and serve as common building blocks in the field of pharmaceutical, electronic materials and polymers.<sup>[1]</sup> Concretely speaking, propionitrile, one of the most common low carbon alkanes nitriles, is a significant intermediate for organic syntheses, i.e. Houben-Hoesch reaction,<sup>[2]</sup> as well as for pharmaceuticals, *i.e.* ketoprofen and fragrances.<sup>[1d]</sup> It is precisely because of this pivotal focus that the efficient synthesis of nitriles share an urgent and highly profitable market. These and other applications generate an annual demand for propionitrile of around 20 million tonnes. Within this context, commercial nitriles is mainly produced by ammoxidation method using toxic using harsh, acidic dehydrating reagents and consequently they led to one of the worst environmental disasters.<sup>[3]</sup> Exploring new alternative pathways for realizing the synthesis of nitriles will be of strategic significance for both basic research and industrial production.<sup>[4]</sup> Recently, electrosynthesis which utilize flexible electrical sources to drive the activation and reorganization of chemical bonds has been proposed and shows great potential in chemical synthesis.<sup>[5]</sup> This simple, mild, and lowtoxic synthetic method show great attractiveness to be practiced commercially at small scales in distributed areas and becomes cheaper as the price of renewable electricity produced continues to decline.<sup>[6]</sup> On this account, some materials such as NiSe were exploited as electrocatalyst to drive catalytic primary amines to nitriles.<sup>[7]</sup> This electrochemical induced C-N bond activates dehydrogenation directly into a C=N bond may provide important insights into alternative pathways for realizing synthesis of nitriles. More meaningfully, this anodic oxidation process could be coupled with water reduction to generate hydrogen simultaneously.<sup>[5a, 8]</sup> However, this promising topic has not been fully explored for the understanding the chemical bond activation conversion process and optimizing the conversion efficiency. In this regard, it is expected to design effective catalyst models to understand performance relationship with structure and to steer efficient catalysts.

neering



 Propylamine + water
 Electrolyser
 Propionitrile + hydrogen

 Schematic 1. An electrochemical route to propionitrile. (a) Illustration of the current industrial route. (b) Proposed electrochemical route for the synthesis of propylamine from propionitrile.
 Propionitrile + hydrogen

Essentially the direct production of nitriles from primary amines mainly depends on the activated dehydrogenation of the C (sp<sup>3</sup>)-H/N (sp<sup>3</sup>)-H.<sup>[1c]</sup> Notably, the effective chemisorption and subsequent multi-electron transfer reactions of amino group

## **RESEARCH ARTICLE**



**Figure 1.** Preparation and characterization for the vacancies-rich (VR) and vacancies-poor (VP) Ni(OH)<sub>2</sub> atomic layer. (a) Schematic illustration of controllably synthesized of VR-Ni(OH)<sub>2</sub> and VP-Ni(OH)<sub>2</sub>. (b-d) TEM, HRTEM and HAADF-STEM image of the VP-Ni(OH)<sub>2</sub>, respectively. (e-g) TEM, HRTEM and HAADF-STEM image of the VR-Ni(OH)<sub>2</sub>, respectively.

would be key factors in this organic synthesis.<sup>[9]</sup> Forcing on the first issue, the bonding mode of R-NH<sub>2</sub> in the amine group is unequal sp<sup>3</sup> hybridization, so that a lone pair electrons exists in the N atom. Therefore, it is reasonably believed that constructing positive charge sites in surface of a catalyst could attract the lone pair electrons of amine group. Meanwhile, the attacks of chemical bonds via the electrophilic or nucleophilic surface of the catalyst is a widely used way to boosts the formation of intermediates and ultimately speed up organic reactions in reviewing most organic reactions.<sup>[10]</sup> Obviously, the positive charge sites also act as a similar electrophile in organic reactions to activate inert C (sp<sup>3</sup>)-H/N (sp<sup>3</sup>)-H bonds.<sup>[11]</sup> On account of aforementioned analysis, we thus reasoned that surface local charge density regulation is an effective strategy to synergistically resolve adsorption and cleavage issues. Based on the use of vacancy to modify the surface structure of materials, the vacancy-induced local electropositive site drives the electrooxidation of amino C-N bonds to nitrile C=N bonds can be anticipated in catalysts with surface deficiency. To go further, the atomic thickness not only favors building clear atomic structure, but also enables the majority of vacancies distribution on the surface.<sup>[12]</sup> Bearing it in mind, we pay our attention to the atomically thin layers with rich surface defects and fully exposed active sites shall be an ideal structural model of pursuing catalytic primary amines to nitriles.

Herein, a model of Ni(OH)<sub>2</sub> atomic layer with surface deficiency would be a promising candidate, thanks to its wide applications in small molecule electrooxidation (such as water, methanol, ethanol).<sup>[13]</sup> In this process, we achieved the controlled synthesis of multi-vacancy ultrathin Ni(OH)<sub>2</sub> nanosheets through

*in situ* electrochemical transformation from Ni-MOFs nanosheets. Density functional theory calculations revealed that defectinduced local lean electron of catalyst surface will promote the electrooxidation of amino C-N bonds to nitrile C=N bonds. Thus, the as prepared multi-vacancy ultrathin Ni(OH)<sub>2</sub> nanosheets exhibited a small potential of 1.36 V to drive 10 mA cm<sup>-2</sup> and simultaneous possess a high Faradaic efficiency of 96.5% at the potential of 1.38 V for propylamine electrooxidation to propionitrile. In particular, *in situ* Fourier transform infrared (FT-IR) spectroscopy precisely verified the transformation process of amino C-N bonds to nitrile C=N bonds.

#### **Results and Discussion**

Vacancies-rich Ni(OH)<sub>2</sub> (VR-Ni(OH)<sub>2</sub>) atomic layer was synthesized through *in situ* electrochemical topological transformation from ultrathin metal-organic frameworks (MOFs) nanosheets (Figure 1a). A two dimensional layered Ni-MOFs ([Ni<sub>3</sub>(OH)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O) with strong hydrogen bonds was as a precursor (Figure S1).<sup>[14]</sup> Initially, ultrathin Ni-MOFs nanosheets was prepared by a self-assembly process (Figure S2a and S3). Subsequently, *in situ* electrochemical topological transformation strategy was used to fabricated vacancies-rich Ni(OH)<sub>2</sub> (VP-Ni(OH)<sub>2</sub>) was obtained by similar routine from alkali soaked Ni-MOFs nanosheets (AS-Ni(OH)<sub>2</sub>) (Figure S2b and S4). TEM image in Figure 1b and 1e reveals that the *in situ* 

### **RESEARCH ARTICLE**



**Figure 2**. The characterization for vacancy. (a) XRD patterns. (b) XPS Ni 2p spectra. (c) XPS O 1s spectra. (d) Ni K-edge XANES spectra. (e) Ni K-edge EXAFS  $k^3(\chi k)$  oscillation functions and (f) the corresponding FT curves.

transformed samples all maintained a sheet-like morphology. Meanwhile, vertically distributed sheets in the TEM images reveal the average thickness of VR-Ni(OH)<sub>2</sub> and VP-Ni(OH)<sub>2</sub> are 2.2 nm and 2.1 nm (Figure S5), respectively. The atomic thickness ensures that the defects of the construction are distributed on the surface. Furthermore, the interlayer spacing extracted by HRTEM (Figure 1c and 1f) are corresponding to specific crystal of hexagonal Ni(OH)<sub>2</sub>, demonstrating the formation of pure Ni(OH)<sub>2</sub>. In consideration of the conversion process, this result also suggest that unstable MOFs materials often act as pre-catalysts during anodic electrooxidation process. The scanning transmission electron microscopy-high-angle annular dark field (HAADF-STEM) images show that abundant nanopores distributed on the surface of the obtained VR-Ni(OH)<sub>2</sub> (Figure 1g), which are consistent with our previous research work.[13c] Predictably, the existence of nanopores on the nanosheet can effectively enrich the reaction molecules and promote permeation through the nanopore, leading to significant improvement of the catalytic performance.<sup>[13c, 15]</sup> In addition, their X-ray diffraction pattern for the accumulated powder sample could be readily indexed to Ni(OH)<sub>2</sub> (JCPDS NO. 14-0117) (Figure 2a). The broader diffraction peaks of VR-Ni(OH)<sub>2</sub> than VP-Ni(OH)<sub>2</sub> may be caused by structure microdistortions in the crystal.<sup>[16]</sup>

To accurately characterize the defect of the obtained nanosheets, X-ray photoelectron spectroscopy (XPS) was first conducted. As shown in Figure 2b, the Ni 2p is no obvious difference between VR- and VP-Ni(OH)2. The specific Ni 2p3/2 and Ni 2p<sub>1/2</sub> peaks are located at 856.3 eV and 873.9 eV, and the binding energy is separate into 17.6 eV, indicating that Ni was +2 oxidation state.<sup>[15]</sup> Observingly, their O 1s core level spectrum in Figure 2c clearly showed three distinct peaks: namely the peak of lattice oxygen at 531.4 eV, the peak of oxygen vacancy at 532.3 eV and the peak of adsorbed H<sub>2</sub>O at 533.6 eV.<sup>[17]</sup> However, VR-Ni(OH)<sub>2</sub> transformed by Ni-MOFs has a significantly enhanced peak of 532.3 eV which indicates that obtained by Ni-MOFs possess larger concentration of oxygen vacancies than those obtained by AS-Ni(OH)2.<sup>[17b]</sup> To further explore atomic structure, X-ray absorption fine structure spectroscopy (XAFS) was also employed. As shown in Figure 2d, the absorption edge of VR-Ni(OH)<sub>2</sub> are consistent with Ni-MOFs, VP-Ni(OH)<sub>2</sub> and commercial Ni(OH)<sub>2</sub> (Bulk Ni(OH)<sub>2</sub>), indicating that the valence state of Ni has not changed after the conversion, which is completely in accord with the result from the Ni 2p analysis in XPS. Meanwhile, compared with AS-Ni(OH)<sub>2</sub> and Bulk Ni(OH)<sub>2</sub>, the white line of VR-Ni(OH)<sub>2</sub> and VP-Ni(OH)<sub>2</sub> has a noticeable decline, and means that the geometric local structure (such as coordination number, bond length) around Ni atom has changed slightly.<sup>[12a]</sup> Thus, the Ni K-edge extended XAFS (EXAFS)  $k^2 \chi(k)$ oscillation curve derived from Figure 2d was presented in Figure 2e, and displays a significant amplitude difference in 2-8 Å in changed by the local structure distortion of NiO<sub>6-x</sub> polyhedron.<sup>[12b]</sup> Furthermore, from the Fourier transform curves (FTs) of  $k^2 \chi(k)$ spectra (Figure 2f and Table S1), the Ni-O peak (2.01 Å) for VR-Ni(OH)<sub>2</sub> present a shift in the position towards a lower length. Meanwhile, the intensity of the Ni-O peak (2.01 Å) and Ni-Ni peak (3.06 Å) for VR-Ni(OH)<sub>2</sub> was significantly reduced. Strikingly, fitted Ni-O, Ni-Ni coordination number for VR-Ni(OH)<sub>2</sub> are much lower than AS-Ni(OH)<sub>2</sub>, VP-Ni(OH)<sub>2</sub>, suggesting the presence of abundant oxygen and Ni vacancies in VR-Ni(OH)2.[11, 18] Noticeably, VP-Ni(OH)<sub>2</sub> compared to AS-Ni(OH)<sub>2</sub> has a similar but relatively weak trend as VR-Ni(OH)2, indicating that nickel hydroxides will adaptively form only a small number of vacancies during the amine electrooxidation process. In general, combined with the XPS results, vacancy-confined Ni(OH)<sub>2</sub> atomic layer were controllably synthesized via in situ electrochemical transformation of the unstable MOFs, which revealed the unstable MOFs usually as a pre-catalysts. In consideration of the special structure of the selected MOFs, the formation mechanism of defects is simply deduced. Acceptably, during electrochemical operation, hydroxides in electrolytes quickly transported to around Ni atom through strong hydrogen binds existing in Ni-MOFs, and then replaced the coordinated water molecules and carboxylate groups to form Ni(OH)<sub>2</sub>. Under this premise, nucleophilic propylamine can also participate in the coordination reaction with the Ni atom thus acting as a steric hindrance to prevent its combination with hydroxide. In this regard, the Ni(OH)<sub>2</sub> with unsaturated coordination was formed. Notably, this study not only proposes a new method for constructing surface vacancies but also present conclusive evidence for the catalytic performance of MOFs from its derived defect structure.

anuscri

## **RESEARCH ARTICLE**



**Figure 3**. Electrochemical measurement. (a) The normalized polarization curves and (b) the corresponding Tafel plots. (c) Arrhenius plot. (d) Nyquist plots for VR-Ni(OH)<sub>2</sub> in 1m KOH with and without 10 mmol propylamine at 1.4 V (vs RHE). (e) Nyquist plots for VR-Ni(OH)<sub>2</sub> and for VP-Ni(OH)<sub>2</sub> catalysts in 1 M KOH with 10 mmol propylamine at 1.4 V (vs RHE). (f) The corresponding Nyquist plots and (g) Bode phase plots of VR-Ni(OH)<sub>2</sub> at various voltages in 1 M KOH with 10 mmol propylamine. (h) Nyquist plots for VP-Ni(OH)<sub>2</sub> and (i) Bode phase plots of VP-Ni(OH)<sub>2</sub> at various voltages in 1 M KOH with 10 mmol propylamine.

To evaluate the propylamine oxidation reaction (POR) activity of constructed catalyst model, VP-Ni(OH)<sub>2</sub>, as comparison were also carried out. As shown in Figure 3a, VR-Ni(OH)<sub>2</sub> is more easily activated and show decent oxygen evolution performance in 1 M KOH in the absence of propylamine, while the samples still present a unsatisfactory current density response below the potential of 1.55 V. In the presence of 10 mmol propylamine, the apparent POR catalysis is observed with a significant rise of the anode current density for all samples. These result elucidate that POR process is easier than oxygen evolution reaction. Specifically, VR-Ni(OH)<sub>2</sub> only need a potential of 1.36 V to drive 10 mA cm<sup>-2</sup> in the presence of propylamine, which is smaller than that of VP-Ni(OH)<sub>2</sub> (1.42 V). Moreover, the potential required by VR-Ni(OH)<sub>2</sub> to achieve a current density of 50 mA cm<sup>-2</sup> are 1.41 V, which is much lower than that of VP-Ni(OH)<sub>2</sub> (1.50 V). The higher current density indicated that VR-Ni(OH)<sub>2</sub> is an efficient POR catalysts. Furthermore, VR-Ni(OH)<sub>2</sub> present a remarkable low Tafel slope of 31.5 mV dec<sup>-1</sup>, while VP- Ni(OH)<sub>2</sub> shows a Tafel slope of 56.4 mV dec<sup>-1</sup> (Figure 3b), meaning that VR- Ni(OH)<sub>2</sub> has a faster electron-transfer rate for POR. Additionally, turnover frequency (TOF) was also calculated and the higher TOF of VR-Ni(OH)<sub>2</sub> reflected the enhanced intrinsic activity of the active sites (Figure S6). To assess the kinetic barriers involved in POR process, we studied the dependence of the performance on the temperatures for catalysts (Figure S7). The Arrhenius plots can be fitted to a straight line and the slopes represent the electrochemical activation energies.<sup>[19]</sup> Undoubtedly, propylamine electrooxidation reaction more rapidly at raised temperatures on the performance of the nickel hydroxides catalysts.<sup>[20]</sup> As shown in Figure 3c, the electrochemical activation energies for VR-  $Ni(OH)_2$  (24.03 kJ mol<sup>-1</sup>) is lower than for VP-Ni(OH)\_2 (79.30 kJ mol<sup>-1</sup>), indicating that VR- Ni(OH)\_2 has the low kinetic barriers to adsorb propylamine for further activation.<sup>[13c]</sup>

To further illustrate the catalytic kinetics of POR, the electrochemical impedance spectroscopy (EIS) were investigated at different potentials. The Nyquist plots of VR-Ni(OH)2 were combined by the a arc and a steep line in 1 M KOH without propylamine (Figure 3d),<sup>[21]</sup> indicating that  $VR-Ni(OH)_2$  is more inclined to absorb propylamine than hydroxyl, and the absorbing propylamine is rapidly oxidized to generate a fast charge-transfer rate.<sup>[22]</sup> Meanwhile, Figure 3e compares the Nyquist plots of VR-Ni(OH)<sub>2</sub> and VP-Ni(OH)<sub>2</sub> at 1.4 V, and the smaller complete semicircle of VR-Ni(OH)<sub>2</sub> suggest the catalysts has better electronic conductivity and faster charge-transfer rate.[21] Therefore, the increased potential provides more electrons and absorbed propylamine, resulting in a faster charge-transfer rate (Figure 3f). As shown in the Bode phase plots, the frequency peak of VR-Ni(OH)<sub>2</sub> decrease and shifts to lower frequency at the potential of 1.35 V, and then shifts to higher frequency as the potential increases (Figure 3g).<sup>[23]</sup> Interestingly, the Bode phase plots of VP- Ni(OH)<sub>2</sub> is different from its Nyquist plots (Figure 3h), showing a different trend from VR-Ni(OH)2. The frequency peak of VP-Ni(OH)<sub>2</sub> keeps decreasing and moves towards the higher frequency (Figure 3i).<sup>[22]</sup> These result suggest that more propylamine is absorbed on the surface of VR-Ni(OH)2 with a great number of vacancies than VP-Ni(OH)2. At the potential of 1.35 V, the amount of absorbed propylamine is larger than the amount consumed by the electrooxidation on the surface of VR-Ni(OH)<sub>2</sub>, and the increased potential makes the adsorption and

## **RESEARCH ARTICLE**



**Figure 4**. Detection of product and coupling electrolytic water performance. (a) Chronopotentiometric curves of VR-Ni(OH)<sub>2</sub> at different potentials in 1 M KOH with 10 mmol propylamine. (b) <sup>1</sup>H NMR spectra of the collected product at different potentials. (c) FEs of propionitrile at different potentials. (d) The schematic showing the setup for the in-situ IR experiments. (e, f) in situ FTIR spectra for propylamine electrooxidation of VR-Ni(OH)<sub>2</sub>. (g) The schematic showing the homemade propylamine electrolyser using VR-Ni(OH)<sub>2</sub> as the anode and  $CoS_2$ -MoS<sub>2</sub> as the cathode. (h) Current–potential curves in a two-electrode system in 1.0 m KOH with and without 10 mmol propylamine. (i) The voltage of the electrolyzer required for different current densities.

consumption rates tend to balance. Therefore, all of the results indicate that the presence of vacancies for Ni(OH)<sub>2</sub> favored fast charge-transfer rate and easily propylamine adsorption.

The catalysis stability and electrooxidation product were also important considerations. Therefore, propylamine oxidation catalysis was carried out at different potentials (Figure 4a). Stepped-potential electrolyses at each given potential for 2 h were performed to quantify the liquid products by <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) analysis. The results in Figure 4b suggested that the VR-Ni(OH)<sub>2</sub> possess the Faradaic efficiency is as high as 96.5% for producing propionitrile at a moderately potential of 1.38 V (Figure 4c). Meanwhile, the propionitrile yield rate was also calculated as 0.0011 mol mg<sup>-1</sup> h<sup>-1</sup> at 1.38 V. (Figure S8 and Table S2). Notably, the constructed Ni(OH)<sub>2</sub> catalysts realized direct synthesis of nitriles from primary amines, namely C-N bond activates dehydrogenation directly into a C=N bond. To further pinpoint the POR process, in situ Fourier transform infrared (FT-IR) spectroscopy measurement was carried out. The schematic diagram of the in situ experimental device is shown in Figure 4d. In order to more accurately identify the product molecules, before starting the in-situ test, the assembled in-situ FT-IR test device (Figure 4d) has completed background subtraction. FT-IR spectral results in Figure 4e and 4f show the small molecule structure evolution signal during the propylamine electrooxidation process on the surface of VR-Ni(OH)<sub>2</sub>. Obviously, the vibrational peak of C=N at v = 2253 cm<sup>-1</sup> can be immediately observed and it gradually increased with reaction propulsion.<sup>[24]</sup> The timedependent in situ FT-IR further proved that VR-Ni(OH)2 promote amino C-N bonds electrooxidation to nitrile C≡N bonds for realizing synthesis of propionitrile. Under normal conditions, electrochemical selectivity is an important consideration issue. In this study, the tiny amounts of byproducts were also detected, such as propionaldehyde ( $v = 1747 \text{ cm}^{-1}$ ) and carbon monoxide  $(v = 2173 \text{ cm}^{-1})^{[25]}$ , which may result from the unavoidable oxygen exposure in an open environment. Meanwhile, the electrooxidation performance of n-Butylamine confirms that the presence of vacancies can also improve the performance of other primary amines (Figure S9). Combined with the all-around electrochemical testing and in situ spectroscopy, amino C-N bonds could be electrooxidized to nitrile C≡N bonds on the surface of Ni(OH)<sub>2</sub>, which undoubtedly offer an important insight into alternative pathways for accessible nitriles producing. Beyond that, the surface vacancy promote the primary amines electrooxidation performance of Ni(OH)<sub>2</sub>.

As anodic oxidation reaction, this POR process could be coupled with water reduction to generate hydrogen simultaneously. In this regard, a dual-electrode electrochemical configuration with using the previously reported  $CoS_2$ -MoS<sub>2</sub> as the cathode and VR- Ni(OH)<sub>2</sub> as the anode was constructed (Figure 4g).<sup>[26]</sup> The required voltage is 1.48 V to achieve a current density of 10 mA cm<sup>-2</sup> (Figure 4h), which is smaller than the necessary voltage of the overall water splitting (1.74 V). Meanwhile, the voltage gap between hybrid water electrolysis and overall water splitting gradually increased with the raising of current density (Figure 4i). Integrated with the overpotential and current density, the performance of the VR-Ni(OH)<sub>2</sub> is decent

## **RESEARCH ARTICLE**



**Figure 5.** Theoretical simulation. (a) Electrostatic potential maps of propylamine. (b) Charge density of the VR-Ni(OH)<sub>2</sub>. (c) The charge density difference in the perfect Ni(OH)<sub>2</sub> and the isosurfaces level is 0.000968 au. The yellow and blue isosurfaces represent charge accumulation and depletion in the space. (d) The charge density difference in the VR-Ni(OH)<sub>2</sub> and the isosurfaces level is 0.004028 au. (e) The positive charge density difference in the VR-Ni(OH)<sub>2</sub>. (f) The negative charge density difference in the VR-Ni(OH)<sub>2</sub>. (g) The reaction route 1 of propylamine electrooxidation. (h) The reaction route 2 of propylamine electrooxidation.

relative to that of other report organic compound oxidation catalysts (Table S3). Meanwhile, no obvious gas bubbles were produced on the surface of the anode (Figure S10). Therefore, the above result suggested that the VR-Ni(OH)<sub>2</sub> may be a anode candidate to realize the coupled hydrogen evolution from water splitting by integrating propylamine electrooxidation.

This interesting process of bond conversion motivated us to reveal the mechanism in regard to adsorption, activation and electrooxidation catalyst surface defect towards further improving and catalvst performance unlocking other profound electrosynthesis reaction. In this study, the conventional DFT calculations were performed to explore adsorption and dehydrogenation. First, the electrostatic potential of propylamine was proposed in Figure 5a. Clearly, the N atom neighborhood appeared negative potential relative to other groups in propylamine molecule, which may root in the lone pair electrons of unequal sp<sup>3</sup> hybrid orbitals. In this regard, the positive charge sites may directly adsorb propylamine molecules by attracting lone pair electrons.<sup>[27]</sup> Furthermore, the effect of vacancy defects on the surface charge distribution of Ni(OH)<sub>2</sub> is studied (Figure 5b). Due to the absence of atoms, there is a lacking electron density in the vacancy area relative to intact surface. The electron deletion could render vacancy sites more electropositive, which might facilitate the adsorption of the N atom with lone pairs of electrons.[11] To better elucidate the strength of the adsorption, the charge density difference after propylamine adsorption are considered. For the surface of perfect Ni(OH)<sub>2</sub>, the electrons of the N atom tend to flow to the H atom in catalyst lattice, as a consequence, occurring a slight adsorption in the form of hydrogen bonds (Figure 5c and Figure S11). The adsorption energy is only -0.057 eV (Table S2). Specifically, the obvious charge transfer behavior signified the strong adsorption between the vacancies-rich surface and propylamine molecules (Figure 5d). In addition, the corresponding adsorption energy is calculated as -0.662 eV (Table S4), further confirming the direct adsorption. Meanwhile, the critical distance between N atom and Ni atom of VR-Ni(OH)<sub>2</sub> is 2.1 Å, which is much smaller than perfect Ni(OH)<sub>2</sub> (4.3 Å). The huge difference in the critical distance further means that vacancies can provide anchor sites for direct chemisorption of propylamine molecules. However, the formation of anchor sites must require surface defect with a high energy barrier reaching up to 2.59 eV (Figure S12). The considerable reaction energy makes the propylamine adsorption process in perfect Ni(OH)<sub>2</sub> considerably difficult. The positive charge surface of vacancies-rich Ni(OH)<sub>2</sub> may realize propylamine molecules nitrogen adsorption and catalysis directly. To explore the adsorption process in detail, the process of losing and gaining electrons between the vacancies-rich surface and propylamine molecules is presented separately (Figure 5 e and f). Similar to theoretical predictions, the electrons of the N atoms tend to flow to the Ni atoms exposed by the defects (Figure 5d, 5e, 5f and Figure S13). Notably, surface vacancy-induced local electropositive site to directly chemisorption lone pair electrons of propylamine molecules.

Broadly accepted, the first step of dehydrogenation is considered the rate-determining step in the dehydrogenation

### **RESEARCH ARTICLE**

activation reaction of C-N bonds.<sup>[28]</sup> As such, the subsequent chemical activation process was also explored by simulating the first step of dehydrogenation in detail. The first dehydrogenation of propylamine to propionitrile was discussed in two cases: dehydrogenation of N (define as route 1) and adjacent carbons (define as route 2). As show in Figure 5g and 5h, route1 has a smaller reaction energy barrier (1.43 eV) compared with route 2 (1.92 eV). In addition, after dehydrogenation, the Ni-N bond length in route 1 was slightly increased (0.2 Å), which caused N atom to be chemically adsorbed by two Ni sites simultaneously, and facilitates the subsequent dehydrogenation reaction process. These findings further suggested that the vacancy-induced local electropositive site chemisorbs the N atom with lone pairs of electrons and then attack the corresponding N-H bond. In summary, the resolving of vacancies model, local charge distribution and adsorption process will undoubtedly provide important insights for the discovery of more chemical activation processes.

#### Conclusion

Integrating all experiments and theoretical calculation, we proposed vacancies-rich Ni(OH)<sub>2</sub> atomic layer to realize a direct one-step route from the electrooxidation of amino C-N bonds to nitrile C=N bonds for accessible nitriles producing. VR-Ni(OH)<sub>2</sub> were controllably synthesized via in situ electrochemical topological transformation of Ni-MOFs, which revealed the unstable MOFs usually as a pre-catalysts. EXAFS and XPS results clearly reveals the presence of vacancy in Ni(OH)2 atomic layer. Then, the all-around electrochemical testing and in situ spectroscopy suggest the vacancies-rich Ni(OH)<sub>2</sub> efficient promote the electrooxidation of amino C-N bonds to nitrile C≡N bonds. Combined with the theoretical simulation, the vacancyinduced local electropositive site chemisorbs the N atom with lone pairs of electrons and then attack the corresponding N-H bond. Furthermore, this work gains atomic-level insights into vacancies, local charge distribution and adsorption process through semiquantifying the relationships among model, structure and performance, holding promise for unlocking other profound electrosynthesis reaction.

#### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21805102, 21825103, and 51727809), and the Fundamental Research Funds for the Central University 2019kfyXMBZ018).

Keywords: vacancies-rich nickel hydroxides• positive charge surface · C-N bond activates dehydrogenation · local electropositive • amine electrooxidation

- [1] a) F. F. Fleming, L. Yao, P. C. Ravikumar, L. Funk, B. C. Shook, J. Med. Chem. 2010, 53, 7902-7917; b) A. Martin, V. N. Kalevaru, ChemCatChem 2010, 2, 1504-1522; c) R. Y. Liu, M. Bae, S. L. Buchwald, J. Am. Chem. Soc. 2018, 140, 1627-1631; d) X.-Q. Chu, D. Ge, Z.-L. Shen, T.-P. Loh, ACS Catal. 2017, 8, 258-271; e) J. Mao, Z. Wang, X. Xu, G. Liu, R. Jiang, H. Guan, Z. Zheng, P. J. Walsh, *Angew. Chem. Int. Ed.* **2019**, *58*, 11033-11038.
- [2] Y. Sato, M. Yato, T. Ohwada, S. Saito, K. Shudo, J. Am. Chem. Soc.

1995. 117. 3037-3043.

- a) Z. Li, Y. Xiao, Z. Q. Liu, Chem. Commun. 2015, 51, 9969-9971; [3] b) T. Shen, T. Wang, C. Qin, N. Jiao, Angew. Chem. Int. Ed. 2013, 52, 6677-6680; c) T. Wang, N. Jiao, Acc. Chem. Res. 2014, 47, 1137-1145; d) Y. Wang, S. Furukawa, N. Yan, ACS Catal. 2019, 9, 6681-6691.
- R. V. Jagadeesh, H. Junge, M. Beller, Nat. Commun. 2014, 5, 4123. [4] [5] a) B. You, X. Liu, N. Jiang, Y. Sun, J. Am. Chem. Soc. 2016, 138, 13639-13646; b) B. H. R. Suryanto, H.-L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, Nat. Catal. 2019, 2, 290-296; c) Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Norskov, T. F. Jaramillo, *Šcience* **2017**, *355*, eaad4998. P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, E. H.
- [6] Y. De Lura, C. Ham, D. Huggins, C. A. Sarej, T. F. Sarahino, E. H. Sargent, *Science* **2019**, *364*, eaav3506.
   Y. Huang, X. Chong, C. Liu, Y. Liang, B. Zhang, *Angew. Chem. Int.*
- [7] *Ed.* **2018**, *57*, 13163-13166. a) Y. Zhou, Y. Gao, X. Zhong, W. Jiang, Y. Liang, P. Niu, M. Li, G.
- [8] Zhuang, X. Li, J. Wang, Adv. Funct. Mater. 2019, 29, 1807651; b) C. Tang, R. Zhang, W. Lu, Z. Wang, D. Liu, S. Hao, G. Du, A. M. Asiri, X. Sun, Angew. Chem. Int. Ed. 2017, 56, 842-846
- a) J. Vilim, T. Knaus, F. G. Mutti, Angew. Chem. Int. Ed. 2018, 57, [9] 14240-14244; b) H. Liu, C. Xu, D. Li, H.-L. Jiang, Angew. Chem. Int Ed. 2018, 130, 5477-5481.
- K. Kiyokawa, S. Hata, S. Kainuma, S. Minakata, Chem. Commun. [10] 2019, 55, 458-461.
- X. Zhang, Y. Zhao, Y. Zhao, R. Shi, G. I. N. Waterhouse, T. Zhang, Adv. Energy Mater. 2019, 9, 1900881. [11]
- a) J. Huang, J. Chen, T. Yao, J. He, S. Jiang, Z. Sun, Q. Liu, W. [12] Cheng, F. Hu, Y. Jiang, Z. Pan, S. Wei, Angew. Chem. Int. Ed. 2015, 54, 8722-8727; b) X. P. Wang, H. J. Wu, S. B. Xi, W. S. V. Lee, J. Zhang, Z. H. Wu, J. O. Wang, T. D. Hu, L. M. Liu, Y. Han, S. W. Chee, S. C. Ning, U. Mirsaidov, Z. B. Wang, Y. W. Zhang, A. Borgna, J. Wang, Y. H. Du, Z. G. Yu, S. J. Pennycook, J. M. Xue, Energy Environ. Sci. 2020, 13, 229-237
- [13] a) B. Dong, W. Li, X. Huang, Z. Ali, T. Zhang, Z. Yang, Y. Hou, Nano Energy 2019, 55, 37-41; b) U. K. Sultana, J. D. Riches, A. P. O'Mullane, Adv. Funct. Mater. 2018, 28, 1804361; c) W. Wang, Y.-B. Zhu, Q. Wen, Y. Wang, J. Xia, C. Li, M.-W. Chen, Y. Liu, H. Li, H.-A. Wu, T. Zhai, Adv. Mater. 2019, 31, 1900528.
- [14] A. Carton, A. Mesbah, T. Mazet, F. Porcher, M. Francois, Solid State Sci. 2007, 9, 465-471
- Q. Zhou, Y. Chen, G. Zhao, Y. Lin, Z. Yu, X. Xu, X. Wang, H. K. Liu, [15] W. Sun, S. X. Dou, ACS Catal. 2018, 8, 5382-5390.
- a) J. Tian, Y. Leng, Z. Zhao, Y. Xia, Y. Sang, P. Hao, J. Zhan, M. Li, [16] H. Liu, Nano Energy 2015, 11, 419-427; b) T. Ungár, Scr. Mater. 2004, 51, 777-781.
- [17] a) W. Li, F. Li, H. Yang, X. Wu, P. Zhang, Y. Shan, L. Sun, Nat. Commun. 2019, 10, 5074; b) Z.-F. Huang, J. Song, Y. Du, S. Xi, S. Dou, J. M. V. Nsanzimana, C. Wang, Z. J. Xu, X. Wang, Nat. Energy 2019, 4, 329-338.
- Y. Sun, Q. Liu, S. Gao, H. Cheng, F. Lei, Z. Sun, Y. Jiang, H. Su, S. [18] Wei, Y. Xie, Nat. Commun. 2013, 4, 2899.
- [19] B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. García-Melchor, L. Han, J. Xu, M. Liu, L. Zheng, F. P. G. d. Arquer, C. T. Dinh, F. Fan, M. Yuan, E. Yassitepe, N. Chen, T. Regier, P. Liu, Y. Li, P. D. Luna, A. Janmohamed, H. L. Xin, H. Yang, A. Vojvodic, E. H. Sargent, Science 2016, 352, 333-337.
- H. You, Z. Zhuo, X. Lu, Y. Liu, Y. Guo, W. Wang, H. Yang, X. Wu, H. [20] Li, T. Zhai, CCS Chem. 2019, 1, 396-406.
- [21] N. Zhang, Y. Zou, L. Tao, W. Chen, L. Zhou, Z. Liu, B. Zhou, G. Huang, H. Lin, S. Wang, Angew. Chem. Int. Ed. 2019, 58, 15895-15903.
- H. Y. Wang, S. F. Hung, H. Y. Chen, T. S. Chan, H. M. Chen, B. Liu, [22] J. Am. Chem. Soc. 2016, 138, 36-39.
- D. Liu, J. C. Liu, W. Cai, J. Ma, H. B. Yang, H. Xiao, J. Li, Y. Xiong, [23] Y. Huang, B. Liu, Nat. Commun. 2019, 10, 1779.
- C. Ennis, R. Auchettl, M. Ruzi, E. G. Robertson, Phys. Chem. Chem. [24] Phys. 2017, 19, 2915-2925.
- B. Köröglu, Z. Loparo, J. Nath, R. E. Peale, S. S. Vasu, *J. Quant.* Spectrosc. Radiat. Transfer **2015**, *152*, 107-113. C. Li, Y. Liu, Z. Zhuo, H. Ju, D. Li, Y. Guo, X. Wu, H. Li, T. Zhai, Adv. [25]
- [26] Energy Mater. 2018, 8, 1801775.
- [27] H. Li, J. Shang, Z. Ai, L. Zhang, J. Am. Chem. Soc. 2015, 137, 6393-6399
- I. Dutta, S. Yadav, A. Sarbajna, S. De, M. Holscher, W. Leitner, J. K. [28] Bera, J. Am. Chem. Soc. 2018, 140, 8662-8666.

## **RESEARCH ARTICLE**

#### Entry for the Table of Contents



Vacancies-rich  $Ni(OH)_2$  nanosheets were proposed to realize a direct one-step route from the electrooxidation of amino C-N bonds to nitrile C=N bonds for accessible nitriles producing. During the catalytic reaction, the vacancy-induced local electropositive site chemisorbs the N atom with lone pairs of electrons and then attack the corresponding N-H bond.