Mechanistic study of monolayer NiP₂ (100) towards solar hydrogen production

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TOC

Abstract:

Understanding catalytic mechanism at the molecular level is critical to the design and exploration of new materials for solar hydrogen production. Herein, we have first surveyed the catalytic activity towards hydrogen evolution reaction (HER) for all low-index surfaces of different nickel phosphides (Ni₃P, Ni₁₂P₅, Ni₂P, Ni₅P₄, NiP, NiP₂, and NiP₃). It is found that the surface P atoms with only one single PP bond possess excellent HER activity. Accordingly, we then explored monolayer NiP₂ (100) as the cathode material. Comprehensive density functional theory study was employed to verify the HER activity of this material, including the effect of vacancy and doping. Defect-free and Zn-doped monolayer NiP₂ (100) are found to possess excellent HER activity and thermodynamic stability. This crystal facet also has a high density of active sites (0.126 N Å⁻² under an applied over-potential of 200 mV), which is very close to Pt (111) surface (0.132 N Å⁻²). The low surface energy and strengthened bonding imply that the monolayer NiP₂ (100) can be stable and easy to synthesize. This finding not only promotes a comprehensive understanding of Ni_xP_y material towards its catalytic activity for HER, but also suggests a possible new material for the experimentalist in the field.

1. Introduction

The human society is striving to maintain a high-technology lifestyle without causing significant environmental hazards to our planet. Exploration of renewable energy sources is a practical solution to meet the requirements of our continued economic development. Hydrogen, regarded as the future generation of clean fuel, has attracted immense amount of attention in recent years. However, the realization of industrial scale hydrogen production largely depends on the development of cost-effective materials using green production technology. One of the most promising renewable energy technologies is photocatalytic or electrochemical water splitting to generate hydrogen fuel (using electricity generated by solar cells).

Pt is the most effective catalyst for hydrogen evolution reaction (HER), however, its scarcity makes it impossible for practical large-scale applications. This has prompted continued investigation towards seeking new generation of materials for affordable applications.^[1] These materials include transition metals^[2] and their dichalcogenides,^[3] carbides,^[4] borides,^[5] nitrides,^[6] phosphides,^[7] and metal-free carbon nitrides^[8] and so on. Among them, nickel phosphides (Ni_xP_y) hold great promise as a low-cost and earth-abundant catalyst. In this type of compounds, phosphorus has a lower catenation tendency, and displays various kinds of shapes (cages, dumbbell, etc.) and structures (1D to 3D chains). In addition, Ni_xP_y often forms amorphous films that are immune to chemical attack as compared with their crystalline counterparts with grain boundaries. Nickel phosphides generally possess a high stability in acidic solutions and it can only be corroded in hot oxidizing acids such as HNO_3 .^[9] Researches have indicated that Ni_xP_y has more than ten stoichiometric compositions, and some of them have relatively high HER activity.^[10] As known, facet orientations indeed play a crucial role on catalytic activity during an HER process.^[11] Highly-active facet orientations with certain particular exposed atomic configurations are one of the most economical and effective route to further lower the kinetic HER over-potential. Due to the huge number of surfaces and uncertainty in their synthesis conditions, experimentally evaluating all these possibilities is practically prohibitive, if not at all impossible. Theoretical study therefore becomes important, as they will provide good insights at the atomic/molecular level, and the understanding will then guide the design and selection of materials for optimizing the performance of solar energy conversion. There have been some excellent theoretical studies on the active sites and ability of HER.^[12] However, most of them were focused on the position of active site only. It will be ideal for the developed models to offer atomic information to enable an in-depth understanding of corresponding active sites. Therefore, unearthing the key factors affecting the HER activity becomes a pressing task for the design and optimization of efficient catalysts.

In the present work, we firstly investigate the pivotal parameters influencing the HER activity based on the density functional theory (DFT) simulations of Ni_xP_y . According to the survey results, monolayer NiP_2 (100) was selected as a potentially viable material for HER. Detailed theoretical studies were then carried out on defect-free and Zn doped monolayer of NiP_2 (100). Our current study promotes a deep comprehension of this material for its catalytic ability and stability.

2. Computational Methods

CASTEP module (Accelrys Inc., San Diego, CA, USA) is used to optimize the structures and calculate the energies. During the calculations, the exchange-correlation energy was calculated

using the Perdew-Burke-Ernzerh generalized gradient approximation.^[13] The ultrasoft pseudopotential method, considering the ionic cores of Ni-3d⁸4s² and P-3s³3p², was used to describe the electron-ion interaction in reciprocal space. The Broyden-Fletcher-Goldfarb-Shanno algorithm with line search was selected as the minimization algorithm. The energy cutoff is 380 eV and the SCF tolerance is 5.0×10⁻⁷ eV atom⁻¹. The quality of the *k*-points samplings is set to ensure the actual spacing is close to 0.05 Å⁻¹. The convergence tolerances are in total energy of within 5.0×10⁻⁶ eV atom⁻¹, maximum ionic Hellmann-Feynman force of within 0.01 eV Å⁻¹, maximum stress of within 0.02 GPa, and maximum ionic displacement of within 5.0×10⁻⁴ Å. This method has been verified in our previous publications.^[14]

The surfaces, containing at least 6 layers, were obtained from the bulk Ni₃P, Ni₁₂P₅, Ni₂P, Ni₅P₄, NiP, NiP₂, and NiP₃, as shown in Figure S1 in the Support Information (SI) with a vacuum region of 15 Å. Considering the symmetry, all low-index surfaces with different terminations were chosen during calculation. Different terminations are denoted using capital letters A, B, C and D, when applicable.

The different energies are calculated according to the following eqs.^[15]

Atomization energy:

$$E_{\text{atomisation}} = E_{\text{sys}} - n_{\text{Ni}} E_{\text{Ni atom}} - n_{\text{P}} E_{\text{P atom}} \quad (1)$$

Bond energy:

$$E_{\text{bond}} = E_{\text{atomisation}} / (2n_{\text{Ni}} + 1.5n_{\text{P}}) \quad (2)$$

Vacancy formation energy

$$\Delta E_{\text{vac}} = E_{\text{sys}} - n_{\text{Ni}} (E_{\text{Ni atom}} + 2E_{\text{bond}}) - n_{\text{P}} (E_{\text{P atom}} + 1.5E_{\text{bond}}) \quad (3)$$

Defect formation energy

$$\Delta E_{\text{defect}} = E_{\text{sys}} - n_{\text{M}} E_{\text{M atom}} - n_{\text{Ni}} (E_{\text{Ni atom}} + 2E_{\text{bond}}) - n_{\text{P}} (E_{\text{P atom}} + 1.5E_{\text{bond}}) \quad (4)$$

The surface energy, adsorption energy and Gibbs free energy of adsorption hydrogen atom are calculated by eqs. (5-7).^[16]

$$E_{\text{sur}} = (E_{\text{slab}} - n_{\text{Ni}} E_{\text{Ni atom}} - n_{\text{P}} E_{\text{P atom}} + n_{\text{Ni}} E_{\text{f Ni}_x\text{P}_y} + \Delta\mu_{\text{P}}(yn_{\text{Ni}}/x - n_{\text{P}})) / (2A) \quad (5)$$

$$\Delta E_{\text{ads}} = E[\text{Ni}_x\text{P}_y + \text{H}] - E[\text{Ni}_x\text{P}_y] - 1/2 E[\text{H}_2] \quad (6)$$

$$\Delta G = E[\text{Ni}_x\text{P}_y + \text{H}] - E[\text{Ni}_x\text{P}_y] - 1/2 E[\text{H}_2] + \Delta E_{\text{ZPE}} - T\Delta S_{\text{H}} \quad (7)$$

where E_{sys} and E_{slab} are energies of the investigated system and slab model, $E_{\text{Ni atom}}$ and E_{P} are energies per atom of the metallic (M = Ni, Co, Cu, Zn, Fe, Mn, Cd) and black P, $E_{\text{f Ni}_x\text{P}_y}$ is the formation energy of Ni_xP_y , n_{Ni} and n_{P} are the number of Ni and P atoms in the slab model, and A is the surface area of the slab. $E[\text{Ni}_x\text{P}_y + \text{H}]$ is the optimized energy of the system with H atom adsorbed on the Ni_xP_y facet. $E[\text{Ni}_x\text{P}_y]$ is optimized the energy of Ni_xP_y surface, and $E[\text{H}_2]$ means the average energy of a gas phase H_2 molecule. ΔE_{ZPE} is the zero-point energy considered as 0.05 eV. T is the absolute temperature, $-T\Delta S_{\text{H}}$ denotes the contribution of entropy at temperature K , which equals to 0.20 eV at 298 K.^[17] The calculated energies of species are given in Table S1. The exchange current at overpotential $\eta = 100$ mV can be determined based on the calculated ΔG .^[18]

3. Results and Discussion

3.1 The activity survey of Ni_xP_y

As known, the best catalyst has a Gibbs free energy of H^* absorption equal to zero following either the Volmer-Tafel or the Heyrovsky mechanism.^[19] In this work, the ΔG values of all low surface energy (thus stable) facets of the different types of Ni_xP_y were calculated to reveal the origin of the catalytic activity. The relationship between ΔG with charge state and bond number are shown in Figure 1. All stable facets are listed in Table S2.

Figure 1. (a) The relationship between Mulliken charge and ΔG ; (b) The relationship between Hirshfeld charge and ΔG ; (c) The relationship between number of PP bond and ΔG ; (d) Local magnification the relationship between number of PP bond and ΔG . Double and triple PP bond are not considered. Detailed data and geometric structure can be found in Table S2 and Figure S2-S8.

The relationship between the charge state and applied over potential was analyzed in this work. As indicated in Figure 1, there is no obvious connection between charge and HER activity of Ni_xP_y material either based on the Mulliken or Hirshfeld charge. Furthermore, it is found the neighboring P atoms have greatly affect the HER activity. The $|\Delta G|$ are localized in a small region: the number of PP bond is either 0 or 1, as shown in Figure 1c. It has been verified by previous experiments^[10] and theoretical prediction^[20] that high HER activity is associated with the situation when the P atoms are only connected with neighboring Ni atoms. It is interesting to note that some of the $|\Delta G|$ values are nearly zero if there are only one PP bond (Figure 1d). Therefore, the surface P atom with one single PP bond is expected to exhibit the best HER activity. Among different surfaces with one PP bond, NiP_2 (100) surface has the highest density of active sites (to be discussed later). It also possesses a clear layer-by-layer crystal structure (Figure 2a) that makes it possible to form a monolayer that may exhibit the typical two-dimensional (2D) properties such as large electrochemical surface areas, high porosity for fast mass transfer, and excellent structure rigidity to ensure high stability.^[21] In order to verify this, detailed calculation about monolayer of NiP_2 (100) is carried out next.

3.2 Geometric structure and electronic characteristics of monolayer NiP_2 (100)

The optimized bulk NiP₂, NiP₂ (100) and monolayer NiP₂ (100) facets are manifested in Figure 2.

Figure 2. (a) The geometric structure of bulk NiP₂, NiP₂ (100) and monolayer NiP₂ (100). Violet and blue spheres stand for P and Ni atoms, respectively. The bonds are displayed with the bond length tolerance from 0.6 to 1.185; (b) PDOS of bulk NiP₂, NiP₂ (100) and monolayer NiP₂ (100), and the electron density difference map of monolayer NiP₂ (100) surface with potential isovalue equals to 5.0 eV are inserted in, where a loss of electrons is indicated in blue while electron enrichment is indicated in red.

Figure 2a shows there are four coordination for Ni and P in bulk NiP₂. The Ni connects with four neighbor P, and P connect with two neighbor P and two neighbor Ni. The NiP₂ (100) surface are only terminated by P-P bond. For unrelaxed slab of NiP₂ (100), the Ni and P atoms are non-coplanar on the surface. Four Ni atoms are located in the middle, and four P atoms are located above these Ni atoms while another four P atoms are below. The four P atoms above only have three coordination. In the case of relaxed NiP₂ (100) slab, the Ni and P atoms in the surface will move inward and making themselves coplanar. The inward movement also leads to the formation of NiNi bond between first layer and second layer. When monolayer NiP₂ (100) is generated, all of the Ni atoms have four bonds with neighbors P, while all of P atoms possesses three bond: two with neighbors Ni and one with neighbor P. The Ni and P atoms are densely packed in a regular atomic-scale pentagon pattern, which is similar to graphene, the well-known 2D material. As illustrated in Figure 2b, we found that the band gap of bulk NiP₂ is around 0.60 eV, which is consistent with previous experimental results (0.50 eV-0.73 eV).^[22] The valence band maximum is formed by Ni 3d orbitals, while the conduction band minimum is made up of Ni 3d and P 3p resonance peaks. For the NiP₂ (100) facet, the zero band gap indicates this surface become a conductor, and Ni 3d and P 3p orbitals afford the conductivity of NiP₂ (100) facet. When the monolayer NiP₂ (100) is formed, partial density of states (PDOS) at the Fermi level are increased further due to the appearance of unsaturated bond. This indicates the monolayer NiP₂ (100) may display remarkable electron mobility at room temperature.

Forming vacancy and doping with another element are two of the important strategies to improve catalytic properties of materials. Therefore, the effect of different vacancy and doping are

investigated. [Figure 3](#) shows the optimized geometric structure and defect formation energy of different vacancy and doping of monolayer NiP_2 (100). The vacancy formation energies in monolayer NiP_2 (100) facets indicate Ni vacancy is easier to form than P vacancy. After the Ni vacancy is formed, the neighbor P atom will move and generate new bonds, namely, the double PP bond and single NiP bond. However, there are no obvious structure change when P vacancy is formed, although the neighbor bond lengths are decreased. For the elemental doping, several positive bivalent metal atoms (Co, Cu, Zn, Fe, Mn, Cd) are considered. As shown in [Figure 3](#), Zn is the most stable dopant with defect formation energy at 0.22 eV. Furthermore, there is no obvious structure change after doping expect for Cd doping.

Figure 3. The optimized geometric structure and defect formation energy of different vacancy and doping of monolayer NiP_2 (100). More details about formation energies can be found in [Table S3](#).

3.3 Activity for HER

Figure 4. Free energy profile of H₂ generation on different active site (a) NiP₂ (100) with different layer, where Pt (111) surface is displayed for comparison; (b) monolayer NiP₂ (100) with Ni and P vacancy; (c) **P sites on Co, Cu, Zn, Fe, Mn and Cd doped monolayer NiP₂ (100)**; (d) **metal sites on Co, Cu, Zn, Fe, Mn and Cd doped monolayer NiP₂ (100)**. Yellow spheres stand for H atoms, violet spheres stand for P atoms, blue spheres stand for Ni atoms and the doped atoms are manifest with element symbol near the corresponding atoms.

ΔG for different kinds of monolayer NiP_2 (100) facets are indicated in Figure 4. Figure 4a shows the ΔG value when the number of layers changes from 1 to 5. It is found that H^* is stable when adsorbed on the Top P site on the basis of the minimum energy of the system, which is agreeable with previous researches where P was found to be the active site for HER.^[23] When there is only 1 layer, only one type (P1) atom is considered because all P atom on the surface are nearly same. Where there are 2 to 5 layers, two types of P atoms are considered, one connected with sublayer P atom and another connect with sublayer Ni atom. As indicated in Figure 4a, the ΔG of H^* for the 1-layer P1 and 2-layer P1 are -0.14 eV. When the layer number is larger than 2, the $|\Delta G|$ increases greatly and not suitable for HER. Therefore, mono- and double layered NiP_2 (100) are able to bond the atomic hydrogen while still able to desorb H_2 easily. Figure 4b manifest the effect vacancy on the catalytic activity. As indicated, $|\Delta G|$ for most sites are increased compared with defect-free surface, indicating the activity will greatly decrease when vacancies are formed on the surface. The effect of different doping are displayed in Figure 4c. The influence can be divided into are three categories. The first simultaneously increases the activity of P1 and P2 (Zn); the second makes one P more active while another P less active (Cu, Fe, Mn and Cd); the third sees the decrease in the activity of all P atoms (Co). Besides the P sites, the metal sites may also be active during HER. Figure 4d indicates that most of H atom on metal sites are moved into top P site or bridge metal-P site on monolayer NiP_2 (100) expect for the Co, Fe and Mn. On these three metal sites, ΔG for Mn site is -0.03 eV. Therefore, Mn doped NiP_2 could be a good candidate for water splitting. This finding is consistent with a recent experimental report in that Mn-doped NiP_2 showed increased HER activity.^[24] Based on our prediction, this increase will not be as significant as Zn doping. However, there has been no experimental report on the HER activity of Zn-doped NiP_2 . Therefore, we would recommend future experiment on Zn-doped monolayer NiP_2 (100). Figure 5 shows a summary of the exchange current for HER and density of active sites on bulk NiP_2 (100), monolayer NiP_2 (100) and Zn doped monolayer NiP_2 (100) surfaces.

Figure 5. (a) The exchange current for HER over NiP_2 (100), monolayer NiP_2 (100), 12.5% Zn doped monolayer NiP_2 (100) surfaces, Pt (111), and Ni (111), are manifest based on the calculated hydrogen chemisorption energy. The experimental data (Exp.) for Ni, Pt from Ref. [25] are also added for comparison; (b) The density of active sites, defined as the number of active site per unit surface area, on different monolayer NiP_2 (100) surfaces, with Pt (111) added for comparison. The number of active sites is obtained

by counting the number of sites where the $|\Delta G|$ (Gibbs free energy of adsorption hydrogen atom) is smaller than the over-potential.

Figure 5 indicates the over-potential on monolayer NiP_2 (100) and Zn doped monolayer NiP_2 (100) are -0.14 and -0.03 eV, respectively. Both are much better than bulk NiP_2 (100). The number of active sites for Zn doped monolayer NiP_2 (100) is $0.126 \text{ N } \text{\AA}^{-2}$ under applied 200 mV over-potential, which is very close to one of Pt (111) surface ($0.132 \text{ N } \text{\AA}^{-2}$). When compared with monolayer of MoS_2 , there is no obvious difference for the over-potential for HER. The main difference lies with the number of the active sites. For MoS_2 , it has been found only the edge sites of crystalline MoS_2 are active, while the basal plane is inactive for HER.^[26] Therefore we expect the number of active sites is much lower in MoS_2 . To the contrary, the basal plane of monolayer NiP_2 (100) has the excellent HER performance and its density is close to Pt (111). Furthermore, S vacancy is often induced to improve the HER activity on MoS_2 , however, its introduction will reduce the stability of MoS_2 .^[26] This dilemma does not exist in the monolayer NiP_2 (100) as discussed above. Based on our study, monolayer NiP_2 (100), particularly the one with Zn-doping, will greatly improve the HER activity. It can be considered as the new generation of cathode materials for large-scale applications from activity perspective. Recently, researchers obtained direct evidence that the porous 2D NiP_2 have excellent HER activity.^[27] We speculate this might be due to the formation of monolayer layer at certain locations within the porous structure.

3.4 Stability analysis

Surface energy is the key parameter to assess surface stability. Figure 6 manifests the surface energies for each low-index surfaces of NiP_2 and the surface energy change along with different layers of NiP_2 (100).

Figure 6. (a) Surface energies of the most stable surface terminations. Lines parallel to the horizontal axis represent stoichiometric terminations and lines with negative slopes are for the P-rich terminations; (b) the bond length of bulk NiP_2 , NiP_2 (100) and monolayer NiP_2 (100), where the last column (Ave.) in each group is the average value of d₁, d₂ and d₃.

Comparing with other phosphides, bulk NiP_2 is thermodynamically favorable when $\Delta\mu_p$ changed from -0.07 eV to -0.22 eV.^[14a] Considering contributions of temperature effect and interface relaxation, the $\Delta\mu_p$ is expanded from 0 eV to -0.30 eV during the surface energy calculation. As indicated in Figure 6a. The (100)A is the most stable surface among all low-index surfaces of NiP_2 , which is consistent with previous experimental result that (200) planes of NiP_2 is the easy exposed surface).^[27b] Combined with the geometric structure in Figure 2, we found the (100)A surface terminates with four P-P bonds with a length of 2.102 Å while Ni atoms have four coordination with four neighbor P atoms. Therefore, the stable surface is NiP_4 tetrahedron with three- and four-coordinated P atoms. In addition, the surface energy still remains low when the NiP_2 (100) is changed from 5 layer to 1 layer. The lower surface energy indicates it is highly likely that monolayer NiP_2 (100) can be synthesized in experiment. Furthermore, Ni atoms have four coordination in the monolayer of NiP_2 (100). The saturated Ni atoms ensure the stability of monolayer (100) surface because phosphorus often generally possess high corrosion resistance due to the low catenation tendency and formed superstructures such as cages, dumbbell, chains etc.^[9] Furthermore, the average bond length of monolayer NiP_2 (100) (2.18 Å) is decreased when compared with bulk NiP_2 (100) (2.21 Å). This makes the surface atoms more tightly packed and contributes to the stability of monolayer NiP_2 (100), as shown in Figure 6b.

4. Conclusions

In this paper, understanding of the catalytically active sites of Ni_xP_y at the molecular level is proposed based on a comprehensive theoretical analysis. We found that the surface P atom with only one single PP bond will have excellent hydrogen evolution reaction (HER) activity. Based on this finding, we explore monolayer NiP_2 (100), as a candidate for cathode material in HER. DFT simulations were performed to verify the HER activity of this material, including the effect of different doping and vacancies. The calculated hydrogen chemisorption energies are -0.14, and -0.03 eV, respectively, for monolayer NiP_2 (100) and Zn doped monolayer NiP_2 (100). Moreover, the density of active sites monolayer NiP_2 (100) is $0.126 \text{ N } \text{\AA}^{-2}$ under an applied over-potential of 200 mV, which is very close to Pt (111) surface ($0.132 \text{ N } \text{\AA}^{-2}$). This study also found that NiP_2 (100) is the most stable surface among all the low-index surfaces of NiP_2 . Monolayer of NiP_2 (100) may be easy to be synthesized because the formation of NiP_2 (100) only need to break P-P with a length of 2.102 Å. Therefore, monolayer NiP_2 (100) and Zn doped monolayer NiP_2 (100) could be exploited in experiment to improve the HER catalytic performance. This work provides a new insight for designing new 2D phosphides as a low-cost and highly efficient HER catalyst. This method can also be used to quickly develop other new materials and guide the experimental scientists for selective synthesis.

Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's website.

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Conflicts of Interest

The authors declare no competing financial interest.

Keywords

phosphides, nickel phosphides, water splitting, hydrogen evolution reaction, DFT calculations

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- [1] S. H. Hsu, J. Miao, L. Zhang, J. Gao, H. Wang, H. Tao, S. F. Hung, A. Vasileff, S. Z. Qiao, B. Liu, *Adv Mater.* **2018**, *22*, 1707261.
- [2] J. R. McKone, B. F. Sadler, C. A. Werlang, N. S. Lewis, H. B. Gray, *ACS Catal.* **2013**, *3*, 166–169.
- [3] a) Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara, T. F. Jaramillo, *Nano Lett.* **2011**, *11*, 4168–4175; b) J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou, Y. Xie, *Adv. Mater.* **2013**, *25*, 5807–5813; c) D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. Alves, T. Fujita, M. Chen, T. V. Asefa, B. Shenoy, G. Eda, M. Chhowalla, *Nat. Mater.* **2013**, *12*, 850–855; d) J. Yang, D. Voiry, S. J. Ahn, D. Kang, A. Y. Kim, M. Chhowalla, H. S. Shin, *Angew. Chem. Int. Ed.* **2013**, *52*, 13751–13754.
- [4] a) W. F. Chen, C. H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu, R. R. Adzic, *Energ Environ. Sci.* **2013**, *6*, 943–951; b) H. Wang, N. Yang, W. Li, W. Ding, K. Chen, J. Li, L. Li, J. Wang, J. Jiang, F. Jia, Z. Wei, *ACS Energy Lett.* **2018**, *3*, 1345–1352.
- [5] H. Vrubel, X. L. Hu, *Angew. Chem., Int. Ed.* **2012**, *51*, 12703–12706.
- [6] B. F. Cao, C. M. Veith, J. C. Neufeld, R. R. Adzic, P. G. Khalifah, *J. Am. Chem. Soc.* **2013**, *135*, 19186–19192.
- [7] a) Y. Feng, X. Y. Yu, U. Paik, *Chem. Commun.* **2016**, *52*, 1633–1636; b) Y. Men, P. Li, J. Zhou, G. Cheng, S. Chen, W. Luo, *ACS Catal.* **2019**, *9*, 3744–3752; c) K. Wang, B. Huang, F. Lin, F. Lv, M. Luo, P. Zhou, Q. Liu, W. Zhang, C. Yang, Y. Tang, Y. Yang, W. Wang, H. Wang, S. Guo, *Adv. Energy Mater.* **2018**, *8*, 1801891; d) K. Xu, Y. Sun, Y. Sun, Y., Zhang, G. Jia, Q. Zhang, L. Gu, S. Li, Y. Li, H. J. Fan, *ACS Energy Lett.* **2018**, *3*, 2750–2756.
- [8] a) C. Merlet, B. Rotenberg, P. A. Madden, P.-L. Taberna, P. Simon, Y. Gogotsi, M., Salanne, *Nat. Mater.* **2012**, *11*, 306–310; b) S. Meng, B. Li, S. Li, S. Yang, *Mater. Res. Express.* **2017**, *4*, 055602.
- [9] Gerasimov, M. V., Simirskii, Y. N., *Metallurgist.* **2008**, *52*, 477–481.
- [10] a) Z. Huang, Z. Chen, Z. Chen, C. Lv, H. Meng, C. Zhang, *ACS Nano.* **2014**, *8*, 8121–8129; b) García-Muelas, R., Li, Qiang, Lopez, N., *J. Phys. Chem. B.* **2018**, *122*, 672–678; c) L. G. Feng, H. Vrubel, M. Bensimon, X. L. Hu, *Phys. Chem. Chem. Phys.* **2014**, *16*, 5917–5921; d) Y. Shu, Y. K. Lee, S. T. Oyama, *J. Catal.* **2005**, *236*, 112–121; e) Y. Pan, Y. Liu, J. Zhao, K. Yang, J. Liang, D. Liu, W. Hu, D. Liu, Y. Liu, C. Liu, *J. Mater. Chem. A* **2015**, *3*, 1656–1665; f) J. P. Eric, R. M. James, G. R. Carlos, J. B. Adam, M. W. Alex, S. L. Nathan, E. S. Raymond, *J. Am. Chem. Soc.* **2013**, *135*, 9267–9270. g) H. Zhao, S. T. Oyama, H. J. Freund, R. Włodarczyk, M. Sierka, *Applied Catalysis B: Environmental* **2015**, *164*, 204–216.
- [11] a) J. Pan, G. Liu, G. Q. Lu, H. M. Cheng, *Angew. Chem., Int. Ed.* **2011**, *50*, 2133–2137; b) J. Hermann, M. Trachta, P., Nachtigall, O. Bludsky, *Catal. Today* **2014**, *227*, 2–8; c) J. N. Wilson, H. Idriss, *J. Amer. Chem. Soc.* **2002**, *124*, 11284–11285; d) H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Nature* **2008**, *453*, 638–642. e) J. Zhu, F. Fan, R. Chen, H. An, Z. Feng, C. Li, *Angew. Chem.* **2015**, *127*, 9239–9242; f) T. Tachikawa, T. Ochi, Y. Kobori, *ACS Catal.* **2016**, *6*, 2250–2256.

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- [12] a) R. B. Wexler, J. M. P. Martinez, A. M. Rappe, *ACS Catal.* **2017**, *7*, 7718–7725; b) P. Liu, J. A. Rodriguez, *J. Am. Chem. Soc.* **2005**, *127*, 14871–14878; c) M. H. Hansen, L.-A. Stern, L. Feng, J. Rossmeisl, X. Hu, *Phys. Chem. Chem. Phys.* **2015**, *17*, 10823–10829.
- [13] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *77*, 3865 – Published 28 October 1996; b) Erratum *Phys. Rev. Lett.* **1997**, *78*, 1396
- [14] a) J. Hu, S. Zheng, X. Zhao, X. Yao, Z. Chen, *J. Mater. Chem. A* **2018**, *6*, 7827–7834; b) J. Hu., W. Chen, X. Zhao, H. Su, Z. Chen, *ACS Appl. Mater. Interfaces* **2018**, *10*, 5475–5484.
- [15] a) G. Liu, A. W. Robertson, M. J. Li, W. H. Kuo, M. T. Darby, M. H. Muhieddine, Y. Lin, K. Suenaga, M. Stamatakis, J. H. Warner, S. C. Tsang, *Nature Chem.* **2017**, *9*, 810–816. b) F. He, K. Li, G. Xie, Y. Wang, M. Jiao, H. Tang, Z. Wu, *Phys. Chem. Chem. Phys.* **2016**, *18*, 12675–12681.
- [16] J. Hu, X. Zhao, W. Chen, H. Su, Z. Chen, *J Phys. Chem. C* **2017**, *121*, 18702–18709.
- [17] Q. Tang, D. Jiang, *ACS Catal.* **2016**, *6*, 4953–4961.
- [18] a) J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandalov, U. Stimming, *J. Electrochem. Soc.* **2005**, *152*, J23–J26; b) J. Kibsgaard, C. Tsai, K. Chan, J. D. Benck, J. K. Nørskov, F. Abild-Pedersen, T. F. Jaramillo, *Energy Environ. Sci.* **2015**, *8*, 3022–3029.
- [19] a) B. Hinemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Hørch, I. Chorkendorff, J. K. Nørskov, *J. Am. Chem. Soc.* **2005**, *127*, 5308–5309. b) Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, Z. Qiao, *Nat. Commun.* **2014**, *5*, 3783; c) J. K. Nørskov, T. Bligaard, J. Rossmeisl, C. H. Christensen, *Nature Chem.* **2009**, *1*, 37. d) H. Tang, K. Dou, K. Kaun, Q. Kuan, S. Yang, *J. Mater. Chem. A* **2014**, *2*, 360–364. e) Y. Ito, W. Cong, T. Fujita, Z. Tang, M. Chen, *Angew. Chem. Int. Ed.* **2015**, *54*, 2131–2136.
- [20] J. Hu, X. F. Cao, X. Zhao, W. Chen, G.-P. Lu, Y. Dan, Z. Chen. *Front. Chem.* **2019**, *7*, 444.
- [21] a) D. Voiry, R. Fullon, J. Yang, C. Silva, R. Kappera, I. Bozkurt, D. Kaplan, M. J. Lagos, P. E. Batson, G. Gupta, A. D. Mohite, L. Dong, D. Er, V. B. Shenoy, T. Asefa, M. Chhowalla, *Nature Mat.* **2016**, *15*, 1003–1009. b) L. Cheng, D. Zhang, Y. Liao, H. Zhang, Q. Xiang, *Solar RRL*, **2019**, *3*, 1900062; c) D. Han, Y. Xin, Q. Yuan, Q. Yang, Y. Wang, Y. Yang, S. Yi, D. Zhou, L. Feng, Y. Wang, *Solar RRL*, **2019**, *3*, 1970064; d) F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, V. Pellegrini, *Science* **2015**, *347*, 1246501; e) X. Zhang, Z. Luo, P. Yu, Y. Cai, Y. Du, D. Wu, S. Gao, C. Tan, Z. Li, M. Ren, T. Osipowicz, S. Chen, Z. Jiang, J. Li, Y. Huang, J. Yang, Y. Chen, C. Ang, Y. Zhao, P. Wang, L. Song, X. Wu, Z. Liu, A. Borgna, H. Zhang, *Nature Catal.* **2018**, *1*, 460–468. f) X. Zhang, Z. Luo, P. Yu, Y. Cai, Y. Du, D. Wu, S. Gao, C. Tan, Z. Li, M. Ren, T. Osipowicz, S. Chen, Z. Jiang, J. Li, Y. Huang, J. Yang, Y. Chen, C. Ang, Y. Zhao, P. Wang, L. Song, X. Wu, Z. Liu, A. Borgna, H. Zhang, *Nature Catal.* **2018**, *1*, 460–468; g) Y. Chen, K. Yang, B. Jiang, J. Li, M. Zeng, L. Fu, *J. Mater. Chem. A* **2017**, *5*, 8187–8208.
- [22] a) F. Hulliger, *Phys. Lett.* **1963**, *4*, 282–283; b) J. P. Odile, S. Soled, C. A. Castro, A. Wold, *Inorg. Chem.* **1978**, *17*, 283–286.
- [23] L. Jin, H. Xia, Z. Huang, C. Lv, J. Wang, M. G. Humphrey, C. Zhang, *J. Mater. Chem. A* **2016**, *4*, 10925–10932.
- [24] X. Wang, H. Zhou, D. Zhang, M. Pi, J. Feng, S. Chen, *J. Power Sources* **2018**, *387*, 1–8.
- [25] a) W. S. Zhi, K. Jakob, F. D. Colin, C. Ib, K. N. Jens, F. J. Thomas, *Science* **2017**, *355*, eaad4998; b) G. Li, D. Zhang, Q. Qiao, Y. Yu, D. Peterson, D. Zafar, R. Kumar, S. Curtarolo, F. Hunte, S. Shannon, Y. Zhu, W. Yang, L. Ca, *J. Am. Chem. Soc.* **2016**, *138*, 16632–16638.
- [26] a) T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Hørch, I. Chorkendorff, *Science* **2007**, *317*, 100; b) H. I. Karunadasa, E. Montalvo, Y. J. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* **2012**, *335*, 698; J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan, Y. Xie, *J. Am. Chem. Soc.* **2013**, *135*, 17881.
- [27] a) P. Jiang, Q. Liu, X. Sun, *Nanoscale* **2014**, *6*, 13440–13445; b) Z. Pu, Y. Xue, W. Li, I. S. Amiin, S. Mu, *New J. Chem.* **2017**, *41*, 2154–2159.