Acidic Media Regulated Hierarchical Cobalt Compounds with Phosphorous Doping as Water Splitting Electrocatalysts

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Facile synthesis of elaborate nanostructured transition metal compounds with tunable components remains challenging because multiple synthetic procedures or complex manipulation are normally involved. Herein, an acid-etching strategy is applied to Co, in which the composition and morphology of the resultant materials are tunable. Specifically, a novel two-tiered Co(CO₃)_{0.5}(OH)·0.11H₂O nanosheet is formed, part of which decomposes to produce hierarchical Co(CO₃)_{0.5}(OH)·0.11H₂O/Co₃O₄ nanocomposite by tuning the etching condition. The composite shows bifunctional electrocatalytic capability towards the oxygen evolution and hydrogen evolution reactions (OER and HER). Moreover, the phosphorous dopant is introduced to boost the catalytic activity, especially in the HER. Density functional theory calculations reveal that the phosphorous dopant can dramatically push the binding energy to the ideal value, thus improving the HER performance. Computed results indicate that partial orbitals of the P atom are above the Fermi level and the P atom enhances the charge density of the neighboring Co atom, which optimizes the H* binding. In addition, an efficient overall water splitting configuration is performed with the integration of the P-doped Co compound catalysts. The acid-etching methodology inspires more novel nanostructured and multicomponent metal compounds for prominent electrocatalysis.

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can be found under https://doi.org/10.1002/aenm.202100358.

DOI: 10.1002/aenm.202100358

1. Introduction

Water electrolysis in alkaline intermediates could be an ideal route for amenable industrial production of renewable hydrogen (H₂) fuel.^[1-5] Low-cost transition metal-based compounds have been widely investigated in pursuit of alternatives of noble metal electrocatalysts in water splitting.^[6-15] It is solidly revealed that elaborate structures are central to high-efficient catalytic activity (showing structure-determining-activity) among these catalysts.^[16-20] On the other hand, conventional synthesis relies on insubordinate hydrolysis of transition metal ions in alkaline media, which normally results in unsatisfied architectures. Accordingly, many complex manipulations have been adopted to enhance catalytic efficiency, including secondary component coupling, post-vacancy introduction, conducting support engineering, and so on.[21-31] These implementations will bring inevitably excessive complexity to the desired facile synthesis.

In previous work, we demonstrated that using the facile acid-etching strategy novel nanostructured materials can be readily constructed.^[32-34] Basically, metals whose reduction potentials are below zero (H+/H) can be oxidized by protons to generate metal cations, which can serve as the metal source for hydrolysates. For example, two-tiered Ni(OH)₂ nanosheet was obtained directly on Ni foam by pH self-regulation in HCl etching media. Meanwhile, ultrathin nanosheet (sub-1 nm) was achievable simply by adjusting the acidity of the etching solution. Other than geometric structure engineering, acid-etching can determine the facet of the hydrolysate through regulation of the crystal monomer supersaturation. In the acid-etched Fe (or NiFe alloy) case, high-index (012) facet exposed hematite nanocubes were constructed, which is scarcely achievable via the conventional synthesis.^[34] It is mentioned that these acid-etched hydrolysates as electrocatalysts have exhibited superiority over that of the conventional hydrolysates in water splitting. Notably, the hydrolysates that have distinct solubility product constants (K_{sp}) show dissimilar morphologies (geometry and facet). Therefore, more transition metals are expected to be

enforced timely using the acid-etching strategy, which could enrich the abundance of novel transition metal compounds and efficient electrocatalysts.

Herein, we apply the acid-etching strategy to metallic Co, which undergoes an unexpected composition evolution in the etching process. Two-tiered Co(CO₃)_{0.5}(OH) · 0.11H₂O nanosheets are pre-formed, which further undergo decomposition, leading to a resultant of hierarchical $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O/Co_3O_4$ nanocomposites. The as-prepared composite shows bifunctional catalytic ability towards oxygen evolution and hydrogen evolution reactions (OER and HER). Furthermore, facile phosphorous doping is adopted to convert the composite to P-doped Co₃O₄, which boosts markedly the catalytic performance, especially the HER. A lower H* binding energy (-0.15 eV) is revealed on the Co-site of the P-doped Co_3O_4 than that of the undoped counterpart (-0.3 eV) by density functional theory (DFT) calculations, which accounts for the improved HER performance. Besides, electrocatalytic overall water splitting with a low overpotential of ≈ 1.6 V is performed with the integration of the P-doped Co₃O₄ bifunctional catalysts.

2. Results and Discussion

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The composition evolution of the acid-etched Co and the subsequent fabrication of P-doped Co_3O_4 are schematically illustrated in **Figure 1**. In a relatively low concentration acid media (0.25 mM, 18 h), a two-tiered mono-component $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ nanosheet is formed. The formation of the two-tiered nanosheet structure follows the pH self-regulation mechanism.^[32,33] With prolonged etching time (0.25 mM, 24 h) or a high concentration acid (0.45 mM, 18 h), hierarchical $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O/Co_3O_4$ nano-composite (denoted as Co-NC) is produced. The subsequent formation of Co_3O_4 is ascribed to the partial decomposition

of the $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ species. To introduce the phosphorous dopant, the composite is thermally treated in a reducing atmosphere produced by the pyrolysis of NaH₂PO₂. Meanwhile, the nanosheet counterpart will undergo pyrolysis, which leads to the resultant of hierarchical P-doped Co_3O_4 .

The composition of the acid-etched Co resultants in various conditions is confirmed by the X-ray diffraction (XRD) patterns shown in Figure 2a. All the peaks of 0.25 mM acid-etched Co (18 h, blue curve) can be indexed to the orthorhombic Co(CO₃)_{0.5}(OH) · 0.11H₂O (JCPDS No. 48-0083),^[35] indicating a mono-component of the resultant. Interestingly, no intentional carbon source is added in the etchant, while carbonate is formed. No participation of carbonate is observed in the acid-etched Ni case. This might be ascribed to stronger binding ability between Co_{3}^{2+} and CO_{3}^{2-} , whose K_{sp} is about three orders of magnitude lower than that of the NiCO₃. The carbon source is believed to be the dissolved CO₂ in the solution.^[36] Moreover, both prolonged etching time (0.25 mM, 24 h) and 0.45 mM acid-etched (18 h) cases will produce precipitates, whose peaks (black curve) match with that of the cubic Co₃O₄ (JCPDS No. 42-1467). Hence, bicomponent resultant can be realized when applying the acid-etching strategy to Co. After the thermal treatment in the presence of NaH₂PO₂ (red curve), three main diffraction peaks of (111), (311), and (400) planes are observed, which demonstrates that the essential Co₃O₄ component is preserved. Meanwhile, the peaks of Co(CO3)_{0.5}(OH) · 0.11H₂O are diminished because it undergoes pyrolysis, which results in Co₃O₄ species.

Scanning electron microscopy (SEM) was captured to reveal the morphology of the acid-etched Co. The 0.25 mM acid-etched (18 h) sample shows nanosheet arrays on the Co surface (Figure 2b). Two-tiered nanosheets with distinct sizes are observed in tracking the structural evolution processes (Figure S1, Supporting Information). This unique structure is similar to that of the acid-etched Ni, consolidating the



Figure 1. Schematic illustration of the structure and composition evolution of the acid-etched Co and phosphorous doping process.





Figure 2. a) XRD patterns of two-tiered $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ (blue), Co_3O_4 powder (black), and P-Co_3O_4 (red); all #peaks refer to $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ (JCPDS No. 48-0083); all *peaks refer to Co_3O_4 (JCPDS No. 42-1467); b-d) SEM images of two-tiered $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$, hierarchical Co-NC, and P-Co₃O₄, respectively; e) HRTEM image of P-Co₃O₄; inset, SAED pattern; f) AFM image and height profiles.

pH self-regulation growth mechanism.^[27,28] With prolonged etching time (24 h), Co₃O₄ nanoparticles are produced on the nanosheets and in the solution, forming hierarchical Co-NC (Figure 2c and Figure S2a, Supporting Information). Sporadic corroded nanosheets are found among the nanoparticles, demonstrating that they are probably induced by the decomposition of the nanosheets. Moreover, the 0.45 mM acid-etched (18 h) sample shows a similar hierarchical structure, indicating that excessive nanosheets will decompose to form nanoparticles (Figure S2b, Supporting Information). A typical transmission electron microscope (TEM) image confirms the novel two-tiered and hierarchical structure of the Co-NC (Figure S3, Supporting Information). A high-resolution TEM (HRTEM) image of the nanosheet displays a lattice spacing of 0.264 nm, corresponding to the (221) plane of the Co(CO₃)_{0.5}(OH) · 0.11H₂O (Figure S4, Supporting Information). The thickness of the nanosheet is ≈ 3 nm revealed by the side-view TEM image (Figure S5, Supporting Information). As for the nanoparticle, the diameter is ≈80 nm and the observed lattice spacing is 0.286 nm, which corresponds to the (220) plane of the Co₃O₄ (Figure S6, Supporting Information). The thermally-treated Co-NC preserves the hierarchical structure as displayed in Figure 2d. The observed lattice spacing of 0.284 nm corresponds to the (220) plane of Co_3O_4 and the selected area electron diffraction (SAED) pattern along the [111] zone indicates a single crystalline character (Figure 2e). Meanwhile, the atomic force microscopy image verifies the uniform thickness (\approx 3 nm) of the nanosheets (Figure 2f), which matches with the TEM result. Energy-dispersive X-ray spectroscopy coupled with TEM was performed to verify the phosphorous dopant (Figure S7, Supporting Information). The Co, O, and P elemental maps present uniform distribution, indicating a homogeneous P doping. Hence, the Co-NC has successfully converted to hierarchical P-doped Co₃O₄ (denoted as P-Co₃O₄) through the facile treatment.

X-ray photoelectron spectroscopy (XPS) measurement was performed to analyze the surface composition and the

valence state. As shown in the Co 2p spectra, the ratio of $Co^{2+}/$ Co^{3+} of the Co-NC is 1.37, which is higher than the stoichiometric proportion of Co₃O₄ because of the 2+ valence state of the Co(CO₃)_{0.5}(OH) · 0.11H₂O species (Figure S8, Supporting Information). In contrast, the ratio reaches 3.5 for the P-Co₃O₄, which indicates that partial Co^{3+} is reduced to Co^{2+} on the surface (Figure 3a). The deconvoluted peaks in the P 2p spectrum located at 129.6, 130.4, and 133.5 eV can be assigned to P 2p1/2, P 2p3/2 and for P-O species, respectively (Figure 3b).^[37] As for the O 1s spectra, a noticeable positive shift is observed in the $P-Co_3O_4$ (Figure 3c). This might be induced by the reduction of Co species and the dopant of P. The deconvoluted peaks at 531.5 and 532.5 eV can be assigned to oxygen vacancies and P-O species, respectively.^[24,37] Moreover, the XPS survey spectrum presents that the atomic ratio of P to O is \approx 9% in the P-Co₃O₄ (Figure S9, Supporting Information).

The electrocatalytic HER activity was evaluated by the polarization curves scanned in the three-electrode configuration (Figure 4a). The Co-NC sample shows an overpotential of 161 mV at the current density of 10 mA cm⁻², which is superior to that of the bare Co but inferior to Pt (85 mV) and P-Co₃O₄ (80 mV). Though showing little difference at low current densities, the P-Co₃O₄ exhibits a much lower overpotential of (173 mV) compared to that of Pt (285 mV) at a high current density of 70 mA cm⁻². This suggests that the phosphorous dopants can enhance markedly the HER activity, making the P-Co₃O₄ a promising catalyst for large-scale H_2 production through water splitting. Correspondingly, the P-Co₃O₄ presents a small Tafel slope (55 mV dec⁻¹), which is comparable to that of Pt (51.4 mV dec⁻¹) and much lower than the Co-NC electrode (108.8 mV dec $^{-1}$, Figure 4b). This indicates that the HER on the P-Co₃O₄ electrode probably follows the Volmer-Heyrovsky mechanism.[38] Moreover, the electrochemical surface area (ECSA) is analyzed to estimate the accessible active sites (Figure S10, Supporting Information). The P-Co₃O₄ electrode displays a higher ECSA (10.7 mF cm⁻²)



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Figure 3. a,b) XPS Co 2p and P 2p spectrum of P-Co₃O₄, respectively; c) O 1s spectra of Co-NC and P-Co₃O₄.

than that of the Co–NC (4.3 mF cm⁻²), indicating more active sites of P-Co₃O₄. Besides, the electrochemical impedance spectroscopy (EIS) was investigated to reveal the kinetics of charge transfer (Figure S11, Supporting Information). The P-Co₃O₄ electrode has a lower series resistance (1.95 Ω) and charge transfer resistance (4.6 Ω) compared to that of the Co–NC electrode (2.2 and 9.4 Ω), demonstrating a preferable charge transfer in P-Co₃O₄.

DFT calculations were performed to understand the markedly enhanced HER activities induced by the phosphorous dopant (see computation details in Supporting Information). Figure 4c,d show the optimized atomic structures of the H* intermediate binding on the Co-site of Co₃O₄ and P-Co₃O₄, respectively (see top-view structures in Figure S12, Supporting Information). The adsorption free energy (ΔG_{H^*}) diagram at an equilibrium potential for the HER pathway is depicted in Figure 4e. For the undoped Co₃O₄, the ΔG_{H^*} on Co-site is -0.3 eV, which deviates from the optimal value (0 eV) most,^[29] indicating a most sluggish HER activity. The ΔG_{H^*} on the P-site of the P-Co₃O₄ is -0.22 eV, which is slightly lower than that of the Co-site of Co₃O₄. Remarkably, the ΔG_{H^*} is optimized significantly (-0.15 eV) on the Co-site (adjacent to P), which indicates the markedly improved HER activity of the P-Co₃O₄. To further explain the catalytic properties before and after the P dopant from the electronic level, their charge densities and density of states (DOS) were analyzed. The DOS diagram shows that partial orbitals of the P atom are above the Fermi level, which weakens its ability to adsorb hydrogen (Figure 4f). Moreover, when the O atom is replaced by the less electronegative P, more charges are transferred to the neighboring Co due to

the low charge density on P (Figure S13, Supporting Information), which will result in weaker adsorption of H* intermediates. According to the Sabatier principle, the undoped Co₃O₄ interacts too strongly with the H*, while the interaction can be weakened by the P dopant. Therefore, the ΔG_{H^*} on P-doped Co₃O₄ is optimized, leading to enhanced HER activity.

The OER behaviors were investigated by the polarization curves as shown in Figure 5a. The overpotential of the P-Co₃O₄ electrode is 283 mV, which is about 40 mV ahead of the Co-NC. The corresponding Tafel slope of the P-Co₃O₄ is 85.3 mV dec⁻¹, which is smaller than that of the Co–NC counterpart (Figure 5b). Though not as obvious as the HER activity, the OER performance is also enhanced after the introduction of phosphorous dopant. Galvanostatic measurements were conducted to evaluate the durability of the electrodes as OER and HER catalysts, respectively. As displayed in Figure 5c, the augment of the overpotential is low to 15 mV after 60 h, demonstrating outstanding stability working in the alkaline electrolyte. Moreover, the increment of the overpotential is 26 mV after the consecutive HER test, indicating decent durability. The SEM and TEM images of P-Co₃O₄ after the stability test show that the morphology and crystallinity have a negligible change, indicating the durable structure of P-Co₃O₄ (Figure S14, Supporting Information). Moreover, the main peaks of the XRD pattern and P 2p peaks of the XPS spectrum are retained after testing, which demonstrates stable components of the P-Co₃O₄ and barely P dissolution (Figure S15 and S16, Supporting Information).

Thanks to the improved activity of the $P-Co_3O_4$ in both HER and OER, a full water splitting configuration is built based on the bifunctional electrocatalysts (Figure 5d). In the two-electrode







Figure 4. a) HER polarization curves; b) Tafel slopes; c,d) H* intermediate binding on optimized atomic structures of the Co-site of Co₃O₄ and P-Co₃O₄, respectively; e) Gibbs free energy (ΔG_{H^*}) diagram; f) Calculated DOS of Co₃O₄ and P-Co₃O₄. The Orange dashed line denotes the position of the Fermi level.

mode, a low voltage of 1.6 V is needed to deliver a current density of 10 mA cm⁻², which is about 120 mV ahead of the device based on the undoped Co-NC electrodes. At the current density of 20 mA cm⁻², the Faradaic efficiencies for both H_2 and O_2 are calculated to be 100% (Figure S17, Supporting Information). Moreover, the cell voltage increases only 22 mV after a 20 h consecutive test, implying good stability of the device (Figure S18, Supporting Information). The low cell voltage of the P-Co₃O₄ competes with many reported transition metal-based electrocatalysts in full water splitting (Table S1, Supporting Information).

3. Conclusion

In summary, the structural and component evolutions have been revealed in the acid-etching Co case, which can be readily tuned by the etching conditions. A novel hierarchical bicomponent resultant is obtained, which shows bifunctional electrocatalytic capability towards both OER and HER. Moreover, the phosphorous dopant is introduced to further enhance the catalytic performance. DFT calculations demonstrate that the binding energy of H* is much lower on the Co-site of the P-Co₃O₄ than that of the undoped counterpart, which elucidates the markedly improved HER activity. Besides, an efficient full water splitting is demonstrated based on the bifunctional electrocatalysts. The acid-etching strategy offers great potentiality in constructing novel nanostructured and multicomponent metal compounds for advanced electrocatalysis.

4. Experimental Section

Synthesis of Two-Tiered Co(CO₃)_{0.5}(OH)·0.11H₂O Nanosheet, Co-NC, and P-Co₃O₄: A piece of Co foam (1 × 4 cm) was washed by 1 M HCl for the removal of oxidation layers on the surface. Then, the foam was immersed into 0.25 mM HCl aqueous solution, and heated up to 80 °C for 18 h. The foam was washed with deionized water and dried at room







Figure 5. a) OER polarization curves; b) Tafel slopes; c) Galvanostatic stability test; d) Polarization curves of two-electrode full water splitting.

temperature. The nanocomposites can be obtained by two routes: i) prolong the reaction time to 24 h in 0.25 mM HCl aqueous solution at 80 °C; ii) use more concentrated etchant (0.45 mM HCl aqueous solution) and maintain at 80 °C for 18 h. To obtain the P-doped Co₃O₄, the as-obtained Co-NC was put downstream in a porcelain boat with 50 mg NaH₂PO₂ at the upstream of a tube furnace. Then the furnace was heated to 280 °C at a ramping rate of 2 °C min⁻¹ and held for 1 h under Ar atmosphere. After cooling down to room temperature, the P-doped Co₃O₄ nanocomposites were obtained.

Computation Method: The computation details were shown in the Supporting Information.

Electrochemical measurements: The electrochemical performance of all samples was evaluated in 1 M KOH aqueous solution (pH = 13.8) at room temperature (25 °C). In the three-electrode configuration, a graphite rod and Hg/HgO electrode were used as the counter and reference electrode, respectively. All polarization curves were scanned at 2 mV s⁻¹ without *iR* compensation. In the two-electrode full water splitting configuration, two Co-NC or P-Co₃O₄ electrodes were used as anode and cathode, respectively. ECSA was derived from the electrochemical double-layer capacitance. EIS was measured with frequencies ranging from 100 000 to 0.1 Hz.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

D.S. and J.S. contributed equally to this work. H.W. thank the financial support from the Program of Qilu Young Scholars of Shandong University (No. 62460082063152). This work was also supported by the National Key Research and Development Program of China (No. 2017YFA0204800) and the National Natural Science Foundation of China (Grant No. 21525315).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

acid-etching, cobalt compounds, DFT calculations, electrocatalysts, water splitting

Received: January 30, 2021 Revised: April 2, 2021 Published online: April 24, 2021

- F. Yang, Y. Chen, G. Cheng, S. Chen, W. Luo, ACS Catal. 2017, 7, 3824.
- [2] N. Jiang, B. You, M. Sheng, Y. Sun, Angew. Chem., Int. Ed. 2015, 54, 6251.
- [3] J. Zhang, Y. Liu, C. Sun, P. Xi, S. Peng, D. Gao, D. Xue, ACS Energy Lett. 2018, 3, 779.
- [4] Z. Wang, H. Liu, R. Ge, X. Ren, J. Ren, D. Yang, L. Zhang, X. Sun, ACS Catal. 2018, 8, 2236.
- [5] S. Piontek, C. Andronescu, A. Zaichenko, B. Konkena, K. junge Puring, B. Marler, H. Antoni, I. Sinev, M. Muhler, D. Mollenhauer, B. Roldan Cuenya, W. Schuhmann, U.-P. Apfel, ACS Catal. 2018, 8, 987.
- [6] L. Han, S. Dong, E. Wang, Adv. Mater. 2016, 28, 9266.

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- [7] Y. Shi, B. Zhang, Chem. Soc. Rev. 2016, 45, 1529.
- [8] C. Tang, R. Zhang, W. Lu, L. He, X. Jiang, A. M. Asiri, X. Sun, Adv. Mater. 2017, 29, 1602441.
- [9] C. Wang, J. Jiang, T. Ding, G. Chen, W. Xu, Q. Yang, Adv. Mater. Interfaces 2016, 3, 1500454.
- [10] X. Long, G. Li, Z. Wang, H. Zhu, T. Zhang, S. Xiao, W. Guo, S. Yang, J. Am. Chem. Soc. 2015, 137, 11900.
- [11] T. Ouyang, X.-T. Wang, X.-Q. Mai, A.-N. Chen, Z.-Y. Tang, Z.-Q. Liu, Angew. Chem., Int. Ed. 2020, 59, 11948.
- [12] X.-T. Wang, T. Ouyang, L. Wang, J.-H. Zhong, Z.-Q. Liu, Angew. Chem., Int. Ed. 2020, 59, 6492.
- [13] X.-T. Wang, T. Ouyang, L. Wang, J.-H. Zhong, T. M, Z.-Q. Liu, Angew. Chem., Int. Ed. 2019, 58, 1329.
- [14] T. Ouyang, Y.-Q. Ye, C.-Y. Wu, K. Xiao, Z.-Q. Liu, Angew. Chem., Int. Ed. 2019, 58, 4923.
- [15] C. Huang, T. Ouyang, Y. Zou, N. Li, Z.-Q. Liu, J. Mater. Chem. A 2018, 6, 7420.
- [16] D. McAteer, I. J. Godwin, Z. Ling, A. Harvey, L. He, C. S. Boland, V. Vega-Mayoral, B. Szydłowska, A. A. Rovetta, C. Backes, J. B. Boland, X. Chen, M. E. G. Lyons, J. N. Coleman, *Adv. Energy Mater.* 2018, *8*, 1702965.
- [17] Y. Li, J. Liu, C. Chen, X. Zhang, J. Chen, ACS Appl. Mater. Interfaces 2017, 9, 5982.
- Y. Zhao, X. Zhang, X. Jia, G. I. N. Waterhouse, R. Shi, X. Zhang,
 F. Zhan, Y. Tao, L.-Z. Wu, C.-H. Tung, D. O'Hare, T. Zhang,
 Adv. Energy Mater. 2018, 8, 1703585.
- [19] U. P. Suryawanshi, U. V. Ghorpade, D. M. Lee, M. He, S. W. Shin, P. V. Kumar, J. S. Jang, H. R. Jung, M. P. Suryawanshi, J. H. Kim, *Chem. Mater.* **2020**, *33*, 234.
- [20] B. Qiu, L. Cai, Y. Wang, Z. Lin, Y. Zuo, M. Wang, Y. Chai, Adv. Funct. Mater. 2018, 28, 1706008.
- [21] W. Y. Lim, Y. F. Lim, G. W. Ho, J. Mater. Chem. A 2017, 5, 919.

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- [22] Z.-Z. Luo, Y. Zhang, C. Zhang, H. T. Tan, Z. Li, A. Abutaha, X.-L. Wu, Q. Xiong, K. A. Khor, K. Hippalgaonkar, J. Xu, H. H. Hng, Q. Yan, *Adv. Energy Mater.* 2017, *7*, 1601285.
- [23] J. Li, M. Yan, X. Zhou, Z.-Q. Huang, Z. Xia, C.-R. Chang, Y. Ma, Y. Qu, Adv. Funct. Mater. 2016, 26, 6785.
- [24] Z. Cai, Y. Bi, E. Hu, W. Liu, N. Dwarica, Y. Tian, X. Li, Y. Kuang, Y. Li, X.-Q. Yang, H. Wang, X. Sun, Adv. Energy Mater. 2018, 8, 1701694.
- [25] Y. Wang, Y. Zhang, Z. Liu, C. Xie, S. Feng, D. Liu, M. Shao, S. Wang, Angew. Chem., Int. Ed. 2017, 56, 5867.
- [26] Y. Xin, X. Kan, L. Y. Gan, Z. Zhang, ACS Nano 2017, 11, 10303.
- [27] C. Tsai, H. Li, S. Park, J. Park, H. S. Han, J. K. Nørskov, X. Zheng, F. Abild-Pedersen, *Nat. Commun.* 2017, *8*, 151131.
- [28] H.-Y. Wang, Y.-Y. Hsu, R. Chen, T.-S. Chan, H. M. Chen, B. Liu, Adv. Energy Mater. 2015, 5, 1500091.
- [29] E. Hu, J. Ning, D. Zhao, C. Xu, Y. Lin, Y. Zhong, Z. Zhang, Y. Wang, Y. Hu, Small 2018, 14, 1704233.
- [30] J. S. Kim, B. Kim, H. Kim, K. Kang, Adv. Energy Mater. 2018, 8, 1702774.
- [31] C. Gu, S. Hu, X. Zheng, M. R. Gao, Y. R. Zheng, L. Shi, Q. Gao, X. Zheng, W. Chu, H. B. Yao, J. Zhu, S. H. Yu, *Angew. Chem.*, *Int. Ed.* 2018, 57, 4020.
- [32] H. Wu, X. Lu, G. Zheng, G. W. Ho, Adv. Energy Mater. 2018, 8, 1702704.
- [33] H. Wu, T. Zhu, X. Lu, G. W. Ho, J. Mater. Chem. A 2017, 5, 24153.
- [34] H. Wu, T. Yang, Y. Du, L. Shen, G. W. Ho, Adv. Mater. 2018, 30, 1804341.
- [35] Y. Wang, H. Xia, L. Lu, J. Lin, ACS Nano 2010, 4, 1425.
- [36] K. Ding, X. Zhang, J. Li, P. Yang, X. Cheng, CrystEngComm 2017, 19, 5780.
- [37] K. Liu, F. Wang, P. He, T. A. Shifa, Z. Wang, Z. Cheng, X. Zhan, J. He, Adv. Energy Mater. 2018, 8, 1703290.
- [38] Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri, X. Sun, Angew. Chem., Int. Ed. 2014, 53, 6710.