

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

Accepted Article

- **Title:** Bimetallic Zn/Fe Polyphthalocyanine Derived Single-Atom Fe-N4 Catalytic Site : A Superior Tri-Functional Catalyst for Overall Water Splitting and Zn-Air Battery
- Authors: Yuan Pan, Shoujie Liu, Kaian Sun, Xin Chen, Bin Wang, Konglin Wu, Xing Cao, Weng-Chon Cheong, Rongan Shen, Aijuan Han, Zheng Chen, Lirong Zheng, Jun Luo, Yan Lin, Yunqi Liu, Dingsheng Wang, Qiang Zhang, Chen Chen, and Yadong Li

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.201804349 Angew. Chem. 10.1002/ange.201804349

Link to VoR: http://dx.doi.org/10.1002/anie.201804349 http://dx.doi.org/10.1002/ange.201804349

WILEY-VCH

WILEY-VCH

Bimetallic Zn/Fe Polyphthalocyanine Derived Single-Atom Fe-N₄ Catalytic Site: A Superior Tri-Functional Catalyst for Overall Water Splitting and Zn-Air Battery

Yuan Pan⁺, Shoujie Liu⁺, Kaian Sun, Xin Chen, Bin Wang, Konglin Wu, Xing Cao, Weng-Chon Cheong, Rongan Shen, Aijuan Han, Zheng Chen, Lirong Zheng, Jun Luo, Yan Lin, Yungi Liu, Dingsheng Wang, Qing Peng, Qiang Zhang, Chen Chen,* Yadong Li

Abstract: Developing an efficient single-atom materials (SAMs) synthesis methodology and exploring the energy-related catalytic reaction are important but still challenging. Herein, we report a novel polymerization-pyrolysis-evaporation (PPE) strategy to synthesize Ndoped porous carbon (NPC) anchored atomically dispersed Fe-N₄ catalytic site derived from predesigned bimetallic Zn/Fe polyphthalocyanine. Experiments and theorv calculations demonstrate the formed Fe-N₄ site exhibits superior tri-functional electrocatalytic performance for oxygen reduction, oxygen evolution and hydrogen evolution reactions. In overall water splitting and rechargeable Zn-air battery devices comprising Fe-N₄ SAs/NPC catalyst, it exhibits high efficiency and extraordinary stability. Interestingly, our current PPE method is a general strategy for preparing M SAs/NPC (M = Co, Ni, Mn), which brought forward a new perspective for designing various SAMs for catalytic application.

Single-atom materials (SAMs), which can reach the highest catalytic performance in catalysis field due to the maximum atom utilization efficiency, have attracted increasing attention in various catalytic systems¹⁻⁸. However, single atoms (SAs) are easy to migrate and agglomerate during catalytic process, so preparing and stabling SAMs remain to be a significant issue up to now. A series of strategies have been explored for preparing metal SAMs, such as atomic layer deposition⁹, coprecipitation¹⁰, chemical synthesis¹¹, wet impregnation¹², and pyrolysis of metal organic frameworks¹³ or organic polymers¹⁴. Nevertheless, these methods suffer from harsh reaction conditions, multi-step synthesis process or the environmental pollution due to the waste solvent. Therefore, the development of novel SAMs synthesis methodology and the exploration of catalytic application is necessary but still challenging.

Electrochemical reactions including oxygen reduction/ evolution reaction (ORR/OER) and hydrogen evolution reaction (HER) are significantly important in energy-related applications¹⁵. An efficient multi-functional electrocatalysts play important roles

Dr. Y. Pan, Dr. S. Liu, K. Wu, X. Cao, W. C. Cheong, R. Shen, Dr. A. [*] Han, Z. Chen, Prof. D. Wang, Prof. Q. Peng, Prof. C. Chen, Prof. Y. Li Department of Chemistry, Tsinghua University, Beijing 100084 (China) E-mail: cchen@mail.tsinghua.edu.cn Dr. Y. Pan, K. Sun, Y. Lin., Prof. Y. Liu, State Key Laboratory of Heavy Oil Processing China University of Petroleum (East China), Qingdao 266580 (China) Dr. S. Liu, K. Wu College of Chemistry and Materials Science Anhui Normal University, Wuhu 241000 (China) X. Chen Department of Chemistry, University of Science and Technology Beijing, Beijing, 100083, China Dr. B. Wang, Prof. Q. Zhang Department of Chemical Engineering, Tsinghua University, Beijing 100084 (China) Prof. L. Zheng Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China Prof. J. Luo Center for Electron Microscopy, Tianjin University of Technology, Tianjin, 300384, China These authors contributed equally to this work. Supporting information for this article is given via a link at the end of the document.

in these renewable energy technologies¹⁶. At present, noble metals-based catalysts show excellent electrocatalytic performance for these reactions, but it is far from application because of its high price and scarcity¹⁷. Therefore, the development of non-noble metal catalysts is the hotspot in these research field. Recently, non-noble-metal-based heteroatom-doped carbon materials have become one of the most promising alternatives due to the strong interactions between metal and heteroatom species in the carbon framework¹⁸. Up to now, the electrochemical reaction catalyzed by tri-functional atomically dispersed catalysts and the understanding of active sites have seldom been investigated.



Figure 1. (a) synthesis scheme (b) TEM (the inset is SAED image), (c) HRTEM, (d) HAADF-STEM and EDS mapping images, C (red), N (yellow) and Fe (green), (e) AC HAADF-STEM of the Fe-N₄ SAs/NPC.

Herein, we put forward a facile and effective "polymerization-pyrolysis-evaporation (PPE)" strategy to synthesize N-doped porous carbon (NPC) anchored atomically dispersed Fe-N₄ site derived from predesigned bimetallic Zn/Fe polyphthalocyanine (ZnFe-BPPc). Benefiting from the synergistic effects between atomically dispersed Fe-N₄ catalytic site and porous conductive carbon networks, the Fe-N₄ SAs/NPC catalyst can be used as an efficient tri-functional electrocatalyst for overall water splitting and Zn-air battery. Interestingly, various M SAs/NPC (M = Co, Ni, Mn) can be obtained by varying metal precursors, demonstrating the generality of this strategy.

The highlight of our synthetic strategy only includes two steps: (1) polymerization and (2) high temperature pyrolysis of

ZnFe-BPPc. We synthesized ZnFe-BPPc conjugated polymer networks with homogeneous distributions of Zn and Fe (Figure S1) by a low-temperature solvent-free solid phase synthesis in a muffle furnace (Figure 1a). Pyromellitic dianhydride, which connected by two pairs of available anhydride group convert phthalocyanine monomer to polymer¹⁹. Meanwhile, the proper diameter of the large ring cavity in the phthalocyanine structure (0.27 nm) can accommodate a variety of metals (e.g. Zn, Fe, Co, Ni, Mn) with smaller radius to form phthalocyanine metal coordination polymers. PPc linkers could provide coordination environment which may led to the partly exchange between metals residing in PPc nodes and other metals, the spatial distance of metal sites were further adjusted. If the doping metal can be removed selectively and the remaining metal can be reduced in situ, SAMs with different metal can be achieved. Therefore, we select Zn as doping metal and the intentional addition of Zn²⁺ can replace a certain proportion of Fe³⁺ as ZnFe-BPPc. Subsequent pyrolysis of ZnFe-BPPc at 920 °C for 3 h, the Zn atoms were evaporated and the formation of Fe-Fe bonds at high temperature was prevented. PPc linkers converted to NPC simultaneously, and single-atom Fe in situ anchored on NPC was prepared finally. By a series of exploration experiments, we found that the mole ratio of Zn/Fe is important for the synthesis of SAMs (Figure S2-S4). The Fe-N₄ SAs/NPC can be successfully synthesized when the mole ratio of Zn/Fe is 30/1 (feed ratio). However, the Fe-Fe bonds aggregated and formed nanoparticles (NPs) rapidly without the addition of Zn (Scheme S1).

Transmission electron microscopy (TEM) (Figure 1b) reveals that Fe-N₄ SAs/NPC keeps thin graphene-like layered structure of the initial Zn₃₀Fe₁-BPPc. High-magnification TEM (HRTEM) (Figure 1c) shows fringe spacing of about 0.34 nm corresponding to the (002) lattice plane of graphitic carbon. The ring-like selected area electron diffraction (SAED) image (inset of Figure 1c) indicates poor crystallinity. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) images indicate C, N, and Fe elements are distributed uniformly over the entire NPC (Figure 1d). Inductively coupled plasma optical emission spectrometry (ICP-OES) reveals that the content of Fe is 1.96 wt. % (Table S1). Aberration-corrected HAADF-STEM (AC HAADF-STEM) (Figure 1e) shows the highly dispersed sparking points without obvious aggregation, confirming the single-atom feature. N2 adsorption-desorption isotherms reveal typical type-IV with a distinct hysteresis loop, indicating micro/meso porous structure, and the size mainly concentrated in 0.6 and 3.8 nm (Figure S5), respectively. The Fe-N₄ SAs/NPC catalyst shows a large Brunauer-Emmett-Teller surface area of 111.7 $m^2 \cdot g^{-1}$ and pore volume of 0.15 cm³ \cdot g^{-1}.

X-ray diffraction (XRD) patterns and TEM reveal the formation process of Fe-N₄ SAs/NPC (Figure S2-S4). Without the addition of Zn, the pyrolysis of pure FePPc resulted in the formation of Fe₃C and Fe NPs. The Fe₃C NPs can be etched in 0.5 M H₂SO₄ at 80 °C for 12 h (Figure S6). With the increase of Zn/Fe mole ratio from 2/1 to 30/1, the Fe NPs peaks disappear gradually, which indicates that Zn plays a positive role in the formation of Fe-N₄ SAs/NPC. This may be because the evaporation of Zn2+ sites generates uncoordinated N sites to stabilize Fe SAs during pyrolysis. X-ray photoelectron spectroscopy (XPS) reveals that the coexistence of three types N species including pyridinic (398.6 eV), pyrrolic (400.4 eV), and graphitic (401.3 eV) (Figure 2a). From the Raman spectrum



-5 0 5 Velocity (mm s⁻¹) Figure 2. (a) N 1s XPS and (b) N K-edge NEXAFS spectra. (c) XANES of Fe K-edge (the inset is magnified image). (d) FT at R space (the inset is Fe atomic structure model, C (golden), N (silvery) and Fe (orange)). (e) ⁵⁷Fe Mössbauer transmission spectra. (f) WT of the Fe K-edge.

10

-10

Synchrotron-radiation-based X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were carried out to demonstrate the electronic structure and coordination information. The C K-edge (Figure S8) demonstrates the C-N-C defect sites existed in the carbon lattice. From the N K-edge spectrum (Figure 2b), three obvious peaks can be found, assigning to a π^* -transition in the aromatic C-N-C portion of the pyridinic site (peak a) and N-3C bridging of the graphitic site (peak b), and σ^* -transition of the C-N bond (peak c)²⁰. For the Fe K-edge spectrum, the absorption threshold position of Fe-N₄ SAs/NPC located between the FeO and Fe₂O₃, which indicates that the valence of Fe in Fe-N₄ SAs/NPC is situated between +2 and +3 (Figure 2c). From the Fourier-transformed (FT) k³-weighted EXAFS (Figure 2d), one main peak at 1.4 Å can be observed, corresponding to the Fe-N first coordination shell. Compared with Fe foil, FeO and Fe₂O₃, no Fe-Fe coordination peak at 2.2 Å can be detected, demonstrating the atomic dispersion Fe was anchored on NPC. Only one intensity maximum at about 4 Å⁻¹ can be observed from the wavelet transform (WT) contour plots of Fe-N₄ SAs/NPC (Figure 2f), which can be assigned to Fe-N coordination. Compared with the WT plots of Fe foil, FeO and Fe₂O₃, no Fe-Fe signal was detected. The EXAFS fitting results (Figure S9. Table S2) indicate that the first shell of the Fe atom showed a coordination number of 4. Therefore, the central Fe atom is coordinated by 4 N atoms (inset of Figure 2d). The Fe-N₄ catalytic site was further demonstrated by Mössbauer spectroscopy analysis (Figure 2e, Table S3). Three doublets D1, D2, and D3 can be fitted, assigning to intermediate-spin $Fe^{II}N_4/C$, low-spin Fe^{II}N₄/C, and high-spin N-Fe^{III}N₂₊₂/C, respectively²¹⁻²⁴.



WILEY-VCH



Figure 3. LSV curves and free energy diagrams for (a, d) ORR (1) Fe-N₄ and (2) Fe-C₄, (b, e) OER and (c, f) HER. Schematic of (g) water splitting and (j) Zn-air battery. (h) LSV curve of the Fe-N₄ SAs/NPC electrodes (iR compensation, the inset is chronopotentiometric curve at different current densities). (i) Charge-discharge polarization curve and power density plot. (k) Charge-discharge cycling performance.

The ORR activity was first measured by linear sweep voltammetry (LSV) (Figure 3a), cyclic voltammetry (CV) (Figure S10) and Tafel plot (Figure S11) in 0.1 M KOH using rotating disk electrode (RDE). The Fe-N₄ SAs/NPC catalyst exhibits the highest activity in term of the most positive onset (E_{onset} = 0.972 V) and half-wave potential ($E_{1/2} = 0.885$ V). According to LSV curves with different rotation rate and the Koutecky-Levich plot (Figure S12), the calculated electron transfer number is 3.84, which is close to the theoretical. The H₂O₂ yield of Fe-N₄ SAs/NPC catalyst (Figure S13) kept below 12 % at the potential from 0.4 to 1.0 V and decreased to 0.52 % at 0.8 V vs. RHE, revealing the high ORR selectivity. Hardly any change in CV was observed after 5000 cycles (Figure S14a), suggesting the excellent stability. After the injection of 1.0 M CH₃OH into electrolyte, no obvious change in the LSV curve, indicating superior tolerance to methanol (Figure S14b).

The OER and HER performance was further examined in 1 M KOH. The Fe-N₄ SAs/NPC catalyst exhibits the highest catalytic activity (Figure 3b) with a small overpotential of 0.43 V at 10 mA·cm⁻² and Tafel slope of 95 mV·dec⁻¹ than that of Fe NPs/NPC, NPC, commercial RuO₂ and IrO₂ (Figure S15) for OER. The Fe-N₄ SAs/NPC also possesses the smallest charge

transfer resistance (R_{ct}) (Figure S16) and largest double-layer capacitance (Figure S17). For HER, the 20% Pt/C catalyst shows the highest HER activity. The Fe-N₄ SAs/NPC catalyst (Figure 3c) also exhibits optimum catalytic activity with a small overpotential of 0.202 V at 10 mA·cm⁻ ², Tafel slope (123 mV·dec⁻¹) and R_{ct} are smaller than that of Fe NPs/NPC and NPC (Figure S18-19). Meanwhile, the Fe-N₄ SAs/NPC shows excellent stability in long-term electrochemical process, this electrolysis could be sustained for at least 70000 s (Figure S20). Moreover, the morphology can be preserved and elements have uniform distribution over the entire NPC after the long-term electrolysis (Figure S21). The positive E1/2 for ORR and low overpotentials for both HER and OER are comparable with other reported bi/tri-functional catalysts (Table S4).

Density functional theory calculations were further conducted to explain the postive role of Fe-N₄ catalytic site compared with Fe-C₄ site or Fe₆-cluster (Figure S22, Table S5-S9). For each step during the ORR process (Figure 3d), the free energy at Fe-N₄ catalytic site catalyst are lower than that of Fe-C₄ site at 0.4 and 1.15 V. Moreover, in the step of the

increment of free energy, the Fe-C₄ site needs higher energy barrier, suggesting the ORR take place easily at Fe-N₄ catalytic site. The free energy change (Δ G) along the OER pathway was also calculated to quantify the theoretical overpotential (Figure 3e). The conversion of O* to OOH* is the rate-determining step. The calculated overpotential is 0.01 V for Fe-N₄, lower than that of Fe-C₄ (1.04 eV) and Fe₆-cluster (4.35 eV). Moreover, for the HER, the Δ G_{H*} of Fe-N₄ catalytic site is about 0.25 eV, which is smaller that of Fe-C₄ (0.41 eV) and Fe₆-cluster (2.18 eV), suggesting the more favorable H* adsorption kinetics on Fe-N₄ site can significantly improve the ORR, OER and HER activity.

Encouraged by the superior tri-functional ORR, OER and HER performances of Fe-N₄ SAs/NPC electrocatalyst, we assembled a water electrolyzer (Figure 3g) and a Zn-air battery (Figure 3j) for practical application. For the overall water-splitting, the Fe-N₄ SAs/NPC electrodes just needs low potential of 1.67 V to drive a current of 10 mA·cm⁻² (Figure 3h). It also exhibits extraordinary stability as the current density various between 10 and 100 mA·cm⁻² during the 23 h electrocatalysis process (inset of Figure 3h). For the Zn-air battery, the Fe-N₄ SAs/NPC catalyst exhibits lower charge-discharge voltage gap (1.45 V at 50 mA·cm⁻²) and larger power density (232 mW·cm⁻²) than that of Pt/C+Ir/C-based battery (1.59 V at 50 mA·cm⁻² and 52.8 mW·cm⁻²) (Figure 3i and Figure S23), reflecting enhanced rechargeability of the Zn-air battery. Additionally, it also exhibits excellent stability without obvious voltage change after 108 cycles (36 h) (Figure 3k).

WILEY-VCH



Figure 4. HAADF-STEM and EDS mapping images of (a) Co SAs/NPC and (d) Ni SAs/NPC, C (blue), N (red) and Co or Ni (green), AC HAADF-STEM of (b) Co SAs/NPC and (e) Ni SAs/NPC. (c, f) FT at R space.

We extended our PPE strategy to synthesize other metal SAMs by changing metal precursors. Various M SAs/NPC (M = Co, Ni, Mn) can be synthesized and characterized by the high temperature pyrolysis of $Zn_{30}Co_1$ -BPPc (Figure S24), $Zn_{30}Ni_1$ -BPPc (Figure S25) and $Zn_{30}Mn_1$ -BPPc (Figure S26). For example, without the addition of Zn, the pyrolysis of pure CoPPc also resulted in the formation of Co NPs (Figure S27-S29). When the mole ratio of Zn/Co reached to 30/1, Co atoms were atomically anchored on NPC, as demonstrated by EDS mapping (Figure 4a), AC-HAADF-STEM (Figure 4b) and EXAFS (Figure 4c, Figure S30). Similarly, Ni SAs/NPC (Figure 4d-f, Figure S31), Mn SAs/NPC (Figure S32) can be synthesized, revealing the generality of PPE strategy.

In summary, a novel PPE strategy is presented to synthesize a serials of single-atom metal (M = Fe, Co, Ni, Mn) sites anchored on N-doped porous carbon. Significantly, the Fe-N₄/NPC catalyst shows superior tri-functional electrocatalytic performance for overall water splitting and Zn-air battery. This work not only designs an efficient tri-functional electrocatalyst but also provides a novel PPE strategy for preparing SAMs, which further broadens the synthetic methodology of materials with atomic level and energy-related catalytic applications.

Acknowledgements

This work was supported by the National Key R&D Program of China (2017YFA0700101, 2016YFA0202801), the National Natural Science Foundation of China (21573119, 21590792, 21521091, 21390393, U1463202), China Postdoctoral Science Foundation (2017M610076) and Beijing Natural Science Foundation (2184104).

Keywords: Single-atom Fe-N₄ site • polymerization-pyrolysisevaporation strategy • EXAFS • electrochemistry • generality

- [1] J. Jones, H. Xiong, A. T. DeLaRiva, E.J. Peterson, H. Pham, S.R. Challa, G. Qi, S. Oh, M. H. Wiebenga, X. I. P. Hernández, Y. Wang, A. K. Datye, *Science* **2016**, 353, 150-154.
- [2] B. Qiao, J. X. Liang, A. Wang, C. Q. Xu, J. Li, T. Zhang, J. (Jimmy) Liu, Nano Res. 2015, 8, 2913-2924.
- [3] X. Wang, W. Chen, L. Zhang, T. Yao, W. Liu, Y. Lin, H. Ju, J. Dong, L. Zheng, W. Yan, X. Zheng, Z. Li, X. Wang, J. Yang, D. He, Y. Wang, Z. Deng, Y. Wu, Y. Li, *J. Am. Chem. Soc.* **2017**, *139*, 9419-9422.

- [4] Y. Cao, S. Chen, Q. Luo, H. Yan, Y. Lin, W. Liu, L. Cao, J. Lu, J. Yang, T. Yao, S. Wei, Angew. Chem. Int. Ed. 2017, 56, 12191-12196. Angew. Chem. 2017, 129, 12359-12364.
- [5] H. Zhang, J. Wei, J. Dong, G. Liu, L. Shi, P. An, G. Zhao, J. Kong, X. Wang, X. Meng, J. Zhang, J. Ye, *Angew. Chem. Int. Ed.* **2016**, *55*, 14310-14314. *Angew. Chem.* **2016**, *128*, 14522-14526.
- [6] Y. Chen, S. Ji, Y. Wang, J. Dong, W. Chen, Z. Li, R. Shen, L. Zheng, Z. Zhuang, D. Wang, Y. Li, *Angew. Chem. Int. Ed.* **2017**, *56*, 6937-6941. *Angew. Chem.* **2017**, *129*, 7041-7045.
- [7] H. Fei, J. Dong, M. J. Arellano-Jiménez, G. Ye, N. D. Kim, E. L. G. Samuel, Z. Peng, Z. Zhu, F. Qin, J. Bao, M. J. Yacaman, P. M. Ajayan, D. Chen, J. M. Tour, *Nat. Comm.* **2015**, *6*, 8668.
- [8] X. Li, W. Bi, M. Chen, Y. Sun, H. Ju, W. Yan, J. Zhu, X. Wu, W. Chu, C. Wu, Y. Xie, J. Am. Chem. Soc. 2017, 139, 14889-14892.
- [9] H. Yan, H. Cheng, H. Yi, Y. Lin, T. Yao, C. Wang, J. Li, S. Wei, J. Lu, J. Am. Chem. Soc. 2015, 137, 10484.
- [10] B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, Nat. Chem. 2011, 3, 634.
- [11] J. Deng, H. Li, J. Xiao, Y. Tu, D. Deng, H. Yang, H. Tian, J. Li, P. Ren, X. Bao, *Energy Environ. Sci.* **2015**, *8*, 1594-1601.
- [12] C. H. Choi, M. Kim, H. C. Kwon, S. J. Cho, S. Yun, H. T. Kim, K. J. J. Mayrhofer, H. Kim, M. Choi, *Nat. Commun.* **2016**, *7*, 10922.
- [13] P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei, Y. Li, *Angew. Chem. Int. Ed.* **2016**, *55*, 10800-10805. *Angew. Chem.* **2016**, *128*, 10958-10963.
- [14] M. Zhang, Y. G. Wang, W. Chen, J. Dong, L. Zheng, J. Luo, J. Wan, S. Tian, W. C. Cheong, D. Wang, Y. Li, *J. Am. Chem. Soc.* **2017**, *139*, 10976-10979.
- [15] J. Luo, J. H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. G. Park, S. D. Tilley, H. J. Fan, M. Grtzel, *Science* **2014**, *345*, 1593-1596.
- [16] K. Liu, H. Zhong, F. Meng, X. Zhang, J. Yan, Q. Jiang, Mater. Chem. Front., 2017, 1, 2155-2173.
- [17] B. Y. Xia, Y. Yan, N. Li, H. B. Wu, X. W. D. Lou, X. Wang, *Nat. Energy* 2016, *1*, 15006.
- [18] Y. C. Wang, Y. J. Lai, L. Song, Z. Y. Zhou, J. G. Liu, Q. Wang, X. D. Yang, C. Chen, W. Shi, Y. P. Zheng, M. Rauf, S. G. Sun, *Angew. Chem. Int. Ed.* **2015**, *54*, 9907-9910. *Angew. Chem.* **2015**, *127*, 10045-10048.
- [19] Z. Zhang, M. Dou, H. Liu, L. Dai, F. Wang, Small, 2016, 12, 4193-4199.
- [20] P. Chen, T. Zhou, L. Xing, K. Xu, Y. Tong, H. Xie, L. Zhang, W. Yan, W. Chu, C. Wu, Y. Xie, *Angew. Chem. Int. Ed.* **2017**, *56*, 610-614. *Angew. Chem.* **2017**, *129*, 625-629.
- [21] U. I. Kramm, M. Lefevre, N. Larouche, D. Schmeisser, J. P. Dodelet, J. Am. Chem. Soc. 2014, 136, 978-985.
- [22] W. Liu, L. Zhang, X. Liu, X. Liu, X. Yang, S. Miao, W. Wang, A. Wang, T. Zhang, J. Am. Chem. Soc. 2017, 139, 10790-10798.
- [23] U. I. Kramm, J. Herranz, N. Larouche, Thomas M. Arruda, M. Lefevre, F. Jaouen, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, S. Mukerjeec, J. P. Dodelet, *Phys. Chem. Chem. Phys.* 2012, 14, 11673-11688.
- [24] Y. Zhu, B. Zhang, X. Liu, D. W. Wang, D. S. Su, Angew. Chem. Int. Ed. 2014, 53, 10673-10677. Angew. Chem. 2014, 126, 10849-10853.
- [25] N. R. Sahraie, U. I. Kramm, J. Steinberg, Y. Zhang, A. Thomas, T. Reier, J. P. Paraknowitsch, P. Strasser, *Nat. Commun.* 2015, 6, 8618.

WILEY-VCH

Entry for the Table of Contents

Layout 2:

COMMUNICATION



Single-Atom Catalyst: A novel polymerization-pyrolysis-evaporation (PPE) strategy was developed to synthesize N-doped porous carbon (NPC) anchored atomically dispersed Fe-N₄ site as a superior tri-functional catalyst for overall water splitting and Zn-air battery. The PPE method is a general strategy for preparing M SAs/NPC (M = Fe, Co, Ni, Mn) materials.

Yuan Pan+, Shoujie Liu+, Kaian Sun, Xin Chen, Bin Wang,Konglin Wu, Xing Cao, Weng-Chon Cheong, Rongan Shen, Aijuan Han, Zheng Chen, Lirong Zheng, Jun Luo, Yan Lin, Yunqi Liu, Dingsheng Wang, Qing Peng, Qiang Zhang, Chen Chen,* Yadong Li

Page No. – Page No.

Bimetallic Zn/Fe Polyphthalocyanine Derived Single-Atom Fe-N₄ Catalytic Site : A Superior Tri-Functional Catalyst for Overall Water Splitting and Zn-Air Battery