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Hierarchical 3D porous carbon with facilely accessible Fe–N_4 single-atom sites for Zn–air batteries†

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Here, we report a highly efficient ORR electrocatalyst with Fe–N_4 active sites uniformly dispersed on a three-dimensional (3D) interconnected porous nitrogen-doped carbon network synthesized by pyrolyzing SiO_2@ZIF-8 composites loaded with iron salts. The as-prepared single-atom Fe 3D-ordered mesoporous carbon (SA-Fe-3DOMC) possesses a high specific surface area of 1357.8 m^2 g^{-1} and a high Fe loading of 0.84 wt% as well. Benefiting from these favourable structural properties, SA-Fe-3DOMC exhibits a superior ORR half-wave potential ($E_{1/2}$) of 0.901 V and negligible activity loss (only 3 mV) after 10 000 cycles in alkaline media, surpassing the state-of-the-art Pt/C electrocatalyst. Particularly, an integrated zinc–air battery with SA-Fe-3DOMC as the air electrode shows a remarkable peak power density (140 mW cm^{-2}) and a high specific capacity (786.6 mA h g^{-1}), demonstrating great potential for practical application.

Zinc–air batteries (ZABs) have received significant attention as promising next-generation batteries because of their high power density, high specific energy, low cost, environmental friendliness and good safety.[1–3] However, the oxygen reduction reaction (ORR) at the cathode is subject to sluggish kinetics and usually requires high overpotentials.[4] In order to speed up the ORR and make ZABs more energy-efficient, suitable electrocatalysts are always needed.[5–7] Although precious metals and their alloys remain as outstanding candidates for catalyzing the ORR, their practical applications have been significantly hampered by the prohibitive cost and scarcity of precious metals.[8–12] Therefore, it is important to develop high-performance inexpensive catalysts to replace precious metals.[13,14]

To date, Fe single-atom catalysts (SACs) dispersed as Fe–N_4 active sites on a porous carbon matrix have been regarded as one of the most efficient ORR electrocatalysts owing to their high activity, durable stability and maximum atom utilization.[15–17] In general, Fe SACs can be obtained by direct pyrolysis of mixtures of N- and C-containing precursors and Fe salts, followed by acid washing.[18,19] However, iron species are prone to agglomerate during the pyrolysis process, forming iron-based nanoparticles or clusters that are difficult to remove, thus blocking the formation of Fe–N_4 active sites.[20] Moreover, inaccessible pores will be generated owing to the random mixing of the N–C precursors and Fe salts. This leads to some buried Fe–N_4 active sites that cannot be exposed at the three-phase interface, thus reducing the utilization of Fe SACs.[21–24] Thus, an ideal Fe SAC should possess highly accessible Fe–N_4 active sites and a porous network that can facilitate the transport of electrons, oxygen and water.[25] A three dimensional (3D) ordered porous architecture with open channels would be suitable to maximize the accessibility of active sites, but suffers from the limitation of a low specific surface area and cannot support more Fe–N_4 active sites.[26,27] Considering these issues collectively, a 3D-ordered large-pore structure with suitable micropores and mesopores will be highly desirable, which facilitates the exposure of active sites and mass transfer.[28–30]

Herein, we have designed 3D-ordered porous nitrogen-doped carbon with accessible Fe–N_4 active sites as an efficient electrocatalyst for the ORR. Remarkably, the as-prepared SA-Fe-3DOMC possessed a high specific surface area of 1357.8 m^2 g^{-1} and a high Fe loading (0.84 wt%). The electrochemical results demonstrated that SA-Fe-3DOMC exhibited excellent ORR catalytic activity and stability, with $E_{1/2}$ increased to 0.901 V while the current almost remained similar after 10 000 potential cycles from 0.6 V to 1 V in alkaline media. Furthermore, an integrated ZAB with SA-Fe-3DOMC as the air electrode showed a remarkable peak power density (140 mW cm^{-2}) and a high

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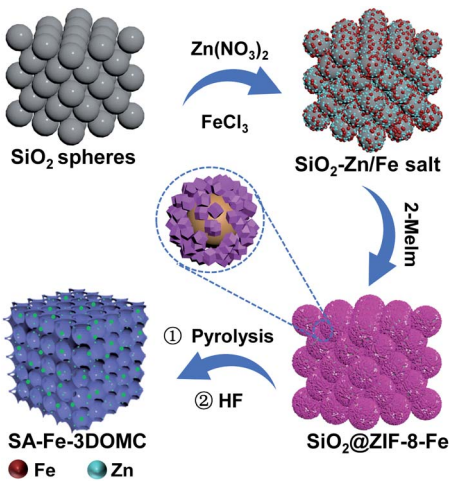
specific capacity (786.6 mA h g^{-1}), demonstrating great potential for practical application.

The synthetic procedure of the SA-Fe-3DOMC catalysts is illustrated in Scheme 1. Briefly, silica nanospheres with a size of 180–200 nm were first modified with Fe^{3+} ($FeCl_3 \cdot 6H_2O$) and Zn^{2+} ($Zn(NO_3)_2 \cdot 6H_2O$) (Fig. S1a, ESI†). The subsequent *in situ* growth of ZIF-8 embedded the silica nanospheres into the MOF precursors (Fig. S1b, ESI†).[26] After carbonization at 900 °C and HF etching, SA-Fe-3DOMC was obtained, showing a honeycomb-like structure and uniform pores with a diameter ranging from 180 to 200 nm (Fig. 1a, b, S1c and d, ESI†), matching well with the size of silica templates. Consistently, a well-defined interconnected macroporous structure with a 10 nm-thick wall was identified by transmission electron microscopy (TEM) (Fig. 1c). Moreover, Fig. 1d reveals that no nanoparticles were detected in the high-angle annular dark field-scanning transmission electron microscope (HAADF-STEM) observation. Elemental mapping images clearly demonstrated the homogeneous distribution of C, N, O and Fe in SA-Fe-3DOMC (Fig. 1e), indicating that iron atoms exist in the carbon matrix as atomically dispersed actives sites. Moreover, the HAADF-STEM image of SA-Fe-3DOMC exhibited that abundant and isolated Fe atoms with brighter spots were indeed atomically dispersed on the porous carbon matrix (Fig. 1f), which was a piece of strong evidence for the successful synthesis of single atoms.[27,28]

The XRD patterns of N–C, SA-Fe-3DOMC and Fe–N–C-50 showed almost the same diffraction peaks centered at around 24.7° and 43.6° (Fig. 2a), which are assigned to the (002) and (101) lattice planes of graphitic carbon, respectively.[31,32] Remarkably, no peaks belonging to Fe and Zn species were observed, confirming the absence of crystalline Fe and Zn particles in SA-Fe-3DOMC. The Fe loading amount of SA-Fe-3DOMC was measured to be 0.84 wt% by inductively coupled plasma-mass spectrometry (ICP-MS). The Raman spectra of the three samples exhibited two prominent peaks at 1340 cm^{-1} and 1590 cm^{-1}, which are ascribed to the D-band (sp^3 disordered carbon) and G-band (sp^2 graphitic carbon), respectively



Scheme 1 Schematic illustration of the synthesis of SA-Fe-3DOMC.

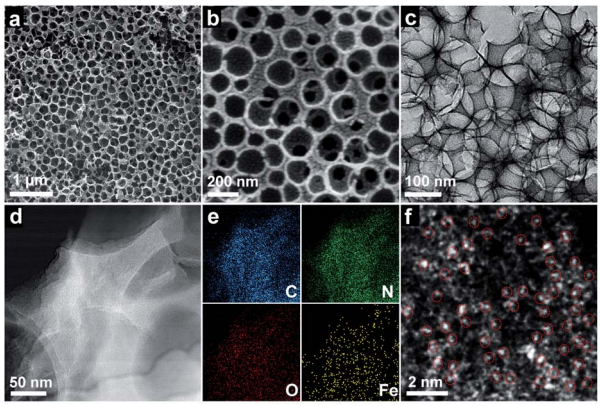


Fig. 1 (a and b) SEM images of SA-Fe-3DOMC. (c) TEM image of SA-Fe-3DOMC. (d) HAADF-STEM image of SA-Fe-3DOMC and (e) corresponding elemental images. (f) AC-HAADF-STEM image of SA-Fe-3DOMC.

(Fig. 2b).[33] The intensity ratio I_D/I_G values for N–C, SA-Fe-3DOMC and Fe–N–C-50 were calculated to be 0.96, 0.93 and 0.95, indicating that SA-Fe-3DOMC possessed a much higher graphitization degree than the other two counterparts.

The pore structures of the as-synthesized catalysts were further characterized by N_2 adsorption–desorption measurements. All catalysts presented a characteristic type IV isotherm, suggesting the presence of abundant mesopores in the samples. Furthermore, a rapid adsorption of N_2 at relatively low pressure (P/P_0 < 0.1) was observed, indicating that micropores can be speculated in the sample (Fig. 2c).[34,35] With the increased number of Fe salts, the specific surface area dramatically decreased from 1681.6 m^2 g^{-1} for N–C to 1357.8 m^2 g^{-1} for SA-Fe-3DOMC and to 629.7 m^2 g^{-1} for Fe–N–C-50. Moreover, the

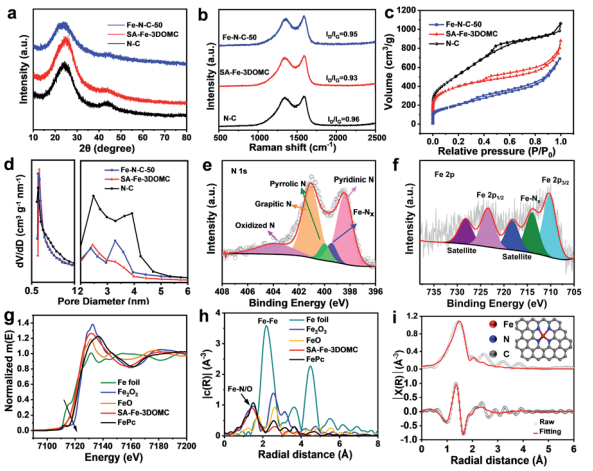


Fig. 2 (a) XRD spectra, (b) Raman spectra, (c) N_2 adsorption/desorption isotherms and (d) pore size distributions of N–C, SA-Fe-3DOMC and Fe–N–C-50. (e) The N 1s high resolution spectrum of SA-Fe-3DOMC. (f) Fe 2p high-resolution spectra. (g) Fe K-edge XANES spectra and (h) Fourier transforms of the Fe K-edge EXAFS oscillations of Fe foil, FeO, Fe_2O_3, SA-Fe-3DOMC, and FePc. (i) FT-EXAFS curve fitting of SA-Fe-3DOMC in *R* space.

pore distribution revealed two sharp peaks at 0.565 nm and 2 to 4 nm (Fig. 2d), implying that a large number of micropores and mesopores were formed,[36] owing to the evaporation of Zn species and the catalytic effect of Fe salts, respectively.[37,38] Notably, the higher specific surface area and abundant pores facilitate the exposure of more Fe–N_x active sites, resulting in better ORR catalytic performance.

The elemental chemical state of the obtained catalyst surface was analysed by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of SA-Fe-3DOMC presented showed the presence of C (89.28 at%), N (4.63 at%), O (5.04 at%), and Fe (1.05 at%) (Fig. S2a, ESI†). The C 1s spectrum of SA-Fe-3DOMC was resolved into C–C (~284.7 eV), C–N (~286.2 eV) and C–O (~289.0 eV), suggesting that heteroatom N was successfully doped into the porous carbon network (Fig. S3, ESI†).[39] The high-resolution N1s spectra of N–C, SA-Fe-3DOMC and Fe–N–C-50 can be deconvoluted into pyridinic-N (~398.5 eV), pyrrolic-N (~400.1 eV), graphitic-N (~401.1 eV) and oxidized-N (~403.9 eV). In addition, a peak at 399.6 eV assigned to Fe–N_x species was observed in both SA-Fe-3DOMC and Fe–N–C-50 (Fig. 2e, S2b and c, ESI†).[28] Furthermore, SA-Fe-3DOMC possessed the highest proportion of pyridinic N and graphitic N compared to the other two counterparts (Fig. S4, ESI†), which is beneficial for regulating the properties of the Fe–N–C catalyst.[39] The Fe 2p high-resolution spectra of SA-Fe-3DOMC and Fe–N–C-50 can be convolved into Fe $2p_{3/2}$ (710.0 eV) and Fe $2p_{1/2}$ (723.7 eV), with peaks around 725.5 eV and 716.1 eV classified as the satellite peaks of Fe, while the peak at 713.2 eV could be assigned to Fe–N_x species (Fig. 2f and S2d, ESI†).[40,41] Linear fitting curve of Fe foil, FeO, Fe_2O_3 and SA-Fe-3DOMC were derived from corresponding Fe K-edge X-ray absorption near edge structure (XANES) position. The iron K-edge XANES position of SA-Fe-3DOMC was located close to that of FeO (Fig. 2g and S9, ESI†), indicating that the valence state of Fe in SA-Fe-3DOMC was close to +2.[42,43] The Fourier-transform (FT) of k^3-weighted extended X-ray absorption fine structure (EXAFS) revealed a predominant peak at 1.50 Å in R space for SA-Fe-3DOMC (Fig. 2h), ascribed to the Fe–N(O) coordination. No Fe–Fe coordination peak (at 2.2 Å) was observed for SA-Fe-3DOMC, further demonstrating the absence of metallic Fe.[44] The EXAFS fitting results were used to indicate the coordination environments of Fe in SA-Fe-3DOMC (Fig. 2i and Table S1, ESI†), which revealed that the Fe atoms in SA-Fe-3DOMC were coordinated with four N atoms, indicating a high probability that the active sites in SA-Fe-3DOMC could be Fe–N_4.[45]

The electrocatalytic activity of NC, SA-Fe-3DOMC and Fe–N–C-50 was first evaluated by cyclic voltammetry (CV). Apparently, the CV curves of all samples showed obvious oxygen reduction peaks under O_2-saturated conditions (Fig. 3a, S5a and b, ESI†), and a more positive oxygen reduction peak of SA-Fe-3DOMC was observed, indicating a superior catalytic activity. Moreover, linear sweep voltammetry (LSV) curves recorded by using a rotating disk electrode (RDE) at 1600 rpm were used to investigate the ORR activities in O_2-saturated 0.1 M KOH solution. The SA-Fe-3DOMC catalyst exhibited the highest ORR catalytic activity with an onset potential (E_{onset}) of 0.994 V, a $E_{1/2}$ of 0.901 V and a diffusion-limited current densities of 5.696 mA

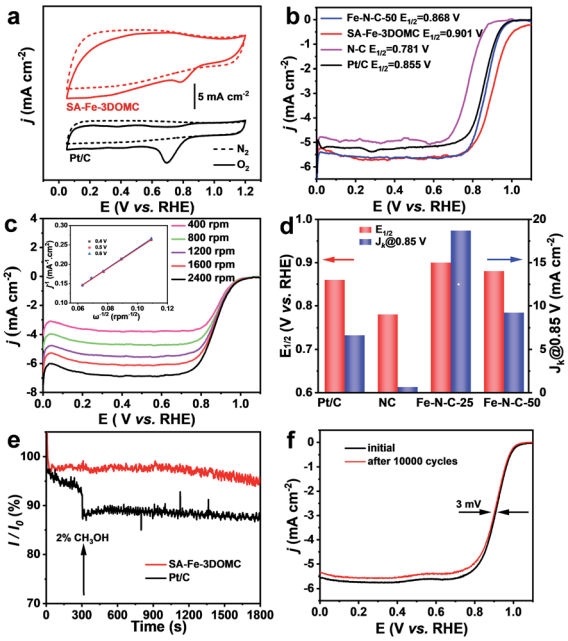


Fig. 3 (a) CV curves in O_2- and N_2-saturated 0.1 M KOH solution. (b) LSV of Pt/C, N–C, SA-Fe-3DOMC, and Fe–N–C-50 in O_2-saturated 0.1 M KOH at 1600 rpm. (c) RDE curves of SA-Fe-3DOMC from 400 rpm to 2400 rpm (inset: K–L plots at 0.4 V, 0.5 V and 0.6 V). (d) Comparison of kinetic current density (j_k) and $E_{1/2}$ for Pt/C, N–C, SA-Fe-3DOMC, and Fe–N–C-50. (e) Chronoamperometric curves of SA-Fe-3DOMC and Pt/C before and after the addition of 2% (v/v) methanol in O_2-saturated 0.1 M KOH. (f) ORR polarization curves of SA-Fe-3DOMC before and after 10 000 cycles.

cm^{-2}, which were much higher than those of commercial Pt/C (0.946 V, 0.855 V, and 5.228 mA cm^{-2}), Fe–N–C-50 (0.955 V, 0.868 V, and 5.608 mA cm^{-2}) and NC (0.876 V, 0.781 V, and 4.982 mA cm^{-2}) (Fig. 3b). To further explore the ORR pathway of SA-Fe-3DOMC, LSV curves were recorded at different rotation speeds (from 400 to 2400 rpm). As depicted in Fig. 3c, the Koutecky–Levich (K–L) plots of SA-Fe-3DOMC showed good linearity and a similar slope, demonstrating that the ORR takes place on the SA-Fe-3DOMC catalyst in a similar way at different potentials. The average electron transfer number of SA-Fe-3DOMC calculated from the K–L plot at 0.4–0.6 V was about 3.7, reflecting an approximate $4e^-$ oxygen reduction pathway (inset of Fig. 3c). RRDE measurements demonstrated very low H_2O_2 yields (3.4–5.1%) and electron transfer numbers in the range of 3.7–3.8 for the SA-Fe-3DOMC catalyst in the potential range from 0.2 to 0.8 V (Fig. S6a and b, ESI†). Fig. 3d further shows the kinetic current density (j_k) of N–C, SA-Fe-3DOMC, Fe–N–C-50 and commercial Pt/C. Remarkably, the j_k of SA-Fe-3DOMC reached as high as 18.70 mA cm^{-2} at 0.85 V, and it was almost 2.8-fold that of commercial Pt/C (6.63 mA cm^{-2}).

In addition, the methanol crossover effects on SA-Fe-3DOMC and Pt/C catalysts were measured in O_2-saturated 0.1 M KOH at 0.6 V. With the addition of 2% (v/v) methanol, a sharp decay in current density was immediately detected for Pt/C (Fig. 3e). In contrast, there was no noticeable variation in current density for SA-Fe-3DOMC, showing a better tolerance to methanol

crossover. The ORR stability of SA-Fe-3DOMC and commercial Pt/C was further investigated by an accelerated durability test (ADT). As illustrated in Fig. 3f, the $E_{1/2}$ of SA-Fe-3DOMC displayed a negligible negative shift of only 3 mV after 10 000 potential cycles from 0.6 V to 1 V. In comparison, the commercial Pt/C showed a severe loss of 12 mV (Fig. S7, ESI†). As shown in Fig. S8,† the morphology and corresponding elemental distribution of SA-Fe-3DOMC before and after 10 000 cycles remain almost unchanged, further confirming the robust properties of SA-Fe-3DOMC. These results suggested that the SA-Fe-3DOMC catalyst has superior electrocatalytic activity and durability in alkaline medium, making it very attractive as a cost-effective electrocatalyst alternative to replace Pt-based counterparts for the ORR.

To further reveal the potential of the SA-Fe-3DOMC electrocatalyst for practical applications, a liquid ZAB was assembled, where carbon paper loaded with SA-Fe-3DOMC and a gas diffusion layer was used as the air electrode (Fig. 4a). Such a battery afforded a stable open-circuit voltage (1.48 V), which was more positive than that of the Pt/C-based battery (1.37 V) (Fig. 4b), confirming outstanding catalytic performance. As shown in Fig. 4c, the battery with SA-Fe-3DOMC exhibited a peak power density of 140 mW cm^{-2}, which was superior to that with Pt/C (124.5 mW cm^{-2}). A typical constant current discharge test also was performed at different current densities (Fig. 4d). Apparently, the voltage gap between SA-Fe-3DOMC and commercial Pt/C widened with the increase of current density, suggesting that the well-designed interconnected 3D nanoporous structure facilitated the mass transfer, especially at higher current densities.[46] When normalized to the consumed Zn during a long-term constant current discharge process at 10 mA cm^{-2}, the SA-Fe-3DOMC battery exhibited a much higher specific capacity with a value of 786.6 mA h g^{-1}, which means that the utilization of catalysts is equal to 95.9% since the theoretical capacity is 820 mA h g^{-1} (Fig. 4e). Moreover, the SA-Fe-3DOMC-based battery can provide electrical energy for 8 light-emitting diodes (LEDs) (Fig. 4f), demonstrating great potential for practical applications.

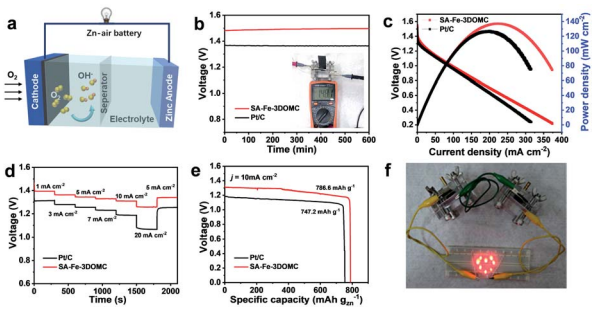


Fig. 4 (a) Schematic of ZABs using SA-Fe-3DOMC as the cathode. (b) Open-circuit plots of Pt/C and SA-Fe-3DOMC. (c) Discharge polarization curves and corresponding power density curves of ZABs respectively with Pt/C and SA-Fe-3DOMC as the cathodes. (d) Discharge curves of ZABs at different current densities. (e) Specific capacities of ZABs using SA-Fe-3DOMC and Pt/C as the cathode at 10 mA cm^{-2}. (f) A demonstration of an LED screen, powered by two ZAB sets.

In summary, we designed and synthesized a SA-Fe-3DOMC electrocatalyst with high ORR catalytic activity, using a SiO_2-embedded Zn-MOF assisted strategy. The achieved SA-Fe-3DOMC showed an excellent $E_{1/2}$ of 0.901 V and a high durability of only 3 mV decrease after 10 000 potential cycles, surpassing the state-of-the-art Pt/C in alkaline medium. For ZAB applications, the as-prepared SA-Fe-3DOMC electrocatalyst also exhibited an outstanding peak power density of 140 mW cm^2 and a superior specific capacity of 786.6 mA h g^{-1}. Collectively, the hierarchical pores generated by SiO_2 and Zn species as porogens allowed the facile access of the single-atom active sites, providing effective strategies not only for seeking alternatives to Pt/C catalysts but also to develop more catalysts for various energy conversion devices, such as CO_2 reduction, water splitting, and N_2 fixation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 F. Meng, H. Zhong, D. Bao, J. Yan and X. Zhang, *J. Am. Chem. Soc.*, 2016, **138**, 10226–10231.
2 W. Wang, M. Tang, Z. Zheng and S. Chen, *Adv. Energy Mater.*, 2019, **9**, 1803628.
3 J. Pan, Y. Y. Xu, H. Yang, Z. Dong, H. Liu and B. Y. Xia, *Adv. Sci.*, 2018, 51700691.
4 D. Wang, H. Xu, P. Yang, X. Lu, J. Ma, R. Li, L. Xiao, J. Zhang and M. An, *J. Mater. Chem. A*, 2021, **9**, 13678–13687.
5 P. Wei, X. G. Li, Z. M. He, X. P. Sun, Q. R. Liang, Z. Y. Wang, C. Fang, Q. Li, H. Yang, J. T. Han and Y. H. Huang, *Chem. Eng. J.*, 2021, **422**, 130134.
6 H. Luo, W. J. Jiang, S. Niu, X. Zhang, Y. Zhang, L. P. Yuan, C. He and J. S. Hu, *Small*, 2020, **16**, 2001171.
7 X. Li, Y. Liu, H. Chen, M. Yang, D. Yang, H. Li and Z. Lin, *Nano Lett.*, 2021, **21**, 3098–3105.
8 I. S. Amiinu, X. Liu, Z. Pu, W. Li, Q. Li, J. Zhang, H. Tang, H. Zhang and S. Mu, *Adv. Funct. Mater.*, 2018, **28**, 104670.
9 Q. C. Xu, H. Jiang, Y. H. Li, D. Liang, Y. J. Hu and C. Z. Li, *Appl. Catal., B*, 2019, **256**, 117893.
10 R. Wu, Y. Song, X. Huang, S. Chen, S. Ibraheem, J. Deng, J. Li, X. Qi and Z. Wei, *J. Power Sources*, 2018, **401**, 287–295.
11 L. Zhao, R. Wu, J. Wang, Z. Li, X. Wei, J. S. Chen and Y. Chen, *J. Energy Chem.*, 2021, **60**, 61–74.
12 Y.-N. Chen, Y. Guo, H. Cui, Z. Xie, X. Zhang, J. Wei and Z. Zhou, *J. Mater. Chem. A*, 2018, **6**, 9716–9722.

13 P. T. Liu, D. Q. Gao, W. Xiao, L. Ma, K. Sun, P. X. Xi, D. S. Xue and J. Wang, *Adv. Funct. Mater.*, 2018, **28**, 1706928.
14 M. Zhang, Q. Dai, H. Zheng, M. Chen and L. Dai, *Adv. Mater.*, 2018, **30**, 1705431.
15 X. Luo, X. Wei, H. Wang, W. Gu, T. Kaneko, Y. Yoshida, X. Zhao and C. Zhu, *Nano-Micro Lett.*, 2020, **12**, 163.
16 Z. Zhang, X. Gao, M. Dou, J. Ji and F. Wang, *J. Mater. Chem. A*, 2017, **5**, 1526–1532.
17 Y. Yan, H. Y. Cheng, Z. H. Qu, R. Yu, F. Liu, Q. W. Ma, S. Zhao, H. Hu, Y. Cheng, C. Y. Yang, Z. F. Li, X. Wang, S. Y. Hao, Y. Y. Chen and M. K. Liu, *J. Mater. Chem. A*, 2021, **9**, 19489–19507.
18 J. Zhang, X. Dong, W. Xing, Y. Luo, Y. Chen, Y. Xue, C. Zhang, J. Chen, G. Wang and R. Wang, *Chem. Eng. J.*, 2021, **420**, 129938.
19 D. Wang, H. Xu, P. Yang, L. Xiao, L. Du, X. Lu, R. Li, J. Zhang and M. An, *J. Mater. Chem. A*, 2021, **9**, 9761–9770.
20 Y. Qiao, P. Yuan, Y. Hu, J. Zhang, S. Mu, J. Zhou, H. Li, H. Xia, J. He and Q. Xu, *Adv. Mater.*, 2018, **30**, 1804504.
21 Y. C. Guo, L. Feng, C. C. Wu, X. M. Wang and X. Zhang, *J. Catal.*, 2020, **390**, 213–223.
22 R. Jiang, L. Li, T. Sheng, G. Hu, Y. Chen and L. Wang, *J. Am. Chem. Soc.*, 2018, **140**, 11594–11598.
23 H. W. Liang, W. Wei, Z. S. Wu, X. Feng and K. Mullen, *J. Am. Chem. Soc.*, 2013, **135**, 16002–16005.
24 Y. Li, J. Gao, F. Zhang, Q. Qian, Y. Liu and G. Zhang, *J. Mater. Chem. A*, 2018, **6**, 15523–15529.
25 S. Lee, D. H. Kwak, S. B. Han, Y. W. Lee, J. Y. Lee, I. A. Choi, H. S. Park, J. Y. Park and K. W. Park, *ACS Catal.*, 2016, **6**, 5095–5102.
26 A. I. Douka, Y. Xu, H. Yang, S. Zaman, Y. Yan, H. Liu, M. A. Salam and B. Y. Xia, *Adv. Mater.*, 2020, **32**, 2002170.
27 Y. J. Deng, B. Chi, X. L. Tian, Z. M. Cui, E. S. Liu, Q. Y. Jia, W. J. Fan, G. H. Wang, D. Dang, M. S. Li, K. T. Zang, J. Luo, Y. F. Hu, S. J. Liao, X. L. Sun and S. Mukerjee, *J. Mater. Chem. A*, 2019, **7**, 5020–5030.
28 X. Zhang, X. Han, Z. Jiang, J. Xu, L. Chen, Y. Xue, A. Nie, Z. Xie, Q. Kuang and L. Zheng, *Nano Energy*, 2020, **71**, 104547.
29 Y. Yan, P. Zhang, Z. Qu, M. Tong, S. Zhao, Z. Li, M. Liu and Z. Lin, *Nano Lett.*, 2020, **20**, 7662–7669.
30 M. Liu, P. Zhang, Z. Qu, Y. Yan, C. Lai, T. Liu and S. Zhang, *Nat. Commun.*, 2019, **10**, 3917.
31 G. Gan, X. Li, L. Wang, S. Fan, J. Mu, P. Wang and G. Chen, *ACS Nano*, 2020, **14**, 9929–9937.
32 J. Han, X. Meng, L. Lu, J. Bian, Z. Li and C. Sun, *Adv. Funct. Mater.*, 2019, **29**, 1808872.
33 Y. Wang, R. Gan, H. Liu, M. Dirican, C. Wei, C. Ma, J. Shi and X. Zhang, *J. Mater. Chem. A*, 2021, **9**, 2764–2774.
34 B. Chen, X. He, F. Yin, H. Wang, D.-J. Liu, R. Shi, J. Chen and H. Yin, *Adv. Funct. Mater.*, 2017, **27**, 1700795.
35 B. Li, Y. Yan, C. Shen, Y. Yu, Q. Wang and M. Liu, *Nanoscale*, 2018, **10**, 16217–16230.
36 Q. Y. Zhou, Z. Zhang, J. J. Cai, B. Liu, Y. L. Zhang, X. F. Gong, X. L. Sui, A. P. Yu, L. Zhao, Z. B. Wang and Z. W. Chen, *Nano Energy*, 2020, **71**, 104592.
37 Y. Zhou, Y. Yu, D. Ma, A. C. Foucher, L. Xiong, J. Zhang, E. A. Stach, Q. Yue and Y. Kang, *ACS Catal.*, 2020, **11**, 74–81.
38 G. Chen, P. Liu, Z. Liao, F. Sun, Y. He, H. Zhong, T. Zhang, E. Zschech, M. Chen, G. Wu, J. Zhang and X. Feng, *Adv. Mater.*, 2020, **32**, 1907399.
39 H. Zhang, S. Hwang, M. Wang, Z. Feng, S. Karakalos, L. Luo, Z. Qiao, X. Xie, C. Wang, D. Su, Y. Shao and G. Wu, *J. Am. Chem. Soc.*, 2017, **139**, 14143–14149.
40 X. Xie, L. Peng, H. Yang, G. I. N. Waterhouse, L. Shang and T. Zhang, *Adv. Mater.*, 2021, **33**, 2101038.
41 L. Lin, Q. Zhu and A. W. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 11027–11033.
42 K. Yuan, D. Lutzenkirchen-Hecht, L. Li, L. Shuai, Y. Li, R. Cao, M. Qiu, X. Zhuang, M. K. H. Leung, Y. Chen and U. Scherf, *J. Am. Chem. Soc.*, 2020, **142**, 2404–2412.
43 Y. Yan, S. Liang, X. Wang, M. Zhang, S.-M. Hao, X. Cui, Z. Li and Z. Lin, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, **40**, 118.
44 Z. Zhang, J. Sun, F. Wang and L. Dai, *Angew. Chem., Int. Ed. Engl.*, 2018, **57**, 9038–9043.
45 J. Chen, H. Li, C. Fan, Q. Meng, Y. Tang, X. Qiu, G. Fu and T. Ma, *Adv. Mater.*, 2020, **32**, 2003134.
46 M. G. Park, D. U. Lee, M. H. Seo, Z. P. Cano and Z. Chen, *Small*, 2016, **12**, 2707–2714.