Assembling pore-rich FeP nanorods on the CNT backbone as an advanced electrocatalyst for oxygen evolution

Yan, Ya; Zhao, Bin; Yi, Sung Chul; Wang, Xin

2016

Yan, Y., Zhao, B., Yi, S. C., & Wang, X. (2016). Assembling pore-rich FeP nanorods on the CNT backbone as an advanced electrocatalyst for oxygen evolution. *Journal of Materials Chemistry A*, 4(33), 13005-13010.

<https://hdl.handle.net/10356/84616>

<https://doi.org/10.1039/C6TA05317C>

© 2016 The Author(s) (Royal Society of Chemistry). This is the author created version of a work that has been peer reviewed and accepted for publication by *Journal of Materials Chemistry A*, The Author(s) (Royal Society of Chemistry). It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1039/C6TA05317C>].

Downloaded on 26 Apr 2023 13:21:39 SGT

Assembling pore-rich FeP nanorods on the CNT backbone as an advanced electrocatalyst for oxygen evolution

Ya Yan ^{a,b}, Bin Zhao ^a, Sung Chul Yi ^{c,*}, Xin Wang ^{b,*}

^a School of Materials Science & Engineering, University of Shanghai for Science and Technology, 516 Jungong Road, Yangpu District, Shanghai 200093, China

^b School of Chemical and Biomedical Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798 Singapore

^c Department of Chemical Engineering, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea

* Corresponding authors. E-mail: WangXin@ntu.edu.sg (X.W); scyi@hanyang.ac.kr (S.C.Y.)

Abstract

Electrocatalytic water splitting is a promising mean for clean energy production. There is a great need to develop low cost, efficient and durable electrocatalysts for such purpose. Herein, we report a novel hierarchical nanostructure composed of FeP porous nanorods on CNT backbones. The directed growth of α -FeO(OH) nanospindles on CNTs was first realized via a bottom-up assembly, followed by phosphorization transformation. When evaluated for electrocatalytic water splitting reaction, these hierarchical structures exhibited superior oxygen evolution performance due to their advantageous structural features.

Water splitting is a promising approach to enable the storage of intermittent solar and wind energies in the form of chemical fuels, namely hydrogen and oxygen.¹⁻⁴ High overpotentials are normally required in order for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) to proceed at decent rates.⁵⁻¹⁰ Of the two half reactions, OER is intrinsically more sluggish as it requires a total of four redox equivalents per turnover, and results in the formation of two O-O bonds.^{11, 12} Therefore, the employment of an efficient electrocatalyst is necessary to increase the reaction rate, reduce overpotential, and enhance energy conversion efficiency. RuO₂ and IrO₂ are currently the most active catalysts for OER. However, Ru and Ir are scarce resources and very expensive.^{13, 14} Research for more efficient and economical OER catalysts remains an ongoing challenge.^{15, 16}

Recently, metal (including cobalt, nickel, and iron) phosphides have gained much attention for their dominant catalytic activity in HER.¹⁷⁻²¹ However, metal phosphides have rarely been applied as electrocatalysts for OER.^{22, 23} Most recently, Hu et al. showed that Ni₂P, which is an efficient hydrogen-evolution electrocatalyst, is also highly active for oxygen evolution.²² They found that the active form of the catalyst for OER is a core-shell Ni₂P/NiO_x assembly that is generated in-situ under catalytic conditions. This finding was further evidenced by the work from Paik et al. for the investigation of a Ni-P catalyst.²⁴ Motivated by the success of the nickel phosphide as efficient electrocatalyst for OER, we aimed to study the catalytic properties of iron phosphide for oxygen evolution.

Here, we report a novel hierarchical nanostructure composed of porous FeP nanorods grafted on CNT backbones (denoted as FeP@CNT). These nanostructures were achieved via a bottom-up assembly of α -FeO(OH) nanospindles on CNTs (denoted as FeO(OH)@CNT). FeO(OH)@CNT subsequently underwent *in situ* phase and structure transformation by phosphorization. The as-prepared FeP@CNT experienced dramatic structural changes under anodic potentials and this process engendered unique local compositions. More importantly, FeP@CNT displayed excellent OER performances, which were comparable to iridium based catalysts. Furthermore, the activated catalyst also achieved remarkable durability. The outstanding electrocatalytic activity of FeP@CNT can be attributed to its unique hybrid structure. FeP@CNT is rich in nanopores, and the *in situ* generated oxidized iron species served as active sites for OER. To the best of our knowledge, the nano-composite of porous FeP nanorods-coated CNT hierarchical structure has not been reported and applied in the field of OER.

The synthetic strategy used to fabricate the FeP@CNT hierarchical structure is illustrated in Fig. 1. In the first step, FeO(OH) nanospindles were selectively grown onto mildly oxidized multi-wall CNTs (see experimental section in the Supporting Information for CNT oxidation) by solvothermal reaction of FeSO₄·7H₂O at 120 °C. A glycerol/water (volume ratio=1/3) mixed solvent was used to facilitate the formation of nanospindle-structured FeO(OH)@CNT. Ferric ions from the dissolved FeSO₄·7H₂O would interact with the functional groups on the CNT surface, and ensured the selective nucleation and growth of FeO(OH) nanospindles on the CNTs.²⁵⁻²⁷ The crystallographic structure and phase purity of the

FeO(OH)@CNT samples was determined by X-ray powder diffraction (XRD). All the diffraction peaks can be assigned to tetragonal α -FeO(OH) (JCPDS no. 29-0713) (Fig. 2a). Scanning electron microscope (SEM) characterization revealed that FeO(OH)@CNT consisted of highly entangled CNTs whose entire surface was uniformly decorated with nanospindles (see Supporting Fig. S1, Fig. 2b and c). Further characterization by transmission electron microscopy (TEM) showed that the as-obtained α -FeO(OH) nanospindles were between 100-150 nm in length and possessed diameters that were several nanometres wide (Fig. 2d). High-resolution (HR) TEM characterization of the selected area further evidences the presence of an interlayer spacing of ca. 2.53 Å (Fig. 2d inset), which corresponds to the (101) plane of α -FeO(OH). Meanwhile, the surface composition of the α -FeO(OH)@CNT was also investigated by X-ray photon spectroscopy (XPS) (Fig. S2).

The second step features a solid/gas-phase reaction at 300 °C which introduces P into the α -FeO(OH) structure (see Fig. 1). NaH₂PO₂ was used as a precursor to generate the PH₃ gas. PH₃ then reacted with the α -FeO(OH) nanospindles on CNTs to form the final FeP (JCPDS no. 65-2595) nanorods on CNT backbones. This outcome was confirmed by XRD analysis (Fig. 3a). Furthermore, SEM showed that thermal conversion of α -FeO(OH) nanospindles to FeP nanorods underwent a pseudomorphic transformation process due to their structural similarity (Fig. 3b). During the phosphorization process, certain level of porosity was introduced into the resulting structures as a result of the volume reduction associated with the phase transformation from low density α -FeO(OH) (3 g cm⁻³) to denser FeP with a density of 6.74 g cm⁻³.²⁸ Accordingly, the specific surface area (calculated by the Brunauer-Emmett-Teller (BET) method) of the samples increased from about 55 m² g⁻¹ (for FeO(OH)@CNT) to 98 m² g⁻¹ after phosphorization, while the overall hierarchical nanostructure was maintained (see Supporting Fig. S3). Porous structure of the nanowires was easily observed upon closer examination of the FeP nanorods with TEM (Fig. 3c) and this is consistent with the BET results. The lattice fringes of the FeP nanorods were imaged by HRTEM (Fig. 3d). The interplanar spacing of 2.51 Å observed corresponds to the (102) plane of FeP (Fig. 3d inset), which is consistent with our XRD results.

In addition, it was observed that crystalline regions of the porous FeP nanorods are surrounded by thick amorphous-like shells (~4 nm) (indicated by the yellow circles in Fig. 2d), composed of Fe, P, O as characterized by energy dispersive spectroscopy (EDS) under scanning TEM (STEM) mode (see Supporting Fig. S3). Such amorphous outer layers have also been observed in other metal phosphide nanostructures.^{23, 29, 30} Further STEM-EDS line profiling spectra illustrated that the Fe and P overlap quite well cross the nanorod (Fig. 4a and b). This suggests that P has been uniformly doped into the crystal structure of porous nanorods. It is also evident from the EDS line profiling that the surface has higher P contents compared with the core sides of the porous nanorod, which are in agreement with the TEM observation. Besides, the average atomic ratio of P/Fe in the nanorods was calculated to be 1.09 from the EDS spectrum (Fig. S4). This value is consistent with the expected 1:1 FeP stoichiometry.

We further investigated the surface composition and oxidation states of the FeP@CNT through XPS. The XPS survey spectrum (see Supporting Fig. S5a) shows that the sample surface consists of O, C, Fe and P

elements. Residual oxygen-containing functionalities in the CNTs and surface oxidation of FeP nanorods likely contributed to the O element observed (see Supporting Fig. S5b). This is consistent with the EDS analysis. High-resolution XPS spectra (see Supporting Fig. S5c) of the C1s core level can be deconvoluted into two main peaks. The main peak at 284.7 eV is assigned to sp^2 -hybridized graphite-like carbon atom while the peak around 286.6 eV is attributed to the carbon atom bound to one oxygen atom. This is consistent with the reported values for acid-treated CNTs.³¹ In the Fe 2p core level spectrum (Fig. 4), one broad core doublet at 712.3 and 726.2 eV was observed. This doublet likely arises from the native (amorphous) oxide layers present at the surface, in agreement with the TEM observation.³² Another set of sharp peaks is observed at a lower binding energies of 707.3 eV ($2p_{3/2}$)/ 720.1 eV ($2p_{1/2}$) and these peaks can be attributed to FeP.^{33, 34} The P 2p core level spectrum (Fig. 4d) of the FeP@CNT exhibits two peak regions, with one centred at the binding energy of 129.3 and 130.1 eV (P $2p_{3/2}$ and $2p_{1/2}$). These peaks can be assigned to low-valence P (FeP in this case). The other peak at 133.7 eV is characteristic of phosphate-like P.^{35, 36} The existence of the high oxidation state P could be ascribed to surface oxidation under ambient conditions as has been previously observed for metal phosphide materials.³⁵

This unique hybrid structure is expected to exhibit superior electrochemical performance, owing to the integration of several advantageous structural features within the catalyst. Specifically, the highly conductive and flexible CNT backbone can provide a three-dimensional (3D) electronic network to facilitate charge transfer.^{5, 37, 38} Furthermore, the porous FeP nanorods grafted on the CNT backbone can enhance electrochemical activity and mechanical integrity of the electrode due to their large surface area, nanoscale diffusion length (typically a few nanometres) and sufficient internal pores and void space.³⁸ In comparison, electrodes composed of nanoparticles usually experience severe agglomeration with most of their active interfaces eliminated when evaluated for the water splitting.^{21, 39}

Next, we investigated the redox behaviours of FeP@CNT upon potential cycling that covered the OER region. Fig. 5a displays the first and second scans of linear sweep voltammetry (LSV) for FeP@CNT, measured in 1.0 M KOH solution (see Supporting Information for details). The first oxidative sweep of the FeP@CNT produced prominent anodic currents with a huge preoxidation peak over the broad potential range prior to the onset of OER (~ 1.5 V vs. RHE). Compared to the corresponding second scan, the highly extensive oxidative currents measured during the first scan implies that irreversible oxidative transformation of FeP occurred during the first scan. On the basis of the general electrochemical redox states of iron upon potential bias, it is suggested that the Fe II species present on the surface of FeP are oxidized to higher valent states ($\geq 3+$).⁴⁰ Clearly, steady-state OER performance of the catalyst will be defined by the nature of FeP@CNT that is present after its transformation.

In the light of the anodic behaviour of the present FeP@CNT, we then assessed the OER performances of the steady-state catalyst. Fig. 5b shows OER polarization curves of the iron-based materials (FeP@CNT and Fe_2O_3 @CNT, Fig. S6) and precious metal catalysts (IrO_2). The catalysts were deposited onto a glassy carbon

working electrode at similar catalyst loadings and measured on a rotating disk electrode (RDE) in 1.0 M KOH solution. The anodic current density recorded with the FeP@CNT catalyst showed a sharp onset of OER current at ~ 1.48 V vs. RHE (corresponding to an overpotential of 250 mV, see Fig. S7 for the more detailed information for determining the onset potential). To reach the current density of 10 mA cm^{-2} , an overpotential of only 300 mV was required. The IrO_2 catalyst afforded a similar onset potential, but its OER current density fell below that of our FeP@CNT at ~ 1.53 V vs. RHE. Further analysis of its catalytic kinetics by Tafel plots (Fig. 5c) resulted in a Tafel slope as low as of 53.0 mV dec^{-1} . This value is smaller than that of Fe_2O_3 @CNT (67.0 mV dec^{-1}) and is also comparable with one of the best commercial OER catalysts, IrO_2 (50.0 mV dec^{-1}). This suggests a faster kinetics on the FeP@CNT. According to electrochemical impedance spectroscopy (EIS) measurements (Supporting Fig. S8), the activated catalyst exhibited the smallest charge transfer resistance at OER-occurring potential (1.6 V), when compared to Fe_2O_3 @CNT and IrO_2 . This observation implies that FeP@CNT is highly efficient in shuttling charges during catalytic turnover. These benefits of the activated FeP@CNT might be from its morphological advantages and unique surface nature in the local environments. Concerning the low onset, high current density and small Tafel slope, the OER catalytic activity of the FeP@CNT compares favourably to the most of state-of-the-art OER electrocatalysts (see Supporting Table S1 for detailed comparison). The Faraday efficiency of OER in basic medium was also monitored during a 120 min galvanostatic electrolysis (Fig. 5d). The amount of oxygen evolved during electrolysis corresponded to the theoretical Faraday yield. Moreover, the FeP@CNT hierarchical structures exhibited very good durability, when biased galvanostatically at 10 mA cm^{-2} on the FeP@CNT electrodes, the catalyst showed a nearly constant overpotential with merely 50 mV increase during 14 h of continuous operation (Figure 4b inset). Afterwards, to verify the surface composition of the FeP@CNT after the stability test, XPS profiles were recorded from the catalyst (Fig. S9), which exhibited a shift of the Fe 2p main peak along with diminished shoulder features (Fe-P) compared with the original state, indicating a transition of the original FeII species to higher oxidation states after stability test.

Additionally, the electrocatalytic property of freshly synthesized FeP@CNT for HER in base solution (1.0 M KOH) is also investigated as shown in Supporting Fig. S10. Different from the anode sweeps, no redox switching peaks were observed during the consecutive cathodic scans in the HER region, indicating no change of the surface structure and composition for the as-prepared FeP@CNT. As expected, the FeP@CNT electrode showed comparable or even better electrocatalytic property than most of other reported iron phosphides electrocatalysts for HER in alkaline solution (see Supporting Table S2). To be specific, to achieve a current density of 10 mA cm^{-2} , the FeP@CNT hierarchical electrocatalyst only requires overpotential of 110 mV (Fig. S7a). The Tafel slope of FeP@CNT nanostructures is 51 mV dec^{-1} (Fig. S7b), suggesting a Volmer-Heyrovsky mechanism for HER. Finally, a practical investigation on the bifunctional performance of FeP@CNT for overall water electrolysis is demonstrated in a two-electrode alkaline electrolyzer (Fig. S11). It showed a current density of 10 mA cm^{-2} at about 1.77 V vs. RHE, representing a combined overpotential of only about 540 mV for HER and OER.

The remarkable activities of the hierarchical FeP@CNT nanostructure is mainly attributed to the following aspects. First, incorporation of highly conductive and flexible CNT backbone into iron phosphides improves the conductivity and charge transfer capability. Second, uniform morphology and porous structure were expected to maximize the number of exposed active sites for electrochemical reactions, and facilitate the diffusion of reactants in the electrolyte. Third, the *in-situ* generated oxidized iron species on the surface of FeP nanorods can act as active sites for catalytic reactions. More importantly, metallic iron phosphides with high electrical conductivity can facilitate electron transfer.^{23, 41, 42} Thus, synergistic effects might exist between the FeP core and the surface oxidized iron species, which requires further study for confirmation.

In summary, an advanced FeP@CNT hierarchical nanostructure has been constructed by bottom-up assembly of α -FeO(OH) nanospindles on CNTs and *in situ* transformation to porous FeP nanorods by phosphorization. As a result of their desirable nanoporous structure and *in situ* generated OER active oxidized iron species upon anodic potentials, the steady-state FeP@CNT hierarchical nanostructure showed remarkable OER activity that compared favourably to iridium catalyst. FeP@CNT also exhibited remarkable durability. In addition, the as-obtained FeP@CNT hierarchical nanostructure displayed excellent electrocatalytic activity for HER. These findings not only extend the family of CNT-supported functional nanomaterials but also highlight the potential application of iron phosphides as efficient electrocatalysts for OER.

Acknowledgment

This project is funded by the academic research fund AcRF tier 1 (M4011253 RG 7/14) and tier 2 (M4020246, ARC10/15), Ministry of Education, Singapore and The Program for Associate Professor of Special Appointment (Young Eastern Scholar) at Shanghai Institutions of Higher Learning (QD2016013). We also acknowledge financial support by Defence Acquisition Program Administration and Agency for Defence Development under the contract UD120080GD, Republic of Korea.

Electronic supplementary information (ESI) available: Experimental section and figures. See DOI:

References

1. A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253-278.
2. Y. Jiao, Y. Zheng, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, **44**, 2060-2086.
3. M. Ledendecker, S. Krick Calderón, C. Papp, H.-P. Steinrück, M. Antonietti and M. Shalom, *Angew. Chem. Int. Ed.*, 2015, doi: 10.1002/anie.201502438.
4. H. Wang, H. W. Lee, Y. Deng, Z. Lu, P. C. Hsu, Y. Liu, D. Lin and Y. Cui, *Nat. Commun.*, 2015, **6**, 7261.
5. M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei and H. Dai, *J. Am. Chem. Soc.*, 2013, **135**, 8452-8455.
6. Y. Yan, B. Xia, Z. Xu and X. Wang, *ACS Catal.*, 2014, **4**, 1693-1705.
7. M.-R. Gao, J.-X. Liang, Y.-R. Zheng, Y.-F. Xu, J. Jiang, Q. Gao, J. Li and S.-H. Yu, *Nat. Commun.*, 2015, **6**.
8. Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec and S. Z. Qiao, *ACS Nano*, 2014, **8**, 5290-5296.
9. Z. Huang, Z. Chen, Z. Chen, C. Lv, H. Meng and C. Zhang, *ACS Nano*, 2014, **8**, 8121-8129.
10. S. Cobo, J. Heidkamp, P. A. Jacques, J. Fize, V. Fourmond, L. Guetaz, B. Joussetme, V. Ivanova, H. Dau, S. Palacin, M. Fontecave and V. Artero, *Nat. Mater.*, 2012, **11**, 802-807.
11. T. A. Betley, Q. Wu, T. Van Voorhis and D. G. Nocera, *Inorg. Chem.*, 2008, **47**, 1849-1861.
12. R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 2008, **47**, 1697-1699.
13. T. Reier, M. Oezaslan and P. Strasser, *ACS Catal.*, 2012, **2**, 1765-1772.
14. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446-6473.
15. P. Du and R. Eisenberg, *Energy Environ. Sci.*, 2012, **5**, 6012-6021.
16. D. U. Lee, P. Xu, Z. P. Cano, A. G. Kashkooli, M. G. Park and Z. Chen, *J. Mater. Chem. A*, 2016, **4**, 7107-7134.
17. Y. Shi and B. Zhang, *Chem. Soc. Rev.*, 2016, **45**, 1529-1541.
18. J. Wang, W. Cui, Q. Liu, Z. Xing, A. M. Asiri and X. Sun, *Adv. Mater.*, 2016, **28**, 215-230.
19. P. Xiao, W. Chen and X. Wang, *Adv. Energy Mater.*, 2015, **5**, doi:10.1002/aenm.201500985.
20. Z. Pu, Q. Liu, P. Jiang, A. M. Asiri, A. Y. Obaid and X. Sun, *Chem. Mater.*, 2014, **26**, 4326-4329.
21. J. Tian, Q. Liu, Y. Liang, Z. Xing, A. M. Asiri and X. Sun, *Acs Appl Mater Inter*, 2014, **6**, 20579-20584.
22. L. A. Stern, L. G. Feng, F. Song and X. L. Hu, *Energy Environ. Sci.*, 2015, **8**, 2347-2351.
23. J. Ryu, N. Jung, J. H. Jang, H.-J. Kim and S. J. Yoo, *ACS Catal.*, 2015, **5**, 4066-4074.
24. X.-Y. Yu, Y. Feng, B. Guan, X. W. Lou and U. Paik, *Energy Environ. Sci.*, 2016.
25. Z. Wang, D. Luan, S. Madhavi, Y. Hu and X. W. Lou, *Energy Environ. Sci.*, 2012, **5**, 5252-5256.
26. Y. Gu and F. Jérôme, *Green Chem.*, 2010, **12**, 1127.

27. Y. Q. Liang, Z. D. Cui, S. L. Zhu and X. J. Yang, *Electrochim. Acta*, 2010, **55**, 5245-5252.
28. Y. Piao, J. Kim, H. B. Na, D. Kim, J. S. Baek, M. K. Ko, J. H. Lee, M. Shokouhimehr and T. Hyeon, *Nat. Mater.*, 2008, **7**, 242-247.
29. J. Park, B. Koo, K. Y. Yoon, Y. Hwang, M. Kang, J.-G. Park and T. Hyeon, *J. Am. Chem. Soc.*, 2005, **127**, 8433-8440.
30. H. Kim, Y. Chae, D. H. Lee, M. Kim, J. Huh, Y. Kim, H. Kim, H. J. Kim, S. O. Kim, H. Baik, K. Choi, J. S. Kim, G.-R. Yi and K. Lee, *Angew. Chem.*, 2010, **122**, 5848-5852.
31. T. I. T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin and N. M. D. Brown, *Carbon*, 2005, **43**, 153-161.
32. A. P. Grosvenor, B. A. Kobe, M. C. Biesinger and N. S. McIntyre, *Surf. Interface Anal.*, 2004, **36**, 1564-1574.
33. C. Qian, F. Kim, L. Ma, F. Tsui, P. Yang and J. Liu, *J. Am. Chem. Soc.*, 2004, **126**, 1195-1198.
34. C. Y. Son, I. H. Kwak, Y. R. Lim and J. Park, *Chem. Commun.*, 2016, **52**, 2819-2822.
35. P. Jiang, Q. Liu, Y. Liang, J. Tian, A. M. Asiri and X. Sun, *Angew. Chem. Int. Ed.*, 2014, **53**, 12855-12859.
36. E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, *Angew. Chem. Int. Ed.*, 2014, **53**, 5427-5430.
37. Q. Liu, Z. Pu, A. M. Asiri and X. Sun, *Electrochim. Acta*, 2014, **149**, 324-329.
38. Y. Yan, X. Ge, Z. Liu, J.-Y. Wang, J.-M. Lee and X. Wang, *Nanoscale*, 2013, **5**, 7768-7771.
39. Z. Zhang, B. Lu, J. Hao, W. Yang and J. Tang, *Chem. Commun.*, 2014, **50**, 11554-11557.
40. R. D. Smith, M. S. Prevot, R. D. Fagan, S. Trudel and C. P. Berlinguette, *J. Am. Chem. Soc.*, 2013, **135**, 11580-11586.
41. Y.-P. Zhu, Y.-P. Liu, T.-Z. Ren and Z.-Y. Yuan, *Adv. Funct. Mater.*, 2015, **25**, 7337-7347.
42. Y. Yan, B. Y. Xia, X. Ge, Z. Liu, A. Fisher and X. Wang, *Chem. Eur. J.*, 2015, **21**, 18062-18067.

Figures and captions

Fig. 1 Schematic illustration of the formation of the hierarchical FeP@CNT hybrid material for OER catalysis. The FeP@CNT is synthesized through two steps including solvothermal growth and solid/gas-phase phosphorization.

Fig. 2 (a) XRD pattern, (b, c) FESEM images, and (d) TEM image of FeO(OH)@CNT hierarchical structures (inset is the HRTEM image of the selected area).

Fig. 3 (a) XRD pattern, (b) FESEM image, (c) TEM image and (d) HRTEM image of FeP@CNT hierarchical structures (inset is the enlarged HRTEM image of selected area).

Fig. 4 (a) STEM image of as-prepared FeP@CNT. (b) EDS line profiling spectra of a FeP nanorod (inset: a STEM image of the FeP nanorod marked with a profile path selected from image a). (c-d) Fe 2p and P 2p core level XPS spectra of FeP@CNT.

Fig. 5 (a) LSV scans (iR -compensated), (b) iR -corrected OER polarization curves and (c) corresponding Tafel plots measured in 1.0 M KOH. (d) Faradic efficiency of the OER catalysed by FeP@CNT in 1.0 M KOH at the overpotential of 370 mV (inset: galvanostatic electrolysis in 1.0 M KOH at 10 mA cm^{-2} over 14 h).

Graphical abstract

A porous FeP nanorods on CNT backbones (FeP@CNT) catalyst is designed for efficient OER and the effect of the unique structure on the OER performance is also investigated.