Phosphorus-Doped CuCo₂O₄ Oxide with Partial Amorphous Phase as a Robust Electrocatalyst for the Oxygen Evolution Reaction

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It is highly desirable to develop efficient and low-cost electrocatalysts for the oxygen evolution reaction (OER) to improve the efficiency of water electrolysis. Here, we report a strategy doping with a small amount of phosphorus to make inactive and low-cost spinel CuCo₂O₄ (CCO) turn into high-efficiency and superior to the noble metal catalyst RuO2. The spinel CuCo₂O₄-P_{0.5} (CCP_{0.5}) shows the best OER performance with a small overpotential of 290 mV at a current density of 10 mA cm⁻² and a low Tafel slope of 68 mV dec⁻¹ in an alkaline

1. Introduction

Global climate concerns caused by the rapid depletion of fossil fuels (coal, petroleum, and natural gas, etc) have made it imperative to develop sustainable and environmentally friendly energy sources.^[1–3] Hydrogen is recognized as a promising renewable energy source because of its high efficiency and zero CO₂ emission characteristics.^[4-6] However, developing efficient and clean hydrogen production technologies remains a challenge due to inefficient and costly water electrolysis.^[7–8] The electrolysis of water involves with hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).^[9-10] The efficient water electrolysis is especially hampered by the sluggish kinetics of the OER at the anode because it is a four-electron

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electrolyte. The phosphorus doping induces the production of an amorphous phase that provides a large number of active sites, and the synergistic effect of the crystalline phase and amorphous phase significantly improves the OER activity of CCO. It is also revealed that the conductivity of CCO is improved compared with pristine CCO. Our work highlights that nonmetallic element doping is an effective strategy to greatly enhance the OER performance of spinel transition metal oxide electrocatalysts.

and uphill reaction.^[11–13] Generally speaking, noble metal-based catalysts such as RuO₂ and IrO₂ show the high catalytic activity towards OER in alkaline electrolyte.^[14] Unfortunately, the use of these materials increases the cost of electrolytic water technology.^[15-16] Therefore, it is critical to develop highly efficient and inexpensive OER electrocatalysts to boost water electrolvsis.

The inexpensive transition metal-based compounds have received tremendous attention and believed to have good electrochemical activities for OER.^[17-18] In particular, the spinel AB_2O_4 (A, B=transition metal) oxides that consist of 3d transition metals have shown their potential of catalytic performance for OER, such as MnCo₂O₄, CoFe₂O₄, CoAl₂O₄, and $NiCo_2O_4$.^[19-24] Here we focus on spinel CuCo_2O_4 that is widely used in supercapacitors, electrochemical sensors, and oxygen reduction reactions.^[25-26] The unique spinel structure should also made it a promising OER catalyst. However, the spinel CuCo2O4 shows low electric conductivity and insufficient exposure of active sites,^[27] which greatly hindered its further improvement of electrochemical activity. In spinel oxide only 1/8 of the tetrahedral interstices and 1/2 the octahedral interstices are filled with metal cations in the crystal lattice, and the remaining unoccupied interstices tend to make the spinel an open structure to accommodate the migration of cations.^[28-29] Generally speaking, introducing other atoms into the lattice can greatly affect the electronic structure of the pristine catalyst, enhance the intrinsic activity of the catalyst and the conductivity.^[30]

Recent studies have proved that the construction of a partial amorphous phase in the catalyst is beneficial to improve the activity of the catalyst and reduce the overpotential of the reaction.^[21,31] Amorphous materials have the unique advantages of long-range disorder and isotropy.^[32] Many dangling bonds in the amorphous phase increase the surface energy, which is generally beneficial for the adsorption of the reaction intermediate.^[33] The presence of a large proportion of the coordination with unsaturated atoms in the amorphous phase can introduce a large number of defects that can provide active sites for catalysis,^[34] thus improving the reaction kinetics of catalysts. However, pure amorphous catalysts increase the space resistance of the electron transport due to dangling bonds, and their conductivity is worse than that of corresponding crystalline catalysts.^[33] Experimental and theoretical calculation studies have shown that partially amorphous catalysts have more OER catalytic potential than pure amorphous or crystalline catalysts.^[35-36] For example, Song et al. uses a surface fluorination strategy to achieve partial amorphous in the catalyst and thus reduce OER reaction overpotential.^[37] Therefore, it is highly desirable to combine the advantages of both amorphous and crystalline in CuCo₂O₄.

Here, we report a strategy that promotes the occurrence of the partial amorphous phase of inexpensive spinel $CuCo_2O_4$ (CCO) by doping with small amount phosphorus and improve its OER catalytic activity. Experiments of phosphorus doping with different content were carried out with CCO. $CuCo_2O_4$ – $0.5(CCP_{0.5})$ exhibits excellent OER catalytic activity and longterm stability in 1.0 M KOH with an overpotential of 290 mV at a current density of 10 mA cm⁻², and its Tafel slope is as low as 68 mV dec⁻¹, which is better than the benchmark RuO₂ catalyst and many transition metal-based oxides for OER. Our work highlights that doping with non-metallic elements is an effective strategy to optimize the electronic configuration and surficial partial amorphization of inexpensive spinel transition metal oxide electrocatalysts to greatly enhance OER activity.

2. Results and Discussion

 CCP_{x} (x \approx 0–1.0) catalysts were successfully synthesized by the hydrothermal method followed by annealing as described in the experimental section. The SEM image of CCP_{0.5} in Figure 1a and Figure 1b indicating that the particles are the agglomeration of small nanoparticles, and with the sizes of about 1-1.9 µm. HRTEM was performed to investigate the microscopic crystal structure of CCP_{0.5}. Figure 1c confirms that the CCP_{0.5} micron-sphere composes of small nanoparticles. As shown in Figure 1d-e, both crystalline and amorphous phases exist in CCP_{0.5.} which can be ascribed to P doping hampering crystallization. It is considered that the synergistic effect between crystalline and amorphous phases promotes the rapid transport of electrons and improves the electrochemical catalytic activity of the catalyst.^[38] In the crystalline region of Figure 1d and 1e, the lattice fringe spacings of 0.25, 0.471 and 0.289 nm corresponds to the (311), (111), and (220) facet of the cubic phase spinel CCO, respectively.^[26,39-40] Furthermore, HAADF-STEM (Figure 1f) and EDX elemental mapping images (Fig-



Figure 1. a) and b) SEM, c) TEM, d) and e) HRTEM images of CCP_{0.5}; f) The HAADF-STEM image and g-j) corresponding EDX element mapping images of CCP_{0.5}, Cu-blue, Co-yellow, O-red, P-orange.

ure 1g-j) indicate that Cu, Co, O, and P are uniformly distributed, which confirming that P is doped into CCO lattice. Those results show that P doping into CCO inducing partial amorphization.

XRD was performed to study the structure of CCP_x. Figure 2a shows the XRD pattern of CCP_x ($x \approx 0-1.0$) which can be defined as the cubic phase CuCo₂O₄ (JCPDS 01–1155). As the phosphorus content increased, the position of the diffraction peak of CCP_x have no shifted (the enlarged spectra in Figure S2) and no diffraction peaks of other metal P oxide phases were observed, which indicates that no other phase can be observed. On the other hand, as the increase of phosphorus content, it could be observed that the intensity of the XRD peaks for CCP_x decreased and the grain size smaller (Supplementary Information Table S1), implying that the crystallinity of CCP_x decreased with the increase of P content. This can be attributed to the phenomenon of partial amorphization of the catalyst caused by phosphorus doping induced lattice distortion.

XPS was carried out to study the elemental composition and the chemical state of CCP_x . The XPS survey spectrum of



Figure 2. a) XRD patterns of CCO, CCP_{0.25}, CCO_{0.5}, CCP_{0.75}, and CCP.



Figure 3. XPS spectra of the $CCP_{0.5}$: (a) Cu 2p, (b) Co 2p, (c) P 2p and (d) O 1s electrons.

CCP_{0.5} (Supplementary Information Figure S3) shows that only Cu, Co, O, and P elements are present. In particular, P 2 s and 2p electrons are detected confirming the successful doping of P into the spinel CCO.^[41] The high-resolution XPS spectrum of Cu 2p electrons (Figure 3a) shows that the two main peaks at the binding energies of 934.6 eV and 954.4 eV can be classified to Cu $2p_{3/2}$ and $2p_{1/2}$ electrons of Cu^{2+[42]} and two satellite (named as "Sat.") peaks at 962.2 eV and 942.2 eV are also detected, respectively. The high-resolution XPS spectrum of Co 2p electrons (Figure 3b) can be deconvolved into two main peaks, which are assigned to Co $2p_{3/2}$ and $2p_{1/2}$ electrons, respectively. At 780.1 eV and 795.3 eV of the Co $2p_{3/2}$ and $2p_{1/2}$ electrons correspond to Co²⁺, while the binding energie located at 782.3 eV and 797.5 eV correspond to Co³⁺, respectively.^[43] There are two satellites peaks at 787.4 eV and 803.4 eV of Co. Additionally, the high-resolution XPS spectrum of P 2p electrons (Figure 3c) shows a wide peak at 133.3 eV, which can be ascribed to P-O bonds in the CCP_{0.5}.^[44] Figure 3d shows the high-resolution O 1s XPS spectrum, which is deconvolved into four peaks. In general, the peak (O1) at 529.3 eV is associated to the typical metal-oxygen (M–O–M) bond.^[45] The characteristic peak (O2) at 530.4 eV corresponds to oxygen or hydroxyl groups adsorbed on the surface.^[46] The characteristic peak (O3) at 531.6 eV can be assigned to the oxygen defect with low coordination,^[47] while the peak (O4) located at 532.9 eV is associated with surface physical adsorption and chemical adsorption of molecular water or carbonate.^[48] For CCO and CCP_{0.5}, the ratios of the four types of oxygen are calculated from the area of the fitted sub-peak, and the results are listed in Table. S3 (Supplementary Information). Interestingly, the ratio of oxygen/hydroxyl adsorbed on the surface and lattice oxygen remains approximately the same after P doping, while the proportion of oxygen defects with low coordination greatly increased. The doping of high valence states easily leads to the accumulation of defects and the formation of partially disordered structure in metal oxides, which are conducive to the formation of new active sites in the electrochemical process.^[44] Furthermore, the XPS atomic percentage (Supplementary Information Table. S4) indicates that the P content in CCP_{0.5} is approximate 16.75%, and that for the $CCP_{0.25}$, $CCP_{0.75}$, and CCPare approximate 12.75%, 19.34% and 21.08%, respectively. The result indicates that the P atoms have been successfully doped into CuCo₂O₄ lattice.

The electrocatalytic OER performance of CCP_x ($x \approx 0-1.0$) was measured in 1.0 M KOH with a three-electrodes system. As shown in Figure 4a, all CCP_x ($x \approx 0.25-1.0$) shows better catalytic performance than CCO, indicating that doping P atoms into CCO are beneficial to enhance the OER performance. The OER performance of CCP_x is closely related to the amount of P. As shown in Figure 4a and 4c, the overpotential of CCP_{0.5} catalyst is only 290 mA at a current density of 10 mA cm⁻², while that for CCO, CCP_{0.25}, CCP_{0.75}, and CCP are 423, 320, 310, and 345 mV, respectively. The catalytic activity of commercial RuO₂ was also evaluated and compared with CCP_{0.5}. RuO₂ requires an overpotential of 336 mV to achieve the same current density. Those results indicate that CCP_{0.5} shows a lower overpotential than the benchmark noble metal-based RuO₂ catalyst and many



Figure 4. a) LSV curves of CCP_x ($x \approx 0-1.0$) and that of RuO₂ in 1.0 M KOH solution at a scan rate of 5 mV s⁻¹; b) the corresponding Tafel slops of CCP_x ($x \approx 0-1.0$) and RuO₂; c) comparison of the overpotentials and Tafel slops of CCP_x ($x \approx 0-1.0$) and RuO₂; d) ElS curves of CCP_x ($x \approx 0-1.0$); e) ECSA of the CCP_x ($x \approx 0-1.0$) tested by the double-layer capacitances; f) the chronoamperometry measurement of CCP_{0.5} at 1.52 V for 19 h in 1.0 M KOH solution.

previously reported transition-metal oxides (as summarized in Table S5), indicating that the developed $CCP_{0.5}$ catalyst is promising for large-scale application.

In addition, Tafel slopes are estimated to obtain OER reaction kinetics information.^[49] As shown in Figure 4b, the Tafel slopes of CCP_{0.25}, CCP_{0.50}, CCP_{0.75}, and CCP catalysts are decreased to 79, 68, 71, and 94 mVdec⁻¹, respectively, in comparison to the pristine spinel CCO (136 mVdec⁻¹), indicating that P doping can boost OER kinetic rate. As is clearly shown in

Figure 4c, within a certain range, the OER reaction kinetics rate of the catalyst is positively correlated with the phosphorus content. It is considered that P doping into CCO can greatly affect the electronic structure of the pristine catalyst and induce the catalyst to produce a partial amorphous phase to provide more catalytically active sites. However, with the further increase of phosphorus concentration, the OER reaction kinetics is hindered, which indicating that CCP_{0.5} is the best result for the combination of the effect of the partial amorphous and the effect of the optimization of the electronic structures.Electrochemical impedance spectroscopy (EIS) was performed to evaluate the electrode reaction kinetics of the catalysts.^[13,50] As shown in Figure 4d, CCP, ($x \approx 0.25-1.0$) all show smaller chargetransfer resistance than pristine CCO. The electrochemical equivalent circuit is shown in Figure S4 (Supplementary Information). The charge-transfer resistance of CCO is 23.4 Ω_{r} while that for $CCP_{0.5}$ is 5.92 Ω , which indicates that a faster electron transfer process was conducted in CCO after P-doping. To determine the electrochemically active surface areas (ECSA) of the catalysts, the double-layer capacitance (C_{dl}) method was performed by measuring the current density of the non-Faraday region. Figure S5 (Supplementary Information) shows the corresponding cyclic voltammetry (CV) curves which are tested at various scanning rates (20 mVs⁻¹ to 120 mVs⁻¹). The C_{dl} of CCO, CCP $_{0.25}$, CCP $_{0.50}$, CCP $_{0.75}$, and CCP catalysts are 0.88, 7.16, 6.15, 5.36, and 7.52 mF cm⁻², respectively, (Figure 4e) indicating that P doped samples expose more active site for OER and therefore has better OER catalytic activity. Interestingly, the ECSA of CCP_{0.5}, which has the best OER catalytic activity, is slightly lower than CCP_{0.25} and CCP. This further proves that the OER activity of the CCP_x is not just determined by the active surface area. To exclude the contribution of the increased ECSA, the LSV curves of CuCo₂O₄–P_x ($x \approx 0.0-1.0$) was normalized by ECSA. As shown in the Figure S6 (Supplementary Information), $CuCo_2O_4-P_{0.5}$ (CCP_{0.5}) showed lower potential than $CuCo_2O_4$ (CCO) at the same current density, indicating that moderately phosphorus-doped CuCo₂O₄ had higher intrinsic activity than the pristine CuCo₂O₄.^[51]

The OER stability of an electrocatalyst is another critical parameter for practical application. The electrochemical stability of the CCP_{0.5} and CCO catalyst is evaluated by chronopotentiometry measurement. As shown in Figure S7 (Supplementary Information) and Figure 4f, the current density of CCO decreased by 25% after 9 h under constant voltage while the CCP_{0.5} has no obvious decrease in OER current density after 19 h test, which indicates that the $CCP_{0.5}$ catalyst is robust for long-term catalyze OER. Furthermore, phosphorus doping is beneficial to improve the stability of CCO. In order to explore the relationship between the stability and structure of the catalyst, the SEM test was carried out for the catalyst after 5,000 cycles working. As shown in Figure S9 (Supplementary Information), it can be seen that the nanoparticles piled on the particle surface have no other obvious changes. It shows that the oxygen evolution reaction has little effect on the microscopic morphology of CCP_{0.5}. So, the catalyst has good structural stability.

3. Conclusions

In summary, phosphorus-doped $CuCo_2O_4$ with a partial amorphous phase have been successfully prepared as a highly efficient and stable OER catalyst. It was found that $CCP_{0.5}$ exhibited advanced catalytic activity with an overpotential of 290 mV at a current density of 10 mA cm⁻² and a Tafel slope of 68 mV dec⁻¹, which is much better than the benchmark OER

catalyst RuO₂. The improved catalytic activity of CCP_x(x \approx 0.25–1.0) compared to CCO can be attributed to the phosphorus doping and the partial amorphous phase characteristics of the catalyst, improve the electronic conductivity of CuCo₂O₄ and generates abundant active sites. This effective strategy of phosphorus-doped spinel inducing partial amorphous phase production to enhance CCO electrocatalytic OER activity is also expected to be used in the design of other catalysts in the future.

Experimental Section

Chemicals and materials

Cobalt(II) nitrate hexahydrate (98.5%, Sinopharm), copper(II) nitrate trihydrate (99%, Sinopharm), urea (99%, Sinopharm), phosphoric acid (85%, Sinopharm), ketjen black (EC-300 J, Lion Corporation), isopropanol(99.7%, Sinopharm), ethanol absolute (99.7%, Sinopharm), ruthenium(IV) oxide (99.9%, Mackin), potassium hydroxide (95%, Aladdin), Nafion solution (5%, Dupont), and deionized water (18.2 M Ω cm⁻¹) were used as received.

Synthesis of phosphorus-doped CuCo₂O₄

CuCo₂O₄ samples were named after the amount of phosphorus added in the experiment. CuCo₂O₄ samples with the phosphorus added amount of 0 mmol, 0.25 mmol, 0.5 mmol, 0.75 mmol, and 1 mmol were named as CCO, CCP_{0.25}, CCP_{0.5}, CCP_{0.75}, and CCP. In the first step, cobalt(II) nitrate hexahydrate(Co(NO₃)₂·6H₂O) and copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) were dispersed in isopropanol solution at a molar ratio of 2: 1. Then 30 mmol urea was added and sonicated for 2 h to form a homogeneous solution. Next, certain amounts of the phosphoric solution were added to the former solution. The solution was transferred to 100 ml Teflon-lined autoclave and heated at 120 °C for 16 h. The resulted materials were washed several times with ethanol and deionized water by centrifugation and dried at 60 °C to obtain the precursors. Finally, the precursors were annealed at 500 °C for 6 h in the air to obtain the catalysts.

Material characterizations

X-ray powder diffractometer (XRD) was tested on Miniflex 600 using Cu–K_α radiation with a scanning speed of 4° per minute. Scanning electron microscopy (SEM) images were recorded on JSM6700 (JEOL). Transmission electron microscope (TEM) and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were performed on an FEI field-emission microscope (FEI Tecnai G2 F30) operated at 200 kV. X-ray photo-electron spectroscopy (XPS) was performed on an ESCALAB 250Xi using monochromatized Al K_α radiation (15 kV, 10 mA). The binding energy of the collected spectrum was calibrated with reference to the C 1s binding energy (284.8 eV).

Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (Autolab, PGSTAT302 N) with a three electrodes system. Graphite rod and Hg/HgO (1 M KOH, aqueous, MMO) was used as the counter and reference electrodes, respectively. 10 mg of catalyst and 2 mg of Ketjen Black added into the solution of 390 μ L of ethanol, 1560 μ L of deionized water, and 50 μ L of 5% Nafion solution to form ink solution after sonication for 40 min. 10 μ L of the prepared ink was drop-casted on a glassy carbon electrode and dried at room temperature to form the working electrode (the loading of the catalyst was 255 μ g cm⁻²).

The O₂-saturated 1.0 M KOH solution was used as an electrolyte. During the test, magnetic stirring (600 $rmin^{-1}$) was used to remove the formed O₂ bubbles on the working electrode. Before the test, the cyclic voltammetry (CV) activation was performed from 1.1 to 1.7 V vs. hydrogen electrode (RHE) at a scanning rate of 50 mVs⁻¹ until the material reached a stable state. All potentials were converted to a RHE scale through the following equation: E(vs. RHE) = E(vs. Hg/HgO) + 0.098 + 0.059 × pH. Linear sweep voltammetry (LSV) was tested at a scan rate of 5 mV s⁻¹ and without internal resistance (iR) compensation. The Tafel slopes of the catalysts were obtained to study the electrocatalytic kinetics of the OER through the equation $\eta = a + b \log j$. In which j, a, b, and η represented the current density, fitting parameter, Tafel slope, and overpotential respectively. The electrochemical double-layer capacitance (C_{dl}) can be obtained by measuring the current density at different scan rates (20, 40, 60, 80, 100, 120 mV s⁻¹) on the non-Faraday region by cyclic voltammetry. The ECSA normalized current density calculation formula of CuCo₂O₄– P_x (x \approx 0.0–1.0) catalyst is as follows: ECSA normalized current density = current × Cs/C_{dl}. Cs is the specific capacitance. Based on the Cs value of OER catalyst in alkaline solution reported previously, 0.040 mF cm⁻² was used as the Cs value in this study.^[52] Electrochemical impedance spectroscopy (EIS) was recorded at 1.52 V (versus RHE) with an amplitude of 10 mV and the frequency from 10^6 to 10^{-2} Hz. Chronopotentiometry measurement was used to evaluate the stability of the catalysts at 1.52 V (versus RHE).

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] N. T. Suen, S. F. Hung, Q. Quan, N. Zhang, Y. J. Xu, H. M. Chen, Chem. Soc. Rev. 2017, 46, 337.
- [2] W. Tong, M. Forster, F. Dionigi, S. Dresp, R. Sadeghi Erami, P. Strasser, A. J. Cowan, P. Farràs, *Nat. Energy.* 2020, *5*, 367.
- [3] J. Zhu, L. Hu, P. Zhao, L. Y. S. Lee, K. Y. Wong, Chem. Rev. 2020, 120, 851.
- [4] Y. Chen, H. Li, J. Wang, Y. Du, S. Xi, Y. Sun, M. Sherburne, J. W. Ager, 3rd, A. C. Fisher, Z. J. Xu, Nat. Commun. 2019, 10, 572.
- [5] X. Zhang, H. Xu, X. Li, Y. Li, T. Yang, Y. Liang, ACS Catal. 2015, 6, 580.
- [6] R. Beltrán-Suito, P. W. Menezes, M. Driess, J. Mater. Chem. A 2019, 7, 15749.
- [7] A. Sivanantham, P. Ganesan, S. Shanmugam, Adv. Funct. Mater. 2016, 26, 4661.

- [8] S. Sultan, M. Ha, D. Y. Kim, J. N. Tiwari, C. W. Myung, A. Meena, T. J. Shin, K. H. Chae, K. S. Kim, *Nat. Commun.* **2019**, *10*, 5195.
- [9] Y. Tan, M. Luo, P. Liu, C. Cheng, J. Han, K. Watanabe, M. Chen, ACS Appl. Mater. Interfaces. 2019, 11, 3880.
- [10] L. Li, L. Song, H. Xue, C. Jiang, B. Gao, H. Gong, W. Xia, X. Fan, H. Guo, T. Wang, J. He, *Carbon* 2019, 150, 446.
- [11] Y. Wang, C. Xie, Z. Zhang, D. Liu, R. Chen, S. Wang, *Adv. Funct. Mater.* **2018**, *28*.
- [12] M. Chauhan, S. Deka, ACS Applied Energy Materials 2019, 3, 977.
- [13] S. Pan, X. Mao, J. Yu, L. Hao, A. Du, B. Li, Inorg. Chem. Front. 2020, 7, 3327.
- [14] Z. Zhang, J. Zhang, T. Wang, Z. Li, G. Yang, H. Bian, J. Li, D. Gao, RSC Adv. 2018, 8, 5338.
- [15] F. Urbain, R. Du, P. Tang, V. Smirnov, T. Andreu, F. Finger, N. Jimenez Divins, J. Llorca, J. Arbiol, A. Cabot, J. R. Morante, *Appl. Catal. B* 2019, 259.
- [16] Y. Xu, W. Bian, J. Wu, J.-H. Tian, R. Yang, *Electrochim. Acta.* 2015, 151, 276.
- [17] A. T. Aqueel Ahmed, B. Hou, H. S. Chavan, Y. Jo, S. Cho, J. Kim, S. M. Pawar, S. Cha, A. I. Inamdar, H. Kim, H. Im, *Small* **2018**, *14*, e1800742.
- [18] Y. Gong, J. Wang, Y. Lin, Z. Yang, H. Pan, Z. Xu, Appl. Surf. Sci. 2019, 476, 600.
- [19] W. Bian, Z. Yang, P. Strasser, R. Yang, J. Power Sources. 2014, 250, 196.
- [20] H. Fang, T. Huang, D. Liang, M. Qiu, Y. Sun, S. Yao, J. Yu, M. M. Dinesh, Z. Guo, Y. Xia, S. Mao, J. Mater. Chem. A 2019, 7, 7328.
- [21] X. Ji, X. Ren, S. Hao, F. Xie, F. Qu, G. Du, A. M. Asiri, X. Sun, Inorg. Chem. Front. 2017, 4, 1546.
- [22] A. Rebekah, E. Ashok Kumar, C. Viswanathan, N. Ponpandian, Int. J. Hydrogen Energy. 2020, 45, 6391.
- [23] T. Wu, S. Sun, J. Song, S. Xi, Y. Du, B. Chen, W. A. Sasangka, H. Liao, C. L. Gan, G. G. Scherer, L. Zeng, H. Wang, H. Li, A. Grimaud, Z. J. Xu, *Nat. Can.* 2019, *2*, 763.
- [24] Y. Gong, Z. Yang, Y. Lin, J. Wang, H. Pan, Z. Xu, J. Mater. Chem. A 2018, 6, 16950.
- [25] Y. Wang, H. Ji, W. Liu, T. Xue, C. Liu, Y. Zhang, L. Liu, Q. Wang, F. Qi, B. Xu, D. C. W. Tsang, W. Chu, ACS Appl. Mater. Interfaces 2020, 12, 20522.
- [26] R. Ning, J. Tian, A. M. Asiri, A. H. Qusti, A. O. Al-Youbi, X. Sun, *Langmuir* 2013, 29, 13146.
- [27] A. A. Yadav, Y. M. Hunge, S. B. Kulkarni, C. Terashima, S. W. Kang, J. Colloid Interface Sci. 2020, 576, 476.
- [28] Y. Zhou, S. Sun, C. Wei, Y. Sun, P. Xi, Z. Feng, Z. J. Xu, Adv. Mater. 2019, 31, e1902509.
- [29] Y. Gong, H. Pan, Z. Xu, Z. Yang, Y. Lin, M. Zhang, Int. J. Hydrogen Energy. 2018, 43, 14360.
- [30] C. Guo, X. Sun, X. Kuang, L. Gao, M. Zhao, L. Qu, Y. Zhang, D. Wu, X. Ren, Q. Wei, J. Mater. Chem. A 2019, 7, 1005.
- [31] H. Ren, X. Sun, C. Du, J. Zhao, D. Liu, W. Fang, S. Kumar, R. Chua, S. Meng, P. Kidkhunthod, L. Song, S. Li, S. Madhavi, Q. Yan, ACS Nano 2019, 13, 12969.
- [32] M. Li, L. Tao, X. Xiao, X. Jiang, M. Wang, Y. Shen, ACS Sustainable Chem. Eng. 2019, 7, 4784.
- [33] M. Ju, X. Wang, X. Long, S. Yang, CrystEngComm 2020, 22, 1531.
- [34] J. Han, J. Zhang, T. Wang, Q. Xiong, W. Wang, L. Cao, B. Dong, ACS Sustainable Chem. Eng. 2019, 7, 13105.
- [35] M. Kuang, J. Zhang, D. Liu, H. Tan, K. N. Dinh, L. Yang, H. Ren, W. Huang, W. Fang, J. Yao, X. Hao, J. Xu, C. Liu, L. Song, B. Liu, Q. Yan, *Adv. Energy Mater.* 2020, 202002215.
- [36] Q. Kong, W. Feng, Q. Zhang, P. Zhang, Y. Sun, Y. Yin, Q. Wang, C. Sun, *ChemCatChem* 2019, 11, 3004.
- [37] H. Han, H. Choi, S. Mhin, Y.-R. Hong, K. M. Kim, J. Kwon, G. Ali, K. Y. Chung, M. Je, H. N. Umh, D.-H. Lim, K. Davey, S.-Z. Qiao, U. Paik, T. Song, *Energy Environ. Sci.* 2019, *12*, 2443.
- [38] M. Jiang, J. Li, J. Li, Y. Zhao, L. Pan, Q. Cao, D. Wang, Y. Du, Nanoscale 2019, 11, 9654.
- [39] D. Prasad, K. N. Patil, J. T. Bhanushali, B. M. Nagaraja, A. H. Jadhav, *Catal. Sci. Technol.* **2019**, 9, 4393.
- [40] S. Liu, K. S. Hui, K. N. Hui, ACS Appl. Mater. Interfaces 2016, 8, 3258.
- [41] S. V. Mohite, R. Xing, B. Li, S. S. Latthe, Y. Zhao, X. Li, L. Mao, S. Liu, Inorg. Chem. 2020, 59, 1996.
- [42] H. Xie, S. Chen, F. Ma, J. Liang, Z. Miao, T. Wang, H. L. Wang, Y. Huang, Q. Li, ACS Appl. Mater. Interfaces 2018, 10, 36996.
- [43] W. Yan, Z. Yang, W. Bian, R. Yang, Carbon 2015, 92, 74.
- [44] Z. Li, L. Lv, J. Wang, X. Ao, Y. Ruan, D. Zha, G. Hong, Q. Wu, Y. Lan, C. Wang, J. Jiang, M. Liu, *Nano Energy* 2018, 47, 199.

- [45] W. Yan, W. Bian, C. Jin, J.-H. Tian, R. Yang, *Electrochim. Acta.* 2015, *177*, 65.
- [46] Z. Zou, T. Wang, X. Zhao, W.-J. Jiang, H. Pan, D. Gao, C. Xu, ACS Catal. 2019, 9, 7356.
- [47] Y. S. Park, M. J. Jang, J. Jeong, S. M. Park, X. Wang, M. H. Seo, S. M. Choi, J. Yang, ACS Sustainable Chem. Eng. 2020, 8, 2344.
- [48] Y. Yang, L. Dang, M. J. Shearer, H. Sheng, W. Li, J. Chen, P. Xiao, Y. Zhang, R. J. Hamers, S. Jin, Adv. Energy Mater. 2018, 8.
- [49] S. Zhao, J. Berry-Gair, W. Li, G. Guan, M. Yang, J. Li, F. Lai, F. Cora, K. Holt, D. J. L. Brett, G. He, I. P. Parkin, *Adv. Sci.* 2020, *7*, 1903674.
- [50] L. Yang, J. Han, J. Zhang, Y. Li, W. Wang, L. Cao, B. Dong, *ChemElectroChem* **2020**, *7*, 3991.
- [51] S. Niu, W. J. Jiang, T. Tang, L. P. Yuan, H. Luo, J. S. Hu, Adv. Funct. Mater. 2019, 29.
- [52] C. C. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc. 2013, 135, 16977.

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Phosphorous doping: CuCo₂O₄ has been successfully prepared and its OER performance has been further optimized by doping with different amounts of phosphorus. The optimized samples showed significant improvement in OER activity in 1 M KOH and had good stability. The non-metallic P-doping strategy improves the conductivity of the catalyst and introduces partial amorphous phase. The synergistic effect between the crystalline phase and the amorphous phase can provide more catalytic active sites, thus significantly reducing the OER overpotential of the catalyst.



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Phosphorus-Doped CuCo₂O₄ Oxide with Partial Amorphous Phase as a Robust Electrocatalyst for the Oxygen Evolution Reaction