Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Ni_2P hollow microspheres for electrocatalytic oxygen evolution and reduction reactions

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General methods and materials. All chemical reagents, including nickel nitrate hexahydrate $Ni(NO_3)_2•6H_2O$, sodium hypophosphite monohydrate $NaH_2PO_2•H_2O$, ethanol, isopropyl alcohol, cyclohexane, oleylamine, potassium hydroxide KOH, Nafion, and carbon black were purchased from commercial suppliers and were used as received without further purification. Milli-Q water of 18 MΩ cm was used in all experiments. SEM images were obtained on a Hitachi SU8020 cold-emission field emission scanning electron microscope (FE-SEM) with an accelerating voltage of 5 kV. The morphology was also examined by TEM (FEI, Tecnai G2 F20). The EDX spectra of the catalyst loaded on carbon cloth were obtained by a FEI Quanta 200. XPS was measured on a Kratos AXIS ULTRA using monochromatic Al Kα X-ray (hν = 1486.6 eV) with photoelectron take-off angle of 90° with respect to surface plane. The C 1s peak at 284.8 eV from the adventitious carbon was used for binding energy calibration. The Ni/P atomic ratio was detected by aurora M90 of Bruker. Bruker D8 ADVANCE (Cu Kα radiation) in the grazing incidence measurement mode was used to record XRD patterns of the catalyst. The Brunauer-Emmett-Teller (BET) surface area was measured on an ASAP 2020 of Micromeritics instrument corp, using the multipoint BET method and the following equation. All samples used were prepared through centrifugation and re-dispersion.

$$\frac{1}{v[(p_0/p)-1]}=\frac{c-1}{\upsilon_m c}\left(\frac{p}{p_0}\right)+\frac{1}{\upsilon_m c}$$

Sythesis of Ni_2P microspheres. The Ni_2P hollow microsphere was synthesized *via* a facile two-step strategy, including hydrothermal synthesis of $Ni(OH)_2$ followed by phosphorization with NaH_2PO_2 under argon. First, $Ni(NO_3)_2 \bullet 6H_2O$ (0.436 g, 1.50 mmol) was dissolved in 30 mL of ethanol, and then 3 mL of oleylamine and 15 mL of ethanol were quickly added with strong stirring. After half an hour, the resulted homogeneous solution was transferred into a 100-mL Teflon-lined autoclave and was heated to 180 °C for 12 h. After cooling to room temperature, the formed $Ni(OH)_2$ precipitates were collected and rinsed with cyclohexane, distilled water, and ethanol, and was then dried under vacuum at 60 °C for 6 h. Next, $Ni(OH)_2$ and NaH_2PO_2 (with a molar ratio of 1:3) were put at two separate positions in a porcelain boat with NaH_2PO_2 at the upstream side of the furnace. The sample was heated at 300 °C for 60 min under argon, and then was naturally cooled to ambient temperature under argon.

Electrochemical studies. All electrochemical experiments were performed using a CH Instruments (Model CHI660D Electrochemical Analyzer) at 23 °C. Carbon cloth with or without catalysts was used as the working electrode, Ag/AgCl (KCl saturated) was used as the reference electrode, and a Pt wire was used as the counter electrode. All electrochemical measurements were performed in 1.0 M KOH for OER and 0.1 M KOH for ORR. All LSV measurements were conducted with *i*R compensation. For experiments conducted with or without O_2, the solutions were saturated by bubbling high-purity O_2 or N_2 for at least 30 min before analysis. For rotating ring-disk electrode measurements, a bipotentiostat (Model CHI 832 Electrochemical Analyzer) and a rotating ring-disk electrode with a rotating glassy carbon (GC) disk electrode and a platinum ring electrode (ALS RRDE-2) were used. The collection efficiency of the ring-disk electrode was evaluated with the $[Fe(CN)_6]^{3-/4-}$ redox couple and was calculated to be 0.47. All potentials reported in this work were referenced to RHE unless otherwise stated.

The preparation method of the working electrodes is as follows. For OER, 5 mg of catalyst powder was dispersed in 1.0 mL of 3:1 v/v water/isopropyl alcohol mixed solvent with 45 μL of Nafion solution (5 wt %, Sigma-Aldrich). The mixture was then ultrasonicated for about 0.5 h to generate a homogeneous ink. Next, 10 μL of the dispersion was transferred onto the carbon cloth electrode (0.25 cm^2), leading to a catalyst loading of 0.20 mg/cm^2. Finally, the as-prepared catalyst film was dried at room temperature. For comparison, a bare carbon cloth electrode was also dried for electrochemical measurement. Electrochemical impedance spectroscopy (EIS) was recorded on an indium tin oxide (ITO, 0.25 cm^2) electrode over a frequency range from 0.01 Hz to 0.1 MHz at the amplitude of the sinusoidal voltage of 5 mV under 0.6 V (vs Ag/AgCl) in a 1.0 M KOH solution. For EIS and electrochemically active surface area (ECSA), the catalysts were loaded on ITO (0.2 mg cm^{-2}) electrodes without Nafion. The ECSA values can be calculated using the equations below:

$$i_c = \nu C_{dl} \qquad (1)$$

$$\mathrm{ECSA} = C_{dl}/C_s \qquad (2)$$

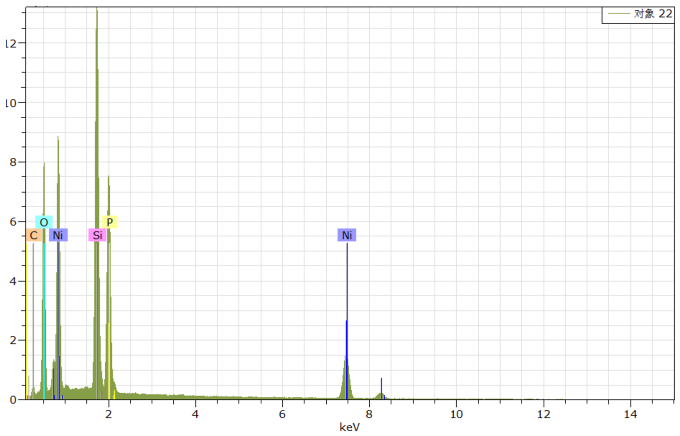
where i_c is the charging current, ν is the scan rate, and C_s is the specific capacitance (27 μF cm^{-2}, Ref *J. Am. Chem. Soc.* **2013**, *135*, 16977-16987).

For ORR, 1.0 mg of catalyst powder and 1.0 mg of carbon black was dispersed in 1.0 mL of 3:1 v/v water/isopropyl alcohol mixed solvent with 45 μL of Nafion solution (5 wt %, Sigma-Aldrich). The mixture was then ultrasonicated for about 0.5 h to generate a homogeneous ink. Next, 5 μL of the dispersion was transferred onto the RDE electrode (0.125 cm^2), leading to a catalyst loading of 0.04 mg/cm^2. Finally, the as-prepared catalyst film was dried at room temperature.

We used rotating-disk electrode (RDE) measurements to explore the ORR kinetics of the Ni_2P/C hybrid in 0.1 M KOH, and the n value can be calculated using the Koutecky-Levich (K-L) analysis：

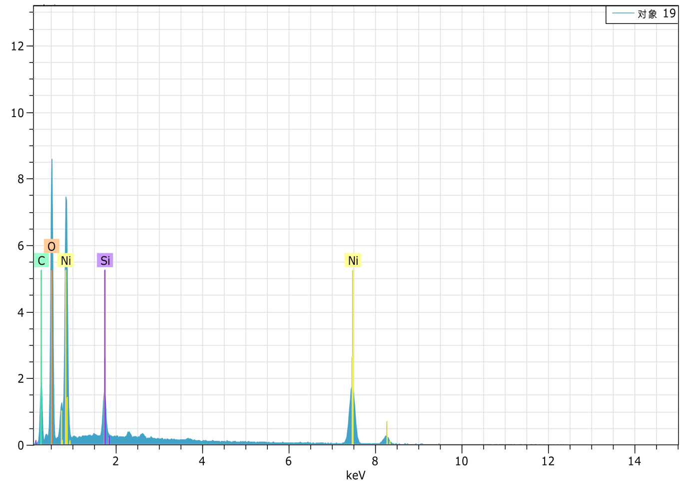
$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{j_d}=-\frac{1}{nFkC_{O_2}}-\frac{1}{0.2nFD_{O_2}^{2/3}v^{-1/6}C_{O_2}\omega^{1/2}}$$

where j is the measured current density, j_k and j_d are the kinetic and diffusion-limited current densities, respectively, k is the rate constant for ORR, F is the Faraday constant (96485 C mol^{-1}), n is the number of electrons transferred per molecule of O_2, ω (rpm) is the rotation rate, C_{O_2} is the concentration of O_2 in the bulk solution, D_{O_2} is the diffusion coefficient of O_2, and v is the kinematic viscosity of the solution. The constant 0.2 is adopted when the rotation speed is expressed in rpm.



Element	*Wt%*	*At%*
CK	2.71	6.76
OK	20.45	26.88
SiK	7.59	8.10
NiK	52.65	38.30
PK	20.63	19.96

Figure S1. EDX of Ni_2P. The atom ratio of Ni and P is 38.30:19.96.



Element	***Wt%***	***At%***
CK	15.21	29.67
OK	33.11	48.49
SiK	2.77	2.31
NiK	48.91	19.53

Figure S2. EDX of $Ni(OH)_2$. The atom ratio of Ni and O is 19.53:48.49.

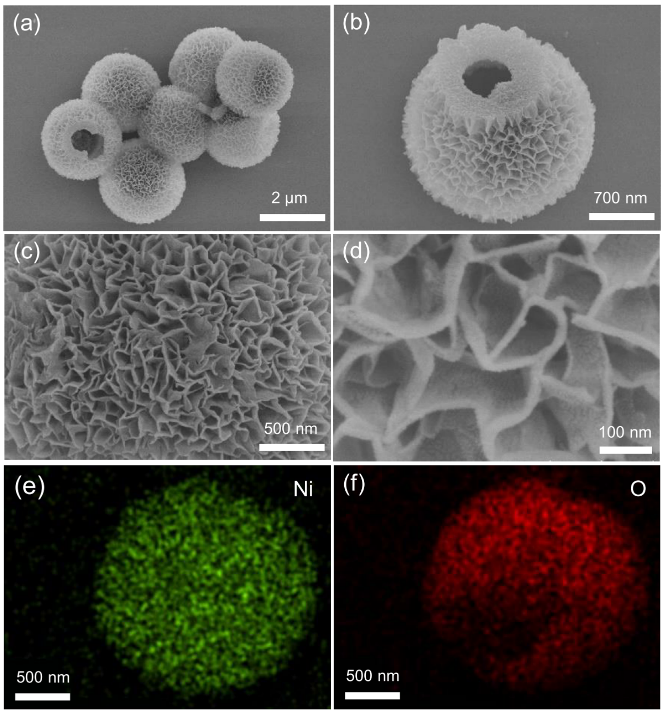


Figure S3. (a-d) SEM and (e, f) elemental mapping images of $Ni(OH)_2$.

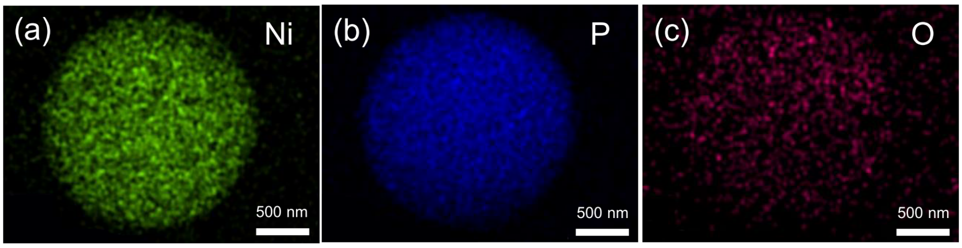


Figure S4. (a-c) elemental mapping images of Ni_2P.

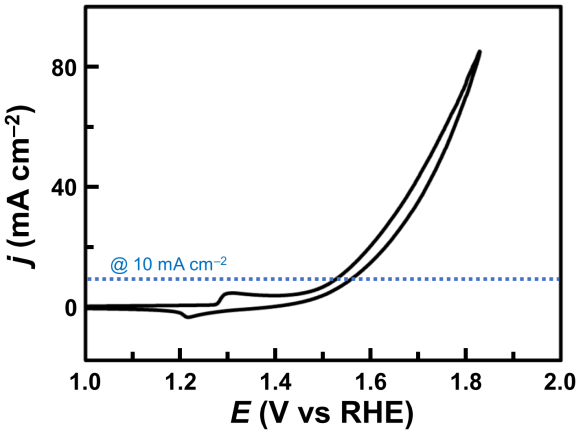


Figure S5. CV of Ni_2P coated on carbon cloth electrode in 1.0 M KOH. Scan rate is 5 mV s^{-1}.

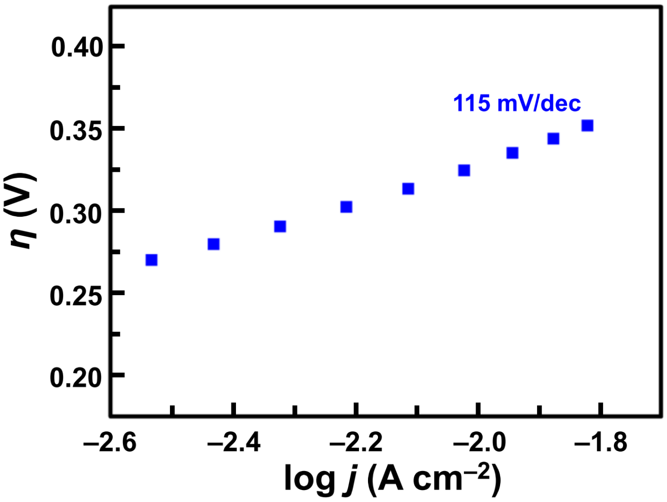


Figure S6. Tafel plot of Ni_2P.

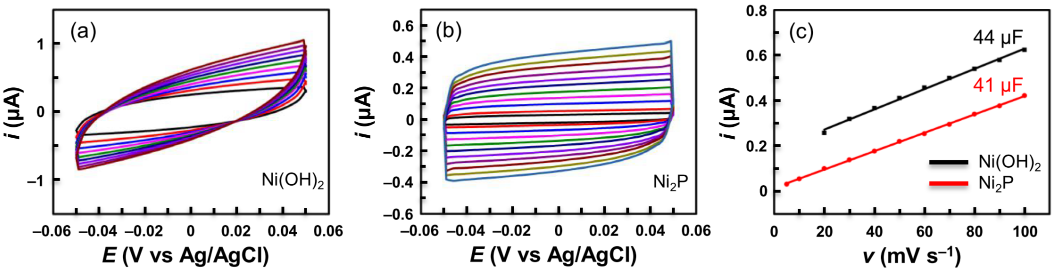


Figure S7. Charging currents of (a) $Ni(OH)_2$ and (b) Ni_2P recorded in the non-Faradaic potential region at different scan rates. (c) Cathodic charging currents of $Ni(OH)_2$ and Ni_2P at 0 V vs Ag/AgCl plotted against scan rates.

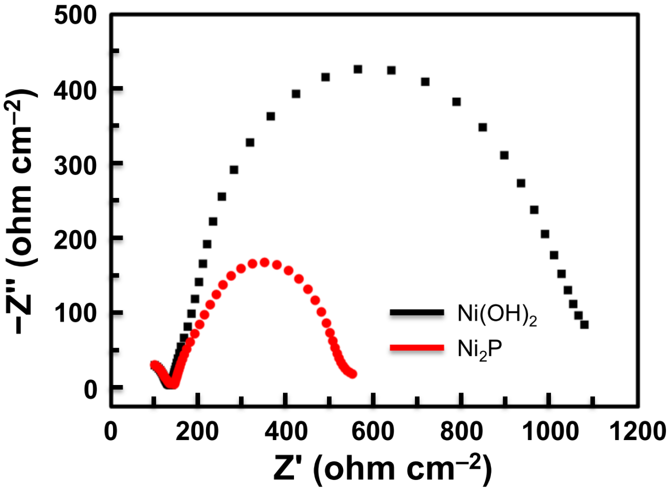


Figure S8. EIS Nyquist plots of Ni_2P and $Ni(OH)_2$.

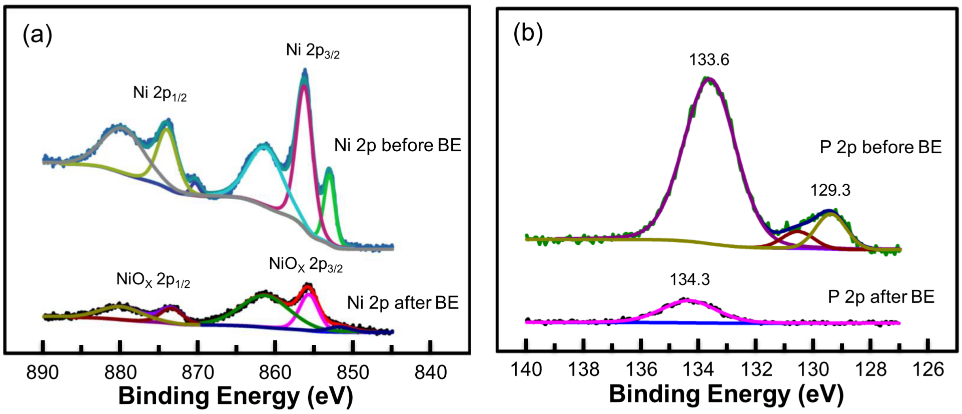


Figure S9. (a) XPS spectra of Ni 2p before (top) and after (bottom) bulk electrolysis. (b) XPS spectra of P 2p before (top) and after (bottom) 10-h bulk electrolysis.

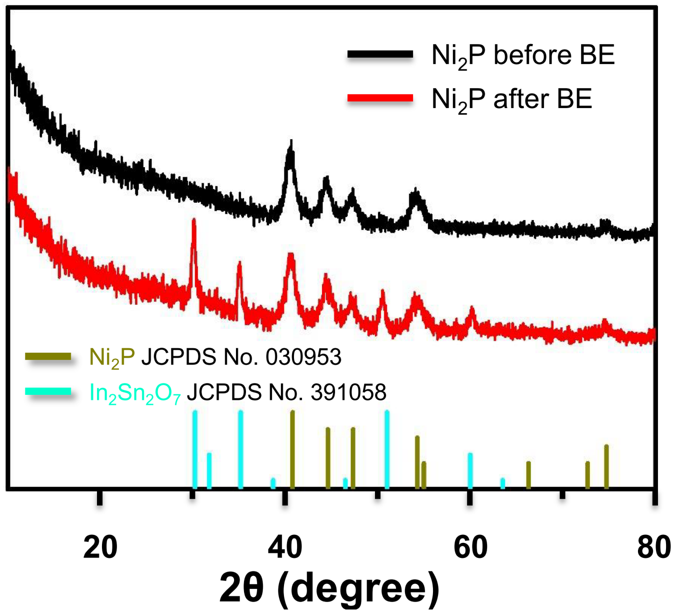


Figure S10. The grazing-incidence XRD patterns of the catalyst loaded on an ITO electrode before and after electrolysis, confirming the presence of Ni_2P in the catalyst bulk phase after electrolysis. In order to use the grazing-incidence XRD, the catalyst was loaded directly onto an ITO electrode without Nafion. As a result, some catalysts have exfoliated from the electrode, leading to the detection of $In_2Sn_2O_7$ signals from ITO.

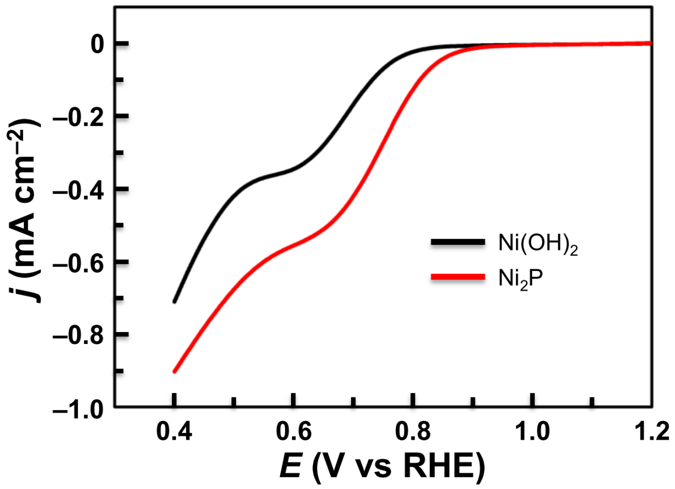


Figure S11. LSV of O_2 reduction at GC disk electrode coated with Ni(OH)$_2$ or Ni$_2$P in an O_2-saturated 0.1 M KOH solution at 1600 rpm.

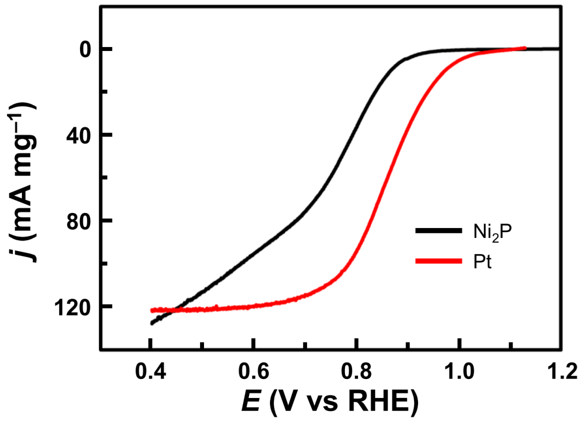


Figure S12. LSV of ORR at catalyst-coated GC disk electrodes in O_2-saturated 0.1 M KOH solution at 1600 rpm. The currents of carbon black supports are subtracted from those of the Ni_2P/C and Pt/C materials for direct comparison.

Table S1. Comparison of OER non-noble-metal phosphide electrocatalysts.

Catalyst	η (at 10 mA/cm^2)	Loading	Electrolytes	Ref.
Ni_2P	280 mV [a]	0.20 mg/cm^2	1 M KOH	***This work***
$Ni(OH)_2$	390 mV [a]	0.20 mg/cm^2	1 M KOH	***This work***
CoP/C	340 mV [a]	0.71 mg/cm^2	1 M KOH	*ACS Catal*. **2015**, *5*, 6874
Ni_2P/FTO	400 mV [b]	0.10 mg/cm^2	1 M KOH	*Chem. Commun*. **2015**, *51,* 11626
FeP@Au	320 mV [a]	0.20 mg/cm^2	1 M KOH	*J. Mater. Chem. A* **2016**, *4,* 9750
NiCoP/rGO	270 mV [a]	0.15 mg/cm^2	1 M KOH	*Adv. Funct. Mater*. **2016**, *26* , 6785
CoFeP	370 mV [a]	0.57 mg/cm^2	0.1 M KOH	*Angew. Chem. Int. Ed*. **2015**, *54,* 9642
CoP/C	360 mV [a]	0.40 mg/cm^2	0.1 M KOH	*ACS Catal*. **2015**, *5,* 4066
CoP	400 mV [a]	0.10 mg/cm^2	1 M KOH	*ACS Appl. Mater. Interfaces* **2016**, *8*, 2158
CoMnP	330 mV [a]	0.28 mg/cm^2	1 M KOH	*J. Am. Chem. Soc*. **2016**, *138*, 4006
$Fe_{1.1}Mn_{0.9}P$	350 mV [a]	0.28 mg/cm^2	1 M KOH	*Chem. Mater*. **2017**, *29*, 3048
Ni_2P nanoparticles	290 mV [a]	0.14 mg/cm^2	1 M KOH	*Energy Environ. Sci*. **2015**, *8*, 2347
Ni-P	300 mV [a]	0.20 mg/cm^2	1 M KOH	*Energy Environ. Sci*. **2016**, *9*, 1246
Ni_2P@C/G	285 mV [a]	0.25 mg/cm^2	1 M KOH	*Chem. Commun*. **2017**, *53*, 8372
Ni_2P/C	270 mV [a]	2.0 mg/cm^2	1 M KOH	*Chem. Mater*. **2017**, *29*, 8539
C@Ni_8P_3/NF	267 mV [a]	1.9 mg/cm^2	1 M KOH	*ACS Appl. Mater. Interfaces* **2016**, *8*, 27850
$Ni_{12}P_5$/FTO	280 mV [b]	1.0 mg/cm^2	1 M KOH	*ACS Catal*. **2017**, *7,* 103
CoP@RGO	280 mV [a]	0.28 mg/cm^2	1 M KOH	*J. Am. Chem. Soc*. **2016**, *138*, 14686
Co-P films	345 mV [a]	1.0 mg/cm^2	1 M KOH	*Angew. Chem. Int. Ed*. **2015**, *54*, 6251
$NiPS_3$@NiOOH	350 mV [a]	0.38 mg/cm^2	1 M KOH	*ACS Catal*. **2017**, *7*, 229

[a] LSV; [b] CV, the oxidation branch.

Table S2. Comparison of ORR non-noble-metal phosphide electrocatalysts.

Catalyst	Half-potential	Loading	Electrolytes	Ref.
Ni_2P/C	0.81 V	0.04 mg/cm^2	0.1 M KOH	***This work***
Ni_2P	0.77 V	0.04 mg/cm^2	0.1 M KOH	***This work***
CoP/C	0.70 V	0.28 mg/cm^2	0.1 M KOH	*Nano Lett.* 2015, *15*, 7616
Co_2P/C	0.76 V	0.07 mg/cm^2	0.1 M KOH	*ACS Nano*. 2015, *9*, 8108
Co_2P@CoNPG	0.81 V	2 mg/cm^2	0.1 M KOH	*Electrochim. Acta.* 2017, *231*, 344
NP-PC-0.5	0.75 V	0.2 mg/cm^2	0.1 M KOH	*Electrochim. Acta.* 2017, *248*, 11
Co_xP-CNTs-1000	0.76 V	-	0.1 M KOH	*Chem. Commun.* 2015, *51*, 7891
BNC/Co_2P-2	0.80 V	0.2 mg/cm^2	0.1 M KOH	*Chem. Commun.* 2015, *51*, 15015