Supporting information

Ultrasmall $Co_2P_2O_7$ Nanocrystals anchored on Nitrogen-doped Graphene as Efficient Electrocatalysts for Oxygen Reduction Reaction

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Table S1. ORR electrocatalytic properties of the catalysts measured in this work.

Catalysts	Onset potential (V vs.RHE)	Half wave potential (V vs.RHE)	Cathodic Peak potential (V vs. RHE)
$Co_2P_2O_7$/N-rGO-600	0.890	0.742	0.800
$Co_2P_2O_7$/N-rGO-700	0.916	0.770	0.816
$Co_2P_2O_7$/N-rGO-800	0.934	0.766	0.823
$Co_2P_2O_7$/N-rGO-900	0.878	0.747	0.805
Pt/C	0.974	0.772	0.833

$Co_2P_2O_7$/rGO	0.897	0.690	0.785
N-rGO	0.825	0.581	0.699
$Co_2P_2O_7$	0.796	0.398	0.520
rGO	0.648	0.428	0.551

Table S2. Comparison of ORR performance for the Co-based electrocatalysts reported-recently with our $Co_2P_2O_7$/N-RGO-800 catalyst.

Catalysts	Electrolyte	Cathodic peak potential (V vs. RHE)	Onset potential (V vs. RHE)	Tafel slope (mV/dec)	Loading mass (mg cm^{-2})	Reference
$Co_2P_2O_7$/N-RGO-800	**0.1M KOH**	**0.823**	**0.934**	**66.1**	**0.2**	**This work**
Co_2P@CoNPG	0.1M KOH	0.82	0.90	69	2.0	*Electrochim. Acta* 2017, **231**, 344.
CoO@N/S-CNF	0.1M KOH	0.74	0.84	/	0.08	*Carbon* 2016, **106**, 84.
CoNP@NC/NG	0.1M KOH	0.78	0.93	56	0.08	*J. Mater. Chem. A* 2016, **4**, 10575.
CoP NCs	0.1M KOH	0.86	0.92	72.1	0.2	*Adv. Mater.* 2018, **30**, 1705796.
$Co(PO_3)_4$/RGO	0.1M KOH	0.82	0.91	75	0.1	*Electrochim. Acta* 2017, **227**, 310.
$Co_2P_2O_7$/NPGA	0.1 M KOH	0.82	0.91	/	0.25	*ACS Sustain. Chem. Eng*. 2018, **6**, 9793.
$Co_3(PO_4)_2$C-N/rGOA	0.1M KOH	0.837	0.968	35	0.25	*Energy & Environ. Sci.* **2016**, 9, 2563.
$Na_2CoP_2O_7$	1M NaOH	0.71	0.86	96	0.13	*ChemElectroChem* 2018, **5**, 153.

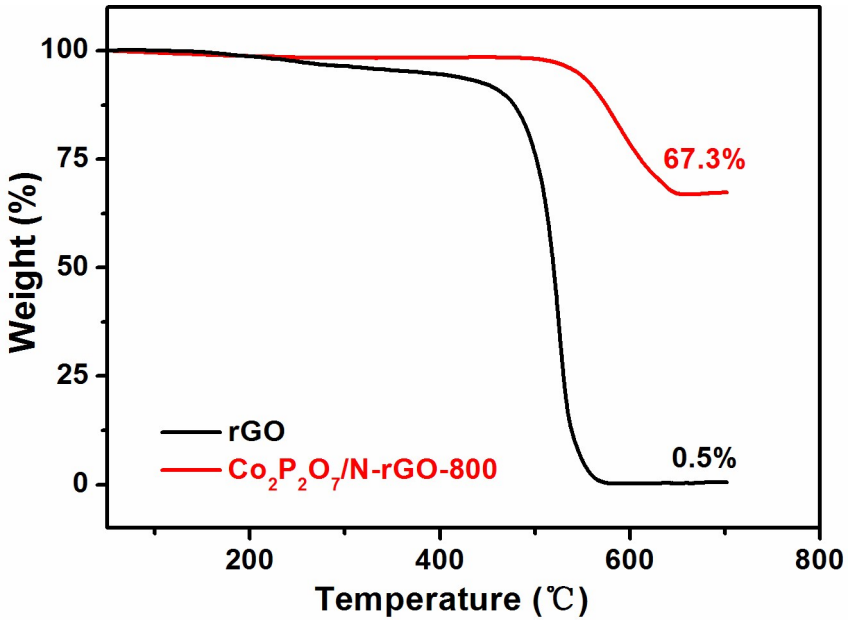
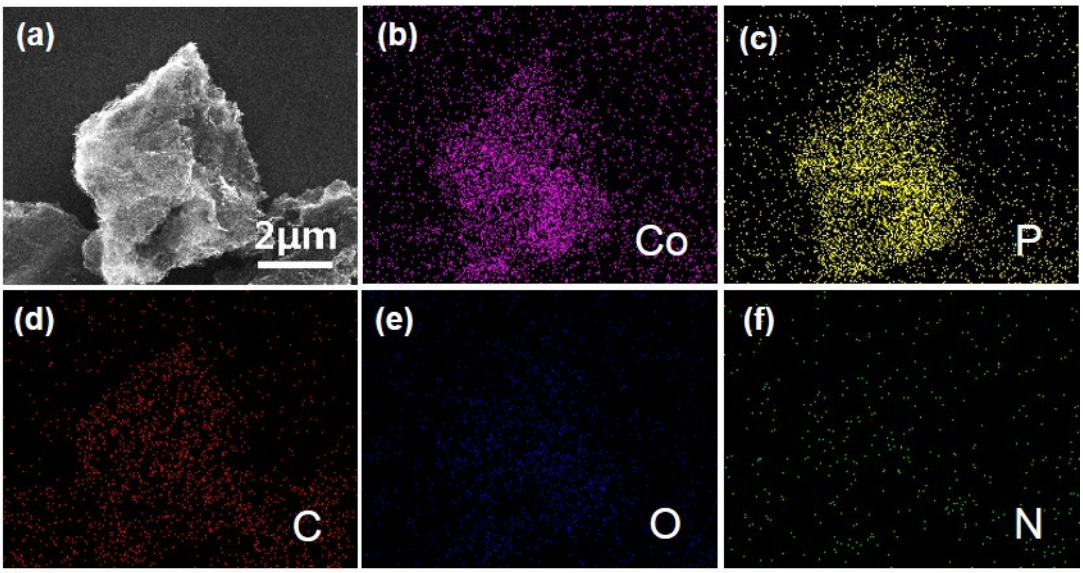


Fig. S1 TGA profiles of the $Co_2P_2O_7$/N-rGO-800 composite and rGO.



(h)

Element	*Wt%*	*At%*
CK	52.54	65.18
NK	11.62	12.36
OK	17.09	15.92
PK	07.88	03.79
CoK	10.87	02.75
Matrix	Correction	ZAF

Fig. S2 (a) SEM image, (b-f) corresponding EDS element mapping, (g) EDS spectrum, and (h) elemental composition of the $Co_2P_2O_7$/N-rGO-800.

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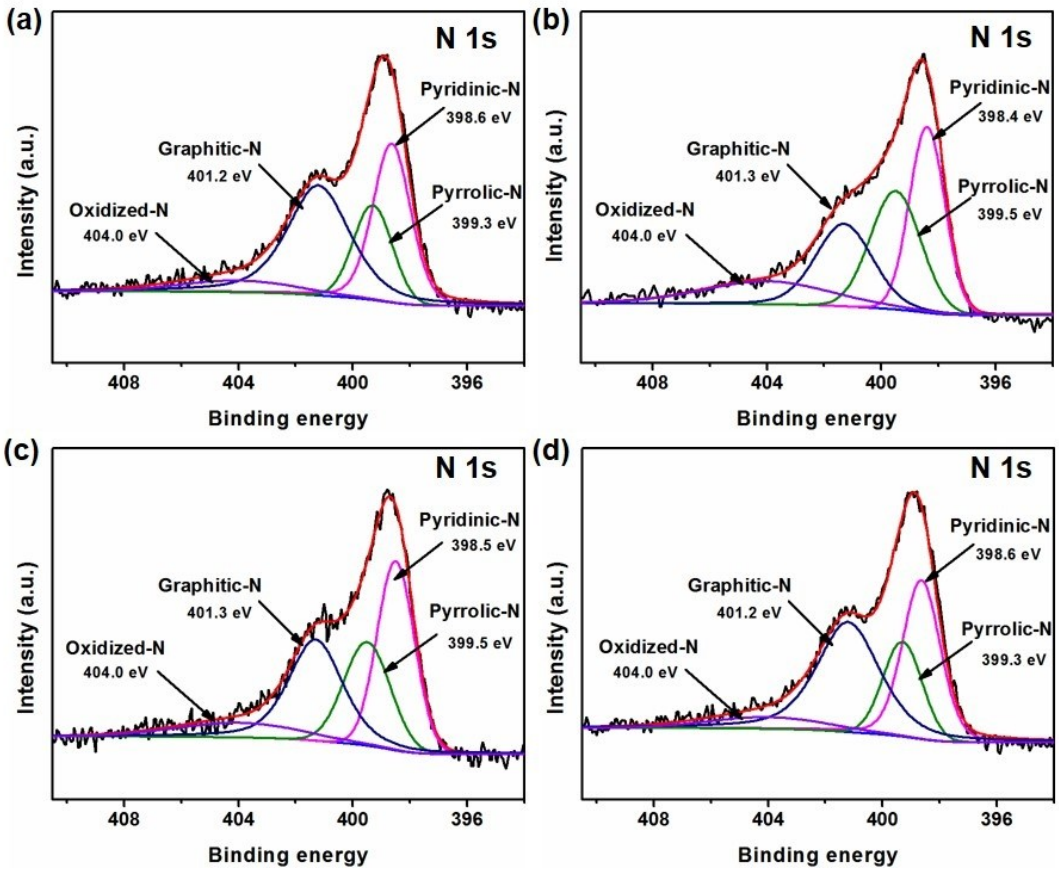

Fig. S3 High-resolution XPS spectra of N 1s for the composites synthesized at various temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C.

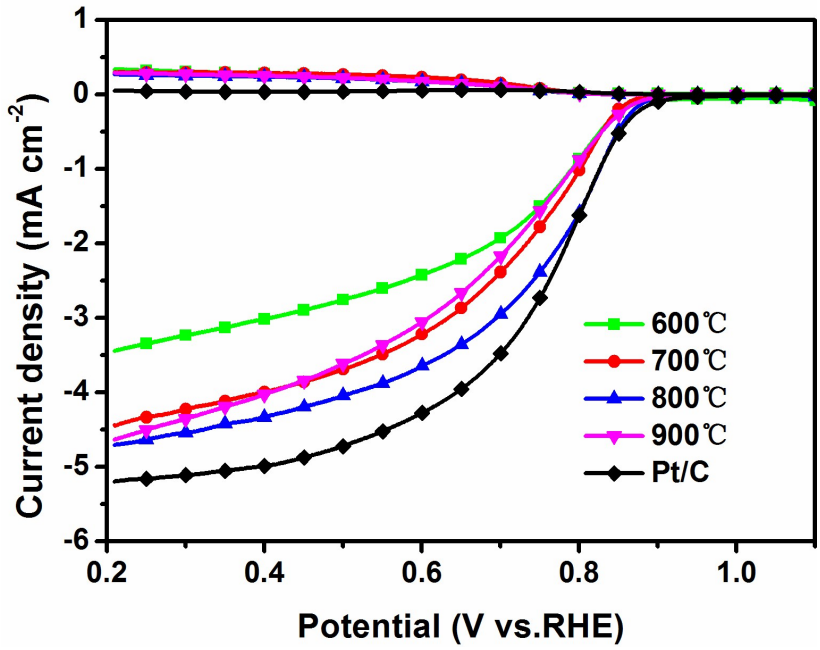

Fig. S4 RRDE voltammograms for the various $Co_2P_2O_7$/N-rGO samples and the Pt/C catalyst recorded in 0.1 M KOH solution at a rotation rate of 1800 rpm.

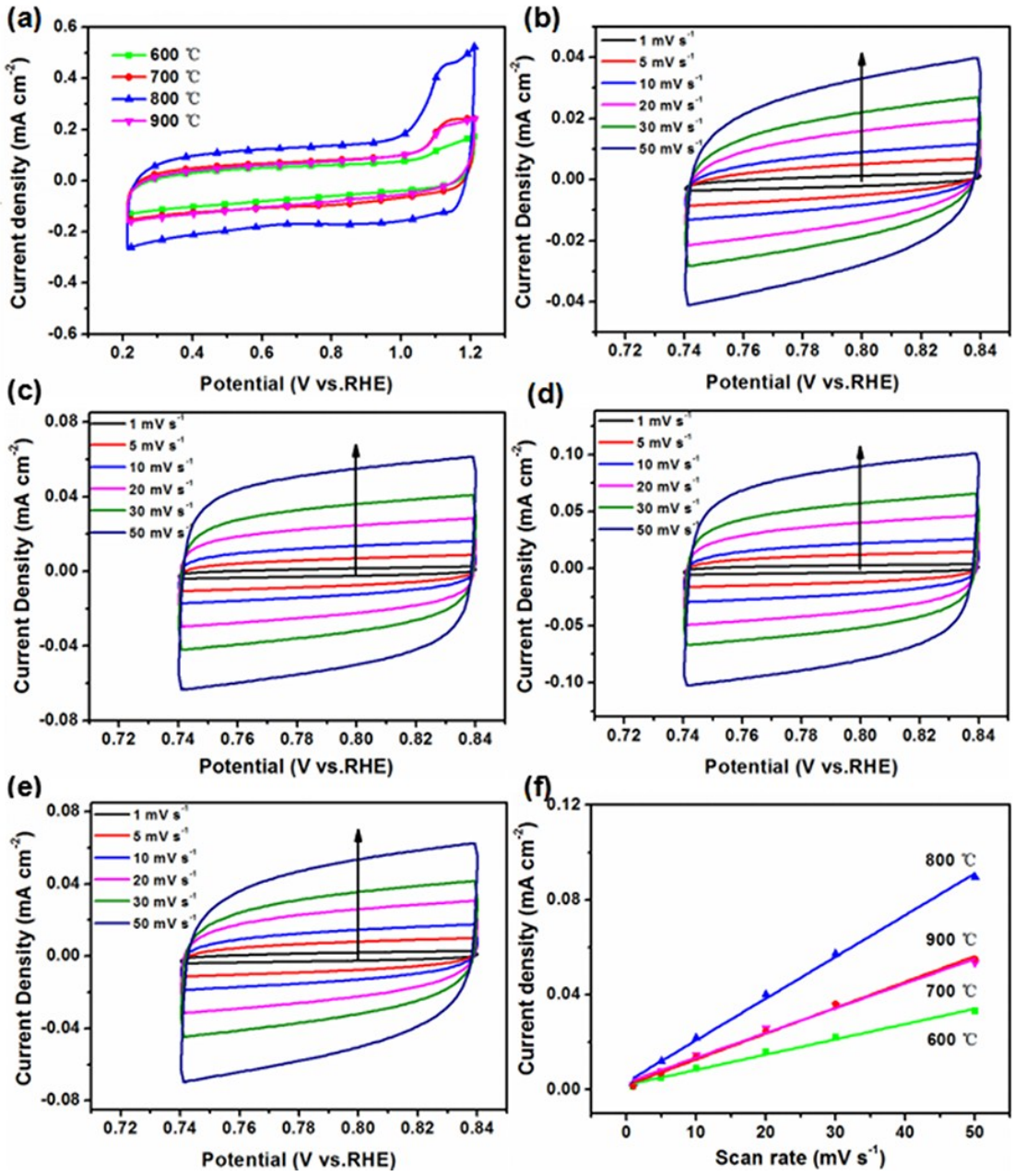

Fig. S5 (a) Cyclic voltammograms of $Co_2P_2O_7$/N-rGO in N_2-saturated 0.1 M KOH at 50 mV s^{-1}. Cyclic voltammograms in the potential range of 0.74-0.84 V vs RHE for various catalysts in N_2-saturated 0.1 M KOH at different scan rate: (b) $Co_2P_2O_7$/N-rGO-600, (c) $Co_2P_2O_7$/N-rGO-700, (d) $Co_2P_2O_7$/N-rGO-800, and (e) $Co_2P_2O_7$/N-rGO-900. (f) Dependence of current densities as a function of scan rate at 0.8 V (vs RHE).

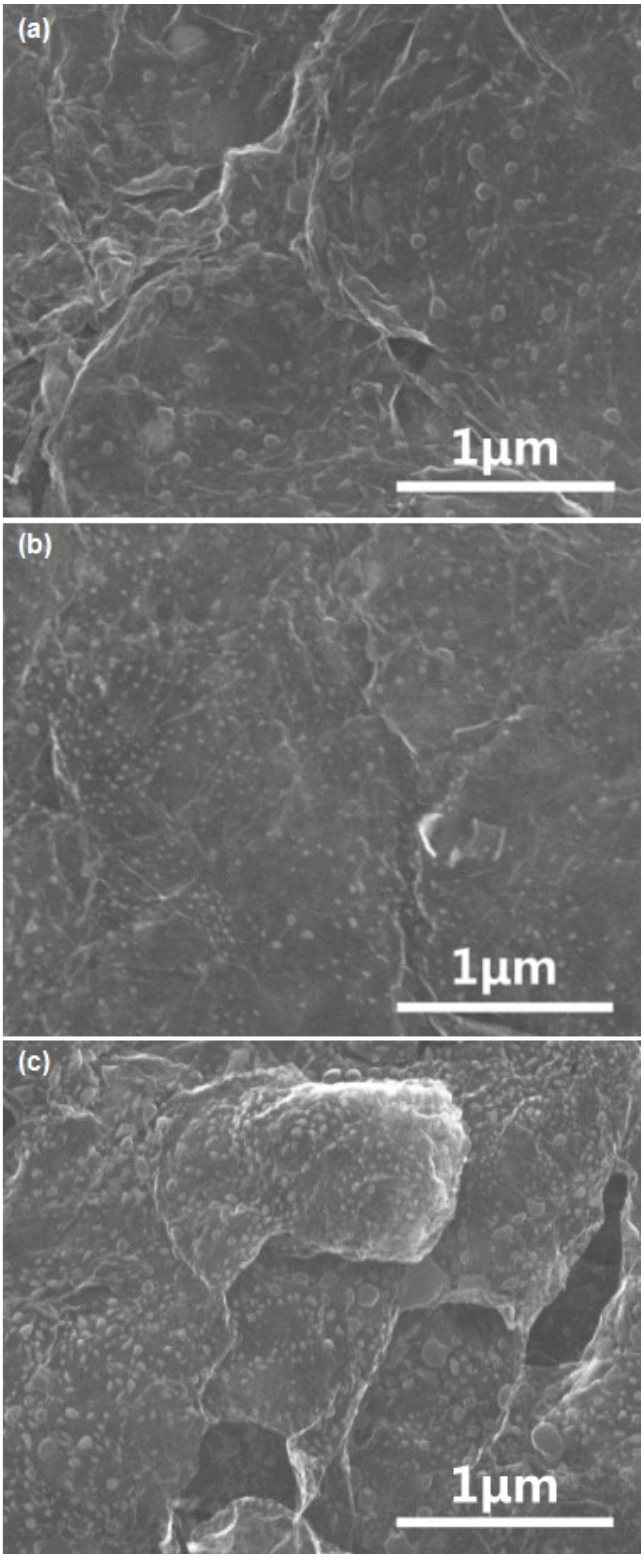

Fig. S6 SEM images of the $Co_2P_2O_7$/N-rGO-800 synthesized at different Co and P precursor amount: (a) 0.2 mmol; (b) 0.4 mmol; (c) 0.8 mmol.

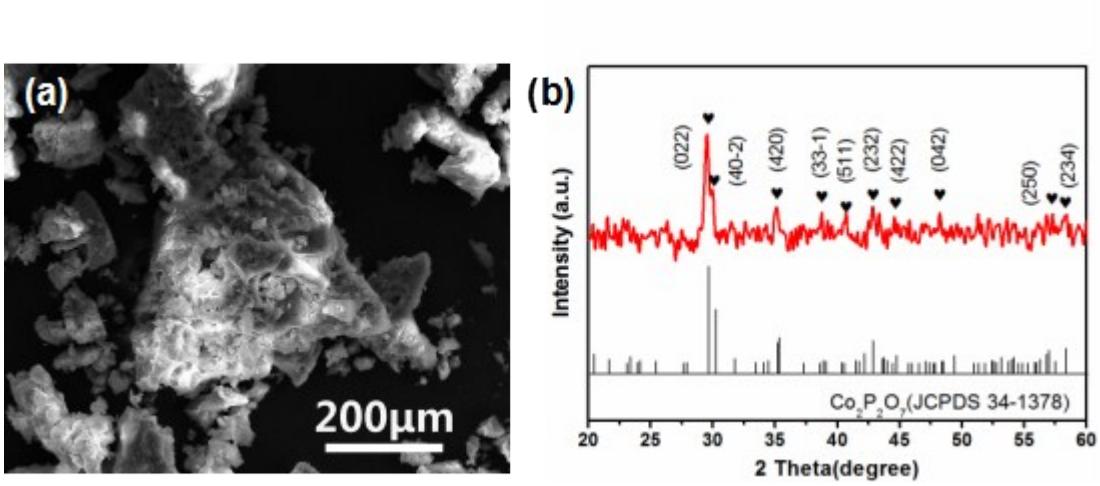

Fig S7 (a) SEM image and (b) XRD pattern of the bulk $Co_2P_2O_7$ synthesized at 800 °C.

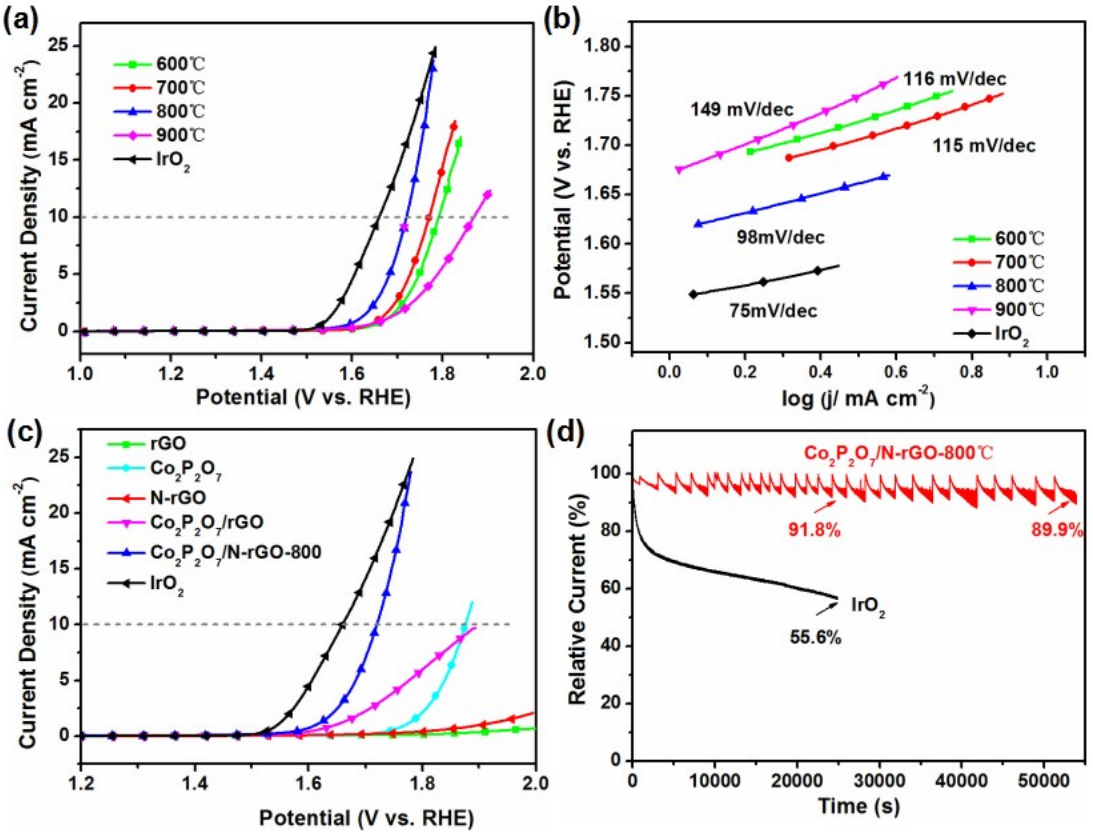

Fig. S8 OER polarization curves (a) and corresponding Tafel curves (b) for the $Co_2P_2O_7$/N-rGO synthesized at different temperatures and the IrO_2 catalyst at rotation rate of 1800 rpm in O_2-saturated 0.1 M KOH electrolyte; (c) OER polarization curves of the $Co_2P_2O_7$/N-rGO-800 composite catalyst and other control samples; (d) Chronoamperometric stability of the $Co_2P_2O_7$/N-rGO-800 and the IrO_2 catalyst at 1.76 V (vs RHE).

Measurement of electrochemical surface area of various $Co_2P_2O_7$/N-rGO catalysts (ECSA).

The electrochemical surface area (ECSA) of investigated catalysts was estimated based on the electrochemical double layer capacitance(C_{dl}).[1] In N_2-saturated 0.1 M KOH solution, a potential range of 0.74-0.84 V vs.RHE (Fig. S5a) with no apparent faradaic behaviors occurred was choosen as the potential window to record the CV curves with various scan rates (Fig. S5b-e). As shown in Fig. S5f, the dependence of the current density on the scan rate in this region is liner for all samples, corresponding to the capancitance charging behavior. The ECSA was determined according to following equation by assuming a C_{dl} capacitance of 60 μF cm^{-2}.[2] ECSA = Q/m*C_{dl}, where Q = S/v (S: peak area, v: scan rate). Therefore, the ECSAs of were 30.9, 50.0, 79.9, 47.5 m^2 g^{-1} for $Co_2P_2O_7$/N-rGO-600, $Co_2P_2O_7$/N-rGO-700, $Co_2P_2O_7$/N-rGO-800, and $Co_2P_2O_7$/N-rGO-900, respectively.

Electrochemical measurements for OER

To obtain a clear understanding of OER performance of as-prepared catalysts, various electrochemical tests were also performed in a conventional three-electrode cell similar to that for ORR tests. The catalyst loading were 0.2 mg cm^{-2} for all of the catalysts, including the commercial IrO_2.

Linear sweeping polarization curves (LSV), electrochemical impedance spetroscopy (EIS) and i-t chronoamperometric responses were carried out to study the electrochemical activity of the samples. All measurements were measured in 0.1 M KOH electrolyte. A nitrogen-saturated environment was achieved by flowing N_2 through the electrolyte before the measurement for approximately 30mins. LSV curves were recorded within the potential range from 1.0 V to 2.0 V (vs. RHE) and at a potential scanning rate of 5mV s^{-1} with the electrode rotation speed of 1800 rpm. EIS tests were measured in the frequency range from 100 kHz to 0.01 Hz. All of the potentials in this study were iR-corrected (where i represent the measured current and

R refers to the ohmic resistance of the electrolyte calculated from the high frequency response of the electrochemical resistance spectrum) and referenced to the reversible hydrogen electrode according to the equation: $E_{RHE} = E_{SCE} + 1.012V$. The stability of the samples were tested by the i-t chronoamperometric responses at 1.76 V (vs. RHE): 54000s for $Co_2P_2O_7$/N-rGO while 25000s for IrO_2.

Supplymentary Reference

1 X. Han, F. Cheng, T. Zhang, J. Yang and H. Y. J. Chen, *Advanced Materials*, 2014, **26**, 13, 2047-2051.

2 X. Han, X. Wu, C. Zhong, Y. Deng, N. Zhao and W. Hu, *Nano Energy* 2017, **31**, 541-550.