Supporting Information

N-, P-, and O-doped porous carbon as advanced trifunctional metal-free electrocatalysts

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Details of calculation sections

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Number of Figures: 14

1. Calculation of electron transfer number (n) and % HO_2^- for oxygen reduction reaction:

The electron transfer numbers (n) per O_2 involved in ORR were calculated from the slopes of the Koutecky-Levich plots according to the following equations:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k}$$

Where j is the measured current density, j_k and j_l are the kinetic and diffusion-limiting current densities, ω is the rotating rate of electrode (rpm). B is determined from the slope of the Koutecky-Levich plots according to the following Levich equation.

$$B = 0.2nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6}$$

Where n is electron transfer number per oxygen molecule, F is Faraday constant (96485 C mol^{-1}), C_{O2} is the bulk concentration of O_2 (7.8×10^{-7} mol cm^{-3}), υ is the kinetic viscosity of electrolyte (0.01 cm^2 S^{-1}). D_{O2} is the diffusion coefficient of O_2 in 0.1 M KOH (1.8×10^{-5} cm^2 S^{-1}).

Hydrogen peroxide yields and the electron transfer number (n) were calculated by the following equations:

$$\%(HO_2^-) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}}$$

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}}$$

Where I_d is disk current, I_r is ring current, the collection efficiency (N) was determined to be 0.40 by using 10 mM $K_3[Fe(CN)_6]$.

Citing: *J. Am. Chem. Soc. 2012, 134, 3517.*

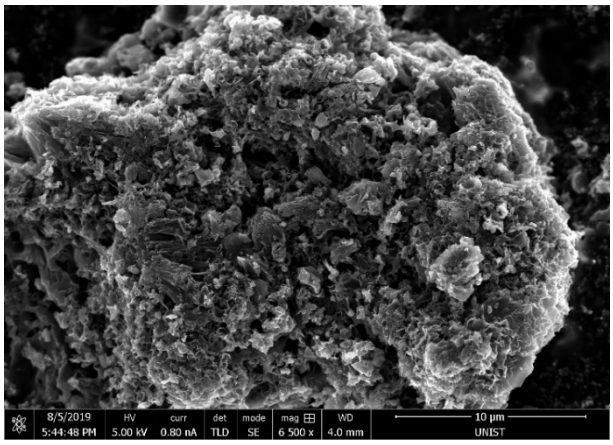

Figure S1 SEM image of NPOCs.

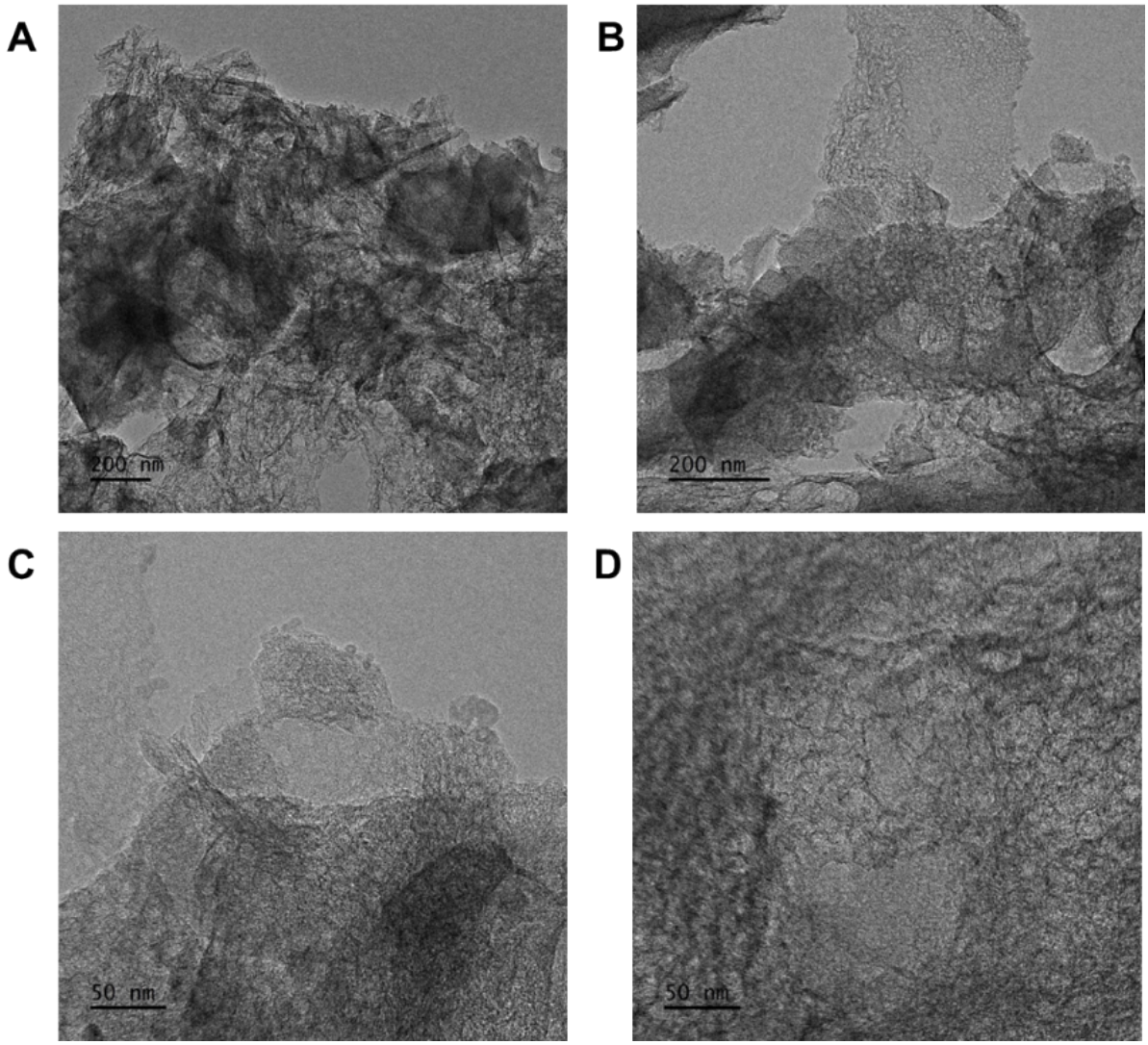

Figure S2 TEM images of NPOCs

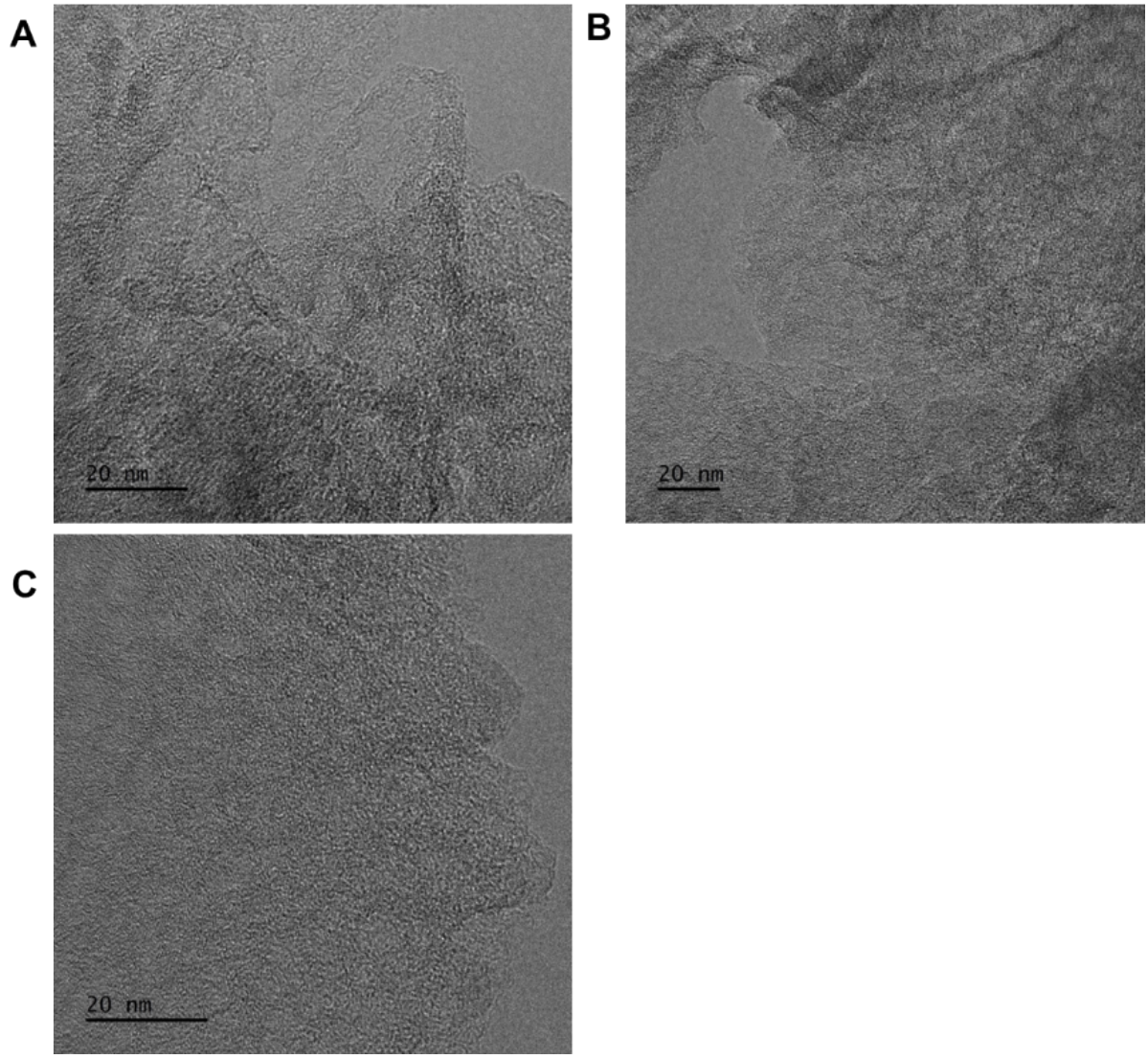

Figure S3 HRTEM images of NPOCs.

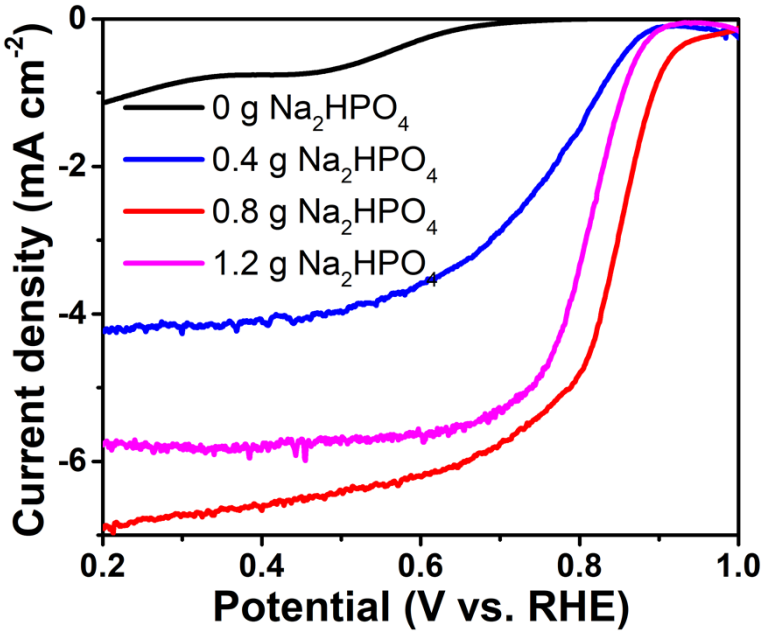

Figure S4 The effect of the additive amount of phosphorus source on ORR activity.

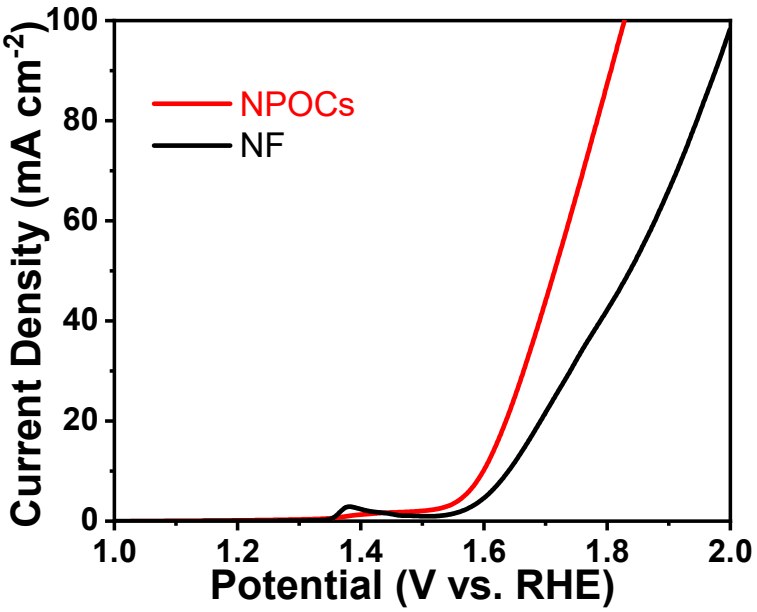

Figure S5 The comparison between blank NF and NPOCs of OER activity.

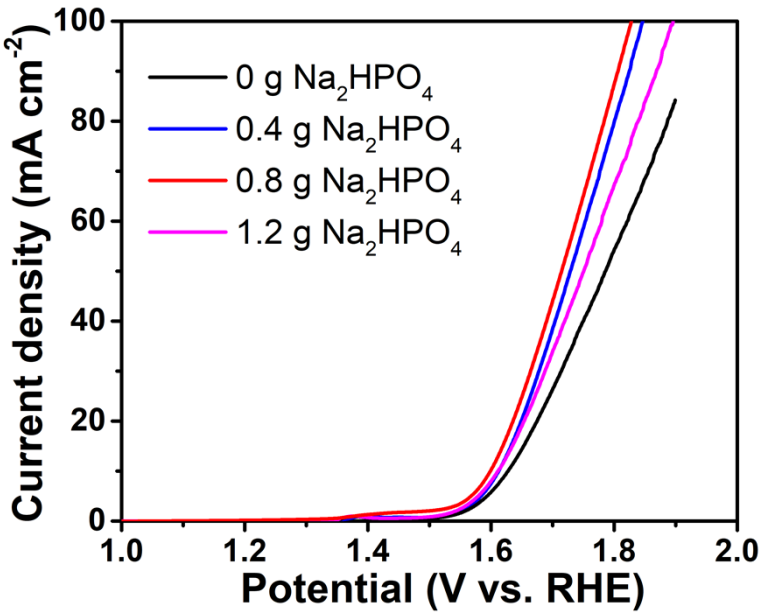

Figure S6 The effect of the additive amount of phosphorus source on OER activity.

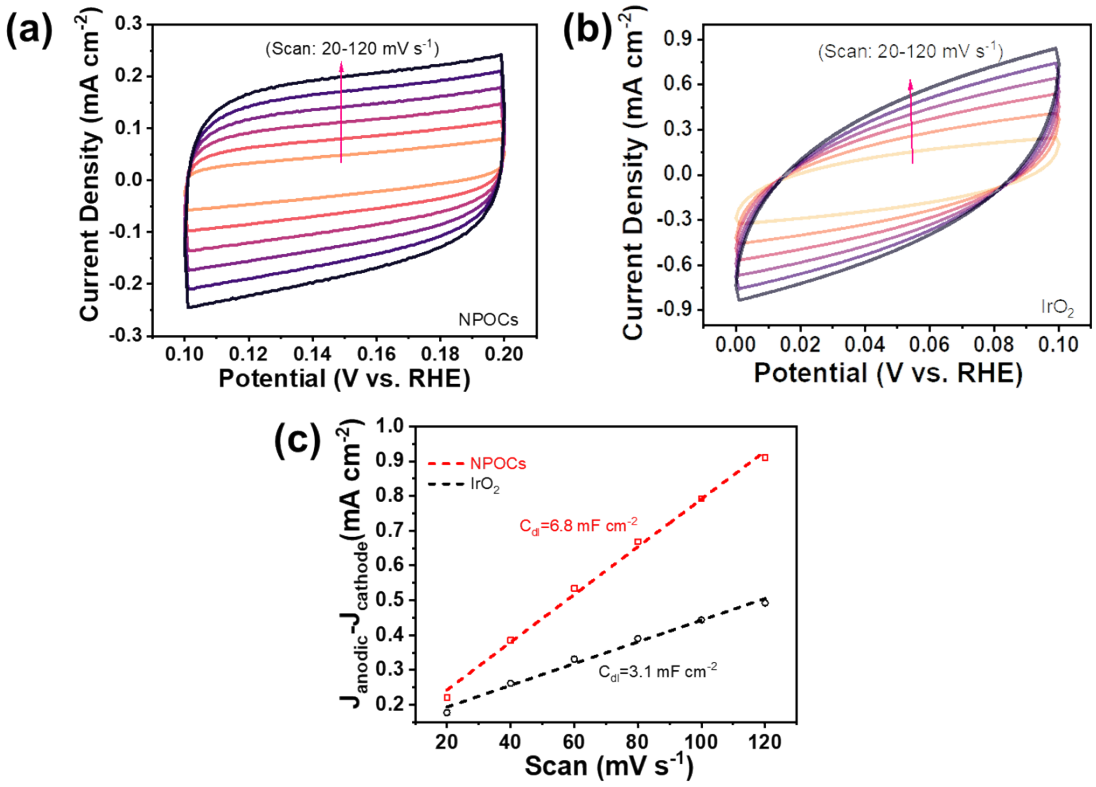

Figure S7 The CV curves recorded at different scan rates for (a) NPOCs, (b) Commercial IrO_2. (c) Double-layer capacitance (C_{dl}).

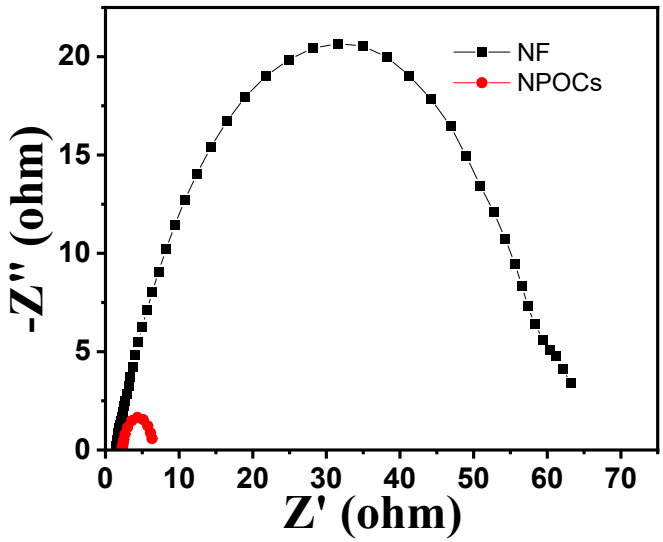

Figure S8 Nyquist plots of blank NF and NPOCs.

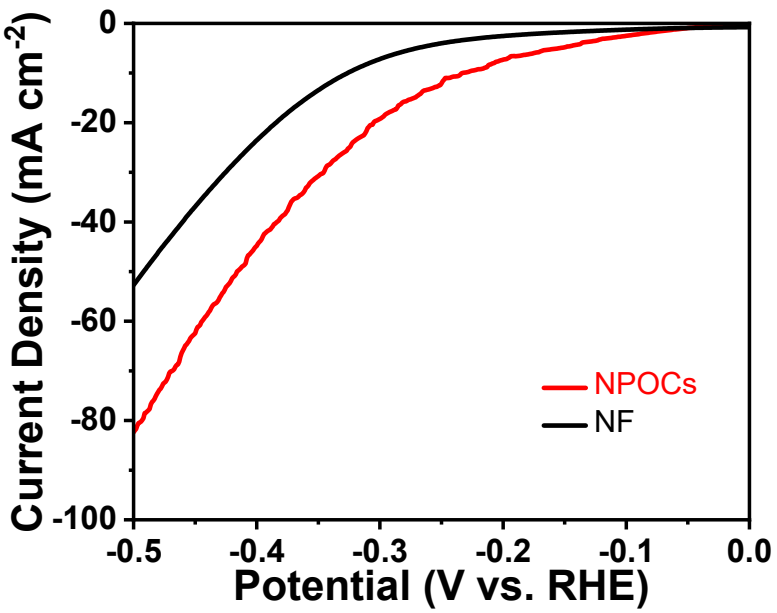

Figure S9 The comparison between blank NF and NPOCs of HER activity.

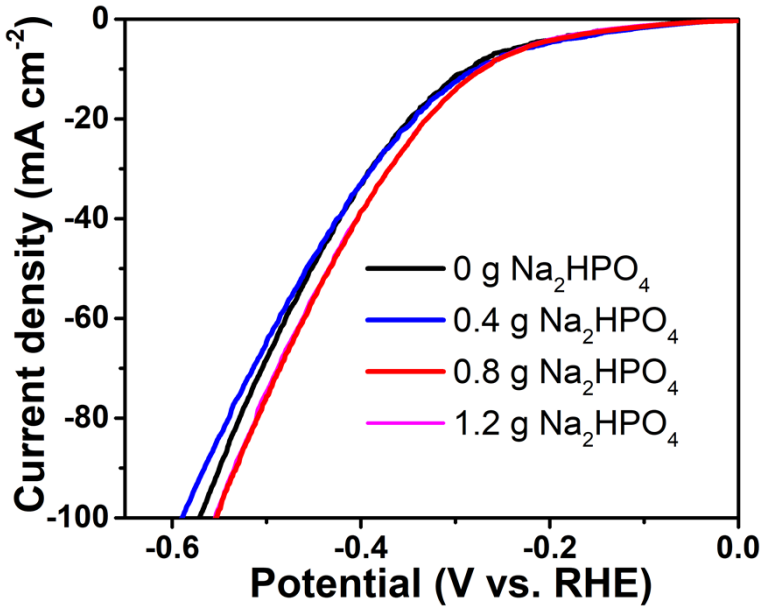

Figure S10 The effect of the additive amount of phosphorus source on HER activity.

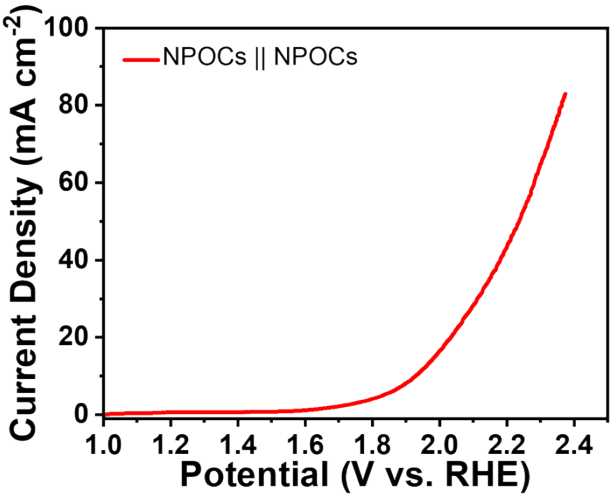

Figure S11 Overall catalytic water splitting activity of NPOCs in 1 M KOH.

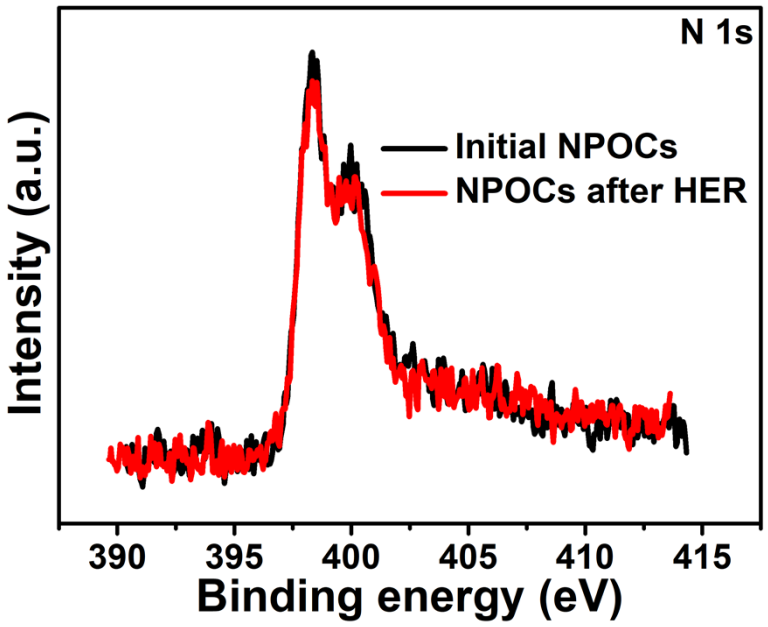

Figure S12 The comparison of N 1s between initial NPOCs and NPOCs after HER.

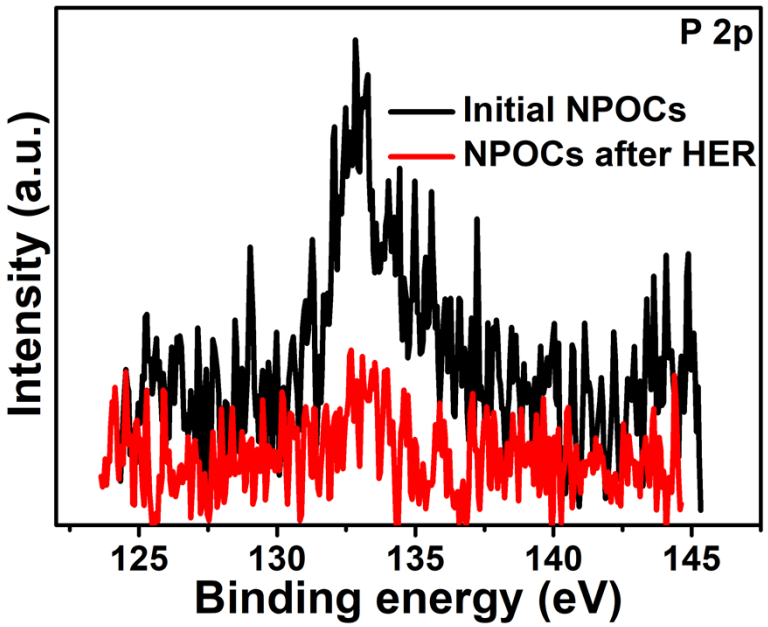

Figure S13 The comparison of P 2p between initial NPOCs and NPOCs after HER.

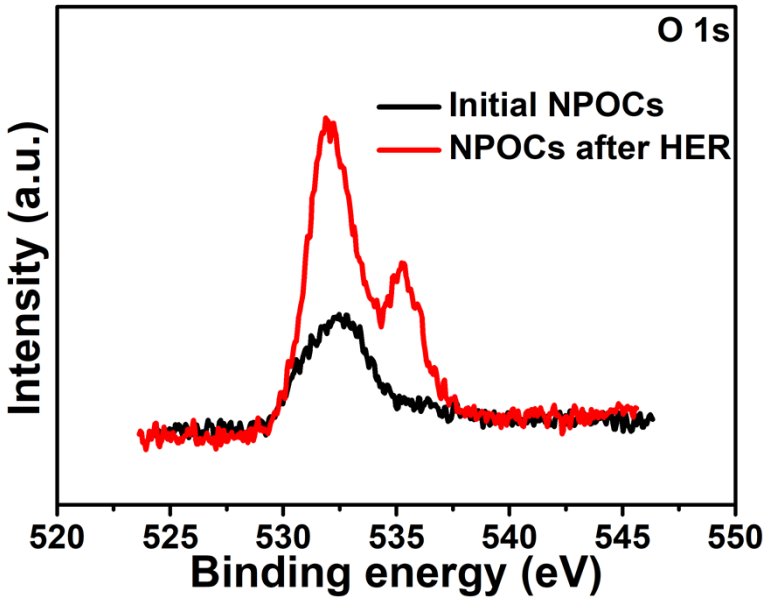

Figure S14 The comparison of O 1s between initial NPOCs and NPOCs after HER.