

## Supporting Information

### Crystallinity Dependence for High-Selectivity Electrochemical Oxygen Reduction to Hydrogen Peroxide

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## 1. Experimental section

Typically, 2mg HATP·6HCl (2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloric acid salt) was dissolved in 20 mL dimethyl sulfoxide and heated to 50 °C with stirring in a 50 mL single-mouth flask. The flask was placed in an oil bath and stirred for 10 min at a rotating speed of 300 rpm. Subsequently, in another glass reaction vial, 2mgNiCl<sub>2</sub>·6H<sub>2</sub>O (nickel (II) chloride hexahydrate) was dissolved in 4 mL H<sub>2</sub>O, and the solution was added into the heated flask, and kept the solution in the heated flask stirring under 50 °C for another 10 minutes. After then, 100 μL NH<sub>3</sub>·H<sub>2</sub>O was added into the flask carefully with changing the temperature of the oil bath to 60 °C. After 12 hours reaction, the resulting black powder was collected by centrifuging, washing with distilled water and ethanol several times. The solid was then dried at 60 °C overnight. Thereafter, the dry sample black powder 2-Ni<sub>3</sub>(HITP)<sub>2</sub> was obtained. 5-Ni<sub>3</sub>(HITP)<sub>2</sub>, 10-Ni<sub>3</sub>(HITP)<sub>2</sub>, 20-Ni<sub>3</sub>(HITP)<sub>2</sub> samples were synthesized in a same process by changing the amount of HATP·6HCl and NiCl<sub>2</sub>·6H<sub>2</sub>O to 5, 10, 20 mg accordingly.

## 2. Electrochemical Characterization

The oxygen reduction reaction (ORR) performances of the resultant catalysts were

measured using a commercial potentiostats combined with the rotating ring-disk electrode (RRDE) technique in a standard three-electrode configuration electrochemical cell. The as-prepared catalyst ink, consisting of catalyst powder, water, ethanol and Nafion solution was carefully dropped on the RRDE electrode. Graphite rod and saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. Prior to ORR measurement, scanning cycle voltammetry (CV) in N<sub>2</sub>-saturated 0.1M KOH and O<sub>2</sub>-saturated 0.1M KOH were tested. No obvious oxygen reduction peaks were observed in the N<sub>2</sub>-saturated solution.

For the electrode preparation process, 1 mg of catalyst powder was dispersed into a mixture solution of 30  $\mu$ L of Nafion (5%, Sigma Aldrich), 250  $\mu$ L of ethanol, and 750  $\mu$ L of distilled water. And then put the solution in an ultrasonic water bath to form homogeneous catalyst ink. After that, 5  $\mu$ L of the dispersion was transferred onto the rotating ring disk electrode with a diameter of 5 mm. The catalysts loading was 25.6  $\mu$ g/cm<sup>2</sup>.

### 3. Calculation Methods

**Mass activity.** The mass activity (MA, A  $\cdot$  g<sup>-1</sup>) values were calculated from the electrocatalyst loading  $m$  and the measured current density  $j$  (mA  $\cdot$  cm<sup>-2</sup>) near at  $\eta = 250$  mV based on the relation<sup>1</sup>:

$$MA = j / m$$

**Selectivity and Electron Transfer Number.** The selectivity for hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can be obtained by measuring the currents of O<sub>2</sub> reduction at the disk and H<sub>2</sub>O<sub>2</sub>

oxidation at the Pt ring of RRDE electrode. The number of electron transferred and selectivity based on RRDE measurements were calculated by the equation<sup>2</sup>:

$$H_2O_2(\%) = 200 \times \frac{I_r / N}{I_d + I_r / N}$$

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

Where  $I_d$  is the disk current,  $I_r$  is the ring current, and  $N=0.44$  is the Pt ring current collection efficiency.

To extract information regarding the correlation between the kinetics activity and the mass transport of reactants, Koutecky-Levich (K-L) plot was acquired from the polarization curves at various rotation speeds. The electron transfer number was determined by the Koutecky-Levich equations<sup>3</sup>:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

In which the B factor was given by

$$B = 0.62nFC_oD_o^{2/3}V^{-1/6}$$

Where  $n$  is the number of electrons transferred during the oxygen reduction reaction,  $J$  is the measured current density,  $J_K$  and  $J_L$  are the kinetic and limiting current densities,  $\omega$  is the angular velocity of the disk ( $\omega = 2\pi N$ ,  $N$  is the linear rotation speed),  $F$  is the Faraday constant (96485 C mol<sup>-1</sup>),  $D_o$  is the diffusion coefficient of O<sub>2</sub> in the 0.1 M KOH solution ( $1.9 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>),  $C_o$  is the bulk concentration of O<sub>2</sub> ( $1.2 \times 10^{-3}$  mol L<sup>-1</sup>) and  $V$  is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>).

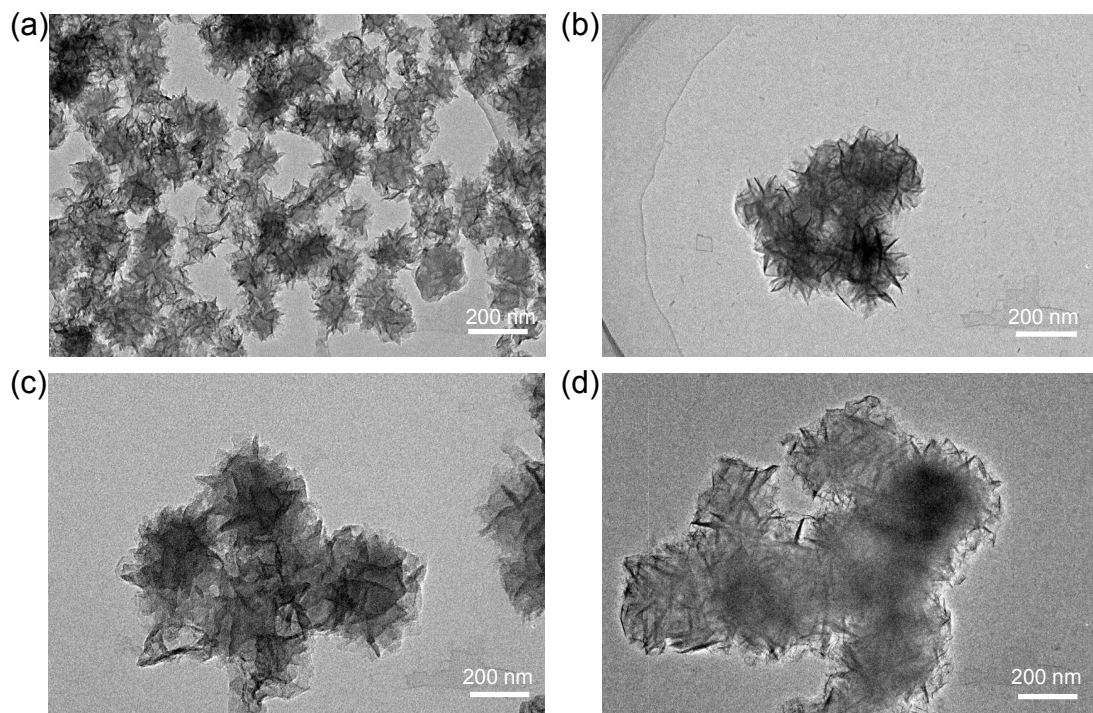
**Electrochemically Active Surface Area.** The electrochemically active surface area (ECSA) for each system was estimated from the electrochemical double-layer

capacitance ( $C_{dl}$ ) of the catalytic surface. To measure double-layer charging via CV, a potential range in which no apparent Faradaic processes occur was determined from static CV. This range is typically a 0.1 V potential window, and the charging current,  $i_c$ , is then measured from CVs at multiple scan rates ( $v=20, 40, 60, 80, 100$  mV/s) in the non-Faradaic region. The  $C_{dl}$  can be given by  $i_c = v C_{dl}$ . The ECSA of a catalyst sample is calculated from the double-layer capacitance according to the following equation<sup>4</sup>:

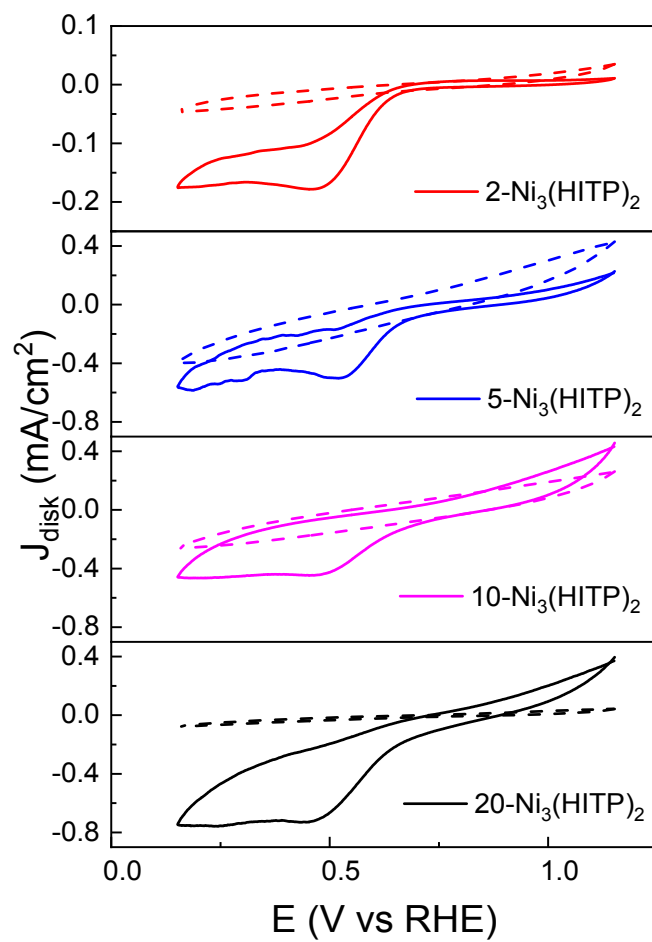
$$ECSA = \frac{C_{dl}}{C_s \cdot L}$$

where  $C_s$  is the specific capacitance of the sample and the typical values are in the range of  $C_s = 0.02-0.06$  mF/cm<sup>2</sup>. For our estimation of the surface area, we used a general  $C_s = 0.04$  mF/cm<sup>2</sup>.  $L$  is the loading of catalyst given in mg cm<sup>-2</sup>.

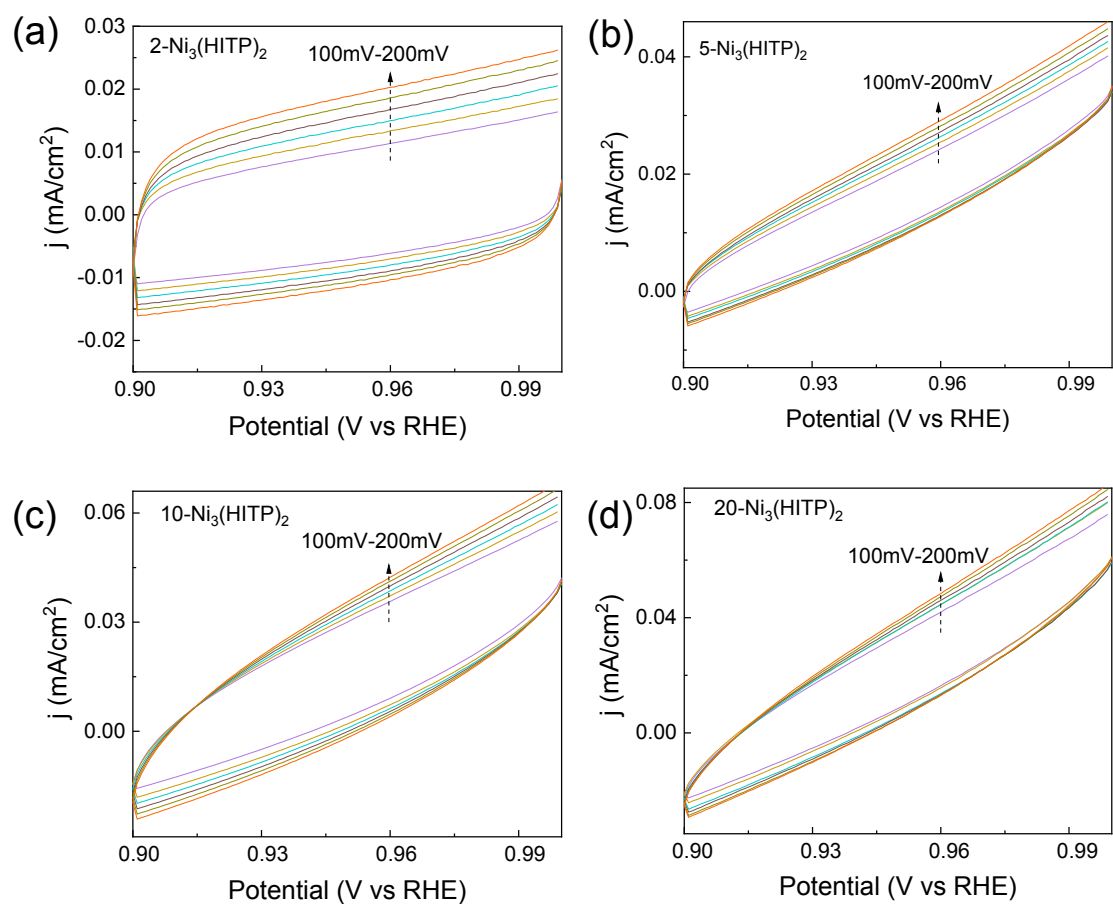
## 4. Supplementary Figures and Tables



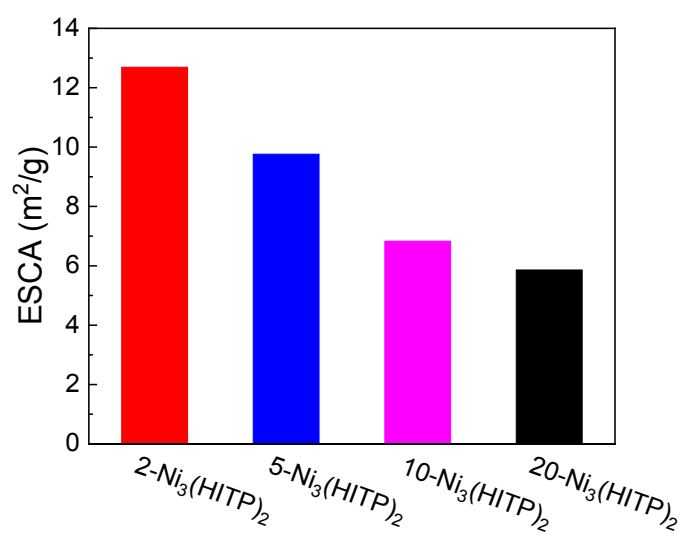
**Figure S1.** TEM images of (a) 2- $\text{Ni}_3(\text{HITP})_2$ , (b) 5- $\text{Ni}_3(\text{HITP})_2$ , (c) 10- $\text{Ni}_3(\text{HITP})_2$ , and (d) 20- $\text{Ni}_3(\text{HITP})_2$ .



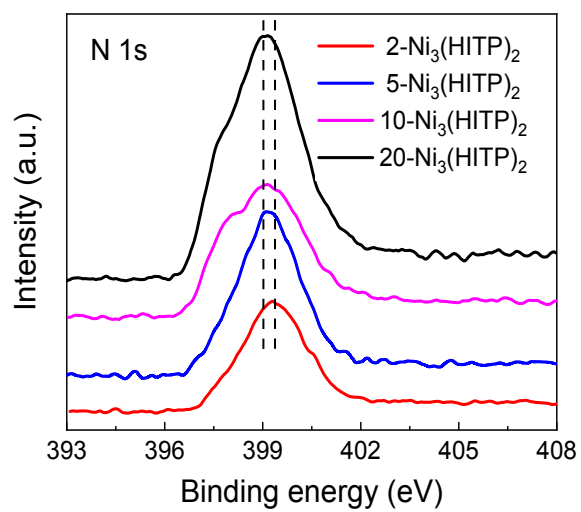
**Figure S2.** Electrochemical cyclic voltammetry curves of 2-Ni<sub>3</sub>(HITP)<sub>2</sub>, 5-Ni<sub>3</sub>(HITP)<sub>2</sub>, 10-Ni<sub>3</sub>(HITP)<sub>2</sub>, 20-Ni<sub>3</sub>(HITP)<sub>2</sub> under 1600 rpm in 0.1 M KOH, O<sub>2</sub>-saturated solution (solid line), N<sub>2</sub>-saturated solution (dash line).



**Figure S3.** The CVs measured at different scan rates of 100, 120, 140, 160, 180, and 200  $\text{mV s}^{-1}$ .



**Figure S4.** ESCA values calculated from  $C_{dl}$  for 2-, 5-, 10- and 20- $\text{Ni}_3(\text{HITP})_2$ .



**Figure S5.** N XPS spectra of 2-, 5-, 10-, and 20-Ni<sub>3</sub>(HITP)<sub>2</sub>.



## References

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