

## **Ultra-small RuO<sub>2</sub>/NHC nanocrystal electrocatalysts with efficient water oxidation activities in acidic media**

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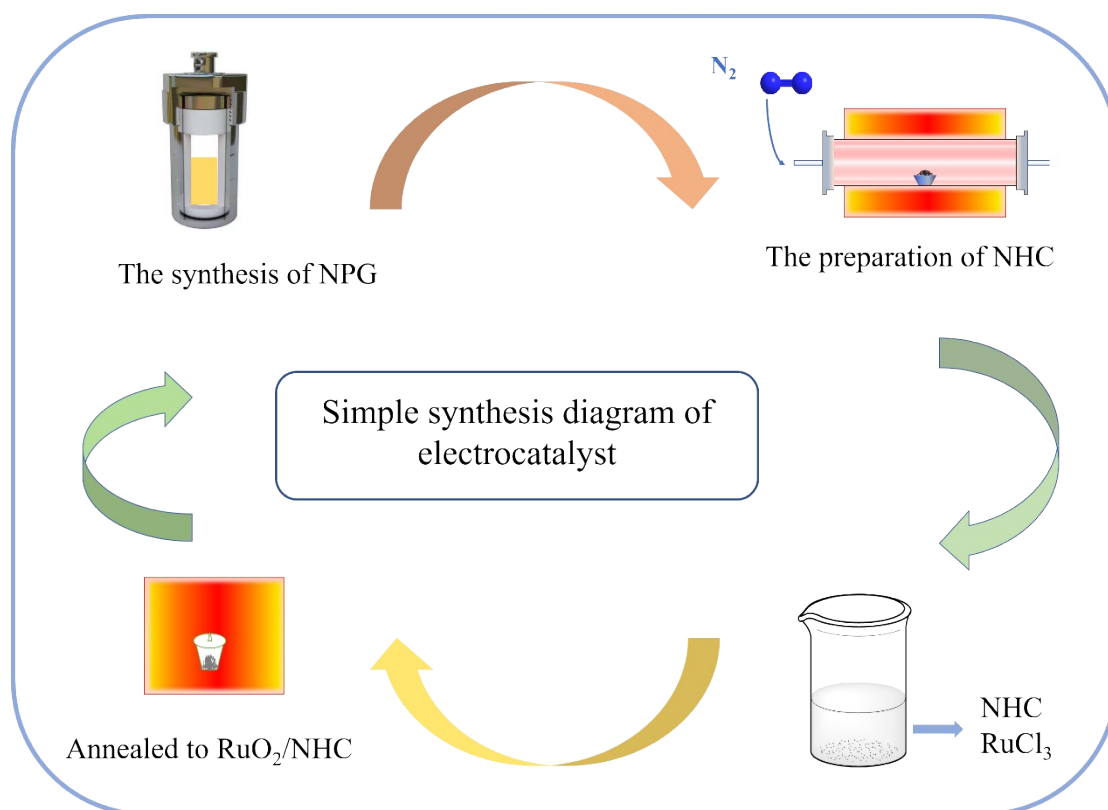


Fig S1. Simple synthesis flow diagram of electrocatalyst  $\text{RuO}_2/\text{NHC}$ .

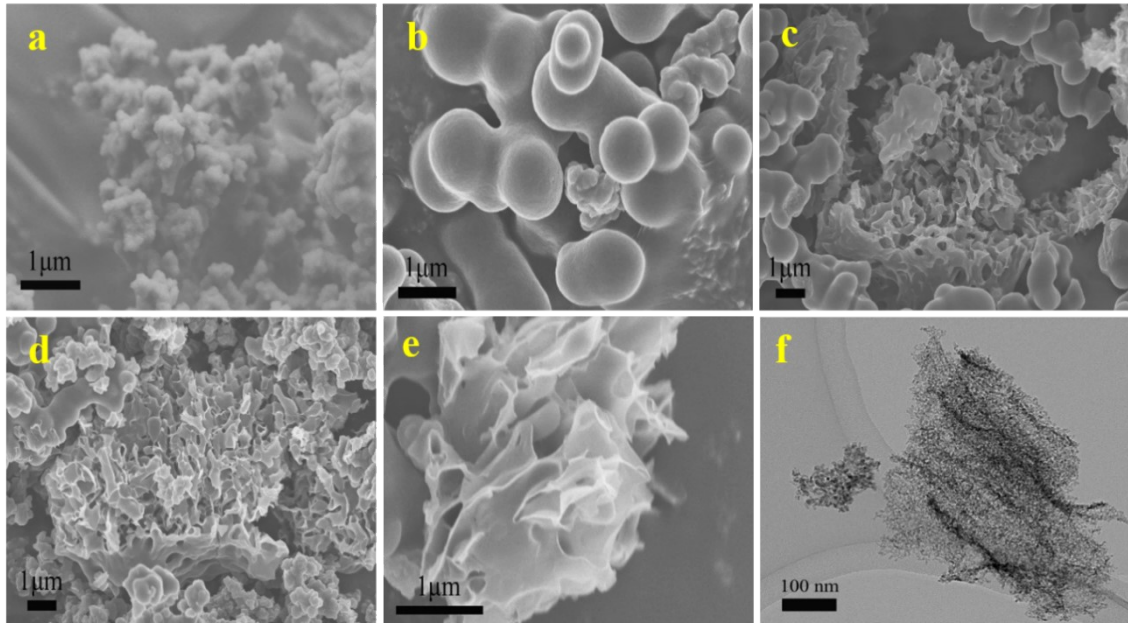


Fig S2. SEM of a) NPG; b) NHC<sup>0</sup>; c) NHC<sup>1</sup>; d) NHC<sup>2</sup>; e) NHC<sup>4</sup> and f) TEM of RuO<sub>2</sub>/NHC<sup>3</sup>.

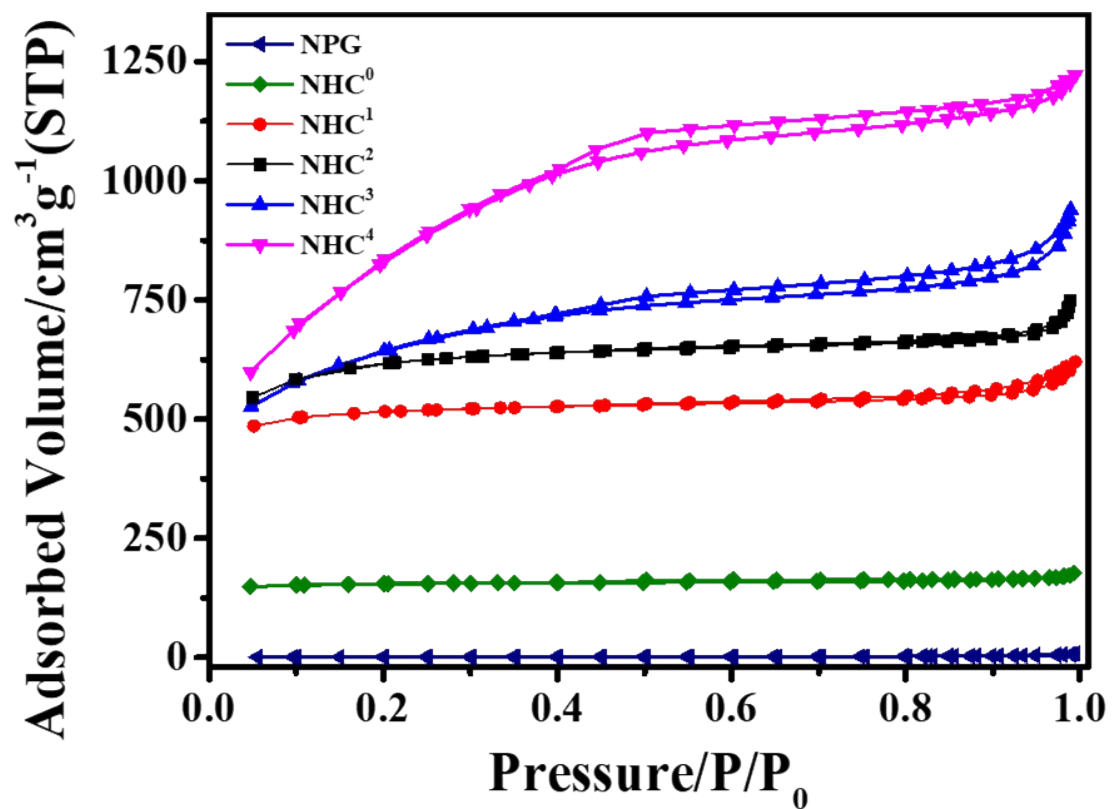


Fig S3. Nitrogen adsorption-desorption isotherms of different supporter samples.

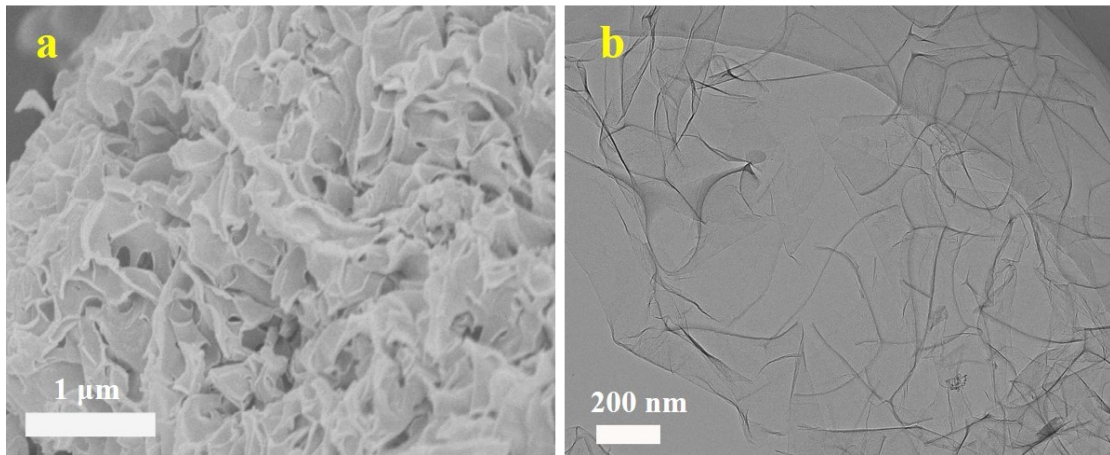


Fig S4. a) SEM of NHC<sup>3</sup> and b) TEM image of NHC<sup>3</sup>.

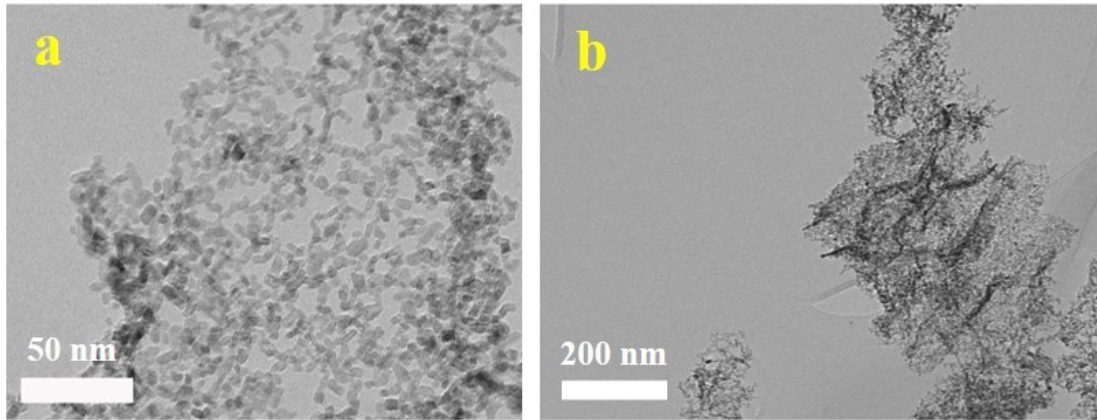


Fig S5. TEM of  $\text{RuO}_2/\text{NHC}^3$  at different multiples.

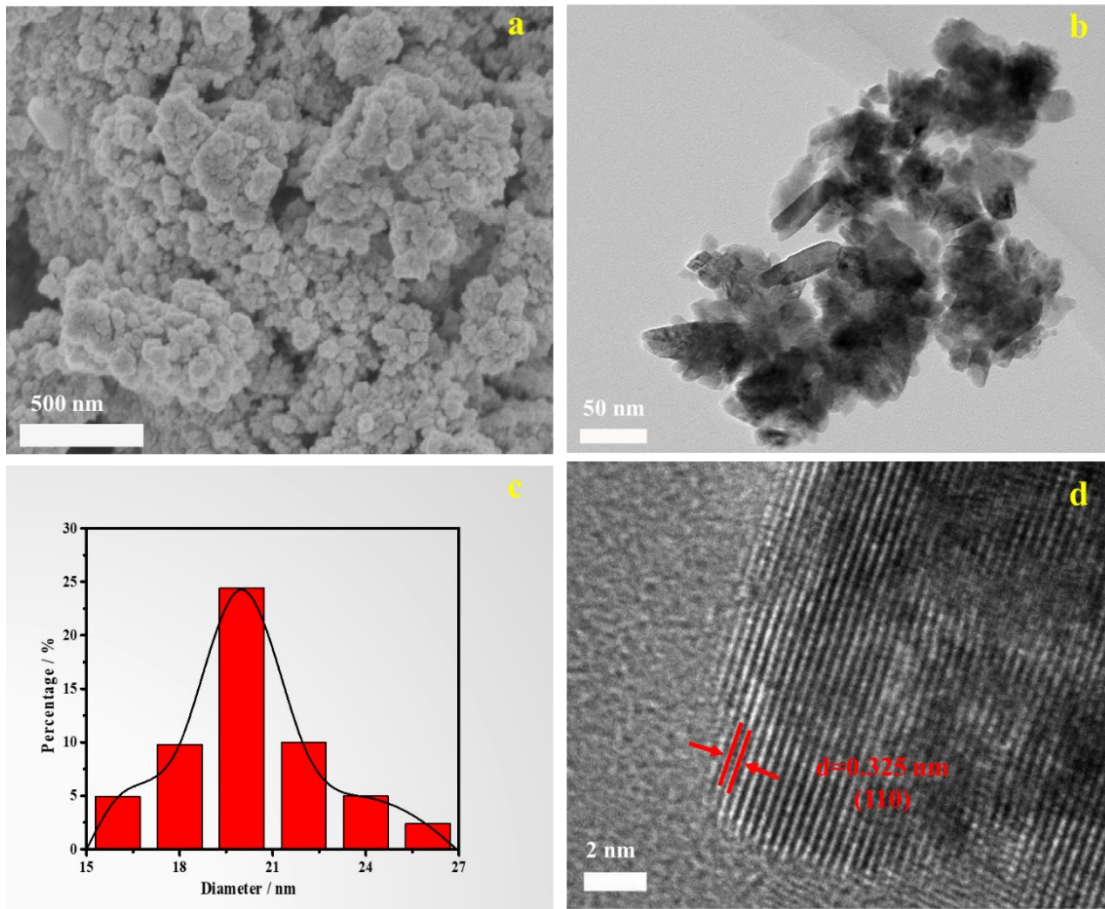


Fig S6. a) SEM of RuO<sub>2</sub>; b) TEM image of RuO<sub>2</sub>; c) particle size image of RuO<sub>2</sub> and d) HR-TEM image of RuO<sub>2</sub>.

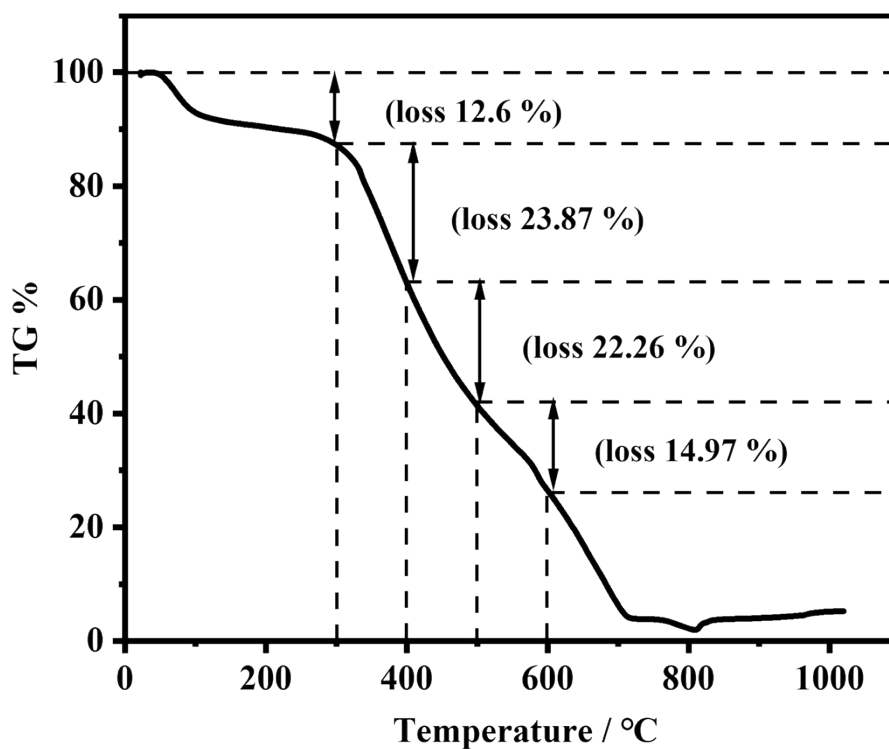


Fig S7. TGA plot of precursor of RuO<sub>2</sub>/NHC in 20 mL/min air atmosphere with temperature ramping 10 °C/min.



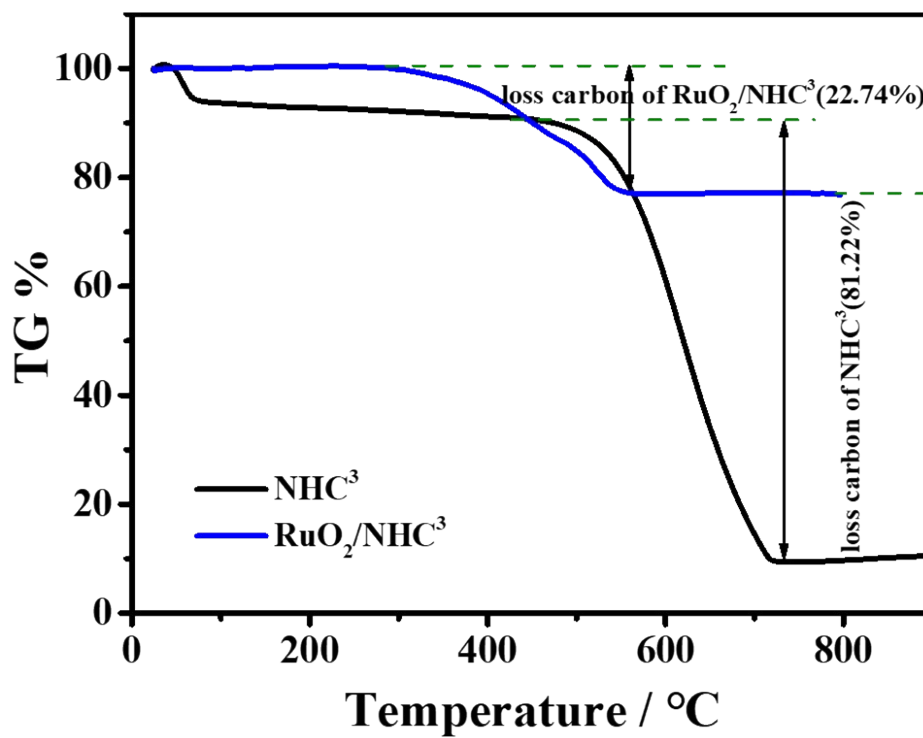


Fig S8. TGA plot of RuO<sub>2</sub>/NHC<sup>3</sup> and NHC<sup>3</sup> in 20 mL/min air atmosphere with temperature ramping 10 °C/min.

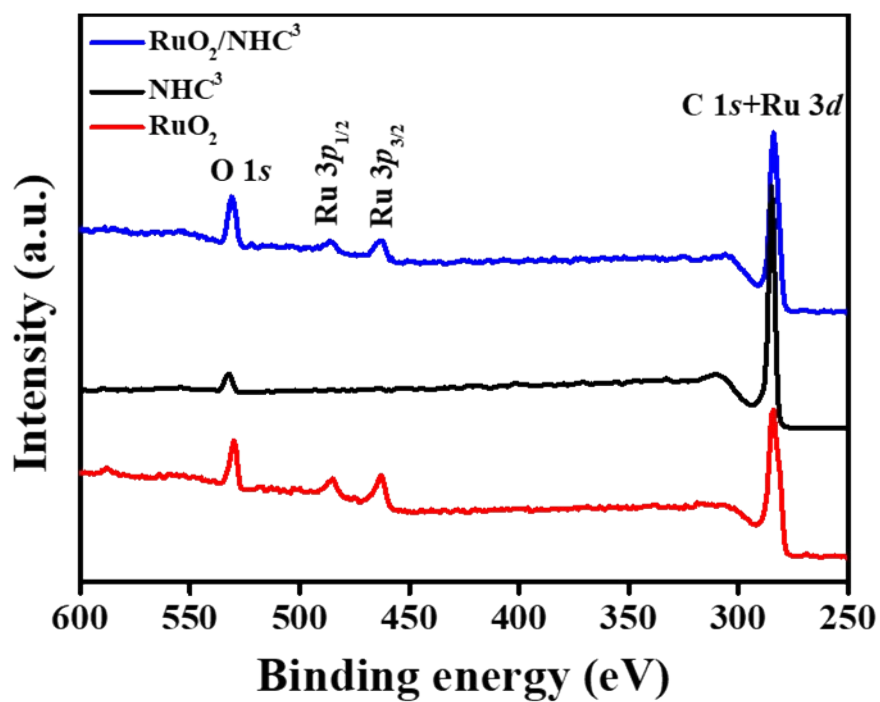


Fig S9. XPS survey spectra of NHC<sup>3</sup>, RuO<sub>2</sub>/NHC<sup>3</sup> and RuO<sub>2</sub> electrocatalysts.

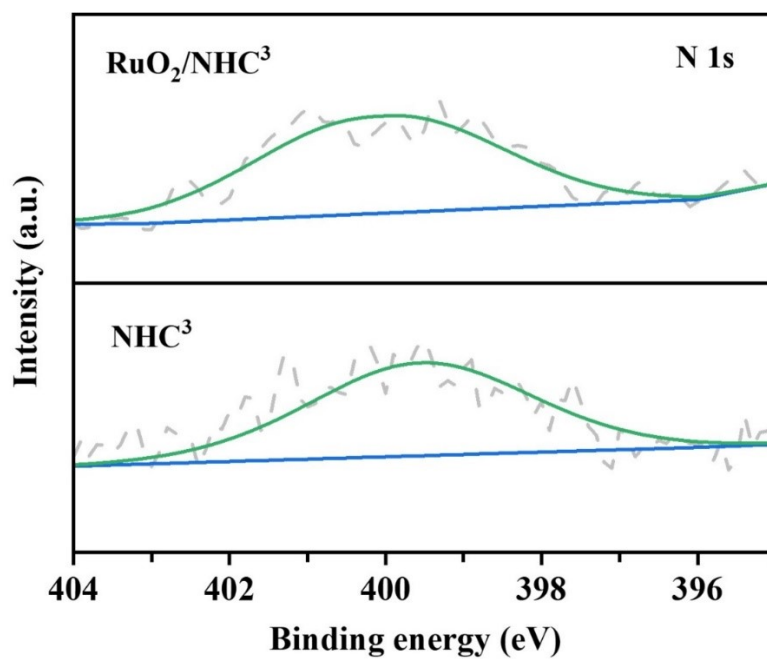


Fig S10. High resolution XPS spectra of N 1s of electrocatalysts RuO<sub>2</sub>/NHC<sup>3</sup> and NHC<sup>3</sup>.

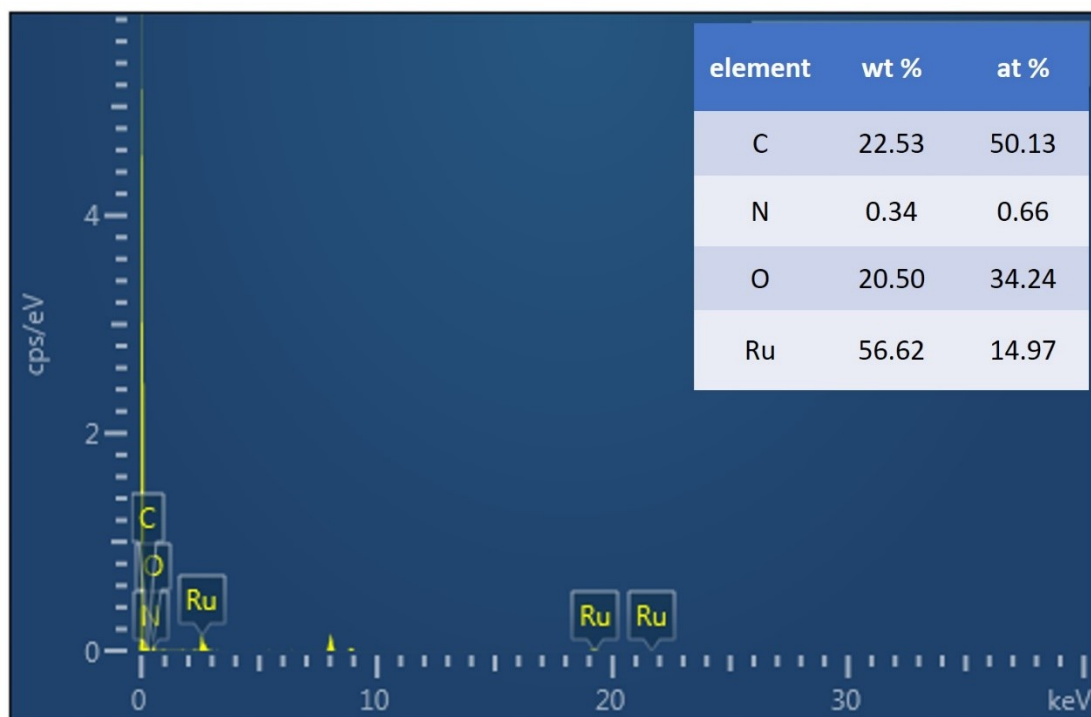


Fig S11. EDS analysis for RuO<sub>2</sub>/NHC<sup>3</sup>.

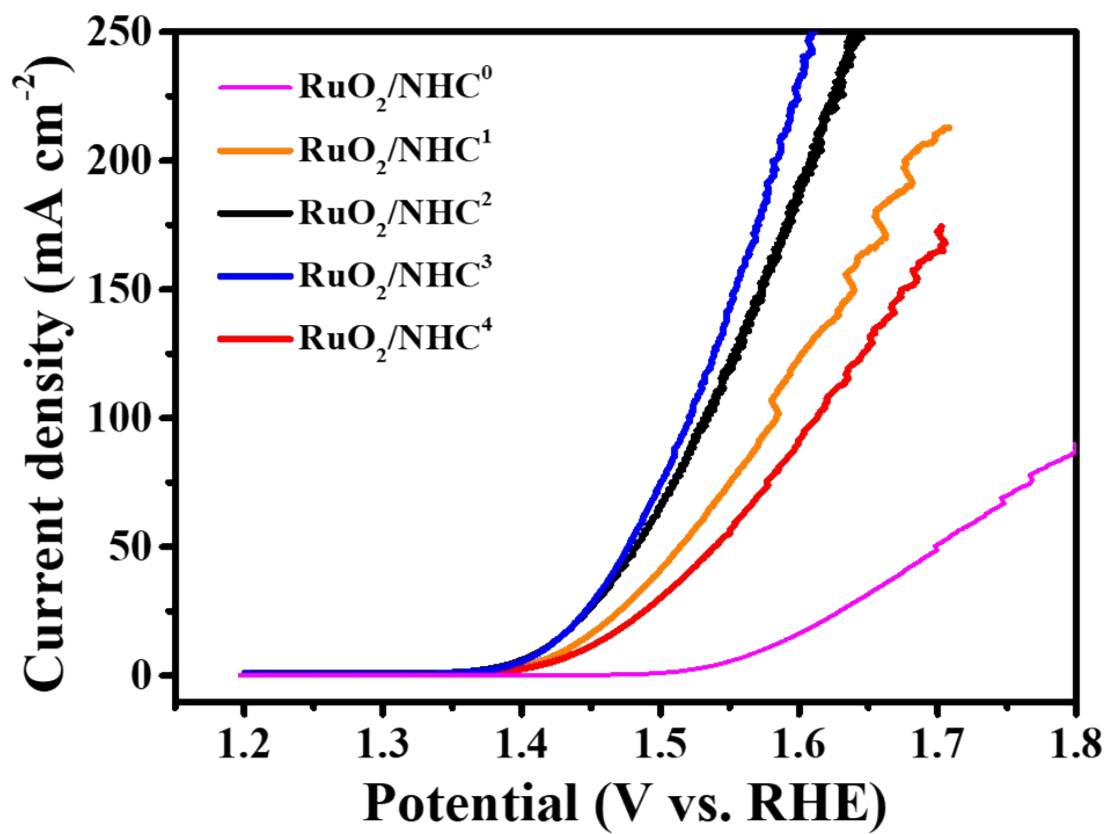


Fig S12. Polarization curves of RuO<sub>2</sub>/NHC<sup>0</sup>, RuO<sub>2</sub>/NHC<sup>1</sup>, RuO<sub>2</sub>/NHC<sup>2</sup>, RuO<sub>2</sub>/NHC<sup>3</sup>, RuO<sub>2</sub>/NHC<sup>4</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

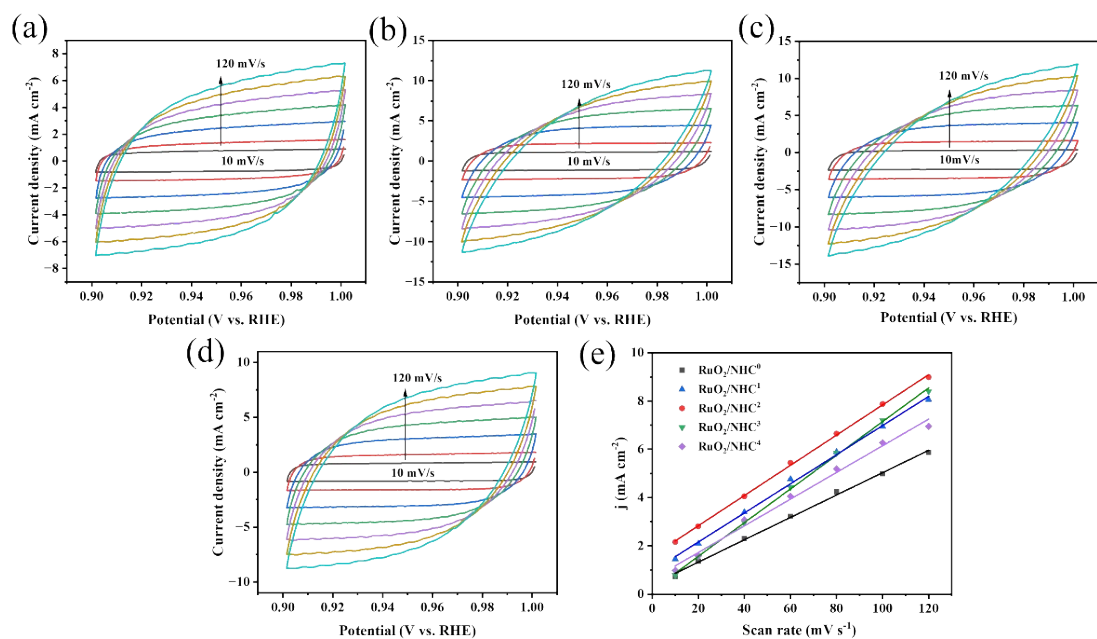


Fig S13. CV curves of a) RuO<sub>2</sub>/NHC<sup>0</sup>, b) RuO<sub>2</sub>/NHC<sup>1</sup>, c) RuO<sub>2</sub>/NHC<sup>2</sup> and d) RuO<sub>2</sub>/NHC<sup>4</sup> e) Current density as a function of the scan rate for different samples for OER.

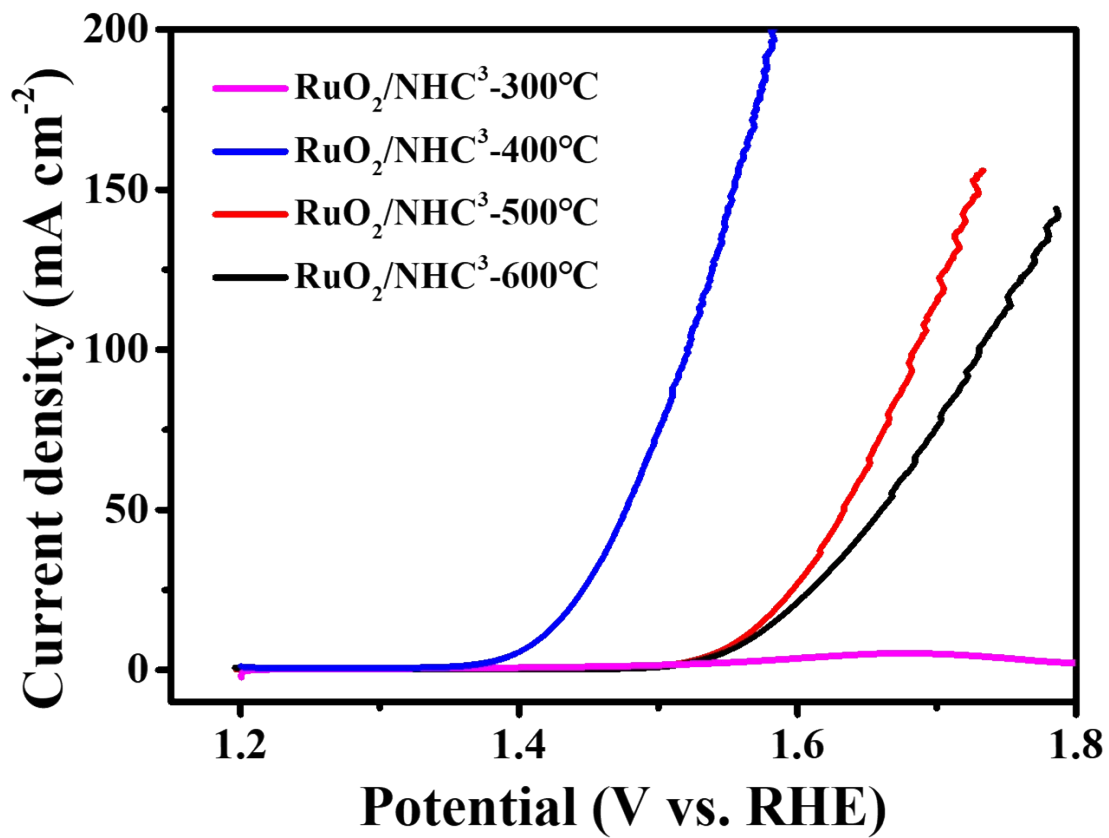


Fig S14. Polarization curves of RuO<sub>2</sub>/NHC<sup>3</sup>-300 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-400 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-500 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-600 °C.

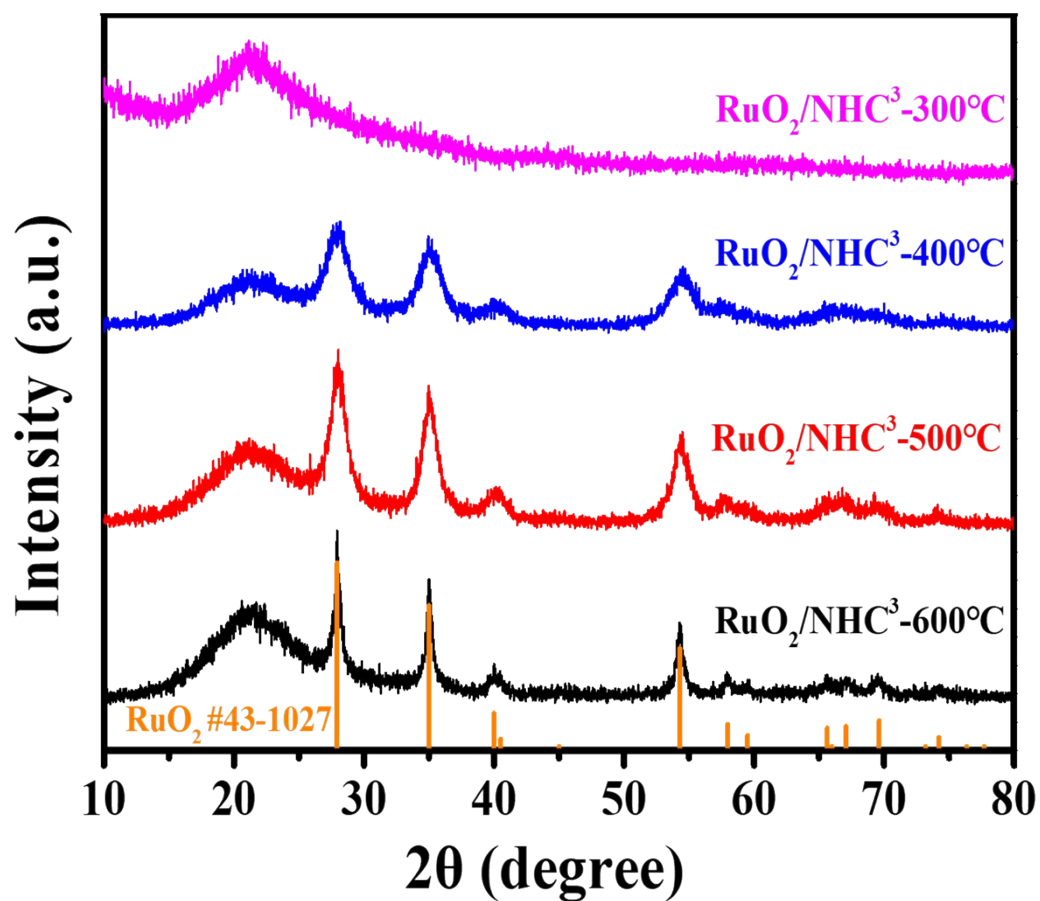


Fig S15. XRD pattern of RuO<sub>2</sub>/NHC<sup>3</sup>-300 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-400 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-500 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-600 °C.



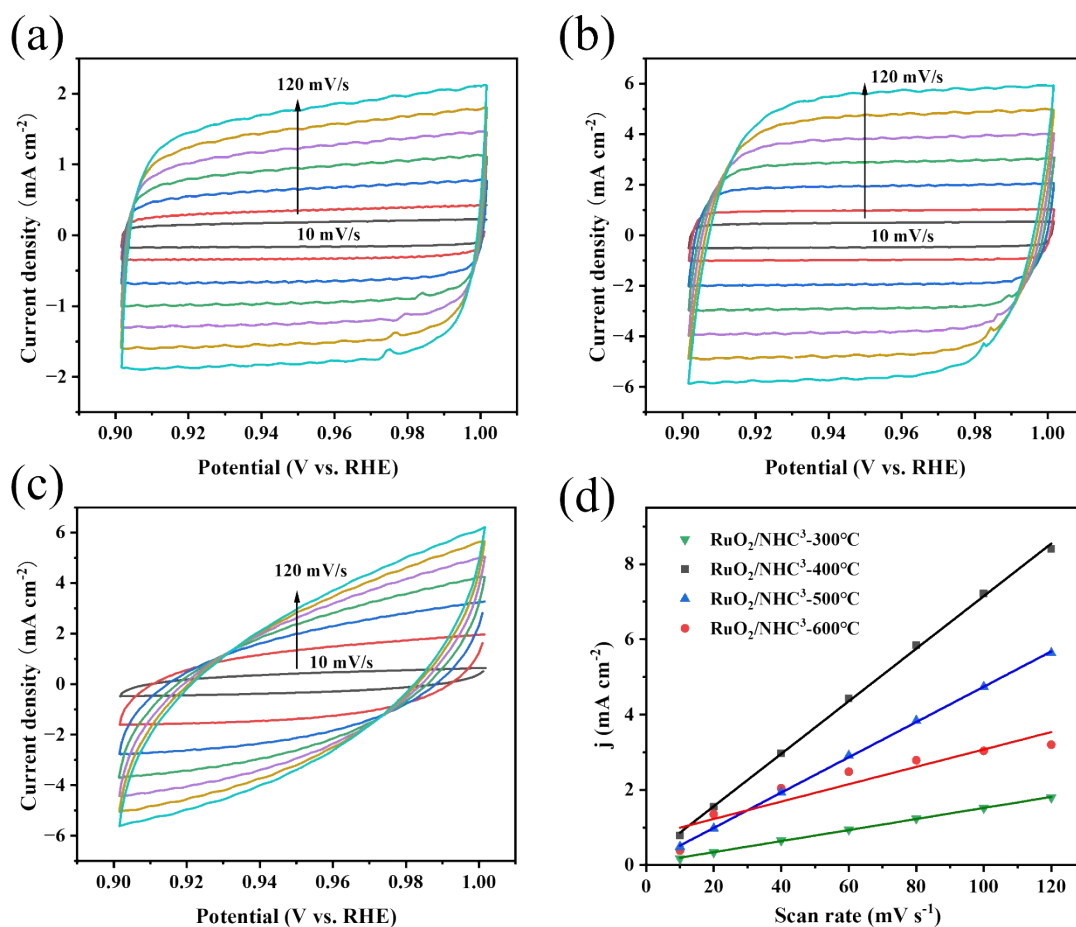


Fig S16. CV curves of a) RuO<sub>2</sub>/NHC<sup>3</sup>-300 °C, b) RuO<sub>2</sub>/NHC<sup>3</sup>-500 °C, c) RuO<sub>2</sub>/NHC<sup>3</sup>-600 °C and d) Current density as a function of the scan rate for different samples for OER.

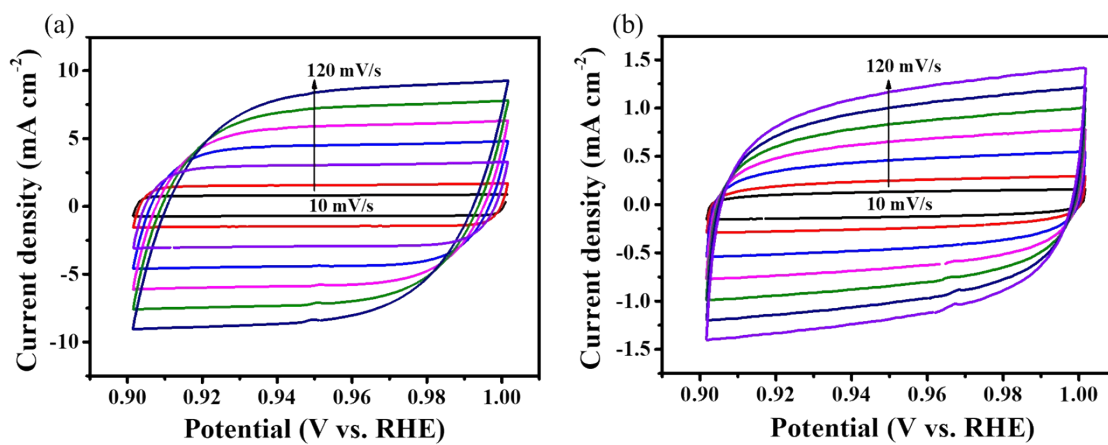


Fig S17. CVs measured at different scan rates from 10 to 120 mV/s of (a)  $\text{RuO}_2/\text{NHC}^3$  and (b)  $\text{RuO}_2$ .

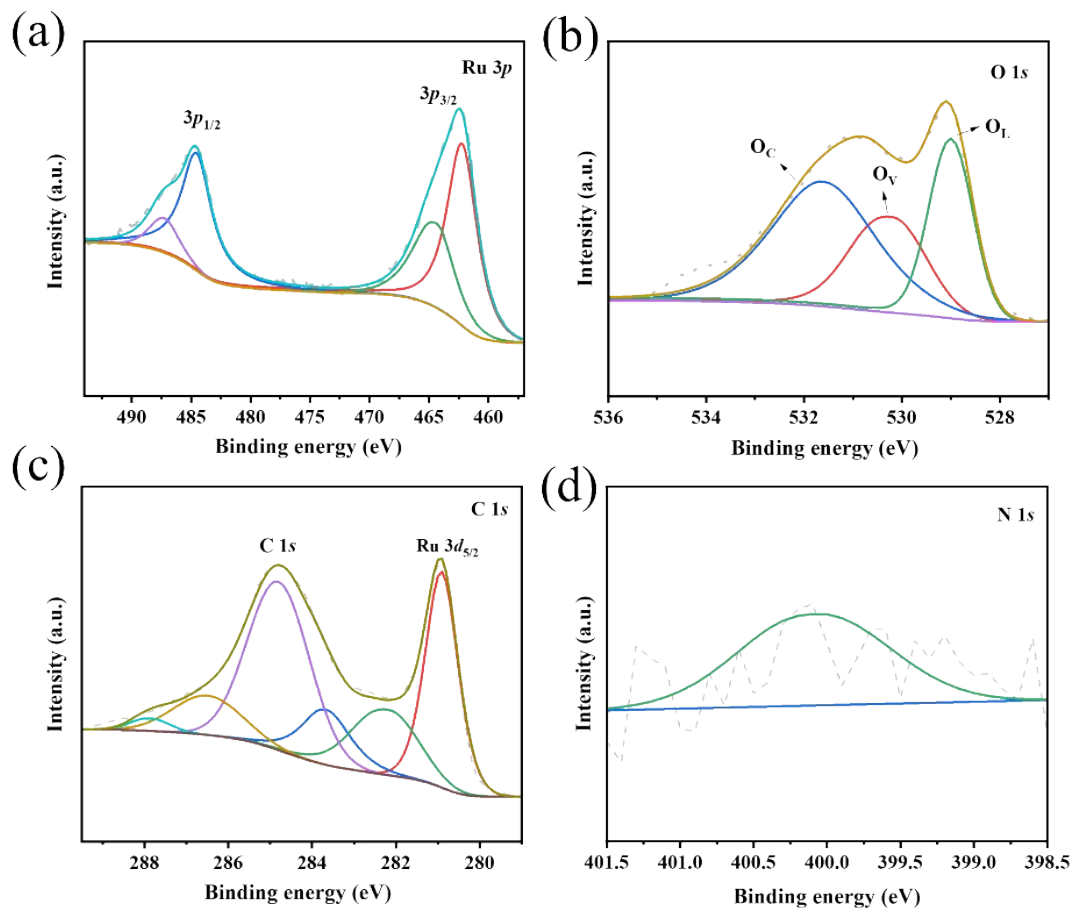


Fig S18. a) Ru 3p, b) O 1s, c) C1s and d) N 1s XPS spectra of RuO<sub>2</sub>/NHC<sup>3</sup> after long time chronopotentiometry test.

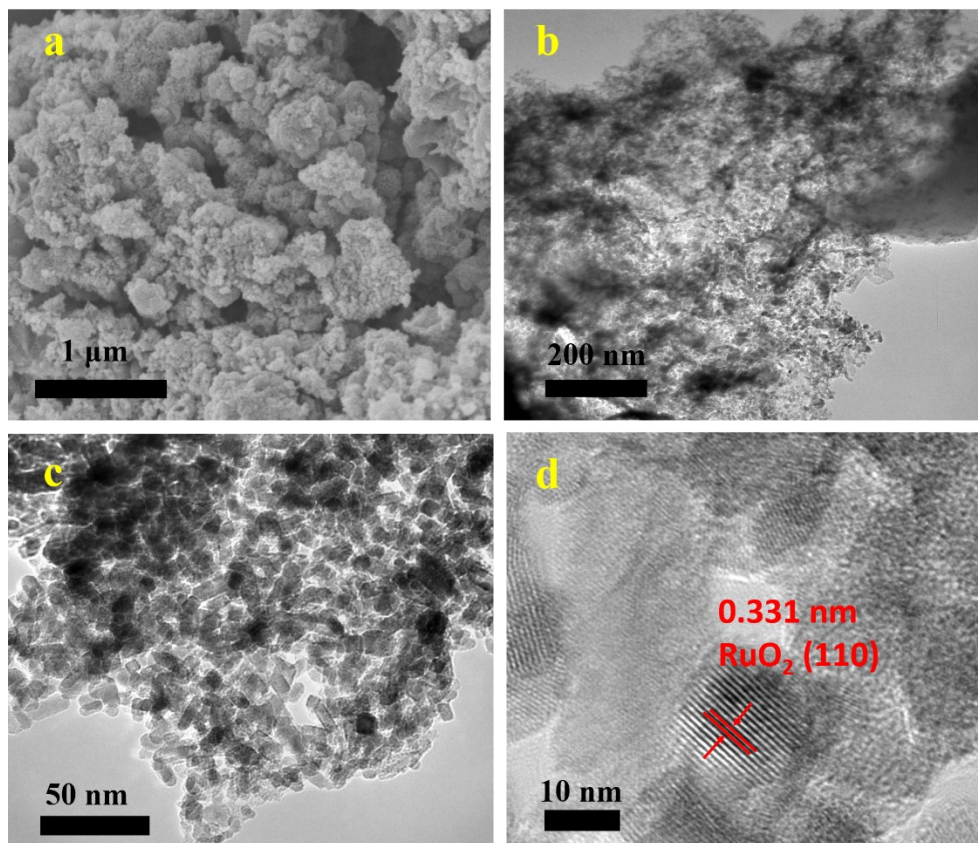


Fig S19. a) SEM, b-c) TEM image and d) HR-TEM image of RuO<sub>2</sub>/NHC<sup>3</sup> after long time chronopotentiometry test.

Table S1. BET surface area and overpotential at 10 mA/cm<sup>2</sup> of various samples.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Sample	η <sub>10</sub> (mV)
NPG	4	RuO <sub>2</sub> /NPG	NA
NHC <sup>0</sup>	468	RuO <sub>2</sub> /NHC <sup>0</sup>	344
NHC <sup>1</sup>	1563	RuO <sub>2</sub> /NHC <sup>1</sup>	202
NHC <sup>2</sup>	1894	RuO <sub>2</sub> /NHC <sup>2</sup>	185
<b>NHC<sup>3</sup></b>	<b>2107</b>	<b>RuO<sub>2</sub>/NHC<sup>3</sup></b>	<b>186</b>
NHC <sup>4</sup>	2998	RuO <sub>2</sub> /NHC <sup>4</sup>	215

Table S2. The  $C_{dl}$  and ECSA of RuO<sub>2</sub>/NHC<sup>0</sup>, RuO<sub>2</sub>/NHC<sup>1</sup>, RuO<sub>2</sub>/NHC<sup>2</sup>, RuO<sub>2</sub>/NHC<sup>3</sup> and RuO<sub>2</sub>/NHC<sup>4</sup> for OER.

Sample	$C_{dl}$ (mF/cm <sup>2</sup> )	ECSA (cm <sup>2</sup> /mg)
RuO <sub>2</sub> /NHC <sup>0</sup>	46.3	1157.5
RuO <sub>2</sub> /NHC <sup>1</sup>	60.3	1507.5
RuO <sub>2</sub> /NHC <sup>2</sup>	62.6	1565
<b>RuO<sub>2</sub>/NHC<sup>3</sup></b>	<b>69.8</b>	<b>1745</b>
RuO <sub>2</sub> /NHC <sup>4</sup>	55.3	1382.5

Table S3. The  $C_{dl}$  and ECSA of RuO<sub>2</sub>/NHC<sup>3</sup>-300 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-400 °C, RuO<sub>2</sub>/NHC<sup>3</sup>-500 °C and RuO<sub>2</sub>/NHC<sup>3</sup>-600 °C for OER.

Sample	$C_{dl}$ (mF/cm <sup>2</sup> )	ECSA (cm <sup>2</sup> /mg)
RuO <sub>2</sub> /NHC <sup>3</sup> -300 °C	14.7	367.5
<b>RuO<sub>2</sub>/NHC<sup>3</sup>-400 °C</b>	<b>69.8</b>	<b>1745</b>
RuO <sub>2</sub> /NHC <sup>3</sup> -500 °C	46.9	1172.5
RuO <sub>2</sub> /NHC <sup>3</sup> -600 °C	23.1	577.5

Table S4. Parameters of  $R_s$  and  $R_{ct}$  acquired through fitting EIS spectra.

electrocatalyst	$R_s$ (ohm)	$R_{ct}$ (ohm)
<b>RuO<sub>2</sub>/NHC<sup>3</sup></b>	<b>1.60</b>	<b>0.4189</b>
RuO <sub>2</sub>	1.898	5.04
NHC <sup>3</sup>	19.98	1.716



Table S5. Comparison of the Ru-based electrocatalysts reported in representative literature under acidic electrolyte.

Catalysts	Electrolyte	$\eta(\text{mV})$ at 10 $\text{mA}/\text{cm}^2$	Stability	Ref
<b>RuO<sub>2</sub>/NHC<sup>3</sup></b>	<b>0.5 M H<sub>2</sub>SO<sub>4</sub></b>	<b>186</b>	<b>27 h at 10 mA/cm<sup>2</sup></b>	<b>This work</b>
RuCo@NG/N-GNs	0.5 M H <sub>2</sub> SO <sub>4</sub>	209	10 h at 10 mA/cm <sup>2</sup>	1
1D-RuO <sub>2</sub> -CN <sub>x</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	250	lost ~32% current after 55 h of scan	2
IrO <sub>2</sub> -BN-rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	300	45 h at 10 mA/cm <sup>2</sup> and 5 mA/cm <sup>2</sup>	3
NaRuO <sub>2</sub> nanosheets	0.1 M HClO <sub>4</sub>	255	6 h at 1 mA/cm <sup>2</sup>	4
Cu-doped RuO <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	188	8 h at 10 mA/cm <sup>2</sup>	5
a/c RuO <sub>2</sub>	0.1 M HClO <sub>4</sub>	205	60 h at 10 mA/cm <sup>2</sup>	6
Cr <sub>0.6</sub> Ru <sub>0.4</sub> O <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	178	10 h at 10 mA/cm <sup>2</sup>	7
RuO <sub>2</sub> /(Co, Mn) <sub>3</sub> O <sub>4</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	270	24 h at 10 mA/cm <sup>2</sup>	8
Sn-RuO <sub>2</sub> @NPC	0.5 M H <sub>2</sub> SO <sub>4</sub>	178	150 h at 10 mA/cm <sup>2</sup>	9
COOH-MWNTs	0.5 M H <sub>2</sub> SO <sub>4</sub>	265	10 h at 10 mA/cm <sup>2</sup>	10
2D D-RuO <sub>2</sub> /G	0.5 M H <sub>2</sub> SO <sub>4</sub>	169	2000 cycles	11
RuB <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	223	10 h at 10 mA/cm <sup>2</sup>	12
Ru@IrO <sub>x</sub>	0.05 M H <sub>2</sub> SO <sub>4</sub>	282	24h at 1.55 V	13
RuMn NSBs	0.5 M H <sub>2</sub> SO <sub>4</sub>	196	125 h at 10 mA/cm <sup>2</sup> for RuMn NSBs-250  RuMn NSBs-300	14
3D Ru/RuO <sub>2</sub> @N-rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	234	10 h at 10 mA/cm <sup>2</sup> in 1.0 M KOH for Ru/RuO <sub>2</sub> @N-rGO  Ru/RuO <sub>2</sub> @N-rGO	15
Zn-doped RuO <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	206	30 h at 10 mA/cm <sup>2</sup>	16

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