Electronic Supplementary Information (ESI)

Hierarchically interconnected nitrogen-doped carbon nanosheets for efficient hydrogen evolution reaction

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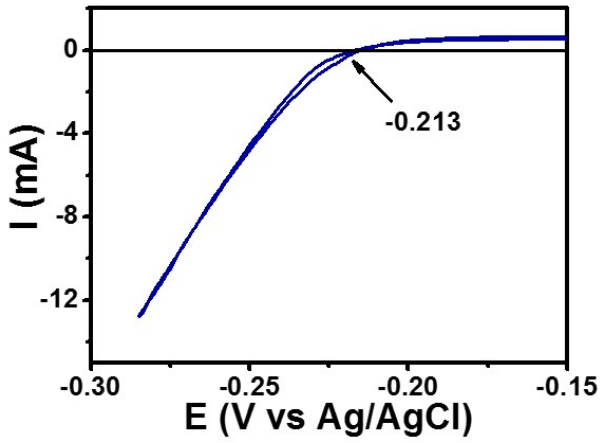

Fig. S1 Calibration of Ag/AgCl reference electrode in 0.5 M H_2SO_4. The reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE). The calibration was conducted in a H_2-saturated electrolyte with Pt wires as both the working electrode and counter electrode. CVs were performed at a scan rate of 1 mV s^{-1}, and the averaged value of the two potentials at which the anodic and cathodic scan crossed zero current was taken to be the thermodynamic potential for the hydrogen electrode reaction. Accordingly, E (RHE) = E (Ag/AgCl) + 0.213 V.

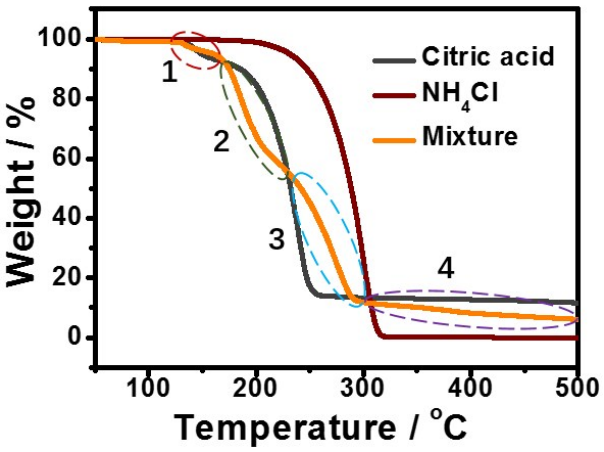

Fig. S2 Thermogravimetry (TG) analysis of the citric acid-ammonium chloride (NH_4Cl) mixture independently compared with citric acid and NH_4Cl. The TG curve of the mixture can be devided into four regions: where 1) the crystal water in citric acid evaropated; 2) citric acid dehydrated; 3) NH_4Cl decomposed; and 4) the gas-foamed carbon was further carbonized and NCNS was finally obtained.

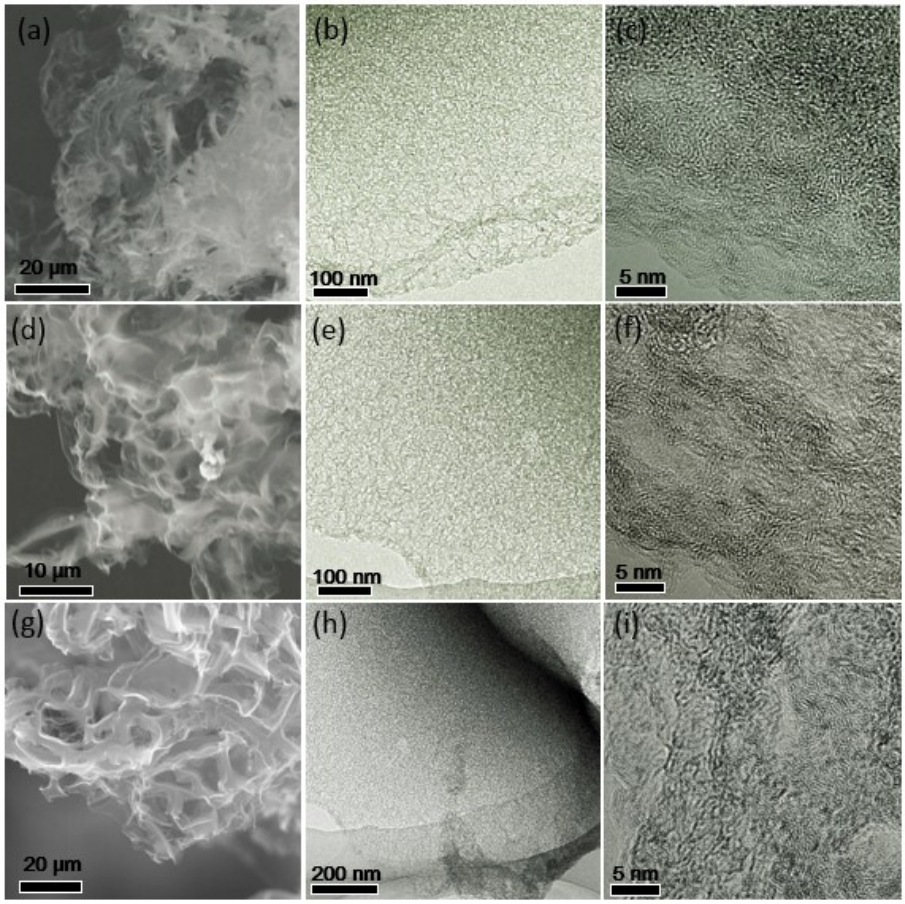

Fig. S3 SEM and TEM images of (a-c) NCNS-800, (d-f) NCNS-900 and (g-i) NCNS-1100, respectively, showing similar morphology compared to that of NCNS.

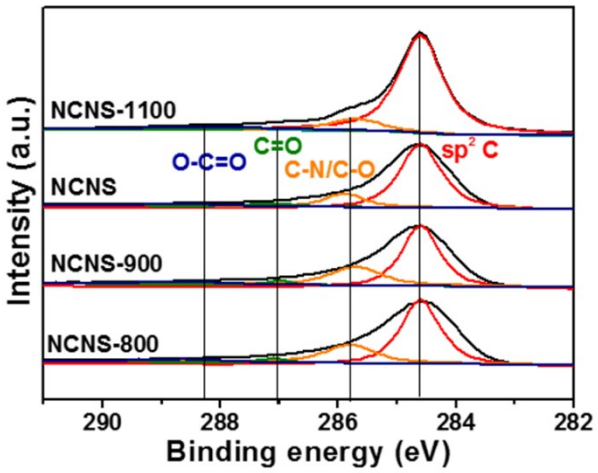

Fig. S4 High-resolution C 1s XPS spectra of the samples. The main peak centred at about 284.6 eV is attributed to the graphitic sp^2 carbon whereas the additional component centred at 285.6 eV is assigned to C−N. The weak peak at 287.3 eV could be assigned to C=O while the broad band at 288.4 eV may ascribe to typical O−C=O.

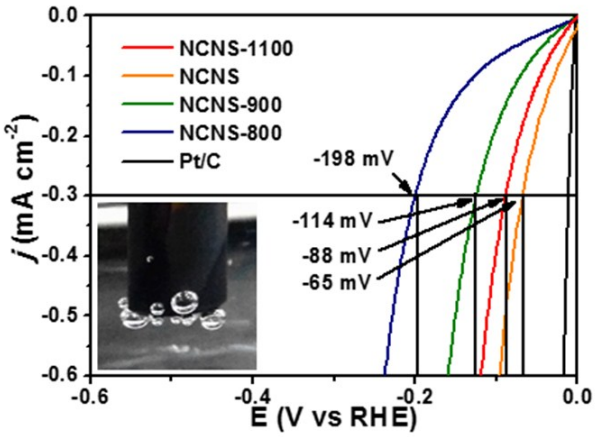

Figure S5 The enlarged view of the LSVs in the Figure 3a. Inset is the photograph of the obvious hydrogen bubbles generated on the NCNS-1000 modified glassy carbon electrode during the LSV scanning.

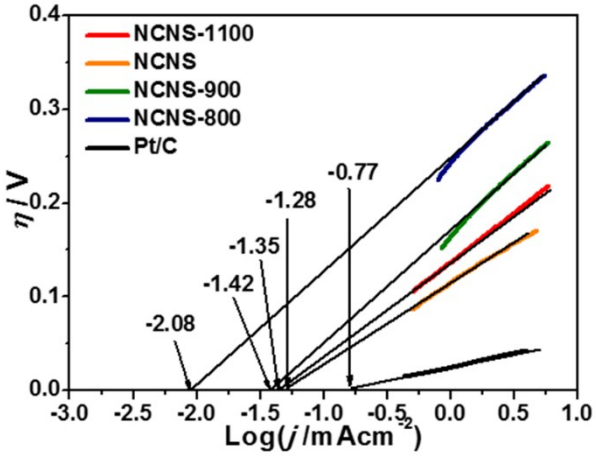

Fig. S6 Tafel plots of these catalysts. To obtain the exchange current density, the Tafel plots are extrapolated to the j axis.

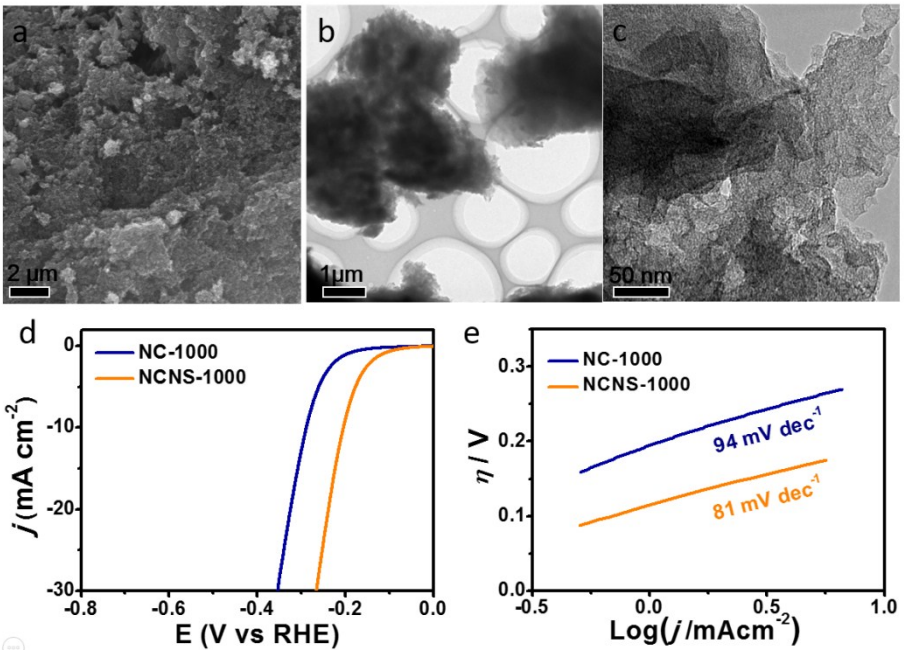

Fig. S7 SEM (a), TEM (b, c) images of NC-1000. LSV (d) and corresponding Tafel plots (e) for NC-1000 and NCNS-1000 in 0.5 M H_2SO_4.

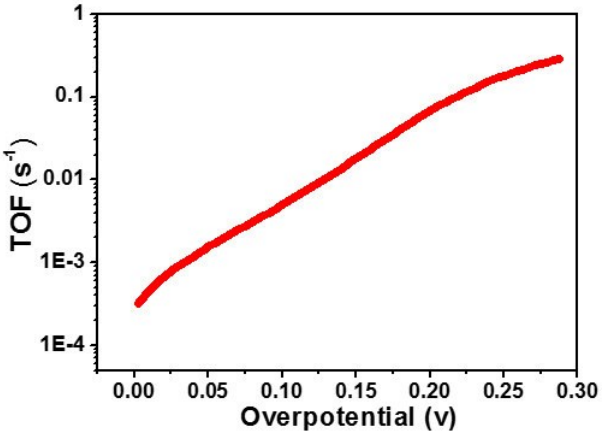

Fig. S8 Turnover frequency plot vs. overpotential in acidic medium for NCNS. Turnover frequency (TOF) is calculated as below:

The per-site TOF value was calculated according to the following equation:

TOF (H_2/s) = total hydrogen turnovers per geometric area/ active sites per geometric area (1)

The number of total hydrogen turnovers was calculated from the current density extracted from the LSV polarization curve according to:

total hydrogen turnovers = (j mA/cm^{-2}) ((1C/s)/1000mA) (1 mol e$^-$/(96485.3 C)) ((1 mol)/2 mol e$^-$) ((6.022×10^{23}) / (1 mol H_2)) = 3.12×10^{15} (H_2/s)/cm^2 per mA/cm^2 (2)

The number of active sites in NCNS catalyst was calculated from the mass loading on the glassy carbon electrode, the graphitic N contents (calculated form the atomic contant, which is determined to be 3.41 wt%) and the graphitic N atomic weight, assuming each graphitic N center accounts for one active site:

active sites = ((catalyst loading per geometric area ((x g)/cm^2) × N wt%)/(N M_W

(g⁄mol)))((6.022×10^{23} N atoms)/(1 mol N)) = ((0.286 × 10^{-3} g⁄cm^2 × 3.41 wt%)/(14 g⁄mol))((6.022×10^{23} N atoms)/(1 mol N)) = 4.2 × 10^{17} N sites per cm^2 (3)

Finally, the current density from the LSV polarization curve can be converted into TOF values according to:

TOF = ((3.12 × 10^{15})/(4.2 × 10^{17})) × j = 0.0074 × j.

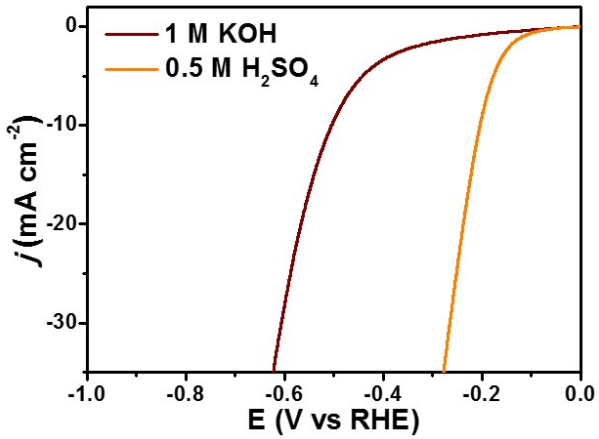

Fig. S9 The LSV curves of NCNS-1000 in 0.5 M H_2SO_4 (acid) and 1 M KOH (alkaline), respectively.

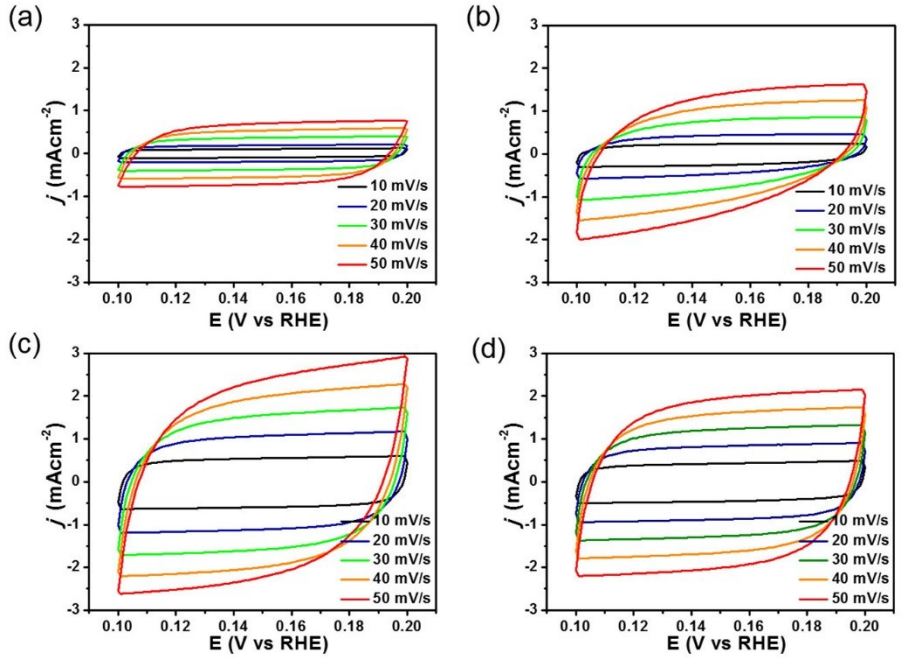

Fig. S10 Cyclic voltammograms of NCNS-800 (a), NCNS-900 (b), NCNS (c) and NCNS-1100 (d) under different scan rates in 0.5 M H_2SO_4. The C_{dl} is estimated by plotting the Ja-Jc at 0.15 V (vs. RHE) against the scan rate, where the slope is twice that of C_{dl}.

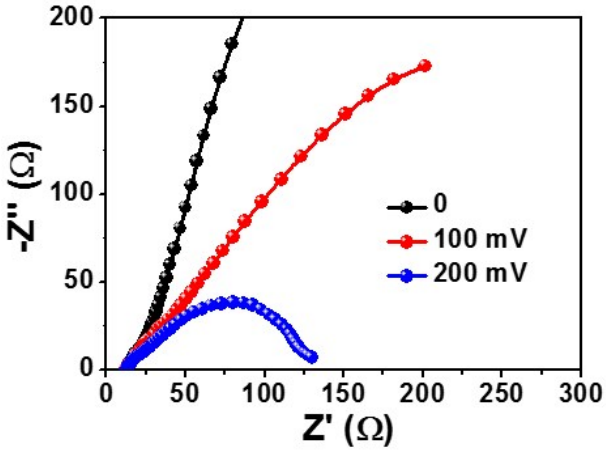

Fig. S11 Electrochemical impedance spectra of NCNS-1000 in 0.5 M H_2SO_4 at overpotentials of 0, 100, 200 mV, respectively.

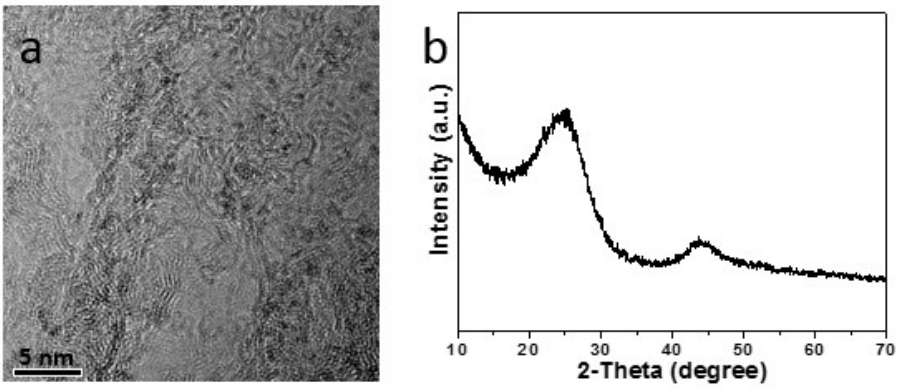

Fig. S12 TEM image and XRD pattern of NCNS-1000 after HER long-term stability test. Note that the long-term stability test was carried out by depositing the sample on the nickel foam. After the operation, the sample was collected by sonication and then characterized by XRD.

Table S1 Element composition for the three samples.

Element	*C (at%)*	*N (at%)*	*O (at%)*
NCNS-1100	90.7	3.7	5.6
NCNS-1000	88.1	5.4	7.4
NCNS-900	85.9	5.9	8.2
NCNS-800	83.9	6.3	9.8

Table S2. Comparison of HER performance for N-doped carbon metal-free catalysts.

Catalysts	η_0 *(mV)*	η_{10} *(mV)*	*b (mV dec^{-1})*	j_0 *(μA cm^{-2})*	*Ref.*
NCNS-1000	-65	203	81	50	This work
N,S- graphene	-130	280	80.5	--	1

C_3N_4@NG	<-100	240	51.5	0.35	2
N,P-C network	-60	~180	89	160	3
N,P-graphene	<-200	420	91	0.24	4
g-C_3N_4 NRs-G	-80	207	54	39.8	5
PNC	-4	62	45.9	--	6
NHC	-65	180	--	--	7

η_0: onset potential.

η_{10}: overpotential at current density of 10 mA cm^{-2}.

b: Tafel slope.

j_0: exchange current density.

References

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