Supplementary Data

Ball-milling synthesis of N-graphyne with controllable nitrogen doping sites for efficient electrocatalytic oxygen evolution and supercapacitor

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1. Calculation

1) The calculated process of electrochemical surface area:

The electrochemical surface area (ECSA) is calculated by the measured double layer capacitance (Cdl) of the catalysts surface. In a typical procedure, a potential range in which no apparent Faradaic processes happened was determined from static CV. All measured current in this non-Faradaic potential region is hypothesized to be owing to double-layer charging. The charging current ic was measured from the CVs at different scan rates, as displayed in Figure S1. The relation between ic, C_{dl}, and scan rate (v) is as follows ,

$$i_c = \nu C_{dl}$$

Hence, the slope of ic as a function of v gives a straight line with a slope equal to Cdl (Figure 4d).

The ECSA of a catalyst sample is calculated from the Cdl according to the equation,

$$\text{ECSA}=\frac{C_{dl}}{C_s}$$

where C_s is the specific capacitance of the sample. The C_s is equal to 0.040 mF cm^{-2} in 1 M KOH according to the previous reports.

2) The calculation of Gibbs free energy change:

The thermodynamic feasibility for the synthesis of N-graphyne using CaC_2 and Pyrazine is examined by the calculation of Gibbs free energy change. One molecule (N) N-graphyne and 2N CaH_2 formed by N pyrazine molecule and 2N CaC_2 are supposed as a model. Moreover, E, N, and N_A represent the bond energy of chemical bond, the number of atoms, and avogadro constant, respectively.

Enthalpy change:

$$\Delta H = H_{N-graphyne} - H_{pyrazine} - H_{CaC_2} + H_{CaH_2}$$

$$= \frac{6N}{N_A}(E_{\text{pyrazine}} + E_{C-C} - E_{\text{pyrazine}} - E_{C-H}) + \frac{3N}{N_A}(\Delta H_{CaH_2} - \Delta H_{CaC_2})$$

$$= \frac{4N}{N_A}(332 - 414) + \frac{2N}{N_A}(-181.5 + 62.8)$$

$$= -565.4\frac{N}{N_A}KJ$$

This reaction is an exothermic reaction.

Eutropy change:

$$\Delta S = S_{N-graphyne} - S_{\text{pyrazine}} + S_{CaH_2} - S_{CaC_2} + \Delta S_{mix}$$

$$= \frac{1}{N_A}\Delta_f S_{N-graphyne} - \frac{N}{N_A}\Delta S_{pyrazine} + 2\frac{N}{N_A}(\Delta S_{CaH_2} - \Delta S_{CaC_2}) + \Delta S_{mix}$$

$$= \frac{1}{N_A}\Delta S_{N-grapyne} - \frac{N}{N_A}\Delta S_{pyrazine} + 2\frac{N}{N_A}(41.4 - 70.3) + \Delta S_{mix}$$

$$= \frac{1}{N_A}\Delta S_{N-graphyne} - 61\frac{N}{N_A} + \Delta S_{mix}(J/K)$$

Thereinto,

$$\Delta S_{mix} = k\ln\frac{(3N+1)!}{3N!} - k\ln\frac{(N+3N)}{(3N)!\cdot N!} = k\ln(3N+1) - \ln\frac{4^4}{3^3}\ln(J/K)$$

Gibbs free energy change:

ΔG=ΔH-TΔS

$$=-565400\frac{N}{N_A}-\frac{T}{N_A}\Delta S_{N-graphyne}+61\frac{N}{N_A}+kT\ln(3N+1)-\ln\frac{4^4}{3^3}KNT$$

$$=-\frac{T}{N_A}\Delta S_{N-graphyne}-kT\ln(3N+1)-kN(\frac{565400}{R}-\frac{61T}{R}-\ln\frac{4^4}{3^3}T)$$

Thereinto:

$$-\frac{T}{N_A}\Delta S_{N-graphyne}<0$$

$$-kT\ln(3N+1)<0$$

When T < 9000 K,

$$-kN(\frac{565400}{R}-\frac{61T}{R}-\ln\frac{4^4}{3^3}T)<0$$

That is ΔG < 0.

Thus, the reaction should be a spontaneous process in common temperature.

2. Characterization

Figure S1

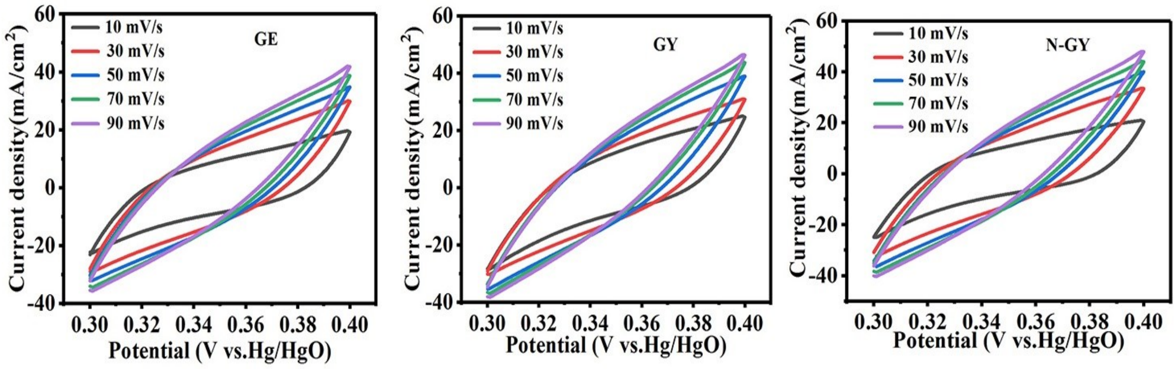

Figure S1. Cyclic voltammetry (CV) curves of graphene (GE), γ-graphyne (GY), and N-graphyne (N-GY) with different scan rates (10-90 mV/s) in the region of 0.30-0.40 V (vs. Hg/HgO)

Table S1 Electrocatalysts for OER

Electrocatalysis materials	Electrolyte	Current density	Overpotential (mV)	Tafel slope (mV/dec)	References
$Co_3(OH)_2(HPO_4)_2$/NF	1M KOH	100 mA/cm^2	240	69	S1
Ni_2P-VP_2/NF	1M KOH	100 mA/cm^2	398	49	S2
NiTe/NiS	1M KOH	100 mA/cm^2	104	49	S3
$NdNiO_3$	0.1M KOH	100 mA/cm^2	350	45.9	S4
NiCo/$NiCo_2S_4$/NiCo @NF	1M KOH	100 mA/cm^2	294	60	S5
Ni-Fe-OH/Ni_3S_2@NF	1M KOH	100 mA/cm^2	310	93	S6
NiFe Nanosheet @NF	1M KOH	100 mA/cm^2	290	52	S7
$Na_{1-x}Ni_yFe_{1-y}O_2$ @NF	1M KOH	100 mA/cm^2	290	44	S8
NiCoP @NF	1M KOH	100 mA/cm^2	370	116	S9
Ni_2P @NF	1M KOH	100 mA/cm^2	390	85	S10
$Ni_{0.51}Co_{0.49}P$ @NF	1M KOH	100 mA/cm^2	480	43	S11

Electrocatalysis materials	Electrolyte	Current density	Overpotential (mV)	Tafel slope (mV/dec)	References
NiFe-P @NF	1M KOH	100 mA/cm^2	240	73	S12
Ni-Fe/graphene @NF	1M KOH	100 mA/cm^2	398	39	S13
CoNiCH @NF	1M KOH	100 mA/cm^2	104	/	S14
$FeNi_2S_4$/GO @NF	0.1M KOH	100 mA/cm^2	350	66	S15
CoMoNiS @NF	1M KOH	10 mA/cm^2	113	58	S16
Fe-$NiSe_2$	1M KOH	100 mA/cm^2	350	83	S17
Au@Ni_2P	1M KOH	100 mA/cm^2	360	50	S18
IrO_2/NiO @NF	1M KOH	100 mA/cm^2	320	41.8	S19
FeOOH/$Ni(OH)_2$ @NF	1M KOH	100 mA/cm^2	250	70	S20
NCFO @NF	1M KOH	100 mA/cm^2	320	56	S21
3DG−Au-Ni_3S_2 @NF	1M KOH	100 mA/cm^2	380	150	S22
Ni_7S_6 @NF	0.1M KOH	30 mA/cm^2	280	119	S23
Ni−Tan @NF	1M KOH	100 mA/cm^2	230	33.5	S24
FeOOH/$Ni(OH)_2$ @NF	1M KOH	100 mA/cm^2	250	70	S25
WC @NF	1M KOH	100 mA/cm^2	400	52	S26
NiV LDH	1M KOH	100 mA/cm^2	280	55.3	S27

Electrocatalysis materials	Electrolyte	Current density	Overpotential (mV)	Tafel slope (mV/dec)	References
Ni_5Co_3Mo−OH @NF	1M KOH	100 mA/cm^2	290	56.4	S28
$CePO_4/NiCo_2O_4$ @NF	1M KOH	100 mA/cm^2	360	74	S29
MnPx/MoPy @NF	1M KOH	100 mA/cm^2	380	105	S30
Co-NiMoN @NF	1M KOH	100 mA/cm^2	380	73	S31
NiFe-OH @NF	1M KOH	100 mA/cm^2	228	22.6	32
$(Ni,Fe)_3S_2$/NF @NF	1M KOH	10 mA/cm^2	246	41	S33
NiO/NiS @NF	1M KOH	40 mA/cm^2	200	60	S34
FeOOH/NFG @NF	1M KOH	100 mA/cm^2	280	36.2	S35
γ-graphyne @NF	1M KOH	100 mA/cm^2	336	130	S36
N-graphyne	**1M KOH**	**100 mA/cm^2**	**285**	**122**	**This work**

Table S2 Supercapacitor electrode materials

Supercapacitor materials	Scan rate (A/g)	Capacity (F/g)	Reference
N-Doped Graphene Aerogel	0.5 A/g	112.1 F/g	S37
N, P Co-Doped Graphene	1 A/g	416 F/g	S38
N, P co-doped Graphene	0.25 A/g	202 F/g	S39
N/P codoped porous carbon-coated graphene	0.5 A/g	134 F/g	S40
NS-PCMSs	0.1 A/g	271 F/g	S41
CNSs	0.5 A/g	227 F/g	S42
Carbon nanosheets	1 A/g	241 F/g	S43
Graphene-Based Porous Materials	1 A/g	214 F/g	S44
All-In-One Flexible Graphene	2 mV/s	237 F/cm^3	S45
Alkynyl Carbon Materials	0.2 A/g	76 F/g	S46
Graphdiyne nanostructures	5A/g	41 F/g	S47
γ-graphyne	0.2 A/g	81 F/g	S48
N-graphyne	**1 A/g**	**235 F/g**	**This Work**

Table S3 The fitting results of EIS spectra

Electrodes	$R_i(\Omega/cm^2)$	CPE-T	CPE-P	$R_{ct}(\Omega/cm^2)$
GE	0.758	0.414	0.760	1.208
GY	0.774	0.277	0.823	0.393
N-GY	0.744	0.332	0.778	0.357

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