Supporting Information

Converting benzene into γ-graphyne and its enhanced electrochemical oxygen evolution performance

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1. CALCULATION

1) Calculation of Gibbs free energy change:

The thermodynamic calculation of the synthesis of γ-graphyne is supplied as follow.

A model that one γ-graphyne molecule and 3N CaH_2 are formed by N benzene molecule and 3N CaC_2 is supposed.

Enthalpy change:

$$\Delta H = H_{\gamma-graphyne} - H_{benzene} + H_{CaH_2} - H_{CaC_2}$$
$$= \frac{6N}{N_A}\left(E_{C-C(benzene)} + E_{C-C} - E_{C-C(benzene)} - E_{C-H}\right) + \frac{3N}{N_A}\left(\Delta_f H^{\theta}_{CaH_2} - \Delta_f H^{\theta}_{CaC_2}\right)$$
$$= \frac{6N}{N_A}(332 - 414) + \frac{3N}{N_A}(-181.5 + 62.8)$$
$$= -849\frac{N}{N_A}\ (kJ)$$

This reaction is an exothermic reaction.

Entropy change:

$$\Delta S = S_{\gamma-graphyne} - S_{benzene} + S_{CaH_2} - S_{CaC_2} + \Delta S_{mix}$$
$$= \frac{1}{N_A}\Delta_f S^{\theta}_{\gamma-graphyne} - \frac{N}{N_A}\Delta_f S^{\theta}_{benzene} + 3\frac{N}{N_A}\left(\Delta_f S^{\theta}_{CaH_2} - \Delta_f S^{\theta}_{CaC_2}\right) + \Delta S_{mix}$$
$$= \frac{1}{N_A}\Delta_f S^{\theta}_{\gamma-graphyne} - \frac{N}{N_A}(1733) + 3\frac{N}{N_A}(41.4 - 70.3) + \Delta S_{mix}$$
$$= \frac{1}{N_A}\Delta_f S^{\theta}_{\gamma-graphyne} - 260\frac{N}{N_A} + \Delta S_{mix}\ (J/K)$$

In which

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

Gibbs free energy change:

$$\Delta G = \Delta H - T\Delta S$$

$$= -849000\frac{N}{N_A} - \frac{T}{N_A}\Delta_f S^{\theta}_{\gamma-graphyne} + 260\frac{N}{N_A}T + kTln(3N+1) - ln\frac{4^4}{3^3}kNT$$

$$= -\frac{T}{N_A}\Delta_f S^{\theta}_{\gamma-graphyne} - kTln(3N+1) - kN(\frac{849000}{R} - \frac{260T}{R} - ln\frac{4^4}{3^3}T)$$

Define $\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$, and

$$\Delta G_1 = -\frac{T}{N_A}\Delta S_{\gamma-graphyne} < 0$$

$$\Delta G_2 = -kTln(3N+1) < 0$$

$$\Delta G_3 = -kN(\frac{849000}{R} - \frac{260T}{R} - ln\frac{4^4}{3^3}T)$$

When $T < 3043.7K$,

$\Delta G_3 < 0$, $\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 < 0$

The reaction should be a spontaneous process in common temperature.

2. CHARACTERIZATIONS

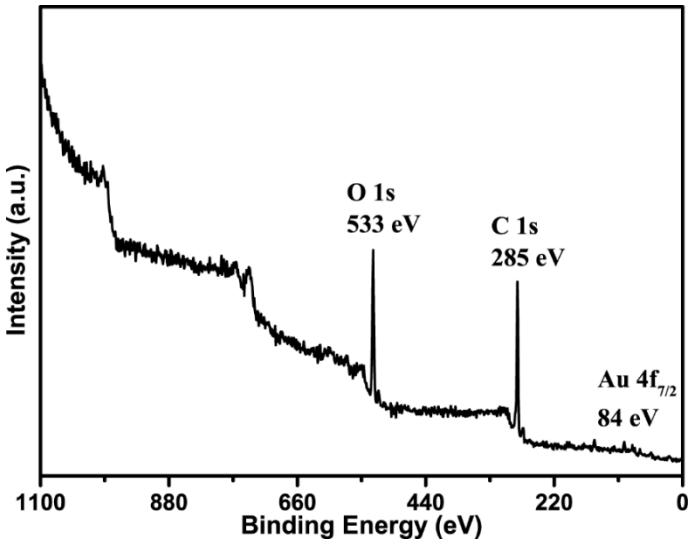

Figure S1 XPS survey spectrum of the sample.

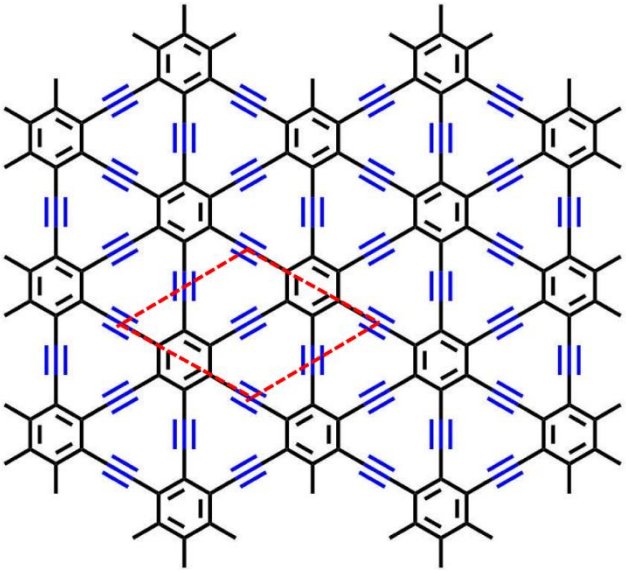

Figure S2 The chemical structural formula of γ-graphyne. (The red dashed line indicates the rhombohedral unit cell)

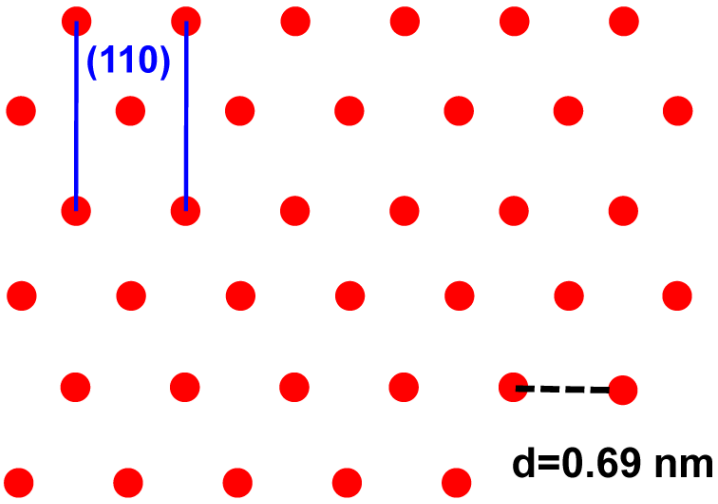

Figure S3 The crystal lattices of γ-graphyne.

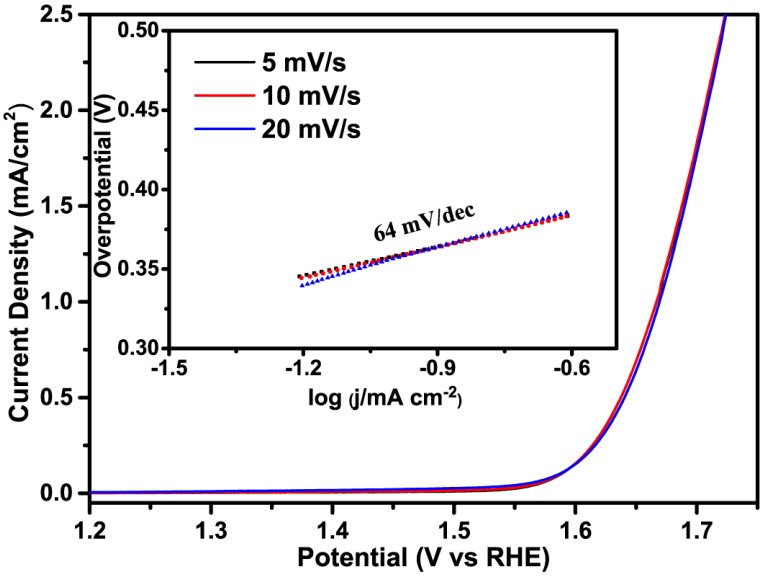

Figure S4 LSV curves of γ-graphyne/GC electrode at different scan rate in 1 mol·L^{-1} KOH electrolyte. (inset: Tafel curves)

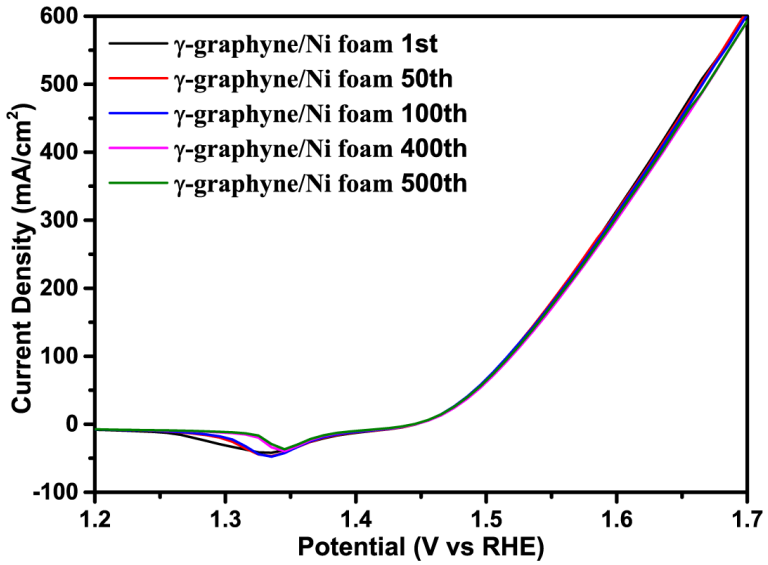

Figure S5 Negative polarization curves at different cycles for Ni foam and γ-graphyne/Ni foam electrodes in 1 mol·L^{-1} KOH solution.

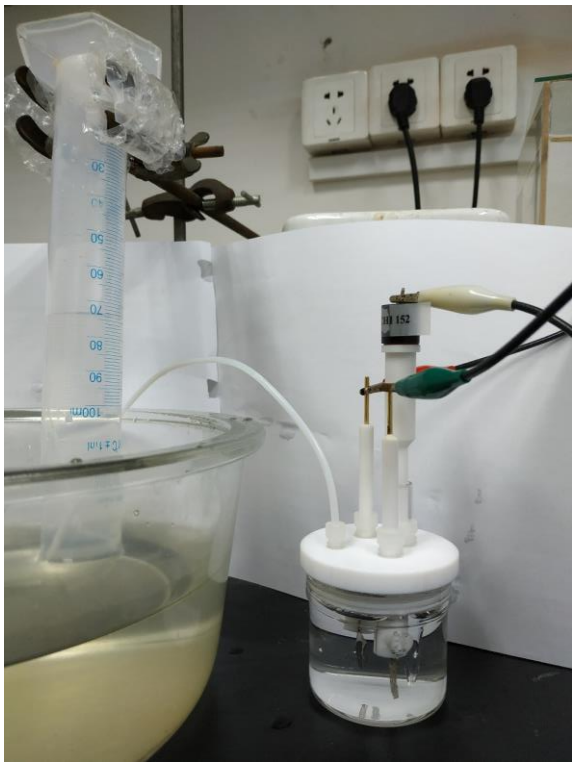

Figure S6 The gases collection device by water displacement.

Figure S7 The photo of electrolytic tank after reaction.

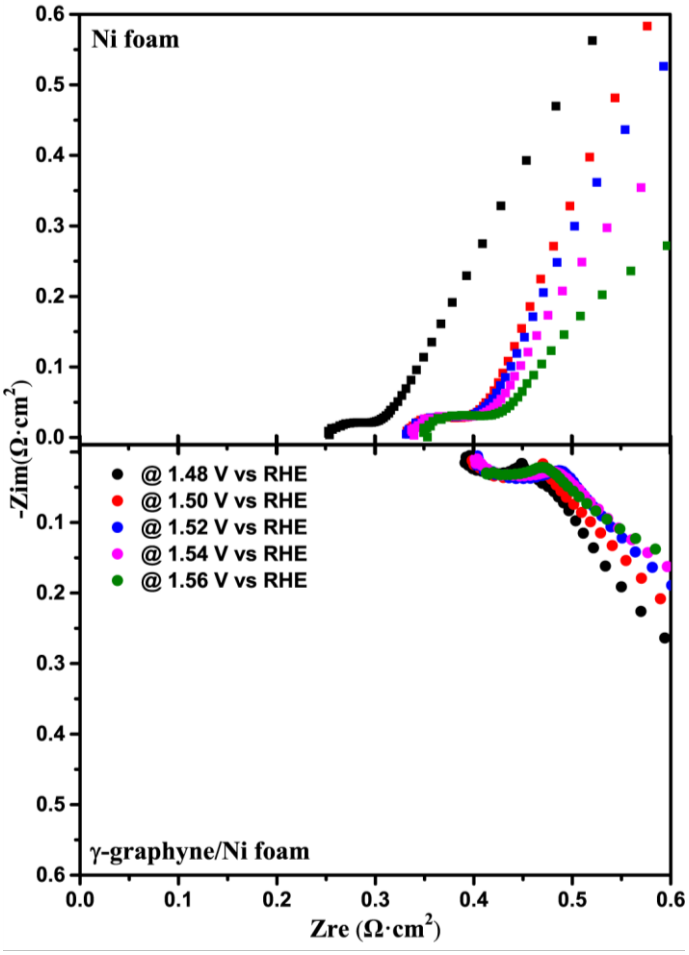

Figure S8 The enlarged view of EIS Nyquist plots (Figure 5A) at high frequencies.

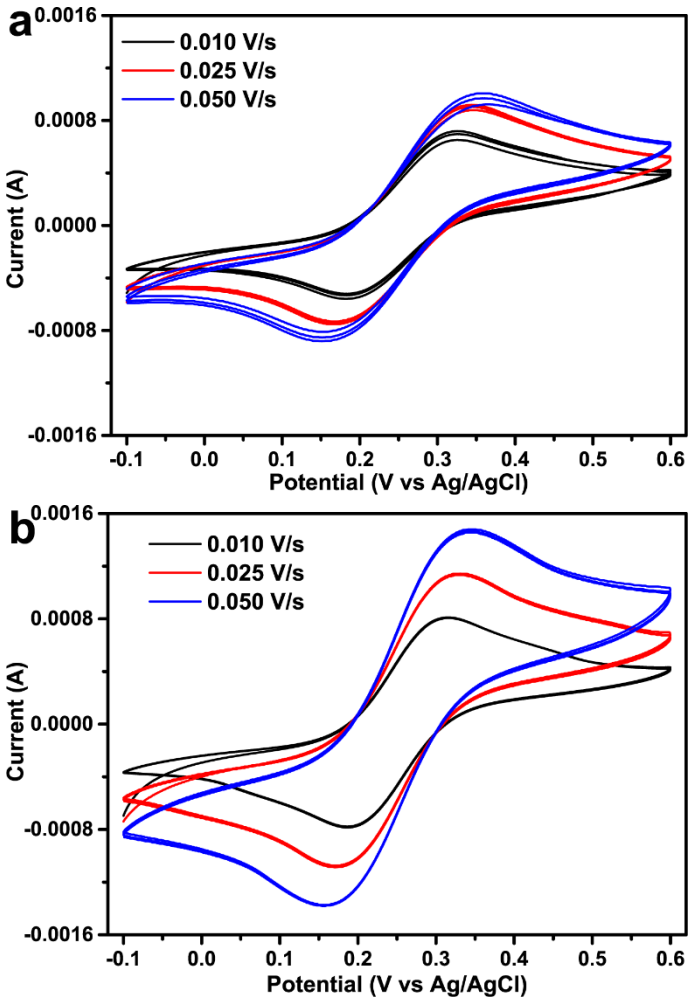

Figure S9 CV curves of (a) Ni foam and (b)γ-graphyne/Ni foam electrodes in 0.5 mol·L^{-1} $K_3Fe(CN)_6$/ $K_4Fe(CN)_6$ solution at various scan rates.

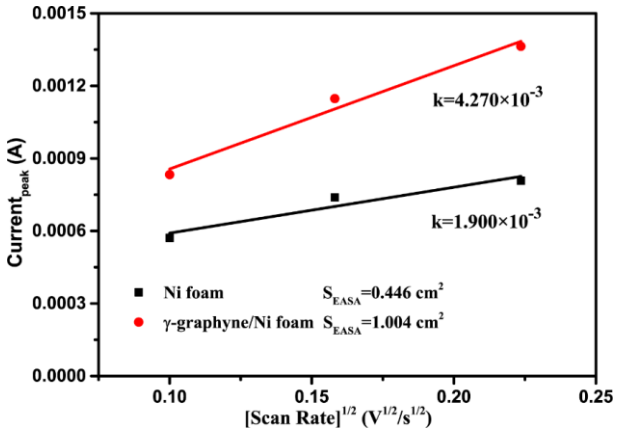

Figure S10 The linear relationship of peak current and the square root of scan rate obtained from CV curves of Ni foam and γ-graphyne/Ni foam electrodes in $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution (0.5 mmol·L^{-1}) at various scan rates.

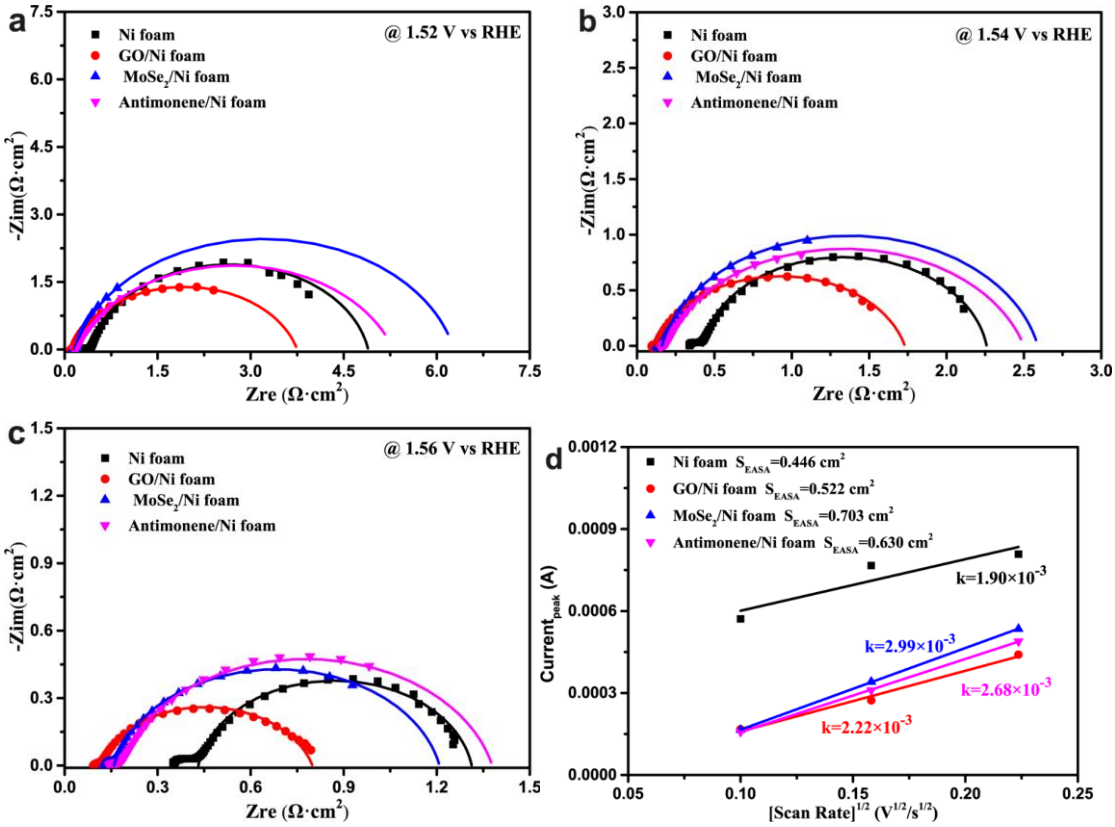

Figure S11 EIS Nyquist plots and fitting data for Ni foam, graphene oxide/Ni foam, $MoSe_2$/Ni foam and antimonene/Ni foam electrodes in 1 mol·L^{-1} KOH solution at (a) 1.52 V (vs RHE), (b) 1.54 V (vs RHE) and (c) 1.56 V (vs RHE); (d) The linear relationship of peak current and the square root of scan rate obtained from their CV curves in $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution (0.5 mmol·L^{-1}) at various scan rates.

Table S1 The fitted impedance data based on RCR equivalent circuit for γ-graphyne/GC electrode.

Electrodes	Overpotential (V)	R_i (Ω/cm^2)	CPE-T	CPE-P	R_{ct} (Ω/cm^2)
γ-graphyne/GC	0.35	0.79	0.01	0.8	165
	0.33	0.77	0.01	0.79	305
	0.31	0.71	0.01	0.77	677
	0.29	0.72	0.01	0.78	1889
	0.27	0.71	0.01	0.76	3709

Ri is internal resistance, CPE is constant phase element, Rct is the charge transfer at the working electrode/electrolyte interface.

Table S2. The fitted impedance data based on RCR equivalent circuit for Ni foam and γ-graphyne/Ni foam electrodes.

Electrodes	Overpotential (V)	R_i (Ω/cm^2)	CPE-T	CPE-P	R_{ct} (Ω/cm^2)
Ni foam	0.33	0.43	0.1	0.9	0.9
	0.31	0.41	0.1	0.91	1.8
	0.29	0.41	0.1	0.89	4.5
	0.27	0.40	0.1	0.84	12.5
	0.25	0.31	0.1	0.78	49.8
γ-graphyne/Ni foam	0.33	0.47	0.3	0.77	0.5
	0.31	0.48	0.3	0.76	0.9
	0.29	0.49	0.3	0.75	1.6
	0.27	0.47	0.3	0.73	3.6
	0.25	0.44	0.3	0.68	11.1

R_i is internal resistance, CPE is constant phase element, R_{ct} is the charge transfer at the working electrode/electrolyte interface.

Table S3 The fitted impedance data based on RCR equivalent circuit for graphene oxide(GO)/Ni foam, $MoSe_2$/Ni foam and antimonene/Ni foam electrodes.

Electrodes	Overpotential (V)	R_i (Ω/cm^2)	CPE-T	CPE-P	R_{ct} (Ω/cm^2)
GO/Ni foam	0.33	0.11	0.26	0.82	0.69
	0.31	0.12	0.27	0.84	1.61
	0.29	0.12	0.3	0.83	3.63
$MoSe_2$/Ni foam	0.33	0.16	0.66	0.87	1.05
	0.31	0.16	0.72	0.87	2.43
	0.29	0.16	0.76	0.86	6.12
antimonene/Ni foam	0.33	0.18	0.69	0.85	1.2
	0.31	0.18	0.74	0.82	2.32
	0.29	0.18	0.81	0.8	5.12

R_i is internal resistance, CPE is constant phase element, R_{ct} is the charge transfer at the working electrode/electrolyte interface.