

Electronic Supplementary Information

Ultrafine Rh nanocrystals immobilized on 3D boron and nitrogen co-doped graphene-carbon nanotube networks: high-efficiency electrocatalysts towards methanol oxidation reaction

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Supplementary Results



Fig. S1 The synthetic process for the 3D $(\text{BNG})_7-(\text{CNT})_3$ hydrogel. It includes: (1) mixture of GO suspension, CNTs and NH_4BF_4 by magnetic stirring and ultrasonic treatment; (2) generation of 3D BNG-CNT hydrogels by a solvothermal co-assembly process.

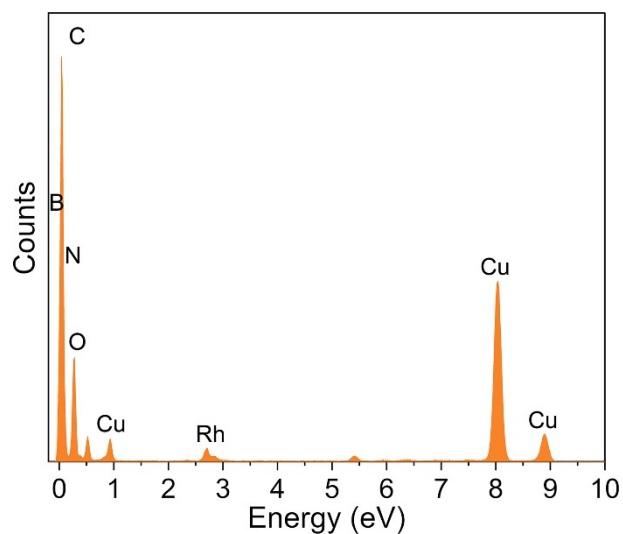


Fig. S2 EDX spectrum of 3D Rh/(BNG)₇-(CNT)₃ catalyst verifies the presence of B, N, C, and Rh components in the hybrid. Since the sample was held on a Cu grid, Cu signals were also detected.

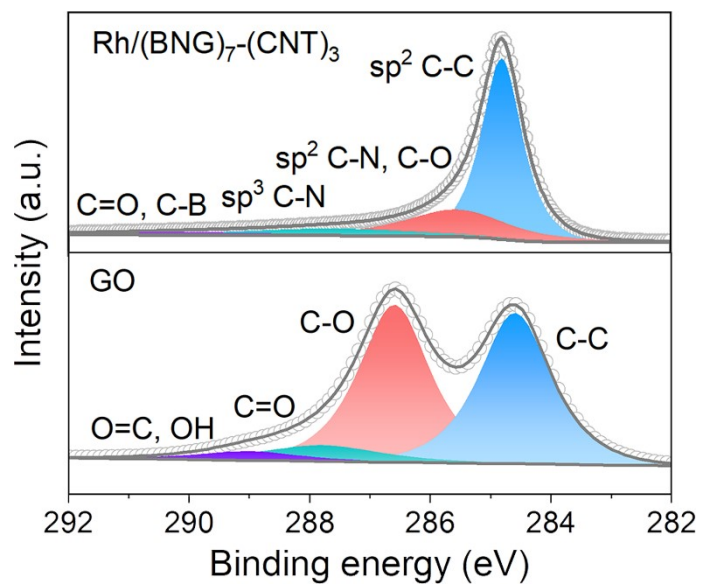


Fig. S3 High-resolution C 1s spectra of the Rh/(BNG)₇-(CNT)₃ and GO materials.

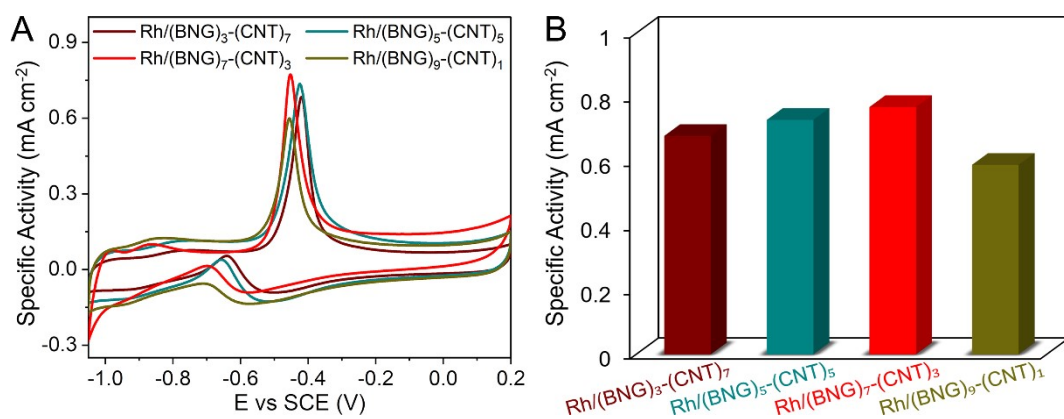


Fig. S4 (A) ECSA-normalized CV curves of Rh/BNG-CNT architectures with different BNG/CNT ratios in a mixture of 1 M KOH and 1 M CH₃OH at 50 mV s⁻¹. (B) ECSA-normalized specific activities for different catalysts.

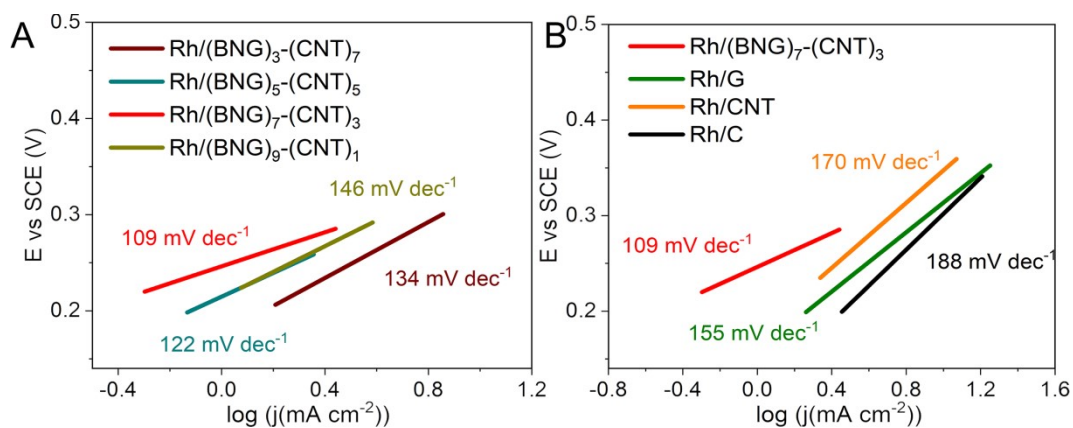


Fig. S5 Tafel curves of (A) the Rh/BNG-CNT architectures with varying BNG/CNT ratios, and (B) Rh/(BNG)₇-(CNT)₃, Rh/G, Rh/CNT, and Rh/C in a mixture of 1 M KOH and 1 M CH₃OH at 50 mV s⁻¹.

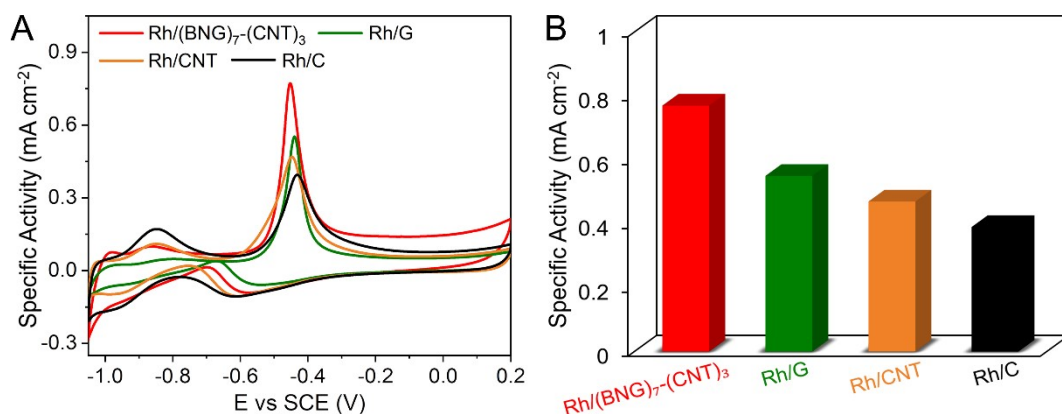


Fig. S6 (A) ECSA-normalized CV curves of the Rh/(BNG)₇-(CNT)₃ and other reference catalysts in a mixture of 1 M KOH and 1 M CH₃OH at 50 mV s⁻¹. (B) ECSA-normalized specific activities for different catalysts.

Table S1. Methanol oxidation behaviors on different catalysts.

Electrode	ECSA (m ² g ⁻¹)	Mass activity (mA mg ⁻¹)	Specific activity (mA cm ⁻²)
Rh/(BNG) ₃ -(CNT) ₇	63.3	432.5	0.68
Rh/(BNG) ₅ -(CNT) ₅	77.5	570.4	0.73
Rh/(BNG) ₇ -(CNT) ₃	105.4	814.0	0.77
Rh/(BNG) ₉ -(CNT) ₁	59.7	357.5	0.59
Rh/G	52.2	288.5	0.55
Rh/CNT	44.8	210.2	0.46
Rh/C	36.0	142.3	0.39
Pt/C	60.6	292.8	0.48
Pd/C	68.3	270.3	0.40

Table S2. Comparison of methanol oxidation behavior on the 3D Rh/(BNG)₇-(CNT)₃ and various Rh-based electrocatalysts.

Catalyst	ECSA (m ² g ⁻¹)	Mass activity (mA mg ⁻¹)	Scan rate (mV s ⁻¹)	Electrolyte	Reference
Rh/(BNG) ₇ -(CNT) ₃	105.4	814.0	50	1 M KOH + 1 M CH ₃ OH	This work
Rh nanosheets	45.5	333	50	1 M KOH + 1 M CH ₃ OH	[22]
Rh nanotubes	60.9	325	50	1 M KOH + 1 M CH ₃ OH	[61]
Rh nanospheres	50.7	292	50	1 M KOH + 1 M CH ₃ OH	[62]
Rh sheets/ graphene	48.6	264.0	50	1 M KOH + 1 M CH ₃ OH	[20]
Rh/doped graphene	81.4	721.5	50	1 M KOH + 1 M CH ₃ OH	[25]
Rh/carbon nanohorns	102.5	784.0	50	1 M KOH + 1 M CH ₃ OH	[23]

Table S3. The charge-transfer resistance (R_{ct}) of different catalysts.

Catalyst	R_{ct} value (Ω)	Error (%)
Rh/(BNG) ₇ -(CNT) ₃	14.9	2.4
Rh/G	20.6	1.5
Rh/CNT	22.1	3.4
Rh/C	6664.0	3.8