**Electronic Supplementary Information** 

## Immobilizing ultrasmall Pt nanocrystals onto 3D interweaving BCN nanosheet-graphene networks enables efficient methanol oxidation

## reaction

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## Supplementary Results:



Fig. S1 Typical FE-SEM images of the bulk g-C<sub>3</sub>N<sub>4</sub> powder at different magnifications.



Fig. S2 Typical FE-SEM images of the exfoliated  $g-C_3N_4$  nanosheets at different magnifications.



**Fig. S3** HR-TEM image of the 3D Pt/BCN-G nanoarchitecture shows the lattice fringes of graphene nanosheets.



**Fig. S4** (a) Low-magnification HAADF-STEM and the corresponding elemental mapping images reveal the homogeneous dispersion of (b) C, (c) B, (d) N and (e) Pt elements in the Pt/BCN-G nanoarchitecture.



**Fig. S5** EDX spectrum of the 3D Pt/BCN-G nanoarchitecture verifies the presence of C, B, N and Pt components in the hybrid.



Fig. S6 High-resolution C 1s XPS spectrum of GO, indicating that the carbon sheets possess a

large number of oxygen functional groups.



**Fig. S7** The ECSA-normalized CV curves of (a) the Pt/BCN-G electrodes with different BCN/G ratios, and (b)  $Pt/(BCN)_7$ -G<sub>3</sub>, Pt/G, Pt/BCN, Pt/CNT, and Pt/C electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M CH<sub>3</sub>OH solution at 50 mV s<sup>-1</sup>.



**Fig. S8** (a) LSV curves of (a) the Pt/BCN-G electrodes with different BCN/G ratios and (b)  $Pt/(BCN)_7-G_3$ , Pt/G, Pt/BCN, Pt/CNT, Pt/C and Pt/CN electrodes in 0.5 M  $H_2SO_4$  and 1 M  $CH_3OH$  solution at 50 mV s<sup>-1</sup>.



**Fig. S9** (a-b) FE-SEM images and (c) corresponding Pt size distribution of the Pt/BCN-G catalyst after the long-term stability test.

Catalyst	B (at%)	N (at%)
Pt/(BCN) <sub>1</sub> -G <sub>9</sub>	1.0	2.6
Pt/(BCN) <sub>3</sub> -G <sub>7</sub>	1.7	7.7
Pt/(BCN) <sub>5</sub> -G <sub>5</sub>	4.8	12.8
Pt/(BCN) <sub>7</sub> -G <sub>3</sub>	6.6	18.0
Pt/(BCN) <sub>9</sub> -G <sub>1</sub>	8.5	23.2

**Table S1** The B and N contents in various Pt/BCN-G catalysts.

**Table S2** Compiled study comparing CV results for different catalysts.

Electrode	ECSA	Mass activity	Specific activity
	(m² g⁻¹)	(mA mg⁻¹)	(mA cm <sup>-2</sup> )
Pt/(BCN) <sub>1</sub> -G <sub>9</sub>	69.9	680.1	0.97
$Pt/(BCN)_3-G_7$	79.2	806.5	1.02
$Pt/(BCN)_5-G_5$	110.4	1213.5	1.10
$Pt/(BCN)_7-G_3$	121.2	1782.2	1.47
$Pt/(BCN)_9-G_1$	93.6	946.3	1.01
Pt/G	43.3	438.5	1.01
Pt/BCN	24.6	221.5	0.9
Pt/CNT	31.9	297.7	0.93
Pt/C	29.7	262.5	0.88

**Table S3** Comparison of methanol oxidation behavior of the 3D  $Pt/(BCN)_7$ -G<sub>3</sub> catalyst with various state-of-the-art Pt-based electrocatalysts.

Electrode	ECSA (m <sup>2</sup> g <sup>-1</sup> )	Mass activity (mA mg <sup>-1</sup> )	Electrolyte	Ref.
Pt/(BCN) <sub>7</sub> -G <sub>3</sub>	121.2	1782.2	0.5 M H <sub>2</sub> SO <sub>4</sub> +1 M CH <sub>3</sub> OH	This work
Pt/[BMIM]BF <sub>4</sub> /CNT	N. A	155.0	0.5 M H <sub>2</sub> SO <sub>4</sub> +1 M CH <sub>3</sub> OH	[48]
Pt/imidazolium- salt/CNT	67.6	410.0	0.5 M H <sub>2</sub> SO <sub>4</sub> +0.5 M CH <sub>3</sub> OH	[22]
Pt/N-doped graphene	N. A	376.2	0.5 M H <sub>2</sub> SO <sub>4</sub> +0.5M CH <sub>3</sub> OH	[49]
$Pt/RGO-Ti_3C_2T_x$	90.1	1102.0	0.5 M H <sub>2</sub> SO <sub>4</sub> +1 M CH <sub>3</sub> OH	[37]
Pt/RGO/CNT	117.3	691.1	0.5 M H <sub>2</sub> SO <sub>4</sub> +1 M CH <sub>3</sub> OH	[50]
Pt/G-C <sub>3</sub> N <sub>4</sub>	69.0	621.8	0.5 M H <sub>2</sub> SO <sub>4</sub> +1 M CH <sub>3</sub> OH	[39]
Pt/RGO-MoS <sub>2</sub>	104.3	737.8	0.5 M H <sub>2</sub> SO <sub>4</sub> +1 M CH <sub>3</sub> OH	[51]
PtPd dendrites/RGO	81.6	647.2	0.5 M H <sub>2</sub> SO <sub>4</sub> +1 M CH <sub>3</sub> OH	[52]