# Electronic Supplementary Information

# *In situ* self-assembled N-rich carbon on pristine graphene as a highly effective support and cocatalyst of Pt nanoparticles for superior catalytic activity toward methanol oxidation

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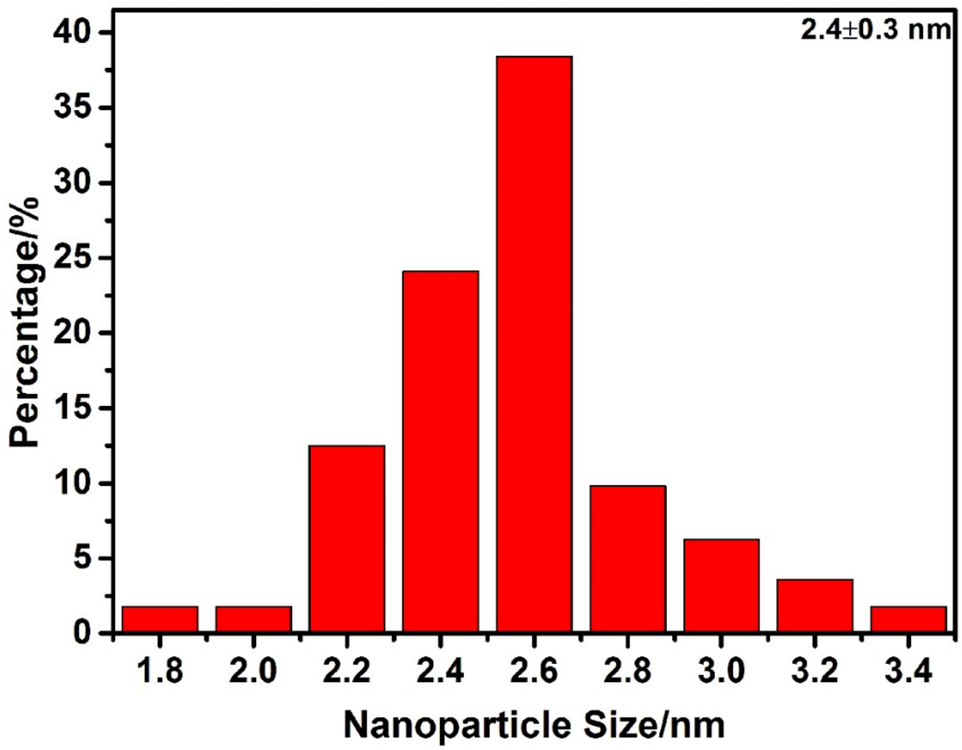


**Fig. S1** Size distribution of Pt NPs in G@NC@Pt.

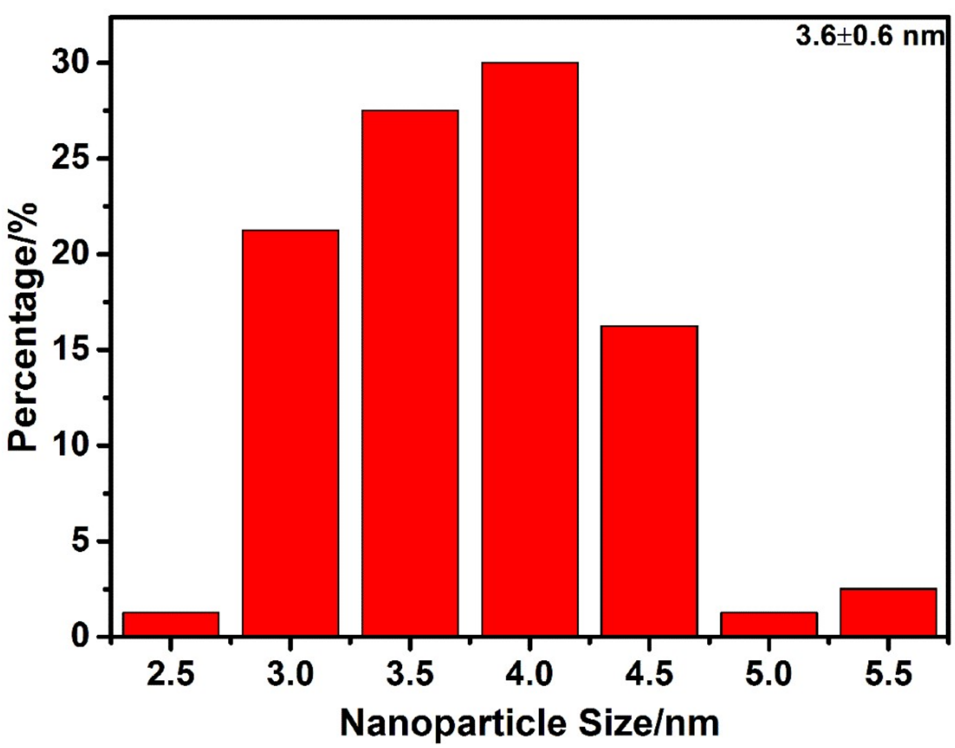


**Fig. S2** Size distribution of Pt NPs in G@NC@Pt (2:5).

**Table S1** Detailed comparison of G@NC@Pt with state-of-the-art commercial Pt/C catalysts and representative noncovalently functionalized carbon supported Pt catalysts.

| Catalyst | Forward peak current density (A $mg^{-1}$ Pt) | Onset potential (V) | Scan rate (mV $s^{-1}$) | Electrolyte | Ref. |
|---|---|---|---|---|---|
| Commercial Pt/C (20%, JM) | 0.354 | ~0.58 (vs. RHE) | 50 | 0.5 M $H_2SO_4$ | 1 |
| commercial Pt/C (20%, Alfa Aesar) | 0.212 | ~0.2 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | 2 |
| Commercial Pt/C (20%, JM) | 0.1845 | ~0.38 (vs. SCE) | 50 | 1.0 M $H_2SO_4$ | 3 |
| Commercial Pt/C (20%, JM) | 0.295 | 0.26 (vs. Ag/AgCl) | 50 | 0.5 M $H_2SO_4$ | 4 |
| Commercial Pt/C (20%, JM) | ~0.202 | ~0.25 (vs. SCE) | 20 | 0.5 M $H_2SO_4$ | 5 |
| Commercial Pt/C (20%, E-TEK) | ~0.105 | ~0.4 (vs. Ag/AgCl) | 50 | 0.5 M $H_2SO_4$ | 6 |
| Pt−$TiO_2$−rNHGO | 0.591 | ~0.30 (vs. Ag/AgCl) | 50 | 0.5 M $H_2SO_4$ | 7 |
| Pt@RFC | 0.657 | 0.36 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | 8 |
| Pt/NCNTs-500 | 0.80 | 0.23 (vs. SCE) | 20 | 0.5 M $H_2SO_4$ | 9 |
| PMo/Pt/MWCNT | 0.1647 | 0.2 (vs. Ag/AgCl) | 50 | 1.0 M $H_2SO_4$ | 10 |
| Pt/$TiO_2$@NC−NCNTs | 0.577 | ~0.27 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | 11 |
| Pt/G-NCNTs | 0.74 | ~0.45 (vs. RHE) | 50 | 0.5 M $H_2SO_4$ | 12 |
| Pt-PVP-GNF | ~0.235 | 0.55 (vs. NHE) | 20 | 0.5 M $H_2SO_4$ | 13 |
| Pt/e-RGO-SWCNT | 0.192 | ~0.45 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | 14 |
| Pt/PANI-HPMo-GS | 0.322 | 0.2 (vs. SCE) | 20 | 0.5 M $H_2SO_4$ | 15 |
| Pt-RGO/PF | 0.404 | ~0.23 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | 16 |
| Pt-CQD/RGO | 0.529 | ~0.25 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | 17 |
| Pt/$(LDCNT)_3$-$(NG)_7$ | 0.872 | ~0.20 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | 18 |
| Pt/$G_5$-$(PCNT)_5$ | 0.618 | ~0.25 (vs. SCE) | 20 | 1 M $H_2SO_4$ | 19 |
| Pt/CNTs@TiCoN | 0.92 | ~0.32 (vs. Ag/AgCl) | 50 | 0.5 M $H_2SO_4$ | 20 |
| Pt/$Ti_{0.5}Cr_{0.5}N_2$/G | 0.785 | 0.46 (vs. RHE) | 50 | 0.5 M $H_2SO_4$ | 21 |
| G-Cys-Au@Pt | 0.674 | 0.23 (vs. SCE) | 50 | 0.1 M $H_2SO_4$ | 22 |
| G@NC@Pt | 0.961 | 0.20 (vs. SCE) | 50 | 0.5 M $H_2SO_4$ | This work |

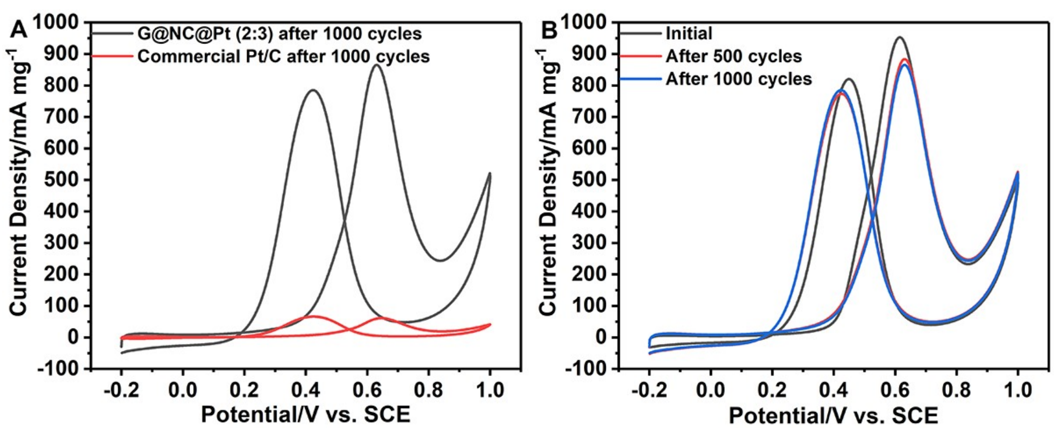


**Fig. S3** (A) CV curves of G@NC@Pt (2:3) and commercial Pt/C after measuring CV for 1000 cycles in 1 M $CH_3OH$ + 0.5 M $H_2SO_4$. (B) Initial CV curve of G@NC@Pt (2:3) and those after 500 and 1000 cycles of the ADT tests carried out in 1 M $CH_3OH$ + 0.5 M $H_2SO_4$.

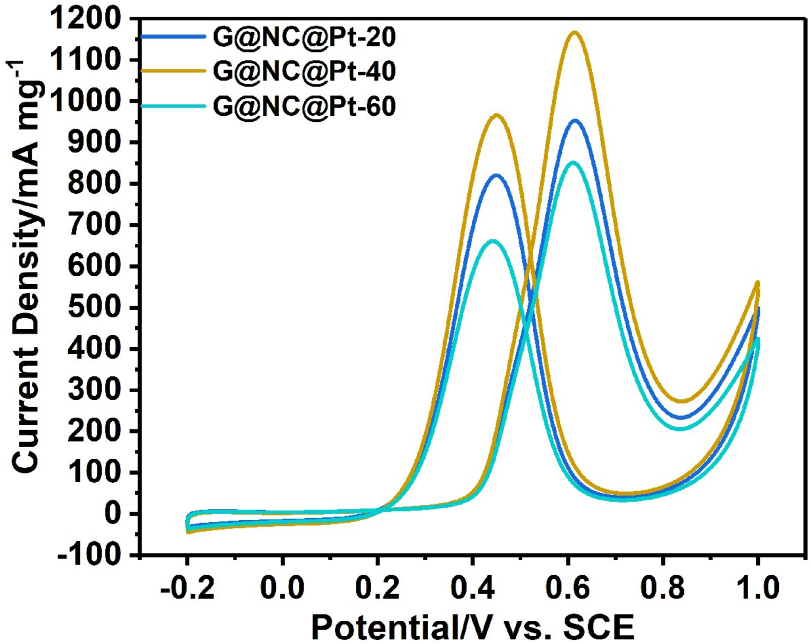


**Fig. S4** CV curves of G@NC@Pt with different Pt loadings.

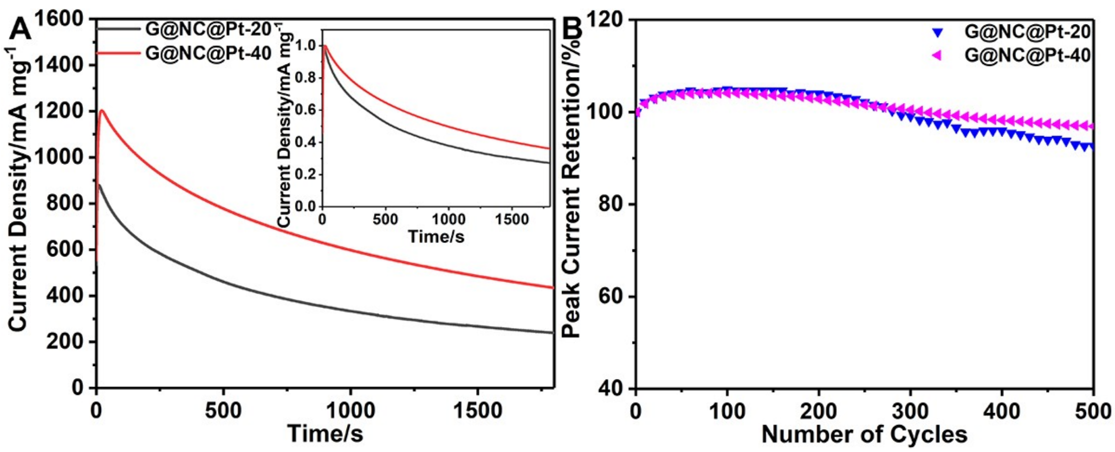


**Fig. S5** (A) Chronoamperometric curves of G@NC@Pt with 20% and 40% loadings. (B) The remaining percentage of peak current for G@NC@Pt with 20% and 40% loadings after measuring CV for different numbers of cycles. The inset of (A) shows the normalized current density versus time curves obtained from the chronoamperometric curves.

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