Supporting Information

Fabrication of Graphene-Porous Carbon-Pt Nanocomposite with High Electrocatalytic Activity and Durability for Methanol Oxidation

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Experimental Section

Preparation of CMK-3

CMK-3 was synthesized using SBA-15 as the template,[1] and sucrose as the carbon source. In brief, 1.25 g of sucrose and 0.14 g of H_2SO_4 were dissolved in 5 g of H_2O and 1 g of SBA-15 was added to this solution. After stirring for 0.5 h, the mixture was heated at 100 °C for 6 h and subsequently at 160 °C for another 6 h. The resulting product was impregnated again with an aqueous solution consisting of 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 g of H_2O. After heat treatment at 100 °C and 160 °C, the mixture was carbonized at 900 °C for 3 h under N_2 protection. Finally, CMK-3 was obtained by the removal of the silica template using a 10 wt% HF solution at room temperature, and collected by centrifugation, washed with deionized water, and dried at 60 °C.

Preparation of graphene oxide

Graphene oxide (GO) was synthesized from natural graphite powders by a modified Hummer's method. In brief, 5 g of graphite powder and 5 g of $NaNO_3$ were added into 230 mL of 98% H_2SO_4 under stirring in an ice bath. 30 g of $KMnO_4$ was slowly added to the mixture under stirring for 15 min below 5 °C. The mixture was then heated at 35 °C for 30 min. Subsequently, 460 mL of distilled water was slowly added into the above mixture,

followed by stirring the mixture at 98 °C for more than 15 min. The mixture was further diluted with 1400 mL of distilled water and the reaction was terminated by adding 25 mL of 30 % H_2O_2. Meanwhile, the color of the solution turned from dark brown to bright yellow. The resulting mixture was filtered and washed with distilled water several times to remove residual acids and salts. As-prepared GO was dispersed in water by ultrasonication for 30 min, followed by a low-speed centrifugation to get rid of any aggregated GO nanosheets.

1 D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548–552.

G-mSiO$_2$ template

G-mSiO$_2$ herein was used as a hard template to prepare G-mC. The N_2 adsorption/desorption isotherm of G-mSiO$_2$ shows a type IV curve with a H1 hysteresis loop (**Fig. S1A**), indicating that G-mSiO$_2$ is a typical mesoporous material containing uniform pores with a diameter of ~2.2 nm (**Fig. S1B**). The surface area and pore volume of G-mSiO$_2$ are ~1004 m^2 g^{-1} and 0.92 cm^3 g^{-1}, respectively. SEM image (**Fig. S1C**) reveals that G-mSiO$_2$ is a large-scale 2D nanosheet covered by a mesopore structure (width: 0.5~1.0 μm, length: 0.5~1.0 μm, thickness: 20~50 nm). Only C, O, Si elements can be detected in the EDX spectrum of G-mSiO$_2$ (the inset of **Fig. S1C**), implying the formation of 2D mesoporous silica on both sides of graphene nanosheets. The uniform mesopores of G-mSiO$_2$ were further confirmed by TEM though the mesopore structure is slightly disordered (**Fig. S1D**).

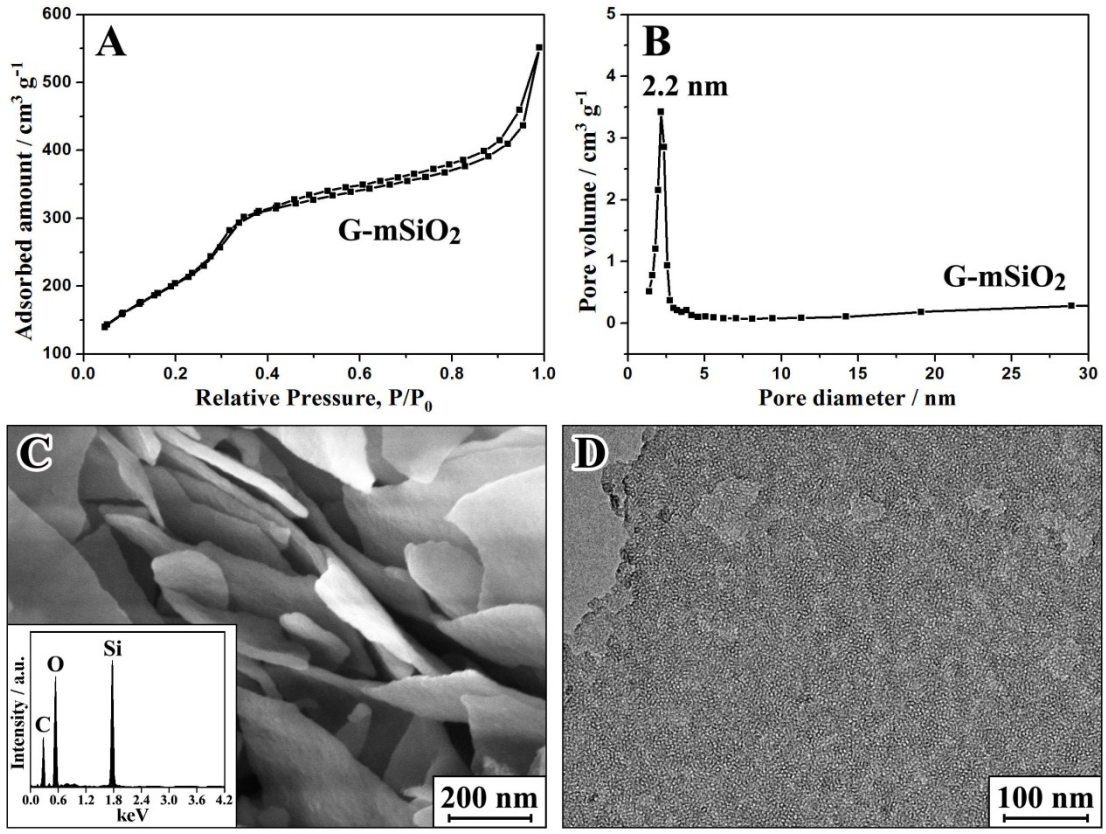

Fig. S1 (A) N_2 adsorption/desorption isotherm, (B) the pore size distribution, (C) SEM and (D) TEM images of G-mSiO$_2$. The inset of (C) is the EDX spectrum of G-mSiO$_2$.

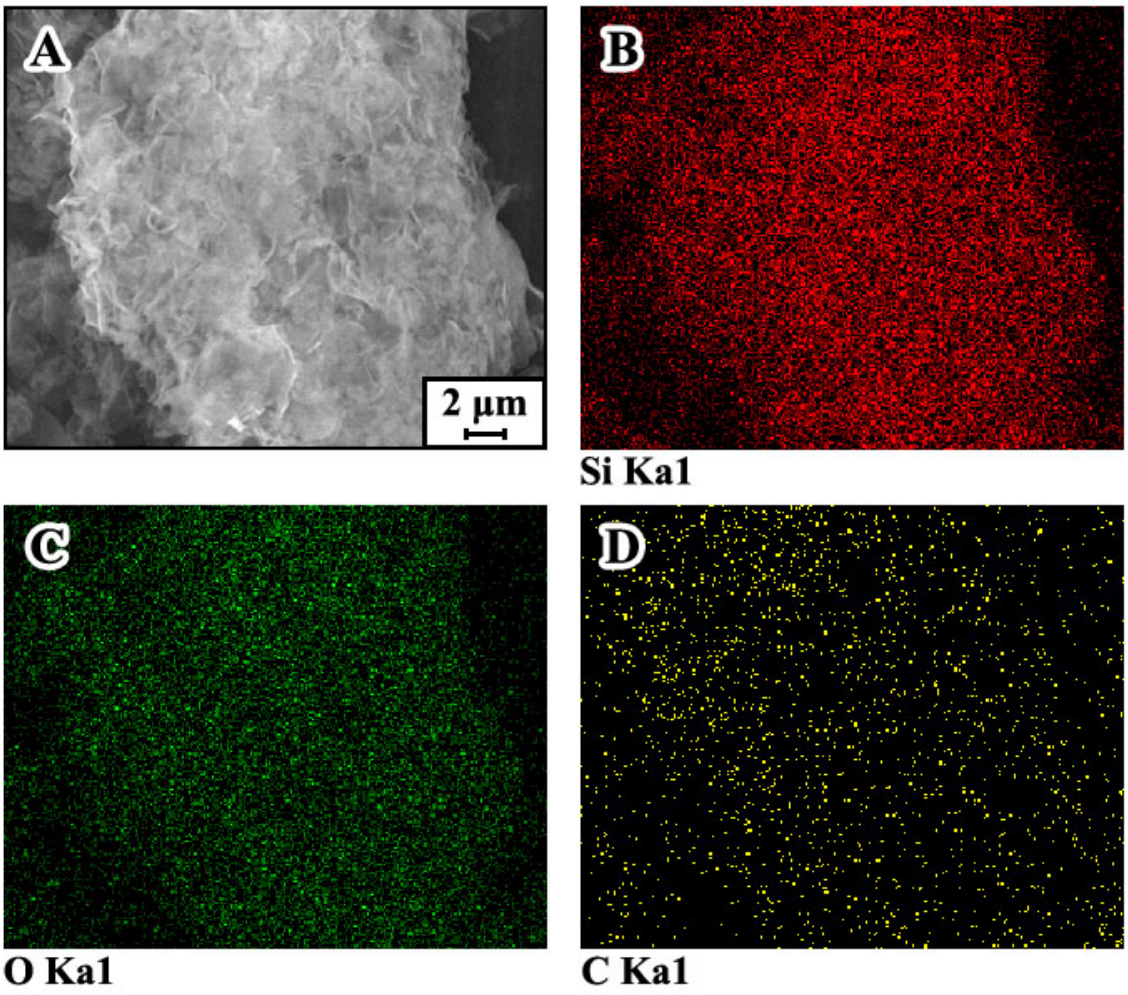

Fig. S2 SEM–EDX mapping: (A) SEM image of G-mSiO_2 and (B–D) corresponding EDX mapping images of Si, O and C elements, respectively.

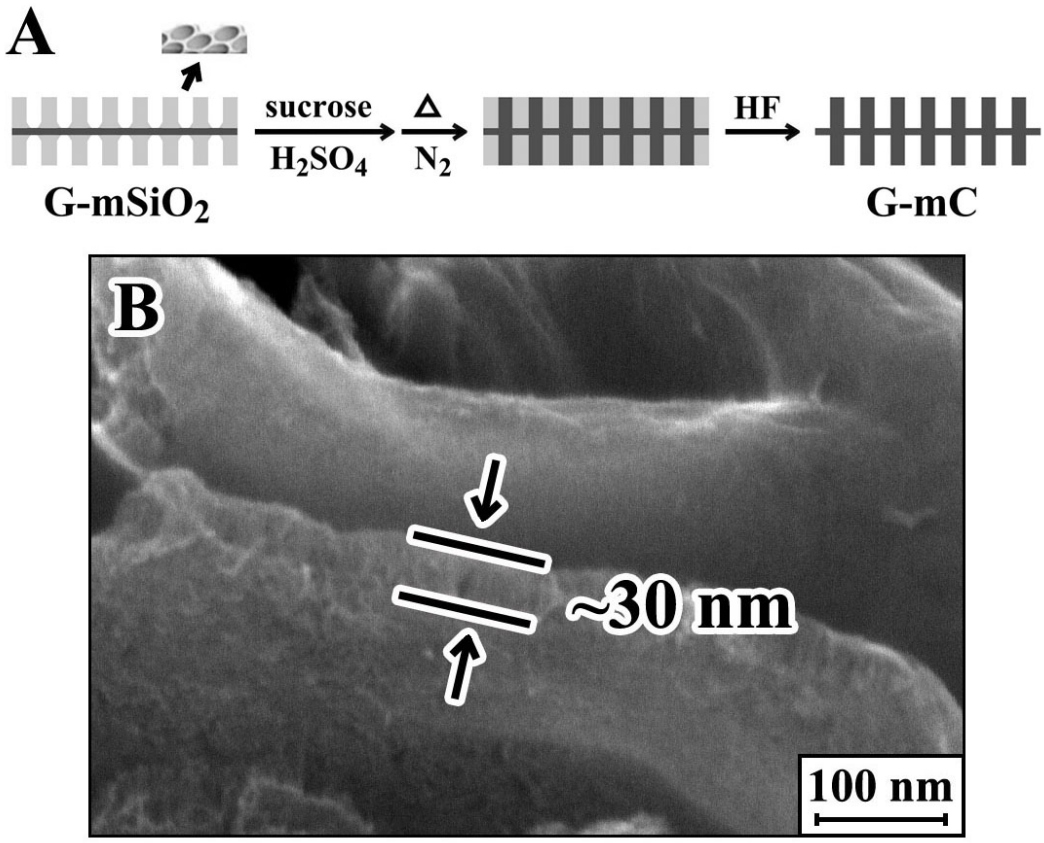

Fig. S3 (A) Schematic illustration of the synthesis route for G-mC. (B) SEM image of the cross-section of G-mC.

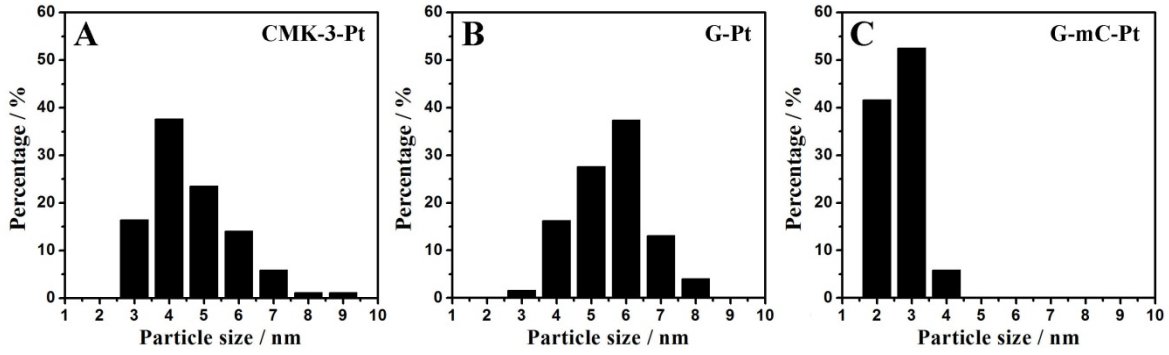

Fig. S4 Size distribution histograms of Pt nanoparticles supported on (A) CMK-3, (B) graphene, and (C) G-mC.

Table S1. Mean particle sizes and contents of Pt in CMK-3-Pt, G-Pt, G-mC-Pt and their ECSA, onset potential, forward peak current density (I_f), I_f/I_b ratio, R_{ct} values

Sample	CMK-3-Pt	G-Pt	G-mC-Pt
Particle size of Pt / nm	4.7±0.3	5.8±0.4	2.6±0.2
Pt content / wt%	18.5	18.1	19.0
Pt content (after cycles) / wt%	17.4	16.4	18.8
ECSA / $cm^2\ mg^{-1}$	204.8	417.5	639.5
Onset potential / V	0.084	0.068	0.065
I_f / mA cm^{-2}	0.55	0.90	1.78
I_f/I_b	1.72	2.83	3.39
R_{ct} / Ω	39.0	2.9	8.5

Carbon supports

The mesoporous structures of CMK-3 and G-mC were confirmed by N_2 adsorption/desorption technique. The isotherms of CMK-3 and G-mC show type IV curves with a H1 hysteresis loop (**Fig. S5A** and **S5C**), indicative of the mesoporous nature of CMK-3 and G-mC. The pore size distributions of CMK-3 and G-mC (**Fig. S5B** and **S5D**) calculated using the BJH model show only one peak at about 3.7 and 2.3 nm, respectively, revealing that these mesoporous carbons possess uniform pores. The BET surface areas, pore sizes and pore volumes of CMK-3, stacked graphene nanosheets (GN), G-mC as well as these Pt-loaded carbon supports are displayed in **Table S2**. It is indicated that the surface areas and pore volumes of CMK-3 and G-mC decreased after loading Pt nanoparticles, but the pore size does not change, suggesting that most Pt nanoparticles formed inside the pores of CMK-3 and G-mC.

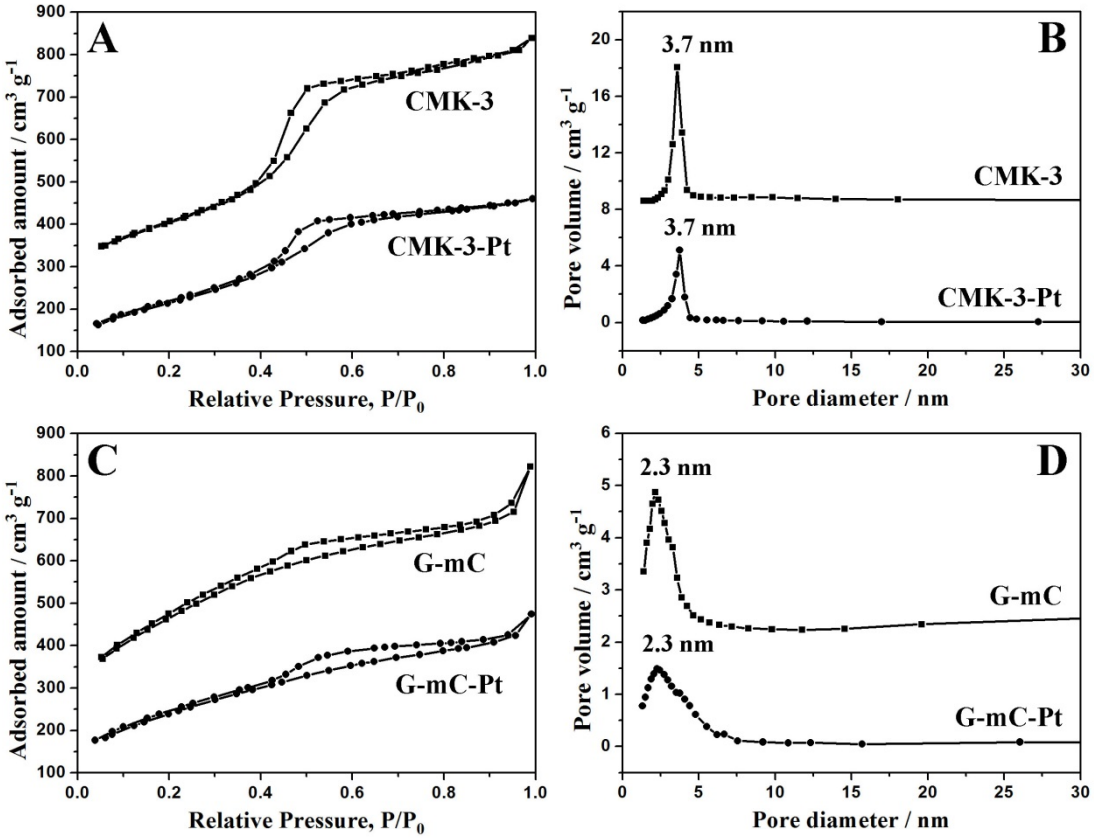

Fig. S5 N_2 adsorption/desorption isotherms and the pore size distributions of (A, B) CMK-3 and CMK-3-Pt, (C, D) G-mC and G-mC-Pt.

Table S2. Structural parameters of CMK-3, CMK-3-Pt, GN, G-Pt, G-mC and G-mC-Pt.

Sample	Pore size / nm	Pore volume / $cm^3\ g^{-1}$	Surface area / $m^2\ g^{-1}$
CMK-3	3.7	1.24	1185
CMK-3-Pt	3.7	0.68	818
GN	N/A	N/A	428
G-Pt	N/A	N/A	214
G-mC	2.3	0.93	1253
G-mC-Pt	2.3	0.58	754

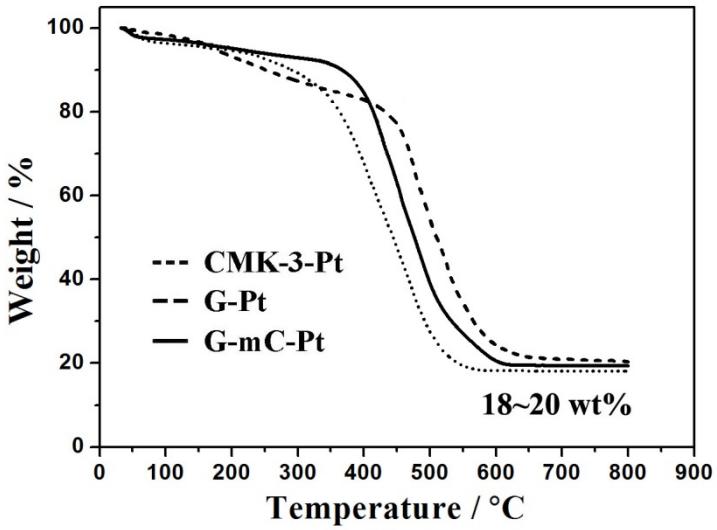

Fig. S6 TGA curves of CMK-3-Pt, G-Pt, and G-mC-Pt.

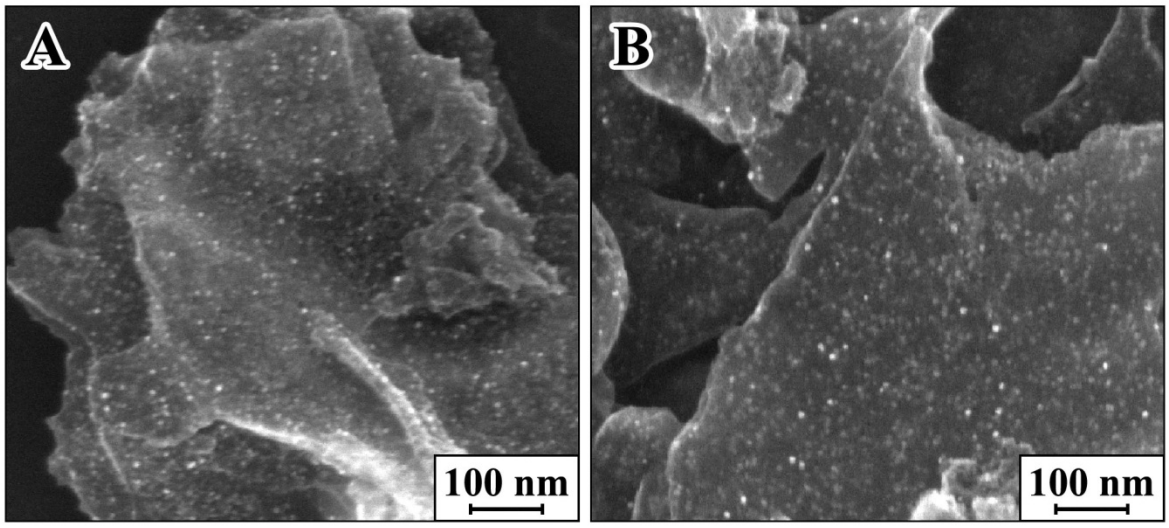

Fig. S7 TEM images of G-mC-Pt (A) before and (B) after 200 cycles.

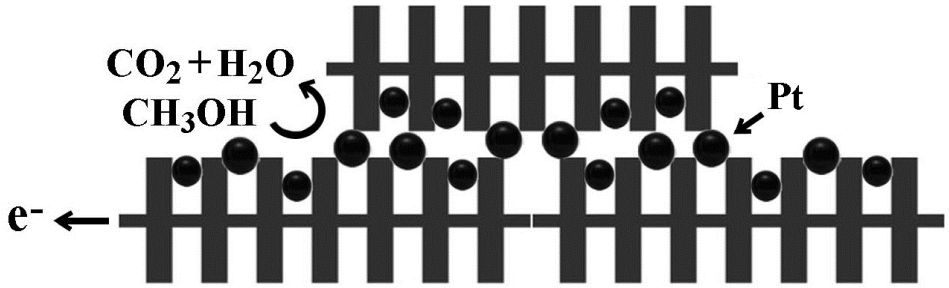

Fig. S8 The illustration of the electrochemical reaction path of G-mC-Pt.