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Supporting Information Available

Graphene-Porous Carbon-Pd/SnO_2 Nanocomposite with Enhanced Electrocatalytic Activity and Durability for Methanol Oxidation

Lirui Nan, Zetan Fan, Wenbo Yue,* Qiao Dong, Lisha Zhu, Liu Yang, and Louzhen Fan*

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China

* Corresponding author

Yue WB, Fax: +86 (0)10 58802075; Tel: +86 (0)10 58804229; E-mail: wbyue@bnu.edu.cn

Fan LZ, E-mail: lzfan@bnu.edu.cn

Experimental Section

Preparation of G-mSiO_2

G-mSiO_2 was synthesized using Cetyltrimethylammonium bromide (CTAB) as the template. In a typical synthesis, 0.03 g of GO was dispersed in 100 mL of deionized water, and 0.04 g of NaOH and 1 g of CTAB were then added into this GO solution by ultrasonication for 2 h. Subsequently, the solution was heated at 40 °C and 1 mL of TEOS was dropwise added into the solution. After stirring for 12 h, the suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 100 °C for 3 days. The precipitate was collected by centrifugation, washed with deionized water, and dried at 60 °C. The dried powder was further heated under N_2 atmosphere at 900 °C for 3 h to completely remove CTAB template. Finally, G-mSiO_2 was obtained after cooling down to room temperature.

Preparation of CMK-3 and G-mC

CMK-3 was synthesized using SBA-15 as the template, 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.

G-mC was synthesized using G-$mSiO_2$ as the template,[1] and sucrose as the carbon source, which is similar to the preparation of CMK-3 except G-$mSiO_2$ instead of SBA-15.

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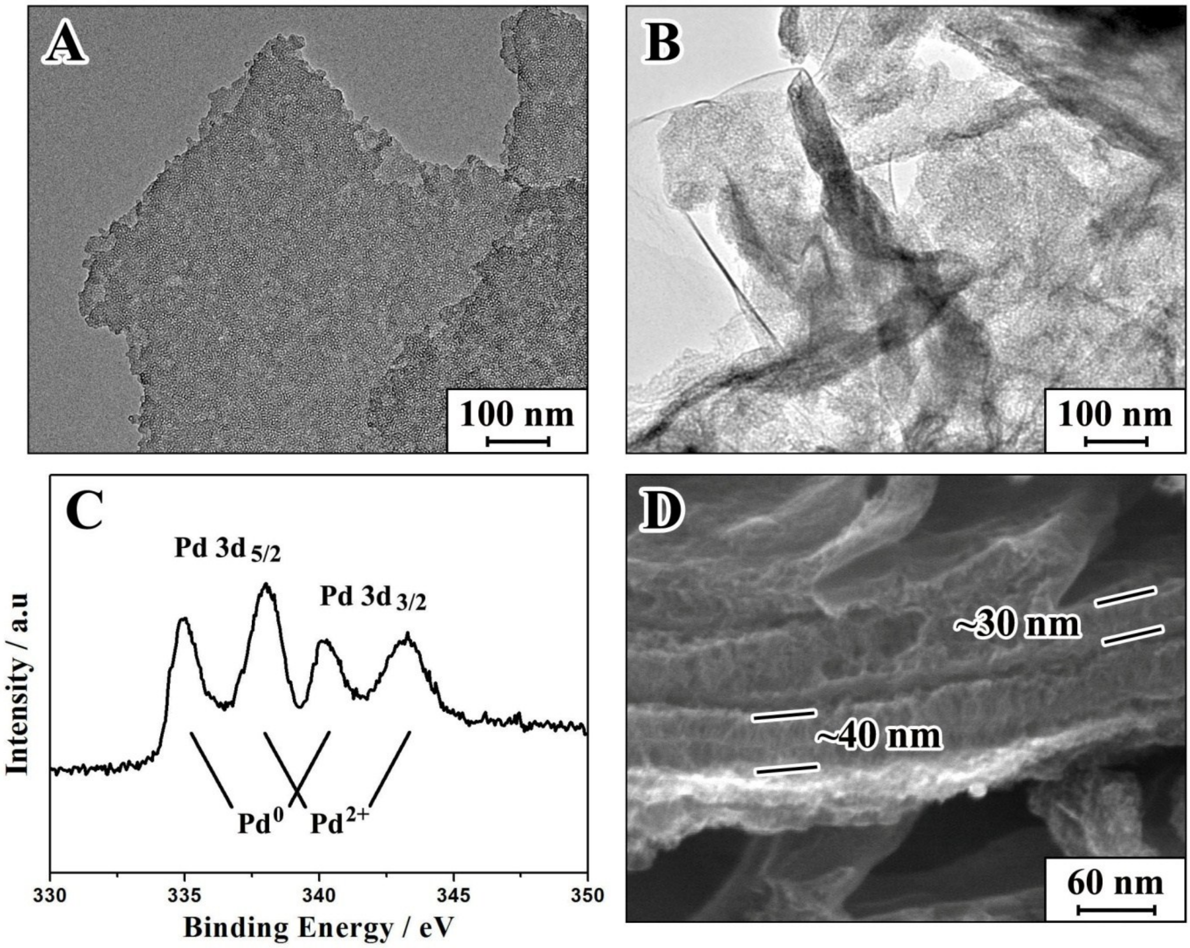

Fig. S1 TEM images of (A) G-mSiO_2 and (B) G-mC. (C) Pd 3d XPS spectrum of G-mC-Pd/SnO_2 prepared without using $NaBH_4$. (D) SEM image of the cross-section of G-mC.

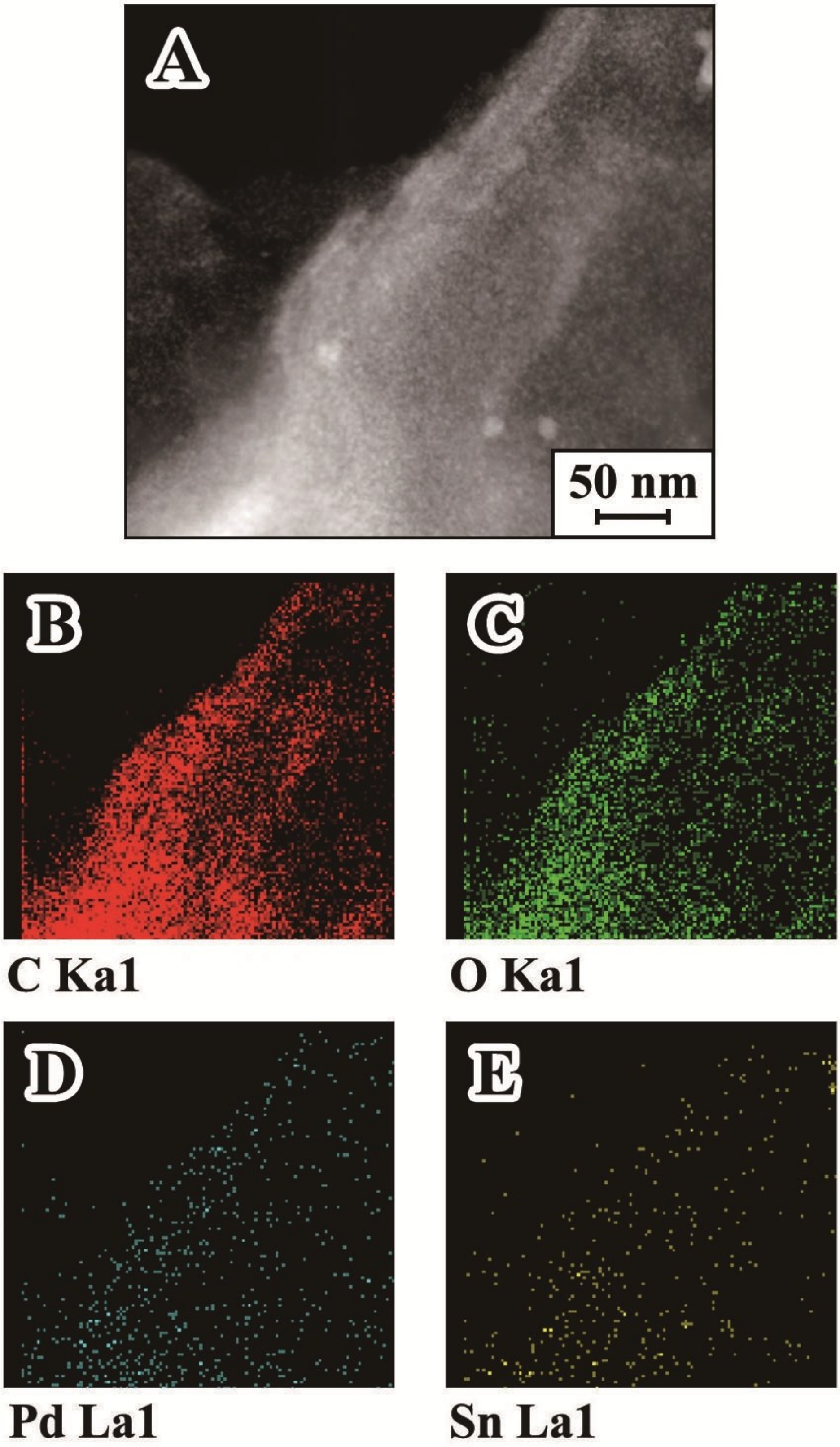

Fig. S2 TEM-EDX mapping: (A) TEM image of G-mC-Pd/SnO_2 and (B–E) corresponding EDX mapping images of C, O, Pd and Sn elements, respectively.

Carbon supports

The porosities of CMK-3, CMK-3-Pd/SnO_2, G-mC and G-mC-Pd/SnO_2 were investigated by N_2 adsorption/desorption technique. The isotherms of CMK-3 and G-mC (**Fig. S3A** and **S3C**) show type IV curves with a H1 hysteresis loop, and the pore size distributions (**Fig. S3B** and **S3D**) show only one peak at about 3.6 and 2.6 nm, indicating that CMK-3 and G-mC are mesoporous carbons with uniform pore structure. **Fig. S4** shows the TGA curves of G-mSiO_2 and G-mSiO_2-C (G-mSiO_2 containing carbon inside the pores), indicating that the contents of porous SiO_2 in G-mSiO_2 and G-mSiO_2-C are ~93.5 and ~57.5 wt%, respectively. Accordingly, the weight ratio of porous carbon to graphene is calculated to be ~9.6. After loading of Pd & SnO_2 nanoparticles, the surface areas of CMK-3 and G-mC decrease from ~1138 and ~1068 $m^2\ g^{-1}$ to ~717 and ~445 $m^2\ g^{-1}$, and the pore volumes decrease from ~1.20 and ~0.71 $cm^3\ g^{-1}$, to ~0.56 and ~0.38 $cm^3\ g^{-1}$, respectively, but the pore sizes do not change. Considering the weight of Pd & SnO_2 (~26.0 wt% for CMK-3-Pd/SnO_2 and ~23.8 wt% for G-mC-Pd/SnO_2), the pore volumes of CMK-3 and G-mC should be ~0.89 and ~0.54 $cm^3\ g^{-1}$ respectively after loading Pd & SnO_2 nanoparticles, much higher than those of CMK-3-Pd/SnO_2 (~0.56 $cm^3\ g^{-1}$) and G-mC-Pd/SnO_2(~0.38 $cm^3\ g^{-1}$), implying that the pores of CMK-3 and G-mC are occupied by Pd & SnO_2 nanoparticles. The BET surface areas, pore sizes and pore volumes of CMK-3, CMK-3-Pd/SnO_2, G-mC and G-mC-Pd/SnO_2 are displayed in **Table S1**.

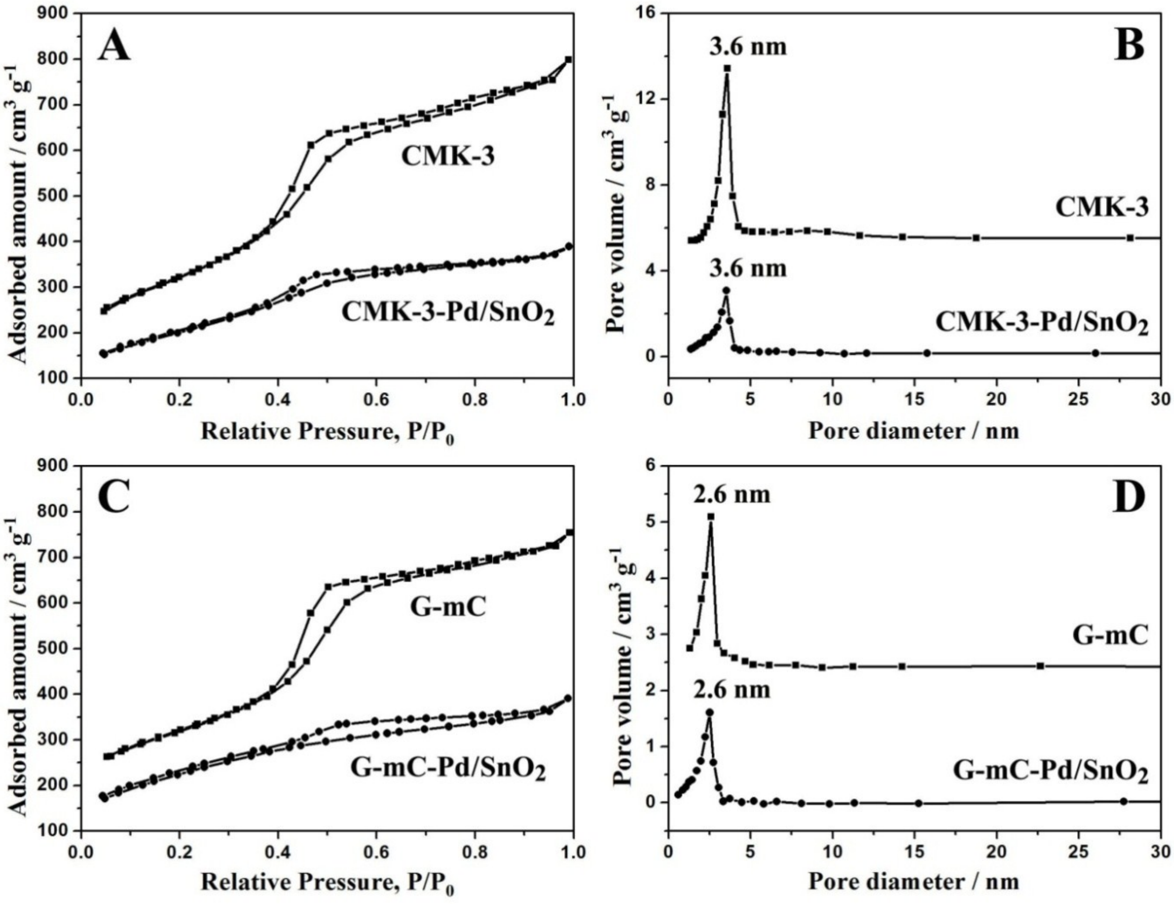

Fig. S3 N_2 adsorption/desorption isotherms and the pore size distributions of (A, B) CMK-3 and CMK-3-Pd/SnO_2, (C, D) G-mC and G-mC-Pd/SnO_2.

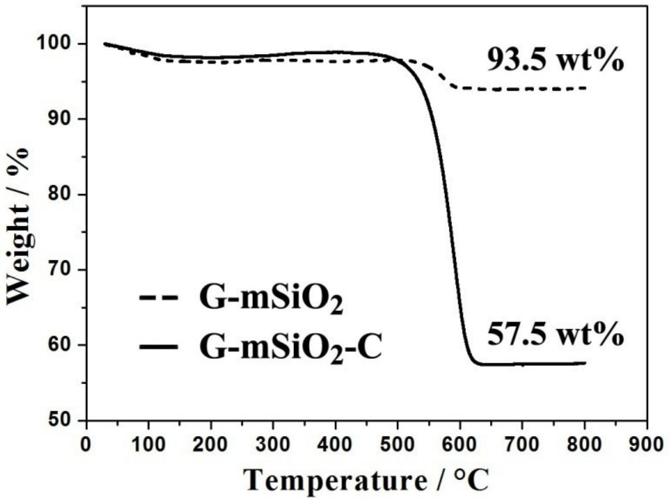

Fig. S4 TGA curves of G-mSiO_2 and G-mSiO_2-C.

Table S1. Structural parameters of CMK-3, CMK-3-Pd/SnO_2, G-mC and G-mC-Pd/SnO_2.

Sample	Pore size / nm	Pore volume / cm^3 g^{-1}	Surface area / m^2 g^{-1}
CMK-3	3.6	1.20	1138
CMK-3-Pd/SnO_2	3.6	0.56	717
G-mC	2.6	0.71	1068
G-mC-Pd/SnO_2	2.6	0.38	445

Table S2. Mean particle sizes and contents of Pd & SnO_2 in CMK-3-Pd/SnO_2, G-mC-Pd/SnO_2, G-mC-Pd, Pd/C and their ECSA, onset potential, forward peak current density (I_f), I_f/I_b ratio, R_{ct} values.

Sample	CMK-3-Pd/SnO_2	G-mC-Pd/SnO_2	G-mC-Pd	Pd/C
Particle size of Pd & SnO_2 / nm	4.6±0.3	2.4±0.1	2.6±0.2	5~7
Pd content / wt%	21.2	19.5	18.8	30
SnO_2 content / wt%	4.8	4.3	N/A	N/A
ECSA / cm^2 mg^{-1}	73.0	116.5	53.0	64.8
Onset potential / V	–0.40	–0.56	–0.38	–0.39
I_f / mA cm^{-2}	5.59	7.81	4.59	4.24
I_f/I_b	6.9	21.0	4.9	2.78
R_{ct} / Ω	23.6	4.9	4.2	33.8

Electrocatalytic performance comparison

The electrocatalytic performance of reported carbon-supported Pd composites is shown in **Table S3** and compared with that of G-mC-Pd/SnO_2. The carbon supports include multiwall carbon nanotube (MWCNT), carbon nanotube (CNT), Vulcan XC 72 (Vulcan), polypyrrole-functionalized graphene (PPy-graphene) and polyvingl pyrrolidone-functionalized graphene (PVP-graphene). Compared to most of reported carbon-supported Pd composites, G-mC-Pd/SnO_2 shows superior electrocatalytic performance, especially good cycling stability. The electrocatalytic activity retention of G-mC-Pd/SnO_2 is maintained at ~85% after 500 cycles, which is not reported previously.

Table S3. The electrocatalytic performance of reported carbon-supported Pd composites and G-mC-Pd/SnO_2.

Sample	ECSA	I_f	I_f/I_b	I_f retention	Ref
Pd/MWCNT	31.6 $m^2\ g^{-1}$	0.16 mA cm^{-2}	N/A	N/A	1
Pd/CNT	32.9 $m^2\ g^{-1}$	19.0 mA cm^{-2}	2.7	N/A	2
Pd/Vulcan	N/A	2.6 mA cm^{-2}	N/A	99.6 % (100th)	3
Pd/ PPy-graphene	35.9 $m^2\ g^{-1}$	265.8 A g^{-1} Pd	4.9	N/A	4
Pd/PVP-graphene	23.2 $m^2\ g^{-1}$	1.1 mA cm^{-2}	N/A	91.6% (50th)	5
G-mC-Pd/SnO_2	11.6 $m^2\ g^{-1}$	7.8 mA cm^{-2}	21.0	85.0% (500th)	This work

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