

Supporting Information

**Ultrathin 2D Semi-ordered Mesoporous Silica Film: Co-operative
Assembly and Application**

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Experimental Section

1. Materials preparation

The aqueous dispersion of graphene oxide (GO, 2.6 wt. %) and reduced graphene oxide (RGO, 4.5 wt. %) were gifted by Ningbo Institute of Material Technology and Engineering, which were directly used as obtained.

Details of the synthesis of SBA-15 were described elsewhere [S1]. Briefly, an aqueous mixture, consisting of 4.0 g tri-block copolymer, EO₂₀PO₇₀EO₂₀ (Pluronic P 123, BASF), 20 mL HCl (37 wt. %) and 9.2 mL tetraethyl orthosilicate (TEOS, 99%), was stirred for 20 h at 35°C and then hydrothermally treated at 100°C for 24 h. Then, the product was filtered, dried and grounded. Finally, the template was removed by the microwave digestion in the mixture of HNO₃ and H₂O₂ [S2]. The same process was repeated to synthesize other silicas in the presence of other templates, which were listed in Table S1. The obtained materials were denoted as SiO₂/GO-*x*. Here, *x* refers to the concentration of the GO solution, *viz.* 1.41, 2.82, 4.23 and 5.64 mg mL⁻¹. The sample synthesized with RGO was denoted as SiO₂/RGO-5.64. The silica denoted as SiO₂/GO-5.64-NP was synthesized without Pluronic P123.

2D nitrogen-doped mesoporous carbon (2DNMC) was synthesized by a nanocasting method [S3]. First, the carbon precursor, phenanthroline, was dissolved in a mixture of ethanol and FeCl₂ solution. Second, the template SiO₂/GO-4.23 was dispersed in the solution and sonicated at room temperature. Third, after the solvent was evaporated, the resultant powders were pyrolyzed at 900 °C for 3 h in argon. Finally, 2DNMC was obtained after a two-step chemical leaching: i) to remove the

silicate template by boiling in 10 M NaOH at 120 °C for 24 h; and ii) to remove the dissolvable iron species by boiling in 0.10 M HClO₄ at 80 °C for 24 h.

2. Physical characterizations

Small angle X-ray diffraction (SA-XRD) measurement was carried out by using a Bruker D8 ADVANCE diffractometer with a Cu K α radiation source operated at 40 keV and at a scan rate of 1° min⁻¹. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 S-TWIN operated at 200 kV. Tapping mode atomic force microscope (AFM) experiment was performed on Bruker Multimode 8. Nitrogen adsorption/desorption isotherms were measured at 77 K using Micromeritics TriStar II 3020 analyzer. The total surface area was analyzed with the well-established Brunauer-Emmett-Teller (BET) method, the microporous surface area was obtained with the MP method (*t*-plot method), and the pore size distribution was analyzed by the Barrett-Joyner-Halenda (BJH) method.

3. Electrochemical tests

The electrochemical test was performed by using a three-electrode cell with an electrochemical work station Zennium (Zahner) at room temperature (25 °C). A gold wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The working electrode was a glassy carbon disk (5.0 mm in diameter, PINE) covered with a thin layer of Nafion-impregnated catalyst. The Pt catalyst loading was 20 $\mu\text{g cm}^{-2}$ for the Pt/C catalyst, and the carbon catalyst loading was 0.5 mg cm^{-2} for the 2D nitrogen-doped hierarchical porous carbon film (2DNMC, see Fig. 6a).

The polarization curve (see Fig. 6b) of the oxygen reduction reaction was collected by scanning the potential from 1.2 down to 0 V at 5 mV s^{-1} in the oxygen-saturated 0.10 M KOH solution under 1600 rpm. For the Pt/2DNMC catalyst, the cyclic voltammogram (see Fig. 6c) was collected to evaluate the performance of the methanol oxidation reaction in an aqueous solution containing 0.50 M CH_3OH + 0.10 M HClO_4 . The scanning rate is 20 mV s^{-1} .

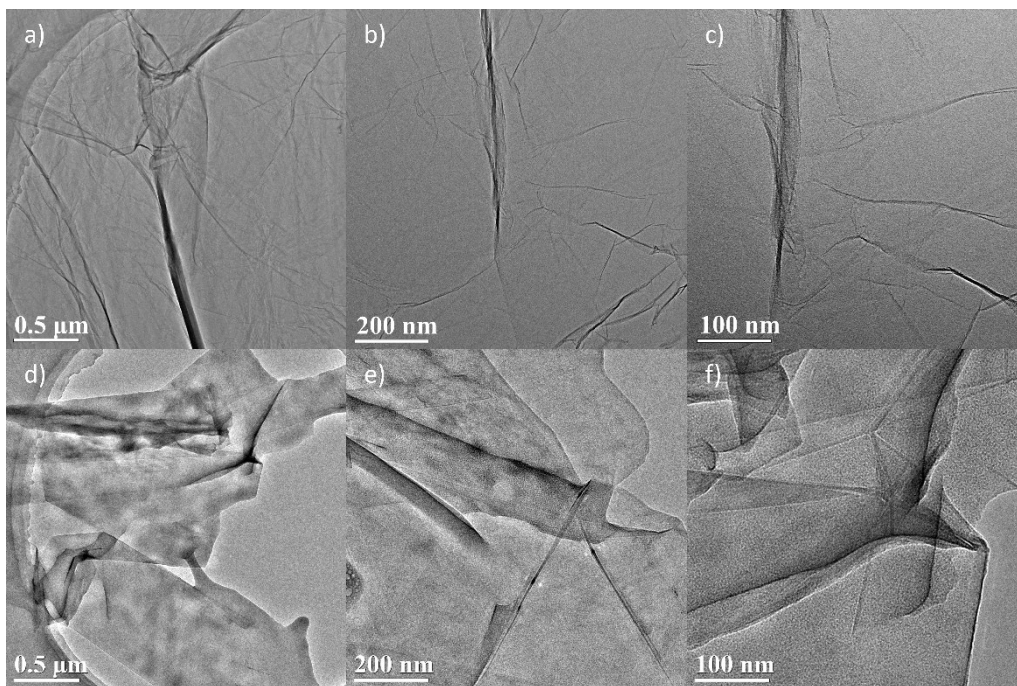


Fig. S1. TEM images of a-c) graphene oxide, d-f) reduced graphene oxide used in the synthesis of the materials.

AFM was used to measure the thickness of the silica film, as shown in Fig. S2.

The thickness of GO and SiO₂/GO-5.64 is found to be 1.0 and 3.0 nm, respectively.

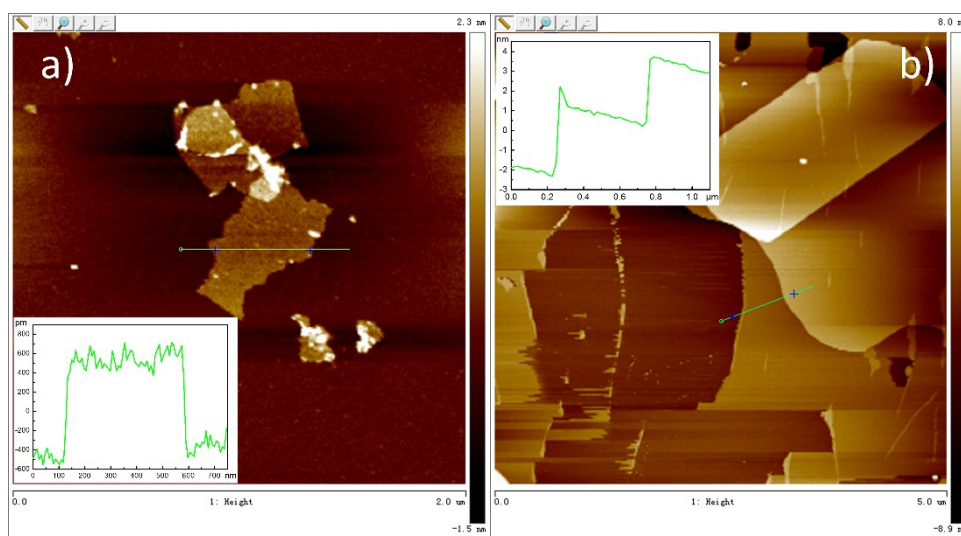


Fig. S2. AFM images of a) GO and b) SiO₂/GO-5.64.

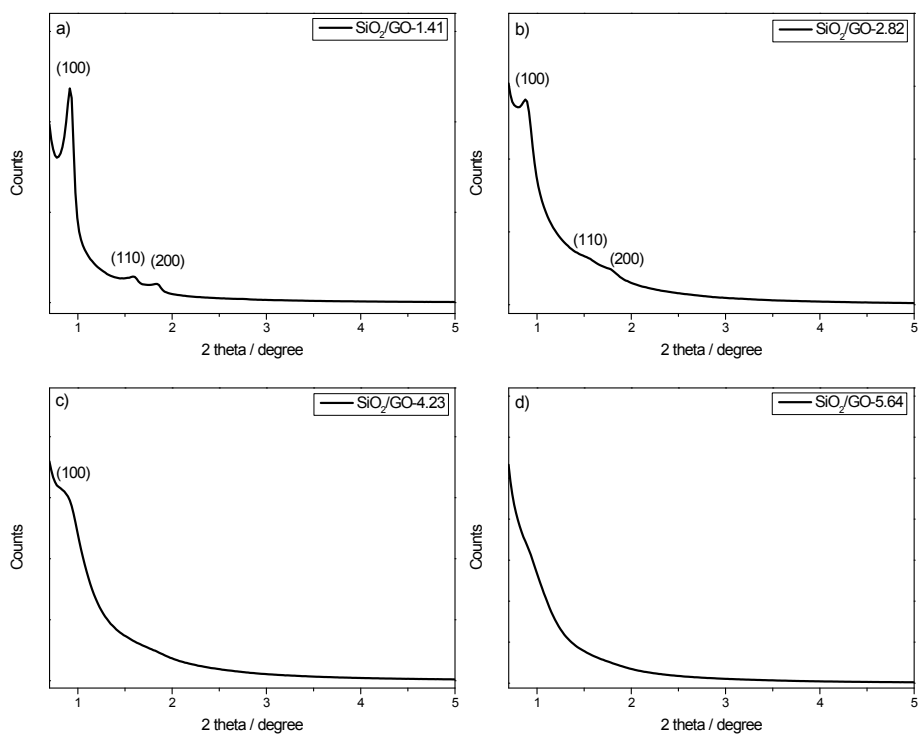


Fig. S3. Small angle X-ray diffraction of SiO₂/GO-*x* (*x*=1.41, 2.82, 4.23, 5.64 mg mL⁻¹).

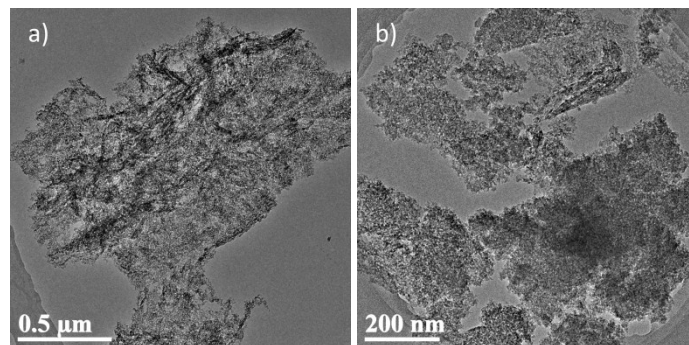


Fig. S4. TEM images of SiO₂/GO-5.64-NP.

The effect of the TEOS amount was investigated at a given GO concentration of 4.23 mg mL^{-1} . TEM images are shown in Fig. S5. It is seen that the three silicas have the same morphology of mesoporous films, and the characteristic size of the silica film increases with the TEOS amount from 9.2 to 27.6 mL. This result suggests that GO acts as the support to assemble the silica precursor and P123 aggregates, and thus directs the formation of 2D silica film.

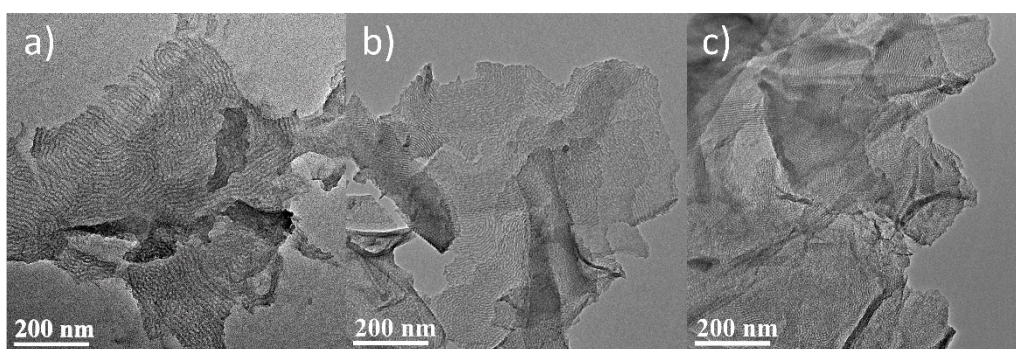


Fig. S5. TEM images of $\text{SiO}_2/\text{GO-4.23}$ synthesized with different TEOS amount: a) 9.2 mL, b) 18.4 mL, and c) 27.6 mL.

Table S1. The synthesized silicas with different combinations of templates.

Sample	TEOS/mL	Concentration of template		
		P123/mmol L ⁻¹	GO/mg mL ⁻¹	RGO/mg mL ⁻¹
SBA-15	9.2	4.72	0	0
SiO ₂ /GO-5.64-NP ^[a]	9.2	0	5.64	0
SiO ₂ /GO-1.41	9.2	4.72	1.41	0
SiO ₂ /GO-2.82	9.2	4.72	2.82	0
SiO ₂ /GO-4.23	9.2	4.72	4.23	0
SiO ₂ /GO-4.23-m	18.4	4.72	4.23	0
SiO ₂ /GO-4.23-n	27.6	4.72	4.23	0
SiO ₂ /GO-5.64	9.2	4.72	5.64	0
SiO ₂ /RGO-5.64	9.2	4.72	0	5.64

[a] The material synthesized without Pluronic P123

Table S2. Pore features of the synthesized silicas.

Sample	$A_{\text{BET}}/\text{m}^2\text{ g}^{-1}$	$A_{\text{MP}}/\text{m}^2\text{ g}^{-1}$	D_{BJH}/nm	$V/\text{cm}^3\text{ g}^{-1}$
SBA-15	806	110	5.7	1.31
SiO ₂ /GO-5.64-NP	598	4	5.3	0.92
SiO ₂ /GO-1.41	824	158	5.9	1.26
SiO ₂ /GO-2.82	782	140	5.9	1.24
SiO ₂ /GO-4.23	811	184	4.8	0.99
SiO ₂ /GO-5.64	812	146	4.7	0.97
SiO ₂ /RGO-5.64	664	107	5.8	1.05

Table S3. Comparison of the ORR performance between 2DNMC and the reported carbon catalysts in literature.

Electrocatalyst	Catalyst loading ($\mu\text{g cm}^{-2}$)	ν (mV s^{-1})	$E_{1/2}$ (V vs. RHE)	I (mA cm^{-2}) @ 0.30 V	Ref.
2DNMC	500	5	~ 0.87	-5.9	This work
CNF@NG	450	10	~ 0.80	-5.0	[S4]
LDH@ZIF-67-800	200	10	~ 0.83	-5.4	[S5]
PMF-800	1200	5	~ 0.86	-5.6	[S6]
C-PY-1000	500	5	~ 0.86	-4.0	[S3]
Zn-ZIF/GO-800	204	10	~ 0.78	-5.1	[S7]
Meso/micro-PoPD	500	10	~ 0.86	-5.8	[S8]

(Test media: 0.10 M KOH; electrode rotating speed: 1600 rpm)

Table S4. Comparison of the MOR performance between 10 wt. % Pt/2DNMC and the reported Pt-based electrocatalysts in literature.

Electrocatalyst	Solution	ν (mV s ⁻¹)	E_{onset} (V vs. SCE)	I_f (mA mg ⁻¹ Pt)	I_f/I_b	Ref.
10 wt.% Pt/2DNMC	0.10 M HClO ₄ + 0.50 M CH ₃ OH	20	0.15	360	1.1	This work
Pt/graphene	0.50 M H ₂ SO ₄ + 0.50 M CH ₃ OH	50	0.25	200	1.0	[S9]
Pt/OMC	0.50 M H ₂ SO ₄ + 0.50 M CH ₃ OH	50	0.25	250	0.83	[S10]
Pt-AO-CNT	0.50 M H ₂ SO ₄ + 1.0 M CH ₃ OH	50	0.17	155	0.94	[S11]
Pt/ND/G-1600-GC	0.50 M H ₂ SO ₄ + 1.0 M CH ₃ OH	20	0.15	98.7	1.0	[S12]
Pt/PANI-HPMo-GS	0.50 M H ₂ SO ₄ + 1.0 M CH ₃ OH	20	0.20	322	1.0	[S13]
Pt/PCN	0.50 M H ₂ SO ₄ + 1.0 M CH ₃ OH	50	0.25	343	0.98	[S14]

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