

Growth of Two-dimensional Silicalite-1 on Graphene Oxide with Controllable Electrical Conductivity

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Supplementary Information

Preparation of silicalite-1/GO composites and characterization methods

The process of synthesis $C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}$ (abbreviated to C_{22-6-6} hereafter) was developed according to Ryoo¹. In brief, 39 g (0.100 mol) of 1-bromodocosane (Tokyo Chemical Industry Co., Ltd) and 172 g (1.000 mol) of N,N,N',N'-tetramethyl-1,6-diaminohexane (TCI) were dissolved in acetonitrile/toluene (AR) mixture (1:1 vol/vol) and heated at 70 °C for 10 h. After 2 h ice-bath, the product was filtered, washed with diethyl ether (AR), and then vacuum rotary evaporated at 60 °C for 1 h, dried in a vacuum oven at 50 °C overnight. Next step, 56.2 g (0.100mol) of the product and 14.8 g (0.120mol) of 1-bromohexane (TCI) were dissolved in 300ml acetonitrile and heated at 90 °C for 10h. The post-treatment process was the same as before. At last, C_{22-6-6} (Br₂) was obtained and served as organic structure directing agent.

Aqueous colloidal suspensions of single layer graphene oxide with a concentration of 5mg/mL prepared according to modified Hummer method were purchased from Suzhou TANFENG grapheme Tech Co., Ltd. The composite synthesis solution was prepared by firstly dissolving a specified amount of the OSDA (C_{22-6-6} , as-synthesized) in deionized water (DI water) at 70 °C for 2 h, ensuring all OSDA were dissolved. A special molar ratio sodium sulfate (Na₂SO₄, Aladdin Industrial Corporation.) and sodium hydroxide (NaOH, Adama Reagent Co., Ltd)

were added into DI water serving as based solution. Thereafter, the silica source (TEOS, TCI), basic solution and different amount of GO solutions were added into OSDA solution. The final molar composition of the synthesis mixture was $7.5\text{C}_{22-6-6} : 100\text{SiO}_2 : 10\text{NaOH} : 25\text{Na}_2\text{SO}_4 : 4000\text{H}_2\text{O} : x\text{GO}$ (x: the weight percent of GO in mixtures). The reaction mixtures were shaken vigorously using vortex mixer for 60s, ensuring good dispersion of GO. Then the mixtures were heated in oil bath at 60 °C for 6 h under stirring, after which a colloidal solution (by visual inspection) was obtained. After cooling to room temperature, the mixtures were transferred into stainless-steel autoclave with HF-washed Teflon lining. Hydrothermal zeolite crystallization was carried out at 150 °C for different times under autogenous pressure and tumbling at 70 r.p.m. After the crystallization, the autoclaves were removed and quenched cool in a water bath. The solid products were recovered by centrifugation at 11000 rpm for 15 min followed by decantation, after which they were redispersed in DI water. This washing treatment was repeated four times until the pH of supernatant below 9.0. The products were then dried at 80 °C overnight. The resulting silicalite-1/GO composites with 5%, 10% and 36% (in theory) by mass are denoted Sil-5%GO, Sil-10%GO and Sil-36%GO, respectively. For comparison, the pure silicalite-1 zeolites were also synthesized under the same conditions except that GO nanosheets solution was not added.

X-ray diffraction (XRD) patterns were obtained on a Bruke AXS D8 ADVANCE diffractometer with $\text{CuK}\alpha$ radiation (40kV, 40mA, $\lambda = 0.1548$ nm), which scans were done in in-plane mode with 2θ varying from 1 to 30° with a step size of 0.02° and dwell time of 0.4s at room temperature. The gap at 2° 2θ was as-broken for clear observation of the special peaks from 2-30°. Scanning electron microscopy (SEM) images were recorded with Hitachi SU-8010 microscope operating at 3kV. High-resolution transmission electron microscope (HRTEM) images were recorded using JEM-2100F (JEOL) operated at an accelerating voltage of 200kV. Raman spectra were obtained with a Thermo SCIENTIFIC DXR Raman Microscope at an excitation line of 663 nm. Nitrogen adsorption and desorption isotherms were measured at 77k on ASAP2020 volumetric adsorption apparatus. Prior

to each measurement, products (0.1 g) were outgassed at 120 °C to vacuum -0.1 MPa. The electrical conductivity of Sil-10%GO composites were measured on a Scribner MTS 740 by using four-point head method.

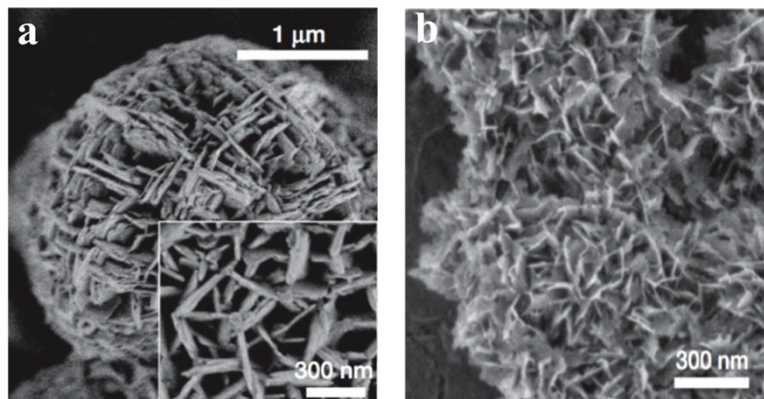


Fig. S1 (a) MFI nanosheets with multilamellar structure in Ryoo's report. SEM image showing that the MFI zeolite had a plate-like morphology that was composed of three-dimensionally intergrown nanosheets. (b) MFI nanosheets with a unilamellar structure. SEM image showing that the MFI zeolite was synthesized in a flake-like morphology.

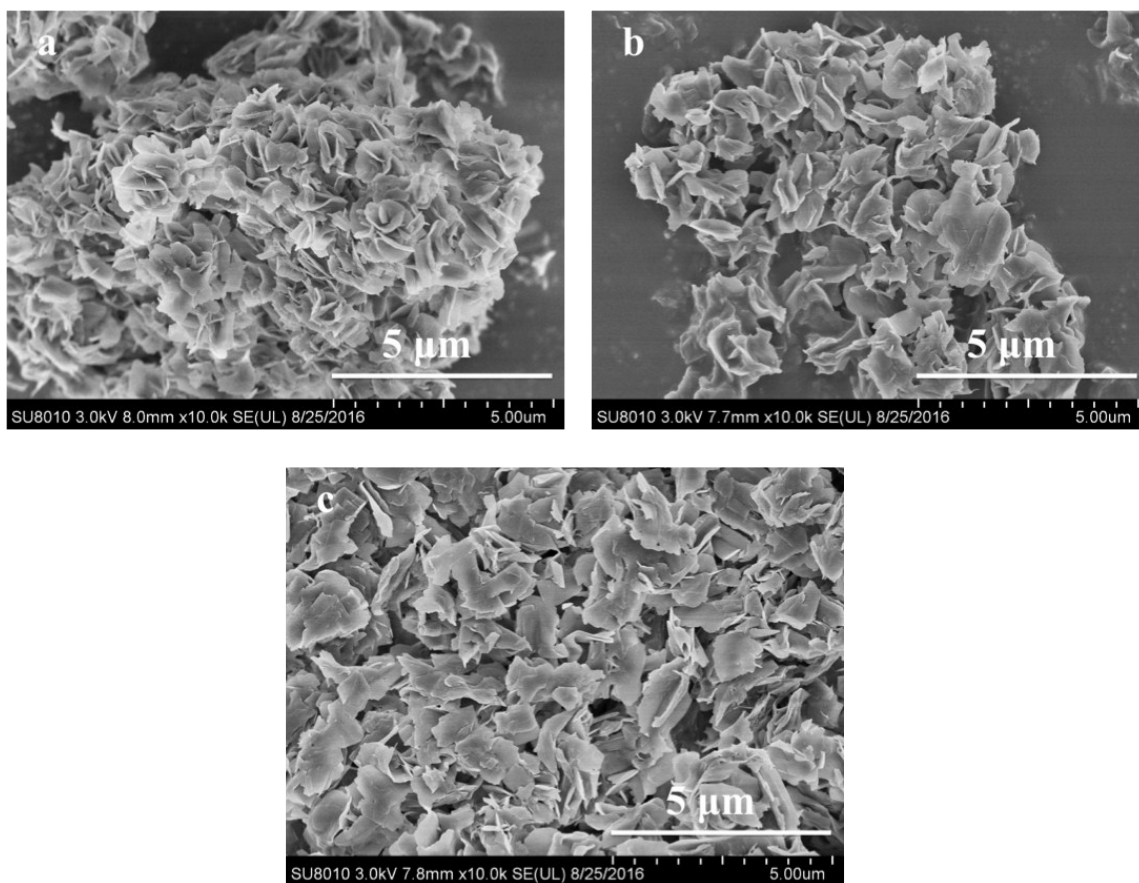


Fig. S2 SEM images of as-synthesized silicalite-1/GO composites: (a) Sil-5%GO, (b) Sil-10%GO, (c) Sil-36%GO.

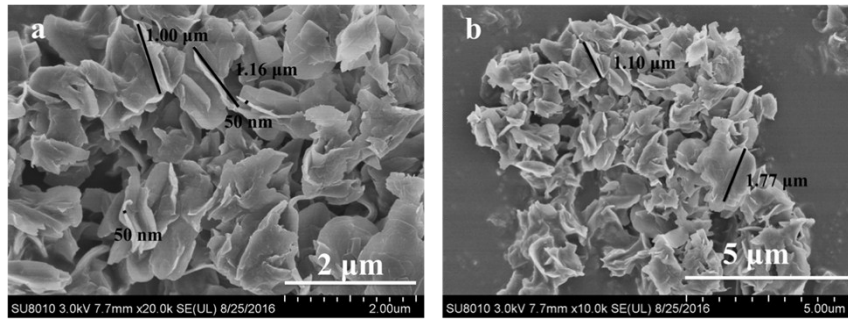


Fig. S3 SEM images of Sil-10%GO. The silicalite-1 exhibited a loose single plates structure with approximately 1-2 μm in length and 50 nm in thickness.

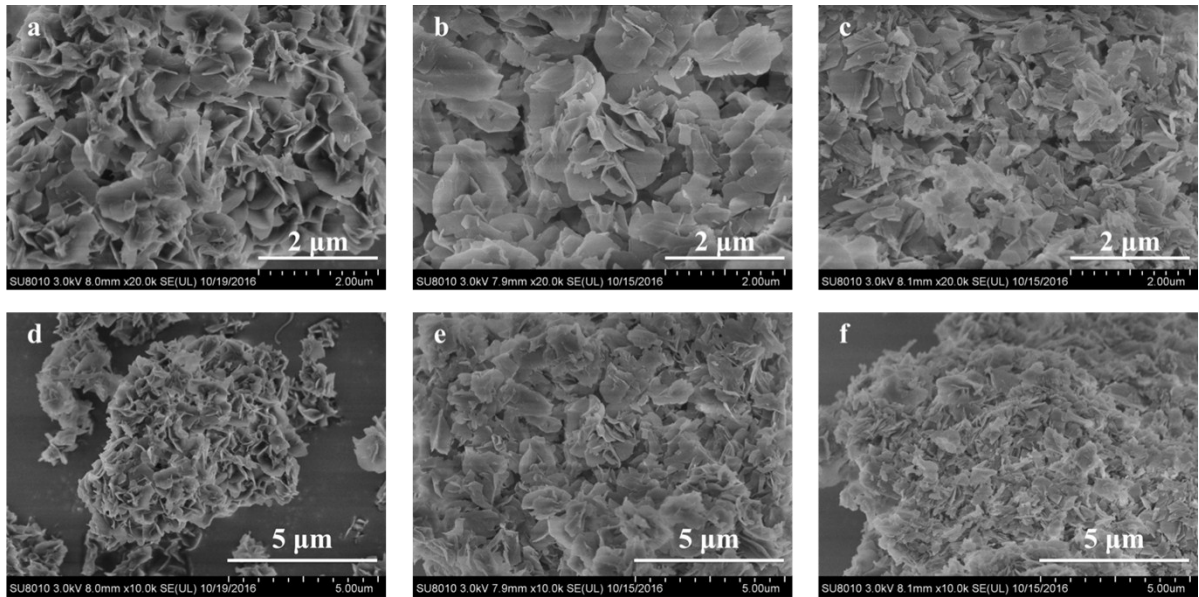


Fig. S4 SEM images of silicalite-1/GO composites synthesized at 150 °C for 8 d then calcined at 550 °C for 6 h under air flow. (a) and (d): Sil-5%GO, (b) and (e): Sil-10%GO, (c) and (f): Sil-36%GO.

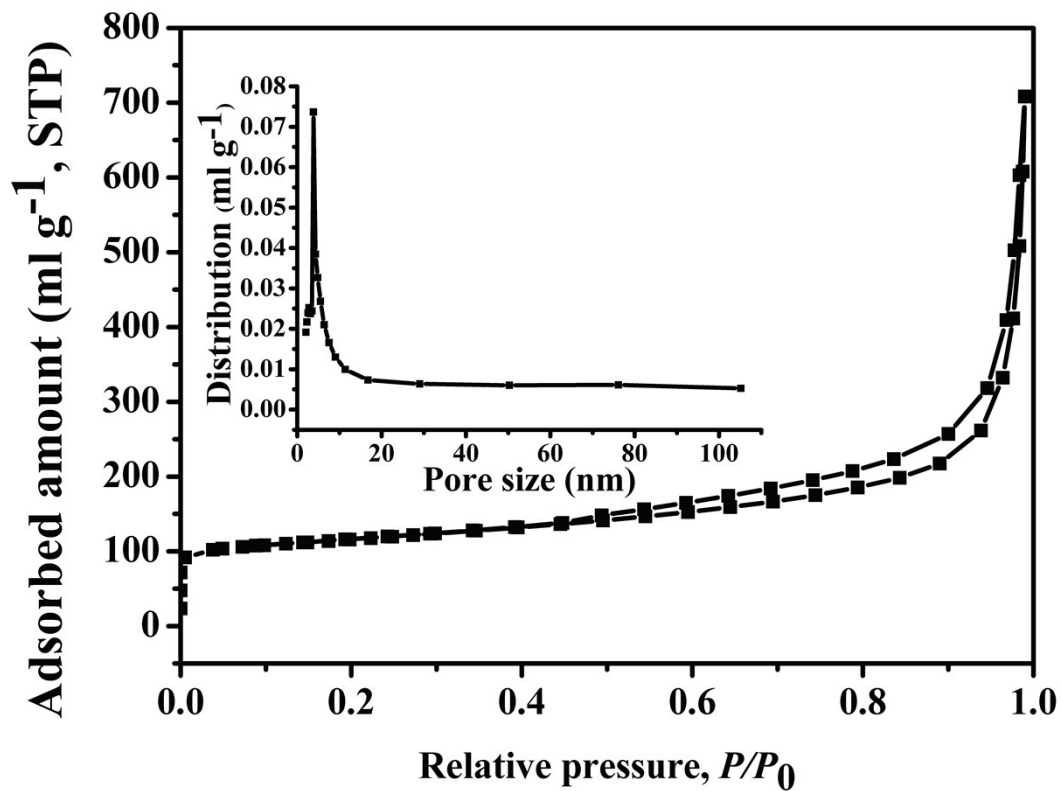


Fig. S5 Nitrogen sorption isotherm curve and pore size distribution of Sil-10%GO calcined at 550 °C for 6 h in air flow.

Reference

1. M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, *Nature*, 2009, **461**, 246-249.