Growth of zeolite crystals with graphene oxide nanosheets

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Supplementary Information

Sample preparation and characterization methods

Graphene oxide (GO) solution with a concentration of 2.1 mg/mL was prepared by exfoliation of graphite according to the reported method. [1] Silicalite synthesis solution was prepared by mixing 1.666 g of 30 wt% Ludox colloidal silica (Sigma-Aldrich) with 0.634 g of 1M tetrapropylammonium hydroxide (TPAOH) aqueous solution (Sigma-Aldrich) in a polypropylene bottle. A different amount of GO solution was added into the silicalite synthesis solution and stirred at room temperature for 4 h, ensuring good dispersion of GO. The resultant solution was dried in a petri dish at 40 °C overnight, and then transferred to a Teflon-lined autoclave, which was pre-filled with 10 g of 1 M TPAOH solution. Hydrothermal zeolite crystallization was carried out at 150 °C for different times. After the crystallization, the sample was washed with deionized water

and then dried at 60 °C overnight. The resulting silicalite-GO composites with 3%, 10% and 20% GO by mass are denoted Sil-3%GO, Sil-10%GO and Sil-20%GO, respectively. For comparison, silicalite crystals were also synthesized under the same conditions except that GO was not added.

To observe the entrapment of GO nanosheets in silicalite crystals, a small portion of Sil-3%GO was further treated in 2 M NaOH solution at room temperature for 4 h to partially dissolve silicalite crystals, followed by washing with deionized water and drying at 60 °C overnight. Two portions of each sample were calcined either under flowing nitrogen at 700 °C for 2 h or under flowing oxygen at 550 °C for 2 h for analysis. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-7001F microscope (JEOL). TEM samples were prepared by dispersing some of the product in butanol by crushing and placing a droplet on a holey-carbon grid. High-resolution transmission electron microscope (HRTEM) images were recorded using a 200 kV JEOL 2011 equipped with a Gatan Ultrascan 1000 CCD system. The instrument has a point resolution of 0.23 nm. X-ray diffraction (XRD) patterns were recorded on a Philips PW1140/90 diffractometer with CuKα radiation (25 mA and 40 kV) at a scan rate of 2°/min and a step size of 0.02°. Nitrogen adsorption–desorption experiments were performed at 77 K on a Micromeritics ASAP 2020MC gas sorption analyser. The electrical conductivity of the Sil-10%GO sample was measured on a Jandel 4-point Conductivity Probe by using a linear arrayed four-point head. Raman spectra were obtained with a Renishaw Invia Raman microscope at an excitation line of 633 nm.

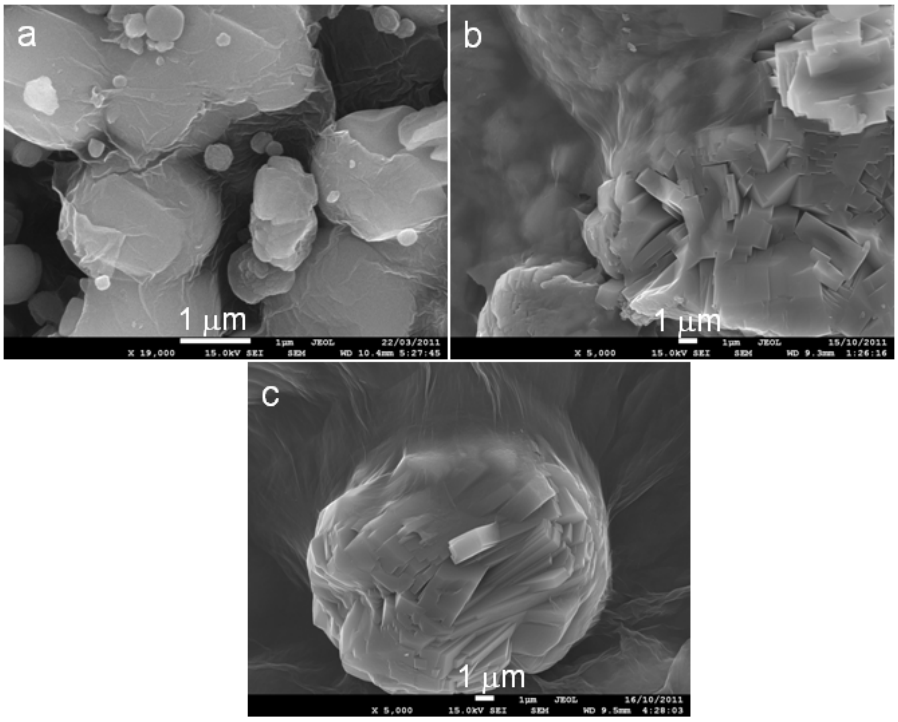


Fig. S1. SEM images of as-synthesized Sil-GO composites: (a) Sil-3%GO, (b) Sil-10%GO, and Sil-20%GO.

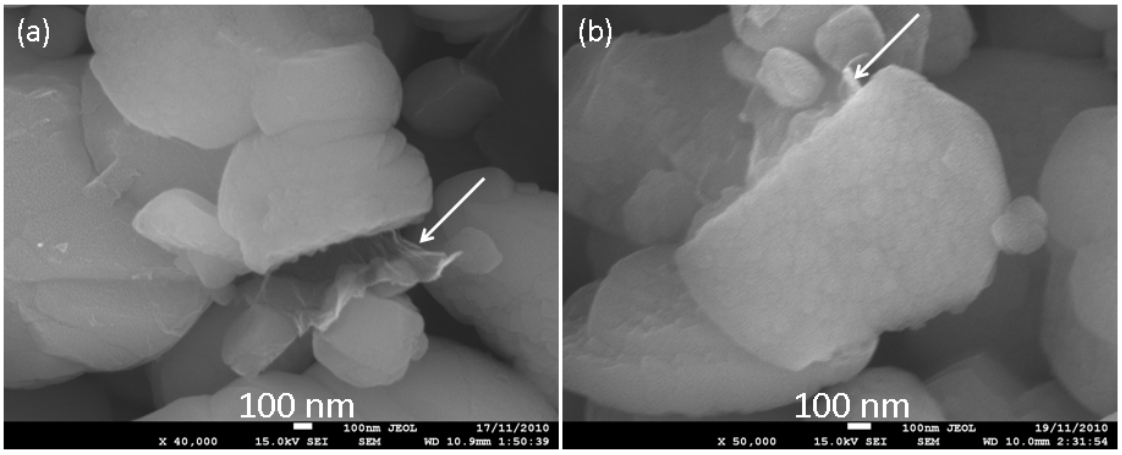


Fig. S2. SEM image of Sil-3% GO composites treated in NaOH solution showing that GO sheets (indicated by arrows) are incorporated into silicalite crystals.

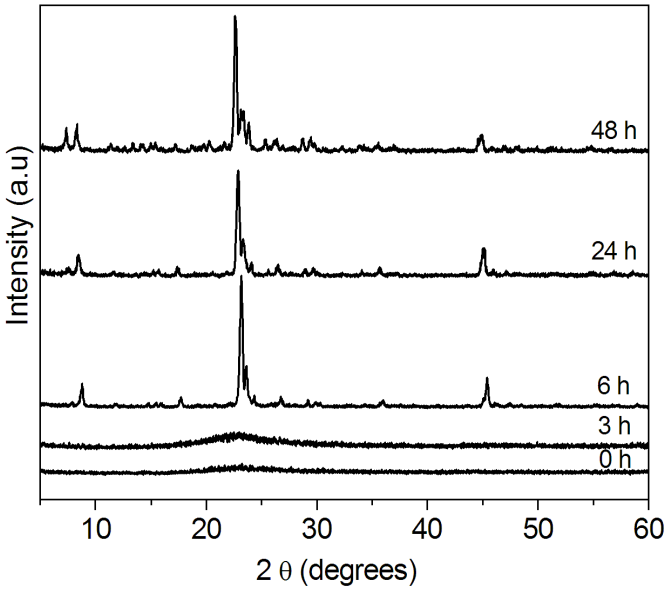


Fig. S3. XRD patterns of silicalite precursor-10 % GO hydrothermally heated at 150 °C for different times.

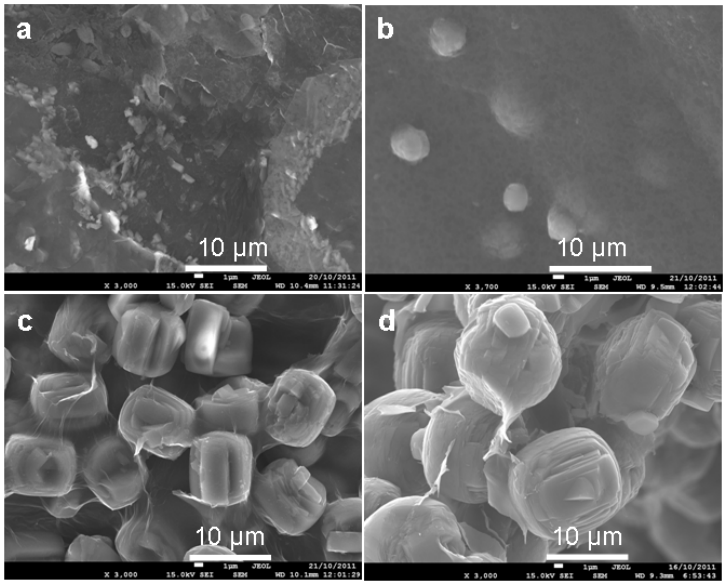


Fig. S4. SEM images of (a) dried silicalite precursor-10% GO, (b) silicalite precursor-10% GO composite hydrothermally treated at 150 °C for 3 h, and (c, d) silicalite-10% GO composites synthesized at 150 °C for different times: (c) 6 h and (d) 24 h.

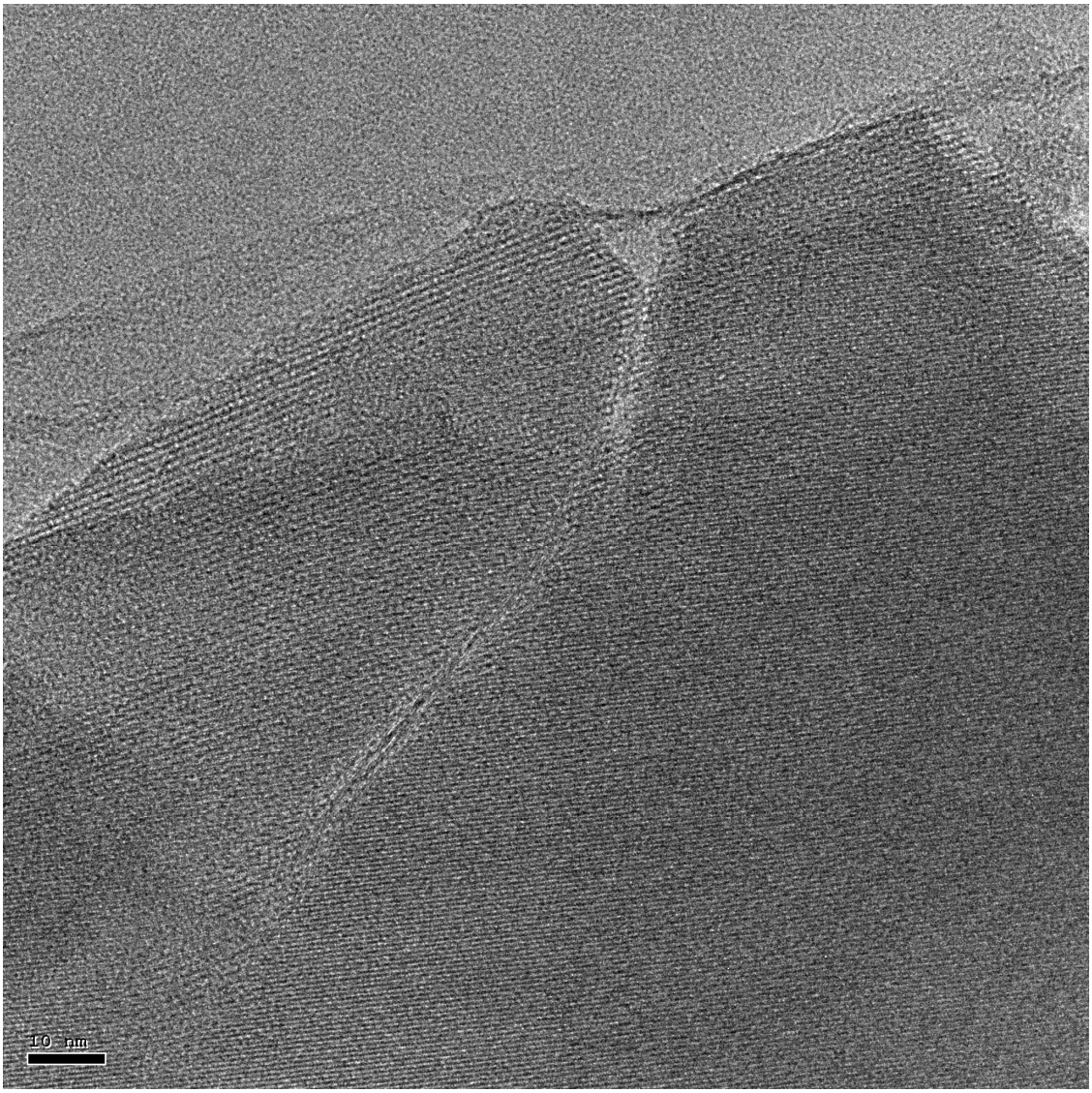


Fig. S5. TEM images of silicalite-GO composite (Sil-10% GO) showing that GO nanosheets are entrapped inside a silicalite crystal.

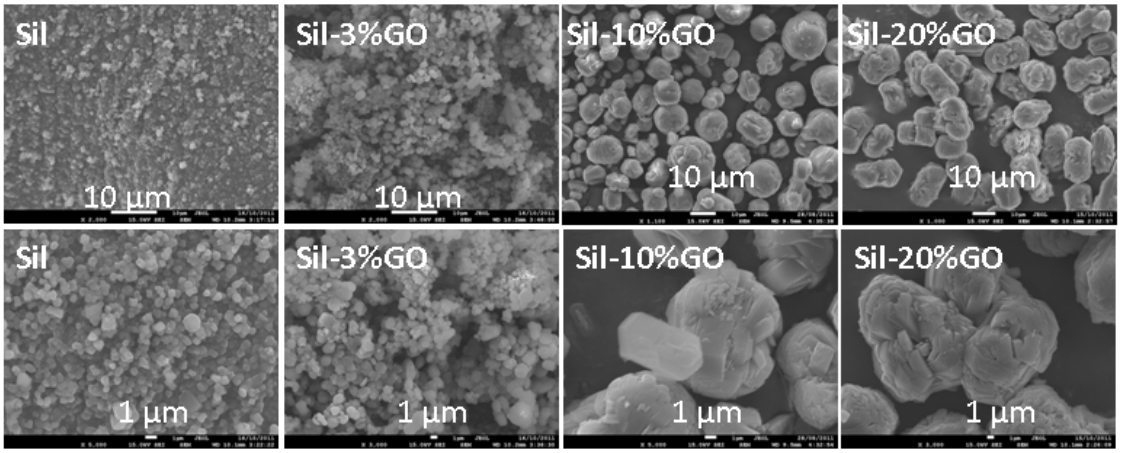
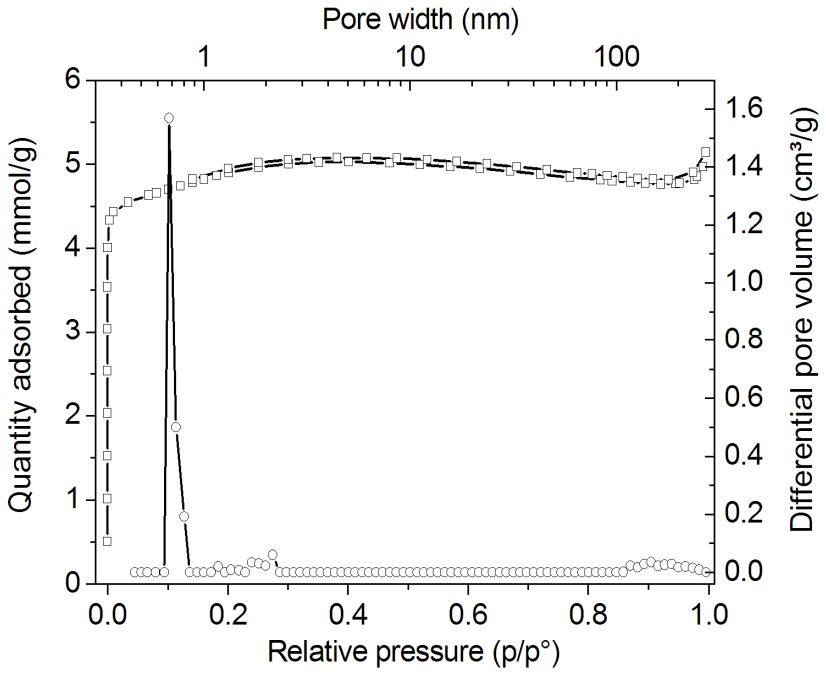
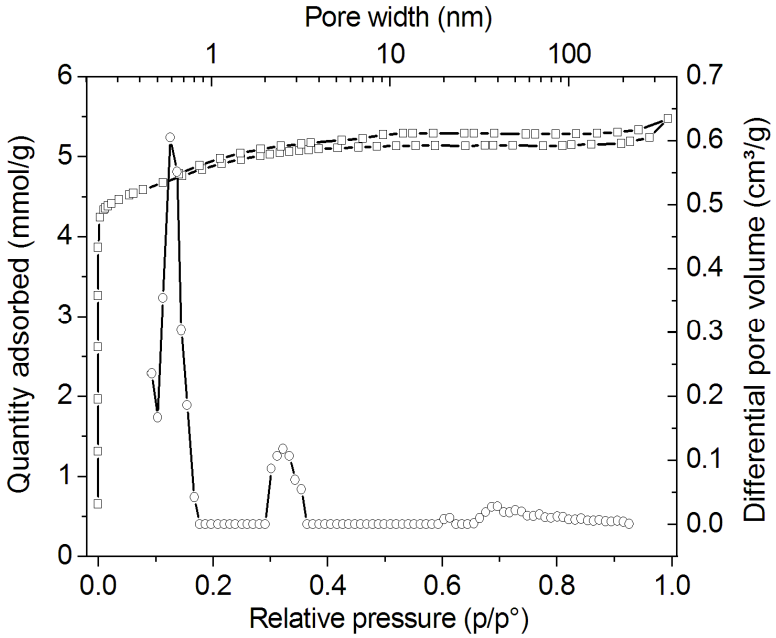


Fig. S6. SEM images of silicalite (Sil) and silicalite-GO composites synthesized at 150 °C for 48 h and then calcined at 550 °C for 2 h in oxygen (upper row: low magnification images; lower row: high magnification images).



(a)



(b)

Fig. S7. Nitrogen sorption isotherm curves and pore size distributions of silicalite-GO composite (Sil-20%GO) calcined (a) at 700 °C for 2 h in nitrogen, and (b) at 550 °C for 2 h in oxygen.

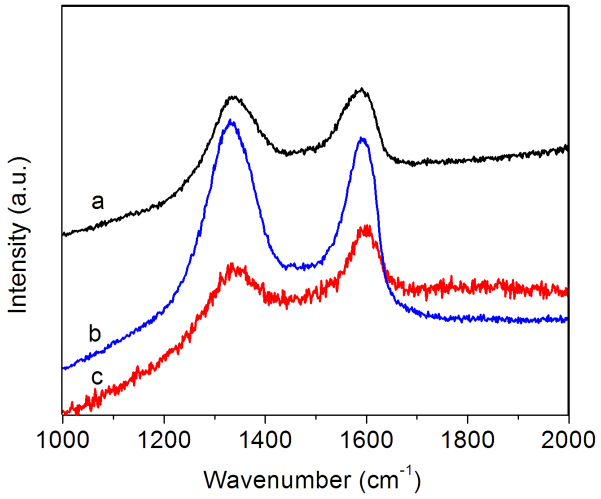


Fig. S8. Raman spectra of (a) silicalite precursor-GO composite, (b) silicalite-GO composite synthesized at 150 ºC, and silicalite-GO composite calcined at 700 ºC for 2 h in nitrogen

Reference

1. D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101-105.