Synthesis of *b*-oriented MFI nanosheet with high-aspect ratio by suppressing intergrowth with 2D GO nanosheet

He Ding, Xiuxiu Ni, Yixiao Zhang, Jingshuang Zhang, Zhouliangzi Zeng, Menglin Qi, Peng Bai and Xianghai Guo*

Department of Pharmaceutical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China
Key Laboratory of Systems Bioengineering (Ministry of Education), Tianjin University, Tianjin, 300350, P. R. China
*Corresponding author.

Preparation of organic-structure directing agent (OSDA)

The process of synthesis $C_{22\text{-}6\text{-}6}$ was prepared according to Ryoo[1]. In brief, 1-bromodocosane and N,N,N',N'-tetramethyl-1,6-diaminohexane with molar ratio of 1:10 were dissolved in acetonitrile/toluene mixture (1:1 vol/vol). After reacting at 70 °C for 10 h, the product was filtered and evaporated to remove superfluous solvent. Next step, the first-step product and 1-bromohexane with molar ratio of 1:1.3 were dissolved in acetonitrile and heated at 90 °C for 10h. The post-treatment process was the same as before, and then $C_{22\text{-}6\text{-}6}$ (Br_2) was obtained and served as organic structure directing agent.

Optimization Process of Synthesis Temperature

The synthesis temperature from 150 °C to 220 °C had been investigated. When the temperature was beyond 180 °C, the structure-directing agents ($C_{22\text{-}6\text{-}6}$) were unstable in the synthesis system and lost their activity gradually. The Sil-10%GO samples synthesized at 160 °C, 170 °C and 180 °C were characterized by SEM (Fig. S1). It was obviously to observe that there were still lots of amorphous silica attaching on the surface of product, which meant they didn't fully crystallize. For higher temperature, the as-synthesized sample aggregated densely with three-dimensional intergrowth. After some experiments, it suggested that 150 °C was the best synthesis temperature for growth of silicalite-1/GO composites.

Calculation Method

The theoretical value is calculated as $W_{GO}/(W_{GO}+W_{Silicalite\text{-}1})$, where W_{GO} means the practical weight of GO nanosheet in experiment and $W_{Silicalite\text{-}1}$ is calculated from the moles of Si in TEOS.

Table S1. The S_{BET} comparison of all as-synthesized samples before and after calcination.

Sample	Before calcination				After calcination			
	V [cm^3g^{-1}]	S_{BET} [m^2g^{-1}]	S_{EXT} [m^2g^{-1}]	S_{INT} [m^2g^{-1}]	V [cm^3g^{-1}]	S_{BET} [m^2g^{-1}]	S_{EXT} [m^2g^{-1}]	S_{INT} [m^2g^{-1}]
Silicalite-1	0.45	108	108	0	0.47	377	190	187
Sil-10%GO	0.34	65	65	0	0.41	416	253	163
Sil-22%GO	0.20	22	22	0	0.47	397	350	46
Sil-36%GO	0.12	11	11	0	0.40	372	284	88
GO	0	0	0	0	—	—	—	—

The t-plot method was used for estimating the external specific surface of the samples. The internal specific surface are was obtained by subtracting the external surface from S_{BET}.

Table S2. Textural property of calcined samples and silicalite-1 in literature

Sample	V [cm^3g^{-1}]	S_{BET} [m^2g^{-1}]	S_{EXT} [m^2g^{-1}]	S_{INT} [m^2g^{-1}]
silicalite-1(>1000 μm)[2]	0.13	392	182	210
silicalite-1(as-synthesized)	0.47	377	190	187
Sil-10%GO	0.41	416	253	163
Sil-22%GO	0.47	397	350	46
Sil-36%GO	0.40	372	284	88

Note: Ar gas as adsorbate, Navarro et al.[2], micrometer-sized silicalite-1 zeolites. The t-plot method was used for estimating the external specific surface of the samples. The internal specific surface was obtained by subtracting the external surface from S_{BET}.

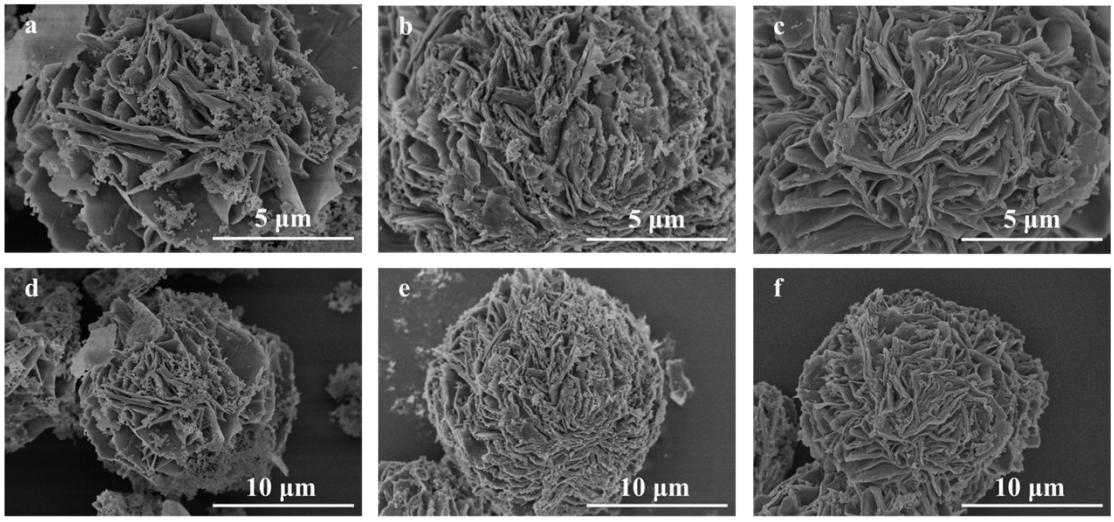

Fig. S1 SEM images of Sil-10%GO synthesized at different temperatures: (a) and (d): 160 °C, (b) and (e): 170 °C, (c) and (f): 180 °C.

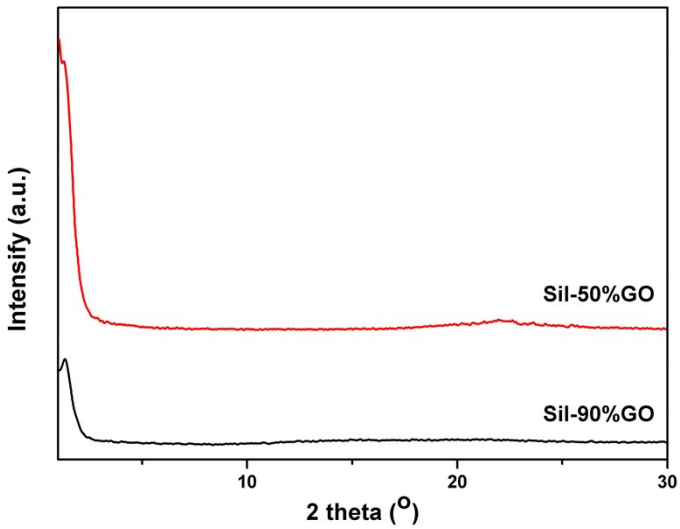

Fig. S2 XRD of Sil-50%GO and Sil-90%GO samples synthesized at 150 °C for 8 d.

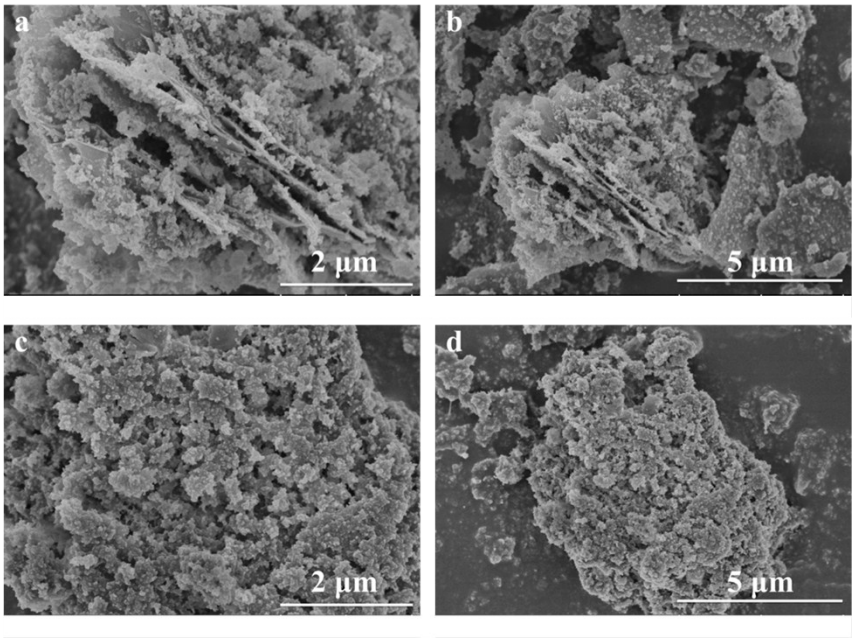

Fig. S3 SEM images of (a) and (b): Sil-50%GO, (c) and (d): Sil-90%GO.

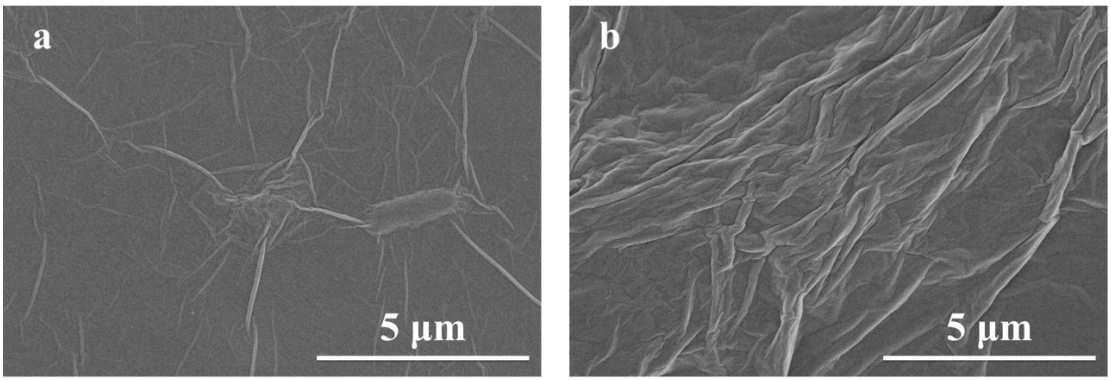

Fig. S4 SEM images of GO nanosheets.

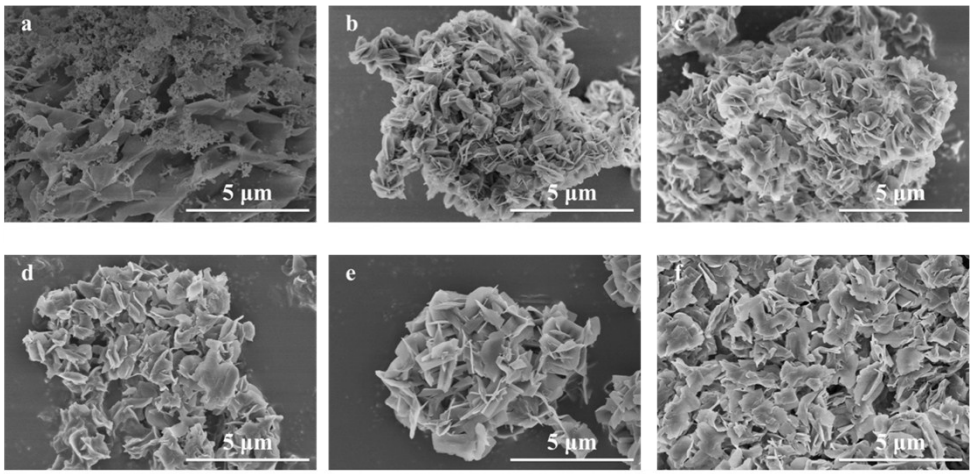

Fig. S5 SEM images of (a) silicalite-1 and (b-f) silicalite-1/GO as-synthesized samples: (b) Sil-1%GO, (c) Sil-5%GO, (d) Sil-10%GO, (e) Sil-22%GO, (f) Sil-36%GO

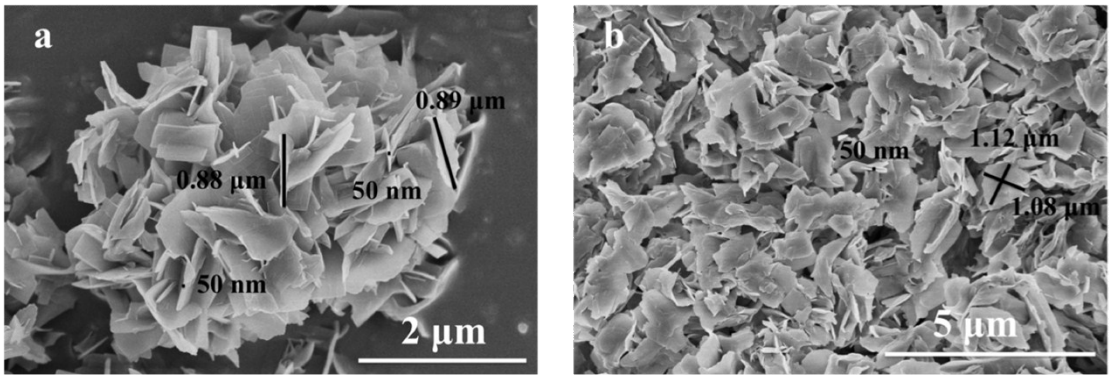

Fig. S6 SEM images of Sil-36%GO

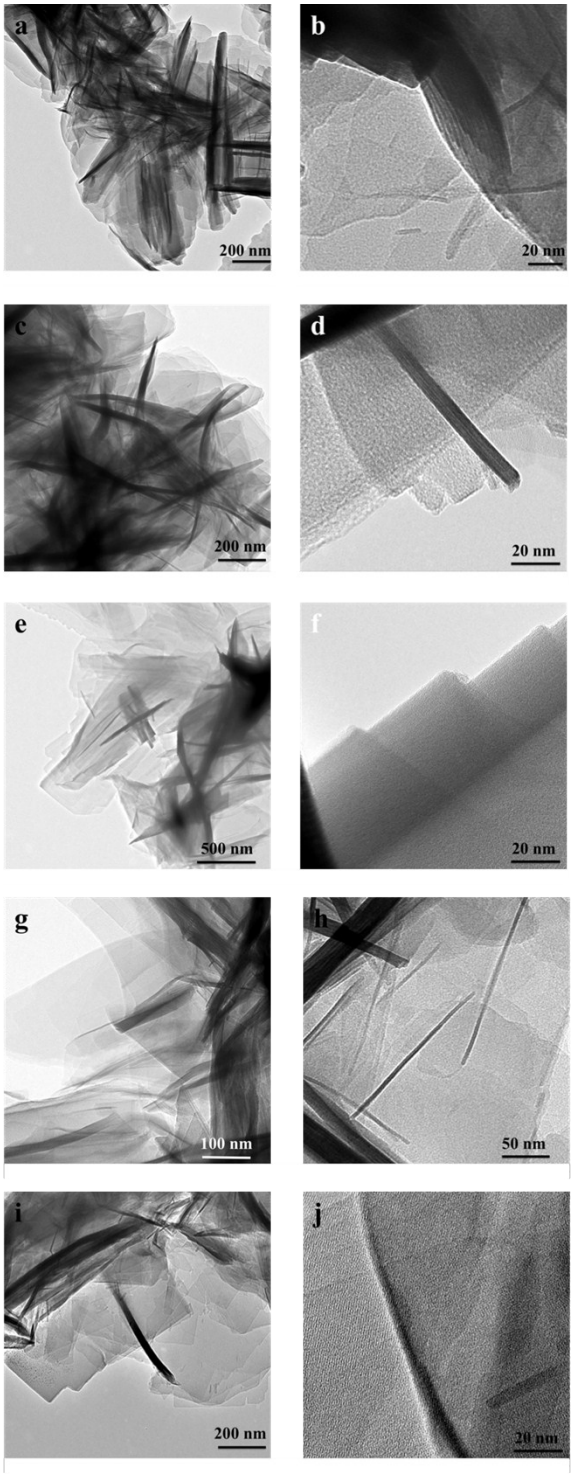

Fig. S7 TEM images of silicalite-1/GO composites synthesized at 150 °C for 8 d, (a) and (b): Sil-1%GO, (c) and (d): Sil-5%GO, (e) and (f): Sil-10%GO, (g) and (h): Sil-22%GO, (i) and (j): Sil-36%GO.

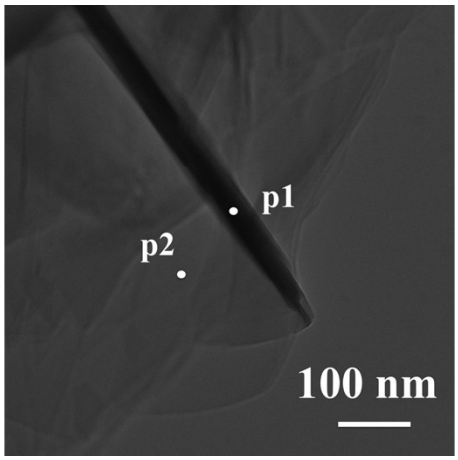

Fig. S8 TEM of Sil-10%GO (p1: point 1, p2: point 2)

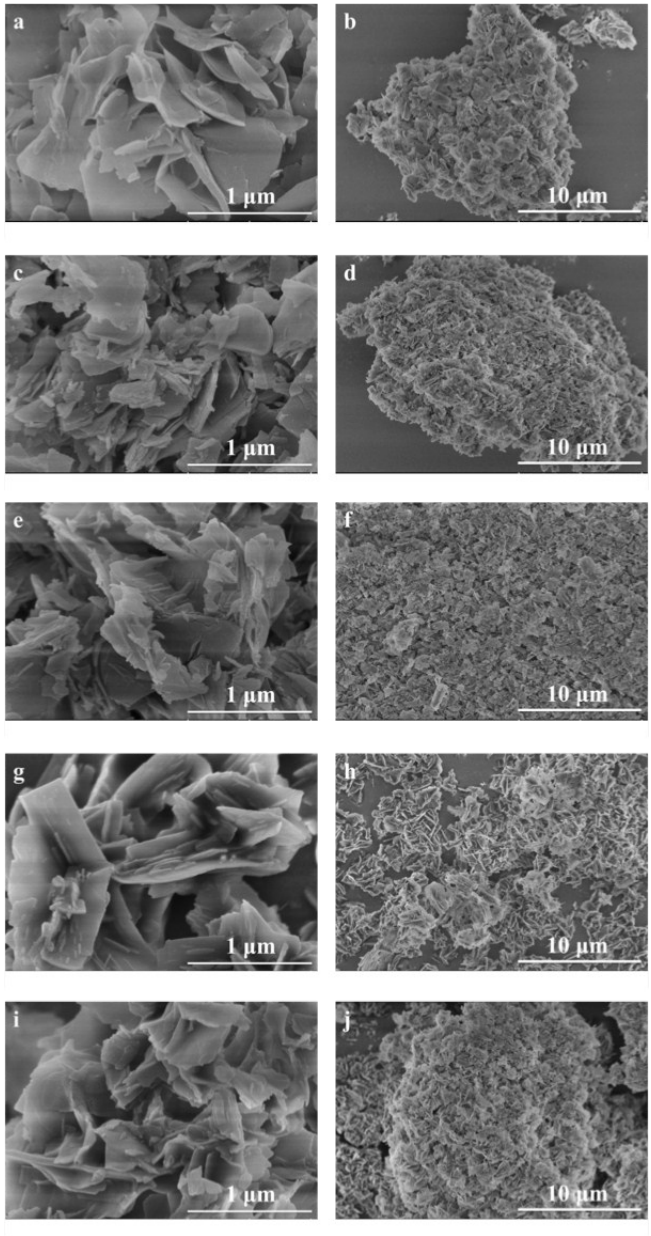

Fig. S9 SEM images of silicalite-1/GO composites synthesized at 150 °C for 8 d then calcined at 550 °C for 6 h under air flow, (a) and (b): Sil-1%GO, (c) and (d): Sil-5%GO, (e) and (f): Sil-10%GO, (g) and (h): Sil-22%GO, (i) and (j): Sil-36%GO.

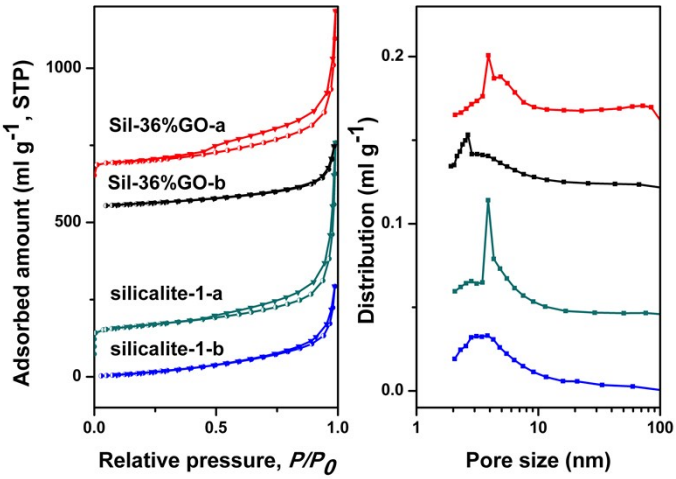

Fig. S10 Nitrogen sorption isotherm curve and pore size distribution of silicalite-1 and Sil-36%GO before and after calcination.

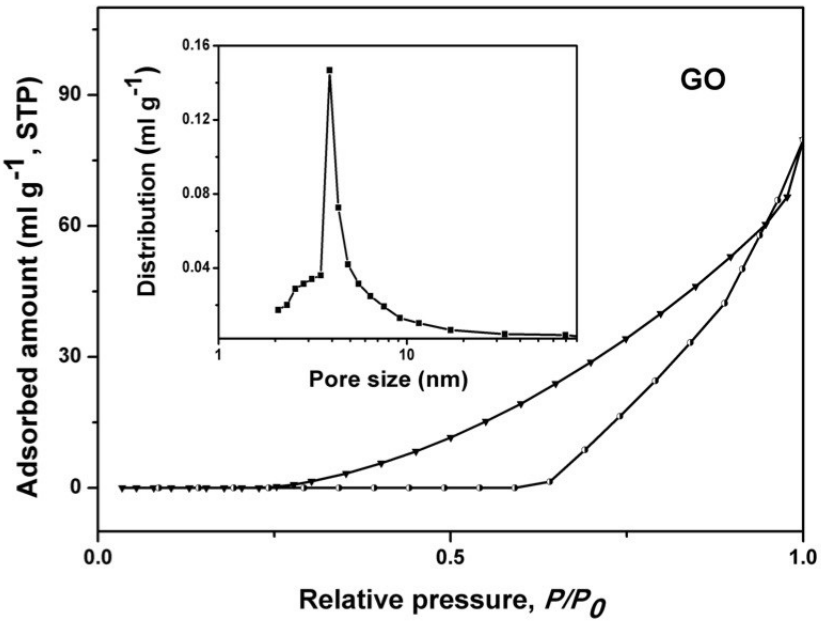

Fig. S11 Nitrogen sorption isotherm curve and pore size distribution of graphene oxide

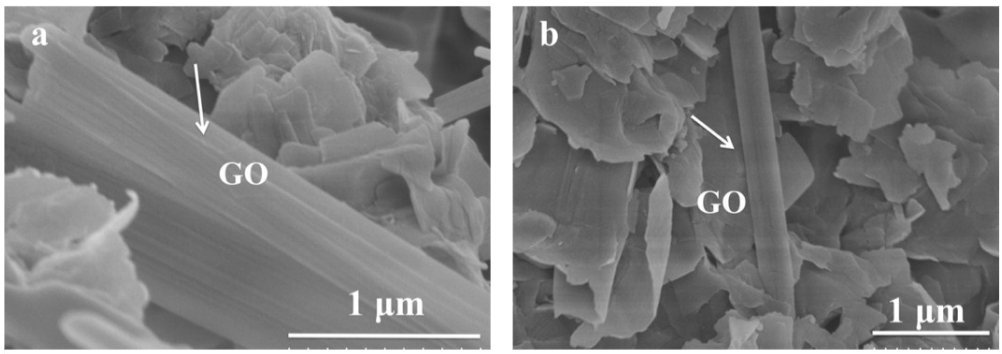

Fig. S12 SEM images of Sil-5%GO after base treatment and water-washing showing that GO nanosheets were wrapped with silicalite-1.

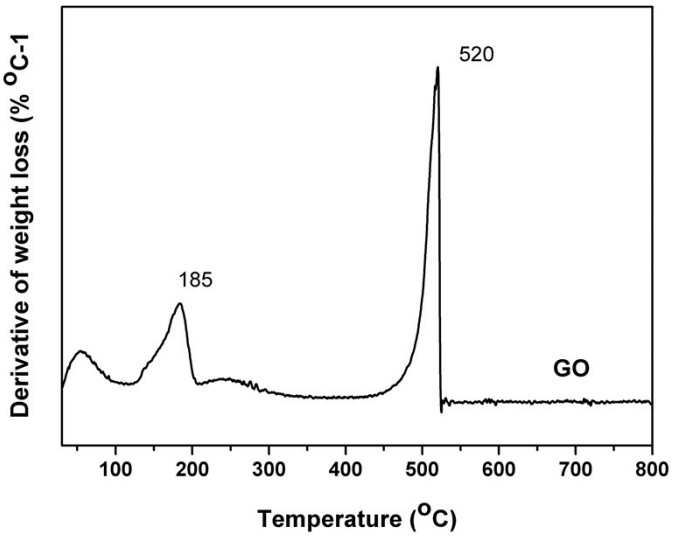

Fig. S13 DTG curves of GO nanosheets

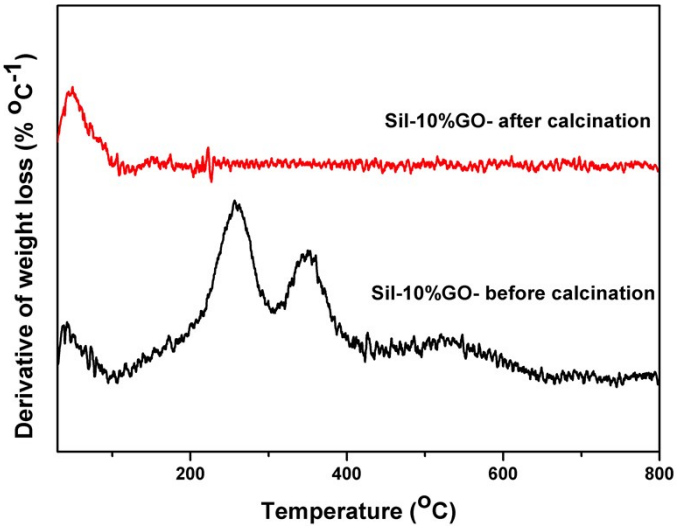

Fig. S14 DTG curves of Sil-10%GO before and after calcination

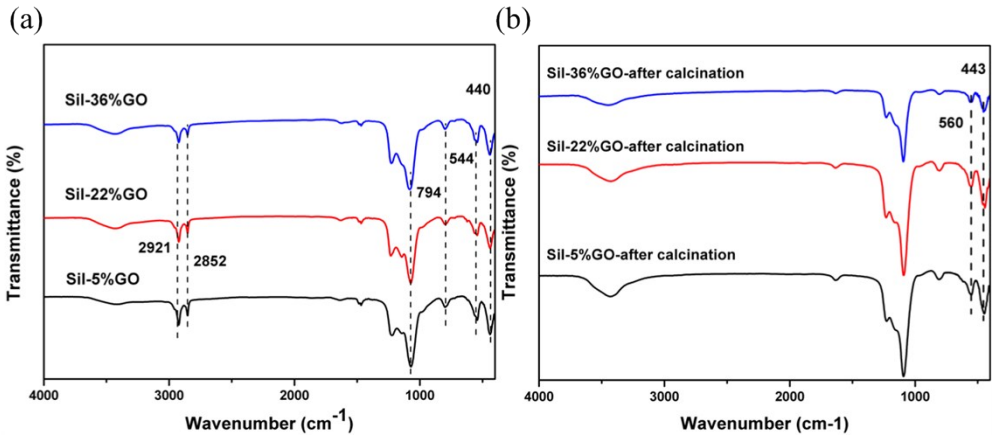

Fig. S15 (a) FT-IR spectra for Sil-5%GO, Sil-22%GO and Sil-36%GO; (b) FT-IR spectra for Sil-5%GO, Sil-22%GO and Sil-36%GO after calcination

Reference：

1. M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, *Nature*, 2009, **461**, 246-249.
2. M. Navarro, E. Mateo, B. Diosdado and J. Coronas, *CrystEngComm*, 2012, **14**, 6016-6022.