

## *Electronic Supplementary Information*

### **Ice Crystal Guided Folding of Graphene Oxides in a Confined Space: A Facile Approach to 1D Functional Graphene Structures**

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## Experimental

### Fabrication of FGOBs and functional FGBs

GO (3 mg/ml) was prepared initially by a modified Hummers method described in our previous report.<sup>1</sup> In order to form air bubbles, GO (3 mg/ml, 10 ml) was stirred with D<sub>400</sub> (60 mg) to form a homogeneous dispersion first. GO bubbles were formed by blowing air (60 ml/min) into the dispersion with a thin glass tube. FGOBs were formed by rapid freezing in liquid nitrogen of the GO containing bubbles followed by freeze drying process. Thermal treatment of the FGOBs was performed under N<sub>2</sub> atmosphere at 500 °C for 60 mins.

### Encapsulating target materials into the FGBs

$\beta$ -FeOOH nanorods (precursor of Fe<sub>3</sub>O<sub>4</sub> nanorods) were prepared according to the literature.<sup>2</sup> TiO<sub>2</sub> nanoparticles (P25) were purchased from Evonik Degussa, Germany. The commercial P25 was used directly without further treatment. Co<sub>3</sub>O<sub>4</sub> was produced by an ethylene glycol mediated precipitation method reported in literature.<sup>3</sup> In a typical procedure to get nanomaterial encapsulated FGBs, target materials such as TiO<sub>2</sub> (30 mg) or Co<sub>3</sub>O<sub>4</sub> (40 mg), or their precursors such as  $\beta$ -FeOOH nanorods (48 mg) were separately mixed with GO/D<sub>400</sub> mixture (GO 20 ml, 3 mg/ml and D<sub>400</sub> 120 mg) before the formation of bubbles. Then, hybrid air bubbles containing GO and the target nanomaterials were formed by blowing air into the dispersion. Note that the presence of TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> or  $\beta$ -FeOOH does not affect the formation of GO bubbles, which is the key factor to successfully encapsulate target nanomaterials into the FGOBs. Subsequent liquid nitrogen shock cooling and freeze drying resulted in specific nanomaterials

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encapsulated FGOBs. Finally, the hybrid FGOBs were transformed to  $\text{TiO}_2@\text{FGBs}$ ,  $\text{Co}_3\text{O}_4@\text{FGBs}$ , and  $\text{Fe}_3\text{O}_4@\text{FGBs}$ , respectively by annealing under  $\text{N}_2$  atmosphere at  $500\text{ }^\circ\text{C}$  for 60 mins.

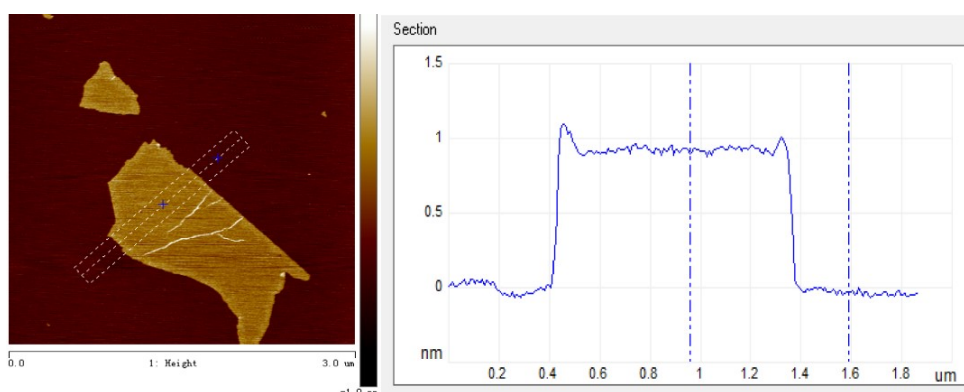
### **Characterization**

SEM images were taken on a NOVA NanoSEM 450 Field Emission Scanning Electron Microscope (Oxford Instrument, INCA Wave). The thickness of GO was measured using AFM (Multimode 8, Bruker). Zeta potential of the samples was obtained by a Malvern Zetasizer Nano-ZS analyzer. A Modular CAM 200 Optical Contact Angle and Surface Tension Meter (KSV Instruments) was employed to measure the surface tension. Optical microscope images were obtained by an Olympus GX71 optical microscope equipped with a DP25 Digital Camera (Olympas Corporation, Japan). Fourier transform-infrared (FTIR) spectrum was recorded with Thermo Nicolet 6700 FTIR Spectrometer. The *in-situ* X-ray diffraction experiment was performed on an Inel powder diffractometer ( $\text{Co K}\alpha$ ,  $\lambda=0.1789\text{ nm}$ ) equipped with a Debye-Scherrer CPS120 position-sensitive detector, allowing for rapid XRD data acquisition. A FEI TF30 transmission electron microscope was employed to investigate the detailed structure of the FGBs.

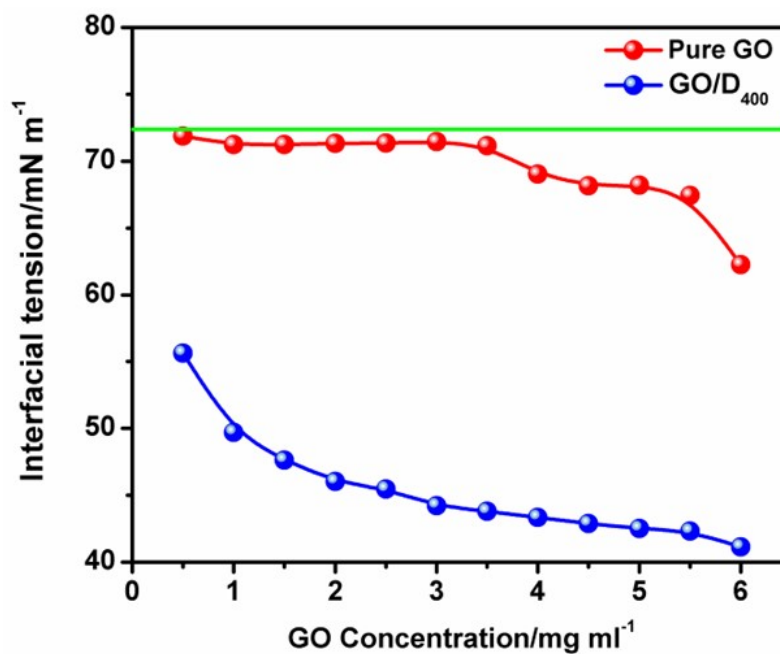
### **Electrochemical Measurements**

The electrochemical measurements were conducted using CR2016 coin cells with pure lithium foil as the counter and reference electrode at room temperature. The working electrode consists of  $\text{Fe}_3\text{O}_4@\text{FGB}$ , Super P and polyvinylidene difluoride (PVDF) in a weight ratio of 8:1:1. A solution of 1.0 M LiPF<sub>6</sub> in ethylene carbonate:diethyl carbonate

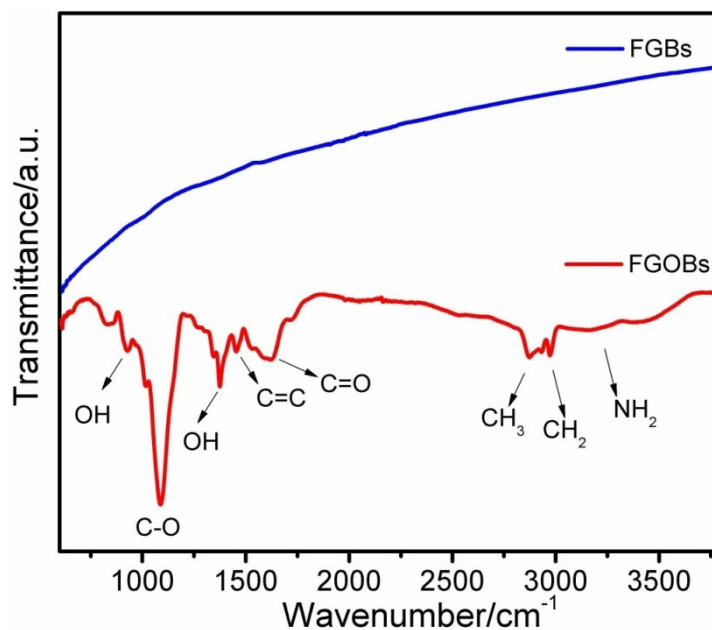
(EC:DEC, 1:1 by weight) was used as the electrolyte. Cell assembly was carried out in an Ar-filled glovebox with the concentration of moisture and oxygen below 1.0 ppm. The galvanostatic charge/discharge tests were performed using a LAND CT2001A battery tester at different current densities within a cut-off voltage window of 0.01-3.0 V.



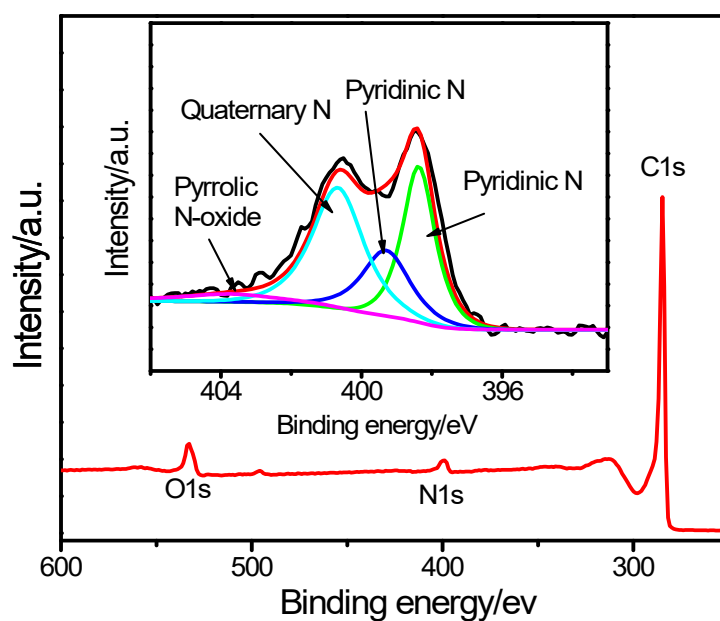
**Fig. S1.** AFM image of GO sheets laying over a Si/SiO<sub>2</sub> substrate and the corresponding height profile.



**Fig. S2.** Effect of D<sub>400</sub> on the surface tension of GO dispersion with different concentrations (GO/D<sub>400</sub> = 2 in all the samples).

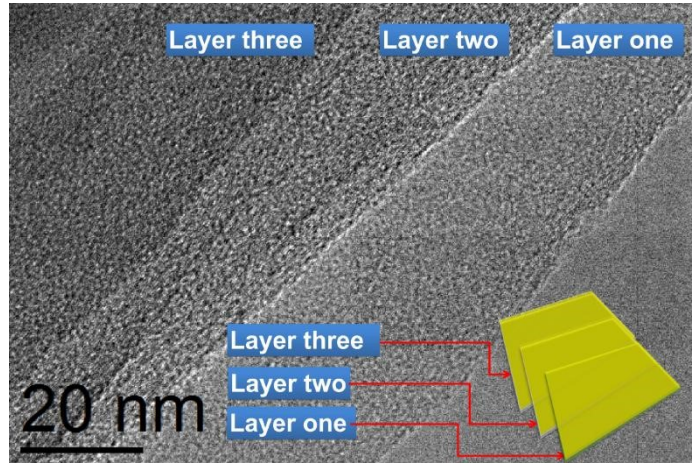


**Fig. S3.** ATR-FTIR spectra of FGOBs and FGBs.

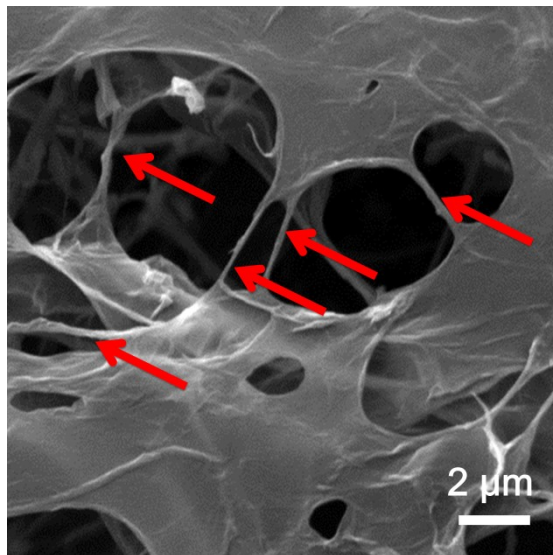


**Fig. S4.** XPS spectrum of the FGBs, inset is deconvoluted curves of N 1s.

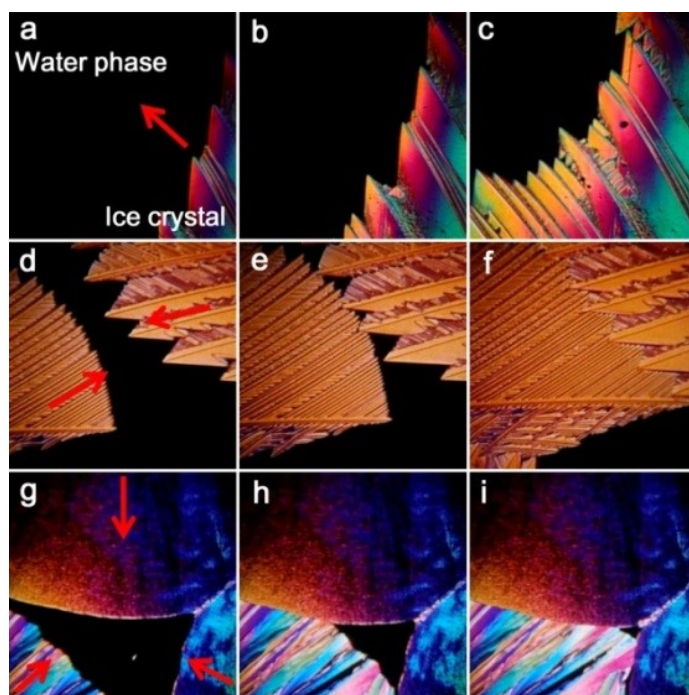
The N 1s spectrum of the FGBs can be deconvoluted into four different kinds of N species,<sup>4</sup> including pyridinic N (398.3 eV), pyrrolic N (399.2 eV), quaternary N (400.7 eV), and N-oxides of pyridinic N (403.6 eV), suggesting that N atoms originating from D<sub>400</sub> have been successfully incorporated into the final graphene structure (Fig. S4).



**Fig. S5.** Higher magnification TEM image of the edge of a typical FGB showing the face to face stacking of graphene layers as a result of the accordion folding process.

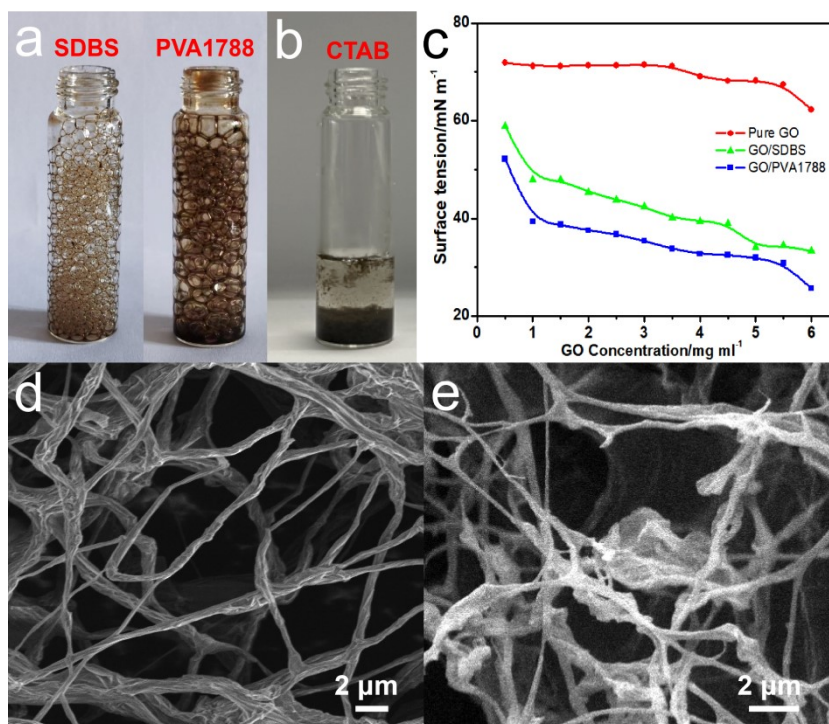


**Fig. S6.** Higher magnification SEM image of the sample demonstrated in Fig. 2d.

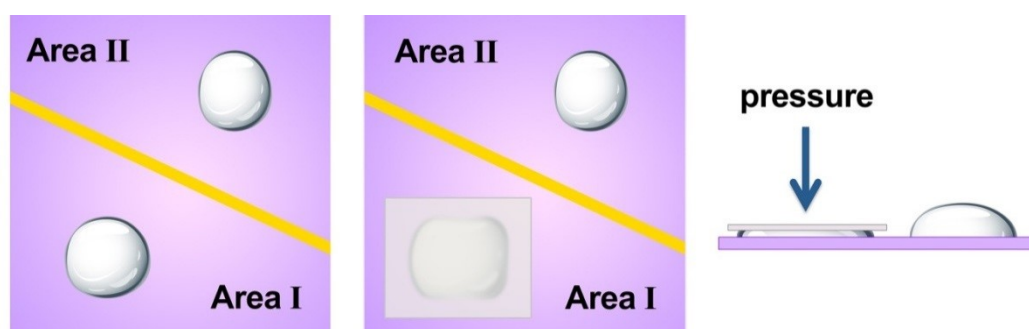


**Fig. S7.** Snapshots of the ice crystallization process.<sup>5</sup> a-c) One ice crystal domain has grown along the direction of the crystallization. d-f) Two ice crystal domains have grown in opposite directions and finally meet with each other. g-i) Three ice crystal domains come together. Red arrows indicate the direction of the crystallization.

As demonstrated in Fig. S7d-f, GO sheets in the suspension will be rejected from the solid phase and eventually move into the water phase (dark area in Fig. S7a-c). As the ice crystals organize into shape and meet with each other, GO sheets between them will eventually be squeezed into the final compact belt conformation in the manner of accordion fold (Video S1). Fig. S6g-i present another situation, in which the flat GO sheets will be forced to fold by more than one (such as three) ice crystal domains.



**Fig. S8.** a) Digital images of air bubbles formed by GO/SDBS and GO/PVA1788 mixtures. b) Digital image of GO precipitation caused by CTAB. c) Effect of SDBS and PVA1788 on the surface tension of GO dispersion with different concentrations (GO/Surfactant = 2 in all samples). d) SEM image of FGOBs formed from GO/SDBS air bubbles. e) SEM image of FGOBs formed from GO/PVA1788 air bubbles.



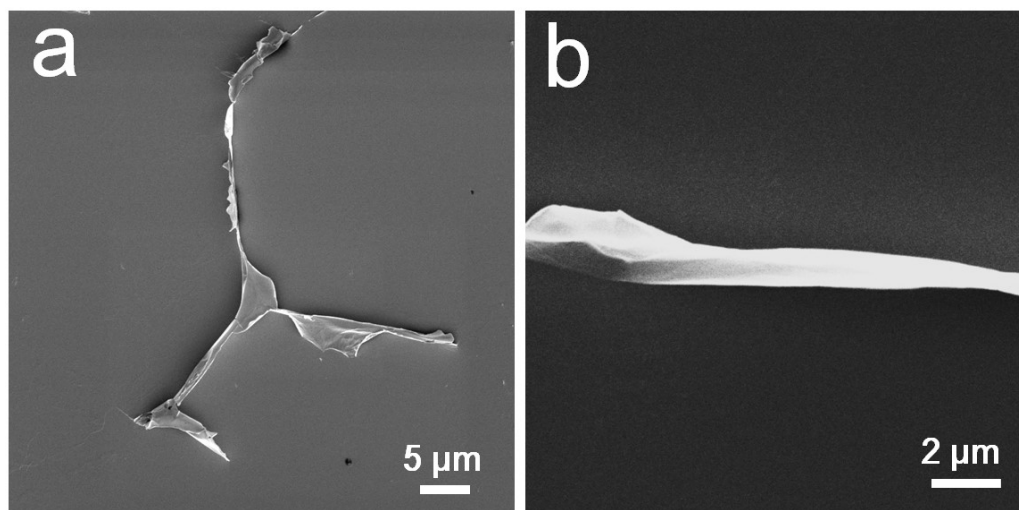
**Fig. S9.** Schematic diagrams of the procedure to create a confined space (water membrane) and the free space on the same surface.

As shown in Fig. S9, the surface of a Si wafer is divided into two areas (Area I and Area II). Then two drops of GO dispersion (3 mg/ml) are placed on the surface of Area I and Area II, respectively. In order to create a confined space on the surface of a Si wafer, another smaller Si wafer is put on the top of the GO droplet located in area I and pressed (150 kPa). Subsequently, a

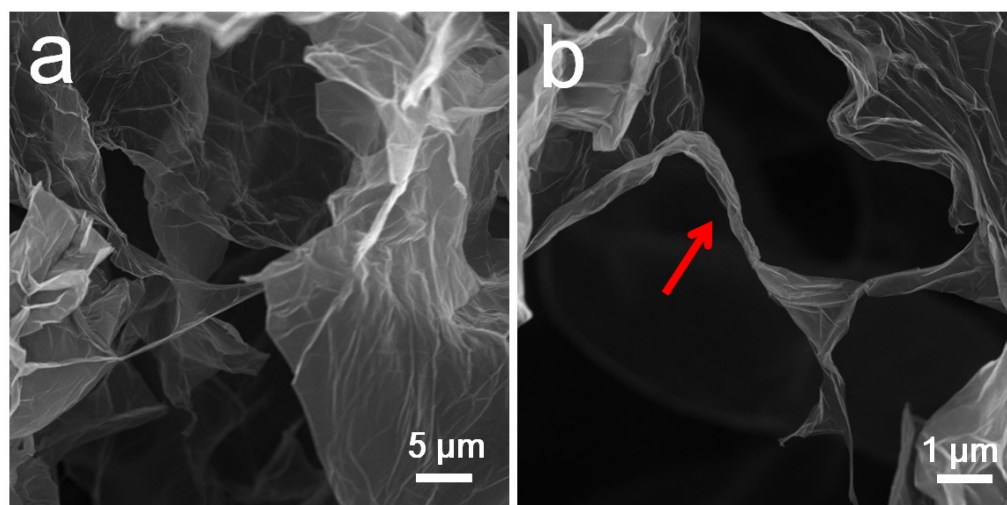


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thin water membrane is formed within the confined space created by two Si wafers. For comparison, another GO droplet located in area II is denoted as free droplet.



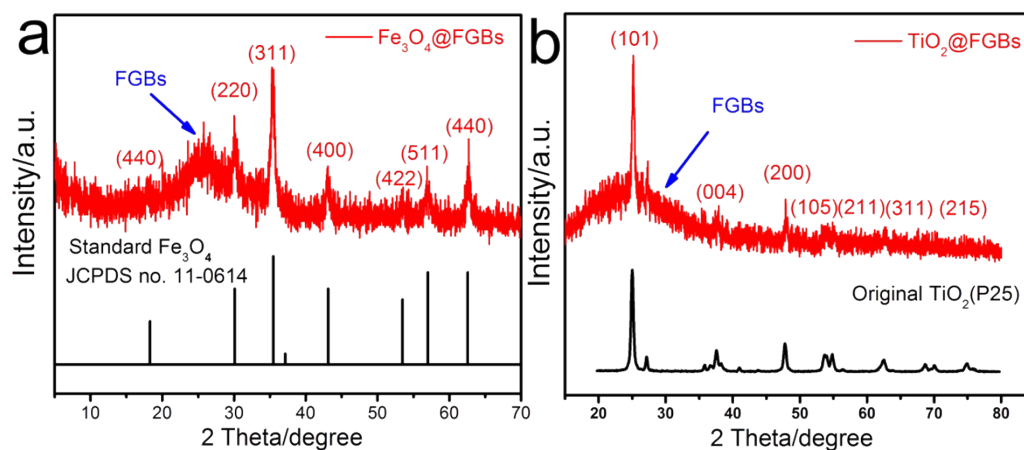
**Fig. S10.** a) SEM image of the 1D folded GO structure on the surface of Si wafer (Area I). b) SEM image of a strip of the FGOBs.



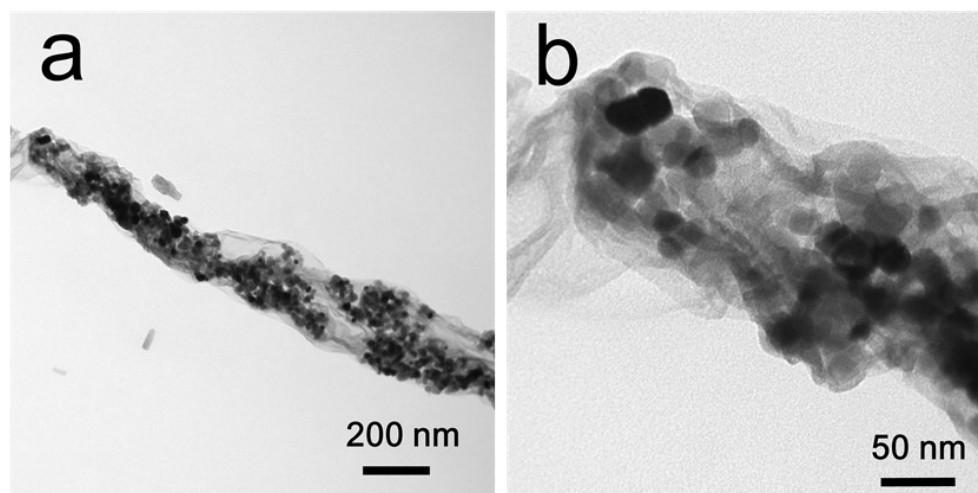
**Fig. S11.** a) Detailed SEM image of the macroporous structure formed in area II. b) SEM image of a strip of FGOBs existed in the macroporous structure.

Area II features macroporous structure that is formed by randomly stacking of graphene nanosheets (Fig. S11a). Previously, much attention has been paid to the direct synthesis of bulky, porous materials via the freeze casting of specific solutions. However, the conformational variations of the flat 2D graphene sheets were poorly investigated. Here we observe that ice casting in a

confined 2D space can result in the folding of flexible GO nanosheets and produce 1D FGOBs in a large scale. Interestingly, some small belts (or partially folded graphene sheets) can also be identified in the stacked structure at higher magnifications (Fig. S11b).



**Fig. S12.** a) XRD patterns of standard Fe<sub>3</sub>O<sub>4</sub> and the as-prepared Fe<sub>3</sub>O<sub>4</sub>@FGBs; b) XRD patterns of original TiO<sub>2</sub> (P25) and the as-prepared TiO<sub>2</sub>@FGBs.



**Fig. S13.** a) TEM image of one strip of the Co<sub>3</sub>O<sub>4</sub> nanoparticles encapsulated FGBs (Co<sub>3</sub>O<sub>4</sub>@FGBs). b) Higher magnification TEM image of the tip.

## References

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