Electronic Supporting Information (ESI)

Growth of 2D sheets of a MOF on graphene surfaces to yield composites with novel gas adsorption characteristics

Ram Kumar, Kolleboyina Jayaramulu, Tapas Kumar Maji* and C. N. R. Rao*

Experimental Section:

Graphite powder, Cadmium perchlorate hydrate and 2,3-Pyridinedicarboxylic acid were obtained from Sigma Aldrich. 4,4′-Azopyridine was synthesized using the procedure reported in literature.[1] Methanol, $KMnO_4$, $NaNO_3$ and other chemicals were obtained from Merck chemicals.

Synthesis of GO and BFG:

Graphite oxide was prepared using a modified Hummers and Offeman method.[2] In a typical synthesis 1.5 g graphite powder and 1.5 g of $NaNO_3$ were slowly added to 75 ml conc.H_2SO_4 and allowed to mix properly under constant stirring for 10 min. In the uniform mixture 10 g $KMnO_4$ was added and transferred to an oil bath maintained at 40 °C. The mixture was allowed to stir for next 30 min. Very viscous dark brown product was formed due to the oxidation of graphite. In the uniform viscous product 75 ml deionized water was added and the temperature of oil bath was raised to 75 °C. The stirring was performed for another 15 min with oil bath maintained at 75 °C. In 150 ml warm water (~ 70 °C) 15 ml H_2O_2 (30%) was mixed and added to the reaction mixture. The Colour of dispersion changed from dark brown to yellow. Obtained product was centrifuged and washed several times with water to remove excess acid. Washed product was again dispersed in water and dialysis was performed till dialysate became neutral. Dialysed product was centrifuged to remove excess water. Obtained solid product was transferred to petridish and stored under vacuum for drying.

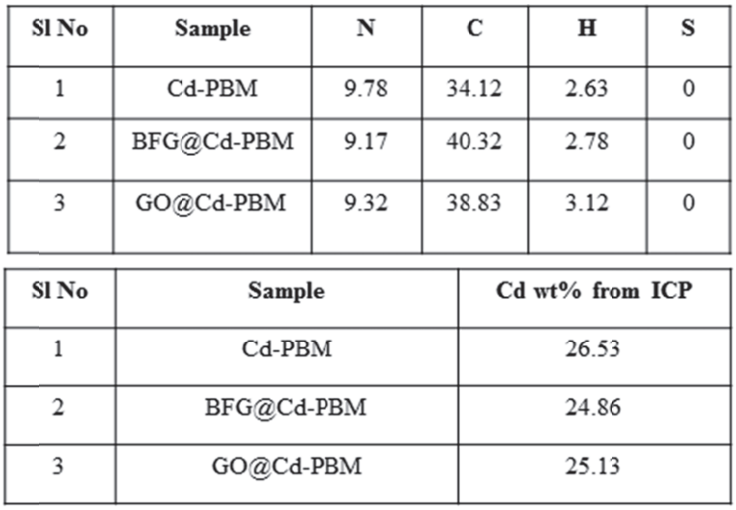
Reduction of GO with Sodium borohydride and Benzoic acid functionalization was performed using the procedure given in literature.[3] Infrared spectrum of BFG is given in Fig. S1.

Synthesis of CAP-GO, CAP-BFG and CAP

In 50 ml water 22 mg GO was dispersed by sonication for 2 hrs. The wt% was calculated based on the obtained solid product of pristine MOF. In the uniform colloidal dispersion Cd (II) ion (~ 0.5 mmol, $Cd(ClO_4)_2 \cdot xH_2O$) was added and allowed to stir for next 15 min. After 15 min Na_2pyrdc (0.5 mmol) and methanolic solution (25 ml) of azpy (0.5 mmol) was slowly added and allowed to stir overnight. Product was centrifuged and washed with water. Obtained product was dried under vacuum at room temperature. BFG@Cd-PBM was obtained by same procedure except the initial dispersion of BFG was obtained by sonication in water maintained at pH 10. Cd-PBM was obtained by simple mixing and overnight stirring of ligand solution with metal ion solution.[4] Phase purity of obtained product was checked by matching powder X-ray diffraction pattern with simulated pattern. Known weight of pristine MOF and composites (between 2 mg to 2.5 mg) were dissolved in high purity conc. HNO_3 and diluted to 10 ml and ICP analysis was carried out with respect to known standard.

Liquid phase exfoliation of BFG@Cd-PBM:

BFG@Cd-PBM was exfoliated in methanol by ultrasonication. The composite was dispersed with a concentration of 1 mg/ml in methanol and sonicated in bath sonicator (Branson-3510) for 90 minutes. The dispersion was centrifuged at 3000 rpm for 30 minutes. Middle portion of supernant was collected and drop casted on Si/SiO_2 substrate for AFM analysis. Colloidal dispersion was drop casted on NaCl window and IR spectrum of exfoliated nanocomposite was collected. The obtained colloidal dispersion of exfoliated sheet was stable for month.



Sl No	Sample	N	C	H	S
1	Cd-PBM	9.78	34.12	2.63	0
2	BFG@Cd-PBM	9.17	40.32	2.78	0
3	GO@Cd-PBM	9.32	38.83	3.12	0

Sl No	Sample	Cd wt% from ICP
1	Cd-PBM	26.53
2	BFG@Cd-PBM	24.86
3	GO@Cd-PBM	25.13

Table 1. Elemental and ICP-OES analysis of pristine MOF and composites.

Characterization:

Powder X-ray diffraction (PXRD) pattern of obtained composites were recorded on a Bruker D8 Discover instrument using Cu-Kα radiation. Morphology of BFG@Cd-PBM, GO@Cd-PBM and Cd-PBM were characterized with Transmission electron microscopy (TEM) (JEOL JEM-3010 with an accelerating voltage at 300 KV). SEM images were obtained from Nova Nano SEM 600, FEI Company. AFM was carried out using Innova scanning probe microscope. Raman spectra of the samples were recorded in backscattering arrangement, using 514.53 nm Ar^+ laser using LabRam HR 800 spectrometer. Thermogravimetric analysis (TGA) was carried out under nitrogen (flow rate of 50 mL/min) with Metler Toledo TGA-850 TG analyzer in the temperature range between 30 °C – 600 °C at a heating rate of 5 °C / min. Infra-red spectrums of the compounds were recorded on a Bruker IFS 66v/S spectrophotometer using the KBr pellets in the region 4000-400 cm^{-1}. IR spectrum of exfoliated BFG@Cd-PBM was recorded by drop casting MeOH colloidal dispersion on NaCl crystal and drying in 100 °C oven to remove solvent. X-ray photoelectron spectra (XPS) were recorded in an Omicron Nanotechnology Spectrometer with Mg Kα as the X-ray source. Samples for XPS were prepared by dropcasting on a Si substrate with native oxide layer. Elemental analysis was carried out using a FLASH 2000 elemental analyzer. Inductively coupled plasma optical emission spectroscopy was carried out using a Perkin-Elmer Optima 7000 DV instrument.

Gas adsorption measurement:

The adsorption isotherms for N_2, (at 77K), and CO_2 (at 195 K) gases were carried out using *QUANTACHROME AUTOSORB-1C* analyzer. The solvent adsorption isotherms MeOH (at 293 K) and H_2O (at 298 K) were measured using BELSORP aqua-3 volumetric adsorption instrument from BEL, Japan. Known weights (100-125 mg) of the as-synthesized samples were placed in the sample cell. Prior to measurements, the samples were dried under high vacuum at 373 K for 12 h to remove the adsorbed water molecules. The adsorbate was charged into the sample tube, and change of the pressure was monitored. The degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations for measurement were computer-controlled and automatic.

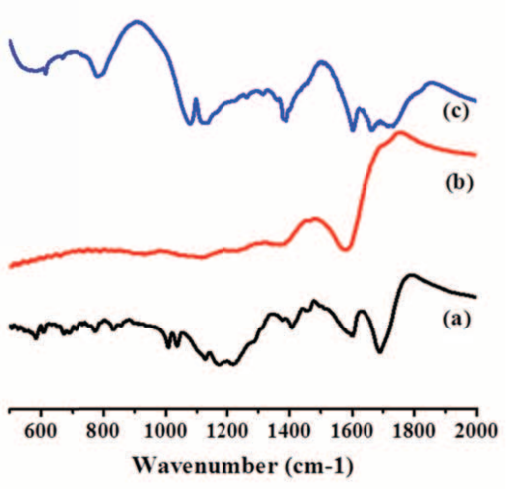


Fig. S1. Infrared spectrum of (a) BFG (black), (b) RGO (red) and (c) GO (blue).

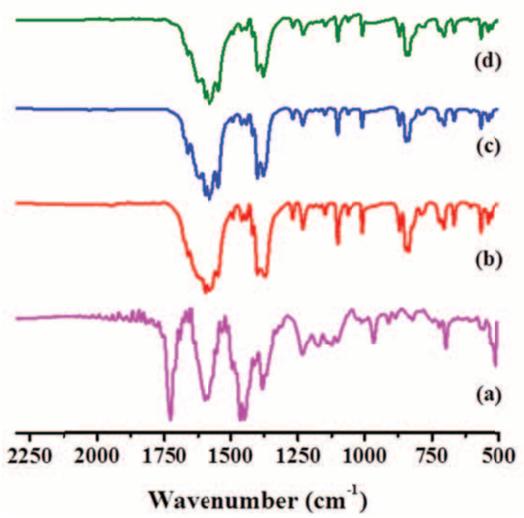


Fig. S2. Infrared spectra of (a) Exfoliated BFG@Cd-PBM (magenta) (b) Cd-PBM (red), (c) BFG@Cd-PBM (blue) and (d) GO@Cd-PBM (olive)

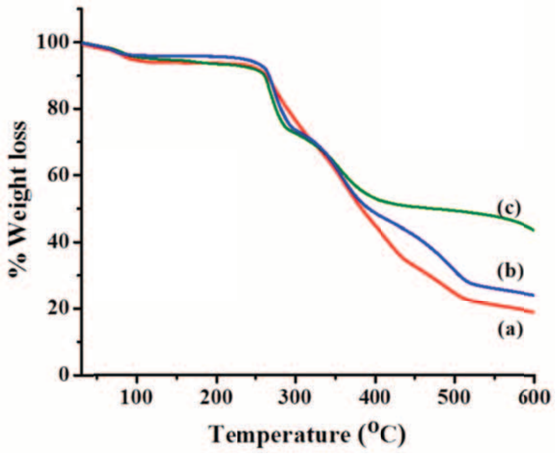


Fig. S3. TG analysis of (a) Cd-PBM (red), (b) BFG@Cd-PBM (blue) and (c) GO@Cd-PBM (olive) at heating rate 5 °C min^{-1} under N_2 atmosphere.

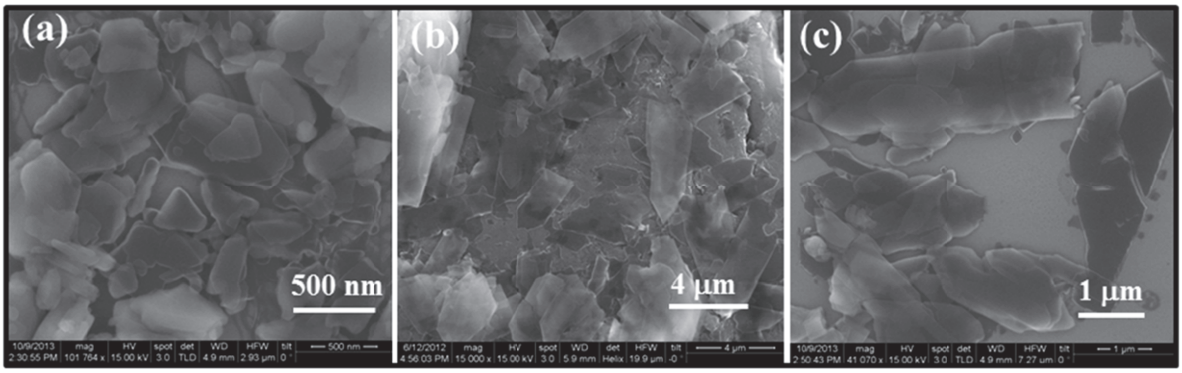


Fig. S4. FESEM images of (a) Cd-PBM, (b) BFG@Cd-PBM and (c) GO@Cd-PBM showing increase in lateral dimension of crystals in composites in comparison to pristine MOF.

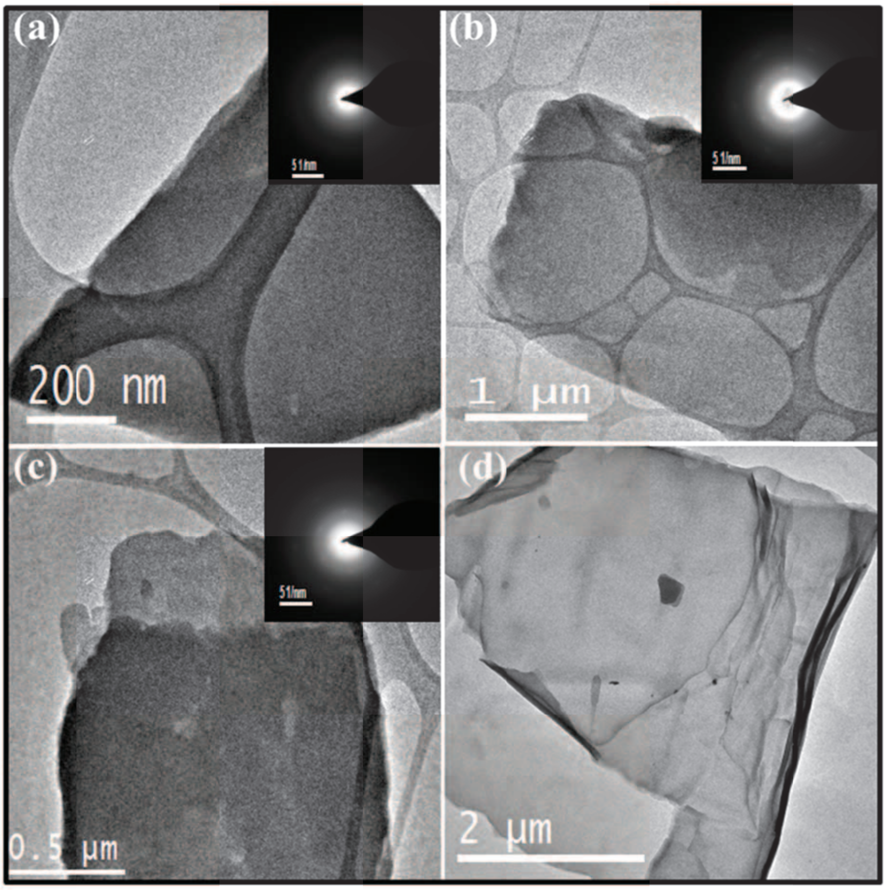


Fig. S5. TEM images of (a) Cd-PBM, (b) BFG@Cd-PBM (c) GO@Cd-PBM and (d) Partially exfoliated BFG@Cd-PBM after 30 min sonication in MeOH.

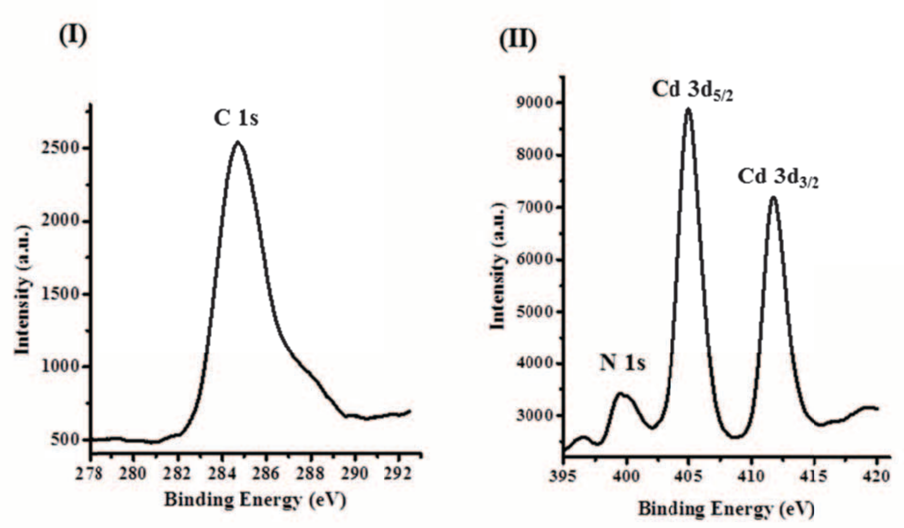


Fig. S6. (I) High resolution C 1s X-ray photoelectron spectra of Cd-PBM. (II) High resolution N 1s and Cd 3d spectra of Cd-PBM.

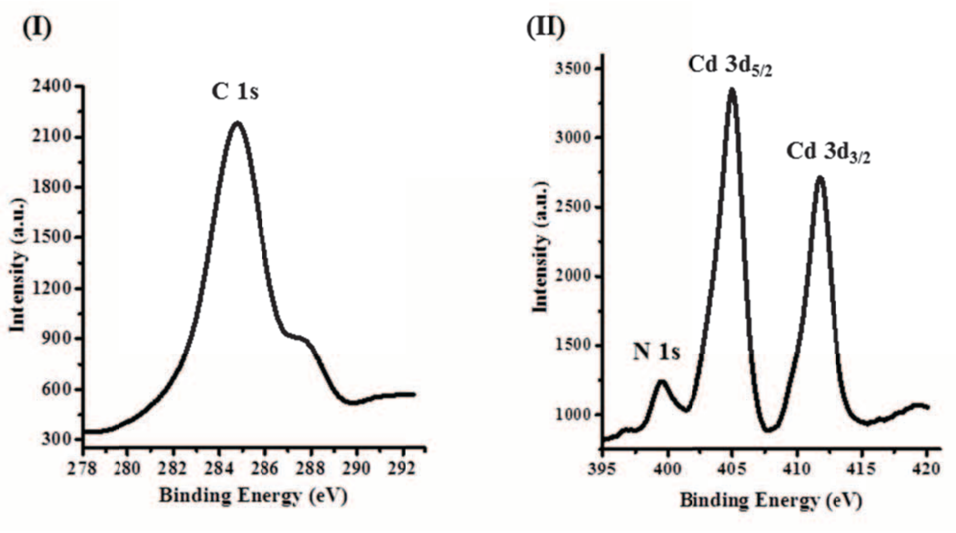


Fig. S7. (I) High resolution C 1s X-ray photoelectron spectra of BFG@Cd-PBM. (II) High resolution N 1s and Cd 3d spectra of BFG @Cd-PBM.

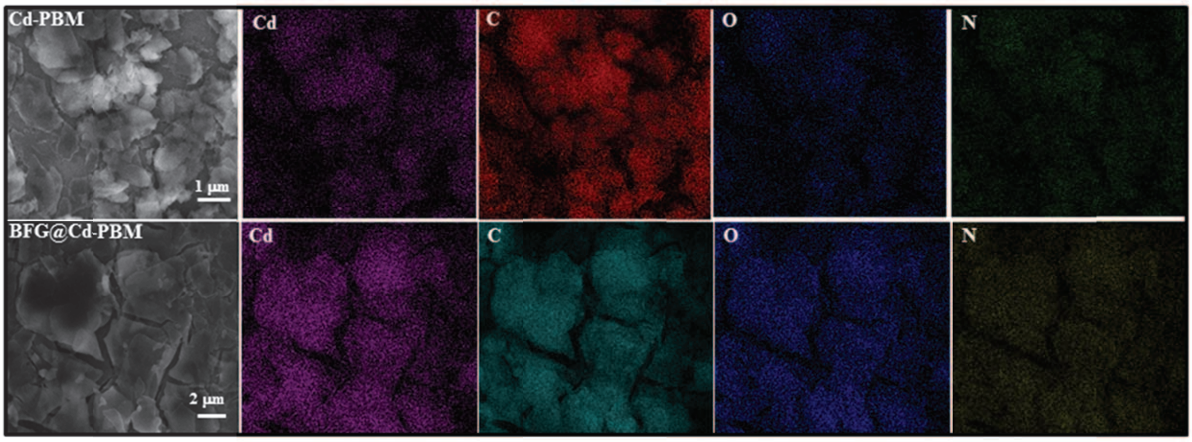


Fig. S8. Elemental mapping of (Top) Cd-PBM and (Bottom) BFG@Cd-PBM showing the homogenity of composites.

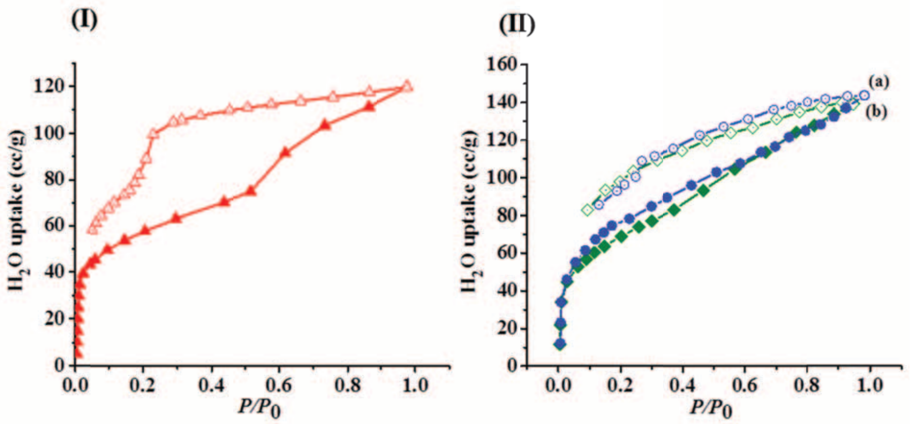


Fig. S9. (I) Water sorption isotherm of Cd-PBM (II a) BFG@Cd-PBM (blue circles) and (II b) GO@Cd-PBM (olive diamond) at 298 K.

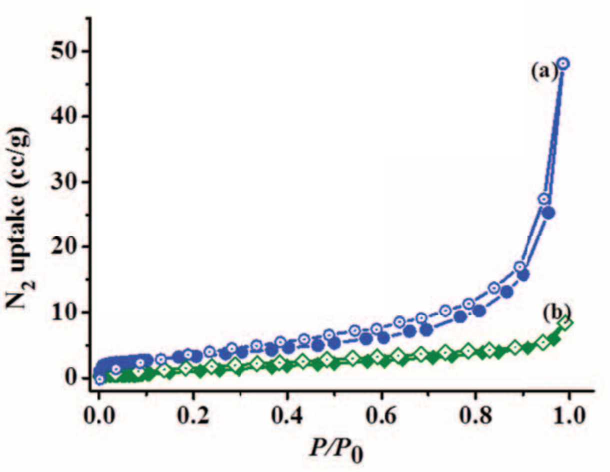


Fig. S10. N_2 adsorption isotherm of (a) BFG@Cd-PBM (blue circles) and (b) GO@Cd-PBM (olive diamond) at 77 K and 1 atm.

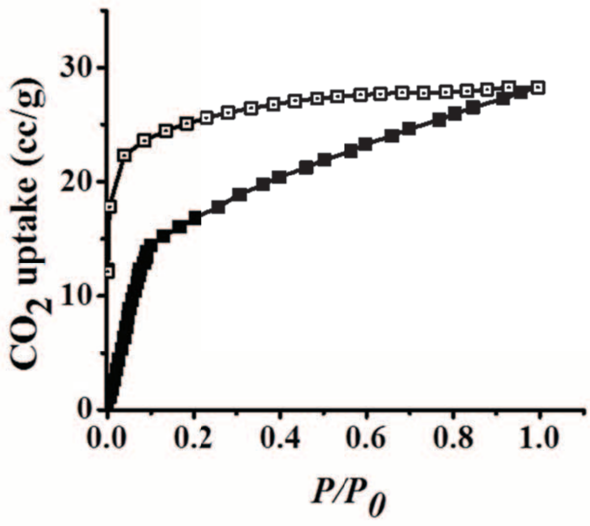


Fig. S11. CO_2 sorption isotherm of physical mixture containing 10 wt.% BFG (benzoic acid functionalized graphene) and Cd-PBM at 195 K.

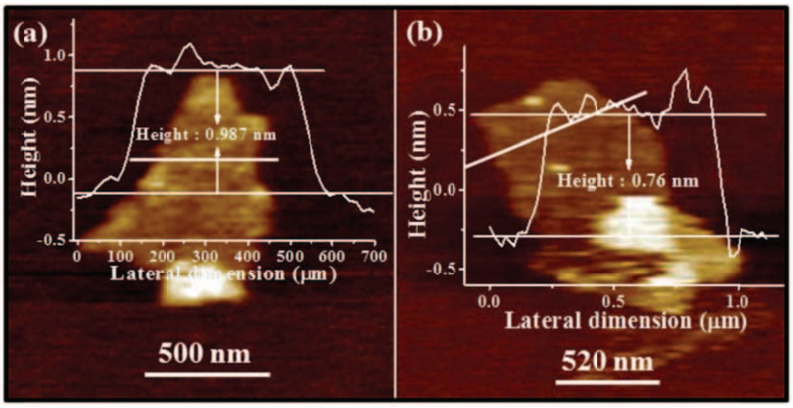


Fig. S12. AFM height profile of (a) GO (average height = 0.987 nm) and (b) BFG (average height = 0.76 nm)

References:

(1) (a) Brown, E. V.; Granneman, G. R. *J. Am. Chem. Soc.*, 1975, **97**, 621; (b) Theilmann, O.; Saak, W.; Haase, D.; Beckhaus, R. d. *Organomet.*, 2009, **28**, 2799.

(2) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.*, 1958, **80**, 1339.

(3) Jahan, M.; Bao, Q.; Yang, J.-X.; Loh, K. P. *J. Am. Chem. Soc.*, 2010, **132**, 14487.

(4) Kanoo, P.; Sambhu, R.; Maji, T. K. *Inorg. Chem.,* 2010, **50**, 400.