Supporting information

Nanosized Cu-MOF induced by graphene oxide and enhanced gas storage capacity

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Fig. S1 (A) Dicopper (II) tetracarboxylate building block for Cu-BTC;
(B) [Cu₃(BTC)₂(H₂O)₃]n polymer framework viewed down the [100] direction, showing nanochannels with fourfold symmetry.



Fig. S2 SEM micrograph of Cu-BTC crystals.



Fig. S3 $[Cu_3 (BTC)_2 (H_2O)_3]_n$ polymer framework viewed down the [100] direction, showing a hexagon.



Fig. S4 (a) Cu adsorbed on the defect of GO; (b) Cu adsorbed on the –OH group of the GO surface; (c) Cu adsorbed on the –O– group of the GO surface.





Fig. S5 HRTEM images of (A) CG-3,(B) CG-9 and (C) CG-15.



Fig. S6 Carbon dioxide storage plotted against total volume of pores.





The FT-IR spectra of the materials were recorded. The range above 2000 cm⁻¹ does not present features relevant to this analysis, so only the range between 500 and 2000 cm⁻¹ is reported. The vibrational peaks of GO are consistent with fingerprint groups such as carboxylic species; hydroxyl species and epoxy species (C=O, 1720-1740 cm⁻¹; OH deformation, ~1390 cm⁻¹; C-O stretching, 1230-1250 cm⁻¹; C-O-C stretching, ~1060 cm⁻¹; C=C from unoxidized sp² CC bonds, 1630-1650 cm⁻¹).



Fig. S8 TGA plots of the parent materials and the composites.

The thermal decomposition of GO can be accompanied by a vigorous release of gas, resulting in a rapid thermal expansion of the material. This is evident by both a large volume expansion and a larger mass loss (from flying GO debris in the TGA instrument) at a rapid heating regime (5 ⁰C/min). Therefore, we did the TGA experiment of GO at a lower heating regime (1 ⁰C/min) for precision analysis. The difference of the hypothetical values between weight loss percentage of Cu-BTC and composites can be ignored taking into account the percentage of each component in the composites and the weight loss percentage of GO and Cu-BTC alone. Eq. (1) provides the details of the calculation:

 $X_{n} = X_{GO} \times \text{wt.}\%_{GO} + X_{Cu-BTC} \times \text{wt.}\%_{Cu-BTC}$ (1)

where "X_n" is the weight loss percentage of composite CG-n to determine, "X_{GO}" and "X_{Cu-BTC}" are the weight loss percentage of GO and Cu-BTC separately, and "wt.%_{GO}" and "wt.%_{Cu-BTC}" are the weight percentages of GO and Cu-BTC in CG-n.

 X_{Cu-BTC} - X_{CG-3} =0.73%; X_{Cu-BTC} - X_{CG-9} =2.2%; X_{Cu-BTC} - X_{CG-15} =3.6%; (X_{GO} = 42.6% and X_{Cu-BTC} = 66.8% at 500 ⁰C)

The TGA curves (see below figure) for the composites look rather similar to that of Cu-BTC, but the major weight loss related to the GO in composite is absent. An explanation should be the formation of the composites via interaction between the cupric ions from Cu-BTC and the epoxy groups on the surface of GO, which prevents the decompose of GO at lower temperature.



Fig. S9 Adsorption isotherms of Cu-BTC(A), CG-3(B) and CG-15(C) for CO₂, CH₄ and N₂ at 273K.



Fig. S10 Initial slope calculation of Cu-BTC (A), CG-3 (B), CG-9 (C) and CG-15 (D) for CO₂, CH₄ and N₂ isotherms collected at 273K.