

Supporting Information

Electrochemical Performance of Graphene Copper Oxide Composites Synthesized from Metal-organic Framework (Cu-MOF)

Zhengang Guo^{#, a}, M.V. Reddy^{#, a}, Bee Min Goh,^a Angela Koh Phei San,^{a, b} Qiaoliang Bao,^a and Kian Ping Loh^{a*}

^a Graphene Research Center, Department of Chemistry, National University of Singapore, Singapore 117542

^bNUS Grad Sch for Int Sci & Eng

Corresponding Author (K. P. Loh): chmlohkp@nus.edu.sg

Authors with equal contribution

1. SEM image of the few-layered G flakes after ball milled. PXRD data of graphite, Few-layer graphene flake and Cu-MOF-G (Fig S1).
2. SEM images of Cu-MOF and Cu-MOF-G (Fig S2).
3. Raman depth mapping of the Cu-MOF-G and Cu-MOF crystal (Fig S3).
4. Recovery of graphene inside the Cu-MOF-G crystal after dissolving crystal in phosphate buffer. (Fig S4).
5. TGA data showing decomposition profile of Cu-MOF, Cu-MOF-G, CuO and CuO-G. (Fig. S5 and S6).
6. FTIR spectra of Cu-MOF, Cu-MOF-G, DMTA (blue), DMTP (red) and DHTP (Fig S7 and S8, Table S1, S2 and S3).
7. Figure S9-S12, ¹H and ¹³C NMR data.
8. Figure.S13: Cyclic voltammetry (CV) studies of (a) CuO-220°C, (b) CuO-G-220°C, Voltage range, 0.005-3.0V; Scan rate: 0.058mV/sec.
9. Figure S14. Cyclic voltammetry (CV) studies of Cu-MOF and discharge-charge cycling profiles, Scan rate and current rates.

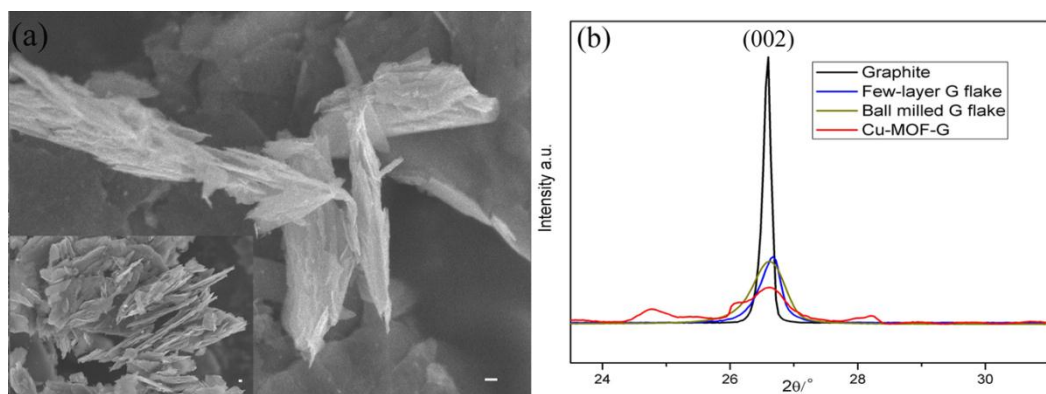


Figure S1. SEM image of the few-layered G flakes after ball milling (a), Scale bar, 100 nm. PXRD data of graphite (black), few-layer graphene flake (blue), ball milled graphene flake (dark yellow) and Cu-MOF-G (red). The (002) XRD peak of exfoliated few-layer graphene flake is of reduced intensity relative to graphite.

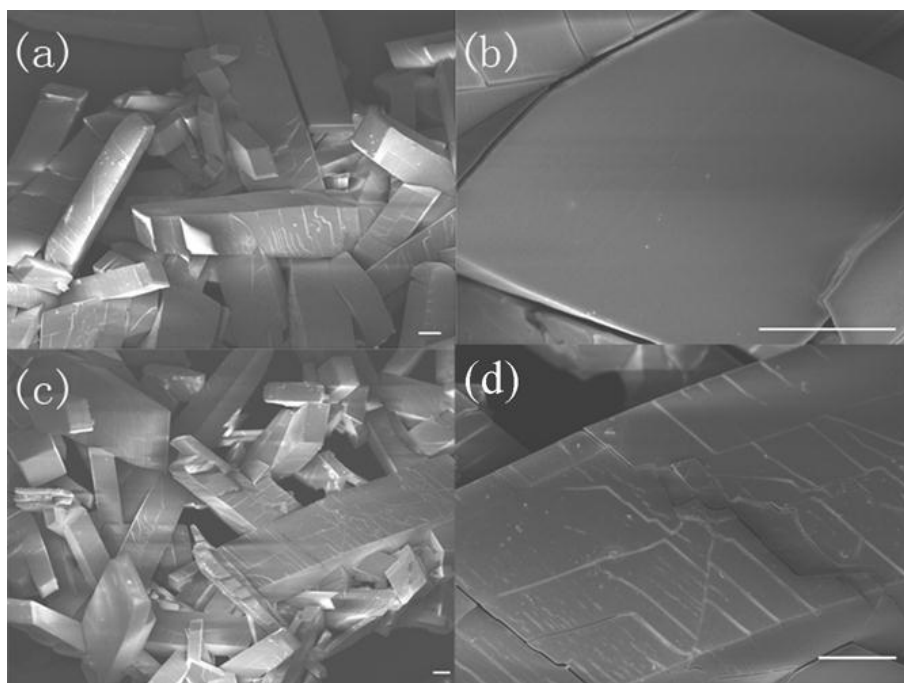


Figure S2. SEM images of Cu-MOF (a and b) and Cu-MOF-G (c and d). Scale bar, 10 μm .

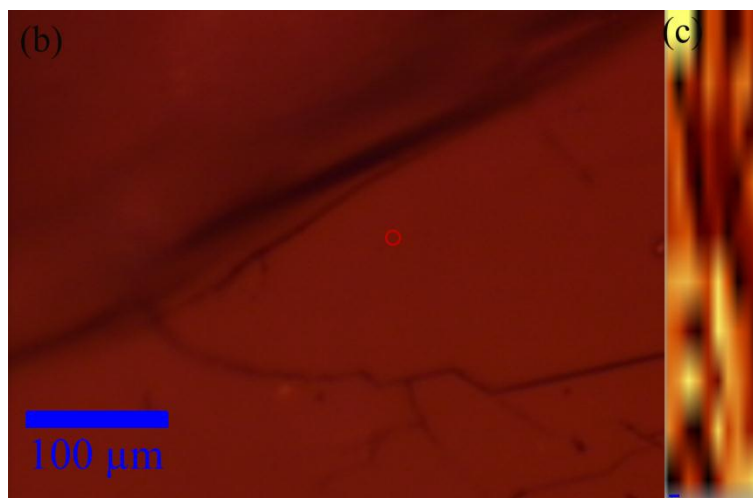
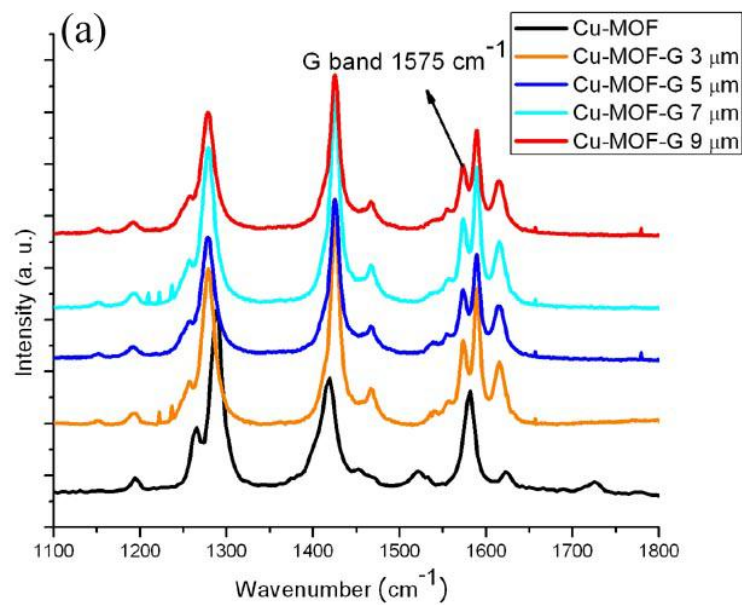


Figure S3. Raman depth mapping of Cu-MOF-G with G band at 1575 cm^{-1} at the depth of 3 μm , 5 μm , 7 μm and 9 μm . (a) Optical image of the depth mapping of Cu-MOF-G (b) The distribution of G inside Cu-MOF-G, the yellow areas shows the signal of G (c, scan width, 1 μm ,

bar scale, 0.1 μm).

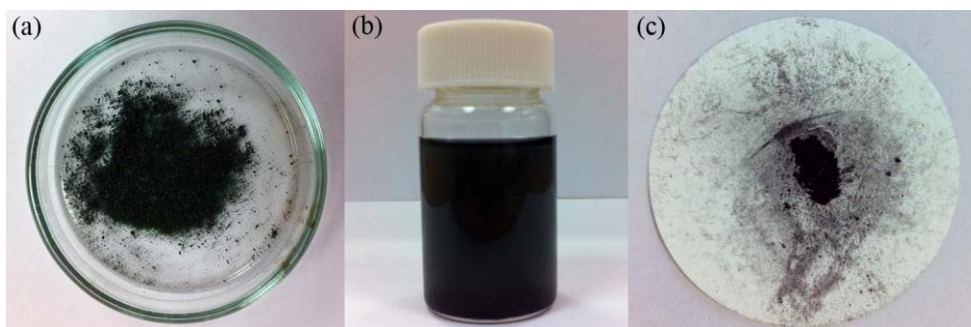


Figure S4. In order to get the ratio of graphene inside composites, 120mg of Cu-MOF-G crystals (a) was dissolved by phosphate buffer (b), and centrifuged. After washing with water and acetone, followed by drying in oven at 80 °C, the weight of collected graphene powder was about 5.6 mg (c). With this method, the weight ratio of graphene in Cu-MOF-G composites was calculated to be about 4.7%.

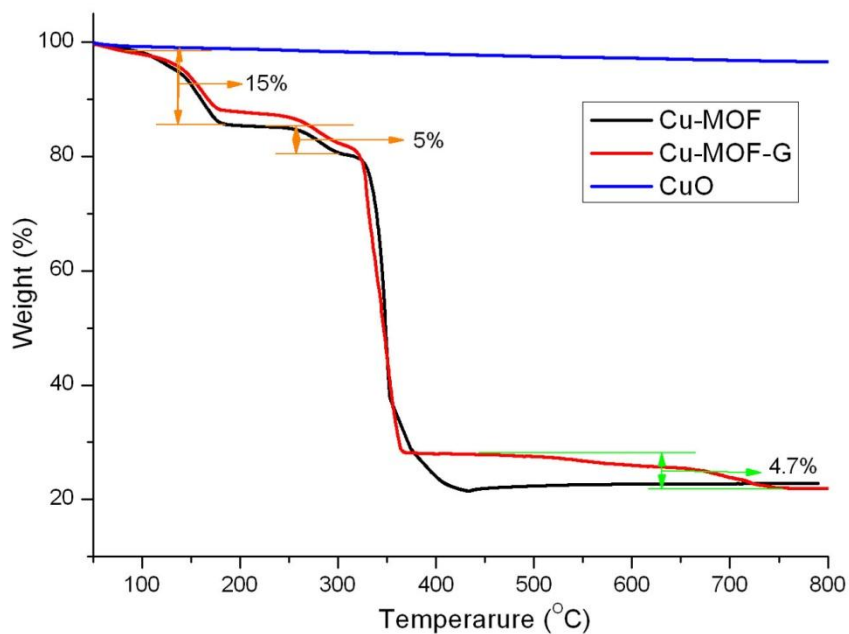


Figure S5. TGA data of Cu-MOF (black), Cu-MOF-G (red) and CuO (blue) synthesized from Cu-MOF at 220 °C in air.

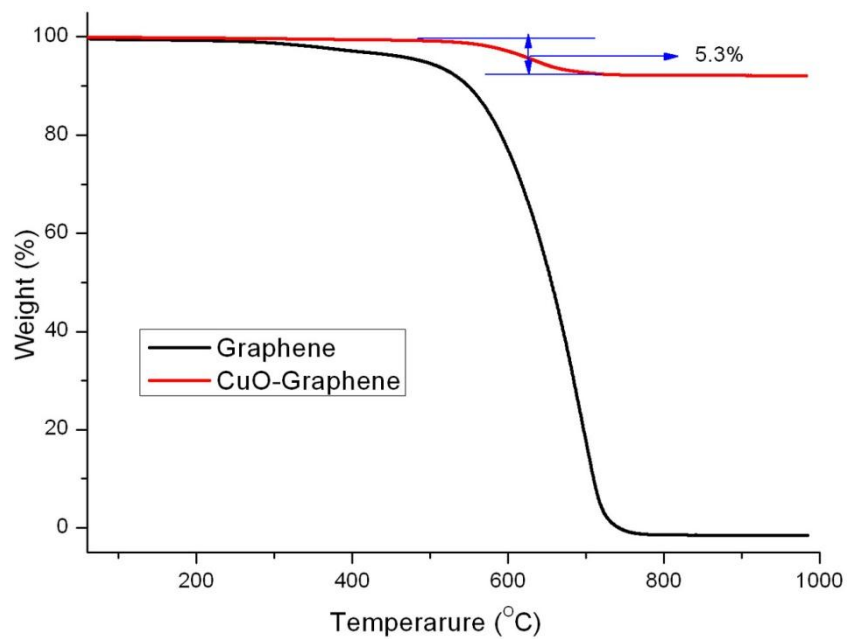


Figure S6. TGA data of graphene and CuO-G in air.

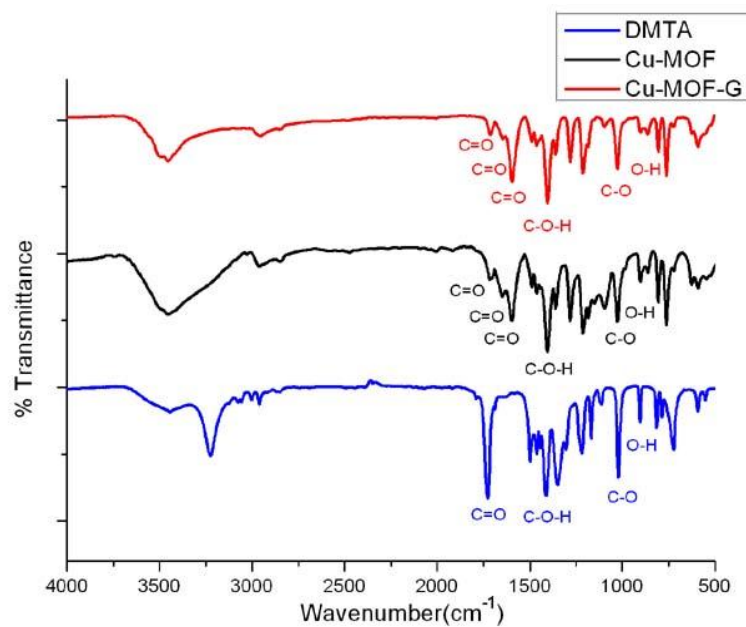


Figure S7. FTIR spectra of DMTA (black), Cu-MOF (ii) and after (iii) heated at 220 °C for for 2h. Cu-MOF-G before (ii) and after (iii) heated at 220 °C for 2h.

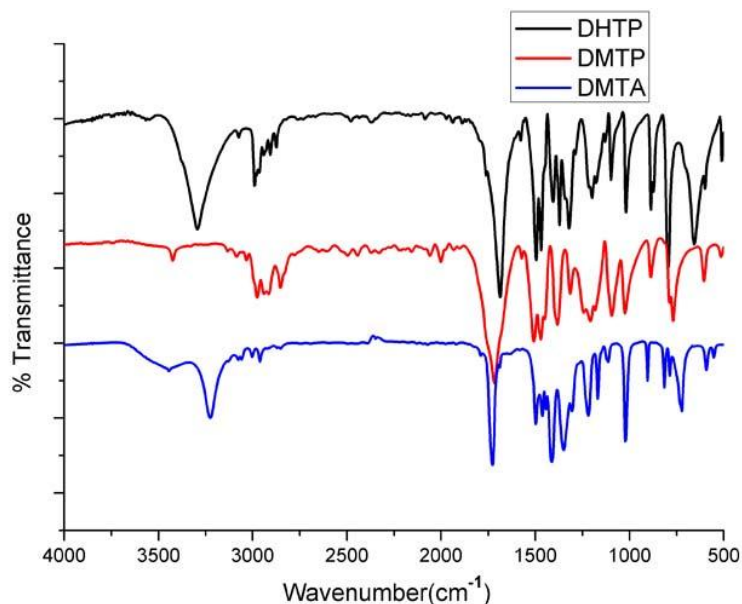


Figure S8. FTIR spectra of DMTA (blue), DMTP (red) and DHTP (black).

The IR spectra of Cu-MOF are shown in Fig. S7, the peak of 1725 cm^{-1} is ascribed to the C=O stretch absorption of carboxyl group in DMTA, and the peaks at 1496 , 1463 and 1446 cm^{-1} are assigned to C=C stretch mode vibration of the benzene ring. The C-O-H bend in-plane mode occurs at peak of 1415 cm^{-1} . The peaks of 1220 and 1168 cm^{-1} are due to the stretching modes of C-OCH₃ and O-CH₃ groups, respectively. The C-OH stretch absorption is at 1020 cm^{-1} . The vibration at 937 cm^{-1} is due to O-H (hydroxyl group) bend out-of-plane mode. The observed bands are similar to those reported in literature¹. After assembly to form Cu-MOF, there are three C=O absorption peaks. The peak of 1712 cm^{-1} is assigned to the carbonyl group which is coordinated with the Cu(II) ions. Other carbonyl groups are from the guest DMTA molecules which are located in the one-dimensional channels by hydrogen bonds. As a result, the absorptions of 1650 and 1602 cm^{-1} are ascribed to vibrations of hydrogen-bonded carbonyl monomer and hydrogen-bonded carbonyl dimer².

In the FTIR data of Cu-MOF-G, the corresponding carbonyl absorptions are changed to 1716, 1646 and 1596 cm^{-1} for Cu-MOF-G (Fig. S7). Other absorption assignments can be found in Table S1-S3. There are no additional peaks in Cu-MOF-G compared with Cu-MOF, which indicates that no new covalent bonds were formed during the self-assembly process after introduction of exfoliated graphene and non-covalent interactions may mediate the interactions between G and MOF.

Table S1. FTIR peaks assignments of DMTA.

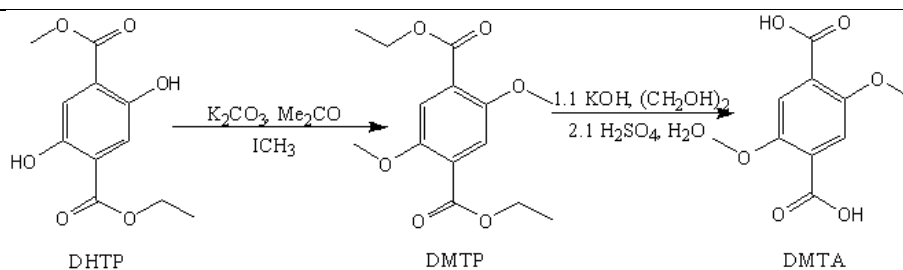
1791 cm^{-1}	C=O	1725 cm^{-1}	C=O	1496 cm^{-1}	C=C
1463 cm^{-1}	C=C	1446 cm^{-1}	C=C	1415 cm^{-1}	C-OH
1220 cm^{-1}	C-OCH ₃	1168 cm^{-1}	CO-CH ₃	1020 cm^{-1}	C-O
937 cm^{-1}	O-H				

Table S2. FTIR peaks assignments of Cu-MOF.

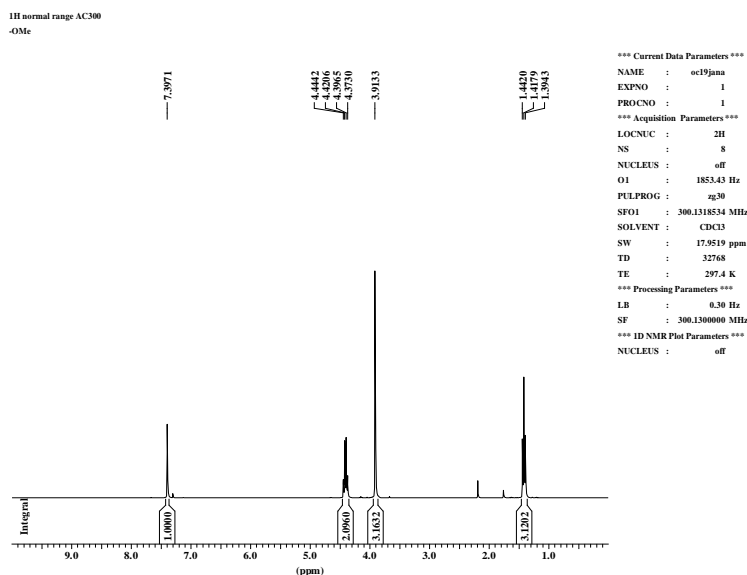
1712 cm^{-1}	C=O	1650 cm^{-1}	C=O	1602 cm^{-1}	C=O
1492 cm^{-1}	C=C	1467 cm^{-1}	C=C	1440 cm^{-1}	C=C
1403 cm^{-1}	C-O-H	1214 cm^{-1}	C-OCH ₃	1184 cm^{-1}	O-CH ₃
1029 cm^{-1}	C-O	902 cm^{-1}	O-H		

Table S3. FTIR peaks assignments of Cu-MOF-G.

1716 cm ⁻¹	C=O	1646 cm ⁻¹	C=O	1596 cm ⁻¹	C=O
1492 cm ⁻¹	C=C	1461 cm ⁻¹	C=C	1407 cm ⁻¹	C-O-H
1211 cm ⁻¹	C-OCH ₃	1180 cm ⁻¹	O-CH ₃	1025 cm ⁻¹	C-O
898 cm ⁻¹	O-H				



Scheme 1. Synthesis of DMTA (2,5-imethoxyterephthalic acid).



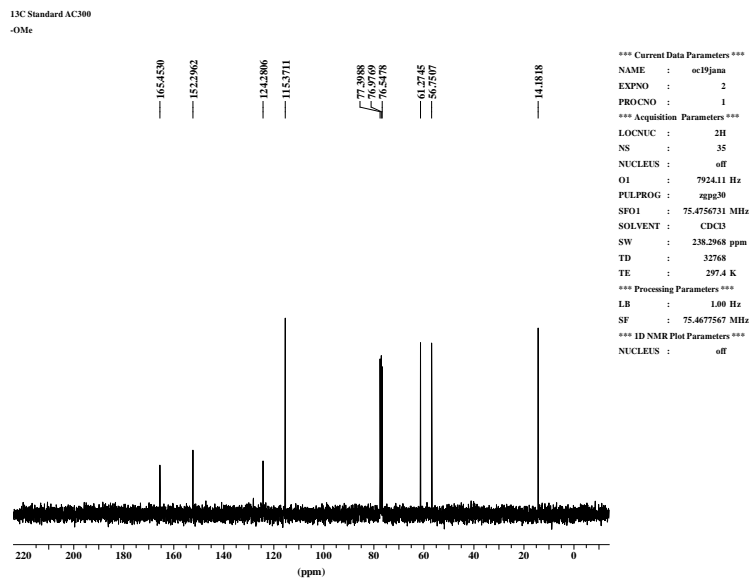


Figure S10. ^{13}C NMR spectra of DMTP in CDCl_3 .

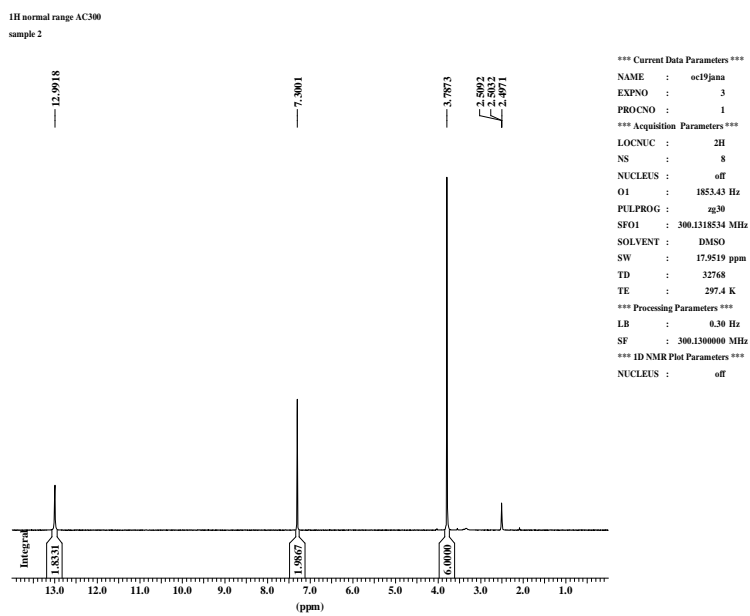


Figure S11. ^1H NMR spectra of DMTA in DMSO.

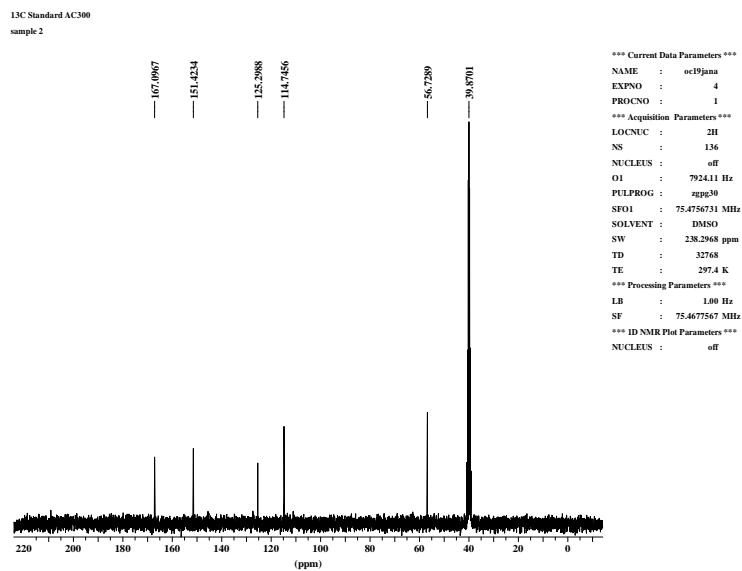


Figure S12. ^{13}C NMR spectra of DMTA in DMSO.

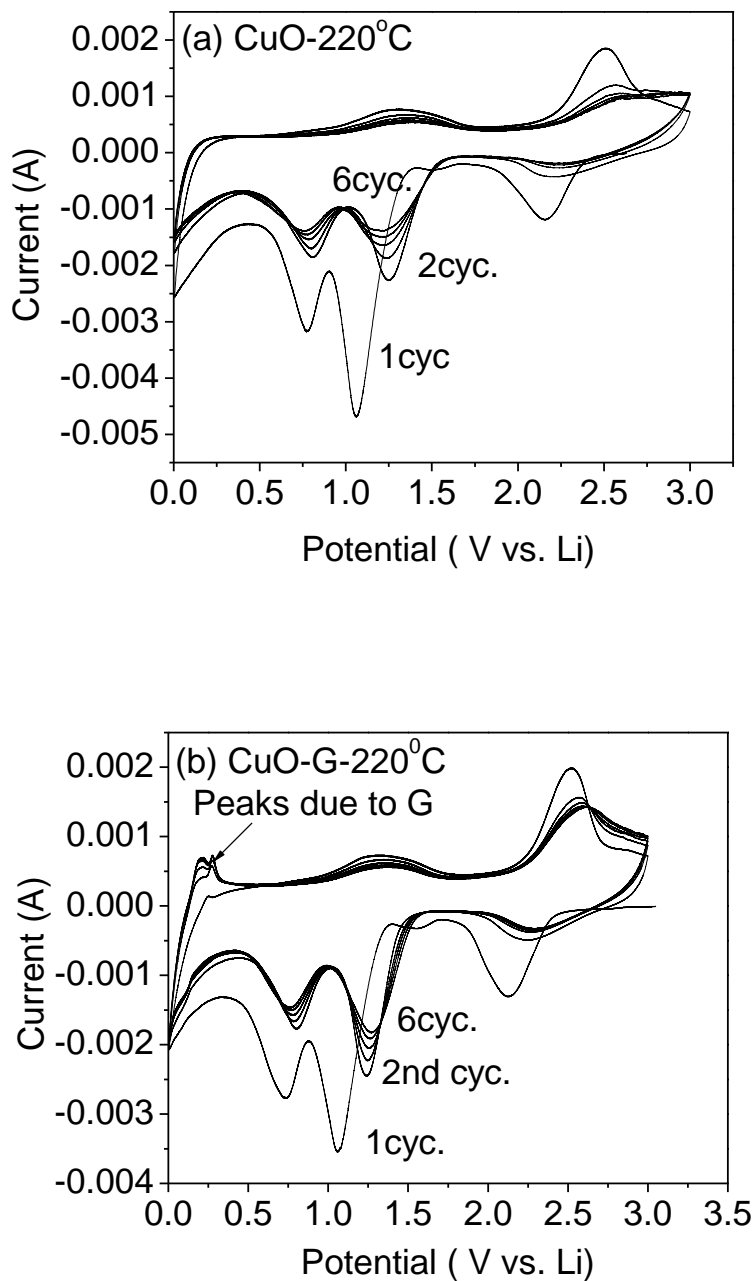


Figure S13. Cyclic voltammetry (CV) studies of (a) CuO-220°C, (b) CuO-G-220°C, Voltage range, 0.005-3.0V; Scan rate: 0.058mV/sec.

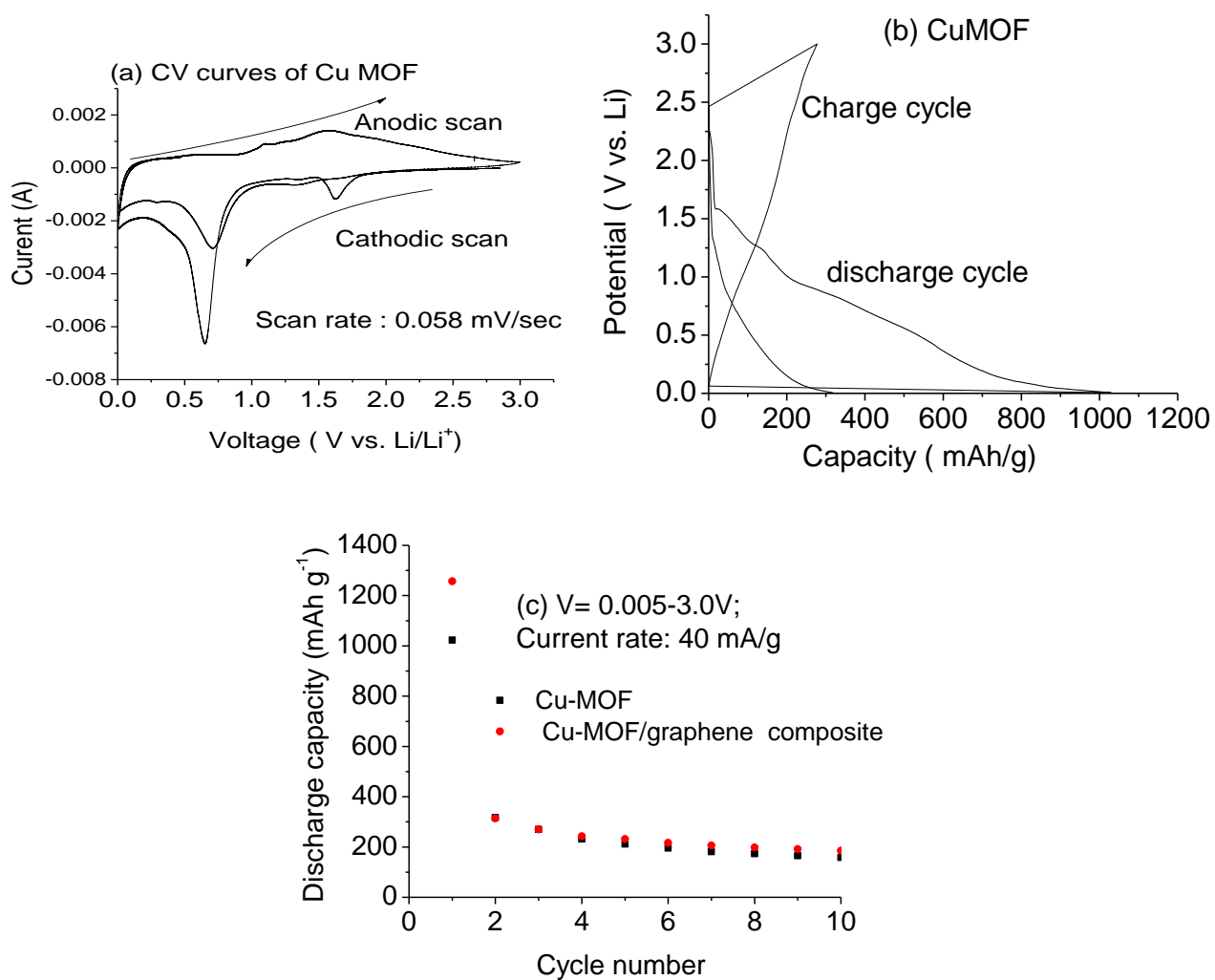


Figure S14. Cyclic voltammetry (CV) studies of Cu-MOF and discharge-charge cycling profiles, Scan rate and current rate are shown in fig.

REFERENCES

- (1) Jiang, D. M.; Urakawa, A.; Yulikov, M.; Mallat, T.; Jeschke, G.; Baiker, A. *Chem-Eur J* **2009**, *15*, 12255.

(2) Jacob, C.; Chandra, A. K. *Spectrochim Acta A* **1981**, 37, 1071.