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Cu-BTC MOF / Graphene-based hybrid materials as low concentration ammonia sensors

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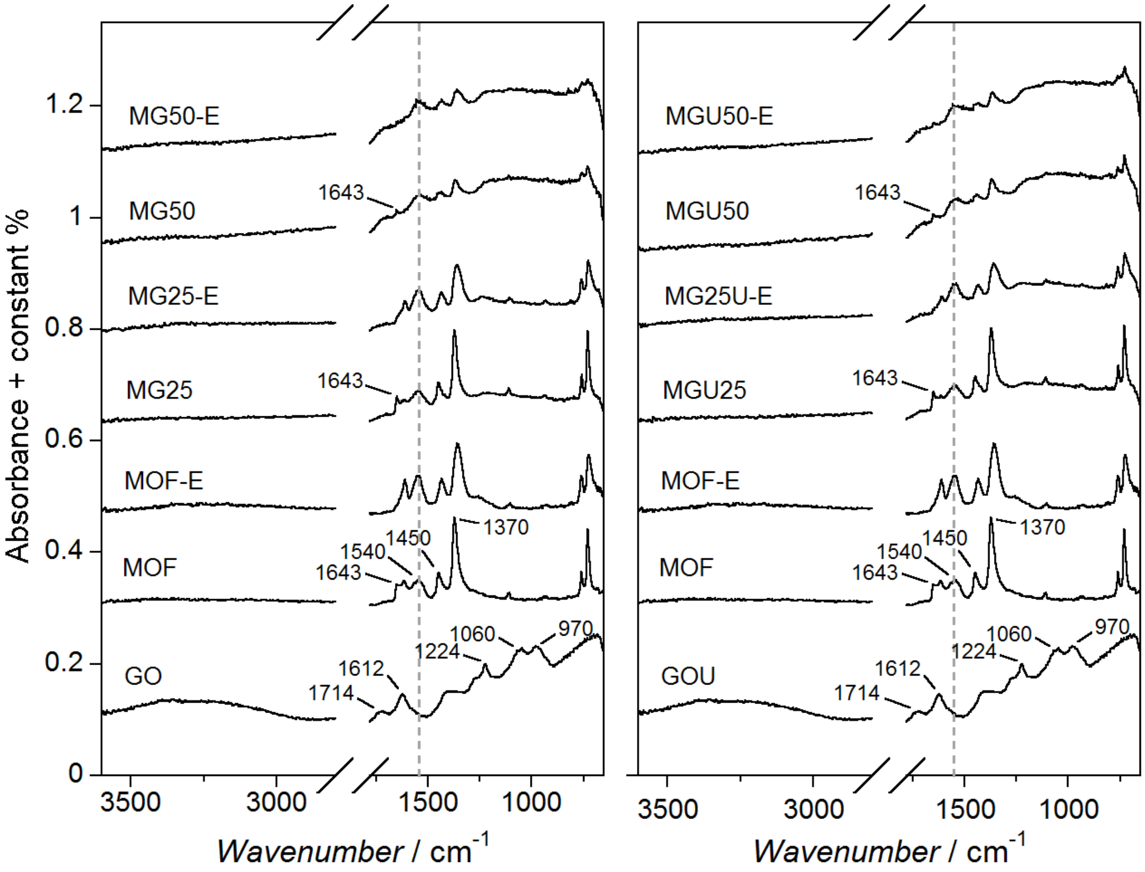

Fig. S1. FT-IR spectra of MOF (HKUST-1), GO/GOU and hybrid materials.

The FT-IR spectra of the parent materials, as well as the hybrids before and after exposure to ammonia are presented in Fig. S1. For GO, the wide band at 3000-3650 cm^{-1}, is attributed to the C-OH group of graphite oxide,[1] while the peak at 1714 cm^{-1}, is attributed to the stretching vibration of C=O bonds in carbonyl and carboxylic groups. The intense band at 1060 cm^{-1} is related to the vibration of C-O bond, while the peak at 1612 cm^{-1} is assigned to oxygen surface groups such as cyclic ethers. Finally the peaks at 1224 cm^{-1} and 970 cm^{-1} are related to epoxy/peroxide groups. The former peak may be also attributed to the asymmetric vibration of S=O in sulfonic groups. GOU exhibits similar spectra to that of GO due to present of small amount of urea. It is worth mentioning that the band at 1240 cm^{-1} is more intense for GOU than for that for GO, and this is related to the contribution of the vibrations of the N-H bond. At the same time, the intense band at 1060 cm^{-1}, which is related to the C-O bond, is weaker in the case of GOU, indicating that carboxylic groups are involved in acid-base reactions with urea [1].

For the initial MOF, the peaks between 1300 and 1700 cm^{-1} are related to the carboxylate ligands of BTC coordinated to the copper sites. More precisely, the peaks at 1370 cm^{-1} and 1450 cm^{-1} represent the symmetric stretching vibrations of the carboxylate groups in BTC, while the bands at 1540 cm^{-1} and 1643 cm^{-1} represent the asymmetric stretching vibrations of the carboxylate groups in BTC.[2] The peak at 1108 cm^{-1} is assigned to the C-O stretching mode of C-OH groups.

The FT-IR spectra of the four hybrid materials tested exhibit features similar to the initial MOF.[3] However, the changes in the environment of the carboxylate ligands which are likely related to the distortion of the MOF structure caused by the incorporation of GO and the interaction of the ligands with the graphene phase, are seen from the variations in the ratios of the bands between 1370 – 1643 cm^{-1}. It is also notable that increasing the GO and GOU contents, the intensity of the above bands decreases, which might be related to the smaller the amount of MOF in the hybrid materials. The appearance of a new peak at ~ 1643 cm^{-1} for the hybrid materials could be also attributed to the presence of GO and GOU.

After ammonia adsorption, a broadening of the bands at 729, 735, 1370 and 1450 cm^{-1} is observed. Moreover, the intensity of the band at 1540 cm^{-1} increased due to a change in the coordination of the carboxylate ligands from BTC.[3] The absence of the band at 1643 cm^{-1} for the exhausted samples, excludes the presence of the acidic form of BTC. Hence, we hypothesize that the carboxylate groups of BTC react with ammonia producing $(NH_4)_3$BTC when the hybrid materials are exposed to NH_3.[3] For MOF-GOU hybrid materials, the increased intensity of the band at 1540 cm^{-1} can be attributed to the alkyl ammonium groups from urea.[1]

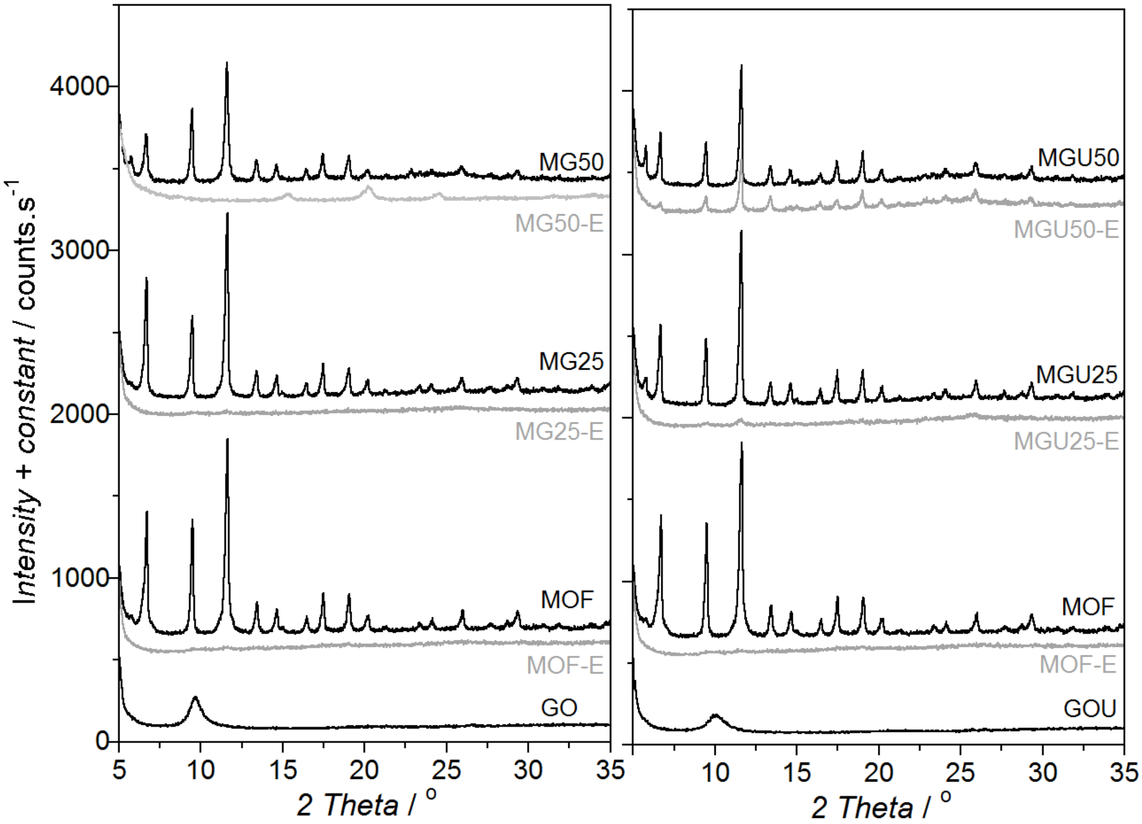

Fig. S2. X-ray diffraction patterns of MOF (HKUST-1), MOF-GO and MOF-GOU hybrid materials.

X-ray diffraction patterns of the parent materials, as well as the hybrid materials before and after exposure to ammonia are presented in Fig. S2. GO exhibits the characteristic peak at $2\theta = 10^o$. For GOU this peak is slightly shifted toward higher angle, indicating that the reaction of urea with GO result to a decrease in the interlayer distance. The MOF exhibits the characteristic peaks related to its crystalline structure which are reflections belonging to CuO.[4] Both GO and

GOU hybrid materials exhibit a characteristic d_{002} peak at 2Θ p 11.4, however, due to the exfoliation of these phases during preparation the rather broad peak observed for the two graphitic phases is not present on the XRD pattern of the mixtures. The diffraction patterns of the hybrid materials are very similar to those of the initial MOF.

After ammonia adsorption, the intensity of the characteristic peaks attributed to MOF significantly decreases, especially for MG1 and MGU1, where the crystallographic structure is lost. Interestingly, for the materials with 50 % GOs some crystallinity remains. This might be related to their limited porosity that hinders the gas access into the micropores. That could explain the short breakthrough times of these materials, since 100 ppm of NH_3 in the outlet gas would be recorded sooner than all adsorption centers get exhausted. This is further supported by the smaller extent of decreases in porosity after ammonia exposure in comparison with the materials containing 25 % GO.

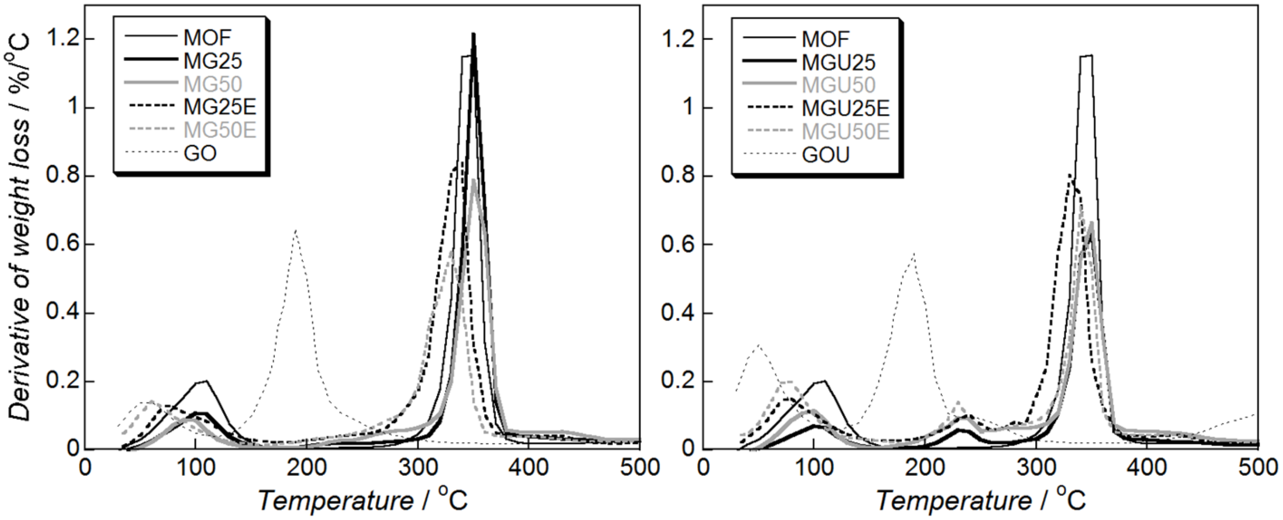

Fig. S3. DTG curves for GO, GOU, MOF (HKUST-1) and hybrid materials.

The DTG curves obtained from the thermal analyses of our materials are presented in Fig. S3. For GO and GOU the observed characteristic peak at 190°C, is related to the decomposition of epoxy groups.[5] For the initial MOF a peak at about 100°C is related to the removal of solvent while another one at about 350 °C is attributed to the collapse of the MOF structure and consequent release of CO_2.[6,7] The hybrid materials and their exhausted counterparts exhibit DTG curves similar to the initial MOF. For the exhausted samples however, the peak at 350 °C is shifted to a lower temperature. During exposure to ammonia, the crystalline structure of MOF collapses and ammonium salt species are formed. The weaker bonding between the copper centers and BTC ligands upon ammonia complexation, leads to a lower decomposition temperature of the MOF structure as seen in Fig. S3. Finally, for the MGU hybrid materials, the peak at around 230°C is linked to the removal of $-NH_2$ moiety.[1,5]

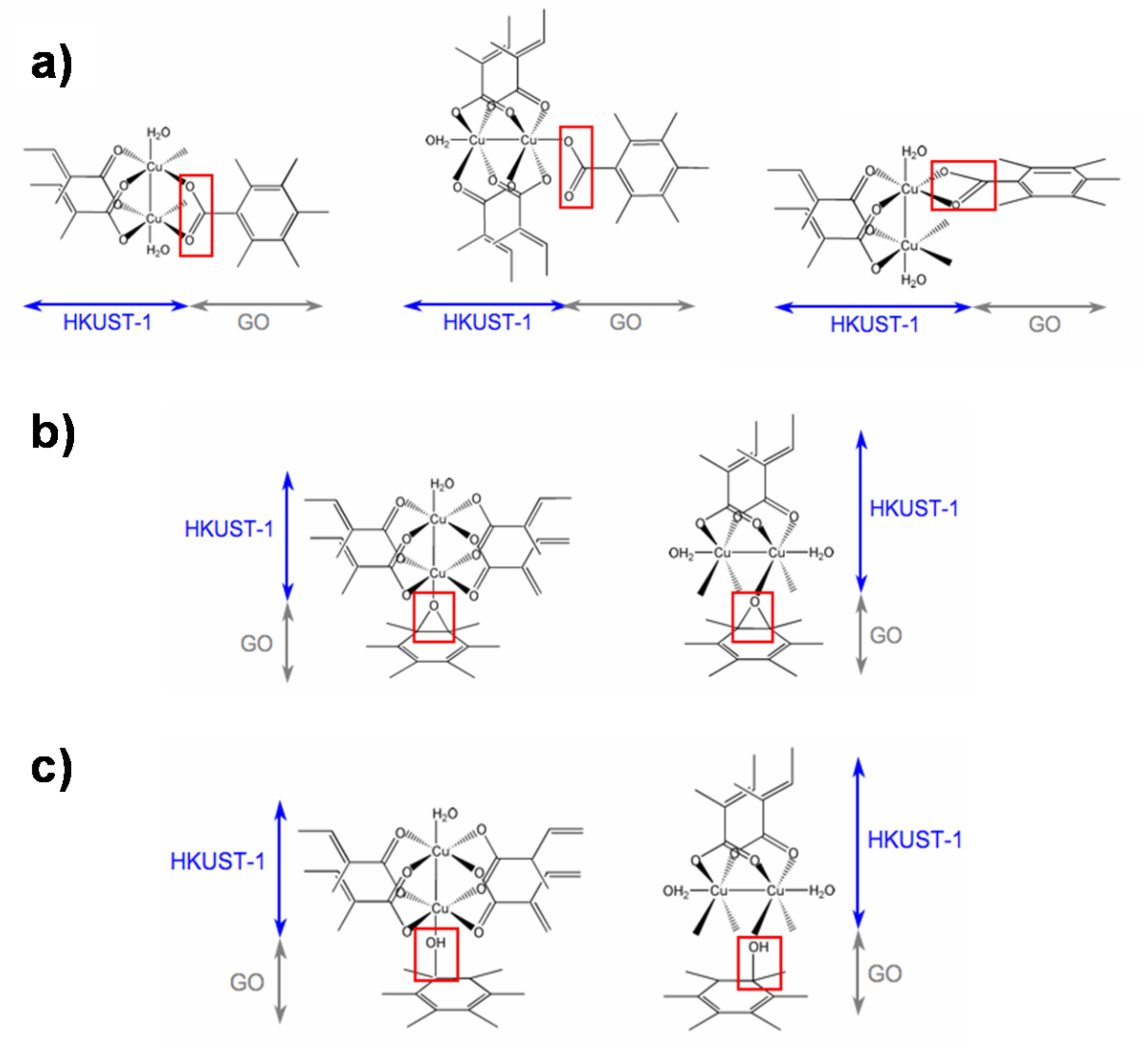

Fig. S4. Details of the possible interactions between the copper sites of HKUST-1 and the a) carboxylic, b) epoxy and c) hydroxyl groups of GO. Reprinted from Ref. (6), Copyright 2011, with permission from Elsevier.[6] Note: The examples of the bonds include the presence of water on the copper centers. There is no water in our system.

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