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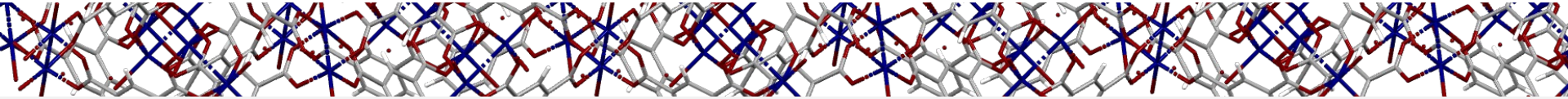

Catalytic and adsorptive properties of HKUST-1/GO composites

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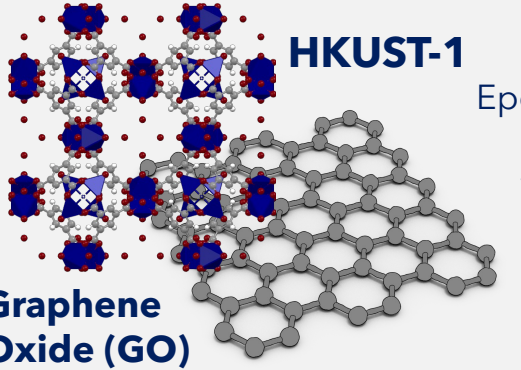
INTRODUCTION



HKUST-1

Graphene Oxide (GO)

HKUST-1/GO

Epoxy and hydroxyl groups on GO surface can react with metal ions in MOFs.

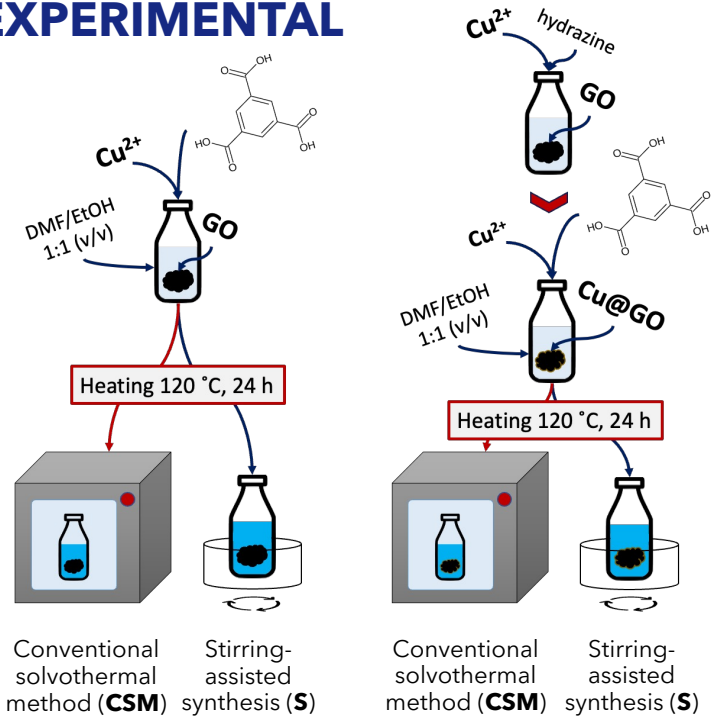
Introduction of GO into MOFs can improve their adsorptive, photochemical, conductive and electric properties [1].

THE AIM OF THE RESEARCH

Investigation of the influence of **synthesis method** of **HKUST-1/GO** on:

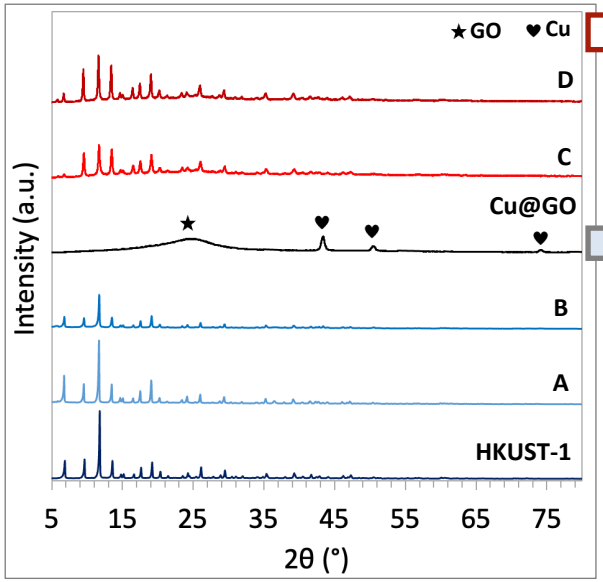
- ✓ its physicochemical properties,
- ✓ its performance in sorption and oxidation of methylene blue (MB).

EXPERIMENTAL

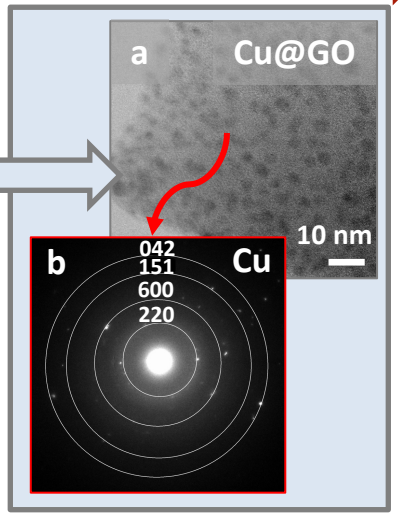


[1] L. Li, X.L. Liu, H.Y. Geng, B. Hu, G.W. Song, Z.S. Xu *J. Mater. Chem. A*, 2013,1, 10292-10299

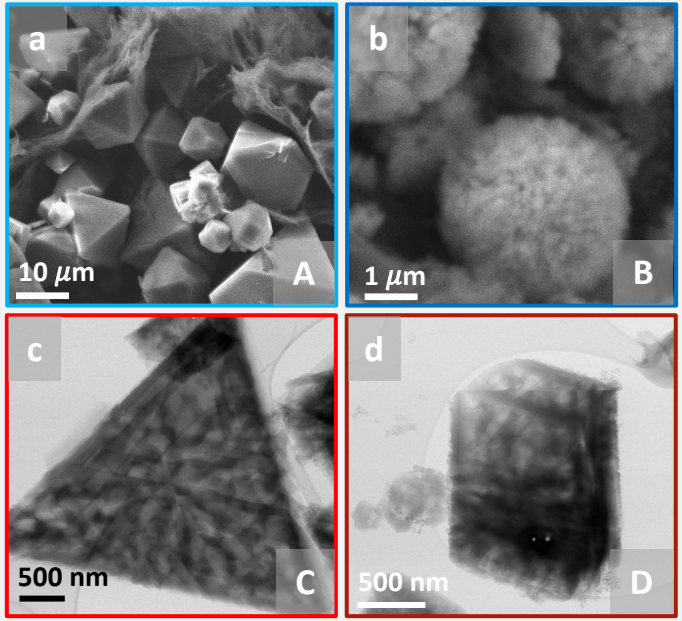
STRUCTURE AND MORPHOLOGY



XRD patterns of HKUST-1, its composites with GO:
A (HKUST-1/GO(CSM)), B (HKUST-1/GO(S)),
C (HKUST-1/Cu@GO(CSM)), D (HKUST-1/Cu@GO(S))
and Cu@GO.



TEM (a) of Cu@GO
and SAED (b) of Cu.



SEM (a,b) and TEM (c,d) of HKUST-1 composites with GO:
A (HKUST-1/GO(CSM)), B (HKUST-1/GO(S)),
C (HKUST-1/Cu@GO(CSM)), D (HKUST-1/Cu@GO(S)).

- ✓ **In all composites the structure of HKUST-1 is present.**
- ✓ XRD, TEM and SAED confirmed the presence of Cu nanoparticles in Cu@GO.

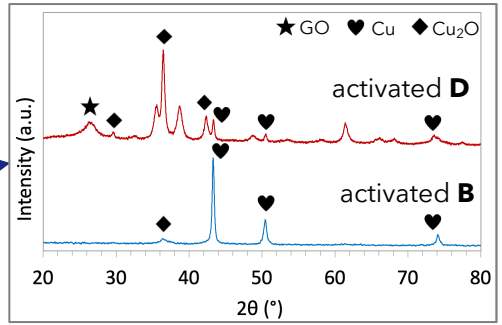
- ✓ Good distribution of HKUST-1 and graphene in the composite can be achieved when GO is decorated with CuNPs prior to the reaction.
- ✓ When GO is not decorated with CuNPs, good distribution of both components in the composite can be achieved only when stirring is applied.

ACTIVATION OF HKUST-1 COMPOSITES

B (HKUST-1/GO(S))
D (HKUST-1/Cu@GO(S))

500 ˚C/10 h
flowing Ar

activated **B**
activated **D**



XRD patterns of activated B (activated HKUST-1/GO(S)), activated D (activated HKUST-1/Cu@GO(S)).

Activation (carbonisation) of HKUST-1/GO composites leads to formation of Cu and Cu_2O supported on carbon matrix.

TEXTURAL PROPERTIES

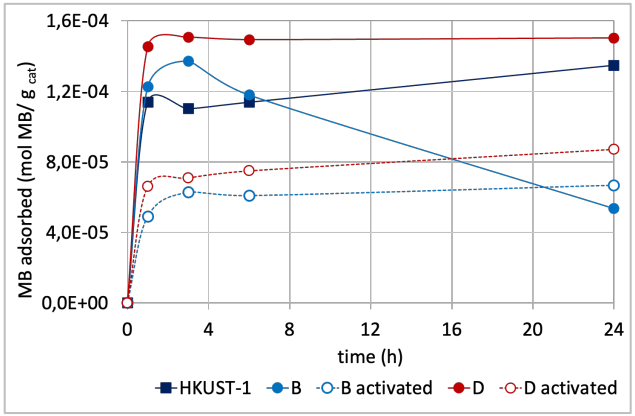
Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	D (nm)
HKUST-1	1050	0.51	0.45	1.9
A	>1	0.01	-	83.3
B	29	0.10	-	14.2
C	386	0.43	0.15	4.5
D	398	0.44	0.16	4.9
B activated	**10**	0.11	0.01	8.0
D activated	**114**	0.29	0.5	42.4

Textural properties of HKUST-1 and its composites with GO: A (HKUST-1/GO(CSM)), B (HKUST-1/GO(S)), C (HKUST-1/Cu@GO(CSM)), D (HKUST-1/Cu@GO(S)), activated B and activated D.

- ✓ **Introduction of GO** to HKUST-1 **= reduction of S_{BET}**.
- ✓ Pre-decoration of GO with Cu (Cu@GO) leads to more developed surface area of a composite and activated composite.

S_{BET} =BET specific surface area, V_{total}=total pore volume, V_{micro}=micropores volume, D=mean pore diameters

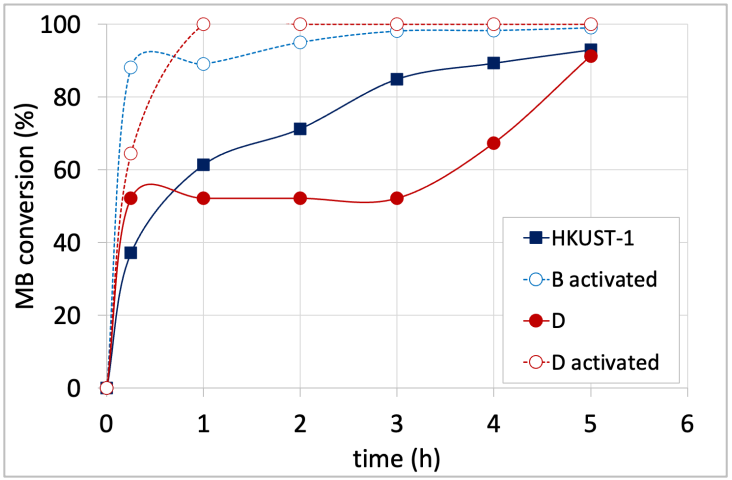
ADSORPTION OF METHYLENE BLUE



Adsorption of MB on HKUST-1, B (HKUST-1/GO(S)), activated B, D (HKUST-1/Cu@GO(S)) and activated D.

- ✓ **HKUST-1/Cu@GO (D) show the highest MB sorption capacity**. It is caused by composite high specific surface area and larger pore diameters than in the case of HKUST-1.

OXIDATION OF METHYLENE BLUE



MB conversion versus time over HKUST-1, activated HKUST-1/GO(stirring) (B activated), HKUST-1/Cu@GO(CSM) (D), activated HKUST-1/Cu@GO(CSM) (D activated).

- ✓ **Activation (carbonisation) of HKUST-1/GO and HKUST-1/Cu@GO significantly improves its performance in MB oxidation** within first 4 hours of experiment. The increase in activity is linked to the exposure of Cu_2O and Cu active sites.
- ✓ After 5 hours of test-run the MB conversion was similar for HKUST-1 and HKUST-1/Cu@GO (ca. 91%) and activated composites (ca. 100%).

CONCLUSIONS

- ✓ **Preparation of HKUST-1/GO composites characterised by even distribution of both components requires stirring** (for unmodified GO), **or pre-decoration of GO with CuNPs.**
- ✓ Pre-decoration of GO with CuNPs allows obtaining composites with HKUST-1 of developed surface area.
- ✓ Such materials show improved performance in MB sorption.
- ✓ Activation (carbonisation) of HKUST-1/GO composites lead to exposition of Cu and Cu_2O active sites that are evenly distributed in the carbon matrix and are active in MB oxidation.