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Supplementary Information

Rapid microwave synthesis of sustainable magnetic framework composites of UTSA-16(Zn) with Fe_3O_4 nanoparticles for efficient CO_2 capture

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Contents

1 Citrate-coated Fe_3O_4 nanoparticles (MNP-CA)

1.1 Size distribution of MNP-CA agglomerates

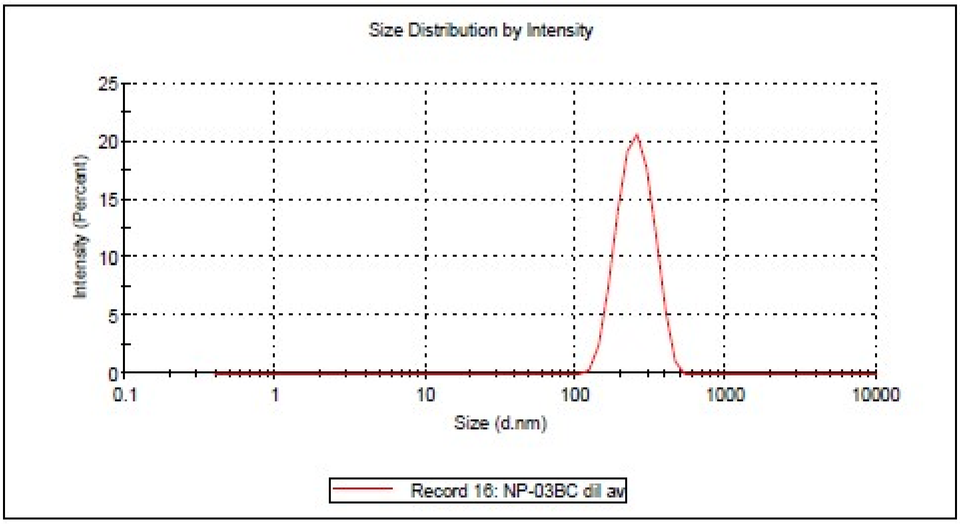

Figure S1: Size distribution by intensity measured by dynamic light scattering, showing the hydrodynamic size of MNP-CA agglomerates.

1.2 Zeta potential of MNP-CA in water

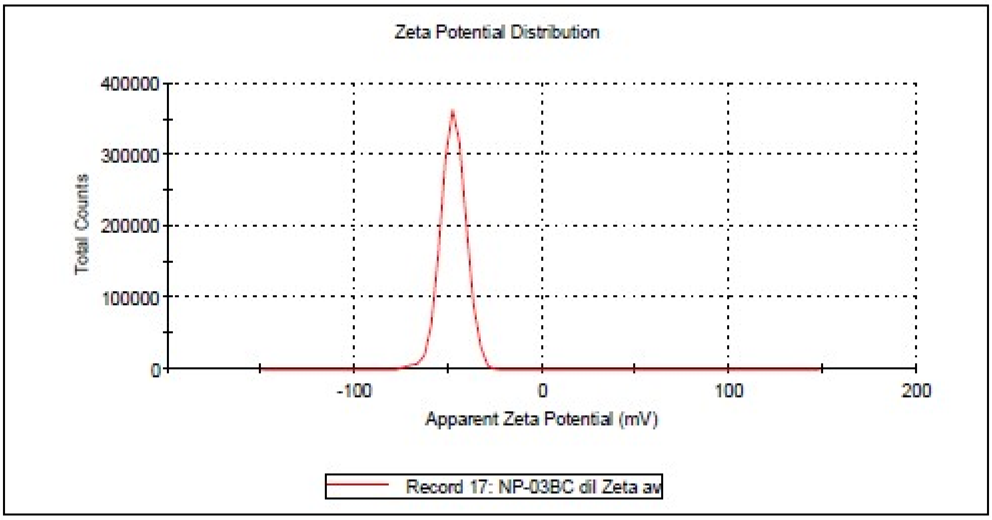

Figure S2: Zeta potential distribution for MNP-CA dispersed in water.

2 Synthesis and CO_2 adsorption of pristine MOF UTSA-16(Zn)

2.1 Synthesis of UTSA-16(Zn)

$Zn(AcO)_2.2H_2O$ (0.439 g, 2 mmol), citric acid monohydrate (0.420 g, 2 mmol) and KOH (0.34 g, 5.2 mmol) were dissolved in H_2O (5 mL) in a 35 mL microwave vial. EtOH (5 mL) was added and stirred (10 min) before the vial was sealed and irradiated under autogenous pressure with stirring at a maximum forward power of 300 W (commercial CEM discover microwave reactor, dynamic mode, T = 25-150 °C, t = 0-60 min). After the reaction, the vial was cooled in the microwave cavity with air, then the product was collected by washing out the vial with H_2O:EtOH 1:1 (20 mL) followed by centrifugation. The product was then washed by centrifuge with MeOH (3 x 30 mL, 4200 RPM, 20 mins) before drying in an oven (50 °C, >4 h).

2.2 Synthesis optimisation and CO_2 adsorption of UTSA-16(Zn)

The synthesis of UTSA-16(Zn) has been reported via a solvothermal route (120 °C for 2 days)[1] or more rapidly at 90 °C for 4 h using microwave heating.[2] In this work we further optimised the preparation of UTSA-16(Zn) before investigating its synthesis in the presence of MNP-CA for the production of MFCs. Figure S3A shows the washing procedure used to activate the MOF post-synthesis. Previous work used anhydrous MeOH and Et_2O with 2 days of soaking[2]. For large scale applications the use of Et_2O is strongly discouraged due to safety concerns around its volatility and flammability[3]. The use of anhydrous solvents and 2 days of soaking and replenishing would also be limiting at scale, due to the cost and volumes of solvents required, and the timescales for soaking. Figure S3A shows the washing and activation of the MOF without anhydrous solvents. Removing the Et_2O solvent wash, and 2 days of soaking, had no effect on CO_2 adsorption performance. An optimised reduced washing procedure of 3 x 30 mL MeOH was therefore selected for future batches. It should be noted that in this study, CO_2 adsorption was measured using the more efficient and time-saving evaluation of gravimetric gas uptake using TGA[4]. Using non-anhydrous solvents and a gravimetric test set-up, the value of CO_2 adsorption obtained using the previously mentioned published microwave method (90 °C, 4 h)[2] was 3.5 mmol/g, so this value was used for comparisons during method optimisation.

To maximise the energy and time efficiency of the synthesis, the reaction temperature and duration were optimised using a microwave method. Although slight improvements to yield and CO_2 adsorption capacity were made with longer durations and higher temperatures, most progress made was only up to 60 °C and in the first 10 minutes (Figure S3B,C). These results show for the first time that UTSA-16(Zn) MOF could be synthesised with a high yield (0.31 g, 77%) in a rapid and energy-efficient manner (60 °C, 10 min microwave synthesis). Microwave-synthesised UTSA-16(Zn) exhibits a CO_2 adsorption capacity of 3.4 mmol/g (Figure S3B) and apparent BET surface area of 741 m^2/g (Figure S3A). These results further support our previous reports of MOF synthesis using selective microwave heating[5–9].

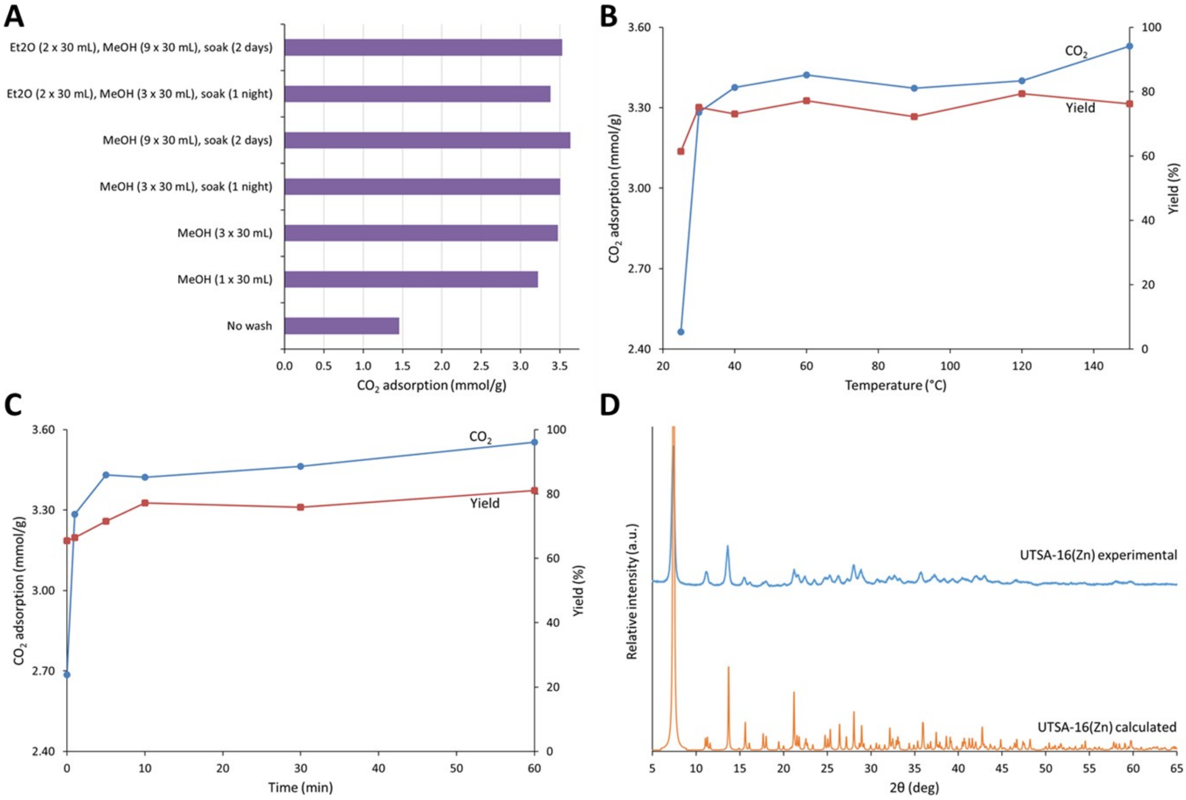

Figure S3: All CO_2 adsorption measured gravimetrically by TGA. A: a comparison of washing and activation techniques for UTSA-16(Zn) produced at 90 °C for 4 h. B: CO_2 adsorption against temperature for UTSA-16(Zn) produced at 10 min. C: CO_2 adsorption against time for UTSA-16(Zn) produced at 60 °C. D: PXRD patterns of UTSA-16(Zn), calculated using Mercury software[10] and experimental produced at 60 °C for 10 min. All UTSA-16(Zn) materials were synthesised using microwave heating.

3 UTSA-16(Zn)@MNP-CA magnetic framework composites (MFCs)

3.1 BET surface area and CO_2 adsorption analyses comparison of MFCs

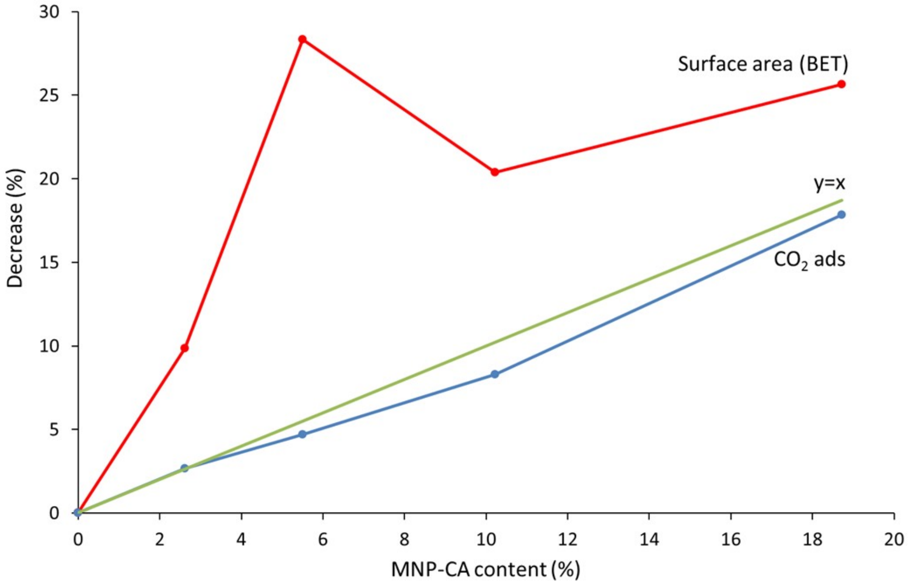

Figure S4: Decrease in CO_2 adsorption capacity and apparent BET surface area plotted against MNP-CA content for UTSA-16@MNP-CA MFCs. A line for y=x represents MNP-CA content for comparison.

3.2 Thermal decomposition of MFCs

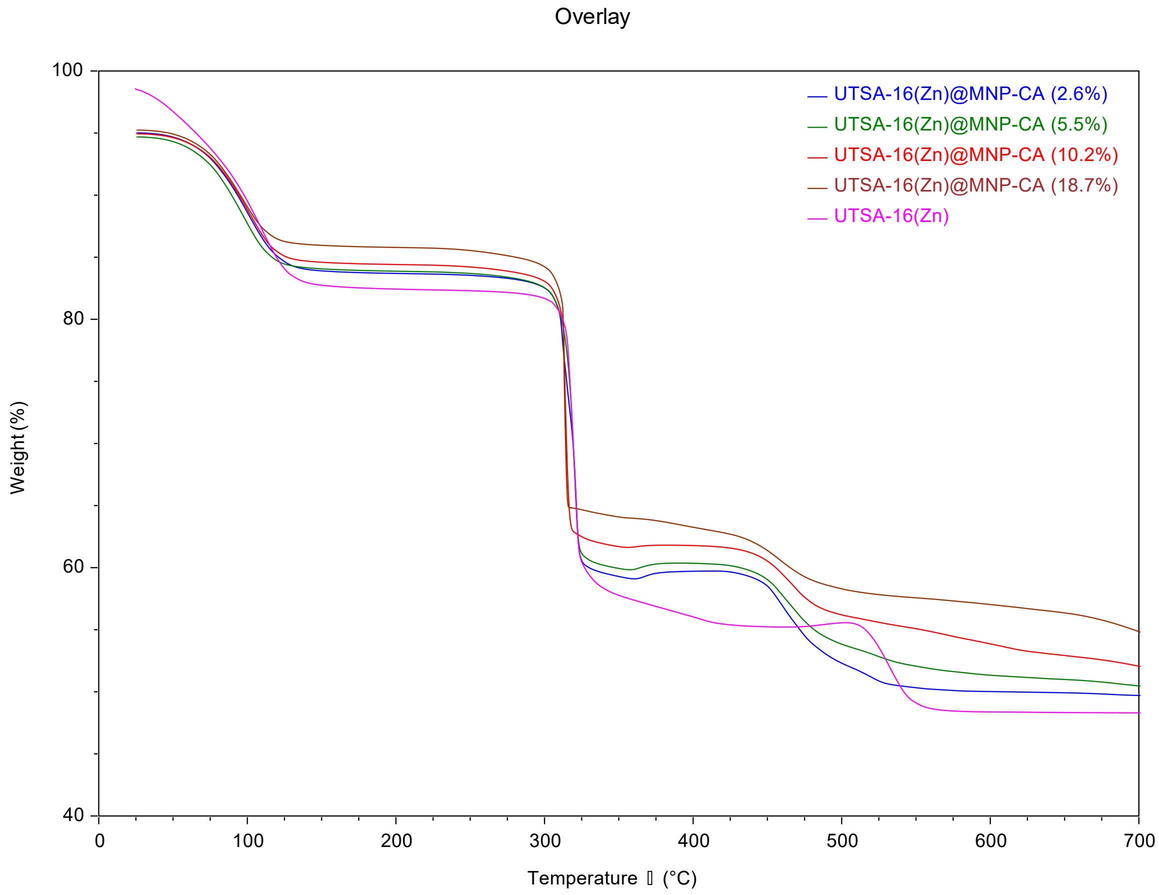

Figure S5: TGA thermograms showing thermal decomposition of UTSA-16(Zn)@MNP-CA with various loadings of MNP (see legend) and pristine UTSA-16(Zn). Measurements conducted under air at a ramp rate of 10 °C/min.

3.3 SEM and EDX image analyses of MFCs

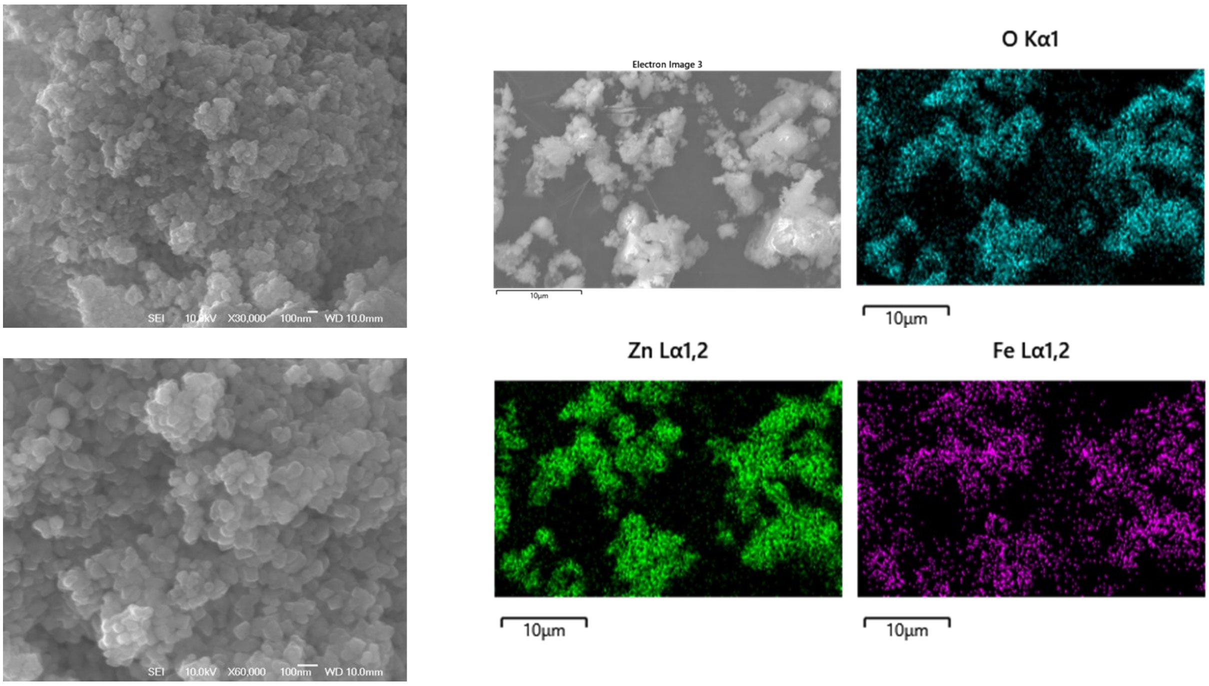

Figure S6: Left: SEM images of UTSA-16(Zn)@MNP-CA (18.7%). Right: elemental mapping by EDX of the same material, Zn (green) showing the distribution of the UTSA-16(Zn) MOF and Fe (pink) showing the distribution of the Fe_3O_4 magnetic nanoparticles. Blue shows the distribution of O atoms, present in both UTSA-16(Zn) and Fe_3O_4.

Data Access - All data created during this research are openly available from the University of Nottingham data repository at DOI: 10.17639/nott.7348

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