Electronic Supporting Information for

HKUST-1 growth on glassy carbon

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1. Materials. All starting compounds and solvents were used as received from commercial sources without further purification unless otherwise noted. Aqueous solutions were prepared using deionised Millipore Milli-Q water (>18 MΩ cm). The tetrafluoroborate salts of 4-carboxymethylbenzenediazonium and benzenediazonium were prepared using standard procedures.[1]

2. Electrochemistry. All electrochemical experiments were conducted at room temperature under a nitrogen atmosphere using a computer-controlled Ecochemie Autolab PGSTAT 30 potentiostat equipped with GPES software. Cyclic voltammetry (CV) was performed with glassy carbon (GC) plates (9 mm × 9 mm) as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode for aqueous solutions and Ag/$AgNO_3$ (0.1 M $AgNO_3$, 0.1 M NBu_4BF_4 in CH_3CN) for non-aqueous solutions as the reference electrodes, and platinum wire as the counter electrode.

3. Growth of HKUST-1 on GC plates

Method A: HKUST-1 growth on grafted GC substrates.

Covalent grafting of functional groups to GC surface. A circular patch (5 mm diameter) of the GC plate surface was exposed to an electrochemical cell solution as described elsewhere.[2] Grafting using the 4-carboxybenzenediazonium cation was performed in an aqueous electrolyte by an *insitu* method, whereas grafting of the methyl 4-carboxybenzenediazonium and benzenediazonium cations was performed in a non-aqueous electrolyte solution. In the former method, a solution of $NaNO_2$ (10 mM) and *p*-aminobenzoic acid (10 mM) in 0.5 M HCl was employed to generate the diazonium cation. Subsequent surface derivatisation was carried out by electrochemical reduction of the diazonium cation by scanning the potential from 0 to -0.60 V vs Ag/AgCl at 100 mV/s for 3 cycles.

In the non-aqueous method, a 1 mM solution of the tetrafluoroborate salt of the diazonium cation and 0.1 M NBu_4BF_4 (as supporting electrolyte) was prepared using dry acetonitrile as the solvent. Electrochemical grafting was performed at a scan rate of 100 mV/s for 3 cycles from 0.20 to -0.60 V vs $Ag/AgNO_3$ (for phenyl) or 0.60 to -0.80 V vs $Ag/AgNO_3$ (for methyl 4-carboxybenzenediazonium). Following grafting, the GC plates were washed and dried under a stream of N_2 gas.

HKUST-1 growth on functionalised GC plates. Benzene-1,3,5–tricarboxylic acid (H_3BTC) (0.25 g, 1.18 mmol) was dissolved in 7.5 mL of a 1:1 mixture of ethanol/dimethylformamide and combined with a solution of copper(II) nitrate trihydrate (0.52 g, 2.15 mmol) in 3.75 mL of water in a 20 mL scintillation vial. The resultant mixture was stirred vigorously for 10 minutes before the functionalised GC plates were introduced into this solution and heated in an oven at 85 °C for 19 hours. The major planar surfaces of the plates were oriented perpendicular to the base of the vial to avoid crystal deposition by gravity. The reaction mixture was cooled to room temperature and the plates were washed with fresh ethanol then dried in air.

Microwave heating. The precursor solution for the HKUST-1 was prepared by dissolving H_3BTC (2.0 mmol) and copper(II) nitrate trihydrate (3.65 mmol) in a water-ethanol mixture (24 mL, 1:1 v/v). The 4-carboxyphenyl-functionalised GC substrate was immersed into this solution then heated in a microwave synthesizer (CEM) for 3 mins at 100 C using a microwave power of 300 W. The GC substrates were subsequently washed with ethanol and slowly dried under air. The density of HKUST-1 crystals on the GC plate was less than that observed following conventional heating.

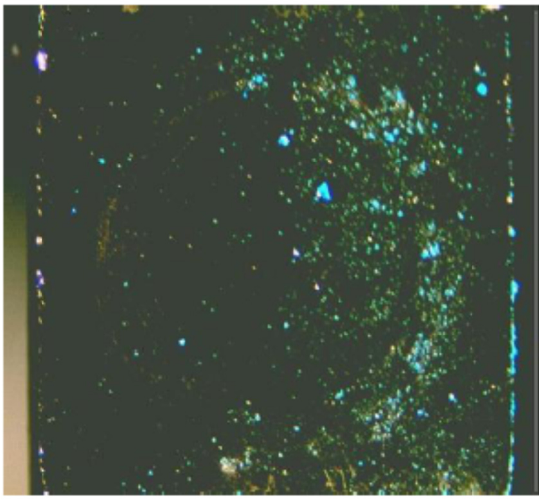

Figure S1. Optical image of HKUST-1 grown using method A on a GC substrate grafted with a circular patch of methyl 4-carboxyphenyl groups. These grafted groups do not promote growth of HKUST-1.

Method B: HKUST-1 growth on roughened GC substrates.

*Surface roughening:*GC substrates were roughened using P120 silicon carbide paper. The roughened substrates are henceforth referred to as GC-r. The GC-r substrates were sonicated in deionised water then washed with a stream of deionised water to remove any particulate matter.

Seeding GC-r substrates: Seeding solutions of HKUST-1 were synthesized as follows: Benzene-1,3,5–tricarboxylic acid (0.25 g, 1.18 mmol) was dissolved in 7.5 mL of a 1:1 mixture of ethanol/dimethylformamide and combined with a solution of copper(II) nitrate trihydrate (0.52 g, 2.15 mmol) in 3.75 mL of water in a 20 mL vial. After stirring the solution vigorously for 10 minutes, the GC-r substrates were dipped into the solution for a period of 2 – 3 minutes then removed from the solution and heated in an oven at 100 °C for 12 – 15 minutes. The substrates were removed from the oven, cooled to room temperature, sonicated in ethanol, washed with a stream ethanol, and dried with a stream of compressed air. The dipping-heating-sonicating-washing-drying procedure was repeated three times.

Secondary growth:Secondary growth of HKUST-1 was achieved by placing the seeded GC-r substrates in a mixture of benzene-1,3,5–tricarboxylic acid (0.25 g, 1.18 mmol), dissolved in 7.5 mL of a 1:1 mixture of ethanol/dimethylformamide,and copper(II) nitrate trihydrate (0.52 g, 2.15 mmol), dissolved in 3.75 mL of water. The seeded supports and solution were contained in a 20 mL scintillation vial, which was sealed and heated in an oven at 85 °C for 19 hours before being cooled to room temperature. The GC plates were orientated perpendicular to the base of the vial to avoid the deposition of crystals by gravity. The substrates were further washed with a stream of ethanol and dried using a stream of nitrogen gas.

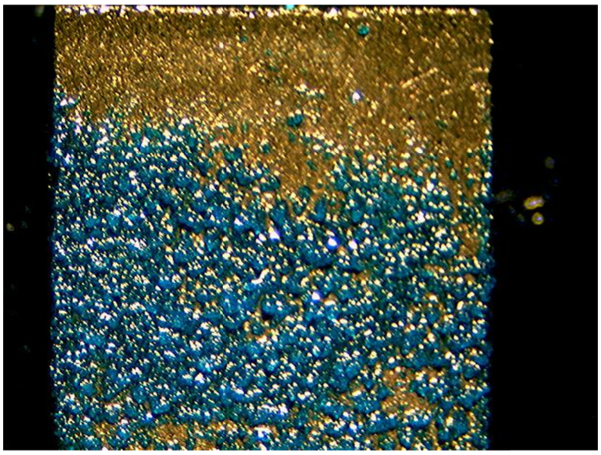

Figure S2. Optical image of HKUST-1 grown using method B on a GC substrate roughened with SiC paper then grafted with phenyl groups.

References

1. Saunders, K. H.; Allen, R. L. M., *Aromatic Diazo Compounds*. 3rd ed.; Edward Arnold: London, 1985.
2. Brooksby, P. A.; Downard, A. J., *Langmuir* **2004**, *20*, 5038-5045.