

Elaboration of Metal Organic Framework Hybrid Materials with Hierarchical Porosity by Electrochemical Deposition-Dissolution

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Supporting Information

The hierarchically structured macro-/microporous HKUST-1 composites were prepared by following the protocol described hereafter.

In the first step, silica particles with a diameter of $\sim 1 \mu\text{m}$ were prepared. Then, a colloidal crystal of the obtained silica particles was fabricated on a gold electrode by the LB technique.¹ After that, the voids of the template were filled with copper of a well-defined thickness via electrodeposition.² Then, the silica template was removed to provide the 3D ordered macroporous Cu electrode with an inverse opal structure. In the last step, the Cu surface was transformed into HKUST-1 via the electrochemical dissolution of Cu in the presence of the organic ligands leading to the direct crystallization of the MOF.

Preparation of the silica colloidal template via LB technique

A colloidal solution of silica particles with a diameter of $\sim 1 \mu\text{m}$ was prepared according to the Stöber method using tetraethyl orthosilicate (TEOS), 25% ammonia solution, and an ethanol solution (absolute ethanol diluted with ultrapure water (resistivity $\geq 18 \text{ M}\Omega\cdot\text{cm}$, Millipore)) as the silica source, catalyst and solvent, respectively.³ The obtained silica particles were then

functionalized with aminopropyltriethoxysilane (APTES) to create the amine (NH₂)-terminated alkyl chains on the particles⁴. This functionalization is very important in order to improve the hydrophobicity of the particles providing stable Langmuir films of the particles.⁵

Synthesis of silica colloidal crystals by the LB technique

The colloidal crystals were obtained following a literature procedure.⁶ In brief, a LB trough (NIMA Technology, model 622) equipped with two symmetrical barriers was used. The reservoir, barriers and dipping well of the instrument were cleaned with analytical grade chloroform (CHCl₃) several times before use. Ultrapure water was filled into the reservoir. A certain amount of the functionalized silica beads was isolated from the synthesis solution by centrifugation and washed several times with absolute ethanol to remove the residues. The washed beads were redispersed in a solution of chloroform-ethanol 80-20 v/v. The obtained suspension was spread at the air-water interface drop by drop. After solvent evaporation, the barriers were slowly closed at a controlled rate. As a result, the silica particle layer was compressed forming a Langmuir film. Along with this compression, surface pressure-area isotherms were recorded. The compression was stopped when the surface pressure increased and reached the target pressure of 4 mN/m (see Fig. S1). Commercial Au-coated glass slides (ACM, VILLIERS SAINT FREDERIC, France) with a 300nm thick gold layer were cut into small pieces and then treated twice in a piranha solution (a mixture containing 3:1 v/v concentrated sulfuric acid (conc. H₂SO₄) and hydrogen peroxide) for 15 min to remove organic contaminants. In this specific case gold has been used as a conducting electrode layer, but in principle any other material, including transparent ITO can be used instead. The slides were then washed several times with ultrapure water. The prepared slides were attached to the dipper by using removable and re-usable glue pads and then dipped through the Langmuir film of silica beads with a controlled rate of 63 mm/min. Then, the slides were pulled up through the film with a rate of 1 mm/min. During the dipping-raising process, the surface pressure was kept constant at 4 mN/m. The desired number of silica layers was transferred to the surface of the Au slides layer-by-layer by repeating the dipping-raising process.

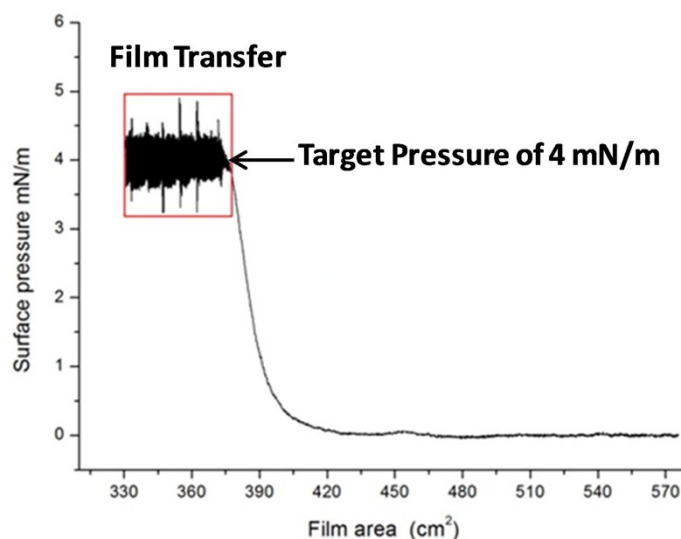


Fig. S1. Surface pressure-area isotherms obtained during the compression of the film of 1 μm -silica particles. After the surface pressure reached the target pressure of 4 mN/m, the deposition of the Langmuir film of silica spheres onto gold-coated glass slides was performed.

Electrosynthesis of 3D ordered macroporous Cu electrodes

The voids of the colloidal template were filled with Cu via electrochemical deposition. A suitable potential for the deposition was chosen by performing cyclic voltammetry (CV) of the Cu plating bath (CUBRAC 660) (see Fig. S2). When scanning the potential of the electrode from 0V towards more negative values and back, one can clearly observe a negative reduction current in the whole potential window with a maximum around -0.47V. We therefore concluded that in principle a potential in the range from 0.00 V to -0.47 V should be suitable for Cu deposition. However when applying too much driving force the copper deposit tends to be rough and thus less negative potentials (-0.05V) have been mostly used in this study. Before deposition, the slides with the silica colloidal template were soaked in the plating bath for at least 10 min to ensure the penetration of the solution into the voids of the template. The gold slide coated with the silica colloidal template was used as the working electrode in a three-electrode cell. A platinum mesh and a silver-silver chloride electrode (Ag/AgCl, sat. KCl) were used as the counter and reference electrodes, respectively. The electrodes were connected to a potentiostat/galvanostat (μ -Autolab Type III equipped with the GPES software). The electrochemical deposition of copper was performed at a given voltage and deposition time in order to infiltrate the desired number of bead layers with metallic copper. After the deposition, the Cu-coated slides were washed with

ultrapure water and dried with air. Then, they were immersed into 5% hydrofluoric solution for ~10 min to remove the silica beads. It should be mentioned that the soaking time should not exceed 10 min in order to prevent the Cu surface from damage. As a result, ordered macroporous Cu electrodes were obtained.

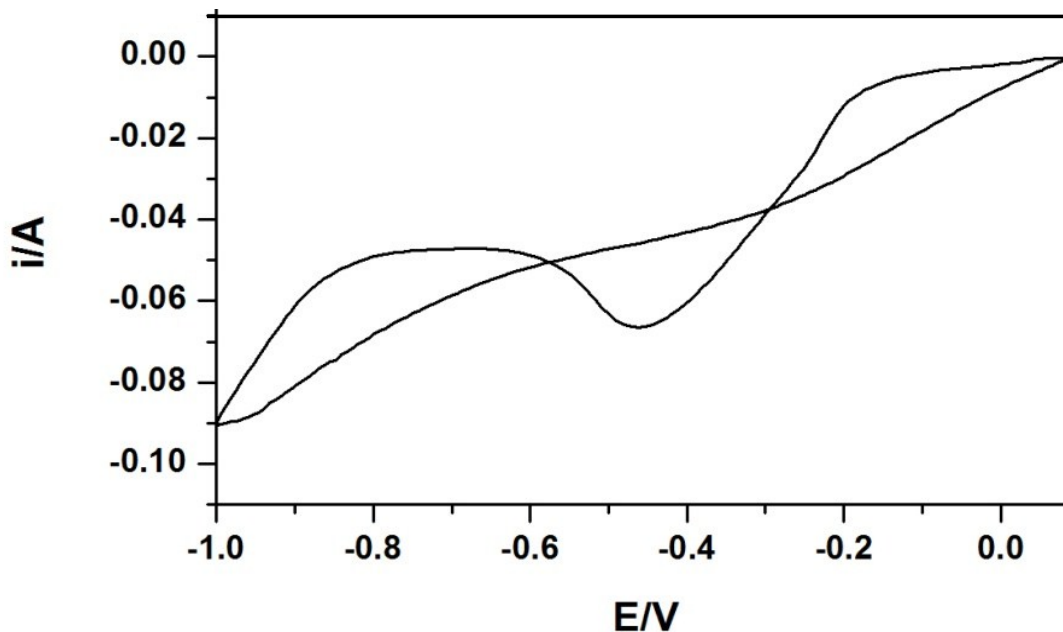


Fig. S2. Cyclic voltammogram of the Cu plating bath recorded at a scan rate of 100 mV/s and room temperature. Flat Au-coated glass slide, Pt mesh and Ag/AgCl electrodes were used as the working, the counter and reference electrodes, respectively. Potentials are given vs. Ag/AgCl.

Transformation of ordered macroporous Cu electrodes into HKUST-1

The electrochemical dissolution of Cu was performed in the presence of the organic ligand, 1,3,5-benzenetricarboxylic acid (BTC). A 3D ordered macroporous Cu electrode was used as the working electrode. The electrode was pretreated for 15 min in 10% H₂SO₄ to remove residual copper oxide contaminations that may occur by oxidation of the Cu surface in air. A silver electrode and a platinum mesh were used as a pseudo reference and a counter electrode, respectively. The experiments were performed in a home-built electrochemical cell (Fig. S3) composed of reaction compartments that are separated by Nafion membranes. The separated compartments prevent polymerization of BTC molecules, causing their removal from the working solution, and eventually disturbing the reaction occurring at the working electrode. The

working electrode compartment was filled with 0.05 M BTC solution in ethanol containing 0.2 M tributylmethylammonium methylsulfate (MTBS) as supporting electrolyte. The counter electrode compartment was filled with the MTBS solution.

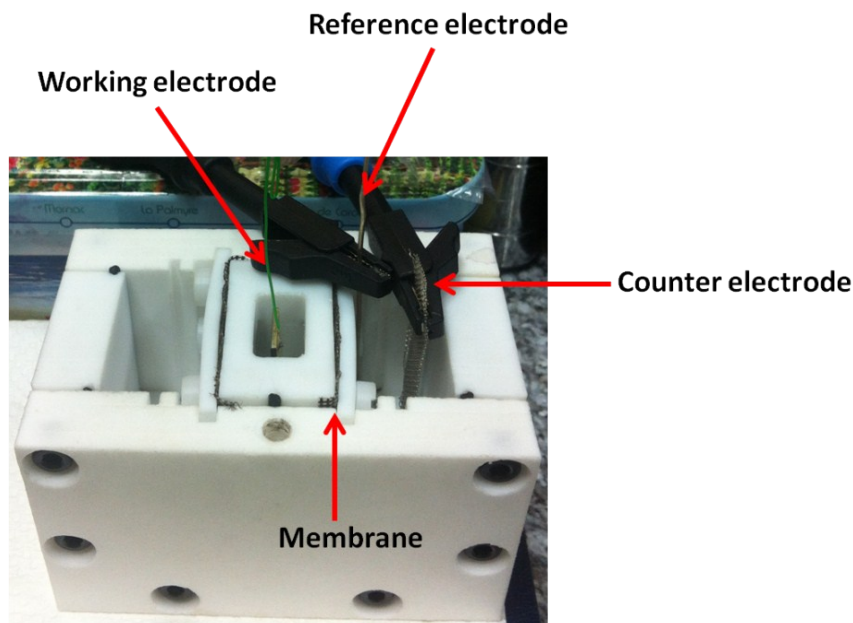


Fig. S3. Photograph showing the experimental set up for the transformation of the Cu surface of the ordered macroporous Cu electrodes into HKUST-1 via the electrochemical dissolution of Cu in the presence of the organic ligand.

Characterizations

The characteristics of the obtained materials were analyzed by Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) analyses and Atomic Force Microscopy (AFM). The FT-IR spectra of the samples were recorded by using a TENSOR 27 (Bruker) FT-IR spectrometer (with KBr pellets) in the range 400-4000 cm^{-1} with a resolution of 4 cm^{-1} . The SEM images were taken with a HITACHI S4700 FESEM and HITACHI TM-1000 SEM with an accelerating voltage of 5 kV equipped with an EDS2006 model 550i EDS analyzer. The powder X-ray diffraction patterns were recorded from the powder that has been mechanically removed from the sample surface. The D8 ADVANCE X-Ray diffractometer was operated at 35 kV and 45 mA with $\text{CuK}\alpha$ radiation. The AFM images were recorded on a Veeco Multimode 8 SPM (see below).

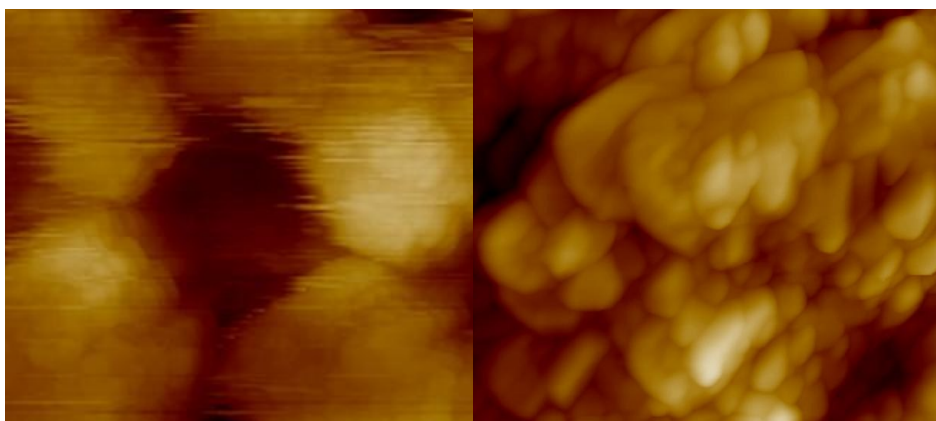


Fig. S4. Typical AFM images of the surface of a macroporous copper electrode (3/2 layers of pores), which has been partially transformed into HKUST-1. The oxidation was carried out at 0.125 V for 60 s, like for images of Figure 6c and 6d in the main manuscript. The left image (1.8 μm size) shows one single pore surrounded by MOF and the right image (500nm size) is a zoom on the HKUST-1 crystallites which are present at the border of the pore.

References

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