



Metal-organic framework templated electrodeposition of functional gold nanostructures



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ABSTRACT

Utilizing a pair of quick, scalable electrochemical processes, the permanently porous MOF HKUST-1 was electrochemically grown on a copper electrode and this HKUST-1-coated electrode was used to template electrodeposition of a gold nanostructure within the pore network of the MOF. Transmission electron microscopy demonstrates that a proportion of the gold nanostructures exhibit structural features replicating the pore space of this ~1.4 nm maximum pore diameter MOF, as well as regions that are larger in size. Scanning electron microscopy shows that the electrodeposited gold nanostructure, produced under certain conditions of synthesis and template removal, is sufficiently inter-grown and mechanically robust to retain the octahedral morphology of the HKUST-1 template crystals. The functionality of the gold nanostructure within the crystalline HKUST-1 was demonstrated through the surface enhanced Raman spectroscopic (SERS) detection of 4-fluorothiophenol at concentrations as low as 1 μ M. The reported process is confirmed as a viable electrodeposition method for obtaining functional, accessible metal nanostructures encapsulated within MOF crystals.

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1. Introduction

Metal-organic frameworks (MOFs) are a well-established family of nanoporous material whose framework is constructed from metal based inorganic clusters connected by heteroatom-containing organic linker molecules. MOFs have been investigated for a diverse range of applications [1]. Although they exhibit excellent properties for many of these applications in their pure form, the inclusion of MOFs as components in composite materials has provided many new exciting opportunities for their application in other areas [2].

The encapsulation of nanostructures within preformed MOF crystals [3], or during MOF crystal growth [4], have been demonstrated to be very effective methods to obtain composites with exciting properties [2]. A diverse range of nanostructured materials, including nanostructured carbon [5], polymer [6], metal

hydride [7], polyoxometalate [8], metal oxide [9], metal nitride [10] and metal [11], have been incorporated into individual, or aggregates of, MOF crystals. A diverse range of different techniques have been employed in the synthesis of a variety of different encapsulated nanostructured metal/MOF composites [12–19], for application in areas such as substrates for surface enhanced Raman spectroscopy (SERS) [12] and catalysis [16–18]. A particularly elegant example of a truly MOF-templated metal nanostructure appears to be that reported by Voloskiy et al. [19] These workers used a judicious choice of solvent/reducing agent to synthesize ~3 nm diameter Au and Pd nanowires that appear to be truly templated by the one dimensional ~3 nm diameter pores of MOF-545.

Amongst the wide variety of different techniques utilized to obtain encapsulated nanostructured metal/MOF composites, electrodeposition stands out, surprisingly, as being the least developed. Electrodeposition should have the advantage over other techniques for the deposition of nanostructures within MOF pore structures due to its ability to plate topologically demanding nanoscale features [20]. To the best of the authors' knowledge, there has been only one report of the use of electrodeposition to

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obtain a metal/MOF composite that involved forming metal sheets by electroreduction and agglomeration of the constituent metal ions of the layered MOF. This electrodeposition process involved destruction of the MOF itself [13]. Limited evidence for the presence of metal sheets on the external surface of the remaining MOF crystallites was provided for this poorly characterized metal/MOF composite formed by a non-templated electrodeposition process. On the contrary, templated electrodeposition has been successfully utilized to prepare composites of encapsulated metal nanostructures within other porous materials including anodized alumina [21], mesoporous silica [22], and hierarchical mesoporous silica/anodized alumina [23]. Aligned arrays of ~ 350 nm long and ~ 65 nm diameter Au nano-rods were fabricated within large pore anodized alumina [21] and much thinner, ~ 7 nm diameter and hundreds of nm long, Pd nanowires were produced by encapsulation within smaller pore diameter mesoporous silica [22]. It has also been shown that a supercritical fluid based electrolyte can be used with mesoporous silica coatings to template the electrodeposition of ~ 3 nm diameter Cu nanowires [20]. The random nature of the pores of the mesoporous silica resulted in relatively poor alignment of the nanowires [22] in contrast to those formed in the well aligned pores of the anodized alumina [21]. Subsequently, these two porous materials were combined to achieve the templated electrodeposition of well aligned nanowires, ~ 10 nm in diameter and hundreds of nm long, of Ag, Cu and Te [23]. Nanoporous MOFs have the potential to provide a similar combination of ordered porosity, matched with an even smaller pore size, yielding the potential to electrodeposit nanostructures with minimum dimensions of < 2 nm embedded in a porous material. Previous work using nanoporous zeolites as templates for electrodeposition reported the formation of isolated metal nanoparticles only within the pore structures rather than extended nanostructures, with no precise determination of the deposited metal particle size or distribution [24].

In order to utilize MOFs for templated electrodeposition they must be attached to an electrode surface as a single crystal or a well intergrown coating of crystals. One method to achieve the latter is the electrochemical anodic dissolution method, whereby a well intergrown coating of MOF crystals is formed directly on the surface of a metal anode by the application of a potential between two metal electrodes, of the metal of the desired MOF, immersed in an electrolyte solution containing the organic linker of the desired MOF [25]. The resultant MOF crystals provide for a relatively continuous and defect free coating that has the added advantage of being strongly adhered to the electrode surface [26]. A variety of carboxylate and imidazole-based MOF coatings have been formed using this route [25–30] including the archetypal copper trimesate MOF, HKUST-1 $\text{Cu}_3[\text{C}_6\text{H}_3(\text{CO}_2)_3]_2(\text{H}_2\text{O})_3$ [31]. HKUST-1 is assembled from $\text{Cu}_2(\text{H}_2\text{O})_2$ dimer units and tridentate trimesate (benzene-1,3,5-tricarboxylate) groups to form a three-dimensional framework structure containing a three-dimensional channel system. The channels consist of alternating cavities of ~ 1.4 nm pore diameter and ~ 1.1 nm pore diameter connected through pores of ~ 1.0 nm diameter as shown in Fig. 1 [32]. There are also smaller ~ 0.5 nm diameter cavities present in the structure between the larger cavities.

In this work we demonstrate for the first time that a porous MOF, HKUST-1, can be used successfully to template electrodeposition of a metal, gold, nanostructure within the pore network of the MOF and that a proportion of the nanostructures exhibit structural features replicating the pore space of the MOF. The high surface area, rough nature of the HKUST-1 encapsulated gold nanostructure is shown to act as an ideal surface enhanced Raman spectroscopic (SERS) substrate.

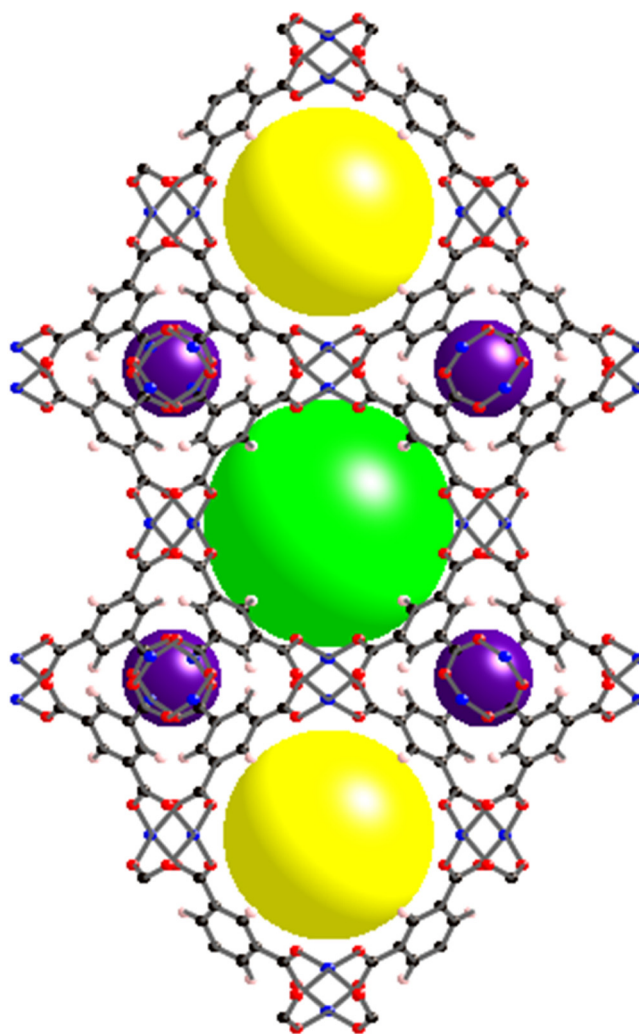


Fig. 1. Structure of HKUST-1 displaying the cavities of ~ 1.4 nm pore diameter (green sphere), ~ 1.1 nm pore diameter (yellow sphere) and ~ 0.5 nm diameter (purple sphere). Key Cu – blue, O – red, C – black, H – pink. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Materials

Cu foil (oxygen free high conductivity), 4-fluorothiophenol (98 +%) and sodium tetrachloroaurate dihydrate $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ (99.99%) were obtained from Alfa Aesar. Hydrochloric acid HCl (37%) and hydrogen peroxide H_2O_2 (30%) were obtained from Fisher Scientific. Repro rubber (thin pour) was obtained from Flexbar. Tetrabutylammonium chloride TBACl (99%) was obtained from Fluka. Deionized water ($18.2 \text{ M}\Omega \text{ cm}$) was obtained from a Milli-Q Millipore Direct 8 purification unit. 1,3,5-benzenetricarboxylic acid BTC (95%), dimethyl sulfoxide DMSO ($\geq 99.9\%$), ethanol ($\geq 99.8\%$), methanol ($\geq 99.9\%$) and methyltributylammonium methyl sulfate MTBAMS ($\geq 95\%$) were obtained from Sigma Aldrich.

2.2. HKUST-1 coating synthesis

Two Cu foil electrodes (each $\sim 16 \text{ cm}^2$) were coated on one side with Repro rubber, which was left to set, rendering that side electro-chemically inactive. The Repro rubber coated Cu foil electrodes were then immersed, active sides face to face and ~ 2 cm

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