Advances in Nanoporous Gold Synthesis

John W. Overcash Literature Seminar November 5, 2009

Nanoporous gold is, as the name implies, gold which contains pores on the order of a few nanometers to a few hundreds of nanometers in size. Due to the very small size of the features, nanoporous gold has many applications such as gas storage, actuation, catalysis (both as a catalyst and a catalyst support), sensing, and plasmonics.[1] Recently, nanoporous gold was used to create the first man-made surface chemistry-driven actuation.[2] The synthesis of nanoporous gold can be broken into two main classes: dealloying methods and templating methods.

Dealloying is a selective corrosion process where the less-noble constituent of an alloy is removed, usually by dissolving it in a corrosive environment with an applied potential (electrochemical dealloying) or without (chemical dealloying). For example, floating commercially available white gold leaf (a Au/Ag alloy with a 1:1 weight ratio) on a nitric acid solution will remove the Ag atoms and leave behind a sponge-like, bicontinuous, nanoporous gold structure (Figure 1).[3] By controlling the temperature of dealloying, the amount of the alloying metal, the potential applied, the time of dealloying, and the corrosive used, the size of the pores and ligaments within this porous gold can be fine-tuned. Pore sizes as small as ~3 nm have been published.[4]

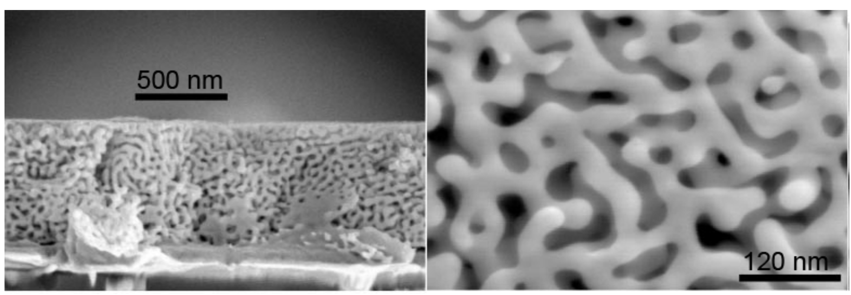

Figure 1: SEM micrographs of nanoporous gold by dealloying of Ag/Au alloys.

A recent extension of the dealloying process was used by Jia, et al. to create a nanoporous gold film directly on a gold electrode using multicyclic potential scans.[5] $ZnCl_2$ in benzyl alcohol was used as the electrolyte. First, a cathodic potential scan was performed which electrodeposited Zn onto the gold electrode surface. A Zn/Au alloy was formed at the interface due to an elevated electrolyte temperature. The Zn/Au alloy was then dealloyed in a subsequent anodic potential scan. These scans were repeated (up to 20 times) to create a nanoporous gold film (Figure 2). The roughness of the electrode after dealloying was estimated to be 560. The nanoporous gold film electrode was then compared to a polished gold electrode using cyclic and square wave voltammetry on standard systems ($Fe(CN)_6^{3-/4-}$, $Fe^{2+/3+}$, and $Cu^{2+/+}$). In all cases, significantly greater electrochemical signal, up to a 7000-fold increases, was observed.

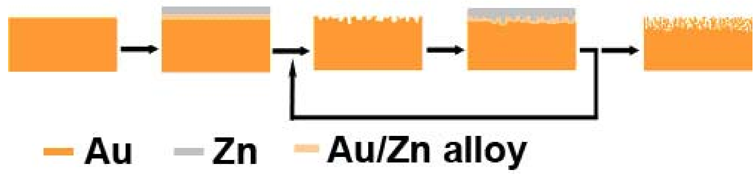

Figure 2: Schematic of nanoporous gold film electrode fabrication.

Template methods, while typically requiring more steps and more time than dealloying methods, allow for long-range order, which is beneficial for plasmonic materials.[6] Templating also allows for hierarchical structures as gold takes the shape of whatever template it is applied to. Recently, Bao, et al. were able to use diatom frustules as templates for nanoporous gold.[7] Diatoms (unicellular algae) create their own nanostructured silica microshells (frustules), which are unique for each species. To use these frustules as a template, the silica is first reduced to Si by a reaction with gas phase Mg:

$$2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + Si(s) \quad (1)$$

The MgO and Si form a continous, interpenetrating network of both phases which replicates the initial shape. Removal of the MgO by HCl solution produces a nanoporous Si template with the same structure as the original SiO_2 frustule. BET analysis showed the specific surface area of the frustules increased from 1.7 m^2/g to 541 m^2/g after the removal of the MgO. Au deposition onto the nanoporous Si template was easily accomplished by electroless gold deposition from a commercially available solution. They then used NaOH to remove the Si template. The results showed that the free-standing, nanoporous gold product retains the morphology of the biosilica frustule template (Figure 3).

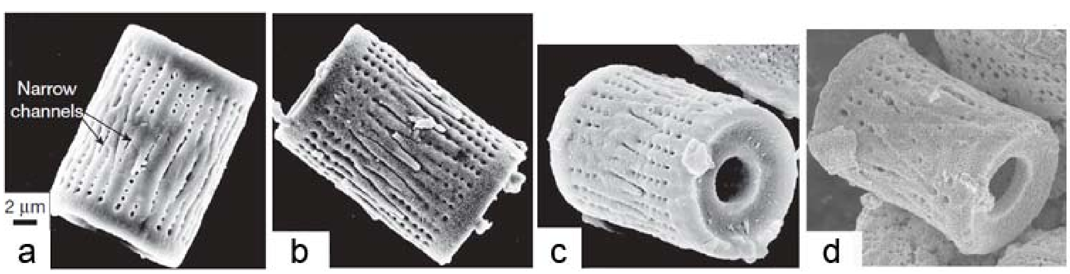

Figure 3: Morphology of frustule made of a) silica b) MgO/Si c) silicon and d) gold.

By combining the dealloying and templating methods, completely synthetic hierarchical porous gold materials can be synthesized. This was realized by Nyce, et al.[8] First, gold was deposited onto micon-sized polystyrene (PS) beads using an electroless deposition method. This step was followed by electroless deposition of silver onto the PS/Au spheres. These beads were then slip cast to form a monolith and heated at to remove the PS and alloy the Au and Ag. Finally, dealloying of the cast Au/Ag alloy resulted in nanoporosity of the material (Figure 5). BET analysis showed the surface area of the hierarchical gold foam to be 1.48 m^2/g, comparable to that of dealloyed gold. The larger pores in this material (from the PS template) facilitate mass transport, while the smaller pores (formed by dealloying) increase the surface area dramatically. This method gives an facile method for the tuning of both the small pores (by adjusting the dealloying parameters) and the large pores (by adjusting of the PS bead size) allowing for the adjustment of the properties for photonic and plasmonic applications.[6]

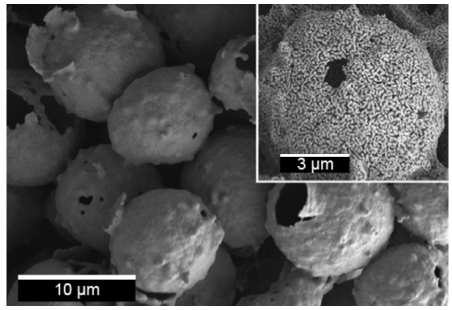

Figure 4: Fracture surface of monolithic Ag/Au shells before dealloying and (inset) after.

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