Electrochemical Fabrication of Nanoporous Gold

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SUPPORTING INFORMATION

1. Electrochemical etching cells

We used two electrochemical cells for gold etching [1], as shown in Figures S1 (a) a static 2-electrode cell holding a volume of ~5 mL and with an exposed gold electrode area of 1.5 cm^2 and (b) a stirred 3-electrode cell holding volume of ~25 mL with an exposed gold electrode area of 0.15 cm^2 .



Figure S1. (a, b) 2- and 3-electrode electrochemical cells used for etching and (c, d) their corresponding *I-V* curves recorded in HF/DMF (1:1, v/v), respectively. The potential scanning rates are indicated in figures. The inset in (c) shows the dependence of peak area (at 1.5-1.9 V) on the potential scanning rate and the inset in (d) shows the amplified peak at ~1.8 V.

The shape of the I-V curves (Figures S1 (c, d) looks similar to the break-through current which is observed for a semiconductor [2-6]. The two electrochemical cells' I-V curves, however, exhibit difference and thus compared. For the static 2-electrode electrochemical cell, a current peak at 1.5-1.9 V is observed in Figure S1 (c) likely due to formation of oxide because its potential position and current height are shown to be dependent upon the potential scanning rate. The inset shows that the peak area is decreasing with the increase of the potential scanning rate which implies a diffusion-controlling process [1]. The peak area, for example, ~8 mC at 1.33 V/s, is much larger than the charge needed to form a monolayer of oxide ($\sim 0.6 \text{ mC}$ for $\sim 1.5 \text{ cm}^2$), suggesting the formation of multilayer or the dissolution of oxide [5]. In the stirred 3-electrode cell, however, this oxidation peak was much smaller (Figure S1 (d) and inset) due to the small working area ($\sim 0.15 \text{ cm}^2 vs \sim 1.5 \text{ cm}^2$) and the stirring of the solution. The current oscillations or noise at > 0.1 A particularly in Figure S1 (d) are related to the evolution of gas (oxygen) at the electrode surface due to anodic electrolysis of water. Note two different reference electrodes were used, platinum grid in static cell (also as a cathode so that the reduction of water to emit hydrogen provided a stable reference system) and silver wire (quasi-reference electrode) in the stirred cell.

2. Etching of gold in HCl/DMF

Figure S2 (a) shows the porous structure in the central part of a cyclic domain (not shown) with a size of $10-30 \mu m$ developing on a gold surface during etching in HCl/DMF, supporting the assumption on the etching mechanism in which oxide is critical for pore formation whilst etching species (HCl or HF) promotes oxide's dissolution [2, 3]. Figure S2 (b) indicates that etching is more prevalent at the edge of the domain than in the central part. There appears to be three neighbouring cyclic domains outside of which a triangle is formed. The domain may be a result of the evolution of bubbles which shield the gold film in this region from any further etching [3, 7, 8]. At the edge of bubble evolution, reagent

concentration is increased due to solution convection, and etching is accelerated in this region giving rise to the increased pore size observed in Figure S2 (b). It supports the hypothesis that convection can accelerate the reaction process for pore etching.

Further etching results in arrow-head like structures observed in Figure S2 (c). At the meeting area of three neighbouring domains, the gold layer has been partly removed by overetching. Inset shows a large field view of the structures which appear to be firework-like domains, indicating only the first generation of nuclei (at the central point) grow into cyclic domains [2, 4].



Figure S2. SEM images of the etched gold in 1:9 (v/v) HCl/DMF at 10 V for 10 s (a, b), for 20 s (c) or in 1:9 (v/v) NH₃/DMF at 10 V for 60 s (d) using stirred etching cell. (a) is the central part of a cyclic domain whereas (b, c) the edge parts. The insets in (c, d) are images of low magnification.

3. Etching of gold in NH₃/DMF

Figure S2 (d) shows etched fracture domains in NH₃/DMF. The gold film has been lifted up to form grooves. The expanded volume should come from the formation of silicon oxide on the bottom [2, 4]. When the etching was continued, the structure was developed into the stacks of silicon oxide (not shown), suggesting NH₃/DMF is not a suitable etching solution for gold because the gold oxide cannot be effectively dissolved into it [9-13].

4. Characterization of thiol-derivatized SWCNT

The condensation reaction between carboxylated single walled carbon nanotubes (SWCNTs) and cysteamine was characterized by the appearance of strong C-H stretching vibrations at 2935 and 2891 cm⁻¹, and amide I band at 1634 cm⁻¹ in the FT-IR spectrum (Figure S3 (a)) [146]. TGA results show weight losses of 2.6, 8.9 and 13.2 % between 120 to 600 °C for pristine SWCNTs, carboxylated-SWCNTs, and the cysteamine functionalized-SWCNTs, respectively (Figure S3 (b)). The difference in weight loss of carboxylated-SWCNTs and the cysteamine functionalized-SWCNTs is attributed to the presence of cysteamine molecules on the surface of the SWCNTs.



Figure S3. FT-IR spectra (a) and TGA curves (b) of SWCNT. The functionalized SWCNTs are indicated in figures. The TGA curves in (b) were recorded in a nitrogen atmosphere at heating rate of $10 \,^{\circ}$ C/min.

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