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Supplementary Information

Simple, Highly-Efficient Route to Electroless Gold Plating on Complex 3D Printed Polyacrylate Plastics

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Materials and General Characterizations.

The preparation of 1,6-hexanediol diacrylate-based 3D objects (HDDA)¹ and pentaerythritol triacrylate-based 3D objects (PETA)² were described elsewhere.

Tomography of the gold coated samples were performed at beamline 8.3.2 at the Advanced Light Source (Lawrence Berkeley National Laboratory, Berkeley, CA, USA) using a monochromatic beam at an energy of 17 keV. A PCO.Edge detector with a frame size of 2560×2160 combined to a LuAg scintillator were used to collect projected images. Lenses of $5 \times$ and $2 \times$ magnification were used, resulting in an effective pixel resolution of 1.3 µm and 3.25 µm for the HDDA-Au and PETA-Au, respectively. Data sets of 1025 transmitted projections were collected with a 1500 ms exposure time over 180 degrees rotation range. The projection images were conventionally normalized with empty-beam images and 3D volumes were reconstructed via a filtered back projection algorithm using Livermore Tomography Tools software (LLNL, Livermore, USA).

Morphology and composition of fractured samples were investigated with a Jeol JSM-7401F scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) in a lower secondary electron image (LEI) mode with no sputter coating.

Attenuated total reflection (ATR)-IR spectra were recorded on a Perkin Elmer Spectrum GX FTIR-ATR. Spectra are averaged over ca. 15 scans with a resolution of 4 cm⁻¹.

Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/DSC 3+ system at a heat rate of 10 °C/min under an air flow of 50 mL/min.

BET surface areas were measured by nitrogen adsorption porosimetry with a Micromeritics Instrument ASAP 2000 after degassing at 100 °C for 12 h.

Preparation of 4-Dimethylaminopyridine-Stabilized Gold nanoparticle (Au-DMAP)

Gold nanoparticles stabilized with 4-dimethylaminopyridine (Au-DMAP) were prepared, as similarly to the literature procedure.³ Typically, gold (III) chloride trihydrate (HAuCl₄·3H₂O, 0.35 g) was dissolved in water (30 mL) and added to tetraoctylammonium bromide (1.1 g) dissolved in toluene (80 mL). Then, freshly prepared NaBH₄ (0.4 g) dissolved in water (25 mL) was slowly added to the mixture and stirred for ~1 h. After the reaction, the organic layer was taken and washed with H₂SO₄ (0.1 M, 100 mL), NaOH (0.1 M, 100 mL), and water (100 mL). For the phase transfer, 4-dimethylaminopyridine (DMAP, 0.98 g) was dissolved in water (80 mL) and mixed with the as-prepared gold nanoparticle mixture in toluene. After the completion of spontaneous phase transfer, the aqueous phase was taken, diluted with additional water (240 mL), and stored in a refrigerator until further use.

Preparation of Au-coated HDDA (HDDA-Au)

For the surface modification, a HDDA piece (~9 mg, $5 \times 5 \times 2 \text{ mm}^3$, ~150 µm line width) was first put to aqueous HCl (37%, 4 mL) in a small vial, mixed by using a vortex mix, and allowed to sit for 1-2 days. The HCl was decanted, and the acid-treated HDDA (HDDA-COOH) was repeatedly washed with a small amount of fresh DI water by using a vortex mixer and dipped in water (400 mL) for 1 day. When the HDDA-COOH was dried, the weight loss of ~1–2 mg was typically observed. For the seeding, the HDDA-COOH was transferred to the suspension of Au-DMAP nanoparticle (~4 mL) and allowed to sit for 1-2 days. Then, the excess Au-DMAP suspension was decanted, and the seeded HDDA was repeatedly washed with DI water by using a vortex mixer and dipped in water (400 mL) for 1 day. For the electroless Au plating, the seeded HDDA was immersed in hydroxylamine hydrochloride (NH₂OH·HCl, 80 mg) in water (4 mL) and then HAuCl₄·3H₂O (10 mg) was added. The plating reaction was completed in ~5 minutes. After the reaction, the suspension was decanted, and the gold-coated HDDA (HDDA-Au) was repeatedly washed with DI water by using a vortex mixer and dipped in water (400 mL) for 1 day. Then, the HDDA-Au was air-dried under ambient condition.

Preparation of Au-coated PETA (PETA-Au)

A PETA piece (~1 mg, ~5 mm diameter, ~2 mm height, ~150 µm thickness, sub-µm feature size) was first put to aqueous HCl (37%, 4 mL) in a small vial, mixed by using a vortex mix for a few seconds, and allowed to sit for 1 days. Then, the HCl was decanted, and the acid-treated PETA (PETA-COOH) was repeatedly washed with a small amount of fresh DI water using a vortex mixer and dipped in water (400 mL) for 1 day. For the seeding, the PETA-COOH was dipped into a suspension of Au-DMAP nanoparticle (~4 mL) and allowed to sit for 1-2 days. Then, the excess Au-DMAP suspension was decanted, and the seeded PETA was repeatedly washed with DI water using a vortex mixer and dipped in water (400 mL) for 1 day. For the electroless Au plating, the seeded PETA was immersed in

hydroxylamine hydrochloride (NH₂OH·HCl, 80 mg) in water (4 mL) and then HAuCl₄·3H₂O (10 mg) was added. The plating reaction was completed in ~5 minutes. After the reaction, the suspension was decanted, and the gold-coated PETA (PETA-Au) was repeatedly washed with DI water using a vortex mixer and dipped in water (400 mL) for 1 day. Then, the PETA-Au was air-dried under ambient condition.

Formation of Porous Au Foams through the Thermal Baking

The dried gold-coated samples of HDDA-Au and PETA-Au were placed in a small ceramic crucible and put into a tube furnace. After attaching all fittings to the quartz tube, air flow was adjusted and purged for a few minutes prior to the baking. For the baking of samples, the samples were heated to 400 °C at a rate of 5 °C/min, held at 400 °C for 8hr, and then cooled to RT at a rate of 10 °C/min.

Henderson-Hasselbalch Equation

The Henderson-Hasselbalch equation (eq.1) tells us the ratio of the concentrations of conjugate acid and base at the pH of a solution and acid dissociation constant, pK_{a} , for the acid, as follows:

$$HA \leftrightarrow H^{+} + A^{-}$$

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$$

$$-\log [H^{+}] = -\log K_{a} + \log \frac{[A^{-}]}{[HA]}$$

$$pH = pK_{a} + \log \frac{[A^{-}]}{[HA]}$$
(1)

The p K_a value of acrylic acids is known to be between 4 and 5. At neutral pH 7, the concentration of A⁻, [A⁻], (negative charge) must be ~100 to 1,000 times of [HA] (neutral).

Nanoindentation

Mechanical properties of gold foams were characterized with a MTS XP Nanoindenter equipped with a 496 μ m-diameter sapphire spherical indenter. Before indentation, a gold foam monolith was attached to silicon wafers with epoxy. A series of load-unload indents were carried out in laboratory air at room temperature, and load-displacement curves during the unloads were used to determine the unloading stiffness, *S*, the contact depth, *h*_c, the contact area, *A*, and the contact radius, *a*, following the Oliver-Pharr data analysis procedure. More details on indentation experiments and the analysis could be found elsewhere.^{4,5}

Fig. S8 shows a representative load-displacement (*P-h*) curve and the converted indentation stress-strain curve for the gold foam (~ 0.6 ± 0.1 g/cm³) prepared by our standard procedure. The nanoindenter is fundamentally a load-controlled instrument. We measure the resultant displacement as a known force is applied to the indenter. Interestingly, we often observed a sudden increase in the displacement without a significant load increase in the *P-h* curve. The indentation stress-strain curve clearly shows a yield point and is typical of a material that cold-draws with necking down of the cross-section in a limited area of the specimen.

Electric Conductivity of Gold Foams

Our gold foam was so conductive that it was not possible to directly measure a resistance using a multi-meter. Here, we developed a simple experimental set-up to measure a conductivity using Keithley 2400 source meter (**Fig. S9**). From the resistances difference (0.2 Ohm = 0.78-0.58) and shape of the sample ($1.7 \times 1.7 \times 0.6$ mm³, 0.68 g/cm³), the conductivity was estimated to be ~ 9.0×10^3 S/m. This confirmed that our gold foams had a very good electrical conductivity although it was still ~2 orders of magnitude smaller than a theoretical maximum of the gold.

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	Sample ^a	t	HAuCl ₄ ·3H ₂ O	$W_{\rm Au}{}^b$	W_{HDDA}^{c}	$W_{\rm Au}/W_{ m HDDA}$	Au thickness	
		(min)	(mg)	(%)	(%)		(µm)	
-	A1	1	10	6.0	94.0	0.06	0.12	
	A2	5	10	16.4	83.6	0.20	0.38	
	A3	60	10	18.1	81.9	0.22	0.42	
	B1	5	2	6.6	93.4	0.07	0.14	
	B2	5	5	9.5	90.5	0.10	0.20	
	В3	5	10	16.4	83.6	0.20	0.38	
	B4	5	20	29.3	70.7	0.41	0.80	

Table S1. Preparation of HDDA-Au samples with a different thickness of Au coatings

^{*a*} Samples were prepared by immersing the seeded HDDA in a solution of NH₂OH·HCl (80 mg) and HAuCl₄·3H₂O (*x* mg) in water (4 mL) for the duration, *t* (min). ^{*b*} W_{Au} was determined from a TGA curve to be a residual weight at 800 °C. ^{*c*} $W_{HDDA} = 100 - W_{Au}$

	size (cm)			weight	volume	density
	X	у	Z	(mg)	(cm ³)	(mg/cm ³)
before	0.45	0.45	0.17	7.0	0.035	202
after	0.16	0.15	0.07	1.0	0.0017	590

Table S2. Bulk densities of HDDA-Au (before) and PµSL-Au (after) samples



Fig. S1 SEM image of the HDDA-Au having a part of gold coatings peeled off. The gold has a bright color while the dark area indicates uncoated polymer surface.



Fig. S2 SEM images of HDDA-Au.



Fig. S3 Use of tin/palladium (Sn^{2+}/Pd^{2+}) as a seeding catalyst for electroless gold plating. Prior to a tin sensitization, a HDDA substrate was treated with HCl, and the same hydroxylamine procedure was used for electroless Au plating.



Fig. S4 Control over the thickness of Au coatings on HDDA substrates. Different HDDA-Au samples were prepared by changing (a) the duration of a plating reaction and (b) the amount of $HAuCl_4 \cdot 3H_2O$ salts added to a plating solution. Thickness of Au coatings were related to the residual weight at 800 °C in a TGA curve.





(b) Fig. S5. (continued)



(c)



(d)



















Fig. S6. SEM images of PµSL-Au.



Fig. S7 SEM images of PETA-Au. (a, b) a fractured piece at a low maginification, (c, d) the inner/outer surface and (e, f) the inside of the sample.





Fig. S8 (a, b) SEM images for a fractured piece of the TPL-Au sample at low/high magnifications. The TPL-Au sample was prepared by baking PETA-Au at 400 °C, 8h in air.





Fig. S9 Mechanical properties of gold foams. (a) Load-displacement curve obtained with a spherical indenter. (b) Indentation stress-strain curve for the gold foam.





(b)

Fig. S10 Electrical conductivity of gold foams. (a) Experimental set-up developed to measure a conductivity of gold foam sample. (b) Enlarged view of a sample in the set-up.

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