Supporting Information

Fabrication of Paper-templated Structures of Noble Metals

Dionysios C. Christodouleas[1], Felice C. Simeone[1], Alok Tayi[1], Sonia Targ[1], James C. Weaver[2], María Teresa Fernández-Abedul[3], George M. Whitesides[1,2*]

[1]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, United States

[2]Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, MA, United States

[3] Departamento de Química Física y Analítica, Universidad de Oviedo, Asturias, Spain

[*] Corresponding author E-mail: gwhitesides@gmwgroup.harvard.edu

Experimental Section

Materials. As precursors of metals and metal oxides, we used $AuCl_3$, $AgNO_3$, $PtCl_4$, $RhCl_3$, $Pd(NO_3)_2$, $IrCl_3$, $RuCl_3$, $AlCl_3$, $TiCl_3$ purchased from Sigma Aldrich. As templates, we used: i) Whatman® Chromatography paper Grade A (20 cm x 20 cm) purchased from Sigma Aldrich, ii) cotton-lace, cotton-fabric and polyurethane sponge purchased from local stores. Stainless steel meshes (Type 316, 16×16, wire diameter 0.018 inch, and Type 304, 400×400, wire diameter 0.001 inch) were purchased from McMaster-Carr and cut in pieces (5 x 5 cm).

For electrochemical experiments, we used a gold rod (99.99% trace metals basis) with 2 mm diameter, a platinum rod (99.95% trace metals basis) with a 1 mm diameter, a platinum mesh (99.9% trace metals basis), a gold foil (99.9% trace metals basis) and a general purpose, Ag/AgCl, reference electrode purchased from Sigma Aldrich.

Fabrication of Paper-templated Structures. We used a solid-ink printer (Xerox ColorQube 8880) to pattern chromatography paper, by printing wax on paper, and to define hydrophilic regions of various shapes [1]. We then heated the patterned paper at 130 °C for 2 minutes to allow wax to penetrate inside the paper and form hydrophobic barriers [1].

We used a pipette to add a solution of metal precursor to the hydrophilic region of the paper template (see the amount added for each paper-templated structure in Table S-3). We let the structures dry at 70 °C for around 30 minutes.

Using a pair of scissors, we cut out the patterned area of the paper template (i.e., hydrophobic barriers). We placed the paper loaded with the metal precursors between two layers of stainless steel mesh and placed it in a furnace pre-heated at 550 °C in air; for the fabrication of the Pd, the Ag-Pd, and the TiO_2 structures, the furnace was pre-heated at 850 °C. We left the structures in the furnace for two minutes and then let them cool down to room temperature. We carefully removed the structures from the stainless steel mesh to obtain free-standing, almost flat, paper-templated structures.

Fabrication of Fabric-templated and Sponge-templated Silver Structures. To produce fabric-templated structures, we used pieces of fabric (i.e., lace, cotton cloth) composed of cotton 100% as templates, and a 3 M solution of Ag^+ as silver precursor. We dipped the templates in the solution of the metal precursor for 5 minutes and then let them dry at 70 °C for around 30 minutes. Once dried, we burned the templates loaded with the precursor in a furnace pre-heated at 550 °C.

To produce the sponge-templated structures, we used pieces of polyurethane sponges as templates. We dipped the templates in a 3 M solution of Ag^+, then let them dry at 70 °C for around 30 minutes. Once dried, we burned the templates loaded with the precursor in a furnace pre-heated at 550 °C.

Characterization: Scanning electron microscopy (SEM) images and Energy Dispersive Spectroscopy (EDS) spectra were obtained using a Vega 3 microscope (Tescan). X-ray photoelectron spectroscopy (XPS) spectra were obtained using a K-Alpha XPS system (Thermo Scientific). Multipoint BET surface area analysis with krypton was performed using an Autosorb iQ analyzer (Quantachrome) at Quantachrome's Materials Characterization Laboratory (Florida, USA). Cyclic voltammograms were obtained using an electrochemical analyzer (model Autolab PGSTAT302N, Metrohm). Electrical measurements were performed using a source meter (model 2400, Keithly).

Estimation of the Electrochemically Active Surface Area of Paper-templated Structures: We estimated the electrochemically active area of gold and platinum paper-templated structures using the capacitive currents recorded in cyclic voltammetry experiments [2]. We measured: i) the values of the capacitance of the electrochemical double-layer of paper-templated electrodes, and ii) the values of the capacitance of the electrochemical double-layer of gold and platinum rod electrodes with known surface area and composition (purity 99.99 %). In all experiments, we used a platinum mesh as counter electrode and a commercial Ag/AgCl electrode as reference electrode. All

measurements were performed with an electrochemical analyzer (model Autolab PGSTAT302N, Metrohm).

For all electrodes (i.e., paper-templated, and rods), we used Eq. S-1 to estimate the values of their capacitance C_τ from the capacitive currents measured in cyclic voltammograms recorded in 5 mM $Fe(CN)_6^{4-}$ + 0.5 M KCl (See Figure S-7).

$$C_\tau = \frac{dQ}{dE} = \frac{i_c \cdot dt}{dE} = \frac{i_c}{v} \quad \text{(S-1)}$$

Here, i_c (A) is the average capacitive current measured in a narrow range of applied potentials in the cyclic voltammogram recorded at a scan rate v (V/s); the slope of i_c *vs.* v gives C_τ.

We used the values of C_τ to estimate the electrochemically active surface area A of the paper-templated structure by using Eq. S-2:

$$A = \frac{C_{PT}}{C_R} = \frac{i_c}{v \cdot C_R} \quad \text{(S-2)}$$

Where C_{PT} was the capacitance of the paper templated structures, and C_R the capacitance of the Au and Pt electrodes with known surface area.

Specifically, we recorded cyclic voltammograms in solutions of $Fe(CN)_6^{4-}$ (5 mM $Fe(CN)_6^{4-}$ in 0.5 M KCl) at seven scan rates (10, 25, 50, 75, 100, 125, and 150 mV/s) using four different electrodes: i) a gold paper-templated electrode (with geometric surface area equal to 75 mm^2 and weight equal to 10.1 mg); ii) a platinum paper-templated electrode (with geometric surface area equal to 79 mm^2 and weight equal to 6.9 mg); iii) a gold rod electrode (with geometric surface area equal to 197.7 mm^2); and iv) a platinum rod electrode (with geometric surface area equal to 114.0 mm^2). For these electrodes, we measured the average of the capacitive currents during both the positive (i_a) and negative potential sweep (i_c) in a range of applied potentials where no redox reactions occur (i.e., -0.09 V to -0.13 V for gold electrodes, and -0.18 V to -0.22 V for platinum

electrodes). We then plotted the capacitive currents *vs.* the scan rate, and, using Eq. S-1, we estimated: i) the value of C_{PT} for the paper-templated gold electrode, ii) the value of C_{PT} for the paper-templated platinum electrode, iii) the value of C_R for the gold rod electrode, iv) the value of C_R for the platinum rod electrode. The rod electrodes were flat and polished, therefore we assumed that their geometric area coincided with their electrochemically active surface area. We used the values of C_R and the values of C_{PT} for the paper-templated electrodes to estimate the electrochemically active surface area of the paper-templated electrodes through Eq. S-2. We calculated an electroactive area to be 0.025 m^2/g for paper-templated gold, and 0.105 m^2/g for paper-templated platinum Pt.

Fabrication of Conductive Silver Lines Using a Laser Cutter. We soaked a sheet of chromatography paper in a 1 M solution of Ag^+ for 10 minutes, let it dry, and then placed it inside a laser cutter (Versa Laser). We then used the software of the laser cutter to adjust the power of the laser beam (50 W, 10.6 μm) to 7% and the speed of the cutting process to 60% and upload the template of the predefined pattern. These settings partially burn the paper in a predefined pattern, resulting in the creation of well-defined metallic silver lines. After the silver pattern formed on the paper, we soaked the entire sheet of paper in an aqueous solution under agitation for one hour to dissolve most of the unreacted silver ions from the paper. Figure 3A and 3B show two SEM images of two paper sheets with embedded lines and EDS maps (Figure 3C and 3D) confirmed that the lines were composed primarily of silver.

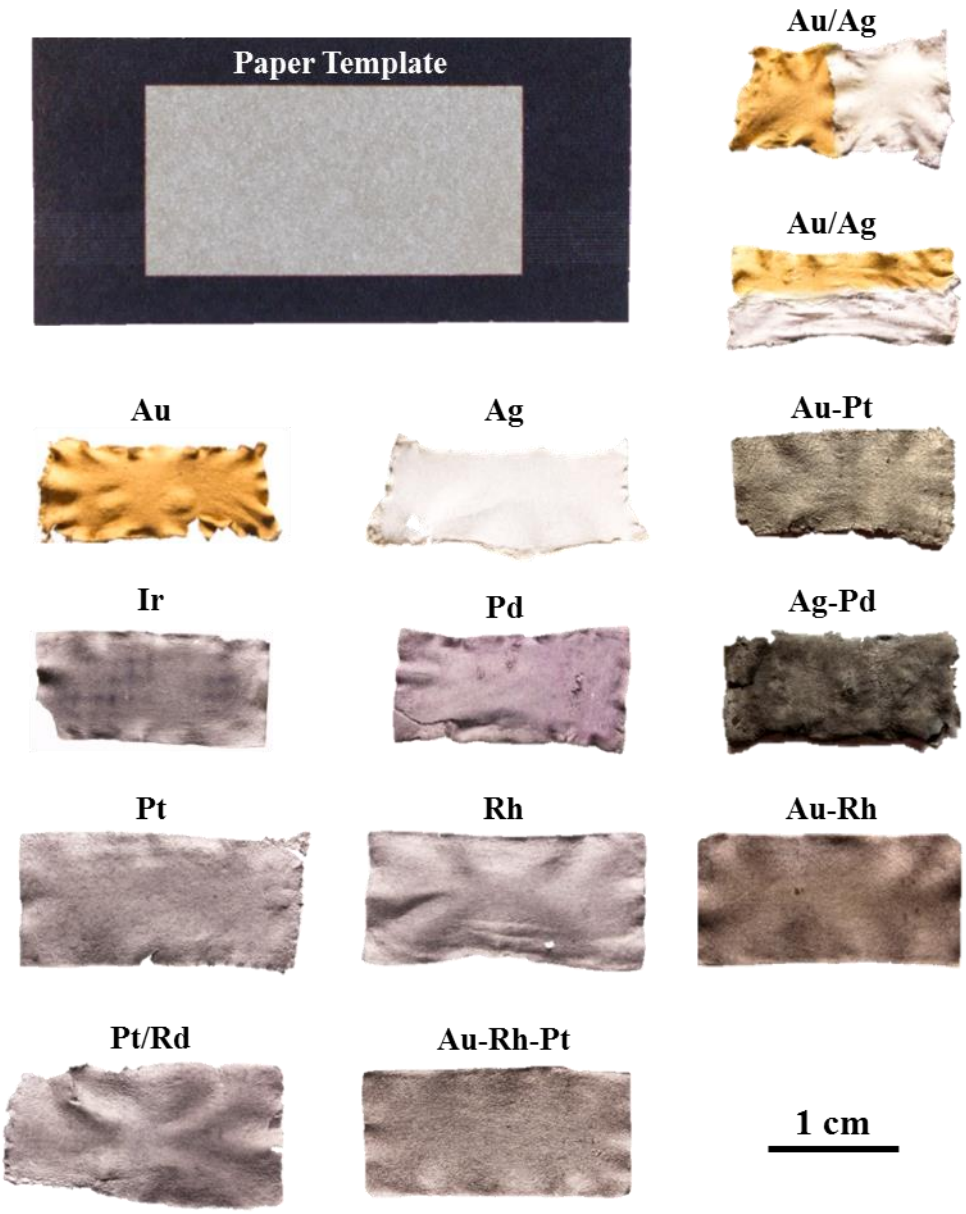

Figure S-1. Photos of a paper template and of a series of paper-templated structures of different composition. The label above each structure describes the composition of the structure. The same scale bar applies to all structures, including the paper template.

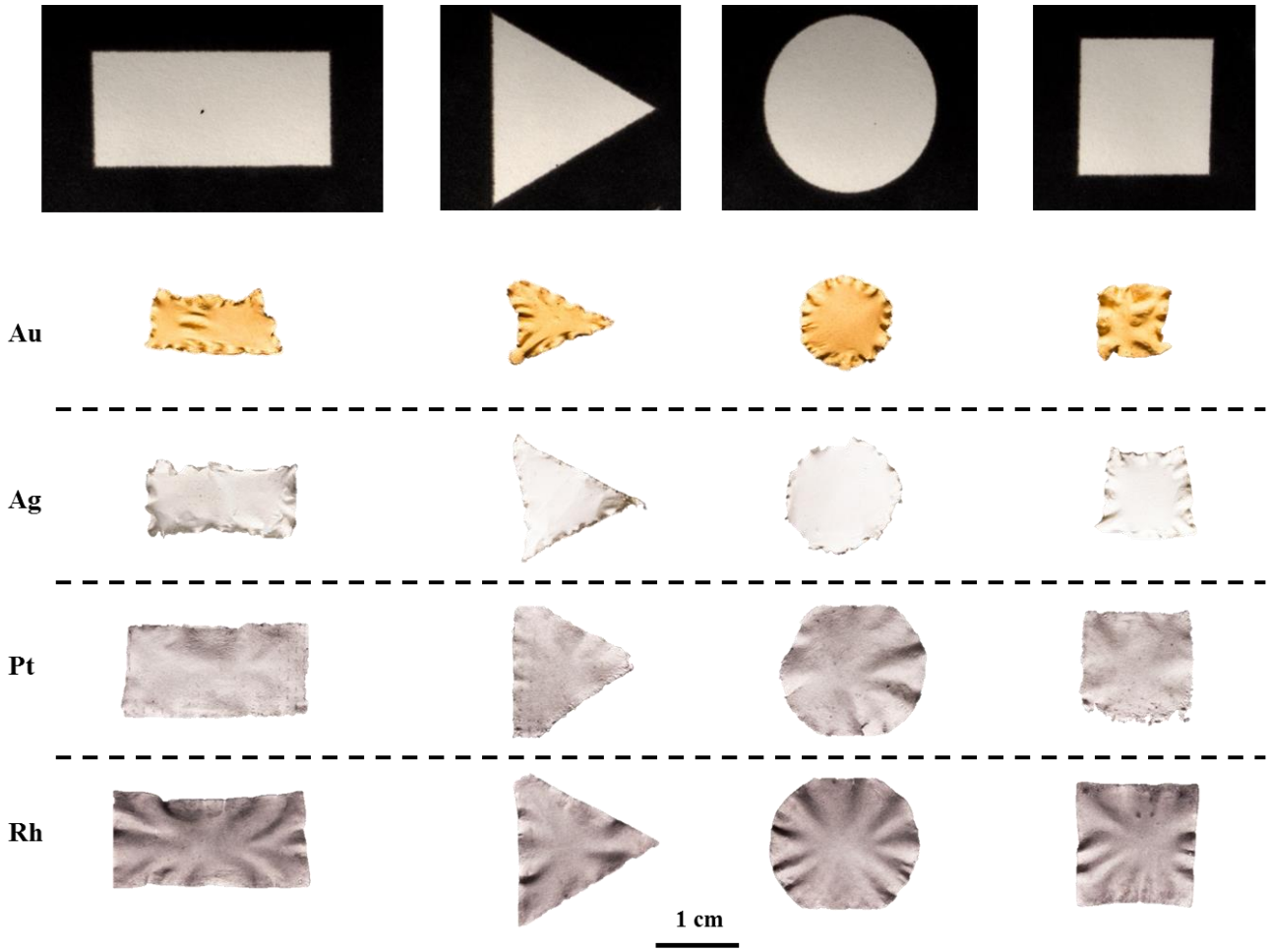

Figure S-2. Photos of the paper template (top line) and the resulting paper-templated structures of gold, silver, platinum and rhodium, (from top to down) with rectangular, triangular, circular and square shape. The same scale bar applies to all structures, including the paper templates.

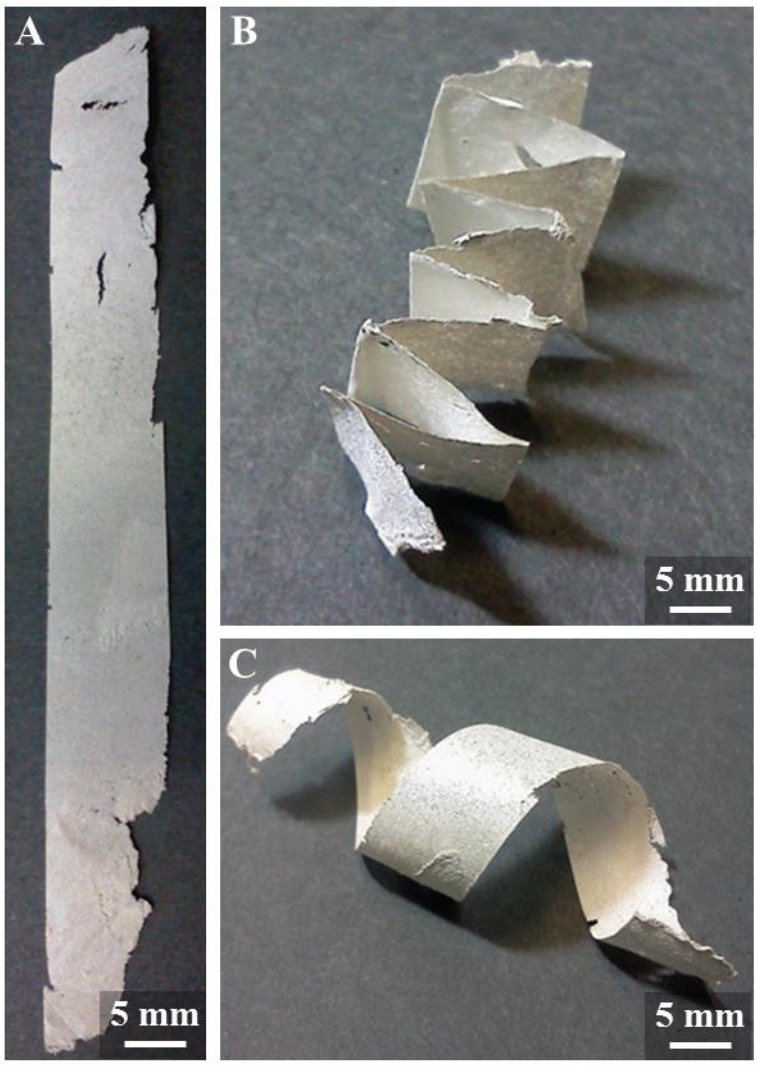

Figure S-3: Photos of a paper-templated silver structure (left side) when is folded (upper right) and scrolled (lower right)

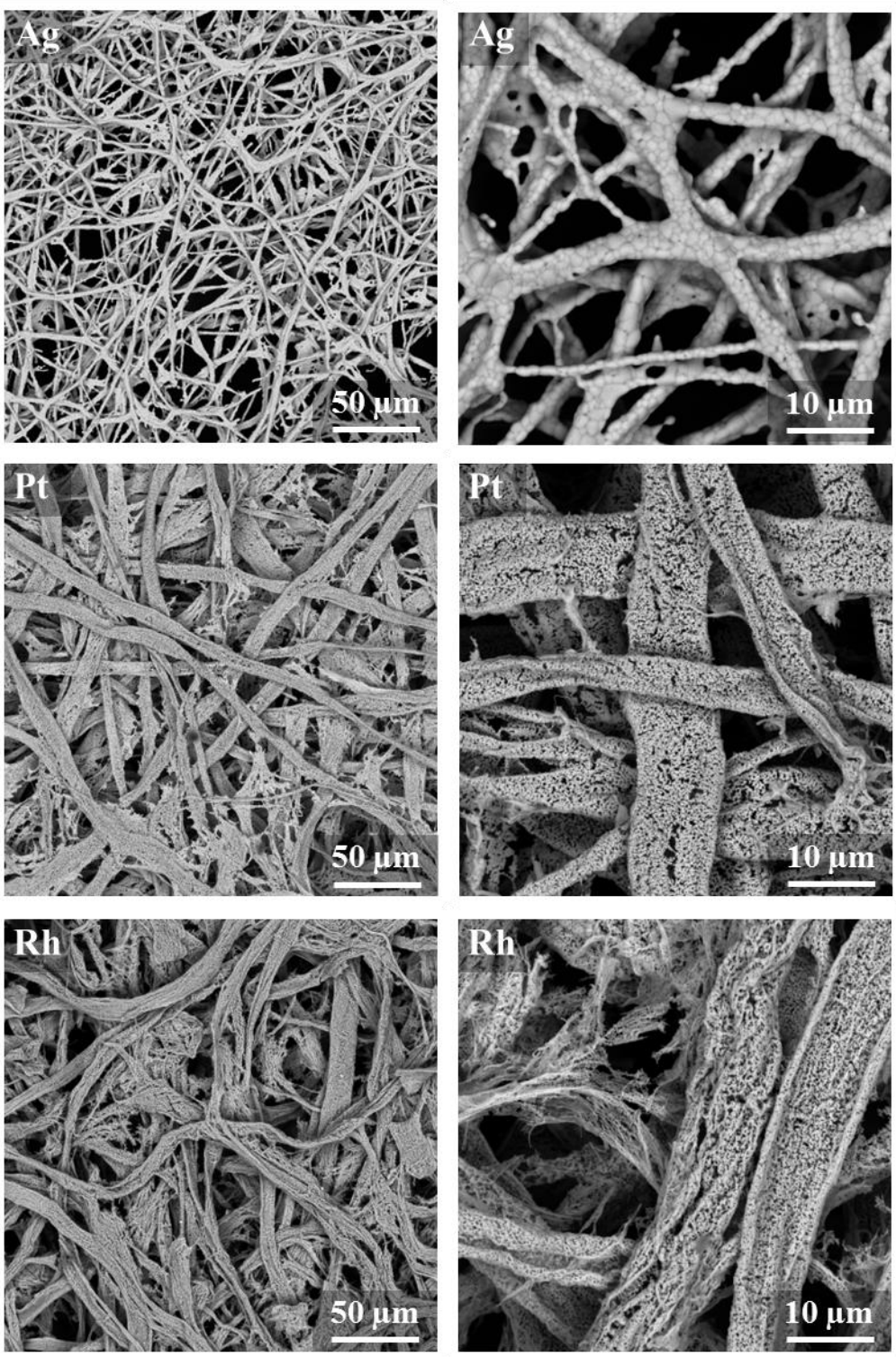

Figure S-4. SEM images, at two different magnifications, of a paper-templated structure of silver (Ag), a paper-templated structure of platinum (Pt), and a paper-templated structure of rhodium (Rh).

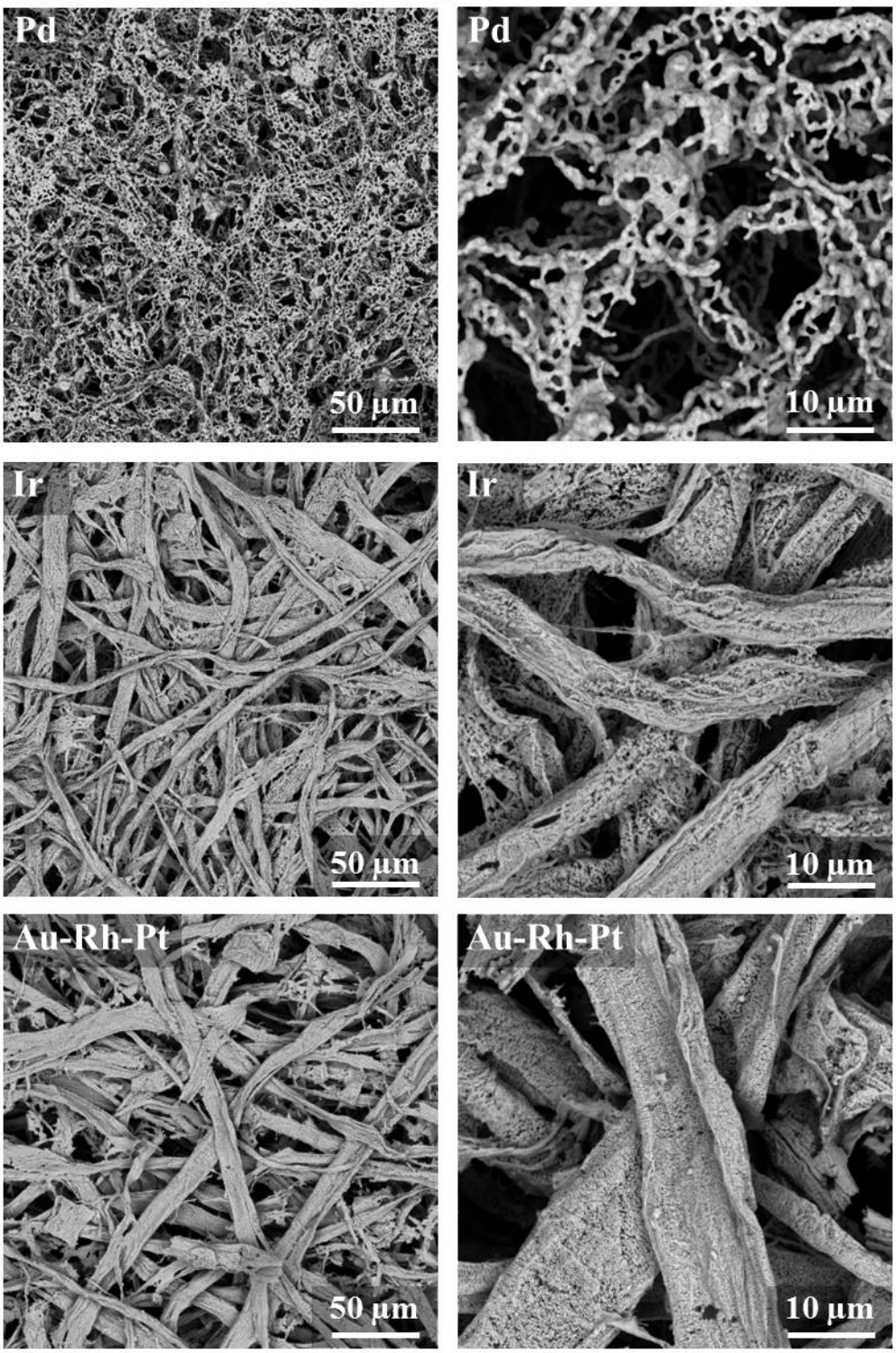

Figure S-5. SEM images, at two different magnifications, of a paper-templated palladium structure (Pd), a paper-templated iridium structure (Ir), and a paper-templated structure composed of gold, rhodium and platinum (Au-Rh-Pt).

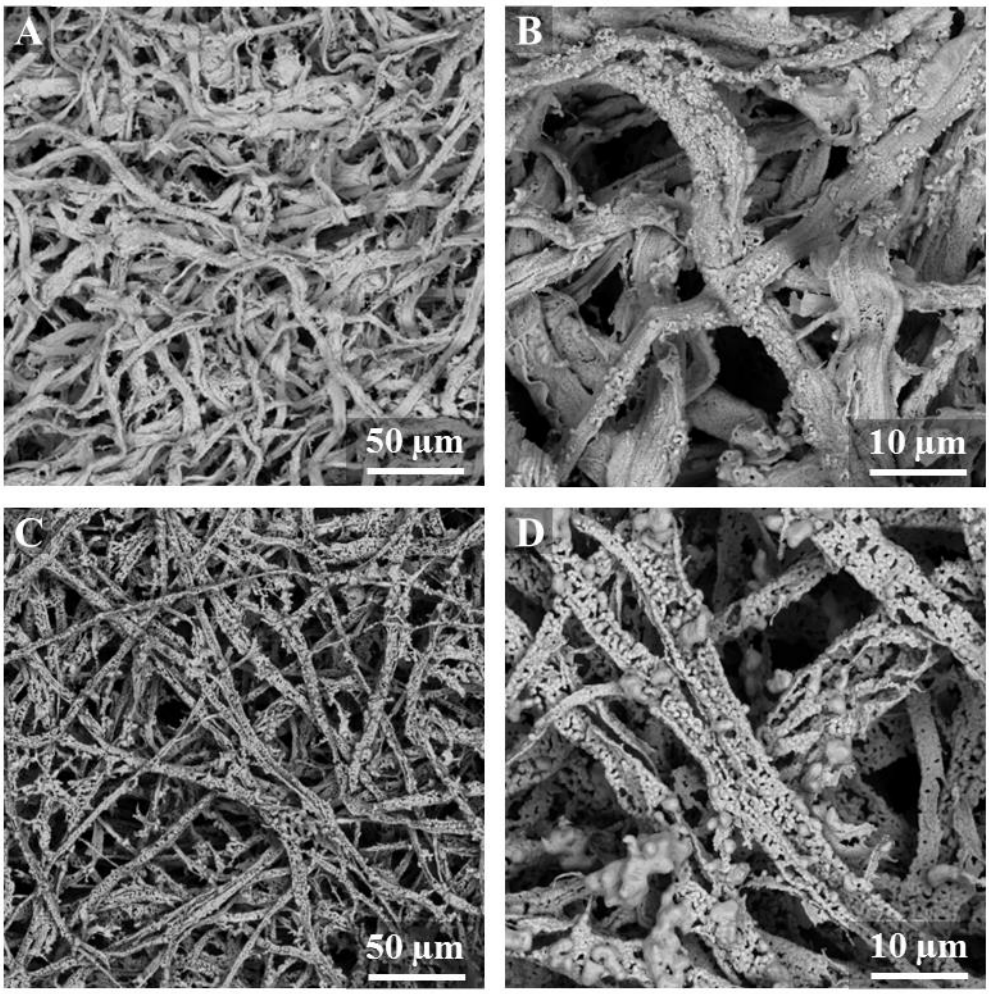

Figure S-6. SEM images of a gold paper-templated structure prepared using 300 µL of 0.5 M $AuCl_3$ (A-B) and a gold paper-templated structure prepared using 100 µL of 0.5 M $AuCl_3$ (C-D).

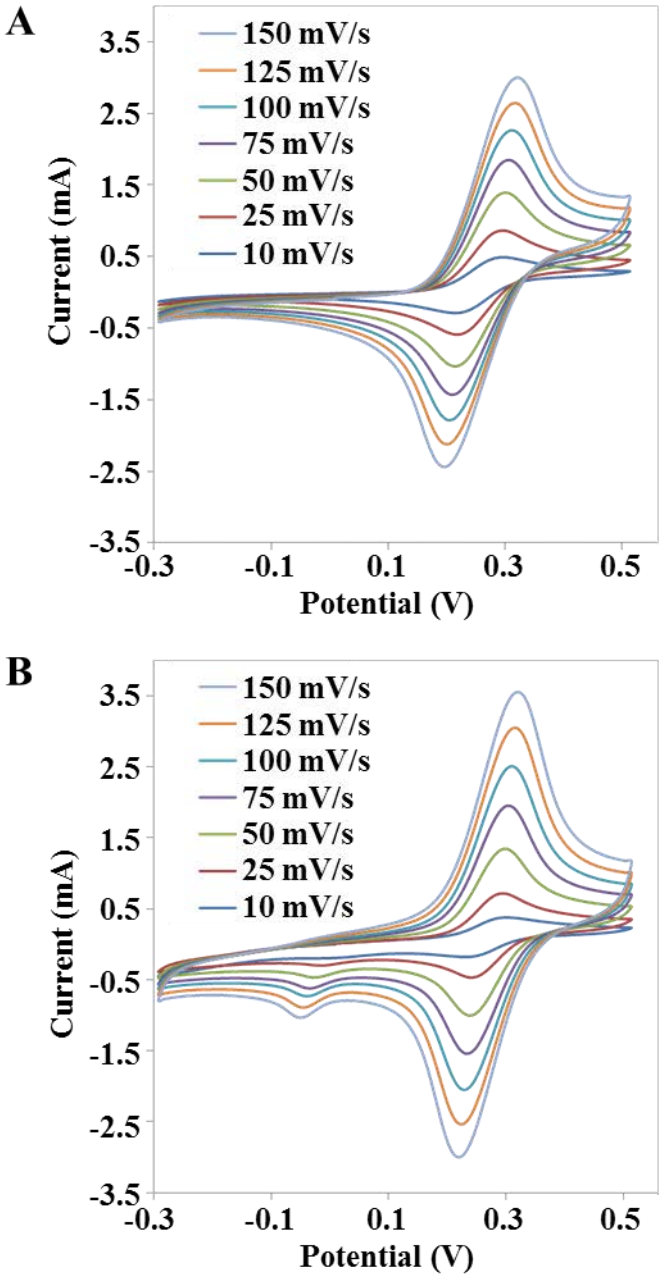

Figure S-7. Cyclic voltammograms in solutions of $Fe(CN)_6^{4-}$ (5 mM $Fe(CN)_6^{4-}$ in 0.5 M KCl) at different scan rates for A) a 75 mm^2 paper-templated gold electrode, and B) a 79 mm^2 paper-templated platinum electrode. We used a platinum mesh as counter electrode, and a commercial Ag/AgCl electrode as reference electrode.

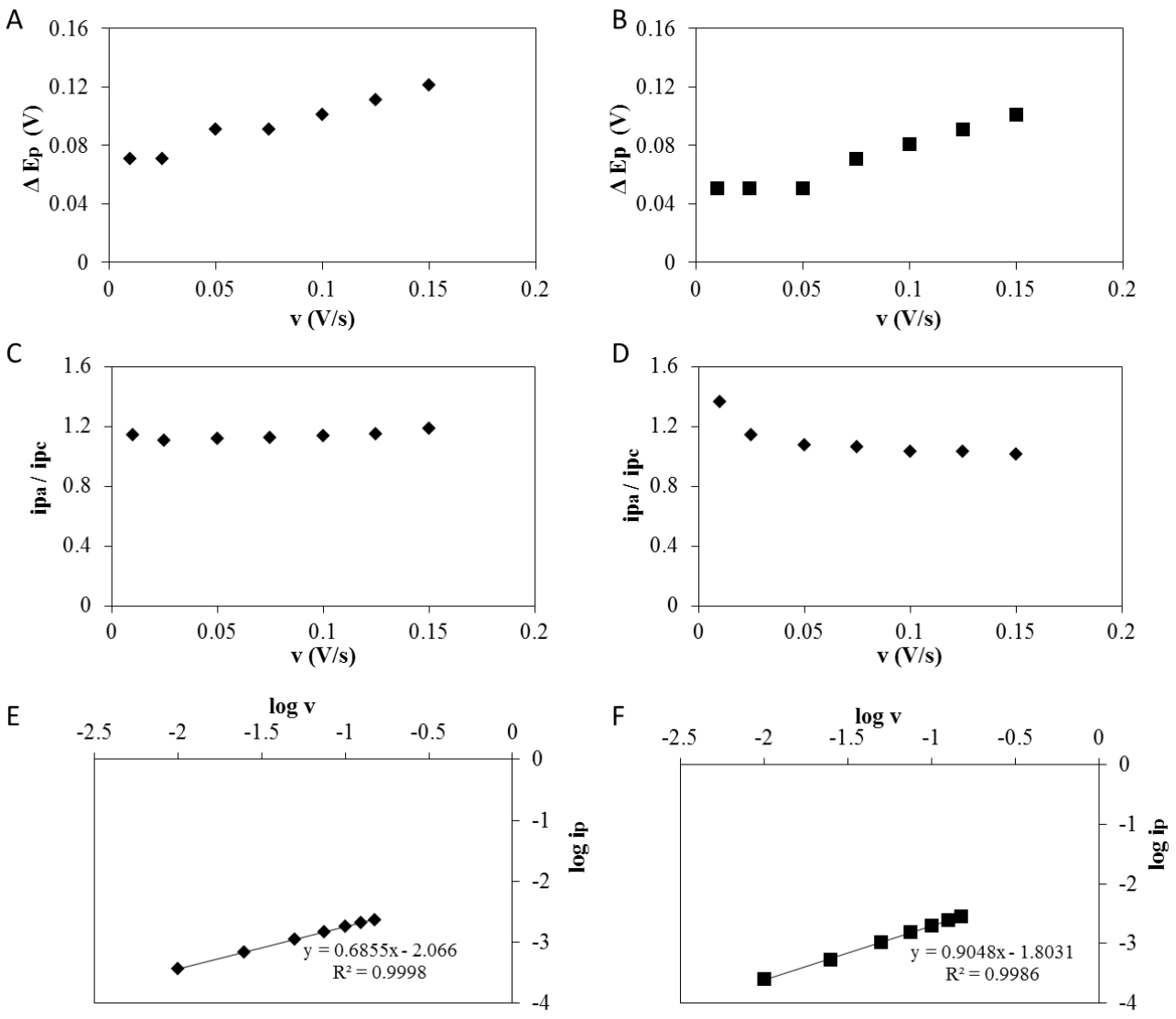

Figure S-8: Separation of peak potentials $\Delta E_p = (E_{pa} - E_{pc})$ *vs.* the scan rate for the paper-templated gold (A), and paper-templated platinum electrode (B) in 5 mM $Fe(CN)_6^{4-}$, 0.5 M KCl. Values of the ratio of anodic to cathodic peak current (i_{pa}/i_{pc}) *vs.* the scan rate for the paper-templated gold (C), and paper-templated platinum electrode (D) in 5 mM $Fe(CN)_6^{4-}$, 0.5 M KCl. Logarithm of the intensity of the anodic peak current *vs.* the logarithm of the scan rate for paper-templated gold (E), and paper-templated platinum (F) in 5 mM $Fe(CN)_6^{4-}$, 0.5 M KCl

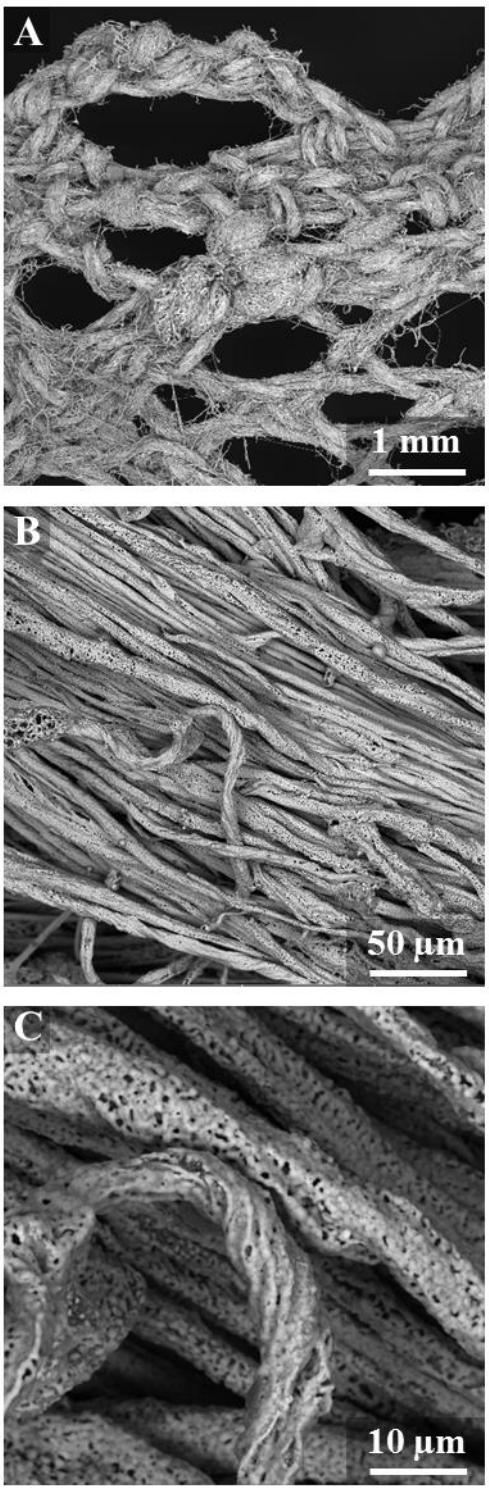

Figure S-9: SEM images at different magnifications of the lace-templated silver structure.

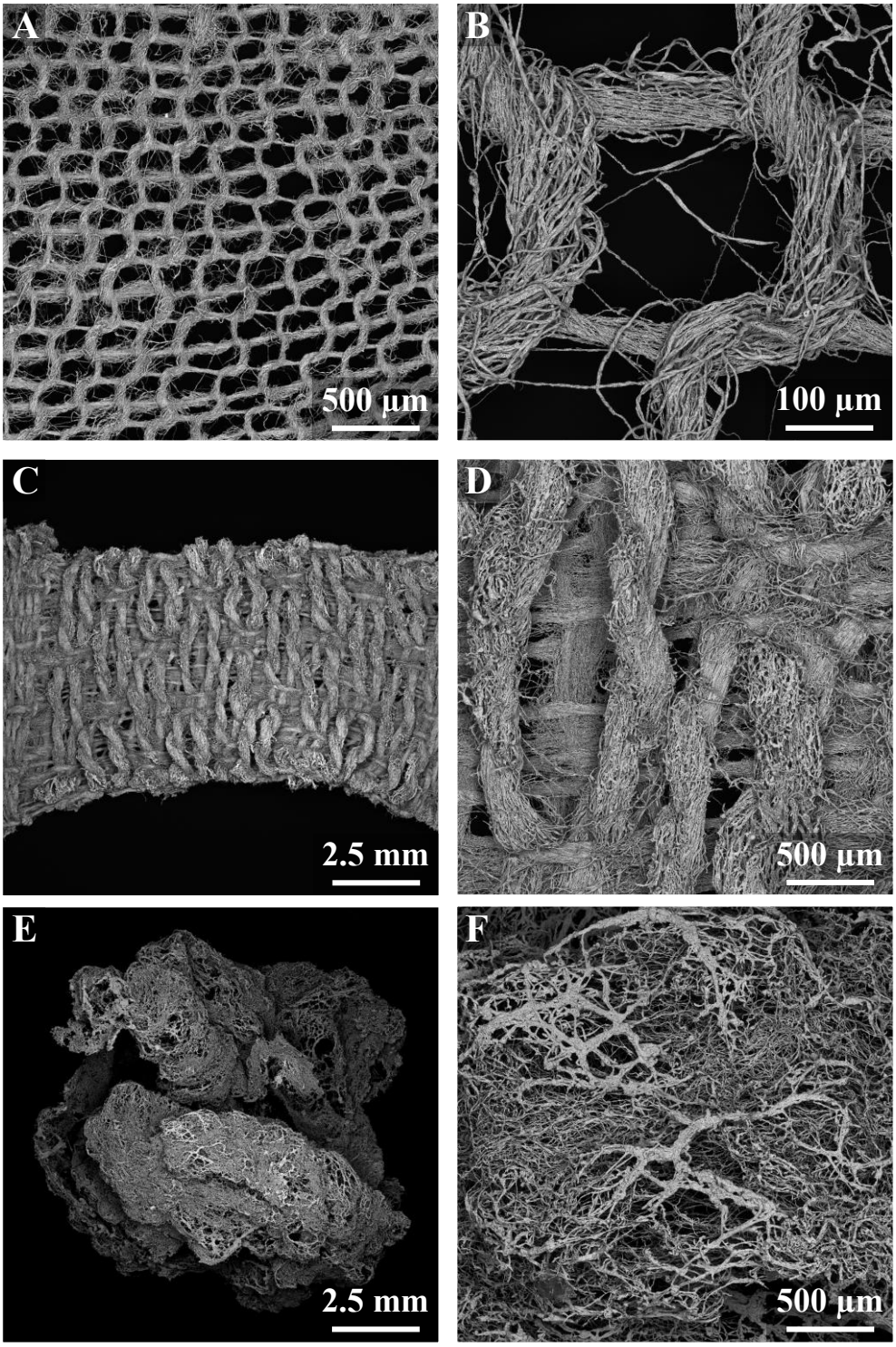

Figure S-10: SEM images at different magnifications of two fabric-templated silver structures (A-D). SEM images of a sponge-templated silver structure at different magnifications (E-F).

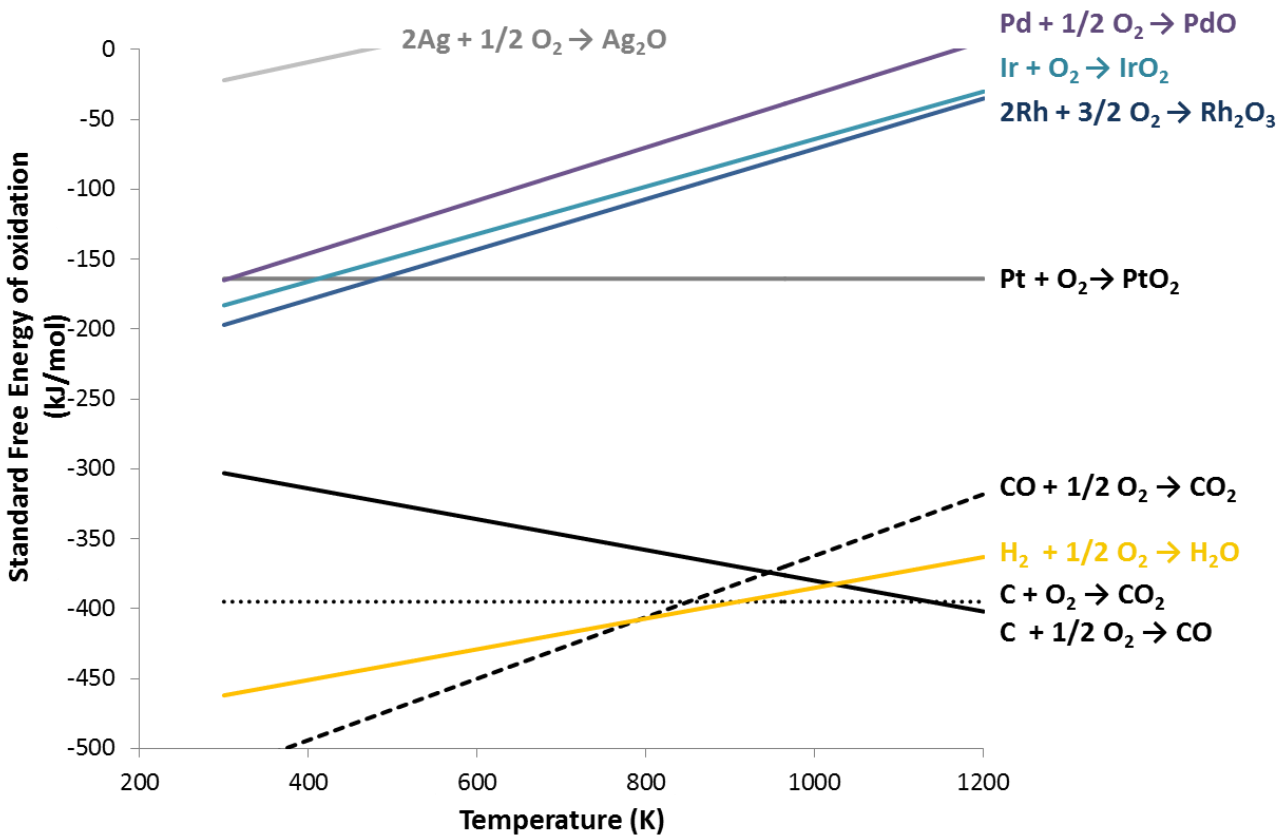

Figure S-11: Ellingham diagrams of the reactions of carbon, hydrogen and noble metals with oxygen (as O_2). To plot the curves, we used the equations that is publicly available at http://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/interactive.php

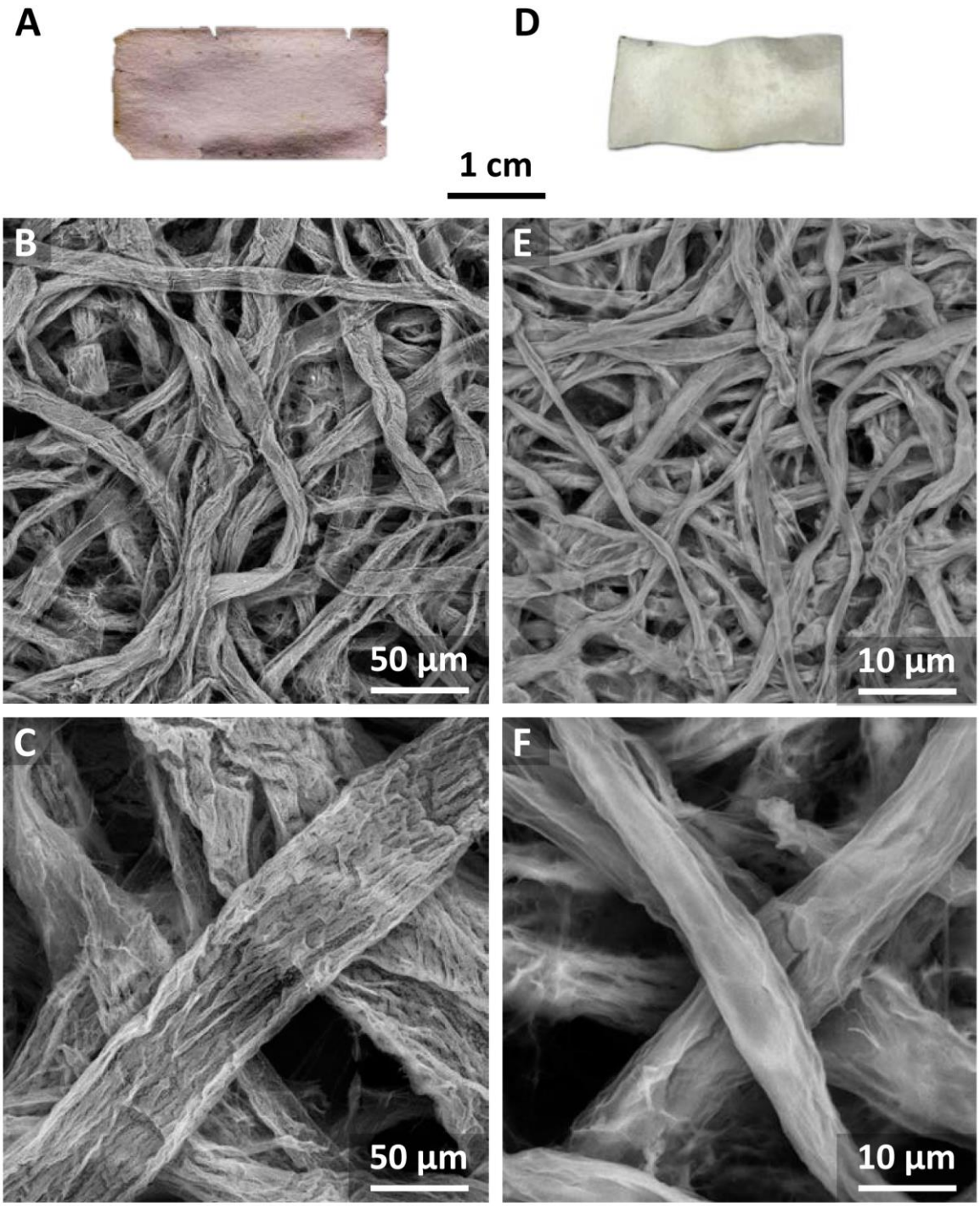

Figure S-12: Photo of a paper-templated structure composed of TiO_2 (A) and two SEM images of the structure at two different magnifications (B-C). Photo of a paper-templated structure composed of Al_2O_3 (D) and two SEM images of the structure at two different magnifications (E-F).

Table S-1: Thickness of the paper-templated structures.

Paper-templated structure	**Thickness (mean ± SD, N=5)[c]**
Au	135 ± 4 µm
Ag	150 ± 20 µm
Pt	90 ± 10 µm
Rh	110 ± 20 µm
Pd	60 ± 4 µm
Ir	50 ± 4 µm
Au/Ag [a]	70 ± 4 µm
Au/Ag [b]	90 ± 20 µm
Pt/Rh	110 ± 20 µm
Au-Pt	110 ± 20 µm
Ag-Pd	150 ± 40 µm
Au-Rd	110 ± 30 µm
Au-Pt-Rh	120 ± 20 µm

[a] Side-by-side configuration . [b] Top-down configuration

Table S-2. Composition of the surface of the paper-templated structures (composed of one noble metal element) in carbon and oxygen before and after removing 10 nm of surface material.

Paper-templated structure	Oxygen atomic %		Carbon atomic %	
	prior	after	prior	after
Au	28	4.4	45	15
Ag	23	2.9	31	7.0
Pt	22	1.1	36	7.0
Rh	40	8.4	30	5.8
Pd	5.5	0.2	43	4.6
Ir	43	18	19	0.1

Table S-3: Solution of metal precursor used for the fabrication of each paper-templated structure.

Paper-templated structure	Precursor	
	Concentration	**Volume**
Au	0.5 M Au^{3+}	300 mL
Ag	0.5 M Ag^{+}	300 mL
Pt	0.5 M Pt^{4+}	200 mL
Rh	0.5 M Rh^{3+}	150 mL
Pd	0.5 M Pd^{2+}	300 mL
Ir	0.5 M Ir^{3+}	300 mL
Au/Ag [a]	0.5 M Au^{3+} / 1.5 M Ag^{+}	75 mL / 75 mL [c]
Au/Ag [b]	0.5 M Au^{3+} / 1.5 M Ag^{+}	75 mL / 75 mL[d]
Pt/Rh	0.5 M Pt^{4+} / 0.5 M Rh^{3+}	50 mL / 50 mL[c]
Au-Pt	0.25 M Au^{3+}, 0.25 M Pt^{4+}	300 mL
Ag-Pd	0.25 M Ag^{+}, 0.25 M Pd^{2+}	300 mL
Au-Rd	0.25 M Au^{3+}, 0.25 M Rh^{3+}	300 mL
Au-Pt-Rh	0.16 M Au^{3+}, 0.16 M Pt^{4+}, 0.16 M Rh^{3+}	300 mL
TiO_2	12 % w/w Ti^{4+}	50 mL
Al_2O_3	2 M Al^{3+}	200 mL

[a] Side-by-side configuration . [b] Top-down configuration

[c] using a multi-channel pipette we added at the same time the solution of one precursor on one of the two short sides of the rectangular paper template, and the solution of the other precursor on the other short side of the rectangular paper template

[d] using a multi-channel pipette we added at the same time the solution of one precursor on the middle of one of the two long sides of the rectangular paper template, and the solution of the other precursor on the middle of the other long side of the rectangular paper template

References

[1] M. M. Hamedi, A Ainla, F. Güder, D. C. Christodouleas, M.T. Fernández-Abedul, G. M. Whitesides. *Adv. Mater.* DOI: 10.1002/adma.201505823.

[2] S. Trasatti, O.A. Petrii, *Pure & Appl. Chem.,* **1991,** *63(5)*, 711