

Honeycomb nanogold networks with highly active sites

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Electronic Supplementary Information

Experimental details

Chemicals

Electrodepositions were performed using KAuBr_4 and H_2SO_4 (Ajax Finechem), which were used as received and made up with deionized water (resistivity of $18.2 \text{ M}\Omega \text{ cm}$) purified by use of a Milli-Q reagent deioniser (Millipore). SERS activity was measured after immersing the samples in an aqueous 1 mM solution of Rhodamine B (Merck) for one hour before the unbound Rhodamine B was washed off with water.

Preparation of E-beam Evaporated Substrate

The metal layers were deposited by a BalzersTM electron beam evaporator. The layer composed of 1000 \AA of Au and 10 \AA of Ti. The films were deposited sequentially by electron evaporation process onto the bare AT-cut quartz substrates. The purpose of the Ti layer is to assist with the adhesion of the Au layer to the substrate surface.

Materials Characterisation

SEM measurements were performed on a FEI Nova SEM instrument with an AMETEK energy dispersive X-ray (EDX) system (Nova 200) operated at an accelerating voltage of 30 kV . Prior to SEM imaging, samples were thoroughly rinsed with Milli-Q water and dried under a flow of nitrogen. X-ray diffraction data were obtained with a Bruker AX 8: Discover with General Area Detector Diffraction System (GADDS). SERS measurements were carried out with a PerkinElmer RamanStation 400 at an excitation wavelength of 785 nm .

Electrochemical Measurements

Cyclic voltammetric experiments were conducted at $(20 \pm 2)^\circ\text{C}$ with a CH Instruments (CHI 760C) electrochemical analyser in an electrochemical cell that allowed reproducible positioning of the working, reference, and auxiliary electrodes and a nitrogen inlet tube. An e-beam evaporated Au film was used as the working electrode which was washed in acetone and methanol followed by

drying in a stream of nitrogen gas prior to use. The reference electrode was Ag/AgCl (aqueous 3 M KCl). For electrodeposition experiments an inert graphite rod (3 mm diameter, Johnson Matthey Ultra ‘F’ purity grade) was used as the counter electrode. Electrochemical depositions were commenced after degassing the electrolyte solutions with nitrogen for at least 10 min prior to any measurement.

Electrochemically Active Surface Area Measurements

The electrochemically active surface area of the materials was determined by cyclic voltammetry in accordance with an established protocol¹. In short, a monolayer oxide was formed on the gold surfaces by cycling the applied potential in a solution of 1 M H₂SO₄. This oxide layer was subsequently reduced in the negative sweep, and the total charge required to reduce the oxide layer was used to calculate the electrochemically active surface area, using a value of 400 $\mu\text{C cm}^{-2}$.

Raman Scattering Measurements

In order to investigate the SERS activity of the gold nanostructures, samples were immersed in a 1 mM solution of rhodamine B for 1 hr followed by washing with Milli-Q water, in a similar procedure to that found in the literature for SERS investigations on solid surfaces^{2,3}. After allowing to air dry, the samples were then analysed using a Perkin Elmer RamanStation 400 (785 nm laser) with an exposure time of 4 s and 30 acquisitions, with background correction enabled.

SERS Enhancement Factor Calculations

The enhancement in the Raman scattering from the honeycomb gold was calculated in accordance with work done previously on 4-mercaptobenzoic acid⁴. As the characteristic rhodamine B peaks could not be seen in the case of the unmodified gold substrate following immersion in rhodamine B (Fig. 3d, black line), a Raman spectrum of rhodamine B powder was taken in order to provide a control for the SERS calculations (Fig. 3d, brown line). SERS enhancement factors were then estimated using the analytical enhancement factor calculation outlined below

$$AEF = \frac{I_{SERS}}{I_{powder}} \times \frac{N_{powder}}{N_{SERS}}$$

I_{SERS} and I_{powder} were calculated by the method described by Zhang et al, based on the peak area at 1506 cm^{-1} . N_{powder} was calculated using the density of rhodamine B (1.31 g cm^{-3}), its molecular weight ($479.02 \text{ g mol}^{-1}$) and the spot size of the instrument ($100 \text{ }\mu\text{m}$). For N_{SERS} the area occupied by each rhodamine molecule across the surface of the samples was taken from work done by Kudelski⁵, who estimated that one molecule of Rhodamine 6G occupied 17 nm^2 of the geometric surface area. It should be noted that this calculation assumes the formation of a complete monolayer of the dye across the surface, and is therefore likely to underestimate the actual enhancement factor of the nanostructured surfaces.

Enhancement factors found were 1.04×10^4 , 1.94×10^3 and 1.32×10^3 for samples prepared at 2 A cm^{-2} from a solution containing 0.1 M KAuBr_4 and $1.5 \text{ M H}_2\text{SO}_4$ for 5, 10 and 30 s respectively at a current density of 2 A cm^{-2} in 0.1 M KAuBr_4 in $1.5 \text{ M H}_2\text{SO}_4$.

Supplementary Figures

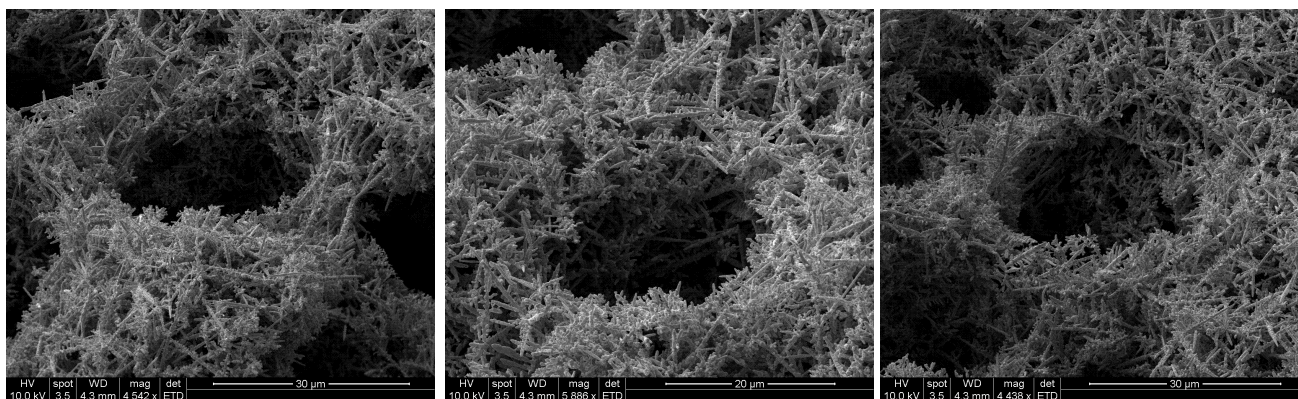


Figure S1: SEM image of a honeycomb gold network taken at a 45° angle. Sample was prepared by depositing 2 A cm^{-2} for 30 s from a 0.1 M KAuBr_4 and $1.5 \text{ M H}_2\text{SO}_4$ solution.

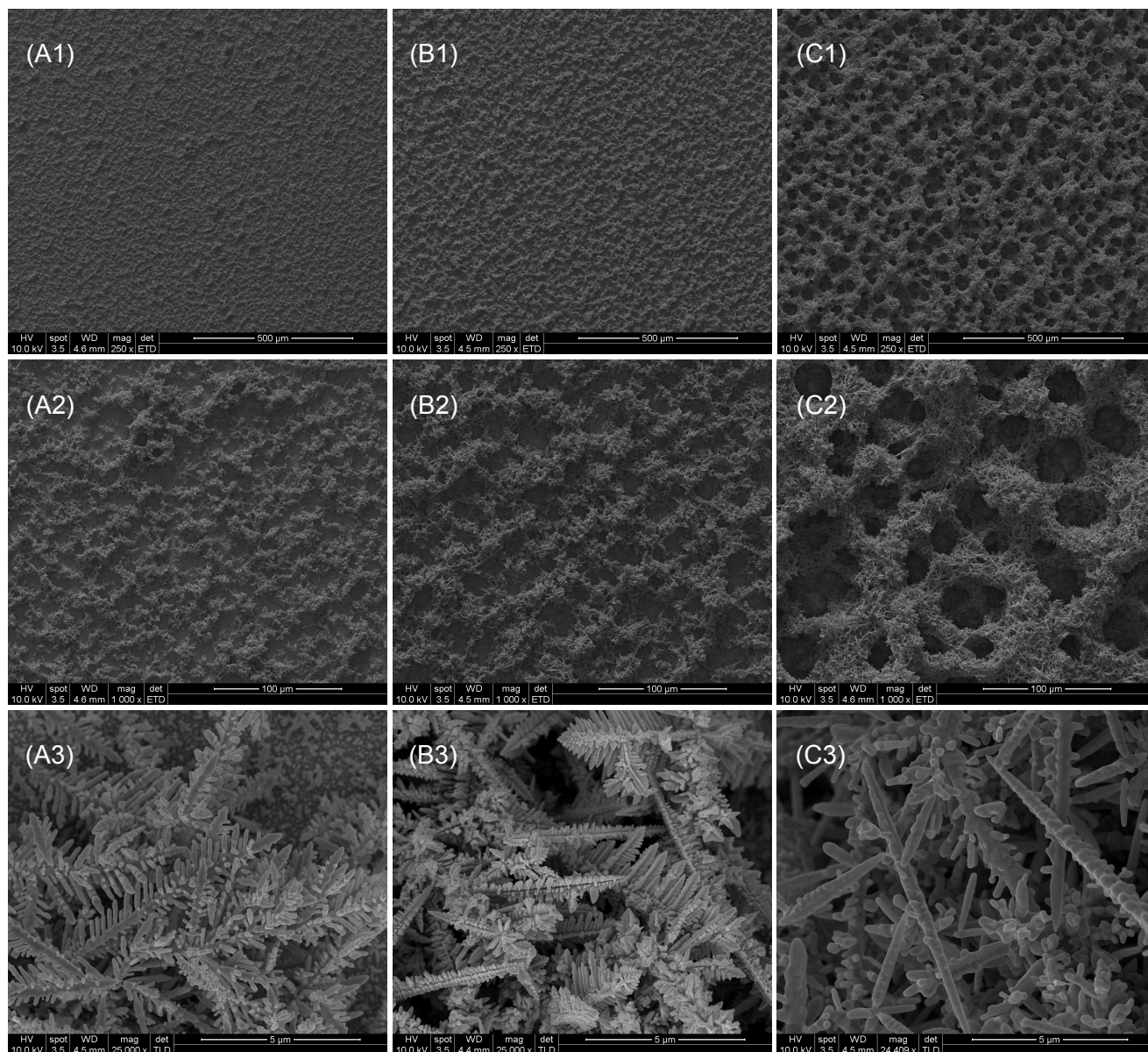


Figure S2: SEM images of honeycomb gold networks deposited for 5 s (A1-A3), 10 s (B1-B3) and 30 s (C1-C3) at 2 A cm^{-2} from a solution of 0.1 M KAuBr_4 and $1.5 \text{ M H}_2\text{SO}_4$.

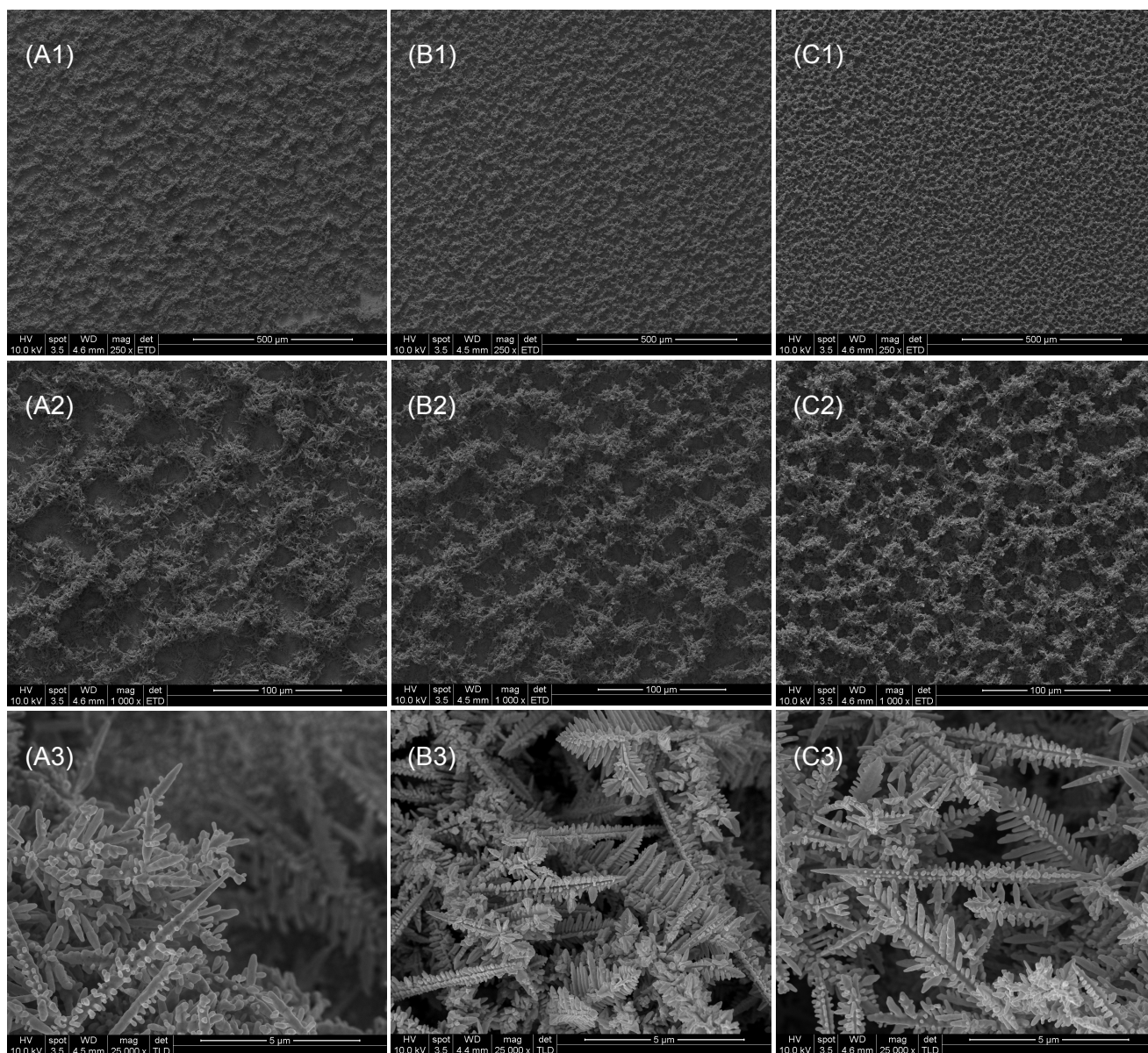


Figure S3: SEM images of honeycomb gold networks deposited for 10 s with current densities of 1 A cm⁻² (A1-A3), 2 A cm⁻² (B1-B3) and 3 A cm⁻² (C1-C3) from a solution of 0.1 M KAuBr₄ in 1.5 M H₂SO₄.

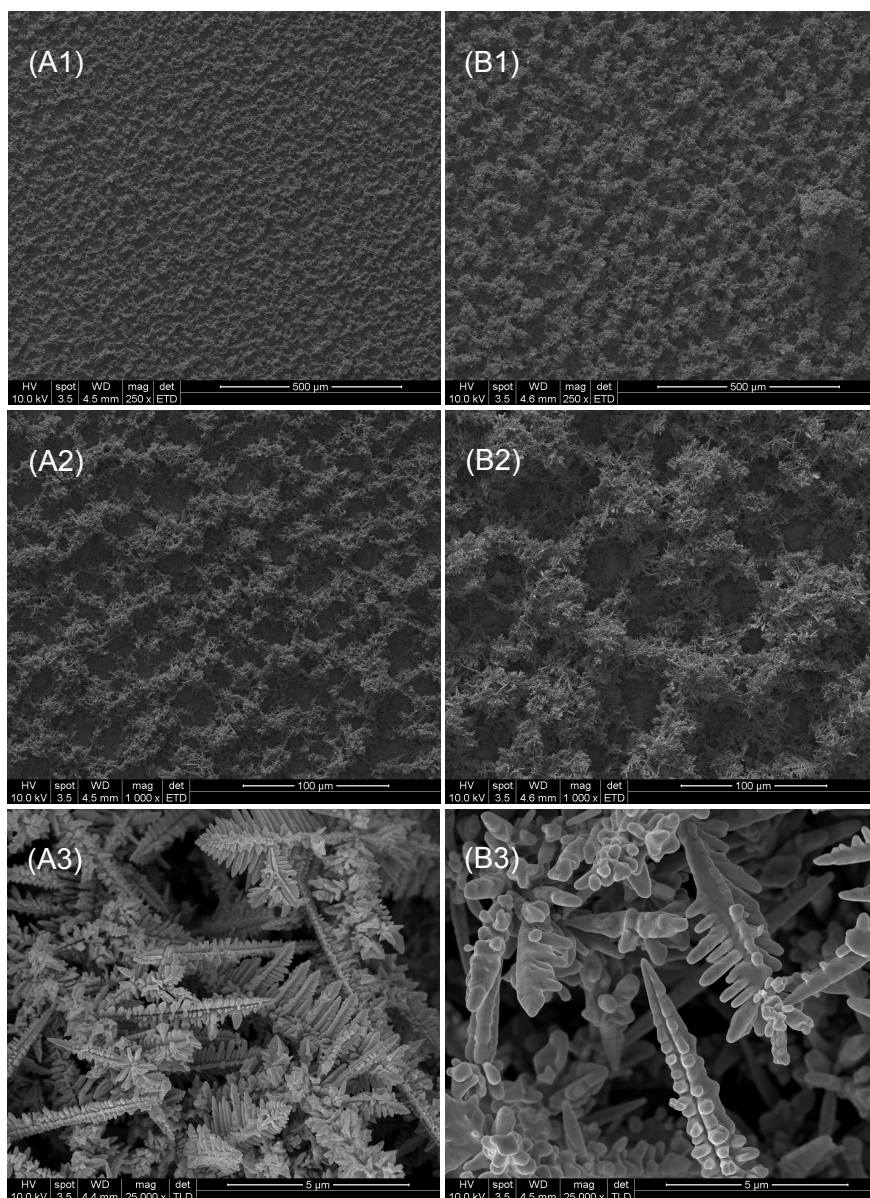


Figure S4: SEM images of honeycomb gold networks deposited for 10 s at 2 A cm^{-2} from solutions containing 1.5 M H_2SO_4 and 0.1 M (A1-A3) or 0.4 M KAuBr_4 (B1-B3).

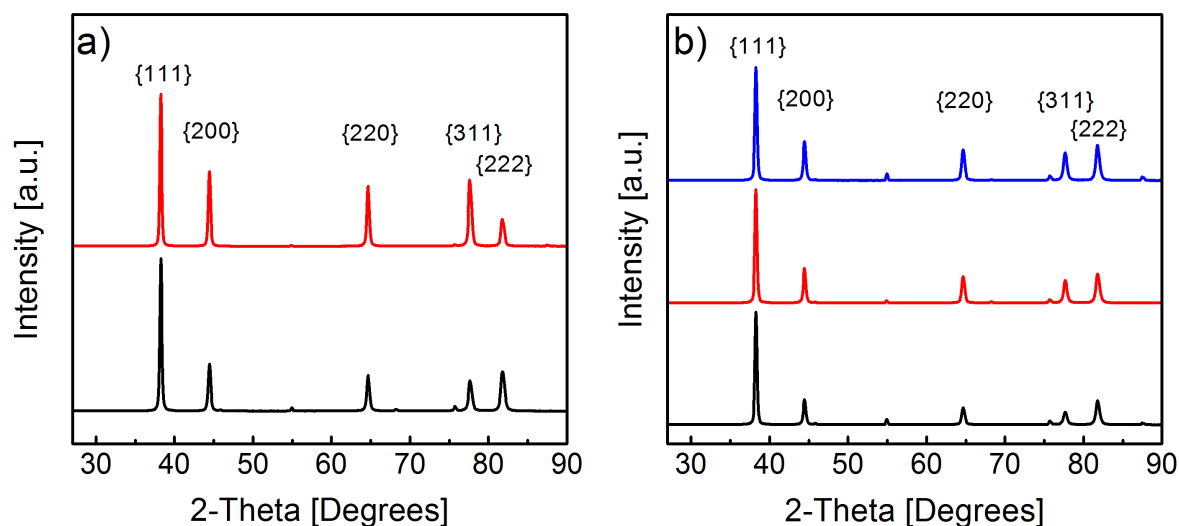


Figure S5: (a) XRD spectra for honeycomb gold deposited from 0.1 M KAuBr₄ (black) and 0.4 M KAuBr₄ (red) for 10 s at 2 A cm⁻². (b) XRD spectra for honeycomb gold deposited from 0.1 M KAuBr₄ for 10 s at 1 A cm⁻² (black), 2 A cm⁻² (red) and 3 A cm⁻² (blue).

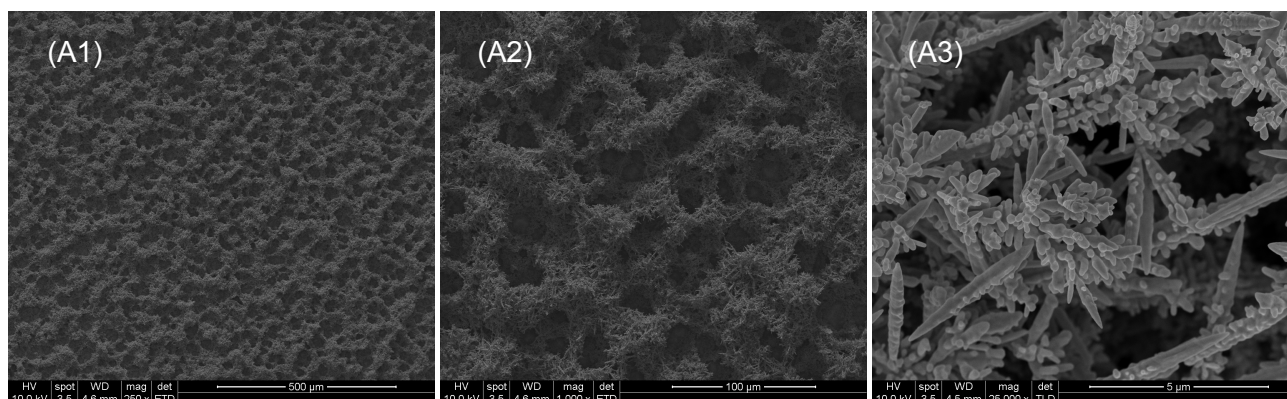


Figure S6: SEM images of honeycomb gold networks deposited for 30 s at 2 A cm⁻² from solutions containing 1.5 M H₂SO₄ and 0.1 M HAuCl₄.

References

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