

Gold nanospikes formed through a simple electrochemical route with high electrocatalytic and surface enhanced Raman scattering activity

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Electronic Supplementary Information

Experimental details

Chemicals

Aqueous 0.5 M H₂SO₄ (Merck) and 1 M NaOH (AnalaR, BDH) solutions were made up with deionized water (resistivity of 18.2 MΩ cm) purified by use of a Milli-Q reagent deioniser (Millipore). H₂HAuCl₄·3H₂O was prepared by dissolving gold (HGR Matthey, 99.999%) in aqua regia and evaporated to dryness. The solid was diluted with Milli-Q water until the desired concentration level which was confirmed using a Perkin Elmer (Model 3110) Atomic Absorption Spectrometer. Pb(CH₃COO)₂·3H₂O (Sigma Aldrich), glucose (Ajax Finechemicals) and Rhodamine B (Merck) were used as received.

Preparation of e-beam evaporated substrate

The metal layers were deposited by a BalzersTM electron beam evaporator. The layer composed of 1000 Å of Au and 10 Å 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.

Electrochemical measurements

Voltammetric experiments were conducted at (20 ± 2)°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. When a 1.6 mm diameter gold electrode (BAS) was used as the working electrode (as in Fig. S4) it was polished with an aqueous 0.3 μm alumina slurry on a polishing cloth (Microcloth, Buchler), sonicated in deionized water for 5 min, and dried with a flow of nitrogen gas prior to use. The reference electrode was Ag/AgCl (aqueous 3 M KCl). For electrodeposition experiments an inert graphite rod (6 mm diameter, Johnson Matthey Ultra “F” purity grade) was used as the counter electrode. For cyclic voltammetric studies (as shown in Figure 2 of the manuscript) the counter electrode

was a Pt wire. All electrochemical experiments were commenced after degassing the electrolyte solutions with nitrogen for at least 10 min prior to any measurement.

All electrocatalytic data have been normalised with respect to the electrochemically active surface area of the electrode determined by calculating the charge required for reducing the monolayer oxide (Figure 2b) as described by Rand and Woods¹.

¹ D. A. J. Rand and R. Woods, *J. Electroanal. Chem.* 1971, **31**, 29.

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. XPS measurements of Au nanospikes were carried out on a VG MicroTech ESCA 310F instrument at a pressure better than 1×10^{-9} Torr. The general scan and C 1s, Au 4f, and Pb 4f core level spectra for the respective samples were recorded with un-monochromatized Mg Ka radiation (photon energy = 1253.6 eV) at a pass energy of 20 eV and electron takeoff angle of 90°. The core level binding energies (BEs) were aligned with the adventitious carbon binding energy of 285 eV.

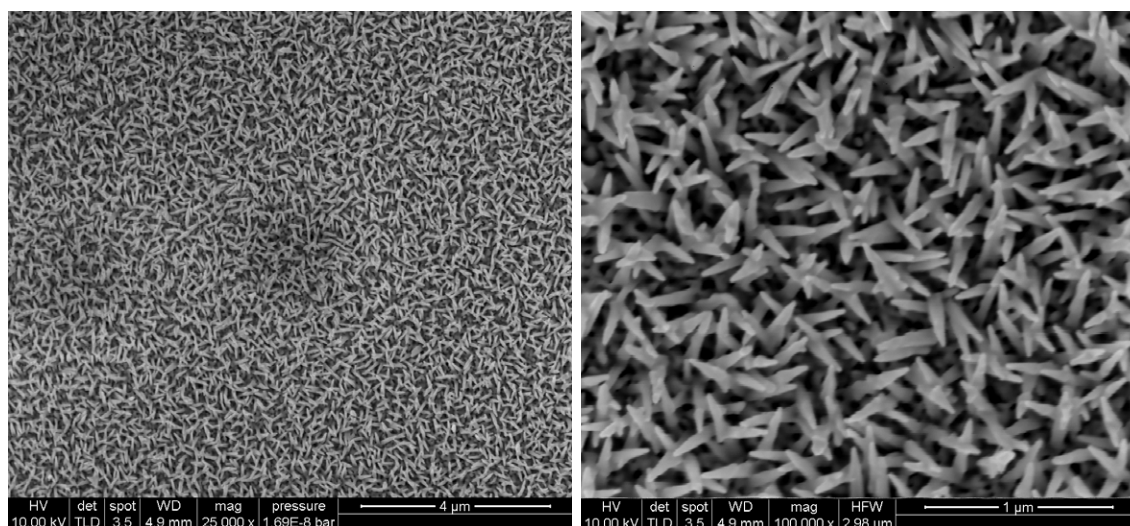


Figure S1: SEM images of gold electrodeposited at 0.05 V for 600 s from 6.9 mM HAuCl₄ containing 0.500 mM Pb(CH₃COO)₂.

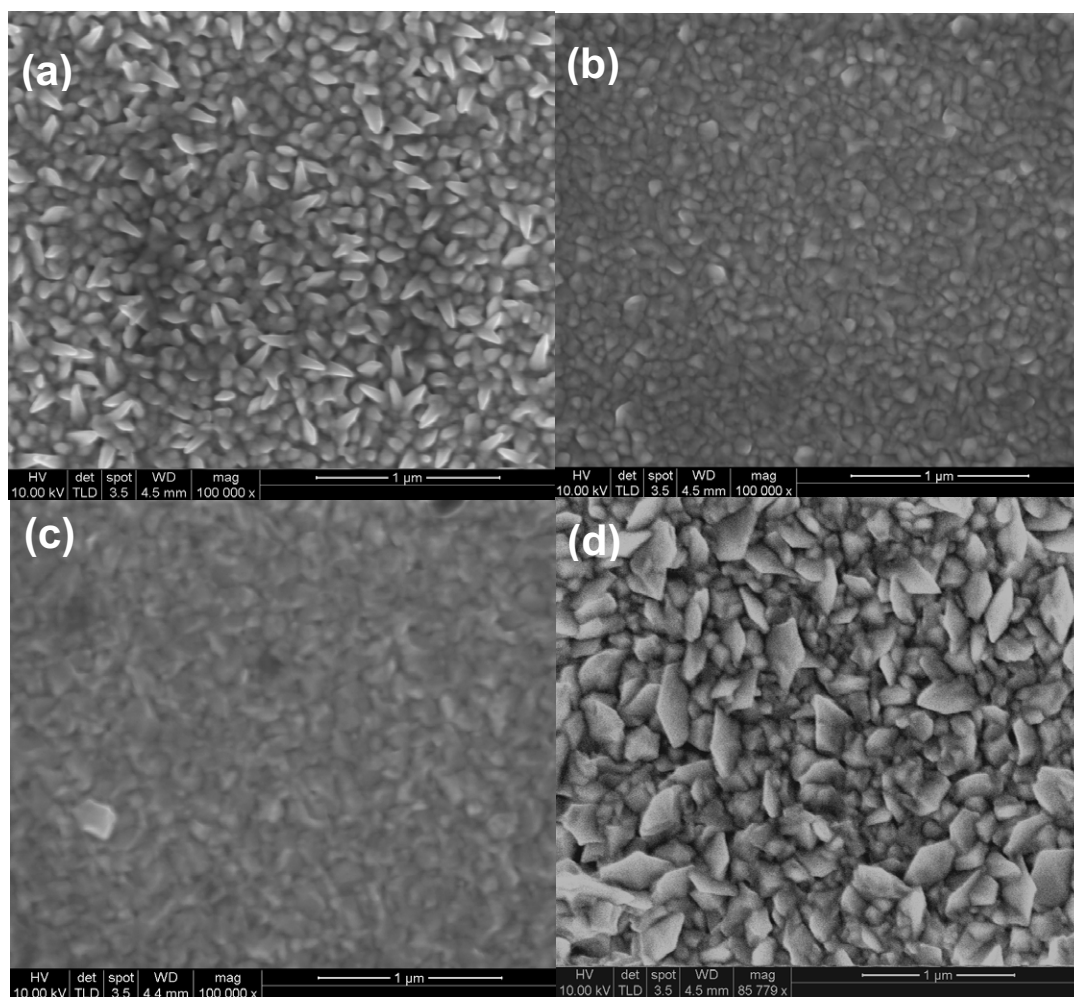


Figure S2: SEM images of gold electrodeposited from a solution containing 6.9 mM HAuCl₄ and 0.5 mM Pb(CH₃COO)₂ at (a) 0.15, (b) 0.25 and (c) 0.45 V for 600s and (d) 0.25 V for 40 min.

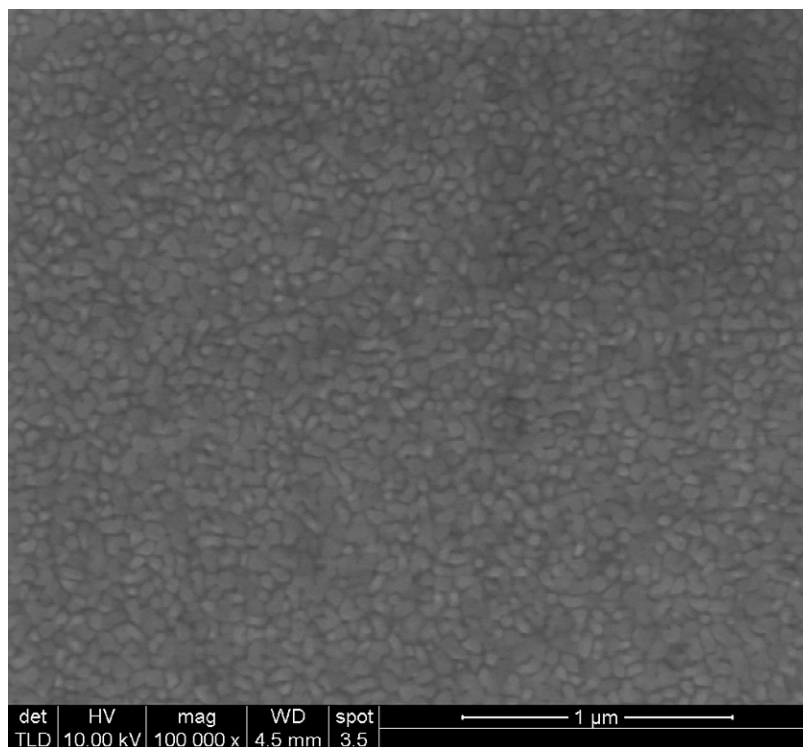


Figure S3: SEM image of e-beam evaporated gold film (200nm) on a quartz substrate.

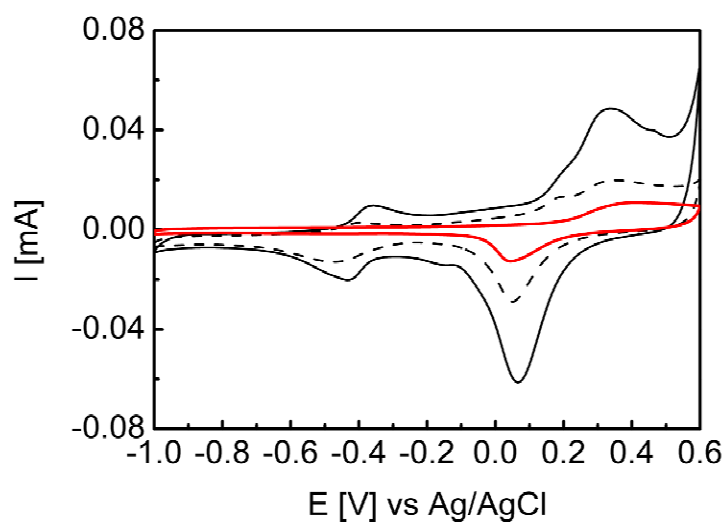


Figure S4: CVs of unmodified Au (dashed), Au nanospikes (solid) and Au electrode (red) recorded at 50 mV s⁻¹ in 1 M NaOH.