Electronic Supplementary Material (ESI) for RSC Advances
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Supplementary information for

Surface enhanced Raman scattering of dendritic Ag nanostructures grown with anodic aluminium oxide

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Experimental Procedure

Simultaneous fabrication of porous aluminium oxide template and nanostructured dendritic Ag

First, the alumina ceramic substrate was rendered electrically conductive with a special mixed bonded silver paste (ESL 9912-A, Electro-Science Laboratories, Inc., USA), where Ag was screen-printed using Ag/polymer paste and then fired at 900°C for 30 min to remove the organic part of paste which was originally developed for chip resistors. In the next step, aluminium was electrodeposited galvanostatically from an ionic liquid (1-ethyl 3-methylimidazolium chloride-aluminium chloride; BASF, Germany) at a current density of 20 $mAcm^{-2}$ for 30 minutes resulting in a thickness of the obtained Al layer of around 10 µm. The obtained layer consisted of pure Al as verified by EDX analysis. The final step was the anodization of the surface using tartaric-sulphuric acid. Therefore a constant voltage of 14 V was applied to the substrate after increasing the voltage for 5 minutes with a linear ramp. During the whole process the temperature was kept constant.

Electron Microscopy

A scanning electron microscopy (SEM) equipped with a focused ion beam (FIB) was used to analyze the surface morphology of the sample during different production steps. An EDX detector within the SEM was used for localized measurements of the atomic composition. For a detailed analysis of the structure of the achieved sample, methods of state-of-the-art transmission electron microscopy (TEM) were used. A TEM sample of a Ag-dendrite was prepared by FIB. The region of interest was protected from damage during cutting by applying a layer of Pt. TEM was carried out using an FEI Titan TEM operating at 300 kV. In addition to TEM images, selected area diffraction patterns were acquired and analyzed to study the crystal structure. Scanning TEM was used to acquire HAADF images. The TEM was furthermore equipped with a Bruker four detector EDX spectrometer, enabling to map the chemical composition of the sample with nanometer resolution.

Raman Spectroscopy

A 100 µM solution of 1-phenylethyl mercaptane (Sigma Aldrich) was prepared using methanol aided by sonification. SERS measurements were obtained after 24h of incubation of the analyte on the substrates. Raman spectra were obtained using a Horiba Jobin Yvon LabRamHR-VIS system using the HeNe laser at wavelength of 632.8 nm with a hole diameter of 500µm and a slit width of 200 µm using a D1 filter with 60s integration time. The total signal integration time was 60s with averaging of 2 scans over 600-2000 cm^{-1}. LabSpec software (v.5.19.17, Horiba) was used to acquire spectra, perform background subtraction and to analyze the spectra.

Additional Raman spectra

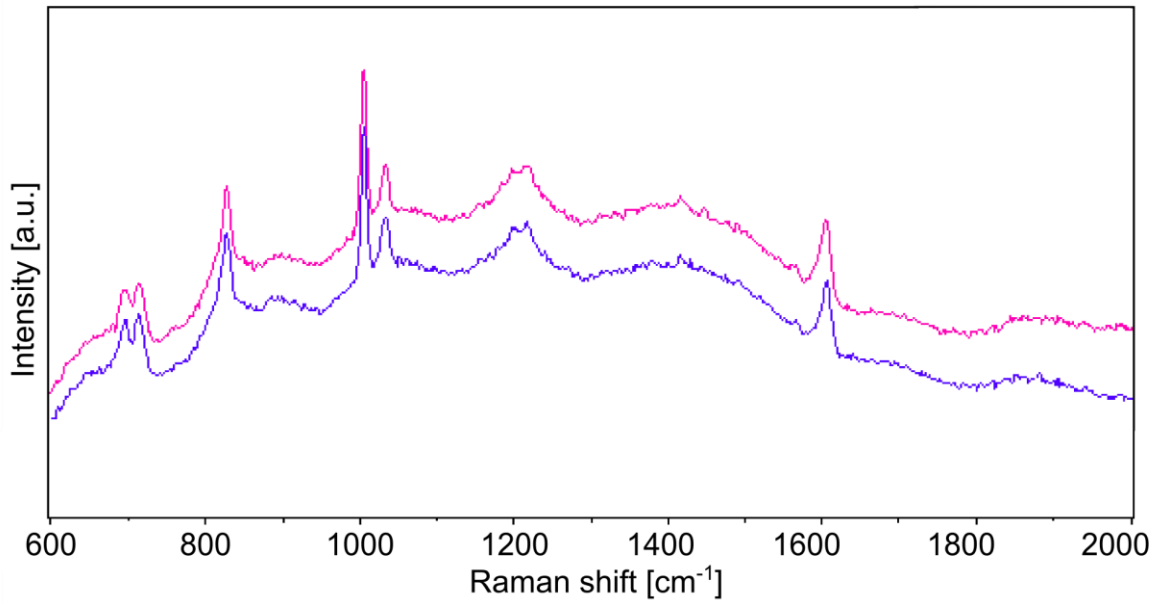

Fig. 1: Raman spectra (raw data, background not subtracted) of two different Ag dendrites as-prepared.

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Calculation of Surface Enhancement: SAM on Nanostructures vs. Solution on AAO

The following equation was used for the calculation of the SERS enhancement factor (EF):

Enhancement Factor (EF) definition:

$$EF = \frac{\frac{I_{\{SERS\}}}{N_{\{SERS\}}}}{\frac{I_{\{Bulk\}}}{N_{\{Bulk\}}}} = \frac{N_{\{Bulk\}} * I_{\{SERS\}}}{N_{\{SERS\}} * I_{\{Bulk\}}} = \mathbf{2\ 10^5}$$

N_{Bulk} and N_{SERS} are the number of phenylethyl mercaptan molecules and I_{Bulk} and I_{SERS} their intensities (thiol peak at 996 cm^{-1}) in the bulk and on the SERS substrate, respectively.

Intensities I (Integrated Peak Area of the peak at 996 cm^{-1})

$I_{SERS} = 74027.1$

$I_{Bulk} = 17341.7$

Number of phenylethyl mercaptan molecules

The Number of 1-phenylethyl mercaptan molecules in the probed solution (N_{Bulk}) was calculated from the thiol bulk density and Raman scattering volume using the following equation. A pure solution was used.

$N_{Bulk} = V * \rho_{Bulk} = d^2 * \frac{\pi}{4} * h * \rho_{Bulk} = 2.3649\ 10^{11}$

(h=500µm=0.005 dm; d=1µm=10^{-5}dm; $\rho_{Bulk}=6.02\ 10^{23}\left[\frac{molecules}{dm^3}\right]$)

The number 1-phenylethyl mercaptan molecules probed on the SERS substrate (N_{SERS}) was calculated from the packing density, the Raman scattering area using the following equations. The concentration of the solution has to be taken into account as a diluted solution was used.

$N_{SERS} = A * \mu_{SAM} = d^2 * \frac{\pi}{4} * \mu_{SAM} * concentration = 5.34\ 10^6$

(d=1µm=10^{-5}dm, $\mu_{SAM} = 6.8\ 10^{16}\ \left[\frac{molecules}{dm^2}\right]$)

The packing density of 6.8 x10^{16} molecules dm^{-2} reported for benzenthiol was used for the calculation [1].

References

[1]A.D. McFarland, M.A.Young, J.A. Dieringer, R.P. van Duyne, J.Phys.Chem B 109 (2005) 11279.