Supplementary information

Scalable Decoration of Au Nanoparticles onto Al nanoconcavities Arrays for Highly Enhanced SERS Detection

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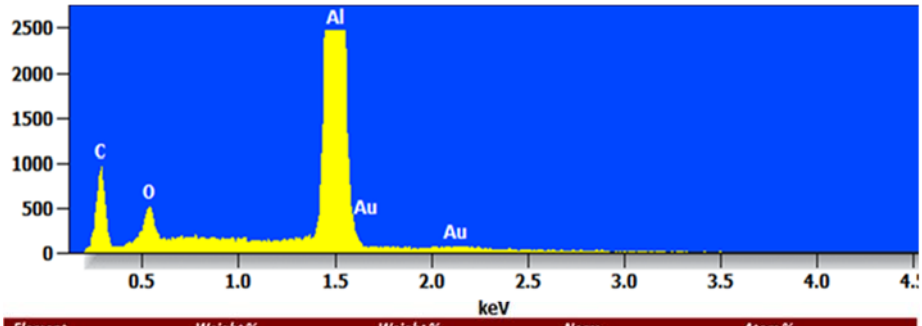
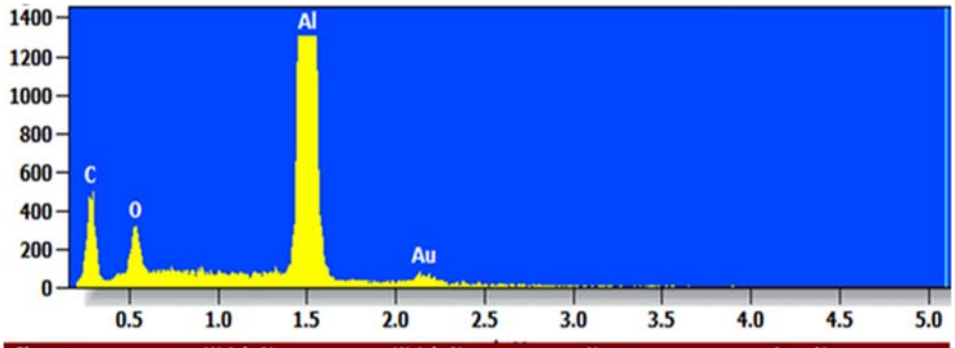
1. Characterization of the Au nanoparticles onto Al nanoconcavities substrates



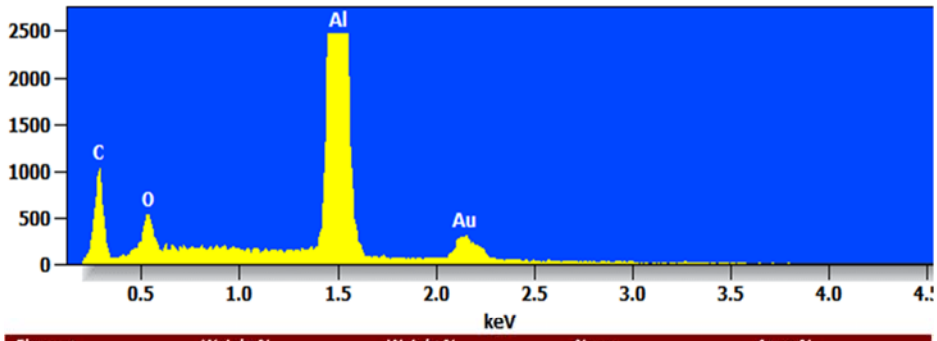
Element	Weight %	Weight % Error	Norm. Wt.%	Atom %
C	5.18	± 0.06	5.18	10.90
O	2.53	± 0.06	2.53	4.00
Al	90.65	± 0.43	90.65	84.89
Au	1.64	± 0.33	1.64	0.21
Total	100.00		100.00	100.00

Figure S1. EDS Spectrum and quantitative analysis of the concave-like structured Al templates with Au sputtering for 20 s and subsequent thermal annealing 400 ºC for 30 min.



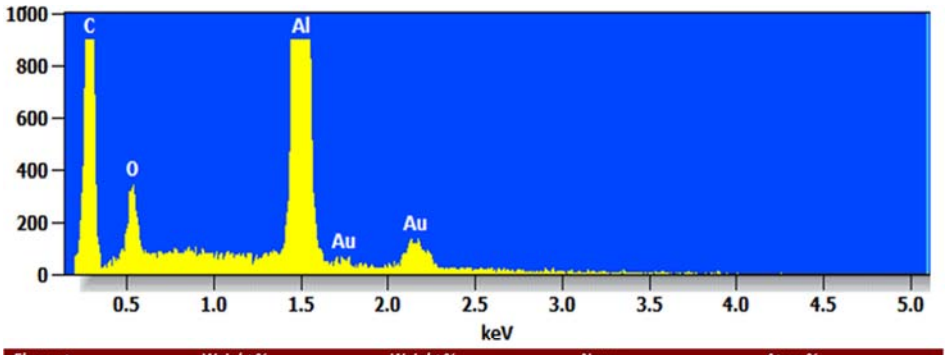
Element	Weight %	Weight % Error	Norm. Wt.%	Atom %
C	5.00	± 0.08	5.00	11.00
O	2.92	± 0.15	2.92	4.81
Al	85.04	± 0.49	85.04	83.24
Au	7.04	± 0.81	7.04	0.94
Total	100.00		100.00	100.00

Figure S2. EDS Spectrum and quantitative analysis of the concave-like structured Al templates with Au sputtering for 60 s and subsequent thermal annealing 400 ºC for 30 min.



Element	Weight %	Weight % Error	Norm. Wt.%	Atom %
C	4.73	± 0.05	4.73	11.41
O	2.49	± 0.10	2.49	4.50
Al	76.07	± 0.38	76.07	81.63
Au	16.72	± 0.67	16.72	2.46
Total	100.00		100.00	100.00

Figure S3. EDS Spectrum and quantitative analysis of the concave-like structured Al templates with Au sputtering for 108 s and subsequent thermal annealing 400 ºC for 30 min.



Element	Weight %	Weight % Error	Norm. Wt.%	Atom %
C	3.43	± 0.05	3.43	8.83
O	2.48	± 0.10	2.48	4.79
Al	72.40	± 0.36	72.40	82.98
Au	21.69	± 0.71	21.69	3.41
Total	100.00		100.00	100.00

Figure S4. EDS Spectrum and quantitative analysis of the concave-like structured Al templates with Au sputtering for 200 s and subsequent thermal annealing 400 ºC for 30 min.

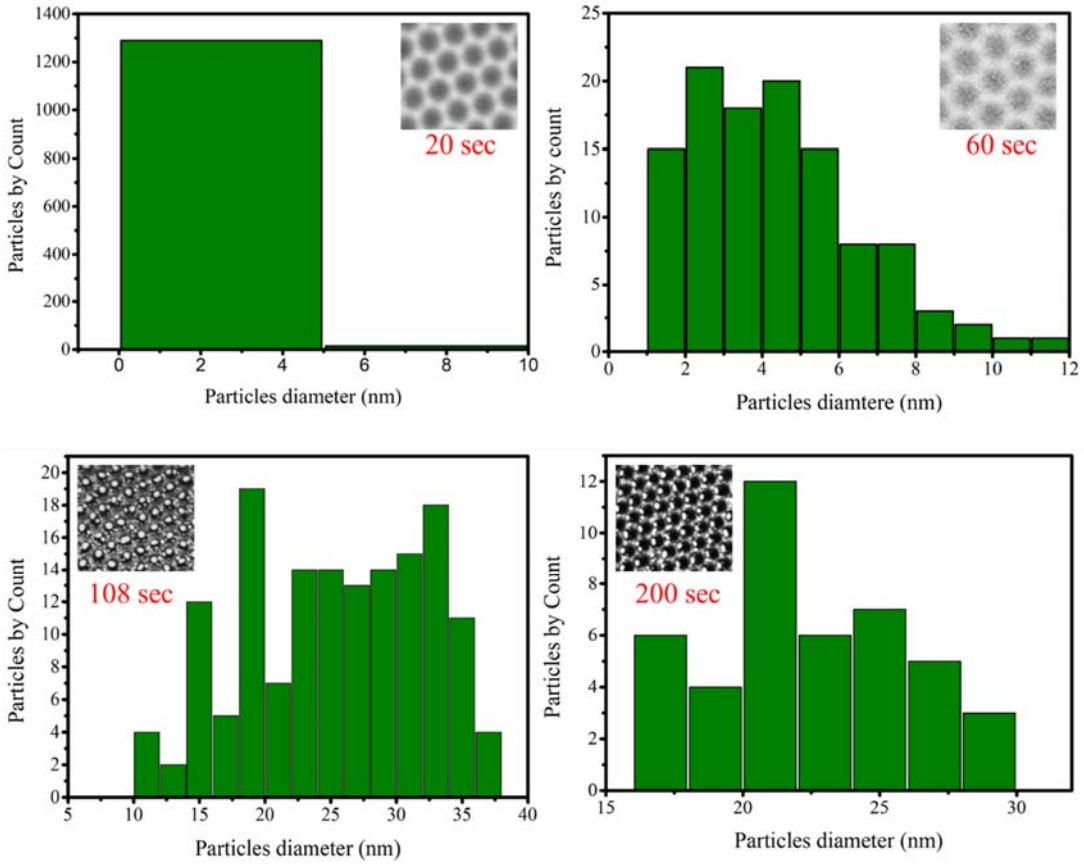


Figure S5. Au particle size distribution histogram for various Au sputtering times after thermal annealing of 400ºC during 30 min.

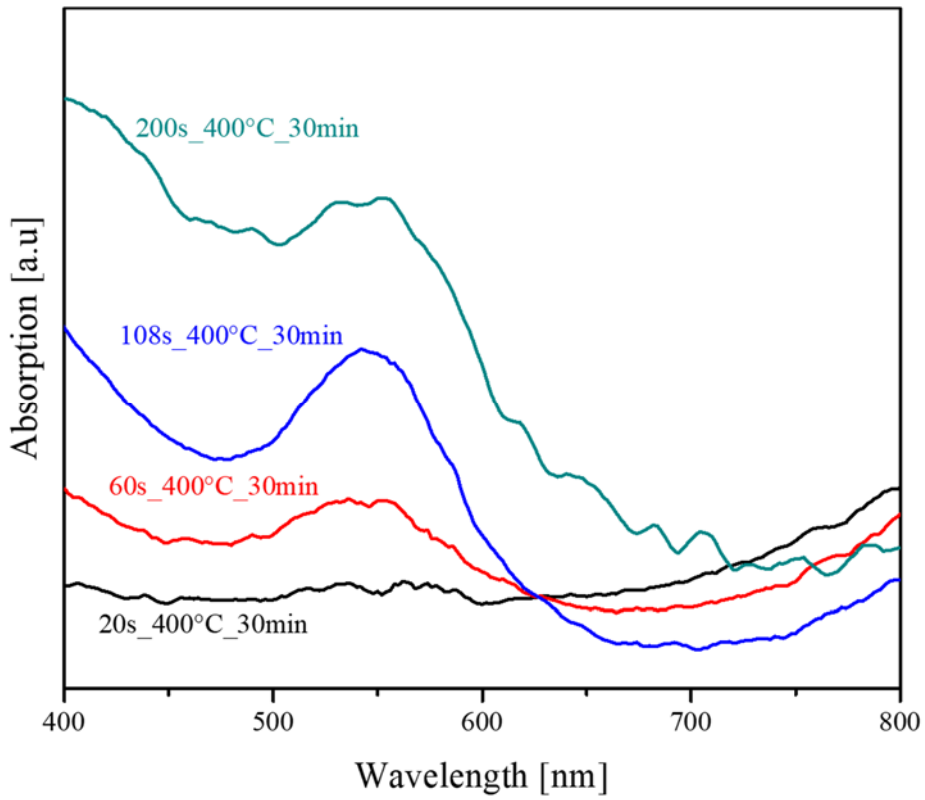


Figure S6. UV-vis absorption spectra of prepared Al-nanoconcavities substrates with 20, 60, 108 and 200 s Au puttering thermally treated at 400 °C for 30 min.

2. SERS Measurements

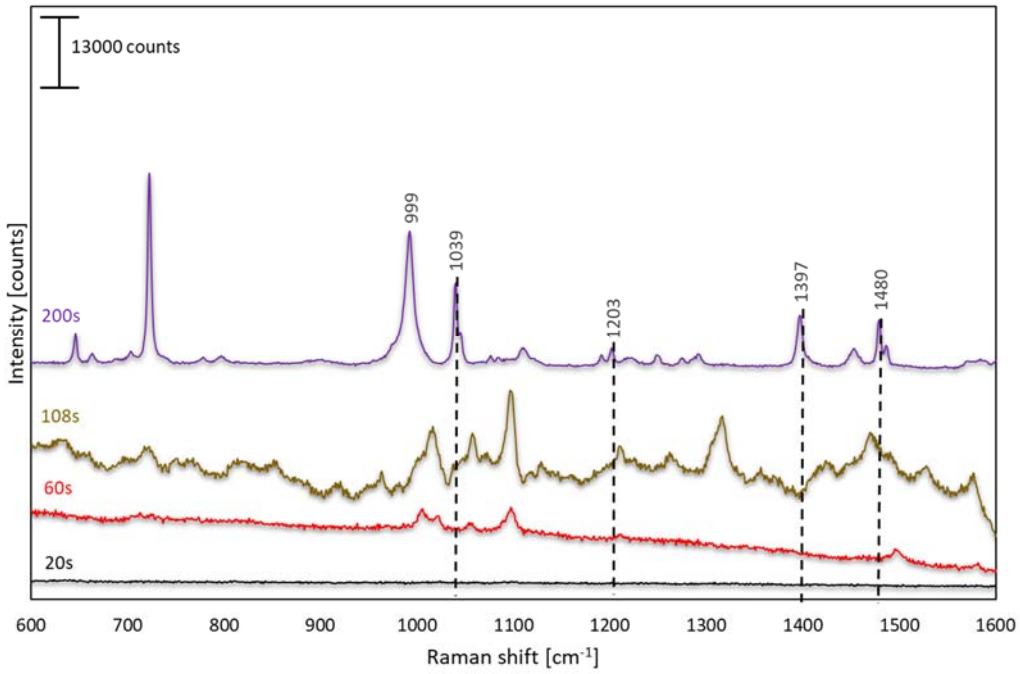


Figure S7. SERS spectra of 20, 60, 108, and 200 s Au sputtered substrates for 350°C during 30 min thermal annealing. The concentration of 4-Mpy was 10^{-7} M for all.

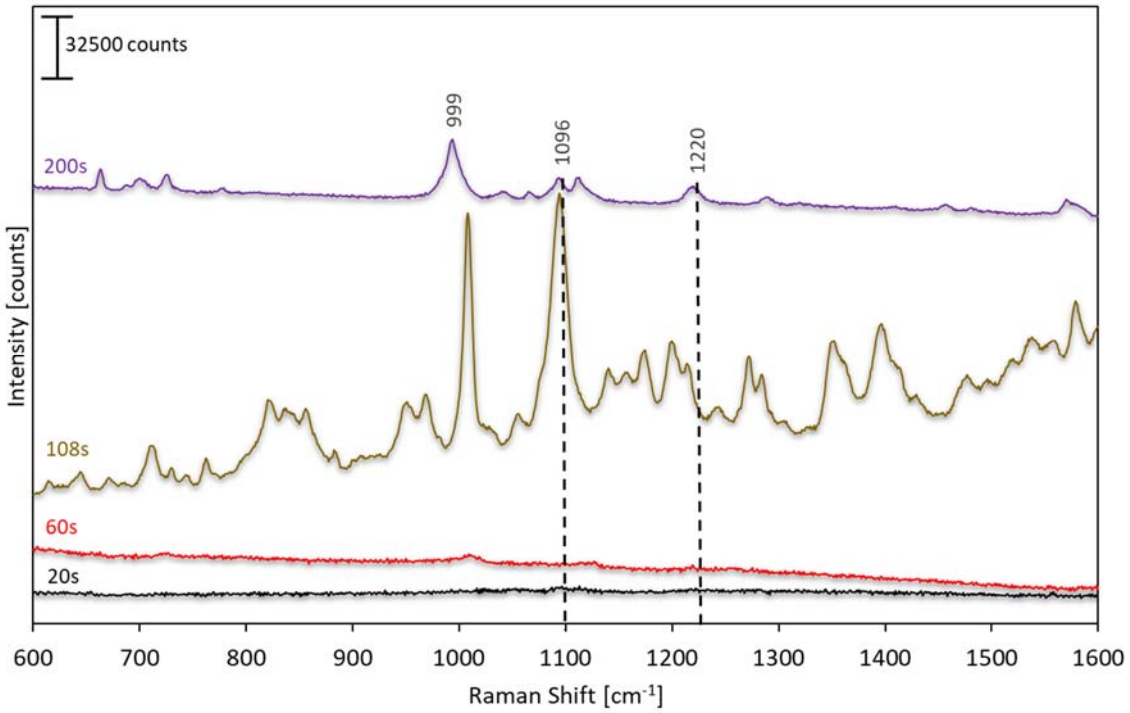


Figure S8. SERS spectra of 20, 60, 108, and 200 s Au sputtered substrates for 400°C during 30 min thermal annealing. The concentration of 4-Mpy was 10^{-7} M for all.

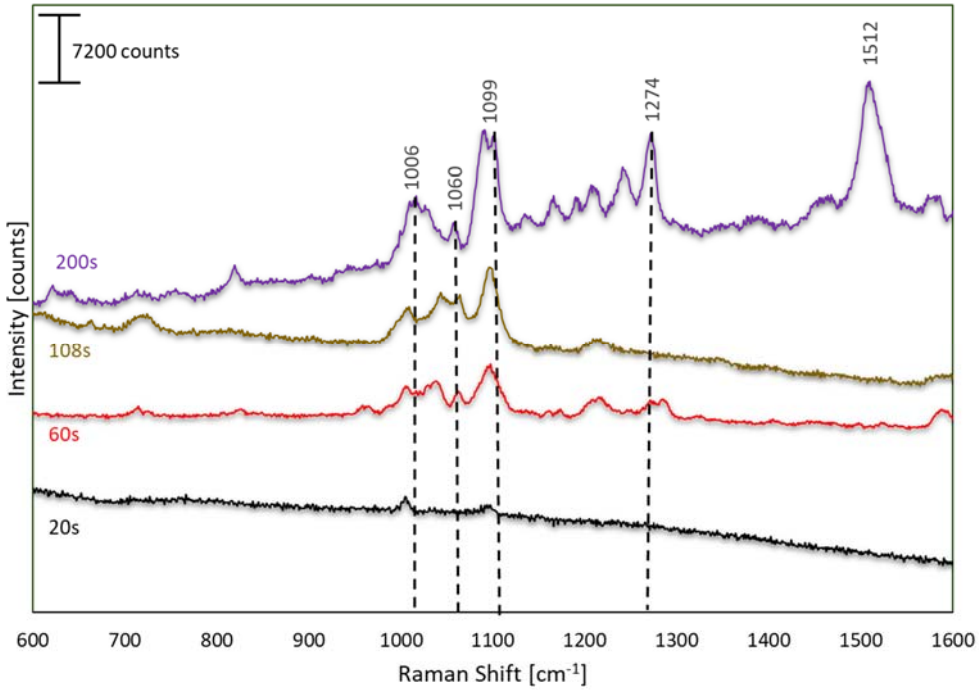


Figure S9. SERS spectra of 20, 60, 108, and 200 s Au sputtered substrates for 400°C during 120 min thermal annealing. The concentration of 4-Mpy was 10^{-7} M for all.

This analysis was conducted using the Raman shift value of 1097 cm^{-1}. The curve serves to identify the region suitable for quantification purposes. The red line denotes the region of insufficient concentration, rendering quantification n unattainable.

3. Calculation of Enhancement factor

A typical method to objectively determine SERS proficiency is the calculation of the enhancement factor (EF). We have followed the most standard and accurate method [1]for its determination, expressed in Equation 1

$$EF = (I_{surf}/ N_{surf}) (I_{bulk} /N_{bulk}) \quad (1)$$

where the intensities of the vibrational modes in the SERS and Raman spectra are denoted as Isurf and Ibulk, respectively, Nbulk is the total number of molecules subjected to Raman spectrum analysis, and the number of molecules subjected to SERS probes is denoted by Nsurf. The expression for the calculation of Nbulk used is Nbulk = A · h · p · Na / M [2], where A is the area of laser spot. h is the penetration depth, p is the density of probe molecule, Na is the Avogadro's number. And M is the molecular weight. Based on the numerical aperture of the long working distance objective (NA = 0.5), we calculated the expected depth of penetration, of 6.28 μm. The area of the laser spot is 2.84 μm^2

(radius of 0.95 μm). Based on these values, we calculate the total number of molecules in the bulk sample, that is N_{Bulk} 1.1×10^{11} molecules.

Many factors are considered when estimating the number of molecules that contribute to the SERS signal on the Al substrate (N_{Surf}). The first is that the amplification is caused only by the Au fractals immediately next to the surface. The 4-MPy molecules are therefore adsorbing onto the Al surface in a flat, parallel orientation, which leads to the second observation. The SERS spectra provide strong evidence for this, namely the presence of non-symmetric modes (b_2). Recent DFT calculations further support this assumption [3, 4] **.** The number of molecules on the surface of the laser (N_{Surf}) is **9.1×10^4 molecules** and is calculated briefly in SI. At the Raman shift of 1097 cm^{-1} for sample prepared for 108 s Au sputtering and thermally annealed at 400 °C for 30 min, the enhancement factor was estimated as EF **1.6×10^7**. While evaluating the EF on various Raman shifts at 1009 cm^{-1} , EF= **3.4×10^7** was determined.

References

1. He, S., et al., *Optimizing the SERS enhancement of a facile gold nanostar immobilized paper-based SERS substrate.* RSC advances, 2017. **7**(27): p. 16264-16272.
2. Muehlethaler, C., et al., *Ultrahigh Raman enhancement on monolayer MoS2.* Acs Photonics, 2016. **3**(7): p. 1164-1169.
3. Gardner, A.M. and T.G. Wright, *Consistent assignment of the vibrations of monosubstituted benzenes.* The Journal of chemical physics, 2011. **135**(11).
4. Birke, R.L. and J.R. Lombardi, *Simulation of SERS by a DFT study: a comparison of static and near-resonance Raman for 4-mercaptopyridine on small Ag clusters.* Journal of Optics, 2015. **17**(11): p. 114004.