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Supplementary Information

Ni/Au hybrid nanoparticle arrays as a highly efficient, cost-effective and stable SERS substrate

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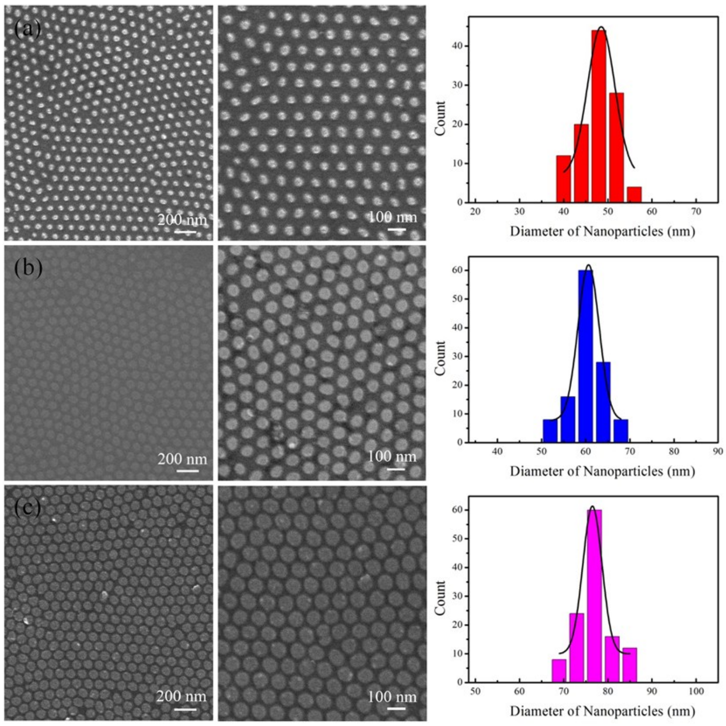

Fig. S1 SEM images of Ni NP arrays with three evaporation thickness of 10 nm (a), 15 nm (b) and 25 nm (c) and the according size distribution of diameter of the three Ni NP arrays.

EF calculation

The enhancement factor (EF) was calculated using the standard formula[1,2]

$$EF = (I_{SERS}/I_{NR})(C_{NR}/C_{SERS})$$

where I_{SERS} and I_{NR} are the integral intensity of the same band obtained by SERS and normal Raman scattering measurements, respectively. C_{SERS} and C_{NR} are the concentration of the CV solution used for SERS and normal Raman scattering measurements, respectively. In this work, C_{SERS} is 10^{-6}, 10^{-7}, 10^{-8}, 10^{-10} M and C_{NOR} is 10^{-3} M. Three main characteristic absorption bands of 1177, 1372, and 1618 cm^{-1} were considered for EF calculation. The calculation results are shown in Tab. S1and Tab. S2.

Another way[3] of EF calculation is

$EF = (I_{SERS}/I_{NR})(N_{NR}/N_{SERS})$

where I_{SERS} and I_{NR} correspond to the integrated intensities obtained by SERS and normal Raman scattering measurements, respectively. N_{SERS} and N_{NR} are the number of molecules probed in the SERS and normal Raman scattering measurements, respectively. I_{SERS} and I_{NR} were determined from the area of the 1177 cm^{-1} band and for the 10^{-6} M CV molecule. N_{NR} was calculated through multiplying molecules concentration C_{NRS} (i.e. $6.022\times10^{23}\times10^{-3}$ molecules/L) by the scattering volume (V) for the normal Raman (non-SERS) measurement[3,4]. N_{SERS} value was determined by calculating the total surface area of upper hemispheres of hexagonally close-packed Ni/Au particles in a circular area (A) of laser spot, assuming a hexagonal close-packed arrangement of CV molecules (d_{CV} = 1.528 nm) on the particle surface. [5]

N_{NR} and N_{SERS} can be calculated form the following equation,

$$N_{NR}= C_{NRS}\, V= C_{NRS}\, A\, h$$

$$N_{SERS}=[2\pi(D/2)^2]/[\pi(d_{CV}/2)^2]\eta NA$$

Where the laser excitation wavelength is 633 nm and the *N.A.* is 0.9; the laser penetration depth, h is approximately 2 μm; the laser spot area A is calculated by the spot diameter (*1.22*×633 nm/N.A.); D (80nm) is the diameter of the 25 nm Ni/20 nm Au nanoparticle; η (0.907) is the duty ratio for the hexagonal close-packed arrangement of CV molecules on the particle surface; N (117 particles/μm^2) is the surface coverage of the particles in the 25 nm Ni/20 nm Au NP arrays substrate, obtained from the SEM image, respectively. The EF is calculated to be 5.79×10^3 for the 10^{-6} M CV as the analyte. N_{SERS} value is a theoretical maximum number of molecules. Therefore, the actual EF is believed to be higher than the value reported herein.

Sample	probing molecule concentration	EF		
		1177 cm^{-1}	1372 cm^{-1}	1618 cm^{-1}
25 nm Ni/20 nm Au	10^{-6} M	2.8×10^6	1.9×10^6	5.7×10^5
45 nm Au	10^{-6} M	2.9×10^6	2.1×10^6	6.0×10^5
30 nm Au	10^{-6} M	2.2×10^6	1.5×10^6	3.3×10^5
20 nm Au	10^{-6} M	1.3×10^6	1.0×10^6	3.1×10^5
10 nm Au	10^{-6} M	9.5×10^5	5.2×10^5	1.9×10^5

Tab. S1. EFs of SERS intensity at three main peaks of 10^{-6} M CV molecule absorbed on the 25 nm Ni/20 nm Au substrate and pure Au NP arrays substrate with different thickness of 10, 20, 30 and 45 nm.

Sample	probing molecule concentration	EF 1177 cm^{-1}	1372 cm^{-1}	1618 cm^{-1}
25 nm Ni/ 20 nm Au	10^{-6} M	2.8×10^{6}	1.9×10^{6}	5.7×10^{5}
	10^{-7} M	1.1×10^{7}	4.6×10^{6}	3.0×10^{6}
	10^{-8} M	8.9×10^{7}	1.4×10^{7}	2.1×10^{7}
	10^{-10} M	4.5×10^{8}	3.1×10^{8}	9.5×10^{7}

Tab. S2 EFs of SERS intensity at three main peaks of CV molecule with four different concentrations absorbed on the 25 nm Ni/20 nm Au substrate

Reference

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