Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Electronic Supplementary Material

Templated gold nanocaps for surface-enhanced Raman scattering (SERS) sensors based on monolayer polystyrene colloidal arrays

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Supporting information to DOI : https://doi.org/10.1039/d4nj01150c

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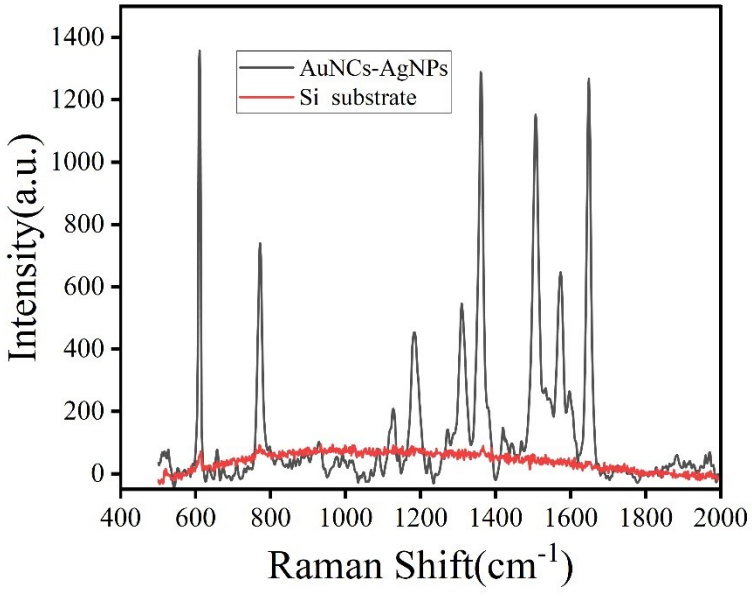

Figure S1. SERS spectra of R6G (1.0×10^{-3} M) absorbed on the AgNPs-AuNCs (black line) and Si substrate (red line). The excitation laser wavelength for Raman measurements is 532 nm, the laser power is 0.1 %, and the acquisition time is 3 s.

To quantitatively evaluate the SERS enhancement factor (EF) of the convex AgNPs-AuNCs substrate, the SERS EF value of R6G was calculated by this equation[S1-S3]:

$$EF = \frac{I_{SERS}}{I_{REF}} \cdot \frac{N_{REF}}{N_{SERS}}$$

Where I_{SERS} is the SERS intensity of band of 614 cm^{-1} of 1×10^{-3} M R6G on the AuNCs-AgNPs, I_{REF} is the normal Raman intensity of 614 cm^{-1} of 1×10^{-3} M R6G on a Si substrate. N_{SERS} and N_{REF} are the number of R6G molecules which excited by the laser. $N_{SERS} = \frac{A_{SERS} \cdot V_{SERS} \cdot C_{SERS} \cdot N_A}{S_{SERS}}$, where S_{SERS} is dispersion area of R6G solution, A_{SERS} and is the area which irradiated by laser in AuNCs-AgNPs, V_{SERS}, and C_{SERS} are volume and concentration of R6G solution in AuNCs-AgNPs, $N_{REF} = C_{REF} V_{REF} N_A$. Similarly, V_{REF} and C_{REF} are volume and R6G on Si substrate, and N_A is the Avogadro constant. Where A_{SERS} = 1.22 λ/NA, λ is incident wavelength (532 nm), NA = 0.5, the laser spot is ~ 1.3 μm^2. Raman test condition (laser power= 0.1%, Acquisition time=3s. Suppose that 100 µL 1×10^{-3} M R6G molecules are uniformly dispersed on the surface of SERS substrate, the surface area is 0.25 cm^2, laser spot (A_{SERS}) was 1.88 μm^2, The intensities at 614 cm^{-1} are 1357 and 63 for SERS substrate and REF Raman testing respectively.

$$N_{SERS} = \frac{1.3\ \mu m^2 \cdot 100\ \mu L \cdot 10^{-3}\ mol/L \cdot N_A}{0.25\ cm^2} = 3.2\times10^9$$

$$N_{REF} = 10^{-3}\ mol/L \cdot 100\ \mu L \cdot N_A = 6.02 \times 10^{16}$$

The EF value of the 614 cm^{-1} band is calculated as follows:

$$EF_{R6G} = \frac{1357}{63} \cdot \frac{6.02 \times 10^{16}}{3.2 \times 10^9} = 4.05\times10^8$$

Table S1. The list of some SERS substrates together with its probe molecules, enhancement factors (EF) and detection limits (LOD).

Fabrication method	Substrate material	Compositions	Analyte	Enhancement factor	LOD (M/L)	References
Self-assembly	Si wafer	AgNPs-AuNCs PS array	R6G	4.05×10^8	10^{-7}	This work
Layer by layer	Si wafer	Au NPs multilayer	R6G	8.6×10^6	-	[S4]
Nanoimprint and sputtering	PDMS[a]	Au NPs	R6G	2.24×10^7	10^{-11}	[S5]
X-ray interference lithography	Si wafer	Au nanodisk	R6G	1.0×10^6	10^{-8}	[S6]
Electrodeposition	PET[b] film	Ag NPs	R6G	3.0×10^7	10^{-9}	[S7]
AAO[c]-electron Beam evaporating	Al[d] base	AgNCs	R6G	3.87×10^6	10^{-5}	[S8]
Direct imprint	PET	Graphene@AuNCs	R6G	-	10^{-6}	[S9]
Laser interference lithography	ITO[e]	Au NPs	R6G	1.25×10^5	10^{-8}	[S10]
Self-assembly	ITO	AuIoN[f]	R6G	1.51×10^6	-	[S11]
Self-assembly	Si wafer	3D SLNA[g]-Ag NPs	R6G	2.0×10^{14}	10^{-15}	[S12]

[a] PDMS: polydimethylsiloxane. [b]PET: polyethylene terephthalate. [c]AAO: anodic aluminum oxide. [d]Al: aluminum. [e]ITO: indium tin oxide. [f]AuIoN: Au Island over Nanospheres. SLNA: “sunflower-like” nanoarrays.

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