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Supporting Information

Invisible-ink-assisted pattern and written surface-enhanced Raman scattering substrates for versatile chem/biosensing platforms

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Table S1. UV-visivle measurements from the three materials of Au_1-, Au_3-, and Au_{10}-SERS substrate group. Each experiment was repeated on three separate substrates.

SERS substrate	Sample 1	Sample 2	Sample 3
Au_1-substrate	526 nm	526 nm	525 nm
Au_3-substrate	530 nm	532 nm	530 nm
Au_{10}-substrate	536 nm	537 nm	536 nm

Table S2. Comparison of the catalysis reaction rate of the 4-NTP with different nanomaterials.

SERS substrate	Reaction rate	Reference
Au-base substrate	2.14×10^{-2} s^{-1}	This work
Au NP-loaded filter paper	6.57×10^{-3} s^{-1}	1
Silver microflowers	1.06×10^{-4} s^{-1}	2
Silver NPs on MgO	9.5×10^{-3} s^{-1}	3
Fe_3O_4/C/Au NPs	4.7×10^{-3} s^{-1}	4
Au NPs/GO	3.1×10^{-3} s^{-1}	5
Ag Nanowire–Au NPs	1.7×10^{-2} s^{-1}	6

Table S3. Comparison of the limit of detection (LOD) of the methylene blue (MB) with different nanomaterials.

SERS substrate	LOD of MB	Paremeter	Reference
Au-base substrate	100 nM (~0.03 ppm)	785 nm; 5 mW; 1 s	This work
AuAg-base substrate	0.5 nM (~0.15 ppb)	785 nm; 5 mW; 1 s	This work
3-D AuAg nano-hollows	50 nM	785 nm; 10 mW; 1 s	11
30s-AgNPs/GF substrate	1 nM	785 nm	12
Ag NPs	200 nM	785 nm; 10 s	13
c-Ag_2O	2 ppm	632.8 nm; 25 mW; 20 s	14
18 ± 2 nm Au NPs	5 ppb	632.8 nm; 2 mW; 10 s	15
Ag nanostructures/PPy	0.2 ppm	632.8 nm; 0.1 mW; 5s	16
TiO_2 microarray	0.01 mM	532 nm	17
Ag NPs on Cu_2O	1 nM	633 nm; 0.1 mW; 10s	18
$(Au@PAAS/LDH)_{10}$ UTF	1 nM (R6G)	633 nm; 0.325 mW; 1 s	19

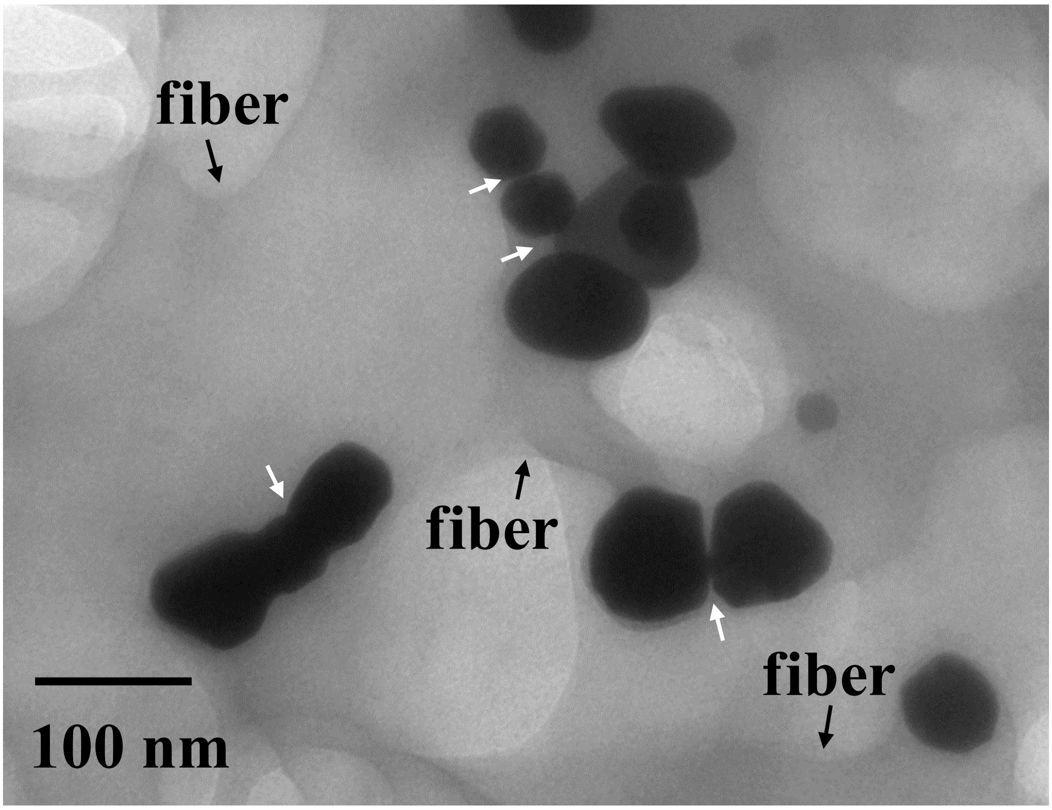

Fig. S1. TEM images of a Au_3-SERS substrate.

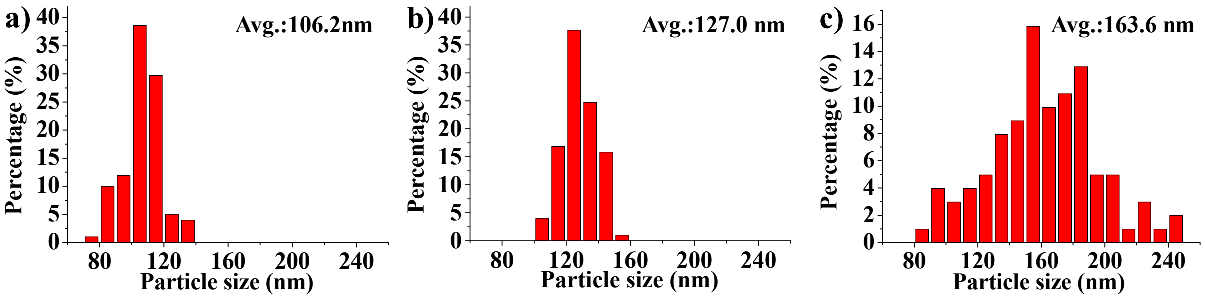

Fig. S2. Percentage and average particle size measurements of Au nanoparticles. a) Au_1-SERS, b) Au_3-SERS, and c) Au_{10}-SERS substrates.

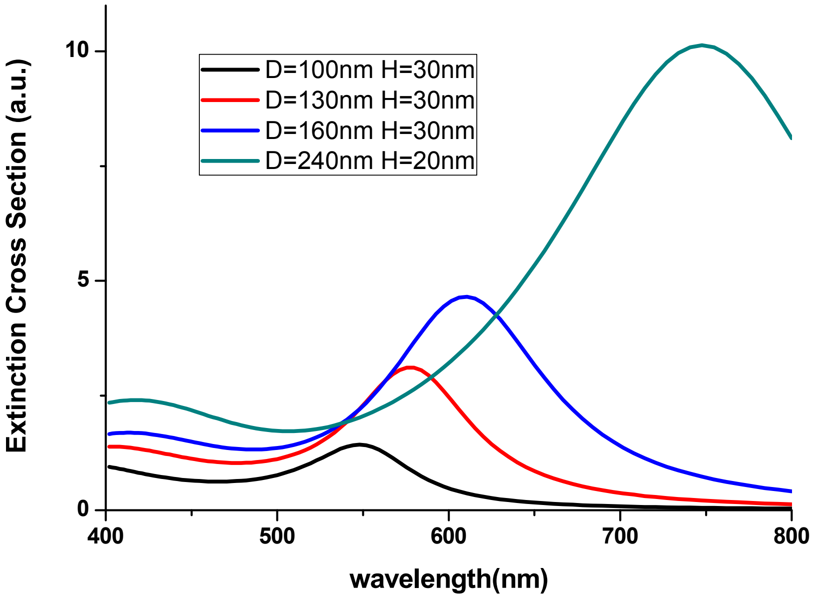

Fig. S3. Extinction spectrum of hexagonal Au nanoparticles with various diameters (D) and thickness (H)

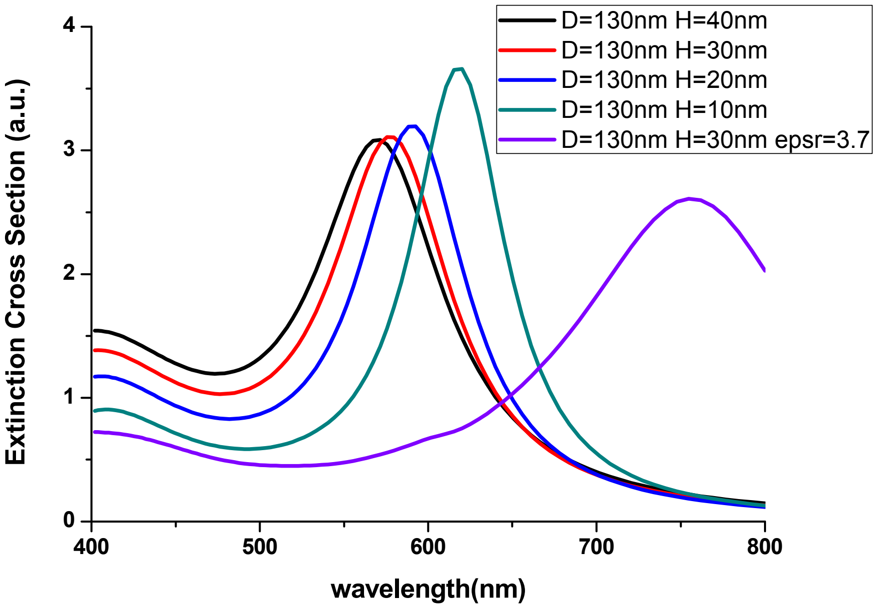

Fig. S4. Extinction spectrum of hexagonal Au nanoparticles with 130 nm in diameter (D) and various thickness (H).

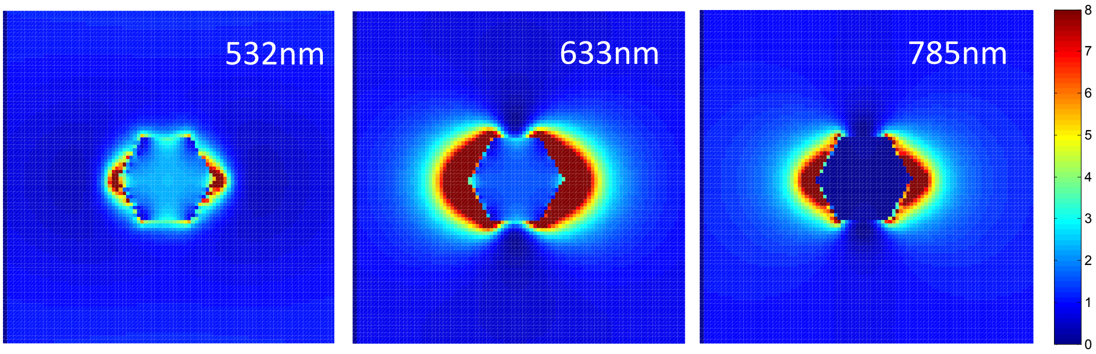

Fig. S5. E^2 Intensity pattern of Hexagonal Au nanoparticle with D=130 nm and H= 30nm at different excitation wavelengths.

After 20 days of storage under different conditions, the Au_3-SERS substrate could retain its SERS activity for reproducible Raman intensity in response to the same MB concentration (Fig. S.5). This high environmental stability under aerobic conditions is highly beneficial for simple packaging of this substrate, in contrast to the oxygen susceptibility of Ag-based SERS substrates.[7]

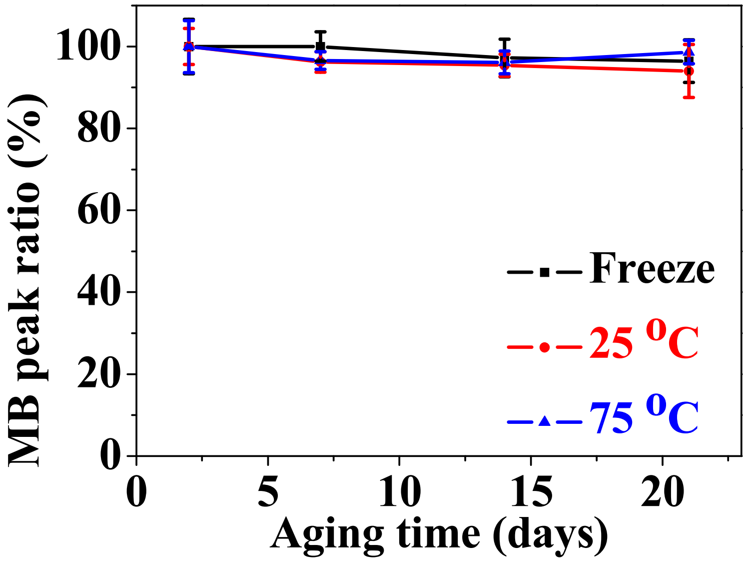

Fig. S6. Stability of the SERS signal of 0.1 mM MB from aged Au_3-based SERS substrates aged at different temperatures.

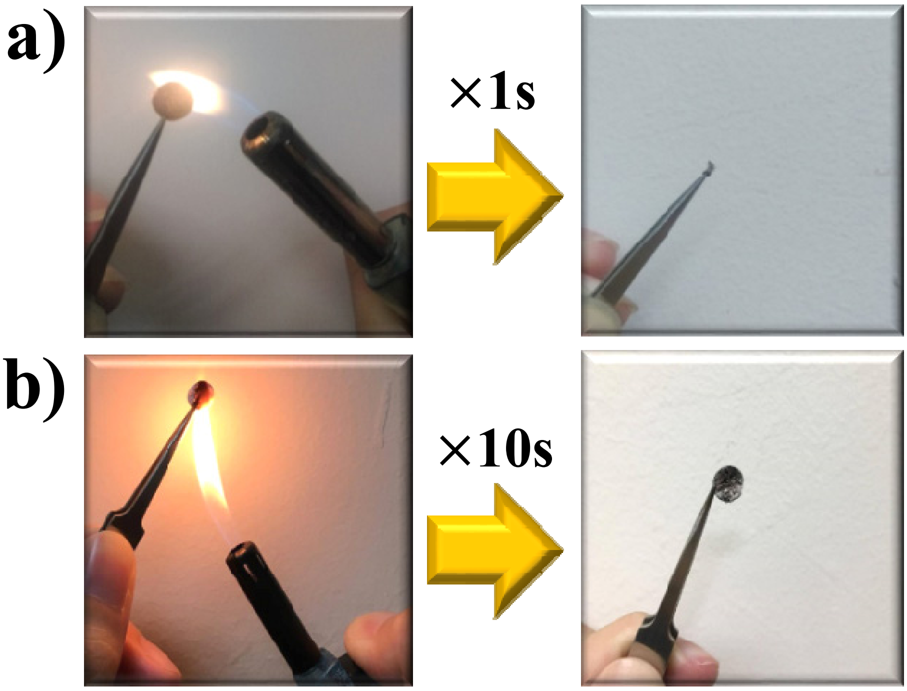

Fig. S7. Flame-burning examination of Au-based substrates. a) Au_3-based SERS substrate and b) SERS product purchased from Ocean Optics (RAM-SERS-AU).

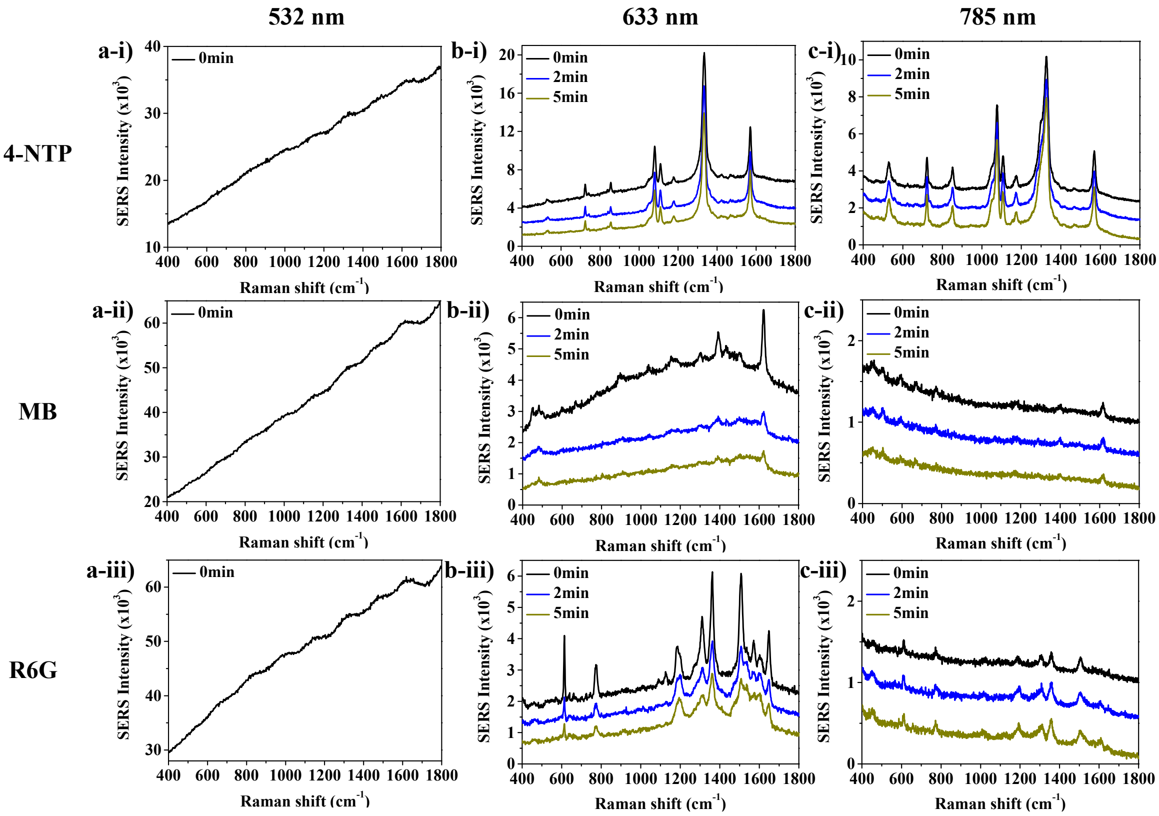

Fig. S8. SERS measurements of i) 4-NTP monolayer, ii) 0.001 mM MB, and iii) 0.01 mM R6G by using laser devices at a) 532 nm, b) 633 nm and c) 785 nm. The normal Raman intensity with different wavelengths was normalize with a silica wafer.

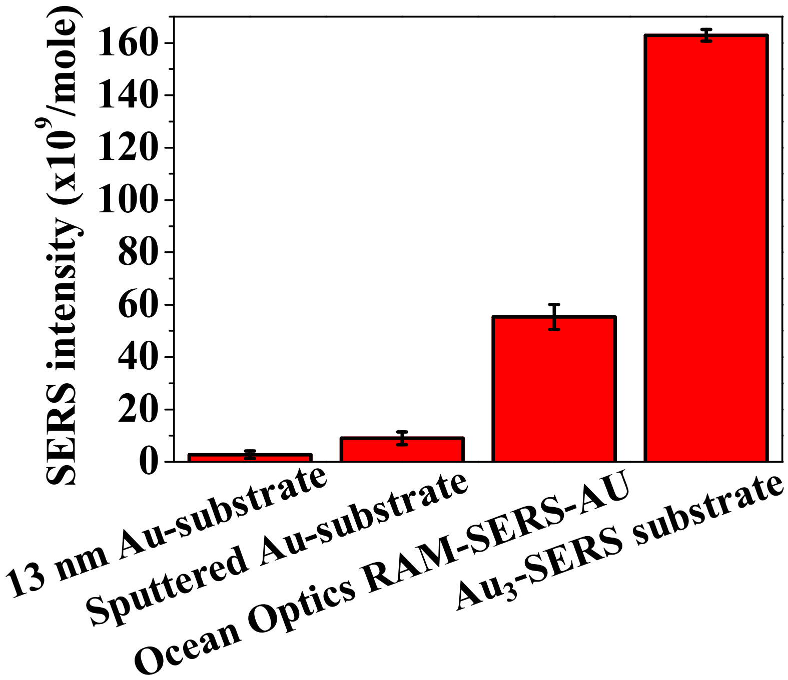

Fig. S9. SERS intensity at 1620 cm^{-1} per mol of metal for the sensing of 0.1 mM MB with different SERS substrates.

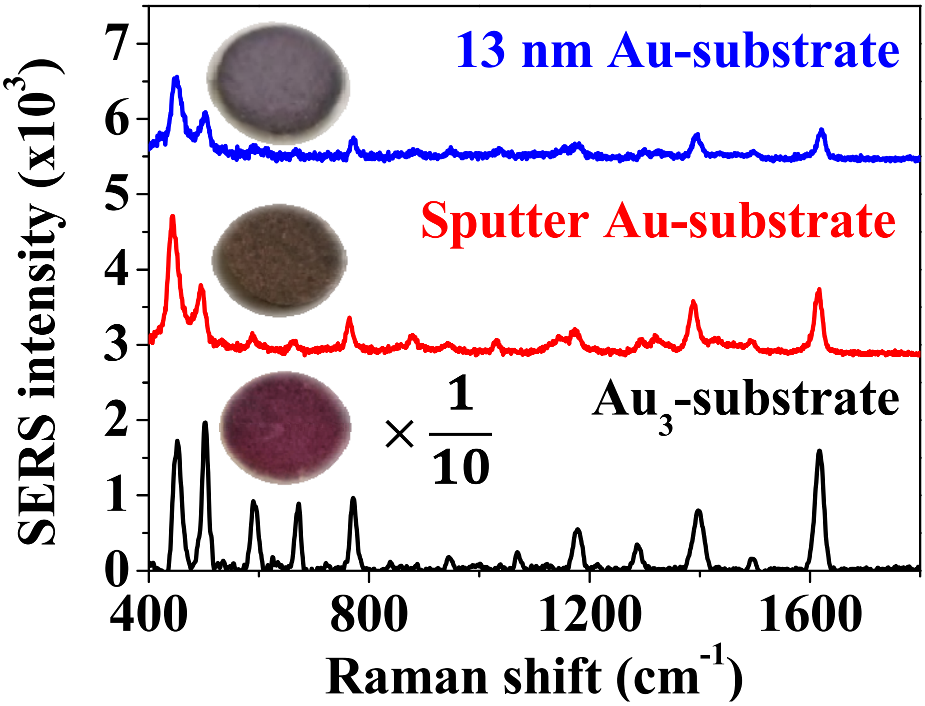

Fig. S10. Photograph and SERS spectra of the 0.1 mM MB on Au$_3$-SERS substrate, the SERS substrate after sputtering of Au nanocrystals (2.5 kV, 10 mA with fine coat ion sputter JFC-1100), and the SERS substrate after being coated with a colloidal Au solution.

Under 74% humidity, slow solution drying under higher humidity and a higher reaction temperature did not yield Au nanoparticles with uniform size through a moderate nucleation and growth process. The resulting Au-based SERS substrates not only showed a certain performance degradation (Fig. S.10.a) but also showed poor reproducibility of the SERS peaks (data not shown). A TNA concentration of 10 mM is the optimal concentration for producing good SERS substrates (Fig. S.10.b). Lower TNA concentrations did not supply adequate electrons to reduce the Au ions, whereas higher TNA concentrations resulted in a large amount of TNA aggregates in the filter paper pores and huge deposition onto the Au nanoparticles. The decrease of the organic shielding effect in the thick coating on the surface of the Au nanoparticles enabled the closer adsorption of the targeted analyte, readily enhancing the EM interaction between the Au nanoparticles and the analyte.

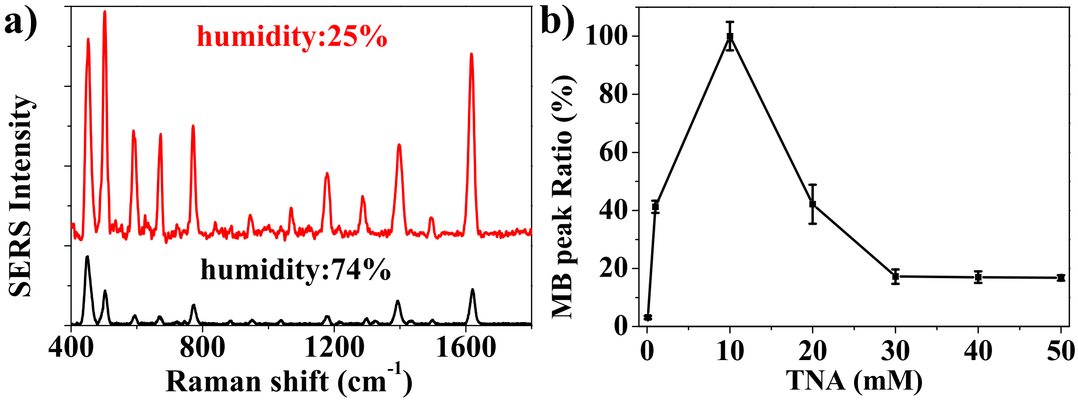

Fig. S11. SERS analysis of MB for the model analysis with different condition. a) Au_3-SERS substrate under different humidity conditions and b) representative SERS profiles recorded at 1620 cm^{-1} with Au_3-SERS substrates prepared at different TNA concentrations.

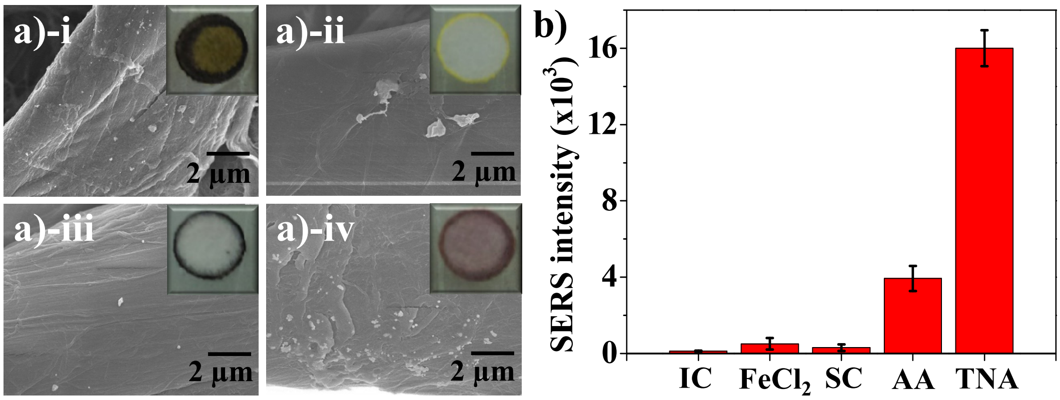

Fig. S12. Preparation of Au_3-based SERS substrates using different reductant. a) SEM images for the preparation of Au_3-based SERS substrates using i) iron chlorophyllin, ii) iron(II) chloride, iii) SC, and iv) L-(+)-ascorbic acid. b) SERS measurements for different Au_3-based SERS substrates shown in a).

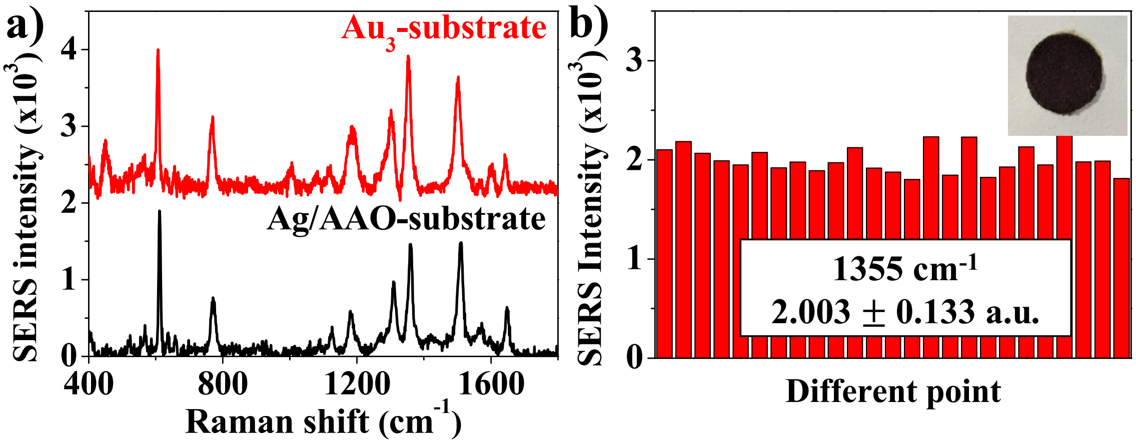

Fig S13. SERS measurements of 0.01 mM R6G with different SERS substrate. a) Au_3-SERS substrate and Ag/AAO-SERS substrate. b) SERS spectra of 0.01 mM R6G with a Au_3-SERS substrate, as recorded at twenty-five different points. The inset in b) is a photograph of the Au_3-SERS substrate onto which 0.01 mM R6G was dropped.

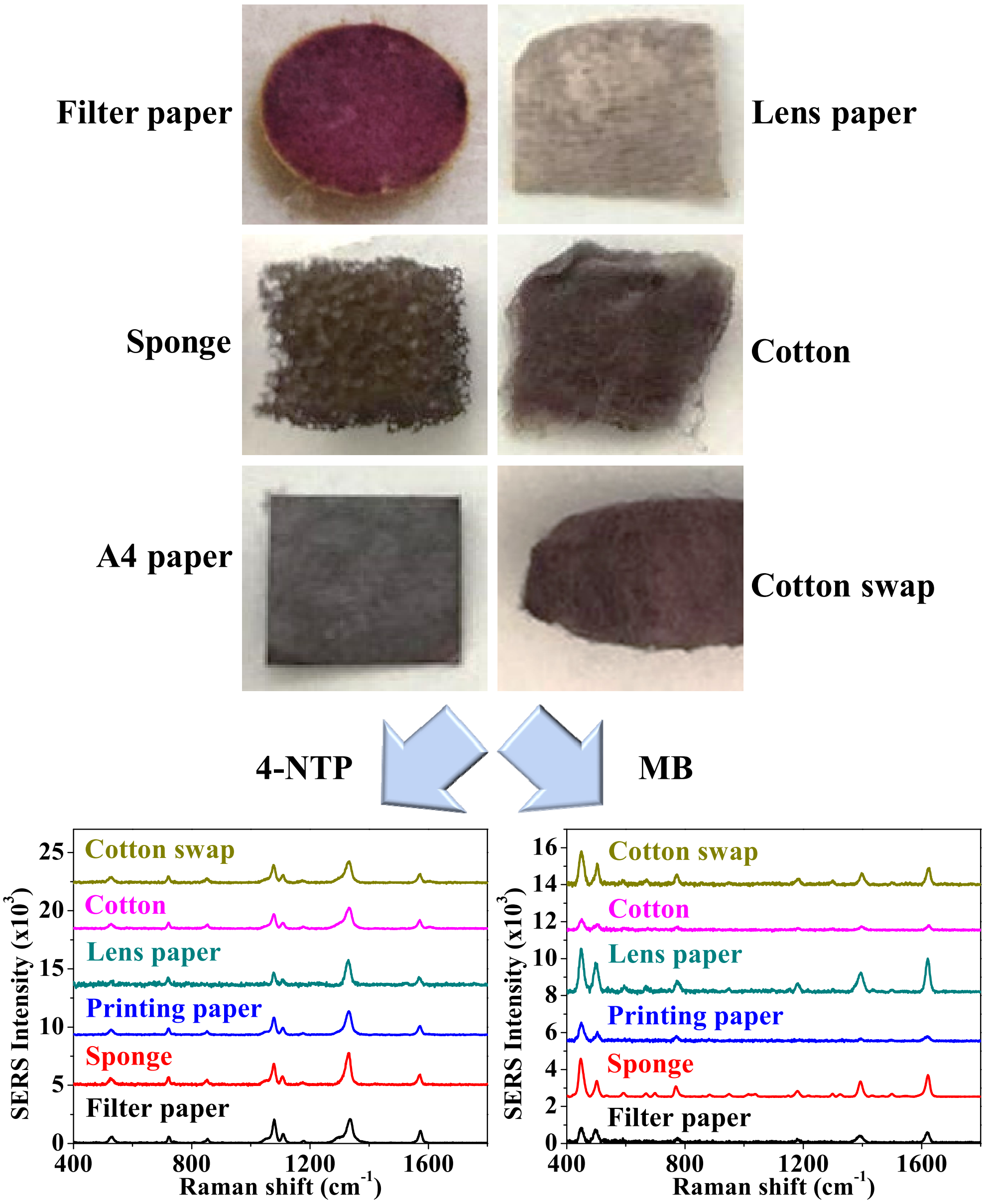

Fig. S14. SERS measurement of the 0.01 mM 4-NTP and 0.01 mM MB with different Au$_3$-SERS materials.

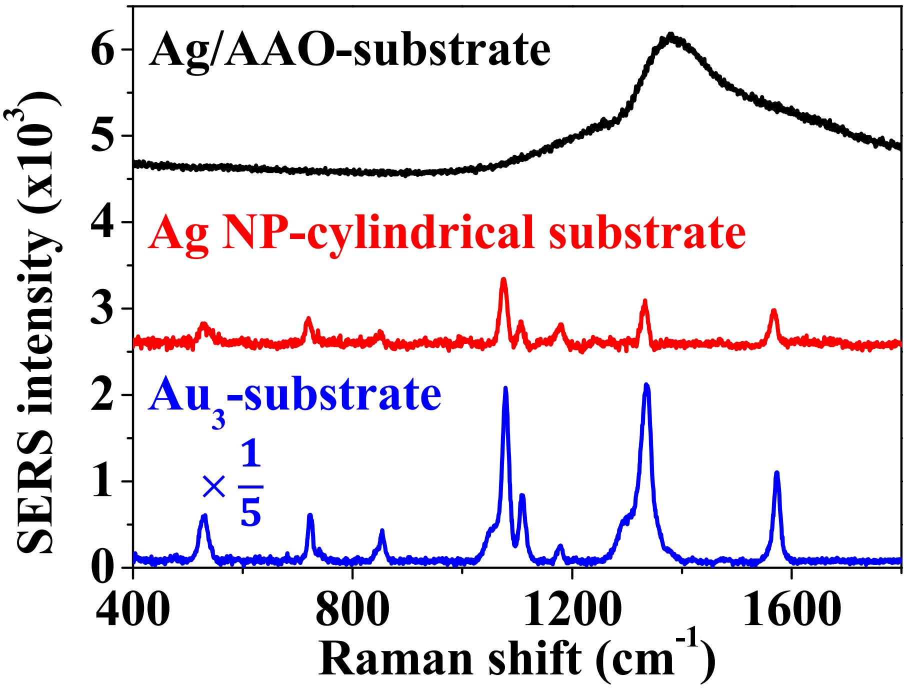

Fig. S15. SERS measurements of 0.01 mM 4-NTP with Au_3-SERS substrate, Ag/AAO-SERS substrate (Bio MA-Tek), and Ag nanoparticle-cylindrical SERS substrate (Yunyang).

We mixed different concentration (0.1 mM-0.001 mM) of melamine in milk solution to mimic contamination in food additive. 675 cm^{-1} (ring breathing II mode) and 983 cm^{-1} (in-plane ring breathing I mode) was obviously produced (Fig. S.15) and could be assigned to the amino group at the melamine.[8-10] 0.01 mM (~ 1.261 ppm) of melamine in milk was detectable. This LOD value is lower than the maximum concentration of 5 ppm allowed by the Taiwan food and drug administration.

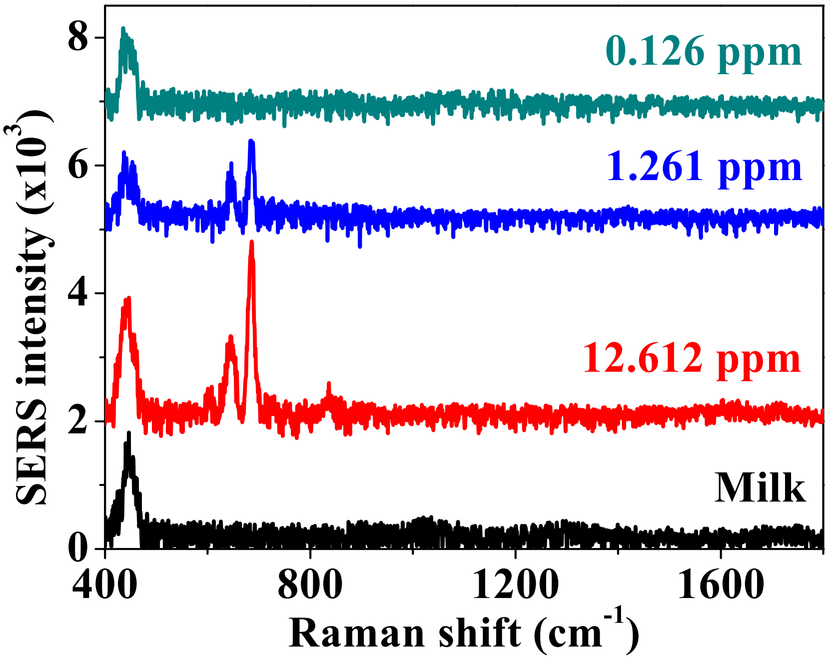

Fig. S16. SERS measurements of mix different concentration melamine in commercial milk product with Au$_3$-SERS substrates.

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