Supporting Information for Amphiphilic Functionalized Acupuncture Needle as

SERS sensor for in situ Multiphase Detection

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Section 1: The morphology characterization of Au-AgN.



Figure S1.The SEM image of the surface of the Ag needle. (a) and (b) represent different magnification of the surface of the Ag needle, (c) and (d) come from different areas of the needle, corresponding to the selected areas in the (b).



Figure S2. XPS spectra of NaCit-Au NPs and PVP-Au NPs, (a) O 1s and (b) Au 4f.



Figure S3. The TEM images of PVP-Au NPs and the distance-distribution histogram of interparticle gap.



Figure S4. The TEM images and the diameter-distribution histogram of PVP-Au NPs.



Figure S5. (a) Raman spectra of 0.1mmol MG molecules from different SERS active silver needles. (b) A line-mapping on 10 random points from different SERS active silver needles were determined by the intensity of SERS spectra at 1614 cm^{-1} .



Figure S6. SEM of (a) NaCit-Au NPs and (b) PVP- Au NPs modified on the Ag needles, the inset are the corresponding Raman mapping images.



Figure S7. The photo and EDS of Au-AgN (yellow parts of needle body are the absorbed Au NPs).



Figure S8. The high magnification SEM image of Au-AgN.

Section 2: The sensitivity of the Au-AgN.



Figure S9. The SERS spectrum of the PVP Au-AgN platform.



Figure S10. SERS spectra of 10⁻⁵ M CV observed on PVP-Au NPs, Ag Needle and Au-AgN platforms. The blank spectrum referring to the spectrum observed on the platforms without the presence of any probe molecule.



Figure S11. SERS of CV molecule at Au-AgN sensor with different Au NP size. Inset: the relationship between the Raman intensity of 1616 cm^{-1} band and the corresponding size of Au NPs.



Figure S12. SEM of the Au NPs with increasing diameters on the Ag Needle. (a) 20 ± 3 nm. (b) 40 ± 4 nm. (c) 55 ± 4 nm. (d) 70 ± 5 nm. (e) 85 ± 10 nm. (f) 95 ± 10 nm.



Figure S13. SERS of CV molecule at Au-AgN sensor with different chain length of PVP polymerization. PVP polymer with the average molecular weight equal to 8k, 10k, 24k, 54k and 130k, respectively. Inset: the relationship between the Raman intensity of 1175 cm⁻¹ band and the corresponding average molecular weight of PVP.



Figure S14. SERS spectra obtained at different concentrations of CV using (a) Au NPs, (b) Ag needle and (c) Au-AgN, (d) comparison of enhancement effect of the three SERS structures.



Figure S15. (a) Raman spectra of 0.1mmol MG molecules from Au NPs on Ag needles and Au NPs on stainless steel needle. (b) A line-mapping on 10 random points from Au NPs on Ag needles and Au NPs on stainless steel needle were determined by the intensity of SERS spectra at 1614 cm^{-1} .

Section 3: The prohibited colorants Detection by Au-AgN.



Figure S16. The SERS spectra using the portable Au-AgN sensor of prohibited colorants: (a) Sudan III; (b) brilliant blue; (c) orange II; (d) sunset yellow.

Section 4: Multiplex Detection in organic by Au-AgN.

Table S1 Raman shifts (cm^{-1}) and assignments for MG (red) and lemon yellow (black).^{1,2}

MG	Lemon yellow	Assignment
724		out-of-plane
797		vibrations of ring C-H
916		of radical orientation
	1056	Phenylalanine
1171		in-plane vibrations of ring C-H
—	1125	Amide III
1219		C-H rocking
	1338	Tryptophan
1365		N-phenyl stretching
1390		N-phenyl stretching
	1443	ν (V=V)
	1503	v(C-C) pigment
	1597	Tyrosine
1616		ring C-C stretching



Figure S17. Au-AgN sensor for dual-analyte (black line) detection of 1μ M 2,2'-bpy and 1μ M 4-Mpy in ethanol. SERS spectra of sole 2,2'-bpy (blue line) and 4-Mpy (pink line) in the ethanol, respectively, were measured as references.

A volume of 2 mL of ethanol with 1μ M 2,2'-bpy of and 1μ M 4-Mpy were detected by the Au-AgN sensor. The SERS spectra of sole 2,2'-bpy and 4-Mpy, respectively, were used as references. As shown in **Figure S17**, the dualanalyte detection by the portable Au-AgN sensor. The comparison between the dual-analyte and single-analyte SERS spectra showed that vibrational bands of both analytes could be seen and detected. The peaks at 1013 and 1307 cm⁻¹ can be assigned to 2,2'-bpy, whereas the peaks at 1078 and 1330 cm⁻¹ are attributed to 4-Mpy (**Table S2**), indicating a good capability of dualanalyte detection by this Au-AgN sensor.³

4-mby	thiram	2,2'-bpy	Assignment
		763	i.p.ring.def
		1013	ring breathing
1078			β(C-H)
1106			ring breathing/C-S
		1307	ring str.(C-C, C-N)
	1139		$\rho\left(\text{CH}_{\scriptscriptstyle 3}\right)\!,\nu\left(\text{C-N}\right)$
1330			β(C-H)
	1379		$\sigma \text{s}(\text{CH}_{\scriptscriptstyle 3}), \nu(\text{C-N})$
		1479	C-Hi.p.def.
	1508		$\sigma s(CH_3), v (C-N)$
1579			v(C-C)

Table S2 Raman shifts (cm⁻¹) and assignments for 4-mpy (red), thiram (blue) and 2,2'-bpy (black).⁴⁻⁷

Section 5: The impact of thickness of the liquid on the SERS intensity



Figure S18. The schematic diagram of measuring the influence of the thickness of the liquid on the intensity of SERS signal.



Figure S19. Illustration of measuring the influence of the thickness of the liquid on the intensity of SERS signal.(a) a self-made device for measuring the influence of the thickness of the solution on the intensity of SERS signal. (b) an adjustable mobile platform with a scale. (c) the accuracy of platform movement can reach 1mm.(d) acquisition spectrum.



Figure S20. The Au-AgN sensor close to the inner wall of the cuvette (a) and corresponding position of the platform (b).



Figure S21. Different positions of needles in the liquid and the corresponding displacement of the platform; (a) 1mm, (b) 2mm, (c) 3mm, (d) 4mm, (e)5mm, (f) 6mm.



Figure S22. SERS of CV molecule at Au-AgN sensor. Liquids between objective lense and Au-AgN sensor has defferent thickness of 1, 2, 3, 4, 5 and 6mm. Inset: the relationship between the Raman intensity of 1175 cm^{-1} band and the corresponding thickness of the solution.

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