Supporting Information

Development of a novel wavelength selection method for the trace determination of chlorpyrifos on the Au@Ag NPs substrate coupled surface-enhanced Raman spectroscopy

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1. The preparation of Au@Ag NPs

First, 0.25 ml of 0.1 M $HAuCl_4$ was added to 100ml of ultrapure water and then heated to boiling temperature under magnetic stirring. After injecting 1.5 ml of 1% sodium citrate, the mixed solution was refluxed for ~30 min until it turned wine red. After gradually cooling to room temperature under stirring, the resulting solution was filtered through 0.22 μm Millipore membrane, and the Au NPs colloid with the size of 30 nm was stored in a refrigerator at 4 ºC for further use. Secondly, 10 ml of Au NPs colloid and 1.5 ml of 0.1 M ascorbic acid were mixed in a round-bottom flask under magnetic stirring. Then 3.5 ml of 1mM $AgNO_3$ was added dropwise to the mixture at a rate of one drop per 30 s. Silver nitrate was reduced by ascorbic acid and the resultant silver continuously grew at the surface of Au seeds. The solution was stirred for an additional 30 min after the wine red of solution changed into orange-yellow.

2. The enhancement factor (EF) of Au@Ag NPs

The EF of Au@Ag NPs is an important parameter which should be estimated. In this study, the EF was calculated using the following formula:

$$EF= (I_{SERS}/I_S) \times (C_S/C_{SERS}) \quad (1)$$

where C_S is the concentration of the analyte that produces a spontaneous Raman signal, and C_{SERS} is the concentration of analyte analyzed in SERS enhancement substrate. The I_S and I_{SERS} represent Raman signals intensity under the above mentioned experimental conditions, respectively. For 2.5×10^{-3} mol/L chlorpyrifos(CPS) standard solution without a SERS amplification effect, the acquired Raman signal intensity at 1260 cm^{-1} was approximately equal to the signal intensity obtained from 1.0×10^{-9} mol/L CPS standard solution deposited with Au@Ag NPs. Hence, the EF is calculated to be 2.5×10^6 and this value is enough for the detection

of CPS residues.

3. The reproducibility of CPS SERS spectra enhanced by Au@Ag NPs

Forty SERS spectra were collected (1.0×10^{-4}, 3.0×10^{-5}, 5.0×10^{-6} and 3.0×10^{-7} mol/L, 10 spectra for each concentration) and RSD values at different Raman characteristic bands were calculated. As shown in Table S1, all RSD values were less than 10%, which indicate that the reproducibility of CPS SERS spectra enhanced by Au@Ag NPs is good.

Table S1 Relative Standard Deviation (RSD, %) of Spectra Intensity Measurements (n=10)

SERS spectra (mol/L)	Wavelength (cm^{-1})					
	626	1085	1160	1260	1455	1570
1.0×10^{-4}	2.3	3.8	3.1	2.9	3.6	5.7
3.0×10^{-5}	3.5	2.4	3.6	4.0	4.2	6.8
5.0×10^{-6}	3.0	6.9	5.5	5.8	6.3	8.6
3.0×10^{-7}	5.7	7.1	6.8	7.6	7.7	8.3
Mean (%)	3.6	5.1	4.8	5.1	5.5	7.4

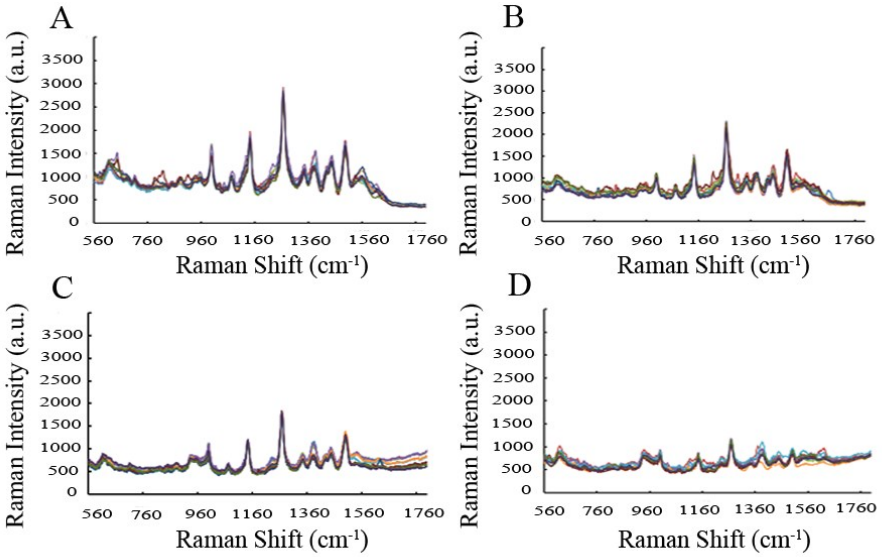

Fig.S1 The CPS SERS spectra collected from 10 samples at the concentration of (A) 1.0×10^{-4} mol/L. (B) 3.0×10^{-5} mol/L. (C) 5.0×10^{-6} mol/L. (C) 3.0×10^{-7} mol/L

4. The pretreatment of tea samples for SERS measurements

Pretreatment of green tea samples was done according to the previous reported literature.[1] In this work, Longjing tea samples were bought from the local supermarket in Zhenjiang (Jiangsu province, China) and the tea samples were intact. First, each sample of 10 g green tea samples was weighted and spiked with different concentration of CPS (1.0×10^{-4}, 1.0×10^{-5}, 1.0×10^{-6}, 1.0×10^{-7}, 1.0×10^{-8} mol/L) then dried at ambient temperature. A total of 50 samples (10 samples for each concentration) were prepared. After that, 10 mL of methylene chloride (CH_2Cl_2) was mixed with 0.25 g spiked tea sample in a 25 mL volumetric flask and ultrasonicated for 1 hr. Then the extract was filtered through Whatman no.1 paper. The extraction

procedure was repeated for three times and the extracts were collected. Then the extract was concentrated to 1 mL in a rotary evaporator and finally dried with a nitrogen stream. Finally, the residue was diluted with 1 mL water containing 5% ethanol then the supernatant was obtained after centrifuging at 6000 rpm for 5 min and the supernatant was filtered through an ENVI-carb extraction column. The filtered solution was used for SERS measurements. Fig. S1 shows the CPS SERS spectra at the concentrations from 1.0×10^{-4} to 1.0×10^{-8} mol /L.

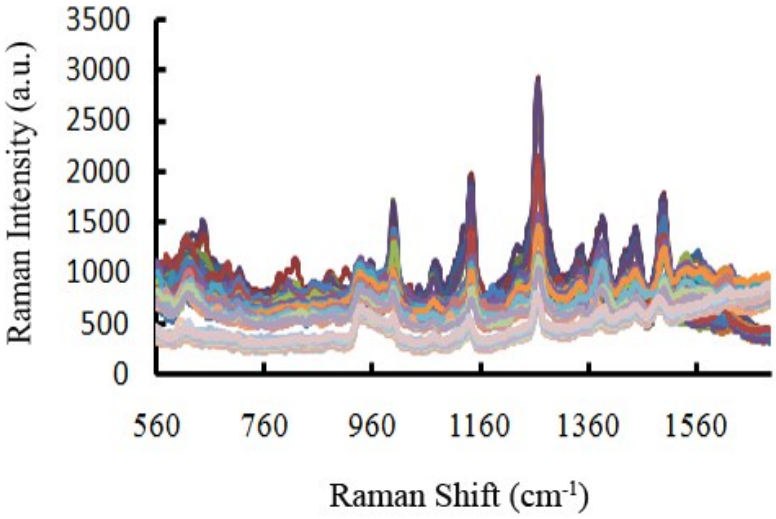

Fig. S2 The CPS SERS spectra with the concentrations from 1.0×10^{-4} to 1.0×10^{-8} mol /L.

5. The pretreatment of tea samples for GC-MS measurements

5 g of spiked tea sample was weighted and grounded using a pulverizer (A11, IKA, Germany) and then sieved by a 60 mesh sieves. The grounded tea sample was put into a 50 mL plastic centrifuge tube to which 10 mL water and 30 mL ethyl acetate were added for extraction. The mixture was homogenized for 2 min and centrifuged at 5000 rpm for 5 min. Thereafter supernatant was collected into a 250 mL round-bottom flask with anhydrous sodium sulfate. The residue was extracted again with 30 mL of ethyl acetate and the supernatant was dehydrated with anhydrous sodium sulfate. The mixture of two extracts was condensed to near dryness by a rotary evaporator in 40 ℃ water bath. Subsequently, the dry residue was dissolved with 2 mL of ethyl acetate/hexane (1:1, v/v) in a round-bottom flask, and the resultant was then subjected to solid phase extraction (SPE).

The active carbon SPE column (ENVI-Carb) was coupled to florisil SPE column (SIMON Florisil). The coupled SPE columns were rinsed with 6 mL of ethyl acetate/hexane (1:1, v/v) in advance. The 2 mL of extract in the round-bottom flask was injected into the coupled SPE columns and eluted with an additional 6 mL of ethyl acetate/hexane (1:1, v/v). The eluate was evaporated to near dryness in 40 ℃ water bath. The residue was dissolved with 1.0 mL of ethyl acetate and transferred into a 2 mL vial for GS-MS analysis.

6. The parameters of GC-MS system

The GC-MS system was equipped with an automatic sampler (AOC-20i+s), automatic injector and fused silica capillary column: HP-5. GC-MS solution software (release version 2.30) was used to obtain and analyze the data. The chromatographic conditions were: the injector was operated in a splitless mode. The column temperature was initially at 50 ℃ for 2 min and then the temperature was heated to 200 ℃ at a rate of 20 ℃/min and was kept for 1 min. The temperature was increased to 270 ℃ at a rate of 5 ℃/min and followed by 10 min stabilization. The injection port temperature was kept at 280 ℃, and the interface temperature at 250 ℃. A sample volume of 1 μL was injected into the instrument using ultra pure helium (purity ≥99.999%) as a carrier gas. The pressure was set to 53.5kPa and gas flow rate at 1.0 mL/min. The mass spectrometer conditions were: electron ionization mode (EI, 70 eV). The temperature of ion source was 230 ℃, and acquisition was in SIM mode. The solvent delay was 9 min. The detector gain was in absolute mode and detector voltage was at 1.0 kV. The scan interval was set to 0.2 s and the selected monitoring ion (m/z) was 197.

Table S2 Models performance results for the siPLS selected spectral intervals combinations

PLS Components	Spectral Interval	RMSECV
5	**[3 4 6 10]**	**0.2600**
5	[2 4 6 10]	0.2722
6	[4 6 9 10]	0.2751
5	[2 6 9 10]	0.2781
4	[2 6 8 10]	0.2795
5	[4 5 6 10]	0.2860
4	[2 5 6 10]	0.2863
4	[2 3 6 10]	0.2865
3	[3 6 9 10]	0.2867
5	[3 5 6 10]	0.2870

Table S3 A list of 184 wavelengths rearranged by mRMR based on wavelengths importance

Rank	Wavelength (cm^{-1})	Rank	Wavelength (cm^{-1})	Rank	Wavelength (cm^{-1})	Rank	Wavelength (cm^{-1})	Rank	Wavelength (cm^{-1})
1	1268	39	1683	77	645	115	1205	153	1405
2	1692	40	999	78	1190	116	636	154	747
3	1385	41	1068	79	979	117	1056	155	751
4	1270	42	1693	80	993	118	1005	156	1046
5	1274	43	1388	81	1242	119	977	157	754
6	1262	44	1217	82	1392	120	1058	158	1050
7	1381	45	1376	83	669	121	1203	159	985
8	1669	46	1677	84	1192	122	1052	160	987
9	1266	47	622	85	1243	123	1207	161	738
10	1272	48	1253	86	1397	124	1032	162	1406
11	1377	49	1687	87	1223	125	642	163	741
12	1697	50	631	88	649	126	1003	164	919
13	1276	51	1245	89	1209	127	1048	165	914
14	626	52	1001	90	656	128	891	166	640
15	1264	53	1670	91	1394	129	1194	167	749
16	1386	54	1070	92	1211	130	663	168	916
17	1695	55	1251	93	972	131	1060	169	712
18	1277	56	1698	94	667	132	968	170	921
19	1072	57	647	95	1062	133	1200	171	736
20	1383	58	1401	96	1395	134	714	172	1038
21	1690	59	1675	97	658	135	983	173	906
22	1374	60	1247	98	1064	136	721	174	912
23	1257	61	1219	99	718	137	1198	175	1042
24	1682	62	995	100	970	138	893	176	925
25	628	63	1680	101	660	139	638	177	908
26	1279	64	1249	102	743	140	895	178	910
27	997	65	1403	103	981	141	900	179	729
28	1679	66	651	104	1196	142	723	180	1036
29	1390	67	1672	105	745	143	1034	181	1593
30	1261	68	929	106	904	144	633	182	1620

31	1255	69	902	107	1201	145	1408	183	1583
32	1700	70	1685	108	654	146	889	184	1551
33	624	71	1221	109	966	147	725		
34	1066	72	989	110	1224	148	923		
35	1688	73	1674	111	898	149	1044		
36	1379	74	1188	112	665	150	727		
37	1259	75	1213	113	975	151	927		
38	1215	76	991	114	1054	152	716		

Reference

[1] H. Ru-Yan, J. Wei-Ting, Q. Xiao-San, W. Xiao-Hui, X. Yu and W. Xiao-Chun, *J. Agric. Food. Chem.*, 2013, **61**, 12565-12571.