

Supporting Material

Synergistic construction of SERS strategy by Fe₃O₄@PDA@AgNPs and GNA: accurate pursuit and efficient detection of probiotics

Shijie Liu^{ab1}, Qian Ding^{ab1}, Huihui Zhi^{ab}, Lijun Zhao^{ab*}, Miaoyun Li^{ab**}, Yanxia Liu^{ab},

Haoyun Li^{ab}, Dong Liang^{ab}, Yaodi Zhu^{ab}, Lingxia Sun^{ab}, Yangyang Ma^{ab}

^a College of Food Science and Technology, Henan Agricultural University,
Zhengzhou, 450002, P.R. China

^b Sauce braised and prefabricated products modern production school enterprise
research and development center, Henan Agricultural University, Zhengzhou, 450002,
P.R. China

¹ These authors contributed equally to this study.

*Corresponding author. Tel.: 86-371-63558150; E-mail: zhaolj2014@126.com

**Corresponding author. Tel.: 86-371-63558150; E-mail: limy7476@126.com

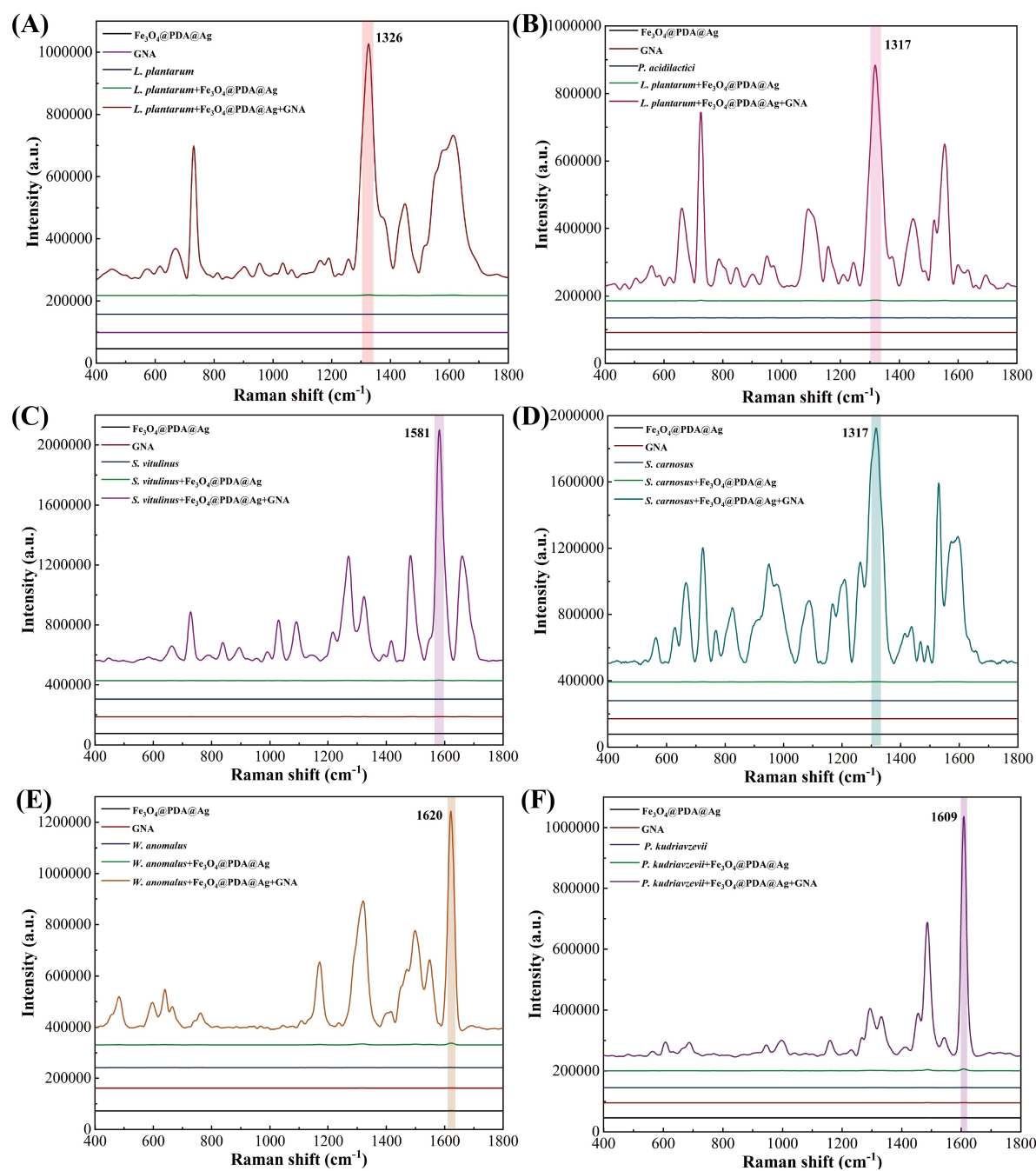


Fig. S1 The Raman spectrum enhancement effect of this strategy on probiotics.

(A)-(D) were the Raman spectra of *L. plantarum*, *P. acidilactici*, *S. vitulinus*, *S. carnosus*, *W. anomalus* and *P. kudriavzevii* before and after the strategy was enhanced respectively.

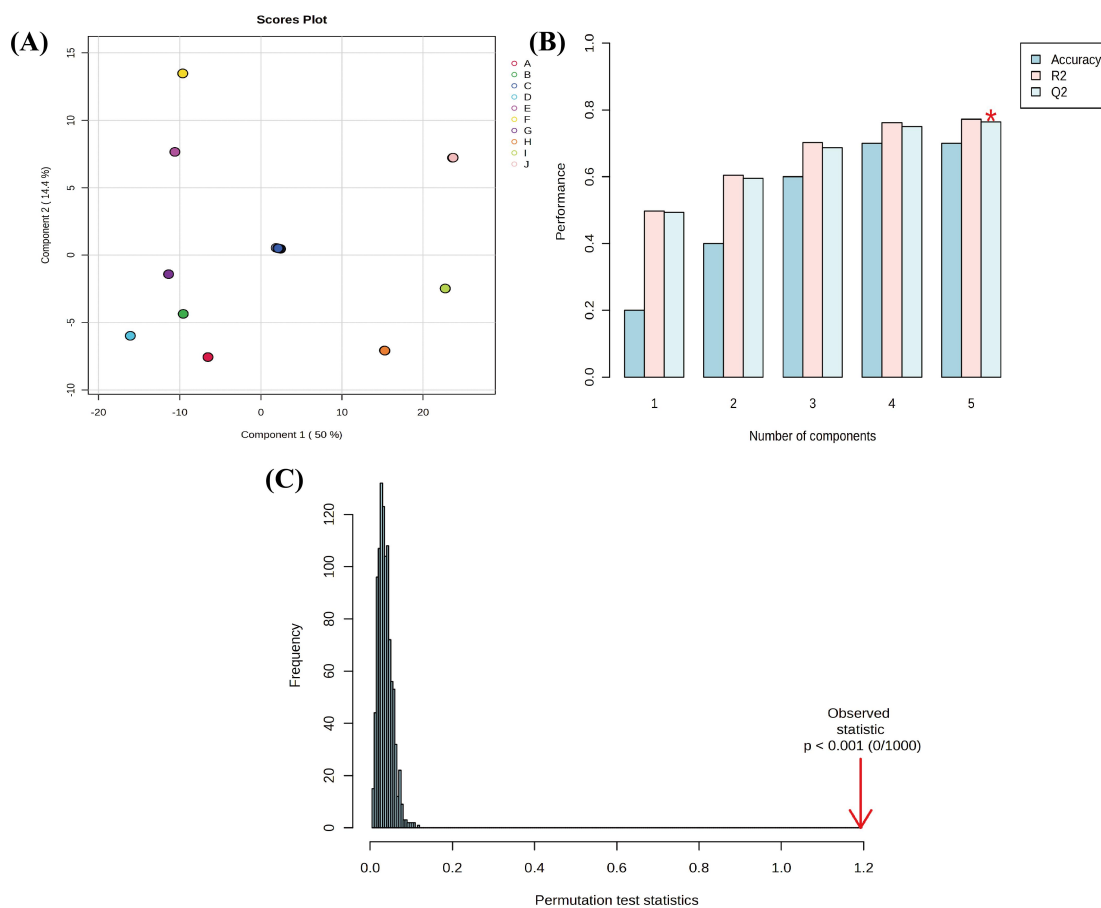


Fig. S2 (A), Classification effect of PLS-DA on SERS spectra of 10 probiotics; (B), 5-fold cross-validation result chart; (C), 1000 replacement checks.

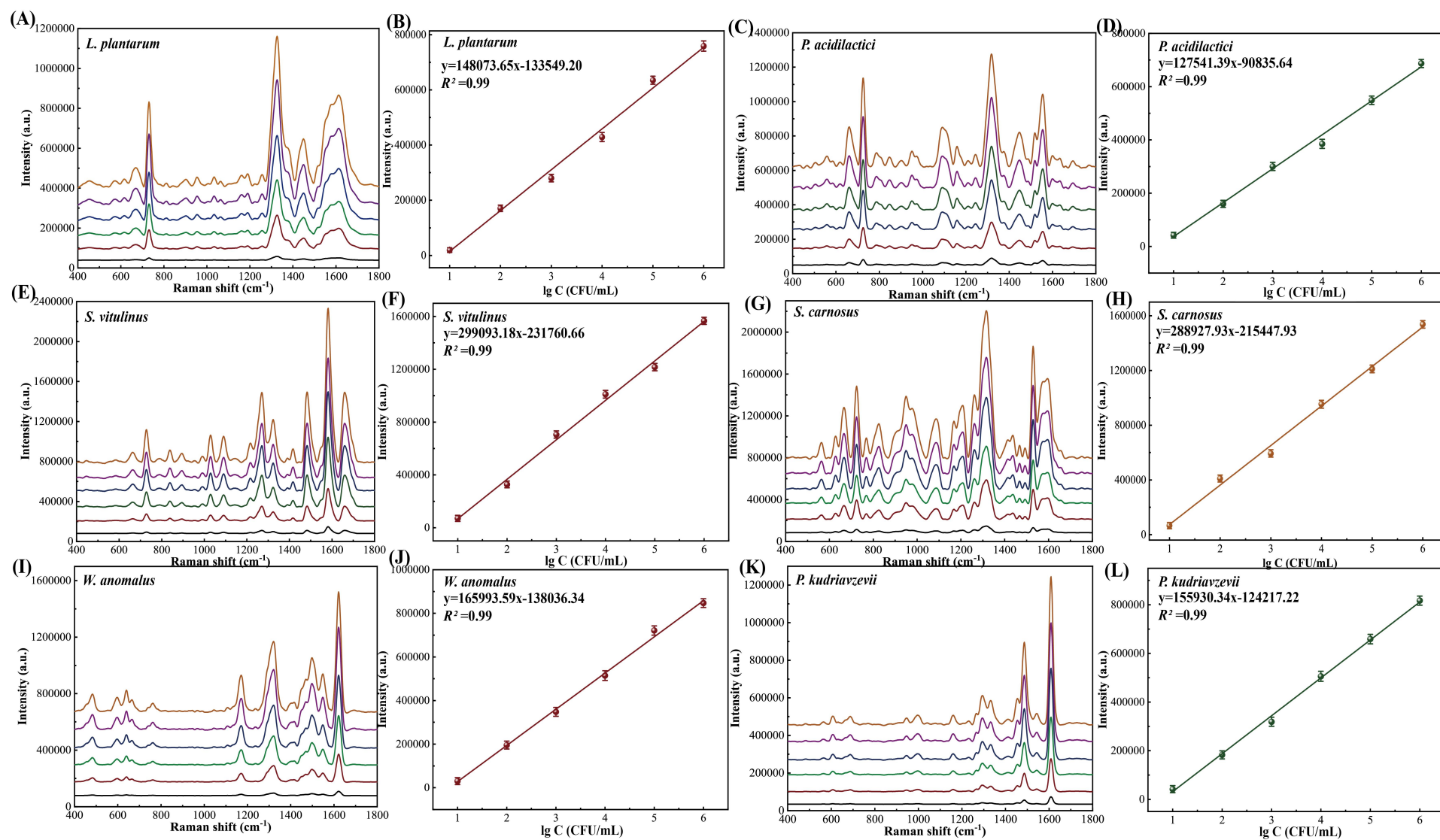


Fig. S3 Quantitative detection. (A) and (B), SERS spectra and the digitized quantitative equation of different concentrations of *L. plantarum*; (C) and (D), SERS spectra and the digitized quantitative equation of different concentrations of *P. acidilactici*; (E) and (F), SERS spectra and the digitized quantitative equation of different concentrations of *S. vitulinus*; (G) and (H), SERS spectra and the digitized quantitative equation of different concentrations of *S. carnosus*; (I) and (J), SERS spectra and the digitized quantitative equation of different concentrations of *W. anomalus*; (K) and (L), SERS spectra and the digitized quantitative equation of different concentrations of *P. kudriavzevii*.

Table S1 Information of strains used in the study

Genus	Species	Source
Lactic acid bacteria genus	<i>Lactiplantibacillus plantarum</i> (<i>L. plantarum</i> HAU L1)	Yogurt
	<i>Latilactobacillus sakei</i> (<i>L. sakei</i> HAU L2)	Yogurt
	<i>Pediococcus pentosaceus</i> (<i>P. pentosaceus</i> HAU P1)	Yogurt
Staphylococcus genus	<i>Pediococcus acidilactici</i> (<i>P. acidilactici</i> HAU P2)	Yogurt
	<i>Staphylococcus vitulinus</i> (<i>S. vitulinus</i> HAU S1)	Air-dried bacon
	<i>Staphylococcus xylosus</i> (<i>S. xylosus</i> HAU S2)	Air-dried bacon
	<i>Staphylococcus carnosus</i> (<i>S. carnosus</i> HAU S3)	Air-dried bacon
Yeasts genus	<i>Wickerhamomyces anomalus</i> (<i>W. anomalus</i> HAU J1)	Traditional jiaotou
	<i>Saccharomyces cerevisiae</i> (<i>S. cerevisiae</i> HAU J2)	Traditional jiaotou
	<i>Pichia kudriavzevii</i> (<i>P. kudriavzevii</i> HAU J3)	Traditional jiaotou

Table S2 SERS enhancement factor of this strategy

Number	Species	Raman shift/cm ⁻¹	Microorg anism	Intensity (a.u.)		EF	
				Microorganism+	Microorganism+	Fe ₃ O ₄ @PDA	Fe ₃ O ₄ @PDA
				Fe ₃ O ₄ @PDA@	Fe ₃ O ₄ @PDA@Ag	@Ag	@Ag
				Ag	+GNA		+GNA
1	<i>L. plantarum</i>	1326	152.67	2065.38	755342.26	1.35×10 ¹	4.95×10 ³
2	<i>L. sakei</i>	1321	152.98	2308.59	832521.74	1.51×10 ¹	5.44×10 ³
3	<i>P. pentosaceus</i>	1613	141.76	2766.61	1098352.19	1.95×10 ¹	7.75×10 ³
4	<i>P. acidilactici</i>	1317	153.52	1939.10	683936.33	1.26×10 ¹	4.46×10 ³
5	<i>S. vitulinus</i>	1581	128.51	2827.21	1564945.71	2.20×10 ¹	1.22×10 ³
6	<i>S. xylosus</i>	1456	109.99	2600.12	1412011.36	2.36×10 ¹	1.28×10 ³
7	<i>S. carnosus</i>	1317	125.58	2693.75	1537959.22	2.15×10 ¹	1.22×10 ³
8	<i>W. anomalus</i>	1620	407.12	6876.17	844552.68	1.69×10 ¹	2.07×10 ³
9	<i>S. cerevisiae</i>	1613	445.19	9419.05	1103948.35	2.12×10 ¹	2.48×10 ³
10	<i>P. kudriavzevii</i>	1609	428.59	6066.84	816041.04	1.42×10 ¹	1.90×10 ³

Table S3 Tentative attribution of Raman shift in SERS spectra of ten common probiotics

Raman shift (cm ⁻¹)										Assignment
<i>L. plantarum</i>	<i>L. sakei</i>	<i>P. pentosaceus</i>	<i>P. acidilactici</i>	<i>S. vitulinus</i>	<i>S. xylophilus</i>	<i>S. carnosus</i>	<i>W. anomalus</i>	<i>S. cerevisiae</i>	<i>P. kudriavzevii</i>	
		481	504		463		482	479		Skeletal modes of carbohydrates(starch)
572	561		558			563			567	Cell wall and cell membrane
	598	598					598	596	606	C-C twisting mode (protein)
617			618		614	627	639			Phenylalanine(skeletal)
668	660	666	661	664	664	665	666	666	687	C-S stretch model of cysteine
730	725		726	727	726	724				Adenine (nucleic acids)
	769	758				768	761	759		NAG, NAM (glycosidic ring mode)
			787	787	799					Cytosine or uracil (nucleic acids)
810						825				O-P-O stretching or tyrosine
	857		846	838						Proline, hydroxyproline and tyrosine
	899			894						Phosphodiester backbone, deoxyribose
903			902							C-COO- stretch (carbohydrates)
954	945	945	950	953	959	950		945	946	Phospholipids N-C stretching
	998	999		991				992	996	Phenylalanine (proteins)
1034	1030			1028	1011					CC ring breathing (polysaccharide)
1064					1069			1047		C-N stretch
	1082		1091	1090	1124	1086	1108			Stretch of O=P-O (nucleic acid)
1160	1163	1163	1159		1156	1168	1170	1163	1159	C-C stretch
1195			1210	1216	1197	1208				CH ₂ stretching, Amide III (protein)
1256	1256		1245		1232	1262	1237			PO ₂ ⁻ expansion, Amide III
				1270					1267	Amide I
					1295				1293	-CH ₂ deformation
1326	1321	1317	1317	1323	1323	1317	1319	1318	1332	Adenine (nucleic acids)
	1376			1389						Amide III
				1416			1417		1409	Symmetric vibration of COO ⁻
1450	1458	1453	1446		1456	1436		1453	1455	C-H deformation (lipids)
				1481		1468			1488	-CH ₂ deformation
	1518	1491	1519			1492	1499	1492		Phenylalanine
		1544	1554		1550	1532	1549	1544	1545	Amine II

1597	1599	1581	1596			Guanine, adenine, and tryptophan (protein)
1613	1613	1632	1625	1620	1613	Amide II (protein)
			1659			Amide I (protein)
		1695				Amide I (unsaturated lipid)

Table S4 Screening results of characteristic peaks of SERS average fingerprint spectrum difference of ten common probiotics based on PLSDA analysis

Variable range	Raman shift/cm-1	Assignment	VIP
X582-X590	1607-1623	Amide II (protein)	2.91
X518-X521	1482-1488	-CH ₂ deformation	2.42
X147-X152	720-731	Adenine (nucleic acids)	1.34
X567-X570	1578-1584	Guanine, adenine, and tryptophan (protein)	1.39
X437-X438	1321-1324	Adenine (nucleic acids)	1.07
X359-X363	1164-1172	C-C stretch	1.06

Table S5 Digitized quantitative equations for SERS spectra of ten common probiotics based on this strategy

Number	Quantitative formula
<i>L. plantarum</i>	$y=148073.65x-133549.20, R^2=0.99$
<i>L. sakei</i>	$y=163348.88x-138514.74, R^2=0.99$
<i>P. pentosaceus</i>	$y=208166.23x-151441.62, R^2=0.99$
<i>P. acidilactici</i>	$y=127541.39x-90835.64, R^2=0.99$
<i>S. vitulinus</i>	$y=299093.18x-231760.66, R^2=0.99$
<i>S. xylosus</i>	$y=269644.59x-227003.92, R^2=0.99$
<i>S. carnosus</i>	$y=288927.93x-215447.93, R^2=0.99$
<i>W. anomalus</i>	$y=165993.59x-138036.34, R^2=0.99$
<i>S. cerevisiae</i>	$y=217024.67x-202330.34, R^2=0.99$
<i>P. kudriavzevii</i>	$y=155930.34x-124217.22, R^2=0.99$