Electronic Supplementary Material (ESI) for Analytical Methods.
This journal is © The Royal Society of Chemistry 2024

Supporting Information

Three-dimensional hotspot structures constructed from nanoporous gold with V-cavity and gold nanoparticles for surface-enhanced Raman scattering

Yang Xu, [a] Yan Wu, [b] Jianjun Wei,*[a] Yuanyu Zhao, [b] Peili Xue, [b]

[a] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China.

[b] Sichuan Science City Hospital, Mianyang 621000, China.

*Corresponding Authors:

Jianjun Wei: weijianjun@scu.edu.cn

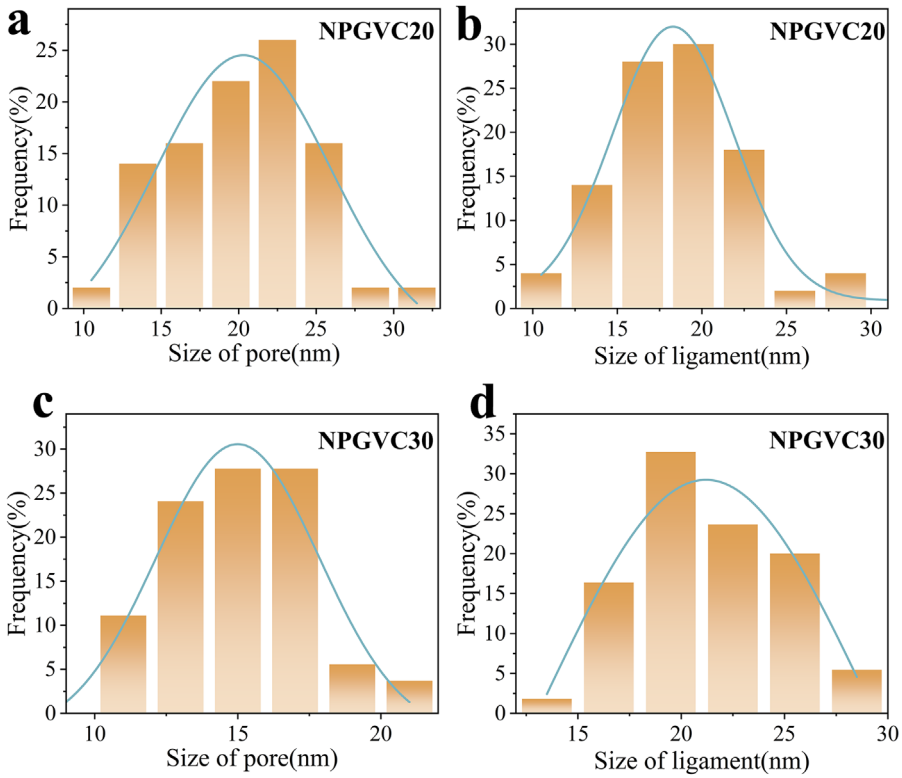

Figure S1. Statistical results of feature size for different NPGVC structure. a, c) The size of pore. b, d) The size of ligament.

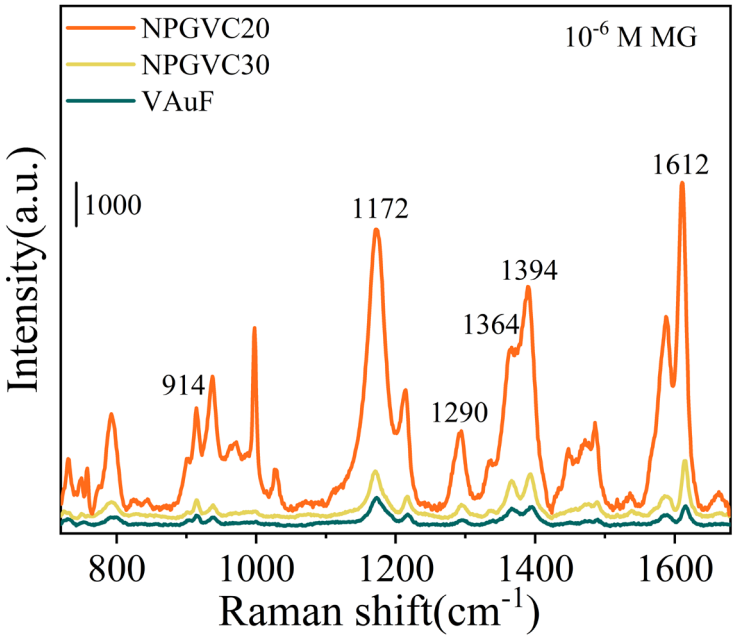

Figure S2. SERS spectra of 10^{-6} M MG molecules on the NPGVC20, NPGVC30, and VAuF.

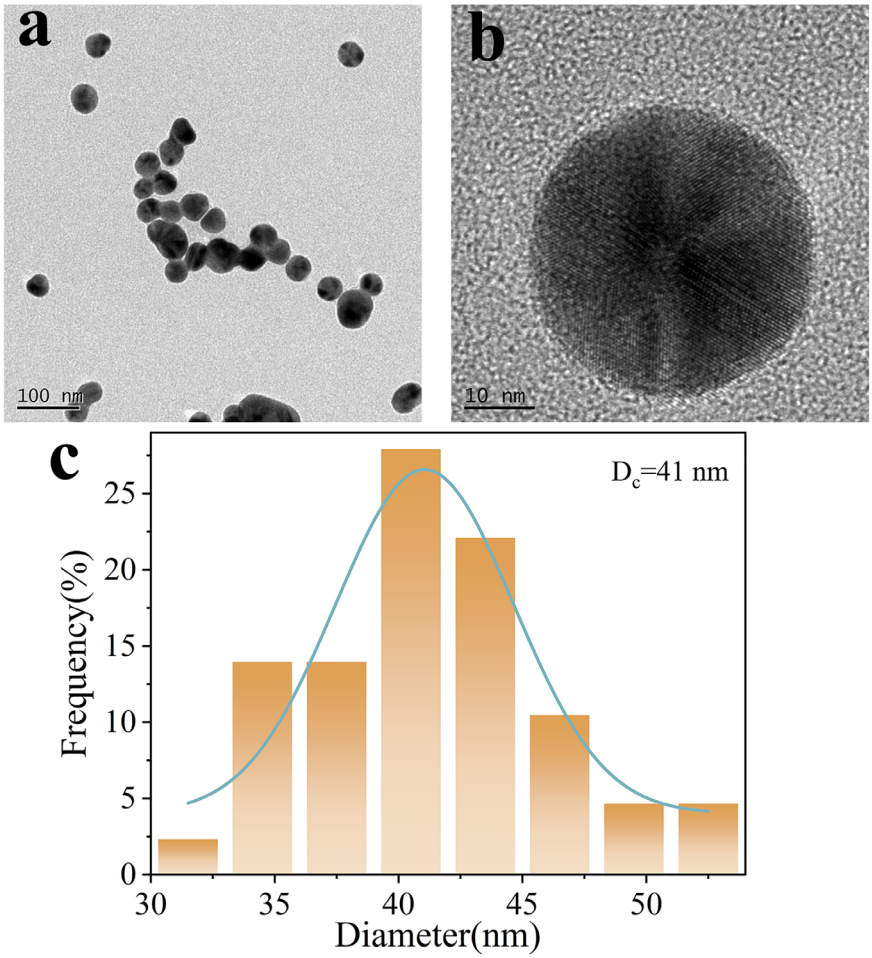

Figure S3. a) TEM images of the prepared AuNPs. b) Statistical results of particle size for AuNPs.

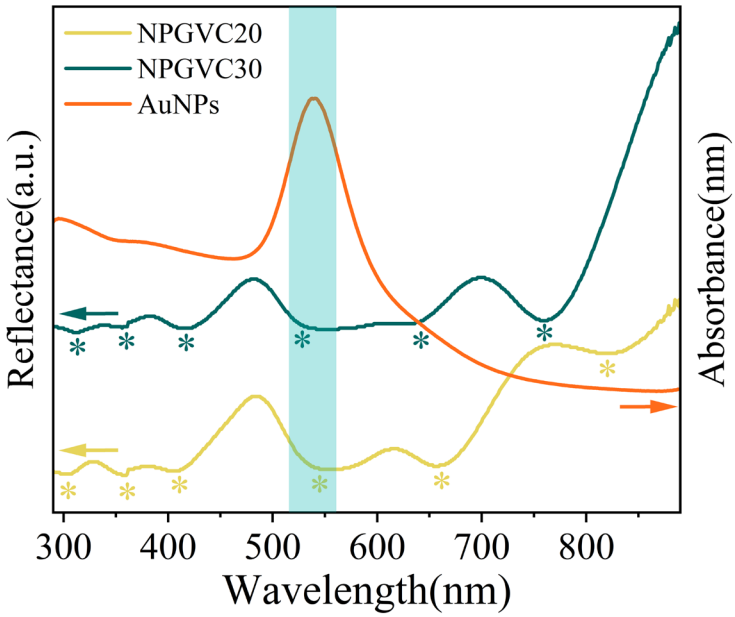

Figure S4. Reflectance spectra of NPGVC20 and NPGVC30; absorbance spectra of AuNPs.

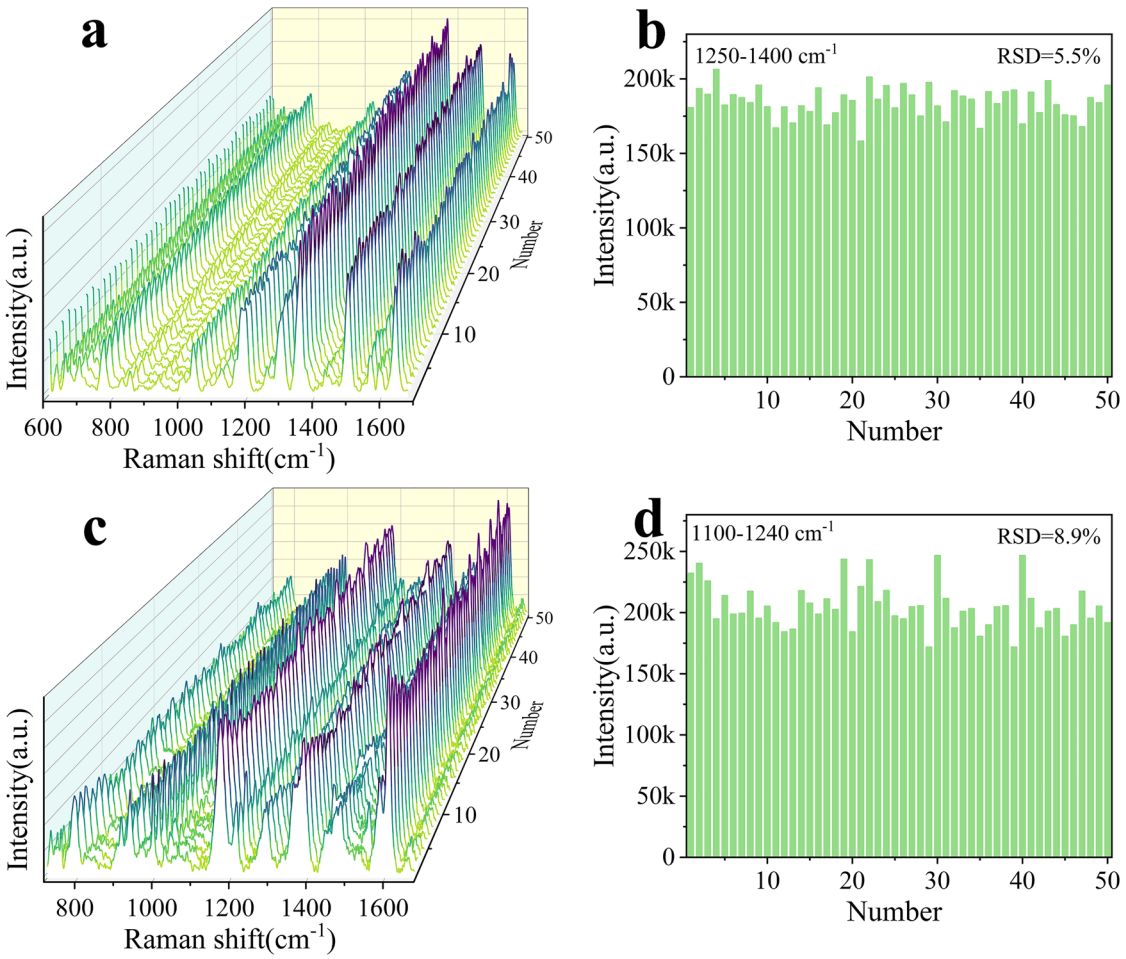

Figure S5. a) SERS spectra of 10^{-7} M R6G obtained at 50 randomly chosen spots on NPGVRC substrate. b) The corresponding relative standard deviation (RSD) values of a) for the integral area in the 1250~1400 cm^{-1}. c) SERS spectra of 10^{-7} M MG obtained at 50 randomly chosen spots on NPGVRC substrate. d) The corresponding RSD values of c) for the integral area in the 1100~1240 cm^{-1}.

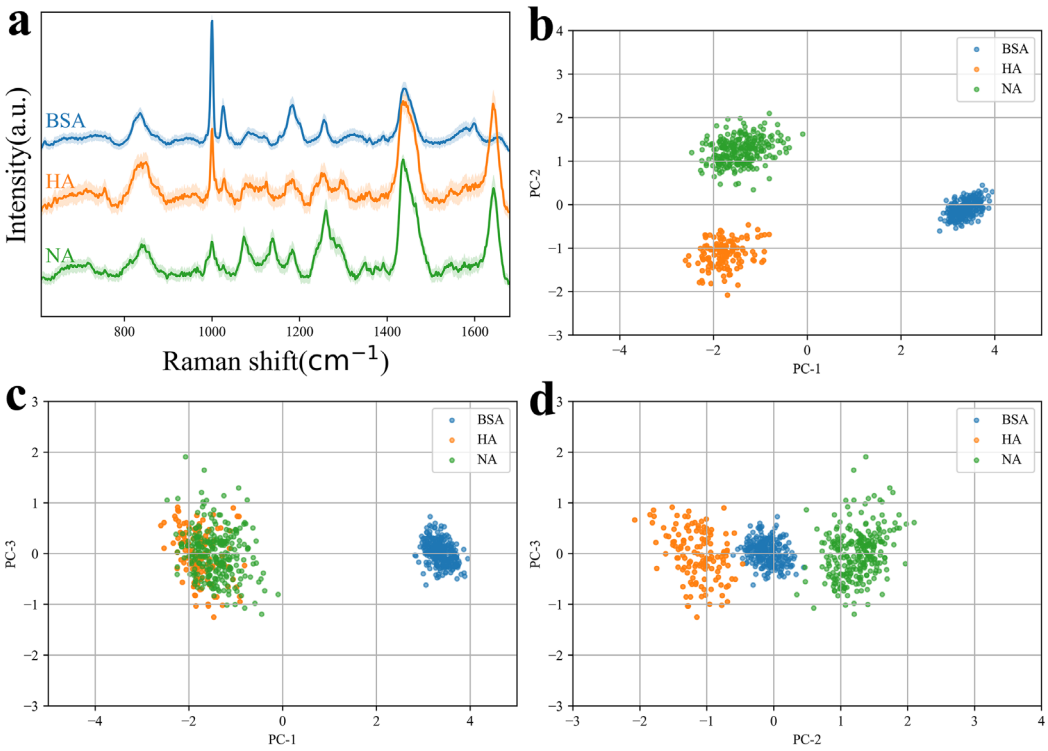

Figure S6. a) SERS spectra of HA, NA, and BSA detected by NPGVRC substrate. b-d) 2D projections of the PCA score plots for the SERS spectra of HA, NA, and BSA.

Table S1. Raman band assignment for the R6G molecule in experiment and theory.[1]

Vibrational mode	Theory (cm^{-1})	Experiment (cm^{-1})
C–C xanthene/phenyl rings bending	615	611
C–H out-of-plane bending	771	772
C–H in-of-plane bending	1175	1184
C–O–C stretching in $COOC_2H_5$ group	1307	1304
C–C stretching in xanthene ring	1351	1360
C–C stretching in xanthene ring	1505	1502
C–C stretching in the phenyl ring	1577	1570
C–C stretching in xanthene ring	1652	1644

Table S2. Raman band assignment for the MG molecule in experiment and theory.[2–4]

Vibrational mode	Theory (cm^{-1})	Experiment (cm^{-1})
Ring skeletal radial vibration	918	914
Aromatic C–H bending in-plane	1172	1172
Aromatic C–H bending in-plane	1289	1290
N–C stretching	1360	1364
C–C and C–H in-plane motions	1395	1394
N–C bonding and C–C stretching	1616	1612

Table S3. Raman band assignment of HA, NA normal spectra, HA and NA SERS spectra.[5–12] Ile: Isoleucine, Trp: Tryptophan, Tyr: Tyrosine, Val: Valine, Ser: Serine, His: Histidine, Glu: Glutamic, Thr: Threonine, Pro: Proline, Asp: Aspartic acid, Phe: Phenylalanine, Arg: Arginine, Gly: Glycine, Lys: Lysine, Met: Methionine, Cys: Cysteine, Ala: Alanine, Gln: glutamine, Gal: Galactose, Man: Mannose, GlcNAc: N-acetyl-D-glucosamine, Fuc: Fucose, Glc: Glucose, str: stretch vibration, def: deformation vibration, ben: bending vibration, sym: symmetrical, asym: asymmetrical.

Raman shift (cm^{-1})				Possible band assignment			Ref.
HA normal	NA normal	HA SERS	NA SERS	Backbone	Side-chain	Glycan	
619	619	620		Amide IV			5, 6
642	642	642			C–S str		5
710	710				C–S str trans, Ile		5, 7
760	760	756	757	Amide V	Trp		5-8
830	830	830	830	C–C str	Tyr, Val, Ile	Gal, Man	7-11
839	843	840	841	C–C str	Tyr, Ser, Val, His		7, 8
852	850	854	855	C–C str	Ile, Tyr, Ala		7, 8
885	884	888	884		Trp, Glu, Thr	Man	7, 8
1004	1004	1001	1001		sym. ring C–C str, Phe		7, 8
1015	1015	1015	1015	C–C str			7, 8
1031	1031	1029	1028		ring CH def, Phe, Gly		7, 8
1064	1064			C–N str	Glu, Ser		7, 8
1075	1075	1077	1074	C–N str	Ile, His, Arg, Glu, Asp	Man	7, 8
1130	1128	1126		C–N str	NH_3^+ def, Trp, Ile, Gly	GlcNAc	5, 7, 8
1138	1139		1137	C–N str	Trp, Ile, Gly		7, 8
1178	1176	1179	1179		Tyr, His		7, 8
1208	1208				Tyr, Phe		7, 8
1245	1246	1245	1246	Amide III (β-sheet, coil)	CH_2 ben, Ile		5, 12
1265	1263	1260	1262	Amide III (α-helix)	CH_2 ben, Ile		5, 11
1300	1301	1302	1302	Amide III (β-turn)	CH_2 ben, Glu, Cys	Gln	5, 12
		1354	1352	C-H def		GlcNAc	7, 8
		1389	1392		COO^- sym str		7, 8
1445	1442	1444	1438	CH_2 def	Gly, Leu, Pro, Trp	Hln	5
1468	1468	1471	1467		Ala		7, 8
1554	1553	1548	1546	Amide II	Trp		5, 7, 8
1655	1654	1644	1644	Amide I			5, 12

Reference

1 H. Watanabe, N. Hayazawa, Y. Inouye and S. Kawata, *J. Phys. Chem. B*, 2005, **109**, 5012–5020.

2 C. Tsai, J. Lin and C. Lin, *Talanta*, 2007, **72**, 368–372.

3 Y. Zhao, Y. Tian, P. Ma, A. Yu, H. Zhang and Y. Chen, *Anal. Methods*, 2015, **7**, 8116–8122.

4 T. T. K. Chi, N. T. Le, B. T. T. Hien, D. Q. Trung and N. Q. Liem, *Commun. Phys.*, 2017, **26**, 261.

5 A. Rygula, K. Majzner, K. M. Marzec, A. Kaczor, M. Pilarczyk and M. Baranska, *J. Raman Spectrosc.*, 2013, **44**, 1061–1076.

6 R. Tuma, *J. Raman Spectrosc.*, 2005, **36**, 307–319.

7 G. Zhu, X. Zhu, Q. Fan and X. Wan, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.*, 2011, **78**, 1187–1195.

8 J. De Gelder, K. De Gussem, P. Vandenabeele and L. Moens, *J. Raman Spectrosc.*, 2007, **38**, 1133–1147.

9 E. Wiercigroch, E. Szafraniec, K. Czamara, M. Z. Pacia, K. Majzner, K. Kochan, A. Kaczor, M. Baranska and K. Malek, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.*, 2017, **185**, 317–335.

10 P. H. Arboleda and G. R. Loppnow, *Anal. Chem.*, 2000, **72**, 2093–2098.

11 G. Cerchiaro, A. C. Sant'Ana, M. L. A. Temperini and A. M. Da Costa Ferreira, *Carbohydr. Res.*, 2005, **340**, 2352–2359.

12 J. Kong and S. Yu, *Acta Biochim. Biophys. Sin.*, 2007, **39**, 549–559.