Electronic Supplementary Material (ESI) for Analyst.

Electronic Supplementary Information

Highly Sensitive AuNSs@AgNR SERS Substrates for Rapid Determination of Aromatic Amines

Qian Zhang,[a] Zhenglin Liu,[a] Hengchang Zhang,[a] Caiqin Han,[a] Ying Wu,[a] Changchun Yan,[a] Ying Liu,[a] Bin Wu,*[b] Guohai Yang,*[c] Peitong Duan*[a,d]

[a.] Jiangsu Key Laboratory of Advanced Laser Materials and Devices, School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, China.

[b.] The 41st Institute of China Electronics Technology Group Corporation, Qingdao 266555, China.

[c.] School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, China.

[d.] National University Science Park, Jiangsu Normal University, Xuzhou 221009, China.

* Corresponding author, E-mail: a. dpthcq@jsnu.edu.cn; b. wubin@ei41.com; c. yangguohai@jsnu.edu.cn

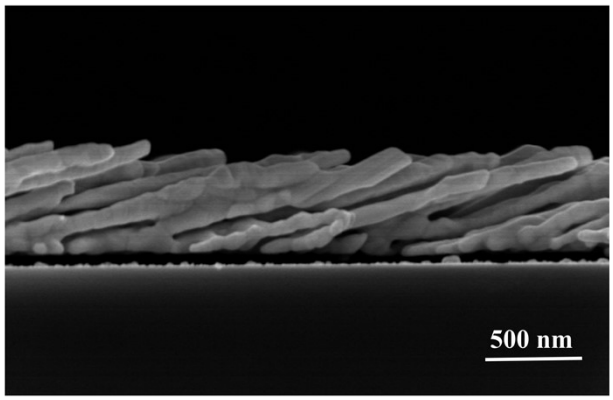

Fig. S1. Cross-sectional view of the AgNR substrate.

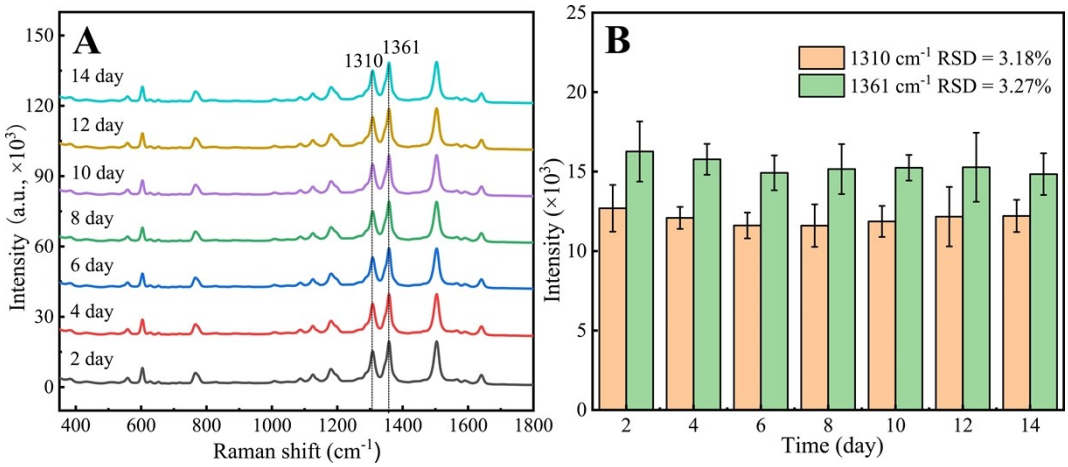

Fig. S2. (A) SERS spectra of R6G collected from AuNSs@AgNR substrate sealed for two weeks; (B) histogram of peak intensity and storage time at 1310 cm^{-1} and 1361 cm^{-1}.

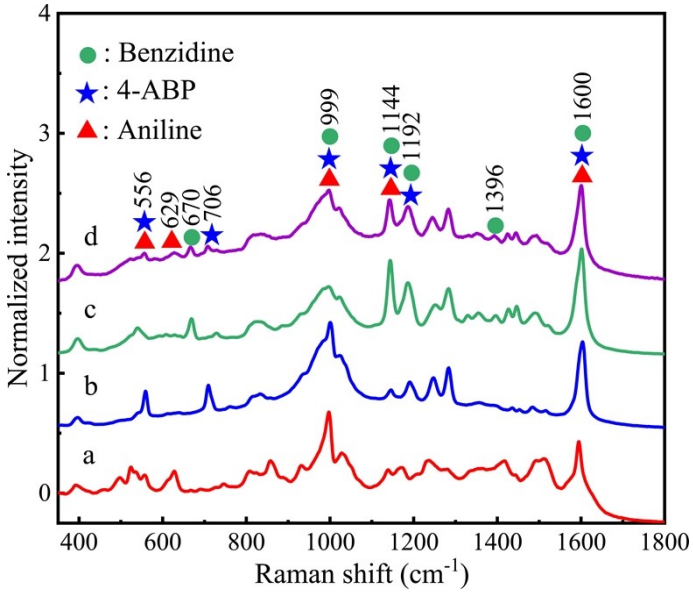

Fig. S3. SERS spectra of (a) aniline, (b) 4-ABP, (c) benzidine, (d) mixture of aniline, 4-ABP and benzidine. All spectra were normalized by the highest peak in each spectrum.

Table S1. Comparison of EFs based on R6G and CV for different nanomaterials.

Probe Molecule	SERS Substrate	EF	Ref.
R6G	Au nanodendrites on tape	1×10^{8}	1
	Rough gold nanoarrays	1.9×10^{7}	2
	HS-β-CD modified silver nanorods	3.2×10^{7}	3
	Urchin-like Ag hemispheres decorated with Ag nanoparticles	1.23×10^{6}	4
	Ag-nanoplates decorated polyacrylonitrile nanopillar	9.6×10^{6}	5
	Urchin-like AuNPs decorated Ag-nanohemisphere nanodot	1.23×10^{7}	6
	Graphene oxide embedded hierarchical silver particles and gold nanostars	2.59×10^{7}	7
	Graphene oxide-wrapped flower-like sliver particles	3.4×10^{5}	8
	β-cyclodextrin coated SiO_2@Au@Ag nanoparticles	2.247×10^{7}	9
	AuNSs@AgNR	4.67×10^{8}	This work
CV	RGO/Au NRs hybrid films	1×10^{3}	10
	Silver nanocubes	3.1×10^{5}	11
	3D silver metallized nanotrenches	1.7×10^{7}	12
	Wafer-scale SERS metallic nanotube arrays	4.21×10^{6}	13
	Twin-ZnSe nanowires	3.02×10^{5}	14
	Silver nanoparticles arrays	1×10^{7}	15
	Au nano-islands@Ag-frustum arrays	2.67×10^{7}	16
	AuNSs@AgNR	1.11×10^{8}	This work

Text S1.

Calculation of the Enhancement Factors (EFs) of AuNSs@AgNR substrates for R6G and CV.

The EFs of AuNSs@AgNR substrates to R6G and CV are calculated by the following formulas:

$$EF = \left(\frac{I_{SERS}}{I_{Raman}}\right) \times \left(\frac{N_{Raman}}{N_{SERS}}\right) \quad (1)$$

$$N_{SERS} = C_{SERS} V_{SERS} \times \frac{S_{Laser}}{S_{SERS}} \times N_A \quad (2)$$

$$N_{Raman} = C_{Raman} V_{Laser} \times N_A \quad (3)$$

I_{SERS} and I_{Raman} are the SERS and Raman peak intensity of R6G at 1361 cm^{-1} and CV at 1177 cm^{-1}. N_{Raman} and N_{SERS} are the quantity of molecules generating Raman signal and SERS signal collected under the light spot. C_{Raman} = 10^{-2} M, C_{SERS} = 10^{-5} M were selected of R6G and CV. S_{SERS} is the dispersion area of the liquid to be measured on the AuNSs@AgNR substrate. In the experiment, V_{SERS} = 2 μL is R6G and CV solution volume, and $S_{SERS} = \pi r^2$ = 3.1 × 10^{-6} m^2 is the actual distribution area of droplets. $S_{Laser} = \pi r^2$ = 7.6 × 10^{-12} m^2 is spot irradiation area on the structure, N_A is the Avogadro constant. V_{Laser} = 2.5 × 10^{-12} m^3 is the volume of solution irradiated in the liquid pool. Finally, the EFs of AuNSs@AgNR substrates for R6G and CV were calculated to be 4.67 × 10^8 and 1.11 × 10^8, respectively.

Text S2.

Calculation of the Enhancement Factors (EFs) of AuNSs@AgNR substrates for benzidine and 4-ABP.

The EFs of AuNSs@AgNR substrates to benzidine and 4-ABP are calculated by the following formulas:

$$EF = \left(\frac{I_{SERS}}{I_{Raman}}\right) \times \left(\frac{N_{Raman}}{N_{SERS}}\right) \quad (1)$$

$$N_{SERS} = C_{SERS} V_{SERS} \times \frac{S_{Laser}}{S_{SERS}} \times N_A \quad (2)$$

$$N_{Raman} = C_{Raman} V_{Laser} \times N_A \quad (3)$$

I_{SERS} and I_{Raman} are the SERS and Raman peak intensity of benzidine at 1600 cm^{-1} and 4-ABP at 556 cm^{-1}. N_{Raman} and N_{SERS} are the quantity of molecules generating Raman signal and SERS signal collected under the light spot. C_{Raman} = 10^{-2} M, C_{SERS} = 10^{-5} M were selected of benzidine and 4-ABP. S_{SERS} is the dispersion area of the liquid to be measured on the AuNSs@AgNR substrate. In the experiment, V_{SERS} = 2 μL is benzidine and 4-ABP solution volume, and $S_{SERS} = \pi r^2$ = 3.1 × 10^{-6} m^2 is the actual distribution area of droplets. $S_{Laser} = \pi r^2$ =

7.6×10^{-12} m^2 is spot irradiation area on the structure, N_A is the Avogadro constant. V_{Laser} = 2.5×10^{-12} m^3 is the volume of solution irradiated in the liquid pool. Finally, the EFs of AuNSs@AgNR substrates for benzidine and 4-ABP were calculated to be 7.38×10^6 and 1.90×10^7, respectively.

References:

1. X. C. He, S. J. Yang, T. L. Xu, Y. C. Song and X. J. Zhang, *Biosens Bioelectron*, 2020, **152**, 112013.
2. C. H. Zhu, Q. S. Zhao, D. X. Huo, X. Y. Hu and X. J. Wang, *Mater Chem Phys*, 2021, **263**, 124388.
3. K. X. Sun, G. W. Meng, Q. Huang, X. L. Zhao, C. H. Zhu, Z. L. Huang, Y. W. Qian, X. J. Wang and X. Y. Hu, *J Mater Chem C*, 2013, **1**, 5015-5022.
4. H. B. Tang, G. W. Meng, Z. B. Li, C. H. Zhu, Z. L. Huang, Z. M. Wang and F. D. Li, *Nano Res*, 2015, **8**, 2261-2270.
5. Z. B. Li, Z. F. Du, K. X. Sun, X. He and B. S. Chen, *Rsc Adv*, 2017, **7**, 53157-53163.
6. H. B. Tang, G. W. Meng, Q. Huang, C. H. Zhu, Z. L. Huang, Z. B. Li, Z. Zhanga and Y. Zhang, *Rsc Adv*, 2014, **4**, 19654-19657.
7. C. Y. Zhang, B. C. Zhao, R. Hao, Z. Wang, Y. W. Hao, B. Zhao and Y. Q. Liu, *J Hazard Mater*, 2020, **385**, 121510.
8. C. Y. Zhang, R. Hao, B. Zhao, Y. Z. Fu, H. J. Zhang, S. Moeendarbari, C. S. Pickering, Y. W. Hao and Y. Q. Liu, *Appl Surf Sci*, 2017, **400**, 49-56.
9. Y. L. Lu, G. H. Yao, K. X. Sun and Q. Huang, *Phys Chem Chem Phys*, 2015, **17**, 21149-21157.
10. P. B. Jimenez-Vara, J. Johny, I. C. Novoa-de Leon, C. Guerrero-Bermea, D. F. Garcia-Gutierrez, D. I. Garcia-Gutierrez, L. Chavez-Guerrero and S. Sepulveda-Guzman, *Mater Lett*, 2020, **265**, 127405.
11. L. Liu, Y. Z. Wu, N. Q. Yin, H. M. Zhang and H. Ma, *J Quant Spectrosc Ra*, 2020, **240**, 106682.
12. A. Colnita, D. Marconi, N. E. Dina, I. Brezestean, D. Bogdan and I. Turcu,

Spectrochim Acta A, 2022, **276**, 121232.

13. Y. C. Lu, W. H. Chiang, C. Y. Liu, J. P. Chu, H. C. Ho and C. H. Hsueh, *Sensor Actuat B-Chem*, 2021, **329**, 129132.
14. G. T. Wang, H. N. Wei, Y. Tian, M. M. Wu, Q. Q. Sun, Z. S. Peng, L. F. Sun and M. Liu, *Opt Express*, 2020, **28**, 18843-18858.
15. S. Augustine, K. P. Sooraj, V. Pachchigar, C. M. Krishna and M. Ranjan, *Appl Surf Sci*, 2021, **544**, 148878.
16. M. Y. Li, J. Wu, C. N. Wang and J. H. Fang, *Vacuum*, 2020, **175**, 109265.