

## **Label-Free and ultrasensitive SERS detection of pesticide residue using 3D hot-junction of Raman enhancing montmorillonite/silver nanoparticles nanocomposite**

Xiaojuan Zhao<sup>a</sup>, Dan Sun<sup>b</sup>, Man Yu<sup>a</sup>, Yan Xu<sup>c</sup>, Hui Xie<sup>a,\*</sup>

a School of Materials Engineering, Xi'an Aeronautical University, Xi'an 710077, China

b School of Pharmacy, Nantong University, Nantong, Jiangsu 226001, China;

c State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry,  
Jilin University, Changchun 130012, P.R. China

\*Corresponding author

E-mail: [xiehui@xaau.edu.cn](mailto:xiehui@xaau.edu.cn).

Postal address: School of Materials Engineering, Xi'an Aeronautical University, Xi'an 710077,  
China

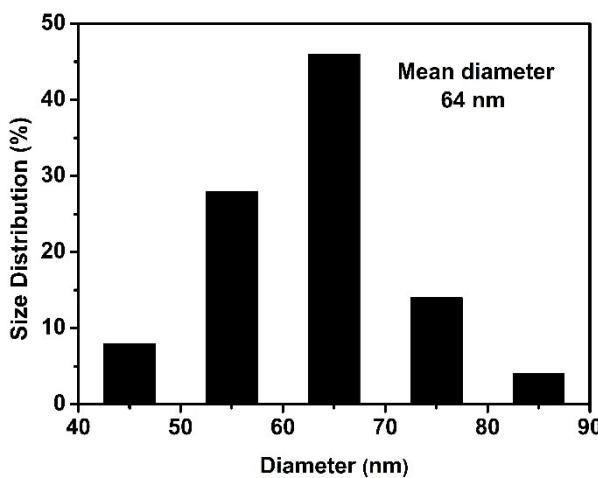


Fig. S1 Histogram of the AgNPs size distribution.

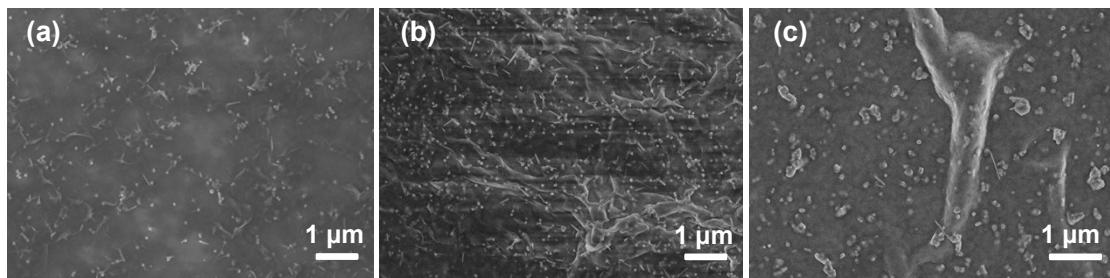


Fig. S2 SEM images of MMT/AgNPs nanocomposite with different volume ratio of MMT and AgNPs:  
(a) 1:7, (b) 1:10 and (c) 1:20.

Table S1 The SERS vibrational band assignments of thiram

Peak position ( $\text{cm}^{-1}$ )	Assignment
561	S–S stretching
931	C=S and $\text{CH}_3\text{N}$ stretching
1143	CN stretching, $\text{CH}_3$ rocking
1378	CN stretching, symmetric $\text{CH}_3$ deformation
1505	CN stretching vibration, $\text{CH}_3$ deformation, $\text{CH}_3$ rocking

Table S2 Comparison of the proposed approach with reported methods for the detection of thiram.

Method	Limit of detection	Detection range	$R^2$	Ref.
Fluorescence	0.1 $\mu\text{g/mL}$	0.5-2.5 $\mu\text{g/mL}$	0.9993	1
Fluorescence	70 nM	0.5-1000 $\mu\text{M}$	0.9926	2
Phosphorescence	25.0 nM	0.05-2.5 $\mu\text{M}$	-	3
Colorimetric	0.036 $\mu\text{M}$	0.1- 100 $\mu\text{M}$	0.95/0.99	4
Colorimetric	19.7 nM	0.025-0.35 $\mu\text{M}$	0.99345	5
Electrochemical	$0.7 \times 10^{-6} \text{ M}$	-	0.99	6
HPLC	0.22 $\mu\text{g/mL}$	0.07-15 $\mu\text{g/mL}$	0.9905	7
Raman	$10^{-7} \text{ M}$	$1.0 \times 10^{-7}$ - $1.0 \times 10^{-3} \text{ M}$	0.9978	8
Raman	50 ng/g	0.1-12 $\mu\text{g/g}$	0.9950	9
Raman	$1.0 \times 10^{-8} \text{ M}$	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-3} \text{ M}$	0.9927	This work

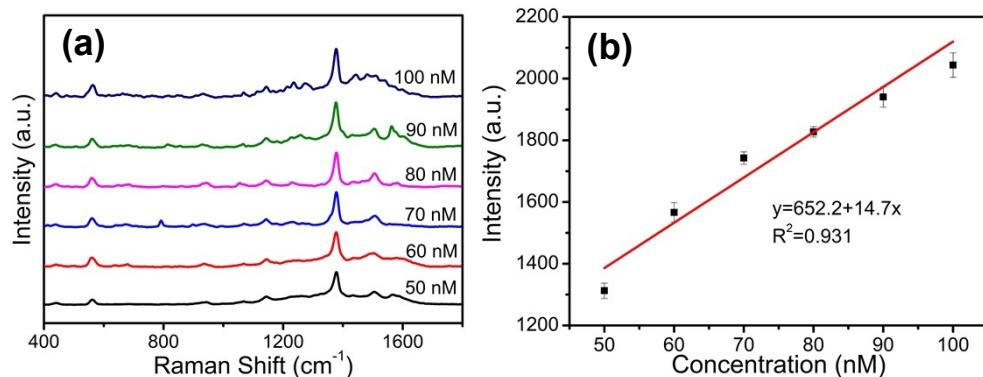


Fig. S3 (a) SERS detection of thiram on the apple. (b) The averaged peak intensities of the 1378  $\text{cm}^{-1}$  as a function of the concentration of thiram on the apple.

## References

1. Z. Tang, Z. Chen and G. Li, Y. Hong, *Anal Chim Acta*, 2020, **1136**, 72.
2. J.R. Bhamore, S. Jha, A.K. Mungara, R.K. Singhal, D. Sonkeshariya and S.K. Kailasa, *Biosens. Bioelectron.*, 2016, **0**, 243.
3. Z. Cheng, K. Zhang, T. Zhao, B. Liu, Z. Wang and Z. Zhang, *Sens. Actuators B Chem.*, 2017, **252**, 1083.
4. V.T. Hoang, N.X. Dinh, N.L.N. Trang, N.T. Khi, N.V. Quy, P.A. Tuan, D.Q. Tri, L.H. Thang T.Q. Huy and A.T. Le, *Mater. Res. Bull.*, 2021, **139**, 111278.
5. C. Zhang, X. Jiang, F. Yu, Y. Liu, Q. Yue, P. Yang and Y. Liu, *Sens. Actuators B Chem.*, 2021, **344**, 130304.
6. P.N. Ragam and B. Mathew, *Int J Environ Sci Te.*, 2020, **17**, 1739.
7. K. Charoenkitamorn, O. Chailapakul and W. Siangproh, *Talanta*, 2015, **132**, 416.
8. A. Jiao, X. Dong, H. Zhang, L. Xu, Y. Tian, X. Liu and M. Chen, *Spectrochim. Acta A.*, 2019, **209**, 241.
9. M. Chen, W. Luo, Q. Liu, N. Hao, Y. Zhu, M. Liu, L. Wang, H. Yang and X.Q. Chen, *Anal. Chem.*, 2018, **90**, 13647.