

Cite this: DOI: 10.1039/c0xx00000x

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PAPER

Cu@Ag/β-AgVO₃ as SERS Substrate for Trace Level Detection of Carbamate Pesticides

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

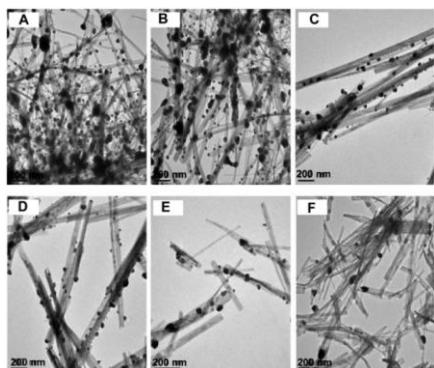


Figure S1. β-AgVO₃ TEM images in NO₃-Ag/NH₄VO₃ different molar ratios: (A) 4:1; (B) 3:1; (C) 2:1; (D) 1:1; (E) 1:2 and (F) 1:4.

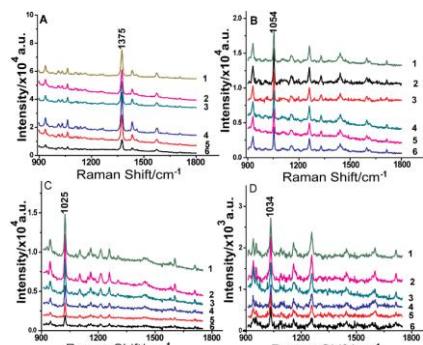
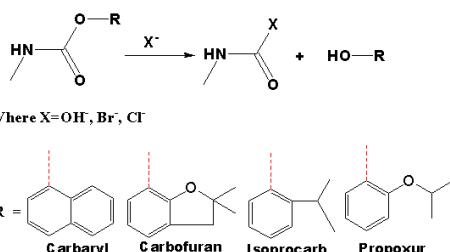


Figure S2. Cu immersion time effect on Cu@Ag/β-AgVO₃ substrate fabrication for carbamate detection. 8.0×10⁻² μM (A) carbaryl, (B) carbofuran, (C) isoprocarb and (D) propoxur. 1-6: 1, 5, 10, 20, 60 and 120 min



Scheme 1. Effect of salt.

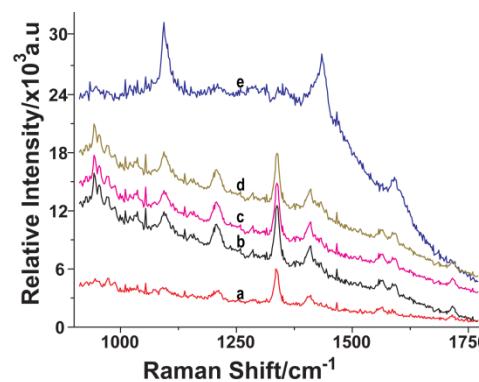


Figure S3. Interference of amino/phosphorous compounds on the detection of carbamate pesticides. (a, c) carbamate pesticides and 20 dATP, (b) carbamate pesticides and (d, e) carbamate pesticides and PPD. Concentration of each pesticides 1.0 μM, dATP (a) 1.0×10² μM and (c) 1.0×10³ μM, and PPD (d) 1.0×10² μM and (e) 1.0×10³ μM.

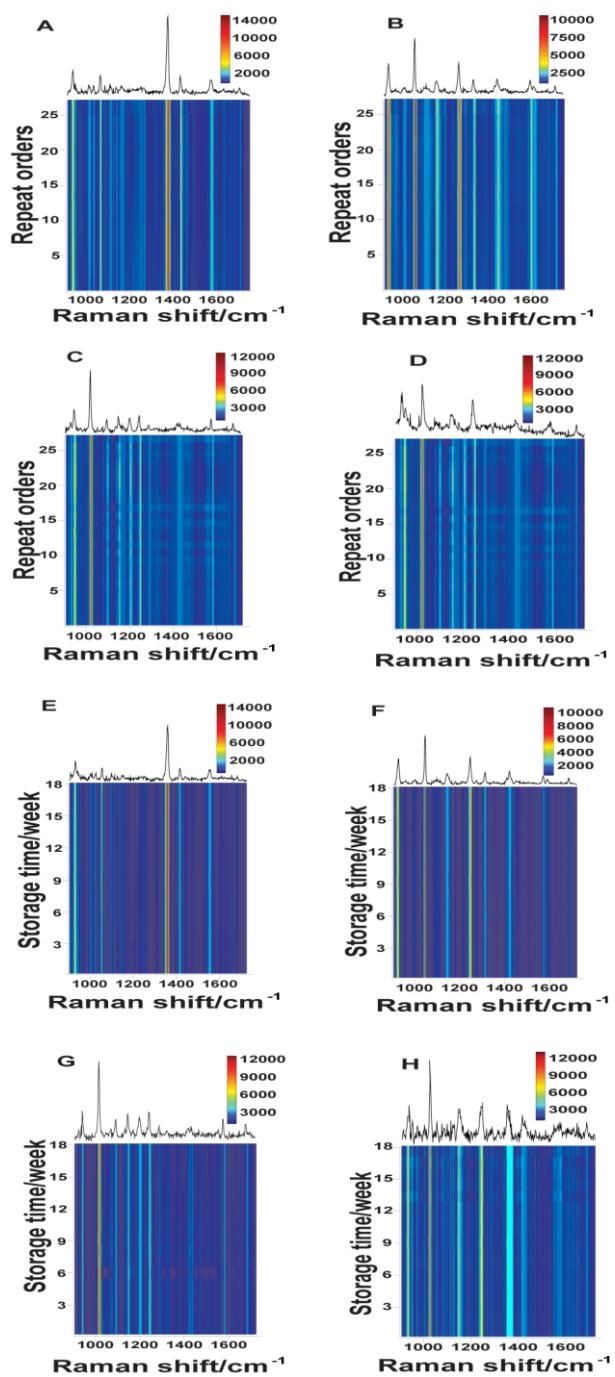


Figure S4. SERS spectra recorded 26 times successively on the same substrate for (A) carbaryl; (B) carbofuran; (C) isoprocarb and (D) propoxur; and SERS spectra at different weeks (18) for (E) carbaryl; (F) carbofuran; (G) isoprocarb and (H) propoxur in $1.0 \times 10^{-1} \mu\text{M}$ of each pesticide.

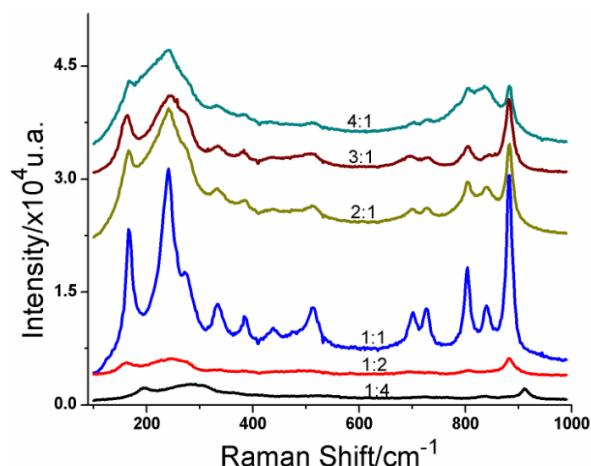


Fig S5. Normal Raman spectra (solid state) of synthesized products in different $\text{AgNO}_3/\text{NH}_4\text{VO}_3$ molar ratios.

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Carbamate pesticides band assignments

The band assignments of these carbamate pesticides on different substrate were done on the basis of general published data.^{1S,2S,3S}

Table S1. Carbamate pesticides peaks assignment

Literature position (cm ⁻¹)	Carbaryl			Carbofuran			Isoprocarb			Propoxur			Proposed assignment
	Ag [a]	NR [b]	TLC [c]	Ag-Cu [d]	NR [b]	Ag-Cu [d]	NR [b]	Ag-Cu [d]	NR [b]	Ag-Cu [d]	NR [b]	Ag-Cu [d]	
988			965	978									O-C stretching
1000-1090	1018, 1058	1010, 1035, 1068, 1115	1020, 1065	978, 1009, 1034, 1065, 1110	1014, 1057	1054	1024, 1099	1025, 1083	1035, 1099	1034, 1090			combination of the aromatic ring breathing mode, CH in-plane bending and CN stretching
1170-1190	1196	1164	1192	1165	1157, 1200	1156, 1194	1164, 1214	1160, 1184, 1212	1160	1158			C-N-CH ₃ asym str
1180-1280	1196	1223, 1270	1192, 1245	1165, 1248, 1266	1200, 1270	1156, 1194, 1263	1214, 1257	1184, 1212, 1260	1270	1255			C-N-C asym str
1214		1223			1200	1194	1214	1212					C=O stretching
1200-1265	1196	1223, 1270	1192, 1245	1248, 1266	1200, 1270	1194, 1263	1214, 1257	1212, 1260	1270	1255			Coupled C-N and C-O stretch
1275		1270	1245	1266	1270	1263		1260	1270	1255			C-C bridge-bands stretching
1285-1365					1270, 1292, 1329	1263,	1302	1302	1296				CH ₂ wag
1380	1363	1375	1370	1377	1330	1329		1384					CH ₃ deformation and symmetric in-plane bending, N-CH ₃ stretch
1400-1500	1447, 1500	1375, 1435	1450, 1500	1434, 1461	1443	1440	1457	1450	1446	1445			v(CC) aromatic (in ring) chain stretch vibrations
1400 - 1470	1447	1375, 1435	1370, 1450	1377, 1434, 1461	1443	1440	1457	1450	1446	1445			C-H bending, CH ₃ , CH ₂ in-plane bending
1500-1600	1500, 1552, 1580	1500, 1552, 1580	1500, 1555, 1585, 1620	1578, 1630	1597	1600, 1613	1603	1605	1597	1600			v(CC) aromatic (in ring) chain stretch vibrations
1500-1600	1500, 1552, 1580	1500, 1552, 1580	1500, 1555, 1585, 1620	1578, 1630	1597	1600	1603	1605	1597	1600			N-H stretc C-N defor
1680 - 1740	1580	1708	1585	1711	1708	1715	1713	1711	1715	1715			C=O stretching

[a]: silver nanoparticles colloids, [b]: Normal Raman in solid state, [c]: TLC plate used with Ag nanoparticles and [d]: Ag/β-AgVO₃/Cu substrate.

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