Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Informations

Combining 3-D Plasmonic Gold Nanorod Arrays with Colloidal Nanoparticles as a Versatile Concept for Reliable, Sensitive, and Selective Molecular Detection by SERS

*Mehmet Yilmaz[1,2], Erhan Senlik[1,2], Erhan Biskin[2,3], Mustafa Selman Yavuz[4], Ugur Tamer[5], Gokhan Demirel[1,3]**

[1]Bio-inspired Materials Research Laboratory (BIMREL), Department of Chemistry, Gazi University, 06500 Ankara, TURKEY

[2]Department of Chemical Engineering, Bioengineering Division, Hacettepe University, 06800 Ankara, TURKEY

[3]Biyomedtek: Center for Bioengineering, 06800 Ankara, TURKEY

[4]Department of Metallurgy and Materials Engineering, Selcuk University, 42075 Konya, TURKEY

[5]Department of Analytical Chemistry, Faculty of Pharmacy, Gazi University, 06330 Ankara, TURKEY

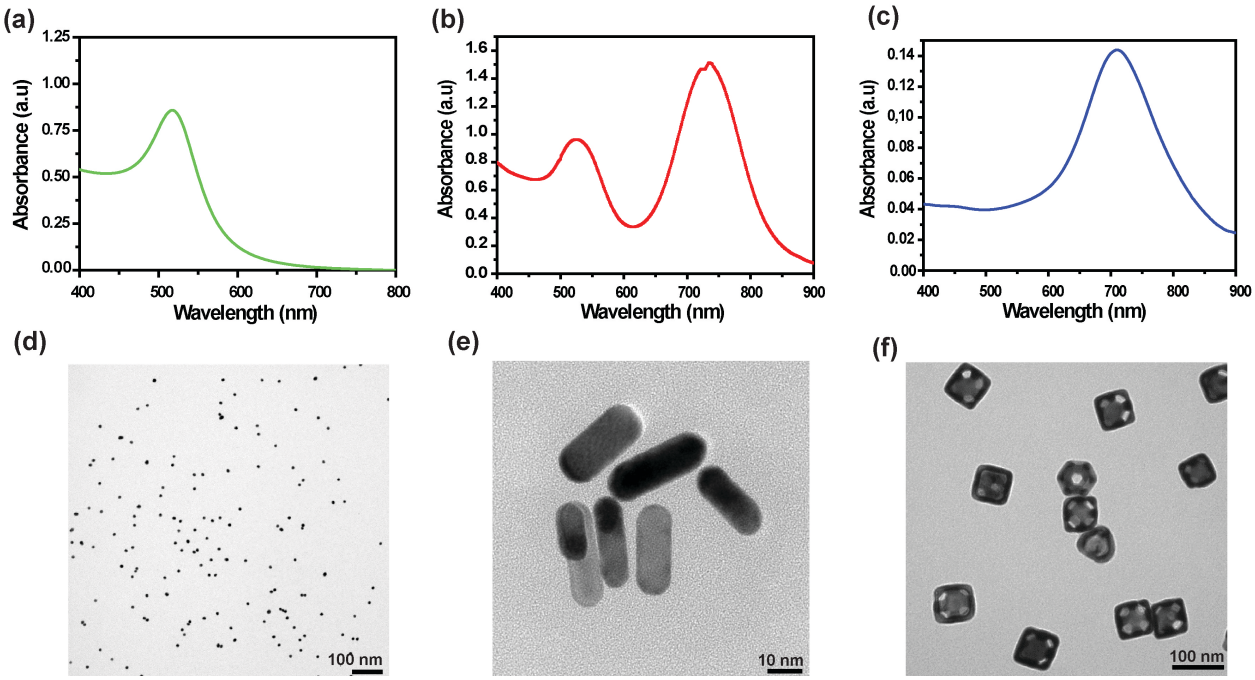

Figure S1. UV/Vis spectra of as-prepared colloidal gold nanoparticles: Gold nanospheres (AuNP) (a), Gold nanorods (AuNR) (b), and Gold nanocages (AuNC) (c). TEM images of synthesized colloidal gold nanoparticles: (a) AuNPs, (b) AuNRs, and (c) AuNCs.

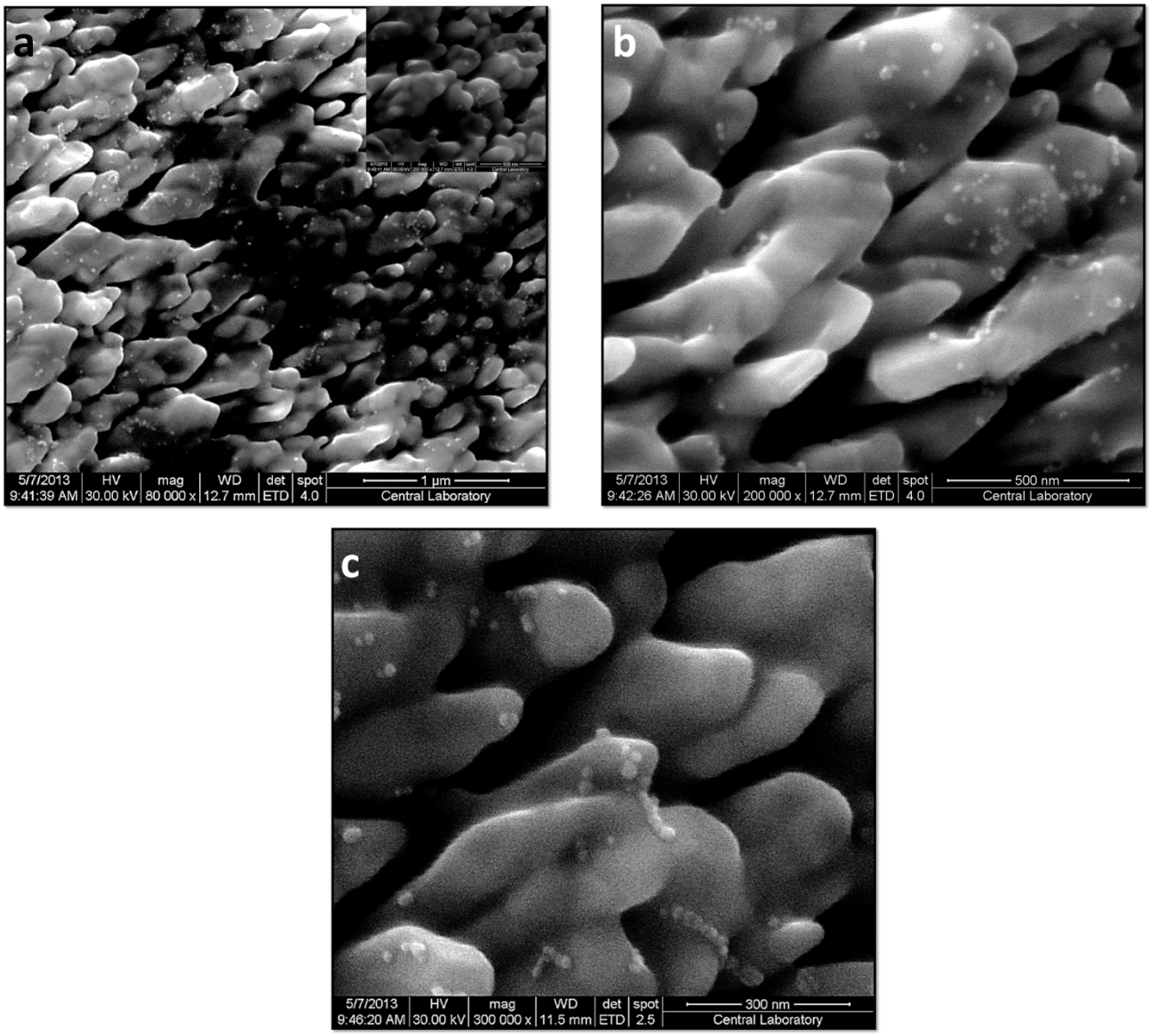

Figure S2. SEM images of colloidal gold nanoparticle decorated gold nanorod arrays: (a) nanospheres (AuNPs), (b) nanorods, and (c) nanocages on gold nanorod arrays (α=10°).

Table S1. The Raman shifts, relative intensities and peak assignments for MB.

Solid MB powder (cm^{-1})[1]	10 μM of MB on GNA and 20 ppm AuNR (cm^{-1})	Reported results (cm^{-1})[2]	Band assignments[1, 2b]
1618 (s)	1618 (s)	1617 (s)	*v*(C–C) ring
		1597 (w)	
1544 (w)	1575 (w)	1513 (w)	v_{asym}(C–C)
1441 (w)	1436 (w)	*1442 (m)*	v_{asym}(C–N)
1396 (m)	1395 (m)	1396 (m)	v_{sym}(C–N)
1331 (w)	1315 (w)		
1272 (w)	1290 (w)	1301 (m)	
1181 (m)	1177 (w)	*1184 (m)*	*v*(C–N)
	1149 (w)	*1121 (m)*	γ(C-H)
1067 (w)	1038 (w)	1030 (m)	β(C-H)
	882 (w)		
768 (w)	770 (m)		
677 (w)	667 (w)	670 (w)	γ(C-H)
	590 (w)	612 (m)	δ(C-S-C)
497 (w)	500 (m)	502 (m)	δ(C-N-C)
445 (s)	449 (s)	449 (m)	δ(C-N-C)

Abbreviations: GNA: Gold nanorod arrays fabricated at 10° of deposition angle; AuNR: colloidal gold nanorods; s, strong; m, medium; w, weak; *v*, stretching; α, in-plane ring deformation; β, in-plane bending; γ, out-of-plane bending; and δ, skeletal deformation.

Table S2. The Raman shifts, relative intensities and peak assignments for DIP.

Solid DIP powders[3] (cm^{-1})	5 ppm of DIP on GNA and 20 ppm AuNR (cm^{-1})	Reported results[3] (cm^{-1})	Band assignments[3]
1569 (m)	1572 (m)	1576 (m)	*v*(C–C) ring
	1518 (m)		v_{asym}(C–C)
1437 (m)	1445 (m)	*1443 (w)*	*v*(C–C) ring
1317 (m)	1370 (s)	1326 (m)	*v*(C–O)
1289 (m)	1298 (m)	1271 (m)	β(C-H)
1146 (m)	1156 (s)	*1150 (m)*	
1080 (w)	1073 (w)	*1060-1095 (m)*	Trigonal ring breathing
987 (s)	998 (w)	996 (s)	Symmetric ring breathing
933 (w)	953 (m)	938 (m)	γ(C-H)
885 (m)	880 (w)	891 (m)	
844 (m)	817 (m)		β(C-CO2)
748 (m)	739 (w)		δ(O-C-O)
639 (m)	655 (w)		γ(C-H)

Abbreviations: GNA: Gold nanorod arrays fabricated at 10° of deposition angle; AuNR: colloidal gold nanorods; s, strong; m, medium; w, weak; *v*, stretching; β, in-plane bending; γ, out-of-plane bending; and δ, skeletal deformation.

Table S3. The Raman shifts, relative intensities and peak assignments for MP.

Solid MP powders[4] (cm^{-1})	5 ppm of MP on GNA and 20 ppm AuNR (cm^{-1})	Reported results[4-5] (cm^{-1})	Band assignments[4-5]
1596 (w)	1587 (w)	1598 (m)	*v*(C–C) ring
1373 (s)	1342 (s)	*1376 (s)*	*v*(N–O)
1216 (m)	1222 (w)	1246 (m)	*v*(C–O) ring
1107 (m)	1158 (m)	1132 (m)	*v*(C–N)
1039 (m)	1028 (w)	*1003 (m)*	*v*(CH_3–O)
857 (w)	853 (w)	*851 (w)*	*v*(N–O)

Abbreviations: GNA: Gold nanorod arrays fabricated at 10° of deposition angle; AuNR: colloidal gold nanorods; s, strong; m, medium; w, weak; *v*, stretching;

Table S4. The Raman shifts, relative intensities and peak assignments for DP.

5 ppm of DP on GNA and 20 ppm AuNR (cm^{-1})	Reported results[6] (cm^{-1})	Band assignments
1584 (m)		
1446 (w)		δ(CH2)
1372 (m)		*v*(C–O)
1279 (m)		β(C-H)
1148 (s)	1149 (s)	γ(C-H)
1056 (w)	*1050 (w)*	β(C-H)
952 (m)	*950 (s)*	γ(C-H)
736 (w)	*720 (m)*	*v*(P–O)
643 (w)		γ(C-H)

Abbreviations: GNA: Gold nanorod arrays fabricated at 10° of deposition angle; AuNR: colloidal gold nanorods; s, strong; m, medium; w, weak; *v*, stretching; β, in-plane bending; γ, out-of-plane bending.

References

1. Xiao, G.-N.; Man, S.-Q., Surface-enhanced Raman scattering of methylene blue adsorbed on cap-shaped silver nanoparticles. *Chem Phys Lett* **2007,** *447* (4), 305-309.
2. (a) Naujok, R. R.; Duevel, R. V.; Corn, R. M., Fluorescence and Fourier Transform surface-enhanced Raman scattering measurements of methylene blue adsorbed onto a sulfur-modified gold electrode. *Langmuir* **1993,** *9* (7), 1771-1774; (b) Ruan, C.; Wang, W.; Gu, B., Single-molecule detection of thionine on aggregated gold nanoparticles by surface enhanced Raman scattering. *J Raman Spectrosc* **2007,** *38* (5), 568-573.
3. Kolomenskii, A.; Schuessler, H., Raman spectra of dipicolinic acid in crystalline and liquid environments. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2005,** *61* (4), 647-651.
4. Wang, J.; Kong, L. T.; Guo, Z.; Xu, J. Y.; Liu, J. H., Synthesis of novel decorated one-dimensional gold nanoparticle and its application in ultrasensitive detection of insecticide. *J Mater Chem* **2010,** *20* (25), 5271-5279.
5. Alak, A. M.; Vo-Dinh, T., Surface-enhanced Raman spectrometry of organo phosphorus chemical agents. *Anal Chem* **1987,** *59* (17), 2149-2153.
6. Yan, F.; Wabuyele, M. B.; Griffin, G. D.; Vass, A. A.; Vo-Dinh, T., Surface-enhanced Raman scattering detection of chemical and biological agent simulants. *Sensors Journal, IEEE* **2005,** *5* (4), 665-670.