Supporting information for

Surface Enhanced Raman Scattering by Graphene-Nanosheet-Gapped Plasmonic Nanoparticle Arrays for Multiplexed DNA Detection

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Table S1. DNA sequences used in this work

Oligonucleotide	Sequence
Cy5 labeled Staphylococcus aureus	Target DNA: 5-TGT TAC GAT TGT GTG AAT ACT CGT CTA ATG TCG TCC TTT G -3 Probe DNA: 5- GTA TTC ACA CAA TCG TAA CA-SH-3 Reporter DNA: 5-Cy5-CAA AGG ACG ACA TTA GAC GA-3
TAMRA labeled Listeria Monocytogenes	Target DNA: 5- CGC GTG TTT CTT TTC GAT TAG GAC TTG CAG GCG GAG -3 Probe DNA: 5-ATC GAA AAG AAA CAC GCG-SH-3 Reporter DNA: 5-TAMRA-CTC CGC CTG CAA GTC CTA-3
HEX labeled E.Coli O157:H7	Target DNA: 5-AGC GTC CGG GAA TTC ACC CGC AAT GGC TTC CAG CAC ATCC-3 Single base mismatch DNA: 5-AGC GTC CCG GAA TTC ACC CGC AAT GGC TTC CAG CAC ATCC-3 Probe DNA: 5-CGG GTG AAT TCC CGG ACG CT-SH-3 Reporter DNA: 5-HEX-GGA TGT GCT GGA AGC CAT TG-3

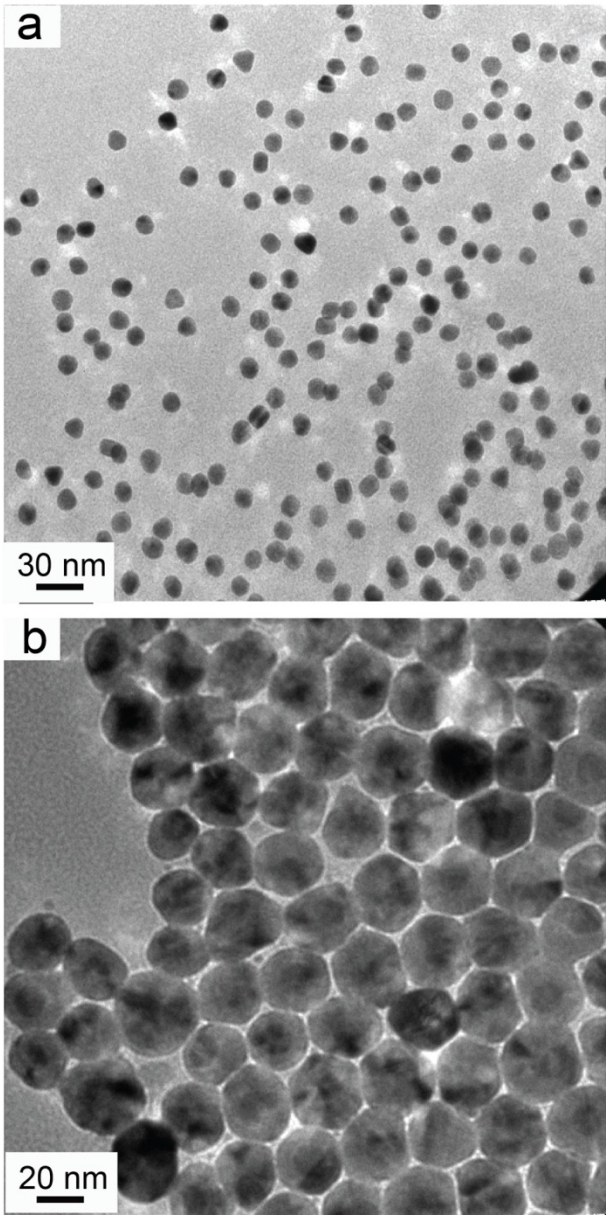

Fig. S1 TEM images of (a) Au NPs and (b) Au@Ag NPs.

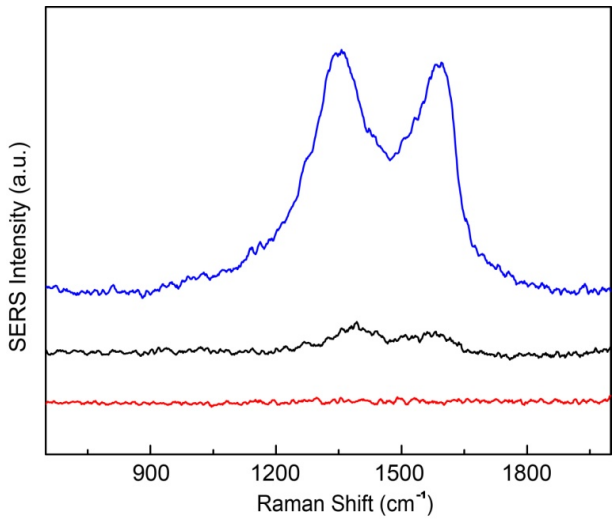

Fig. S2 SERS spectra collected on Au@Ag NP monolayer (red line), Au@Ag-tGO bilayer structure (black line) and Au@Ag-tGO-Au@Ag sandwich type substrate (blue line).

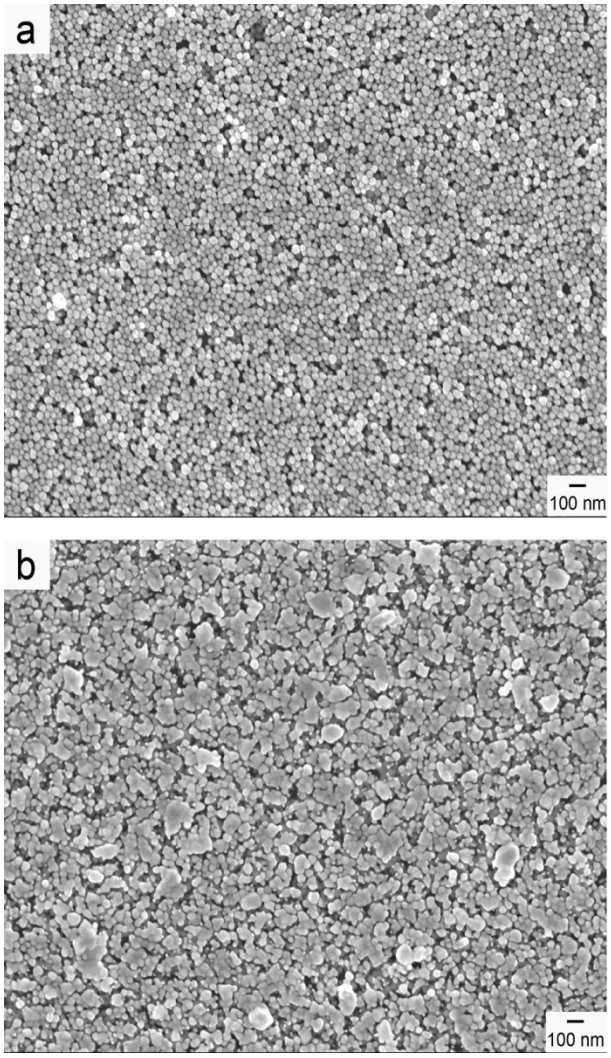

Fig. S3 SEM images of (a) Au@Ag-tGO-Au@Ag sandwich structure with PEGylation and (b) Au@Ag-tGO-Au@Ag sandwich structure without PEGylation.

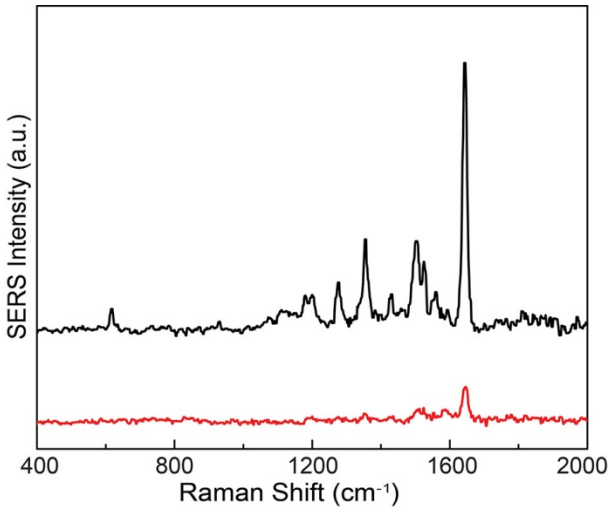

Fig. S4 SERS spectra of RhB on colloidal Au@Ag nanoparticles with (red line) and without (black line) PEG brushes.

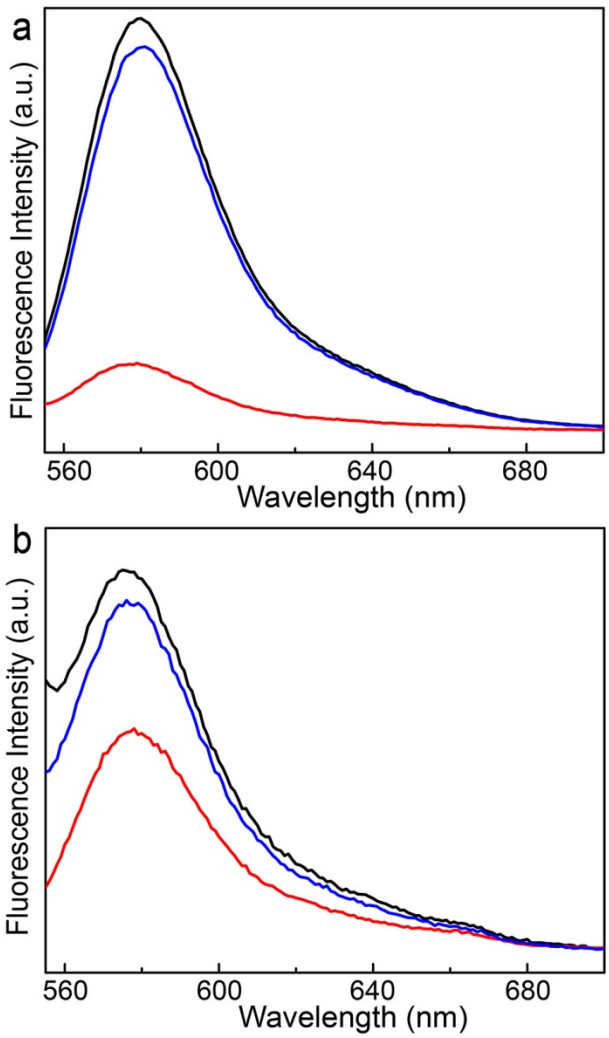

Fig. S5 (a) Fluorescence quenching of TAMRA labeled single-stranded probe DNA (10 nM) (black line) in the presence of citrate stabilized Au@Ag nanoparticles (red line) and PEGylated Au@Ag nanoparticles (blue line). (b) Fluorescence quenching of TAMRA labeled double-stranded DNA (5 nM) (black line) in the presence of citrate stabilized Au@Ag nanoparticles (red line) and PEGylated Au@Ag nanoparticles (blue line).

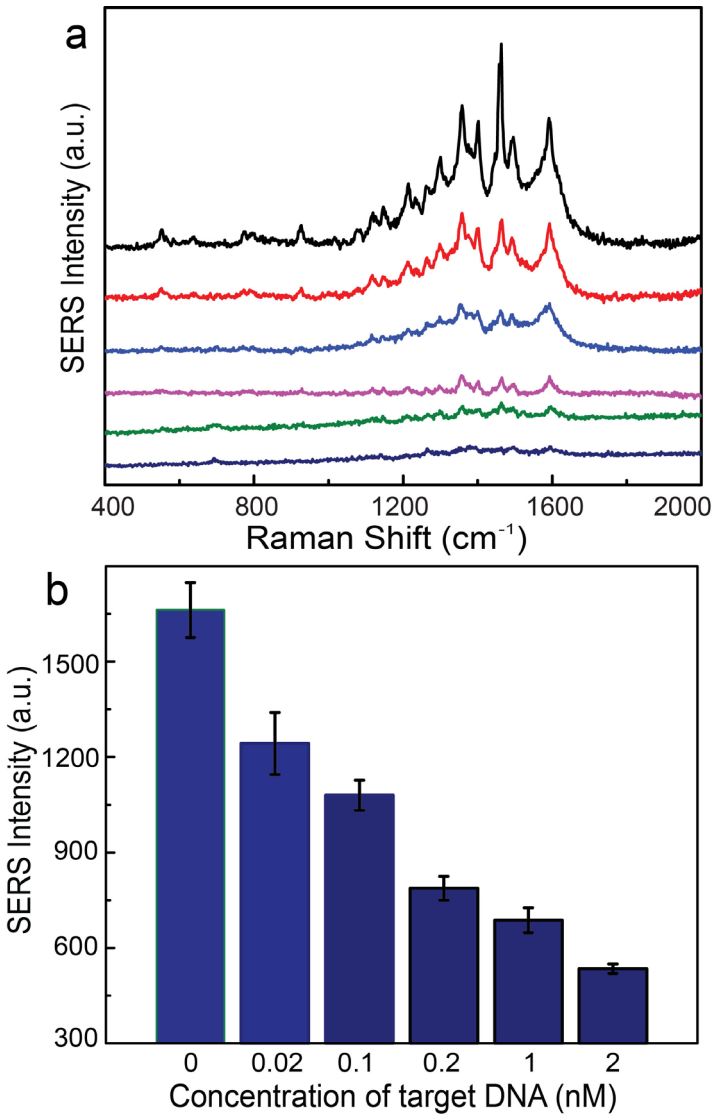

Fig. S6 (a) SERS spectra of Cy5 labeled reporter DNA (50 nM) for the detection of target DNA of different concentrations (from top to bottom: 0, 0.02, 0.1, 0.2, 1.0, and 2.0 nM). Black line is the background spectra of 50 nM reporter DNA in absence of target DNA. (b) SERS peak intensity of Cy5 labeled reporter DNA (50 nM) at 1592 cm^{-1} for the detection of target DNA of varying concentrations.

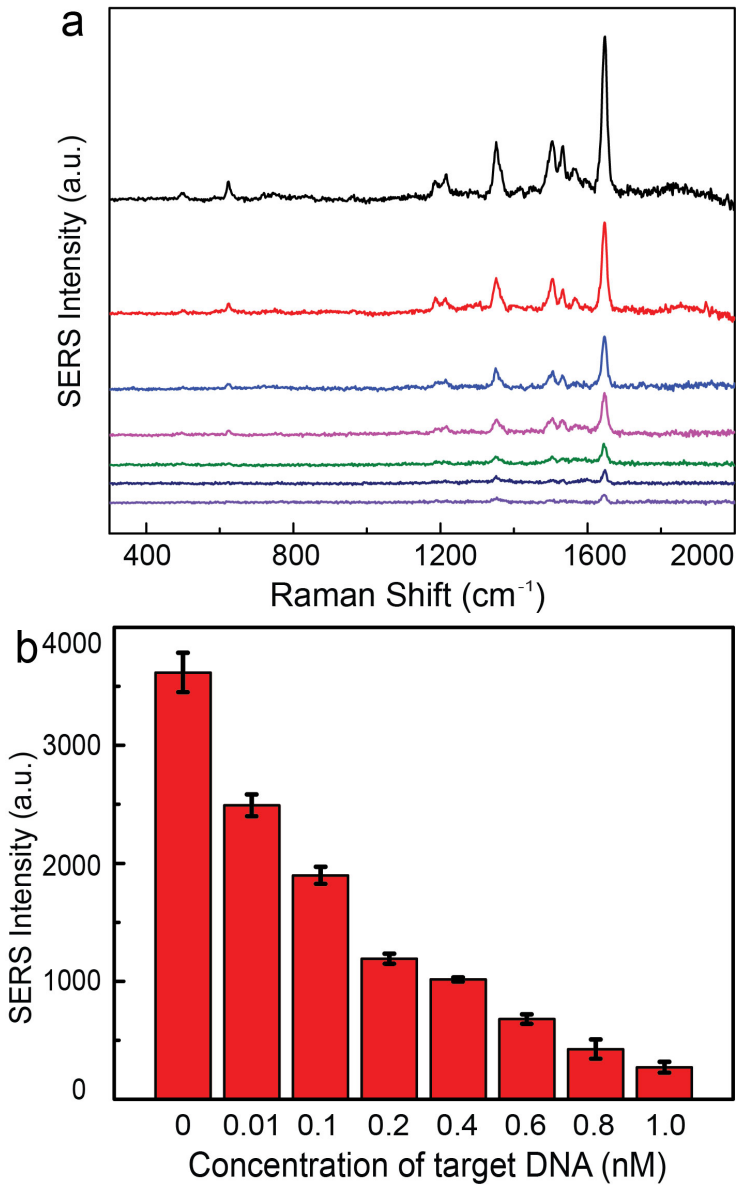

Fig. S7 (a) SERS spectra of TAMRA labeled reporter DNA (20 nM) for the detection of target DNA of different concentrations (from top to bottom: 0, 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 nM). Black line is the background spectra of 20 nM reporter DNA with the absence of target DNA. (b) SERS peak intensity of TAMRA labeled reporter DNA (20 nM) at 1645 cm^{-1} for the detection of target DNA of varying concentrations.

Calculation of enhancement factor (EF)

Quantitative analysis of the enhancement ability of the Au@Ag-tGOtGO-Au@Ag substrate was performed by calculating an enhancement factor of RhB molecules (1 μM, 10 μL) deposited on the substrate.

The enhancement factor (EF) is defined as

$$EF = (I_{SERS} \times N_{normal}) / (I_{normal} \times N_{SERS})$$

where N_{SERS} and N_{normal} are the number of RhB molecules illuminated by the laser under SERS and normal Raman condition. I_{SERS} and I_{normal} correspond to the intensities of the same vibrational mode in the SERS and normal Raman spectra. Intensities of the vibrational band at 1644 cm^{-1} from RhB, which is assigned to aromatic C-C stretching is used in this calculation. Taking laser spot diameter to be 1 μm, scattering area is calculated to be 0.8×10^{-12} m^2 and scattering volume is 9.6×10^{-18} m^3 with penetration depth of 12 μm.

$$N_{normal} = 1.26 g/cm^3 \times 9.6\times10^{-18} m^3 = 2.4\times10^{-16} mol/479.02 g/mol = 2.5 \times10^{-11} mol.$$

$$N_{SERS} = 10 \mu L \times 1 \mu M \times 0.8\times10^{-9} cm^2/1 cm^2 = 0.8\times10^{-20} mol,$$

$$I_{normal} = 326 mW^{-1}S^{-1} \text{ and } I_{sers} = 30000 mW^{-1}S^{-1}$$

$$EF = (30000 mW^{-1}S^{-1} \times 2.5\times10^{-11} mol) / (326 mW^{-1}S^{-1} \times 0.8\times10^{-20} mol)$$

$$EF = 2.7\times10^{8}$$