Electronic Supplementary Information For

Fabrication of a Self-Assembled and Flexible SERS Nanosensor for Explosive Detection at Parts-Per-Quadrillion Levels from Fingerprints

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Spectroscopy and Microscopy Characterization. A Varian Cary 50 Scan UV-visible spectrophotometer was used to collect absorption and extinction spectra in the range of 300-1100 nm. Absorption spectra of Au TNP solutions were obtained by diluting 0.3 mL of reaction solution to a final volume of 2.0 mL with acetonitrile in a 1 cm quartz cuvette. Acetonitrile was used as a background in each run before collecting the absorbance spectra. Background subtracted (using 3M adhesive tape) extinction spectra of our SERS nanosensors were measured in air (pH 7.4) at room temperature. Scanning electron (SEM) and Transmission electron (TEM) microscopy techniques were used to determine the average edge-length of gold nanoprisms used in our SERS nanosensor fabrication.

Synthesis of Gold Triangular Nanoprisms (Au TNPs): Gold triangular nanoprisms (Au TNPs) were synthesized according to our published method with minor modifications.^{1,2} Briefly, Et₃PAu(I)Cl (0.008 g, 0.02 mmol) was dissolved in 10 mL of acetonitrile and stirred for 5 min at room temperature followed by addition of a mixture of 0.085 mL of TOA and 0.3 mL of PMHS. Then the reaction mixture was gradually heated to 40 ^oC. During this time the color of the solution changed from colorless to pink, purple, and then blue. When the solution turned light blue, 9 mL acetonitrile was added to the reaction mixture was monitored through UV-visible absorption spectroscopy to follow the dipole peak position (λ_{LSPR}) of Au TNPs. The reaction mixture was removed from heat once the dipole peak reached at 800 nm in acetonitrile, which represented average edge-lengths of 42 nm.¹⁻⁴ The edge-lengths were confirmed by both TEM and SEM analyses.

Silanization of Glass Coverslips: Glass coverslips were functionalized based on our published procedure.^{1,2} As a first step, coverslips were incubated in RBS 35 detergent solution at 90 °C for 10 min with sonication. The coverslips were then thoroughly rinsed with nanopure water and further incubated in a solution containing concentrated hydrochloric acid and methanol (1:1 v/v) for 30 min. Coverslips were rinsed with nanopure water and placed in a vacuum oven at 60 °C overnight. Next the cleaned coverslips were immersed in a 10% APTES solution in ethanol for 30 min, and then sonicated for 10 min followed by rinsing with ethanol. Finally, these APTES-functionalized coverslips were dried in a vacuum oven at 120 °C for 3 h.

Simulation of Extinction Spectrum and Electromagnetic Field Calculations. Discreet Dipole Approximation (DDA) (DDASCAT+ tool⁵, DDSCAT 7.3⁶) was used as previously described⁷ to calculate the extinction spectra (600-1000 nm, circularly polarized simulating unpolarized) and electromagnetic field (785 nm, linear polarized) for an Au TNP (8 nm thickness, 42 nm edge length. The dielectric constant was from Johnson and Christy⁸) with an ambient medium representative of the ligand environment (TOA, n = 1.4485).

Enhancement Factor Calculations. We followed the literature procedure⁹ to determine the EF of our Au TNP-containing flexible adhesive SERS substrate at the 1380 cm⁻¹ Raman peak (C-N stretch), using Eq. 1. With a 5 μ M diameter laser spot and a TNT molecule foot print of 0.25 nm², N_{Bulk} was determined to be 7.9 x 10⁷. From the SEM analysis, we estimated that ~4% of the 3M tape surface was covered with ~42 nm edge length Au TNPs. Considering Au TNPs are equilateral triangles and a monolayer of TNT molecules was present on the surface of Au TNPs, N_{SERS} was calculated to be 2.9 x 10⁵.

$$EF = \left(\frac{I_{SERS}}{I_{Bulk}}\right) X \left(\frac{N_{Bulk}}{N_{SERS}}\right)$$
 (Eq. 1)

Limit of Detection (LOD) Calculations. We used a sophisticated mathematical equation (Eq. 2) for limit of detection (LOD) calculations.¹⁰ For LOD determination a 1.0 millimolar (mM) stock solution of explosive in methanol was prepared and then various concentrations upto 100 femtomolar (fM) with 10 fold concentration changes were obtained through serial dilutions.

$$LOD_{B} = \overline{Y}_{b} + t_{\alpha}^{n-1} s_{b}^{n-1} \sqrt{\frac{1+1}{n}}$$
 (Eq. 2)

$$\begin{split} &\overline{Y}_b = Average \ blank \ signal \ value \\ &t_{\alpha}^{n-1} = critical \ value \ of \ the \ distribution \\ &s_b^{n-1} = Standered \ deviation \\ &\sqrt{\frac{1+1}{n}} = Replacement \ of \ the \ true \ mean \ by \ \overline{Y}_b, \ n=3 = number \ of \ blank \ spectrum \end{split}$$

Chemometric Analysis. The SERS spectra were automatically baseline corrected by the Foster and Freeman FORAM FireWire instrument software at the time of collection. Some incomplete baseline correction of nM and μ M concentrations of TNT and PETN occurred and the correction was completed in Origin. The baseline corrected spectra were subsequently normalized using the square root of the sum of squares or 2-norm¹¹. Multivariate calibration curves from 100 fM to 100 μ M were obtained with Partial Least Squares (PLS) using the baseline corrected spectra and the log of the concentration using in JMP 13 with the NIPALS method and Leave-One-Out validation. Principal Components Analysis (PCA) on the sample covariance matrix and Discriminant Analysis (DA) on the PCs were conducted using the

normalized spectra and JMP 13. PCA used the Row-Wise method. DA for single concentrations used the linear method with 3 PCs for the quadripartite analysis (PETN, RDX, TNT, blank; n=24). and 2 PCs for tripartite analysis (TNT, TNB, DNB; n=18). DA for the full concentration ranged from 100 fM to 100 μ M using the Quadratic method (4 PCs for pairwise of either RDX or TNT with PETN, n=120; 8 PCs for pairwise of RDX and TNT, n=120; and 8 PCs for tripartite, n=180).



Fig. S1. TEM image of Au TNPs used in our SERS nanosensor fabrication. Average edgelength was determined to be ~42 nm. The scale bar is 200 nm. **Table S1-A.** Experimentally determined SERS peaks for TNT obtained using Au TNP-based nanosensor.

567	-NO ₂ bend in aromatic compound ¹²
598	-NO ₂ bend in aromatic compound ¹²
721	Ring deformation ¹²
860	Nitro phenyl group on TNT $^{13}/2,4,6$ - NO ₂ scissoring ¹⁴
926	2,4,6- NO ₂ scissoring ¹⁴⁻¹⁶
1002	Symmetric ring breathing peak ¹³
1122	-CH in plane bending ¹³ /CH ₃ deformation ¹⁵
1168	Phenyl methyl group ¹³
1234	Ring breathing and bending ¹³ /-C ₆ H ₂ -C vibration ¹⁵
1311	-C-N stretching
1380	Symmetric -NO ₂ stretching ^{13,17}
1558	2,6-NO ₂ asymmetric stretching
1573	2,6-NO ₂ asymmetric stretching ¹⁸ , -C=C aromatic stretching vibration ¹⁵

Table S1-B. Experimentally determined SERS peak for RDX obtained using Au TNP-based nanosensor.

725	Cyclic deformation ¹²
863	-C-N-C ring vibration ¹⁹
1006	Symmetric ring breathing peak/C-C-stretching
1080	-CH ₂ in plane bend ¹⁹
1130	-C-N stretching (non aromatic amines) ¹²
1242	Nitro amine group ¹³ /N-N Stretching, -CH ₂ -scissoring ¹⁹
1331	-CH ₂ wagging band ²⁰ , Ring breathing and bending ^{13,20}
1380	Symmetric -NO ₂ stretching ^{13,20}
1554	2,6-NO ₂ asymmetric stretching ^{16,20}
1581	2,6-NO ₂ asymmetric stretching ^{16,20}

Table S1-B. Experimentally determined SERS peak of PETN obtained using Au TNP-based nanosensor.

1006	-CO stretching + -C-C-C deformation ²¹
1033	-CH ₂ torsion and -C-C-bending ²²
1076	-C-N stretching ¹²
1138	-CH ₂ wagg ²³
1184	-CO stretching ¹⁶ / -C-C-C deformation + CH ₂ wagg ^{21,24}
1392	-NO ₂ symmetric stretching ¹⁶
1435	-CH ₃ antisymmetric Stretching ^{16,21,23}
1577	-NO ₂ asymmetric stretching ^{12,16,24} / C-H bending



Fig. S2. Spectroscopy analysis of various components in the SERS nanosensor: (A) Raman spectrum of 3M adhesive tape, (B) Raman spectrum of 3M adhesive tape containing 6 μ L of 1.0 mM TNT solution, (C) SERS spectrum of our nanosensor, (D) 6 μ L methaol drop-casted on SERS nanosensor, and (E) 6.0 μ L of a 1.0 mM TNT solution drop-casted on SERS nanosensor.



Fig. S3. Representative SERS spectra collected by drop-casting 6.0 μ L of 1.0 μ M TNT on nanosensor: (A) Spectra from nine randomly selected spots from a single nanosensor; (B) spectra from four randomly selected areas of four different SERS nanosensors (1-4, 5-8, 9-12, and 13-16), which were prepared from four different batches of Au TNPs; (C) time dependence of one SERS nanosensor over an entire month; (D) 20 individual nanosensors over the course of 5 months. The error bars in (C) and (D) represent measurements from six spots.



Fig. S4. Histograms of SERS intensity at 1380 cm⁻¹ collected from 9 randomly selected spots on two different nanosensors for (A) 100 pM and (B) 100 fM TNT concentrations.



Fig. S5. SEM image of number 10 glass slide (A) with TNT from thumb impression, and (B) after placing SERS nanosensor onto the glass slide and collecting the sample.



Fig. S6. Microscopy image of a latent fingerprint onto SERS nanosensor transferred from a glass coverslip.

Table S2. Comparison of SERS EF and sensitivity for different substrates prepared with chemically synthesized gold nanostructures for TNT, RDX, and PETN.^a

SERS Substrate	sensitivity/M	SERS EF	explosive type ^b	ref.
4-amino thiol modified gold nanorods doped with silver nanoparticles	0.61 mg/L ⁻¹	N/A	RDX	25
gold nano-dumbbell structures	10 ⁻¹² M	N/A	TNT	26
Fe ₃ O ₄ /Au nanoparticles/lignin modified microspheres	2 pM	1.4 x 10 ⁶	TNT	27
gold nanocage-graphene oxide hybrid platform	10 ⁻¹⁴ , 5 x 10 ⁻¹³	1.6 × 10 ¹¹	TNT, RDX	20
Ni-Au nanocarpet	10 ⁻⁷ /10 ⁻⁶	~10 ¹⁰	TNT, RDX	28
unmodified gold nanoparticles	10 ⁻¹⁰ M	N/A	TNT	29
cylindrical nanopore/gold nanoparticle	3 x 10 ⁻¹⁶ ,	10 ¹² -10 ¹³	TNT	30
Au nanoparticles (~90–100 nm)	0.15 mgL ⁻¹	$\sim 6 \times 10^{4}$	RDX	31
optical fiber probe -coupled with gold bowtie nanostructure arrays	0.9 µM	10 ¹¹	TNT	32
highly ordered Au nanoparticles	10 ⁻⁹ M		TNT	33
popcorn-shaped gold nanoparticle	100 fM	8.4 X 10 ¹¹	TNT	34
TNT-binding peptides appended to gold nanorods	100 pM		TNT	35
cysteine modified gold nanoparticle	2 pM	1 × 10 ⁹	TNT	15
combination of plasmonic gold nanoparticles with TiO ₂	3.1 x 10 ⁻⁸	20 x over conventional SERS	TNT	36
flexible adhesive SERS substrate	0.9 ppt		TNT	Present
containing self-assembled Au	56 ppq		RDX	work
	56 ppq		PETN	

^appt = parts-per-trillion, ppq = parts-per-quadrillion. ^bNo literature report is available on detection of PETN using chemically synthesized gold nanostructures as SERS substrates.

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