

Supplementary information

Digital SERS sensing platform using 3D nanolaminate plasmonic crystals coupled with Au nanoparticles for accurate quantitative detection of dopamine

Wonil Nam^a, Wansun Kim^b, Wei Zhou^{a,*}, Eun-Ah You^{b,*}

^a Department of Electrical and Computer Engineering, Virginia Tech, Blacksburg, Virginia 24061, United States

^b Nanobiosensor Team, Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea

* Corresponding authors:

E-mail addresses: wzh@vt.edu (W. Zhou), eayou@kriss.re.kr (E.-A. You)

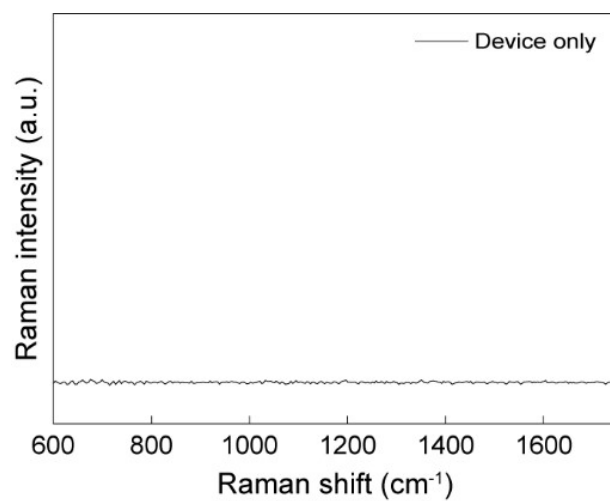


Fig. S1. The averaged spectrum of the 3D NLPC SERS substrates from 400 pixels.

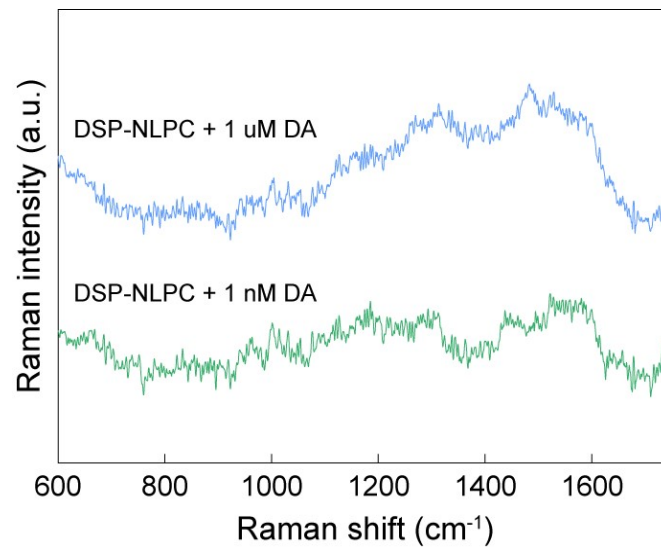


Fig. S2. Raman spectra for DA on DSP-functionalized NLPC substrates at DA concentrations of 1 μ M (blue) and 1 nM (green).

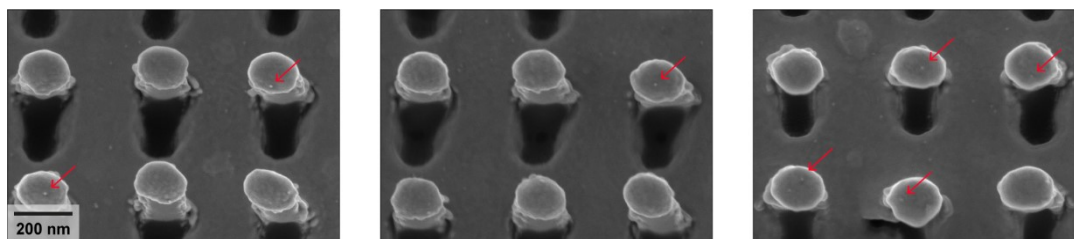


Fig. S3. Top-view SEM images of the 3D NLPC SERS substrate after the detection of 1 nM DA by the dual-recognition method. The red arrows indicate AuNPs.

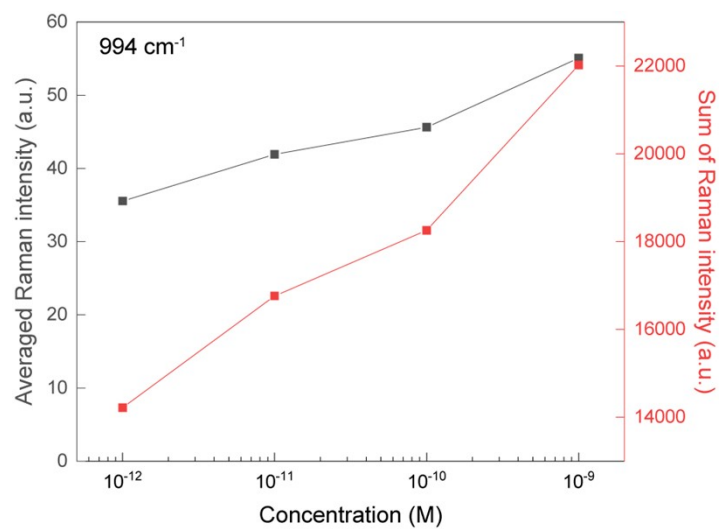


Fig. S4. Average and sum of the Raman intensity using the characteristic peak of 3-MPBA at 994 cm^{-1} for different DA concentrations.

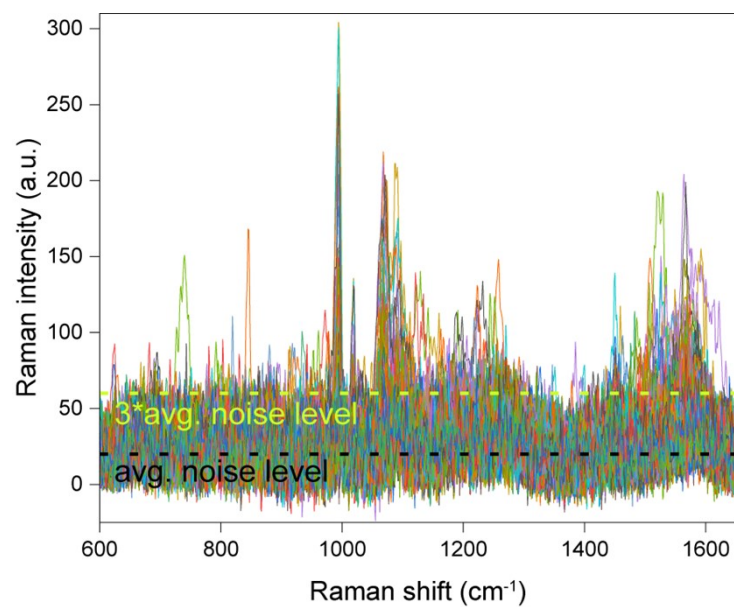


Fig. S5. Threshold value three times higher than the average noise level as determined using 400 Raman spectra for DA-specific dual-recognition assays with 1 nM DA.

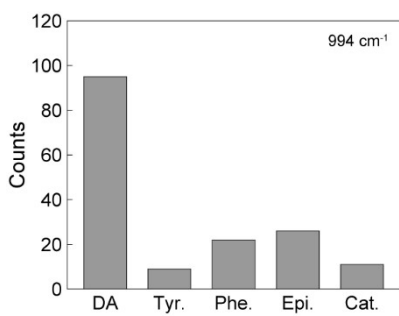


Fig. S6. Digital SERS assay to evaluate DA selectivity. 1 nM of each molecule in aCSF was used. Tyr.; L-tyrosine, Phe.; L-phenylalanine, Epi.; epinephrine, Cat.; catechol.

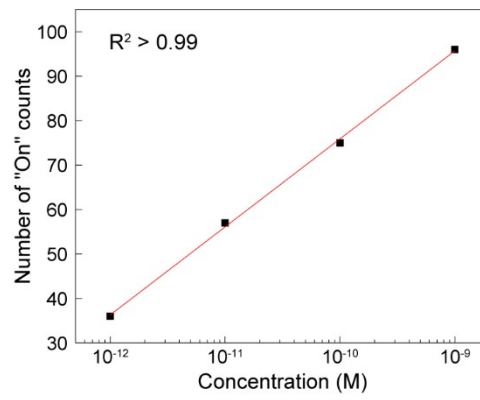


Fig. S7. A linear regression model between DA concentration and the number of "On" counts derived from Fig. 6B results ($\text{Counts} = 19.8\log C + 273.9$, $R^2 > 0.99$).

Table S1. Recovery rate evaluation of the dual-recognition based digital SERS assay for DA detection. A linear regression model in Fig. S7 was used.

Added concentration	Detected concentration	Recovery rate (%)
1 nM	0.922 nM	92.2
100 pM	90.1 pM	90.1
10 pM	9.88 pM	98.8

Table S2. Comparison of this work with previous SERS-based DA sensing works.

Method	DA selectivity	LOD	Dynamic range	Approach	Material	Excitation	Digital assay	Ref.
Label-free	Yes	0.5 nM	0.5 nM ~ 10 uM	Bottom-up	Ag	633 nm	No	33
Label-free	No	100 pM	100 pM ~ 100 uM	Top-down	Graphene-Au	633 nm	No	30
Label-free	No	2.5 uM	2.5 uM ~ 500 uM	Bottom-up	Graphene oxide-Ag	633 nm	No	31
Label-free	No	1 pM	1 pM ~ 1 uM	Top-down	ZnO-Ag	514.5 nm	No	28
Label-free	No	400 pM	400 pM ~ 4 uM	Bottom-up	Ag-Au	532 nm	No	34
Label-free	No	10 nM	10 nM ~ 0.1 mM	Bottom-up	Au	785 nm	No	32
Label-free	Yes	1 uM	1 uM ~ 100 uM	Bottom-up	Ag	514.5 nm	No	35
Labeled	Yes	0.1 pM	0.1 pM ~ 1 nM	Bottom-up	Au	785 nm	No	37
Labeled	Yes	0.01 pM	0.01 pM ~ 10 pM	Bottom-up	Au	633 nm	No	38
Labeled	Yes	1 pM	1 pM ~ 1 uM	Bottom-up	Ag-Au	638 nm	No	55
Labeled	Yes	1 pM	1 pM ~ 1 nM	Top-down	Au	780 nm	Yes	This work