Electronic Supplementary Information

Using Langmuir-Schaefer Technique to Fabricate Large-area Monolayer Films of Ultrathin Au Nanoprisms as SERS-active Substrates

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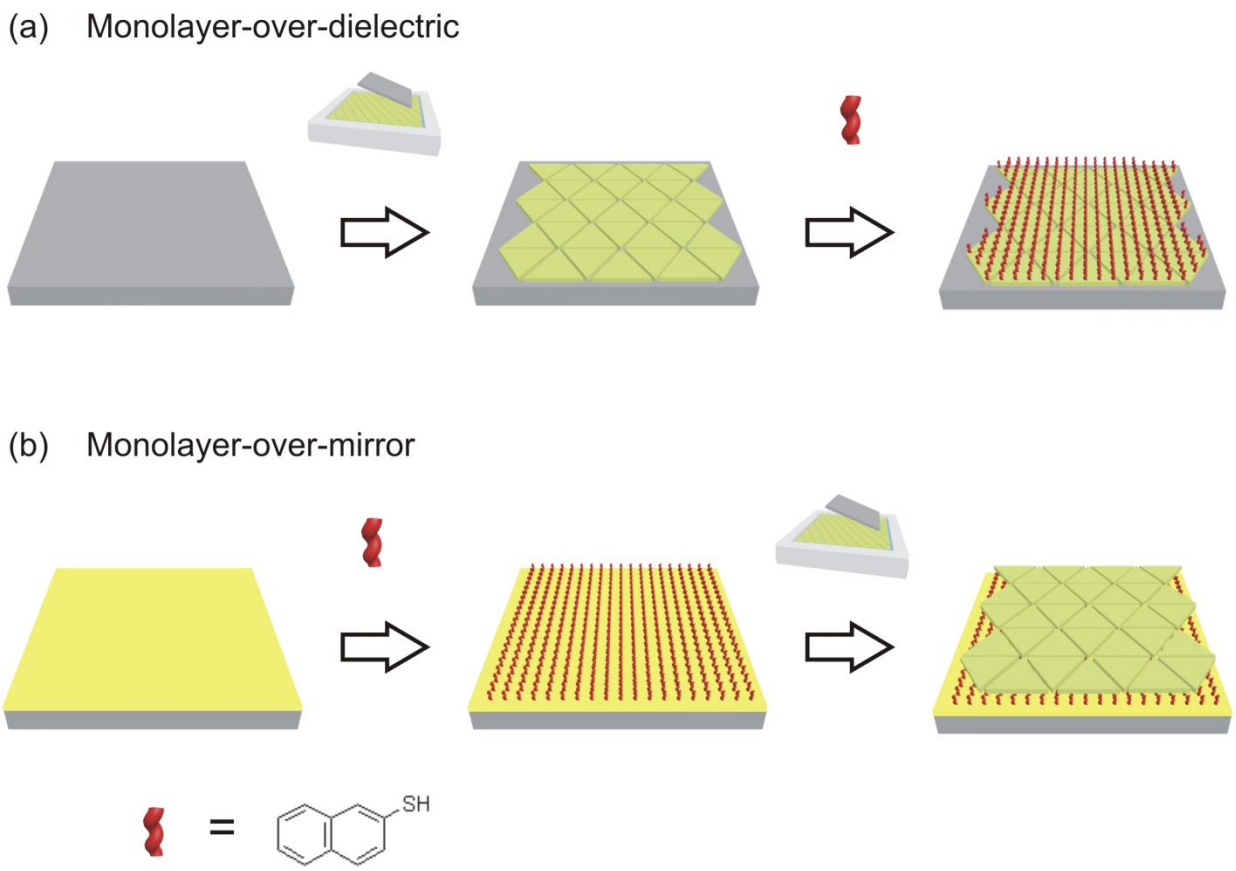

Fig. S1 Schematic illustration of SERS substrates preparation for the (a) monolayer-over-dielectric and (b) monolayer-over-mirror layouts. In (a), film transfer of Au prism monolayers onto Si substrate was carried out, followed by functionalizing with the respective thiol molecules. In (b), the Au coated substrates were first functionalized with the probe molecules before the film transfer.

Calculation of SERS enhancement factor (EF)

$$EF = \frac{I_{Surface}}{I_{solution}} \times \frac{N_{solution}}{N_{Surface}}$$

$I_{surface}$ = 10250 / 1194 (on evaporated Au / on Si; measured using 100 × objective lens)
$I_{solution}$ = 97 (based on 0.2 M 2-napthalenethiol solution, 100 × objective lens)

$N_{solution}$ = number of molecules in solution within the measured laser spot
= $V_{solution}$ × Concentration of molecules ×Avogadro's number

$V_{solution}$ = $\pi \times r^2 \times h$
= $3.142 \times (5\ mm/2)^2 \times 5\ mm$
= $9.817 \times 10^{-17}\ m^3$

$N_{solution}$ = $9.817 \times 10^{-17}\ m^3 \times 0.2\ M\ (= 200\ mol/m^3) \times 6.022 \times 10^{23}$
= 1.182×10^{10}

$N_{Surface}$ = number of molecules on the surface of Au or Au prisms within the measured laser spot

For Au surface
Laser beam diameter = 5 μm (100 × objective lens)
Surface area within the measured laser spot = πr^2
= $3.142 \times (5/2\ \mu m)^2$
= $1.963 \times 10^7\ nm^2$

Surface area of 2-napthalenethiol = 0.244 nm^2/molecule [1]

$N_{Surface}$ = 1.963×10^7 / 0.244 nm^2/molecule
= 8.05×10^7 molecules

EF = [10250/97] x [$1.182 \times 10^{10}/8.045 \times 10^7$]
= 1.55×10^4

For Si surface

Laser beam diameter = 5 μm

Edge length and thickness of prism = 150 nm by 10 nm

Surface area of prism = b x h + 3 x (l x b)
= 134 x 67 + 3 x (134 x 10)
= 12998 nm^2

Surface area within the measured laser spot = πr^2
= $3.142 \times (5/2\ \mu m)^2$
= $1.963 \times 10^7\ nm^2$

Total number of prisms within the measured laser spot

$$= \frac{\text{Surface area within the measured laser spot}}{\text{Projected surface area of a prism}}$$

= $1.963 \times 10^7\ nm^2 / 1.037 \times 10^4\ nm^2$

= 1894 prisms

⇒ Total surface area of prisms within the measured laser spot

= Total number of prisms within the measured laser spot × surface area of each prism

= $1894 \times 12998\ nm^2$

= $2.461 \times 10^7\ nm^2$

Surface area of 2-napthalenethiol = 0.244 nm^2/molecule [1]

$\mathbf{N_{Surface}}$ = $2.461 \times 10^7 / 0.244\ nm^2$/molecule

= 1.009×10^8

EF = [1194/97] x [$1.182 \times 10^{10} / 1.009 \times 10^8$]

= 1.44×10^4

References

1. M. C. S. Pierre, P. M. Mackie, M. Roca and A. J. Haes, *J. Phys. Chem. C*, 2011, **115**, 18511-18517.