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Supporting Information

An Effective Oxide Shell-protected Surface-enhanced Raman Scattering (SERS) Substrates: the Easy Route to $Ag@Ag_xO$- Silicon Nanowire Films via Surface Doping

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1. SERS spectrum on $Ag@Ag_xO$-SiNW substrate of 1×10^{-7} M R6G solution and Raman spectrum of 0.1 M R6G solution

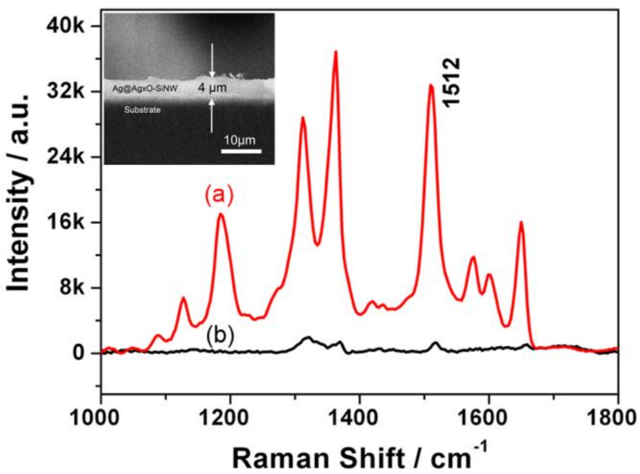

Figure S5. (a) SERS spectrum on $Ag@Ag_xO$-SiNW substrate of 1×10^{-7} M R6G solution; and (b) the Raman spectrum of 0.1 M R6G solution. The inset is the side view of the substrate.

2. The calculation of EF

$EF=\frac{I_{sers}}{I_0}\times\frac{N_0}{N_{sers}}$ is the most widely used definition for the average SERS EF. I_0 and I_{sers} are the peak intensity of regular Raman measurement with 0.1 M R6G methanol solution on ITO glass and SERS measurement with 1×10^{-7} M R6G methanol solution on Ag@Ag_xO-SiNW substrate; and N_0 is the average number of molecules in the scattering volume for the Raman measurement, and N_{sers} is the average number of adsorbed molecules in the scattering volume for the SERS experiments.

N_0 was derived by considering the irradiated R6G solution area A_{laser} (πr_{laser}^2 with r_{laser} = $0.61\lambda_{laser}/NA$), the laser spot depth of focus (2λ / NA^2), and its concentration C_0. N_A is Avogadro constant.

$$A_{laser}=\pi(\frac{0.61\lambda_{\text{laser}}}{\text{NA}})^2=\pi(\frac{0.61\times633\times10^{-8}}{0.9})^2=5.78\times10^{-11}dm^2$$

$$N_0=A_{laser}\times(2\lambda/\text{NA}^2)C_{\text{sers}}\times N_A=5.44\times10^7$$

Sample for SERS measurement was prepared by the addition of 20 μl of 1×10^{-7} M R6G methanol solution onto the given substrate, and dried in room temperature. After the solvent evaporated, the solution formed a 5 mm diameter circular liquid deposit and the probe molecules were uniformly permeated into Ag@Ag_xO-SiNW with thickness of 4 μm (inseted in figure S5). So the density of R6G molecules in the Ag@Ag_xO-SiNW was 1.533×10^{19},

$$(\rho=\frac{20\times10^{-6}\times10^{-7}\times6.02\times10^{23}}{\pi(\frac{0.05}{2})^2\times4\times10^{-5}}=1.533\times10^{19}/dm^3)$$

Owing to the chemical first layer enhancement, the SERS effect is distance-dependent and the SERS signal from molecules on the second monolayer is usually reduced and can be ignored [19]. Assuming laser only penetrate SiNWs surface layer and the diameter of SiNWs is 75 nm. And the R6G molecules on the SiNWs' surface was calculated as 1.129×10^{10} $(1.533\times10^{19}\times\frac{0.075}{2}\times10^{-5}\times\pi(\frac{0.05}{2})^2=1.129\times10^{10}/dm^3)$

$$\text{N}_{\text{sers}}=\frac{A_{laser}}{\pi(\frac{0.05}{2})^2}\times1.129\times10^{10}=332$$

$$EF = \frac{I_{sers}}{I_0} \times \frac{N_0}{N_{sers}} = \frac{32970}{1284} \times \frac{5.44 \times 10^7}{332} = 4.21 \times 10^6$$