



## Supplementary Material

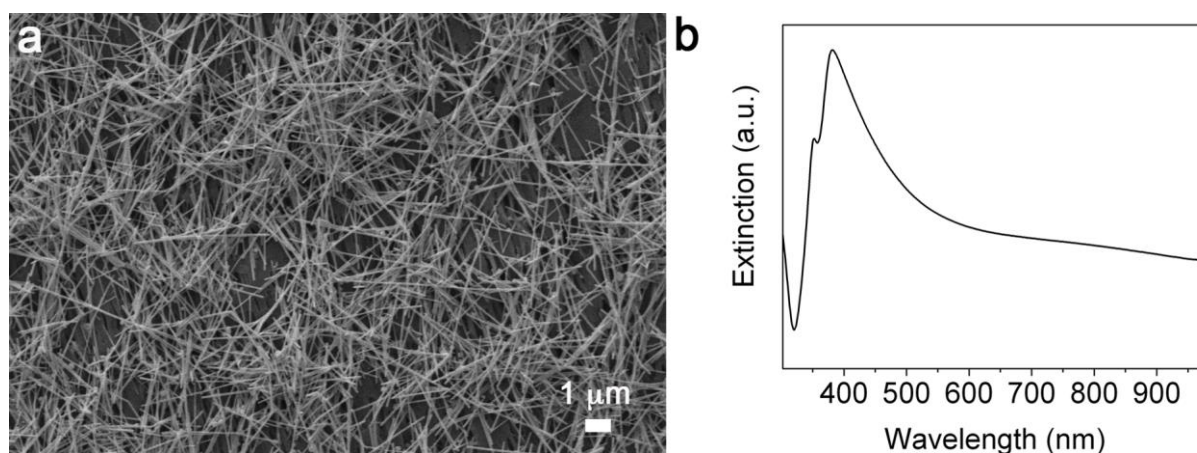
# Cost Effective Silver Nanowire-Decorated Graphene Paper for Drop-on SERS Biodetection

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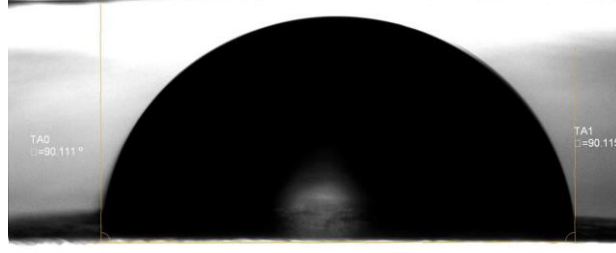
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**Figure S1.** (a) SEM image and (b) UV-vis spectrum of the AgNWs used to prepare the SERS substrates.

**Table S1.** Assignment of main SERS signals of Hb.

Assignment	
$\lambda_{\text{Ex}} = 532 \text{ nm}$	
680	V7
750	V15
1123	V22
1161	V30
1230	V13
1309	V21
1378	V4
1393	V20
1430	V28
1555	V11
1582	V37
1610	V19
1627	V10



**Figure S2.** Contact angle of a 2  $\mu$ L water drop on a AgNWs@graphene spot.

### EF calculation

EF was calculated for the AgNWs@G-paper substrate at the optimal 0.1  $\mu\text{g}/\text{mm}^2$  AgNW density. A 2- $\mu\text{L}$  drop of Hb ( $1 \times 10^{-6}$  M) was dried on a single spot of a laser-patterned AgNWs@PTFE substrate and immediately analysed. SERS maps at  $\lambda_{\text{ex}} = 532$  nm were collected from 3 replica substrates and averaged. Raman measurements on a  $1 \times 10^{-3}$  M Hb solution in water in quartz cuvette (1 cm) were also performed. The EF was calculated by comparing the  $750\text{ cm}^{-1}$  band intensity of Hb in the SERS spectrum ( $I_{\text{SERS}}$ ) with that of the Raman measurement ( $I_{\text{Raman}}$ ) according to the equation:

$$EF = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{Raman}}/N_{\text{Raman}}} \quad (\text{S.1})$$

where

$$N_{\text{Raman}} = C_{\text{molecule}} \times V_f \times N_A = C_{\text{molecule}} \times A_{\text{waist}} \times H_{\text{depth}} \times N_A \quad (\text{S.2})$$

being  $C_{\text{molecule}}$  the concentration of Hb solution used for Raman measurements,  $V_f$  the focal volume,  $A_{\text{waist}}$  the laser spot area in the focal plane,  $H_{\text{depth}}$  the depth-of-field of the objective (10x) and  $N_A$  the Avogadro number,

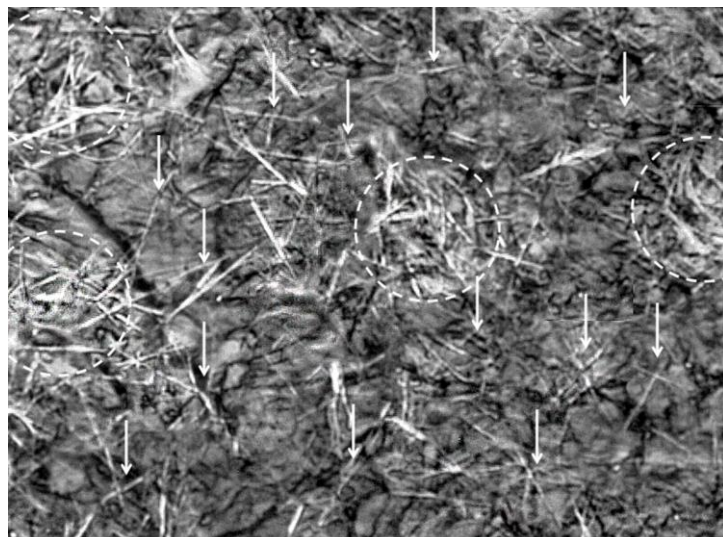
$$N_{\text{SERS}} = D_{\text{AgNWs}} \times A_{\text{waist}} \times A_{\text{eff}}/f_p \quad (\text{S.3})$$

being  $D_{\text{AgNWs}}$  the AgNW density on G-paper,  $A_{\text{eff}}$  the effective area of the hotspot accounting for 98% of the signal, and  $f_p$  the footprint area of Hb molecule.

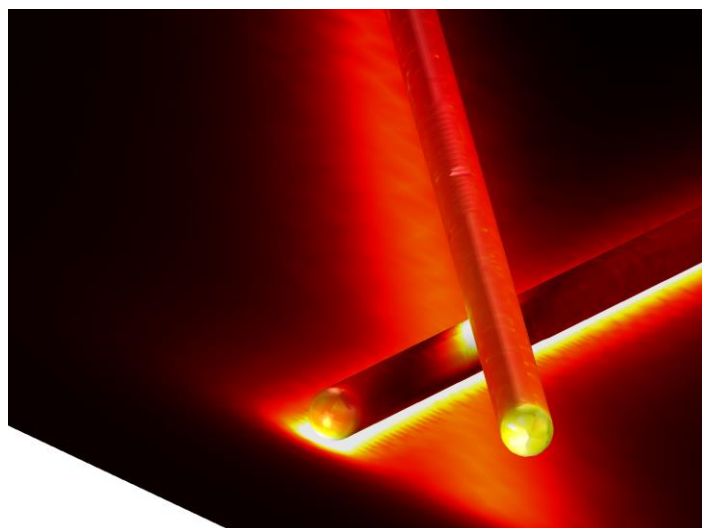
Therefore

$$\frac{N_{\text{Raman}}}{N_{\text{SERS}}} = \frac{C_{\text{molecule}} \times A_{\text{waist}} \times H_{\text{depth}} \times N_A}{D_{\text{AgNWs}} \times A_{\text{waist}} \times A_{\text{eff}}/f_p} = \frac{C_{\text{molecule}} \times H_{\text{depth}} \times N_A \times f_p}{D_{\text{AgNWs}} \times A_{\text{eff}}} \quad (\text{S.4})$$

with  $H_{\text{depth}} = 216\text{ }\mu\text{m}$  at 532 nm,  $f_p = 20\text{ nm}^2/\text{molecule}$  for Hb,  $D_{\text{AgNWs}} = 1.6\text{ AgNWs}/\mu\text{m}^2$  and  $A_{\text{eff}} = 5 \times 10^4\text{ nm}^2$ .  $I_{\text{SERS}}/I_{\text{Raman}}$  is 113 and thus the EF value is  $4 \times 10^6$ .



**Figure S3.** Optical image ( $90\mu\text{m} \times 65\mu\text{m}$ ) of an AgNWs@G-paper substrate. Arrows: isolated AgNWs or forming single junctions with other AgNWs; circles: AgNWs forming more than a single junction with other AgNWs.



**Figure S4.** FEM simulation of a AgNW laying on graphene and surmounted by another crossed wire. SERS hotspots at the graphene/AgNW interface and at the AgNW/AgNW interstitial appear spatially confined. The ratio between the average E-fields values calculated within these hotspots approaches that found by comparing the values of the same hotspots in separate configurations as displayed in Figures. 5a,b.