

Supplementary Material

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

Chiara Amicucci ^{1,2}, Cristiano D'Andrea ¹, Marella de Angelis ¹, Martina Banchelli ¹, Roberto Pini and Paolo Matteini ^{1,*}

¹ "Nello Carrara" Institute of Applied Physics (IFAC) of the Italian National Research Council (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy; chiara.amicucci@unifi.it (C.A.); c.dandrea@ifac.cnr.it (C.D.); m.deangelis@ifac.cnr.it (M.d.A.); m.banchelli@ifac.cnr.it (M.B.); r.pini@ifac.cnr.it (R.P.)

² Department of Industrial Engineering, University of Florence, Via Santa Marta 3, 50134 Florence, Italy

* Correspondence: p.matteini@ifac.cnr.it

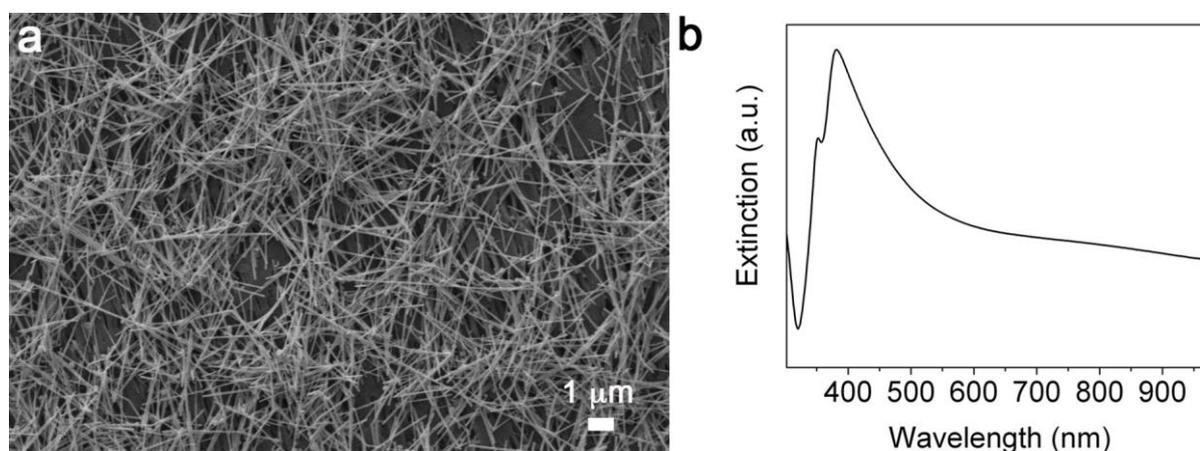


Figure S1. (a) SEM image and (b) UV-vis spectrum of the AgNWs used to prepare the SERS substrates.

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

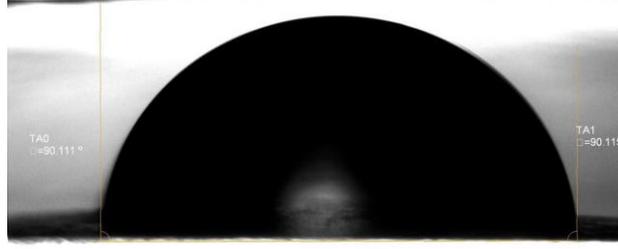


Figure S2. Contact angle of a 2 μ L water drop on a AgNWs@graphene spot.

EF calculation

EF was calculated for the AgNWs@G-paper substrate at the optimal 0.1 μ g/mm² AgNW density. A 2- μ L drop of Hb (1×10^{-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 1×10^{-3} M Hb solution in water in quartz cuvette (1 cm) were also performed. The EF was calculated by comparing the 750 cm^{-1} band intensity of Hb in the SERS spectrum (I_{SERS}) with that of the Raman measurement (I_{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_{molecule} the concentration of Hb solution used for Raman measurements, V_f the focal volume, A_{waist} the laser spot area in the focal plane, H_{depth} the depth-of-field of the objective (10x) and N_A the Avogadro number,

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

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

Therefore

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

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

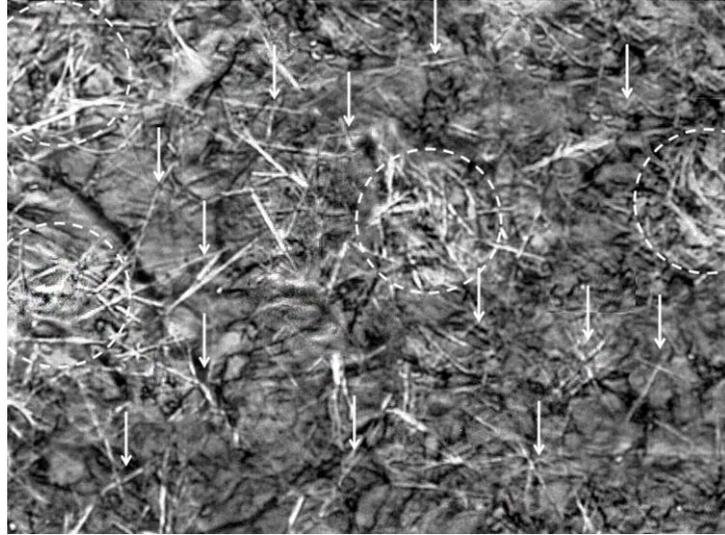


Figure S3. Optical image ($90\mu\text{m} \times 65\mu\text{m}$) of an AgNWs@G-paper substrate. Arrows: isolated AgNWs or forming single junctions with other AgNWs; circles: AgNWs forming more than a single junction with other AgNWs.

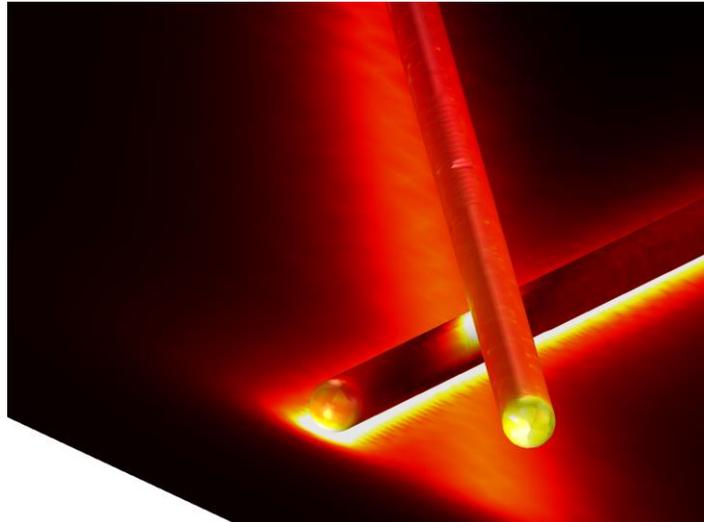


Figure S4. FEM simulation of a AgNW laying on graphene and surmounted by another crossed wire. SERS hotspots at the graphene/AgNW interface and at the AgNW/AgNW interstitial appear spatially confined. The ratio between the average E-fields values calculated within these hotspots approaches that found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