Supporting information for: Remote excitation and detection of surface-enhanced Raman scattering from graphene

Nicolás Coca-López,*,† Nicolai F. Hartmann,‡ Tobia Mancabelli,† Jürgen Kraus,¶ Sebastian Günther,¶ Alberto Comin,‡ and Achim Hartschuh*,‡

†*Department of Chemistry and Center for NanoScience (CeNS), LMU Munich, Butenandtstr. 5-13, 81377 Munich, Germany*

‡*Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, 81377 Munich, Germany*

¶*Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany*

E-mail: nicolas.cocalopez@cup.lmu.de; achim.hartschuh@cup.uni-muenchen.de

Remote excitation and detection of surface-enhanced Raman scattering from graphene: Nanowire B

Figure **S1** shows remote excitation and remote detection of surface-enhanced Raman scattering from graphene. Figures **S1**a,b present the elastic and Raman scattering maps of the NW touching graphene shown in Figure 3 in the main manuscript. After positioning the nanowire parallel to the entrance slit of the spectrometer, we obtain the emission spectra for the different positions along the NW, as was demonstrated in Figure 2 in the main manuscript. If the laser is positioned in the lower terminal of the NW (red arrow in Figure **S1**a), only a spectrally broad and nearly uniform background signal is detected at this position (see Figure **S1**c). This background signal presumably results from the inelastic scattering in the glass substrate, the immersion oil, the microscope objective and possibly from the fluorescence from the PVP poly-

mer wrapping the Ag NWs. The spectrum detected at the distal end of the nanowire which touches the graphene sheet, on the other hand, features the distinct Raman bands of graphene (G, and 2D bands), as can be seen in Figure **S1**c. The observation of Raman scattering at a distance of about 12 μm from the excitation point clearly demonstrates the remote excitation of graphene. As explained in the main text, graphene Raman scattering is generated by propagating SPPs reaching the distal tip after being launched by the laser at the input terminal (see Figure 1 in the main manuscript). Positioning of the laser focus on the upper tip of the NW touching the graphene sheet generates a Raman response which can emit directly into free space (local scattering, Figure **S1**f), or, alternatively, can launch propagating SPPs at the Raman frequency which will scatter out at the other NW end (remote scattering). Because no graphene is present at the distal end at which the Raman scattering signal is observed, this evidences the remote detection of Raman scattering. Importantly, also for this specific NW, both remotely excited and remotely detected Raman signals show comparable intensity (same order of magnitude).

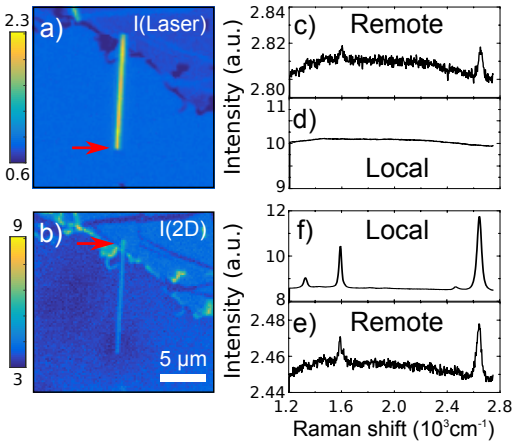

Figure S1: Confocal elastic scattering (a) and 2D Raman band (b) images of a Ag nanowire on glass touching a graphene edge, recorded upon laser excitation at 633 nm. Remote excitation of surface-enhanced Raman scattering from graphene is observed at the remote termination of the nanowire (c) after laser illumination of the termination laying on glass (red arrow in panel (a)), where no Raman features are observed (d). Following local excitation of surface-enhanced Raman scattering (f) at the nanowires tip laying on top of graphene (red arrow in (b)), Raman features are remotely detected at the distal termination of the nanowire (e). Spectra for local and remote positions obtained following the procedure explained in Figure 2 in the main manuscript.

Nanowire-enhanced Raman spectrum of graphene

Figure **S2**a shows a elastic scattering map of the NW laying on graphene already discussed in Figure 4 in the main text. Propagation of SPPs when the excitation is focused on the position marked by the blue circle in Figure **S2**a is shown by the laser elastic scattered light image (see Figure **S2**b). The SERS spectrum of graphene is presented in Figure **S2**c (blue line) in comparison with the Raman spectrum of bare graphene (black line). The increased background observed for the enhanced case is presumably coming from the polymer wrapping the NW. Figure **S2**d shows the spectrum at the right terminal of the NW. At this specific position only the D and G band are present, on top of a stronger signal background. This results from the accumulation of material (i.e. amorphous carbon,[1] smaller/broken nanowires, etc.) at the right terminal, resulting in the observed higher intensity when compared to the left terminal (see Raman scattering map in Figure 4b in the main text).

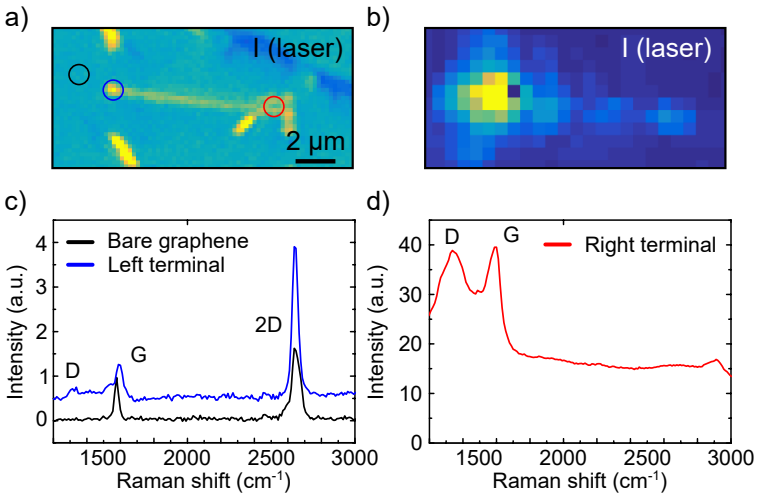

Figure S2: Confocal elastic scattering (a) map of an Ag nanowire on graphene, recorded upon laser excitation at 633 nm. (b) Laser elastic scattered light image obtained when the excitation is focused on the position marked by the blue circle in figure a. (c) Spectra recorded on bare graphene (black) and on the left terminal of the nanowire (blue). The increased background for the latter case is presumably coming from fluorescence and Raman scattering from the polymer wrapping up the NW. (d) Spectrum recorded at the right terminal of the nanowire showing amorphous carbon and a strong background signal, possibly coming from the polymer wrapping the nanowire.

Nanowire on graphene: Experimental and calculated BFP patterns

Figure 4 in the main manuscript shows the qualitative agreement between the experimental and calculated BFP patterns rendered by light emitted at the frequency of the G and 2D Raman bands of a NW on graphene. The patterns are composed of the direct Raman emission pattern of graphene[2] plus the characteristic fringe pattern rendered by back and forth propagating SPPs .[3] To underline the quantitative agreement between experiment and calculation we present here the cross sections of these BFP patterns in Figure **S3**a and b. The cross sections are indicated in the inset as black lines for the experimental patterns and red lines for the calculated ones. The minor non-symmetrical signal contribution visible in the center of the BFP patterns results from additional radiation channels such as photoluminescence and Raman scattering from the NW or material accumulation (see discussion in the main text).

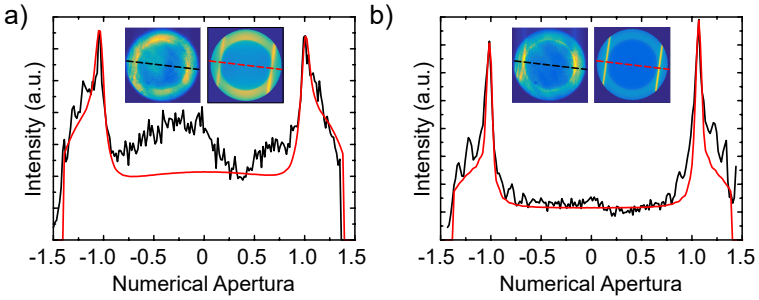

Figure S3: Cross sections of the BFP patterns for scattered light at the 2D (a) and G (b) band frequencies shown in Figure 4 in the main manuscript. The cross sections of the experimental (black line) and calculated (red line) patterns show the good agreement between experiment and calculation. The insets indicate where the cross section were taken.

References

1. Schwan, J.; Ulrich, S.; Batori, V.; Ehrhardt, H.; Silva, S. Raman spectroscopy on amorphous carbon films. *J. Appl. Phys.* **1996**, *80*, 440–447.

2. Budde, H.; Coca-López, N.; Shi, X.; Ciesielski, R.; Lombardo, A.; Yoon, D.; Ferrari, A. C.; Hartschuh, A. Raman Radiation Patterns of Graphene. *ACS Nano* **2016**, *10*, 1756–1763, PMID: 26651030.

3. Song, M.; Dellinger, J.; Demichel, O.; Buret, M.; Des Francs, G. C.; Zhang, D.; Dujardin, E.; Bouhelier, A. Selective excitation of surface plasmon modes propagating in Ag nanowires. *Opt. Express* **2017**, *25*, 9138–9149.