Supporting Information

Laser Treatment of Ag@ZnO Nanorods as Long Life Span SERS Surfaces

M. Macias-Montero,[a]* R. J. Peláez,[b] V. Rico,[a] Z. Saghi,[c] P. Midgley,[c] C. N. Afonso,[b] A.R. González-Elipe,[a] and A. Borras [a]

[a] Nanotechnology on Surfaces Laboratory, Materials Science Institute of Seville (ICMS), CSIC-University of Seville, C/AmericoVespucio 49,41092 Seville, Spain.
[b] Laser Processing Group, Instituto de Optica, CSIC, Serrano 121, 28006 Madrid, Spain.
[c] Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS. UK.

*Corresponding author: maciasmonterom@gmail.com

S1. X-Ray Diffraction of laser treated Ag@ZnO NRs.

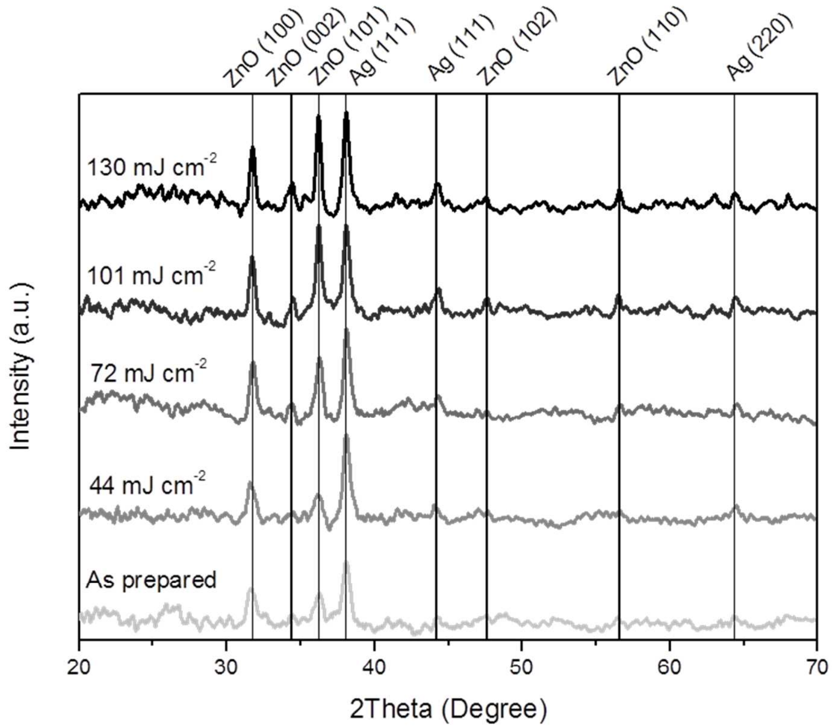

Figure S1: XRD spectra of Ag@ZnO NRs laser irradiated with different fluences as labelled.

S2. Transmission electron microscopy of laser treated Ag@ZnO NRs.

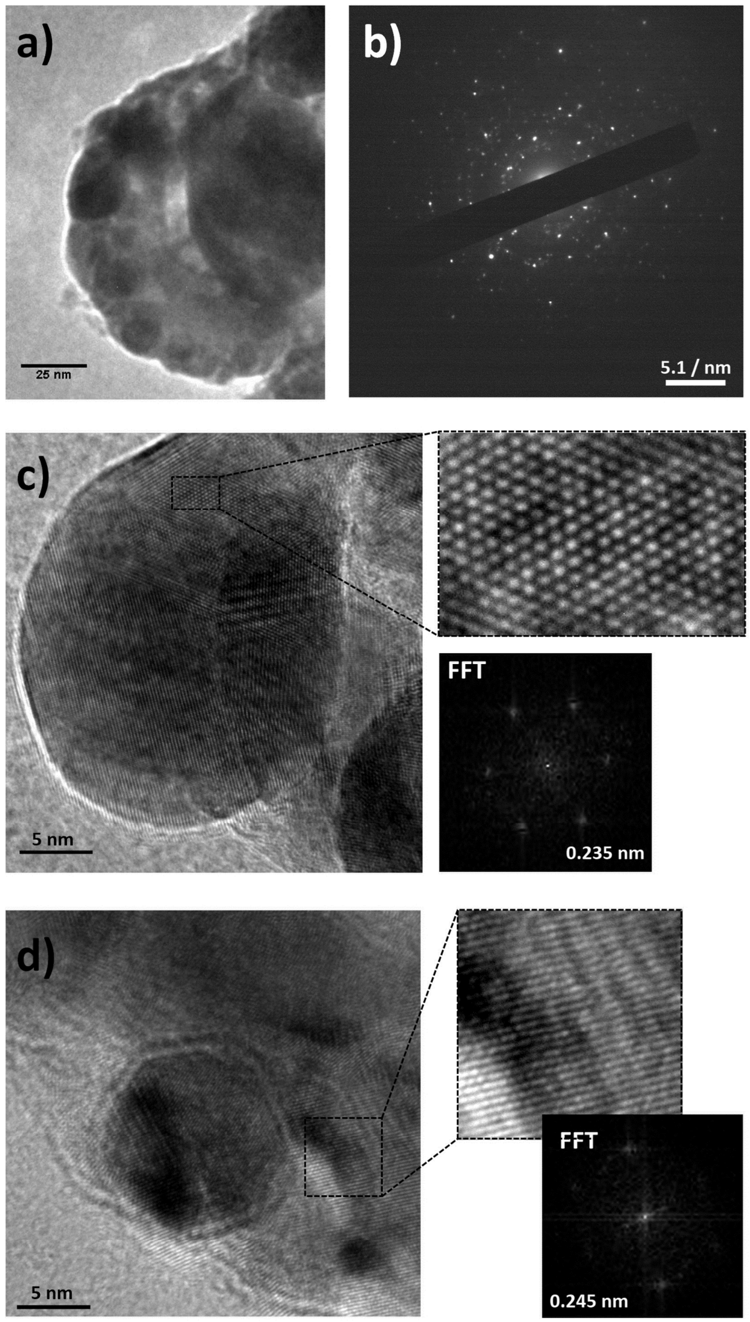

Figure S2: TEM micrographs of a ZnO sphere produced after laser irradiation of Ag@ZnO NRs. a) ZnO particle with Ag NPs inside, b) selected area electron diffraction pattern of the zone displayed in panel a), c) high resolution TEM of an Ag NP on the surface of the ZnO particle, d) high resolution TEM of the ZnO sphere.

S3. Microstructural modification after successive irradiations.

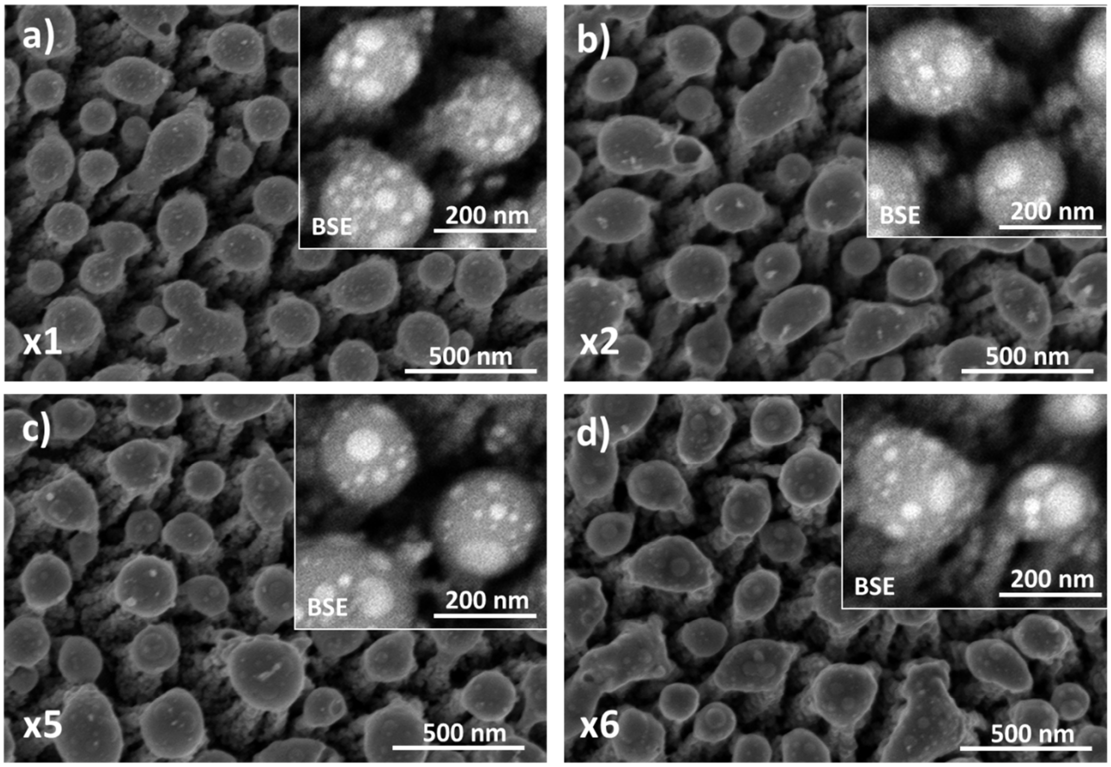

Figure S3: SEM micrographs of Ag@ZnO NRs laser irradiated at a fluence of 72 mJ cm^{-2} with a) 1, b) 2, c) 5 and d) 6 successive pulses.

S4. Water contact angle of Ag@ZnO NRs.

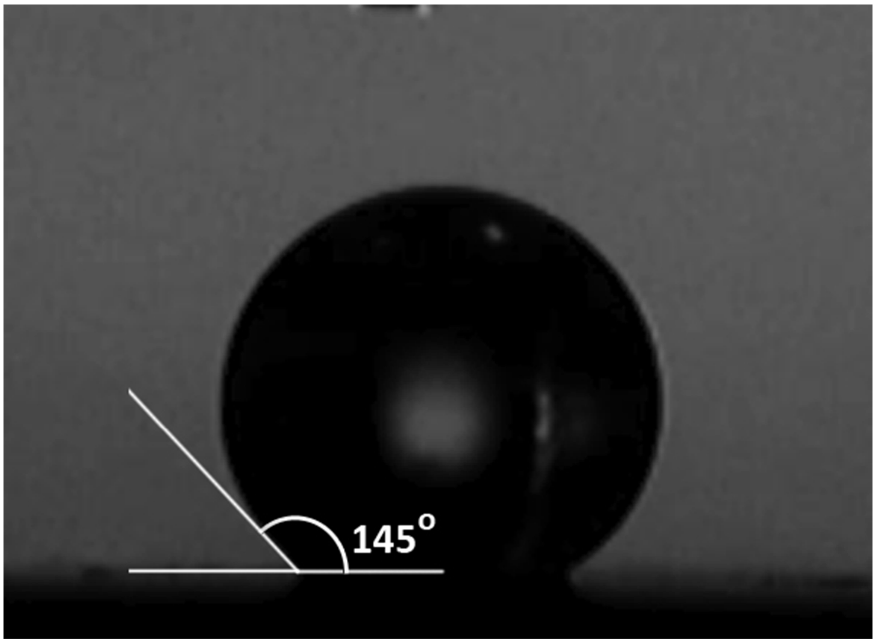

Figure S4: Picture of a water droplet on a Ag@ZnO NRs surface with a contact angle of 145°

S5. Nanocarpet effect on as prepared Ag@ZnO NRs.

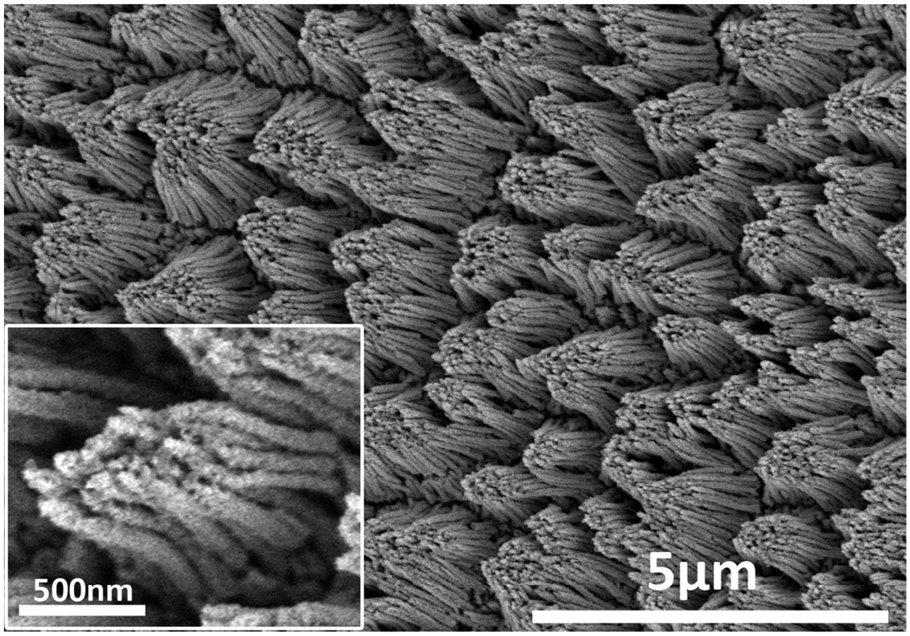

Figure S5: SEM micrographs of Ag@ZnO NRs after water dripping the surface. Inset highlights a NRs bundle.

S6. Calculation of the SERS enhancement factor.

The enhancement factor can be calculated by

$$EF = \frac{I_{SERS}/N_{SERS}}{I_R/N_R}$$

Where I_{SERS} and I_R represent the intensity of the same band of Rh6G (771 cm^{-1} in our case) of SERS and standard Raman spectra respectively, and N_{SERS} and N_R accounts for the number of molecules in the focused incident laser spot in each of the two types of measurements. The number of molecules in the SERS characterization can be estimated knowing that 2 µl droplets with a concentration of 10^{-11} M are deposited over 16 mm^2 samples and that the laser spot is 100 µm. Using these data, we calculate a N_{SERS} of approximately 2.35×10^4 molecules. The same procedure can be followed for the standard Raman measurement, where the concentration used is 10^{-5} M, the droplet volume is 50 µl and a substrate area of 100 mm^2, obtaining approximately 9.42×10^{10}. Regarding the intensity of the signals, the values obtained are I_{SERS} = 420 counts for the as prepared Ag@ZnO NRS and I_R = 1045 counts. Thereby, the enhancement factor is calculated to be 1.6×10^6.

For laser irradiated Ag@ZnO NRs, the same measuring conditions where used obtaining in this case an I_{SERS} of 375 counts. This leads to a slightly lower enhancement factor of approximately 1.4×10^6.

S7. Energy band diagram of Ag-ZnO interface.

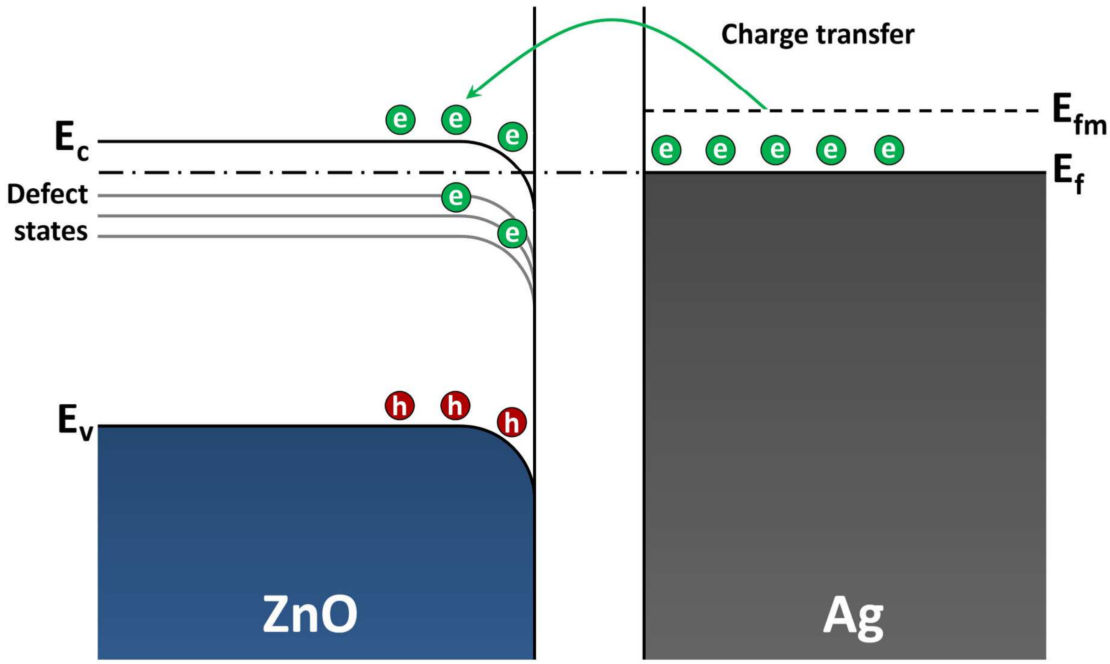

Figure S7: Energy band diagram of Ag-ZnO interface showing the SPR induced electron transfer.