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New Journal of Chemistry

Supporting Information

Hydrophobic Mediated Growth of Galvanic-Nanobuds from Germanium Nanowires for a Highly Tunable SERS substrate

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GeNW SUBSTRATE PROPERTIES

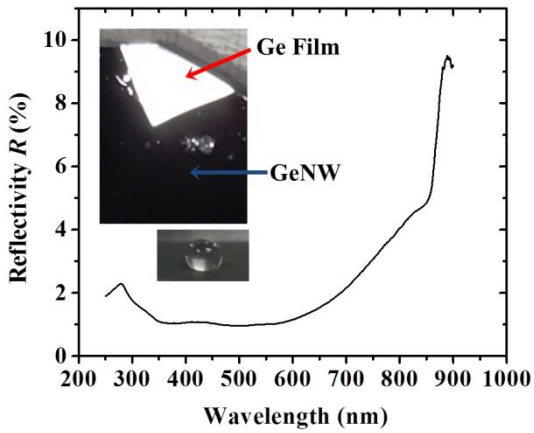


Figure S 1. Reflectance spectrum of GeNW substrate. The spectrum can be compare with the standard reflectivity of Ge wafer (Materials Letters 94 (2013): 86-88). Inset images show the difference between the reflecting Ge film and NW region as well as the hydrophobic nature of the substrate with a water droplet.

VALIDATION OF TEMPORAL SERS PLOT

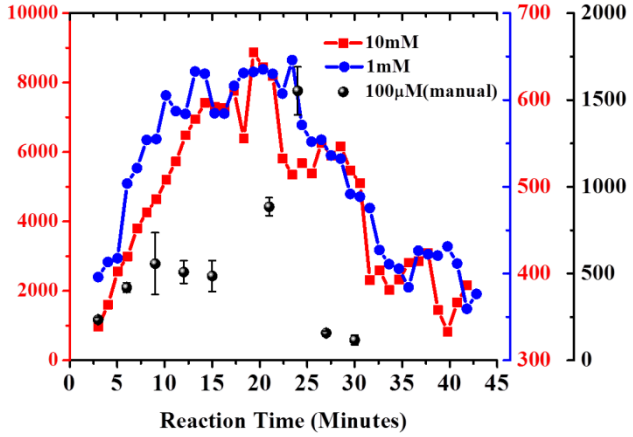


Figure S 2. Temporal plot of the substrates at 785 nm for different concentration of Pyridine.

Concentration of Pyridine does not have any effect on the automated measurement procedure. Multiple substrates were fabricated at different displacement reaction time and the SERS intensity of 100 μM Pyridine was recorded. The intensity trend in the manual experiment should follow that of the automated time mapping. It can be concluded that the resonance is not precisely at 21 min but falls in between 20 to 25 min.

CL MAP ANALYSIS

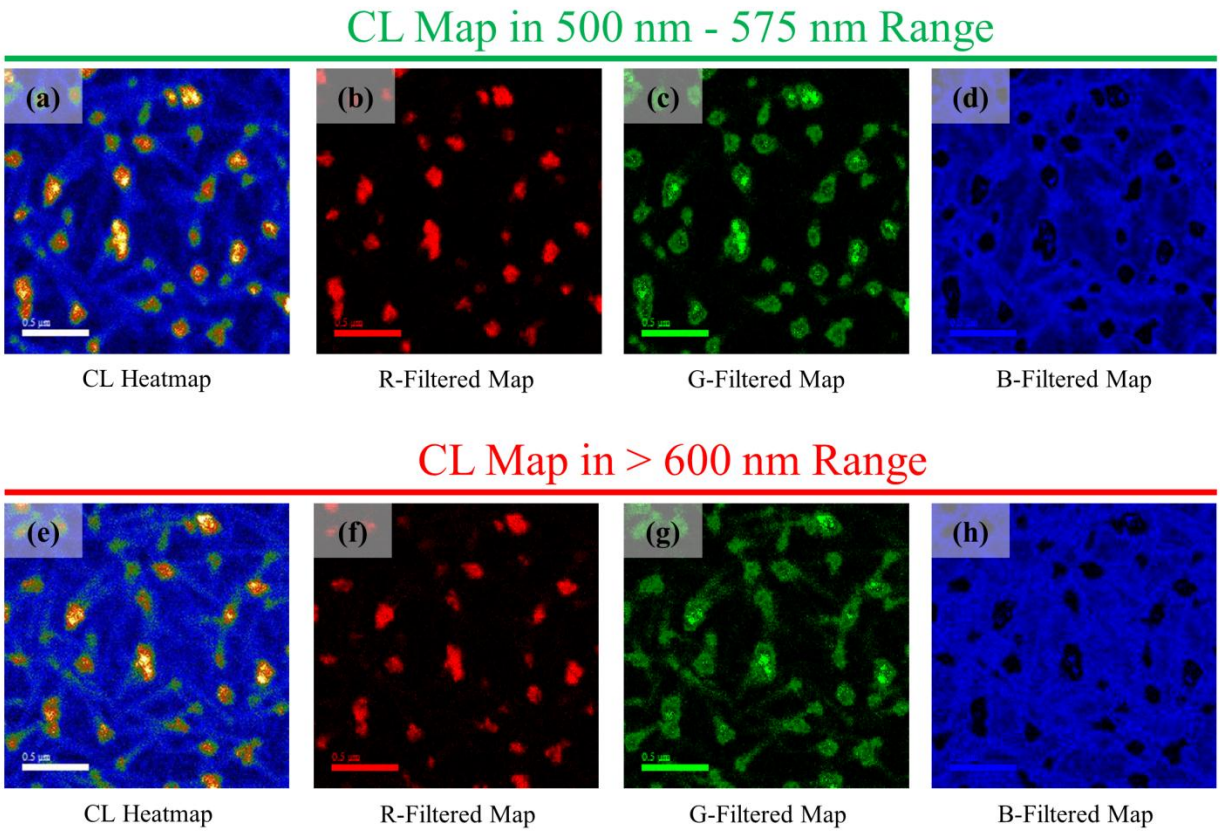


Figure S 3. (a) CL map of substrate tuned to 514 nm using green filter (500-575 nm). (b) R, (c) G, (d) B colour filtered map of the CL map. (e) CL map of substrate tuned to 514 nm using red filter (> 600 nm). (f) R, (g) G, (h) B colour filtered map of the CL map.

Weak CL signal from NWs are observed because of bare GeNWs (Figure S 3). Such luminescence lies below 600 nm (Figure S 5). Hence, the signal is prominent in green spectral band (Figure S 3d) than in red spectral band (Figure S 3h).

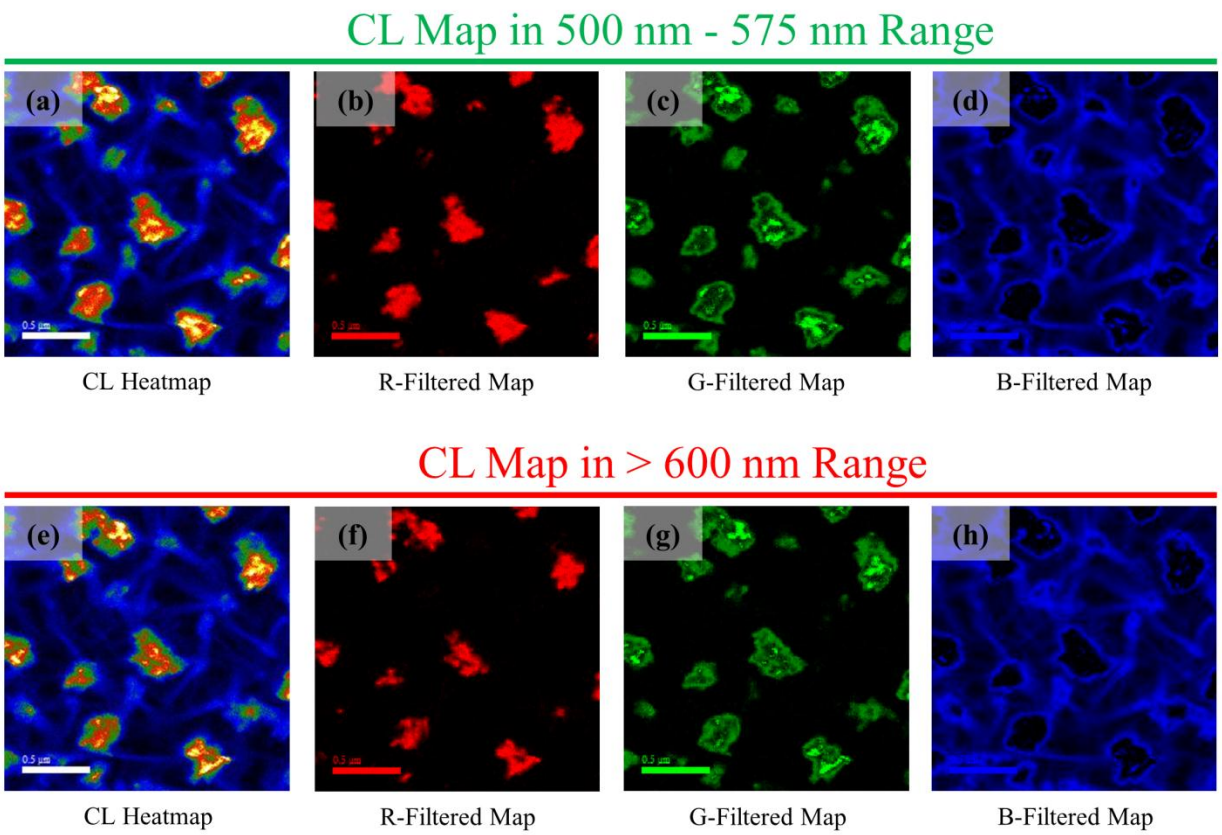


Figure S 4. (a) CL map of substrate tuned to 785 nm using green filter (500-575 nm). (b) R, (c) G, (d) B colour filtered map of the CL map. (e) CL map of substrate tuned to 785 nm using red filter (> 600 nm). (f) R, (g) G, (h) B colour filtered map of the CL map.

Observable CL intensity from NWs in both green and red spectral region (Figure S 4d and h) corresponds to some form of confinement effect rather than CL from bare GeNW. The CL intensity of GeNW is very feeble to contribute to such high signal, at least in the red spectral region (Figure S 5).

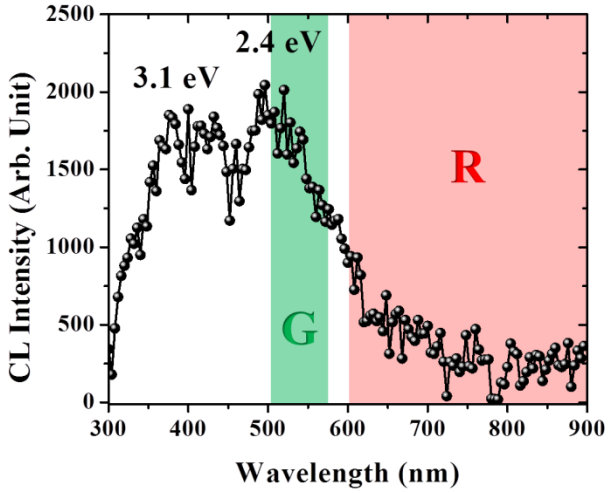


Figure S 5. CL spectrum of bare GeNW. The shaded region is for reference to the filters used in CL mapping. The CL peaks match the corresponding bandgaps reported elsewhere. (*Physical Review B, 1995. 52(3): p. 1452* and *Semiconductor science and technology, 2002. 17(12): p. 1267*)

RAMAN SPECTRA OF R6G

The normal spectra of R6G are provided in Figure S 6 with same experimental specifications as provided in the manuscript.

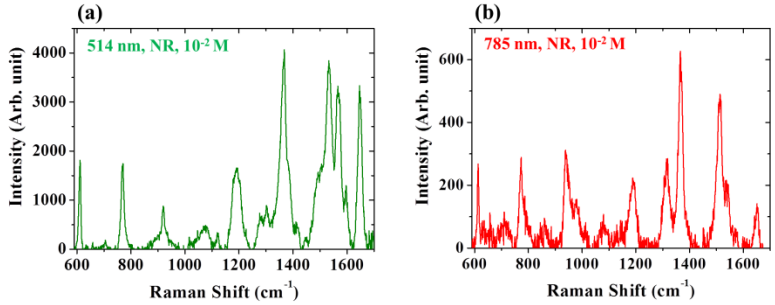


Figure S 6. Normal Raman spectra of 10^{-2} M R6G solution at (a) 514 nm and (b) 785 nm.

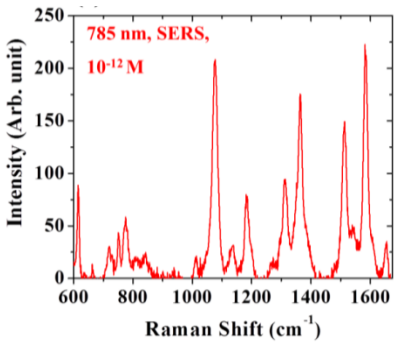


Figure S 7. SERS spectrum of 10^{-12} M R6G solution at 785 nm. The spectrum is obtained by averaging spectra from 50 random spots on a substrate.

The spectrum in Figure S 7 has been obtained by keeping the SERS substrate in 10^{-12} M R6G solution for 2 hours and with the same experimental parameters as mentioned in the main manuscript. The adsorption of molecule on the substrate surface may lead to shift in the observed bands; however, the spectrum is reproducible.

SERS MEASUREMENTS WITH PYRIDINE

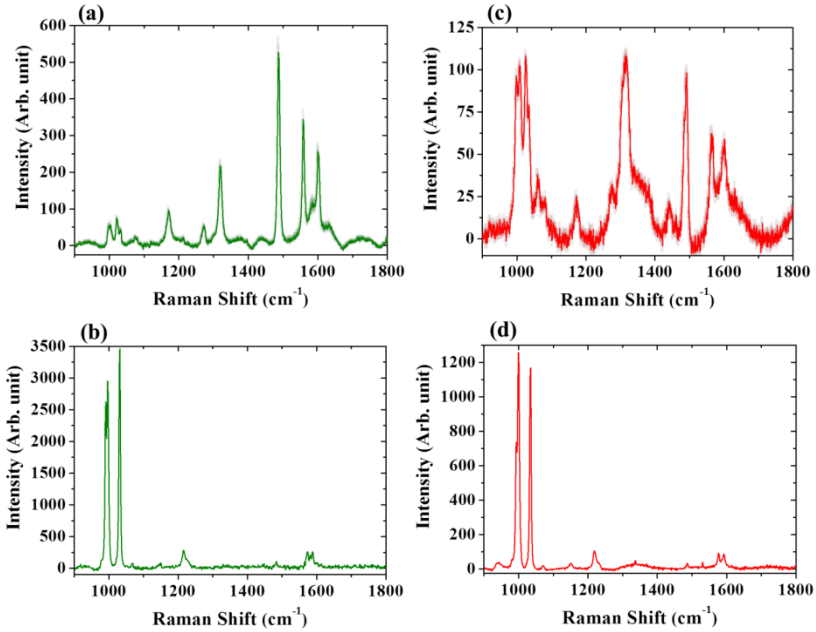


Figure S 8. (a) SERS and (b) normal Raman spectra of Pyridine at 514 nm. (c) SERS and (d) normal Raman spectra of Pyridine at 785 nm.

The spectra in Figure S 8a and b were recorded with 0.76 mW power at the sample and 1 s exposure. The spectra in Figure S 8c and d were recorded with 16.2 mW power at the sample and 1 s exposure. Spectra were acquired with 20xL objective with 0.35 NA. About 10 µl of 10 µm Pyridine was dispensed on the substrates and dried which was followed by Raman measurement. All the EFs represent the Analytical EF using the following equation.

$$AEF = \frac{I_{SERS}/C_{SERS}}{I_{NR}/C_{NR}}$$

MODE ASSIGNMENT

Table S 1. Peak assignment for R6G

Wavenumber (cm^{-1})	Assignment
612, 664, 702	in-plane xanthene ring deformation
774, 920	out-of-plane C-H bend
1084, 1122	in-plane C-H bend
1181	in-plane xanthene ring deformation, C-H bend, N-H bend
1268	C-O-C stretch
1310	in-plane xanthene ring breath, N-H bend, CH_2 wag
1362	xanthene ring stretch, in-plane C-H bend
1507, 1535	aromatic C-C stretch
1576	xanthene ring stretch, in-plane N-H bend
1599, 1606	aromatic C-C stretch
1650	xanthene ring stretch, in-plane C-H bend

TEM CHARACTERIZATION RESULTS

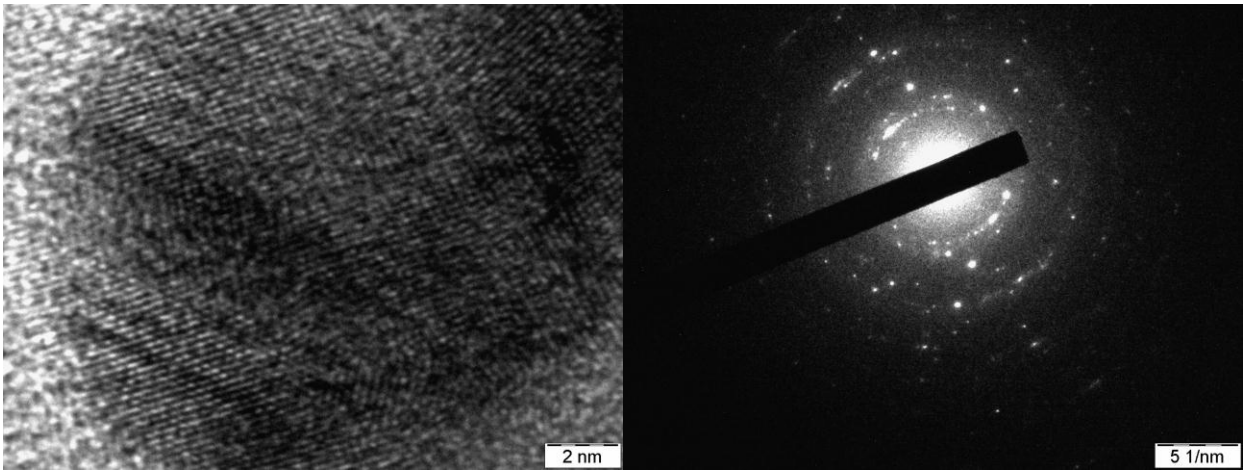
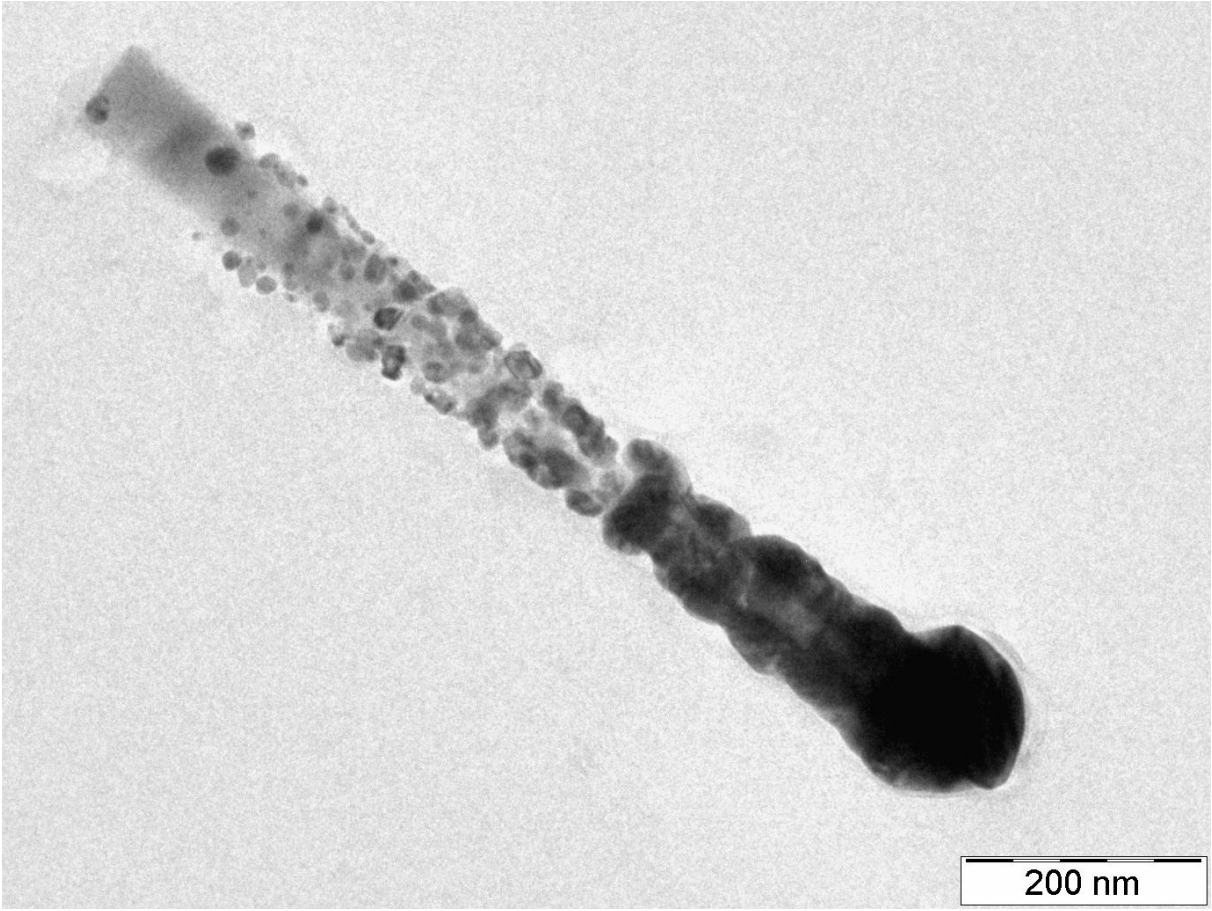
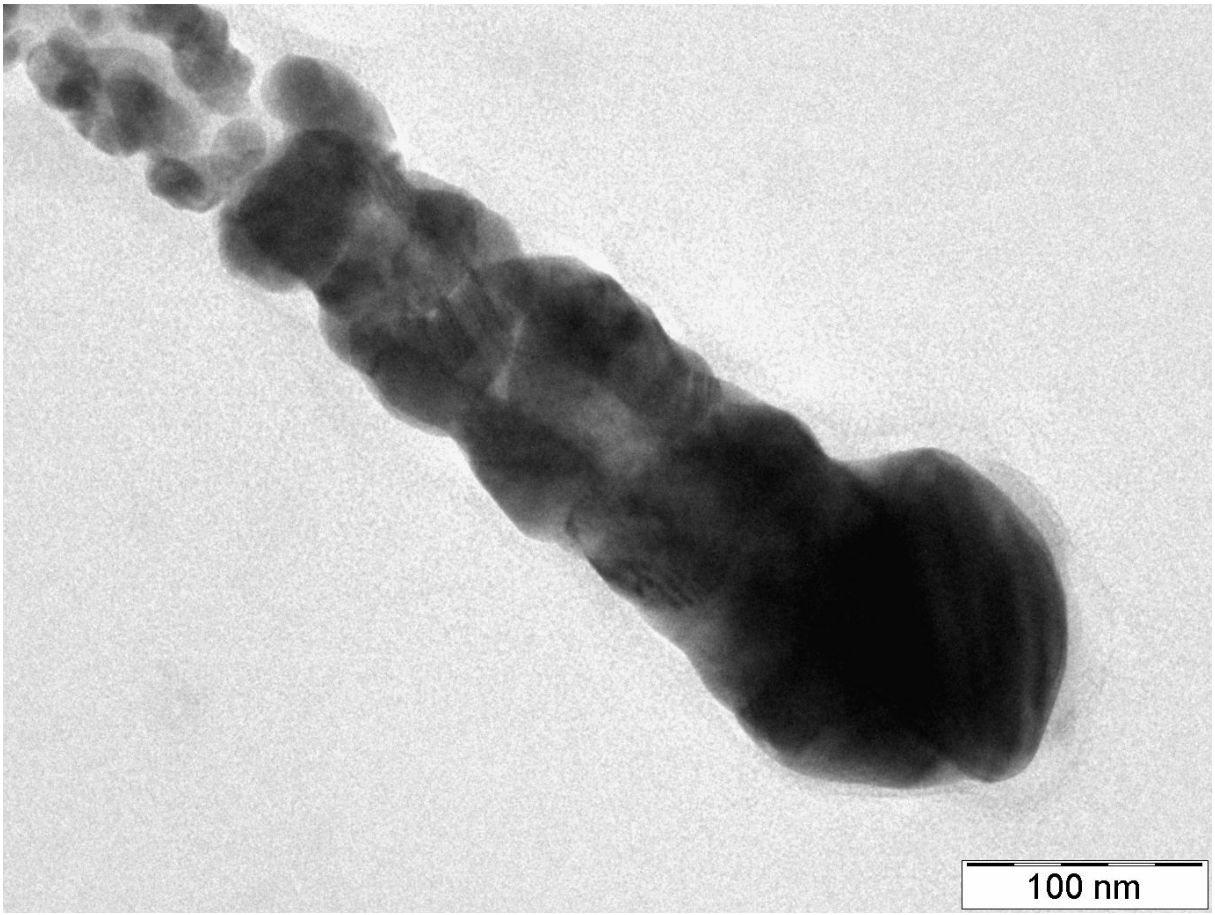
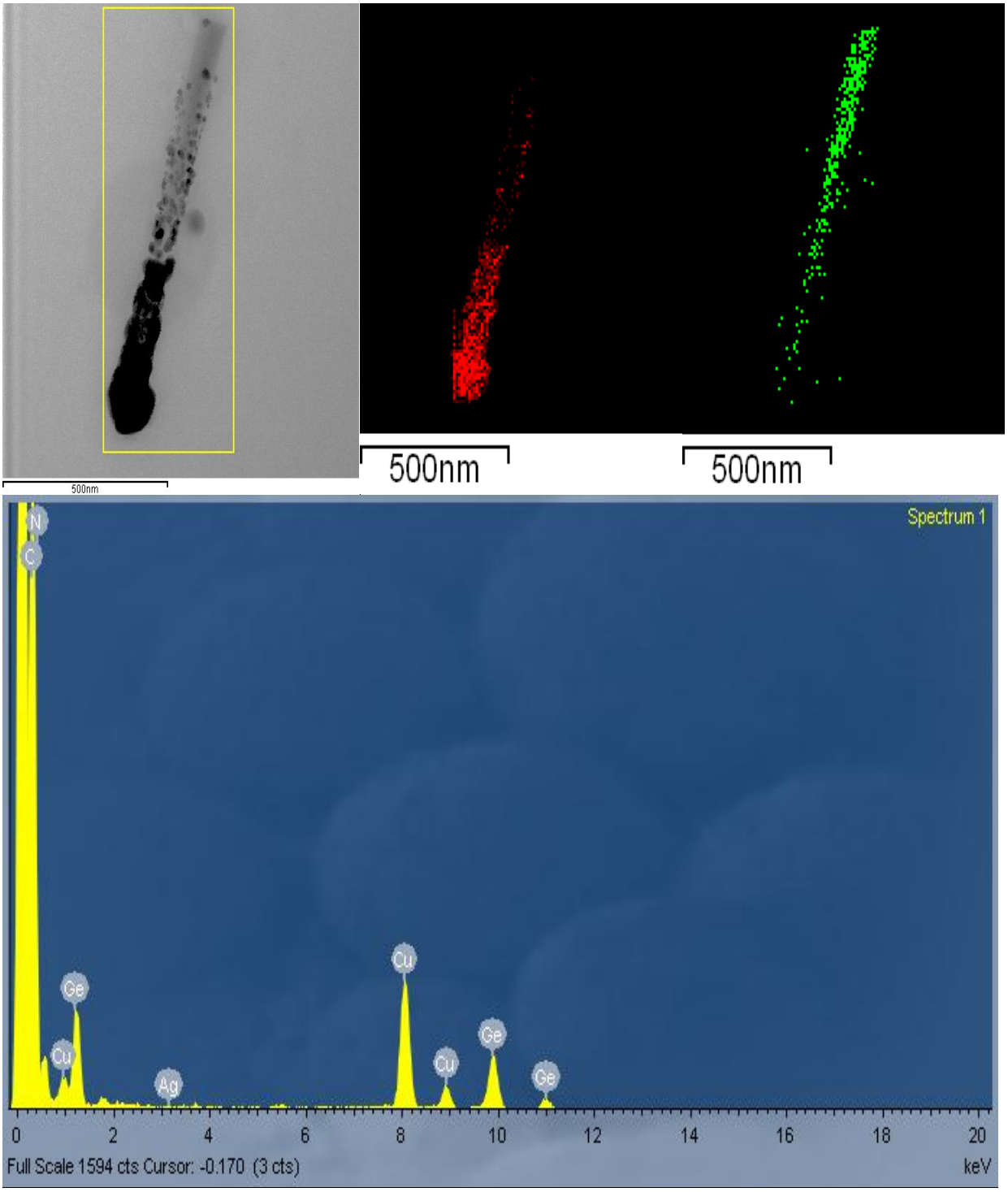


Figure S 9. HRTEM and SAED pattern of Ag cluster in the nanobuds.

The following are the unmodified TEM results provided in the manuscript.




100 nm


500nm
500nm
500nm
Spectrum 1
N
C
Ge
Cu
Ag
Cu
Cu
Ge
Ge
0
2
4
6
8
10
12
14
16
18
20
Full Scale 1594 cts Cursor: -0.170 (3 cts)
keV