Electronic Supplementary Material (ESI) for ChemComm.

Spontaneous Formation and Plasmonic Properties of Ultrathin Gold-Silver Nanorods and Nanowires Stabilized with Oleic Acid

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental section

General

The compound $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]_n$ was synthesized by standard procedures reported in the literature.[1] Oleic acid was purchased from Sigma Aldrich and used without further purification. Experiments have been conducted under air. After reaction the Au-Ag UNWs were separated by centrifugation and washing several times with 3:1 Toluene:ethanol mixtures. All the synthetic approaches described here have been repeated at least twice in order to ensure the reproducibility of the preparation methodology.

Instrumentation

The NMR spectra were recorded on a Bruker Avance 400 spectrometers in d^8-THF solutions. Chemical shifts are expressed relative to $CFCl_3$ (^{19}F external). For GC/MS sample analysis, a Varian 3900 gas chromatograph with a Varian 2100T MS detector (Walnut Creek, CA, USA) was used. SPME injections were carried out in an automated manner using a CombiPal autosampler (CTC Analytics, Zwingen, Switzerland). UV/Vis/NIR spectra were recorded with a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. IR spectra were recorded on a Nicolet Nexus FT-IR. All reported spectra were normalized at 1600 nm. Samples for Transmission Electron Microscopy (TEM) were directly drop-casted from the hexane colloidal dispersions (2-3 drops) to carbon-coated Cu grids. The TEM images were obtained with a a JEOL JEM 2100 microscope. For high resolution electron microscopy (HRTEM) imaging of NPs, selected samples were analyzed by a JEOL JEM 2200-FS microscope, equipped with a Schottky field emission electron source, a spherical aberration corrector of the objective lens, an Omega in-column energy filter, and operating at an acceleration voltage of 200 kV. The same microscope was used in Scanning Transmission Electron Microscopy (STEM) mode and High Angle Annular Dark Field (HAADF) geometry, providing an electron probe of 1 nm, to perform EDS spectra. The latter were collected by using a Bruker X-Flash Silicon Drift detector, with active area of 60 mm^2. For the EDS spectrum analysis the Cliff-Lorimer quantification method was used, linearly modeling the small background contribution to subtract in the

energy ranges of interest, and using a Gaussian function to model both Ag-Lα (and Ag-Lβ) and Au-Lα.

Synthesis of complex $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]_n$

The synthesis of the precursor complex $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]_n$ was previously reported.[1] Briefly, To a CH_2Cl2/Et_2O solution (1:2) of $[Bu_4N][Au(C_6F_5)_2]$ (0.116 g, 0.150 mmol) was added $AgOClO_3$ (0.031 g, 0.150 mmol). A deep-orange solid formed immediately and was filtered after 2 h of stirring.(Yield: 91%).

Synthesis of Au-Ag UNRs (1-3)

Complex $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]_n$ (25.0 mg, 0.018 mmol) was sonicated for 15 minutes in oleic acid (5.0 mL) until a clear colourless solution was formed. The mixture was left, without stirring, at 20 (**1**), 30 (**2**) or 40 ºC (**3**) and light-protected for 72 h hours, forming dark brown solutions with a black solid at the bottom of the glass tube. The solid was separated from the colloidal solution by centrifugation and washing several times with toluene:ethanol 3:1 mixture of solvents. The obtained black solid was dried under vacuum. The black solid obtained was dried and further dissolved in hexane for UV/Vis/NIR and TEM sampling. The IR sampling was carried out by dropcasting a KBr disc with few drops of the hexane colloidal dispersions.

Synthesis of Au-Ag UNWs (4-5)

Complex $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]_n$ (50.0 mg, 0.036 mmol) (4) or (75.0 mg, 0.054 mmol) (**5**) was sonicated for 15 minutes in oleic acid (5.0 mL) in a glass tube until a clear colourless solution was formed. The mixture was left, without stirring, at 30 ºC and light-protected for 72 h hours, forming dark brown solutions with a black solid at the bottom of the glass tube. The solid was separated from the colloidal solution by centrifugation and washing several times with toluene:ethanol 3:1 mixture of solvents. The obtained black solid was dried under vacuum. The black solid obtained was dried and further dissolved in hexane for UV/Vis/NIR and TEM sampling. The IR sampling was carried out by dropcasting a KBr disc with few drops of the hexane colloidal dispersions.

References

[1] E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, R. C. Puelles, A. Laguna, A. A. Mohamed, J. P. Fackler, Jr., *Inorg. Chem.* 2008, **47**, 8069.

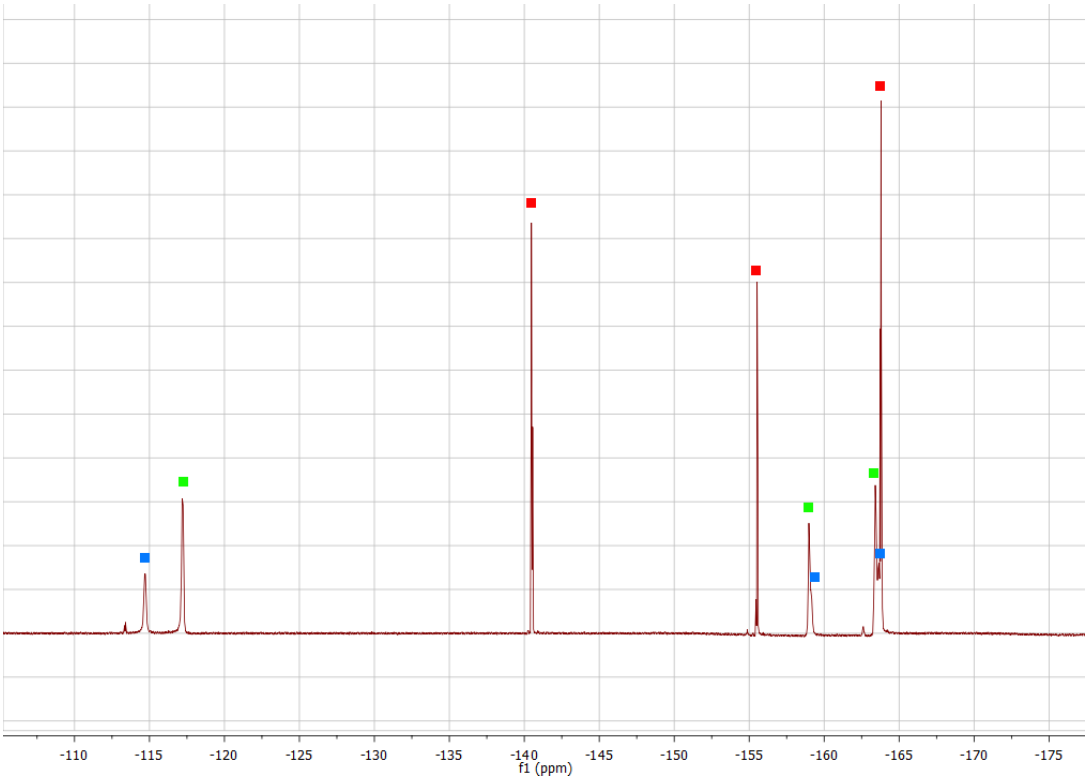


Fig S1. Time-resolved ^{19}F NMR spectra of the decomposition of the complex $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]$ in the presence of 4 equivalents of oleic acid in d_8-THF. The red squares correspond to the signals for C_6F_5H; the blue squares correspond to the C_6F_5 ligands in the $[Au_2Ag_2(C_6F_5)_4(\text{oleic acid})_2]$ complex, the green squares correspond to the C_6F_5 ligand in the $[Au(C_6F_5)(\text{oleic acid})]$ complex. This assignment is similar to the one described for complex $[Au_2Ag_2(C_6F_5)_4(HDA)_2]$ (HDA = Hexadecylamine) (see *J. Mat. Chem. C* **2014**, 2, 2975). Both the formation of C_6F_5H and the intermediate complex $[Au(C_6F_5)(\text{oleic acid})]$ suggests that the pentafluorophenyl ligands act as base and deprotonate oleic acid molecules.

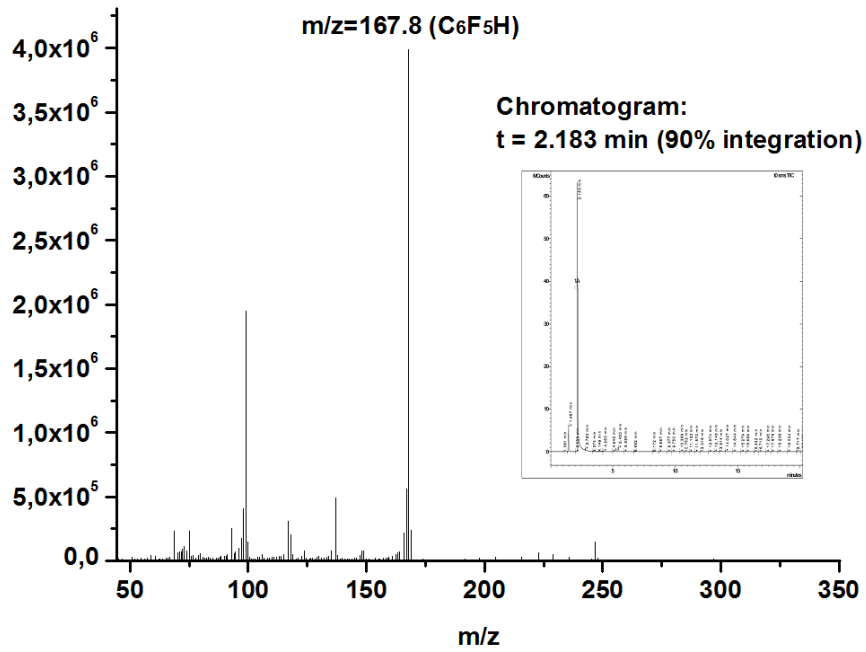


Fig S2 Mass spectrum of the gas phase products of the decomposition of complex $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]$ in the presence of 4 equivalents of oleic acid. The inset shows the headspace solid-phase microextraction gas chromatography mass spectrometry (HS-SPME-GC-MS) chromatogram.

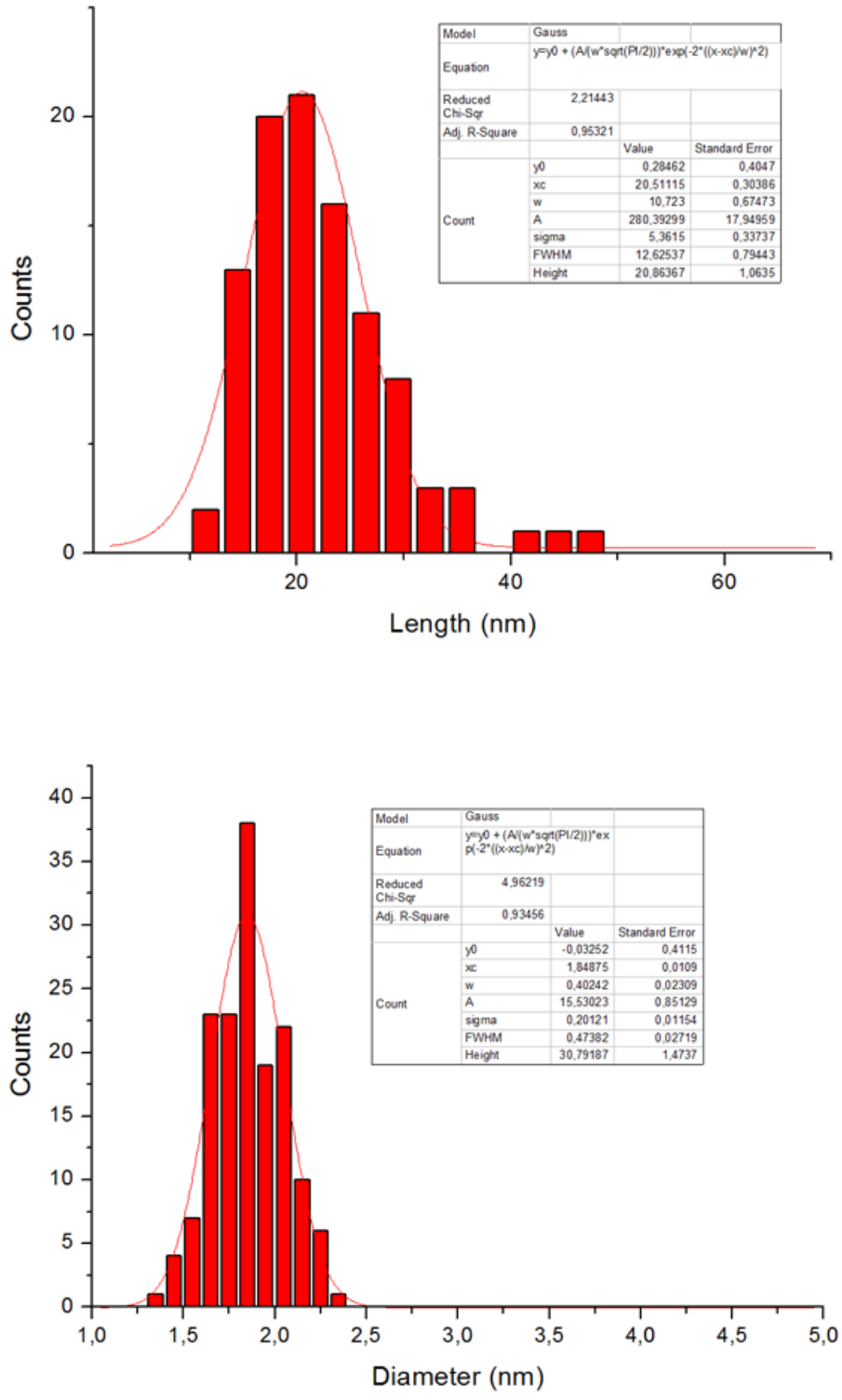
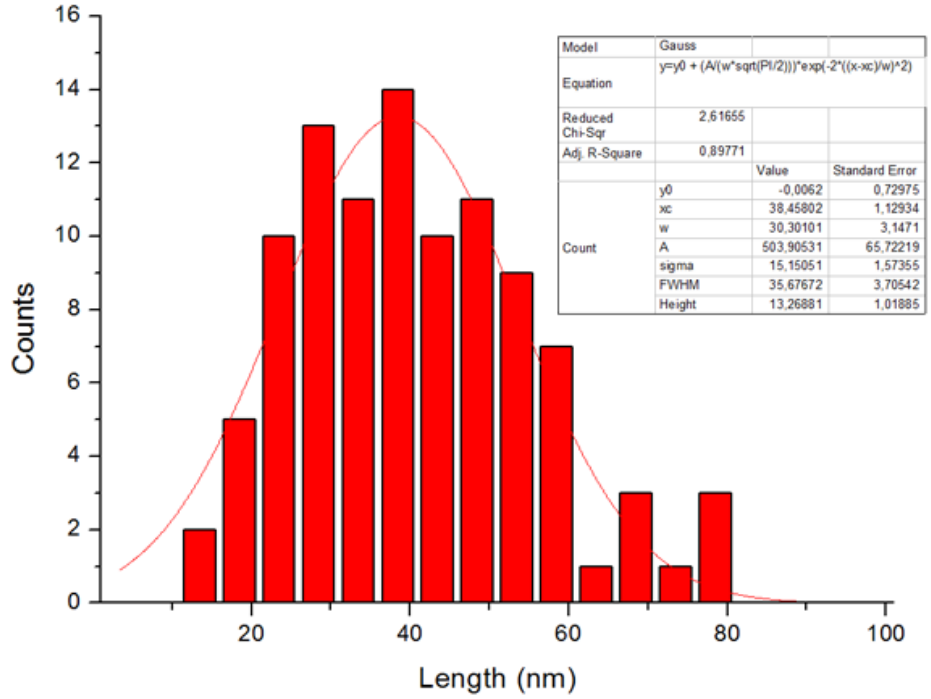


Fig S3 Length distribution (up) and width (bottom) distribution for AuAg UNRs **1**.



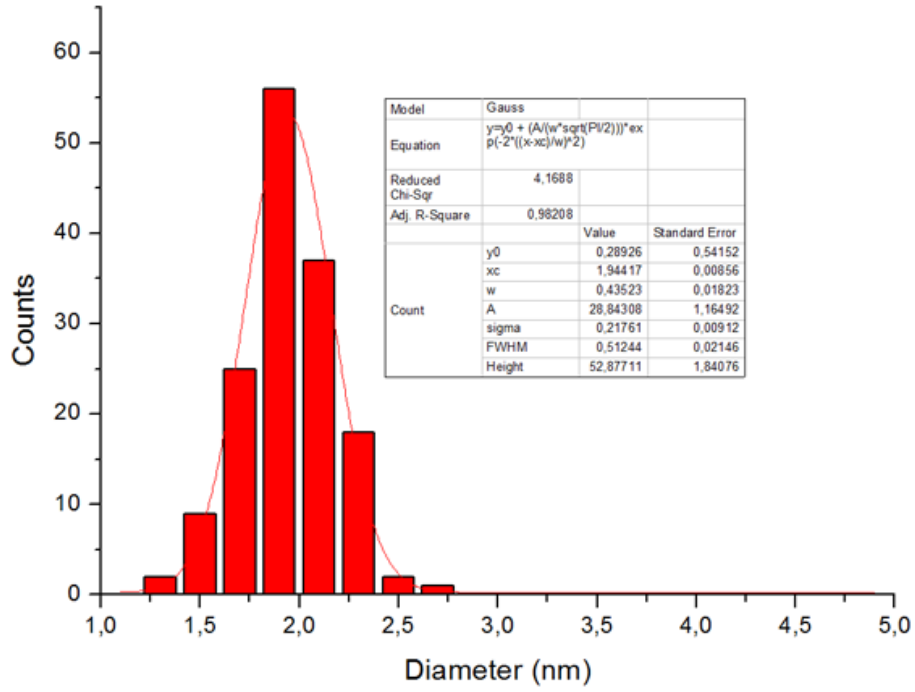
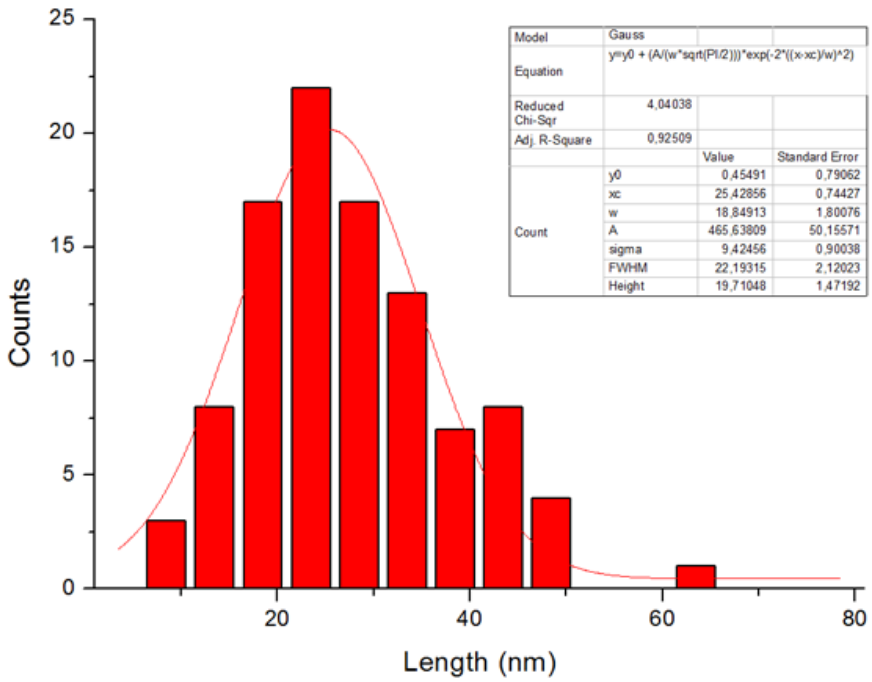


Fig S4 Length distribution (up) and width (bottom) distribution for AuAg UNRs **2**.



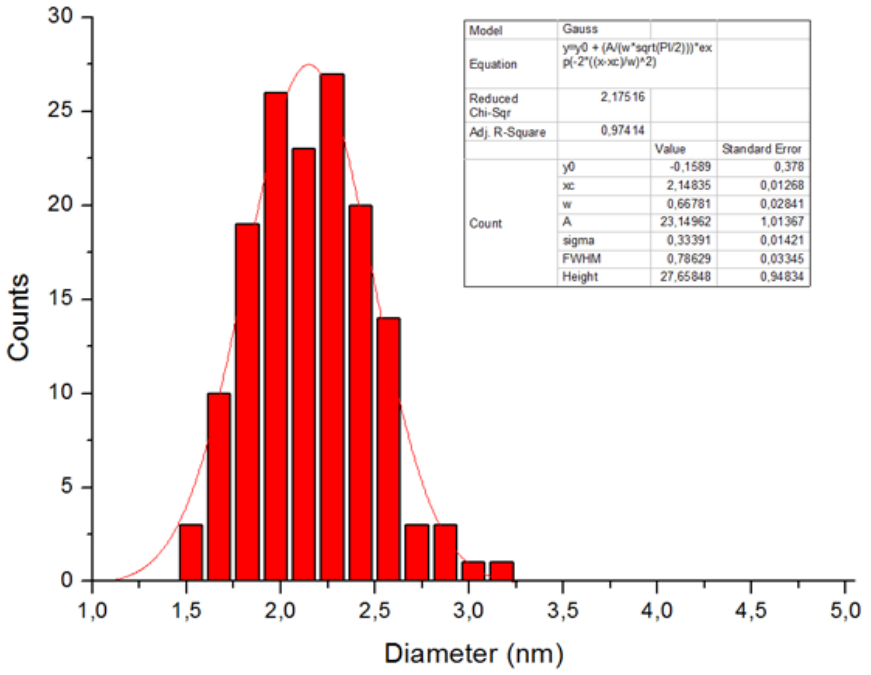
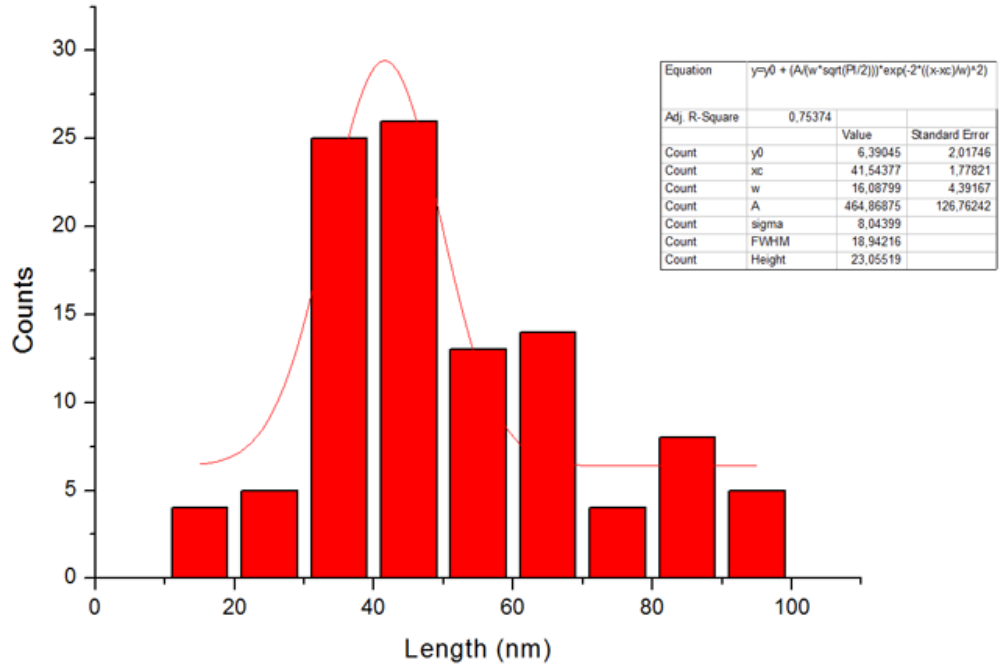
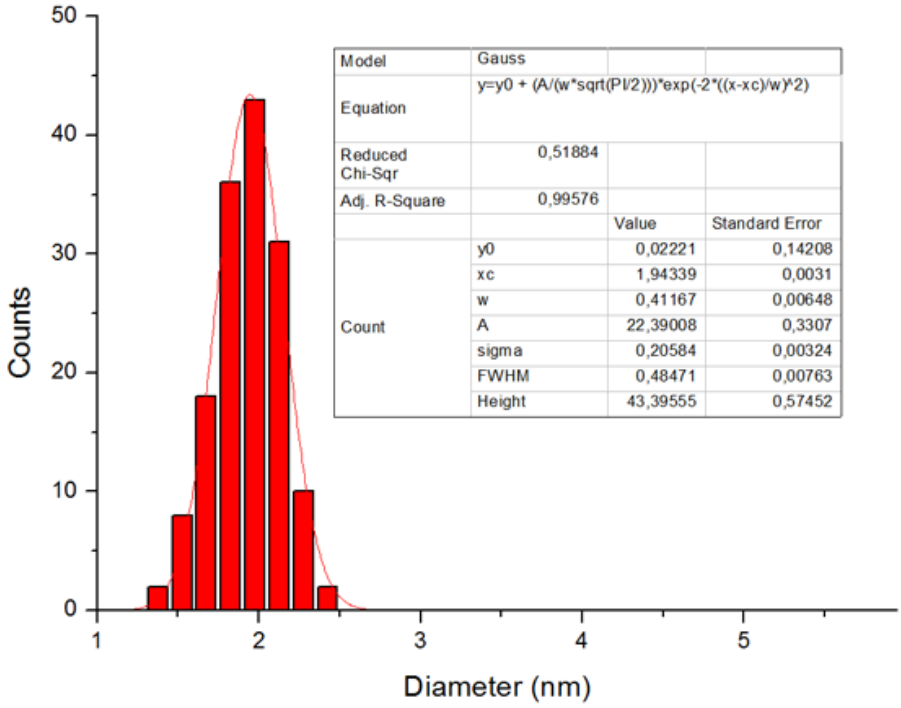


Fig S5 Length distribution (up) and width (bottom) distribution for AuAg UNRs **3**.

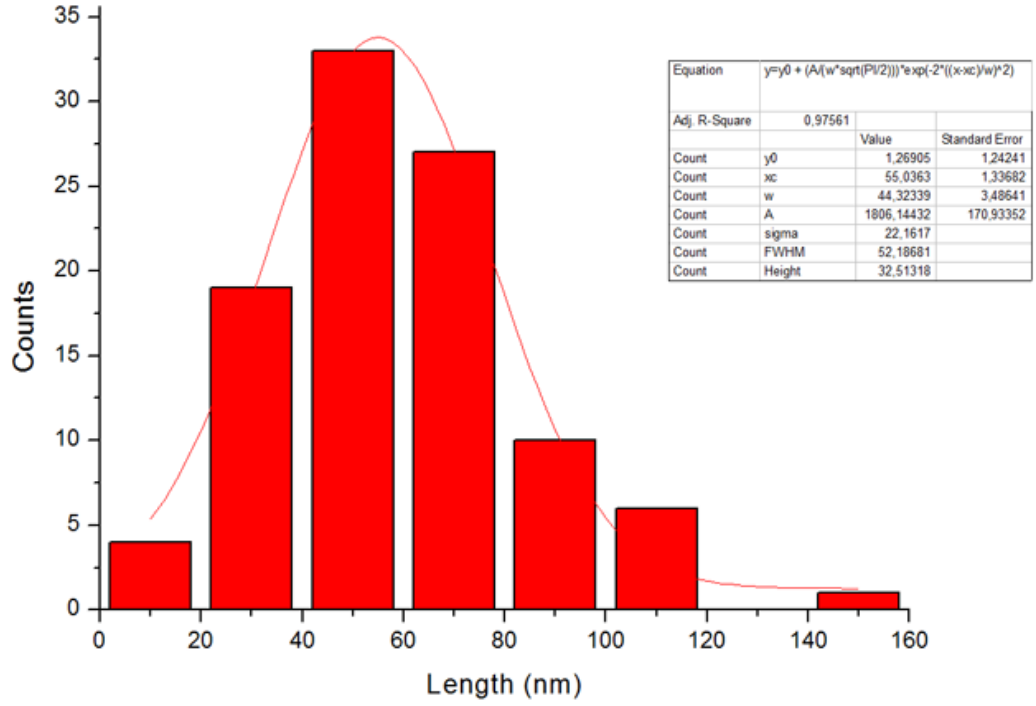


Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Adj. R-Square	0,75374		
		Value	Standard Error
Count	y0	6,39045	2,01746
Count	xc	41,54377	1,77821
Count	w	16,08799	4,39167
Count	A	464,86875	126,76242
Count	sigma	8,04399	
Count	FWHM	18,94216	
Count	Height	23,05519	

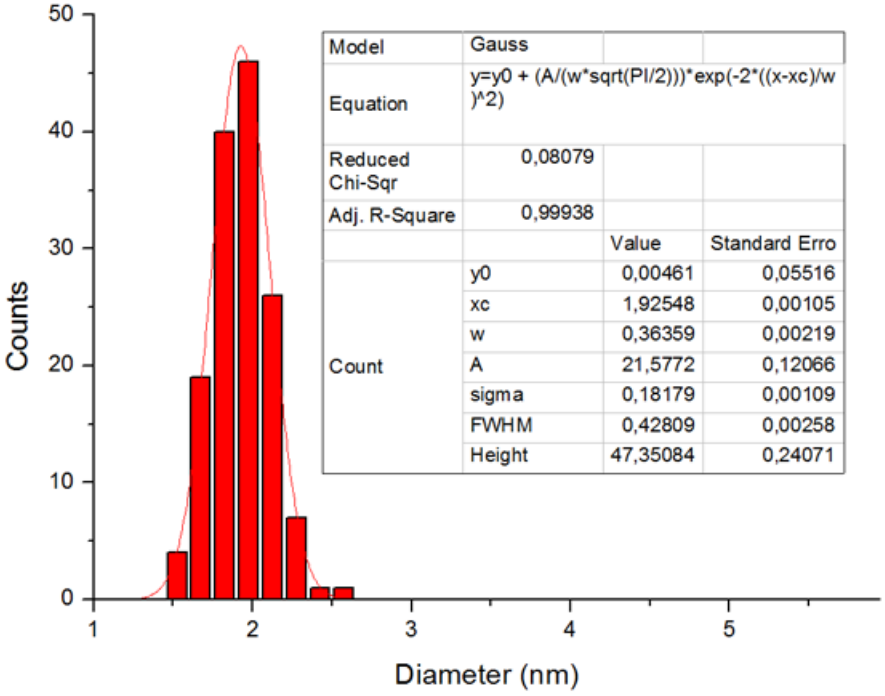


Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	0,51884		
Adj. R-Square	0,99576		
		Value	Standard Error
Count	y0	0,02221	0,14208
Count	xc	1,94339	0,0031
Count	w	0,41167	0,00648
Count	A	22,39008	0,3307
Count	sigma	0,20584	0,00324
Count	FWHM	0,48471	0,00763
Count	Height	43,39555	0,57452

Fig S6 Length distribution (up) and width (bottom) distribution for AuAg UNWs **4**.



Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Adj. R-Square	0,97561		
		Value	Standard Error
Count	y0	1,26905	1,24241
Count	xc	55,0363	1,33682
Count	w	44,32339	3,48641
Count	A	1806,14432	170,93352
Count	sigma	22,1617	
Count	FWHM	52,18681	
Count	Height	32,51318	



Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	0,08079		
Adj. R-Square	0,99938		
		Value	Standard Erro
Count	y0	0,00461	0,05516
	xc	1,92548	0,00105
	w	0,36359	0,00219
	A	21,5772	0,12066
	sigma	0,18179	0,00109
	FWHM	0,42809	0,00258
	Height	47,35084	0,24071

Fig S7 Length distribution (up) and width (bottom) distribution for AuAg UNWs **5**.