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SUPPORTING INFORMATION

Exploring the Potential of High Resolution Inductively Coupled Plasma Mass Spectrometry towards non-Destructive Control and Validation of Electroless Gold Nanoparticles onto Silicon Nanowires Hybrids

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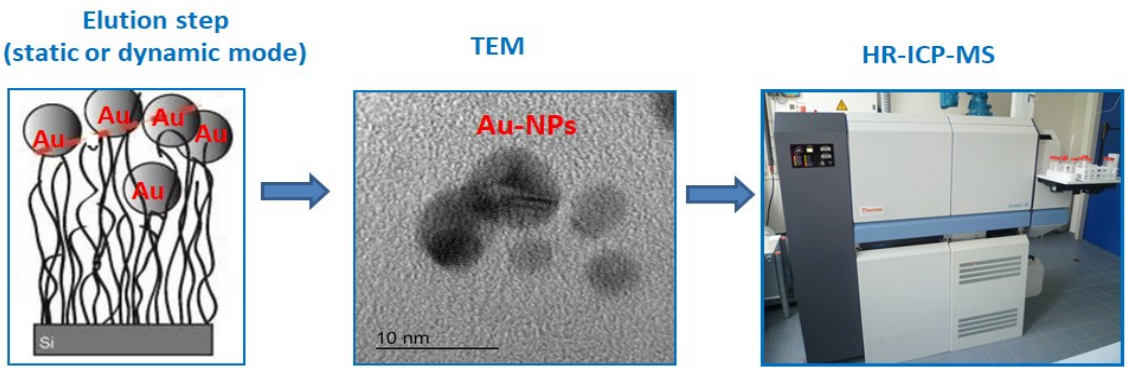
Preparation of SiNWi

Silicon wafers were cut into the samples with a size of 1×1 cm^2. To remove various contaminations from the surface, a standard RCA clean procedure was employed. After ultrasonication in acetone, water and ethanol for 15 min at each step and degreasing in Piranha solution (98% H_2SO_4/30% H_2O_2 = 3:1, v/v) at room temperature for 30 min, the native oxide layer was finally removed in 5% HF for 5 min. For one-step MACE, we have used a water solution containing $AgNO_3$(0.02 M)/HF(2.0 M) for 60 min. At the final step, Si samples were

immersed in the solution of HNO_3 for 10-60 min to remove the silver nanoparticles (AgNPs) from the surface, washed by DI and gently dried in N_2 flow.



Scheme S1. The schematic workflow of the applied elution strategy towards quantification by means of HR-ICP-MS of the unbound or weakly bound AuNPs moved from SiNWi templates depending on the preparation conditions.

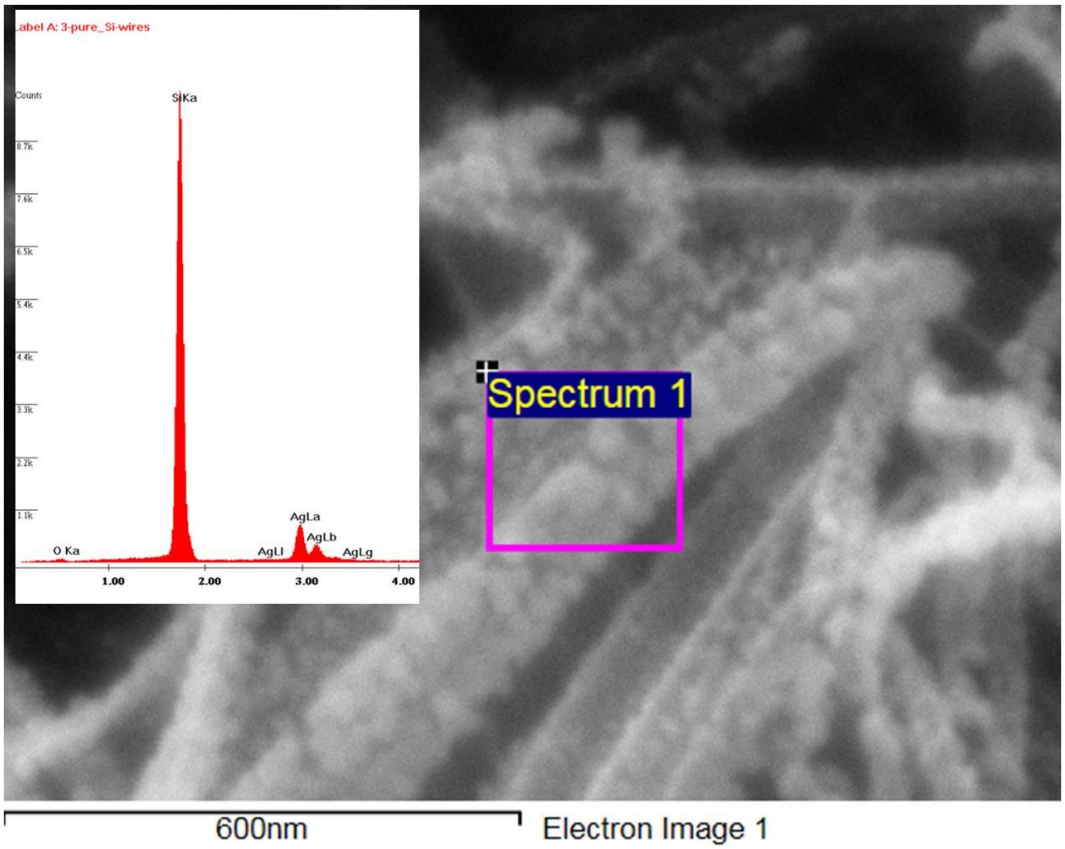


Figure S1. SEM image and EDX spectra of as-prepared intact SiNWi structures.

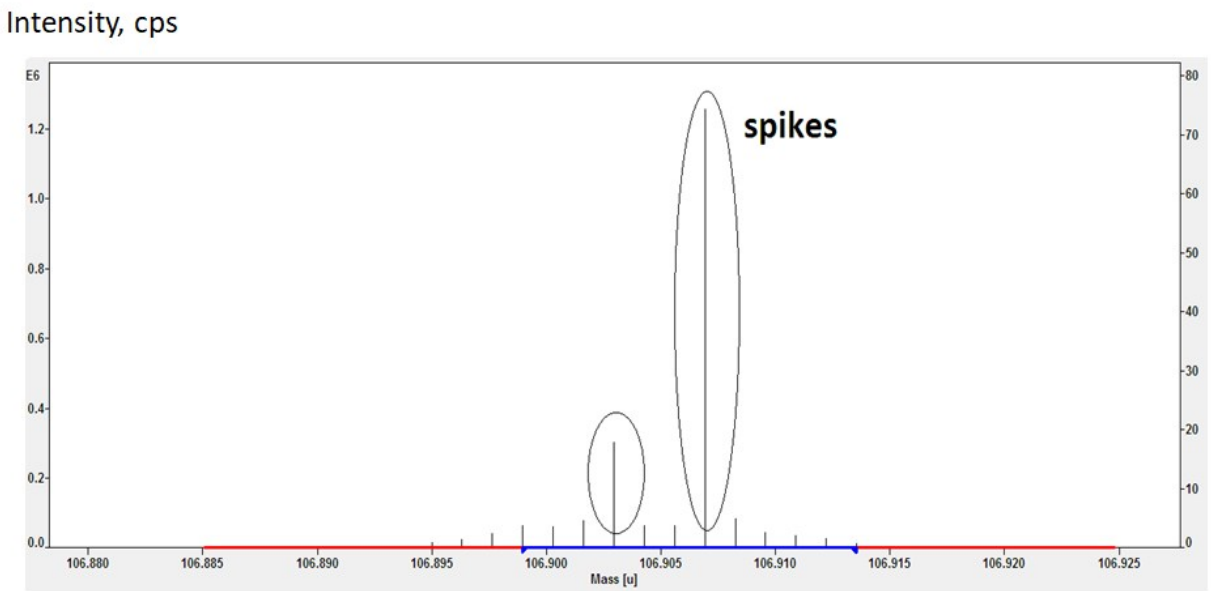


Figure S2. ICP-MS mass spectra of Ag^{107} moved from intact SiNWi substrates dipped into HNO_3 (35%) solution for 10 min.

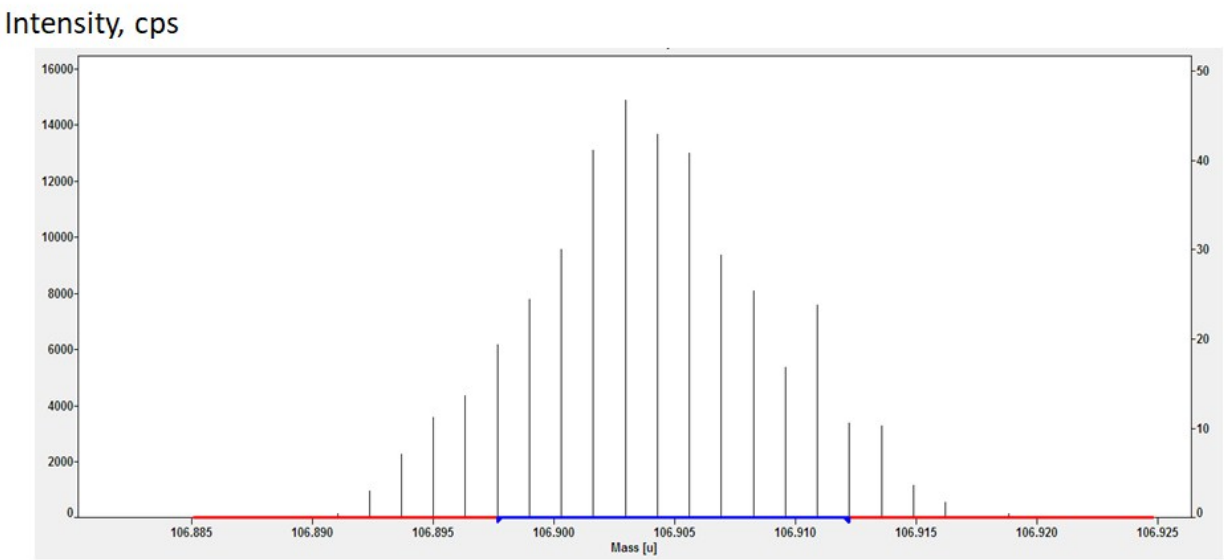


Figure S3. ICP-MS mass spectra of Ag^{107} moved from intact SiNWi substrate after three-step washing process in the same solution for 60 min. NOTE: in both cases (Figure S2, S3) elution experiments were performed at dynamic mode.

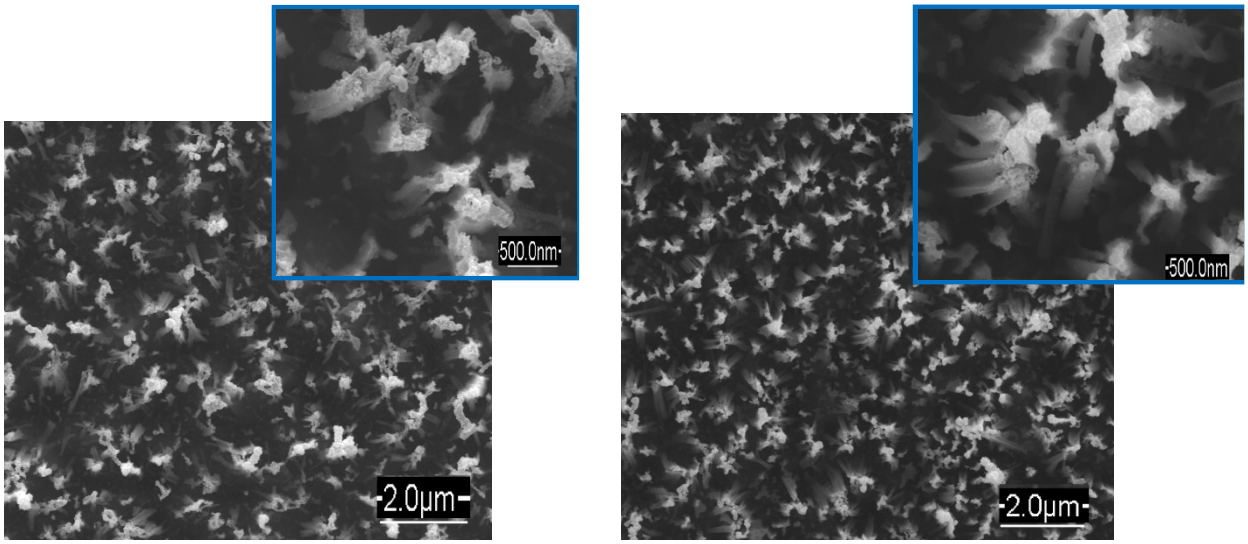


Figure S4. SEM images of intact AuNPs/SiNWi hybrids (*left*) and after ultrasound treatment for 30 min (*right*).

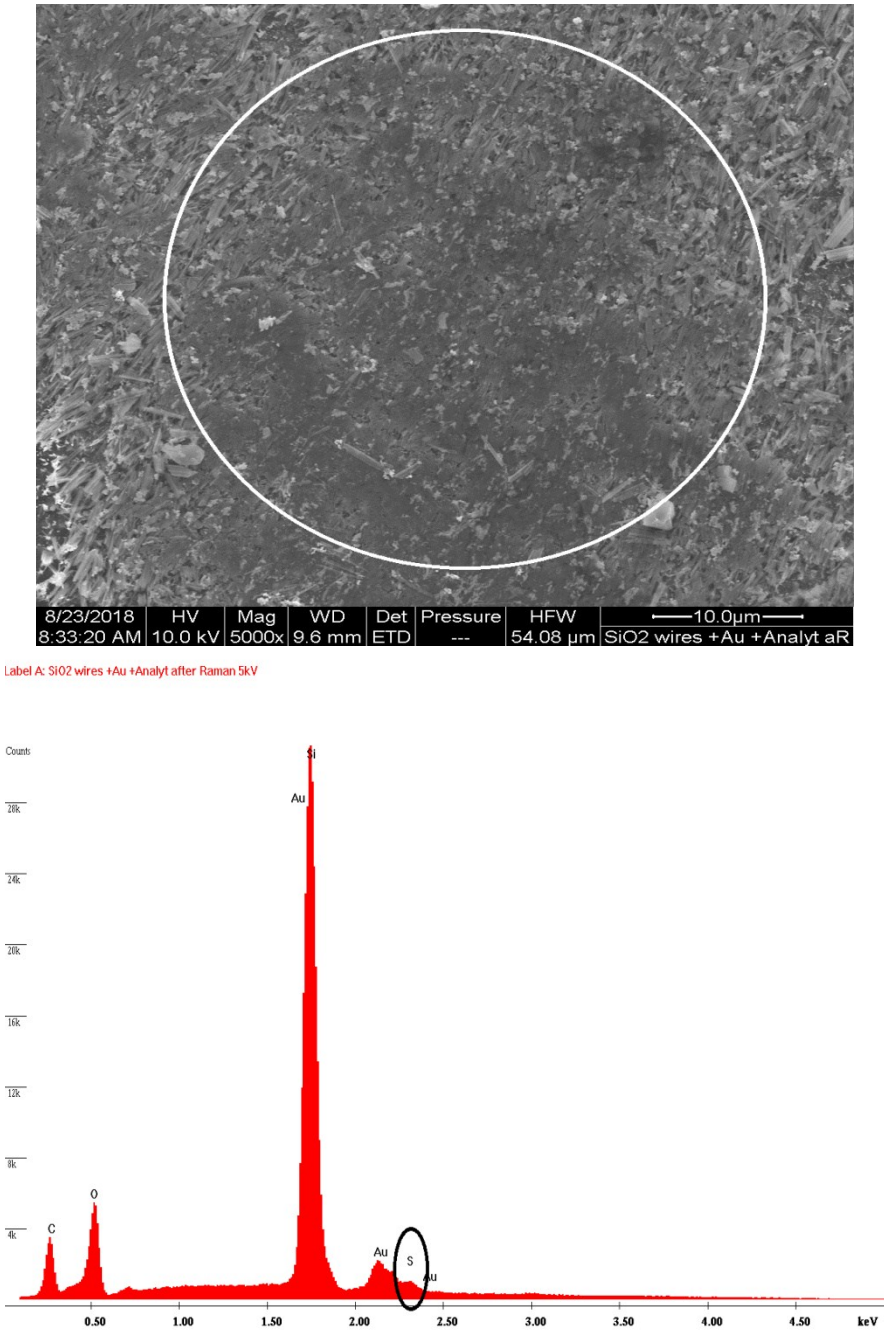


Figure S5. SEM image (*top*) and EDX spectra (*bottom*) of the marked area obtained for 1 M of 1,3-BDT spotted onto the hybrid AuNPs/SiNWi structure prepared at deposition time of 10 min. A slight decrease of secondary electron intensity is noticed in the marked area indicating a thin amorphous layer formation. No crystal formation was observed. NOTE: S-Kα-line seen on EDX spectra is attributed to the thiol group of 1,3-BDT.

Table S1 – The general Ag and Au content found at trace levels in water by ICP-MS after immersion of the AuNPs/SiNWi structures prepared at 10 min of deposition (dynamic pre-treatment mode)

	Ag_{107} MR≥4000*	Au_{197} MR≥4000
Calibration formula**	Y=63.66·X – 2078 R^2=0.9998	Y=44.56·X – 28320 R^2=9999
Content of de-bound Ag and Au found in water as a result of ions migration from hybrid structures, ppt (RSD, %)		
AuNPs-SiNWi structures, ratio 10:5 (as an example)	2639 (0.62)	223369 (2.64)

*MR – medium resolution;

**The precision of the assay was ≤15% RSD (n=9) and method accuracies between 98.7 and 101.2%.

Table S2. Binding of aromatic thiolates to Au and Ag nano-particles, -structures

Type of substrate	sample	concentration [M]	surface binding	References
50 nm Au	p-XDT	$5 \times 10^{-4} – 3 \times 10^{-8}$	monothiolate	1
10 nm Ag		10^{-6}	dithiolate	
Au-sol	1,4 BDT	5×10^{-5}	monothiolate	2
Ag-sol		$10^{-4} - 3 \times 10^{-8}$	dithiolate	
Ag	1,4 BDT	10^{-6}	dithiolate	3
Ag	1,2 BDT	$10^{-3} – 10^{-5}$	dithiolate	4
Ag	1,4 BDT		dithiolate	
Au			monothiolate	5
30 nm Ag	1,3 BDT	$5 \times 10^{-5} – 5 \times 10^{-3}$	dithiolate	6
Ag	BDT	4×10^{-3}	-	7
Au	4-ABT	10^{-3}	-	8
BDT: benzenedithiolate, p-XDT: p-xylene-α,α'-dithiol, ABT: aminobenzenethiol				

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