

# **High Yield Seedless Synthesis of Mini Gold Nanorods: Partial Silver Decoupling Allows Effective Nanorods Elongation With Tunable Surface Plasmon Resonance Beyond 1000 nm and CTAB-Free Functional Coating for mTHPC Conjugation**

Mike Rozenberg<sup>a</sup>, Matěj Bárta<sup>b</sup>, Anya Muzikansky<sup>a</sup>, Melina Zysler<sup>a</sup>  
Karolína Šišková<sup>b</sup>, Yitzhak Mastai<sup>a</sup> and David Zitoun<sup>\*a</sup>

\*Email: [David.Zitoun@biu.ac.il](mailto:David.Zitoun@biu.ac.il)

a. Department of chemistry and Bar-Ilan Institute of Nanotechnology and Advanced Materials (BINA), Bar-Ilan University, Ramat Gan 5290002, Israel

b. Department of Experimental Physics, Faculty of Science, Palacký University Olomouc, tř. 17. listopadu 12, 77900 Olomouc, Czech Republic

## Synthesis notes

- Stock solutions: AgNO<sub>3</sub> 40 mM – can be used for up to a week after preparation in a polypropylene vial, HQ 0.1M is prepared fresh daily, HAuCl<sub>4</sub> 25mM is used until orange precipitants appear at the bottom – solutions are kept in a fridge at 4 °C.
- CTAB stock of 0.2M is prepared and kept inside a pre-heated incubator at 30 °C.
- The sodium borohydride is taken fresh directly from the glovebox during each synthesis; the container is shaken vigorously for 30 seconds before extraction of the powder from the topmost layer.
- The solution of sodium borohydride should be prepared (weighed before the addition of the gold solution, kept in a sealed vial) right after the addition of the hydroquinone and used for no longer than 1 minute to reduce synthetic inconsistencies, particularly of the width.
- The particles are difficult to centrifuge and obtain high yields at the RPMs provided in this work, often we manage to obtain about 50% yield post three rounds of centrifugation. A better centrifuge and centrifuge tubes could be used to improve yields through increase in the RPM<sup>1</sup>.
- While 43-44 μL of sodium borohydride for the preparation of the elongated mini gold nanorods is possible, we have found the width to be somewhat inconsistent in terms of being below 10 nm, spectrally, they may appear similar. For this reason, we have optimized the synthesis around a volume of 47 μL.
- As previously mentioned<sup>2</sup> the gold solution may induce synthetic variability/inconsistency which we have noticed in our internal testing when preparing different sets of the presented nanoparticles. Deviation from the exact value of roughly ±0.5mM has some effect on the width of the nanorods and to a lesser extent their spectral properties. For this reason in this work throughout our presented experiments, different batches of gold solution have been used to provide improved transparency into the possible obtained widths using our method.
- This synthesis also depends on the purity of the CTAB, if iodide impurities are present then the synthesis will not work<sup>2,3</sup>.
- The aforementioned points also allow the reader to perform failure analysis in case of unsuccessful synthesis in terms of width of the obtained nanoparticles.

Table 1S.Synthetic parameters of the presented samples in this work, MI = Mini index or

Sample (MI-XXX)	Au 25mM Vol. (μL)	Ag 40mM vol. (μL)	HQ 0.1M vol. (μL)	NBH 0.01M vol. (μL)	Decoupled Ag vol. (μL)	Notes:
AU250	250	16	500	50	0	
AU225	225	16	500	50	0	
AU200 = Standard	200	16	500	50	0	
AU165 = Regular	165	16	500	50	0	
MIAU103	103	16	500	50	0	
AU200AG10	200	10	500	50	0	
AU200AG13	200	13	500	50	0	
AG10	165	10	500	50	0	
MIAG19	165	19	500	50	0	
AG23	165	23	500	50	0	
BH60	165	16	500	60	0	
BH70	165	16	500	70	0	
BH83	165	16	500	83	0	
BH127	165	16	500	127	0	
BH150	165	16	500	150	0	
BH175	165	16	500	175	0	
BH200	165	16	500	200	0	
BH225	165	16	500	225	0	
BH250	165	16	500	250	0	
AG80	200	80	500	50	0	
AG46	165	16	500	50	0	
AG80SEED	200	80	500	0	0	As described in the experimental section
AG16AFT30 = BH47AFT30 = AFT30	165	16	500	47	30	
BH50AFT30	165	16	500	50	30	
AFT13	165	16	500	47	13	
AFT15	165	16	500	47	15	
AFT20	165	16	500	47	20	
AAREG	200	16	0	0	0	2 ml of seeds and 100 μL of 0.1M ascorbic acid

sample index in this case.

Table 2S. Full Length, Width, AR and yield data of all samples presented in this work,

Sample (MI-XXX)	Length (nm)	Width (nm)	AR	Length Std (nm)	Width Std (nm)	AR Std	Yield and Notes	LSPR (nm)
Reg	21.28	6.98	3.05	2.77	0.86	0.55	Mini	717.50
Stand	21.20	6.77	3.13	2.71	0.64	0.50	Mini and yield of ~94%	729.00
Au250	-	65.08	-	13.08	-	-	Spherical/Ellipsoidal	552.00
Au225	52.81	26.86	1.97	11.74	2.00	0.46	Not Mini	666.00
Au103	26.87	6.99	3.84	3.42	0.64	0.60	mini	794.00
Au200Ag10	33.09	15.37	2.15	4.76	1.26	0.36	Not Mini	637.00
Au200Ag13	48.17	16.78	2.87	6.42	1.04	0.42	Not Mini	688.00
Ag10	37.61	17.64	2.13	3.52	1.24	0.25	Not Mini	678.00
Ag19	21.28	8.03	2.65	4.27	0.84	0.60	Mini and yield of ~94%	784.00
Ag23	37.33	8.54	4.37	3.92	0.76	0.60	Mini	853.00
BH127	36.41	8.93	4.08	4.34	0.69	0.58	Mini	808.00
BH150	24.25	7.77	3.12	4.04	0.77	0.60	Mini	767.00
BH250	18.79	6.74	2.79	2.47	0.83	0.50	Mini	740.00
BH50Aft30	46.29	7.78	5.95	6.98	0.79	1.08	Mini	960.00
BH47Aft30 = Aft30	66.52	9.62	6.91	8.11	0.91	1.07	Mini and yield of ~96%	1052.00
Aft13	28.44	8.21	3.46	4.71	0.81	0.67	Mini	853.00
Aft15	32.76	7.43	4.41	4.27	0.68	0.70	Mini and yield of ~98%	889.00
Aft20	51.56	8.73	5.91	7.19	0.82	0.99	Mini	1008.00
Ag80 Seeded	21.23	6.18	3.44	3.50	0.87	0.74	Mini	790.50
AA Reg	26.69	7.37	3.62	7.16	1.13	1.12	Mini	771.00

green is for mini samples and red is for non-mini samples.

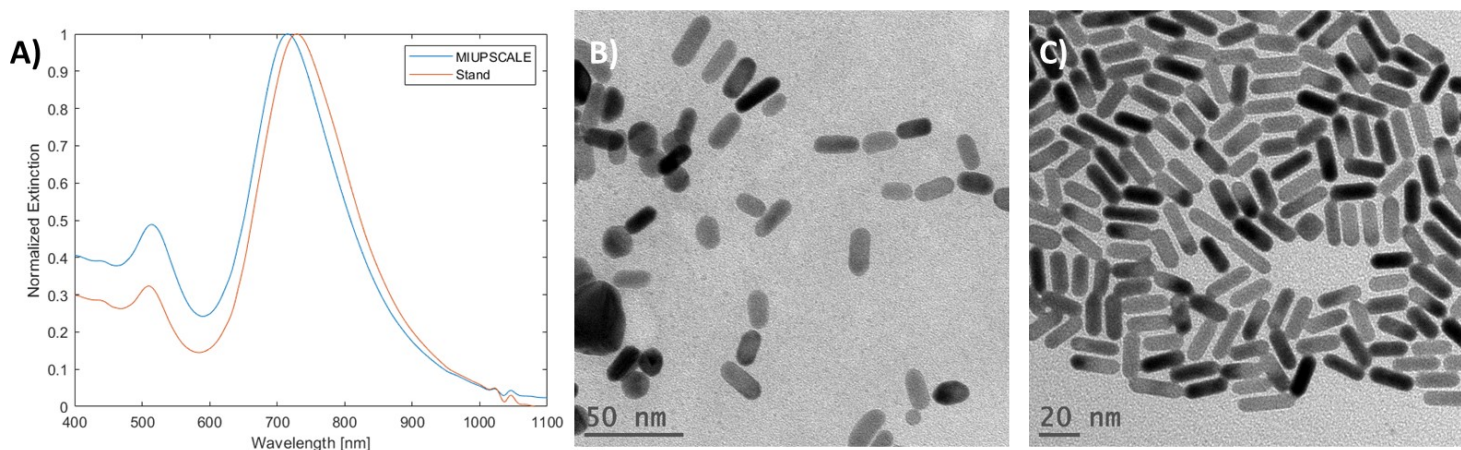


Figure 1S. Characterization and comparison of the Upscaled mGNRs and the standard synthesis by A) UV-vis-NIR and TEM images of the B) Upscaled and C) Standard mGNRs.

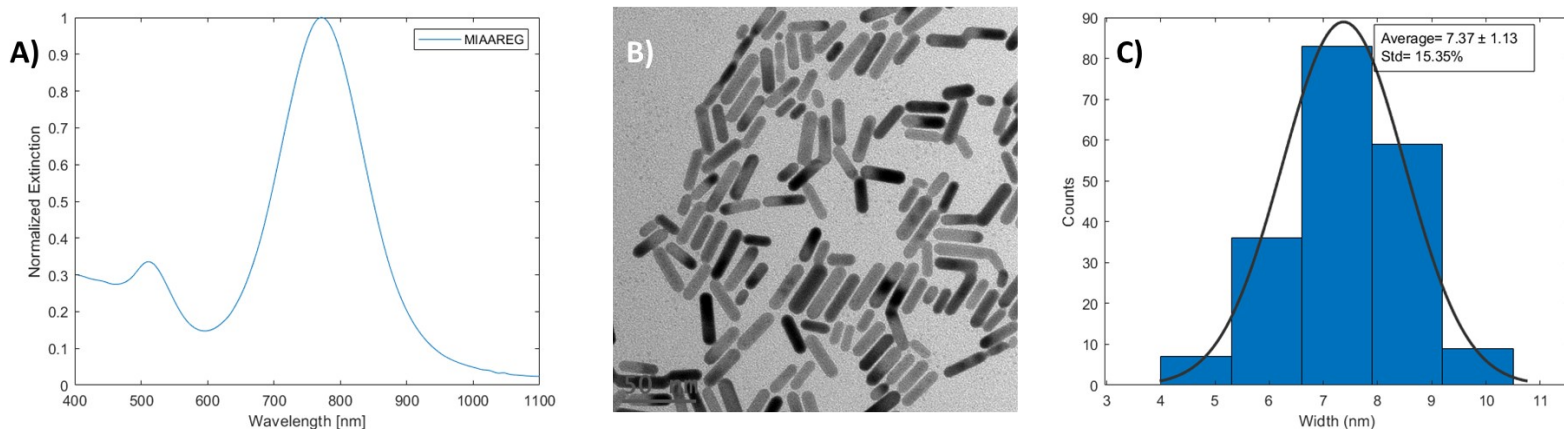


Figure 2S. Characterization of the Ascorbic acid prepared mGNRs by A) UV-vis-NIR B) TEM imaging and C) width histogram indicating the mini designation by width of the GNRs.

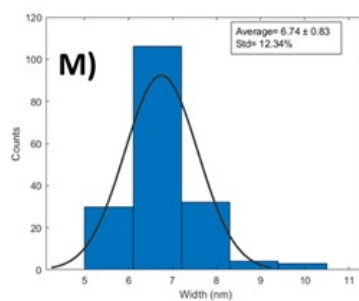
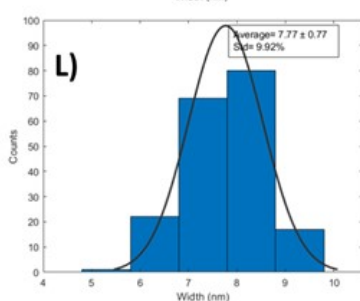
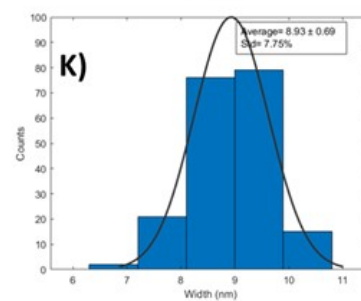
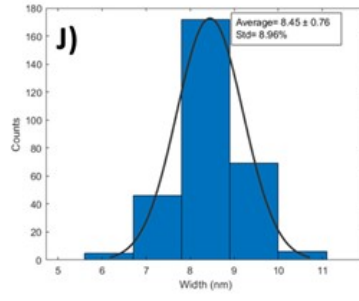
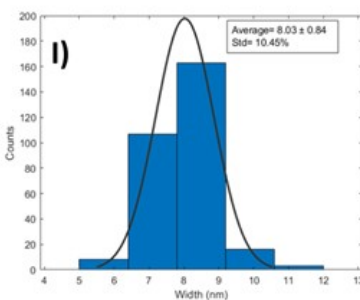
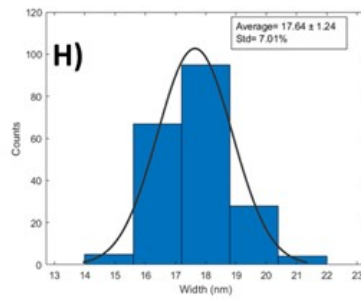
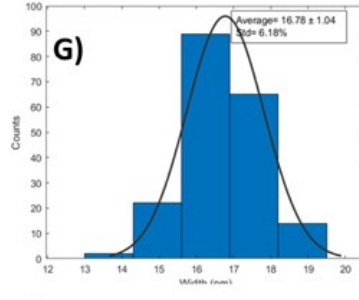
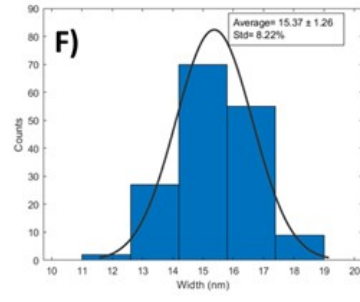
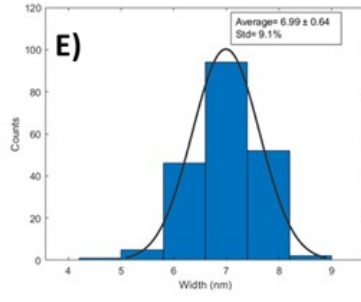
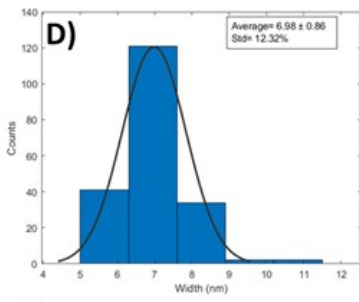
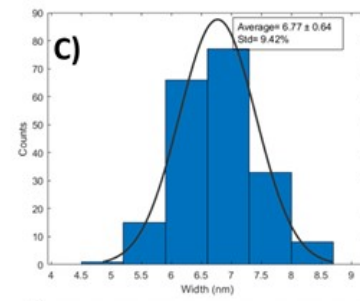
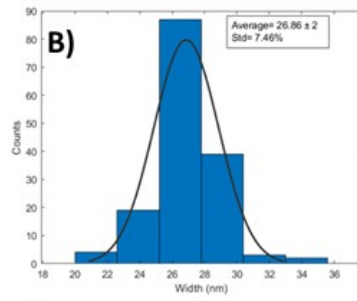
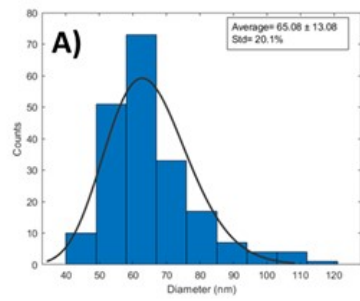


Figure 3S. Diameter and Width Histograms for samples A) Au250 B) Au225 C) Standard D) Regular E) Au103 F) Au200Ag10 G) Au200Ag13 H) Ag10 I) Ag19 J) Ag23 K) BH127 L) BH150 and M) BH250.

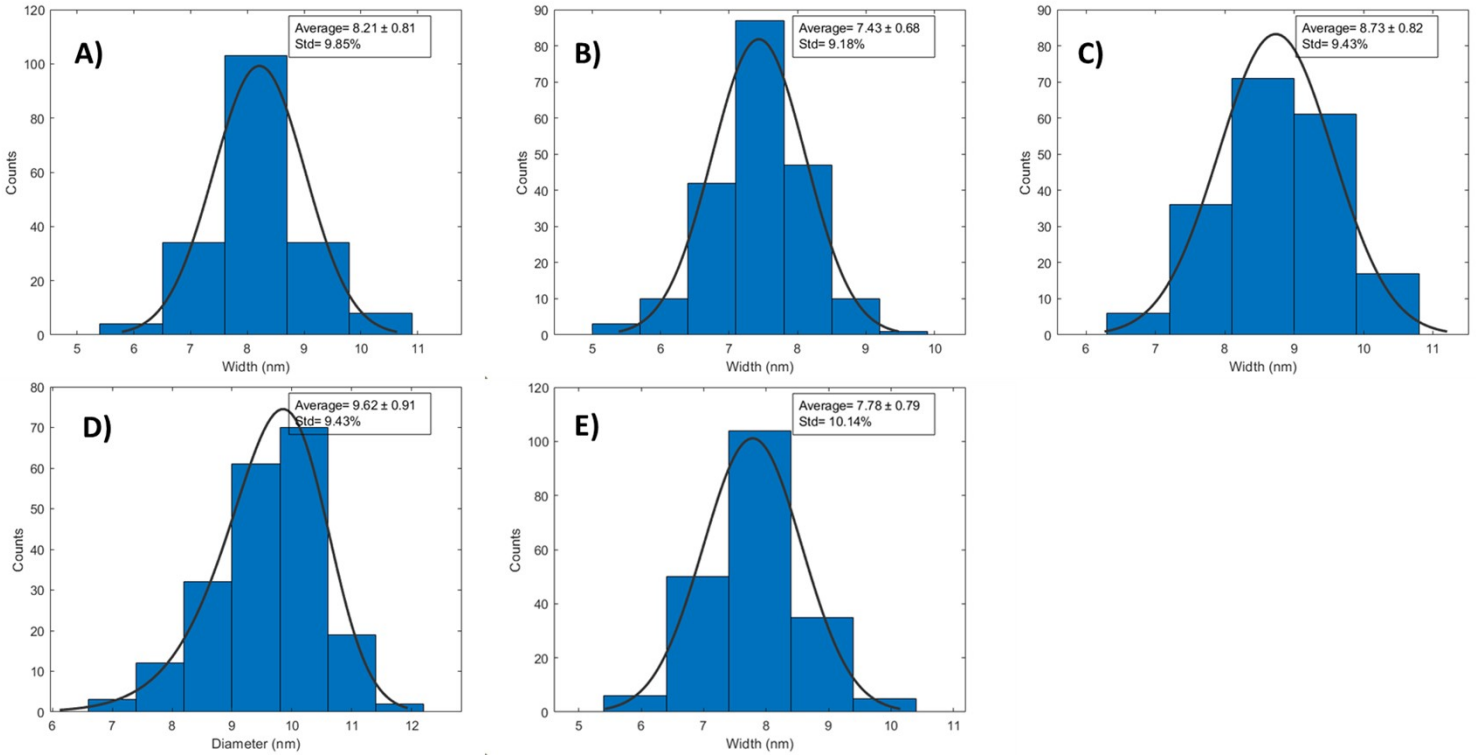


Figure 4S. Width Histograms of the samples with varying silver volumes added 180 seconds after the reaction with A) 13  $\mu$ L (Aft13), B) 15  $\mu$ L (Aft15), C) 20  $\mu$ L (Aft20), D) 30  $\mu$ L (Aft30) and E) pre-optimized reaction with 50  $\mu$ L of NBH used and 30  $\mu$ L of silver stock solution added.

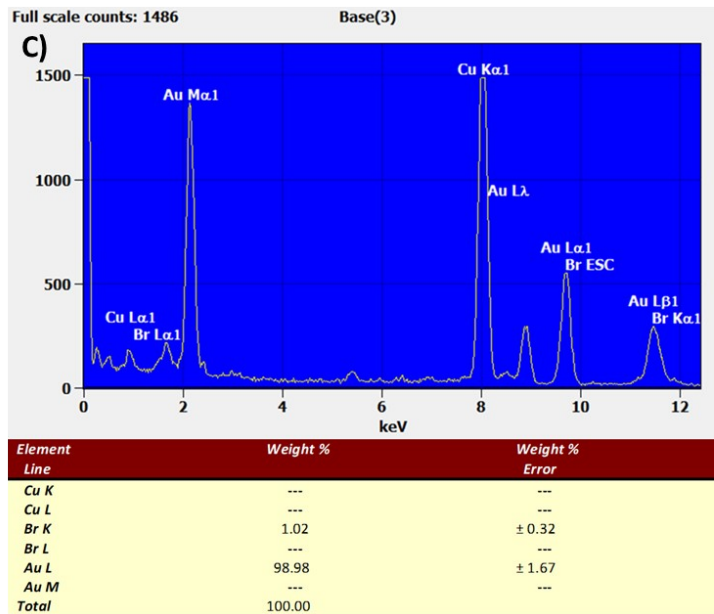
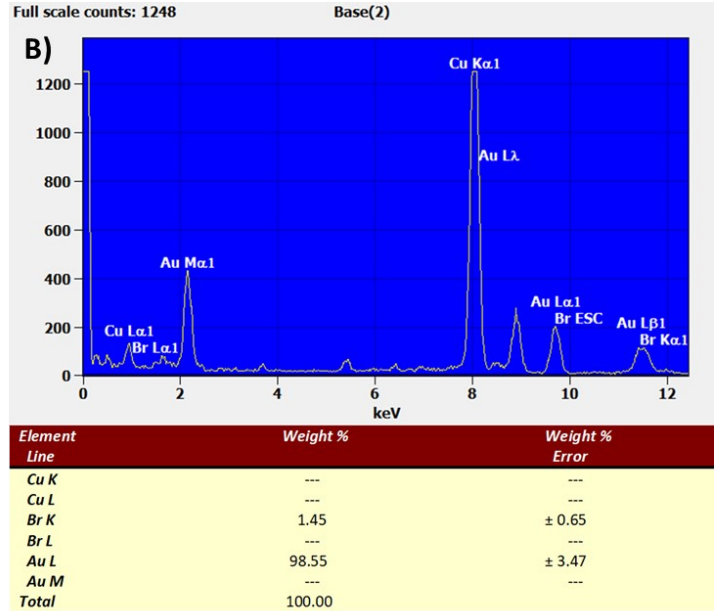
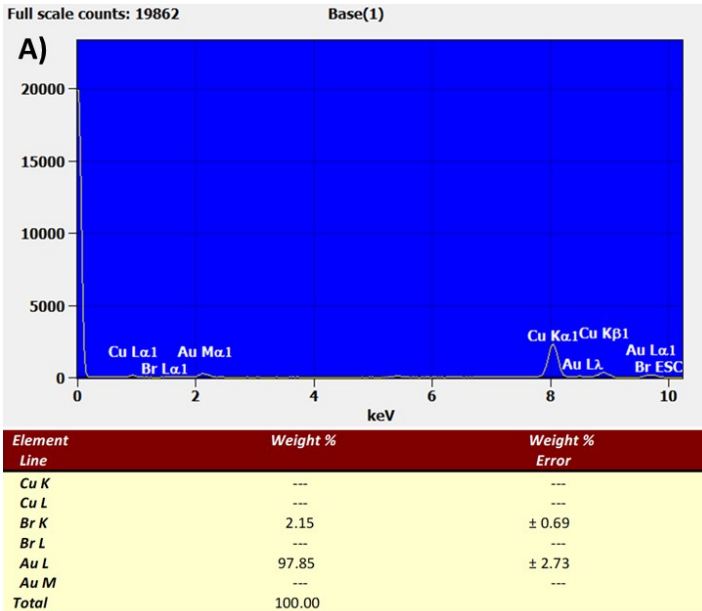


Figure 5S. EDAX spectra and the corresponding elemental analyses of the as-prepared mGNRs, as provided by the software for A) 1<sup>st</sup> spot, B) 2<sup>nd</sup> spot and C) 3<sup>rd</sup> spot on top of the grid, chosen by random with high nanoparticles concentration and relates to the sample in Figure 8B.



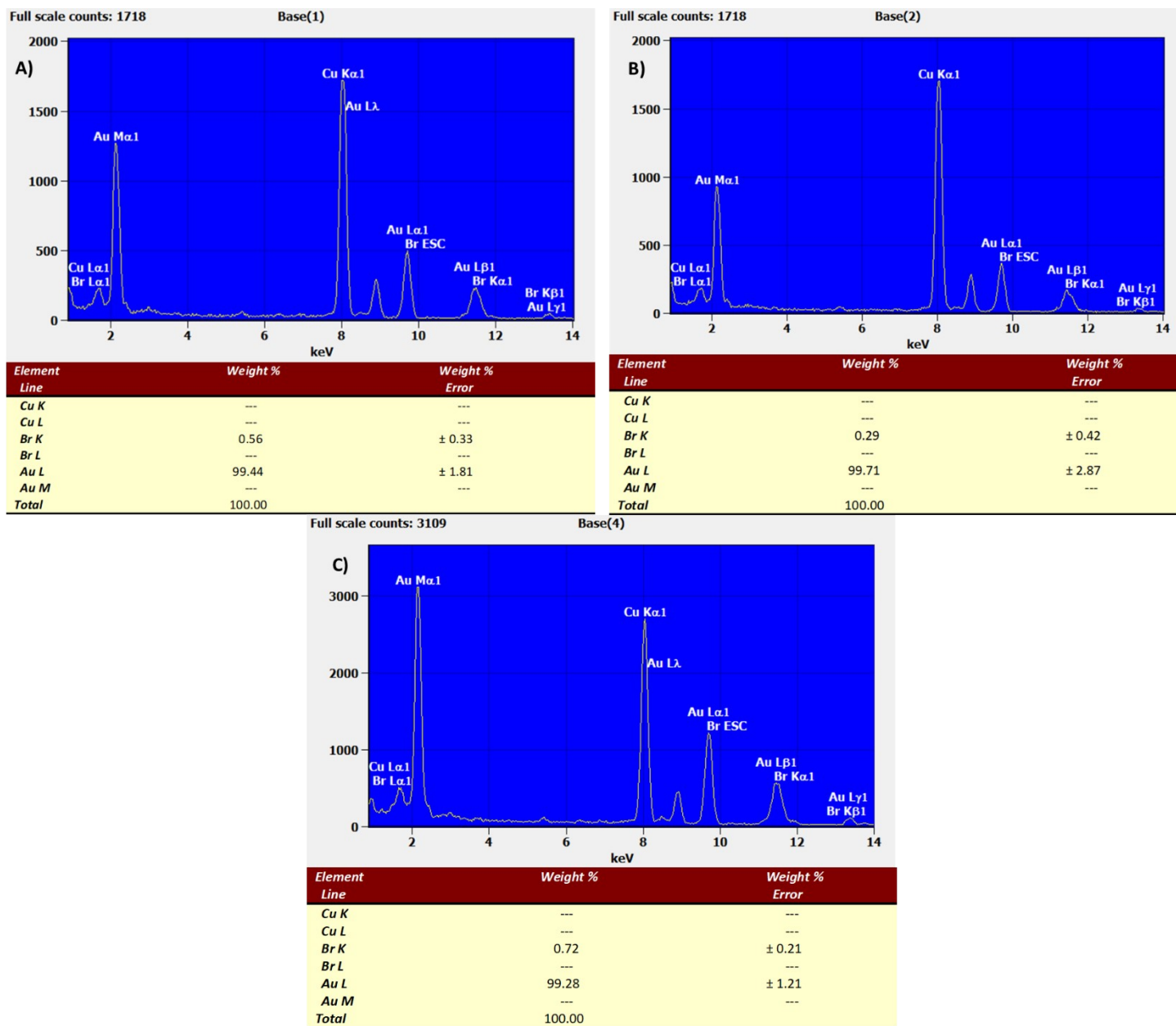


Figure 6S. EDAX spectra and the corresponding elemental analyses of the PSS coated mGNRs, as provided by the software for A) 1<sup>st</sup> spot, B) 2<sup>nd</sup> spot and C) 3<sup>rd</sup> spot on top of the grid, chosen by random with high nanoparticles concentration and relates to the sample in Figure 8C.

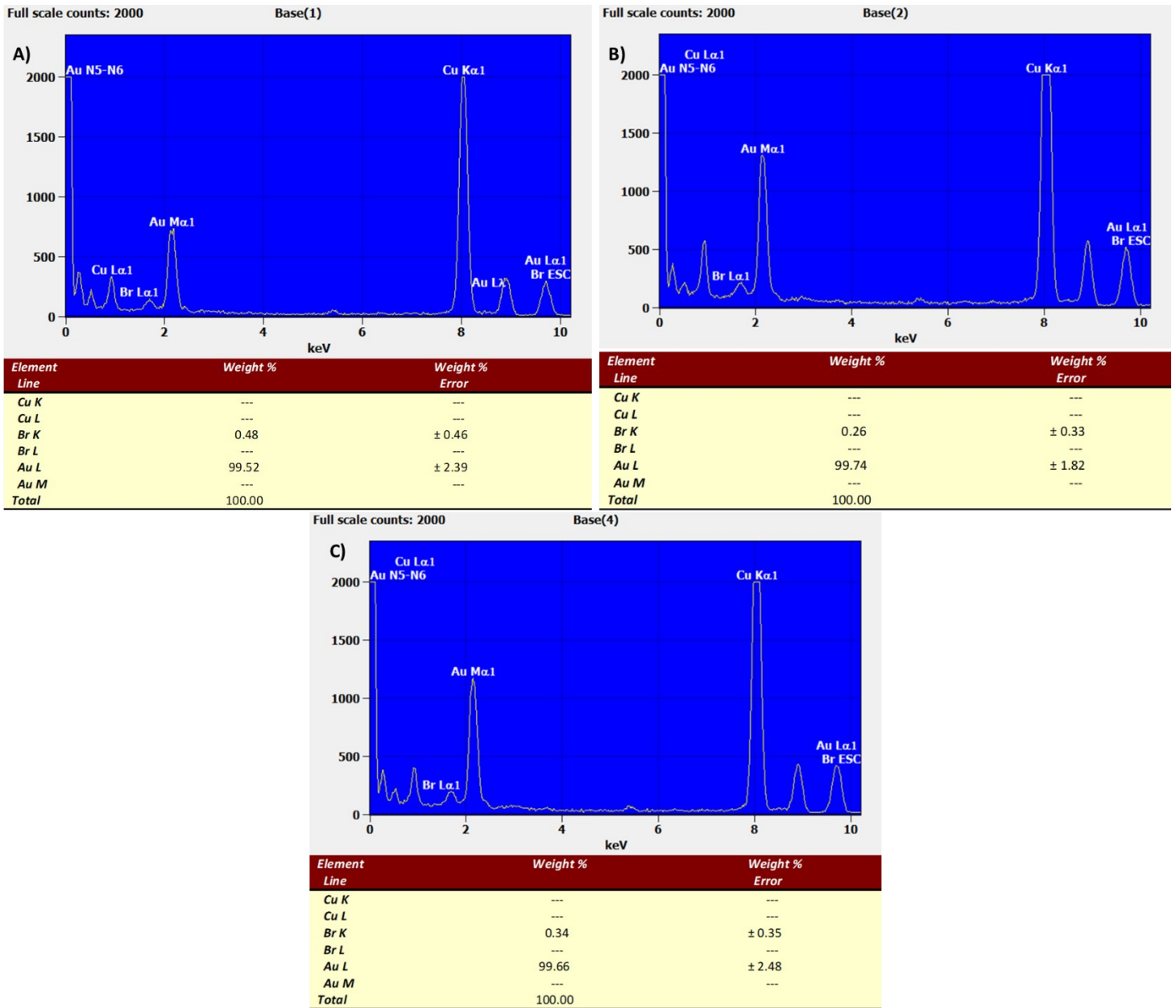


Figure 7S. EDAX spectra and the corresponding elemental analyses of the MPA coated mGNRs, as provided by the software for A) 1<sup>st</sup> spot, B) 2<sup>nd</sup> spot and C) 3<sup>rd</sup> spot on top of the grid, chosen by random with high nanoparticles concentration and relates to the sample in Figure 8D.

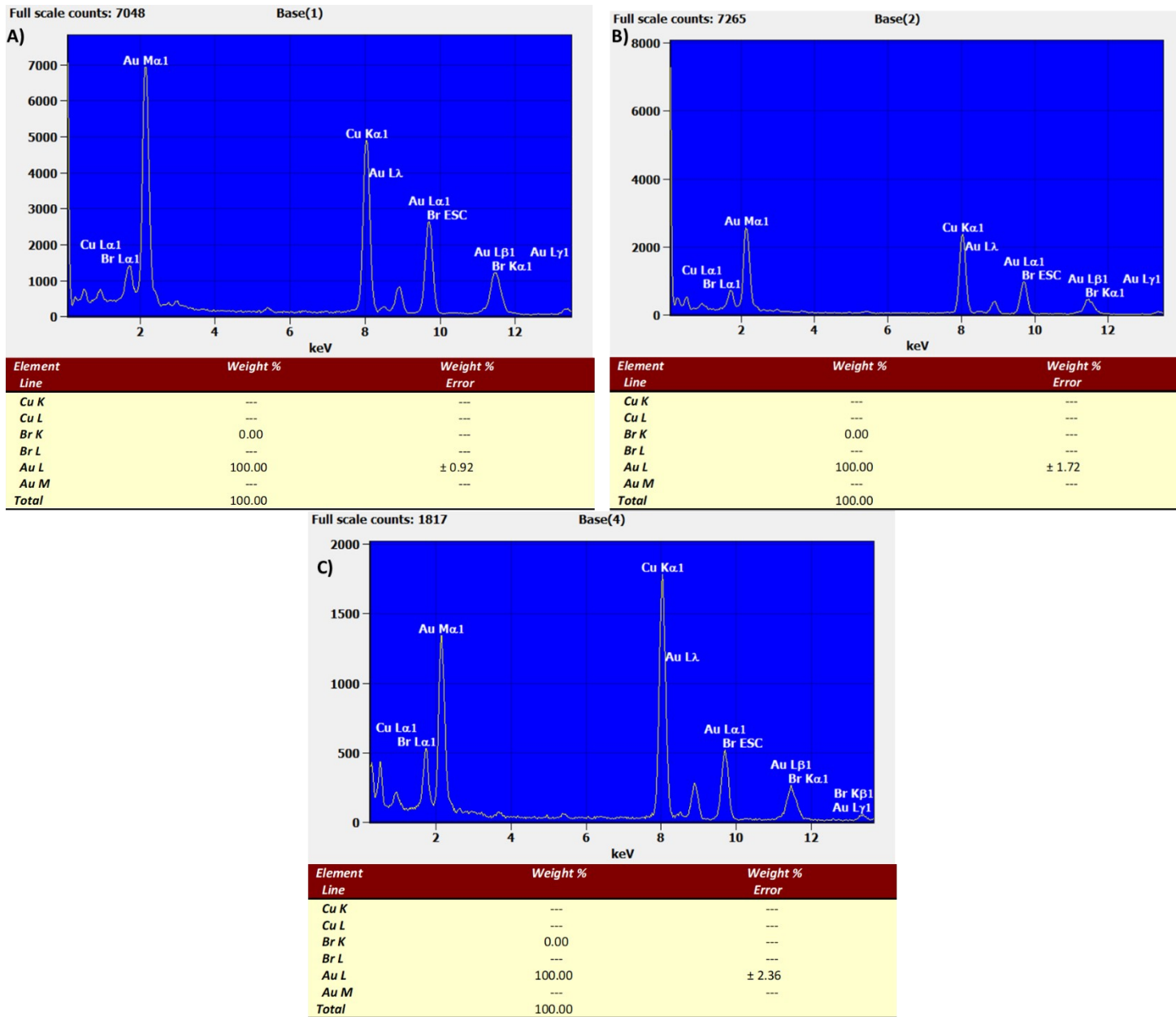


Figure 8S. EDAX spectra and the corresponding elemental analyses of the mTHPC coated mGNRs, as provided by the software for A) 1<sup>st</sup> spot, B) 2<sup>nd</sup> spot and C) 3<sup>rd</sup> spot on top of the grid, chosen by random with high nanoparticles concentration and relates to the sample in Figure 8E.

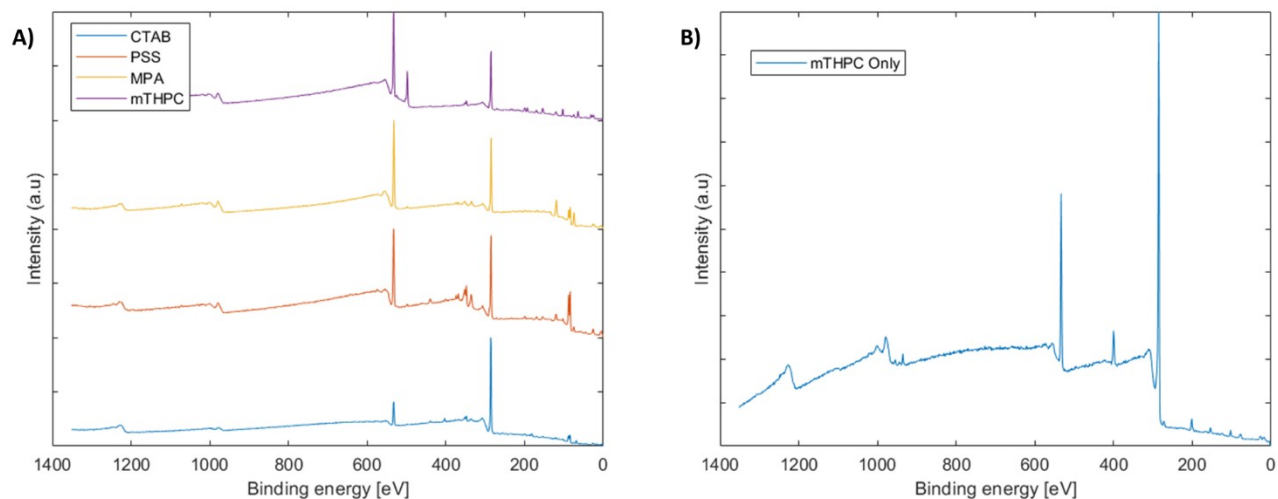


Figure 9S. Complete XPS survey spectra of A) CTAB, PSS, MPA and mTHPC coated gold nanorods and B) reference mTHPC sample.

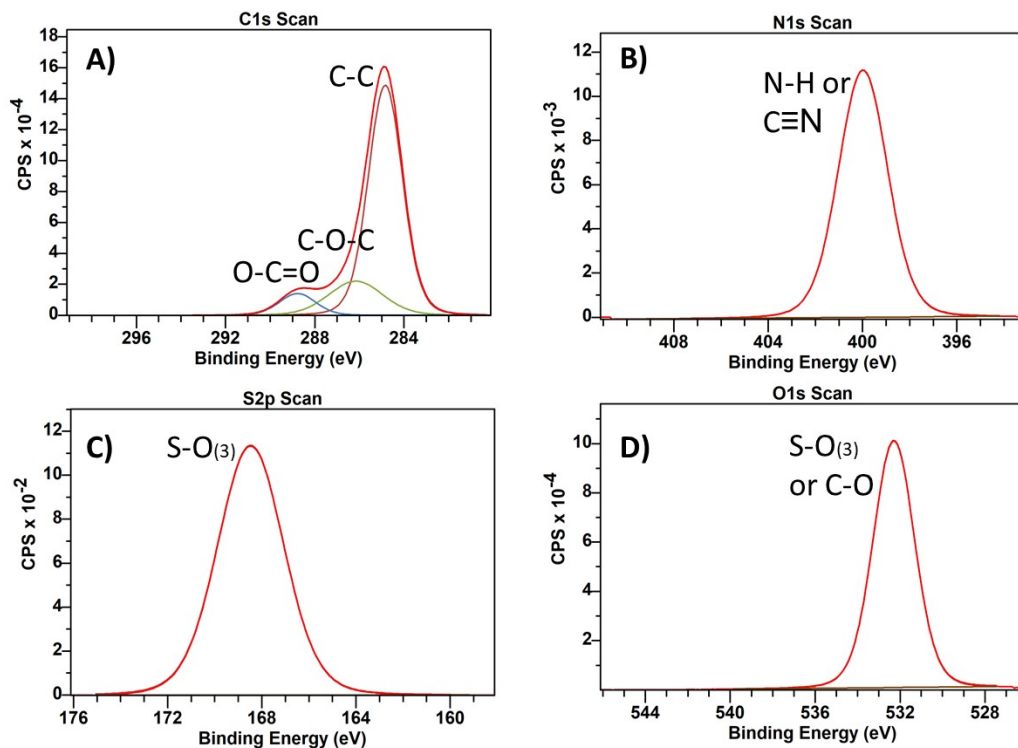
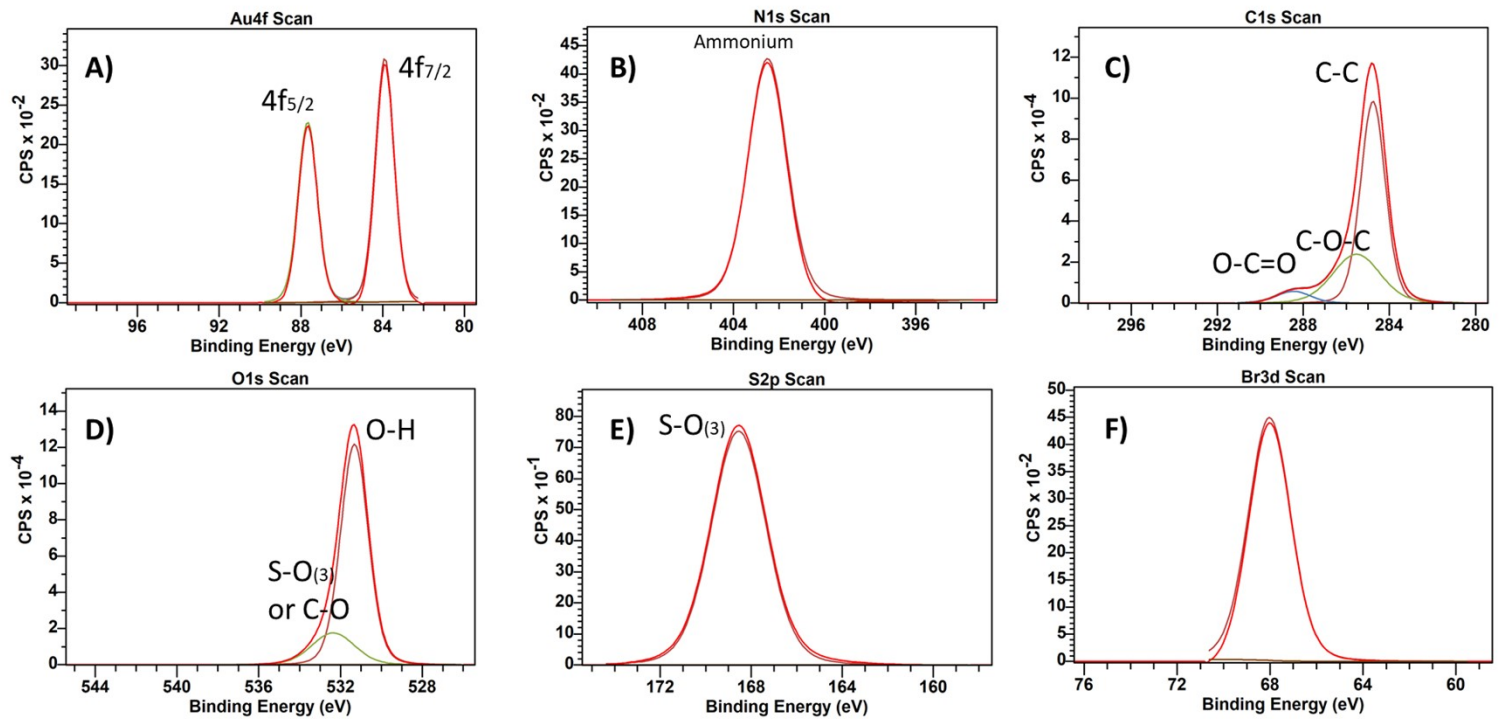


Figure 10S. High-resolution XPS spectra for the Cu tape reference for A) C1s, B) N1s, C) S2p and D) O1s orbitals.

#### XPS Notes:

1. A peak at  $\sim 72\text{eV}$  belongs to  $\text{Al}2\text{p}$  which is from the X-Ray source and is removed manually for the high-resolution spectra.
2. Throughout all samples the N-H (or  $\text{C}\equiv\text{N}$ ) peak at  $\sim 400\text{eV}$  is manually removed as it is a form of contamination from either the device or the tape and has been observed (not shown) on the Al tape/foil as well to avoid confusion with the ammonium peak of the CTAB at higher energies. Additionally for mTHPC (reference and GNR) that does contain the peak at around  $400\text{eV}$ ; the peak is not removed as it is impossible to de-convolute the contribution of each component and is left as is.
3. The sulfate peak is also a form of contamination but is not removed as there is very little concern over confusion of contribution with the exception of PSS, where the contribution from the PSS cannot be deconvoluted from the contamination and as such is left as is. With the exception that the signal strength is sufficiently high in this sample to de-convolute the spin-orbit coupling of the  $\text{S}2\text{p}$  orbital.
4. All samples are calibrated against C-C bond of adventurous carbon for a peak position at  $248.8\text{ eV}$ .

5. All samples containing mGNR possess the Au4f at standard peaks positions for



the spin-orbit coupling with  $4f_{7/2}$  at  $\sim 83.5$  eV and  $4f_{5/2}$  at  $\sim 87.2$  eV

Figure 11S. High-resolution XPS spectra for the as-prepared mGNR for A) Au4f, B) N1s, C) C1s, D) O1s, E) S2p and F) Br3d orbitals.

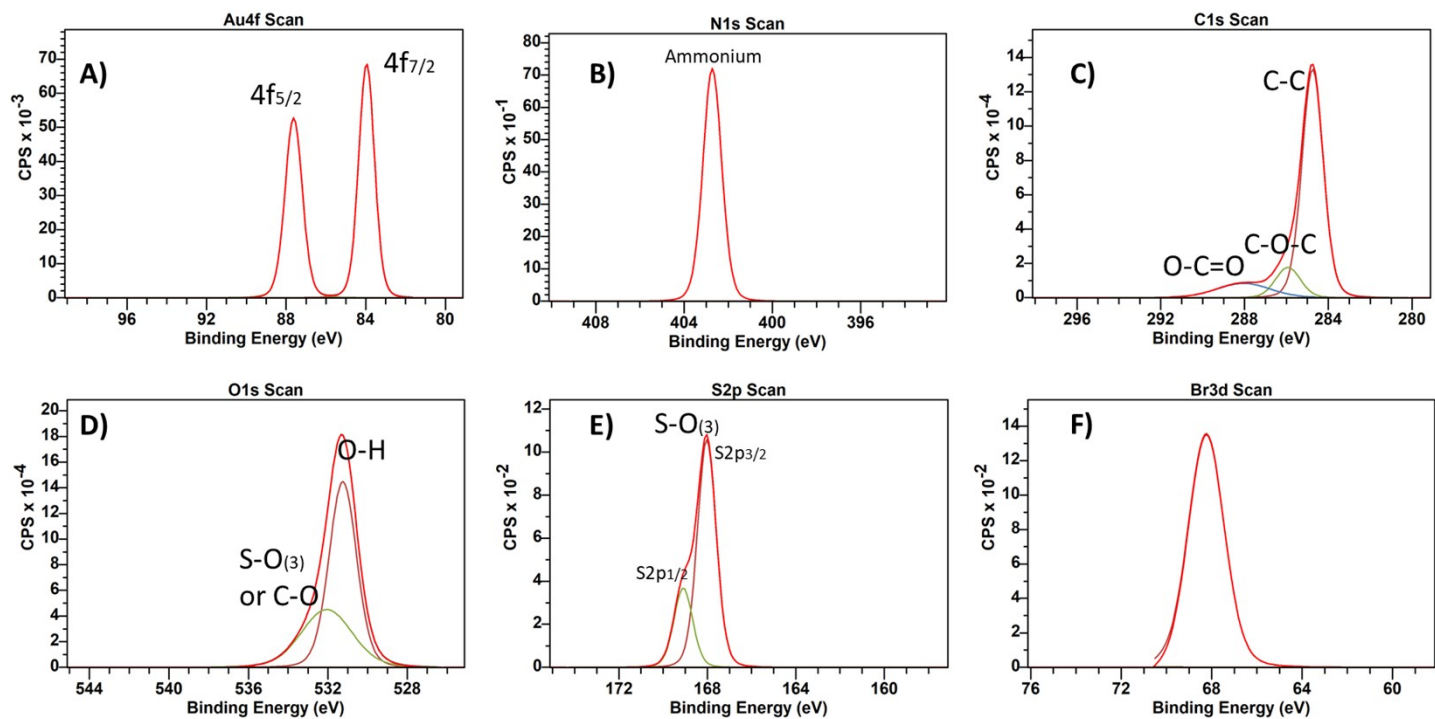


Figure 12S. High-resolution XPS spectra for the PSS coated mGNR for A) Au4f, B) N1s, C) C1s, D) O1s, E) S2p and F) Br3d orbitals.

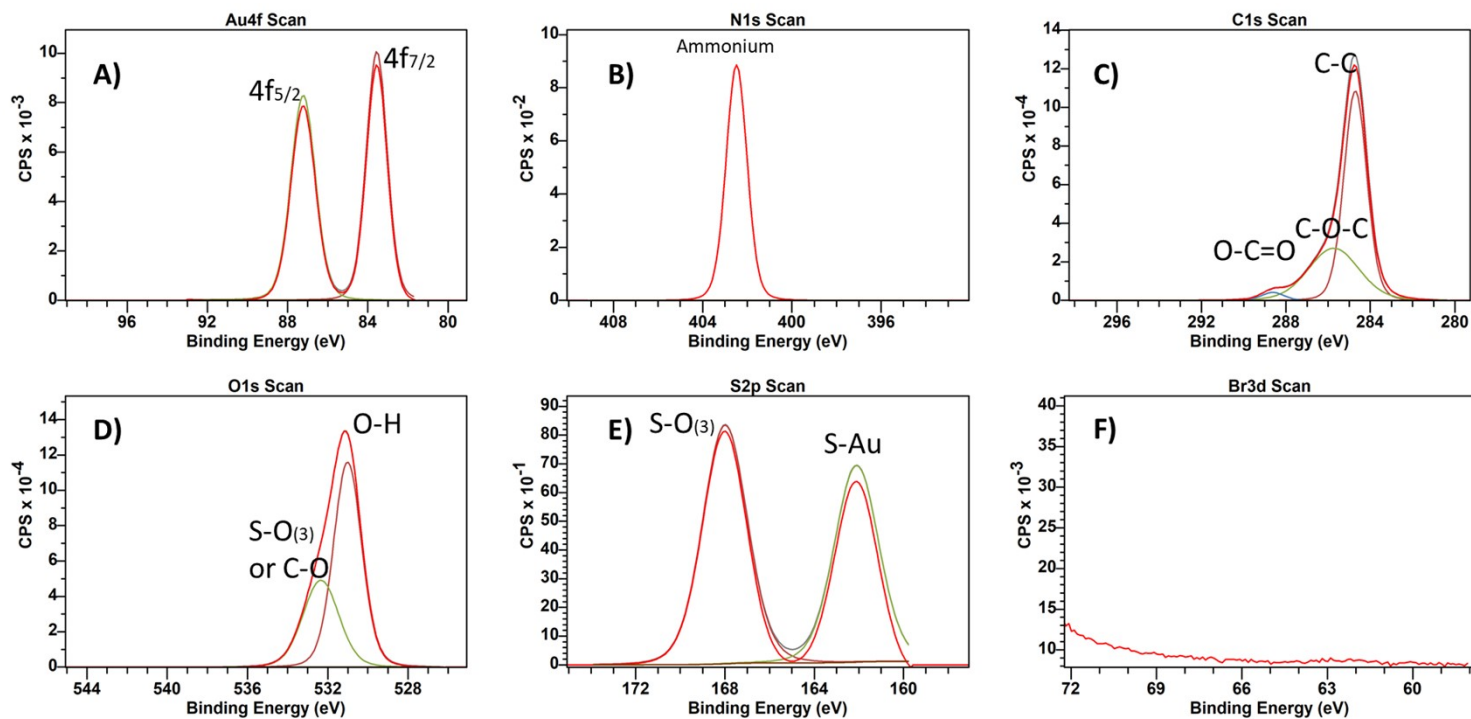


Figure 13S. High-resolution XPS spectra for the MPA coated mGNR for A) Au4f, B) N1s, C) C1s, D) O1s, E) S2p and F) Br3d orbitals.

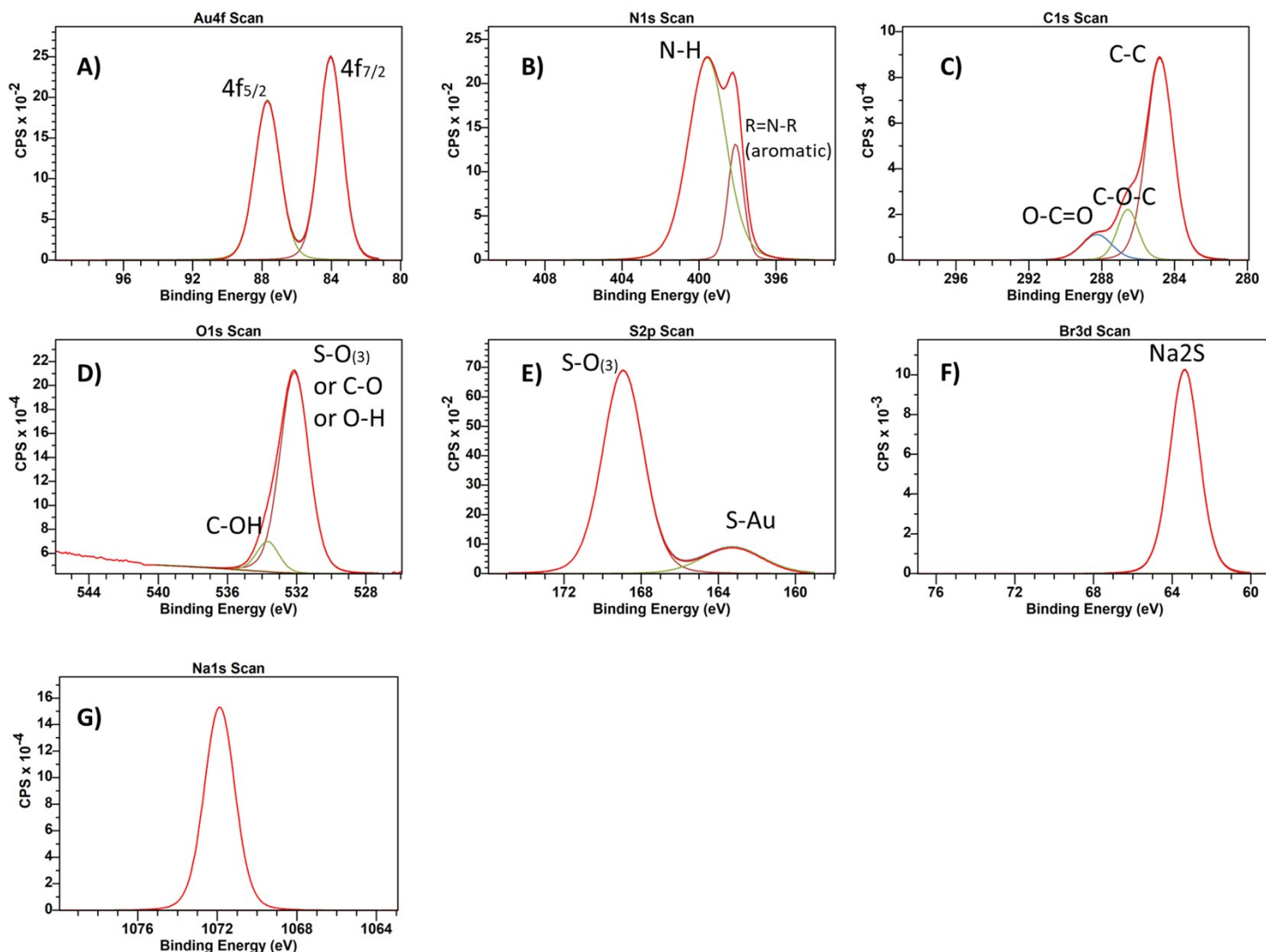


Figure 14S. High-resolution XPS spectra for the mTHPC coated mGNR for A) Au4f, B) N1s, C) C1s, D) O1s, E) S2p, F) Br3d and G) Na1s orbitals.

Figures 13S and 14S notes:

1. There is a sodium contamination (and various other elements which are not identified but are present on the survey of figure 9S for the mTHPC sample since singly deionized water were used for the dialysis instead of doubly deionized water.
2. For this reason the Na1s spectra is added to elucidate the appearance of the peak on the Br3d scan.
3. Both the MPA and mTHPC samples contain the S-Au bond as indicated by the S2p scan at position of ~162.5eV.



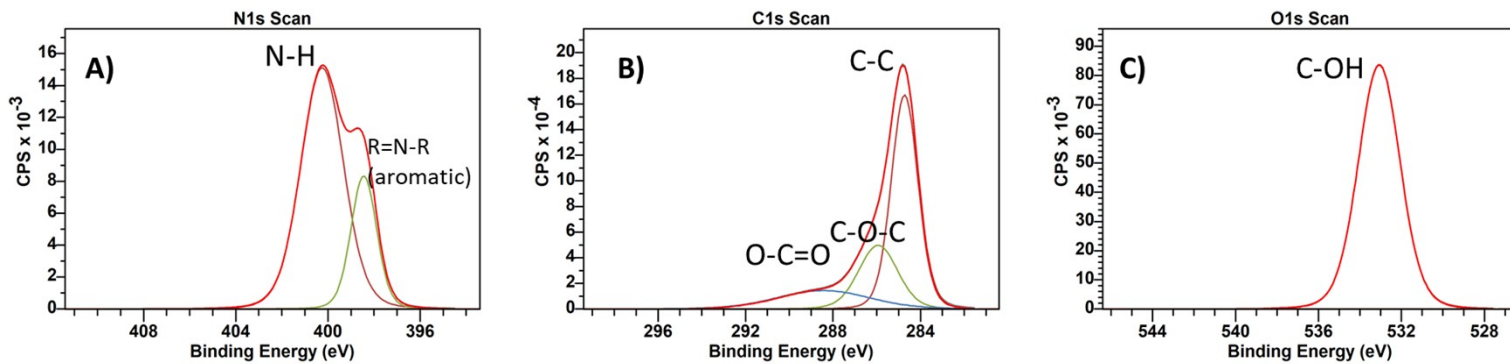


Figure 15S. High-resolution XPS spectra for the mTHPC reference for A) N1s, B) C1s and C) O1s.

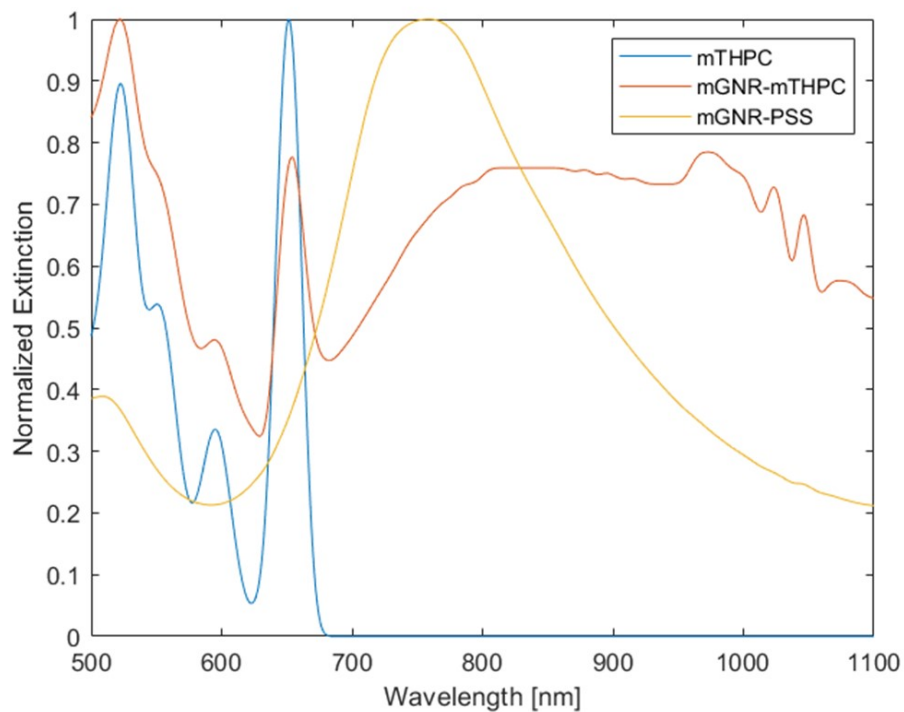


Figure 16S. UV-vis-NIR spectra of mTHPC reference, mGNR with PSS and mGNR with mTHPC.

## References

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- 3 J. E. Millstone, W. Wei, M. R. Jones, H. Yoo and C. A. Mirkin, *Nano Lett.*, 2008, **8**, 2526–2529.