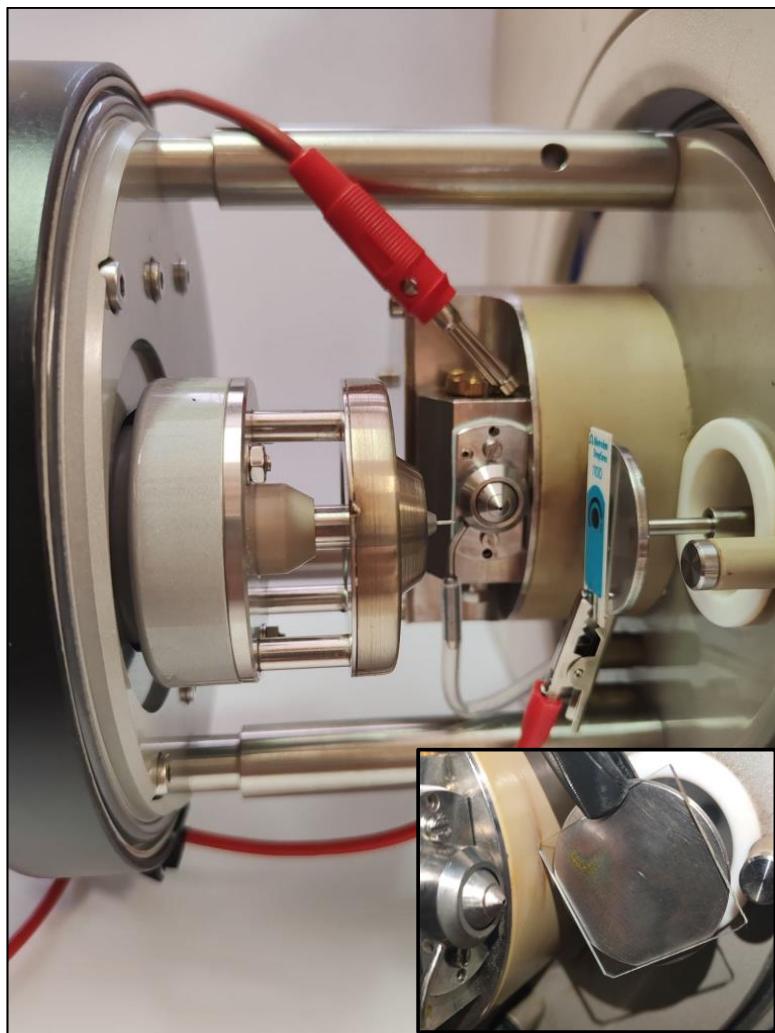


## Supplementary Materials

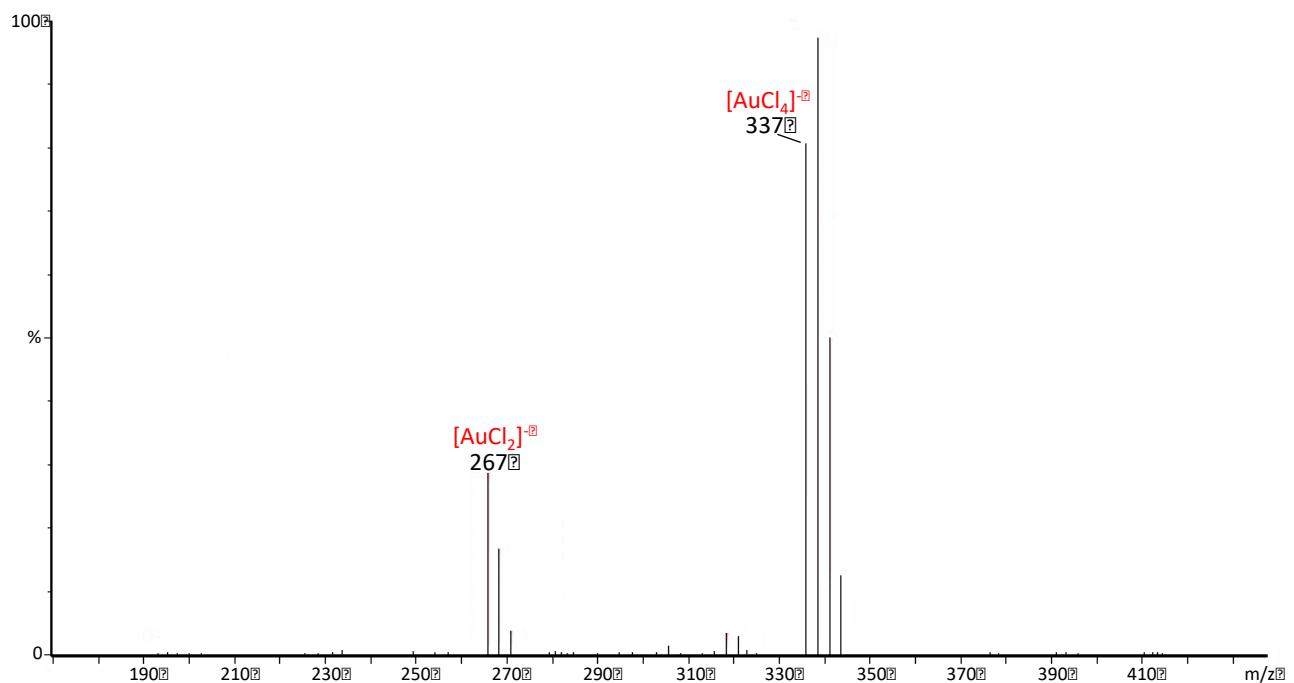
### Charged microdroplets deposition for nanostructured-based electrode surface modification

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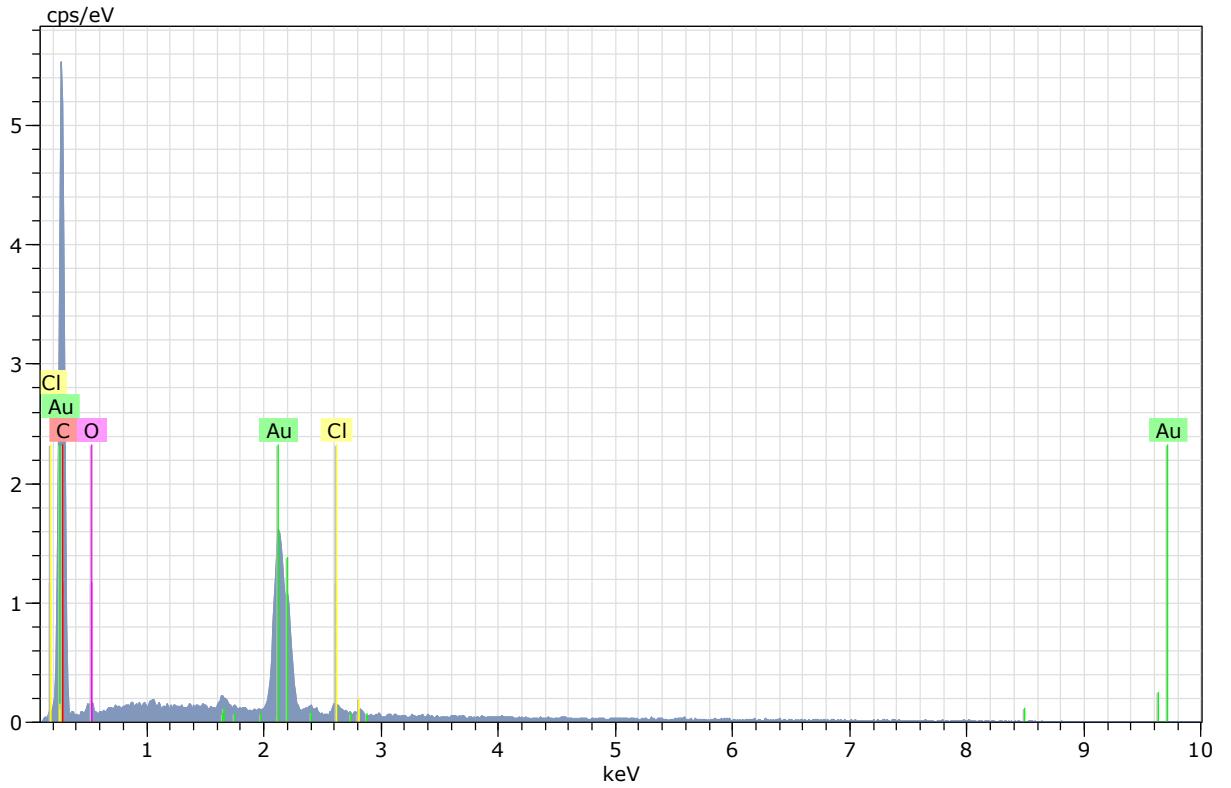
**Figure S1:** ESI Z-spray source apparatus for charged microdroplets deposition onto screen-printed electrodes. Inset: Gold particles deposited onto a glass slide after 1 hour of  $6.4 \times 10^{-4}$  M HAuCl<sub>4</sub> solution deposition.



**Figure S2:** ESI negative mass spectrum of  $6.4 \times 10^{-5}$  M  $\text{HAuCl}_4$  water solution.



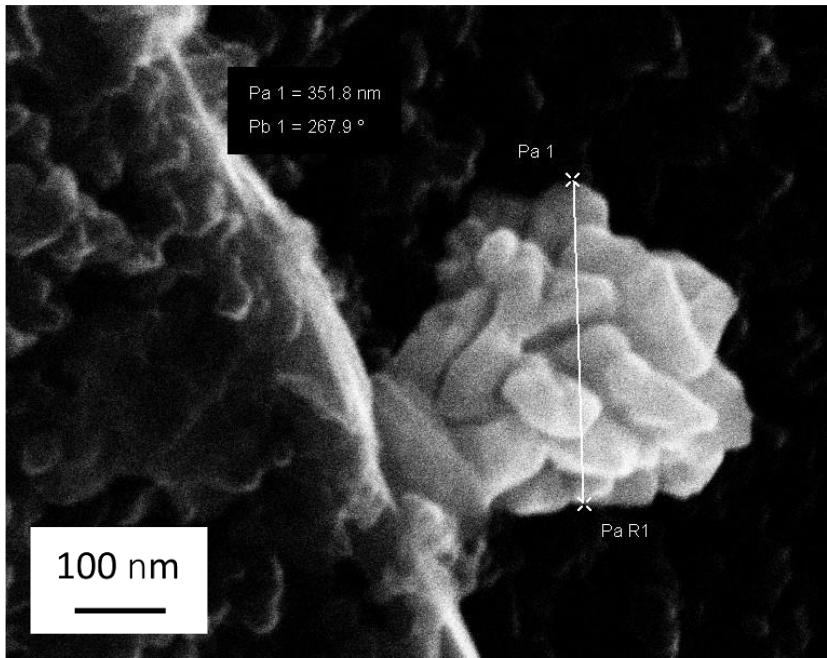
**Figure S3:** ESI positive mass spectrum of  $1 \times 10^{-5}$  M Fc-hexanethiol methanol solution.



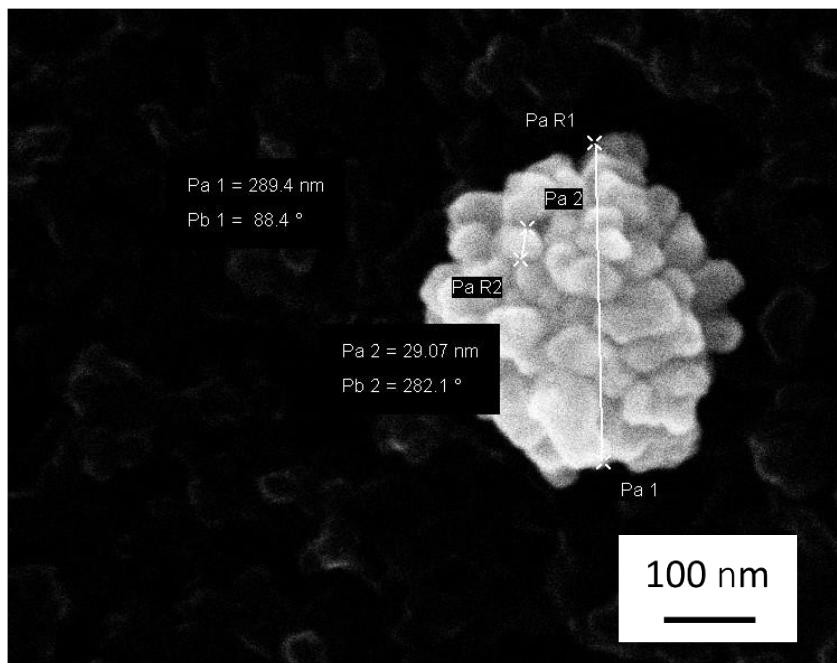
**Figure S4:** EDX analysis of the graphite screen-printed electrode after 10 minutes of microdroplets deposition of HAuCl<sub>4</sub> solution.

**Table S1.** Parameters obtained by EIS fitting.

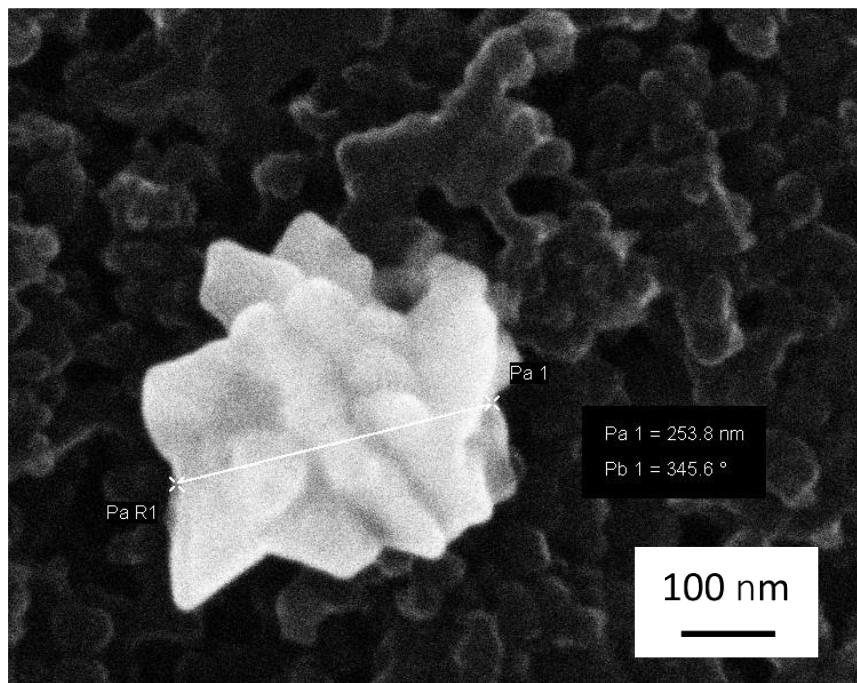
Deposition time	R <sub>CT</sub> ( $\Omega$ )	R <sub>Aul</sub> ( $\Omega$ )	W ( $\sigma$ )
0	3423	/	648
2	2515	/	583
4	1258	479	563
10	1246	186	516



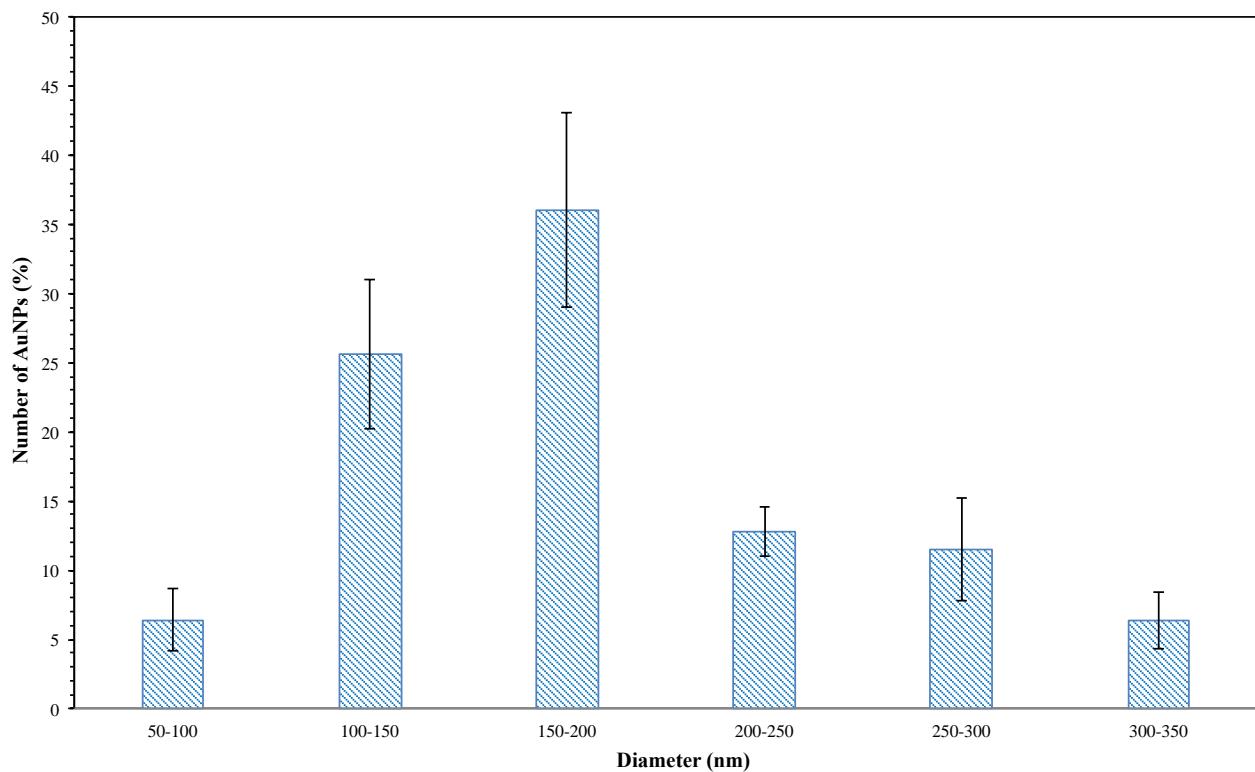
**Figure S5:** SEM image reporting the enlargement of AuNPs aggregates obtained with 2 minutes of deposition.



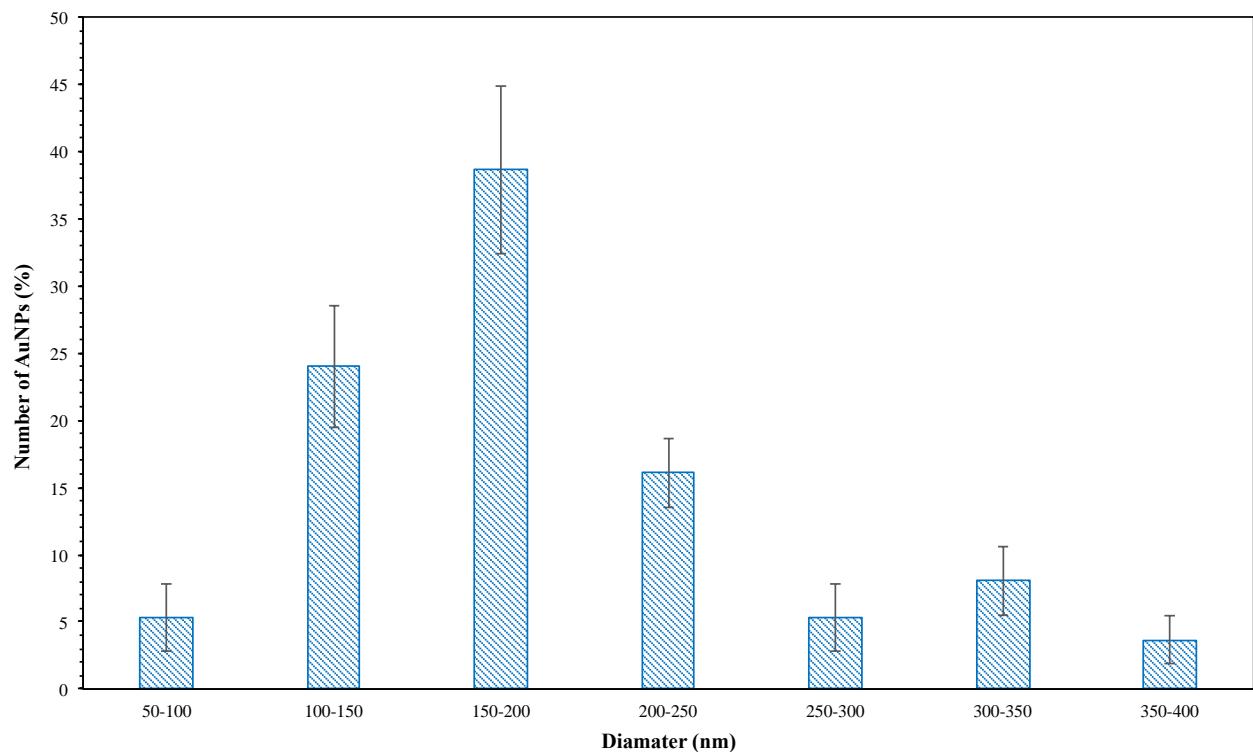
**Figure S6:** SEM image reporting the enlargement of AuNPs aggregates obtained with 4 minutes of deposition.



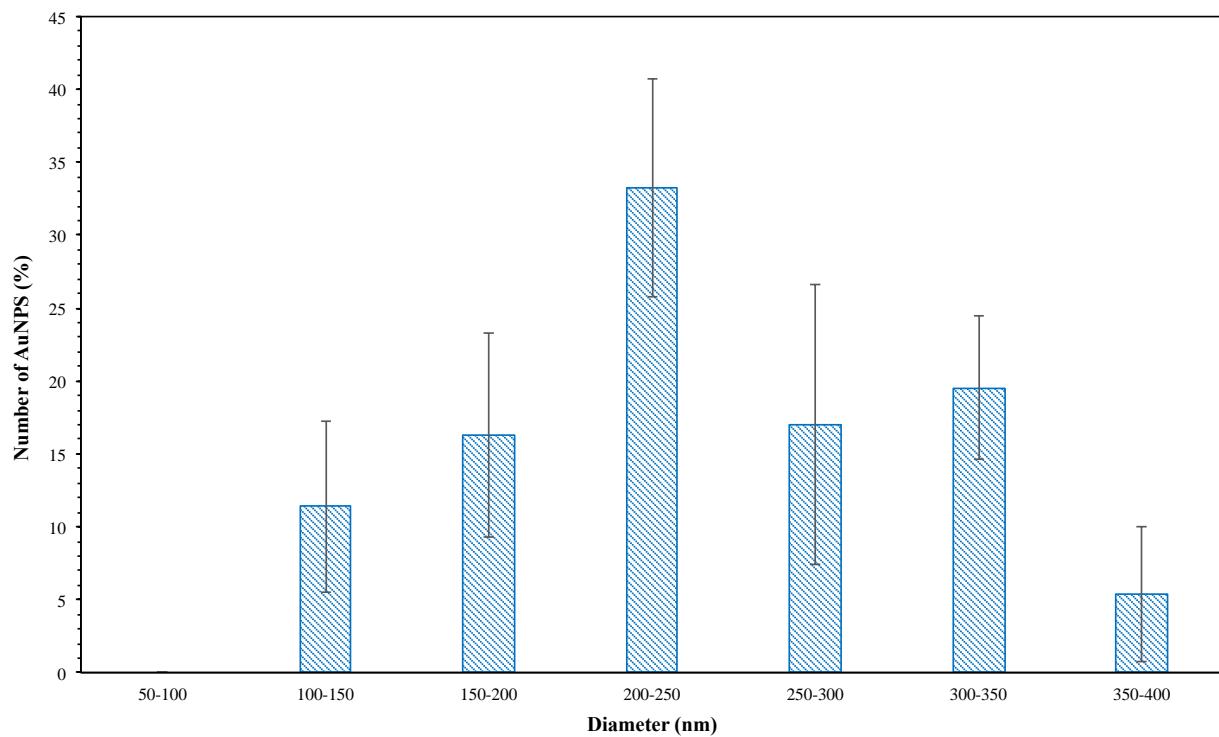
**Figure S7:** SEM image reporting the enlargement of AuNPs aggregates obtained with 10 minutes of deposition.



**Figure S8:** Size distribution of AuNPs after 2 minutes of microdroplets deposition.



**Figure S9:** Size distribution of AuNPs after 4 minutes of microdroplets deposition.



**Figure S10:** Size distribution of AuNPs after 10 minutes of microdroplets deposition.