Supporting Information

Potential-Modulated SERS Profiling via GLAD-Fabricated Ag Nanorod Arrays for Ultrasensitive and Label-Free Spectroelectrochemical Sensing

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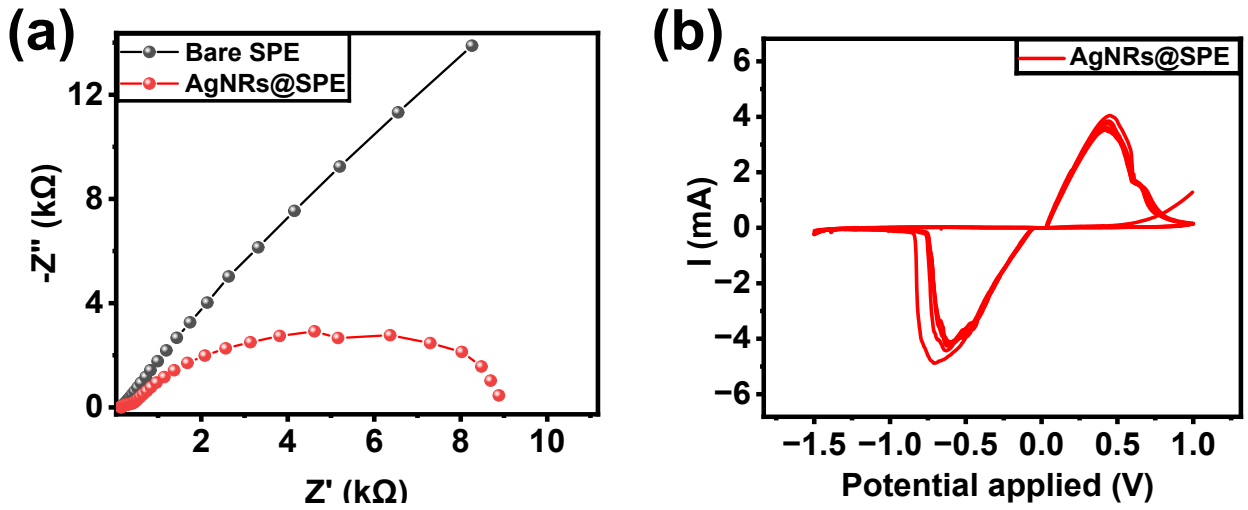

Figure S1. (a) Impedance spectra of bare SPE and AgNRs@SPE at OCP (open circuit potential, i.e., 0 V) from 0.1 Hz to 100 kHz. Initially, 150 µL of 0.1 M KCl was added to the EC-SERS cell containing either the bare SPE or AgNRs@SPE. The charge transfer resistance (R_{ct}), represented by the diameter of the semicircle, reflects the electron transfer rate of the redox reaction on the electrode surface. The R_{ct} of AgNRs@SPE is lower than that of the bare SPE, indicating that the AgNRs coating improves the electrical conductivity of the working electrode. (b) Cyclic voltammogram of AgNRs@SPE. The electrode surface was activated through cyclic voltammetry (CV) by performing 10 cycles at a 100mV s^{-1} scan rate in 0.1 M KCl.

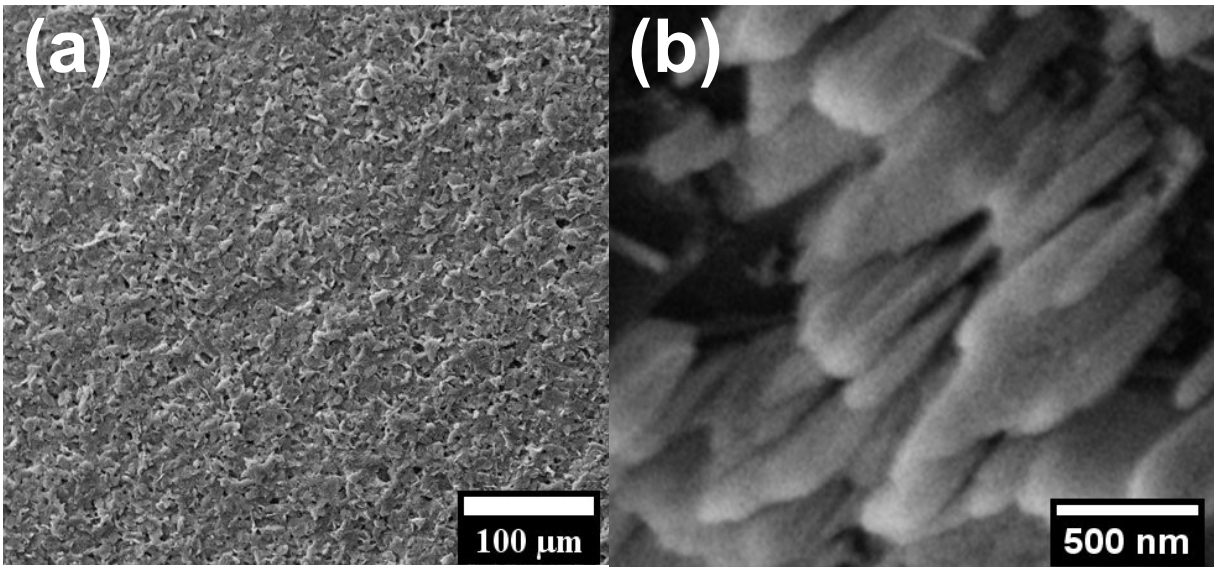

Figure S2.SEM image of (a)Bare SPE (b) Electrochemically activated AgNRs@SPE.

Raman shift (cm^{-1})	
SERS peak of PATP[1] on AgNRs@SPE	**Tentative assignment**
388	X-S
810	Out-of-plane C-H bending
880	aromatic C-H bending
1000	ring breathing mode
1080	C-N stretching + C-S stretching
1177 & 1455	N-N stretching
1597	aromatic C–C ring stretching

X* = Metal **Table S1**: Raman peak assignment of the PATP.[1]

Raman shift (cm^{-1})	
SERS peak of BPE[2,3] on AgNRs@SPE	**Tentative assignment**
879	Out-of-plane ring deformation of the pyridyl ring
1002	Contracting and stretching of the C−C bonds within the aromatic ring
1165-1200	C–H bending and ring vibrational modes
1308	C=C stretching within the aromatic ring
1400	C–H bending
1575-1594	C−N bending
1633	C=C stretching

Table S2: Raman peak assignment of the BPE.[2,3]

Raman shift (cm^{-1})	
SERS peak of Melamine[4] on AgNRs@SPE	**Tentative assignment**
485	interactions between melamine and the AgNRs
541	breathing mode vibrations of the triazine ring.
635	ring deformation or C-N bending vibrations within the triazine ring structure
715	Triazine ring deformation
805	bending mode within the triazine ring structure
1005	symmetric breathing mode of the triazine ring

Table S3: Raman peak assignment of the Melamine.[4]

References

1 A. M. Robinson, S. G. Harroun, J. Bergman and C. L. Brosseau, *Anal. Chem.*, DOI:10.1021/ac2030078.

2 S. K. Gahlaut, D. Savargaonkar, C. Sharan, S. Yadav, P. Mishra and J. P. Singh, *Anal. Chem.*, DOI:10.1021/acs.analchem.9b04129.

3 N. Félidj, S. L. Truong, J. Aubard, G. Lévi, J. R. Krenn, A. Hohenau, A. Leitner and F. R. Aussenegg, *J. Chem. Phys.*, DOI:10.1063/1.1676152.

4 N. T. T. An, D. Q. Dao, P. C. Nam, B. T. Huy and H. Nhung Tran, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, DOI:10.1016/j.saa.2016.06.043.