Electronic Supplementary information

Development of an Electrochemical Surface-Enhanced Raman Spectroscopy (EC-SERS) Aptasensor for Direct Detection of DNA Hybridization

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Figure S-1: (a) UV-visible spectrum of silver nanoparticles prepared by the modified citrate reduction method. (b) TEM image of corresponding silver nanoparticles.



USB Potentiostat Raman Spectrometer

Laptop Computer

Figure S-2: Shows the set-up of the portable EC-SERS system.



Figure S-3: Normal Raman spectra for the four DNA nucleotides (powder): dGMP, dAMP, dCMP, and dTMP. Adenine was measured at medium-high power (46.5 mW) for a time interval of 60 seconds, while the rest were measured at high power (55.9 mW) for a time interval of 60 seconds using 785 nm excitation. All spectra are normalized for both laser power and exposure time.



Figure S-4: Comparison between the adenine base and dAMP at -0.8 V using EC-SERS. Both spectra were collected at medium-high power (46.5 mW) for a time interval of 60 seconds using 785 nm excitation.



Figure S-5: EC-SERS comparison of the four nucleotides, as well as the mixture of bases, at -0.8 V. All the spectra were collected at medium-high power (46.5 mW) for a time interval of 60 seconds.

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Probe (cm ⁻)	Target (cm ⁻)	Probe + Target (cm ²)	Danu assignment
1644	1640	1643	Ring stretching of guanine or v(C=O) ^a
1576	1573	1577	G, A (ring breathing modes of the DNA/
			RNA bases) ^a
	1509		Cytosine ^a
1522		1520	Cytosine, $v(C=C)^{a}$
1476	1471	1478	v(C=C) ^a
	1328	1326	Nucleic acid and phosphates ^a
1348			Nucleic acid mode ^a
1304			v(C-NH ₂) of cytosine ^a
1257		1250	Guanine, cytosine (NH ₂) ^a
1090	1083	1083	Phosphodiester groups in nucleic acids ^a
1017			v(C-O) ribose ^a
	954		Symmetric stretching vibration of $v_1 PO_4^{3-a}$
		858	Phosphate group ^a
787	785	785	-O-P-O-phosphodiester bands in DNA,
			DNA, O-P-O stretching ^a
	730	730	Ring vibration of adenine ^a
685	N/A	681	S-C mode ^a
	663		G, T (ring breathing mode in DNA bases) ^a
595	N/A	586	Ag-S-C-C _{trans} ^b
564	N/A		Ag-S-C-C _{gauche} ^b or cytosine ^a
230	N/A	232	v(Ag-S) ^c

Table S-1: Band assignment for probe, target, and probe + target on AgNP surfaces.

- a) Z. Movasaghi, S. Rehman, I. U. Rehman, Appl. Spectrosc. Rev., 2007, 42, 493-541.
- b) Y. Chen, L. Wu, Y. Chen, N. Bi, X. Zheng, H. Qi, M. Qin, X. Liao, H. Zhang, Y. Tian, *Microchim. Acta*, 2012, **177**, 341-348.
- c) I. Matulaitienė, Z. Kuodis, O. Eicher-Lorka, G. Niaura, *J. Electroanal. Chem.*, 2013, **700**, 77-85.



Figure S-6: EC-SERS anodic signal of probe immobilized on a AgNP electrode, measured at medium-high power (46.5 mW) for a time interval of 60 seconds using 785 nm excitation.



Figure S-7: EC-SERS cathodic signal of a AgNP electrode incubated in 1.0 mM of 12-MDA solution for 2 hours. The signal was measured at 120 mW for a time interval of 60 seconds using the 780 nm high resolution DXR SmartRaman spectrometer.



Figure S-8: SERS signal collected at -1.0 V cathodic for a AgNP electrode initially incubated in 1.0 mM 12-MDA for 2 hours a) 1 month, b) 2 months, c) 6 months, d) 10 months. All spectra were measured at the same parameters, 120 mW for a time interval of 60 seconds using the 780 nm high resolution DXR Raman spectrometer.



Figure S-9: SERS comparison at -1.0 V for probe + target + 12-MDA conducted in 0.1 M NaF measured in a) June, 2012 and b) November, 2014. Both spectra collected at medium-high power (46.5 mW) for a time interval of 60 seconds using 785 nm excitation. Arrows indicate adenine peaks.