SUPPLEMENTARY INFORMATION

Dip-coated carbon nanotube surface deposits as stable, effective response enhancers in pencil lead electrode voltammetry

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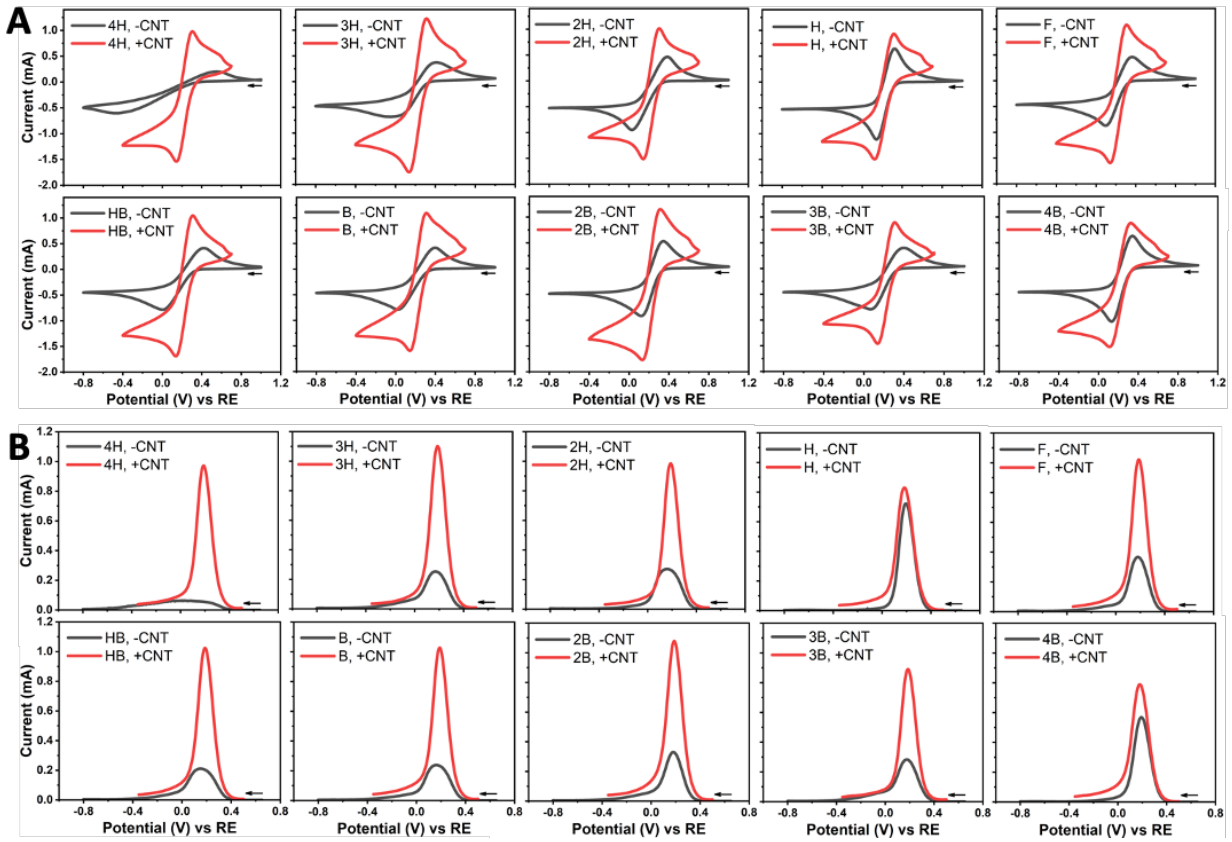

Figure S1: Cyclic (CVs, top two raws) and differential pulse (DPVs, bottom two raws) voltammograms of 100 mM ferricyanide at pencil lead electrodes (PLEs) that were made with 10 pencil leads of the same brand (Pentel AinSTEIN) and diameter (0.5 mm) but of 4H, 3H, 2H, H, F, HB, B, 2B, 3B and 4B hardness/softness grades. Black CVs and DPVs were recorded with PLEs that had no CNT modification while the red CVs and DPVs are responses of the CNT-modified PLE equivalents. The supporting electrolyte for the measurements was 100 mM KCl, the scan speed for CV acquisition was 50 mV/s and the pulse size and time for DPV recordings were 50 mV and 200 ms, respectively. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode.

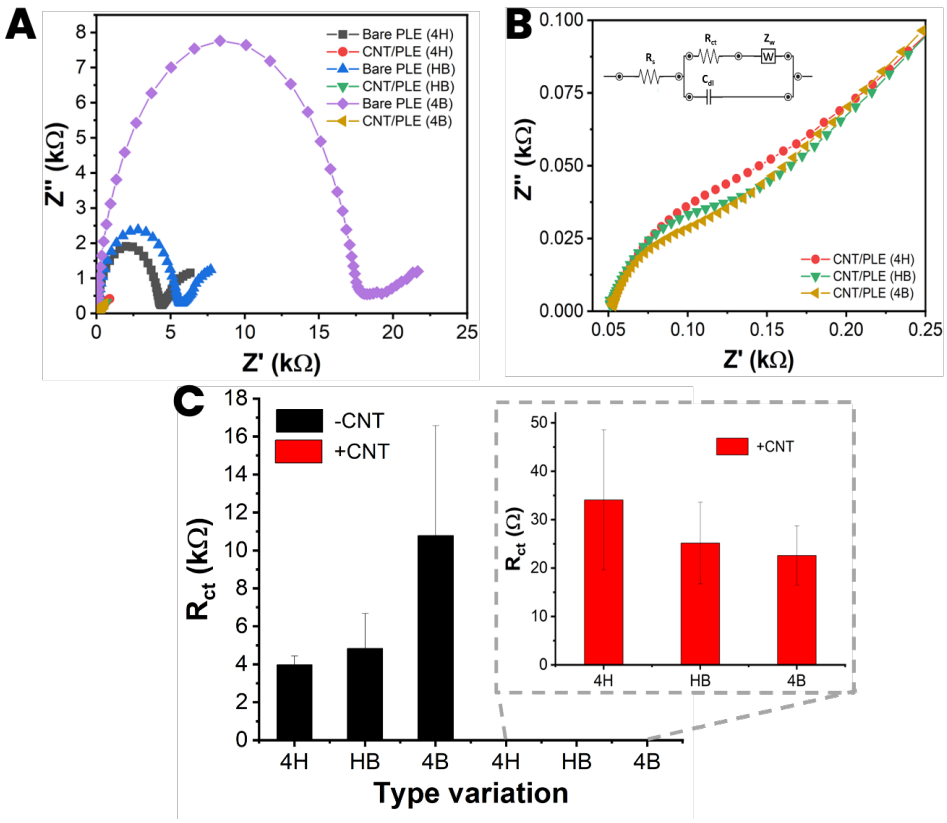

Figure S2: Electrochemical impedance spectroscopy characterization of a Pentel AinSTEIN-based pencil lead electrode regarding the influence of the pencil lead hardness on the bare and CNT-modified sensor's ferricyanide redox responsiveness. (A) Nyquist plots for PLEs that had a H (black square), HB (blue triangle) and 4B (purple square) PL incorporation but no CNT modification and the Nyquist plots for PLEs that H (red circle), HB (green triangle) and 4B (brown triangle) incorporation and a CNT modification. (B) A graphical zoom into the left bottom corner of the plot of the imaginary and real part of the electrode impedance in (A). (C) Bar chart representation of the charge transfer resistances, R_{ct}, of bare (black) and CNT-modified 4H-, HB and 4B-based PLEs. The EC cell was arranged as a three-electrode configuration system with a Pt counter-electrode, a Ag/AgCl/3 M KCl reference and the proposed PLE as working electrode.
Conditions for the PL CNT modification: 10 repetitions of a sequence of 5-s-long immersion into a 5 mg mL^{-1} CNT suspension in DI water with 5-s-long periods of rest in air.
Condition for EIS data acquisition: Frequency range was 100,000 - 0.01 Hz, the AC amplitude 10 mV, and the DC potential was set to open-circuit value of 270 mV. Electrolyte for EIS testing was a 0.1 M KCl solution containing a mixture of 5 mM $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$. R_{ct} value computation assumed for the working electrode the validity of the Randles equivalent circuit.

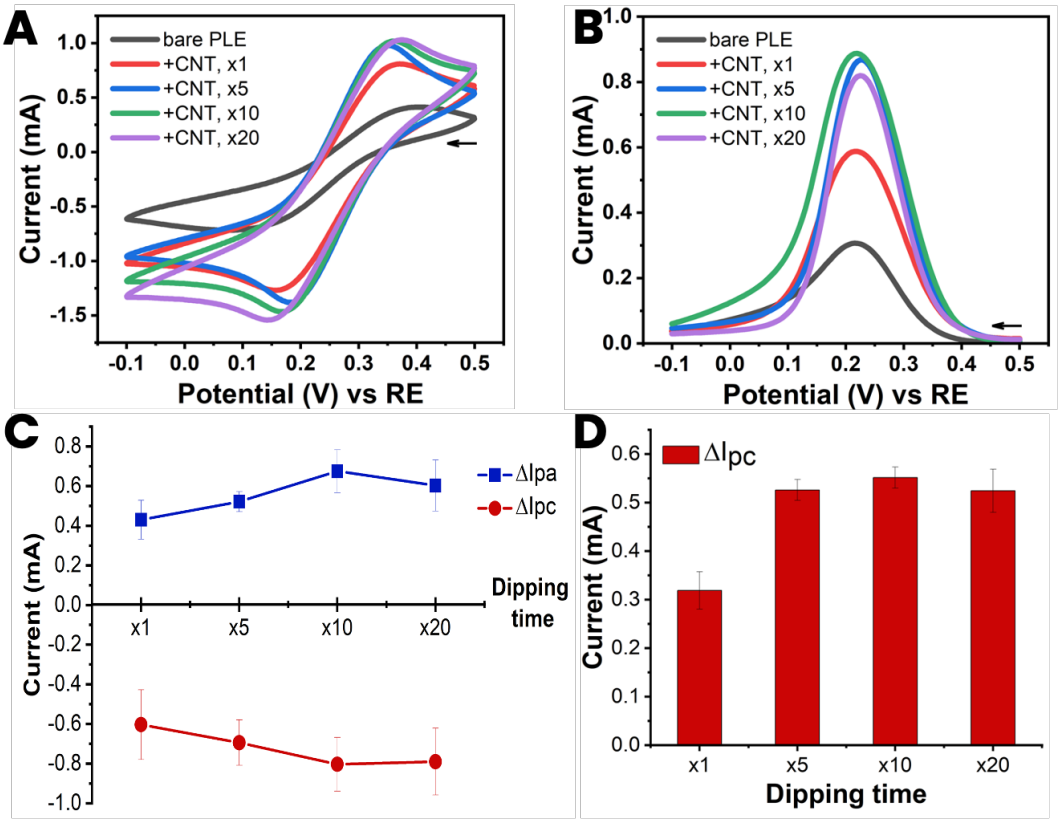

Figure S3: Evaluation of the influence of the number of dip/dry cycles that are performed during CNT modification of PLEs on the ferricyanide redox responsiveness of completed sensors. (A) Cyclic voltammograms (CVs) and (B) differential pulse (DPVs) voltammograms for the Pentel AinSTEIN HB PLEs that were unmodified (black line) or went through a 1 (red line), 5 (blue line), 10 (green line) and 20 (purple line) repeats of the sequence of 5-s-long immersion into a 5 mg/mL CNT suspension in DI water with 5-s-long periods of rest in air. (C) Plot of the gain in the CV ferricyanide reduction (red trace) and ferrocyanide oxidation (blue trace) currents, computed as $\Delta I_p = I_p(PLE_{CNT}) - I_p(PLE_{bare})$, as function of n, the number of dip and dry treatments. (D) Bar chart representation of the gain in the DPV ferricyanide reduction current, computed as $\Delta I_{pc} = I_{pc}(PLE_{CNT}) - I_{pc}(PLE_{bare})$, as function of n, the number of dip and dry treatments. The supporting electrolyte for the CV and DPV measurements was 100 mM KCl, the ferricyanide concentration was 100 mM, the scan speed for CV acquisition was 50 mV/s and the pulse size and time for DPV recordings were 50 mV and 200 ms, respectively. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode.

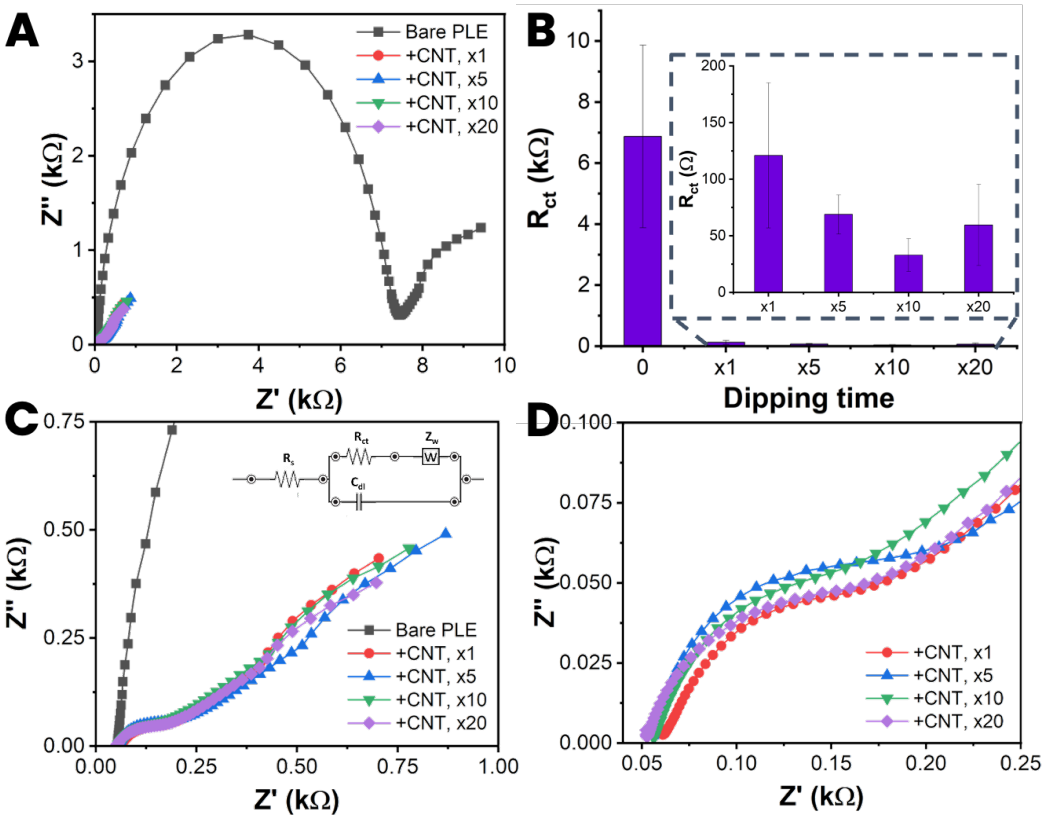

Figure S4: Electrochemical impedance spectroscopy (EIS) evaluation of the influence of the number of dip/dry cycles that are performed during CNT modification of PLEs on the ferricyanide redox responsiveness of completed sensors. (A) Nyquist plots of EIS data for the Pentel AinSTEIN HB-PLEs that were unmodified (black squares) or went through a 1 (red squares), 5 (blue triangles), 10 (green triangles) and 20 (purple squares) repeats of the sequence of 5-s-long immersion into a 5 mg mL^{-1} CNT suspension in DI water with 5-s-long periods of rest in air. (B) Bar chart representation of the charge transfer resistances, R_{ct}, computed for curve fits to the Randles equivalent circuit, as function of n, the number of dip and dry treatments. (C) and (D) are graphical zooms with increasing magnification into the left bottom corner of the plot of the imaginary and real part of the electrode impedance in (A). A three-electrode EC cell was used with a Pt counter and a Ag/AgCl/3M KCl reference electrode.

Conditions for the PL CNT modification: 10 repetitions of a sequence of 5-s-long immersion into a 5 mg mL^{-1} CNT suspension in DI water and 5-s-long periods of rest in air.

Condition for EIS data acquisition: Frequency range was 100,000 - 0.01 Hz, the AC amplitude 10 mV, and the DC potential was set to open-circuit value of 270 mV. Electrolyte for EIS testing was a 0.1 M KCl solution containing a mixture of 5 mM $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$. R_{ct} value computation assumed for the working electrode the validity of the Randles equivalent circuit.

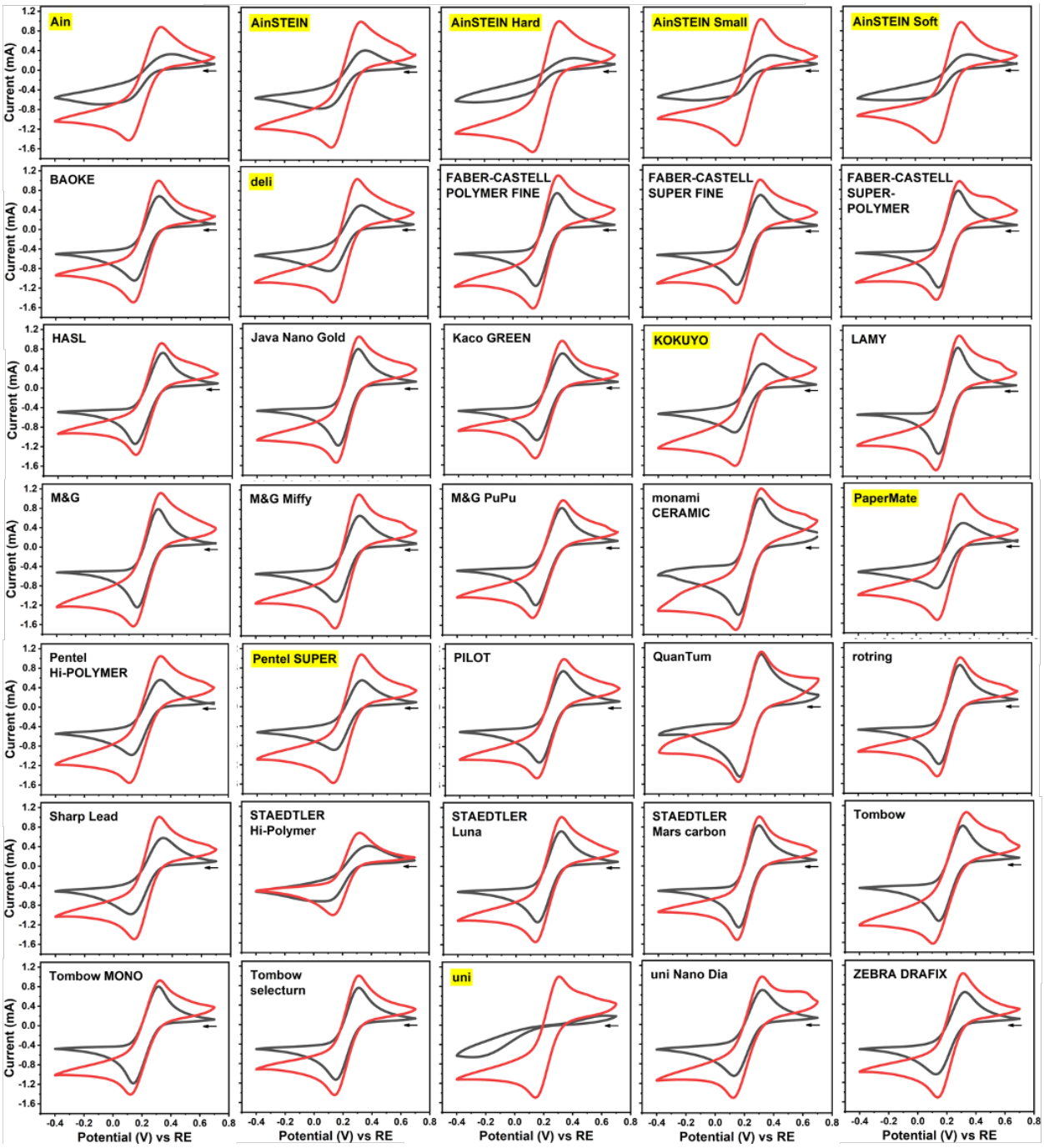

Figure S5: Cyclic voltammograms (CVs) of 100 mM ferricyanide at pencil lead electrodes (PLEs) that were made with 0.5-mm-diameter HB pencil leads of 35 different brands. Black CVs were recorded with PLEs that had no CNT modification while the red ones are the responses of the CNT-modified PLE equivalents. The supporting electrolyte for the measurements was 100 mM KCl, the scan speed for CV acquisition was 50 mV/s. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode. The yellow marked PLE options have been further tested.

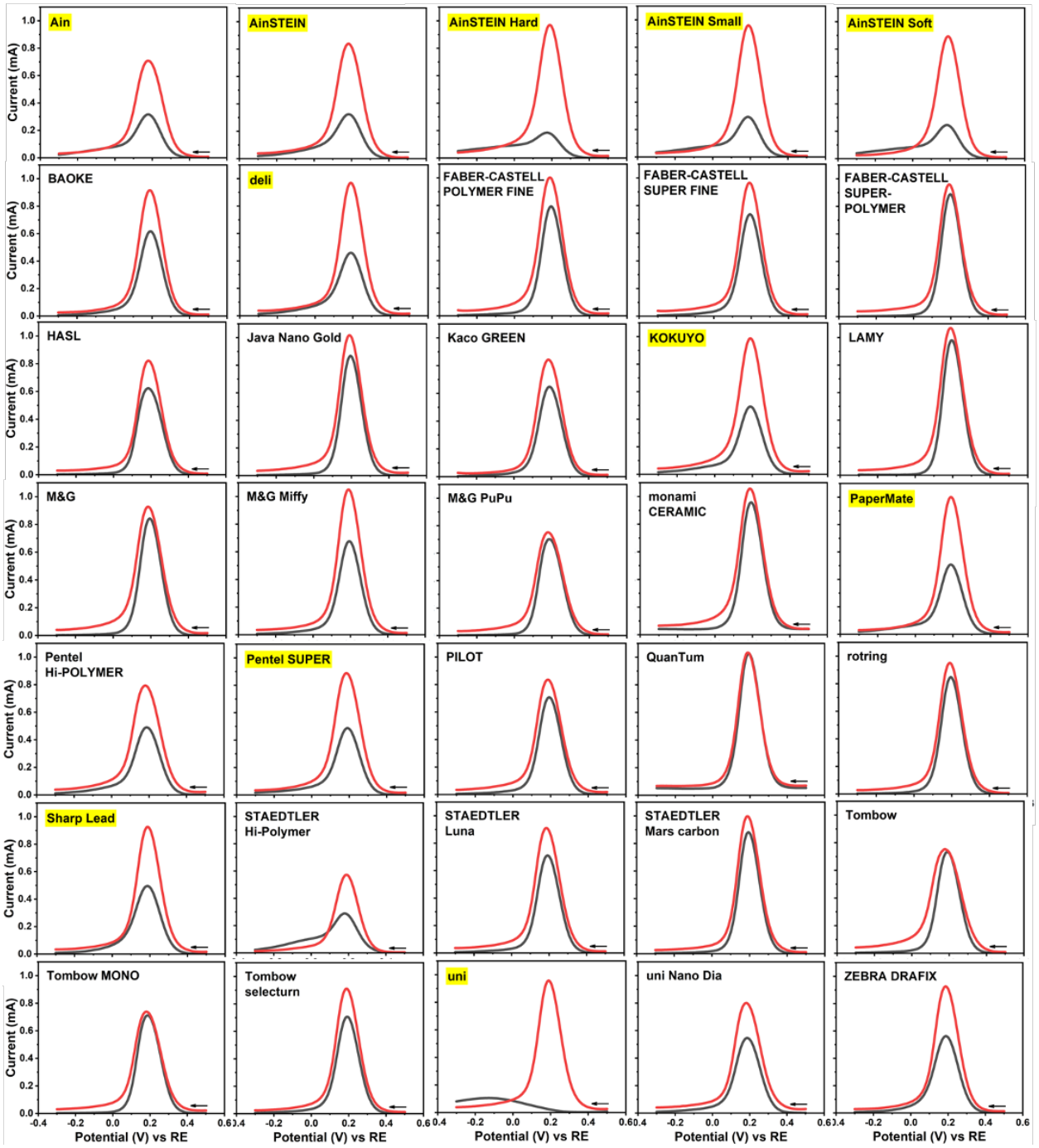

Figure S6: Differential pulse voltammograms (DPVs) of 100 mM ferricyanide at pencil lead electrodes (PLEs) that were made with 0.5-mm-diameter HB pencil leads of 35 different brands. Black CVs were recorded with PLEs that had no CNT modification while the red ones are the responses of the CNT-modified PLE equivalents. The supporting electrolyte for the measurements was 100 mM KCl and the pulse size and time for DPV recordings were 50 mV and 200 ms, respectively. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode. The yellow marked PLE options have been further tested for reproducibility of the CNT modification (Figure S7 and S8).

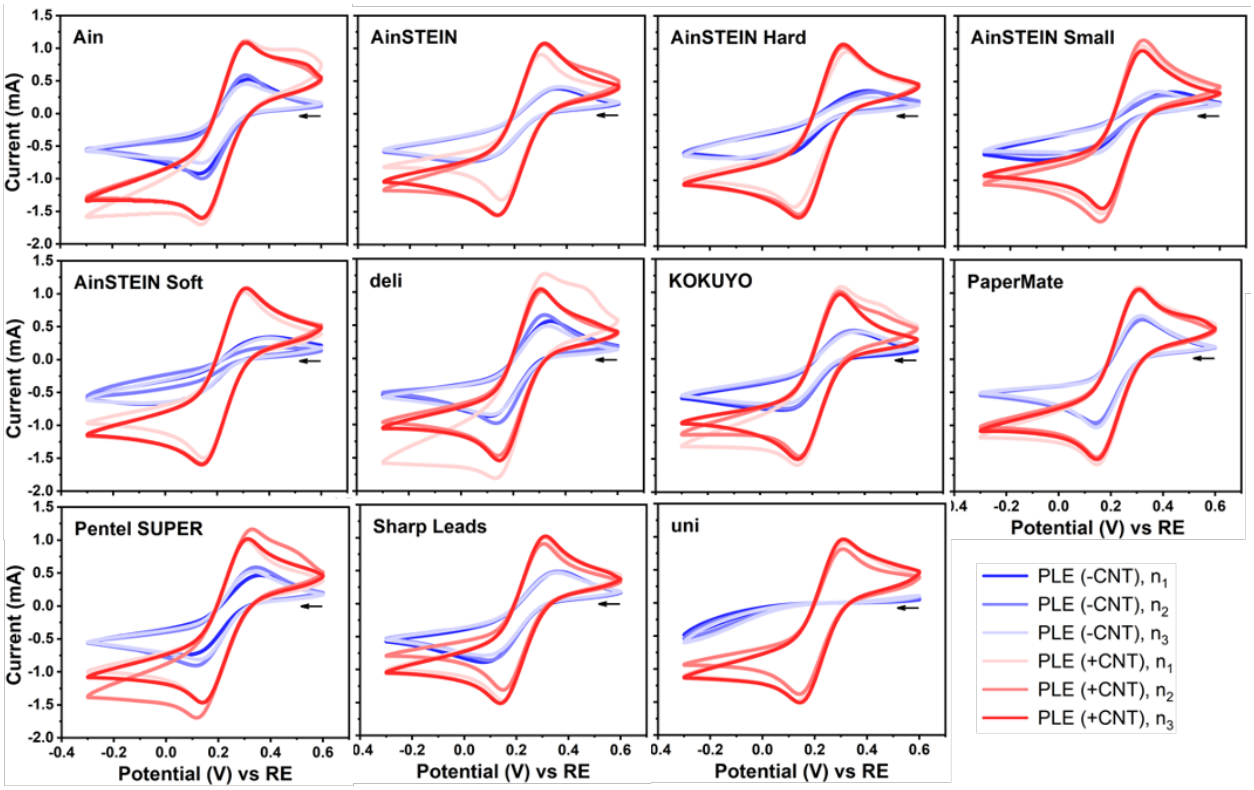

Figure S7: Triplicate repetitions of cyclic voltammograms of 100 mM ferricyanide at 11 different HB-PLEs without (blue) and with (red) CNT modification. The supporting electrolyte for the measurements was 100 mM KCl, the scan speed for CV acquisition was 50 mV/s. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode.

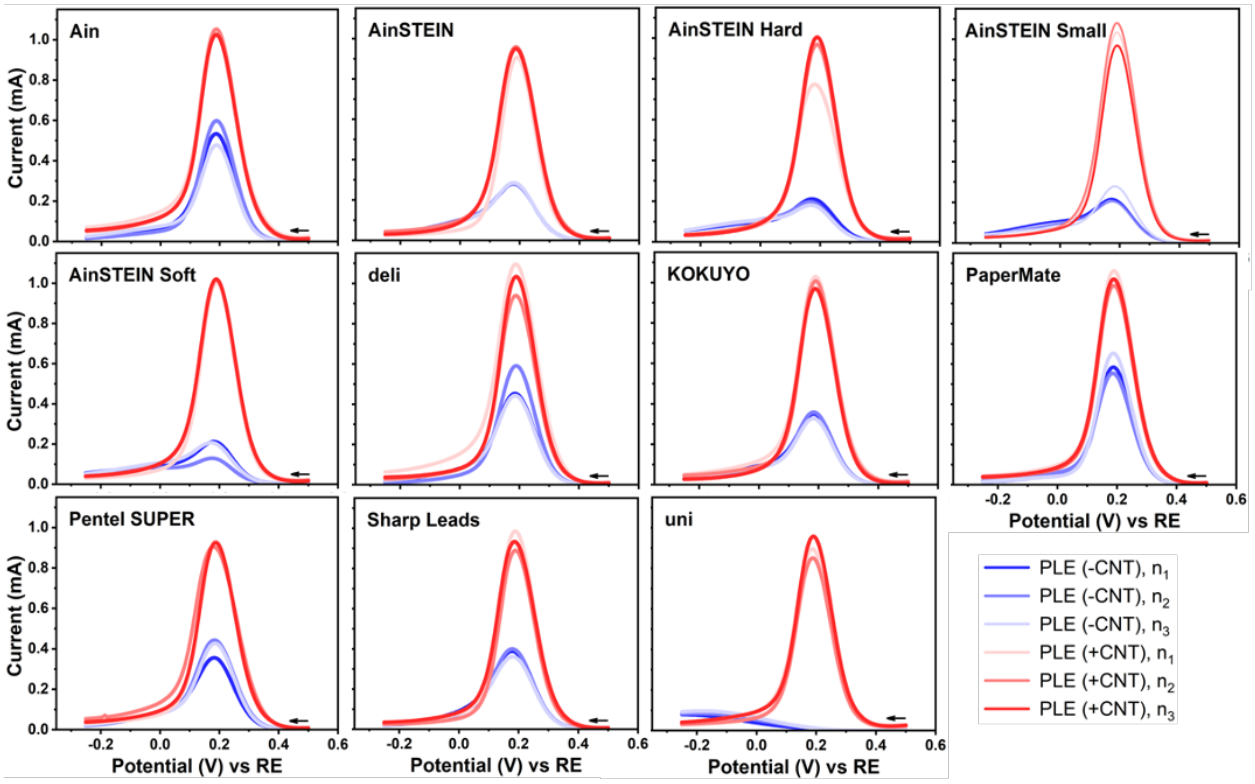

Figure S8: Triplicate repetitions of differential pulse voltammograms of 100 mM ferricyanide at 11 different HB-PLEs without (blue) and with (red) CNT modification. The supporting electrolyte for the measurements was 100 mM KCl, and the pulse size and time for DPV recordings were 50 mV and 200 ms, respectively. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode.

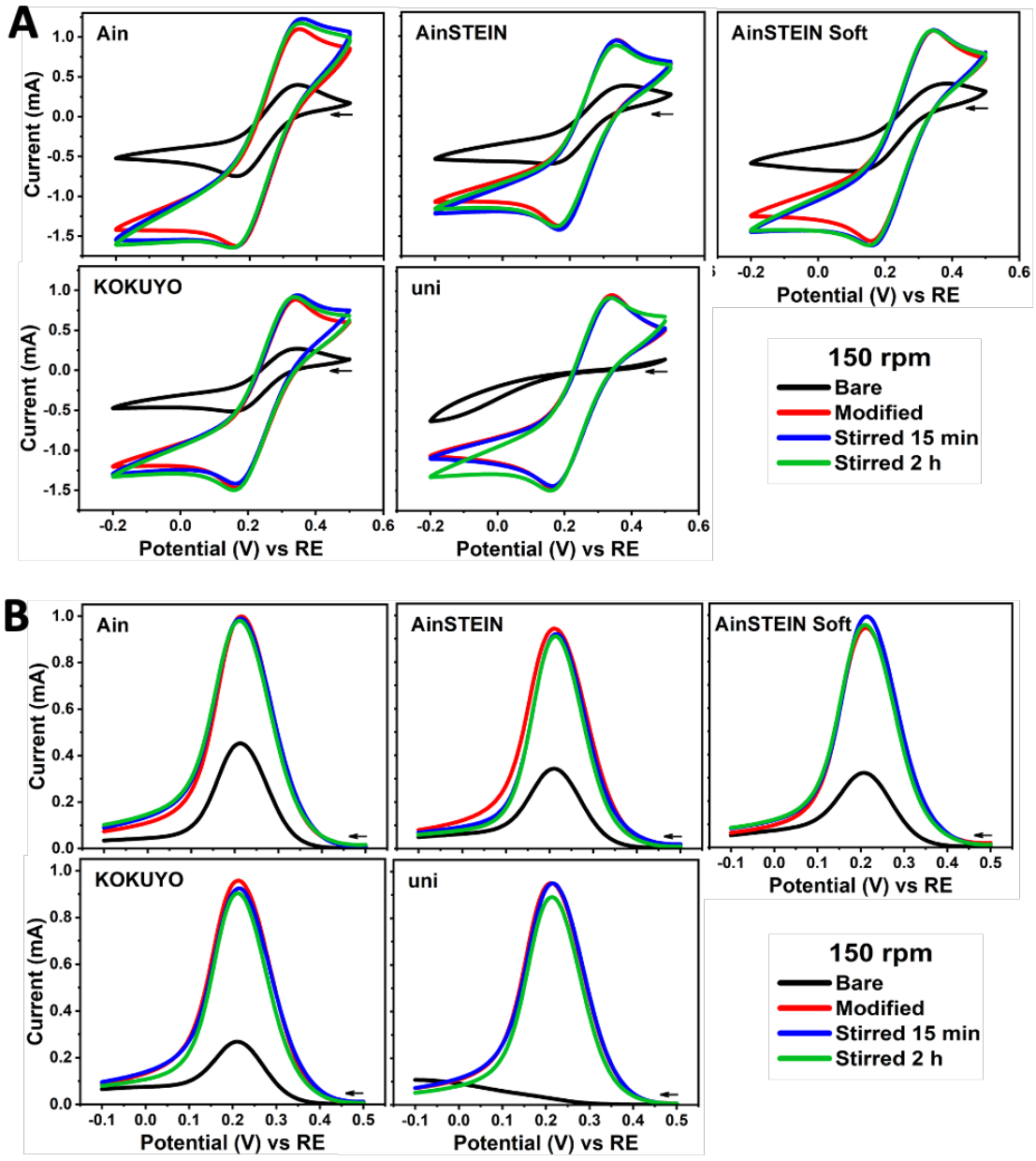

Figure S9: Durability test I with 5 CNT-modified HB pencil lead electrodes. The cyclic (A) and differential pulse (B) voltammograms (DPVs) of 100 mM ferricyanide that were obtained at HB-PLEs (PL brand: uni) without (black) and with (red) CNT modification. The (A) and (B) plot sets also include two voltammograms that were acquired after storage of the sensor tools in stirred DI water. Stirring rates were 150 rpm. Exposure times were 15 min (blue) or 2 hours (green). The supporting electrolyte for the measurements was 100 mM KCl. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode. The scan speed for CV acquisition was 50 mV/s and the pulse size and time for DPV recordings were 50 mV and 200 ms, respectively.

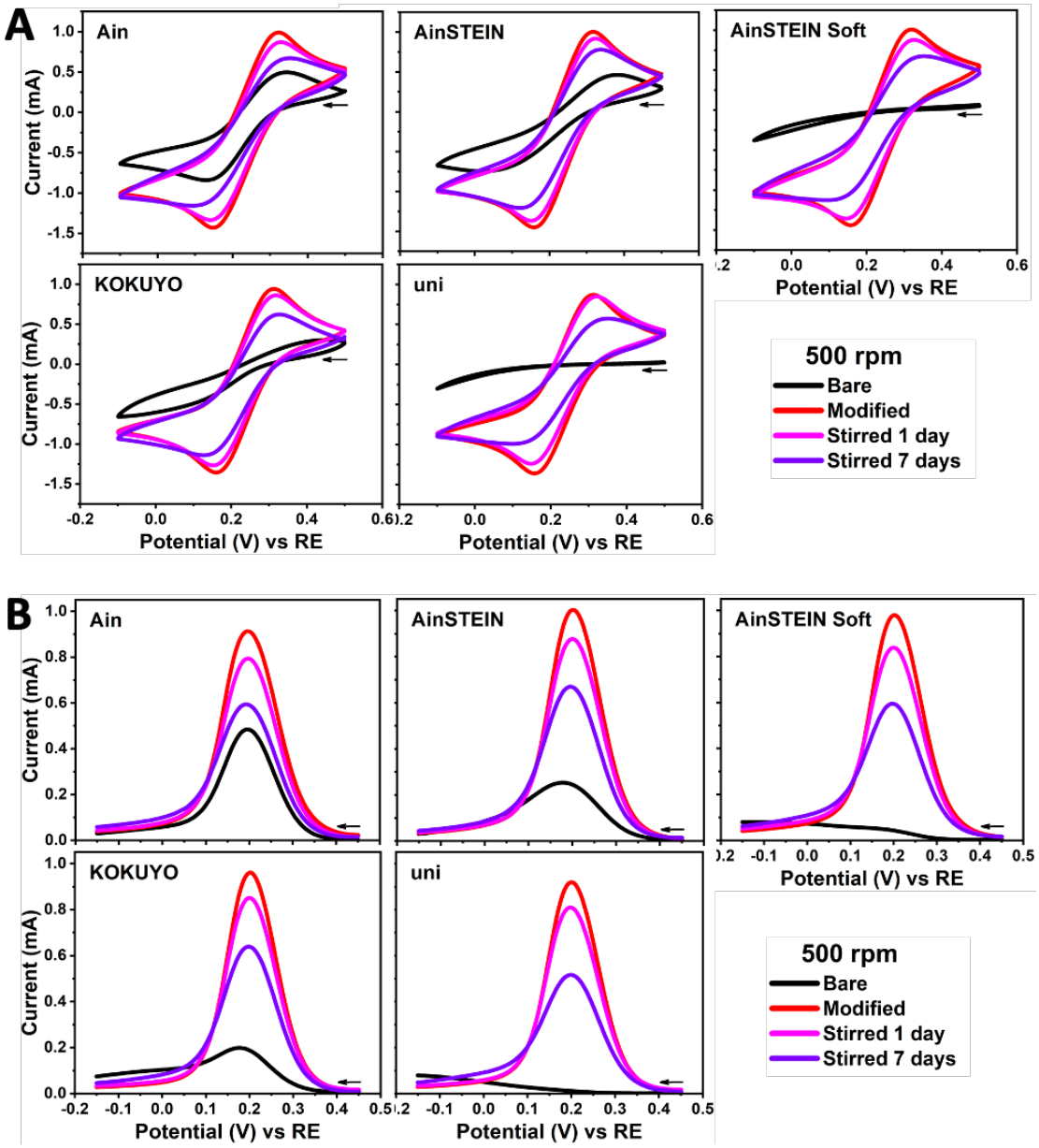

Figure S10: Durability test II with 5 CNT-modified HB pencil lead electrodes. The cyclic (A) and differential pulse (B) voltammograms (DPVs) of 100 mM ferricyanide that were obtained at HB-PLEs (PL brand: uni) without (black) and with (red) CNT modification. The (A) and (B) plot sets also include two voltammograms that were acquired after storage of the sensor tools in stirred DI water. Stirring rates were 500 rpm. Exposure times were 1 day (pink) or 7 days (purple). The supporting electrolyte for the measurements was 100 mM KCl. The EC cell was arranged with a coiled Pt counter and a Ag/AgCl/3M KCl reference electrode. The scan speed for CV acquisition was 50 mV/s and the pulse size and time for DPV recordings were 50 mV and 200 ms, respectively.

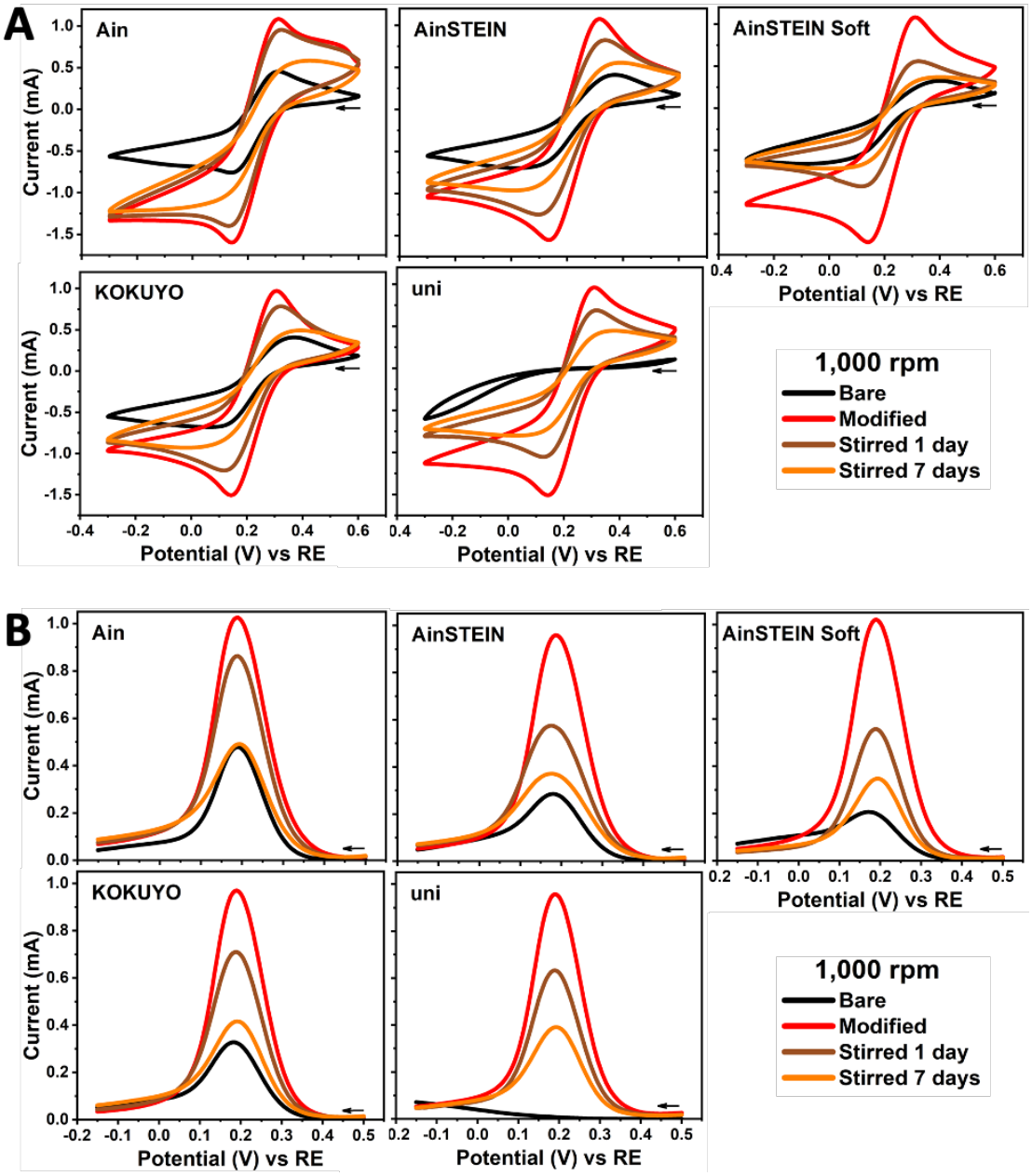

Figure S11: Durability test III with 5 CNT-modified HB pencil lead electrodes. The cyclic (A) and differential pulse (B) voltammograms (DPVs) of 100 mM ferricyanide that were obtained at HB-PLEs (PL brand: uni) without (black) and with (red) CNT modification. The (A) and (B) plot sets also include two voltammograms that were acquired after storage of the sensor tools in stirred DI water. Stirring rates were 1000 rpm. Exposure times were 1 day (brown) or 7 days (orange). The supporting electrolyte for the measurements was 100 mM KCl. The EC cell was arranged with a Pt counter and a Ag/AgCl/3M KCl reference electrode. The scan speed for CV acquisition was 50 mV/s and the pulse size and time for DPV recordings were 50 mV and 200 ms, respectively.

Table S1: The specific conductivity of Pentel AinSTEIN pencil leads of different hardness/softness grades (4H → HB → 4B).

No.	Type	Ø (mm)	L (cm)	R_m (Ω)	R (Ω cm^{-1})	G = 1/R (S cm^{-1})
1	4H	0.5	6	1.3	0.2	4.6
2	3H			1.3	0.2	4.6
3	2H			1.2	0.2	5.0
4	H			1.4	0.2	4.3
5	F			1.3	0.2	4.6
6	HB			1.2	0.2	5.0
7	B			1.2	0.2	5.0
8	2B			1.8	0.3	3.3
9	3B			1.3	0.2	4.6
10	4B			2.0	0.3	3.0

Abbreviations: R_m = Measured resistance in Ohm (Ω), R = Resistivity in Ω cm^{-1}
G = Conductivity in Siemens per cm (S cm^{-1})
L = PL length between multimeter grip points in cm,
Ø = PL diameter in millimeter (mm)

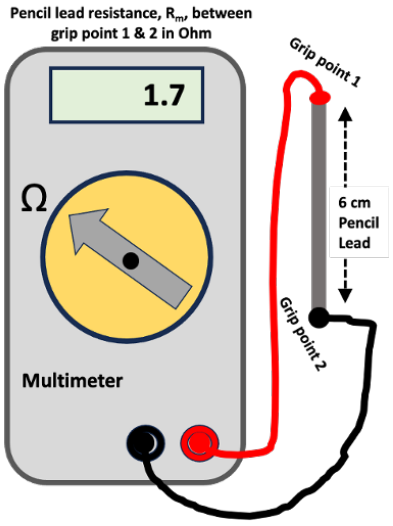

Table S2: Carbon nanotube-based performance enhancement of stationary pencil lead electrodes (PLEs): A comparison of own with published accomplishments.

	PLE Geometry	CNT Type	CNT Preparation	CNT Modification	Add-on Matrix Component	x fold R_{ct} decrease	x fold I_{pc} increase	Ref.
1	Disk	MW-CNT	Suspension in H_2O	Drop & Dry	None	18	4	**1**
2	Disk	SW-CNT	Suspension in DMSO, DMF, THF or H_2O	Drop & Dry	None	7	1.4	**2**
3	Disk	MW-CNT	Suspension in DMF	Drop & Dry	None	11,584	-	**3**
4	Disk	c-MW-CNT	Suspension in DMF	Drop & Dry	None	2	2	**4**
5	Cylindrical	MW-CNT	Suspension in Chitosan/Acetic Acid	ED	Bi-NP/NiO-NP/NaM-NP	75	1.6	**5**
6	Cylindrical	MW-CNT	Suspension in Phosphate Buffer Solution	ED	PoPD	1.4	2	**6**
7	Cylindrical	MW-CNT	Suspension in Chitosan/NaM/Acetic Acid	Dip & Dry	NiO/NaM-NP	12.5	1.5	**7**
8	Cylindrical	c-MW-CNT	Suspension in DMG	ED/Dip & Dry	ꝏ-PEDOT	32.6	1.6	**8**
9	Cylindrical	MW-CNT	Suspension in Chitosan/Acetic Acid/SEP	Dip & Dry	SEP	16.4	3	**9**
10	Cylindrical	MW-CNT	Suspension in Chitosan/Acetic Acid/SMT	Dip & Dry	SMT	6.5	2.5	**10**
11	Cylindrical	c-MW-CNT	Suspension in	Dip & Dry/ED	Au-NP/MIP	2	1.6	**11**
12	Cylindrical	c-MW-CNT	Suspension in DMF	Dip & Dry	None	2	1	**12**
13	Cylindrical[1]	c-SW-CNTs	Suspension in H_2O	Dip and Dry	None	192	2.2	**This work**
	Cylindrical[2]	c-SW-CNTs	Suspension in H_2O	Dip and Dry	None	812	2.1	

Abbreviations: PLE = Pencil lead electrode, CNT = Carbon nanotube, R_{ct} = Charge transfer resistance, I_{pc} = Cathodic cyclic voltammetry current, ED = Electrodeposition, c = carboxylated, DMF = Dimethyl-formamide, DMSO = Dimethyl-sulfoxide, THF, Bi-NP = Bi nanoparticles, NiO-NP = Nickel oxide nanoparticles, NaM-NP = Sodium montmorillonite nanoparticles, PoPD = Poly(o-phenylenediamine), ꝏ-PEDOT = Over-oxidized poly(3,4-ethylenedioxythiophene), SEP = Sepiolite clay, SMT = Sodium smectite, Au-NP = Gold nanoparticles, MIP = Molecular imprinted polymer, THF = Tetrahydrofuran

Notes: 1. The pencil lead was a Pentel AinSTEIN, 2. The pencil lead was a Kokuyo, 3. Cyclic voltammetry used the $[Fe(CN)_6]^{3-}$ anion as redox species, 4. Electrochemical impedance spectroscopy used a $[Fe(CN)_6]^{3-/4-}$ mixture as redox species.

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