Electronic Supporting Information

Concurrent analysis of six NSAIDs in human plasma using polyurethane/B–N–S- co- doped rGO nanofiber-modified glassy carbon electrode followed by EA-SPME

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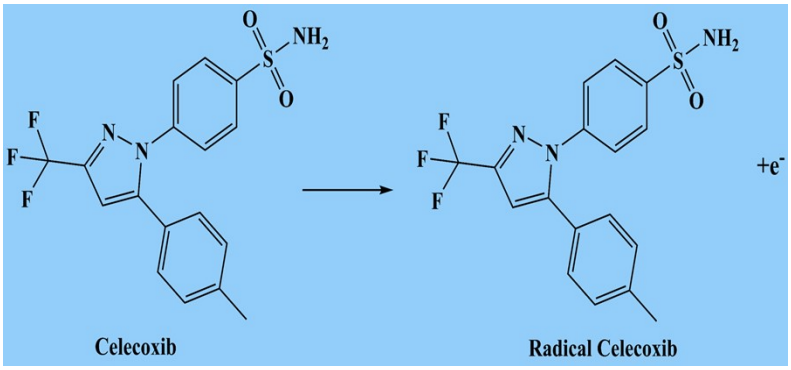
2. Experimental

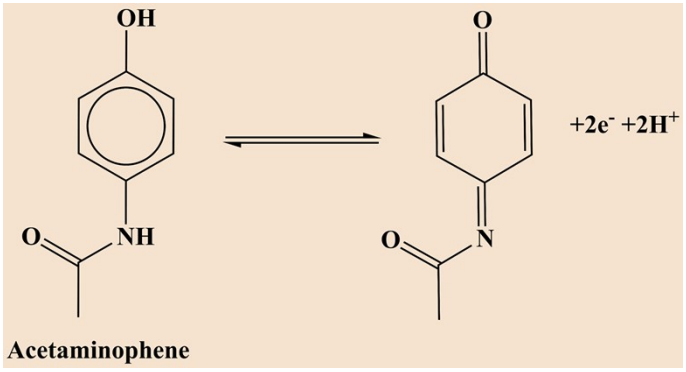
2.1. Materials and chemicals

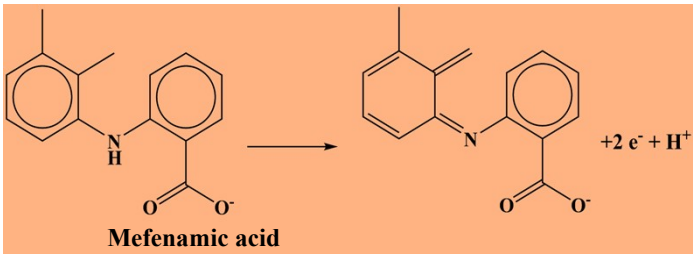
Acetaminophen (AC), naproxen (NAP), celecoxib (CEL), and ibuprofen (IBU) were purchased from Razak Pharmacology (Tehran, Iran). Caffeine (CAF) and mefenamic acid (MEA) were obtained from Alhavi Pharmacology (Tehran, Iran). Sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl), potassium chloride (KCl), monopotassium di hydrogen phosphate (KH_2PO_4), di sodium hydrogen phosphate (Na_2HPO_4), sulfuric acid (H_2SO_4), boric acid (H_3BO_3), thiourea (CH_4N_2S), graphite, and ethanol were procured from Merck (Darmstadt, Germany). Water-based aliphatic polyurethane dispersion based on polyether (PUD-3000) and self-networking acrylic emulsion (NA-68) as a primer were obtained from Simab resin (Tehran, Iran).

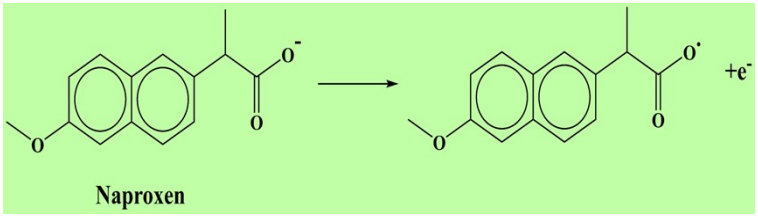
2.2. Apparatus

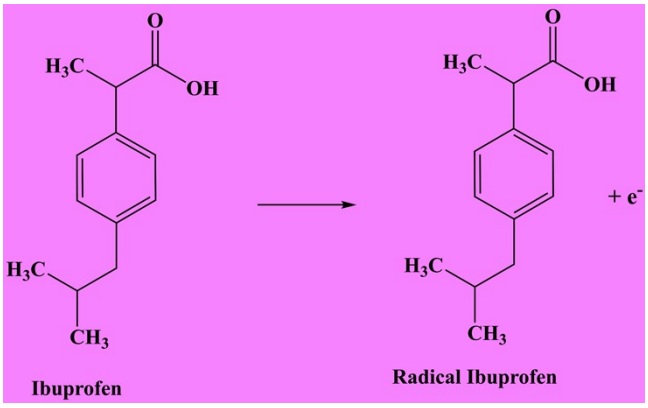
A syringe pump model SP1000HPM (Fanavaran Nano Meghyas, Tehran, Iran) and a high-voltage power supply model HV50P OV (Fanavaran Nano Meghyas, Tehran, Iran) were used to prepare the electrospun nanofibers. The solutions were stirred and heated by a (Heidolph company, Schwabach, Germany) heater-magnetic stirrer. The pH of the solutions was adjusted by a pH meter (Clean company, Model: pH500, Shanghai, China). Electrochemical tests were accomplished by SAMA 500 (from SAMA, Isfahan, Iran). A three-electrode system was applied for the electrochemical tests. A power supply (Padideh Nojen Pars, Model: PNP-1000D, Mashhad, Iran) was used for the electrochemical synthesis of GO from a pure graphite rod. A glassy carbon electrode (from Azar electrode, Urmia, Iran) to collect the electrospun nanofibers on its surface as a modified working electrode, a platinum (Pt) wire electrode as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode were used in this system. A Pt wire electrode (from Azar Electrode, Urmia, Iran) and SCE (from Sentek, England) were used here. Field emission-scanning electron microscopy (FE-SEM) (Zeiss Sigma VP, Model MIRA 3-TESCAN-XMU, Germany) at an accelerating voltage of 20 kV was used for surface morphological characterization of electrospun nanofibers and B-N-S-rGO. The total power dissipation of the PP201 was 200 W. The phase structure of the electrospun nanofibers and B-N-S-rGO was specified with an X-ray diffractometer (Company: STOE-STADV, Darmstadt, Germany). An attenuated total reflection (ATR)-Fourier transforms infrared (FTIR) spectrometer (from THERMO NICOLET, Mundelein, USA) was used to investigate the molecular vibration in electrospun nanofibers and B-N-S-rGO. An oven (from BINDER GmbH, Tuttlingen, Germany) was also used for drying GO powder.











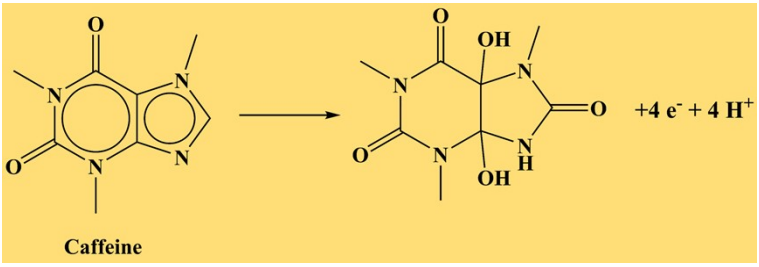


Fig S.1. Chemical structure and electrochemical reaction of six NSAIDs in this study.

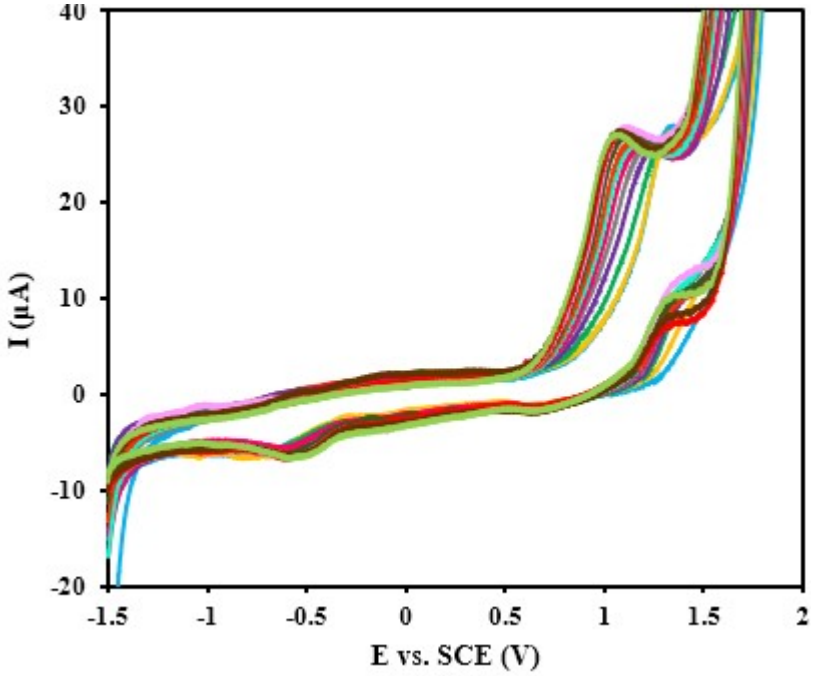


Fig S.2. Cyclic voltammograms of electrochemical reduction of B-N-S-GO to B-N-S-rGO in PBS (pH=7.0) at CPE surface.

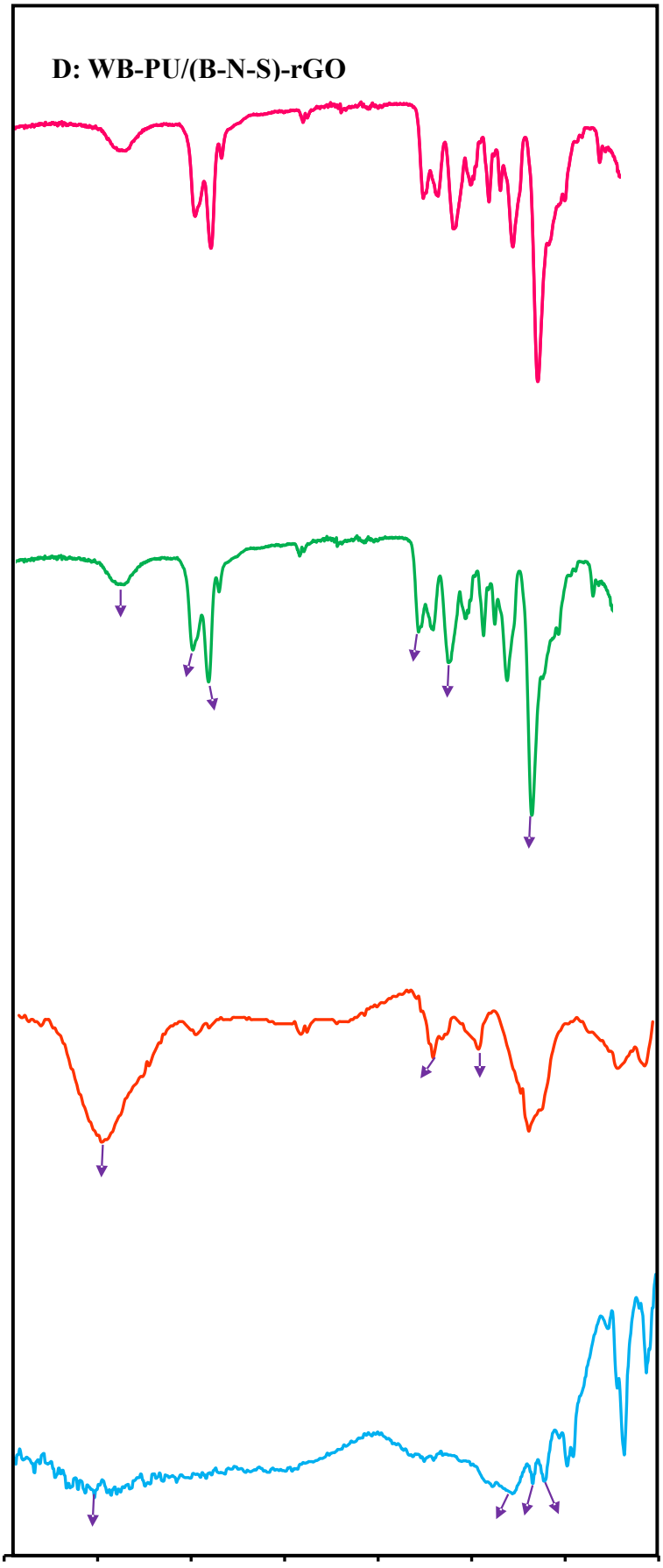


Fig S.3. ATR-FTIR spectrum of A: B-N-S-GO, B: B-N-S-rGO, C: WB-PU and D: WB-PU/(B-N-S-)-rGO.

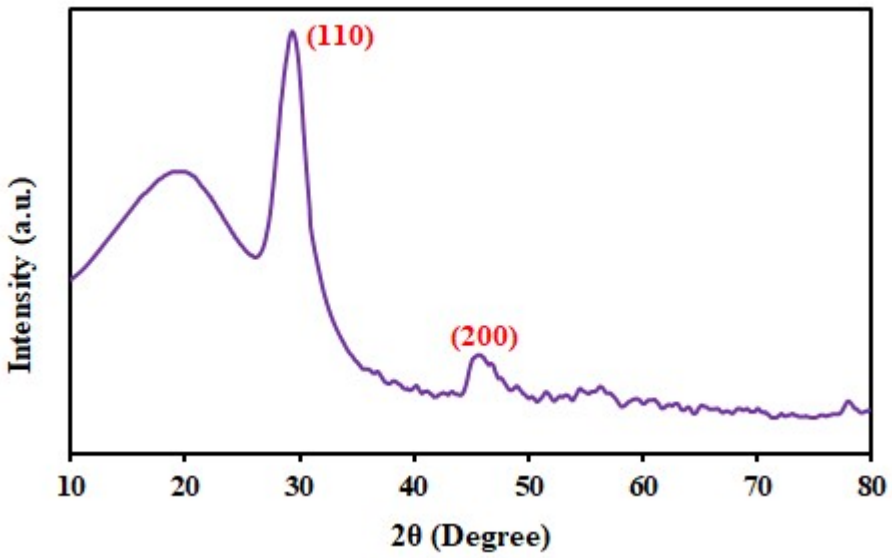


Fig S.4. XRD pattern of WB-PU-(B-N-S-)-rGO electrospun nanofibers.

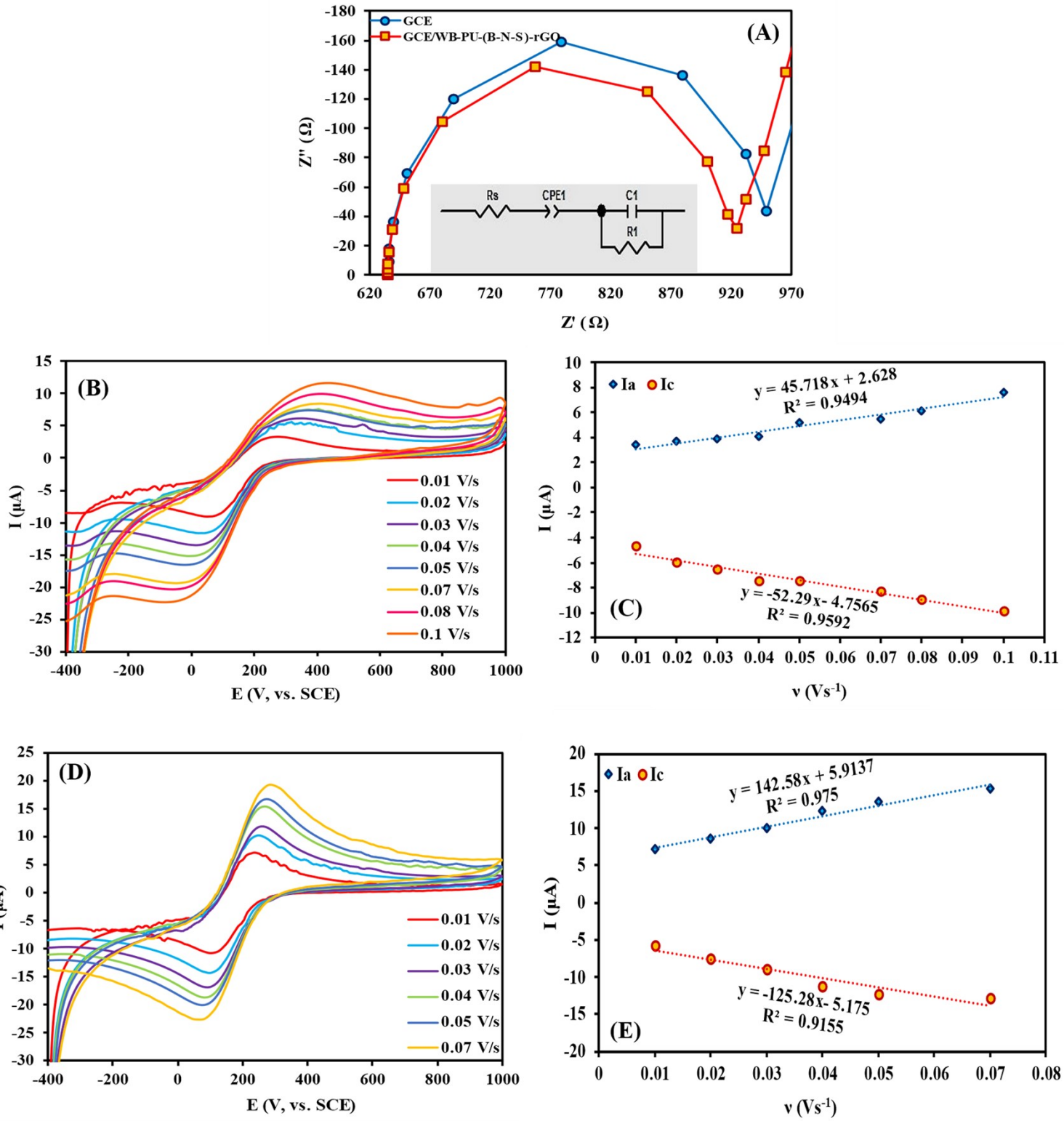


Fig S.5. (A): Nyquist plot of GCE and GCE/WB-PU-(B-N-S) rGO, (B): CVs of ($K_3[Fe(CN)_6]^{-3/-4}$) on the GCE surface at various scan rate, (C): The I-ν plots for Ia and Ic for GCE surface, (D): CVs of ($K_3[Fe(CN)_6]^{-3/-4}$) on the GCE/WB-PU-(B-N-S) rGO surface at various scan rate, E: The I-ν plots for Ia and Ic for GCE/WB-PU-(B-N-S) rGO surface.

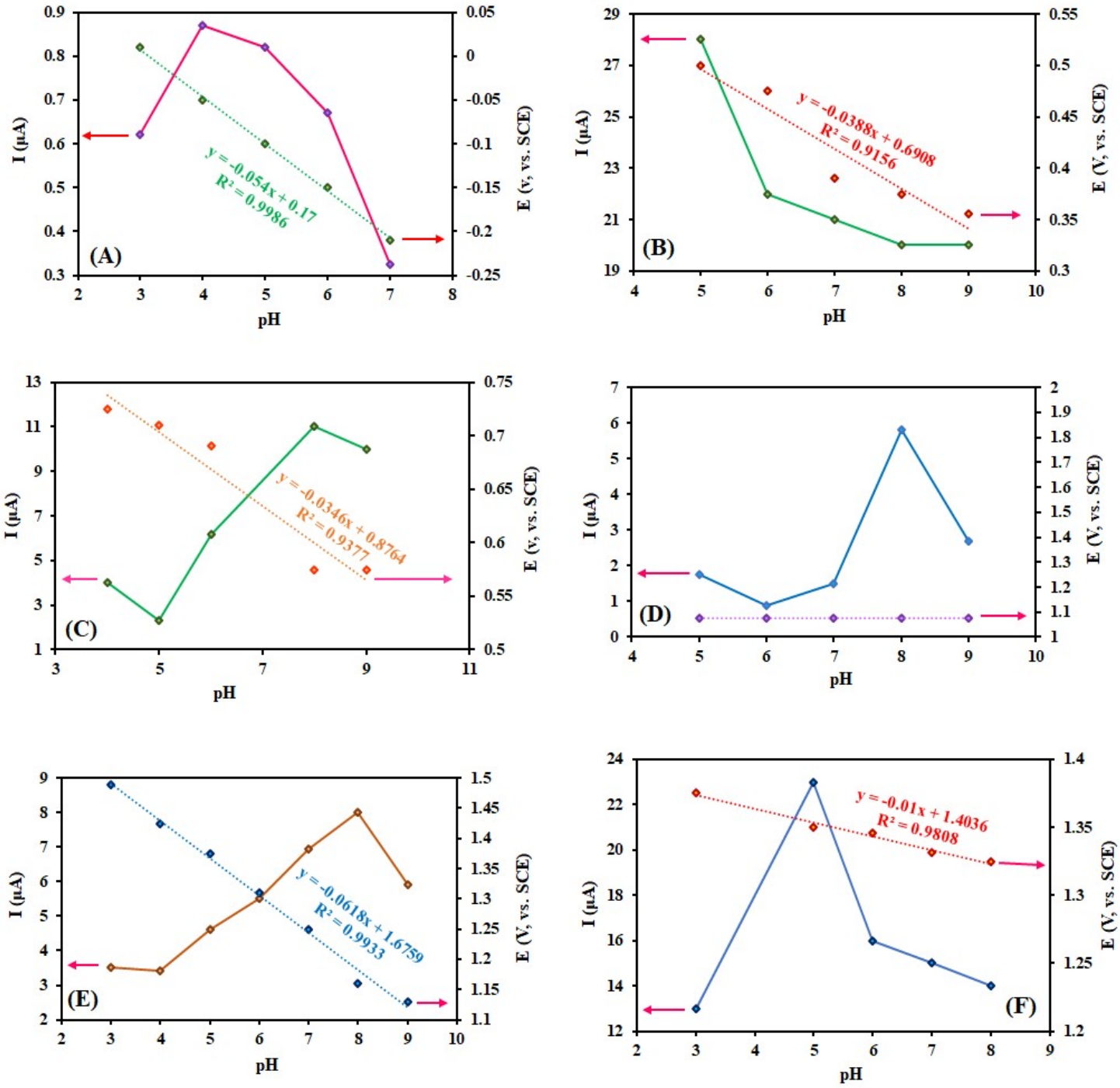


Fig S.6. potential vs. pH and current vs. pH plots of A: CEL (2500 µM), B: AC (5000 µ M), C: MEA (2500 µM), D: NAP (5000 µM), E: IBU (5000 µM) and F: CAF (5000 µM) in PBS at scan rate 0.3 V.s^{-1} (pulse height: 0.025, pulse width: 0.041, H step: 0.025 and T step: 0.083).

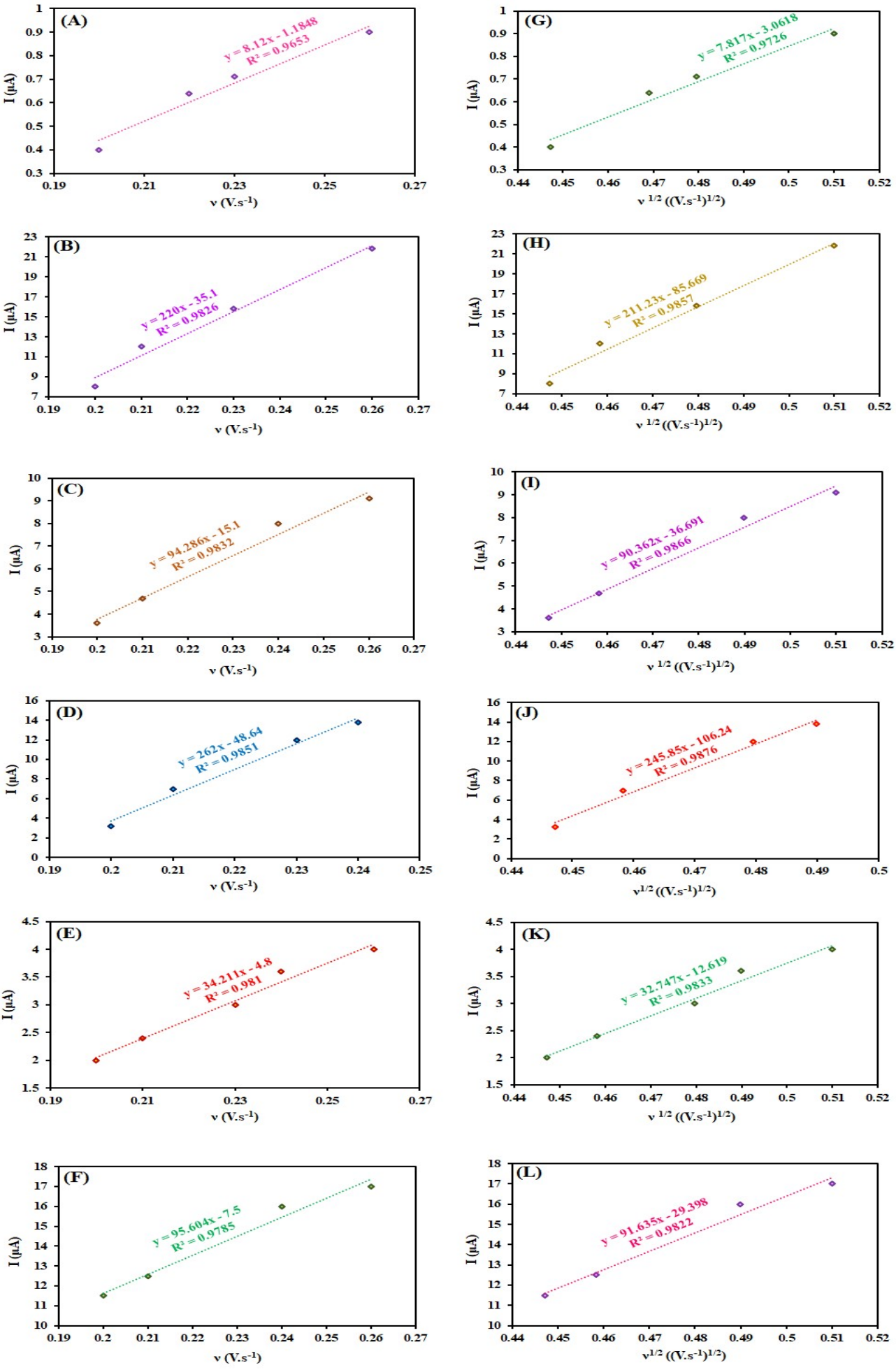


Fig S.7. current vs. scan rate, (A-F), and current vs. (scan rate)$^{1/2}$, (G-L), plots of A, G: CEL (2500 µM), B, H: AC (5000 µ M), C, I: MEA (2500 µM), D, J: NAP (5000 µM), E, K: IBU (5000 µM) and F, L: CAF (5000 µM) in PBS (pH=7).

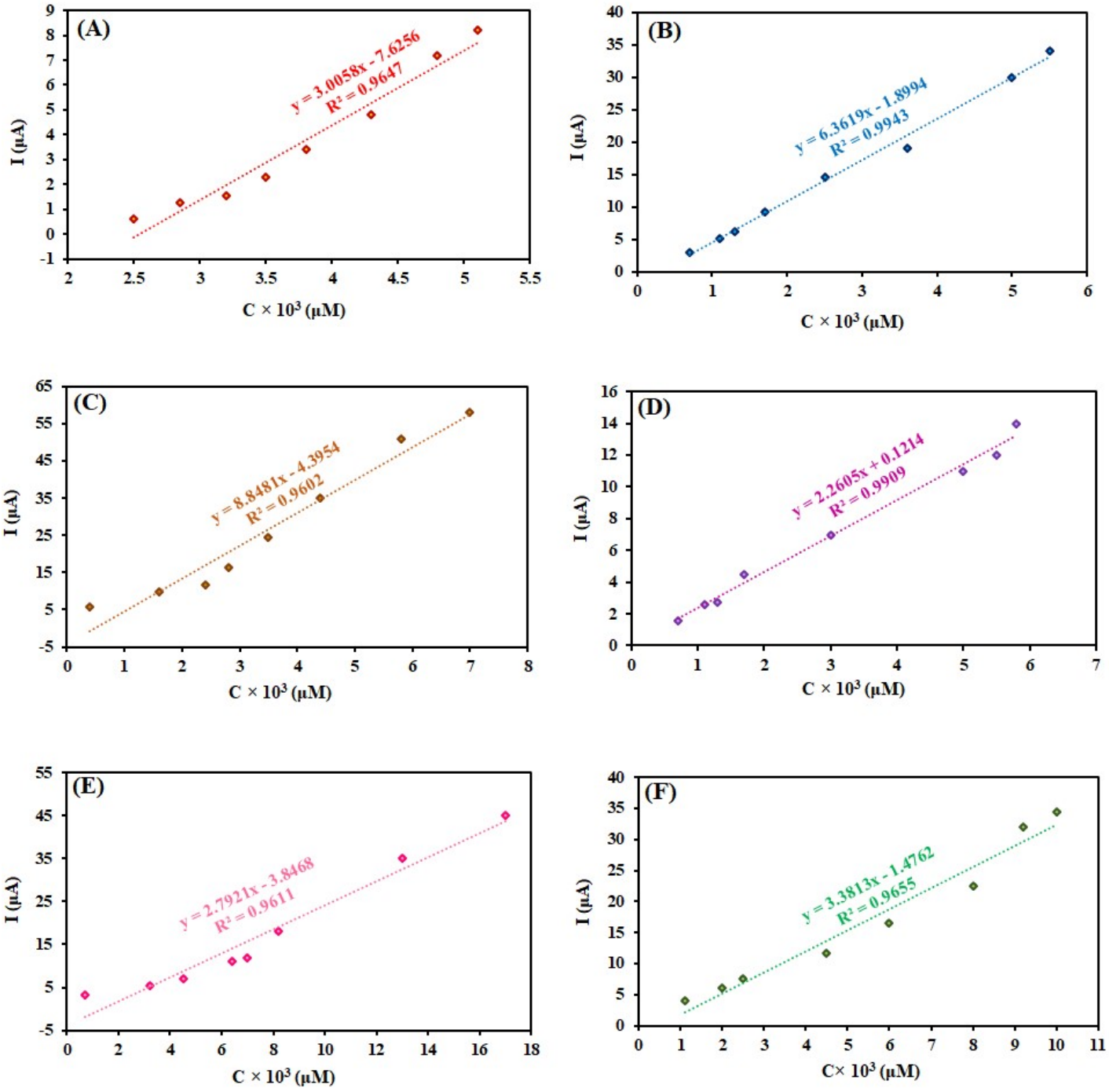


Fig S.8. The current vs. concentration plots of A: CEL, B: AC, C: MEA, D: NAP, E: IBU and F: CAF in PBS (pH=7) at scan rate 0.3 V.s^{-1} (pulse height: 0.025, pulse width: 0.041, H step: 0.025 and T step: 0.083).

Table S. 1. Results of the EIS and CVs of various electrodes in the ($K_3[Fe(CN)_6]^{-3/-4}$) solution.

Electrode	R_{ct}	Slope (I-v)	n	$D_{solution}$ ($cm^2\ s^{-1}$)	A (cm^2)
GCE	320.0	45.7	1	1.7×10^{-6}	20.0
GCE/WB-PU-(B-N-S)-rGO	287.8	142.6	1	1.7×10^{-6}	62.4

Table S. 2. The repeatability investigation of electrochemical biosensor (GCE/WB-PU-(B-N-S)-rGO electrospun nanofibers) in order to simultaneous determination of CEL (3800 µM), AC (2500 µM), MEA (3500 µM), NAP (3000 µM), IBU (7000 µM) and CAF (6000 µM) in PBS solution (pH=7) at scan rate 0.3 V.s-1 (pulse height: 0.025, pulse width: 0.041, H step: 0.025 and T step: 0.083).

Repeatability								
Time No.		2	4	6	8	10	*Accūracy*	%E
Current (µA)	CEL	3.39	3.25	3.17	3.12	3.07	94.11	5.89
	AC	14.48	14.44	14.36	14.29	14.20	95.7	4.30
	MEA	24.49	24.48	24.35	24.24	24.11	95.11	4.89
	NAP	6.95	6.91	6.82	6.75	6.57	94.12	5.88
	IBU	11.97	11.86	11.78	11.62	11.50	92.53	7.47
	CAF	16.46	16.39	16.28	16.15	16.03	93.0	7.0

Table S. 3. The stability investigation of electrochemical biosensor (GCE/WB-PU-(B-N-S)-rGO electrospun nanofibers) in order to simultaneous determination of CEL (3800 µM), AC (2500 µM), MEA (3500 µM), NAP (3000 µM), IBU (7000 µM) and CAF (6000 µM) in PBS solution (pH=7) at scan rate 0.3 V.s-1 (pulse height: 0.025, pulse width: 0.041, H step: 0.025 and T step: 0.083).

Stability							
Time (min)		30	50	70	90	100	RSD (%)
Current (µA)	CEL	3.37	3.31	3.20	3.09	3.01	4.67
	AC	14.45	14.38	14.30	14.22	14.10	0.96
	MEA	24.47	24.37	24.26	24.13	24.06	0.69
	NAP	6.91	6.81	6.63	6.39	6.17	4.61
	IBU	11.93	11.79	11.54	11.31	11.09	2.97
	CAF	16.42	16.32	16.15	16.09	15.97	1.11