Electronic Supplementary Material (ESI) for RSC Advances.

Electrochemical stripping voltametrical sensor based on polypyrrole exfoliated polyetheramine-montmorillonite nanocomposite for nanomolar detection of nifuroxazide

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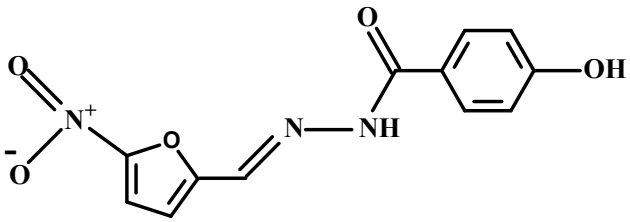
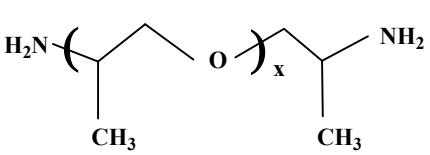
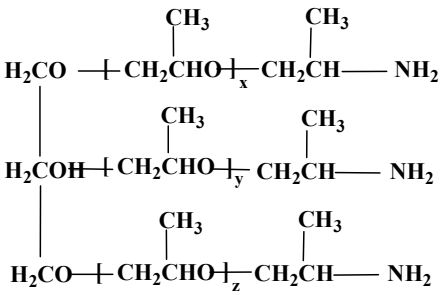


Scheme. S$_1$. Structure of nifuroxazide (NF).





D$_{400}$: x ≈ 6.1 &D$_{2000}$: x ≈ 33

T$_{403}$: x+y+z = 5.3 &T$_{5000}$: x+y+z = 81

Scheme. S$_2$. Structure of Polyoxyalkylene amine $D_{400,}$ $D_{2000,}$ T_{403} andT_{5000}.

2. Experimental

2.1. Materials, equipment, electrochemical liquids, and fabrication of unmodified and modified CPSs

All reagents were in pure form and used as purchased. Pyrrole monomer (Py, reagent grade, 98%), and Iron (III) chloride ($FeCl_3$, reagent grade, 97%) were obtained from Sigma-Aldrich company. Na-Montmorillonite (Na-MMT) was acquired from southern clay products (colloid BP), Inc (Gonzales, Texas, USA) with (114.8 meq/100g) cation exchange capacity. The Na-Montmorillonite clay was dried in a vacuum oven at 100°C for 24 h, yielding the interlayer spacing (d_{001}) was 9.6 Å. Four kinds of polyoxypropylene diamine and triamine (Jeffamine) were ordered from (Huntsman Corporation, TX, USA) including Jeffamine D_{400}, D_{2000}, $T_{403,}$ and T_{5000} with an average molecular mass of 430, 2000, 440, 5000 and the primary amine contents (PACs) are 4.3, 0.97, 6.1, and 0.52 meq/ g, respectively. The commercial capsules of NF (*Antinal* ®200 mg, and Drotazide ® 200 mg), and ultra-pure active powder were ordered from Amoun Pharmaceutical Co., El-Obour City, Egypt.

A Perkin Elmer spectrophotometer and a Phillips Powder-Diffractometer equipped with a Ni-filtered Cu-K_α (λ=1.5418 Å) were used to obtain Fourier transform infrared (FT-IR) spectra and Wide-angle X-ray diffraction (WAXD) patterns of prepared samples, respectively. JEOL JSM 5400 Scanning electron microscopy and a JEOL JEM-100CX electron microscope were used to investigate the morphological structure of MMT and the prepared nanocomposites. In addition, the ultra-thin films of nanocomposites were fabricated for transmission electron microscopy (TEM) analysis by cutting capsules of samples using an ultra-microtome, LKB 8800 ultra-microtome III equipped with a glass knife. The conductivity of MMT and prepared nanocomposites were measured via two probe system of direct current circuit (DC circuit). PC-controlled potentiostat (PAR) Model 273 A and PAR-394 (Princeton Applied Research, Oak Ridge, TN, USA) with the software 270/250-PAR were utilized for the analytical voltammetry measurements.

NF stock (10^{-3}M) and diluted (1.0 to 1000 nM) solutions were prepared in methanol. Urine samples of 3 healthy volunteers were added to a micro-electrolysis cell containing a B-R buffer of pH 5.0 (9: 1, buffer: urine). Britton–Robinson (B–R) universal buffer series (pH

2-11) were prepared by mixing various proportions of boric, phosphoric, and acetic (0.04 M acids) with the NaOH (0.2 M).

5.0 g of carbon powder (CP) was pasted with 1.8 mL of paraffin oil for 1 h to acquire bare carbon paste **[B]** CP. Whereas, 1.0 % **[Ppy / (D_{2000}, D_{400}, T_{5000}, and T_{403})-MMT-50]** nanocomposites modulated CP sensors (**MCPSs**) were constructed by blending 4.95 g of graphite powder, and 0.05 g of modulation material with 1.8 mL paraffin oil to acquire a uniform MCP. The same method was carried out by changing the weight percent of the nanocomposite at the range of 0.5% - 3.0% of **[PDM-50]**. The **[B]** CP, and fabricated MCPSs were inserted into the cavity of the sensor (Inner diameter (ID): 3mm), the superficial of the sensor was smoothed until glossy.

Table. S_1. Composition data of Ppy/ polyetheramine - MMT nanocomposites.

Code	***Polyetheramine-montmorillonite***			**Ppy/ *polyetheramine - MMT***
				Wt %
	Type	***Wt / g***	***Wt %***	
[PDM-10]	D_{2000}-MMT	0.1	10	93.23
[PDM-20]	D_{2000}-MMT	0.2	20	90.22
[PDM-50]	D_{2000}-MMT	0.5	50	66.22
[PD_1M-10]	D_{400}-MMT	0.1	10	88.90
[PD_1M -20]	D_{400}-MMT	0.2	20	85.84
[PD_1M-50]	D_{400}-MMT	0.5	50	83.08
[PTM-10]	T_{5000}-MMT	0.1	10	90.20
[PTM-20]	T_{5000}-MMT	0.2	20	95.94
[PTM-50]	T_{5000}-MMT	0.5	50	76.97
[PT_1M-10]	T_{403}-MMT	0.1	10	92.74
[PT_1M-20]	T_{403}-MMT	0.2	20	86.37
[PT_1M-50]	T_{403}-MMT	0.5	50	70.29

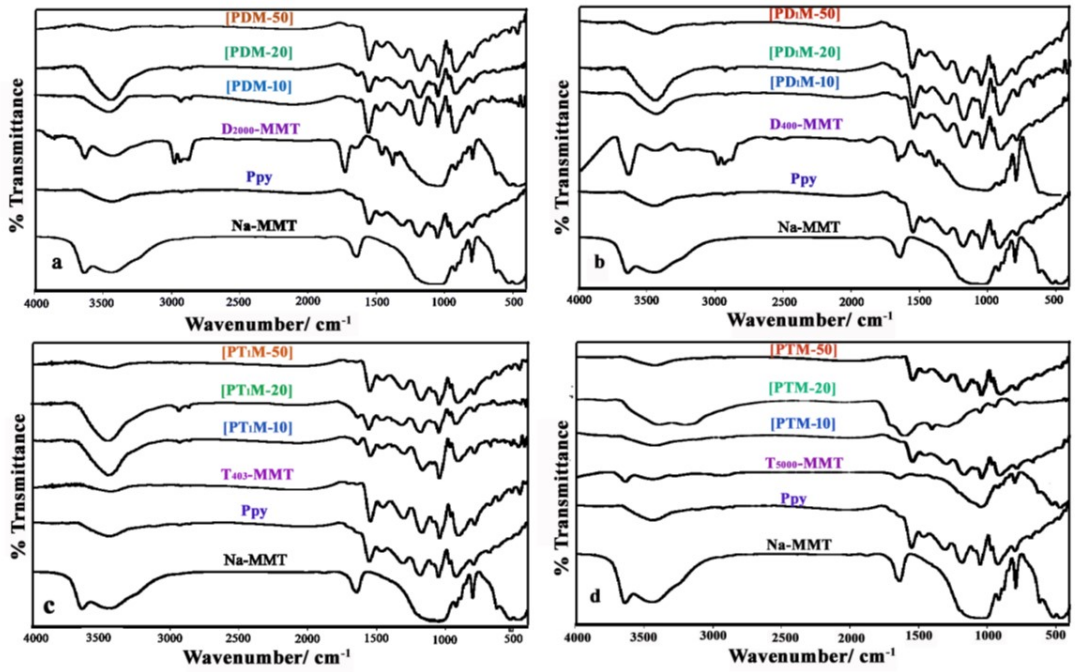


Fig.S1. FT-IR spectra of Na-MMT, Ppy, organoclay, and Ppy/ organoclay nanocomposites at different % of organoclay in the region 4000-400 cm^{-1}.

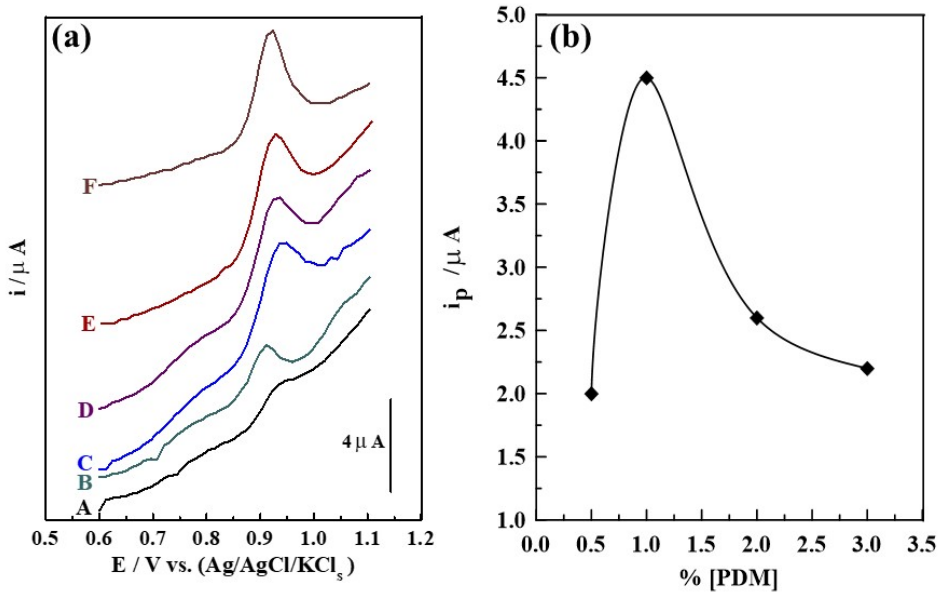


Fig.S$_2$. (a): SW-AdAS voltammograms of 30.0 nM *NF*inpH 5(B-R buffer) at E_{acc}=0.60 V for 10 s at **A) [B]** CPS, **B)** 7.0% **[Na-MMT**, **C)**1.0 % **[PT$_1$M-50]**, **D)**1.0 % **[PTM-50]**, **E)** 1.0 % **[PD$_1$M-50]**, and **F)** 1.0 % **[PDM-50]** MCPSs (f = 100 H$_z$, a = 25 mV and ΔE_s= 10 mV). **(b)** Plot of 30.0 nM *NF* in (pH 5) at E_{acc}=0.6 V for 10 s of different % of **[PDM-50]**.

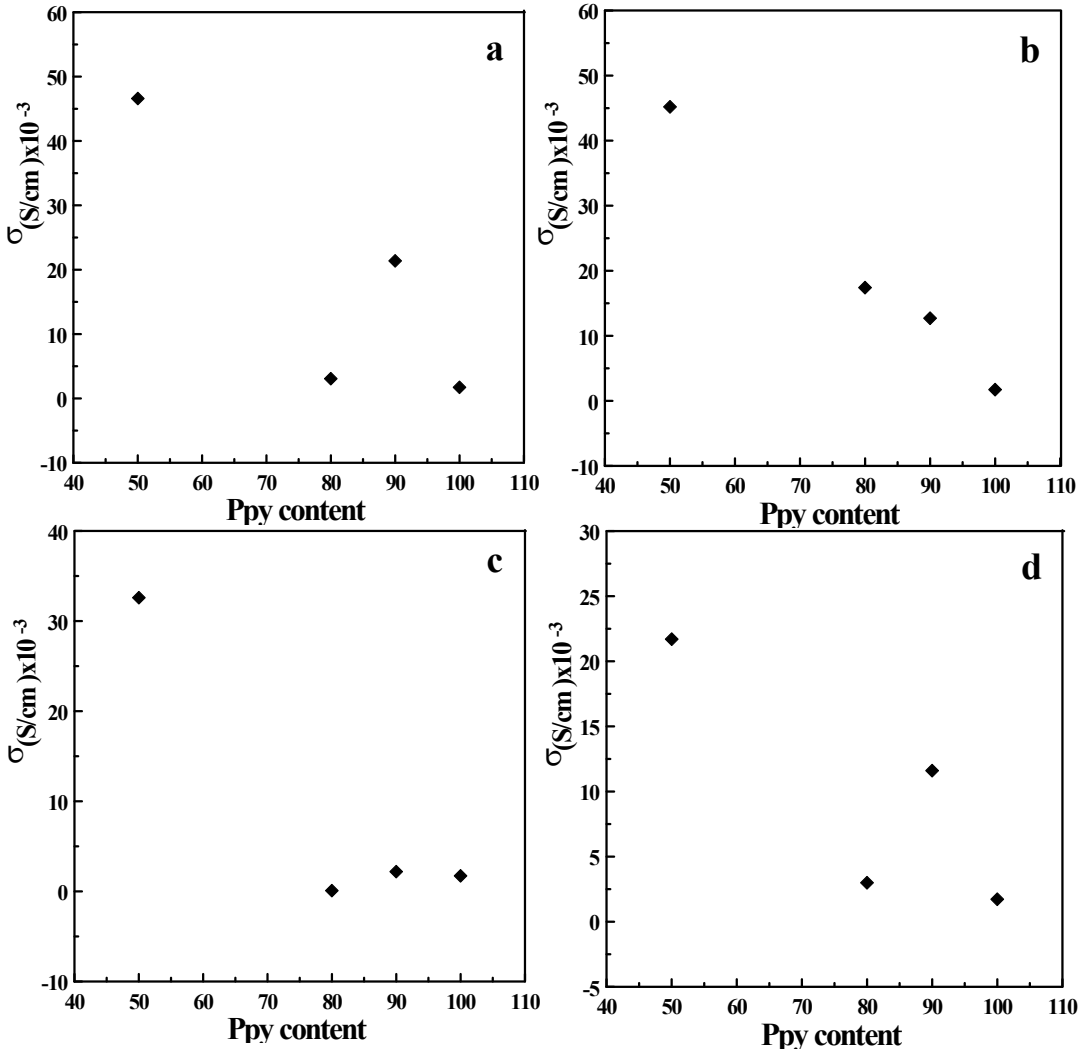


Fig.S$_3$. Conductivity plots of **(a) [PDM]**, **(b) [PTM]**, **(c) [PD$_1$M]**, and **(d) [PT$_1$M]**.

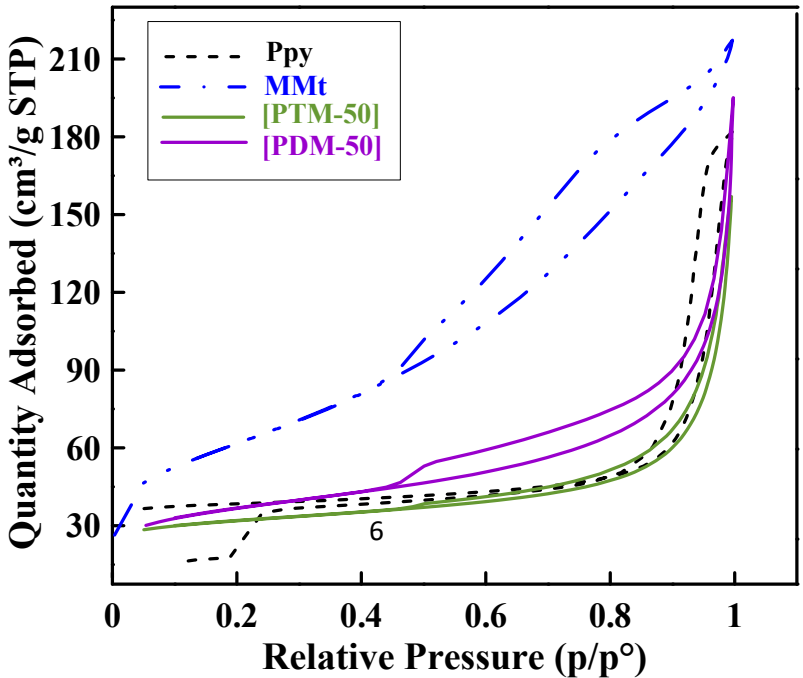


Fig.S4. N_2 adsorption-desorption isotherm of some of prepared materials

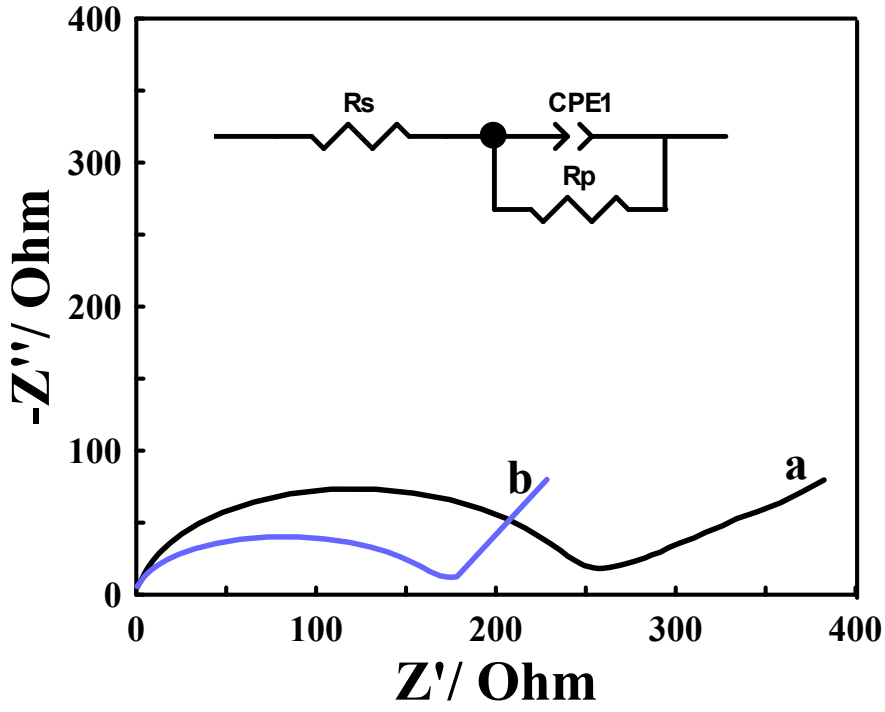


Fig.S5. EIS of **(a) [B]** CPS, and **(b)** 1.0% **[PDM-50]** MCPS.

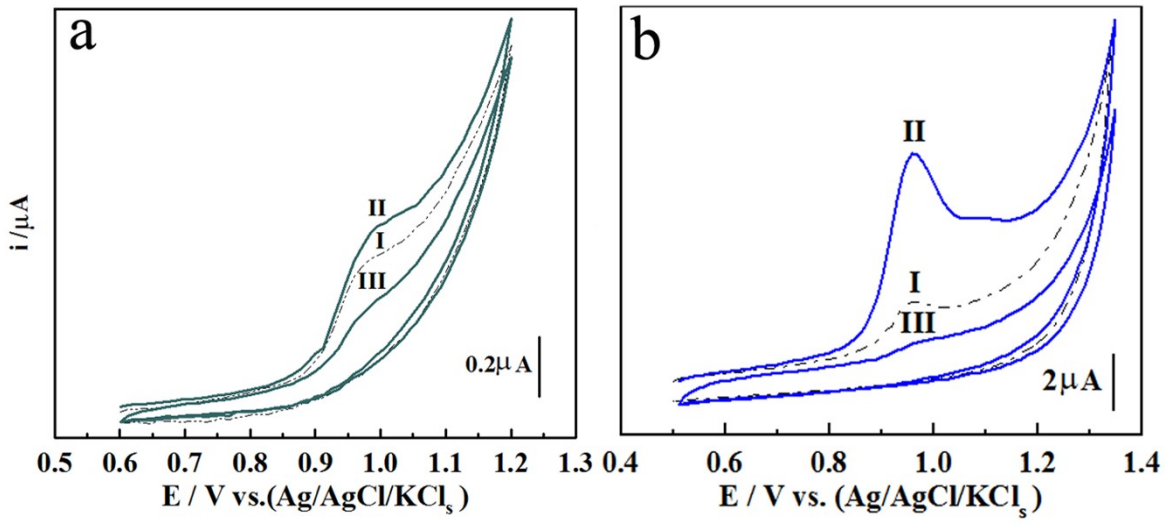


Fig. S6. CVs of 50.0 nM NF (pH 5) utilizing **[B]** CPS **(a),** and 1.0% **[Ppy/ D_{2000}-MMT 50]** MCPS**(b)** at 0.0s (Cycle (I)) for 10.0 s (Cycles; 1st (II) and 2nd (III)) at v=100 mV.s^{-1}.

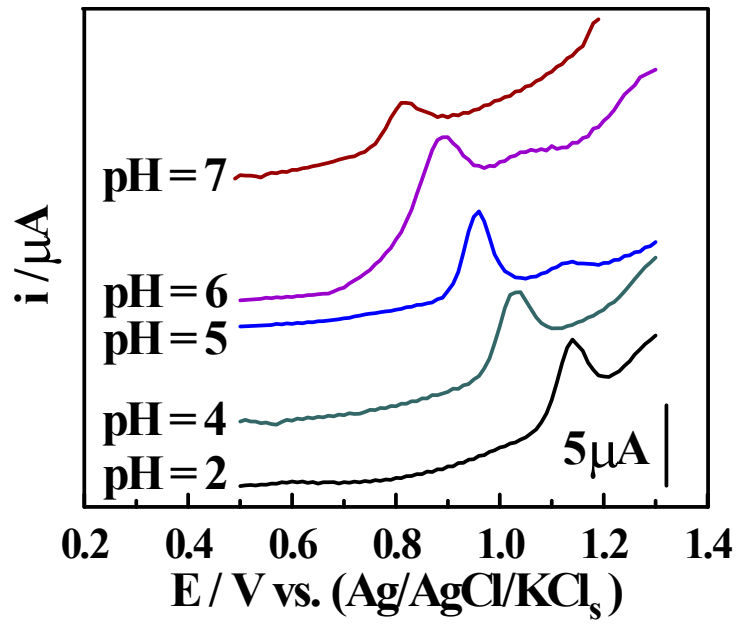


Fig. S7. The effect of using of 30.0 nM NF in series of the B-R buffer upon 1.0 % **[PDM-50]** MCPS ($\boldsymbol{f}$ = 120 Hz, $\boldsymbol{\Delta E_s}$ = 12 mV and, $\boldsymbol{a}$ = 30 mV).

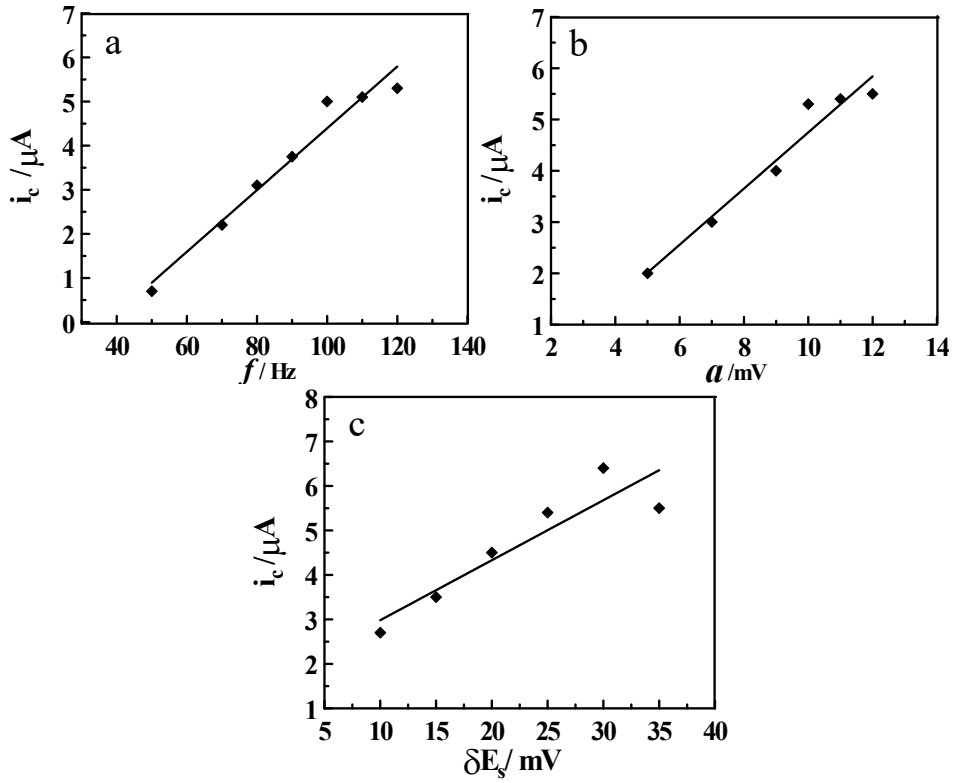


Fig. S8. Effect of pulse parameters of 30.0 nM NF in the B-R universal buffer pH 5 upon 1.0 % **[PDM-50]** MCPS at E_{acc} = 0.5 V for 20 s.

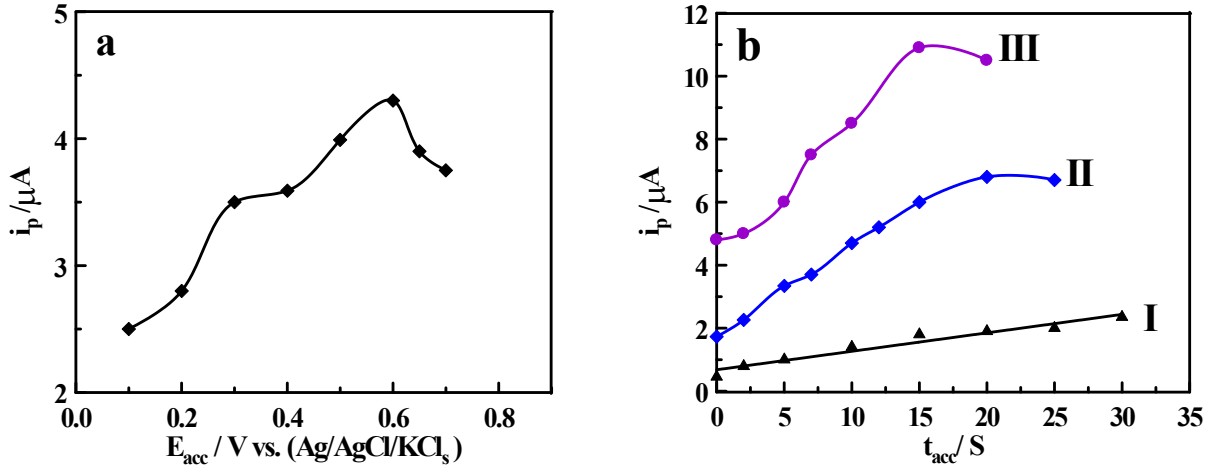


Fig. S9. (a) The effect of $\mathbf{E_{acc}}$ on SW-AdsASVs peaks of 0.1 μM NF in pH 5 upon 1.0 % **[PDM-50]** MCPSfor 20s ($\Delta\mathbf{E_s}$= 12 mV, ***f***= 120 H_z, and ***a***= 30 mV), and **(b)** The effect of the $\mathbf{t_{acc}}$ of (I) 0.01, (II) 0.05, and (III) 0.1μM at $\mathbf{E_{acc}}$= 0.6 V.

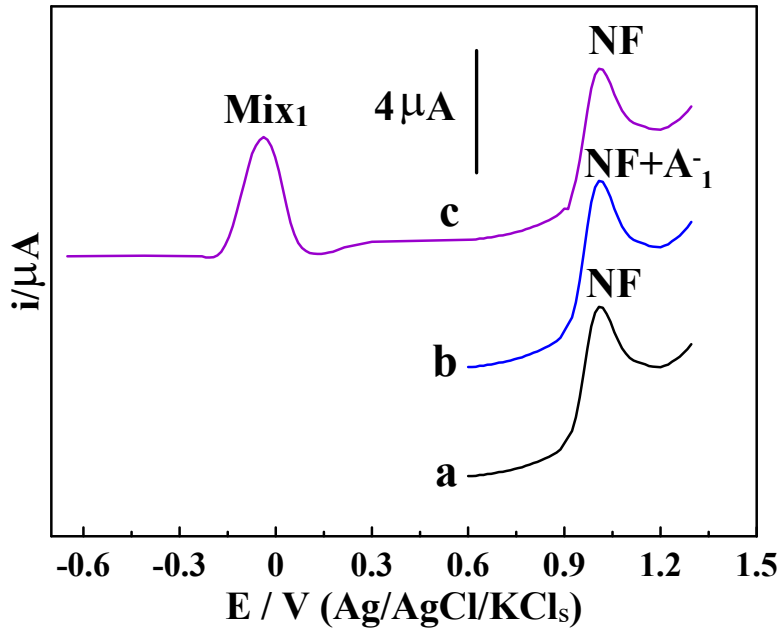


Fig. S_{10}. SW-AdAS voltammetry peaks of **(a)** 20.0 nM NF, **(b)** 20.0 nM NF mixed with 2.0 µM (~100-fold) of A^-_1, and (c) 20.0 nM NF mixed with 20.0 nM of **Mix_1**upon the upon the surface of 1.0 % **[PDM-50]** MCPS.

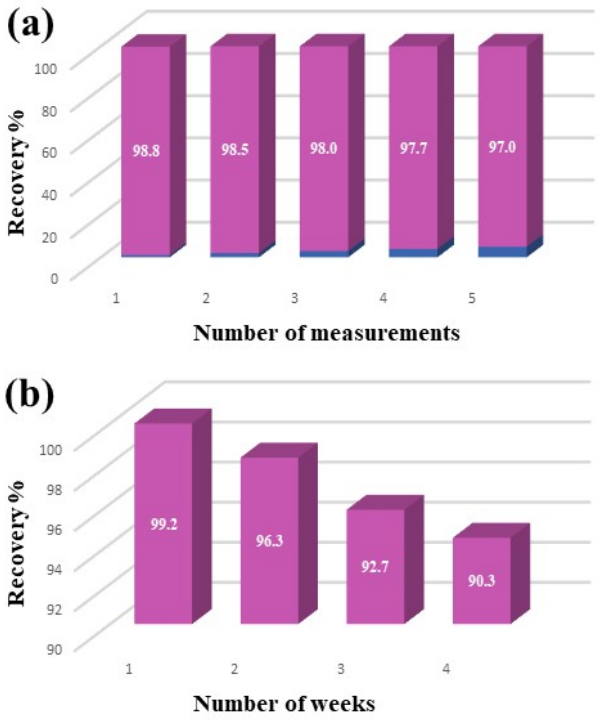


Fig. S_{11}. The reusability **(a)**, and stability**(b)** histogram plots of the 1.0 % **[PDM-50]** MCPS.