Electronic Supplementary Material (ESI) for Analytical Methods.

Synthesis and validation of ultrasensitive stripping voltammetric sensor based on polypyrrole@ZnO/Fe_3O_4 core-shell nanostructure for picomolar detection of artesunate and dopamine drugs

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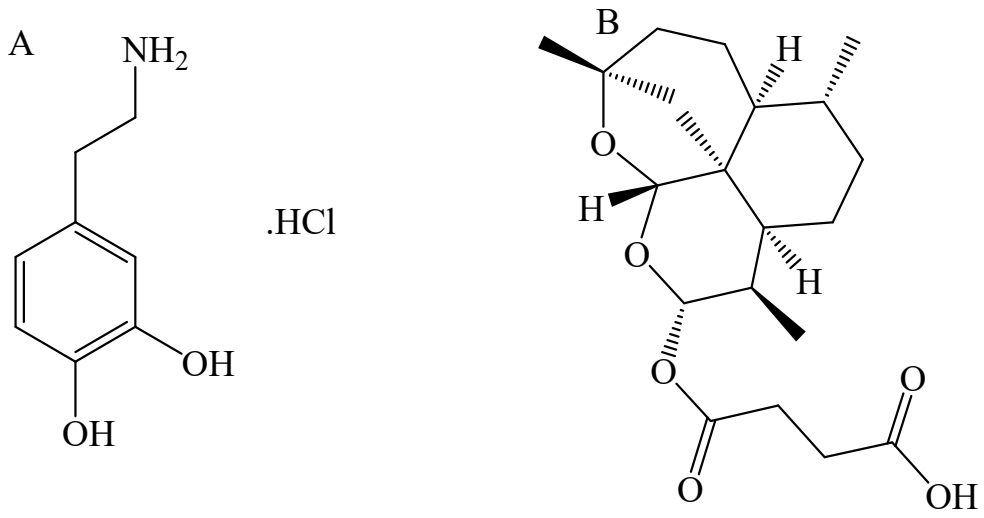


Scheme. S_1: (**A)** Structure of Dopamine (DA), and (**B)** Artesunate (ART)

2.1. Materials and instrumentation

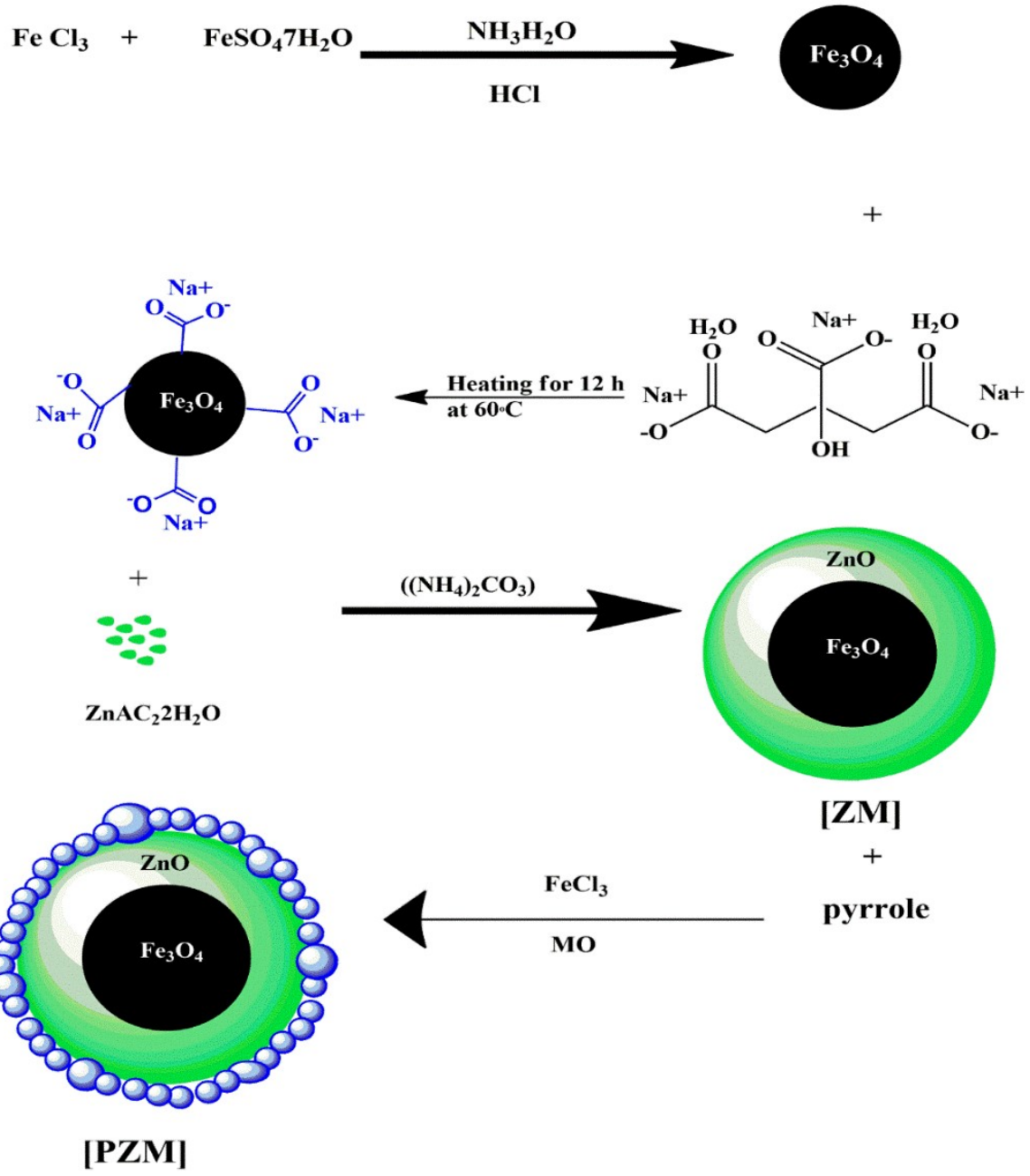
Pyrrole (Ppy, Mallinckrodt, USA, reagent grade, 98%) purified by passing through a column of alumina neutral, sodium citrate (Across, USA, ≥98.0%), acetic acid (HAc, Alfa Asear, AR, 99.7%), phosphoric acid (H_3PO_3, 99.0%), boric acid (H_3BO_3, 99.5%), ammonium carbonate $(NH4)_2CO_3$, and glacial acetic acid (CH_3COOH, 99.0%) were all purchased from Sigma Aldrich. Anhydrous ferric chloride ($FeCl_3$, Alpha Chemika, India Reagent grade, 97%), ferrous sulfate ($FeSO_4.7H_2O$, Oxford Lab Chem, India SISCO, 98%), methyl orange (MO, Pubchem), sodium

hydroxide (NaOH pellets, 98.0%) and hydrochloric acid (HCl, 35%) (Adwic, Egypt), zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, MERCK, Darmstadt), artesunate (ART; $C_{19}H_{28}O_8$, 384.421 g/mol, China), and dopamine HCl (DA, Sigma Aldrich) were purchased and used as received.

The nature of the interaction between functional groups of as-prepared materials in the wave-number range from 400–4000 cm^{-1} sing potassium bromide disc was determined using a Fourier transform infrared spectroscopy (FTIR) instrument (Shimadzu FTIR-8101 A). To characterize the crystalline nature of all as-prepared samples, an X-ray diffractometer (XRD, Philips PW 1710) equipped with Cu-Ka radiation (λ = 1.54060 Å), voltage (40 kV), and current (30 mA) was used with scanning speed of 0.02°/min and 2θ with a range from 2 to 80°. Magnetic hysteresis (M-H) curves of some of the as-prepared materials were measured in a magnetic field in the range of −8 and 8 KOe at room temperature. By adding drops of dispersed materials in a mixture of ethanol and DDW, a high-resolution transmission electron microscopy (HR-TEM) instrument (JEM2100 JEOL) is used to investigate the morphological structure and particle size of **[ZM]**, and **[PZM].** The surface morphology of **[ZM]**, and **[PZM]** was also investigated using scanning electron microscopy (SEM) (SU8000 2.0 kV 4.0 mm × 25.0 K SE (U) equipped with energy-dispersive X-ray spectroscopy (EDX) at an operating voltage of 10 kV. Dynamic light scattering was used to determine the size distribution of the nanoparticle (dynamic light scattering (DLS); Zetasizer Nano ZS; Malvern Instruments, Malvern, UK).

Electrochemical impedance of as-prepared samples was recorded using computer-controlled PAR (Princeton Applied Research, Oak Ridge, TN, USA) potentiostat models Versa STAT 4 using frequency range of 0.1 to 10000 Hz. Voltammetric measurements were performed using computer-controlled electrochemical analyzer models 263A and 394-PAR (Princeton Applied Research, Oak Ridge, TN, USA) with the software package 270/250-PAR. We used a sensor assembly (303A-

PAR) that included a micro-electrochemical cell and a three-sensor system that included a CP as the working sensor, Ag/AgCl/KCls as the reference electrode, and platinum wire as the auxiliary electrode was used. DP-AdCV scans with all as-prepared sensors were tested utilizing a conventional 10-mL volume electrolysis cell containing specific concentration of ART, and DA drug solution mixed with 5 mL of DDW, and then filled with 5 mL of supporting electrolyte (B–R buffer series) under selected preconcentration parameters. DP-AdCV scans were then evaluated after a standing a specific preconcentration time in the selected negative potential range. After each data point was estimated, five-time repetitions were measured in a fresh buffer solution, to refresh the surface of the sensor, under the same potential scan range. The pH drift method [1] has been used to evaluate the pH point of zero charge (pH_{ZPC}) of **[PZM]**. Briefly, different samples of 20 mL 0.01 M $NaNO_3$ solutions was adjusted (pH_i) in the range of 2.0–10 by adding 0.1 M HNO_3 or NaOH. Then, 0.06 g of **[PZM]** was inserted to each sample of $NaNO_3$ solution with continuous stirring for 48 h. The pH of the filtrate solution was recorded (pH_f). Then, the pH_{ZPC} of the **[PZM]** was evaluated from the plot of δpH ($pH_f - pH_i$) vs. pH_i.



Scheme. S_2: Synthesis of **[ZM],** and [**PZM].**

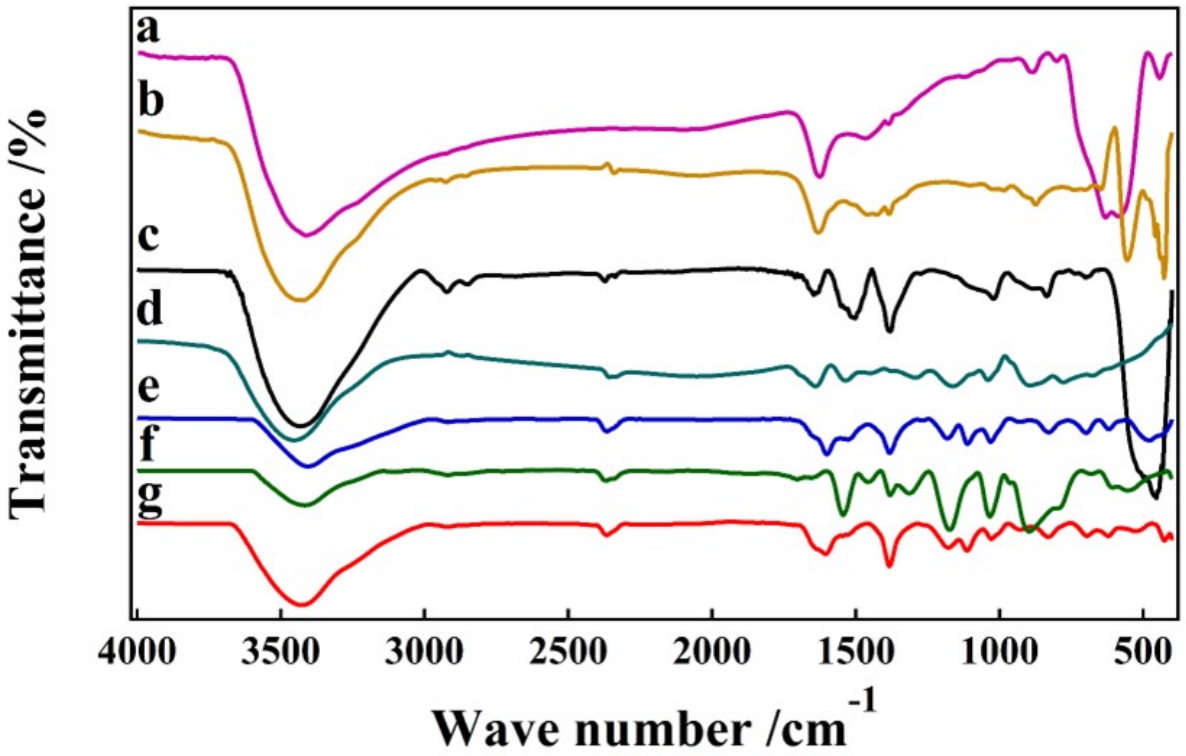


Figure. S_1: FTIR spectra of (a) Fe_3O_4 NPs**,** (b) ZnO NPs, (c) **[ZM]**, (d) Ppy, (e) **[PZ]**, (f) **[PM]**, and (g) **[PZM]**.

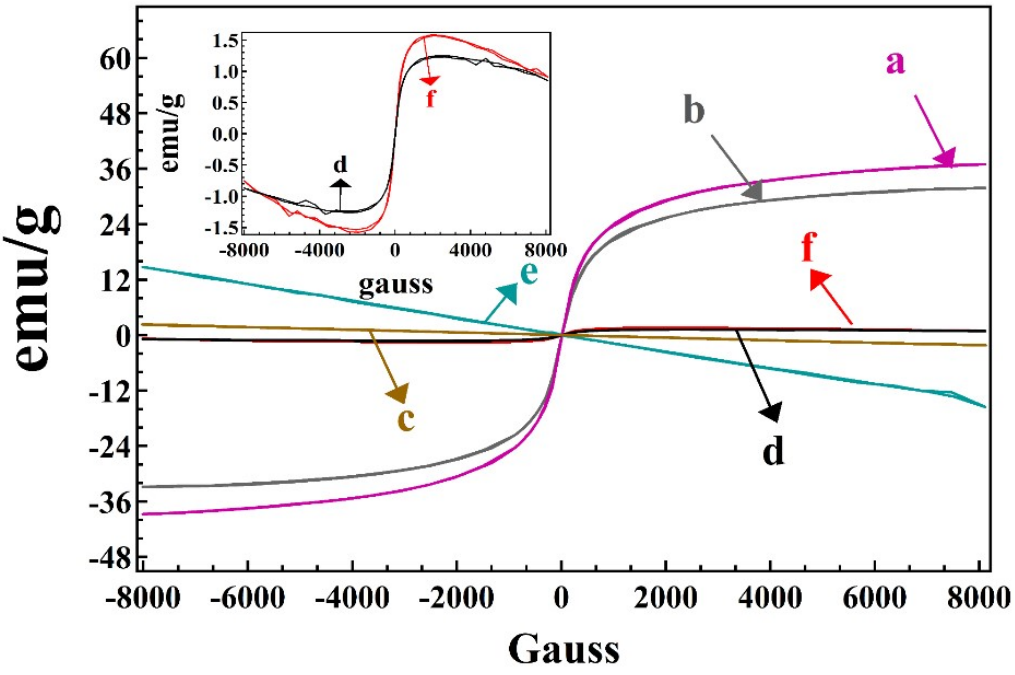


Figure. S_2: Magnetization vs. applied magnetic field at room temperature (a) ZnO NPs, (b) Fe_3O_4 NPs, (c) Cs@Fe_3O_4 NPs, (d) **[ZM]**, (e) Ppy, and (f) **[PZM]**.

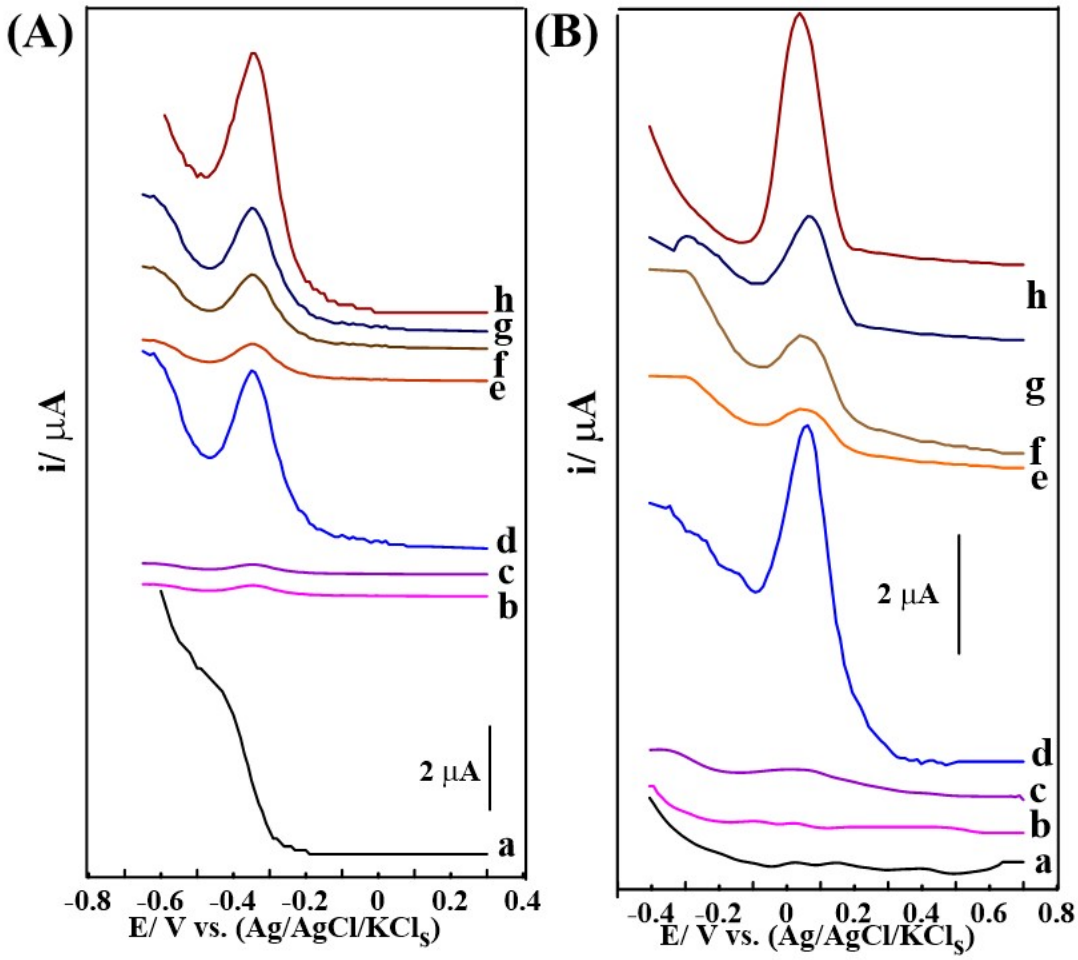


Figure. S_3: DP-AdCV crests of **(A)** 10.0 pM of ART in the BR buffer pH 10, and **(B)** 20.0 pM DA in the BR buffer pH 2for 70s using (a) BCPS, (b) ZnO NPs, (c) Sc@Fe_3O_4 NPs, (d) **[ZM]**, (e) Ppy, (f) **[PZ]**, (g) **[PM]**, and (h) **[PZM]** MCPSs (***v*** =120 mV, and ***a***= 45 mV).

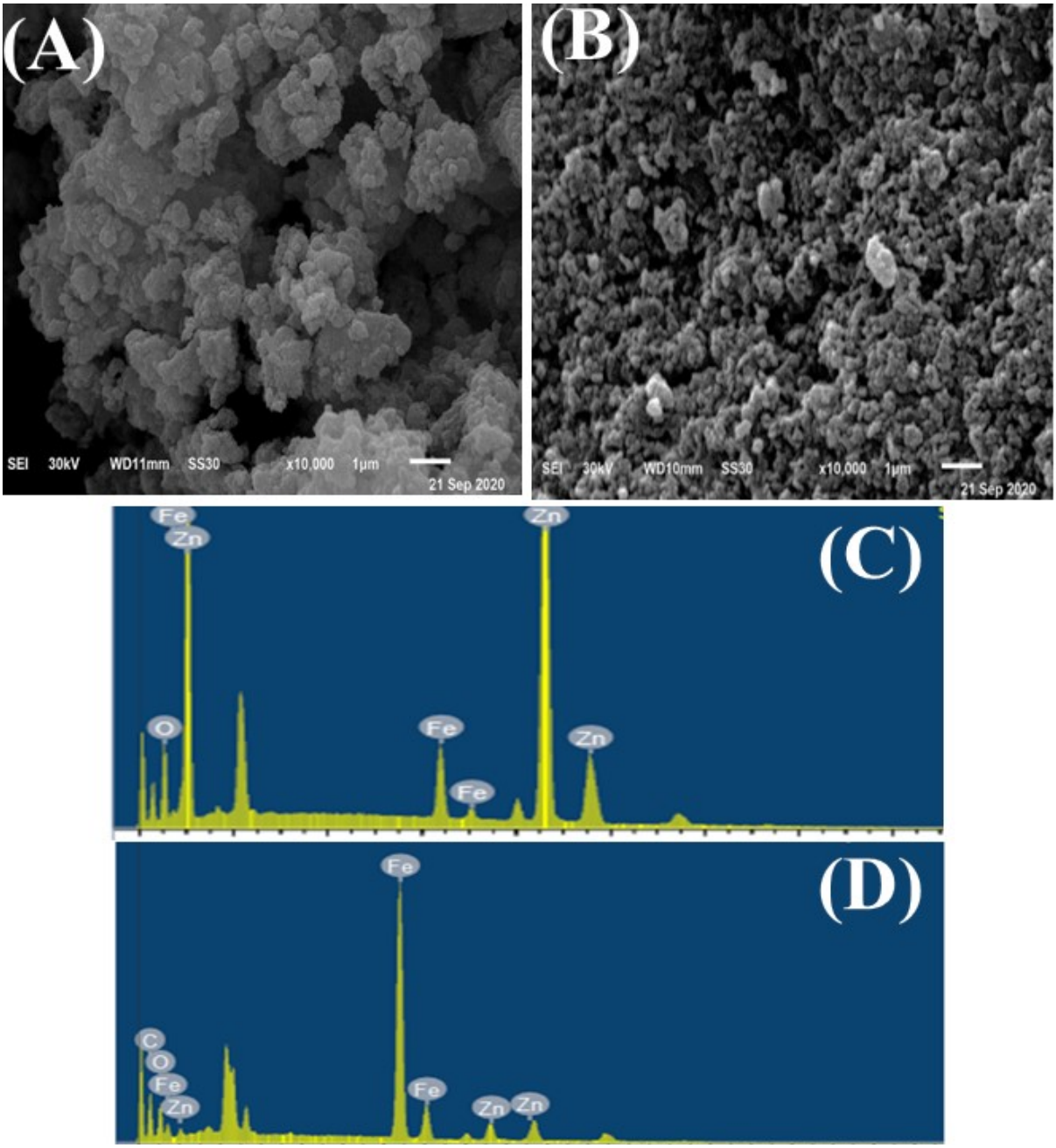


Figure. S_4: SEM images of **(A) [ZM],** and **(B) [PZM]**. The EDX analysis of **(C) [ZM],** and **(D) [PZM]**.

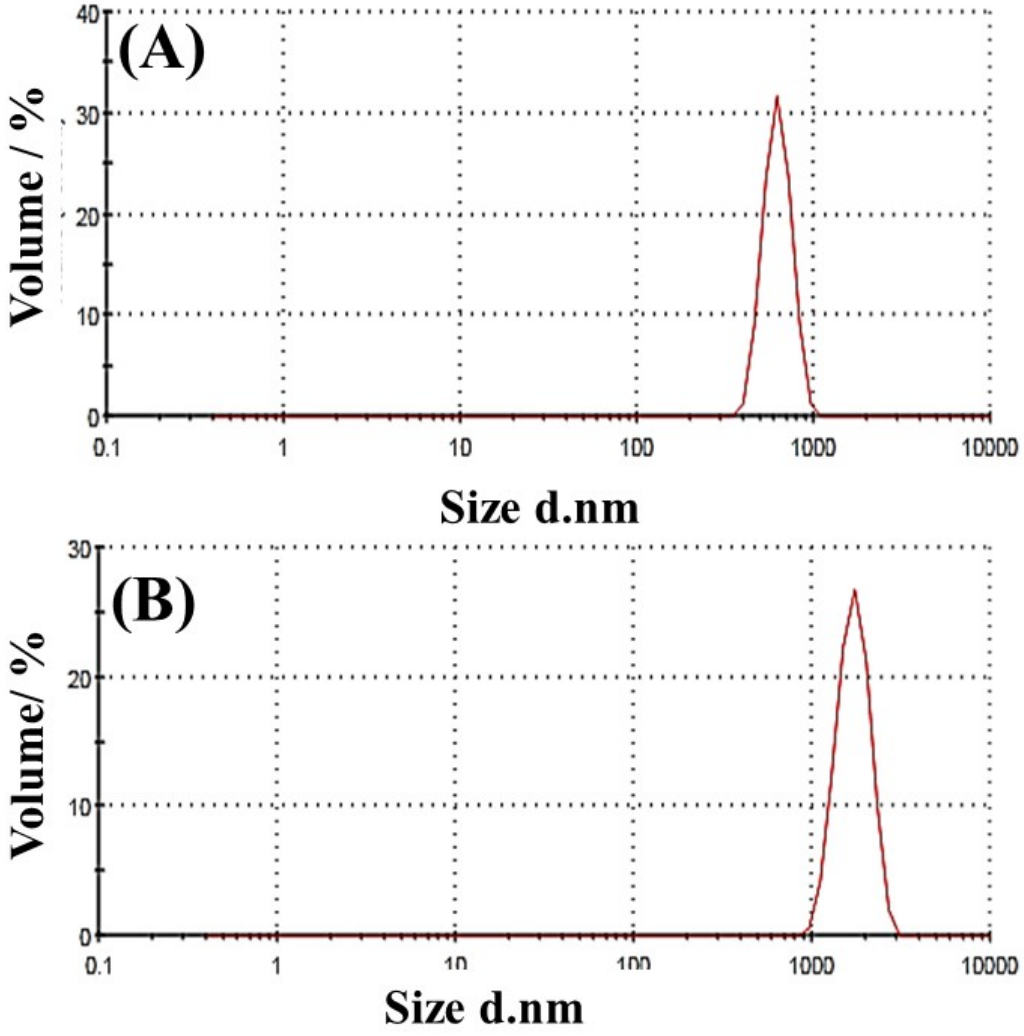


Figure. S_5: Dynamic light scattering (DLS) measurement of **(A) [ZM],** and **(B) [PZM]**.

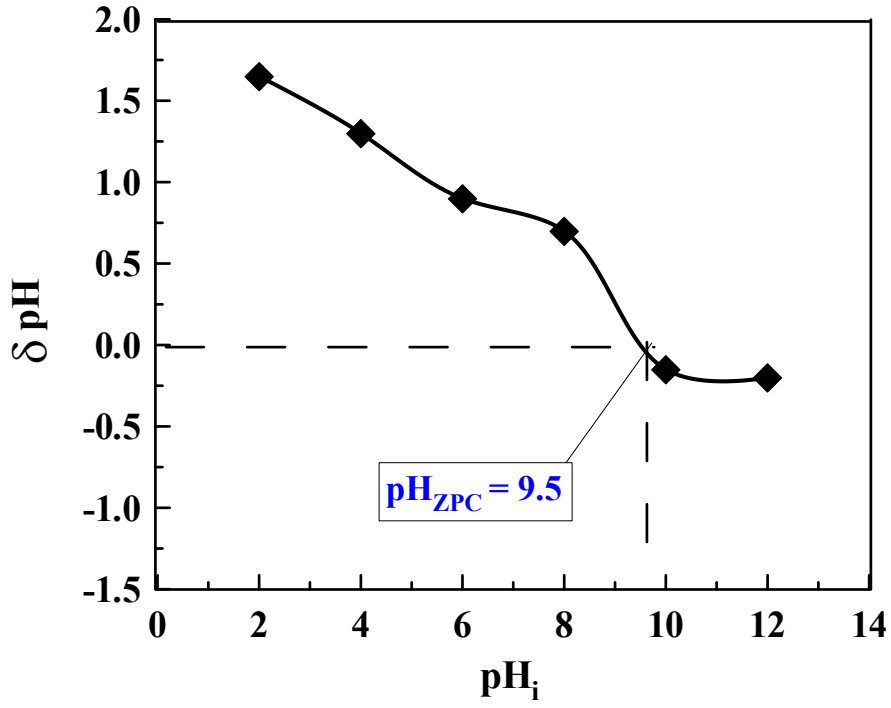


Figure. S_6: The pH_{ZPC} value of **[PZM]**.

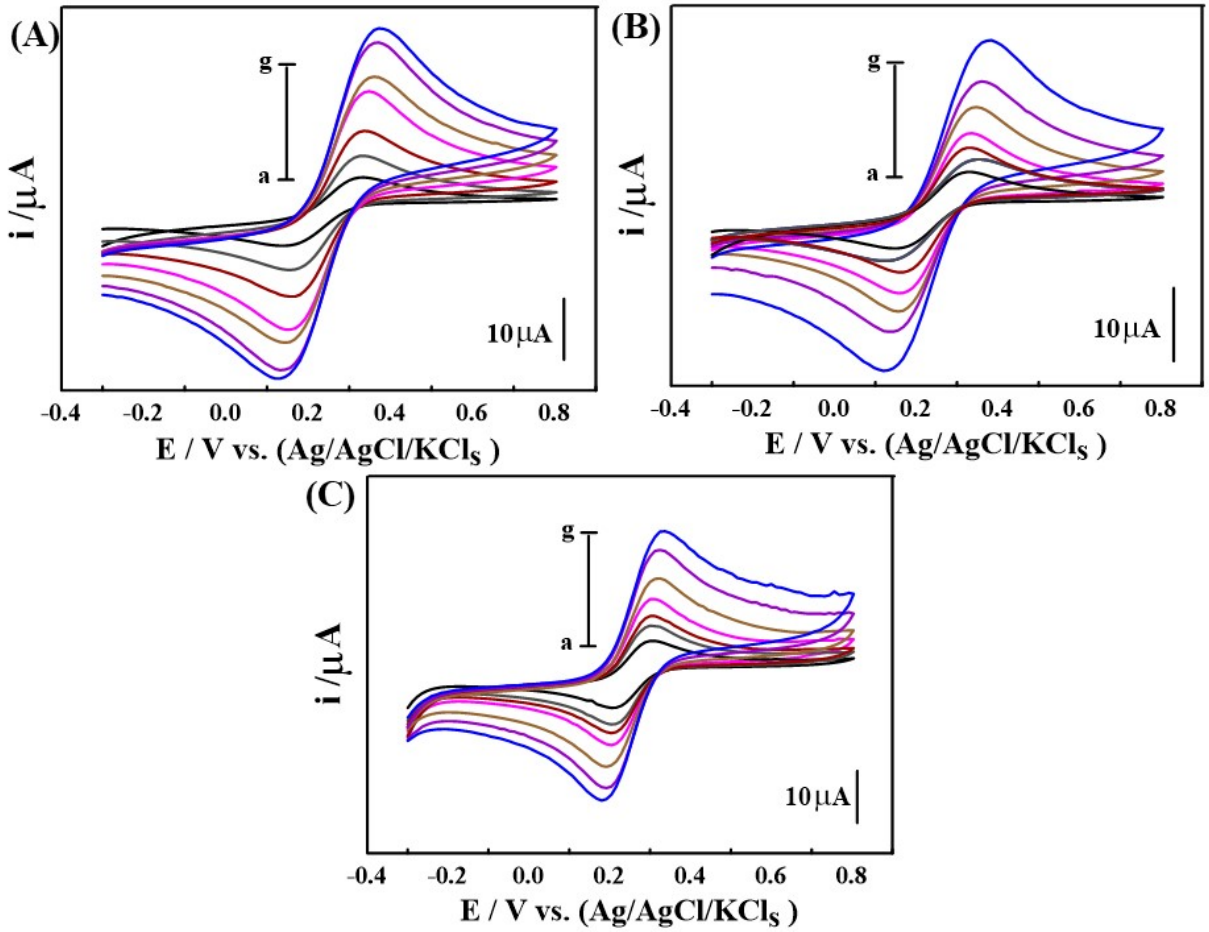


Figure. S$_7$: CVs of 5.0 mM $K_3[Fe(CN_6)]$ in 0.1 M of KCl utilizing **(A)** BCPS, **(B) [ZM]**, and **(C) [PZM]** MCPSs at different $\boldsymbol{\nu} \approx$ (a) 0.02, (b) 0.05, (c) 0.07, (d) 0.1, (e) 0.2, (f) 0.3, and (g) 0.4 mV.s^{-1}.

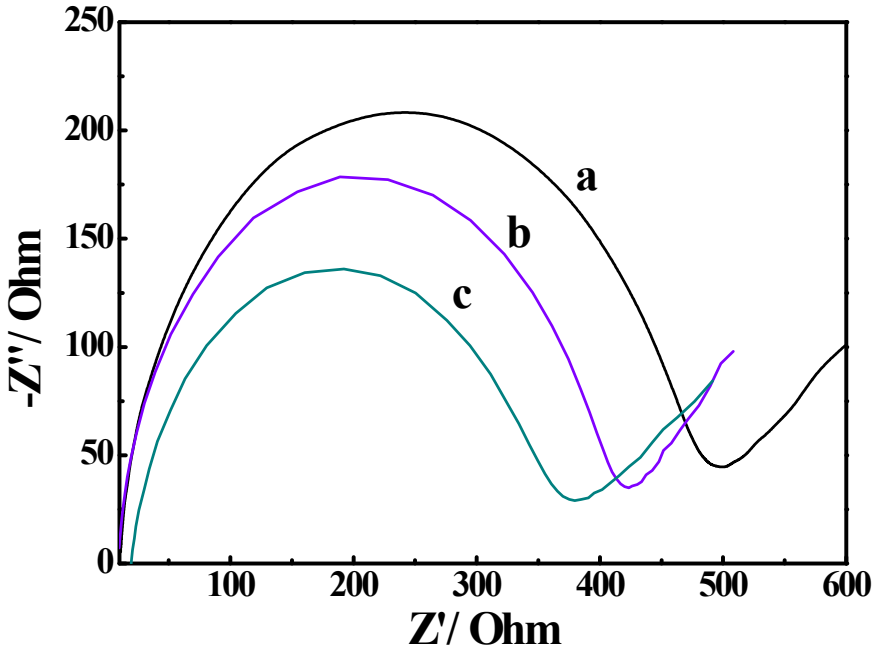


Figure.S$_8$: Nyquist plots of 5.0 mM of $K_3[Fe(CN_6)]$ in 0.1 M of KCl utilizing (a) BCPS, (b) **[ZM]**, and (c) **[PZM]** MCPSs.

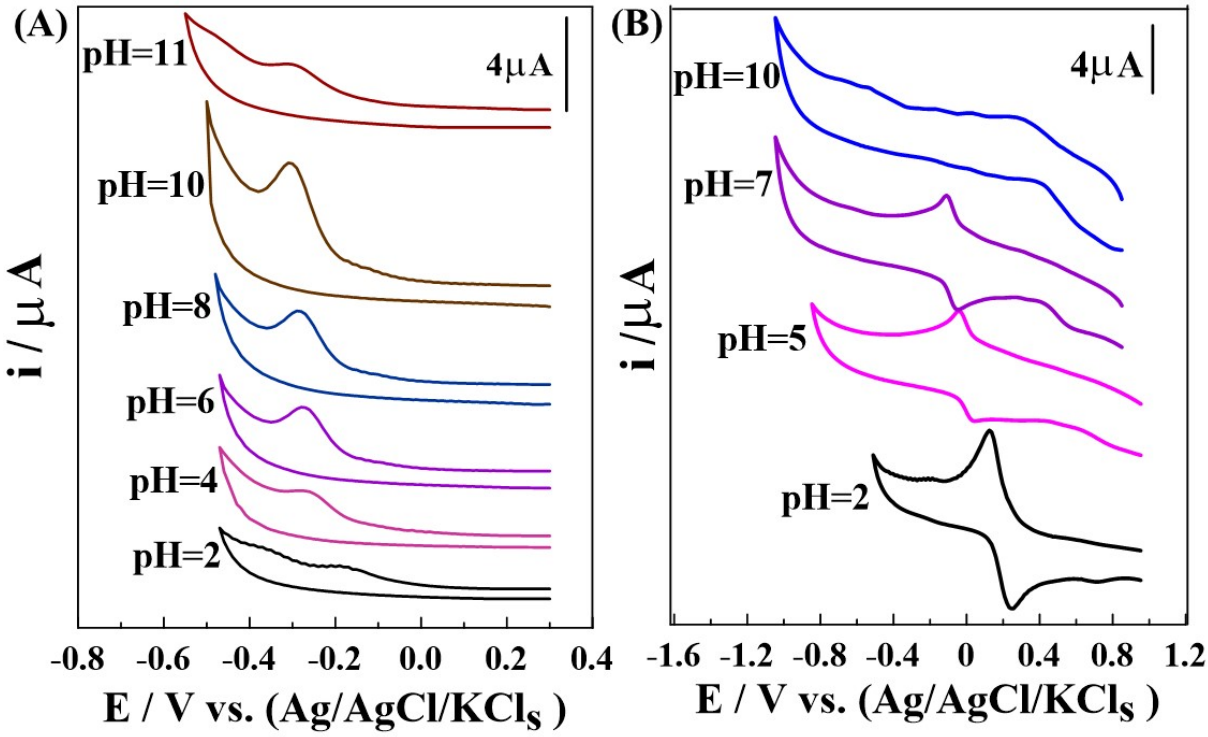


Figure. S$_9$: CVs of **(A)** 0.1 nM of ART, and **(B)** 0.2 nM of DA were estimated using the **[PZM]** MCPS for a series of pH values with B–R universal buffer at v = 100 mV·s^{-1}.

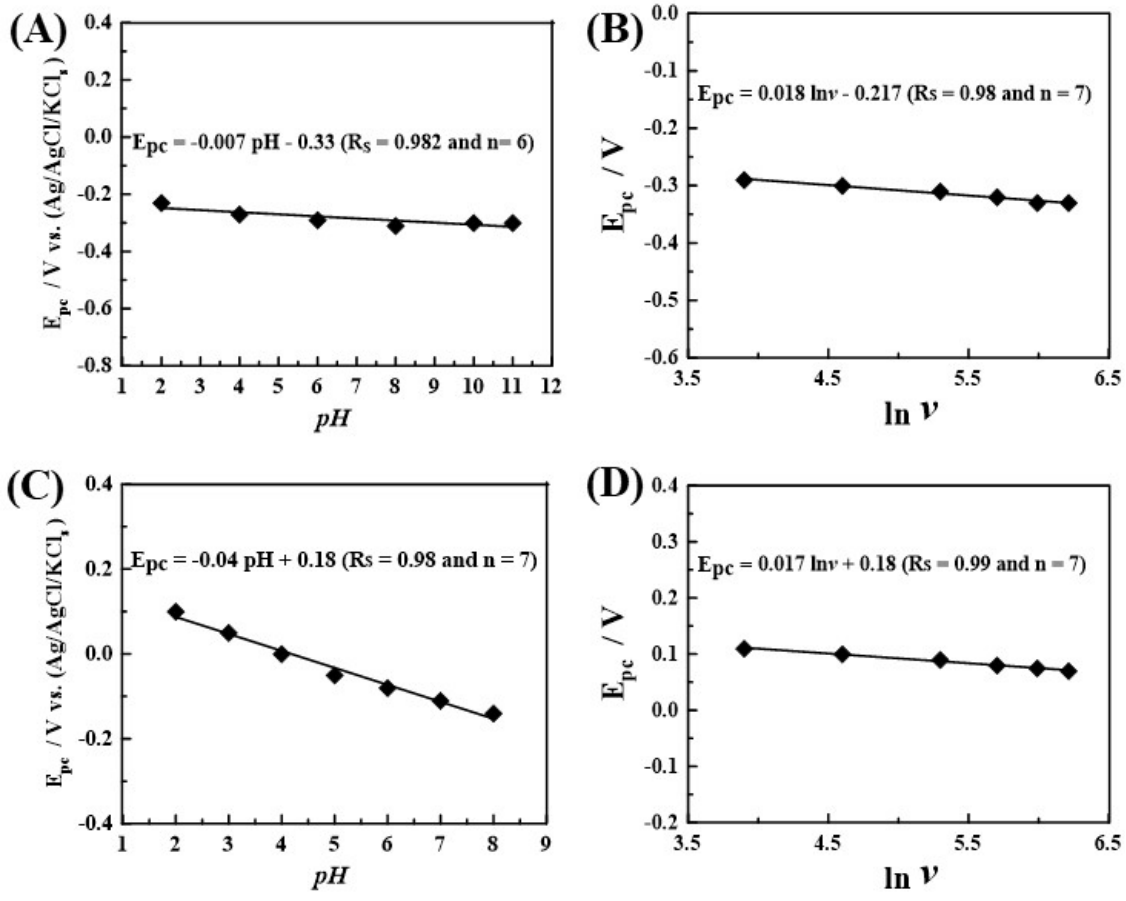


Figure. S_{10}: Plots of **(A)** E_{pc} vs. pH, and **(B)** E_{pc} vs. ln v of 0.1 nM ART *(pH 11)* at $v = 100$ mV·s^{-1} and $v \approx 50 – 500$ mV·s^{-1} ($n = 3$), respectively. Plots of **(C)** E_{pc} vs. pH, and **(D)** E_{pc} vs. ln v of 0.1 nM DA at $v = 100$ mV·s^{-1} and $v \approx 50 – 500$ mV·s^{-1} ($n = 3$), respectively.

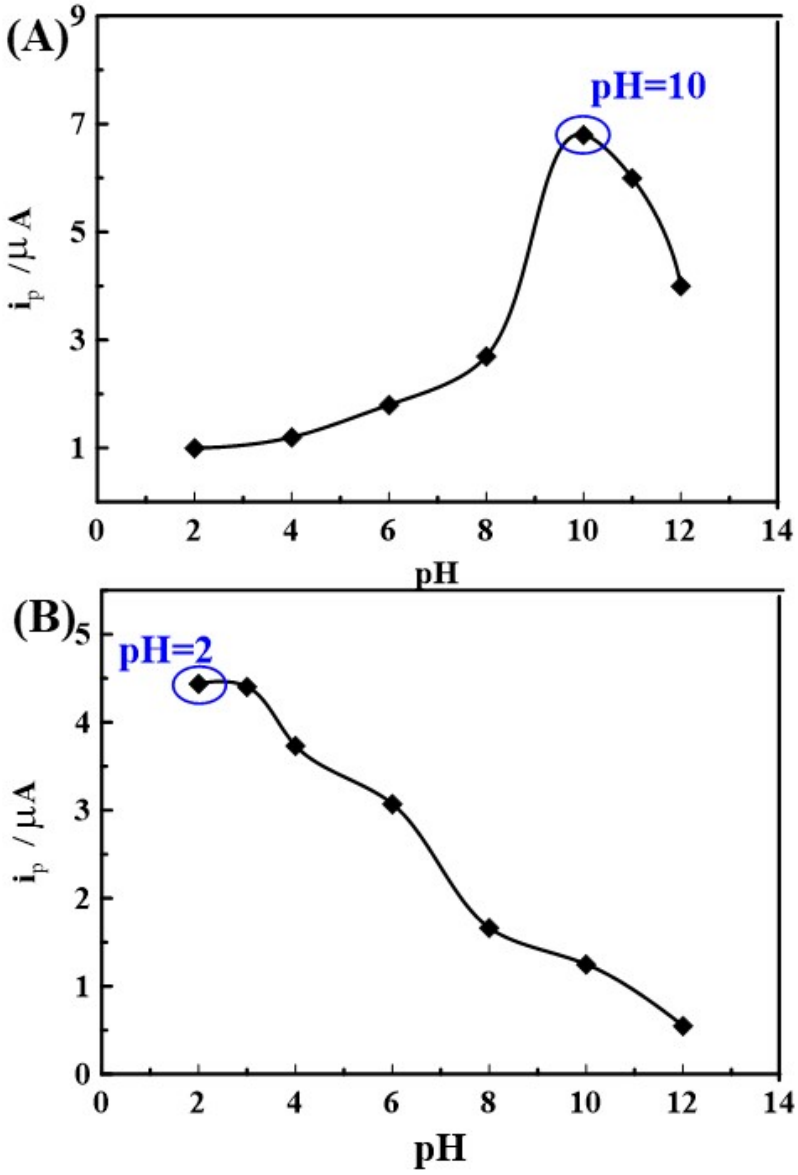


Figure. S_{11}: The plot of the effect of different pH values (B–R universal buffer) of **(A)** 0.1 nM of ART at 0.3 V for 70s, and **(B)** 0.01 nM DA upon **[PZM]** MCPS by DP-AdCV at 0.7 V for 20s (*f*=120 Hz, ***v***=75 mV, and ***a***= 40 mV).

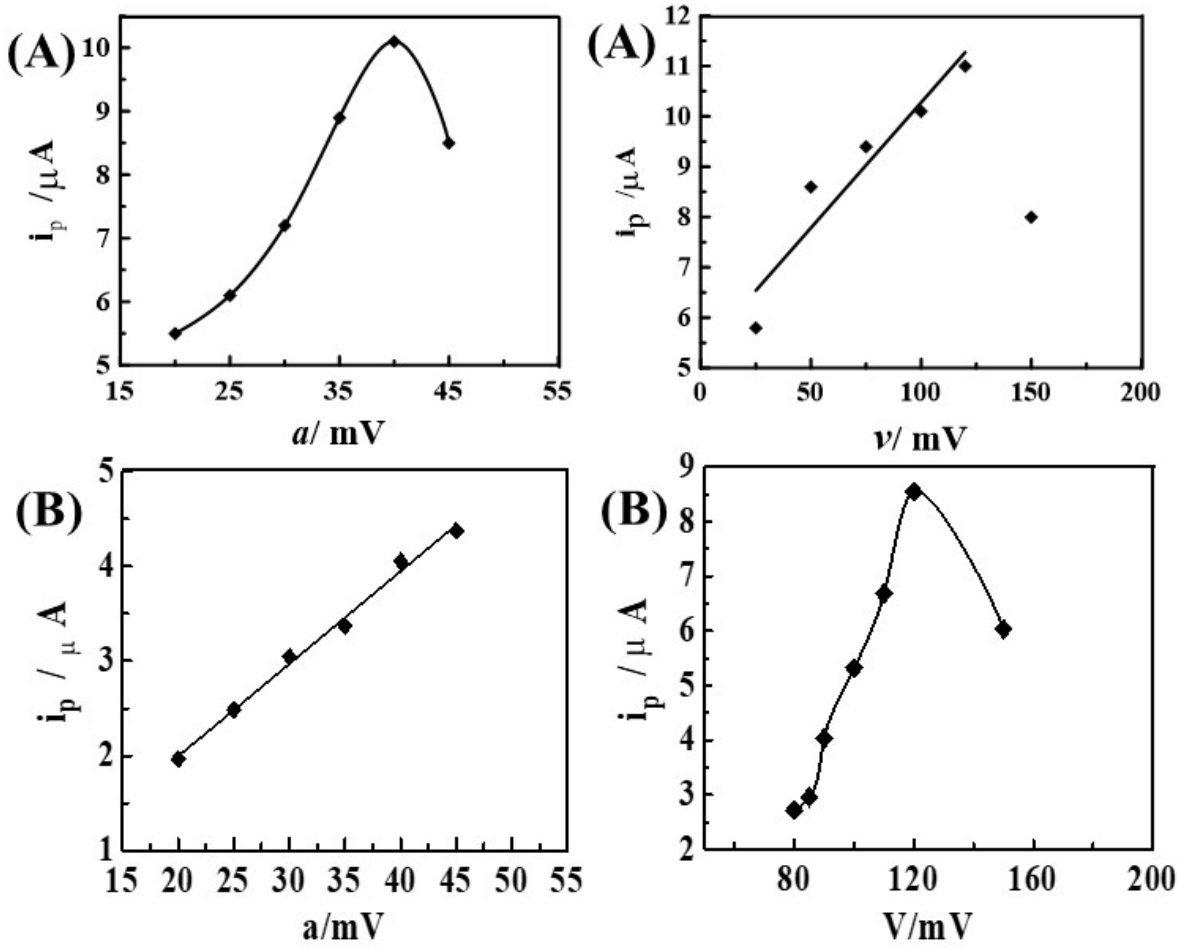


Figure. S_{12}: Influence of pulse amplitude (*a*), and scan rate (*v*) parameters of **(A)** 0.1 nM of ART (pH 10), and **(B)** 0.01 nM DA (pH 2) upon **[PZM]** MCPS by DP-AdCV for 70s, respectively.

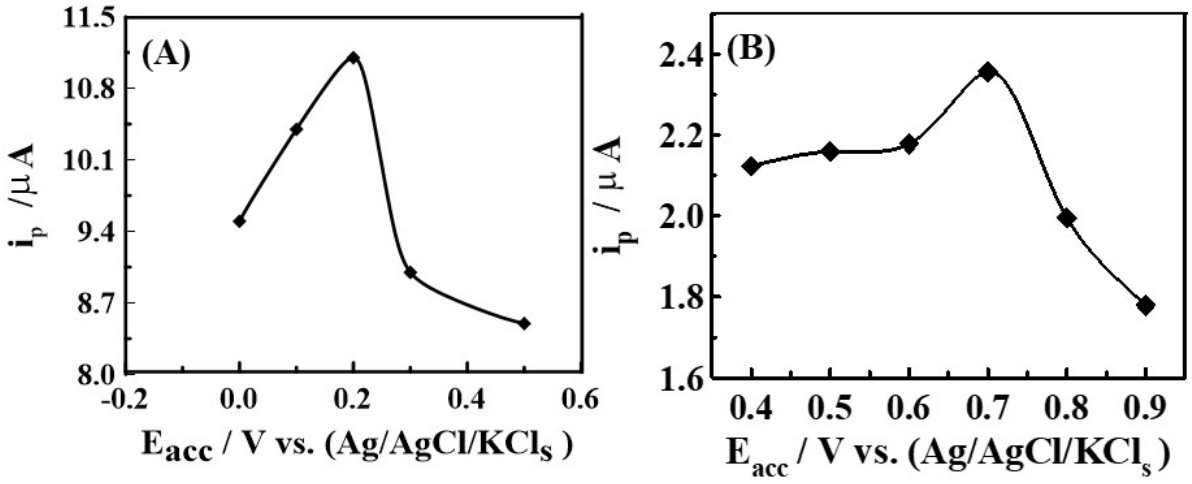


Figure. S_{13}: (A) The effect of $\mathbf{E_{acc}}$ on the DP-AdCV signals of 0.1 nM of ART (pH 10) for 70s, and **(B)** 0.01 nM DA (pH 2) for 40s upon **[PZM]** MCPS by DP-AdCV (***a***= 45 mV, and ***v***=120 mV).

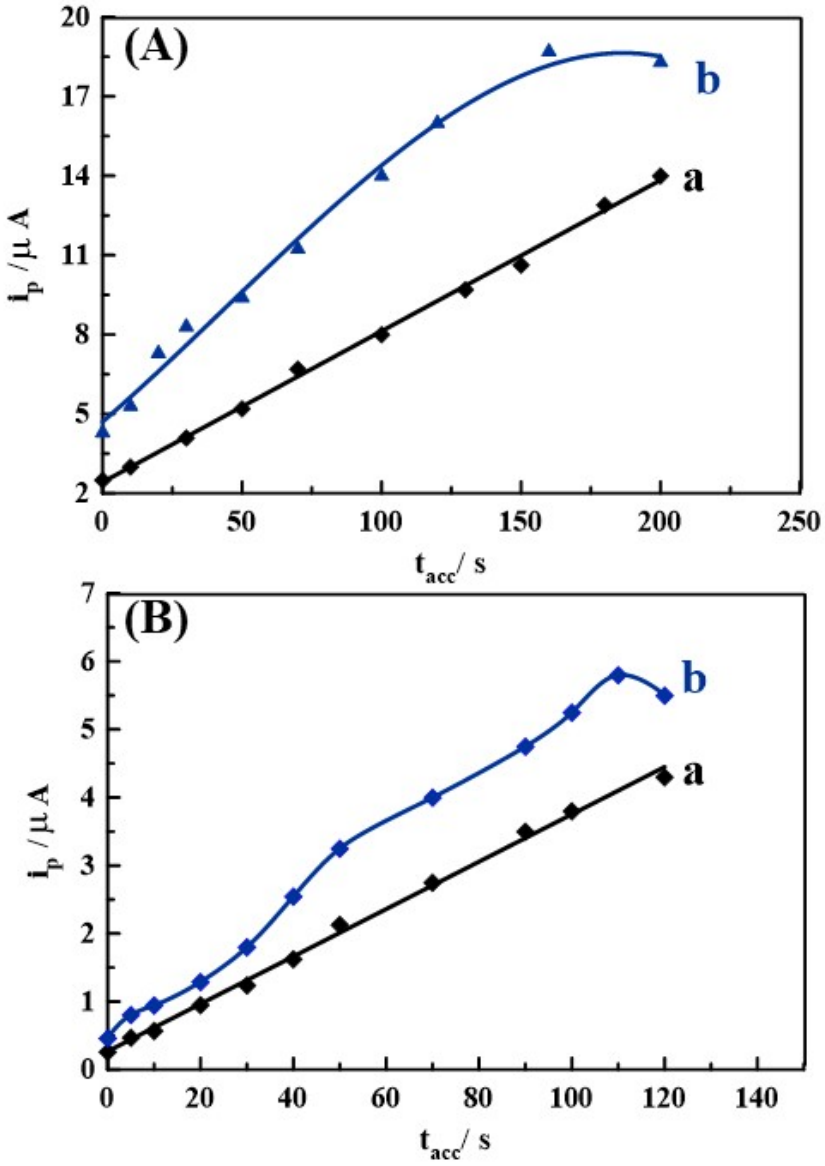


Figure. S_{14}: The effect of t_{acc} on the DP-AdCV signals of **(A)** (a)5.0, and (b)10.0pM of ART (pH 10), and **(B)** (a)10.0, and (b) 15.0 pM of DA (pH 2) on **[PZM]** MCPS (v=120 mV, and a= 45 mV).

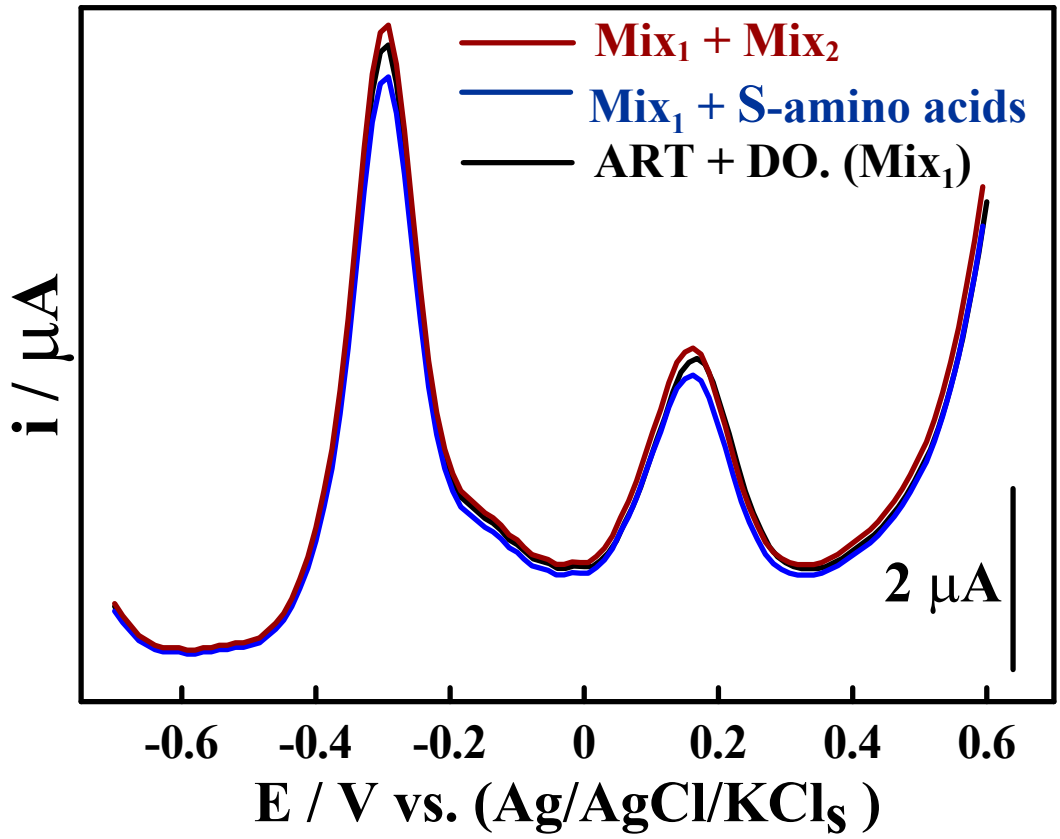


Figure.S_{15}: DP-AdCV scans of 5.0 pM ART + 5.0 pM DA (**Mix_1**) in the presence of 5.0 nM (~100-fold) of (**Mix_2**; Cl^-, CH_3COO^-, CO_3^{-2}, BO_3^{-3}, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}, and SO_4^{-2}), and mixture of S-containing amino acids (cysteine (Cys) and thiamine (TA)).

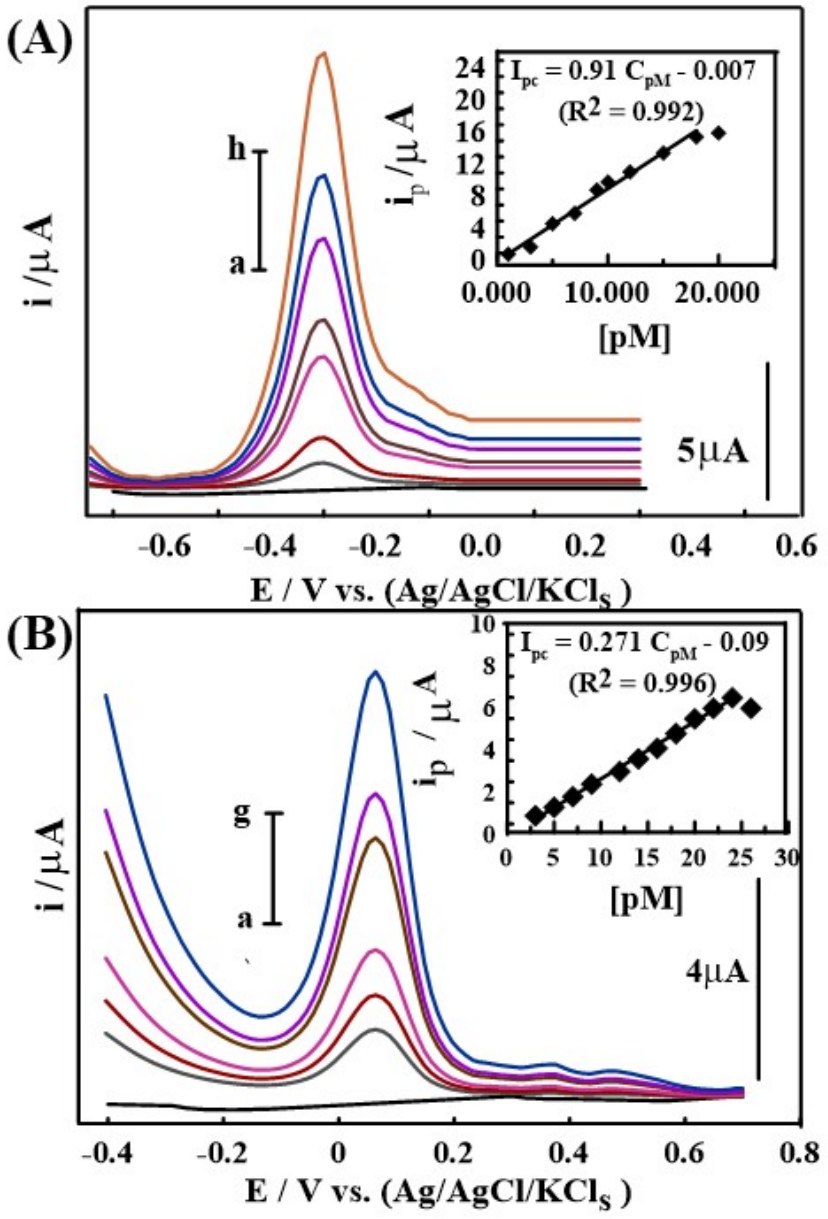


Figure.S$_{16}$: DP-AdCV crests of different amounts of **(A)** ART in the B-R buffer (pH 10) on **[PZM]** MCPS at (***a***= 45 mV, and *v*=120 mV) for t_{acc}= 100s in human urine as follow: (a) Baseline, (b) 1.0, (c) 3.0, (d) 5.0, (e) 7.0, (f) 9.0, (g) 12.0, and (h) 18.0 pM. **(B)** DP-AdCV crests of different amounts of DA in the B-R buffer (pH 2) on **[PZM]** MCPS at (***a***= 45 mV, and *v*=120 mV) for 100s in human urine as follow: (a) Baseline, (b) 5.0, (c) 7.0, (d) 12.0, (e) 16.0, (f) 20.0, and (g) 24.0 pM at (***a***= 40 mV, and *v*=120 mV) for 100 s.

1. J. Rivera-Utrilla, I. Bautista-Toledo, M. A. Ferro-García and C. Moreno-Castilla, *Journal of Chemical Technology & Biotechnology*, 2001, **76**, 1209-1215.