Development of an Electrochemical Sensor Based on Ni-Bio-MOF and Molecular Imprinted Polymer for determination of Diclofenac: electrochemical and DFT investigations

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1.1. Chemicals and Instruments

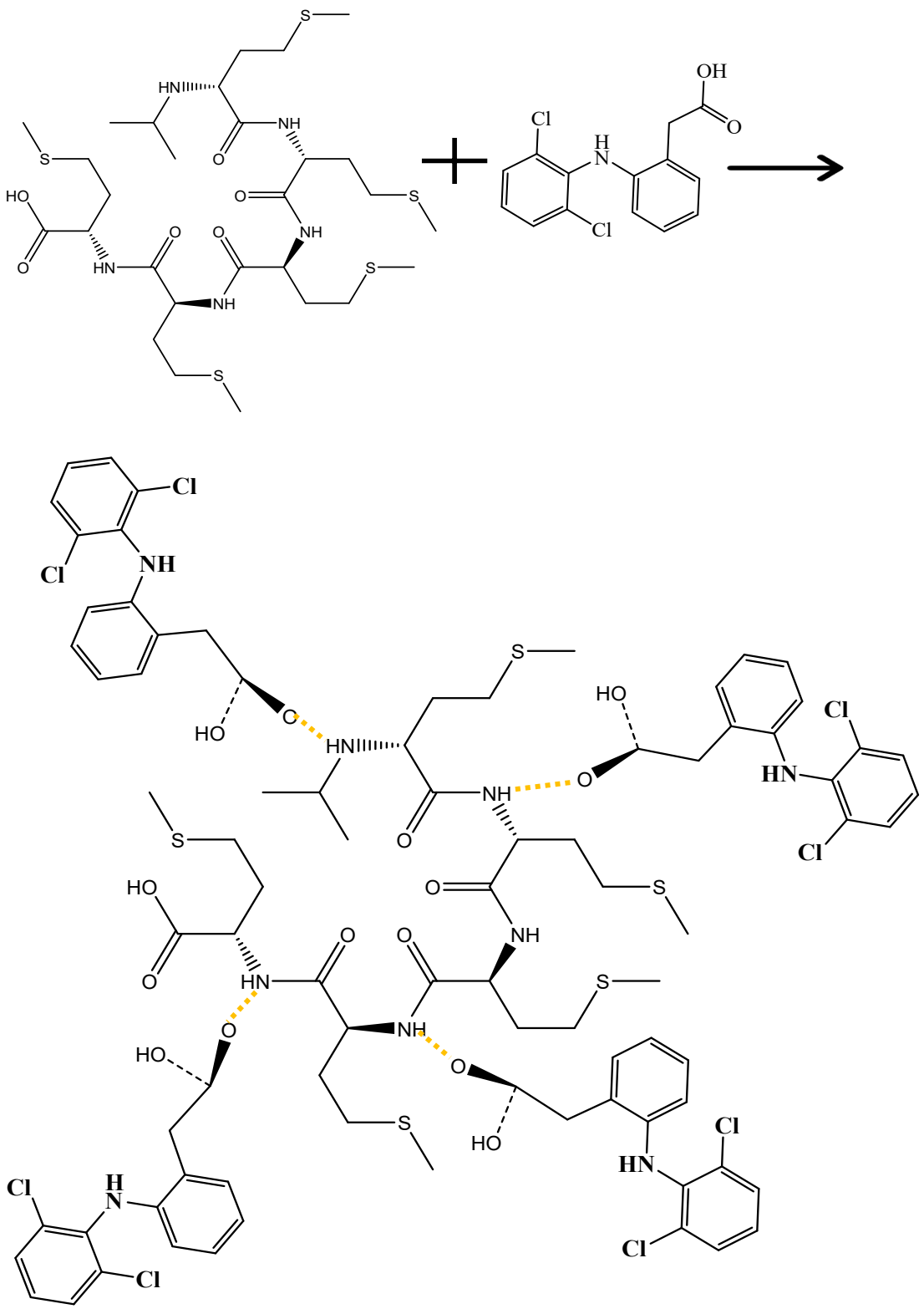
Diclofenac (DCF), L-Methionine (L-Met), Sodium hydroxide, potassium chloride, magnesium dichloride, calcium chloride, Nickel nitrate hexahydrate (Ni $(NO_3)_2$-$6H_2O$, 99 wt.%), ammonium chloride, sodium sulfate, potassium bromide, disodium phosphate, monosodium phosphate, graphite powder (fine powder extra pure), potassium hexacyanoferrate (II) ($K_4Fe(CN)_6$), potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$), glucose, glycine, uric acid, urea, ascorbic acid, diethylether (99 wt.%), ethanol, methanol and acetonitrile were all obtained from Merck company. Terephthalic acid (H_2BDC, 98 wt.%) and N, N-dimethylformamide (DMF, 99 wt.%) were purchased from Sigma-Aldrich Chemical Company. All solutions were prepared with double-distilled water. All experiments were done at room temperature (22-25 °C). Phosphate buffer solution (PBS) was prepared from 0.1M of sodium dihydrogen phosphate and disodium hydrogen phosphate at pH 7. The solution of NaOH was used to adjust the pH of the buffer and PBS was used as a supporting electrolyte. CPE was prepared from powder graphite and paraffin oil. Paraffin oil (d = 0.88 g cm^{-3}) was purchased from Merck company. The regents of organic ligands of amino acid Asparagine (Asn) and BDC, Nickel (II) nitrate hexahydrate, and dimethylformamide (DMF) were used to prepare Ni-Bio-MOF and Ni-MOF. Asn was purchased by Merck company. Solvents of ethanol, acetonitrile, and sodium hydroxide solution were used to remove the template from MIP.

A 691-pH meter (Metrohm) was used for pH measurements. An ultra-pure water system type Aqua Max system (Young-Lin, Hogye-dong, Korea) was used to prepare deionized water. A Tensor 27 (Bruker) instrument was used for ATR-FTIR analysis. The surface properties and morphologies and energy dispersive X-ray analysis (EDS) were examined by field emission scanning electron microscopy with an accelerating voltage of 20 kV (FE-SEM) (MIRA 3,

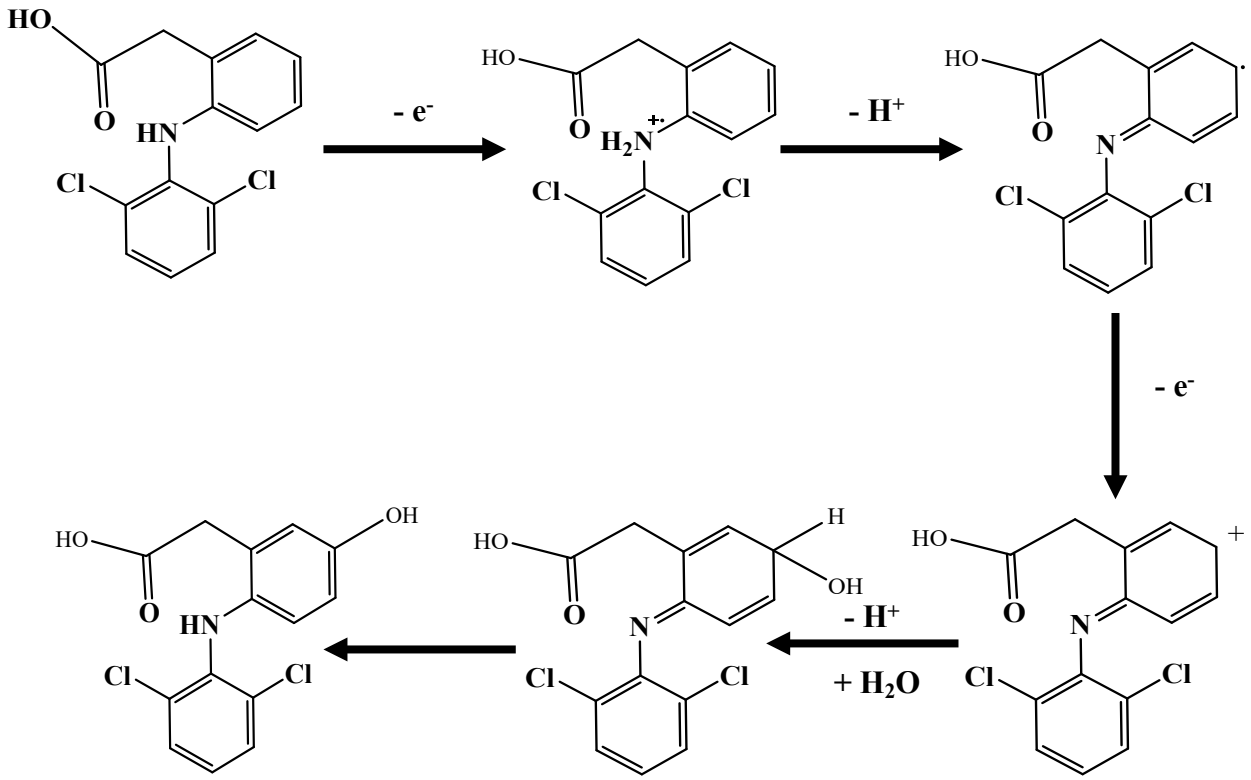
TESCAN, Czech Republic). XPS data for the characterization of the chemical bonding state of the Ni-Bio-MOF were obtained from the XPS (FLEXPS) instrument (Berlin, Germany). A HR-TEM FEI TECNAI F20 instrument was used for HR-TEM images. An XRD XPert PRo MPD instrument was used to identify the compositions of Ni-MOF and Ni-Bio-MOF syntheses and the phases in the materials. BET data for Ni-MOF and Ni-Bio-MOF syntheses were obtained from the BET BELSORP Mini II instrument. A Metrohm Autolab B. V.® Autolab PGSTAT 204 potentiostat/galvanostat (Utrecht, UT, the Netherlands, controlled by NOVA software) was used to carry out all electrochemical experiments. As a working electrode, a bare or modified carbon paste electrode (CPE, diameter=3.5 mm), as a counter electrode, a platinum wire, and as a reference electrode an Ag/AgCl/saturated KCl was used as a three-electrode cell system.

Table S1: Investigation of the anodic peak current intensity of 1.0 μM DCF in the presence and absence of interfering species on the CPE/Ni-Bio-MOF/MIP-PL-Met

Interference (μM)	I_P (μA)	%E (±)
Glucose (1000)	9.46	1.39
Glycine (1000)	9.59	2.79
Uric acid (10)	9.47	1.50
Urea (10)	9.26	-0.75
Ascorbic Acid (1000)	9.46	1.39
Chlorine (100)	9.33	0
Ammonium (100)	9.32	-0.11
Magnesium (100)	9.42	0.96
Sulfate (100)	9.53	2.14
Nitrate (100)	9.32	-0.11
Calcium (100)	9.61	3.00
Bromine (100)	9.38	0.54
Potassium (100)	9.52	2.04
Free	9.33	



Scheme S1. The proposed mechanism for electropolymerization of MIP.



Scheme S2. The proposed mechanism for the electrochemical behavior of DCF

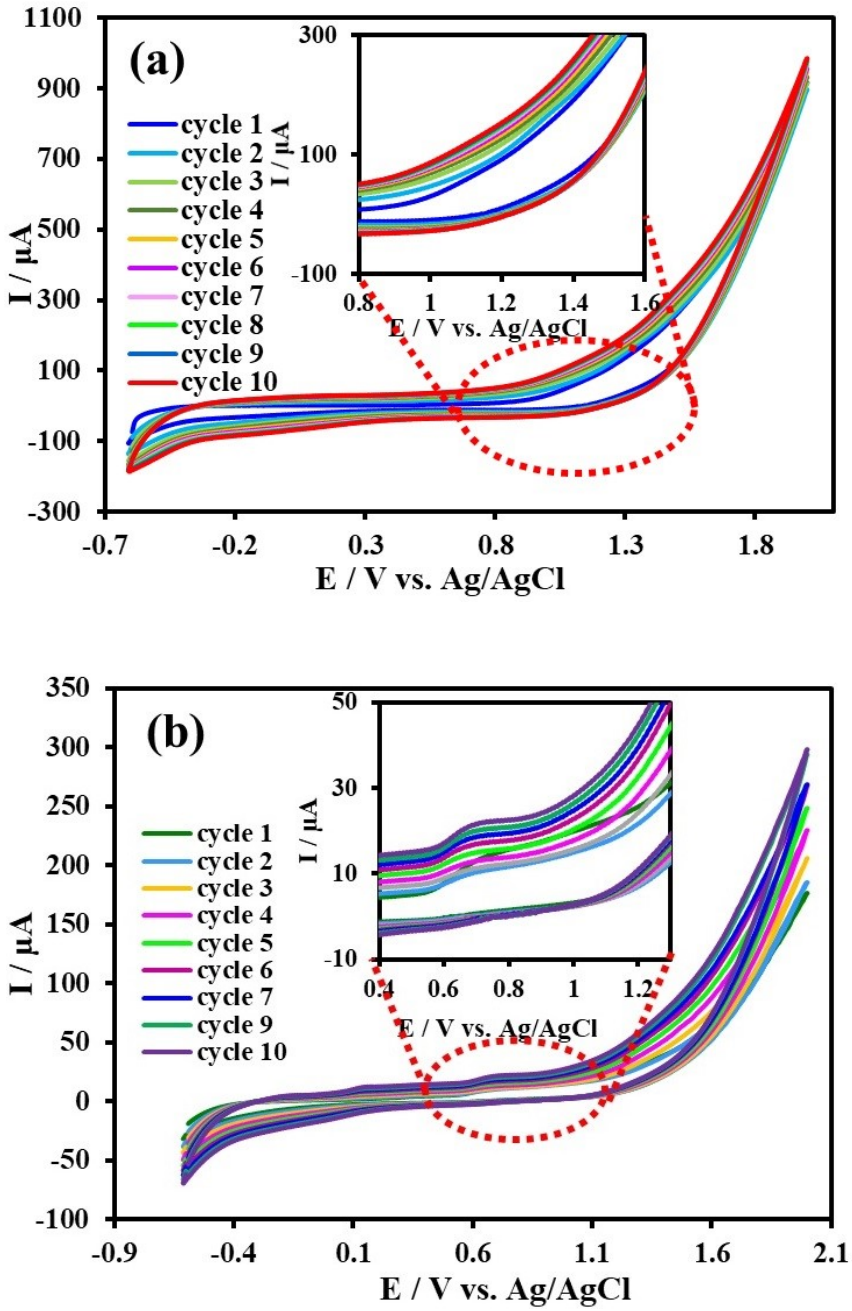


Fig. S1. CVs for the electrochemical polymerization of (a) 0.25 mM L-Met on CPE, and (b) 0.25 mM L-Met with 0.083 mM DCF during the modification of CPE/Ni-Bio-MOF sensor. Deposition conditions: 0.1 M PBS solution (pH 7.0); scan rate 100 mV/s for 10 cycles; potential range of -0.6 to 2.0 V).

Williamson-Hall Equation. The basic form of the Williamson-Hall equation that connects the broadening of X-ray diffraction peaks to crystallite size and strain within the crystal lattice is [*]:

$$\beta Cos\theta = \frac{k\lambda}{D} + 4\varepsilon Sin\theta \qquad \text{S1}$$

where: β is Full Width at Half Maximum (FWHM) of the peak (in radians); θ = Bragg angle (in radians); K = Shape factor (typically around 0.9 for spherical particles); λ = Wavelength of the X-ray; D = Average crystallite size; ε = Microstrain (strain in the crystal lattice). By plotting βCosθ versus 4sinθ, we can calculate micro-strain (ε) from the slope of the linear fit.

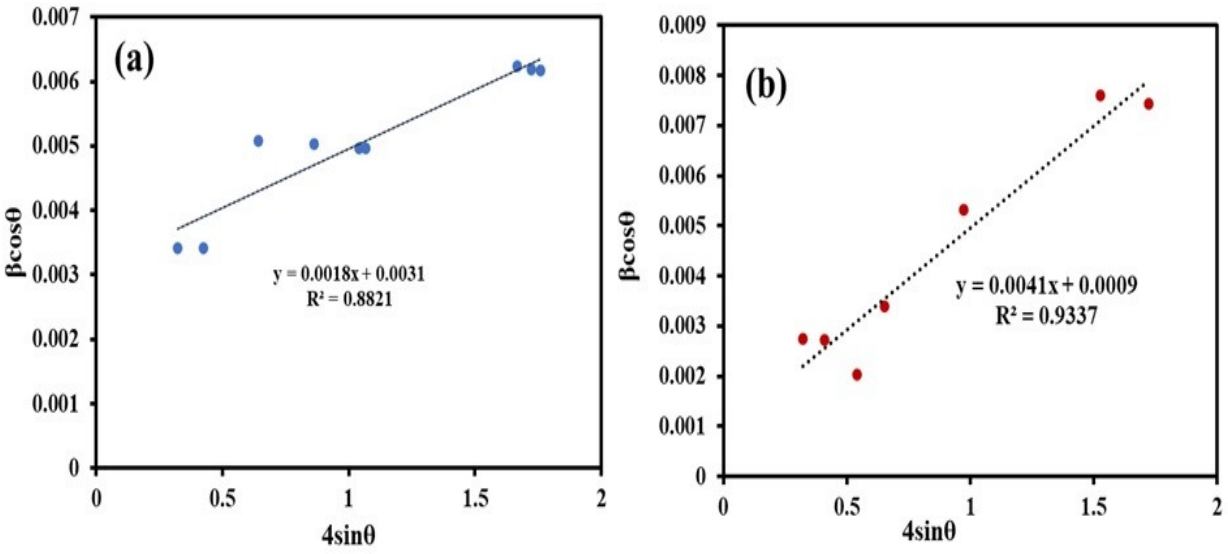


Fig. S2. Microstrain parameters calculation. Williamson-Hall plot of (a) Ni-BDC and (b) Ni-Bio-MOF.

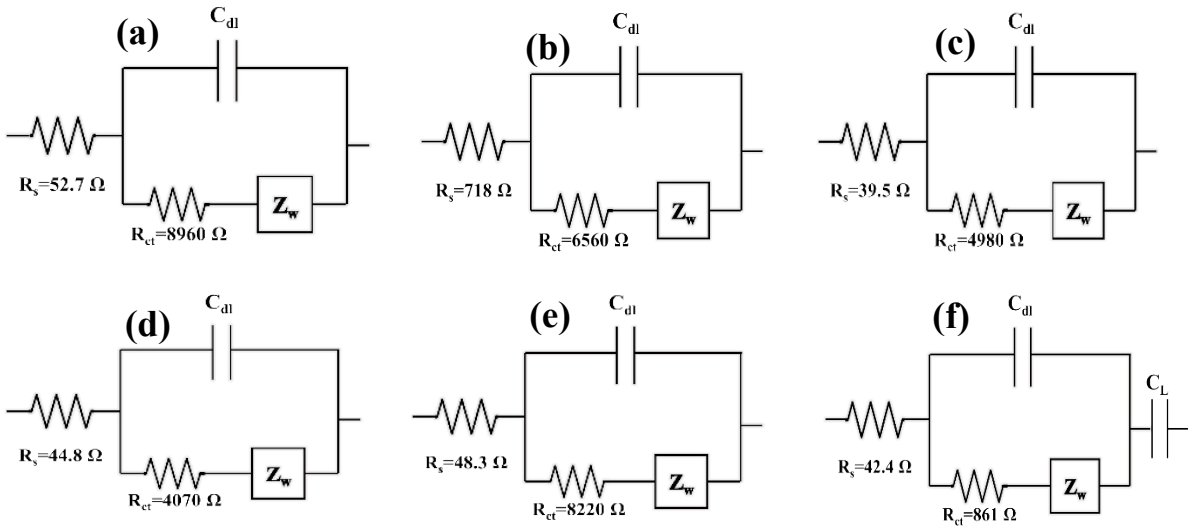


Fig. S3. Equivalent circuits for **(a)** CPE, **(b)** Ni-MOF, **(c)** Ni-Bio-MOF, **(d)** Ni-Bio-MOF/NIP-PL-Met, **(e)** Ni-Bio-MOF/MIP-PL-Met (before removal of template), **(f)** Ni-Bio-MOF/MIP-PL-Met (after removal of template) in 0.1 M KCl solution containing 1.0 mM $K_3Fe(CN)_6$.

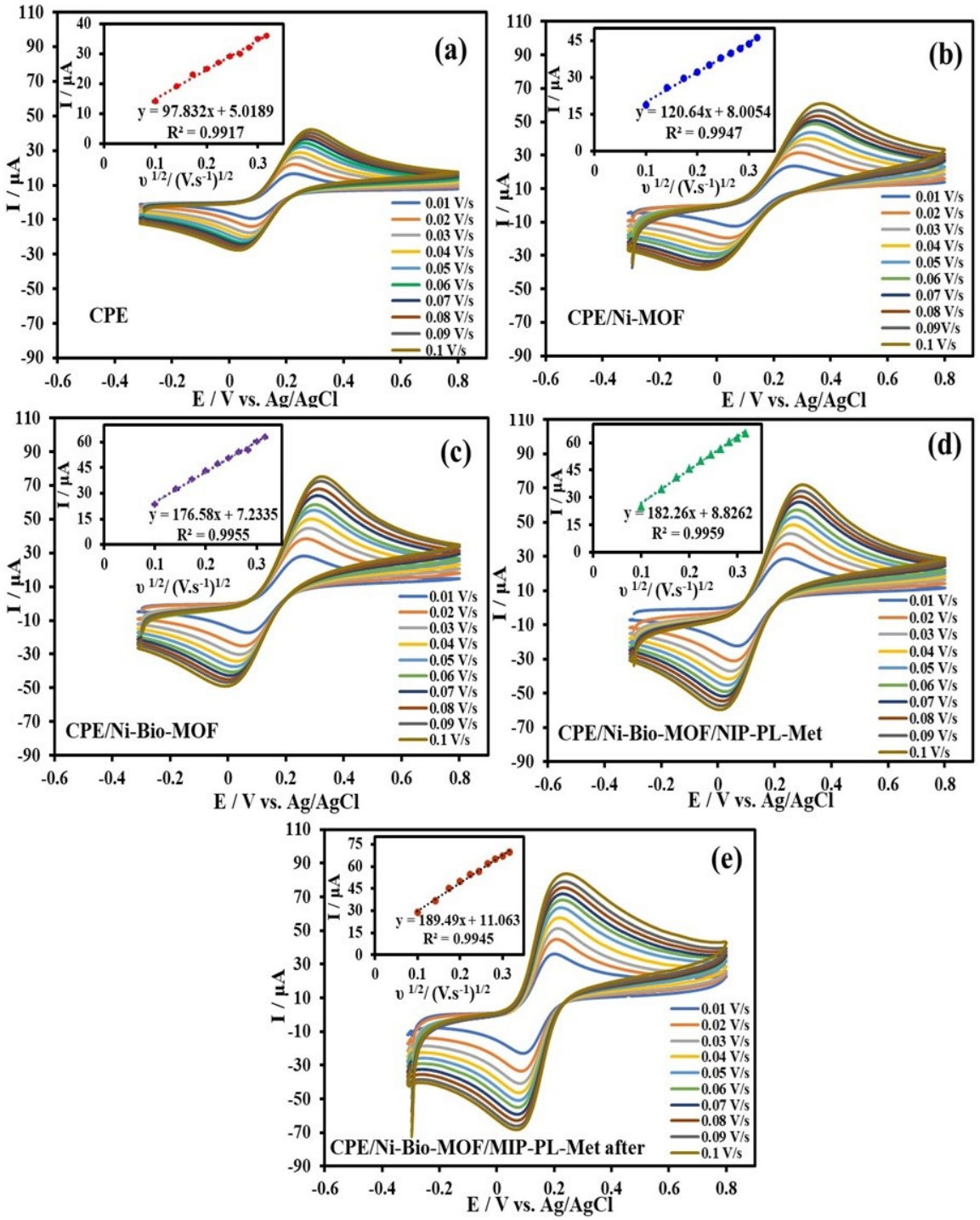


Fig. S4. Cyclic voltammograms of 0.1 M KCl solution containing 5.0 mM $Fe(CN)_6^{3-/4-}$, at different scan rates (10 to 100 mV s^{-1}) at the surface of (a) bare CPE, (b) CPE/Ni-MOF, (c) CPE/Ni-Bio-MOF, (d) CPE/Ni-Bio-MOF/NIP-PL-Met, (e) CPE/Ni-Bio-MOF/MIP-PL-Met (after removal template). Insets: a plot of I_p vs. $\upsilon^{1/2}$ obtained from cyclic voltammograms.

The influence amount of Asn on the synthesis of Ni-Bio-MOF on the response of the electrochemical sensor of CPE/Ni-Bio-MOF/MIP-PL-Met was investigated under the condition best by different Asn amounts (1.0, 3.0, 5.0, 6.0, 7.0 mg). According to the XRD patterns (Fig. S4b), the addition of Asn does not affect the crystallinity of Ni-Bio-MOF, because all samples have relatively high crystallinity. Also, the microstrain values, calculated using the Williamson−Hall (W−H) method, for Ni-Bio-MOF with different Asn amounts (1.0, 3.0, 5.0, 6.0, 7.0 mg), were 0.0017, 0.0041, 0.002, 0.0021, and 0.0023, respectively. These can be attributed to structural defects caused by adding different amounts of ASP to Ni-MOF.

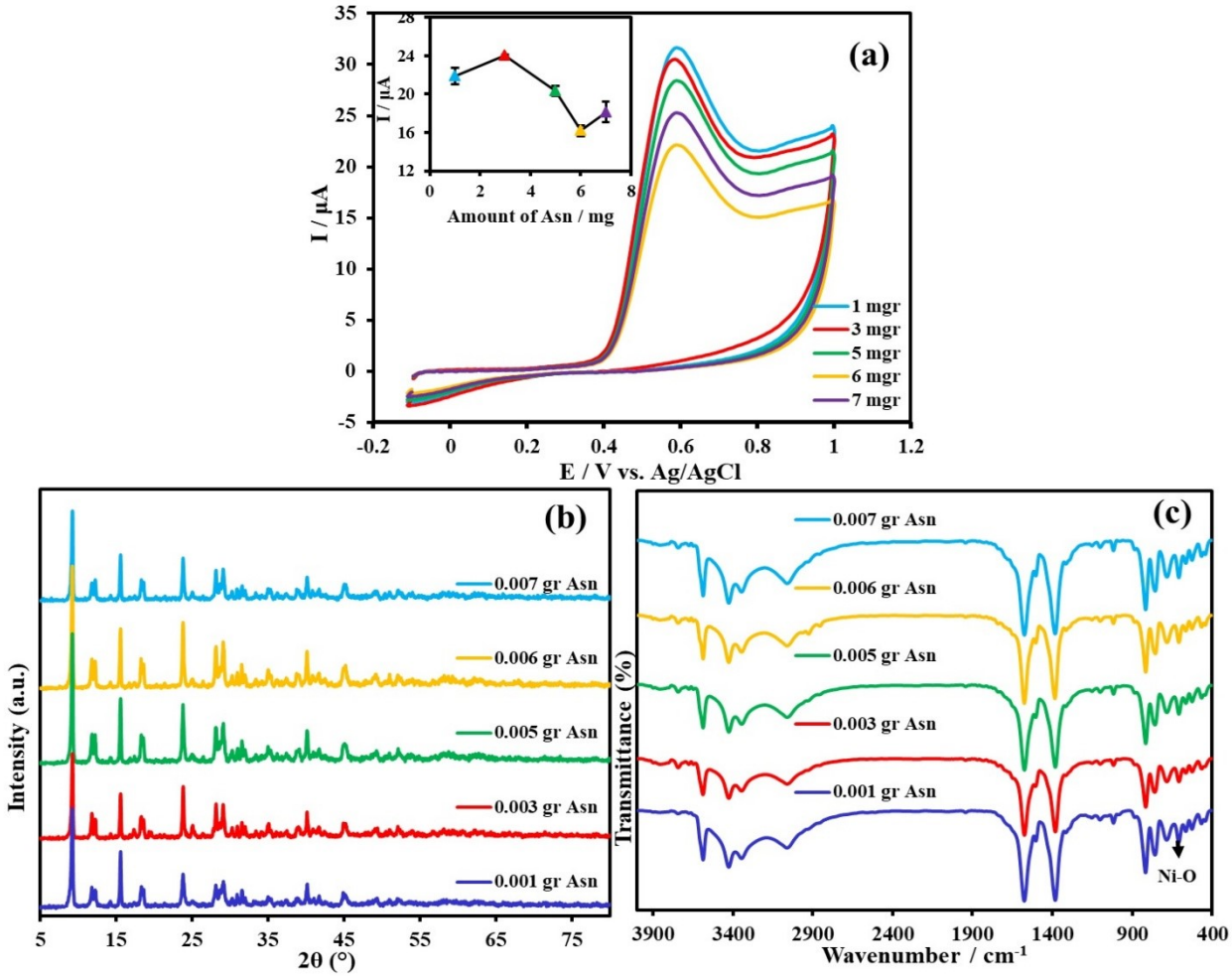


Fig. S5. Optimize the amount of (a) Asn in Ni-Bio-MOF for a 1mM DCF in PBS 0.1M (pH 7.0), Scan rate of 50 mV/s, (b) XRD, and (c) FT-IR for Ni-Bio-MOF in different amounts of Asn.

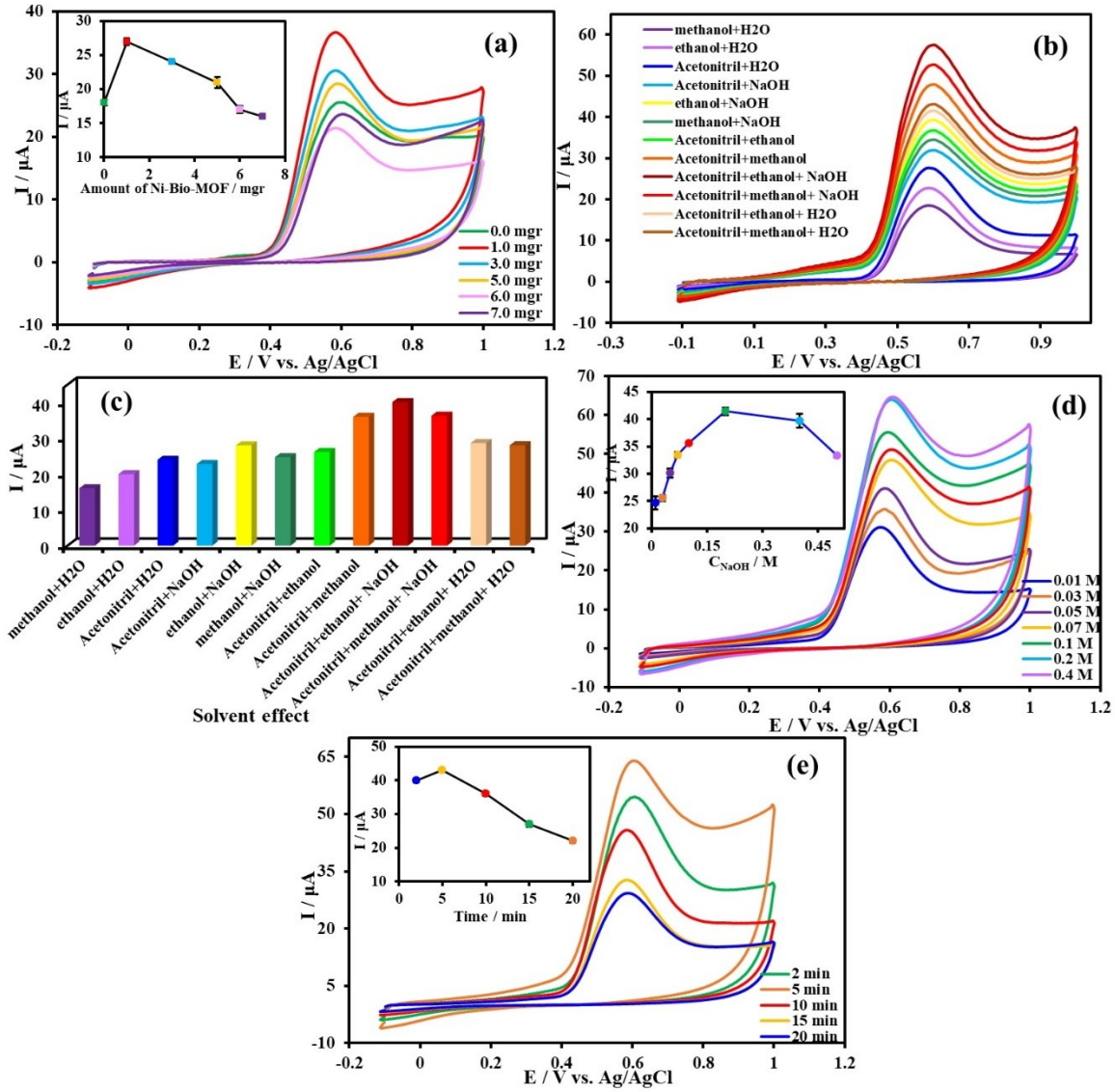


Fig. S6. Optimize the (a) amount of Ni-Bio-MOF in CPE, (b, c) template extraction solvent, (d) the concentration of NaOH, and (e) time of elution for a 1mM DCF in PBS 0.1M (pH 7.0), Scan rate of 50 mV/s.

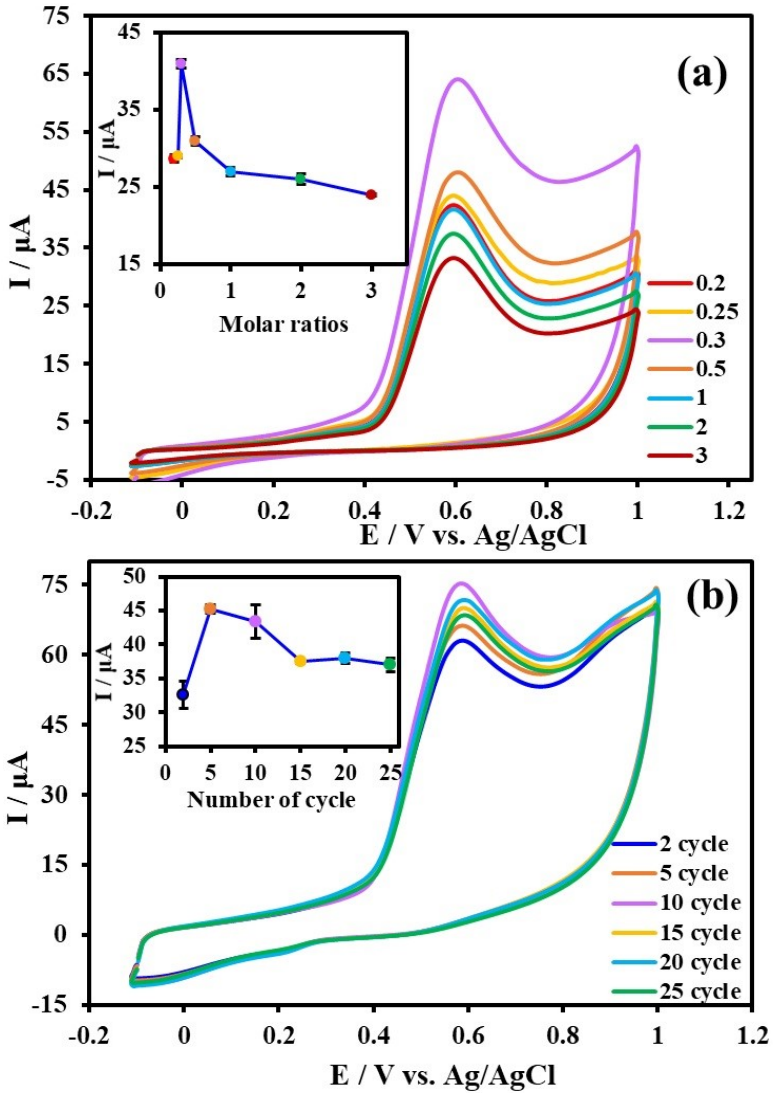


Fig. S7. Optimization (a) ratio template: monomer and (b) the Cycle number of MIP polymerization for a 1 mM DCF in PBS 0.1M (pH 7.0), Scan rate of 50 mV/s.

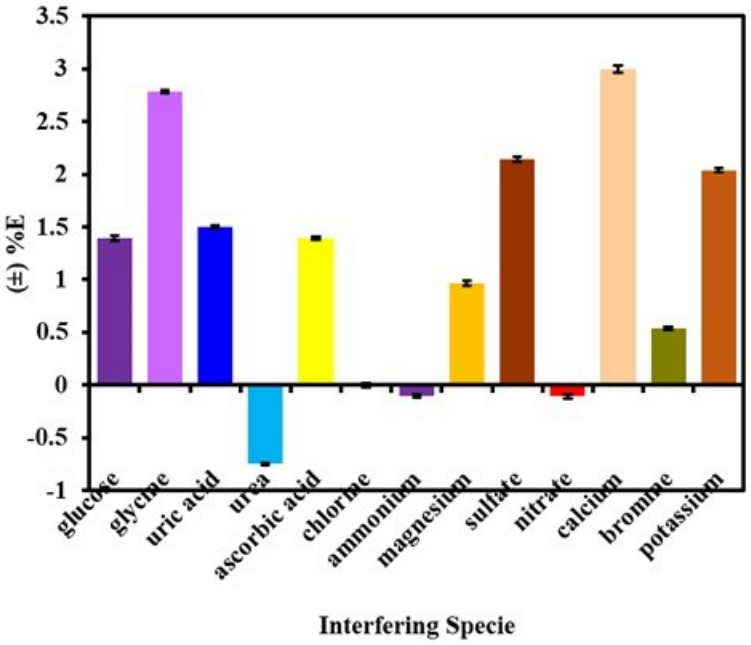


Fig. S8: Effect of various interferences on DCF sensing response of CPE/Ni-Bio-MOF/MIP-PL-Met. Error bars indicate the standard deviations of three repeated measurements.

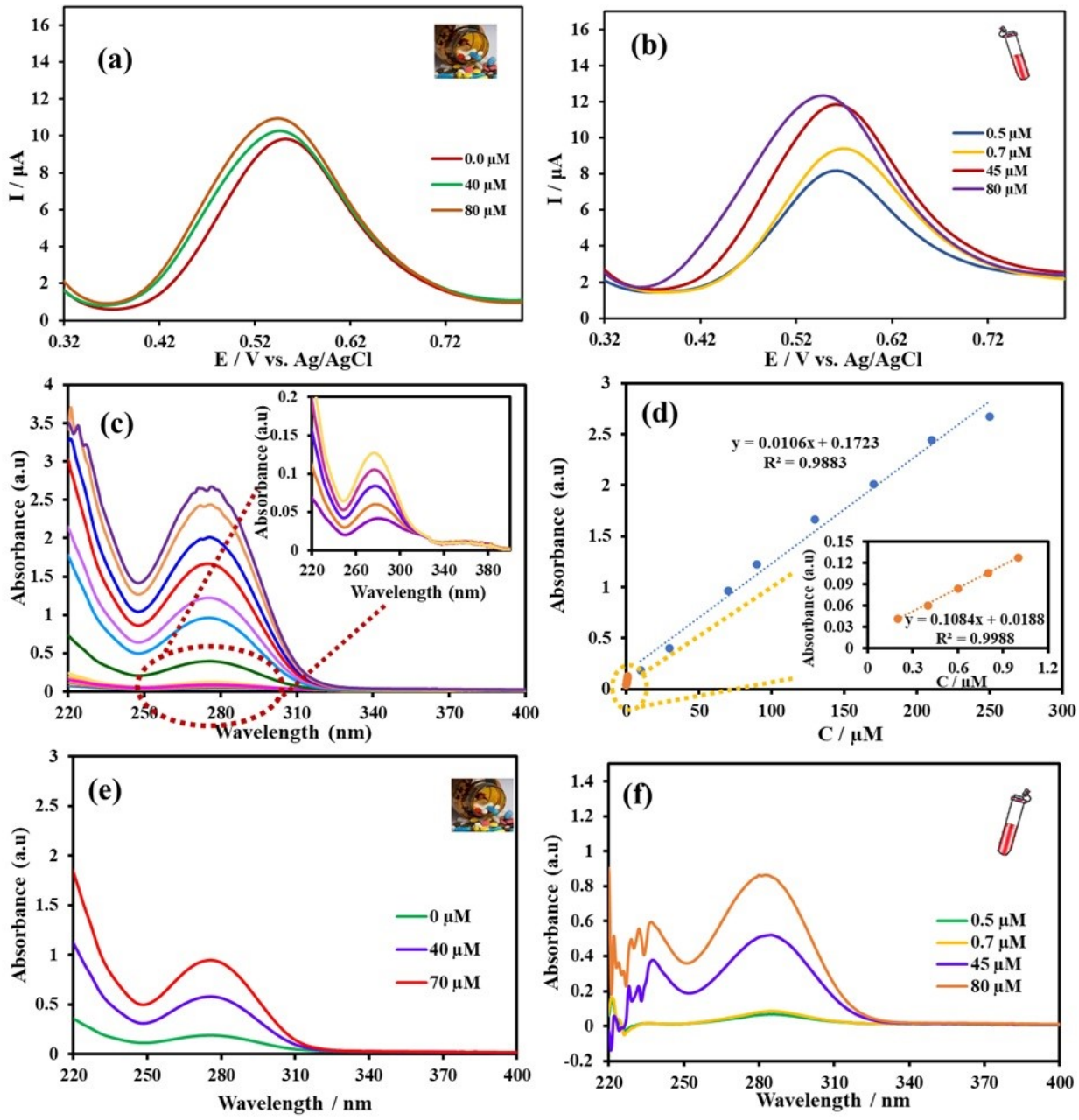


Fig. S9. (a and b) DPV of DCF of tablet and blood serum samples, respectively. (c) UV–Vis spectra of DCF standard solution, and (d) linear calibration curve. (e and f) UV-Vis spectra of DCF of tablet and blood serum samples.