Supplementary Data

Iron-based Metal-Organic Frameworks/Graphene Oxide Composite Electrodes for Efficient Flow-Injection Amperometric Detection of Dexamethasone

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Preparation of graphene oxide (GO)

Graphene oxide was synthesized using a modified Hummer's method are described in the ESI. First, 3 g of graphite was soaked in 360 mL of concentrated H_2SO_4 and 40 mL of concentrated H_3PO_4, and stirred at 55 °C for 30 min. Subsequently, 18 g $KMnO_4$ was added to the mixture. The mixture was alternately stirred and sonicated at 55 °C for 6 h. The mixture was placed in an ice bath and 10 mL of 30% H_2O_2 and 600 mL of water were added. After stirring for 30 min, 100 mL concentrated HCl was added. Finally, the dark brown particles were washed with ethanol and deionized water and filtered. The filtered products were freeze-dried for 12 h to yield GO powder[29].

Synthesis of Fe-based metal organic frameworks, MIL-100(Fe)

For MIL-100(Fe), 2.4 mmol of trimesic acid (H_3BTC) was added to 20 mL of distilled water in a 100 mL size Teflon-lined autoclave and stirred vigorously for 20 min. Then, 3.6 mmol of $FeCl_3 \cdot 6H_2O$ was added to the mixture and stirred for an additional 20 min. A Teflon-lined steel iron autoclave was sealed and maintained at 150 °C for 12 h. The resulting red-brown particles were separated via centrifugation and washed with distilled water. The synthesized particles were soaked in methanol for 36 h and dried at 80 °C for 5 h[30].

Characterization

The size and morphology of the prepared materials were examined by field emission scanning electron microscopy–X-ray dispersive spectroscopy (FESEM-EDS) (ZEISS, MERLIN Compact-Oxford, Aztec ED) and transmission electron microscope (TEM) technique (JEOL JEM 2010). Powder X-ray diffraction (PXRD) patterns were collected using a HORIBA - XGT 5200WR diffractometer (5−80) with Cu Kα radiation (λ =1.54059 Å). For the material functional group analysis, Fourier transform infrared spectroscopy (FTIR) was performed using a BRUKERS, Tensor 27 with a scan range of 4000-530 cm^{-1}. X-ray photoelectron spectroscopy (XPS) data for elemental composition and valence information were collected using an XPS PHI 5600-ci (Physical Electronics, Eden Prairie, MN, USA). All XPS spectra were corrected using the C1s line at 284.5 eV and curve fitting was accomplished using XPS Peak 4.1 software.
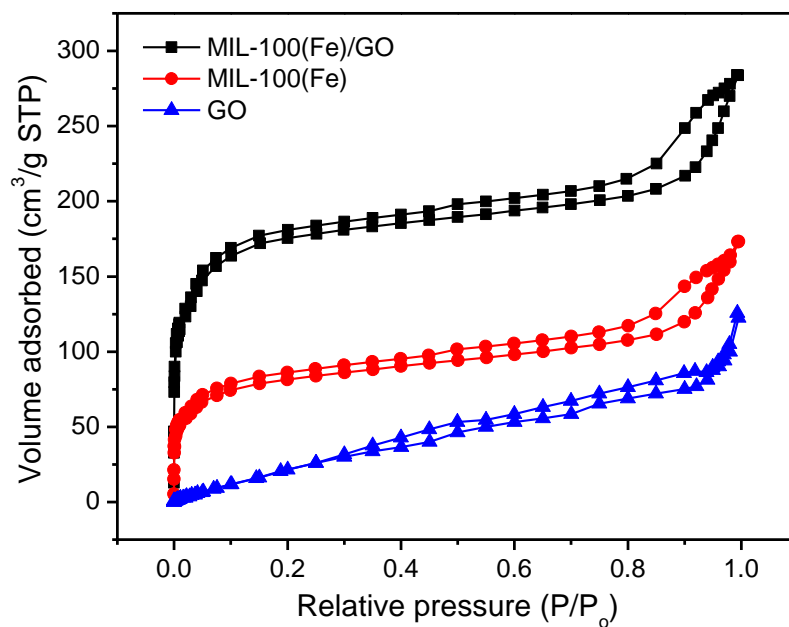
Figure S1 Nitrogen adsorption-desorption isotherm at 77 K of GO, MIL-100(Fe), and MIL-100(Fe)/GO samples.
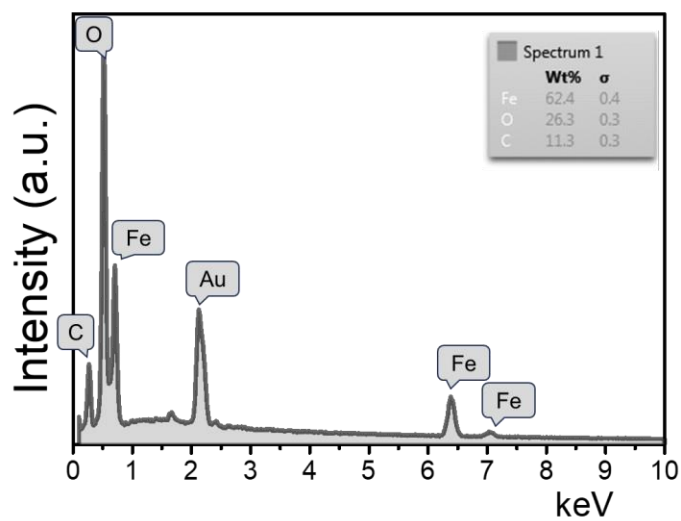
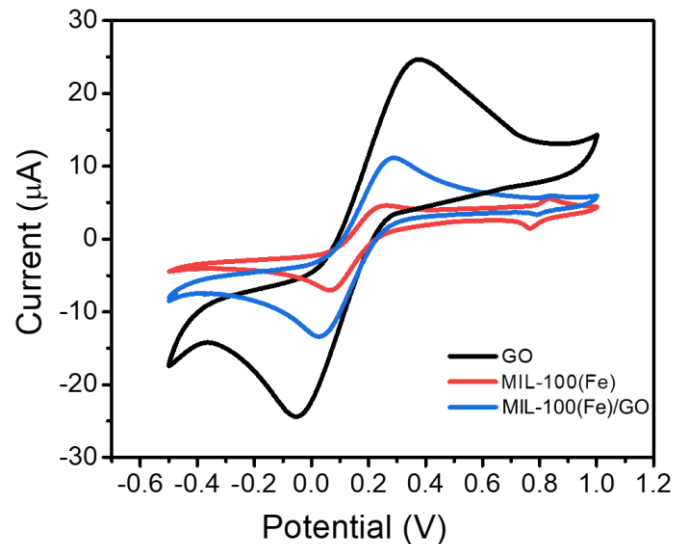

Figure S2 EDS spectrum of MIL-100(Fe).

Figure S3 Cyclic voltammograms of 10 mM ferric/ferrocyanide redox couple in 0.1 M KCl using GO/PGE, MIL-100(Fe)/PGE, and MIL-100(Fe)/GO/PGE.
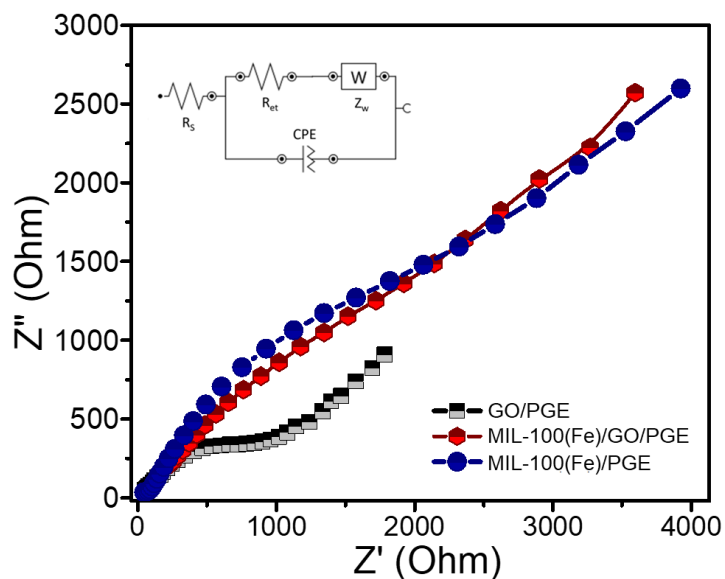

Figure S4 Impedance spectra (Nyquist plots) of 10 mM ferric/ferro-cyanide redox couple in 0.1 M KCl using GO/PGE, MIL-100(Fe)/PGE, and MIL-100(Fe)/GO/PGE (The inset: the equivalent circuit used for the impedance data fitting; Rs is the solution resistance between working and reference electrodes, Zw is Warburg impedance; CPE is the double layer capacitance and Ret is the charge-transfer resistance).
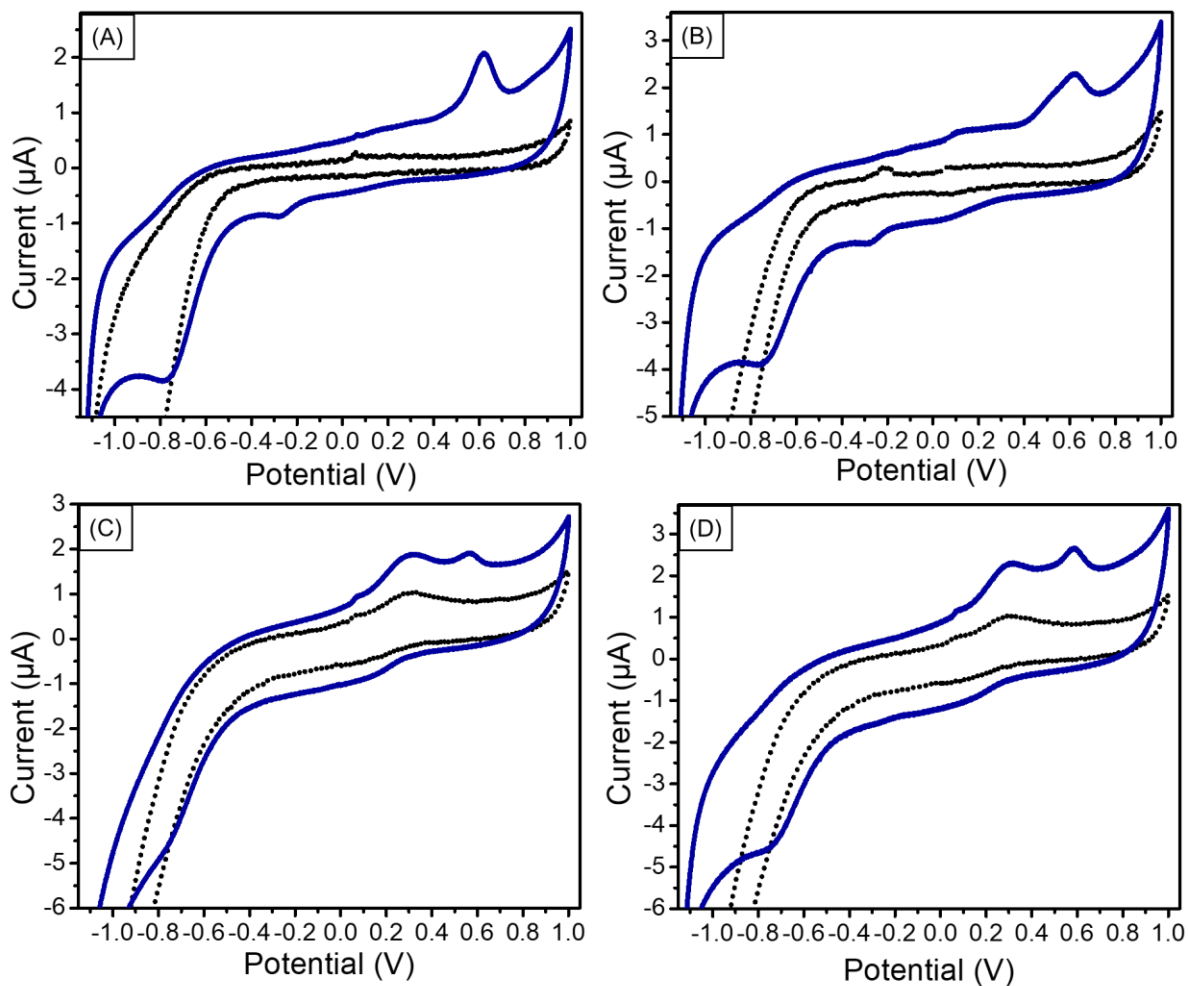
Figure S5 Voltammograms of the electrochemical oxidation of 1.0 mM DEX in 0.04 M BR (pH 2) for (A) Bare PGE, (B) GO/PGE, (C) MIL-100(Fe)/PGE, and (D) MIL-100(Fe)/GO/PGE scanned at 50 mV/s; black dot and blue solid lines correspond to the blank (0.04 M Briton-Robinson buffer) and 1.0 mM DEX solutions, respectively.
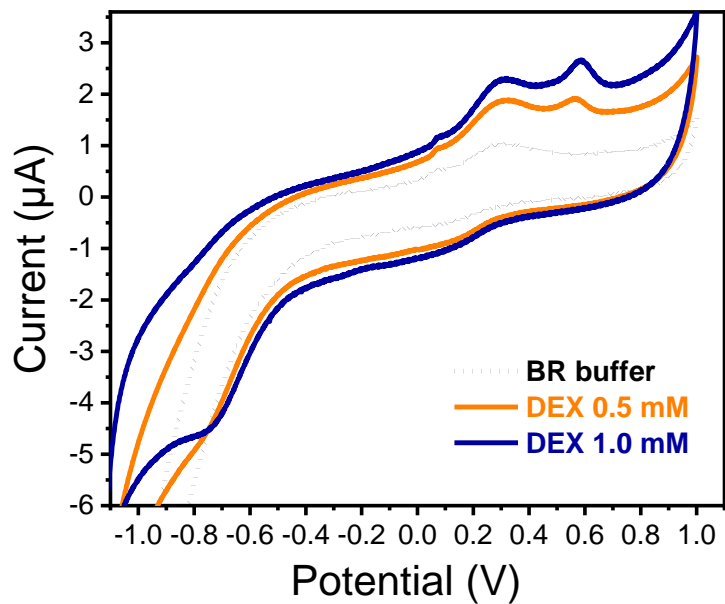
Figure S6 Voltammograms of the electrochemical oxidation of 0.5 and 1.0 mM DEX in 0.04 M BR (pH 2) for MIL-100(Fe)/GO/PGE scanned at 50 mV/s; black dot and solid lines correspond to the blank (0.04 M Briton-Robinson buffer), 0.5 (Orange line) and 1.0 mM (Blue line) DEX solutions, respectively.
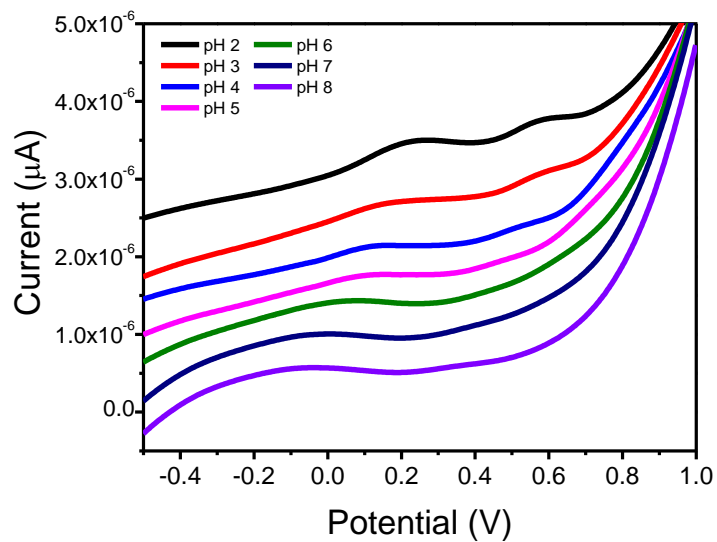
Figure S7 The linear sweep voltammograms of 0.5 mM DEX in in different pH of 0.04 M BR using MIL-100(Fe)/GO/PGE.
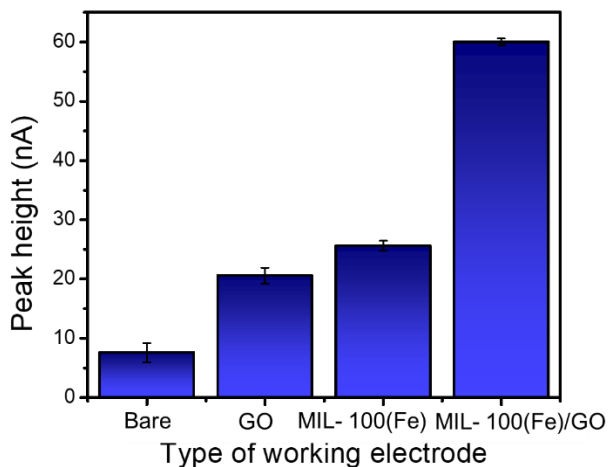

Figure S8 Histograms represent the peak height of different materials compared with bare PGE using 1.0 mM of DEX in a carrier stream of 0.04 M BR buffer (pH 2) in the flow injection system.

Table S1 Real samples analysis for DEX detection using developed method

Sample	Found (mM)	labelled conc. (mM)	%Recovery 20 μM			100 μM			%Error
			Found (μM)	%RR	%RSD	Found (μM)	%RR	%RSD	
D1	2.21	2.12	23.40	105.95	0.27	104.38	102.17	0.52	4.55
D2	2.28	2.12	24.56	111.38	0.19	103.79	101.50	0.58	7.83
D3	0.54	0.53	20.58	100.19	0.02	98.21	97.66	0.30	2.56
S1	ND	-	20.35	101.75	0.04	92.76	92.76	0.63	-
S2	ND	-	20.14	100.7	0.54	103.46	103.46	0.69	-
S3	ND	-	20.46	102.31	0.22	101.57	101.57	0.34	-
S4	ND	-	21.69	108.46	0.07	93.84	93.84	0.87	-
S5	ND	-	20.81	104.07	0.49	97.59	97.59	0.53	-

*D = pharmaceutical sample, S = whitening cream sample, ND = not detectable, RR = recovery,

RSD = relative standard deviation of % recovery

Table S2 Real samples analysis for DEX detection using standard HPLC-DAD method

Sample	%Recovery								%Error
	Found (mM)	labelled conc (mM)	20 µM			100 µM			
			Found (mM)	%RR	%RSD	Found (mM)	%RR	%RSD	
D1	2.18	2.12	23.64	106.53	0.03	104.17	101.84	0.03	3.18
D2	2.25	2.12	21.03	93.91	0.05	110.23	107.98	0.02	6.13
D3	0.53	0.53	17.78	86.25	0.11	100.16	99.63	0.02	0.05
S1	ND	-	19.51	97.57	0.06	102.51	102.51	0.23	-
S2	ND	-	19.35	96.74	0.02	96.22	96.22	0.19	-
S3	ND	-	20.77	103.83	0.01	103.21	103.21	0.01	-
S4	ND	-	19.86	99.31	0.01	100.83	100.83	0.04	-
S5	ND		16.91	84.59	0.03	99.91	99.91	0.05	-

*D = pharmaceutical sample, S = whitening cream sample, ND = not detectable, RR = recovery, RSD = relative standard deviation of % recovery