Supporting Information

Laser-scribed Graphene Electrodes Functionalized with Nafion/Fe_3O_4 Nanohybrids for the Ultrasensitive Detection of Neurotoxin Drug Clioquinol

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Reagents and Materials

Clioquinol (CQL), Nafion (5 Wt%), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), sodium hydroxide (NaOH), potassium chloride (KCl), hydrochloric acid (HCl) and all other interfering species were purchased from Sigma-Aldrich. Polyimide (PI) substrates were purchased from Professional Plastics INC., Taiwan, and used to fabricate LSG electrodes. Iron (III) chloride anhydrous ($FeCl_3$) and Iron (II) chloride tetrachloride ($FeCl_2 \cdot 4H_2O$) were obtained from Alfa Aesar. Potassium ferricyanide ($K_3[Fe(CN)_6]$), and potassium ferrocyanide ($K_4[Fe(CN)_6]$) were purchased from STREM chemicals. Phosphate buffered saline (PBS, pH-7.0) was obtained from Sigma-Aldrich. The polydimethylsiloxane (PDMS) was obtained from Sil-More industrial Ltd., Taiwan. 0.1 M sodium hydroxide (NaOH) is used as the electrolyte for electrochemical tests. All aqueous solutions were prepared using ultrapure water (18.2 MΩ cm) generated by a Direct-Q® 3UV water filtration system. The solvents and chemicals used in this work were of analytical grade and were used as supplied.

Apparatus

The microscopic morphologies of LSG, Fe_3O_4/LSG and Nafion/Fe_3O_4/LSG electrodes were recorded on Zeiss Leo 1530 scanning electron microscopy (SEM, Carl Zeiss microscopy GmbH, Germany) and JEM-2010 (HR) transmission electron microscopy (TEM, Japan). The phase composition and crystal structure of the fabricated LSG, Fe_3O_4/LSG and Nafion/Fe_3O_4/LSG electrodes were performed by X'Pert PRO PANalytical X-ray diffractometer equipped with Ni-filtered Cu-Kα radiation (λ= 0.15465

nm). The Raman spectra were also recorded at ambient temperature with LabRAM xplora Raman spectrometer (Horiba JY Company, Japan). The elemental analysis was performed with an X–ray photoelectron spectroscopy (XPS) AXIS ULTRA DLD ((15 kV) Kratos Analytical, United Kingdom). All the electrochemical measurements including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), differential pulse voltammetry (DPV) and chronoamperometry (CA) were carried-out using a PalmSens4, equipped with PSTrace 5.6 software (PalmSens BV, Houten, The Netherlands).

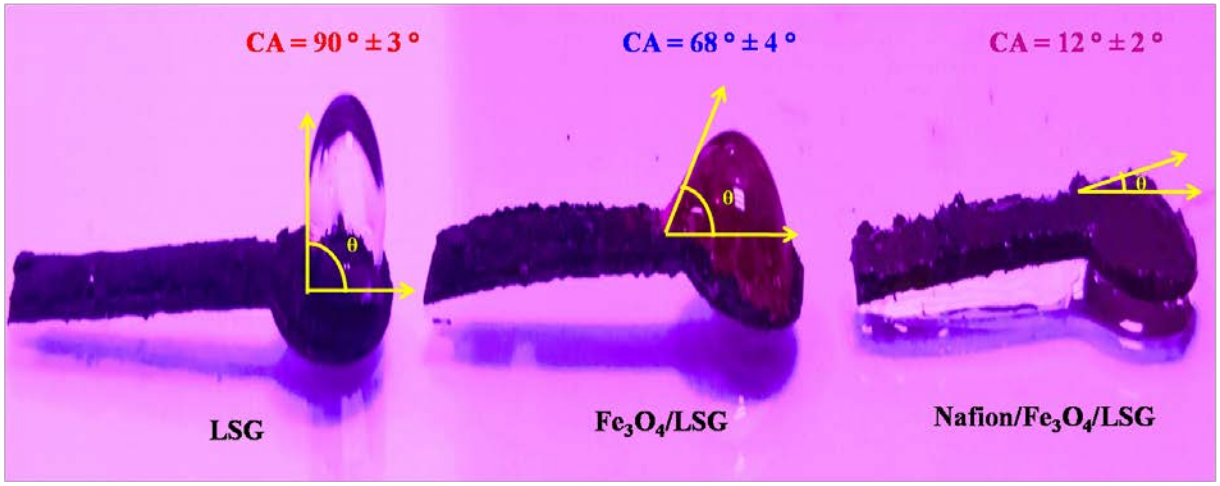

Figure S1. Digital images obtained from measurements of water drop contact angles on LSG, Fe_3O_4/LSG, and Nafion/Fe_3O_4/LSG electrodes.

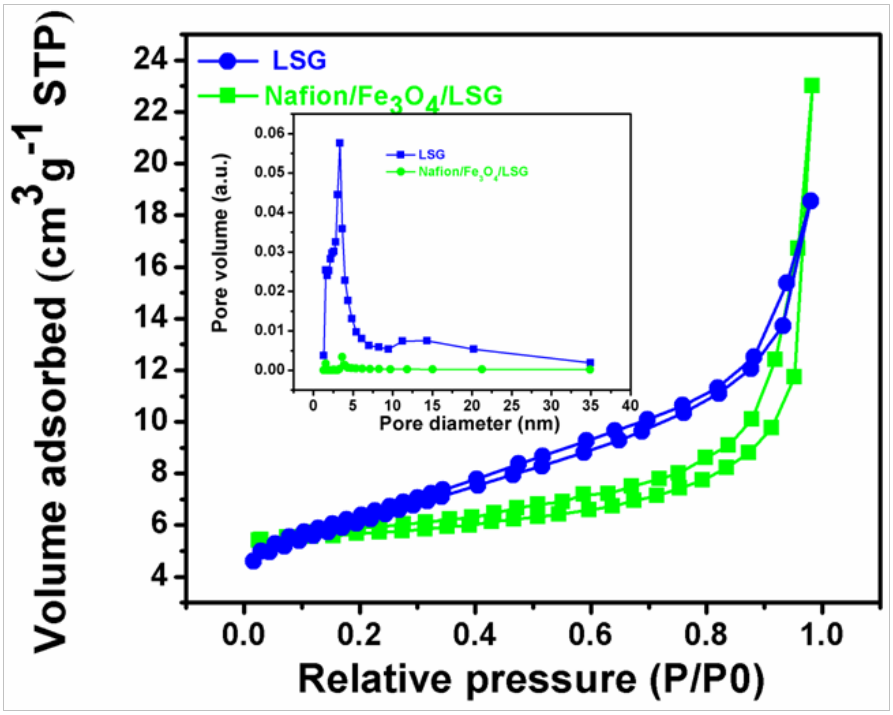

Figure S2. N_2 adsorption–desorption isotherm and pore-size distribution (inset) plot of LSG and Nafion/Fe_3O_4/LSG electrodes.

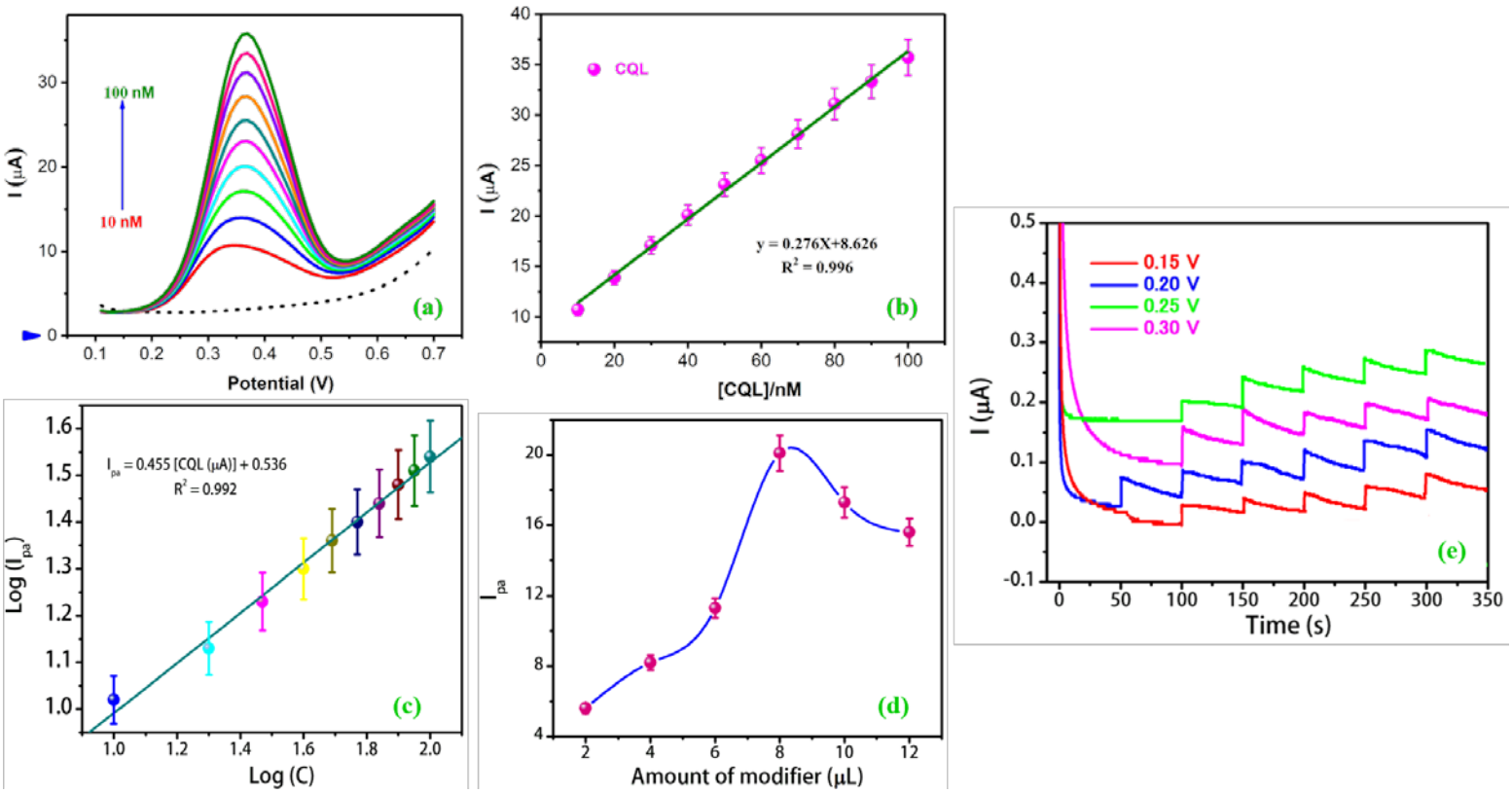

Figure S3. (a) SWV obtained for CQL in the concentration ranging from 10-100 nM. CQL was added in steps of 10 nM each at Nafion/Fe_3O_4/LSG electrode in 0.1 M NaOH. (b) Linearity plot of current vs. concentration. (c) Relationship of logarithm of peak current vs. logarithm of CQL concentration. (d) Effect of modifier amount on the CVs of the fabricated sensor in the presence of 400 nM CQL. (e) CA response of Nafion/Fe_3O_4/LSG at different potentials in 0.1M NaOH with a drop wise addition of 0.01 µM CQL.

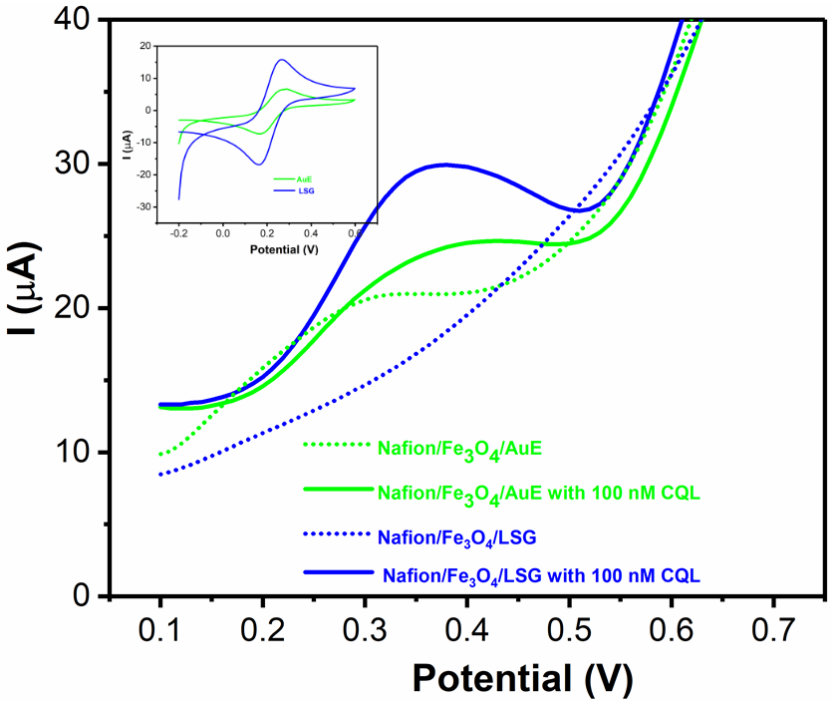

Figure S4. SWV signals observed in a spiked human urine sample (100 nM) from an LSG and AuE modified with Nafion/Fe_3O_4. (Inset: CV scan of an LSG and AuE electrode in a solution containing 1mM $Fe(CN)_6^{3-/4-}$ and 0.1 M KCl at 20 mV/s).

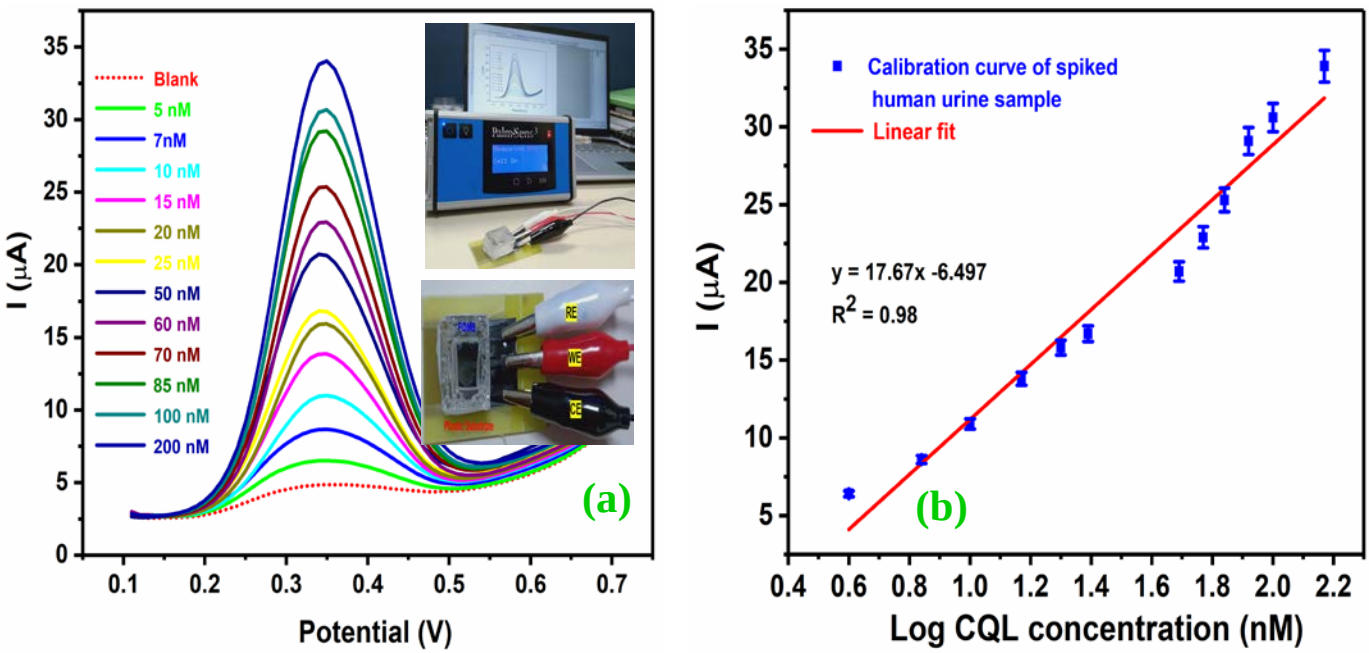

Figure S5. (a) SWV response of the Nafion/Fe_3O_4/LSG upon successive addition of spiked human urine sample (5-200 nM) in 0.1M NaOH by portable biosensor system. (inset: picture of the portable biosensor system). (b) The relationship of logarithm of spiked urine sample concentration vs. peak current response.

Table S1

The determination of CQL in spiked human urine and blood serum samples using Nafion/Fe_3O_4/LSG electrode.

Sample	Added (nM)	Found (nM)	Recovery (%)	[a*]RSD (%, n =3)
Human Blood serum				
	10	9.8	98	0.57
	30	29.6	98.6	0.21
	50	51.3	102.6	2.13
	70	69.7	99.5	2.88
	100	98.8	98.8	1.34
Human urine				
	5	5.1	102	0.12
	10	9.7	97	1.31
	20	20.2	101	1.48
	50	50.3	100.6	2.18
	70	71.3	101.8	0.46
	100	100.8	100.8	0.90

* = mean of replicated measurements (n = 3); [a]RSD = Relative standard deviation

Table S2

The determination of CQL in spiked human urine sample using Nafion/Fe_3O_4/LSG portable mini-electrochemical workstation.

Sample	Added (nM)	Found (nM)	Recovery (%)	[a*]RSD (%, n =3)
Human urine	5	4.56	91.2	0.64
	10	9.84	98.4	0.32
	20	19.87	99.35	1.0
	50	49.65	99.3	1.15
	70	68.95	98.5	0.78
	100	99.32	99.32	1.38
	200	198.53	99.2	2.23

* = mean of replicated measurements (n = 3); [a]RSD = Relative standard deviation