A disposable simultaneous electrochemical sensor array based on molecularly imprinted film at NH_2-graphene modified screen-printed electrode for determination of psychotropic drugs

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Supplemental Information

The FT-IR spectroscopy characterization of the GR-NH2

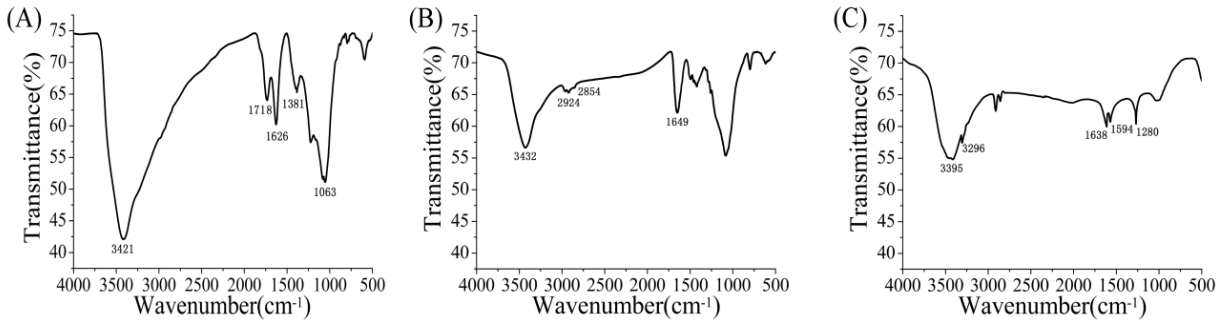

Fig. 1S (A) FT-IR spectrum of GO; (B) FT-IR spectrum of GR; (C) FT-IR spectrum of GR-NH2

The as-prepared GO, GR and GR-NH2 was characterized with FT-IR spectroscopy, as shown in Fig. 1S. In the FT-IR spectrum of GO (Fig. 1S A), we observe a strong and broad absorption at 3421 cm^{-1} due to O-H stretching vibration. The C=O stretching of COOH groups situated at edges of GO sheets is observed at 1718 cm^{-1}. The absorptions due to the O-H bending vibration, epoxide groups and skeletal ring vibrations are observed around 1626 cm^{-1}. The absorption at 1381 cm^{-1} may be attributed to tertiary C-OH groups. The IR spectrum in Fig. 1S B confirms reduction of GO sheets. Here the absorption due to the C=O group (1718 cm^{-1}) is decreased very much in intensity and absorptions at 1626 and 1381 cm^{-1} are absent, suggesting the considerable

deoxygenation by the chemical reduction process. Fig. 1S C showed the IR spectrum of GR-NH_2. A corresponding appearance of a band with lower frequency (1638 cm^{-1}) assigned to the amide carbonyl (C=O) stretch. The NH_2 stretch band appears at 3395 cm^{-1}. The small 3296 cm^{-1} peak may be due to the NH_2 symmetric stretch of the amine group. In addition, the presence of new bands at 1594 and 1280 cm^{-1}, corresponding to N-H in-plane and C-N bond stretching, respectively, further confirms the presence of the amide functional group.

Table S1 Reproducibility experiments of the MIPs sensor.

methcathinone	EC sensor	1	2	3	4	5	RSD
	Current[a](μA)	-17.86	-18.14	-18.20	-17.98	-18.32	1.00%
cathinone	EC sensor	1	2	3	4	5	RSD
	Current[a](μA)	-18.96	-18.52	-18.68	-18.62	-18.64	0.88%

[a]Average of 3 experiment results

Table S2 Repeatability experiments of the MIPs sensor.

methcathinone	solution	1	2	3	4	5	RSD
	Current[a](μA)	-18.28	-18.24	-18.32	-18.30	-18.28	0.16%
cathinone	solution	1	2	3	4	5	RSD
	Current[a](μA)	-18.68	-18.56	-18.74	-18.72	-18.65	0.38%

[a]Average of 5 experiment results

Table S3

Methcathinone				Cathinone			
Samples	Add/ μg mL^{-1}	Recovered[a]/ μg mL^{-1}	Recovery (%)	Samples	Add/ μg mL^{-1}	Recovered[a]/ μg mL^{-1}	Recovery (%)
1	1.63×10^{-5}	1.59×10^{-5}	97.4	1	2.98×10^{-5}	2.94×10^{-5}	98.6
2	8.16×10^{-4}	8.34×10^{-4}	102.2	2	7.46×10^{-4}	7.18×10^{-4}	96.3
3	8.16×10^{-3}	8.04×10^{-3}	98.5	3	8.95×10^{-3}	9.33×10^{-3}	104.2

[a]Mean of 11 determinations±S.D.

After optimization and development of the method, various structural analogs were examined with respect to their interference with the determination of methcathinone and cathinone. Structural analogs such as diethylether, acetone, ephedrin and toluene were investigated. As shown in Table S4, the sensor yielded a small amperometric fluctuation response for the structural analogs with various concentrations level. It was obvious that structural analogs could not rebind on the electrode, and had small response on MIF sensor. Thus they would not interfere with the determination of the methcathinone and cathinone. For NIP sensor, either methcathinone and cathinone or structural analogs, there were very nearly no current responses. This might attribute that there were no suitable sites for methcathinone and cathinone in NIP. Evidently, the strength of rebinding depended on the extent of compatibility of the molecules of compounds being determined and the molecular cavities of MIF. It confirmed that the sensor based on the MIF had a good selectivity of recognition to methcathinone and cathinone.

Table S4

Acrossing reagents[a]	$C_{interfering\ agents}$(ng·mL^{-1}); Current change(μA)[b]					
	0.1	*5*	*25*	*100*	*mean*±SD(μA)	RSD(%)
Cathinone+Diethylether	15.94	15.96	16.02	16.04	15.99±0.05	0.3
Cathinone+Acetone	15.94	15.94	15.98	16.02	15.97±0.04	0.3
Cathinone+Ephedrine	15.94	15.98	16.02	16.06	16.00±0.05	0.3
Cathinone+Toluene	15.94	15.96	16.00	16.02	15.98±0.04	0.3
Methcathinone+Diethylether	13.86	13.88	13.94	13.98	13.92±0.06	0.4
Methcathinone+Acetone	13.86	13.90	13.92	13.94	13.91±0.03	0.2
Methcathinone+Ephedrine	13.86	13.84	13.98	14.02	13.93±0.09	0.7
Methcathinone+Toluene	13.86	13.88	13.94	13.92	13.90±0.04	0.3

[a] containing 0.5 ng mL^{-1} Cathinone or methcathinone and various concentrations of interfering agents. [b] the average value of 11 assays.