Supplementary Material

for

Polydopamine-based molecularly imprinted electrochemical sensor for highly selective determination of ecstasy components

Chen Li[1], Dongfang Han[1], Zhifang Wu[1], Zhishan Liang[1], Fangjie Han[1], Ke Chen[1], Wencai Fu[1], Dongxue Han*[1], Yukai Wang*[2], Li Niu[1]

[1]*Guangzhou Key Laboratory of Sensing Materials & Devices, Center for Advanced Analytical Science, School of Chemistry and Chemical Engineering, c/o School of Civil Engineering, Guangzhou University, Guangzhou 510006, PR China.*

[2] *Guangdong Provincial Key Laboratory of Psychoactive Substances Monitoring and Safety, Anti-Drug Technology Center of Guangdong Province, Guangzhou 510230, PR China.*

* Corresponding authors.

E-mail address: dxhan@gzhu.edu.cn (D. Han); gdgawhk@163.com (Y. Wang)

Materials and reagents

3,4-Methylenedioxyphenethylamine hydrochloride (MDEA) (chemically pure, >95%) was purchased from Beijing InnoChem Science & Technology Co., Ltd. (Beijing, China) and used as template molecule. (±)-3,4-methylenedioxyamphetamine (MDA), (±)-3,4-methylenedioxymethamphetamine (MDMA), (±)-Methamphetamine (MA), Ketanine hydrochloride (Ketanine) and Morphine dissolved in methanol were received from Guangdong Provincial Public Security Department. Dopamine hydrochloride (DA), sucrose, mannitol, vitamin C were bought from Shanghai Aladdin Chemistry Co., Ltd. (Shanghai, China). $Na_2HPO_4 \cdot 3H_2O$, NaH_2PO_4, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6] \cdot 3H_2O$, KCl, HCl, NaOH, H_2SO_4 were of analytical grade and used without further purification.

Phosphate buffered solution (0.1 mol/L PBS, pH 7.5) containing Na_2HPO_4, NaH_2PO_4, NaCl and $[Fe(CN)_6]^{4-/3-}$ (5 mmol/L) prepared in 0.1 mol/L KCl solution containing the equimolar mixture of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6] \cdot 3H_2O$ were used as supporting electrolyte and redox probe, respectively. Ultrapure water (≥18MΩ/cm) was obtained by Millipore ultrapure water system (Shanghai, China) to prepare the aqueous solutions throughout all the work.

Apparatus and instruments

All electrochemical experiments, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV), were performed on CHI660E electrochemical workstation (Shanghai Instrument Co. Ltd., Shanghai, China) by using a classical three-electrode system consisted of an MIP-modified gold disk electrode (Au-E, 3mm diameter) as working electrode, a KCl-saturated Ag/AgCl electrode as the reference electrode and a Pt wire electrode as the auxiliary electrode. Scanning Electron Microscope (SEM) was conducted by Phenom ProX Desktop SEM (Thermo Fisher Scientific Co. Ltd., United States).

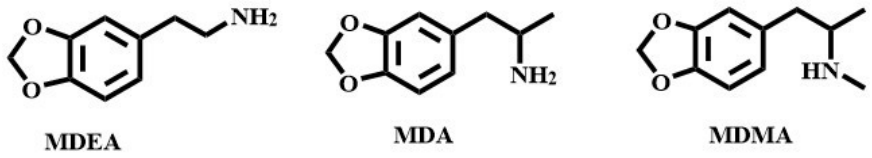

Fig. S1 Chemical structure of MDEA, MDA and MDMA

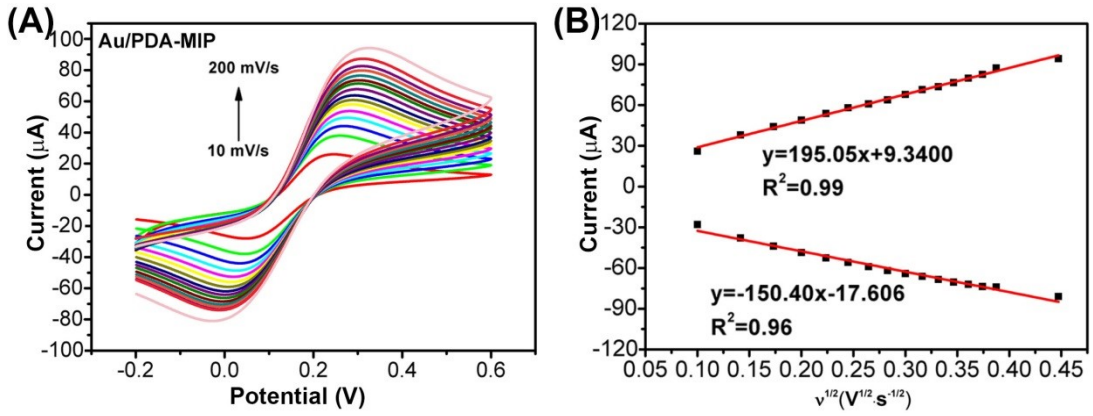

Fig. S2 (A) Cyclic voltammograms of MIP@PDA Au/E in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ solution with 0.1 M KCl at the scan rates from 10 to 200 mV s^{-1}. (B) Calibration curves of anodic and cathodic peak current values versus square root of scan rate.

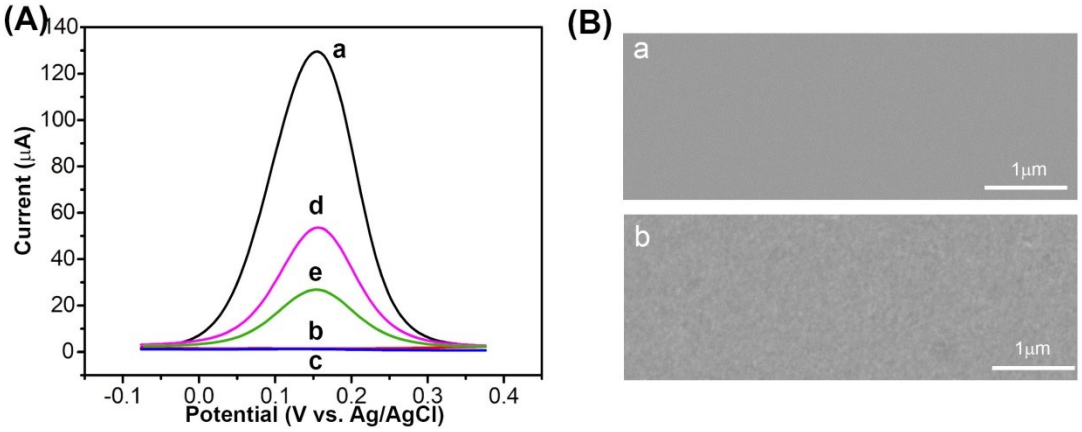

Fig. S3 (A) DPV responses for different steps of MIP@PDA/Au-E in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl: a) bare Au-E; b)MIP@PDA/Au-E; c)NIP@PDA/Au-E; d) MIP@PDA/Au-E after eluted the template molecule; e) MIP@PDA/Au-E after recognized MDA. (B) SEM images of (a) bare Au-E and (b) MIP@PDA/Au-E.

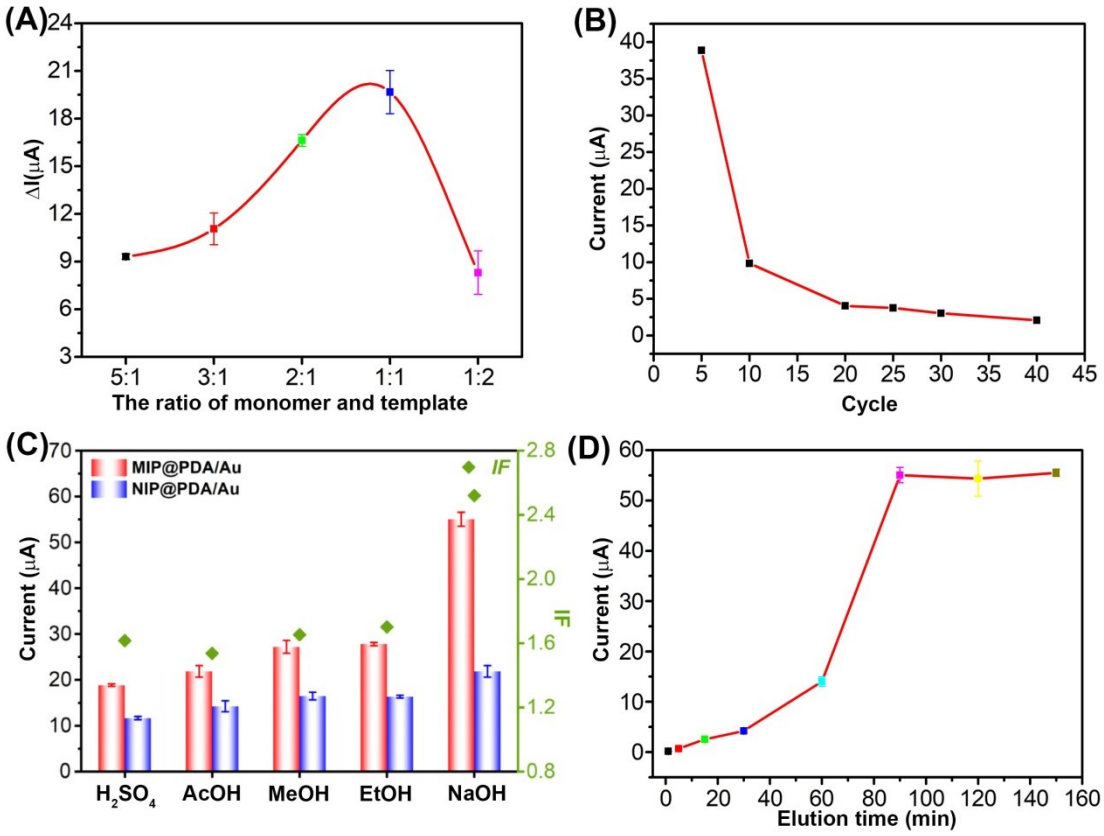

Fig. S4 Optimization of (A) molar ratio of monomer to template, (B) the scan cycles, (C) elution solutions and (D)elution time for modified electrode

Table S1 Selectivity of MIP@PDA Au-E for ecstasy and interfering molecules

Molecules	ΔI_{MIP}/μA	ΔI_{NIP}/μA	IF[a]	β[b]
MDA	19.67	5.45	3.6	1.0
MDMA	18.94	4.89	3.9	0.9
MA	12.53	8.60	1.5	2.5
Morphine	5.09	2.80	1.8	2.0
Ketamine	5.76	5.13	1.1	3.2
Sucrose	4.87	3.18	1.5	2.4
Mannitol	4.87	4.24	1.1	3.1
Vitamin C	1.80	1.17	1.5	2.3

[a] $IF=(\Delta I_{MIP})/(\Delta I_{NIP})$

[b] $\beta=(IF_{MDA}/IF_{interferent})$

Table S2 Detection of MDA and MDMA in urine sample by using MIP@PDA Au-E (*n=3*)

Real sample	Target	Add (uM)	Found(uM)	Recovery (%)	RSD (%)
Urine	MDA	0.50	0.53	106.5	8.63
		1.00	1.06	106.5	1.26
		5.00	5.10	102.0	0.54
	MDMA	0.50	0.50	99.27	0.54
		1.00	1.08	108.0	4.62
		5.00	4.97	99.49	0.92

Table S3 Signals of blank sample for the proposed method

Number	ΔI_{blank}/μA	Number	ΔI_{blank}/μA
1	1.17	7	0.43
2	4.42	8	8.93
3	0.23	9	1.02
4	5.05	10	1.15
5	1.97	Average	3.04
6	6.04	Standard Deviation	2.92

Table S4 The relevant parameters for calculating LOD

Parameter	Value
Noise[a]/μA	2.92
m[b]	11.277
k[c]/μA	24.921
S/N	3
LOD/μM	0.037

[a] is the standard deviation of ΔI_{blank}; [b] is slope of calibration curve; [c] is intercept of calibration curve