Supporting materials

Lignosulfonate situ-modified reduced graphene oxide biosensors for electrochemical detection of dopamine

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1.Preparation of graphene oxide (GO)

GO was prepared by the oxidation of natural graphite powder (325 meshes) according to a modified Hummers' method (Hummers, 1958). Graphite powder (3.0 g) and sodium nitrate (1.5 g) were added to concentrated H_2SO_4 (70 mL) under stirring in an ice bath. $KMnO_4$ (9.0 g) was added slowly to keep the temperature of the suspension lower than 5 °C. Successively, the reaction system was transferred to a 35 ± 5 °C bath and vigorously stirred for about 0.5 h. Then, 150 mL water was added, and the solution was stirred for 15 minutes at 90 ± 5 °C. Additional 500 mL water was added and followed by a slow addition of 15 mL H_2O_2 (30%), turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions, the resulting solid was dried in air and diluted to 600 mL, making a graphite oxide aqueous dispersion, the obtained dispersion was treated in ultrasound for 30 minutes, and then centrifuged at 4,000 rpm for 30 minutes to remove the graphite and graphite oxide residue in the lower layer. Finally, it was purified by dialysis for one week using a membrane with the molar mass cut off of 8,000 to 14,000 g mol^{-1} to remove the remaining metal species.

2. Electrochemical measurements

All electrochemical measurements were performed on an electrochemical workstation (CHI-760E, Austin, Texas) with a standard three-electrode system. A GCE (3 mm in diameter) deposited with the LS-rGO as the modifier, platinum electrode, and saturated calomel electrode were selected as the working electrode, counter electrode, and reference electrode, respectively. The detection is directly conducted in PBS solutions containing different DA, which ~~The sample solutions~~ were purged with nitrogen for about 30 min to remove oxygen prior to the beginning of a series of experiments. The specific parameter settings are as follows: Cyclic voltammetry was carried out at a serious of scan rate from 50 mV s^{-1} to 500 mV s^{-1}, and the quiet time is 5 s, in the potential range of -0.2 V to 0.4 V. All tests were performed in 0.1 mol L^{-1} phosphate buffered saline (PBS) solution with a pH value from 4.0 to 8.0 at 25 °C. Electrochemical impedance spectroscopy (EIS) was performed in 5 mM [Fe (CN)$_6$]$^{4-/3-}$ and 0.1 M KCl solution, at an amplitude of 5 mV in the frequency range between 0.1 Hz and 1000 kHz.
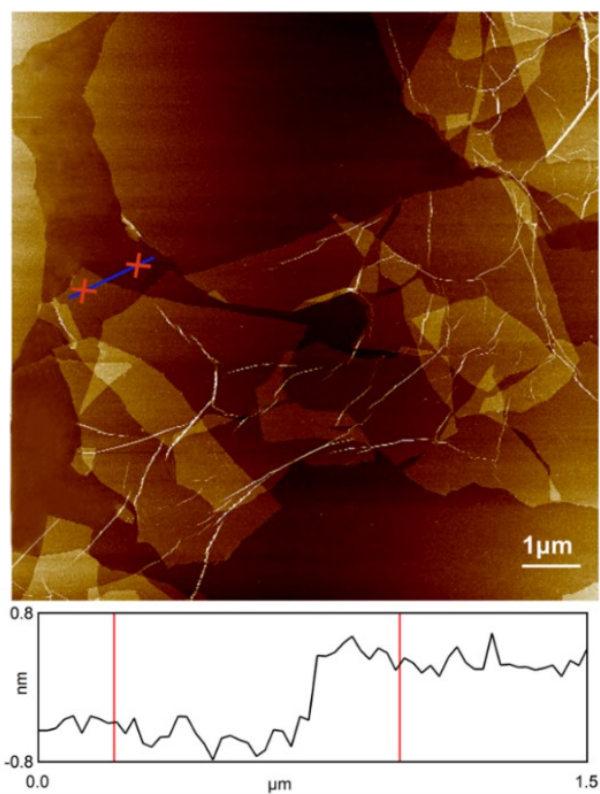
Figure S1. The atomic force microscope (AFM) image and height profile of GO sheets

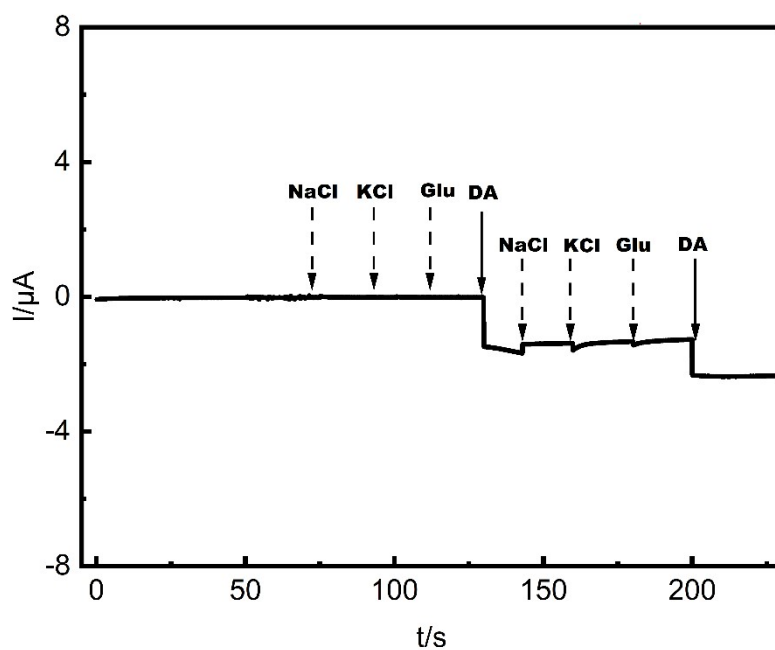on a freshly cleaved mica surface.

Figure S2. i-t curve of LS-rGO sensor, for the addition of 1 μM NaCl, KCl, Glucose,

and 5 μM NaCl, KCl, Glucose respectively at the potential of 0.05 V.

Table S1. Comparison between electrochemical biosensor and other analytical methods

Detection method	advantage	disadvantage
Fluorescence spectrometry	Simple, fast and sensitive operation	fluorescence quenching effect and scattered light interference; The DA detection in complex systems is difficult;
High performance liquid chromatography	Integrating of separation, qualitative analysis and quantitative analysis; Separation and analysis of multiple coexisting substances;	Expensive instrument price; High daily maintenance and analysis cost; Long analysis time;
Capillary electrophoresis	Short separation time; high separation efficiency; small system volume and easy integration of different operation units;	Weak separation capacity; high requirements for PH value; poor reproducibility;
Colorimetry	Fast color rendering; visualization;	Low sensitivity; High purity tested component; Further analysis with other instruments;
Electrochemical analysis method	Simple operation; high sensitivity; good selectivity; In vivo analysis;	The stability needs to be improved; Electrode modification materials need to be developed to improve detection accuracy and sensitivity;

Table S2. Elemental analysis of the rGO and LS-rGO

Sample	C	O	N	S	O/C
rGO	84.30	12.36	3.34	0	14.66
LS-rGO	77.28	19.41	2.42	0.89	25.12

Table S3. Comparison of dopamine detection performance of modified electrodes in different literatures

Materials	Liner range(μm)	Detection limit（μM）	Refs.
TiO2/Gr/GCE	5−200	2	1
Gr/Chitosan/GCE	4.0−100	2.64	2
Au/Cu$_2$O/rGO/GCE	10−90	3.9	3
PG/GCE	5−710	2	4
PANI-H$_2$SO$_4$@Au	10−100	6.7	5
CNF-RGO	10−60	1.16	6
PANI-GO/GCE	2−18	2.0	7
Ni/rGO-oxCNF	10−16	1.64	8
rGO/Au nanoparticles	1−60	0.38	9
GEF/CFE	0.7−45.21	1.91	10
BAMB/Co(OH)$_2$/GO/GCE	3−20,25−100	0.4	11
LS-rGO/GCE	1.08−100	1.08	This work

Table S4. The ionic states of DA in different pH solutions

	H$_3$DA$^+$(%)	H$_2$DA$^+$(%)	HAD$^-$(%)	DA^{2-}(%)
pH 4.7	100	0	0	0
pH 7.0	99	1	0	0
pH 9.2	38.7	58.5	2.8	0
pH 11.7	0	5.1	81.8	13.1
pH 14.6	0	0	0.8	99.2

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