Supporting information

# An electrochemical ratiometric biosensor for the detection of dopamine based on MXene-Au nanocomposite

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## 1. Experimental sections

### Regents and instruments

5 mg·mL$^{-1}$ multilayer $Ti_3C_2T_x$ MXene solution was purchased from Beike 2D Materials Co. Ltd (Suzhou, China). Methylene blue, $HAuCl_4 \cdot 3H_2O$, and dopamine were bought from Aladdin Reagent (Shanghai) Co. Ltd. $K_3[Fe(CN)_6]$, $Na_2HPO_4$, $NaH_2PO_4$, and KCl were purchased from Shanghai Macklin Biochemical Co., Ltd. The above reagents were analytically pure and used without further treatment. Milli-Q water purification system was employed to produce the ultrapure water (18.2 MΩ·cm) used in this work.

Transmission electron microscopy (TEM) images were observed on a JEM-2100 instrument. X-ray diffraction (XRD) measurements were conducted on a Rigaku Smartlab diffractometer with Cu Kα radiation. All the electrochemical measurements were performed on a CHI660E electrochemical station (Shanghai CH Instruments Co. Ltd) with three-electrode system: modified glassy carbon electrode as working electrode, platinum wire as counter electrode and Ag/AgCl (3 M KCl) as reference electrode.

### Synthesis of MXene-Au nanocomposite

MXene-Au was prepared based on the reported reference [24] with minor modification. First, 0.2 mL MXene solution (5 mg·mL$^{-1}$) was dropped into 4.8 mL water and sonicated for 30 min. Next, 1.0 mL $HAuCl_4$ (20 mM) was dropped into the above solution. After reacting for 5 min under continuously stirring, the mixture was centrifugated and washed three times with water. Finally, MXene-Au nanocomposite was obtained by drying the precipitate at 60℃ for 12 h in vacuum.

### Synthesis of MB-MXene-Au nanocomposite

1.0 mg MXene-Au nanocomposite was added into 1.0 mL 25 μM methylene blue (MB) solution and sonicated for 1 h. The superfluous MB was removed by centrifugation and washing.

### Fabrication of MB-MXene-Au/GCE

First, glassy carbon electrode (GCE) was polished with $Al_2O_3$ suspension on polishing cloth. After being washed with water and ethanol, the performance of GCE

was tested by scanning the cycle voltammetry of $[Fe(CN)_6]^{3-/4-}$ in 0.10 M KCl solution. Then the electrode was rinsed well with water and dried with nitrogen. Next, 6 μL 1 $mg \cdot mL^{-1}$ MB-MXene-Au solution was dropped on the electrode surface and dried naturally. Finally, 6 μL 0.025% Nafion was added on MB-MXene-Au/GCE to immobilize MB-MXene-Au on the electrode firmly.

**Electrochemical measurements**

Nafion/MB-MXene-Au/GCE was immersed into 5 mL pH 6.0 PBS containing different concentration of dopamine for electrochemical detection.

Differential pulse voltammetry (DPV) was measured with the parameters: +0.5 ~ -0.5V scan range, 4 mV potential increment, 50 mV pulse width, 50 mV amplitude, and 0.5 s pulse period. The electrochemical impedance spectroscopy (EIS) was carried out in 0.1 M KCl solution containing 20 mM $[Fe(CN)_6]^{3-/4-}$ with a frequency range from 0.1 Hz to 100 kHz. The amplitude of the applied sine wave potential was 5 mV and the formal potential of the system was set at +0.22 V.

**2. Figures**

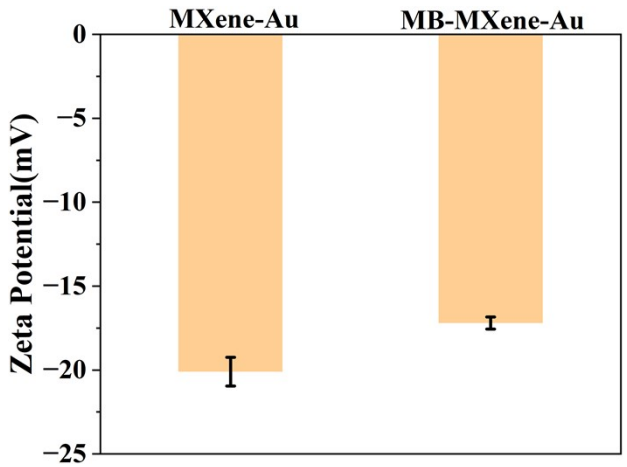


Figure S1. Zeta potential of MXene-Au and MB-MXene-Au

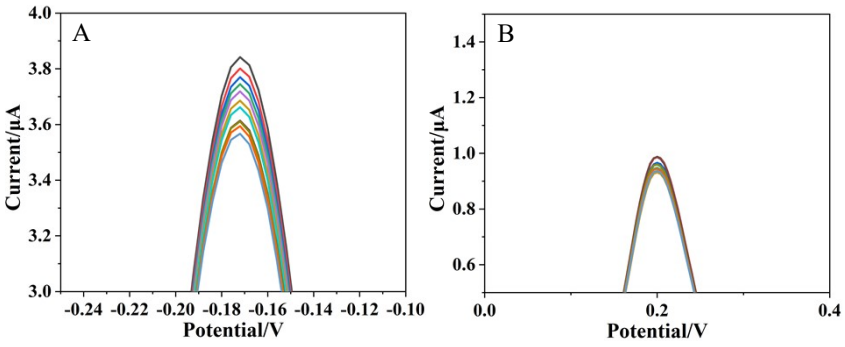


Figure S2. Stability study of the ratiometric biosensor. (A) and (B) are the local enlargement of DPV for MB and DA, respectively.

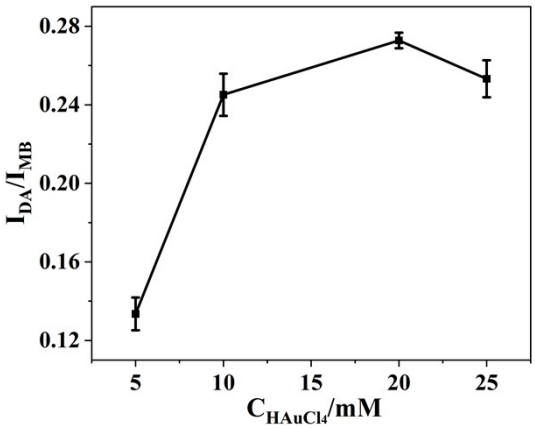


Figure S3. Effect of $HAuCl_4$ concentration on the performance of the ratiometric biosensor.

## 3. Tables

Table S1. Comparison of of DA detection based on various modified nanomaterials

| Modified material | Detection technique | Linear range | Detection limit | Reference |
|---|---|---|---|---|
| Perylene diimide-$Ti_3C_2T_x$ | DPV | 100-1000 μM | 0.24 μM | 1 |
| Ionic liquid/$Ti_3C_2Cl_2$ | DPV | 10-2000 μM | 0.70 μM | 2 |
| $Ti_3C_2T_x$/DNA/Pd/Pt | DPV | 0.2-1000 μM | 0.03 μM | 3 |
| $Ti_3C_2$/G-MWCNTs/ZnO | DPV | 0.01-30 μM | 3.3 nM | 4 |
| $Ti_3C_2$/Holey graphene | DPV | 0.5-50 μM | 0.06 μM | 5 |
| SWCNT | DPV | 0.4-150.0 μM | 0.22 μM | 6 |
| S-doped graphene | DPV | 0.2-12 μM | 0.015 μM | 7 |
| N-doped reduced GO | DPV | 0.5-150 μM | 0.41 μM | 8 |
| 3D N-doped graphene | DPV | 1-1000 μM | 0.26 μM | 9 |
| MXene-ERHG[a] | DPV | 0.3-35 μM | 0.071 μM | 10 |
| Cu- MOFs-MWCNTs | Ratiometric DPV | 0.3-40 μM | 0.026 μM | 11 |
| MB[b]/BP[c]-CNT | Ratiometric DPV | 0.5–350 μM | 0.15 μM | 12 |
| MWCNT | Ratiometric DPV | 1.0–20.0 μM | 0.23 μM | 13 |
| $MnO_2$/MWCNT | Ratiometric DPV | 1.0–50.0 | 0.8 | 14 |
| p(XA)[d]/Au/Cu-TCPP | Ratiometric DPV | 5 - 125 μM | 1.0 | 15 |
| MIPs[e]/pThi[f]/Au-Cu alloy | Ratiometric DPV | 0.3–100 μM | 0.1 μM | 16 |
| **MB-MXene-Au** | **Ratiometric DPV** | **0.1–100 μM** | **0.04 μM** | **This work** |

Note:

[a]ERHG: electrochemically reduced holey graphene;

[b]MB: methylene blue;

[c]BP: 4-(pyren-4-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanamide;

[d]pXA: polyxanthurenic acid;

[e]MIPs: molecularly imprinted polymers (MIPs);

[f]pThi: polythionine.

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