

Supporting Information

An Electrochemical Sensor for Sensitive Detection of Dopamine Based on the
COF/Pt/MWCNT-COOH Nanocomposite

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1. Experimental section

Reagents.

1,3,5-Tris(4-aminophenyl)benzene (TAPB) and 2,5-divinylterephthalaldehyde (DVA) were obtained from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. Acetonitrile (CH₃CN), sodium borohydride (NaBH₄), and dopamine (DA) were supplied by Sigma-Aldrich. Carboxylic-functionalized multiwall carbon nanotube (MWCNT-COOH) was obtained in Nanjing XF NANO Materials Tech Co., Ltd (Nanjing China). Potassium tetrachloroplatinate (K₂PtCl₄) was purchased from Strem Chemicals. Acetic acid (CH₃COOH) was provided by Xilong Scientific. Ethanol (CH₃CH₂OH) was purchased from Sinopharm Chemical Reagent Co., Ltd. The phosphate buffer solution (PBS, pH 7.4, 0.1 M) was prepared from Na₂HPO₄ and NaH₂PO₄. Clinical human serum samples were kindly provided by the Second Hospital of Jilin University (Changchun, China). Millipore ultrapure water (18.25 MΩ·cm) was used throughout the experiment.

Apparatuses.

The transmission electron microscopy (TEM) images were acquired by a TECNAI F20 microscope operated at 200 kV. The scanning electron microscopy (SEM) images were obtained on OXFORD Instrument XMAX with a 20 kV accelerating voltage. The Fourier transform infrared (FT-IR) spectra were carried out on a Bruker VERTEX70 spectrometer within the scope of 500-4000 cm⁻¹ (Ettlingen, Germany). The X-ray photoelectron spectroscopy (XPS) measurements were taken on an ESCALAB MK II spectrometer (VG Scientific) using Al Kα as the radiation. The X-ray diffraction (XRD) was performed on a D8 ADVANCE diffractometer (Bruker, Germany) with a Cu-Kα radiation ($\lambda = 0.154$ nm).

Measurements.

All electrochemical experiments were carried out with a CHI660E (Chenhua Instruments, Shanghai, China) electrochemical workstation with a traditional three-electrode system, which is composed of a modified glassy carbon electrode (GCE) ($\Phi = 3$ mm) as the working electrode, a platinum wire as the counter electrode,

and an Ag/AgCl (saturated with KCl) as the reference electrode. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were measured in 0.1 M KCl solution containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The frequency range of EIS was 0.1 Hz - 100 kHz. The applied potential range for CV measurement was from -0.2 to 0.6 V with the scan rate of 100 mV/s. For dopamine (DA) measurement, the differential pulse voltammetry (DPV) was conducted in 0.1 M PBS (pH 7.4). The experiment parameters of DPV were as follows: initial potential 0.0 V, final potential 0.4 V, pulse height 50 mV, step height 4 mV, pulse width 0.05 s. All the electrochemical experiments were carried out at room temperature. To detect DA in human serum, human serum sample was diluted 20-fold using PBS (pH 7.4) buffer. Then the standard addition method was used to evaluate the practical applicability according to the above procedures under the optimized conditions.

Synthesis of materials.

The synthesis of COF was carried out according to a previously reported method with slight change¹. 1,3,5-Tris(4-aminophenyl)benzene (TAPB, 0.08 mmol) and 2,5-divinylterephthalaldehyde (DVA, 0.12 mmol) were ultrasonically dissolved in 10 mL of acetonitrile to obtain a homogenous yellow solution. Next, 1.4 mL of 12 M acetic acid was added into the above solution. After that, the mixed solution was vigorously shaken for 1 min on a vortex mixer and kept standing for two weeks at room temperature. The yellow sediment was collected by centrifugation and washed with ethanol for three times and dried under a vacuum at 60 °C.

The COF/Pt was synthesized as follows. First, 0.5 mg of the as-prepared COF was ultrasonically dispersed in 1 mL ultrapure water for 10 min. Then, potassium tetrachloroplatinate (K_2PtCl_4) aqueous solution (10 mM) with different volumes (5, 10, 20, 40, 80 μL) was injected into the dispersion under mixing. After stirring for 1 h, 0.2 mL of NaBH_4 solution (1.5 mg/mL) was rapidly injected into the above solution and the mixed solution was continued stirring for another 3 h. The precipitate was collected and washed with deionized water for three times. Afterwards, the prepared COF/Pt was dried under a vacuum at 60 °C.

To obtain COF/Pt/MWCNT-COOH, 0.5 mg COF/Pt and MWCNT-COOH with different quantities (0.05, 0.25, 0.5, 2.5, 5 mg) were dissolved in 1 mL of ultrapure water, respectively. Then, the mixture kept ultrasonication for 0.5 h and agitated for another 2.5 h. Finally, the black powder was collected by centrifugation and dispersed in 1 mL of ultrapure water for further use.

Preparation of the modified electrodes.

The GCE was polished with 1.0, 0.3, and 0.05 μm Al_2O_3 powders in sequence followed by successively sonicated in water, ethanol, and water each for 2 minutes, and dried with nitrogen flow for further use. Finally, 12 μL of the above COF/Pt/MWCNT-COOH suspension was dropped on the surface of the pretreated GCE and dried at room temperature without controlling humidity.

2. Supplementary results and discussions

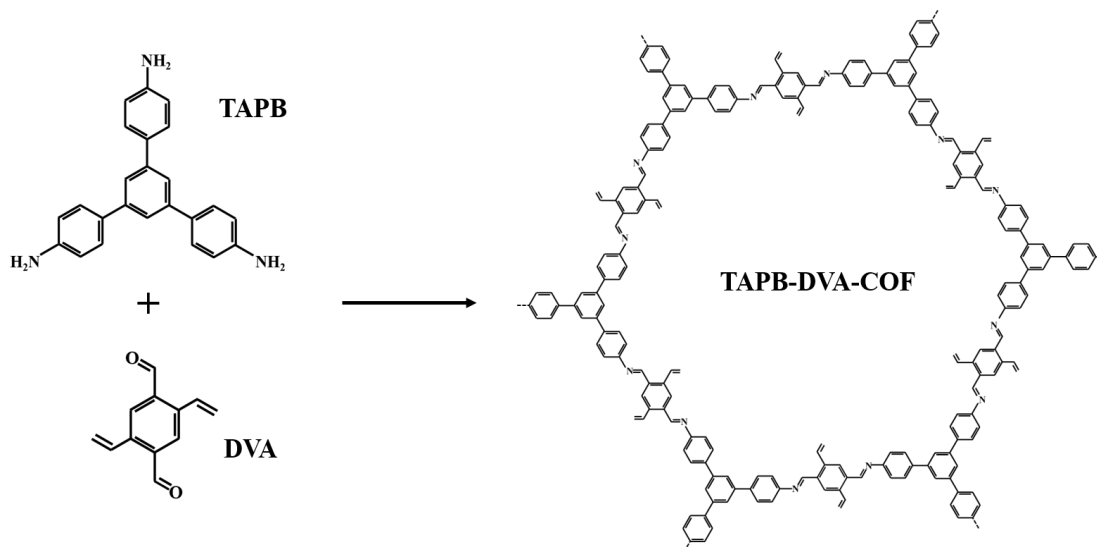


Fig. S1. Schematic illustration of the synthesis and molecular structure of the TAPB-DVA-COF.

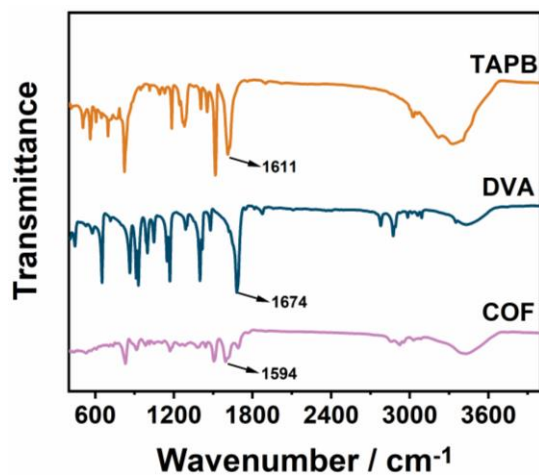


Fig. S2. FT-IR spectra of TAPB, DVA, and COF.

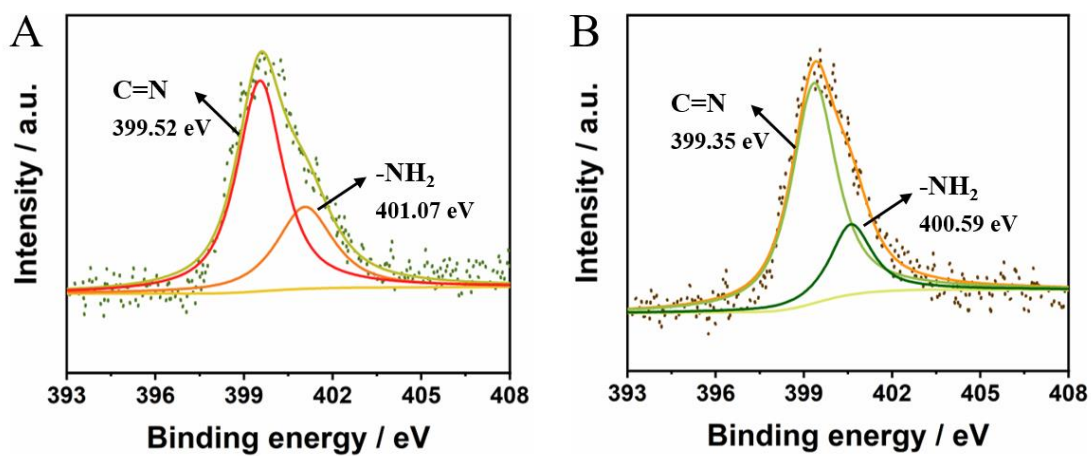


Fig. S3. N 1s region in the XPS of (A) COF and (B) COF/Pt.

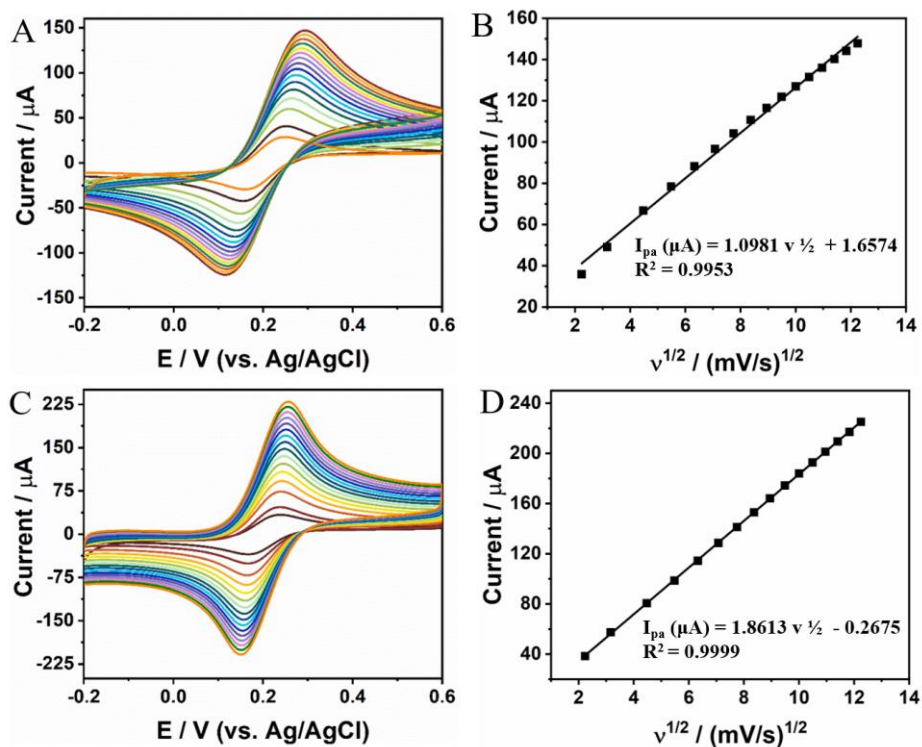


Fig. S4. CV curves and plots of the anodic peak current versus the square root of scanning rate for (A, B) bare GCE and (C, D) COF/Pt/MWCNT-COOH/GCE in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution containing 0.1 M KCl.

The electroactive surface areas of the bare GCE and COF/Pt/MWCNT-COOH/GCE were evaluated by following equation: $I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$, where I_p is the anodic or the cathodic peak current (A), n refers to the electron transfer number, A is the electroactive surface area (cm^2), D is the diffusion coefficient of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ($\text{cm}^2 \text{ s}^{-1}$), C is the concentration of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe (mol cm^{-3}), and $v^{1/2}$ is the square root of scan rate (V s^{-1}). For our experimental system, $n = 1$ and $D = 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

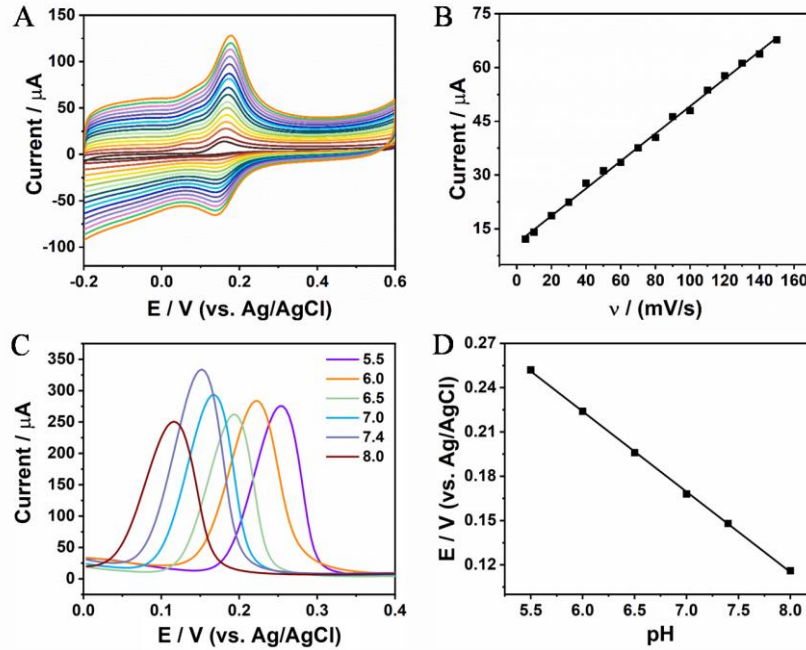


Fig. S5. (A) CV curves and (B) corresponding linear relationship of anodic peak currents against the scan rates of COF/Pt/MWCNT-COOH/GCE in 0.1 M PBS (pH = 7.4) containing 0.5 mM DA at different scan rates (5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150 mV/s). (C) DPV curves and (D) corresponding linear relationship of solution pH versus the redox peak potential of COF/Pt/MWCNT-COOH/GCE in 0.1 M PBS containing 0.5 mM DA.

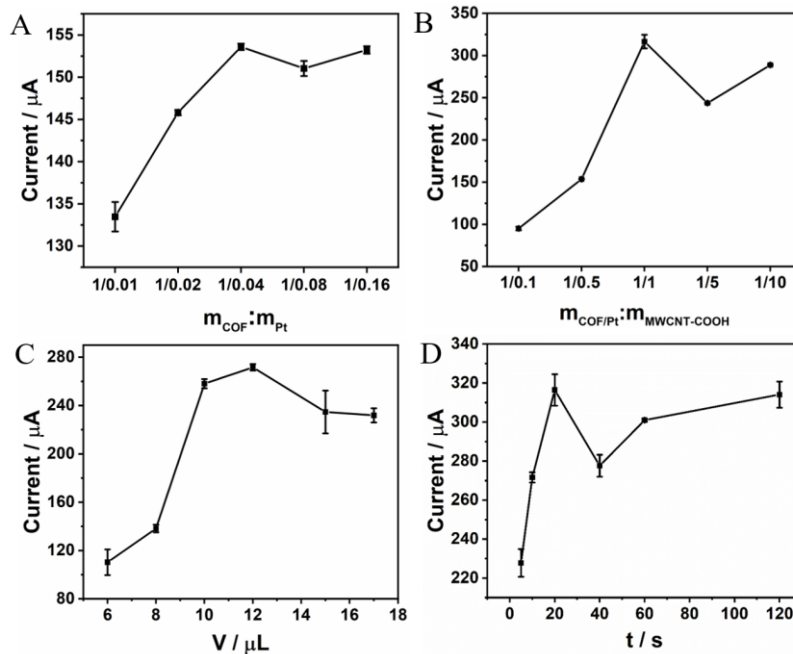


Fig. S6. The effect of (A) mass ratio of COF : Pt, (B) mass ratio of COF/Pt : MWCNT-COOH, (C) the load of COF/Pt/MWCNT-COOH, and (D) the accumulation time on the DPV peak current. The electrolyte was 0.1 M PBS containing 0.5 mM DA.

In order to improve the analytical performance, the mass ratios of COF : Pt nanoparticles and COF/Pt : MWCNT-COOH, the load of COF/Pt/MWCNT-COOH, and the accumulation time on DPV response of the proposed sensor in 0.1 M PBS containing 0.5 mM DA were investigated (Fig. S6). As shown in Figs. S6A-B, the DPV signals increase with the decrease of the mass ratios of COF : Pt and COF/Pt : MWCNT-COOH, and reach their maximums when the mass ratios are 1/0.04 and 1/1, respectively. With further increase of Pt nanoparticles and MWCNT-COOH loading, the DPV response declines slightly. The reason might be ascribed to that the excess loading of Pt nanoparticles and MWCNT-COOH covered the adsorption sites on COF and hampered the enrichment of DA, thus lowered the electrochemical response. Therefore, these mass ratios of COF : Pt (1/0.04) and COF/Pt : MWCNT-COOH (1/1) were selected as the optimal values to prepare COF/Pt/MWCNT-COOH.

The proper load volume of the prepared material on the surface of GCE and accumulation time can improve the detection performance of DA. As shown in Fig. S6C, the peak current increases with the increasing load volume of the COF/Pt/MWCNT-COOH until reaches the maximum value at 12 μ L. After that, the peak current decreased due to the fact that the dense material on electrode surface was unfavorable to the electron transfer. Thus, 12 μ L was chosen as the optimal load volume of COF/Pt/MWCNT-COOH. Fig. S6D shows the effect of accumulation time on DPV signal. The current peak increased sharply with the increase of accumulation time from 5 to 20 s, and reached its maximum at 20 s. Therefore, the accumulation time of 20 s was used in the next measurements.

Table S1. Comparative study of different modified electrodes towards the electrochemical determination of DA.

| Electrodes | Linear range/ μM | LOD/ μM | Reference |
|--------------------------------------|-----------------------------|--------------------|-----------|
| 3D N-doped graphene | 3-100 | 0.001 | 2 |
| AuNPs-PT3BA-PPO | 0.05-30 | 0.02 | 3 |
| 3D-rGO/ β -CD | 0.5-100 | 0.013 | 4 |
| AgPd@Zr-MOF | 2-42 | 0.1 | 5 |
| TiO ₂ /graphene | 5-200 | 2 | 6 |
| HNP-PtTi alloy | 4-500 | 3.2 | 7 |
| Poly(4-aminobutyric acid) | 5-100 | 1 | 8 |
| Graphene | 4-100 | 2.64 | 9 |
| Fe ₂ O ₃ -NrGO | 0.5-340 | 0.49 | 10 |
| COF/Pt/MWCNT-COOH | 2-500 | 0.67 | This work |

Table S2. Determination of DA in real samples using COF/Pt/MWCNT-COOH/GCE sensor.

| Serum Sample | Added/ μM | Determined/ μM | Recovery/% | RSD/% |
|--------------|----------------------|---------------------------|------------|-------|
| 1 | 15 | 15.4 | 102.7 | 2.9 |
| 2 | 300 | 332.7 | 110.9 | 6.0 |
| 3 | 400 | 382.2 | 95.7 | 2.7 |
| 4 | 500 | 458.4 | 91.7 | 2.0 |

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