

Supporting information

Graphdiyne Chelated AuNPs for Ultrasensitive Electrochemical Detection of Tyrosine

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Part 1: Experimental methods

Reagents and apparatus. GDY and AuNPs were obtained from Jiangsu XFNANO Nano Materials Tech Co., Ltd. (China). Ethanol (EtOH), CaCl₂, NaCl, KCl, glucose (Glu), glutathione (GSH), NADH, phenylalanine (Phe), phenol (PhOH), lactic acid (LA), Urea, uric acid (UA), ascorbic acid (AA), dopamine (DA) and tyrosine (Tyr) were purchased from Aladdin. PBS and Nafion were purchased from Sigma-Aldrich. Deionized (DI) water was used for all aqueous solutions. The morphology and structure of the materials were checked using field emission scanning electron microscopy (FESEM, JEOL/JSM-IT800), transmission electron microscope (TEM, FEI G2F20). X-ray photoelectron spectroscopy (XPS, Escalab 250xi, Thermo Scientific) was utilized to analyze the valence states of elements. UV–vis spectra of different materials were recorded using Shimadzu UV–vis spectrophotometer (UV-2550, Japan). Zeta potential measurements were performed with Malvern Zetasizer Nano ZS 90 (Malvern, UK).

Preparation of GDY@AuNPs-based sensing platform. GCEs (d=3 mm) were polished by 0.05 and 0.3 μm alumina slurry and followed by ultrasonically cleaning in ethanol and DI water for 50 s to a shining surface, respectively. For synthesis of GDY@AuNPs (1:3, v/v), 1 mL of 1 mg mL⁻¹ GDY solution (50% ethanol in DI water) mixed with 3 mL of 0.05 mg mL⁻¹ AuNPs, and stirred with 1000 r for 12 h. After reaction, 5 μL of the mixture were cast on the GCE surface. Optimization of the volume ratio

of GDY to AuNPs was further conducted, and the other proportions of GDY@AuNPs (1:2 and 1:4) were also prepared by the same procedure. The modified electrodes were used in all electrochemical experiments. Electrochemical measurements were performed on a CHI 660E electrochemical workstation with a three-electrode system composed of a GCE working electrode, a platinum plate counter electrode, and an Ag/AgCl reference electrode.

Part 2: Additional table and figures

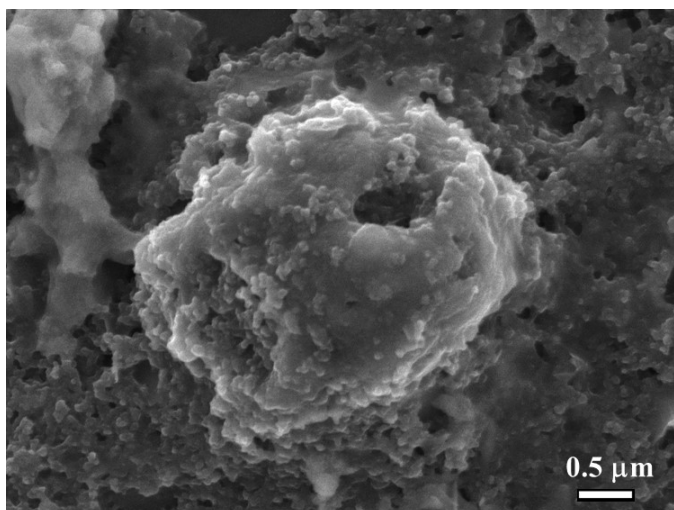


Fig. S1. FESEM image of GDY@AuNPs.

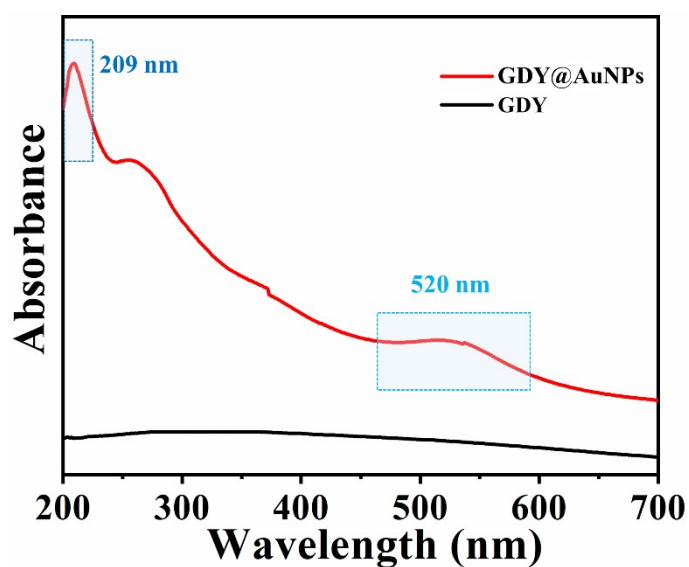


Fig. S2. UV-vis adsorption spectra of GDY (black) and GDY@AuNPs (red).

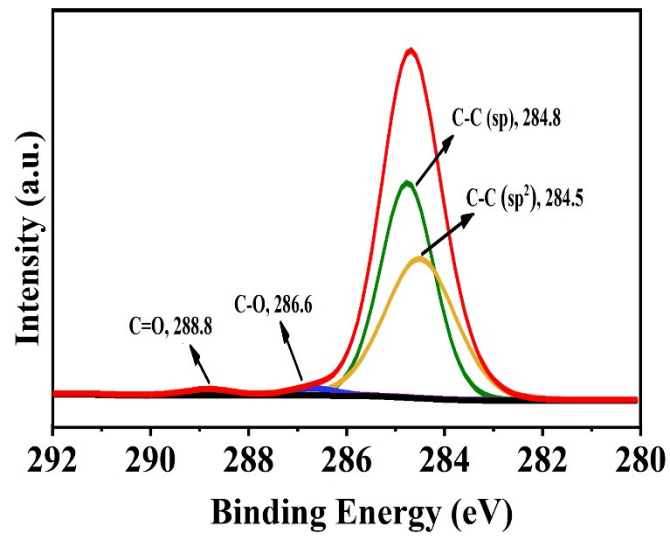


Fig. S3. XPS C 1s patterns of GDY.

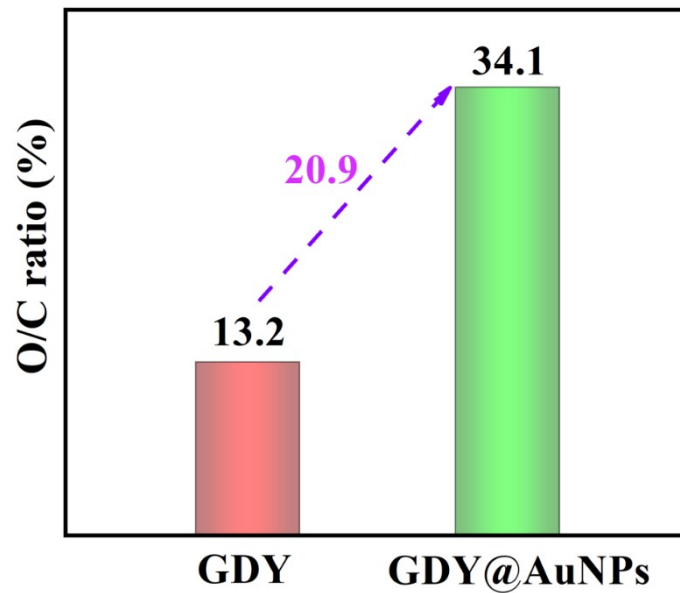


Fig. S4. Histogram of O/C ratio (red: GDY, green: GDY@AuNPs).

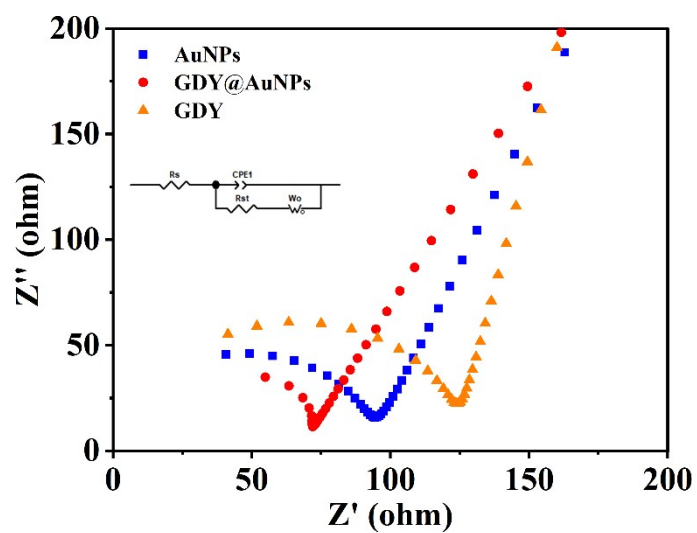


Fig. S5. EIS of GDY@AuNPs (red), GDY (orange) and AuNPs (blue) in presence of 100 μM Tyr in 0.01 M PBS.

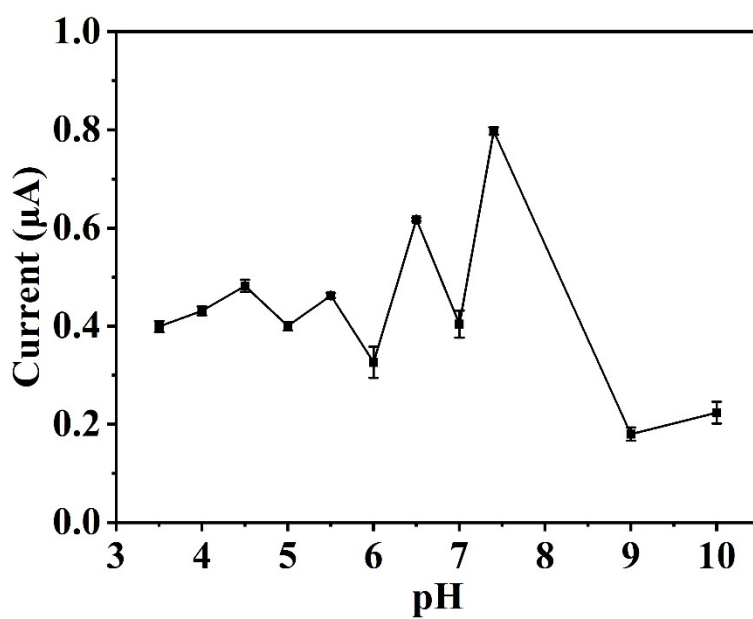


Fig. S6. The peak currents of the DPV curves obtained under different pH values containing 100 μM Tyr.

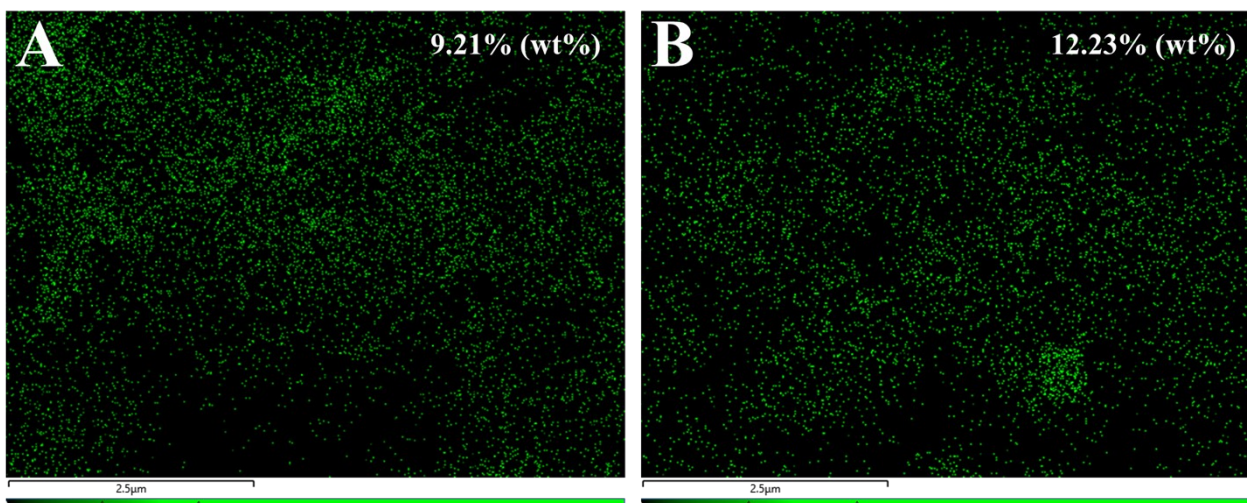


Fig. S7. The element mapping of oxygen before (A) and after (B) DPV electrochemistry experiments.

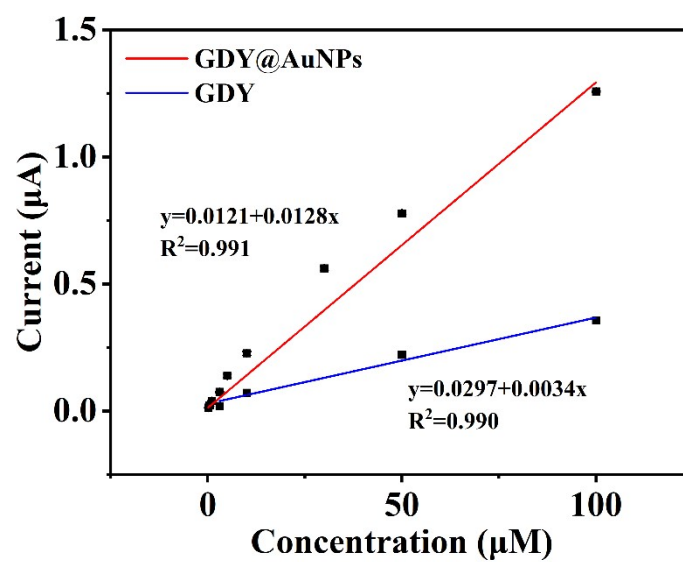


Fig. S8. The relationship of the DPVs peak currents with the concentrations of Tyr (red: GDY@AuNPs, blue: GDY).

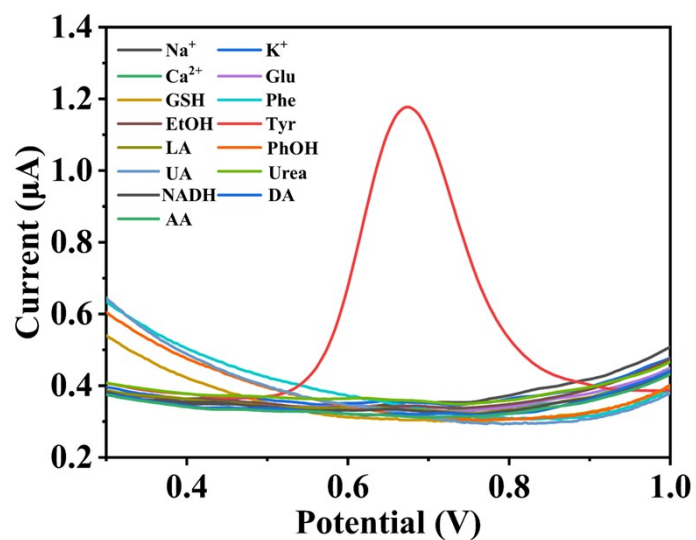


Fig. S9. Selectivity testing of GDY@AuNPs toward Tyr (0.01 M PBS, Tyr: 100 μM , Na^+ : 500 μM , K^+ : 500 μM , Ca^{2+} : 500 μM , Glu: 500 μM , GSH: 500 μM , Phe: 500 μM , EtOH: 500 μM , LA: 500 μM , PhOH: 500 μM , UA: 500 μM , Urea: 500 μM , NADH: 500 μM , DA: 500 μM and AA: 500 μM).

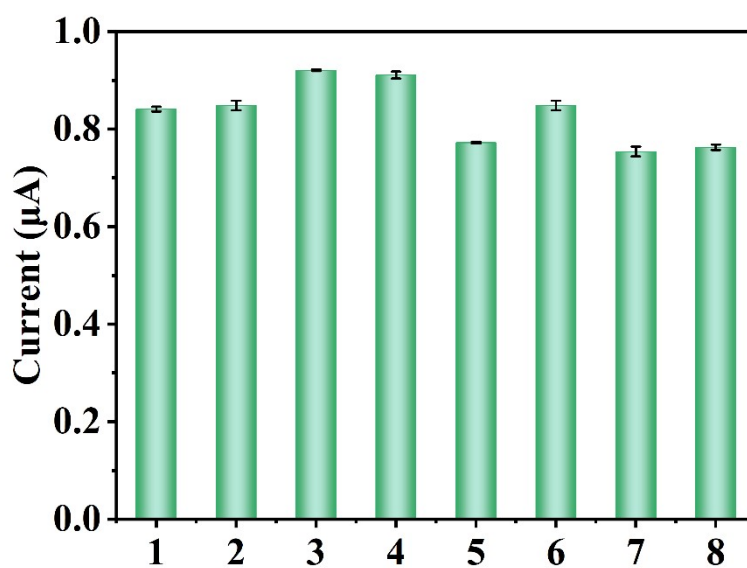


Fig. S10. Reproducibility testing of GDY@AuNPs-based sensors toward 100 μM Tyr.

Table S1. Comparison of different sensors for detecting Tyr.

Sensing material	Analytical method	Liner range (μM)	Detection limit (μM)	References
GDY@AuNPs	DPV ^[a]	0.1-100 100-600	0.1	This work
AuNPs/MWCNT ^[b]	DPV	0.4-80	0.21	1
PABSA ^[c] /AuNPs	DPV	1-100	0.04	2
MWCNT/Nafion	DPV	2-120	0.8	3
AuNPs/poly (trisamine)	DPV	3.9-61.8	0.9	4
MXene/CNTs/CuMOF	DPV	0.53-232.46	0.19	5
GNS ^[d]	DPV	5-120	0.02	6
GR ^[e]	SWV ^[f]	0.8-60	0.07	7

[a] DPV: differential pulse voltammetry; [b] MWCNT: multi-walled carbon nanotube; [c] PABSA: polymer sulfanilic acid; [d] GNS: graphene nanosheets; [e] GR: graphene; [f] SWV: square wave voltammetry.

Table S2. Recovery study of GDY@AuNPs-based sensor performed by added standard Tyr in human sweat.

Tyr added (μM)	Tyr found \pm s.d. (μM)	Recovery (%)
10	10.13 \pm 0.08	101.30 \pm 0.80
30	29.90 \pm 0.03	99.66 \pm 0.10
50	50.04 \pm 0.23	100.09 \pm 0.46
200	200.56 \pm 1.30	100.28 \pm 0.65
500	499.94 \pm 3.15	99.99 \pm 0.63

References

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