Electronic Supplementary Information

Tyrosinase-catalyzed polymerization of L-DOPA (versus L-tyrosine and dopamine) to generate melanin-like biomaterials for immobilization of enzymes and amperometric biosensing

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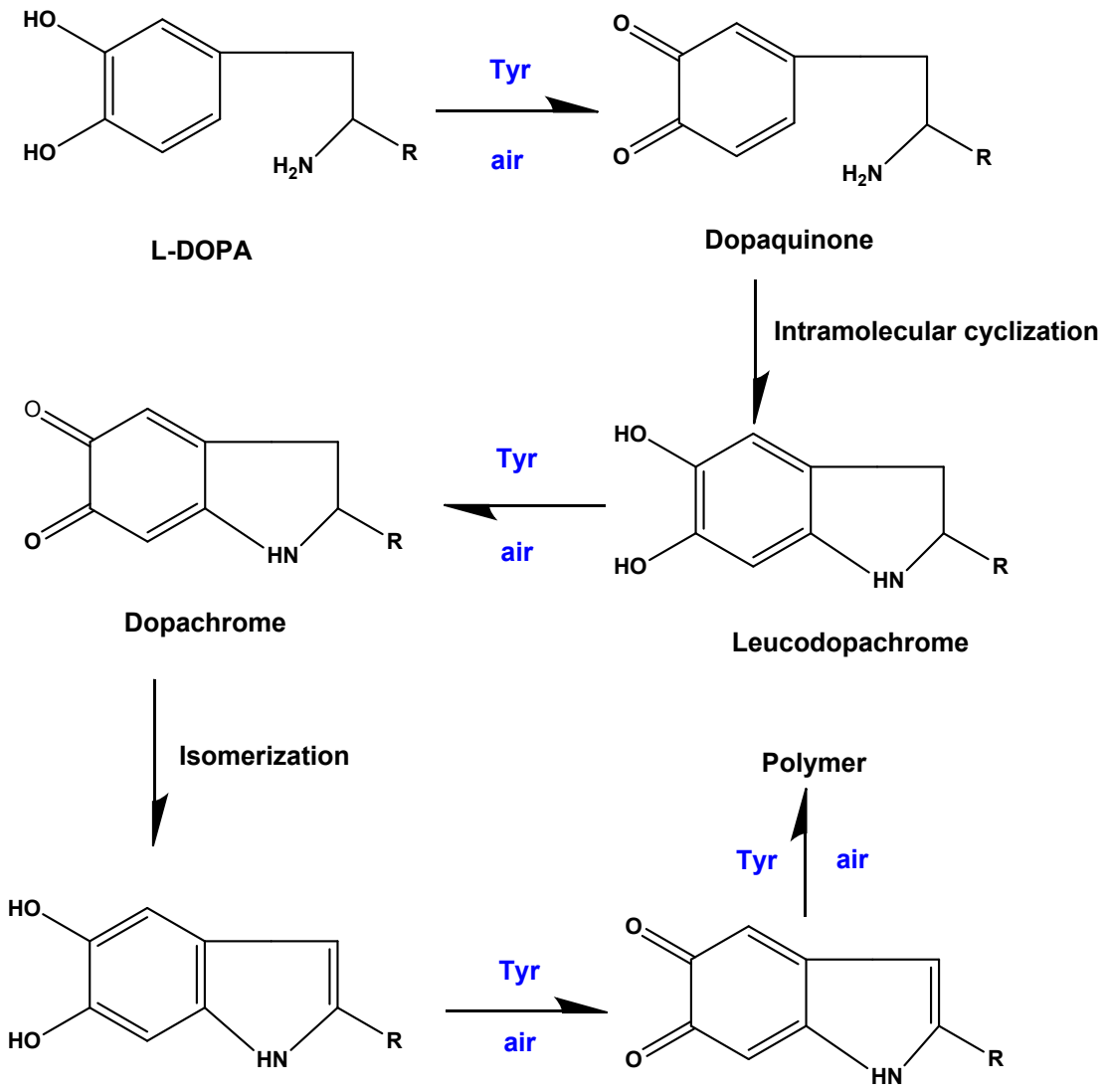
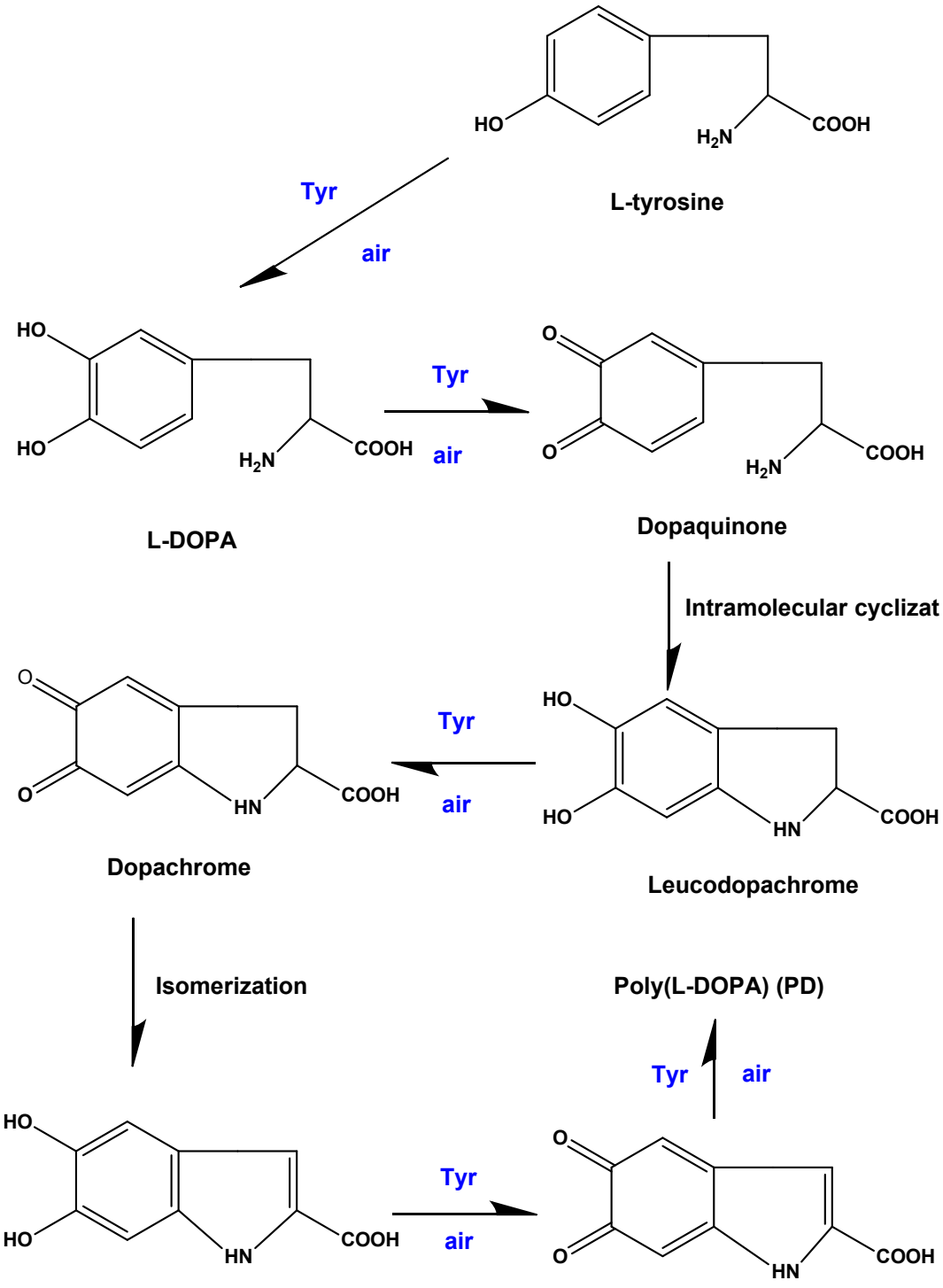


Scheme S1. The possible pathways for Tyr-catalyzed oxidation and polymerization of L-DOPA (R=COOH) and DA (R=H). The denominations here are given for L-DOPA only and those for DA can be inferred simply by using the phrase dopamine instead of the phrase dapa, e.g., from dopachromine to dopaminechromine.



Scheme S2. The possible Tyr-catalyzed pathway for oxidation and polymerization of L-tyrosine.

Table S1. Catechol-biosensing performance of some enzyme electrodes reported in literatures and developed in this work

Enzyme electrode	*S* / mA mM^{-1} cm^{-2}	LOD / μM	LDR / μM	reference
Tyr-PPy/GCE	0.0015	2.0	-	[1]
Tyr/Co_3O_4/GMC	6.4	0.025	0.05-130	[2]
Tyr-AuNC-(PSS-AuNC)$_2$-MPA-AuNP-SPCE	13.72	0.0004	0.01-80	[3]
PD-Tyr-MWCNTs/GCE	4.66	0.04	0.4-87	this work
PD-Tyr-GO/GCE	3.00	0.03	0.4-87	this work
CS-Tyr/GCE	2.25	0.04	0.4-77	this work
Nafion-Tyr/GCE	1.43	0.1	0.4-67	this work
PD_C-Tyr/GCE	2.86	0.04	0.4-87	this work
PD-Tyr/GCE	4.29	0.07	0.4-57	this work
poly(L-tyrosine)-Tyr/GCE	1.09	0.08	0.4-137	this work
PDA-Tyr/GCE	1.75	0.09	0.4-117	this work

PPY: polypyrrole; MEBCs: metal-organic coordination polymers-enzyme biocomposites; GMC: graphitized ordered mesoporous carbon; AuNC: gold nanocubes; SPCE: screen printed carbon electrode; PD_C: chemical oxidative polymerization of L-DOPA by using $K_3Fe(CN)_6$ as an oxidant.

Table S2. Performance comparison among some typical glucose biosensors based on immobilized GOx

Enzyme electrode	Sensitivity / $\mu A\ mM^{-1}\ cm^{-2}$	LOD / μM	LDR / μM	reference
GOx-P*o*AP/platinized GCE	~57	0.5	1-1000	[4]
CS-GOx-AuNP/Au	-	2.7	5-2400	[5]
PDA-GOx/Au	3.81	3	50-9000	[6]
Pt/mesoporous carbon-GOx-gelatin/GCE	8.5	1	40-12000	[7]
Au-PtNPs/CNTs/GOx/CS/GCE	122	0.2	1-7000	[8]
MWCNTs-CS-GOx/Au	6.7	2	5-8000	[9]
CS-Fc/MWCNTs/GOx/GCE	21.9	6.5	20-5360	[10]
PDA-GOx-Lac-MWCNTs /Pt	68.6	0.5	10-3700	[11]
PD-GOx-Tyr/Pt	78.6	0.1	2-5700	this work
PD-GOx-Tyr-GO/Pt	74.3	0.5	2-2700	this work
PD-GOx-Tyr-MWCNTs /Pt	64.3	0.5	2-3700	this work
poly(L-tyrosine)-GOx-Tyr/Pt	59.1	1	2-5700	this work
PDA-GOx-Tyr/Pt	45.7	1	2-6700	this work

P*o*AP: poly(*o*-aminophenol); PPY: polypyrrole; PtNPs: Pt nanoparticles; CNTs: carbon nanotubes.

Table S3. Results obtained in analysis of several human serum samples with the PD-GOx-Tyr/Pt electrode*

	Determined by biosensor (mM)	Determined in hospital (mM)	Bias (mM)	Standard added (mM)	Found (mM)	Recovery
1	4.97	4.88	+0.09	5.00	4.60	92.0
2	4.41	4.45	-0.04	5.00	5.25	105
3	4.39	4.28	+0.11	5.00	5.20	104
4	4.29	4.2	+0.09	5.00	4.92	98.4
5	4.83	4.77	+0.06	5.00	4.80	96.0

* Fresh serum samples were first analyzed at Hunan Normal University Hospital with a Biochemical Analyzer (Mindray BS-300, Shenzhen Mindray Biomedical electronics Co., Ltd.) based on the well-known GOx-peroxidase spectrophotometric method. The samples were then analyzed at the PD-GOx-Tyr/Pt electrode. Serum sample (0.100 mL) was added into 10.0 mL PBS at pH 7.0, and the current response was recorded at 0.50 V vs. SCE for glucose analysis.

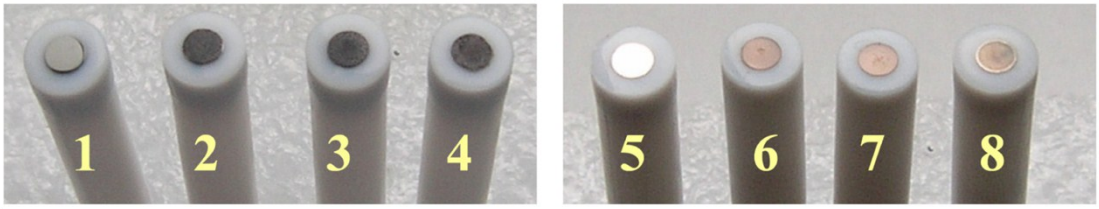


Fig. S1. Digital pictures of the surfaces of bare GCE (1), PD-Tyr/GCE (2), PDA-Tyr/GCE (3), and poly(L-tyrosine)-Tyr/GCE (4) (left) as well as bare Pt (5), PD-Tyr/Pt (6), PDA-Tyr/Pt (7), and poly(L-tyrosine)-Tyr/Pt (8) (right) after water rinse and air drying.

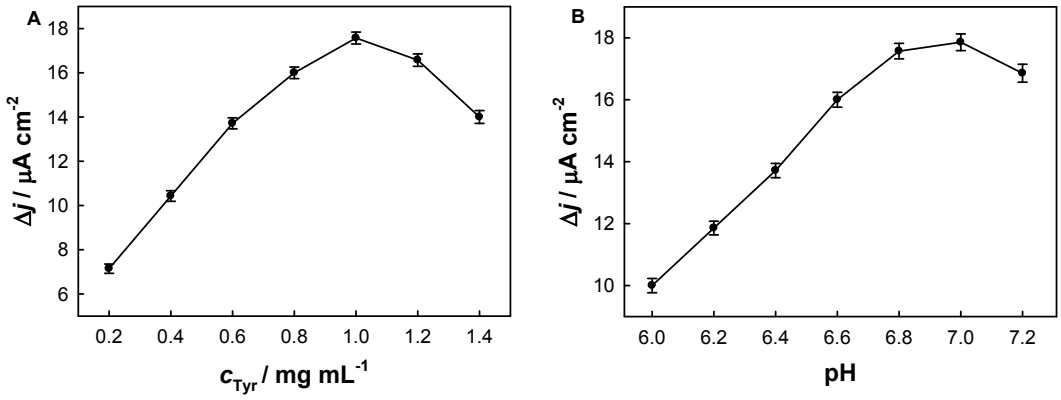


Fig. S2. Optimization of Tyr concentration and biosensing solution pH on the stable current response at PD-Tyr/GCE in stirred PBS containing 0.004 mM catechol. Applied potential: -0.1 V vs. SCE. The responses here are discussed as follows. The current response notably increased with the increase of Tyr concentration from 0.2 to 1.0 mg mL^{-1}, then decreased slightly with the further increase of Tyr concentration to 1.4 mg mL^{-1}, so 1.0 mg mL^{-1} Tyr was used in subsequent experiments. In addition, the maximum response of the biosensor occurred at pH 7.0 that fits the enzyme activity, so 0.1 M PBS with pH 7.0 was selected for future experiments.

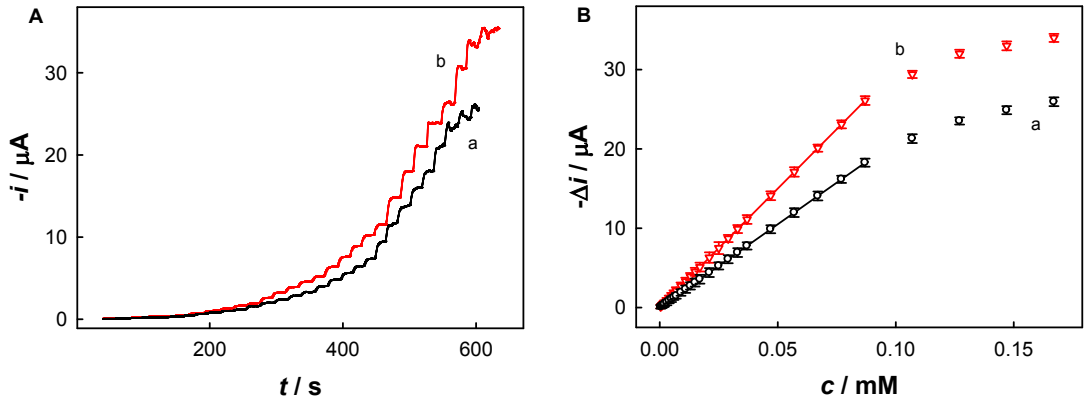


Fig. S3. Time-dependent current response (A) to successive additions of catechol into stirred 0.1 M PBS (pH 7.0) under air atmosphere and the calibration curves (B) at PD-Tyr-GO/GCE (a), PD-Tyr-MWCNTs/GCE (b). Applied potential: -0.1 V vs. SCE.

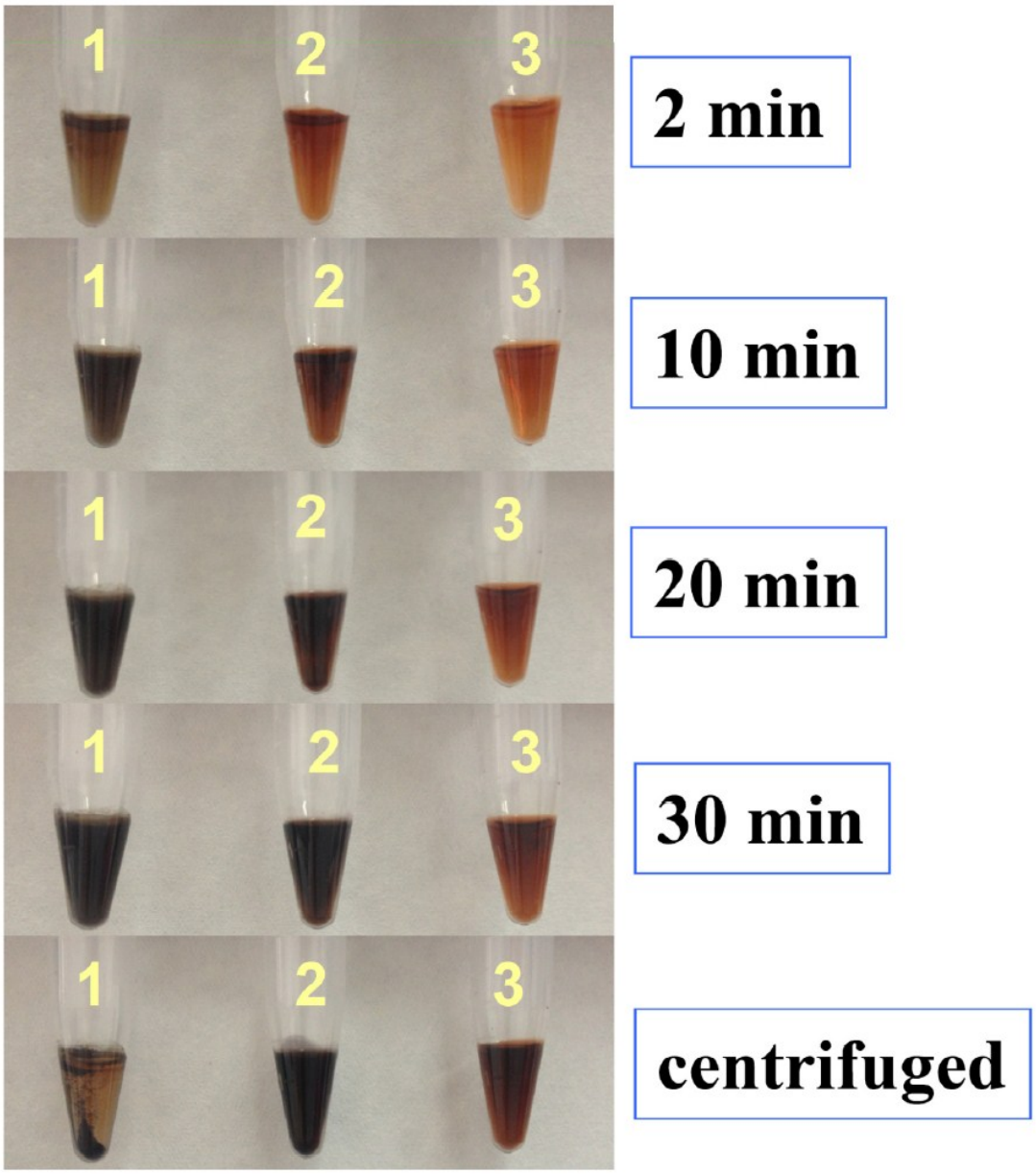


Fig. S4. The digital pictures of 5 mM L-DOPA + 1 mg mL^{-1} Tyr (1), 5 mM DA + 1 mg mL^{-1} Tyr (2), and 5 mM L-tyrosine + 1 mg mL^{-1} Tyr (3) after reactions for various time periods (2, 10, 20 or 30 min) and finally a centrifugation immediately after the 30-min reactions.

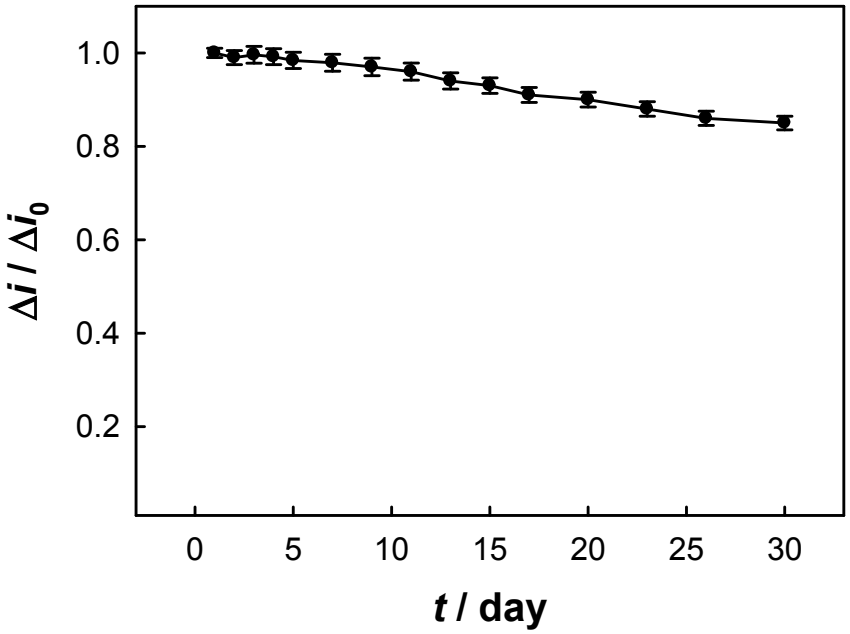


Fig. S5. The storage stability of PD-Tyr/GCE under storage condition (as a dry state in a refrigerator at 4 ^{o}C).

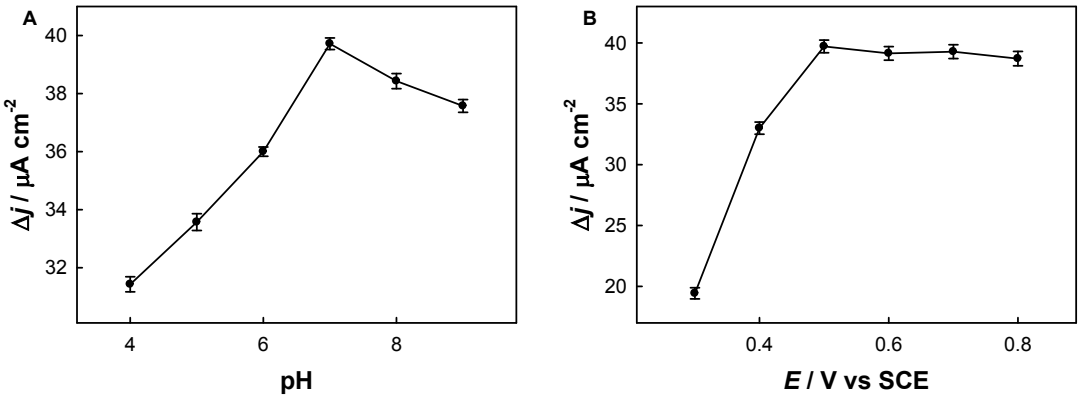


Fig. S6. Effects of solution pH (applied potential: 0.5 V vs. SCE) and applied potential (solution pH 7.0) on the stable current density response at PD-GOx-Tyr/Pt in stirred PBS containing 0.5 mM glucose. The responses here are discussed as follows. The maximum response of the biosensor occurred at pH 7.0 that fits the enzyme activity, so 0.1 M PBS with pH 7.0 was selected for future experiments. Δj increased rapidly with the change of applied potential from 0.30 to 0.50 V vs. SCE and then increased slowly from 0.50 to 0.8 V vs. SCE, due to the increased driving force for the fast oxidation of H_2O_2 at the higher potential. To minimize interferences and current noise at high potentials, 0.50 V vs. SCE was selected as the applied potential for amperometric measurement.

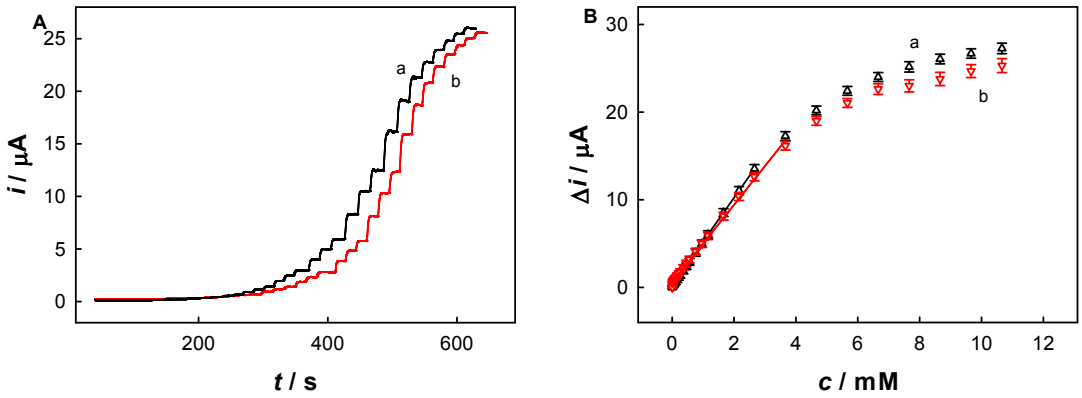


Fig. S7. Time-dependent current responses (A) to successive additions of glucose into stirred 0.1 M PBS (pH 7.0) and the calibration curves (B) at PD-GOx-Tyr-GO/Pt (a) and PD-GOx-Tyr-MWCNTs/Pt (b) electrodes. Applied potential: 0.50 V vs. SCE.

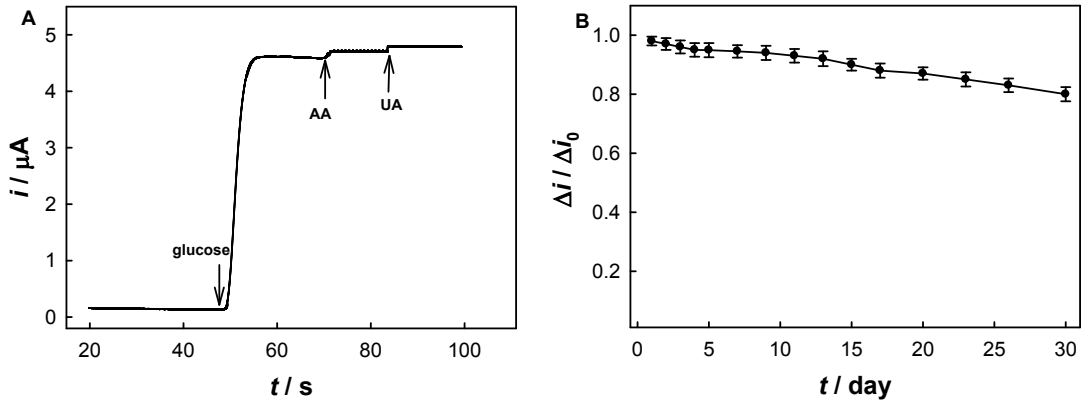


Fig. S8. (A) Amperometric response obtained at PD-GOx-Ty/Pt electrode in PBS (pH 7.0). The arrows show the moments of injections of 1 mM glucose, 0.2 mM ascorbic acid (AA), and 0.2 mM uric acid (UA). Applied potential: 0.5 V vs. SCE. The addition of AA or UA only yielded within 4% of the glucose response here. (B) The storage stability of PD-GOx-Tyr/Pt electrode under storage conditions (as a dry state in a refrigerator at 4 ^{o}C).

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