In situ spontaneous reduction synthesis of spherical Pd@Cys-C_{60} nanoparticles and its application in nonenzymatic glucose biosensors

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1. Materials and methods

1.1. Materials

Potassium tetrachloropalladate was purchased from Sigma (St. Louis, MO, USA), Fullerene (C_{60}) was purchased from YongXin Chemical Reagent Co., (Puyang, China), L-cysteine (Cys) was purchased from KeLong Chemical Reagent Co., (Chengdu, China). Phosphate buffer solutions (PBS) with various pH values were prepared with 0.1 M KH_2PO_4 0.1 M Na_2HPO_4. The supporting electrolyte was 0.1 M KCl. All chemicals and solvents used were of analytical grade. Double distilled water was used throughout all experiments.

1.2. Apparatus and measurements

Electrochemical measurements were carried out on a CHI 660D electrochemical workstation (CH Instruments Co., China). The electrochemical cell contained a three-electrode system where bare or modified glassy carbon electrode (4.0 mm in diameter) was used as a working electrode, platinum wire as an auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. Transmission electron

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microscopy (TEM) was carried out on a TECNAI 10 (Philips Fei Co., Hillsboro, OR). The UV-Vis absorption spectra were recorded in the range of 200-800 nm, using a UV-Vis spectrometer (UV-Vis 8500). The FT-IR spectra were recorded on a Nexus 670 FT-IR spectrophotometer (Nicolet Instruments) using a KBr pellets. All the electrochemical experiments were carried out at room temperature.

1.3. Preparation of Cys-C_{60} derivatives and spherical Pd@Cys-C_{60} nanoparticles

The Cys-C_{60} derivative was prepared as follows: first, 0.4 g Cys was dissolved in 1 mL NaOH solution, then 8 mL ethanol was added. Subsequently, the Cys mixture solution mentioned above was added to C_{60} toluene solution (1 mg mL^{-1}) with stirring. The color of inorganic layer changed from purple to dark brown, and the organic layer turned almost colorless. After 5 days, the solution was filtered, centrifuged, and washed respectively with ethanol and distilled water for several times. The dark brown product of Cys-C_{60} was dried in vacuum for 24 h at 50 °C.

Then, the obtained powder of Cys-C_{60} (5 mg) was dispersed in distilled water (5 mL), and 100 μL potassium tetrachloropalladate (1 mg mL^{-1}) was added in dropwise with vigorous stirring for 24 h. After the reaction, the mixture was stayed at room temperature for 30 days. The final mixture were centrifuged and washed for several times, and the dark brown product of Pd@Cys-C_{60} was dried in vacuum for 12 h at 50 °C. The obtained nanoparticles were redispersed in distilled water. The typical synthetic process is given in Scheme 1.

1.4. Construction of Pd@Cys-C_{60} modified electrode and glucose biosensor

Glassy carbon electrode (GCE, *diameter 4.0 mm*) was polished with 0.3 and 0.05

μm alumina slurry, and then ultrasonically cleaned in ethanol and water thoroughly. Then it was allowed to dry at room temperature. Following this pretreatment, 20 μL Pd@Cys-C_{60} composites dispersed solution was dropped on the GCE, and then it was allowed to dry in air. The resulting electrode is denoted here as Pd@Cys-C_{60}/GCE, was stored at 4 °C when not used.

2. Results and discussion

To further optimize biosensor for glucose, the effect of applied potential on amperometric current of biosensor was investigated from 0.5 to -0.4 V (see Fig. S1, ESI†). The amperometric current increased followed by the applied potential decreased from 0.5 to -0.4 V, However in order to minimize the effect of interfering of the other electroactive species and get enough current responses, an applied potential of -0.05 V was chosen for measurements.

The effect of pH corresponding to the Pd@Cys-C_{60} electrode was investigated by studying the change of chronoamperometric current. The effect of pH was tested in a series of PBS with pH from 5.0 to 9.0. The experimental result shows the chronoamperometric current increases followed by the pH increasing under constant glucose concentration (0.5 mM). Considering the pH of human blood is about 7.4 and Pd in the alkaline solution is easy to generate the PdOH, which may lead to oxidation of glucose. In this case, pH 7.4 was selected to ensure sensitivity and stability of the sensor.

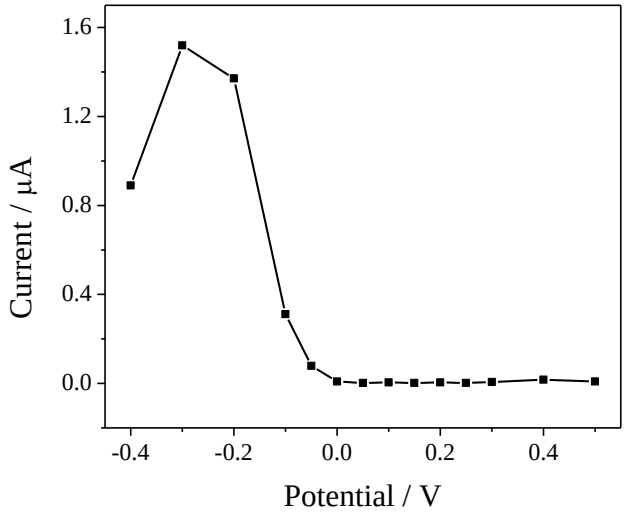

Fig. S1. Influence of the different applied potential of biosensor to 0.5 mM glucose in 0.1 M PBS (pH 7.4).

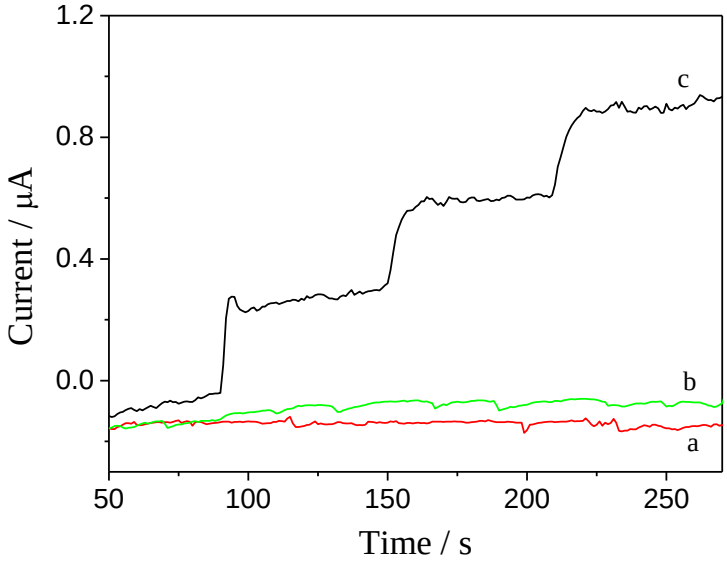

Fig. S2. Amperometric responses of (a) Nafion/Cys-C_{60}/GCE, (b) Nafion/Pd^{2+}(Cys-C_{60})n/GCE, and (c) Pd@Cys-C_{60}/GCE upon successive addition of 0.25 mM glucose in 0.1 M PBS (pH 7.4) at -0.05V..

Table S1 Comparison of performance of some noenzymatic glucose sensor

Materials	Linear range (mM)	Detection limit (μM)	Sensitivity ($\mu AmM^{-1}cm^{-2}$)	Refs.
Nanoporous Pt	1 – 10	97	1.65	1
Au@PdNp	5×10^{-6} to 5×10^{-3}	0.001	–	2
Pt nanotubes	2 – 10	–	0.1	3
BONP/MWCNT	0.0015 – 0.26	0.8	–	4
Pt-PbNAE	0.024 – 11	8	11.25	5
GNPs/MWCNTs/IL	0.005 –0.12	–	–	6
Mesoporous carbon	0.5 – 2.5	0.02	10.81	7
Pt/OMCs/Nafion	0.5 – 4.5	–	16.69	8
Pd@Cys-C_{60}	0.0025 - 1.0	1.0	35.46	This work

Table S2 Effect of the possible interferents in glucose biosensor

Possible interference	Response current(μA)
Glucose (0.5 mM)	0.430
Ascorbic acid (0.1 mM)	0.011
Uric acid (0.1 mM)	0.015
p-Acetamidophenol (0.1 mM)	0.010
Fructose (0.1 mM)	0.029

Table S3. Amperometric determination of glucose in human blood serum samples.

Sample	Concentration (mM)	R.S.D. (%)[a]	Added (mM)	Recovery (%)
1	4.4	2.9	0.5	101.4
2	6.1	3.8	0.5	98.6
3	5.8	1.8	0.5	104.6
4	5.4	2.3	0.5	95.3
5	4.2	3.4	0.5	103.3

[a] R.S.D. (%) calculated from three separate experiments.

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