Electronic Supplementary Information (ESI) for New Journal of Chemistry

Synthesis of novel hedgehog-shaped Bi_2S_3 nanostructure for sensitive electrochemical glucose biosensor

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Experimental

Materials and Reagents: The GOx molecules (EC 1.1.3.4, 108 U mg^{-1}, from Aspergillus niger) were bought from Amresco. Glucose and Nafion were supplied by Sigma-Aldrich. Bismuth nitrate (Bi $(NO_3)_3$), cetyltrimethyl ammonium bromide (CTAB), trimellitic acid ($C_9H_6O_6$), thiourea (CH_4N_2S), anhydrous ethanol, sodium phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), potassium chloride (KCl), potassium ferricyanide ($K_3Fe(CN)_6$), and potassium ferrocyanide ($K_4[Fe(CN)_6]\cdot 3H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Phosphate buffer solution (PBS, 0.1 $mol\cdot L^{-1}$) was the mixture of Na_2HPO_4 and NaH_2PO_4 solutions, and its pH was adjusted by H_3PO_4 or NaOH solution. All reagents used in experiments were of analytical grade.

Apparatus: A CHI 852C electrochemical workstation was from Shanghai Chenhua Instrument Co. Ltd. (China), which was used to carry out electrochemical measurements. A three-electrode system, including a working electrode of glassy carbon electrode (GCE), a reference electrode of saturated calomel

electrode (SCE), and an auxiliary electrode of platinum wire were employed in the experiment. The cyclic voltametric tests were implemented at a scan rate of 100 $mV \cdot s^{-1}$ in a cell with 10.0 mL PBS. All solution pH measurements were conducted on a S-25 digital pH-meter with glass combination electrode. A Hitachi S-4800 scanning electron microscope (Japan) was used to obtain scanning electron micrographs (SEM) at 15 kV of acceleration voltage. X-ray diffractometer spectra were measured by using polycrystalline X-ray diffractometer (XRD, D8 advance, Bruker AXS, Germany). Electrochemical impedance spectroscopy (EIS) was tested in a KNO_3 solution (0.1 $mol \cdot L^{-1}$) including 5 mM of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ within a frequency range from 0.01 to 10 KHz. Fourier transform infrared (FT-IR) spectrum was recorded at a Tensor 27 spectrometer (Bruker Co., Germany).

Synthesis of hedgehog-shaped Bi_2S_3 nanostructure and electrochemical glucose biosensor: Hedgehog-shaped Bi_2S_3 nanostructures were prepared by a composite soft template method by a simple hydrothermal route according to previous research[S1]. Firstly, 0.0210 g of trimellitic acid, 0.0365 g of CTAB, 0.3806 g of thiourea, 0.50 mL of bismuth nitrate solution (0.20 $mol \cdot L^{-1}$) and 9.50 mL of distilled water were transferred into a 50 mL beaker. The system was ultrasonically mixed to obtain a homogeneous light yellow solution. The obtained solution was added to a Teflon-lined reaction kettle, which was placed in a constant-temperature oven for 12 h at 120 ℃. After that, the obtained black precipitates were centrifuged and washed using ethanol and distilled water several times in sequence, and finally dried at 60 ℃ under vacuum for 12 h to obtain black powder product.

The surface of GCEs were polished with 0.3-μm and 0.05-μm alumina slurry (Buhler) in turn, and cleaned carefully using distilled water. High purity N_2 stream was used to dry GCEs at room temperature. Then, 1.0 mg of HS-Bi_2S_3 was weighted to distilled water (1.0 mL) and dispersed by ultrasonication. Next, GOx (1.0 mg) was added into 100 μL of HS-Bi_2S_3 suspension above, and kept shaking for at least 15 min. Next, 5.0 μL of the mixed solution was coated on clean electrodes and dried naturally at room temperature. To avoid the leakage of the GOx from modified GCE, 5.0 μL of Nafion (0.5%) was coated on surface of GOx/HS-Bi_2S_3/GCE. The prepared Nafion/GOx/ HS-Bi_2S_3/GCE was stored in a refrigerator at 4 ℃.

Optimization of electrochemical detection conditions

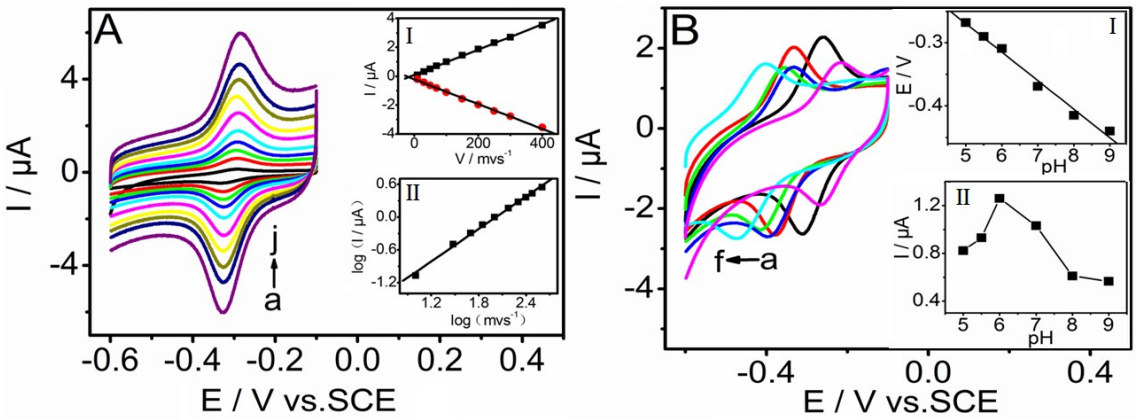

Fig. *S1*. (A) cyclic voltammograms of the Nafion/GOx/HS-Bi_2S_3/GCE in 0.1 M pH 6.0 N_2-saturated PBS at 10, 20, 50, 80, 100, 150, 200 and 300 mV s^{-1} (from a to j), inset I: plots of anodic and cathodic peak currents vs. scan rate, inset II: plot of logarithm of i_{pc} vs. logarithm of v; and (B) Cyclic voltammograms of the Nafion/GOx/HS-Bi_2S_3/GCE in N_2-saturated 0.1 M PBS with different pH values of (a-f) 5.0, 5.5 6.0, 7.0, 8.0 and 9.0 at a scan rate of 100 mV s^{-1}, inset I: plot of formal potential vs. pH, and inset II: plot of peak current vs. pH.

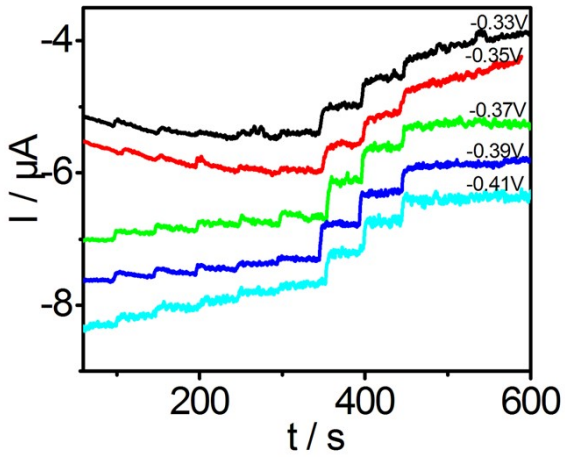

Fig. S2. Amperometric response of Nafion/GOx/Bi_2S_3/GCE at different potential to successive additions of glucose in a stirred 0.1 M pH 6.0 PBS.

Table S1 Detection results of glucose in human serum samples

Sample	Reference method（mM）	Proposed method (mM)	Relative errors (%)
1	4.64	4.43	- 4.5
2	4.88	5.03	3.1
3	5.19	4.80	- 7.5
4	6.39	5.92	- 7.4
5	10.55	10.84	2.7

Reference

S1. M. L. Ye, F. Shi, M. Shen, W. F. Qin, C. L. Ren, Z. J. Yang, *Collioid. Surface. A* 2021, **613**, 126094.