

Electronic Supplementary Information (ESI) for Analyst

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Supporting Information

Urchin-like PtNPs@Bi₂S₃: synthesis and application for electrochemical biosensor

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Experimental

Reagents and instruments

The glucose oxidase (EC 1.1.3.4, 108 U mg⁻¹, from *Aspergillus niger*) was purchased from Amresco. D-(+)-Glucose and Nafion were supplied by Sigma-Aldrich. Chloroplatinic acid (H₂PtCl₆) was purchased from Shanghai Biotech Engineering Co., Ltd. Bismuth nitrate (Bi (NO₃)₃), cetyltrimethyl ammonium bromide (CTAB, (C₁₆H₃₃(CH₃)₃NBr), trimellitic acid (C₉H₆O₆), thiourea (CH₄N₂S), anhydrous ethanol (C₂H₆O), disodium phosphate (Na₂HPO₄), sodium dihydrogen phosphate (NaH₂PO₄), anhydrous ethanol (C₂H₆O) potassium chloride (KCl), potassium ferricyanide (K₃Fe(CN)₆), and potassium ferrocyanide (K₄[Fe(CN)₆]·3H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). The prepared D-(+)-glucose stock solution must be placed at room temperature for 24 h to remove the optical rotation before measurements. The phosphate buffer solution (PBS) was prepared by mixing 0.1 M Na₂HPO₄ and NaH₂PO₄ solutions and its pH was adjusted by using H₃PO₄ or NaOH solution. All other reagents were of analytical grade and distilled water were used in the experiments.

Apparatus

Electrochemical measurements were carried out on a CHI 852C electrochemical workstation (Co., CHI, Shanghai Chenhua, China). All experiments were carried out with a three-electrode system. The modified glassy carbon electrode (GCE), a platinum wire and saturated calomel electrode (SCE) were used as working electrode, auxiliary electrode and reference electrodes. The cyclic voltammetric experiments were implemented at a scan rate of 100 mV s⁻¹ in an electrochemical cell filled with 10.0 mL of PBS. All pH measurements were achieved with S-25 digital pH-meter with glass combination electrode. Scanning electron micrographs (SEM) was observed via using a Hitachi S-4800 scanning electron microscope (Japan) at an acceleration voltage of 15 kV. D8 Advance polycrystalline X-ray diffractometer (XRD, Bruker AXS, Germany) was used to measure X-ray diffractometer spectrum. Electrochemical impedance spectroscopy (EIS) measurements were carried out in 0.1 M KNO₃ solution containing 5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆]. The impedance spectra were recorded at a bias potential of 190 mV within the

frequency range from 0.01 to 10 KHz. A Tensor 27 spectrometer (Bruker Co., Germany) was used to test Fourier transform infrared (FT-IR) spectra.

Synthesis of urchin-like PtNPs@Bi₂S₃ composite nanomaterial

PtNPs@Bi₂S₃ composite nanomaterial was synthesized with a simple hydrothermal route. Firstly, urchin-like Bi₂S₃ nanostructure was synthesized through a composite soft template method by a simple hydrothermal route according to the literature [S1]. Briefly, 60.0 mg of prepared urchin-like Bi₂S₃ was ultrasonically dispersed with 20 mL ethylene glycol, and 2190 μ L of H₂PtCl₆ (10 mg mL⁻¹) was added to the above solution drop by drop. The pH of the mixed solution was adjusted to 11.0 by using NaOH solution (1.0 mol L⁻¹). The prepared system was heated in a Microwave oven (800 w, 2450 MHz) for 6 min (1 time for 1min, totally 6 times). Then the system was allowed to cool to room temperature naturally and filtered with suction. After that, the obtained precipitates were centrifuged and washed with ethanol and distilled water several times in sequence and dried under vacuum at 80 °C for 12 h.

Fabrication of the electrochemical glucose sensor

The GCE was firstly treated with 0.3 and 0.05 μ m alumina slurry (Buhler), and rinsed absolutely with distilled water. The cleaned GCE was dried with high purity nitrogen stream. Next, 1.0 mg of PtNPs@Bi₂S₃ was dispersed in 1.0 mL of distilled water with ultrasonication, and 1.0 mg of GOx was added into 100 μ L of PtNPs@Bi₂S₃ suspension, and kept stirring for 15 minutes. After that, 5.0 μ L of the above suspension was dropped onto the prepared GCE and dried at 4 °C. In order to prevent the leakage of the GOx from modified GCE, 5.0 μ L of 0.5% Nafion was dropped on GOx/PtNPs@Bi₂S₃/GCE. The prepared Nafion/GOx/PtNPs@Bi₂S₃/GCE was dried and stored in a refrigerator at 4 °C before the measurement.

Effects of solution scan rate and pH on the electrochemical behavior at the Nafion/GOx/PtNPs@Bi₂S₃ modified GCE.

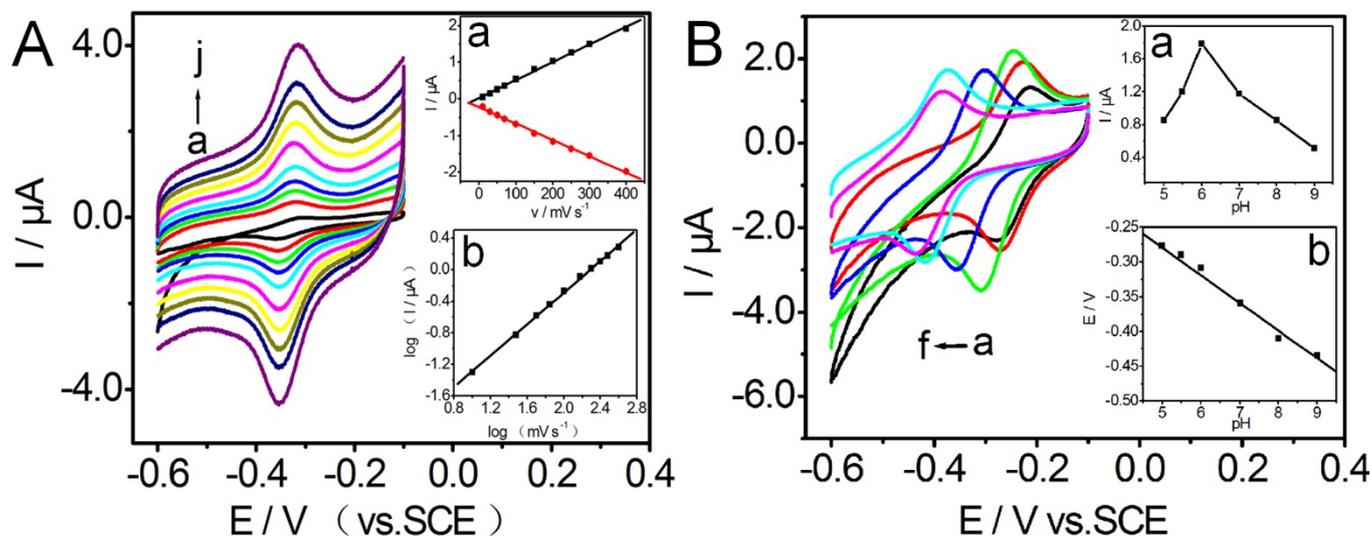


Figure S1 (A) cyclic voltammograms of the Nafion/GOx/PtNPs@Bi₂S₃/GCE in 0.1 M pH 6.0 N₂-saturated PBS at 10, 20, 50, 80, 100, 150, 200, 300, 350, 400 mV s⁻¹ (from a to j), inset I: plots of anodic and cathodic peak currents vs. scan rate, inset II: plot of logarithm of *i*_{pc} vs. logarithm of *v*; and (B) Cyclic voltammograms of the Nafion/GOx/PtNPs@Bi₂S₃/GCE in N₂-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.

Table S1 The content of element of PtNPs@Bi₂S₃ composite.

Element	wt %	at %
Bi	66.76	47.68
S	6.91	32.17
Pt	26.32	20.14

References

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