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TiO_2-SnS_2 nanocomposite as novel matrix for development of enzymatic electrochemical glucose biosensor

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Experimental

Materials and Reagents: GOx (EC 1.1.3.4, 10800 $U \cdot g^{-1}$, derived from Aspergillus niger) was bought from Amresco. D-(+)-Glucoseand Nafion were obtained from Sigma-Aldrich Chemical Company (Mainland, China). Tin (Ⅳ) chloride dehydrate ($SnCl_4 \cdot 5H_2O$), thioacetamide (CH_3CSNH_2), citric acid, and tetrabutyl titanate(TBT) were purchased from Sinopharm Chemical Reagent Co., Ltd. A D-glucose stock solution (0.1 M) was prepared and allowed to mutarotate overnight prior to use. Phosphate buffer saline (PBS, 0.1 M Na_2HPO_4-NaH_2PO_4-KCl) and its different pH values were adjusted with H_3PO_4 or NaOH solutions. All reagents are of analytical grade, and used without purification and prepared using distilled water.

Apparatus: The electrochemical experiments such as cyclic voltammetry (CV) were carried out on a CHI 660E electrochemical workstation (Shanghai Chenhua, China). A three-electrode system was employed with a glassy carbon electrode (GCE, 3 mm in diameter), a saturated calomel electrode (SCE) as reference electrode and Pt wire as the auxiliary electrode. Scanning electron micrographs (SEM, S-

4800, Japan) were obtained at 15 kV acceleration voltage. A FT-IR spectrum was conducted by the German spectrometer of tensor 27 Bruker FT-IR. X-ray photoelectron spectroscopic (XPS) spectrum was obtained with an ESCALAB 250Xi spectrometer (USA).

The synthesis of TiO_2-SnS_2 nanocomposite : The SnS_2 precursor nanomaterials were prepared by a simple hydrothermal procedure[S1]. 5 mM $SnCl_4 \cdot 5H_2O$ was dissolved in 30 mL deionized water with ultrasonic dispersion for 5 min. Then 10 mL 0.5 M of citric acid and 10 mM CH_3CSNH_2 were dropped to the solution. The mentioned solution was dealed with ultrasonic dispersion for 20 min, and finally was put into 50 mL Teflon-lined stainless steel autoclave and heated at the temperature of 160℃ for 12 h. After the autoclave was cooled to room temperature naturally, the yellow precipitate was filtered and washed with deionized water several times. The product was dried in a vacuum at 100 ℃ for 4 h. .

0.4 g SnS_2, 4 mL glacial acetic acid and anhydrous ethanol were added successively in the Teflon liner and mixed homogeneously by stirring. After TBT was dropped to the solution with continuous stirring for 5 min, then the mixture was transferred into Teflon-lined stainless steel autoclave and heated under the temperature of 180 ℃ for 12 h. The yellow precipitate was filtered and washed with deionized water several times. After being dried in a vacuum at 100 ℃ for 4 h,the nanocomposite of TiO_2-SnS_2 was Finally obtained.

Preparation of enzyme biosensor: The GCE was polished with 0.3 and 0.05 μm alumina powder (Buhler), then sonicated in HNO_3/acetone(1:1) and distill water for 20 min, respectively. 1.0 mg TiO_2-SnS_2 was dispersed in 1.0 mL distilled water and sonicated for 30 min. and 10 mg of GOx was added to 1.0 mL the TiO_2-SnS_2 suspension (1.0 $mg \cdot mL^{-1}$) under gentle stirring for 15 min. Afterwards, 5.0 μL of GOx/TiO_2-SnS_2 suspension was coated on surface of GCE and dried in refrigerator. Finally, 5.0 μL of Nafion (0.5%) was dropped on enzyme electrode. The GOx/TiO_2-SnS_2/Nafion/GCE was rinsed thoroughly with distilled water to get rid of the loosely adsorbed GOx molecules. When not in use, the enzyme electrodes were placed in the 0.1M PBS (pH=7.0) and stored at 4 °C in a refrigerator.

References

S1 Z. J. Yang, Y. Tang, J. Li, Y. C. Zhang, X. Y. Hu, *Biosens. Bioelectron.*, 2014, **54** , 528–533.

XPS spectrum for characterization of the biosensor

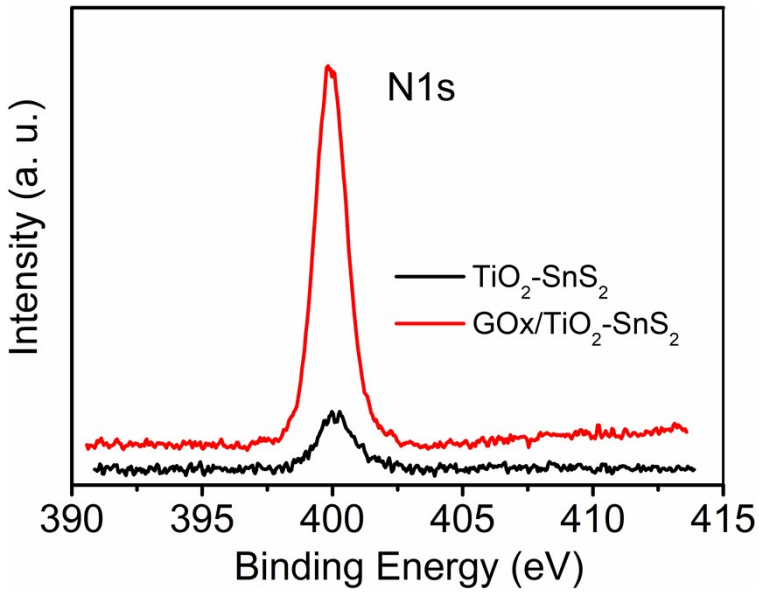

Fig. S1. XPS of N 1s peak of TiO_2-SnS_2 composite and GOx/TiO_2-SnS_2.