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Short communication

ZnO nanorods/Au hybrid nanocomposites for glucose biosensor

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ABSTRACT

ZnO nanorods/Au hybrid nanocomposites (ZnO/Au) with Au nanocrystals growing on the surface of ZnO nanorods were synthesized via a simple and facile hydrothermal route. The prepared ZnO/Au nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM) for the morphology study. The composites had a good electron transferring and biocompatibility. The glucose biosensor was fabricated by entrapping glucose oxidase (GOx) in this composite matrix using cross-linking method with glutaraldehyde and Nafion solutions. The proposed biosensor responded to glucose linearly over concentration range of 0.1–33.0 μM (R^2 = 0.9956), and the detection limit was 10 nM (S/N = 3) at an operating potential of +0.55 V in pH 7.4 phosphate buffered solution (PBS). The biosensor exhibited a high and reproducible sensitivity, short response time (within 5 s), good storage stability and high affinity to GOx (K_M^{app} = 0.41 mM). The effects of electroactive interferents at the testing conditions can be negligible which showed a good selectivity of the biosensor. It is estimated that this ZnO/Au is an attractive material for the fabrication of efficient amperometric biosensors.

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1. Introduction

Glucose is a keen metabolite for living organisms, especially in the case of patients suffering from diabetes. An accurate measurement of glucose level in blood has long been recognized as an important clinical test for diagnosing diabetes mellitus (Rakhi et al., 2009; Poscia et al., 2003). Amperometric enzyme electrodes, based on GOx, have played a leading role for the determination of glucose due to their high sensitivity, repeatability and simple operation. Since the development of the first glucose biosensor, improvement of the response performance of enzyme electrodes has been the main focus of biosensor research (Liu et al., 2010). Gold nanoparticles have been extensively used in biosensor due to their unique capabilities to enhance mass transport, facilitate catalysis, increase surface area, and control an electrode's microenvironment (Rakhi et al., 2009; Scodeller et al., 2008; Du et al., 2007). Searching for new materials and methods for immobilizing enzymes are still very important subjects towards more active and stable biosensors (Yang et al., 2002; Tsai et al., 2005).

Significant research efforts have been taken on multifunctional nanocrystals that comprise two or more different components because of the possibility of combination and integration of properties of the materials together from the viewpoint of technique requirements, which usually cannot be attainable in single-component nanocrystals (Zhang et al., 2008; Lee et al., 2006; Huh et al., 2005). The heterostructures are mainly classified as two types, the core–shell structures (Wang et al., 2006; Green, 2005) and the heterodimer (Casavola et al., 2007; Gu et al., 2005). The core-shell structures, in which a nanocrystalline core is covered by a shell of another or several materials, for instance, two or more types of semiconductors (Dabbousi et al., 1997), semiconductors-magnet (Casavola et al., 2007), metal-semiconductors-magnet (Kim et al., 2005) will improve the original properties of the pure materials. The heterodimer structures, in which two or more inorganic compounds are interconnected through a small interface, such as semiconductor/semiconductor (Halpert et al., 2006), metal/semiconductor (Saunders et al., 2006; Yang et al., 2006), magnet/semiconductor (Buonsanti et al., 2006) and metal/metal (Pellegrino et al., 2006; Choi et al., 2006) can also enhance the properties of pure component.

Zinc oxide (ZnO) nanostructures have significant applications in optics, optoelectronics, sensors, and actuators due to their semiconducting, piezoelectric, and pyroelectric properties (Tseng et al., 2003; Li et al., 2004; Johnson et al., 2004). Extensive efforts have been made to fabricate various kinds of chemical and biochemical sensors based on ZnO nanostructures, such as fluorescent biosensors with nanoscale ZnO platforms (Dorfman et al., 2006; Liao et al., 2007) H_2S gas sensor with single ZnO nanowire (Liao et al., 2007), intracellular pH sensor with ZnO nanorod (Al-Hilli et al., 2006) and ethanol sensor with flowerlike ZnO nanostructure (Feng et al., 2005). Due to their unique properties, these ZnO

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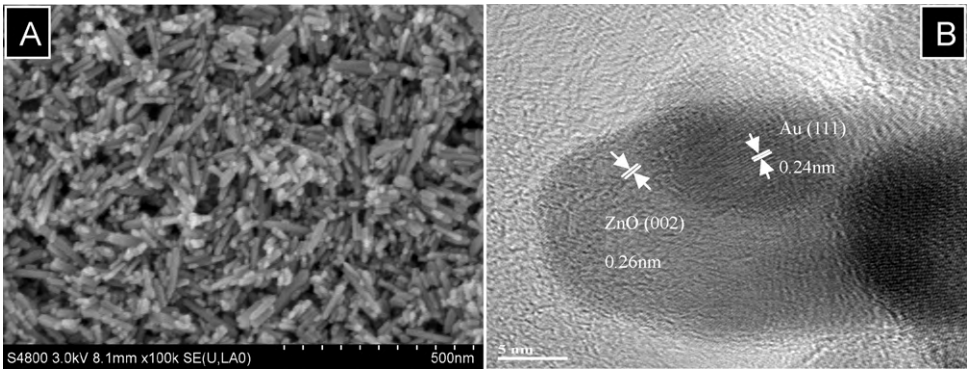

Fig. 1. Typical high-magnification FESEM images (A) and high-resolution TEM images (B) of the as-synthesized ZnO nanorods/Au hybrid nanocomposites.

nanosensors show higher sensitivity and lower limit of detection (LOD) as compared to those prepared from bulk ZnO devices. For enzyme-modified nanosensors, the ZnO nanostructure is one of the most promising substrates for immobilizing enzyme because of their properties including biocompatibility, vast surface-to-bulk ratio, relative chemical stability in physiological environment, and electrochemical activity (Tian et al., 2002; Rodriguez et al., 2000). Moreover, ZnO has a high isoelectric point (IEP) of about 9.5, which should provide a positively charged substrate for immobilization of low IEP proteins or enzyme such as GOx (IEP ≈ 4.2) at the physiological pH of 7.4. In recent years, heterostructures of ZnO/metal nanocomposites (e.g., ZnO/Au (Subramanian et al., 2003; Wang et al., 2007), ZnO/Ag (Zheng et al., 2007)) and their optical properties have attracted intense attention. To our best knowledge, controlled synthesis of water-soluble ZnO/Au hybrid nanocomposites and based electrode enhance the sensitivity for analytes as demonstrated by the detection of glucose without the presence of a mediator has not been reported so far. In this paper, we report a facile solution strategy to synthesize ZnO nanorods/Au hybrid nanocomposites and enhance the sensitivity and LOD of glucose biosensor.

2. Experimental details

2.1. Reagents and apparatus

Glucose, glucose oxidase type VII (136 000 units/g, EC 1.1.3.4. from Aspergillus niger) and Nafion were purchased from Sigma. $Zn(Ac)_2{\cdot}2H_2O$ and other reagents were of analytical grade, purchased from Shanghai Chemical Factory (Shanghai, China). Serum samples were kindly provided by the Hospital of East China Normal University (Shanghai, China) and used with dilution. Amperometric detections were carried out on CHI 660C electrochemical workstation (CH Instruments, USA) with a three-electrode system, a ZnO/Au/GOx/Nafion modified electrode as working electrode, a Ag/AgCl as reference electrode and a platinum electrode as counter electrode. All experiments were performed at ambient temperature ($25 \pm 1\,^{\circ}C$).

The XRD patterns were collected on a Bruker D8 Advance instrument using Cu–Kα radiation. The morphologies of as-prepared product were observed with a JEM-2100 high resolution transmission electron microscope (HRTEM) (JEOL Co. Ltd., Japan) operated at an acceleration voltage of 200 kV and HITACHI S-4800 scanning electronic microscopy (Hitachi Co. Ltd., Tokyo, Japan). UV spectrum was obtained at ambient temperature using a Cary 50 Conc UV–Visible Spectrophotometer (Varian, USA).

2.2. Synthesis of ZnO nanorods/Au nanocomposites

The synthesis of the ZnO nanorods was described in Supplementary data. Gold nanocrystals formed directly onto the ZnO nanorods in the following procedure. The washed ZnO nanorods (0.40 mM) were redispersed in a 50 mL diluted trisodiuom citrate solution by ultrasonic treatment. 0.2 mL of $HAuCl_4$ solution (0.01 M) was dissolved in 10 mL of water and added dropwise into ZnO solution. Then, the mixed solution was stirred at 80 °C for about 12 h. The pink-colored product was then collected by centrifugation and washed with distilled water and ethanol several times for further characterization.

2.3. Preparation of biosensor

For the fabrication of glucose biosensors, the as-synthesized ZnO nanorods/Au hybrid nanocomposites were coated on the pretreated glassy carbon electrode (GCE) (Wei et al., 2010), wetted by PBS solution (pH = 7.4) and dried by high-purity nitrogen gas. For immobilization of GOx, cross-linking method was employed and in a typical reaction process, ~100.0 μL GOx solution, 50.0 μL (2.5%) glutaraldehyde and 50.0 μL (0.5%) Nafion solutions were mixed thoroughly. Thereafter, ~2.0 μL above mixture solution was applied onto the GCE/ZnO/Au electrode surface and allowed to dry in air at room-temperature. Finally, 2.0 μL 0.5% Nafion was further coated on the modified electrode to eliminate the possible fouling and prevent the leaching of the enzyme. When not in use, the modified GCE/ZnO/Au/GOx/Nafion electrodes were stored in PBS at 4.0 °C. The electrochemical experiments were carried with a conventional three-electrode configuration.

3. Results and discussion

3.1. Characterization of ZnO nanorods/Au hybrid nanocomposites

Supplementary Fig. 1A and Fig. 1A exhibits the typical SEM images of as-synthesized ZnO nanorods/Au hybrid nanocomposites which reveal that the obtained structures are grown in very high density and multiply Au decorated ZnO nanorods. This can be attributed to the single ionized oxygen vacancies (V_o^+) on the tip or the side of the ZnO nanorods. The surface energy of the "activated centers" is higher than that of the nonpolar planes and is energetically favored to Au deposition (Diebold et al., 2004). The lengths of the ZnO nanorods range from 50 nm to 100 nm and the diameters of Au nanoparticles are about 15 nm which can be affirmed by Supplementary Fig. 1B and Fig. 1B. The X-ray diffraction patterns are in good agreement with the standard data of typical wurtzite structure of ZnO (JCPDS 36-1451) (Supplementary Fig.

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