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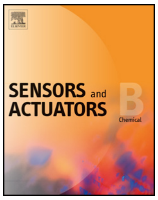

Highly selective H_2O_2 sensor based on 1-D nanoporous Pt@C hybrids with core–shell structure

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ABSTRACT

A strategy of sacrificial template was put forward to prepare porous Pt nanowires core with carbon shell (Pt PNW@C) using Te nanowires as template. These Pt PNW@C hybrids show a highly sensitive response to H_2O_2 oxidation recorded by chronoamperometry at 0.2 V vs. the saturated calomel electrode (SCE). Under optimal conditions, this H_2O_2 transducer displays a linear range of 0.01–1.2 μM with a sensitive of 6.28 $\mu A\,\mu M^{-1}\,cm^{-2}$ ($r = 0.9997$), and a detection limit of 0.002 μM (signal/noise = 3). Moreover, the carbon layer on Pt PNW@C hybrids can greatly enhance the selectivity in H_2O_2 detection in the presence of the common interfering species, such as lactic acid (LA), uric acid (UA), creatinine and glucose, at a positive potential by compared with porous Pt nanowires (Pt PNWs). A glucose biosensor was constructed using this sensitive and selective H_2O_2 transducer combined with glucose oxidase. A calibration curve of glucose concentration can be obtained by measureing enzymatically generated H_2O_2, which shows a linear range from 0.5 to 20 μM with a sensitivity of 0.35 $\mu A\,\mu M^{-1}\,cm^{-2}$ and a detection limit of 0.1 μM.

1. Introduction

Hydrogen peroxide (H_2O_2) is a by-product generated by almost all oxidases in mitochondria. H_2O_2 can diffuse out freely through membranes to reach various cellular compartments [1]. Maintaining H_2O_2 at an appropriate level is essential for intracellular signaling transduction and normal cell functions [2,3]. H_2O_2 is also a major reactive oxygen species involved in various diseases such as cancer, cardiovascular disorders and Alzheimer's disease [4–6]. To better understand the biological effects of H_2O_2, it is critically important to monitor H_2O_2 level in biological environment, especially in cellular environment. Among various measurement used in H_2O_2 detection, the electrochemical approach is of particular interest because of its practical advantages, such as convenience, operation simplicity, low instrumentation expense, and suitability for real-time detection [7].

Horseradish peroxidase has a specific catalysis on H_2O_2 reduction [8,9], but it is susceptible to inactivation under the electrochemical conditions, which limits its application in H_2O_2 detection. Pt-based nanostructures have been explored as alternative electrochemical catalysts for H_2O_2 detection due to their high activity toward H_2O_2 reduction as well as H_2O_2 oxidation [1,6]. However, Pt-based nanostructures were not suitable for selective reduction of H_2O_2 in the presence of oxygen, because it is also active toward oxygen reduction in the potential range applied to H_2O_2 reduction [10]. On the other hand, the direct oxidation of H_2O_2 at common Pt electrodes often requires high overpotential, which is disadvantageous to the sensitive and selective detection of H_2O_2 [11]. Therefore, the quantitative determination of H_2O_2 at physiological pH without interference is of academic and practical interest. Surface modification can remarkably change the catalytic activity of Pt-based nanostructures toward H_2O_2 oxidation, and thus improve the sensitivity and selectivity of these sensors prepared by Pt-based nanostructures in H_2O_2 detection [12,13]. In addition, the electrooxidation of H_2O_2 plays a major role in the development of biosensors based on the determination of enzymatically generated H_2O_2 [14,15].

Herein, a strategy of sacrificial templates was put forward to synthesize porous Pt nanowire core with carbon shell (Pt PNW@C) using Te nanowire as temple. This novel Pt nanostructures can serve as efficient catalysts for H_2O_2 oxidation, and show a high selective and sensitive response to H_2O_2 oxidation even at a high applied potential. This H_2O_2 sensitive sensor can be combined with glucose oxidase and applied in glucose detection.

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2. Experimental

2.1. Reagents and materials

Glucose oxidase (GOx) was extracted from *Aspergillus niger* (Fluka company, 211 U/mg), and used without further purification. Polyvinylpyrrolidone (PVP, molecular weight: 30,000–40,000), hydrazine hydrate (50%, w/w), aqueous ammonia solution (25%, w/w), glutaraldehyde (GA) and albumin from bovine serum (BSA) were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). Other chemical reagents, such as chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$), D-glucose, lactic acid (LA), uric acid (UA), creatinine, sodium tellurite, were analytic pure, and purchased from Acros. Milli-Q system (18.2 MΩ cm) was used for the preparation of all solution.

2.2. Synthesis of core–shell Te NW@C hybrids

Core–shell Te@C nanowire (Te NW@C) hybrids were synthesized by one-pot method, which was similar to the preparation of Te nanowire (Te NW) but in the presence of glucose [17]. Typically, 0.60 g PVP was dissolved in 25 mL of de-ionized water under vigorous magnetic stirring to form a homogeneous solution at room temperature. Then, 0.11 g of Na_2TeO_3 was added into the previous solution and dissolved, followed by the addition of hydrazine hydrate (1 mL), ammonia solution (2 mL) and glucose (1 g). Then, the obtained solution was transferred into the container of Teflon-lined stainless steel autoclave, sealed and maintained at 180 °C for 8 h. Finally, the product was centrifuged and washed with de-ionized water and alcohol, and finally dissolved in 10 mL de-ionized water.

Te NWs were synthesized according to previous reports [16].

2.3. Synthesis of core–shell 1-D nanporous Pt @C hybrids

Te NW@C hybrids were added into 30 mL de-ionized water and followed by adding 0.05 mmol H_2PtCl_6. Pt PNW@C hybrids were obtained after the mixture was continually stirred at 50 °C for more than 24 h. Then, the resulting dispersion was centrifuged and washed with de-ionized water for further use.

Porous Pt nanowire (Pt PNW) was prepared according to previous reports [17].

2.4. Characterization

Transmission electron microscopy (TEM) observation was performed on a JEOL 2010 microscope equipped with an electron energy dispersive X-ray spectroscopy (EDS), operating at 200 kV with a high-brightness LaB_6 electron gun. A drop of 8 μL as-prepared suspension containing Te NW, Pt PNW, Te NW@C or Pt PNW@C hybrids were gently deposited onto a carbon-coated copper grid and dried in air prior to TEM observation.

2.5. Electrochemical investigation

We used a 15 mL glass electrochemical cell containing three electrodes: a glassy carbon disk working electrode (3 mm or 6 mm in diameter) embedded in Teflon, a platinum wire counter electrode (1 mm in diameter, 5 cm in length), and a saturated calomel electrode (SCE) as the reference electrode. Before use, the glassy carbon or bare Pt disk electrodes were polished with 0.5 μm alumina slurry, washed with the de-ionized water, then immersed for 20 min in a sonicator bath, and finally washed with the de-ionized water.

To modify the glassy carbon electrode (GC, 3 mm in diameter) with Pt PNW and Pt PNW@C hybrids, 4.0 mg of these materials were dispersed in 400 μL de-ionized water to form a homogenous catalysts ink by sonication, and then a 5 μL of these catalysts ink was mixed with a 2.5 μL of 0.5% Nafion® 117 ethanol solution. The mixture was spread and air-dried on the electrode at room temperature. For convenience, these modified electrodes were denoted as Pt PNW/GC and Pt PNW@C/GC, respectively.

A three-electrode setup was configured with CHI 660C interfaced to a personal computer at room temperature for the electrochemical characterization. The electrolytic solution was bubbled with nitrogen for 15 min before the electrochemical experiment.

H_2O_2 redox was investigated by cyclic voltammetry in 0.2 M phosphate buffer solution (PBS, pH 7.4) containing 1 mM H_2O_2. These modified glassy carbon electrodes were scanned from −0.4 V to +0.8 V at the scan rate of $50\,mV\,s^{-1}$. H_2O_2 detection was performed under the potentiostatic mode at the operating potential of 0.20 V in 0.2 M PBS (pH 7.4). A rotating disk electrode system (RDE) with a glassy carbon disk (6 mm in diameter) was applied in the amperometric measurement under a rotate rate of 500 rpm, which was controlled by a Pine analytical rotor (Model AFMSRX). For convenience, these modified electrodes were denoted as Pt PNW/RDE-GC and Pt PNW@C/RDE-GC, respectively.

The electrolytic solution was bubbled with nitrogen for 15 min before the electrochemical experiment, and the electrochemical experiments were conducted at the room temperature in ambient condition.

2.6. Preparation of glucose biosensor and detection of glucose

To fabricate glucose biosensor, an aqueous GOx solution was prepared by dissolving 2 mg GOx and 1 mg BSA in 100 μL of PBS solution. Another Pt PNW@C dispersion was prepared by dispersing 1.0 mg Pt PNW@C hybrids in 1 mL of PBS (pH 7.4) solution. Then a 5 μL of the GOx solution and a 5 μL of the Pt PNW@C dispersion was mixed with 4 μL of 0.025% GA, spread, rinsed with the de-ionized water and air-dried on a polished glassy carbon electrode (6 mm in diameter) before use. Glucose detection was also performed at 0.20 V in 0.2 M PBS (pH 7.4), which is controlled by a Pine analytical rotor under a rotate rate of 500 rpm. For convenience, this glucose biosensor was denoted as Pt PNW@C/GOx/RDE-GC.

This glucose sensor was applied in glucose detection in blood sample. The response current was recorded at Pt PNW@C/GOx/RDE-GC in 0.2 M PBS (pH 7.4) after 10 μL serum was added under stirring at a rotate rate of 500 rpm.

3. Results and discussion

3.1. Characterization of Pt PNW@C hybrids

Well-defined Te NW@C hybrids with core–shell structures can be fabricated in one-pot strategy by hydrothermal carbonization of glucose. Fig. 1A and B shows several micron-long Te NWs with high aspect ratios sheathed in the thin carbon cover. The average diameter of inner Te NWs is 10 nm, and the mean thickness of outer carbon layer is 2–3 nm. Upon the basis of the high resolution TEM (HRTEM), as shown in Fig. 1B, it is clear that the *d*-spacing of adjacent fringes on Te NWs is 0.592 nm, corresponding to the (0 0 1) planes of hexagonal lattice of Te [18]. Fig. 1C and D shows that Pt nanowires are covered with thin carbon layer. These as-prepared Pt PNW@C hybrids still remain core-shell structure with 10.5 nm Pt nanowires core and 2–3 nm carbon shell. In addition, different from those smooth Te nanowires, these Pt nanowires are porous, composed of aggregated Pt nanocrystals. The HRTEM image shows the lattice spacing on a single Pt nanocrystal is 0.230 nm, corresponding to the (1 1 1) planes of face-centered cubic lattice of Pt [19]. This