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Nonenzymatic detection of glucose using three-dimensional PtNi nanoclusters electrodeposited on the multiwalled carbon nanotubes

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ABSTRACT

A novel enzyme-free glucose sensor is developed with the three-dimensional (3D) Pt_xNi_{1-x} (x = 0.1–0.9) alloy nanoclusters electrodeposited onto multi-walled carbon nanotubes (MWCNTs). The synthesis, structural, and compositional characterization of 3D Pt_xNi_{1-x}/MWCNTs are reported. Cyclic voltammetry, linear sweep voltammetry, kinetic analysis, electrochemical impedance plots, and amperometric responses exhibit that the 3D Pt_xNi_{1-x}/MWCNTs nanocomposites have more remarkable catalytic performance on the direct oxidation of glucose comparing with the 3D Pt/MWCNTs catalysts and the uniform dispersive morphology Pt_xNi_{1-x}/MWCNTs catalysts. We further investigate how the Pt/Ni atomic ratios of these alloys play a key role in controlling the electrocatalytic activity and thus improve the glucose detection. The optimal Pt/Ni atomic ratio acquired in present experiment condition is 3/7, which proves linearity up to 15 mM of glucose with a sensitivity of 0.94 mA/mMcm^2 and a detection limit of 0.3 μM (S/N = 3) at −0.30 V. Meanwhile, the interference from dopamine, uric acid, *p*-acetamidophenol, ascorbic acid, urea, galactose, lactose and fructose is effectively avoided at this negative potential. The as-synthesized sensor is applicable to the glucose sensing in the real human serum with the concentrations agreeing well with that measured by a hospital. Furthermore, 90% of the surface active sites and the initial sensitivity are retained in continuous tests (31 days), proving favorable long-term stability.

1. Introduction

In recent decades, the emerging desires for glucose sensors with sensitive response, excellent selectivity, good feasibility, and low cost have attracted enormous academic and commercial endeavors [1]. This hot trend is driven by the pharmaceutical and clinical needs as well as by the urgent requirements of healthcare, biological and food surveillance fields [2]. Enzymatic biosensors are considered to be a popular stage due to their significant benefits, such as high sensitivity and excellent selectivity [3]. Nevertheless, to date, several drawbacks of commercialized implanted enzymatic biosensors in long-term clinical practice have not been overcome: i) insufficient long-term stability and the thermal/chemical deformations during fabrication, storage, and use, which originate from inherent fragility of the enzymes; ii) inevitable damaged replies or errant interferences from practical utilization, which can only resort to frequent corrections on compulsion [4].

To solve these problems, nonenzymatic biosensors became a renewed interest engaging major research efforts [5,6], especially the noble metal glucose sensors containing platinum (Pt) [7,8]. Though the early probe of glucose electro-oxidation mechanism investigated that traditional platinum foil electrodes suffered from low sensitivity, sluggish kinetics, catalyst fouling and poor selectivity, the nanometers Pt with higher active surface area applied to glucose detection have evident higher electrocatalytic activity in recent developments. For instance, the high selectivity was obtained because the nanometers Pt as a catalyst favors kinetically-controlled reactions (i.e., the glucose oxidation), not diffusion-controlled reactions (i.e., the oxidation of interferons in body fluids) [9]. Besides this improved selectivity, the nanostruc-

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tured Pt glucose sensors also keep excellent sensitivity, even under the condition of the existence of Cl^- [10]. On the other hand, the Pt based alloys have been proved to be more effective catalysts for glucose oxidation reaction (GOR) and oxygen reduction reaction (ORR), for example, PtRu, PtNi, and PtPb exhibit higher electrocatalysis and corrosion-resistant property than Pt monometallic system [11–14]. In these alloy catalysts, PtNi shows promise for its anticorrosive capacity within the scope of the required voltage due to the passivating role of nickel oxides/hydoxides and the firm integration of Pt and Ni [15]. And, more importantly, the electron transfer from the analytes to the electrodes, which is considered to be one of the most important factors for increasing the sensing efficiency, has to be enhanced for the PtNi alloy electrodes for both the bifunctional mechanism and the electronic effect [16]. At last and most encouragingly, in the recent literatures reported, nickel and nickel oxides/hydroxides are competent to oxidize glucose in mild condition, namely that they are not only promoters but also catalysts for the relevance reaction of glucose sensing [17].

Nowadays, there are many valuable methods by which where various of high sensitive non-enzymatic glucose sensors have been prepared: convention electrodeposition [7,18,19], intense pulse light [9], polyol methods [16], alcohothermal [20], ultrasonic [21–23], electroless plating [24], indirect reduction Pt ions [25,26], microwave thermal [27], or hydrothermal [28]. Taking advantages of carbon nanotubes (CNTs), including the high conductivity, large specific surface areas, and chemical and physical stability, the PtNi alloy/CNTs nanocomposite is considered to be a strong contender for the development of the non-enzymatic glucose detection devices [29]. The PtNi alloy/CNTs nanocomposites, interactively combining the advantages of every part, have performed outstandingly in promoting and stabilizing the reactions [30]. Unfortunately, so far in the literatures the broken bonds of the carbon nanotubes restricted the reaction activity of these nanocomposites, with the depressed electrical conductivity, degraded surface density and weaken mechanical strength [31]. The PtNi catalyst electrodeposited on the carbon nanotubes applied in glucose detection has not been stressed. In addition, for this alloy/CNTs nanocomposite, a further effort is necessitated for the performance improvement and composition analysis.

Herein we report three-dimensional (3D) flowerlike Pt_xNi_{1-x} nanoclusters electrodeposited onto the MWCNTs by an all-electrochemical three-step approach including a key potential pulse sequence in its second step. Compared to the above methods, the proposed electrodeposition protocol does not demand organic solvents [7,19,20,22,23], high temperatures [20,22], separation and purification procedures [20,22,23], and aggressive reductive [25,26], showing the advantages, such as biocompatibility deposits, intact supports, controllable and mild procedure. The application of as-prepared nanocomposites in detection of glucose is evaluated by cyclic voltammetry, linear sweep voltammetry, kinetic analysis, electrochemical impedance plots, and amperometric responses, indicating high sensitive, excellent selective, acceptable linearity range, and remarkable long-term stability. The effect of the control condition and the Pt/Ni composition on the performance of the alloy nanoparticle clusters is also investigated.

2. Material and methods

2.1. Regents and material

α-D(+)-glucose monohydrate (Sigma–Aldrich Co., LLC.), dopamine (DA), ascorbic acid (AA), uric acid (UA), *p*-acetamidophenol (AP), urea, galactose, lactose and fructose were obtained from Shanghai River's electric Co., LTD. Other reagents are as follows: toluene ($C_6H_5CH_3$) (Park Co. Dublin, Ireland), potassium tetrachloroplatinate (II) (K_2PtCl_4) (99.9% Pt), nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) (98% Ni, Sigma–Aldrich Laborchemikalien GmbH, Germany), Nafion (5 wt%, A Johnson Mathey Co., U.S.A.), potassium sulfate (K_2SO_4) (AR, Nacalai Tesque, Inc. Kyoto, Japan), sulfuric acid (H_2SO_4) (AR, BeiHua Chemical Reagent Factory, Beijing, China), and phosphate buffer solution (PBS) (AR, Leici Technology Inc., Shanghai, China). MWCNTs (~90% purity, 7–15 nm, and 0.5–10 μm) (Shenzhen Nanotech. Port. Co., Ltd) were purified in concentrated nitric acid (HNO_3, BeiHua Chemical Reagent Factory, Beijing, China) for ten hours. Deionized water for experiment (ρ=18.5 MΩ cm, 25 ± 1 °C, pH 7) was purified by an ultra pure water system (Milli-Q Co., USA).

2.2. Instruments and apparatus

Electrochemical fabrications and characterization were conducted with a CHI705a electrochemical analyzer (CH Instruments, Inc. USA) using a three-electrode system, where the counter electrode and the reference electrode employed a Pt foil and Ag/AgCl electrode. A 3D Pt/MWCNTs-Nafion electrode, Ni/MWCNTs-Nafion electrode, a Pt_3Ni_7/MWCNTs-Nafion electrode or a 3D Pt_xNi_{1-x}/MWCNTs-Nafion electrode was used as the working electrodes. The morphologies and composition of resulting nanocomposites were characterized by a Hitachi 600 transmission electron microscopes (TEM, Philipps CM20) coupled with energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM, Hitachi S4800), X-ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and an IRIS advantage inductively coupled plasma atomic emission spectroscopy system (ICP-AES, Thermo, USA). The experiments of glucose sensing were recorded with a Keithley 2400 Source Meter (Keithley Instruments Inc. USA). A transformed Cell Culture Incubator (DNP-9082BS-III, Shanghai CIMO Medical Instrument Manufacturing Co., Ltd) was used to conduct the half-cell experiments, assisted by a dissolved oxygen pen (850045 Sper Scientific) and an oxygen monitor controller (ProOx 110, Biospherix, Ltd.).

2.3. Electrodeposition of nanocomposites

The glassy carbon (GC) electrode (3 mm diameter, geometric area ca. 0.28 cm^2, by which the currents divided to obtain the current densities) and a MWCNTs/GC electrode were prepared [32]. The 3D Pt_xNi_{1-x} nanoclusters were electrodeposited on MWCNTs (see Scheme 1) by an all-electrochemical approach based on a three-step method reported in our previous work [33]: (1) The substrates were first anodized in 0.5 M K_2SO_4 for 10 cycles from +1.80 V to −0.40 V (200 mV/s); (2) Pt^{IV} and Ni^{III} complexes were obtained on the MWCNTs surface from the required volumes of 1 M K_2PtCl_4 and 1 M $NiCl_2$ in 0.1 M K_2SO_4 aqueous solutions (pH = 4) with the pulse step process. In this process, the potential was pulsed between 0.30 V and 1.30 V with pulse width 0.0005 s/0.001 s/0.01 s unless the current status was stable; (3) Pt^{IV} and Ni^{III} complexes were converted into 3D Pt_xNi_{1-x} nanoparticle clusters by potential scanning in 0.1 M H_2SO_4 solutions to the steady state (+1.00 V to −0.30 V, 100 mV/s, 10 cycles). Hence, the resulting 3D Pt_xNi_{1-x}/MWCNTs nanocomposites with a flowerlike morphology were formed by using the pulse step process; by contrast, the Pt_xNi_{1-x}/MWCNTs nanocomposites with a uniform dispersion were formed by using cyclic scanning instead of the aforementioned pulse step. For comparison, 3D Pt/MWCNTs or Ni/MWCNTs was also fabricated under the same experimental condition as 3D Pt_xNi_{1-x}/MWCNTs but no $NiCl_2$ precursor was included.

3 μL Nafion (5 wt%) was cast on the prepared 3D Pt_xNi_{1-x}/MWCNTs, Pt_xNi_{1-x}/MWCNTs, 3D Pt/MWCNTs and Ni/MWCNTs electrodes, then dried by airing. The resulting electrodes were denoted below as 3D Pt_xNi_{1-x}/MWCNTs-