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Self-assembly of palladium nanoparticles on functional TiO_2 nanotubes for a nonenzymatic glucose sensor

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ABSTRACT

Polydiallyldimethylammonium chloride, PDDA, was used as a stabilizer and linker for functionalized TiO_2 nanotubes (TiO_2 NTs). Self-assembled process with palladium nanoparticles (NPs) was successfully synthesized and used for the oxidation of glucose on glassy carbon electrodes. Based on the voltammetric and amperometric results, Pd NPs efficiently catalyzed the oxidation of glucose at −0.05 V in the presence of 0.1 M NaCl and showed excellent resistance toward interference poisoning from such interfering species as ascorbic acid, uric acid and urea. To further increase sensitivity, the Pd NPs-PDDA-TiO_2 NTs/GCE was electrochemically treated with H_2SO_4 and NaOH, the glucose oxidation current was magnified 2.5 times than that before pretreatments due to greatly enhancing the electron transport property of the sensor based on the increased defect sites and surface oxide species. In view of the physiological level of glucose, the wide linear concentration range of glucose (4×10^{-7}–8×10^{-4} M) with a detection limit of 8×10^{-8} M (S/N = 3) was obviously good enough for clinical application.

1. Introduction

The current standard of care for treatment of diabetes mellitus includes measurement of physiological glucose levels at least four times daily, coupled with insulin injections to stabilize glucose levels in the normal range [1,2]. Commercially available continuous glucose sensors have recently been reviewed. Most previous studies on these sensors involve use of enzyme glucose oxidase, and then passed to O_2 more commonly with subsequent oxidative detection of H_2O_2 [3]. However, the most serious problem of such sensors is lack of stability and unsatisfactory reproducibility due to the intrinsic nature of enzymes, and the activity of enzyme is influenced readily by temperature, humidity and chemical environment (e.g., pH) [4]. In addition, the interference from some electro-oxidizable species remain as problems for real sensor applications, and reproducibility is also still a critical issue in quality control [5]. In recent years, nanomaterials with special physical and chemical properties have been widely applied in chemsensors and biosensors. Therefore, it is an important strategy in the construction of enzymeless glucose sensors with nanomaterials, because direct electrocatalytic oxidation of glucose at a nonenzymatic sensor would exhibit conveniences and advantages to avoid the drawbacks for enzyme electrode. Especially, the amperometric glucose sensors free from enzymes.

Recently, modification of electrochemical interface with nanosized metal (such as platinum [6,7], gold [8], copper [9] and alloys [10,11,12]) and metal oxide nanostructures (such as MnO_2 [13], ZnO [14], Ag_2O [15] and CuO [16]) has been one of the recent approaches used extensively in the development of sensing platforms. The advantages in tailoring the electrochemical interface with nanoparticles are (i) unique optical, electrical, thermal, catalytic properties and availability of large surface area originating from quantum-size dimensions could change with their sizes and shapes. (ii) High mass transport and enhancement of the electron transfer kinetics, but which is sluggish on the unmodified electrodes, and (iii) increasing the sensitivity and shortening response time, and preventing the undesired electrode reactions to enhance the signal-to-noise ratio.

Palladium nanoparticles (Pd NPs) are one of the most efficient catalysts in the formation of C—C bond and chemical transformation [17], electro-oxidation of formic acid [18] and ethanol electro-oxidation [19]. Xu et al. [20] reported that Pd NPs is a good electrocatalyst for ethanol oxidation and showed higher activity than that of Pt NPs in alkaline media. Moreover, Pd NPs with high electrocatalytic activity and good stability are used in glucose response [21]. The catalytic properties of these metal particles strongly depend on the size, shape, catalyst support etc. [22]. TiO_2 nanotubes (TiO_2 NTs), with high specific surface area, ion-changeable ability, photocatalytic ability, excellent biocompatibility, nontoxic, and good chemical and thermal stability, has attracted considerable interest for conducting support for nanoparticles and sensor substrates [23,24]. Meanwhile, the dispersion of nanometal catalysts on TiO_2 nanostructures can provide new ways to increase the surface

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area and improve the catalyst performance of energy conversion devices. Enhanced electrocatalytic activity of Pd particles dispersed on TiO_2 NTs has already been reported in electrochemical detection of hydrazine [25]. Particularly, compared with the particulate TiO_2 films, the one-dimensional structures show significant enhancement in the electrochemical performance because of improved charge collection efficiency [26].

Herein we report a scalable and ecofriendly method for preparing nanocomposite, where TiO_2 NTs acted as a conducting support for loading Pd NPs. The controlled pre-organization of metal precursor on a conducting support and its subsequent reduction was expected to yield ensembles of nanoparticles. This easy approach for the synthesis of nanoparticles requires less time devoid of using any supplementary capping agents, and the interparticle spacing or the particle coverage on the support can be easily controlled by changing the amount of precursor on the electrode surface. In this work, we found that quaternary ammonium functional groups along the poly (diallyldimethylammonium chloride) (PDDA) [27,28] backbone have a strong electron-accepting ability to withdraw electrons from TiO_2 NTs to induce the net positive charge, and could act as an electrostatic anchor for metal precursor with opposite charge. Thus, the pre-organized Pd precursor located onto the walls of polymer wrapped TiO_2 NTs and chemically reduced to its zero valent state for developing new electrochemical transducers. These characteristics would enhance the rapid transport of surface reaction electrons to the metal substrate, further enhancing the performance of glucose sensor.

2. Experimental

2.1. Reagents

K_2PdCl_4 was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). D-(+)-Glucose was the product of Guangzhou Chemical Reagent Company (Guangzhou, China), and its stock solution was prepared with water. PDDA and TiO_2 nanoparticles (Degussa P25, Germany) were obtained from J&K Chemical Co. Ltd. All other chemicals used were of analytical reagent grade. Ultra-pure water was obtained with a Milli-Q plus water purification system (Millipore Co. Ltd., USA) (18 MΩ).

2.2. Apparatus

Cyclic voltammetric (CV) and chronoamperometric experiments were performed with a CHI 660B electrochemical workstation (CH Instrument Company, Shanghai, China). A conventional two-compartment three-electrode cell with a glassy carbon (GC) working electrode, a Pt wire auxiliary electrode and Ag/AgCl reference electrode. UV–vis spectra (Perkin-Elmer Lambda 900 USA), and crystalline structure of PDDA-TiO_2NTs-Pd NPs hybrid nanostructures were analyzed by powder X-ray diffraction (XRD, X'pert, Philips, Holland). All measurements were conducted at room temperature. Surface morphologies of the samples across the entire substrate were characterized by field-emission scanning electron microscopy (FE-SEM, Nova Nano SEM 230, FEI, USA).

2.3. Preparation of the glucose sensor

The objective of this work is to prepare a TiO_2 NTs-PDDA-supported Pd nano-electrocatalyst for glucose in an alkaline medium. PDDA as an ordinary polyelectrolyte was able to adsorb on the surface of TiO_2 NTs through electrostatic interaction. Inspired by this, PDDA was employed to disperse on the surface of TiO_2 nanotubes, i.e., positively charged PDDA first adsorbed onto the surface of negatively charged TiO_2 NTs (TiO_2 NTs was prepared by hydrothermal method [29]) via the electrostatic interaction. Meanwhile, PDDA act as an electrostatic anchor for $PdCl_4^{2-}$ with opposite charge, and then during the reduction of Pd^{2+} the adsorbed PDDA was expected to act as a stabilizer to make reduced Pd NPs stable in water. Pd nanoparticles have been generated on the modified electrode surface according to Scheme 1.

The TiO_2 NTs were synthesized by hydrothermal method [29] as the following general procedure, 0.4 g TiO_2 nanoparticles (P25) were added into 40 mL of NaOH solution with a concentration of 10 M. Then, the mixture was hydrothermally treated to 140 °C while stirring for 24 h in oil bath. After filtration, the white product was dispersed in 150 mL of 0.1 M HCl by ultrasound, and then was treated with distilled water until pH value was lower than 7. Subsequently, the products were dried at 80 °C and calcined at 400 °C for 3 h to remove any impurity on the TiO_2NTs surface. Finally, the as-prepared TiO_2NTs with well crystallinity was obtained.

PDDA-TiO_2 NTs dispersion was obtained by mixing an optimized amount (0.1 mg) of TiO_2 NTs and 20 μL PDDA in 4 mL distilled water, and sonicated for 30 min at room temperature. PDDA is a highly positively charged species, which can be adsorbed on the surface of TiO_2 NTs and electrodes [30]. To assemble Pd NPs-PDDA-TiO_2 NTs/GCE, 10 μL as-prepared PDDA-TiO_2 NTs solution were dropped on the cleaned electrodes and dried under an infrared lamp at first. Then the PDDA-TiO_2 NTs modified electrode was dipped in 1 mM of K_2PdCl_4 solution for 5 min for the pre-organization of metal precursor with PDDA wrapped TiO_2 NTs. The $PdCl_4^{2-}$-PDDA-TiO_2 NTs/GCE was washed well with water and subsequently soaked in 0.08% (*w*/*v*) aqueous solution of the reducing agent, $NaBH_4$ for 30 min for the reduction of the surface bound Pd complex to metallic Pd NPs.

3. Results and discussion

3.1. Physicochemical characterization

PDDA was positively charged at the experimental condition used in this investigation and it is known to form complex with negatively charged species [31]. The electrostatic interaction of the negatively charged precursor ($PdCl_4^{2-}$) with the positively charged PDDA favors its complexation with quaternary nitrogen of the polymer. And then Pd nanoparticles were assembled onto the TiO_2 NTs surface by the aqueous solution reduction. PDDA plays an important role in the formation of 2D nanowalls of the TiO_2 NTs-PDDA-Pd NPs composite and is also an important factor for improving the stability of the nanocomposite film.

The complexation of $PdCl_6^{2-}$ with PDDA wrapped TiO_2 NTs on the electrode surface and its reduction is confirmed by UV–vis spectra (Fig. 1). UV–vis spectrum of K_2PdCl_4 shows two absorption bands at ~220 and ~275 nm. A broad absorption band for TiO_2 NTs presents at ~325 nm (Fig. 1b), but there are no any other absorption peak that appears while TiO_2 NTs were functionalized by PDDA (Fig. 1c). The band of TiO_2 NTs completely disappears after the $PdCl_4^{2-}$-PDDA-TiO_2 NTs/GCE (Fig. 1d) was soaked in the reducing agent, confirming that the full reduction of K_2PdCl_4 (Fig. 1e). The reduction of preorganized complex resulted in the generation of Pd NPs on the walls of TiO_2 NTs.

The surface morphology and size of surface confined particles have been examined by FE-SEM measurements. Fig. 2(a) displays the SEM image of TiO_2 NTs, with larger surface area are synthesized by hydrothermal method, which were loosely tangled together and the large number of cavities which appeared on the surface of the TiO_2 NTs confirmed their porous characteristics, inducing in high specific surface area to support Pd NPs. Moreover, we can see that TiO_2 NTs arrays consist of 30–50 nm diameter and 2–3 μm long tubes and become crystalline upon annealing. Fig. 2(b) displays the SEM image obtained for the Pd NPs-PDDA-TiO_2 NTs hybrid nanomaterials. Compared with TiO_2 NTs, the hybrid nanomaterials were covered with a layer white membrane, which suggested the presence of PDDA, which adsorbed on the surface of TiO_2 NTs by π–π and electrostatic interaction. But Pd NPs aren't be observed on the walls of TiO_2 NT modified surface. The main reason is due to too small for Pd particles.