Nonenzymatic sensing of glucose using a glassy carbon electrode modified with halloysite nanotubes heavily loaded with palladium nanoparticles

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A B S T R A C T

An efficient and rapid method was developed for the preparation of halloysite nanotubes (HNTs) loaded with Pd nanoparticles (PdNPs) to make a non-enzymatic sensor for glucose. In the preparation step, HNTs self-assembled by sodium dodecylsulfate (SDS) provide an ideal template for loading and arrangement of PdNPs on HNTs. The obtained PdNPs-HNTs nanocomposite material was placed on a glassy carbon electrode to detect glucose. The morphology and composition of the PdNPs-HNTs was investigated by using X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and energy-dispersive X-ray spectrum (EDX). Electrochemical impedance spectroscopy (EIS) reveals charge transfer resistance for the modified electrode. Cyclic voltammetry and amperometry were used to measure the electrocatalytic activity of the PdNP-HNT-modified electrode for non-enzymatic oxidation of glucose. The current response of the PdNP-HNT-modified electrode towards glucose covers two linear regions (0.5 μM to 2.0 mM and 2.0 mM to 15.0 mM). The detection limit is 0.43 μM. The present study indicated that the combination of PdNPs and HNTs endows the sensor with excellent electrocatalytic activity, selectivity, good storage stability and sensitivity.

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1. Introduction

Currently developing the detection of glucose has been one of the important techniques because of not only the increasing and leading diabetes disease but also the crucial requirements in the domains of food, chemistry, biology, and environmental protection [1–4]. There are many techniques applied in glucose detection, such as fluorimetry [5], chromatography [6], colorimetry [7,8], photoelectrochemisty [9], and electrochemistry [10,11]. Among those techniques, electrochemical technique has attracted significant attention due to its advantages in high sensitivity, excellent selectivity and fast response [12]. The electrochemical glucose sensors generally have two main types, the enzymatic [13] and non-enzymatic sensors [14,15]. The majority of these non-enzymatic electrochemical glucose sensors rely on the current response of glucose oxidation directly at the electrode surface. Research on this subject have been focused on the use of transition-metal compound nanostructure such as Ni(OH)$_2$ nanoplates [16], CuO [17], Cu/CuO/ZnO architectures [18] and noble metal such as Pd [19–22], Pt [23,24], Au [25,26] for developing non-enzymatic sensors.

Among those noble metal catalysts, palladium nanoparticles (PdNPs) are one of the most efficient catalysts because of their various advantageous properties, such as the smaller size distribution, bigger

volume percentage of surface atoms and a high binding energy shift and high valence band center downshift with respect to the Fermi level [27]. Moreover, the differences of coordinate bond and the electronic structure between the Pd surface atoms and the internal atoms leading an increase of unsaturation of surface atoms become active sites, thus exhibit excellent catalytic activities. So PdNPs can be widely used in gas sensor [28] and diverse catalytic fields such as electro-oxidation of formic acid [29,30] electrocatalytic for oxygen reduction [31], ethanol [32], automotive exhaust purification [33], organic synthesis reaction [34–40], and so forth. There are also some researches on non-enzymatic glucose biosensors based on PdNPs [21,22]. However, there are weaknesses of palladium catalysts that are deactivated and premature degraded, which include particle growth, coke deposition, coke transformation, and the support material, during the sensing process. This weakness really limits the application of palladium catalysts.

In order to avoid catalyst poisoning, choosing suitable support materials to stabilize the palladium dispersion during the reduction process is especially important. An ideal support material should have the following characteristics: (1) high surface area and abundant active sites for catalyst loading, (2) convenient routes for electron transfer; and (3) low cost and facile preparation [41,42]. The immobilization of metal nanoparticles to nanotubes is of great interest to obtain nanoparticles/nanotube hybrid materials. Halloysite nanotubes (HNTs) are one of promising support materials in the development of catalyst due to their high mechanical strength and chemical resistance. HNTs are

a naturally forming two-layered aluminosilicate ($Al_2(OH)_4Si_2O_5 \cdot nH_2O$) with nanotubular structures [43]. Because of their outstanding characteristics such as natural nanotube, high length-to-diameter (L/D) ratio, low price, etc., HNTs have been attracted researchers attention increasingly. The nanotubular structure of HNTs can also provide a confined space for the metal nanoparticles and reactions [44]. Therefore, HNTs can be explored as a support for active phases in catalysis. The environmental friendly and biocompatible nature enables HNTs to be an infinite possibilities nanomaterial for developing organic/inorganic composites in many fields [45].

In this work, HNTs was used as a support material to make the PdNPs have well dispersion so that the electrocatalytic activity of PdNPs towards glucose oxidation was accomplished. The modification of a glassy carbon electrode (GCE) with the PdNPs-HNTs nanostructures increases its active area and promotes the electron transfer for the glucose oxidation reaction. The PdNPs-HNTs nanostructures catalyze glucose oxidation at a remarkably electrochemical response as well as it is insensitive to interfering agents such as ascorbic acid (AA), uric acid (UA), dopamine (DA). The present study demonstrates that PdNPs-HNTs nanostructures can be a potential catalyst in fabricating novel non-enzymatic glucose sensors.

2. Experimental section

2.1. Reagents

$PdCl_2$ was purchased from Tianjin TianLi Chemical Reagent Ltd. (Tianjin, China). AA, UA, DA, fructose and lactose were purchased from Sigma. High purity HNTs was purchased from Mineral processing plants Lingshou Yanbo. Chitosan (CS, MW 5-6 $\times 10^5$, >90% deacetylation) was purchased from Shanghai Reagent Company. Prior to use, HNTs were treated by sonicating in a mixture of concentrated HNO_3 and H_2SO_4 (at the ratio of 1: 3) for 2 h. The glucose stock solution was allowed to mutarotate at least 24 h before use. All other reagents and chemicals were analytical reagent grade and aqueous solutions were prepared with deionized water from a Millipore system (>18 MΩ cm).

2.2. Apparatus and electrochemical measurements

KQ-800KDE Ultrasonic Cleaner (Kunshan Co. LTD, China) was used to prepare samples. The transmission electron microscope (TEM) image and energy-dispersive X-ray spectrum (EDX) were carried out by Tecnai G^2 F20 S-TWIN (FEI, USA). The X-ray diffraction (XRD) patterns of the samples were observed by D/MAX-3C (Rigaku, Japan).

Electrochemical measurements were carried out in a conventional three-electrode electroanalysis system controlled by EC 550 electrochemical workstation (Gaoss Union Technology Co., Ltd., Wuhan, China) and CHI660 electrochemical workstation (Shanghai CH Instrument Co., Ltd., China). A glassy carbon electrode (3 mm in diameter) modified with the catalysts was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire electrode were used as the reference electrode and the auxiliary electrode, respectively. All potentials were reported with respect to SCE.

2.3. Synthesis of PdNPs-HNTs nanostructures

The procedure used to fabricate PdNPs-HNTs is shown in Scheme 1. For comparison, the PdNPs-HNTs composites with different ratios of Pd/HNTs (1: 4, 1: 8 and 2: 1) were also synthesized. The ratio of Pd/HNTs 1: 4 as an example, the typical synthesis process is as follows: Firstly, 1.0 mL of 0.0564 M $PdCl_2$ aqueous solution was added to a 10.00 mL 0.02 M trisodium citrate solution. Secondly, 10.00 mL of 0.1 M SDS aqueous solution was added to the above solution and stirred for 30 min. Subsequently, excess $NaBH_4$ solution was added in a dropwise manner under stirring condition. Finally, 20 mg HNTs was added into the above solution and stirring overnight. The PdNPs-HNTs composite was recovered from the mixture by centrifugation, rinsed with double distilled water and ethanol 3 times, dried at 60 °C for 12 h.

2.4. Fabrication of the PdNPs-HNTs modified electrode for electrochemical studies

Prior to use, the GCE was polished with 1.0 and 0.3 μm alumina powder successively to obtain mirror like surface, followed by sonication in ethanol solution and doubly distilled water successively. Then, the GCE was allowed to dry in a stream of nitrogen. The PdNPs-HNTs composites (1 mg) were well-dispersed in 1.0 mL DMF by ultrasonic treatment for 10 min. Then the suspension (5 μL) was cast onto the GCE and dried in air at room temperature.

3. Results and discussion

3.1. Morphology and structure characterization of the HNTs and PdNPs-HNTs

The morphologies and structures of the HNTs and PdNPs-HNTs were characterized by TEM. As can be seen from Fig. 1a and b, the majority of the HNTs sample consists of cylindrical tubes of with the diameter of 40–50 nm and length of 400–600 nm. Fig. 1c, d, e and f indicate that the HNTs acted as a substrate and Pd nanoparticles were dispersed on HNTs surfaces, and the average particle size of PdNPs is about 4 to 5 nm. It was obvious that PdNPs aggregate together to form several spheres on the surfaces of the HNTs. These images suggested that PdNPs were successfully attached onto the HNTs surfaces. In order to confirm the composition of the particles, EDX spectra were collected during TEM imaging. EDX patterns shown in Fig. 2 reveal the composites are composed of C, O, Al, Si and Pd elements which suggests PdNPs-HNTs nanocomposites were synthesized successfully.

Fig. 3 shows the powder XRD patterns of pristine HNTs before and after hybridization. The HNTs show a diffraction peak at 2θ = 12.9°, which is related to the 0.725 nm basal spacing for the (001) peak reflection from the walls of coaxial multiwalled nanotubes. Some crystal faces
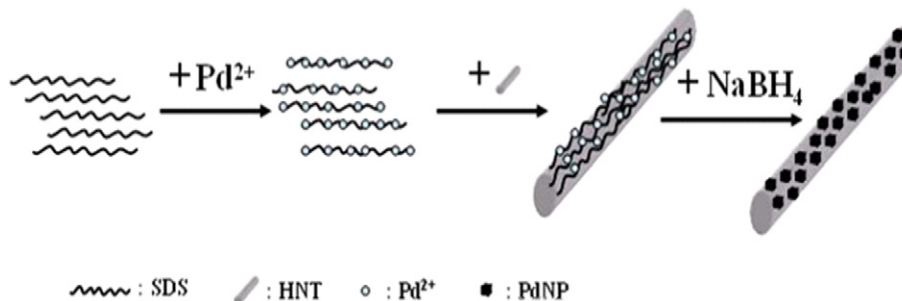
Scheme 1. Schematic procedure of the synthesis of PdNPs-HNTs nanostructures.