Ultrafine palladium nanoparticles grown on graphene nanosheets for enhanced electrochemical sensing of hydrogen peroxide

Xiao-mei Chen [a,c,*], Zhi-xiong Cai [d], Zhi-yong Huang [a], Munetaka Oyama [c], Ya-qi Jiang [b], Xi Chen [b,**]

[a] College of Biological Engineering, Jimei University, Xiamen 361021, China
[b] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China
[c] Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan
[d] Ministry of Education Key Laboratory of Analysis and Detection Technology for Food Safety, Fuzhou University, Fuzhou 350002, China

ARTICLE INFO

ABSTRACT

A nonenzymatic electrochemical method was developed for hydrogen peroxide (H_2O_2) detection using an electrode modified with palladium nanoparticles (PdNPs)-graphene nanosheets (PdNPGNs). Ultrafine PdNPs were homogeneously modified on graphene nanosheets through a facile spontaneous redox reaction and characterized by transmission electron microscopy, energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy technique. Based on the voltammetric and amperometric results, the PdNPGNs-modified glassy carbon electrode (PdNPGNs-GCE) demonstrated direct and mediatorless responses to H_2O_2 at a low potential. The analytical performances of the PdNPGNs-GCE toward H_2O_2 reduction was evaluated in the linear response range from 0.1 μM to 1.0 mM, with a detection limit (S/N = 3) of 0.05 μM. The PdNPGNs-GCE showed excellent resistance toward poisoning from such interfering species as ascorbic acid, dopamine and glucose. Furthermore, the electrochemical sensor presented good characteristics in terms of stability and reproducibility, promising the applicability of this sensor in practical analysis.

1. Introduction

Hydrogen peroxide (H_2O_2), a well-known oxidizing agent, is not only a by-product of a large number of oxidase enzymes, but also an essential mediator in food, pharmaceutical, clinical, industrial and environmental analysis [1,2]. In living organisms, H_2O_2 is a signaling molecule to regulate various biological processes, such as vascular remodeling, immune cell activation and root growth [3]. As a result, there is an ever-growing demand to create high sensitivity, high reliability, rapid, recyclable and low cost H_2O_2 sensors. Electrochemical H_2O_2 sensors, especially nonenzymatic amperometric biosensors, hold a leading position among various biosensors.

Recently, the interest in these enzymeless sensors has been centered on the efforts to find a breakthrough in the electrocatalysts [4–7]. Taking the advantages of catalytic activities, efficient electron transfer rate, and large specific surface area, nanomaterials, especially noble metal nanoparticles modified electrodes usually exhibit high electrocatalytic activities toward H_2O_2

reduction [8–10]. Among these nanomaterials, palladium nanoparticles (PdNPs) are one of the most efficient catalysts, especially in the formation of the C—C bond and chemical transformations such as hydrogenation, hydrodechlorination, carbonylation and oxidation [11,12]. Furthermore, the abundance of Pd on the earth is at least fifty times more than that of Pt [13], which has raised the interest for intensive research on PdNPs in areas of electrocatalysis. In the sensing of H_2O_2, PdNPs show much enhanced catalytic activity for H_2O_2 reduction with the H_2O_2 detection limit reaching 0.1 μM level [14]. Despite this increased activity and sensitivity, probes made from these PdNPs are still not sensitive enough for the determination of H_2O_2 in some special biological systems.

Recent studies have indicated that the size and the distribution of PdNPs play a vital role in the catalytic ability for H_2O_2, and the matrix for the preparation of PdNPs is also very important [15,16]. This gives a hint that the sensitivity of H_2O_2 sensing can be improved greatly by PdNPs with ultrafine size and well dispersion on some proper materials. Moreover, as a famous supporting material, graphene nanosheets (GNs) possess a theoretical surface area of $2630 \, m^2 \, g^{-1}$, which surpasses that of graphite ($10 \, m^2 \, g^{-1}$), and is two folds larger than that of carbon nanotubes ($1315 \, m^2 \, g^{-1}$) [17,18]. Therefore, GNs have received considerable interest for immobilizing nanoparticles on them [19–21].

In our previous study, we discovered a facile method to synthesize high active PdNPs on graphene oxide (GO) nanosheets by the

* Corresponding author. Tel.: +86 592 6181910; fax: +86 592 6180470.
** Corresponding author. Tel.: +86 592 2184530; fax: +86 592 2184530.
E-mail addresses: xmchen@jmu.edu.cn (X.-m. Chen), xichen@xmu.edu.cn
(X. Chen).

galvanic cell effect between $PdCl_4{}^{2-}$ and GO [22]. Previous research based on first-principles calculations indicates that Pd could interact with and bind more strongly to GNs because more interaction states and transmission channels are generated between them, moreover, Pd tends to grow into three-dimensional structures on GNs surfaces [23–25]. This provides a hint that GNs could be an ideal substrate for growing and anchoring PdNPs. In the further research, we found that ultrafine PdNPs can be easily prepared on the GNs by spontaneous redox between $PdCl_6{}^{2-}$ and GNs. Taking the advantage of the ultrafine, well-dispersed, high-yield, "clean" surface (template-free preparation) of PdNPs and the large surface area, high conductivity of GNs, the nano-composite revealed an unusually high electrocatalytic activity and excellent performance for H_2O_2 determination. Under optimized conditions, the linear response of current to H_2O_2 concentration was valid in the range from 0.1 μM to 1.0 mM, with a detection limit (S/N = 3) of 0.05 μM, which is much sensitive than most of the other H_2O_2 sensors. Moreover, the detection was carried out in phosphate buffer solution (PBS) with the pH of 7.4, which is helpful to better understand the effects of H_2O_2 in biological environment. To the best of our knowledge, this is the first time that a PdNPGNs modified electrode has been employed in the development of nonenzymatic H_2O_2 biosensors. This result demonstrated that the applications of a PdNPGNs modified electrode was feasible in H_2O_2 detection and indicated a breakthrough in nonenzymatic sensors using Pd-based electrodes.

2. Experimental

2.1. Materials

K_2PdCl_6 was purchased from Wako Pure Chemicals, Co. Ltd. (Japan); the graphite powder was from Lvyin Co. (China); 5% Nafion ethanol solution and Pd black were from Aldrich Chem. Co. (USA); rod glassy carbon electrodes (GCEs) and Pd electrode were from BAS Co. Ltd. (Japan). All other reagents were of analytical grade

and used without further purification. The pure water for solution preparation was from a Millipore Autopure WR600A system (USA).

2.2. Instrumentation

Morphologies and crystal structures of PdNPGNs observed by TEM and high-resolution TEM (HRTEM) were performed on a JEM-2100 transmission electron microscopy with an acceleration voltage of 200 kV. All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on a copper grid coated with carbon film. Energy dispersive X-ray spectroscopy (EDX) analysis was used to identify the elemental composition of the complex. Electronic binding energies of Pd3d were measured by X-ray photoelectron spectroscopy (XPS) analysis which was performed on a PHI Quantum 2000 Scanning ESCA Microprobe with a monochromatized microfocused Al X-ray source. All the binding energies were calibrated by C 1s as reference energy (C 1s = 284.6 eV). Electrochemical measurements were performed with a CHI 830 Electrochemical Analyzer. A conventional three-electrode system included a GCE coated with PdNPGNs film, a silver auxiliary electrode and a saturated calomel reference electrode (SCE).

2.3. Procedures

GO was prepared according to a modified Hummer's method [26,27]. For the reduction of GO, 50 mg as-synthesized GO was dispersed in 100 mL water to obtain a yellow-brown aqueous solution with the aid of ultrasonication. GNs were achieved by heating the GO aqueous solution in an oil bath at 100 °C for 24 h [28].

In a typical synthesis of ultrafine PdNPs on GNs, homogeneous GNs suspension (5 mL 0.5 mg mL^{-1}) and K_2PdCl_6 (0.5 mL 10 mM) aqueous solution was kept in a vial under vigorous stirring for 60 min at 30 °C. Then, the reaction mixture was washed with pure water and centrifuged to remove the remaining reagents. Before the preparation of the catalysts modified GCE, the GCE was polished with 1, 0.3 and 0.05 μm α-Al_2O_3, sequentially. For coating the GC
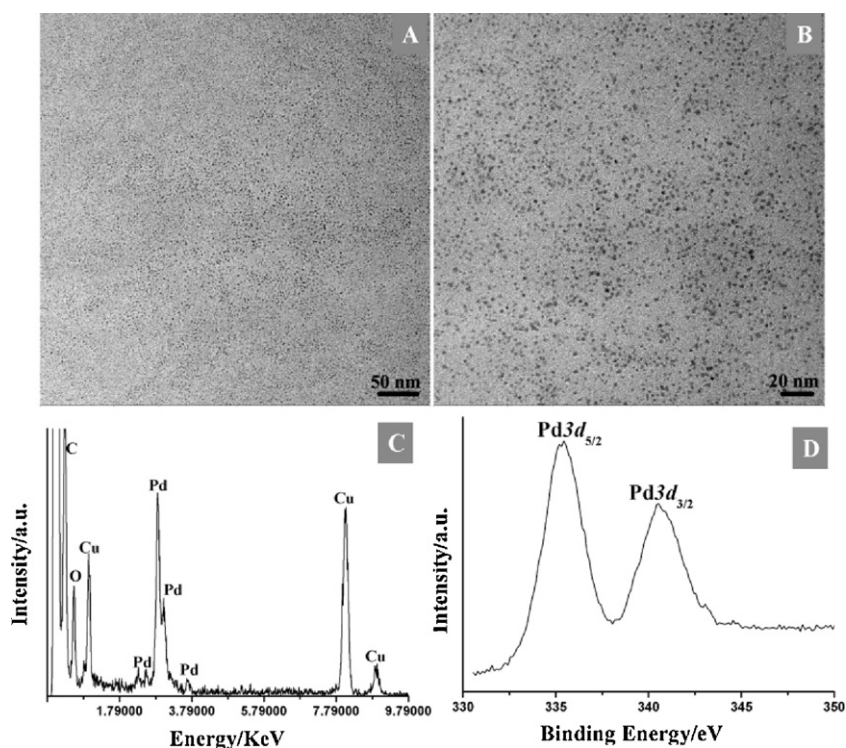

Fig. 1. Representative TEM (A) and HRTEM (B) images of PdNPGNs composite. The EDX (C) and Pd3d XPS spectra (D) of the as-synthesized PdNPGNs composite.