# Detection of hydrogen peroxide at a palladium nanoparticle-bilayer graphene hybrid-modified electrode

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## ARTICLE INFO

## ABSTRACT

We report a nonenzymatic $H_2O_2$ sensor based on a glassy carbon electrode modified with bilayer graphene films (BGFs) that were decorated with well-defined Pd nanoparticles. The BGFs were synthesized with a chemical vapor deposition process, and the Pd nanoparticle films were produced by gas phase cluster beam deposition. The BGFs provide great accessible active surface area and excellent conductive interfaces for electron transfer, which largely enhance the electrocatalytic performance of the modified electrodes. A rapid response time of less than 3 s and a wide linear range from 4 μM to 13.5 mM was exhibited in the amperometric detection of $H_2O_2$.

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## 1. Introduction

Fast quantitative determination of hydrogen peroxide ($H_2O_2$) is important in many fields, such as clinical chemistry, biotechnology, environmental monitoring, pharmaceuticals, and food analysis [1–5]. Among various analytical methods that have been used for the detection of $H_2O_2$, electrochemical (amperometric and potentiometric) techniques have received great attention because of their high efficiency, low cost, and high sensitivity [6–9]. In practice, amperometric determination of $H_2O_2$ is suitable for quick test applications. However, amperometric sensors with bulk electrodes require high overpotential for $H_2O_2$ oxidation, which results in interference from other species in real samples, such as ascorbic acid, urea, and paracetamol [10,11]. Furthermore, the electrode reactions are so irreversible that the responses obtained are usually unstable with poor linearity [12,13]. Efforts have been focused on modifying the electrode surfaces using suitable materials, including enzymes, to improve the selectivity and stability of $H_2O_2$ sensors. Recently, development of enzyme-free electrodes modified with metal nanoparticles (NPs) has become a trend [14–23]. The

nanoparticle-based non-enzymatic $H_2O_2$ sensors were found to be versatile, with a low detection limit and wide response range.

Non-enzymatic $H_2O_2$ sensors based on noble metal nanoparticles, such as silver [24,25], and palladium [26,27], have attracted considerable attention because of their excellent catalytic activity and electrical conductivity. Liao et al. [28] fabricated a highly adhesive Ag nanoparticle coating on a glass carbon electrode (GCE) using gas phase nanoparticle beam deposition. The Ag NP-modified GCE exhibited high electrocatalytic activity toward the reduction of $H_2O_2$ with a detection limit as low as $1 \times 10^{-6}$ M and a very fast response time of less than 1 s. Recently, we used a similar method to fabricate Pd NP-deposited-GCE, which enabled highly selective amperometric detection of $H_2O_2$ at a sufficiently low applied potential ($\sim$−0.12 V) [29]. Although both the lower detection limit and the linear response range of the Pd NP-modified GCE were superior to those of the Ag NP-modified GCE, its response time was approximately one order of magnitude slower.

Graphene sheets (GS) have excellent electrical conduction in two dimensions with good chemical stability. They have been the subject of considerable interest in recent years because of their excellent electrocatalytic activities [6,30–32]. Graphene-metal nanoparticle hybrids may have much higher electrocatalytic activity than that of GS, providing a new way to develop catalytic materials [33]. Phan and Chung synthesized graphene-supported Pd nanocubes for hydrogen detection [6]. Zhou et al. prepared a

Au NP/GS nanocomposite-modified GCE for the detection of $H_2O_2$ [34]. Rosy et al. developed a graphene-modified Pd sensor for the determination of norepinephrine [7]. Until now, GSs used for electrode modifications were generally the chemically reduced graphite oxide (rGO) sheets, with some intrinsic limitations such as a lack of control of the film thickness as well as the use of toxic chemicals. Recently, GSs produced by chemical vapor deposition (CVD) have been considered for electrode modifications [8,9,35,36]. Compared with rGO, they have better quality control and higher electron conductivity. CVD-synthesized bilayer graphene has an electric-field-controllable band gap and thus has attracted special interests [37,38]. However, the chemistry and sensor application of bilayer graphene sheets and their metal NP hybrids have not been much studied. Their electrocatalytic activity and non-enzymatic sensing behavior have not been fully understood.

In this work, for the first time, Pd NPs were deposited on bilayer GSs supported with glass carbon electrodes in the gas phase. The loading amount and size of Pd NPs were well controlled. The electrocatalytic performance of Pd NPs/bilayer graphene films (BGFs)/GCEs toward $H_2O_2$ detection were investigated, with the main focus being their linear response range and response time.

## 2. Materials and method

### 2.1. Preparation of bilayer graphene covered electrodes

BGFs were synthesized by CVD with copper foil as the growth substrate; the details on the fabrication process can be found elsewhere [39]. In order to transfer the bilayer graphene to the electrode, a thin layer of poly(methyl methacrylate) (PMMA) (9% in anisole) was spin-coated on top of the BGF. The copper foil was then submerged in a 1.0 M $FeCl_3$ solution and removed completely after etching for 2 h, leaving a continuous film of PMMA/BGF floating on the solution. The films of PMMA/BGFs were picked up from the solution with a glass slide and washed carefully in deionized water. Finally, the PMMA/BGFs were picked up on the GCE surface from the deionized water and dried in vacuum at 80 °C for 30 min. The PMMA layer was then removed with acetone. Before covered with BGFs, the GCEs (3 mm in diameter) were carefully polished to obtain a mirror-like surface and washed in absolute ethanol and ultrapure water. All the specimens were inspected with an optical microscope to insure that the surfaces of the GCEs were fully covered with BGFs uniformly. BGFs were also transferred to the surface of indium tin oxide (ITO) films. The ITO conductive glass ($10 \times 10\,mm^2$) were purchased from YaRong Chemical Reagent Co. (Nanjing, PR China).

### 2.2. Preparation of Pd NPs and deposition of Pd NPs/BGF hybrid-modified GCEs

Fig. 1 schematically depicts the preparation of Pd NPs/BGF/GCE. Pd nanoparticles were generated by a gas aggregation cluster source. The deposition was performed in a high vacuum chamber equipped with the cluster source. Pd atoms were sputtered from a Pd target in an argon buffer gas (purity, 99.999%) in a liquid nitrogen-cooled aggregation tube. In order to produce Pd nanoparticles with a controlled size, three buffer gas pressures of 90 Pa, 110 Pa, and 130 Pa were used. A stable magnetron discharge ran with an input power of 130 W. Pd nanoparticles were formed in the argon gas through the aggregation process. The nanoparticles were swept by the gas stream into high vacuum through a nozzle, forming a nanoparticle beam with a high speed of ~1000 m/s [40]. The deposition was carried out at a precisely controlled rate of $0.42\,\text{Å}\,s^{-1}$ for 30 min. The corresponding nanoparticle coverage was about 85%, as characterized with transmission electron microscopy.

### 2.3. Chemical reagents

All chemicals from commercial sources were of analytical grade. All solutions were prepared using distilled water.

### 2.4. Characterization

The microstructures of the Pd nanoparticles and Pd NPs/graphene hybrid were characterized with transmission electron microscopy (TEM, TecnaiF20). For TEM, the nanoparticles were either deposited simultaneously on amorphous carbon films supported with copper grids, or deposited on the bilayer graphene transferred on the copper grid surface. The graphene films were characterized using a Raman spectrometer (NTMDT NTEGRA spectra). For Raman spectroscopy, the graphene films were transferred to the surface of a Si wafer.

### 2.5. Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI660D, Shanghai Chenhua Instruments Co., Shanghai, China). A three-electrode cell was used, with a bare or modified electrode as the working electrode, a Ag/AgCl electrode (saturated with KCl) as the reference electrode, and platinum wire as a counter electrode. Phosphate buffer solutions (PBSs) (pH = 7.4, 0.05 M) were used as the electrolyte solution throughout the electrochemical measurements.

## 3. Results and discussion

### 3.1. Characterization of graphene and Pd nanoparticles

In order to investigate the influence of nanoparticle size on the reduction of $H_2O_2$, Pd NPs with three different sizes were prepared by changing the argon gas pressure. Fig. 2 shows TEM images of Pd NPs prepared with different buffer gas pressures. As shown in Fig. 2(a)–(c), the sizes of the Pd NPs increase with increasing argon gas pressure. Corresponding to the buffer gas pressures that were used (90 Pa, 110 Pa, and 130 Pa), the average diameters of the nanoparticles were measured to be ~6.5 nm, 10.6 nm, and 12.0 nm, respectively. The Pd NPs are randomly distributed on the substrate with uniform size. Fig. 2(d) shows a TEM image of Pd NPs deposited on BGF. The sample was prepared with similar experimental condition as that of the NPs shown in Fig. 2(b). We can see that the morphologies of the nanoparticle assemblies of the two samples are quite similar.

Fig. 2(e) shows the Raman spectrum of the graphene sheets used to modify the GCEs. The spectrum reveals two intense peaks at ~1590 $cm^{-1}$ and ~2650 $cm^{-1}$, which can be assigned to the G mode and 2D mode of graphene, respectively. The peak intensity ratio between the G- and 2D-bands was calculated to be ~1.0, and the full width at half-maximum (FWHM) of the 2D-band was ~55 $cm^{-1}$, corresponding well to the Raman characteristic of the AB-stacked bilayer graphene [41]. The high crystallinity of carbon in the bilayer graphene will be highly beneficial for achieving better electronic conduction between adjacent Pd nanoparticles.

### 3.2. Electrocatalytic activity toward $H_2O_2$ reduction

The electrocatalytic activity of Pd NPs/BGF/GCEs toward $H_2O_2$ reduction was investigated by cyclic voltammetry (CV). Fig. 3(a) shows the CV curves obtained for the bare GCE, Pd NPs/GCE, BGF/GCE, and GCE modified with Pd NPs/BGF hybrid, in PBS containing 10 mM $H_2O_2$. For the bare GCE and BGF/GCE, no significant current change could be observed, indicating that there was no electrocatalytic activity toward $H_2O_2$ reduction for them. For the