Silver nanoparticles grafted on poly(1,5-diaminonaphthalene)/graphene for electrocatalytic sensing of hydrogen peroxide

Bui Thanh Duy[1], Nguyen Le Huy[2*], Nguyen Van Anh[1], Nguyen Tuan Dung[2]

[1] School of Chemical Engineering, Hanoi University of Science and Technology, Vietnam
[2] Institute for Tropical Technology, Vietnam Academy of Science and Technology, Vietnam
*Email: huy.nguyenle@hust.edu.vn

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ABSTRACT

In this study, an electrochemical sensor based on silver nanoparticles grafted on poly(1,5-diaminonaphathalene)/graphene (AgNPs-PDAN/Gr) nano-composite has been developed for the sensitive and selective detection of hydrogen peroxide. The key of this study is the combining of the conducting polymer matrix PDAN with AgNPs. The AgNPs were grafted on electrode surface via the functional $-NH_2$ groups of PDAN which enhanced the electron transfer process for detection of hydrogen peroxide. The electrochemical experiments of the obtained sensors were investigated by cyclic voltammetry. It was found that the sensors exhibited good electrocatalytic activity towards hydrogen peroxide reduction with a wider linear range from 0.2 to 120 mM. The sensors performed good selectivity for detection of hydrogen peroxide in the presence of glucose, ascorbic acid, and uric acid.

Introduction

Hydrogen peroxide (H_2O_2) plays an important role in various biological, environmental, chemical, pharmaceutical and clinical processes [1, 2]. It is a by-product which acts as an indicator for numerous enzymatic reactions such as glucose oxidase, lactate oxidase, cholesterol oxidase and so on [3]. It is also employed to treat toxic substances like chlorine, aldehydes, phenols and other aromatic compounds [4]. In particular, the change in H_2O_2 concentration has been demonstrated to be correlated with many diseases, including chronic inflammation, diabetes, neurodegenerative disorders and cancers [5]. Therefore, reliable, sensitive, and rapid quantitative detection of H_2O_2 is of great significance. Many analytical techniques to detect H_2O_2, such as spectrophotometry, fluorescence, electro-chemistry, and chemiluminescence have been reported [1, 2, 4, 6].

Among these, electrochemical techniques offers a high-performance approach for H_2O_2 detection due to their redox behavior [2]. Depending on the electrode materials, kinetics of direct electrochemical reduction of H_2O_2 is different. Therefore, modification of the electrode surface is important to enhance the rate of electrode reactions and hence the decrease of over-potential of redox reactions. Besides, AgNPs has been demonstrated as a electrocatalyst of H_2O_2 reduction [7]. The behavior and kinetics of H_2O_2 reduction could be studied by eletrochemical methods. However, it is coped with the immobilization of AgNPs onto unmodified electrode surface. The combination of a polymer-AgNPs composite electrode have been successfully prepared for determination of H_2O_2, such as AgNPs/polydopamine [8], AgNPs/vinyl polymer [9], AgNPs-chitosan [10], AgNPs-poly[3,4-ethylenedioxy-thiophene] [11], and AgNPs-polyaniline [2], etc.

Here we offer the use of the functional conducting polymer film (PDAN with available free amine groups [12]) which have strong interactions with AgNPs. On the other hand, the combination of graphene and PDAN further improved the electrochemical sensing properties [13]. The PDAN/Gr nanocomposite promises to enhance the effectively electrical conductivity of the polymer film by increasing the active surface area, consequently, to facilite the rate of electron transfer reactions between the target analyte and the electrode surface. In this work, the hydrogen peroxide sensor was successfully fabricated by decorating of AgNPs on PDAN/Gr via the hydrophilic functional $-NH_2$ groups. The preparation and characterization of nanocomposite film was investigated and discussed in detail.

Experimental

Materials and Apparatus

1,5-diaminonaphthalene monomer (DAN) was obtained from Merck. Graphene (Gr, size 1-5 μm, thickness 0.8-1.2 nm) was purchased from ACS Material (Medford, USA), which was dispersed in water with aid of ultrasonic wave. A phosphate buffer solution (PBS, pH 7.4), $LiClO_4$, $HClO_4$, $AgNO_3$, $NaBH_4$, H_2O_2, glucose, ascorbic acid (AA) and uric acid (UA) were from Sigma-Aldrich.

All of the electrochemical experiments were performed with a Palmsens[3] potentiostat (the Netherlands). A conventional three-electrode cell was used, including a platinum rod as a counter electrode, a saturated calomel electrode (SCE) as a reference and a modified glassy carbon electrode (GCE, 1.6 mm in diameter, area of 0.02 cm^2) as a working electrode. Experiments were carried out in non-deaerated solutions, at room temperature. The UV-vis measurements were performed with a UV-vis Aglient 8453 spectrophotometer in quartz cuvettes of 10 mm thickness. Raman spectra were recorded using a Jobin-Yvon LABRAM HR800 microspectrometer, upon a He−Ne laser excitation (632.8 nm) in backscattering mode. Transmission Electron Microscope (TEM) images were taken using Leica LEO 906E instrument operating at 120 kV. Atomic Force Microscope (AFM) of the sample was performed using SPM Nanoscope III (Veeco, Bruker).

Synthesis of colloidal silver nanoparticles

Silver nanoparticles (AgNPs) was synthesized by reducing $AgNO_3$ with $NaBH_4$ as the described in the previous work [14]. Briefly, 25 mL of 2.0 g/L $NaBH_4$ is cooled (ca. 5 °C) and stirred for 20 minutes in a dark glass bottle. Then, 10 mL of 0.02 M $AgNO_3$ was gradually added into the solution (1 drop/s) under vigorous stirring for 6 hrs. Finally, the AgNPs were obtained by centrifugation (10.000 rpm for 15 min), washed several times with distilled water, and dispersed again in pure water.

Fabrication of AgNPs-PDAN/Gr/GCE

The fabrication procedure was presented in scheme 1. The GCE working electrode (diameter of 1.6 mm, area of 0.02 cm^2) was thoroughly polished to a mirror finish using a slurry 0.3 μm α-Al$_2$O$_3$ power on a soft cloth. It was rinsed thoroughly with ethanol and then sonicated in distilled water for 3 min to remove possible contaminants. Next, 5 μL of 0.01 mg/mL Gr solution suspended in water was dropped on the polished GCE electrode and allowed to evaporate at room temperature (denoted Gr/GCE). The Gr/GCE was immersed into a 0.1 M $HClO_4$ solution containing 1 mM DAN monomer and 0.1 M $LiClO_4$. The electropolymerization was carried out using the potentiostatic technique with a constant potential of 0.90 V for 240 s.
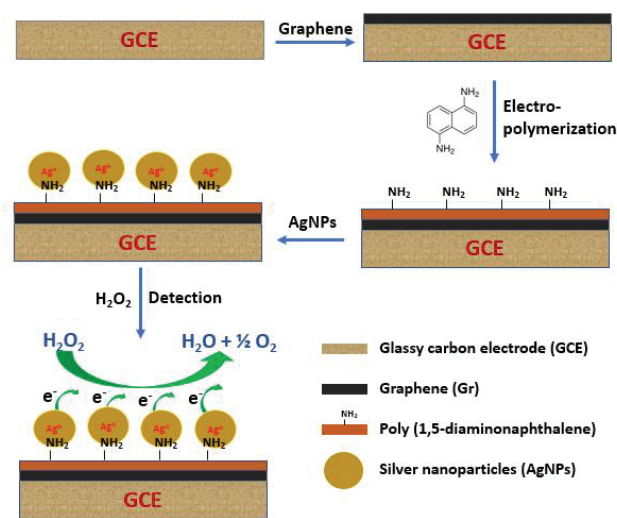
Scheme 1. Schematic representation of the fabrication of AgNPs-PDAN/Gr modified GCE and the mechanism of electrochemical detection of H_2O_2

The obtained PDAN/Gr/GCE was washed with water before it was immersed in the colloidal AgNPs for 2 hrs in order to incorporate AgNPs onto the polymer film. The sensor was rinsed carefully with distilled water and stored until use.

Electrochemical detection of H$_2$O$_2$

Cyclic voltammetry (CV) was used to determine H$_2$O$_2$ with various concentrations ranging from 0.2 to 120 mM (in a stirring PBS, pH 7.4). The CV experiments carried out at a 50 mV/s scan rate, 0.0 to −1.0 V potential range. Similar detection procedures were repeated in the presence of glucose, ascorbic acid (AA) or uric acid (UA).

Results and discussion

Characterization

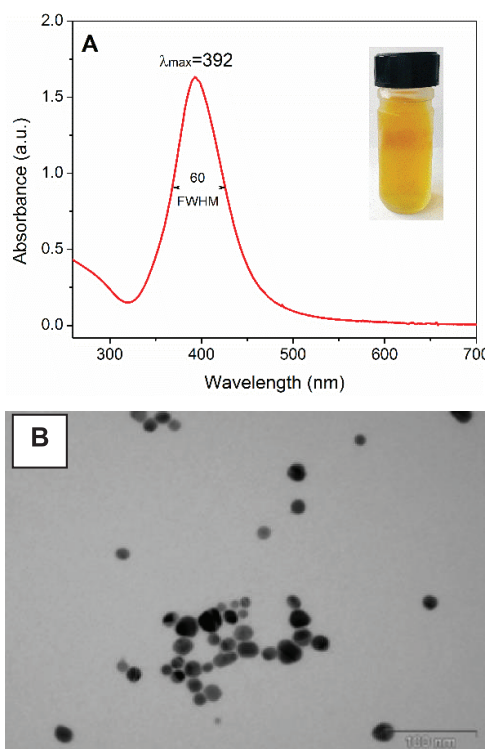Figure 1A showed the UV-vis spectrum of AgNPs dispersion in water and its digital image (insert).

Fig 1. (A) The UV-vis spectrum and digital image (insert) of a synthesized AgNPs solution. (B) TEM images of AgNPs solution.

The surface plasmon resonance with a sharp extinction peak was appeared at *ca.* 392 nm and the full width at half maximum (FWHM) of 60 nm, suggesting that average sizes of AgNPs is about 10-14 nm [15]. The TEM images presented a homogeneous morphology of the obtained AgNPs with a spherical shape. Its average diameter size was estimated via ImageJ softwave to be about 20 nm (Fig. 1B).

Raman spectra of pure Gr, PDAN/Gr and AgNPs-PDAN/Gr are shown in Fig 2, which were used to evaluate the loading of AgNPs on the surface of PDAN/Gr/GCE.
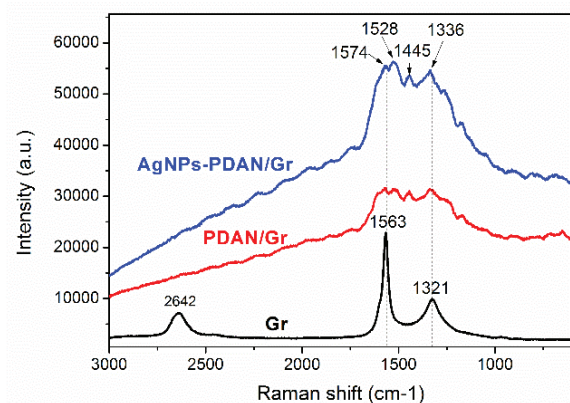

Fig 2. Raman spectra of Gr; PDAN/Gr and AgNPs-PDAN/Gr.

The spectrum of Gr powder shows the D-band (1321 cm^{-1}) may be attributed to defects in the graphene nanosheets or their agglomeration. The sp^2 sites from carbon atoms (C–C) of Gr induce the G-band (1563 cm^{-1}). Whereas another peak at 2642 cm^{-1} (2D-band) induced by the zone-boundary phonons. The Raman spectrum of PDAN/Gr film also confirmed the successful polymerization of DAN on the surface of Gr due to the vibrations of naphthalene ring at 1574, 1528 and 1445 cm^{-1}. The band at 1336 cm^{-1} region corresponds to C–N stretching vibration of polaronic units [16, 17]. In the case of AgNPs grafted PDAN/Gr film, the major Raman features of PDAN/Gr and AgNPs-PDAN/Gr/GCE are similar. However, bands of AgNPs-PDAN/Gr/GCE show somewhat higher intensities. We attribute this enhancement due to the surface-enhanced Raman scattering property of AgNPs. All these results provide an evidence of the interaction between AgNPs and the PDAN deposited onto Gr to form AgNPs-PDAN/Gr nanocomposite.

Furthermore, the morphology of AgNPs-PDAN/Gr film was characterized by AFM image (Fig 4). The results indicated a film uniform-coated with spherical particles.
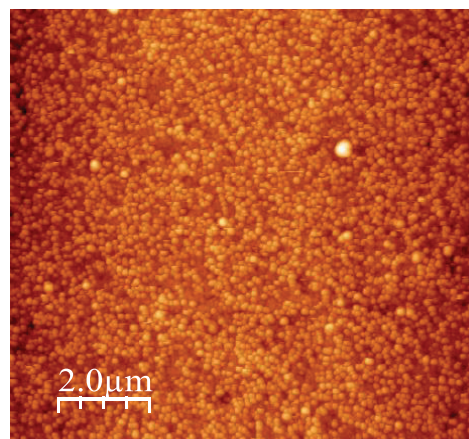

Fig 4. AFM images of AgNPs-PDAN/Gr

Electrochemical behavior

Electrochemical behaviors of bare GCE, PDAN/GCE, PDAN/Gr/GCE and AgNPs-PDAN/Gr/GCE were carried out in PBS using cyclic voltammetry from -0.2 to 0.5 V.
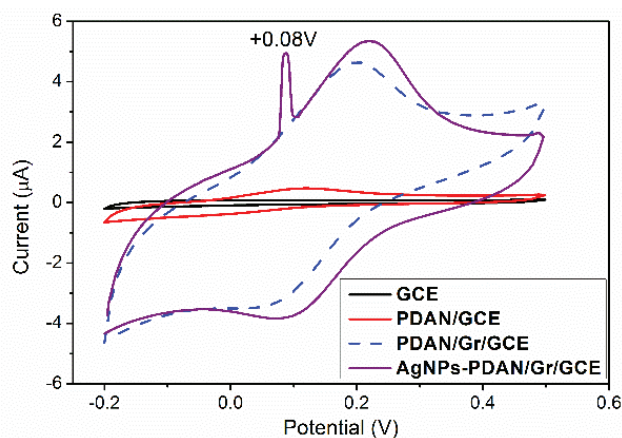

Fig 5. Cyclic voltammetry of bare GCE, PDAN/GCE, PDAN/Gr/GCE and AgNPs-PDAN/Gr/GCE in PBS pH=7.4 at 50 mV/s scan rate.

The bare GCE did not show any significant redox processes whereas PDAN modified electrode clearly showed a typical redox couple of the PDAN [16]. Interestingly, the current intensity of Gr modified GCE was almost 10 times larger than that of pure PDAN. The result confirms the role of Gr in increasing composite conductivity as well as its surface area, two main parameters that can significantly improve the overall sensor performance. In the case of AgNPs grafted PDAN/Gr/GCE, the CV showed a current peak at the potential of +0.08 V corresponding to the oxidative stripping of AgNPs from the modified electrode surface which indicated that AgNPs decorated on PDAN/Gr/GCE surface.

The quantitative determination of H_2O_2 was performed by recording the CV response on AgNPs-PDAN/Gr/GCE corresponging to the spiking of varying concentrations of H_2O_2 in PBS (Fig. 6A).

It can be observed that the H_2O_2 response current appears at the potential range from −0.3 to −0.9 V with a reduction peak current at around −0.6 V. The electrochemical reduction mechanism of H_2O_2 under the catalytic activities of the AgNPs according to the literature [11] is illustrated by the equations below:

$$2Ag + H_2O_2 \rightarrow 2Ag\text{-}OH$$

$$2Ag\text{-}OH + e^- + H^+ \rightarrow Ag + H_2O$$

As can be seen, the increase in the reduction peak current was relative to H_2O_2 concentrations in the range of 0.2 - 120 mM. The calibration curve of

logarithm of H_2O_2 concentration and the current value at -0.6 V was I (μA) = −90.76*$logC_{H2O2}$ (mM) - 89.75 with R = 0.9943.
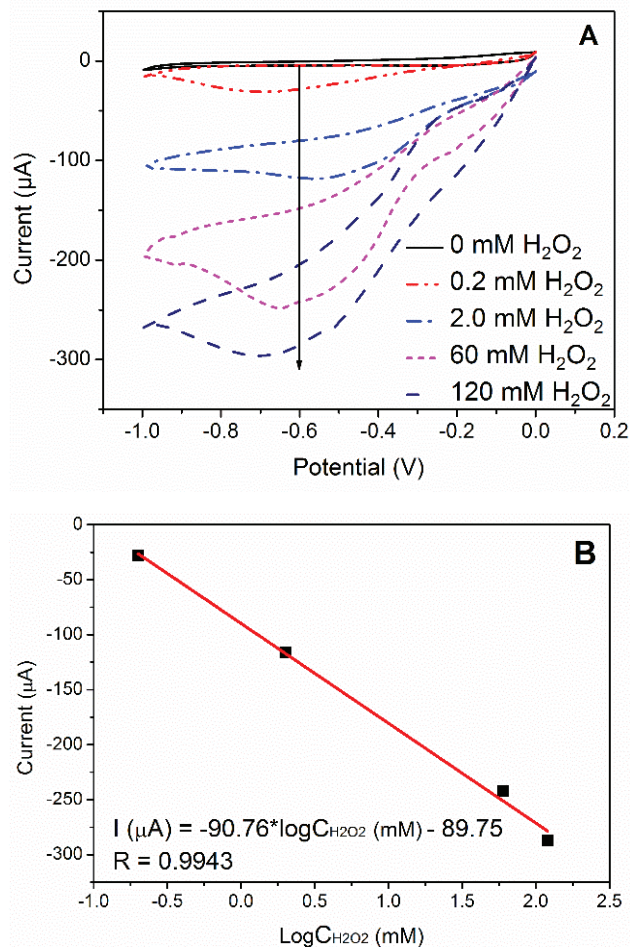

Fig. 6. (A) CVs response of AgNPs-PDAN/Gr/GCE on increasing the concentrations of H_2O_2 (0; 0.2; 2.0; 60; 120 mM) in PBS, pH 7.4; (B) The corresponding calibration curves for H_2O_2 analysis.

The influence of common compounds such as glucose, ascorbic acid (AA), and uric acid (UA) was also investigated. We evaluated CVs response of glucose, AA, and DA (0.5 mM) on AgNPs-PDAN/Gr/GCE (results not shown). These chemical reagents were nearly no obvious current response. Thus, the sensor based AgNPs-PDAN/Gr suggested excellent selectivity for H_2O_2 detection.

Conclusion

The main feature of this work is to fabricate a silver nanoparticle grafted poly(1,5-diaminonaphathalene)/ graphene composite modified glassy carbon electrode by a simple method. The characterization of the composite film confirmed that silver nanoparticles were

uniformly distributed on high conducting film poly(1,5-diaminonaphathalene)/graphene. The electrochemical experiments indicated the non-enzymatic sensor which exhibits a wide linear responding range as well as perfect selectivity for detection of hydrogen peroxide. The high stable and good biocompatible properties of AgNPs and poly(1,5-diaminonaphathalene)/graphene composite films are key for future studies on the biological samples.

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