

## Full Paper

# Silver Nanograins Incorporated PEDOT Modified Electrode for Electrocatalytic Sensing of Hydrogen Peroxide

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Received: November 25, 2008

Accepted: February 16, 2009

## Abstract

A silver nanograins ( $\text{Ag}_{\text{NGs}}$ ) incorporated poly[3,4-ethylenedioxythiophene] (PEDOT) modified electrode was prepared by a simple electrochemical method without using any stabilizer or reducing agent. The surface morphology and thickness of the resulting modified electrode was characterized by using AFM. It was found that the size of the silver particles in the PEDOT modified electrode was smaller than that in the bare electrode. AFM studies also revealed that  $\text{Ag}_{\text{NGs}}$  were uniformly distributed in the PEDOT modified electrode and the thickness of the film was found to be 35 nm. The  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode exhibited good electrocatalytic activity towards the reduction of hydrogen peroxide without an enzyme or mediator immobilized in the electrode. It has shown good amperometric response to hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with a detection limit of  $7 \mu\text{M}$  and a response time of 5 s.

**Keywords:** Silver nanograins, PEDOT,  $\text{H}_2\text{O}_2$ , Amperometry

DOI: 10.1002/elan.200804543

## 1. Introduction

Nanosized metal and semiconductor particles play an important role in many different areas due to their unique properties [1]. Among metal nanoparticle, silver nanoparticles ( $\text{Ag}_{\text{NPs}}$ ) continue to be of great current research interest because of their catalytic properties [2–7] and also silver exhibits the highest electrical and thermal conductivity among all the metals. They have traditionally been explored to use as catalysts in various reactions such as selective butadiene and ethylene oxidation and it is also known for its antibacterial properties and its ability to promote surface enhanced optical phenomena [8].

Conducting polymers have been proven to be suitable host matrices for dispersing metallic particles. The composites of conducting polymer-metal nanoparticles are current research interest [9–11]. The composite of conducting polymer-metal nanoparticles show facile flow of electronic charges and the unique properties that can be achieved with these materials. On the other hand, composite of conducting polymer-metal nanoparticles exhibit exceptional optical and electrical properties than conducting polymer or metal nanoparticle alone [12–16]. It has been also shown that the electrocatalytic properties of nanoparticles are enhanced by the conductive environment provided by the polymeric matrixes [17]. At the same time, because of their high surface to-bulk ratio, nanoparticles significantly affect the matrix leading to some new properties which are not present in either of the pure materials. So, through a suitable

combination of conducting polymers and silver nanoparticles, newly modified surfaces could be generated with higher surface area and enhanced catalytic /electrocatalytic activities.

Among the numerous conducting polymer and conducting polymer-metal nanocomposite [18–22] materials developed and studied over the past few decades, poly(3,4-ethylenedioxythiophene) (PEDOT)-metal nanocomposite material an important class and shows high stability [23]. Since, poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer have a high regularity of the polymeric chain due to the lack of  $\alpha$ - $\beta$  linkages between the monomers [24] and also studies on the behavior of PEDOT in phosphate buffer solutions show a high level of stability when compared to other conducting polymers, suggesting that PEDOT may be a potential candidate for wide range of applications [10]. Recently, Park and co-workers [25] studied current sensing AFM for Ag-PEDOT nanocomposite electrode and Ocypa et al. [20] also characterized Ag-PEDOT nanocomposite electrode but these authors have not utilized this electrode for the electrocatalytic application. Herein, we have reported  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode towards the electrocatalytic reduction of  $\text{H}_2\text{O}_2$ . Here, we take advantage of  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode as signal enhancement for electrochemical sensing of  $\text{H}_2\text{O}_2$  in comparison with Ag electrodeposited in bare electrode.

Since there are several techniques have been adopted for the accurate determination of hydrogen peroxide ( $\text{H}_2\text{O}_2$ )

because it is an essential mediator in food, pharmaceutical, clinical and environmental analysis. Many techniques including titrimetry [26], spectrometry [27], and chemiluminescence [28] have been employed in the determination of  $\text{H}_2\text{O}_2$ . However, these techniques are obviously time-consuming and expensive. Recently, more attention has been paid to the electrochemistry technique owing to its intrinsic sensitivity, high selectivity and simplicity [29]. Electrochemistry technique based on a simple and low cost enzyme electrode has been extensively employed for accurate determination of  $\text{H}_2\text{O}_2$  because of the intrinsic selectivity and sensitivity of enzymatic reactions [30, 31]. Although, a lot of materials have been used to immobilize enzyme on an electrode for retaining the enzymatic biologic activity and electrically connecting the enzyme with the electrode surface, it was ineluctable that these materials might block the electron transfer and biologic activity of the enzyme [32, 33]

Recent studies have showed that  $\text{Ag}_{\text{NPs}}$  exhibited catalytic activity for  $\text{H}_2\text{O}_2$  [34, 35]. In the present study, we prepared silver nanograins incorporated PEDOT modified electrode by electrochemically without using any reducing agent or stabilizer. Silver nanograins incorporated PEDOT modified electrode was utilized for electrocatalytic reduction of  $\text{H}_2\text{O}_2$ .

## 2. Experimental

### 2.1. Reagents and Solutions

EDOT was purchased from (Sigma Aldrich), silver nitrate from (Wako). Stock solutions of  $\text{H}_2\text{O}_2$  were prepared each time freshly from 34% solution (purchased from Wako). All reagents were of analytical grade and used without any further purification. Solutions were prepared with doubly-distilled water. High purity nitrogen was used for deaeration. The buffer and sample solutions were purged with highly purified nitrogen for at least 10 min prior to the experiments. Nitrogen atmosphere was maintained over the solutions during experiments.

### 2.2. Apparatus

Electrochemical experiments were performed with CH Instruments (Model CHI-400) using CHI-750 potentiostat. Glassy carbon electrode (geometric area =  $0.07 \text{ cm}^2$ ) obtained from Bioanalytical Systems (BAS) served as a working electrode. Pt wire act as counter electrode and  $\text{Ag}/\text{AgCl}$  with the saturated  $\text{KCl}$  solution used as reference electrode. All the potentials given in this paper were referred with respect to  $\text{Ag}/\text{AgCl}$  (saturated  $\text{KCl}$  solution) reference electrode. Indium Tin oxide coated glass electrode (ITO electrode) were used to measure AFM of silver nanograins ( $\text{Ag}_{\text{NGs}}$ ) incorporated PEDOT modified surface. Atomic force microscope (AFM) images were recorded by Beijing Nano-Instruments CSPM4000 using tapping mode

operation. Rectangle  $\text{Si}_3\text{N}_4$  cantilevers with a normal force constant,  $0.4 \text{ N/m}$ , a radius of less than  $10 \text{ nm}$  were employed.

### 2.3. Fabrication of Silver Nanograins ( $\text{Ag}_{\text{NGs}}$ ) Incorporated PEDOT Modified Electrode

The PEDOT modified electrode was prepared potentiodynamically by scanning the electrode between  $-0.6$  to  $1.0 \text{ V}$  in aqueous solutions containing  $0.01 \text{ M}$  EDOT,  $0.10 \text{ M}$   $\text{LiClO}_4$  and  $0.050 \text{ M}$  SDS for three potential cycles. And then PEDOT modified electrode was immersed in  $0.1 \text{ M}$   $\text{KNO}_3$  solution containing  $1 \text{ mM}$   $\text{AgNO}_3$  and electrodeposited at  $-0.4 \text{ V}$  for  $45 \text{ s}$  to obtain silver nanograins ( $\text{Ag}_{\text{NGs}}$ ) incorporated PEDOT modified electrode.

## 3. Results and Discussion

### 3.1. Electrochemistry of Silver Nanograins ( $\text{Ag}_{\text{NGs}}$ ) Incorporated PEDOT Modified Electrode

Cyclic voltammograms (CV) was utilized to monitor the redox behaviors of silver electrodeposited and silver nanograins ( $\text{Ag}_{\text{NGs}}$ ) incorporated PEDOT modified electrode in PBS solution, as shown in Figure 1 and modified electrode showed a cathodic peak at  $0.20 \text{ V}$  and a sharp anodic peak at  $0.45 \text{ V}$ . The cathodic peak was ascribed to there reduction of  $\text{Ag}^+$  to form  $\text{Ag}_{\text{np}}$  and the anodic peak was attributed to the stripping of the electrodeposited  $\text{Ag}_{\text{np}}$ . However, when the  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode (Fig. 1b) was scanned in the same solution, the redox peak currents enhanced obviously compared to bare GC electrode. The enhancement in the peak current of  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode due to the interaction of silver nanoparticle with sulfur atom of PEDOT [25, 36].

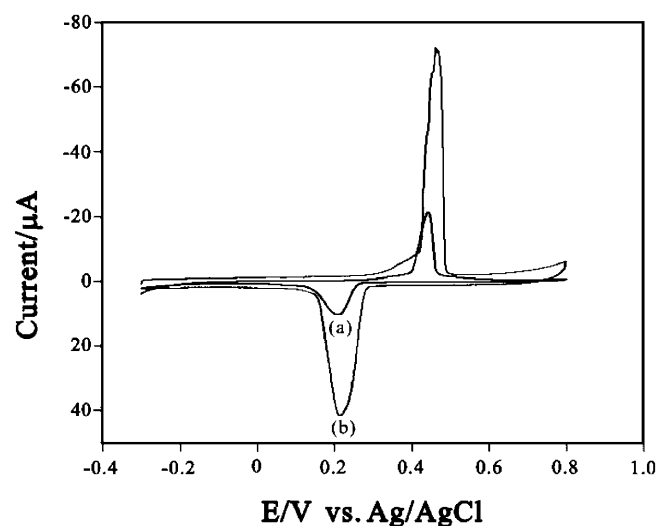


Fig. 1. Cyclic voltammograms of Ag nanoparticle (a) and Ag nanograins incorporated PEDOT (b) modified electrode in the pH 7 PBS solution. Scan rate:  $100 \text{ mV/s}$ .

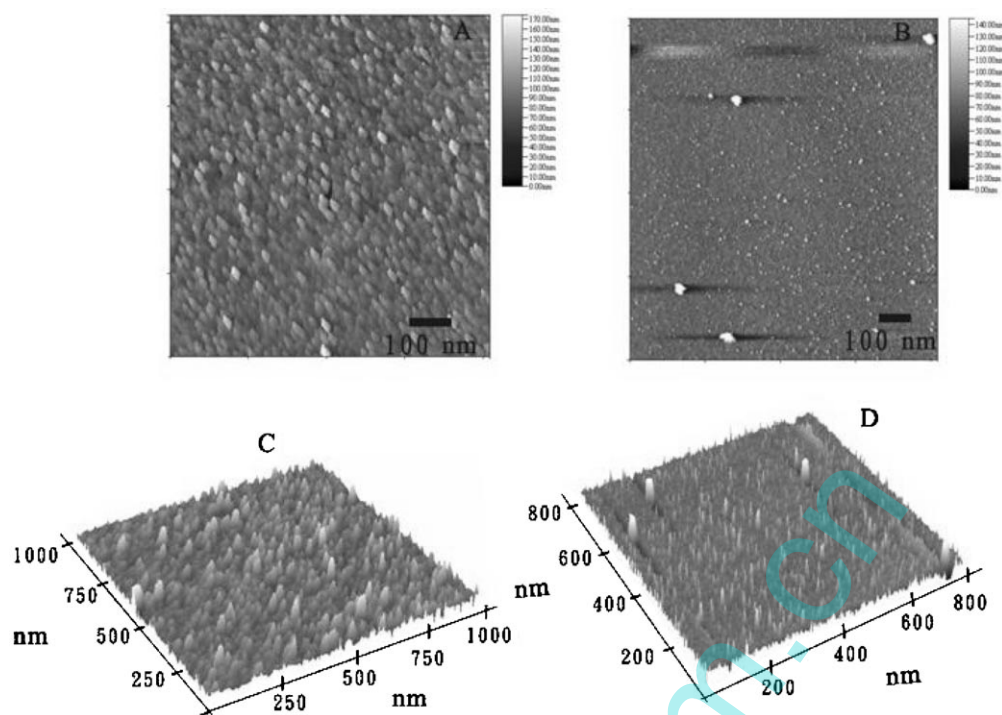


Fig. 2. A) 2D and C) 3D AFM images of silver nanoparticle deposited on ITO glass. B) 2D and D) 3D AFM images of silver nanograins incorporated PEDOT modified ITO glass electrode.

### 3.2. Surface Morphology

Surface morphology of silver particle in bare electrode and Ag<sub>NGS</sub> incorporated PEDOT modified electrode was analyzed by using atomic force microscopy (AFM).

Surface morphology of silver in bare ITO electrode (Fig. 2A) and Ag<sub>NGS</sub> incorporated PEDOT modified electrode (Fig. 2B) is looking smooth and silver particle in bare ITO electrode seems aggregated highly and silver nanograins distributed uniformly in PEDOT modified electrode. The thickness of film was measured by using AFM cross sectional analysis and was found 45 nm, 35 nm for silver in bare ITO electrode and Ag<sub>NGS</sub> incorporated PEDOT modified electrode, respectively. The average particle size of silver in bare ITO glass electrode and in PEDOT modified electrode were 100–150 nm and 50–60 nm, respectively. The decreased particle size of silver into nanograin size in PEDOT modified electrode probably due to conducting polymer matrix may help against agglomeration of silver particle [37]. Moreover, surface roughness of Ag nanoparticle and Ag<sub>NGS</sub> incorporated PEDOT modified electrode was measured by using 2D AFM. It was found that 6 and 10 nm for Ag nanoparticle and Ag<sub>NGS</sub> incorporated PEDOT modified electrode, respectively. The Figures 2C and 2D shows three dimensional AFM image of silver particle in bare ITO electrode and Ag<sub>NGS</sub> incorporated PEDOT modified electrode, respectively.

### 3.3. Electrocatalytic Reduction of H<sub>2</sub>O<sub>2</sub> at Silver Nanograins Incorporated PEDOT Modified Electrode

Ag<sub>NGS</sub> incorporated PEDOT modified electrode exhibited good electrocatalytic behavior towards the reduction of H<sub>2</sub>O<sub>2</sub>. Fig. 3 shows the cyclic voltammograms recorded in the presence of 1 mM H<sub>2</sub>O<sub>2</sub> at bare GC, silver modified, silver nanograins incorporated PEDOT modified electrode in 0.1 M phosphate buffer solution (pH 7.0). There was no response for H<sub>2</sub>O<sub>2</sub> reduction on PEDOT modified electrode. Whereas Ag<sub>NGS</sub> incorporated PEDOT modified electrode exhibited good electrocatalytic behavior towards the reduction of H<sub>2</sub>O<sub>2</sub> without any other mediator/enzyme in the film and reduction peak potential appeared at –0.45 V for H<sub>2</sub>O<sub>2</sub> reduction, was shown in Figure 3c. Silver particle modified electrode shows less catalytic response (Fig. 3b) than Ag<sub>NGS</sub> incorporated PEDOT modified electrode. The enhanced electrocatalytic response of H<sub>2</sub>O<sub>2</sub> due to presence of Ag<sub>NGS</sub> on PEDOT modified electrode. The higher electrocatalytic current of H<sub>2</sub>O<sub>2</sub> in Ag<sub>NGS</sub> incorporated PEDOT modified electrode due to higher surface roughness compared to silver particle modified electrode with features corroborating the observations made in AFM investigations [38]. Cox and co workers have also reported that Ru<sup>II</sup> Den-doped composite electrode shows high sensitivity for determination of 5-Hydroxytryptophan (5-HTPP) which is due to high surface roughness [39]. In general, the presence of metal nanoparticles in electro-

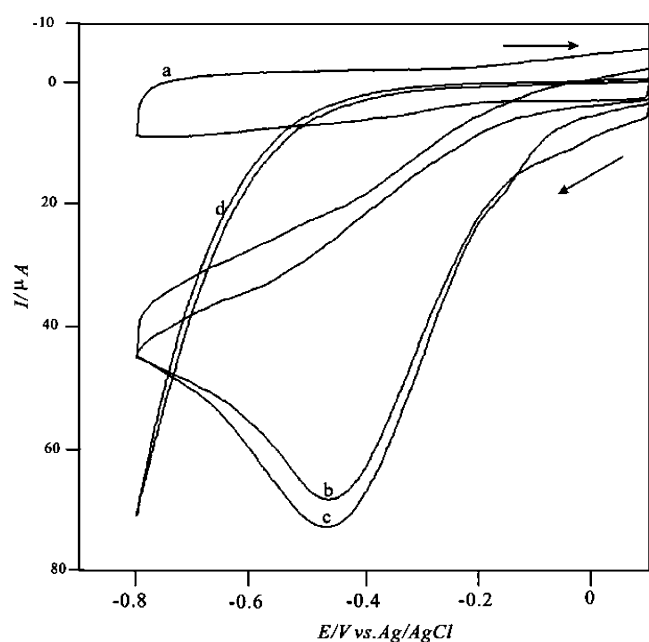
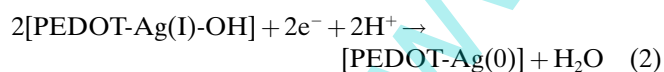
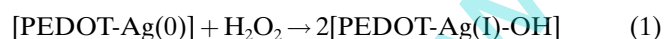


Fig. 3. CVs of different electrodes in pH 7 and 1.0 mM  $\text{H}_2\text{O}_2$ : b) silver nanoparticle modified electrode; c) silver nanograins incorporated PEDOT modified electrode; d) bare GC electrode, and a) CV of silver nanograins incorporated PEDOT modified electrode PBS solution of pH 7 in the absence of 1.0 mM  $\text{H}_2\text{O}_2$ . Scan rate: 50 mV/s.

chemical sensors can decrease the overpotentials of  $\text{H}_2\text{O}_2$  analytes at common unmodified electrodes, in consonance with Ordeig et al. [40]. There was no response on bare GC electrode for  $\text{H}_2\text{O}_2$  in the potential range of 0.1 to  $-0.8$  V which indicates no catalytic reaction of  $\text{H}_2\text{O}_2$ . The possible mechanism of  $\text{H}_2\text{O}_2$  reduction in the silver nanograins incorporated PEDOT modified electrode is reported. First, EDOT-Ag(0) reacts chemically with  $\text{H}_2\text{O}_2$  (Eq. 1) to give argentous hydroxide [41] dispersed in PEDOT (PEDOT-Ag(I)-OH). Subsequently, this species is electrochemically reduced in Eqn. 2 to renewed [PEDOT-Ag(0)].



### 3.4. Amperometric Determination of $\text{H}_2\text{O}_2$ at Silver Nanograins Incorporated PEDOT Modified Electrode

Amperometric response of  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode upon successive addition of 0.1 mM  $\text{H}_2\text{O}_2$  into stirring PBS solution, pH 7 at an applied potential of  $-0.45$  V was illustrated in Figure 4. As  $\text{H}_2\text{O}_2$  was added at regular interval of time into stirring buffer solution,  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode responded rapidly and could attain the steady state current. The response time was ca. 5 s, which indicates a fast electron-transfer process at this electrode. The detection limit was estimated

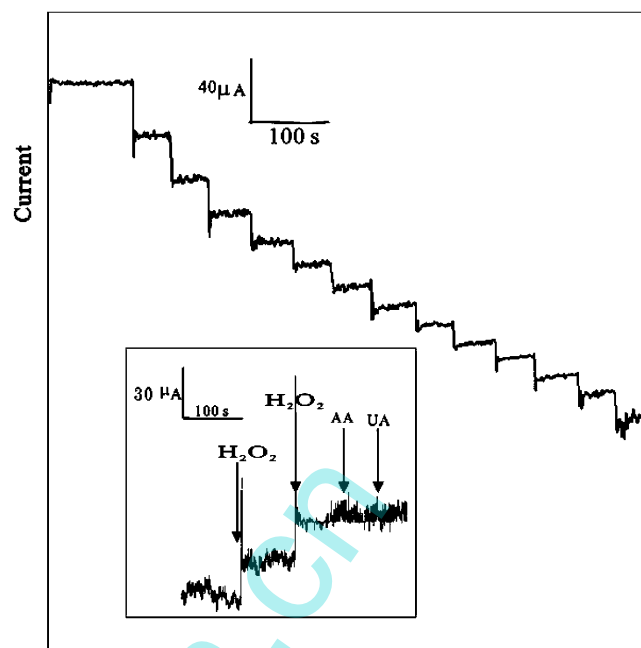


Fig. 4. Amperometric response of the sensor to successive injection of  $\text{H}_2\text{O}_2$  into the stirring PBS. Applied potential:  $-0.45$  V. Inset shows steady-state current response of the as-prepared electrode on injection of 0.01 mM  $\text{H}_2\text{O}_2$ , 0.01 mM  $\text{H}_2\text{O}_2$ , 0.1 mM AA and 0.5 mM UA.

to be  $7 \mu\text{M}$  based on the criterion of signal-to-noise ratio of 3 ( $S/N$  of 3). The detection limit is in general comparable with most of the modified electrode reported in the literature [34, 35, 42–44] (Table 1). The  $RSD$  of  $\text{Ag}_{\text{NGs}}$  incorporated PEDOT modified electrode for 10 successive measurement is 5% for 5 mM  $\text{H}_2\text{O}_2$ , indicating that modified electrode has an excellent reproducibility.

Here, we investigated the interference effect of AA and UA toward the determination of  $\text{H}_2\text{O}_2$ . AA and UA are common existing interfering species in the physiological samples, and their normal concentration ranges are 34–79  $\mu\text{M}$  and 0.18–0.42 mM in the blood of human beings, respectively [45]. Thus, the interfering effect of 0.1 mM AA and 0.5 mM UA compared to 0.01 mM  $\text{H}_2\text{O}_2$  was evaluated at the potential of  $-0.45$  V. As shown in the inset of Figure 4, there was obvious current response with the addition of 0.01 mM  $\text{H}_2\text{O}_2$ . On the contrary, no obvious current response was observed with the addition of 0.1 mM AA and 0.5 mM UA, though the concentration of AA and UA are much higher than that of  $\text{H}_2\text{O}_2$ , demonstrating the interferences of UA and AA were completely avoided.

## 4. Conclusions

The main feature of this work is to fabricate a silver nanograins incorporated PEDOT modified electrode by simple electrochemical method without any stabilizer or reducing agent. The detection of hydrogen peroxide without using of enzyme/mediator in the modified electrode has



Table 1. Comparison of metal nanoparticle modified electrode for hydrogen peroxide determination.

Electrode	Electrolyte	$E_p$ (mV)	Detection limit ( $\mu\text{M}$ )	Reference
GC/Ag nanoparticle	PBS solution	-250	2	[34]
DNA-Ag nanoparticle	PBS solution	-400	1.7	[35]
PVA/Ag nanoparticle	PBS solution	-500	1	[42]
Dendrimer-rhodium nanoparticle	PBS solution	-300	5	[43]
DNA/ $\text{Cu}^{2+}$	PBS solution	-500	0.25	[44]
AgNGs/PEDOT	PBS solution	-450	7	Present study

reported. Electrochemical properties of Ag<sub>NGs</sub> incorporated PEDOT modified electrode has characterized by using cyclic voltammetrically. Surface morphology of modified electrode has analyzed using AFM. It revealed that Ag<sub>NGs</sub> were uniformly distributed in PEDOT modified electrode. Ag<sub>NGs</sub> incorporated PEDOT modified electrode exhibits good electrocatalytic activity towards reduction of H<sub>2</sub>O<sub>2</sub>. It has shown good amperometric response to H<sub>2</sub>O<sub>2</sub> with the detection limit of 7  $\mu\text{M}$ .

## 5. Acknowledgement

This project work was financially supported by the Ministry of Education and the National Science Council of Taiwan (ROC).

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