

Size effects of Pt nanoparticle/graphene composite materials on the electrochemical sensing of hydrogen peroxide and glucose

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Abstract

The electrochemical detection of hydrogen peroxide (H_2O_2) and glucose has attracted much attention recently. Meanwhile, the size of nanoparticles which significantly influences electrocatalytic activity is crucial for electrocatalysts. Hence, in this study we prepared five different graphene/size-selected Pt-modified glassy carbon (GC) electrodes to characterize H_2O_2 level via electrochemical measurements. During the preparation of the nanocomposites, size-selected Pt nanoparticles (NPs) with the mean diameter of 1.3, 1.7, 2.1, 2.9, 4.3 and 13.9 nm were self-assembled onto the graphene surfaces. The electrochemical measurement results are size-dependent for Pt NPs when sensing H_2O_2 and glucose. When all CV results from various electrodes are compared, the Pt-1.7 nm/G-modified GC electrode has the highest reduction current, the best detection limit, as well as the best sensitivity. On the other hand, it was found that the Pt(2.1 nm)-G has the highest Faradic current density for sensing glucose.

1. Introduction

There are many important factors, which can influence the catalytic activity, when dealing with catalysts. [1-9] One of the very important parameters is the size of the nanoparticles. The catalyst effect is a surface phenomenon, and the bulky part the first few layer do not participate in the reaction. Therefore a bulk atom to surface atom ratio is desired to increase the catalytic activity. Another very important parameter concerning the activity of a nanocatalyst is the support material. Recently the graphene powders have been synthesized which possesses a high surface area. This is supposed to be beneficial as the support material for nanoparticle. Therefore, in this study we try to investigate the size effects of Pt nanoparticle supported on graphene. The electrochemical detection of H_2O_2 and glucose was used to evaluate the properties of these graphene-supported Pt catalysts. The size-dependent electrochemical properties will be displayed and discussed in our poster presentation.

2. Experimental

2.1 Preparation of Pt colloidal solution

Pt nanoparticles were synthesized using the polyol method reported in details elsewhere. In short, 0.1163 g of PtCl_4 was dissolved in 12.5 ml of ethylene glycol; stirring and sonication were used to accelerate the dissolution of the salt. In order to control the size of the synthesized particles

the appropriate amount of sodium hydroxide was added to the PtCl_4 solutions so as to obtain the desired pH. The mixture was then stirred at room temperature for 30 min, heated to 160 °C for 3 hr, and finally allowed to cool down to room temperature, forming a platinum colloidal solution (1.3, 1.7, 2.1, 2.9, 4.3 and 13.9 nm).

2.2 Deposition of Pt nanoparticles on graphene

Graphene powders were mixed with the Pt colloidal solutions in a ratio of 80:20 wt. % respectively in a solution containing 2 M sulfuric acid and ethylene glycol in a volume ratio of 1:1. The solution was then stirred for 24 h, and then sonicated using an ultrasonic processor (Part NO. Q700) for 15 min. The resulting solution was filtered to recuperate the catalyst. Five Pt-G catalysts with different average particle sizes were obtained in this manner.

2.3 Electrode preparation and characterization

The catalyst "ink" for electrochemical measurement was prepared with the Pt-graphene powders. More specifically, 3 mL of de-ionized water, 2 mL of ethanol, 60 μL of liquid Nafion and 6 mg of the synthesized Pt particles were sonicated. Transmission electron microscopy (JEOL JEM-1230, 100 kV) was used to characterize sample morphologies. Potentiostat/galvanostat (CHI 405A) was used for electrochemical measurements. The working electrode was glassy carbon (GC) disc electrode on which 10 μL of the catalyst "ink" was deposited and dried at room temperature. A silver/silver chloride (Ag/AgCl) electrode and a large surface area platinum electrode were used as the reference and counter electrode, respectively. All potentials in this study are reported with respect to the Ag/AgCl electrode.

3. Results and discussion

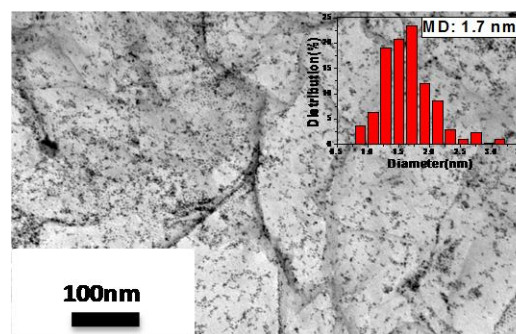


Fig. 1 Transmission electron microscope images of Pt-1.7 nm/G. Histogram in the inset shows the particle size distribution of Pt nanoparticles.

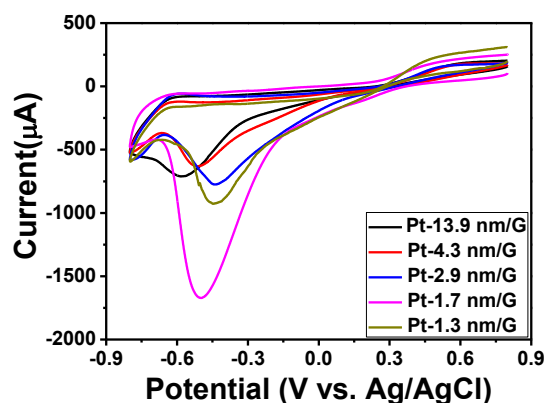


Fig. 2 Cyclic voltammograms of five Pt/G-modified GC electrodes in 0.1 M PBS (pH 7.0) 10 mM H₂O₂. Scan rate: 100 mVs⁻¹.

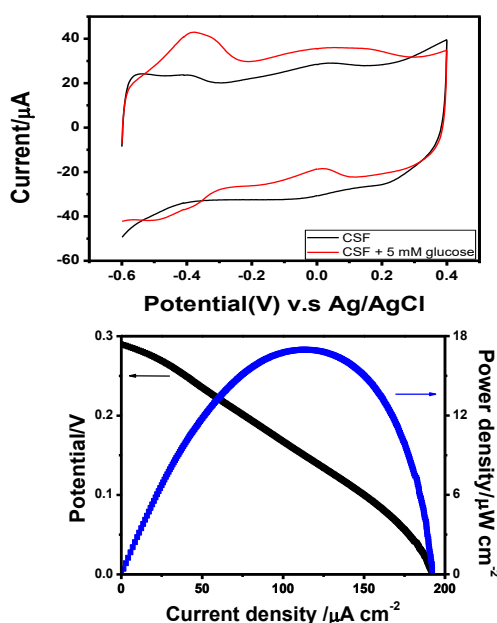


Fig. 3 Cyclic voltammograms of Pt(2.1 nm)-G in the absence (black line) and presence (red line) of 5 mM glucose at a scan rate of 50 mVs⁻¹ in 5 mM CSF, and the maximum power density of Pt(2.1 nm)-G in O₂ saturated CSF with 5 mM glucose at a scan rate of 5 mVs⁻¹.

Pt nanoparticles of different average size varying between 1.7 and 13.9 nm were synthesized using the aforementioned modified polyol method. The sizes of the particles were varied in the different samples by changing the pH of the PtCl₄ solution dissolved in ethylene glycol. Figure 1 shows a representative TEM of the 1.7 nm particles supported on a single G sheet. The inset shows the size distribution of the particles with an average diameter of 1.7 nm which was taken over 300 individual particles from the TEM of the colloidal nanoparticles.

Cyclic voltammograms in Figure 2 illustrate the reduction of H₂O₂ for each catalyst. For the largest size of 13.9 nm, the good reduction current of 673.8 μA can be obtained. For the size lower than 10 nm but higher than 1.5 nm, there are three catalysts containing Pt-4.3 nm/G, Pt-2.9 nm/G, and

Pt-1.7 nm/G. Among these three catalysts, the reduction current will increase along the decrease of particle sizes. Hence the Pt-1.7 nm/G catalyst has the highest reduction current that is 2.5 times higher than that of the Pt-2.5 nm/G one. Fig.3 illustrates the cyclic voltammograms of Pt(2.1 nm)-G with the Faradic current of 19.3 μA/cm². For biofuel cell application, the power density can achieve the 6.8 μW/cm² under saturated oxygen in the CSF solution.

4. Conclusions

In summary, the particles size of Pt colloids can influence the electrochemical properties of Pt/G catalysts for electrochemical sensing of H₂O₂ and glucose. The Pt-1.7 nm/G catalyst has the highest sensitivity up to 1264.6 μAmM⁻¹cm², rapid response time of 1.69 s, low detection limit, and good ECSA in the linear range of 8 μM to 1.5 mM. Among all catalysts, it was found that the smaller Pt particles on graphene would give the higher sensitivity and wider linear range. Thus, the sensitivity of Pt-1.7 nm/G catalyst is 2.5 times higher than that of Pt-13.9 nm/G one. However, after the size is down to 1.3 nm, the linear range of Pt-1.3 nm/G shifts to the high concentration with the much lower sensitivity. On the other hand, the Pt(2.1 nm)-G has the highest Faradic current density for sensing glucose.

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