

# Electrodeposition Fabrication of Pd Nanoparticles on Glassy Carbon Electrode Towards Methanol Oxidation Application

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## ABSTRACT

The present paper reports on the rapid fabrication of Pd nanoparticles on glassy carbon electrode by electrodeposition technique. It suggests that such film exhibits good catalytic activity and stability with respect to methanol oxidation in an alkaline media. It also suggests that the loading of the Pd nanoparticles on the substrate and therefore the effective catalytic area can be tuned by the deposition time used.

**Keywords:** Fuel Cell, Methanol Oxidation, Pd Nanoparticle, Stable Film, Electrodeposition

## 1. INTRODUCTION

Nanostructures exhibit quite unique properties which are quite different from their bulk counterparts and therefore, their synthesis has always been a hot research topic (Burda *et al.*, 2005). Indeed, the past years have witnessed the rapid development of synthetic methods of all kinds of nanostructures (Cushing *et al.*, 2004; Watanabe *et al.*, 2006). Among such nanostructures, gold nanostructures are the most stable and hold great promise as key materials and building block in the 21st century (Daniel and Astruc, 2004) and represent one of the most widely studied nanomaterials so far (Hayat, 1989). It is well-documented that nanoparticles-modified electrodes can exhibit several unique advantages over conventional macroelectrodes such as enhancement of mass transport, catalysis, high effective surface area and control over electrode microenvironment (Katz *et al.*, 2004). Electrodeposition-based cost-effective fabrication

of nanoparticles-modified electrodes has been paid much attention due to its unique properties, such as the requirement of simple instrumentation, the easy control of both the size and morphology of the as-deposited nanostructures through adjusting the electrochemical parameters (Yu *et al.*, 2007).

Direct Methanol Fuel Cells (DMFCs) are intensively studied and considered as possible power sources for electric vehicles and other portable applications in the near future (Chen and Yang, 2003; Wang *et al.*, 2004). The anodic oxidation of methanol on electrode surfaces in acidic medium is a catalytic reaction, giving CO<sub>2</sub> and six electrons. The main factors limiting the practical application of DMFC are the sluggish kinetics of methanol electrooxidation at anode and the poisoning of electrode surfaces. As a result, the development of highly effective methanol electrooxidation catalysts has been paid much attention. Pt exhibits good electrocatalytic performance with respect to the methanol electrooxidation and hence Pt-based nanoparticles are

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intensively used as a catalyst for applications in DMFC (Hsu *et al.*, 2010), but its high cost and limited supply of Pt constitute a major barrier to the development of DMFC. It is therefore highly desirable to develop low-cost non-Pt electrocatalysts with comparable or improved kinetics for methanol oxidation. Indeed, many non-Pt metals have recently been investigated (Jafarian *et al.*, 2006; Heli *et al.*, 2004). Among such metals, Pd is a good electrocatalyst for methanol in alkaline solution (Xu *et al.*, 2007a; 2007b; Singh *et al.*, 2009) and its abundance is at least fifty times more than that of Pt on earth (Liu *et al.*, 2007; 2009). In addition, Ha *et al.* (2005) have demonstrated that Pd and Pd/C catalysts can overcome the CO-poisoning effect and thus lead to high performance in DMFCs. On the other hand, catalyst support is considered as an important factor that influences its activity. Researchers have found that carbon materials can improve the activity and stability of the catalysts employed in fuel cells (Yoo *et al.*, 2008; Bessel *et al.*, 2001; Joo *et al.*, 2006; Bang *et al.*, 2007; Xu *et al.*, 2008; Zhao *et al.*, 2010; Serp *et al.*, 2003; Dong *et al.*, 2010). However, above methods have their inherent drawbacks, such as the pre-synthesis of nanoparticles of catalysts and the modification of both the carbon substrates and the nanoparticles to effectively immobilize the nanoparticles on the substrates. The present paper demonstrates the use of electrodeposition technique to the rapid fabrication of Pd nanoparticles on bare Glassy Carbon Electrode (GCE) surface. It suggests that such film exhibits good catalytic activity and stability for the electrooxidation of methanol. It also suggests that the loading of the Pd nanoparticles on the substrate and therefore the effective catalytic area can be tuned by the deposition time used.

## 2. MATERIALS AND METHODS

H<sub>2</sub>PdCl<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, NaOH, CH<sub>3</sub>OH were purchased from Aladdin Reagent Database Inc. (Shanghai, China) and used as received without further purification. All aqueous solutions were made with double-distilled water. Electrodeposition was carried out with a CHI660D electrochemical workstation (Shanghai, China) in a three electrode cell, with the use of a Ag/AgCl (saturated KCl) as reference electrode, a platinum coil as auxiliary electrode and a Glassy Carbon (GC) disk electrode (3 mm in diameter) as the working electrode. All electrochemical measurements were performed in a conventional three-electrode cell. Scanning Electron Microscopy (SEM) was made on a JSM6330F (JEOL, Japan).

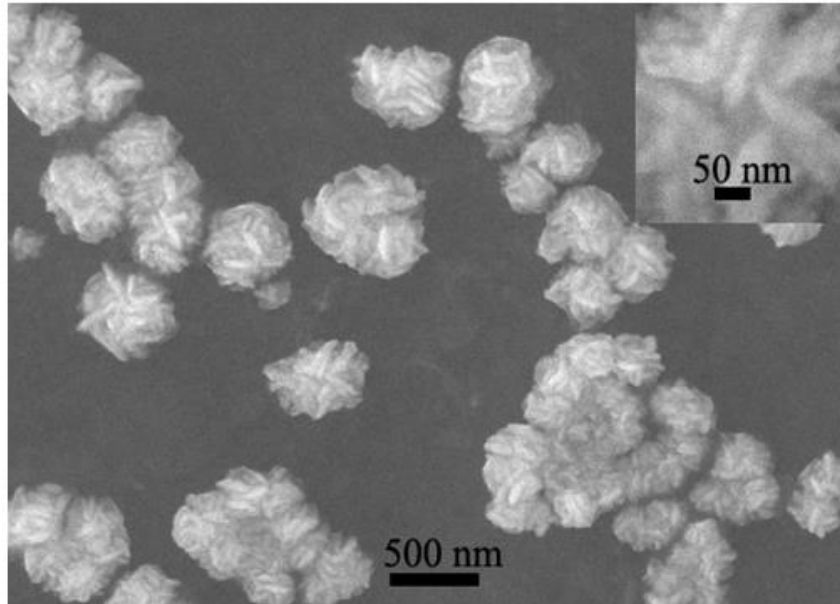
The GCE was pretreated using the following process. First, the surface of a GCE was polished with 1.0 and 0.3 μm α-alumina powders in sequence, rinsed thoroughly with twice distilled water and placed in a water-filled ultrasonic bath over a 2 min period. After dried in air, Pd nanoparticles was grown on the GCE by electrodeposition in a solution containing 5 mM H<sub>2</sub>PdCl<sub>4</sub> and 0.5 M HCl at -0.2 V (vs Ag/AgCl) over a 200 s period (the resulting Pd nanoparticles-supported GCE is denoted as Pd/GCE). After the electrodeposition, the modified electrodes were rinsed twice in water and air-dried at room temperature for characterization and further use.

## 3. RESULTS

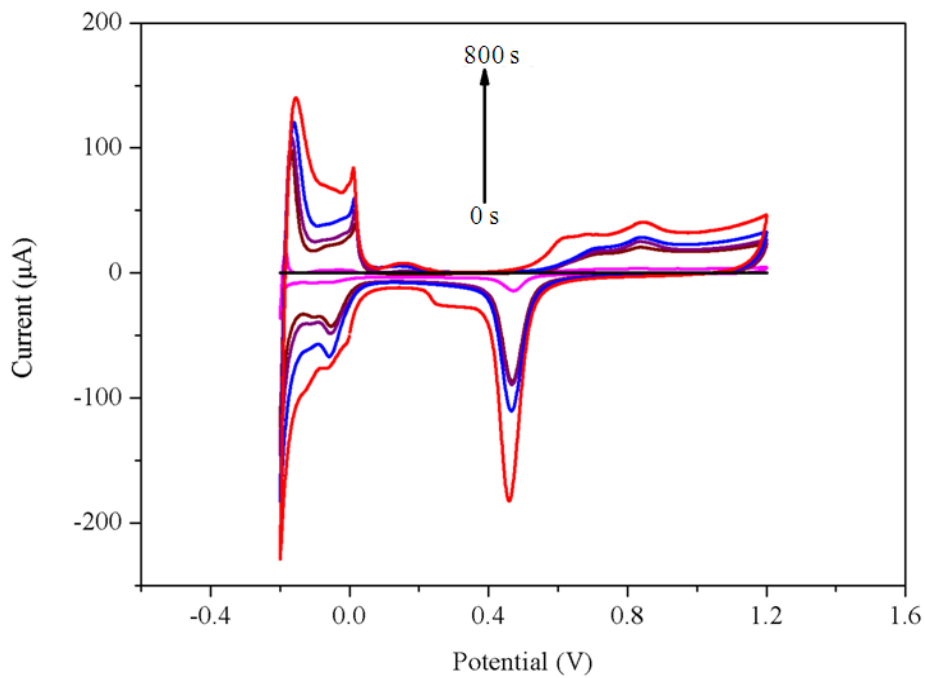
**Figure 1** shows typical SEM image of as-prepared Pd structures, indicating the GCE substrate is covered by flower-like Pd structures with diameters in the range of 300-500 nm. A local view of one Pd flower (inset) further reveals the Pd structure consists of small nanoparticles. It is worthwhile mentioning that such Pd flowers exhibit no observable change on the substrate after it is subjected to a sonication process for several minutes, indicating that the Pd flowers are very stable (Xu *et al.*, 2007a; 2007b; Singh *et al.*, 2009).

**Figure 2** shows CV curves of the Pd/GCE in a 0.5 M NaOH solution at 0.05 V/s. The Pd electrodeposition was performed in solution containing 5 mM H<sub>2</sub>PdCl<sub>4</sub> and 0.5 M HCl at -0.2 V over a period of time of 0, 50, 100, 200, 400 and 800 s. The appearances of well-defined feature peaks of Pd electrodes corresponding to hydrogen adsorption-desorption at -0.1-0 V, below -0.1V is hydrogen absorption and evolution and palladium-oxide formation at 0.6-1.2 V and reduction at 0.46 V, demonstrating the successful deposition of Pd on GCE.

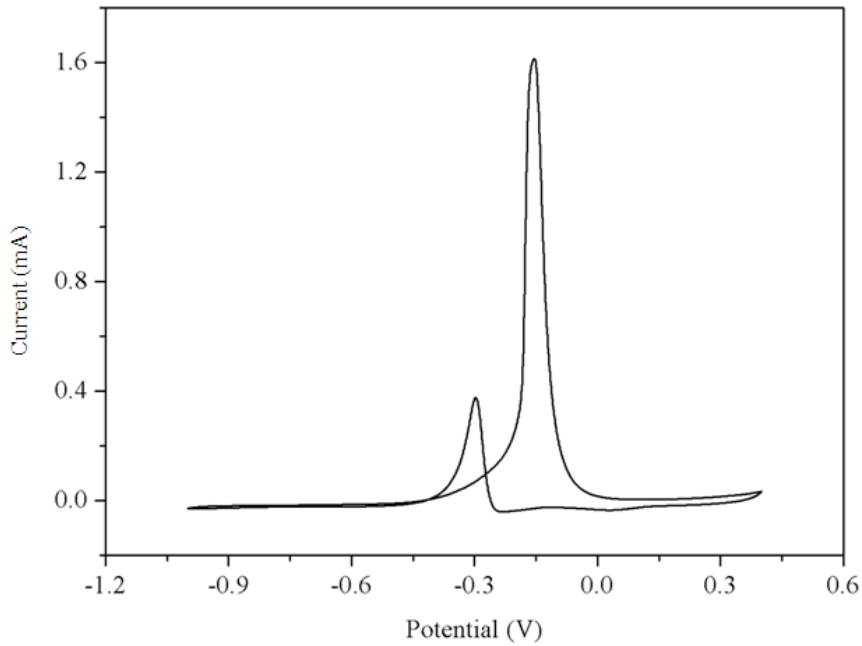
**Figure 3 and 4** shows CV curves of the Pd/GCE in a 0.5 M NaOH solution at 0.05 V/s in the presence of 1.0 M CH<sub>3</sub>OH. The Pd electrodeposition was performed in solution containing 5 mM H<sub>2</sub>PdCl<sub>4</sub> and 0.5 M HCl at -0.2 V over a period of time of 0, 50, 100, 200, 400 and 800 s. It is clearly observed that the peak currents of both the forward and reverse CV scan increase with increase in the deposition time, which can be attributed to that increased deposition time leads to more Pd nanoparticles on GCE surface and hence larger effective catalytic area of Pd as well as higher catalytic current, that is, deposition time can exert good control over the formation of Pd nanoparticles on the electrode surface.



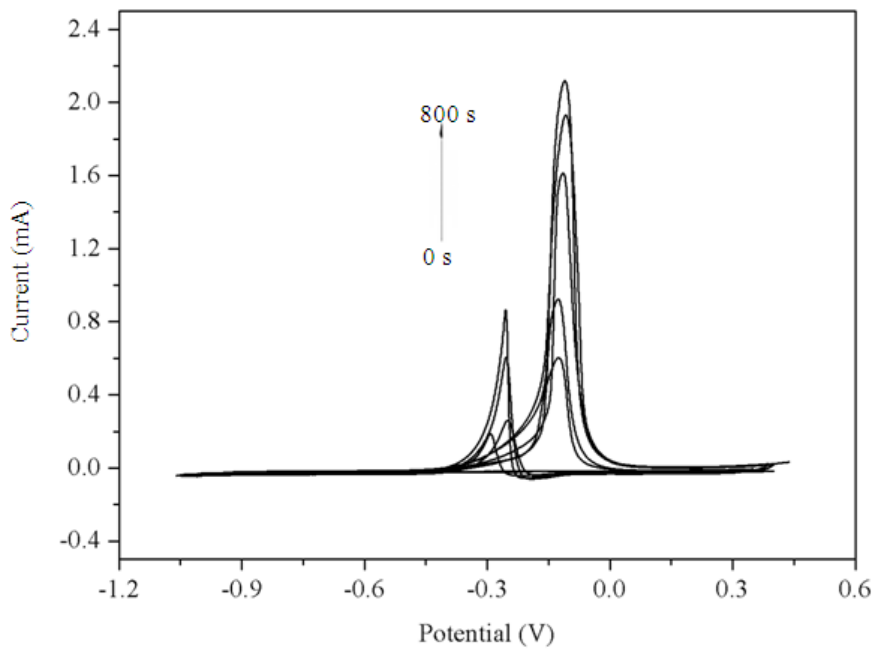
**Fig. 1.** Typical SEM image of the Pd structures electrodeposited on GCE in a solution containing 5 mM  $\text{H}_2\text{PdCl}_6$  and 0.5 M HCL at -0.2 V over a 200-s period. Inset shows the local view of one Pd flower



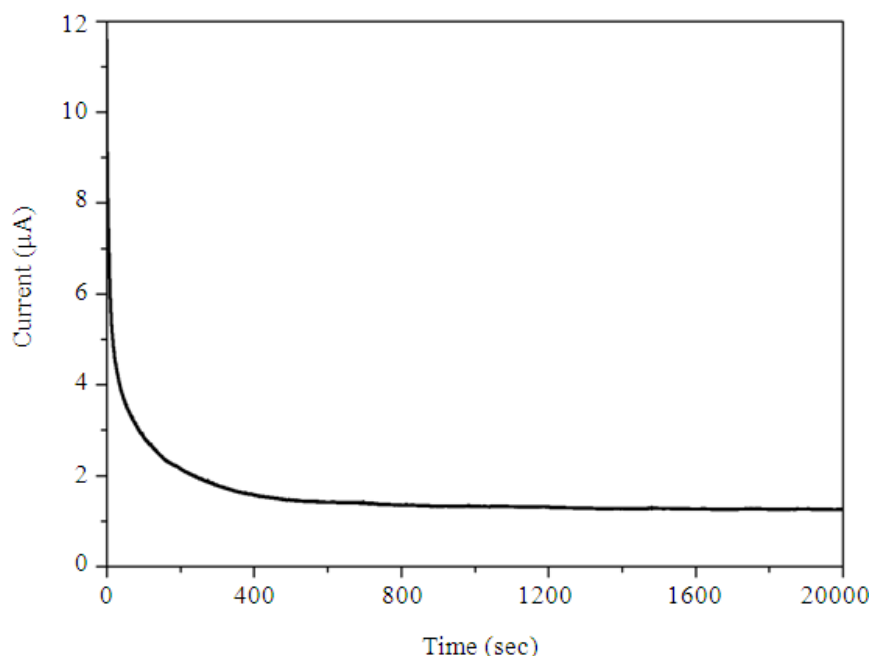
**Fig. 2.** Cyclic voltammery (CV) curves of the Pd/GCE in a 0.5 M NaOH solution at 0.05 V/s. The Pd electrodeposition was performed in solution containing 5 mM  $\text{H}_2\text{PdCl}_4$  and 0.5 M HCL at -0.2 V over a period of time of 0, 50, 100 200, 400 and 800 s



**Fig. 3.** CV curve of the Pd/GCE at 0.05 V/s in a 0.5 M NaOH solution in the presence of 1.0 M CH<sub>3</sub>OH. The Pd electrodeposition was performed in solution containing 5 mM H<sub>2</sub>PdCl<sub>4</sub> and 0.5 M HCl at -0.2 V for 200 s



**Fig. 4.** CV curves of the Pd/GCE in a 0.5 M NaOH solution at 0.05 V/s in the presence of 1.0 M CH<sub>3</sub>OH. The Pd electrodeposition was performed in solution containing 5 mM H<sub>2</sub>PdCl<sub>4</sub> and 0.5 M HCl at -0.2 V over a period of time of 0, 50, 100, 200, 400, 800 s



**Fig. 5.** Chronoamperometry of Pd/GCE in 0.5 M NaOH+1 M CH<sub>3</sub>OH at an constant potential of -0.1V at 25°C

It is well known that the stability of catalysts is important for the application of fuel cell. So the long-term stability of the catalytic performance was then investigated by chronoamperometric measurements where the current density-time (*I-t*) curves at constant potentials were recorded (Chen and Chen, 2011). **Fig. 5** shows the chronoamperometric curves of Pd/GCE in 0.5 M NaOH+1 M CH<sub>3</sub>OH at an applied potential of -0.1 V over 2000 s period. The rapid current decay in the first 100 s showed the poisoning of the electrocatalysts, likely due to the formation of intermediate and some poisoning species during the methanol oxidation reaction (Zhao *et al.*, 2011). With the poisoning of CO-like intermediates, the current density decayed in the first 400 s and attained a steady state thereafter, indicating that these Pd flowers form very stable film on GCE surface and also exhibit stable catalytic performance towards methanol oxidation.

#### 4. DISCUSSION

It can be seen that the peak currents increase with increase in the deposition time, suggesting the loading of Pd on GCE can be simply controlled by varying the deposition time. By means of the reduction chemisorbed

oxygen methods and CV (Grigoriev *et al.*, 2008; Korovin, 1976), the Electrochemical Active Surface area (EAS) of Pd with different electrodeposition time ranging from 0-800 s can be calculated by the following calculation Equation 1 (Nikiforova *et al.*, 2010):

$$EAS = \frac{Q_0}{0.42} \quad (1)$$

where,  $Q_0$  (mC) is the quantity of electricity spent for removal of a monolayer of atomic oxygen adsorbed on the Pd surface, 0.42 mC is the quantity of electricity consumed for an oxygen monolayer formation on a surface area of 1 cm<sup>2</sup>. The EAS of Pd with different electrodeposition time ranging from 0-800 s are thus determined to be 0, 1.141 cm<sup>2</sup>, 1.283 cm<sup>2</sup>, 1.347 cm<sup>2</sup>, 1.87 cm<sup>2</sup>, respectively.

It is also established that the ratio of the forward anodic peak current density ( $I_F$ ) to the reverse anodic peak current density ( $I_R$ ) can be used to describe the catalyst tolerance to CO and other carbonaceous species. In our present study, it is seen that the onset of methanol oxidation peak is about -0.50 V and the peak potential position is at about -0.15 V in the forward scan. Another oxidation peak in the reverse scan is observed at about -0.29 V. The corresponding ratio of  $I_F/I_R$  is measured to be

about 3.9, which is higher than the Pd-modified macroporous Pt (the  $I_F/I_R$  value is 1.18) and the Pd nanoparticles supported on 2-Aminophenoxazin-3-one (APZ) functionalized multi-walled carbon nanotubes (Pd/APZ-MWCNTs) (Du *et al.*, 2009; Xu *et al.*, 2007a) (the  $I_F/I_R$  value is 1.93). It suggests that the Pd film thus formed generates a high complete oxidation of methanol to carbon dioxide. Above observations indicate that GCE-supported Pd film could serve as an ideal candidate for direct methanol fuel cell electrodes.

## 5. CONCLUSION

In summary, electrodeposition has been proven to be an effective method for the rapid fabrication of film of Pd nanoparticles on bare glassy carbon electrode. The resulting film is stable and exhibits good catalytic activity with respect to methanol oxidation in an alkaline media. The loading of the Pd nanoparticles on the substrate can be rationally controlled by the deposition time. Such Pd film may find application in direct methanol fuel cell.

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