Available online at www.sciencedirect.com

ScienceDirect

Electrochemistry Communications 9 (2007) 1725–1729

electrochemistry communications

www.elsevier.com/locate/elecom

# Highly active core–shell Au@Pd catalyst for formic acid electrooxidation

Weijiang Zhou, Jim Yang Lee *

*The Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore*

Received 22 February 2007; received in revised form 9 March 2007; accepted 9 March 2007
Available online 21 March 2007

**Abstract**

Carbon supported bimetallic Au–Pd catalysts with the core–shell structure were prepared by the successive reduction method. TEM, XRD, XPS and UV–vis spectrum were used to characterize the core–shell sample and the monometallic samples. The electrochemical tests (cyclic voltammetry (CV) and chronoamperometry (CA)) showed that the core–shell structure could significantly improve the catalytic activity and stability of Pd in the room temperature electrooxidation of formic acid. The carbon supported pure Au sample showed no activity to the electrooxidation of formic acid and CO. The improvement of activity is ascribed to the interaction between Pd shell and Au core.

*Keywords:* Formic acid electrooxidation; Core–shell; Gold; Palladium

## 1. Introduction

Low-temperature polymer electrolyte membrane (PEM) fuel cells can be run with many different fuels, such as hydrogen [1], methanol [2], ethanol [3] and formic acid [4]. Hydrogen and methanol as a fuel have some notable problems: hydrogen is difficult to store and distribute; and methanol has innate toxicity, sluggish anodic oxidation kinetics, and fuel crossover problem in Nafion® based membranes. There is therefore increasing interest in the search for alterative fuels where these problems may be avoided. Formic acid (FA) as a non-flammable liquid at room temperature and a non-toxic chemical can be a good methanol substitute. The feasibility of direct formic acid fuel cells (DFAFCs) has recently been demonstrated [5]. Although the theoretical energy density of FA (2086 W h/L) is less than half of that of methanol (4690 W h/L), the lower rate of fuel crossover through the Nafion® membrane allows higher fuel concentrations to be used than in the case of direct methanol fuel cells (DMFCs). This is desirable for the design of compact portable power sources. The more facile kinetics of FA electrooxidation at room temperature compared with methanol also allows metals other than Pt to be used as the anode catalyst.

In recent years, Pd has been shown to be a good catalyst for the low temperature electrooxidation of FA [6]. However, the activity and stability of the Pd catalyst are still in need of improvements. The Pd catalytic activity may be increased by the addition of metal or metal oxide promoters [7]. Another effective method of enhancing catalytic activity is the core–shell construction [8–10] of nanosized bimetallic particles. In this work, core–shell Au–Pd nanoparticles supported on carbon black were prepared by the successive reduction, also known as the seed mediated growth method. The method is known for its effectiveness in the size-controlled synthesis of transition metal nanoparticles [11,12]. The supported Au@Pd nanoparticles were used as the anode catalyst for FA electrooxidation, with electrochemical evaluations of activities by cyclic voltammetry (CV) and chronoamperometry (CA), and microstructural characterizations of materials by X-ray diffraction (XRD) and TEM. The experimental results showed significant improvements relative to the monometallic Pd catalysts. It is known that small Pd particles are

---

* Corresponding author. Tel.: +65 65162899; fax: +65 67791936.
*E-mail address:* cheleejy@nus.edu.sg (J.Y. Lee).

1388-2481/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2007.03.016

more active in FA electrooxidation [13,14]. Yet the 7 nm Au@Pd/C catalysts could easily outperform 4 nm monometallic Pd nanoparticles. The specific mass activity of the Au@Pd/C catalyst as measured by CA was also higher than that of commercial Pd catalysts [14]. This is perhaps the first report on the catalysis of FA electrooxidation by bimetallic Au–Pd catalysts with the core–shell structure.

## 2. Experimental

All metal precursor salts (99.99%), trisodium citrate, sodium borohydride, formic acid, perchloric acid and ascorbic acid were purchased from Sigma–Aldrich and used as received. XC-72 R carbon black (Cabot Corp., BET area = 240 $m^2/g$) after refluxing in 5 M $HNO_3$ for 5 h was used as the catalyst support.

Citrate-stabilized Au nanoparticles (seed particles) were prepared by the $NaBH_4$ reduction of 5 mM $HAuCl_4$ aqueous solution in the presence of trisodium citrate in an ice-water bath with stirring [15]. Stirring was continued for 24 h to decompose the un-reacted $NaBH_4$. 100 mM $H_2PdCl_4$ aqueous solution and freshly prepared 100 mM ascorbic acid aqueous solution (in fivefold stoichiometric excess) were added dropwise to the Au hydrosol in succession (ascorbic acid before $H_2PdCl_4$). The colour of the hydrosol changed from red to dark brown in 30 min. Aqueous carbon slurry was added dropwise to the metal hydrosol and stirring was continued overnight. Recovery of the solid product was by means of centrifugation, followed by drying in vacuum (abbreviated henceforth as Au@Pd/C). The atomic ratio of Au to Pd was 2 and the total metal (TM) loading was 10 wt% (2.1 wt% of Pd). Comparative carbon supported monometallic Pd and Au samples (denoted as Pd/C or Au/C, respectively) with the same overall metal loading were prepared by similar procedures. All samples were characterized by TEM, XRD and X-ray photoelectron spectroscopy (XPS).

Electrochemical measurements were carried out in a conventional 3-electrode glass cell under the control of an Autolab potentiostat/galvanostat. The working electrode was a 5 mm glassy electrode pasted with the catalysts sample [3]. A Pt gauze and an Ag|AgCl (3 M KCl) electrode were used as the counter electrode and the reference electrode, respectively. The supporting electrolyte was 0.1 M $HClO_4$ aqueous solution with and without 3 M formic acid depending on the nature of the electrochemical test. For CO-stripping measurements, the catalyst surface was firstly saturated with CO by bubbling CO through 0.1 M $HClO_4$ aqueous electrolyte while holding the working electrode at −0.166 V (*vs* Ag|AgCl) for 15 min. The remaining CO was purged by flowing Ar for 30 min before measurements were made. A scan rate of 5 mV $s^{-1}$ was used for cyclic voltammetry.

## 3. Results and discussion

Fig. 1 shows the TEM images of the Au@Pd/C and Pd/C catalysts. The average diameter of Pd particles in Pd/C from counting more than 250 particles was about 3.8 nm. The specific surface area calculated from this diameter is 131 $m^2/g$ Pd. (The formula $S = 6000/(\rho d)$ was used to estimate the specific surface area of the nanoparticles, assuming spherical geometry. In the formula $\rho$ is the density of Pd and d is the mean particle diameter (nm) from TEM measurements.) The metal particles in Au@Pd/C were larger, at about 7.0 nm, and hence a correspondingly smaller specific surface area. It is interesting to note that the XRD pattern of Au@Pd/C replicated mostly the features of Au/C, without any evidence for the presence of crystalline Pd (Fig. 2). This indicates the absence of large, isolated Pd particles. Pd was therefore present as a thin shell over the Au core. Bulk Au–Pd alloy phases, if any, were not detectable because of the small amount of Pd used. The Au particles in the Au/C sample were also counted and they were marginally smaller than the particles in Au@Pd/C. Fig. 3 shows the UV–vis spectra of the Au hydrosol and the Au@Pd hydrosol before deposition on carbon. The remaining absorption at 520 nm due to the surface plas-

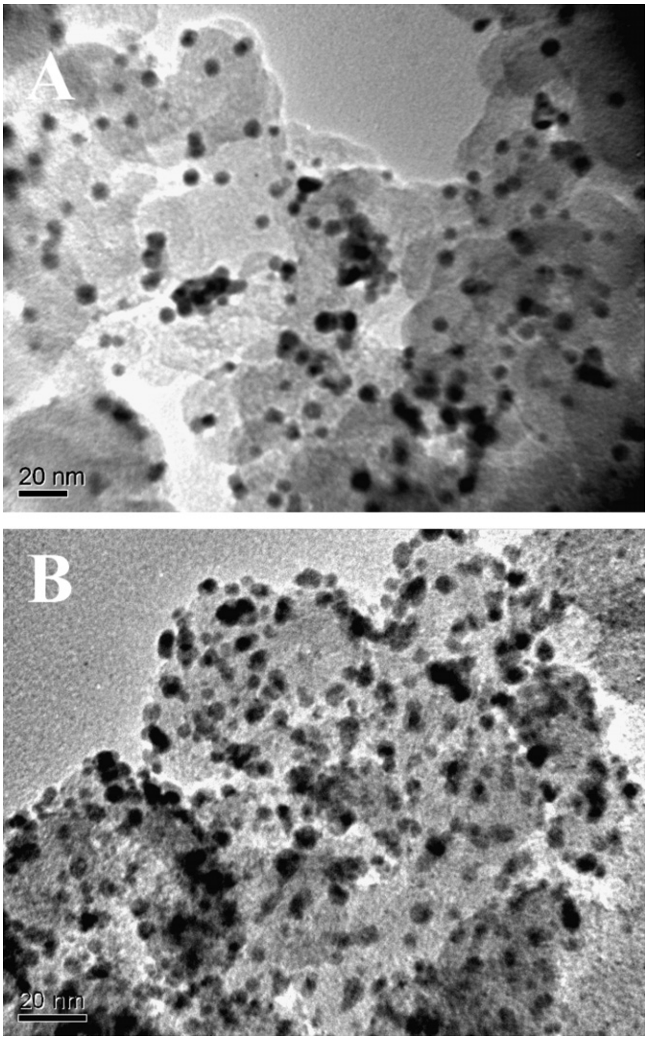

Fig. 1. TEM images of Au@Pd/C (A) and Pd/C (B) catalysts. A JEOL 2010 microscope operating at 200 kV was used to examine the samples.