Materials Chemistry and Physics 143 (2014) 747–753

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Direct electrochemical formation of alloyed AuPt nanostructured electrocatalysts for the oxidation of formic acid

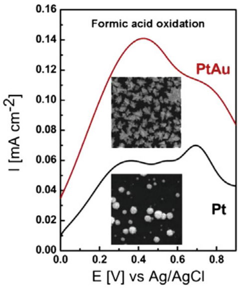
Ali Balkis, Anthony P. O'Mullane*

School of Applied Sciences, RMIT University, GPO Box 2476V, Melbourne, VIC 3001, Australia

HIGHLIGHTS

- Highly anisotropic AuPt alloys can be fabricated via a simple electrochemical method in the absence of surfactants.
- The morphology is controlled by the competing deposition of Au and Pt which is dependent on the applied voltage.
- The AuPt alloys are highly active for formic acid oxidation through the dehydrogenation pathway due to an ensemble effect.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 May 2013
Received in revised form
26 August 2013
Accepted 3 October 2013

Keywords:
Alloys
Nanostructures
Electrochemical techniques
Electrochemical properties

ABSTRACT

The formation of highly anisotropic AuPt alloys has been achieved via a simple electrochemical approach without the need for organic surfactants to direct the growth process. The surface and bulk properties of these materials were characterised by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and electrochemically by cyclic voltammetry to confirm alloy formation. It was found that AuPt materials are highly active for both the model hydrogen evolution reaction and the fuel cell relevant formic acid oxidation reaction. In particular for the latter case the preferred dehydrogenation pathway was observed at AuPt compared to nanostructured Pt prepared under identical electrochemical conditions which demonstrated the less preferred dehydration pathway. The enhanced performance is attributed to both the ensemble effect which facilitates $CO_{(ads)}$ removal from the surface as well as the highly anisotropic nanostructure of AuPt.

1. Introduction

The electrochemical formation of metallic nanostructured materials is a burgeoning area of research interest. This is due to the high level of compositional, shape and size control that is achievable using electrochemical methods under ambient conditions [1–6]. There is a significant amount of literature on the electrodeposition of metallic nanostructures based on gold [7–9], platinum [10–12], palladium [13–15], silver [4,16,17] and copper [18–20] where the influence of size, shape and exposed crystal facets play key roles in electrocatalytic performance [21]. Indeed this approach offers a highly beneficial means to study the electrocatalytic performance of such materials without the complication of organic capping agents that are typically used in the chemical synthesis of nanomaterials to prevent aggregation.

In electrocatalysis the oxidation of small organic molecules in particular has received attention in relation to fuel cell technology [22]. Methanol, ethanol, formaldehyde and also formic acid have been identified as alternative fuels to hydrogen for commercially applicable fuel cells. Although the energy density of formic acid is less than that of methanol it generally has less problems associated with cross over through the electrolyte membrane which therefore

---

* Corresponding author.
E-mail address: anthony.omullane@rmit.edu.au (A.P. O'Mullane).

0254-0584/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matchemphys.2013.10.009

in principle would allow a fuel cell to operate with higher fuel concentrations and thinner membranes [23]. The oxidation of formic acid is known to proceed via a dual path mechanism on platinum, i.e. a preferred dehydrogenation pathway which is direct oxidation to CO_2 and the less preferred dehydration pathway where $CO_{(ads)}$ is generated as an intermediate which poisons the electrocatalyst surface [23,24]. Many strategies have been employed to promote the direct pathway, however a particularly successful approach is using a bimetallic electrocatalyst based on platinum where the secondary metal is typically Au or Pd [23,25–29]. An added advantage of bimetallic systems is that electrodissolution of the electrocatalyst can be minimised [30].

However, in comparison to chemically synthesised bimetallic nanoparticles there have been comparatively fewer studies on the direct electrodeposition of bimetallic nanostructured materials. The advantage of employing bimetallic materials are well known in the areas of catalysis and electrocatalysis, due to the synergistic effect often seen when metals are combined over their individual components. As mentioned previously the AuPt and PtPd combination influences the formic acid oxidation reaction mechanism. Often the synergistic effect is as a result of electronic perturbation effects which influences the adsorption of reactants and intermediates and desorption of products from the surface that can dictate the rate of reaction. Recently Greely et al. have shown by density functional theory calculations the influence of a vast array of bimetallic combinations on the metal–hydrogen bond strength which plays a key role in the hydrogen evolution reaction [31,32]. A key aspect to enhanced formic acid oxidation is the fabrication of an alloyed rather than phase separated material in particular for AuPt [23,25,27]. Due to the miscibility gap between Pt and Au in their binary phase diagram the synthesis of an alloyed material is often challenging [27]. The chemical synthesis of nanostructured AuPt alloys can be quite involved and usually requires organic surfactants and/or elevated temperatures and prolonged reaction times. Therefore the ability to rapidly produce AuPt alloys in the absence of organic moieties would be particularly useful for electrocatalytic applications.

In this work the direct electrodeposition of AuPt nanostructures is reported in the absence of any surfactants from a simple electroplating bath containing equimolar concentration of an aqueous solution containing $HAuCl_4$ and K_2PtCl_4. The morphology and composition is dependent on the applied deposition potential and significantly it is shown that an alloy is formed which is particularly beneficial for the direct oxidation of formic acid.

2. Experimental

2.1. Chemicals

Aqueous solutions of $HAuCl_4$, K_2PtCl_4 (Aldrich), formic acid (Merck), H_2SO_4, HCl (Ajax Finechem) were made up with deionised water (resistivity 18.2 MΩ) purified by use of a Milli-Q reagent deioniser (Millipore). Pt/C −20 wt% Pt on carbon (Alfa Aesar) was used as a commercial catalyst.

2.2. Electrochemical measurements

Cyclic voltammetric experiments were conducted (22 ± 2) °C with a CH Instruments (CHI 760C) electrochemical analyser in an electrochemical cell (BAS) that allowed reproducible positioning of the working, reference, and counter electrodes and a nitrogen inlet tube. The GC electrodes ($0.126\ cm^2$–GC plates ($1 \times 0.75 \times 0.3$ cm) were masked off using Kapton tape) were polished on a polishing cloth (Microcloth, Buehler), and rinsed with Milli-Q water, sonicated in acetone for 5 min and then ethanol for a further 5 min, and dried with nitrogen gas. The reference electrode was Ag/AgCl (aqueous 3 M KCl). For all of the electrochemical experiments carried out, an inert graphite rod (5 mm diameter, Johnson Matthey Ultra "F" purity grade) was used as the counter electrode to prevent contamination by any possible electrolysis products during electrodeposition [33]. To investigate the commercial Pt/C catalyst a total of 5 mg of the catalyst was mixed with 0.12 mL of 5 wt% Nafion in 3.88 mL of ethanol to obtain a suspension. 5 μL of this solution was drop cast onto the GC plate and allowed to dry. All electrochemical experiments were commenced after degassing the electrolyte solutions with nitrogen for at least 10 min prior to any measurement.

2.3. Instrumentation

SEM measurements were performed on a FEI Nova SEM instrument with an AMETEK energy dispersive X-ray (EDX) system (Nova 200) operated at an accelerating voltage of 30 kV. Prior to SEM imaging, samples were thoroughly rinsed with Milli-Q water and dried under a flow of nitrogen. X-ray diffraction (XRD) measurements were conducted on a Bruker AXS X-ray diffraction system with an operating voltage and current of 40 kV and 40 mA with CuKα radiation. XPS was performed using a Thermo K-Alpha instrument at a pressure better than 10^{-9} Torr, with the data being referenced to the adventitious C 1s binding energy of 285 eV.

Table 1 describes the experimental conditions employed to create the samples used in this study. In all cases the electrodeposition time was held constant at 600 s.

3. Results and discussion

Illustrated in Fig. 1 are cyclic voltammograms (CVs) for the electrodeposition of Au, Pt and AuPt on to a GC electrode from electrolytes containing 2.5 mM K_2PtCl_4, 2.5 mM $HAuCl_4$ and an equimolar (2.5 mM) solution of both salts in a supporting electrolyte of 0.1 M HCl respectively. The latter was added to maintain the solubility of the salts in the mixed solution as in its absence a minor brown precipitate was formed presumably due to $Au(OH)_{3(s)}$ [34]. The CVs demonstrate that the electrodeposition of Au is more facile on GC than Pt due to the large difference in the onset potential which occurs at 0.50 V and −0.02 V for Au and Pt respectively. In both cases on the reverse sweep a current cross over is observed which is indicative of a nucleation-growth process [35,36]. It should be noted that the slightly greater increase in current seen at the end of the sweep in the case of Pt electrodeposition is due to the hydrogen evolution reaction (HER). The CV recorded at GC of the mixed salt solution shows two distinct processes, a shoulder at ca. 0.20 V and a broad response from 0.20 V until the end of the reduction sweep. The onset potential occurs at 0.35 V which is less positive than in the case of $HAuCl_4$ only (Fig. 1b). This suggests that the response recorded is not simply a superimposition of the two individual processes and that there may be some speciation changes which makes metal electrodeposition on GC more difficult.

Table 1
Experimental parameters used in the preparation of electrodeposited samples.

Sample no.	Electrodeposition potential [V] vs Ag/AgCl	Electrolyte
		Supporting electrolyte of 0.1 M HCl was used in all cases
S1	−0.20	2.5 mM K_2PtCl_4
S2	−0.20	2.5 mM $HAuCl_4$
S3	0.25	2.5 mM $HAuCl_4$ + 2.5 mM K_2PtCl_4
S4	0.00	2.5 mM $HAuCl_4$ + 2.5 mM K_2PtCl_4
S5	−0.20	2.5 mM $HAuCl_4$ + 2.5 mM K_2PtCl_4