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# Utilising solution dispersed platinum nanoparticles to direct the growth of electrodeposited platinum nanostructures and its influence on the electrocatalytic oxidation of small organic molecules

Benchaporn Lertanantawong<sup>a</sup>, Werasak Surareungchai<sup>b</sup>, Anthony P. O'Mullane<sup>c,\*</sup>

<sup>a</sup> Pilot Plant Development and Training Institute, King Mongkut's University of Technology Thonburi, Bangkok 10150, Thailand

<sup>b</sup> School of Bioresources and Technology, King Mongkut's University of Technology Thonburi, Bangkok 10150, Thailand

<sup>c</sup> School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, QLD 4001, Australia

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## ABSTRACT

The electrodeposition of platinum nanostructures on glassy carbon electrodes in the absence and presence of platinum nanoparticles in the electrolyte is reported. It is found that the presence of platinum nanoparticles has a significant influence on the morphology of the platinum electrodeposited onto the electrode surface. Even though the morphology of the materials is affected, the overall surface area is similar. The electrochemical behaviour of the platinum nanostructures is investigated in 1 M H<sub>2</sub>SO<sub>4</sub> where distinct differences are observed in the exposed surface sites for platinum electrodeposited in the presence of nanoparticles. The influence of these surface sites is then studied for a variety of electrocatalytic reactions such as methanol and ethylene glycol oxidation and the hydrogen evolution reaction. In the case of organic molecule oxidation reactions, the platinum structures created using platinum nanoparticles in the electrodeposition solution exhibited earlier onset potentials and increased current densities compared to those that were electrodeposited in their absence.

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## 1. Introduction

The electrochemical formation of nanostructured materials is a relatively mature field, however, there are consistently new methods and strategies being reported that allow excellent control over composition, size, shape and exposed crystal facets [1–7]. This is particularly useful given the critical role the aforementioned properties play in electrocatalysis, photocatalysis, surface enhanced Raman spectroscopy and electroanalytical chemistry. There are several approaches that can be undertaken to achieve a desired nanostructure such as using hard templates like anodised alumina [8,9], chemical templating with surfactants [10,11], inorganic ions [12,13], *in situ* underpotential deposition of a second metal [14], hydrogen bubbling [4,15–18], or in the absence of any template via appropriate choice of metal precursor concentration and the applied potential/current waveform, time and temperature [19–22]. This illustrates the vast amount of parameters available for the creation of a wide range of interesting materials. The advantage of electrodepositing nanostructured materials is that it is straightforward and can be undertaken under ambient conditions which also ensures good adherence to the underlying support electrode which can be problematic when trying to immobilise chemically synthesised nanomaterials.

Although there have been significant research efforts into reducing the use of Pt as well as finding alternative electrocatalysts to Pt for a variety of important reactions [23–30], the study of nanostructured Pt still remains a relevant topic. In particular the study of small organic molecules such as methanol and ethylene glycol are of interest due to their potential use in direct oxidation fuel cells [31–38]. There have been many interesting insights discovered regarding structure-activity relationships for this material on low index basal planes, stepped surfaces and high energy facets and the link between these observations and chemically synthesised nanoparticles of different size and shape [39–49]. However, establishing this link between well-defined surfaces and small nanoparticles is an ongoing challenge. Therefore, investigating electrodeposited nanostructured surfaces offers an avenue of research into materials with morphological features that are between single crystal surfaces and chemically synthesised nanomaterials.

A recent concept developed by Bard is that of using nanoparticle collisions at an ultramicroelectrode to determine properties such as metal nanoparticle size and the influence of capping agents on electrocatalytic reactions and electron transfer processes [50–54]. Since its inception many others have utilised this approach to investigate the properties of a wide range of dilute nanoparticles in solution [55–62]. The presence of nanoparticles in solution was also reported to significantly influence the diffusion of electroactive species such as ferricyanide to the electrode surface via physical blocking effects [63]. In addition to this blocking effect our recent communication also showed that the

\* Corresponding author.

E-mail address: [anthony.omullane@qut.edu.au](mailto:anthony.omullane@qut.edu.au) (A.P. O'Mullane).

**Table 1**

Electrodeposition conditions used to create Pt nanostructures (concentration of Pt nanoparticles is given in atomic molarity).

Sample no.	Electrodeposition conditions
1	8 mM $K_2PtCl_6$ , $-0.60$ V for 300 s
2	8 mM $K_2PtCl_6$ + 0.26 mM Pt NPs, $-0.60$ V for 300 s
3	8 mM $K_2PtCl_6$ , $-0.60$ V for 600 s
4	8 mM $K_2PtCl_6$ + 0.26 mM Pt NPs, $-0.60$ V for 600 s

presence of gold and silver metal nanoparticles in solution can influence the electrodeposition of gold and silver respectively on glassy carbon electrodes due to interaction between the metal salts and the capping agent of the nanoparticles [64]. In this work we explore this concept further by investigating the influence that Pt nanoparticles in solution have on the electrodeposition of Pt nanostructures and report on the effect that the difference in surface properties has on electrocatalytic activity for technologically important reactions such as methanol and ethylene glycol oxidation. Although there were not significant changes in the surface area of the electrodeposited materials, the effect on their electrocatalytic properties was pronounced and is discussed.

## 2. Experimental

### 2.1. Materials

Aqueous 1.0 M  $H_2SO_4$  and 1.0 M NaOH (Aldrich) solutions were made up with deionized water (resistivity of 18.2 M $\Omega$  cm) purified by use of a Milli-Q reagent deionizer (Millipore). Colloidal Pt nanoparticles capped with citrate, Pt NPs (Nanocomposix, USA) with a mean diameter of  $5 \pm 2$  nm and coefficient of variance of <20%,  $K_2PtCl_6$ , ethylene glycol (Aldrich) and methanol (Merck) were used as received.

### 2.2. Electrochemical measurements.

Electrochemical experiments were performed with a three-electrode system where a 3 mm diameter glassy carbon (GC) electrode was used as the working electrode, a Ag/AgCl (3 M KCl) and platinum wire were used as the reference and counter electrodes respectively. For electrodeposition experiments, plating solutions for the deposition of Pt nanostructures consisted of an aqueous solution of 8 mM  $K_2PtCl_6$  containing 0, 0.05 or 0.26 mM Pt nanoparticles (the concentration is given as atomic molarity where solutions of 0.01 and 0.05 mg/ml of Pt nanoparticles, as quoted by the manufacturer, were employed). The following samples were investigated for electrocatalytic activity and will be referred to by sample name as indicated in Table 1.

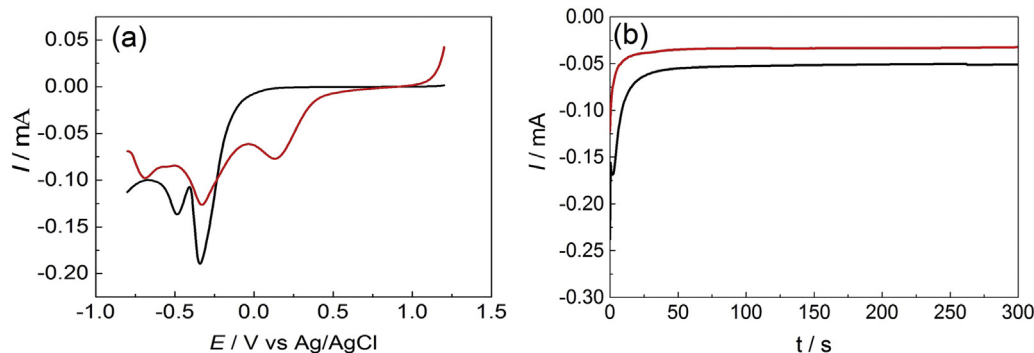
Experiments were undertaken at  $(20 \pm 2)$  °C and all solutions were deaerated with purified nitrogen to remove oxygen for at least 10 min prior to the beginning of all cyclic voltammetric and chronoamperometric measurements. Electrochemical measurements were carried out using an Autolab PGSTAT 10 computer-controlled potentiostat with GPES version 4.9 software (EcoChemie, The Netherlands). Prior to electrodeposition, each GC electrode was polished with aqueous 0.3  $\mu$ m alumina slurry on a polishing cloth (Microcloth, Buehler, USA), thoroughly rinsed with deionized water, sonicated in 95% EtOH and then deionized water for 5 min, rinsed thoroughly by deionized water and blown dry with a flow of nitrogen gas. After electrodepositing Pt nanostructures on a GC electrode it was removed from the plating solution and washed three times with deionized water and dried in a flow of nitrogen gas prior to surface characterization and electrocatalytic experiments. The pH was measured using a Denver instrument model UB-10 (USA).

### 2.3. Physical characterization

Scanning Electron Microscopy (SEM) was performed on an FEI Nova NanoSEM 450 at an operating voltage of 10 kV under high-vacuum conditions. X-ray diffraction data were obtained with a Bruker AX 8: Discover with General Area Detector Diffraction System (GADDS).

## 3. Results and discussion

The electrodeposition of Pt nanostructures was carried out in the presence and absence of citrate capped Pt nanoparticles (Pt NPs) of 5 nm diameter from a solution containing 8 mM  $K_2PtCl_6$  in MilliQ water. Fig. 1a shows linear sweep voltammograms for the electroreduction of  $PtCl_6^{2-}$  ions in the absence (black line) and presence (red line) of Pt nanoparticles. In the absence of nanoparticles in the electrolyte, two distinct reduction peaks are observed at ca.  $-0.33$  and  $-0.49$  V which are attributed to  $PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^-$  and  $PtCl_4^{2-} + 2e^- \rightarrow Pt^0 + 4Cl^-$  respectively [65], however the latter peak could also have a contribution from the direct 4 electron reduction of the Pt salt to Pt metal. The further onset of cathodic current near the end of the sweep is due to the onset of hydrogen ion adsorption on the electrodeposited Pt. Significantly in the presence of Pt NPs all the aforementioned processes shift to less negative potentials and there is an increase in the separation between the electroreduction of  $PtCl_6^{2-}$  and  $PtCl_4^{2-}$  species. This outcome indicates that the overpotential for the electroreduction of  $PtCl_6^{2-}$  to  $PtCl_4^{2-}$  in particular and to a lesser extent  $PtCl_4^{2-}$  to  $Pt^0$  is less when Pt NPs are present in the electrolyte. This is consistent with metal electrodeposition generally being more facile on metals compared to carbon [66] and indicates that Pt NPs are impacting on the electrode surface creating nucleation points for electrodeposition to occur. In addition, from  $-0.50$  V until the end of the sweep, the minor features are likely to be due to the adsorption of



**Fig. 1.** (a) Linear sweep voltammograms recorded at 20 mV s<sup>-1</sup> at a GC electrode in an 8 mM  $K_2PtCl_6$  aqueous solution in the absence (black line) and presence (red line) of 0.26 mM Pt NPs, (b) the corresponding chronoamperometric curves recorded at an applied potential of  $-0.60$  V. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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