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# Electrochemical deposition of Au–Pt alloy particles with cauliflower-like microstructures for electrocatalytic methanol oxidation

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## ABSTRACT

Au–Pt alloy particles with cauliflower-like microstructures of varying Pt/Au ratios were electrodeposited on indium tin oxide (ITO) substrates by constant potential electrolysis at  $E = -0.25$  V. The results of X-ray diffraction and X-ray photoelectron spectroscopy confirm that the bimetallic alloys can be obtained for different Pt/Au ratios including 4/1, 1/1 and 1/4. The formation of alloyed cauliflower-like microstructures may be the result of the fast formation of gold seeds as the core and subsequent simultaneous deposition of Au and Pt from cyclic voltammetric study. The effect of surface composition of Au–Pt alloy particles on electrocatalytic methanol oxidation were investigated in  $H_2SO_4$  solution. The electrocatalytic abilities including electrochemical surface area, peak current density and the turnover number of methanol oxidation follow the order of  $Pt_4Au_1 > Pt > Pt_1Au_1$ . The results can be ascribed to that electronic effect may be prominent while bifunctional effect is insignificant for Au–Pt alloy systems because the electrocatalytic activity of Au is negligible in acidic media. Additionally, the  $Pt_4Au_1$  electrode has superior kinetics of methanol electro-oxidation than monometallic Pt electrode by calculating the electron transfer coefficient ( $\alpha$ ).

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## 1. Introduction

Methanol electro-oxidation, as a promising solution to future energy problems, has received considerable attention due to the possible applications in direct methanol fuel cells (DMFCs), which show high-energy conversion efficiency, low pollutant emission, low operating temperature and the simplicity of handling liquid fuel [1–4]. Over the past

decades, platinum is considered as the most suitable catalyst for methanol oxidation reaction, but a major problem is the poisoning of platinum by CO-like species generated during the electro-catalytic process [5–8]. Therefore, how to keep its activity and durability is of paramount importance. Gold–Platinum catalysts have attracted considerable interest in recent years because of not only their promising catalytic performance, but also the lower price and greater availability

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of gold than that of platinum. The employment of gold in bimetallic Au–Pt catalysts could therefore produce a welcome reduction in the cost of fuel cell installations [9–16].

Several methods have been applied to prepare Au–Pt catalysts, such as co-sputtering [9], crossed-beam pulsed laser deposition [10], microemulsion [11], chemical co-reduction method [12] and electrochemical deposition [13–16]. Amongst these well-developed methods, electrodeposition is a simple method with low cost and easier control. Furthermore, electrodeposition is also a powerful and convenient tool to create hierarchical micro/nanostructures. Hierarchical micro/nanostructures are one type of hyperbranched structures which are generally formed by hierarchical self-assembly of freshly generated precursors under non-equilibrium conditions. They can provide high surface areas, special shapes, and chemical functionality, allowing them promising candidates for the design and fabrication of new functional nanomaterials. For example, porous Pt nano-flowers were obtained by one-step and template-free electrodeposition, and the as-prepared Pt nano-flowers exhibited remarkably higher catalytic activity and stronger poisoning-tolerance for methanol electro-oxidation, compared to conventional nanosized Pt catalysts [17]. Electrochemical deposition was used to prepare palladium nanostructures with a 3D feather-like dendritic morphology [18] or nanoplates [19], both of which exhibited high electrocatalysis activities. We have recently developed an electrodeposition route to fabricate hierarchical dendritic gold microstructures on an indium tin oxide (ITO) substrate without the use of any templates, which displayed multifunctional applications such as electrocatalysis, surface-enhanced Raman scattering, superhydrophobicity and (super)oleophobicity [20]. However, the preparation of bimetallic particles with hierarchical micro/nanostructures by electrodeposition has not been tried as much.

In this study, Au–Pt alloys with cauliflower-like microstructures were fabricated on a surface of indium tin oxide (ITO) substrate by constant potential electrolysis in 0.5 M  $\text{H}_2\text{SO}_4$  containing chloroauric acid and chloroplatinic acid. The resulting bimetallic particles were characterized with scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). It was found that these bimetallic systems demonstrated alloy properties for different Pt/Au ratios including 4/1, 1/1 and 1/4. The electrocatalytic behaviors of Au–Pt alloyed particles for methanol oxidation were investigated in  $\text{H}_2\text{SO}_4$  solutions; the results show a higher catalytic efficiency for  $\text{Pt}_4\text{Au}_1$  composition.

## 2. Experimental

### 2.1. Chemicals

Chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ),  $\text{H}_2\text{SO}_4$  and methanol were all of analytical grade and used without further purification. The solutions were prepared with Milli-Q water (18 M $\Omega$  cm, Millipore).

### 2.2. Electrochemical deposition of Au–Pt alloys

Prior to deposition, the ITO glass was washed with acetone, ethanol and water in sequence by ultrasounds, and then dried in  $\text{N}_2$ . Au–Pt alloys were electrodeposited onto the ITO surface under constant potential electrolysis at  $E = -0.25$  V vs. SCE for 1500 s. The plating bath was the solution of 0.5 M  $\text{H}_2\text{SO}_4$  containing a totaling 10 mM solution of chloroplatinic acid and chloroauric acid, and the molar ratios of chloroplatinic acid and chloroauric acid was adjusted as 5/0, 4/1, 1/1, 1/4 and 0/5, respectively. Herein, the corresponding samples were named as Pt,  $\text{Pt}_4\text{Au}_1$ ,  $\text{Pt}_1\text{Au}_1$ ,  $\text{Pt}_1\text{Au}_4$  and Au.

The co-electrodeposition process of Au and Pt was analyzed with cyclic voltammetry (CV). In CV, the potential was scanned from 1.2 V to  $-0.2$  V at a scan rate of 20  $\text{mV}^{-1}$ .

### 2.3. Electrochemical measurements

The electrochemical measurements were carried out with a 273A electrochemical device (EG&G Princeton Applied Research). The ITO electrode modified with Au–Pt alloys served as a working electrode with an area of 0.196  $\text{cm}^2$ . The counter electrode was a platinum wire and the reference was a saturated calomel electrode (SCE). The CV experiments were performed in 0.5 M  $\text{H}_2\text{SO}_4$  with or without 1 M  $\text{CH}_3\text{OH}$ . After voltammetry in 1 M  $\text{CH}_3\text{OH}$  of 0.5 M  $\text{H}_2\text{SO}_4$  was tested with the same electrodes, chronoamperometry curves for 1500 s were immediately recorded at 0.75 V.

### 2.4. Characterization

The morphologies of the samples were observed by a field emission scanning electron microscope (FE-SEM, JSM-6701F, JEOL Inc., Japan) equipped with Kevex sigma™ energy dispersion X-ray (EDX) analysis tool. EDX spectrum was acquired over a collection time of 100 s using an operation voltage of 10 kV. An X-ray diffraction analyzer (XRD, Rigaku D/max-2400, Cu K-Alpha radiation,  $\lambda = 0.1541$  nm) was used to determine the crystalline structures of the deposits. Chemical composition information about the samples was obtained by X-ray photoelectron spectroscopy (XPS), the measurement was carried out on a multifunctional spectrometer (Thermon Scientific) using Al  $K\alpha$  radiation, and the binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

## 3. Results and discussion

### 3.1. Characterization of the Au–Pt alloyed cauliflower-like particles

Au–Pt bimetallic particles were electrodeposited on the ITO surfaces under a fixed potential electrolysis of  $-0.25$  V for 1500 s in 0.5 M  $\text{H}_2\text{SO}_4$  containing a total 10 mM concentration of  $\text{HAuCl}_4$  and  $\text{H}_2\text{PtCl}_6$  with different molar ratios. To determine whether the Au–Pt bimetallic particles are aggregated together or a formed alloy of the two metals, the detailed XRD characteristics were compared with those of Au, Pt, and Au–Pt bimetallic systems ( $\text{Au}_4\text{Pt}_1$ ,  $\text{Au}_1\text{Pt}_1$ ,  $\text{Au}_1\text{Pt}_4$ ). As shown in

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