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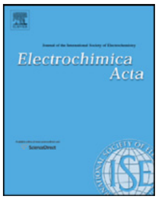

Morphology controlled 1D Pt nanostructures synthesized by galvanic displacement of Cu nanowires in chloroplatinic acid

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ABSTRACT

One-dimensional platinum (Pt) nanostructures with different shape, size, and morphology were synthesized by galvanic displacement of sacrificial Cu nanowires in chloroplatinic acid baths. By increasing the concentration of H_2PtCl_6, the morphology of Pt nanostructures greatly altered from Pt nanoparticles decorated Cu nanowires, Pt coated Cu core–shell nanowires, dense Pt nanotubes to porous Pt nanotubes. At low concentration of H_2PtCl_6 (<1 mM), the Pt content monotonically increased with an increase in $[H_2PtCl_6]$ (upto approx. 80 at.%). The Pt content became independent of $[H_2PtCl_6]$ at higher concentration. The average external diameter and wall thickness of Pt nanotubes decreased with increasing $[H_2PtCl_6]$ suggesting that the dissolution of copper is strongly dependent on $[Cl^-]$, which led to changes in the morphology of Pt nanostructures.

1. Introduction

Recently, metal nanostructures have been extensively studied because of their high chemical reactivity [1]. Specially, metal nanostructures with hollow interiors (nanotube) are useful in the fields of microencapsulation, catalysis, drug delivery, and protection of environmentally sensitive biological species [2]. Platinum (Pt) is a well-known and highly researched noble metal as an electrocatalyst for hydrogen production, fuel cells, and sensors [3–6]. Despite the exorbitant cost of Pt, nanostructured Pt, including nanoparticles [3], nanowires [4,5], nanotubes [6] and nanoporous thin films [7,8], has been investigated because of many advantages including high surface area to volume ratio [6], higher mass activity, specific activity, and durability. It was suggested by many researchers [6,9–12] that further reduction of the size of Pt nanostructures may lead to an increase in the electrocatalytic mass activity and reduce usage of precious Pt catalyst. Inaba et al. [3] reported that Pt nanoparticles in nanometer size (2–5 nm) are commonly used on conductive carbon black (Pt/C) as an electrode catalyst in polymer fuel cells to reduce Pt loading requirements. The specific activity of Pt on conductive carbon black for oxygen reduction strongly depends on the particle size and on the crystal orientation of Pt nanoparticles [13–15]. Han et al. [16] found that the morphology and crystal structure of Pt nanoparticles play important roles in determining the electrocatalyst activities. In addition, Chen et al. [17] reported that nanoelectrodes based on Pt nanotubes synthesized by galvanic replacement (GD) reaction of silver nanowires have been used as electrocatalysts for oxygen reduction. These electrocatalysts have a unique combination of crystallographic parameters and length scales that allow unsupported Pt nanotubes to yield greater durability and activity than their Pt-black and Pt/C counterparts [17].

Several different techniques including impregnation method [18], reduction of K_2PtCl_4 with a capping polymer [3], template-directed electrodeposition [4], and galvanic displacement [6,17,19] have been developed to synthesize Pt nanostructures. Galvanic displacement (sometimes referred to as cementation or immersion plating) is a simple and efficient method to fabricate nanostructures of various metals and semiconductors including nanoparticles [19], nanowires [1,20] or nanotubes [2,21,22]. Unlike electrodeposition, galvanic displacement does not require an external power supply. In addition, it differs from electroless deposition because a reducing agent is not necessary in galvanic displacement. Only limited works for metal nanotubes (Au, Pt, Pd and BiTe) synthesized by galvanic displacement reaction have been reported [2,21,22]. Therefore,

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Table 1
Bath compositions and operation conditions for electrodeposition to synthesize Cu nanowires.

Electrolyte	$CuSO_4$	0.8 M
	H_2SO_4	0.5 M
Operating conditions	Current density	10 mA cm^{-2}
	Time	3 h
	Solution pH	0.5
	Temperature	Room temp.
	Agitation	1″ stir bar 300 RPM

further research efforts are needed to understand the reaction mechanisms and control the processes to synthesize desired nanostructures with specified properties.

In this study, the ability to control size, shape, morphology and structure of 1D Pt nanostructures was demonstrated by galvanic displacement of copper nanowires in chloroplatinic acid electrolytes. The change in Pt nanostructures was studied using open circuit potential (OCP) measurement, scanning electron microscopy (SEM), transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDS) and selective area diffraction (SAD) pattern. The influences of $[H_2PtCl_6]$ on the external diameter and wall thickness of Pt nanotubes were also systematically investigated.

2. Experimental

In order to synthesize 1D Pt nanostructures by galvanic displacement, the sacrificial Cu nanowires, approximately 200 nm in diameter, were synthesized by template-directed electrodeposition method. Commercially available alumina membranes (Whatman Inc. Anodisc 13) with a nominal pore size of 200 nm were used as templates in this study. One side of the template was sputtered with Au using a tabletop sputter coater (Emitech, K550) to form a seed layer. The working electrode was constructed on a glass slide for mechanical support. Double-sided copper tape (3 M, 1182a) was used as an electrical conductive path and an adhesive to secure the template against the slide. The copper tape and edges of the template were insulated using a red mylar insulating tape and coated with Microstop, a dielectric surface coating. Cu nanowires were galvanostatically electrodeposited using a galvanostat/potentiostat (EG&G Princeton Applied Research VMP-2) at 10 mA cm^{-2} for 3 h with a two electrode configuration. A Cu anode was used as a counter electrode. Table 1 lists bath compositions and operating conditions for electrodeposition of the sacrificial Cu nanowires. All solutions were made with ultra-pure water (18 MΩ cm). After electrodeposition of Cu nanowires, the copper tape and mylar tape surrounding the template were removed. The remaining tape and template were detached from the slide by immersing in acetone for 4 h. The template was then washed in acetone under sonication (VWR Sonciator Model 50 D) at power level of 9 for 4 min to remove adhesive residue followed by a detergent under sonication at power level of 9 for 4 min, and rinsed in ultra-pure water. The Au seed layer was mechanically polished from the embedded nanowires in template with 2000 grit SiC paper in water. After the removal of the seed layer, the template was dissolved in 1 M NaOH at room temperature for 2 h. The remaining nanowires were separated from solution by centrifuging at 5000 rpm and washed three times in ultra-pure water, which was the solution for the final nanowire suspension. Good dispersion of nanowires in solution was achieved by intermittent low power (power level of 3) sonic agitation for 5 s. Electrodeposited Cu nanowires were immersed into the chloroplatinic acid electrolyte for galvanic displacement for 12 h. The electrolyte for galvanic displacement consists of ultra-pure water and $H_2PtCl_6{\cdot}6H_2O$, varying the concentration from 0.01 to 100 mM. Solution pH depended on $[H_2PtCl_6]$. Since it is difficult to monitor the effect of $[H_2PtCl_6]$ on galvanic displacement reaction of Cu nanowires to form Pt nanostructures by OCP, OCP measurements were conducted in Cu thin films (0.3 μm thick) electrodeposited on Au/Si substrates, while varying $[H_2PtCl_6]$ from 2.5 to 100 mM. Counter and reference electrodes were Pt mesh and Ag/AgCl (3 M KCl), respectively.

Surface morphology of Pt nanostructures after galvanic displacement was observed using SEM (model: XL30-FEG, Phillips). Composition of Pt nanostructures was determined using EDS (model: INCA energy, Oxford Instrument). TEM (model: JEM-2100F, JEOL) operated at 300 kV accelerating voltage was used to investigate the crystallography of Pt nanostructures. HRTEM image and SAD pattern also were used.

3. Results and discussion

Galvanic displacement of Cu nanowires to form Pt nanostructures is driven by a difference in the redox potential between the sacrificial metal nanowire (Cu) and metal ion (Pt). The anodic dissolution of copper in chloride electrolytes can occur as follows [23,24]:

$$\mathrm{Cu} \leftrightarrow \mathrm{Cu}^{2+} + 2\mathrm{e}^- \quad E^0 = 0.340\,\mathrm{V\,vs.\,SHE} \tag{1}$$

or

$$\mathrm{Cu} + \mathrm{Cl}^- \leftrightarrow \mathrm{CuCl_{ads}} + \mathrm{e}^- \quad E^0 = 0.14\,\mathrm{vs.\,SHE} \tag{2}$$

$$\mathrm{CuCl_{ads}} + \mathrm{Cl}^- \leftrightarrow \mathrm{CuCl_2}^- \tag{3}$$

$$\mathrm{CuCl_{ads}} + 2\mathrm{Cl}^- \leftrightarrow \mathrm{CuCl_3}^{2-} \tag{4}$$

whereas the cathodic deposition of platinum from chloroplatinic acid can occur as follows:

$$\mathrm{PtCl_6}^{2-} + 4\mathrm{e}^- \leftrightarrow \mathrm{Pt} + 6\mathrm{Cl}^- \quad E^0 = 0.744\,\mathrm{V\,vs.\,SHE} \tag{5}$$

In the presence of chloride ions in the solution, cuprous chloride complexes formed on the surface during anodic dissolution of copper [24,25]. The dominant cuprous chloride complex at the surface of copper is strongly dependent on $[Cl^-]$. For $[Cl^-] < 0.05$ M, a considerable amount of the dissolved copper is in the form of Cu^{+2} (Eq. (1)). However, as the concentration of chloride ions increased, $CuCl_2{}^-$ is dominant (Eqs. (2) and (3)). When $[Cl^-] > 0.7$ M, $CuCl_3{}^{-2}$ is the main complex (Eqs. (2) and (4)).

The dependence of surface morphologies of galvanically deposited Pt nanostructures on the concentration of H_2PtCl_6 is shown in Fig. 1. The surface morphology changed from Pt nanoparticles on the sacrificial Cu nanowires (Fig. 1a) → Pt coated Cu core-shell nanowires (Fig. 1b) → dense Pt nanotubes (Fig. 1c) → porous Pt nanotubes (Fig. 1d) as $[H_2PtCl_6]$ increased from 0.01 to 100 mM. Below the concentration of 2.5 mM H_2PtCl_6, Pt nanoparticles or uniform Pt coatings were formed on the surface of Cu nanowires. However, it was clearly observed from TEM analysis that Pt nanotubes started to form above the concentration of 2.5 mM H_2PtCl_6, which will be described later in further detail.

As shown in Fig. 2a, OCP monotonically increased with reaction time followed by plateauing at steady state values. The initial OCPs were approx. 0.05 V vs. Ag/AgCl independent of $[H_2PtCl_6]$. However, the OCPs after galvanic displacement slightly increased from 0.61 to 0.67 V vs. Ag/AgCl with increase in $[H_2PtCl_6]$. The reaction time (i.e. time which requires to reach a steady state OCP) decreased from about 3.5 h to about 40 min with increasing $[H_2PtCl_6]$ from 2.5 to 100 mM. This result may indicate the strong dependence of surface morphology of Pt nanostructures on reaction time of galvanic displacement. That is, there is not enough time to form a uniform Pt particle coating on Cu nanowires or Pt nanotubes (Fig. 1a–c) due to a slow dissolution rate of Cu nanowires and slow deposition rate of Pt at lower concentration of H_2PtCl_6. However, reaction time at high