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Morphology control of noble metal catalysts from planar to dendritic shapes by galvanic displacement

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ABSTRACT

Noble metal electrocatalysts can simply be prepared via galvanic displacement method on a sacrificial substrate, which is advantageous for preparing a uniform and thin catalyst layer. However, it is difficult to control the morphology of deposited metals via galvanic displacement, therefore, there is a limitation to increase the surface area of electrocatalysts. In this study, we demonstrate galvanic displacement for controlling the morphology of Pd, Pt, and Au from planar to whisker shapes by manipulating the dissolution rate of the sacrificial Cu substrate and the mass transport of noble metal ions. The acceleration of the dissolution of sacrificial substrate increases the reduction rate of noble metal, which develops a steep concentration gradient of noble metal ions near the surface of substrate. This induces the selective deposition of noble metal to form a whisker instead of smooth film. To verify the advantage of whisker-type catalysts, the ethanol oxidation with Pd is investigated. Whisker-type Pd shows 21 times higher electrocatalytic performance than planar Pd due to larger surface area. Therefore, it can be suggested that whisker-type catalysts simply prepared by galvanic displacement is applicable for various electrocatalytic reactions.

1. Introduction

The rational design of noble metal catalysts such as Pd, Pt, and Au is of considerable interest because of their superior properties in a number of applications including catalysts, electronics, sensing, photonics, imaging, and biomedicine [1]. Although noble metals are promising catalysts, their high cost represents an obstacle to commercialization [2]. Therefore, extensive studies have focused on improvement of their catalytic activity with a small loading amount by modifying their morphology or controlling their electronic structure. Coating of a substrate with a catalyst of high surface area-to-volume ratio – such as nanoparticles [3], nanowires [4], hollow or porous structures [5,6] – results in enhanced activity due to the dramatically increased surface area. Changes in the d-band center, determined by the alloy composition or the underlying substrate coated by the catalyst, also increase the catalytic performance [7,8].

Catalysts with a large surface area exhibit high catalytic activity due to their high concentration of the active sites for the electrochemical reactions [9]. As mentioned above, the substrate-mediated preparation is one of the most common techniques of fabricating the extended-surface catalysts. A 3D-structured substrate consisting of comparably inexpensive material can be prepared using the anodization method [10], polyol method [11], or hard or soft substrate method [12,13] prior to coating of the catalyst film on the substrate. Noble metal catalysts are then coated on the prepared substrates by galvanic displacement [14–16], electroless deposition [17,18], and electrodeposition [19,20]. However, electroless deposition has several disadvantages, as it is a complex system involving use of various organics in the solution, which makes examination of the deposition characteristics problematic [21]. Furthermore, electrodeposition requires electrical energy for the process and limits the substrates to only conductive materials with low electrical resistance [22]. In contrast, catalyst deposition using galvanic displacement is a facile and economically sustainable method of spontaneous deposition that requires no additional energy supply; deposition occurs simply by immersing a substrate in the solution containing the ionic precursors of metal to be deposited [23,24]. Galvanic displacement is mediated by the difference in standard reduction potentials; the metal substrate is spontaneously oxidized upon coming into contact with an ionized metal source with a more positive reduction potential. The electrons generated from the oxidation reaction, i.e. dissolution of the

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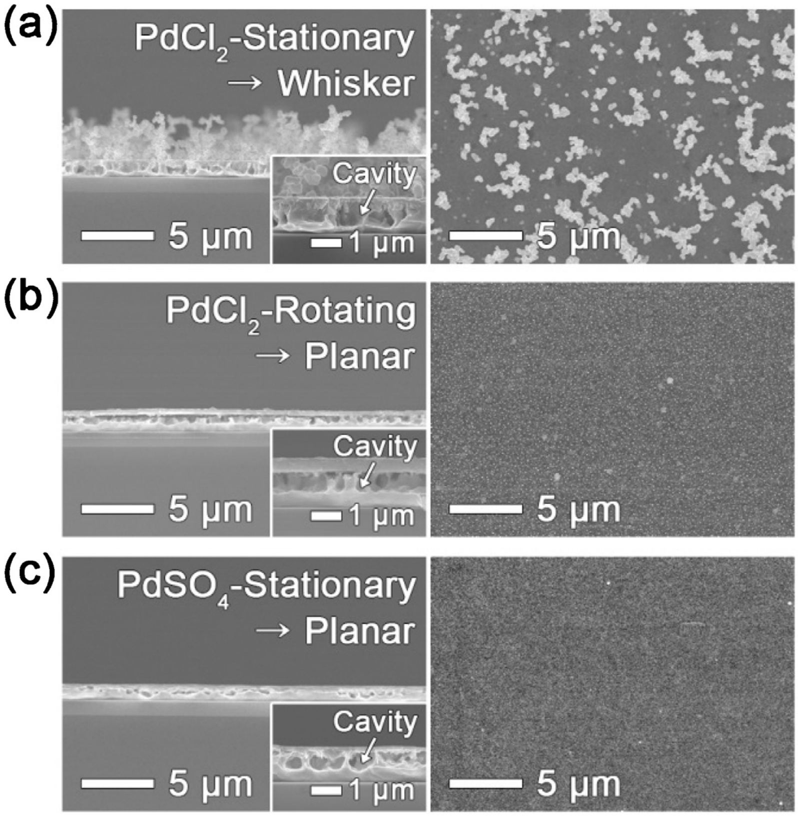

Fig. 1. Surface and cross-sectional images of Pd deposits prepared by galvanic displacement reaction (a, b) in the $PdCl_2$ solution and (c) in the $PdSO_4$ solution. The substrate remained (a, c) stationary for 30 min or (b) rotating at 300 rpm for 2 min during the reaction.

substrate, go towards the reduction reaction, i.e. metal deposition on the substrate.

The metal deposition via galvanic displacement reaction consists of nucleation and growth steps. Nucleated metal particles on the surface at the initial stage of the reaction grow until fully covering the substrate, which generally results in two-dimensional films [25–28]. Therefore, it is hard to control the morphology or increase the surface area via simple galvanic displacement method alone. If one-pot synthesis of catalysts with a large surface area using galvanic displacement from the planar sacrificial substrate can be developed, it can simplify the preparation procedures of electrocatalysts for various electrochemical reactions. Furthermore, the enlargement of surface area can dramatically enhance the electrocatalytic performance of metal deposits.

In this study, we introduced a one-step synthetic approach to synthesis of a whisker catalyst on a flat Cu substrate by galvanic displacement. Mechanistic analyses of Pd whisker formation are presented to elucidate the effects of the mass transport of metal cation and the oxidation rate of the sacrificial Cu substrate on the morphology of metal deposits. We proposed a universal mechanism of controlling the morphology of noble metal (Pd, Pt, and Au) catalysts; i.e., whisker or smooth film prepared via galvanic displacement. Furthermore, Pd-based whisker catalyst for ethanol oxidation was investigated to present the advantages of whisker-type electrocatalysts.

2. Experimental

2.1. Sample preparation

Pd-based catalyst was synthesized simply by dipping Cu substrate in an aqueous solutions containing 0.1 M $HClO_4$ (70%, Junsei) and 3 mM $PdCl_2$ (99%, KOJIMA) or 3 mM $PdSO_4$ (99%, Alfa Aesar). A Cu coupon wafer, whose structure was Cu (PVD, 1 μm)/TaN (PVD, 30 nm)/Ta (PVD, 30 nm)/TaN (PVD, 30 nm)/SiO_2/Si, was used as the sacrificial substrate. Before the galvanic displacement reaction, the Cu substrate was immersed in an aqueous solution of 20.4 mM citric acid (99.5%, Sigma Aldrich) and 35.6 mM KOH (95%, SAMCHUN) for 2 min to eliminate the native Cu oxide. The pretreated wafer was rinsed in deionized water, followed by immersion in the displacement bath. Galvanic displacement was conducted with stationary or 300 rpm-rotating substrate at 25 °C. K_2PtCl_4 (99.99%, Sigma Aldrich) or $AuCl_3$ (99.999%, Sigma Aldrich) (each 3 mM) was also used as a precursor for the Pt and Au displacement, respectively.

2.2. Electrochemical analyses

All electrochemical experiment was conducted in a three-electrode system containing Pt wire as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The effect of counter anions in Pd precursors, Cl^- and SO_4^{2-}, on the kinetics of the oxidation reaction (i.e. dissolution of Cu substrate) was examined by comparing exchange current densities obtained from Tafel plot with a Cu rotating disk electrode (RDE, $A = 0.196\ cm^2$) as a working electrode in (i) 6 mM KCl, 0.1 M $HClO_4$ and (ii) 3 mM K_2SO_4, 0.1 M $HClO_4$ aqueous solutions. Furthermore, cyclic voltammetry was carried out to estimate the diffusion coefficient of the Pd complex with a glassy carbon electrode ($A = 0.196\ cm^2$). The scan rate for cyclic voltammetry was between 10 and 100 $mV\ s^{-1}$. In addition, the electrochemically active surface area of Pd disk ($A = 0.196\ cm^2$) and whisker electrodes was analyzed by cyclic voltammetry in 0.5 M KOH aqueous solution. Pd disk electrode was polished carefully with 0.3 and 0.05 μm alumina powders, and it was rinsed by deionized water with ultrasoni-