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Tailoring nanopores within nanoparticles of PtCo networks as catalysts for methanol oxidation reaction

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A B S T R A C T

It has been recently reported that engineering the pores within alloy nanoparticles leads to improvement in the electrochemical activity of nanoparticle catalysts due to the enhanced electrochemical active surface areas. However, to date, few works have reported the tailoring intraporosity within alloy nanoparticle networks. In this study, a different and innovative approach was adopted to yield a network-like PtCo catalyst composed of intraporous nanoparticles used a cotton-like PtCo precursor material. It was found that the network-like structure and intrapores within the nanoparticles could co-evolve after careful controlled electrochemical dealloying, whereby Pt-rich surface was formed during the leaching out of Co in the first 13th potentiostatic cyclic voltammetry cycles from +0.056 to +1.256 V *vs.* RHE. Electrochemical data also showed that the mass and area activity of the obtained PtCo networks toward methanol oxidation reaction (MOR) was nearly 3.9, 2.0 and 2.1 times higher than that of commercial Pt/C, PtRu/C catalyst respectively, and much higher than that of Pt_3Co networks made of only solid nanoparticles. Moreover, it was observed that such networks exhibited high CO oxidation ability whilst maintaining high catalytic durability under an applied potential of +0.756 V *vs.* RHE. It was found that developing network-like catalysts composed of porous nanoparticles can be an efficient strategy to improve the catalytic activity and durability of fuel cell catalysts.

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1. Introduction

Platinum Group Metals (PGM)- and Pt-based nanomaterials are the most widely used anode and cathode electrocatalysts in low temperature fuel cells (e.g. PEMFC, DMFC etc), which are currently seen as promising energy storage devices to directly and efficiently convert the chemical energy to electrical energy. However, the prohibitive cost of platinum, accounting for over 55% of the total cost of low temperature fuel cell systems, the poor durability and the scarcity in supply largely hindered their large-scale practical applications and market deployment [1]. Therefore, intense R&D efforts have been devoted to improve the inherent activity of Pt-based catalysts as well as reducing the Pt loading without compromising on the overall fuel cell performance [2]. Among these efforts, one efficient route is to create a porous structure of the electrocatalyst yielding large electrochemical surface area, high surface-to-volume ratio, and high gas permeability, in turns resulting in enhanced catalytic performance [3–6]. From the literature, it was found that network-like structures made of solid nanoparticles, such as PtNi, PtCo, PdP, have attracted great attention due to promising and enhanced catalytic performance [7–10]. Moreover, to further improve the catalytic performance, some successful strategies have been developed, for example, by adding non-metallic element such as P, tuning the atomic composition, and optimizing the particle size of the network-like catalysts [11–13].

Recently, nanoporosity in Pt-based alloy nanoparticles, formed via dealloying the alloy nanoparticle precursor, has often been

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reported and found to be an effective method to enhance the electrocatalytic activity [14–19]. This implies that the catalytic activity of the network-like electrocatalysts can be improved by forming porosity within the nanoparticles. On the other hand, porosity within nanoparticles does not evolve for all of PGM- and Pt-based nanoparticles because the initial content of the transition metals need to be high enough and the particle size of the Pt-based alloy nanoparticle precursor must be large enough for pore formation. For example, Snyder et al. and Oezaslan et al. reported that the particle size of $PtNi_3$ and $PtCo_3$ alloy nanoparticles had to reach a critical value of ca. 15 nm and ca. 30 nm respectively in order to yield full porosity within the nanoparticles [18,20]. In the reported network-like electrocatalysts made of alloy nanoparticles [8–11,13,21], particle diameters have been found to be below 10 nm, which are insufficient for forming stable porous structures. Therefore, to engineer porosity with the particles of the network structure at a nanoparticle scale, a suitable precursor must be carefully chosen.

In this study, we report a three-dimensional PtCo network-like structure assembled by the porous PtCo nanoparticles formed by electrochemical dealloying. Herein, the obtained PtCo nanoparticles is a porous network-like structure, which is different from the dense particles of the reported network-like structures [3–13]. In this work, the precursor PtCo particles is a cotton-like alloy, which is different from the dense solid alloy particles used in the previous reports [14–19]. Therefore, the restriction on the sizes of the alloy nanoparticle precursor is broken. This method could be extended to form other alloy with network-like structures assembled by porous nanoparticles. Methanol oxidation reaction (MOR) experiments were conducted on the as-prepared PtCo networks made of porous nanoparticles; it was found that the new material exhibited high catalytic activity than that of the commercial Pt/C, PtRu/C catalysts and the reference Pt_3Co networks composed of the solid nanoparticles.

2. Experimental

2.1. Synthesis

All reagents were of analytic grade, and ultrapure water was used throughout the experiments. Part one: To prepare the flocculent PtCo samples, a solution was prepared as follows: 4 mg $CoCl_2 \cdot 6H_2O$, 0.044 mL H_2PtCl_6 (20 mg mL^{-1}) were dissolved in 60 mL water bubbled continuously with N_2. 10 mL 0.01 mol L^{-1} $NaBH_4$ solution in a constant funnel was added dropwise into the above solution under stirring and N_2 bubbling conditions. Nitrogen acts as a protective gas throughout the reaction, reducing the formation of cobalt oxides. After chemical reaction for 20 min, the resultant precipitate was collected by filtration, then washed with deionized water several times and kept in an ethanol solution. Part two: the electrochemical etching method was used to prepare the

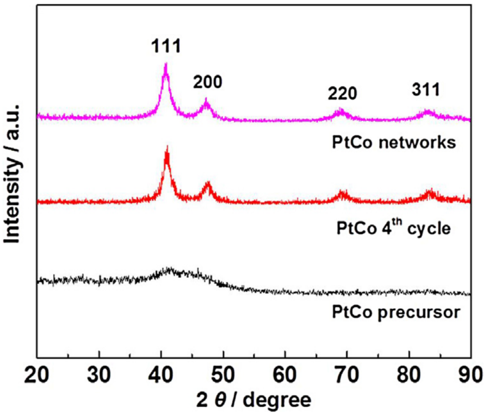

Fig. 1. XRD patterns of the PtCo precursor, PtCo 4th cycle, PtCo networks.

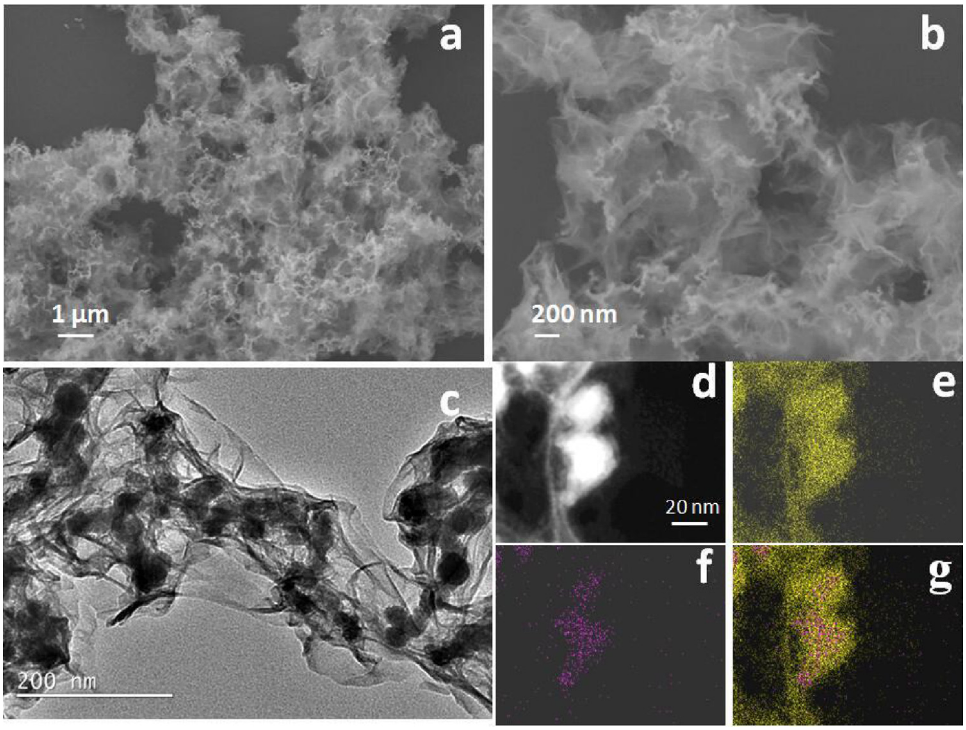

Fig. 2. (a,b) SEM images with various magnifications; (c,d) TEM and STEM images; the EELS-element maps of Co(e) and Pt(f); and (g) the overlapped element map of flocculent PtCo precursor.

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