Applied Catalysis B: Environmental 225 (2018) 84–90

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

# Hollow $PdCu_2$@Pt core@shell nanoparticles with ordered intermetallic cores as efficient and durable oxygen reduction reaction electrocatalysts

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## ARTICLE INFO

*Keywords:*
Polymer electrolyte membrane fuel cell
Oxygen reduction reaction
Hollow nanoparticles
$PdCu_2$@Pt core@shell
Ordered intermetallic core

## ABSTRACT

Carbon-supported hollow $PdCu_2$@Pt core@shell nanoparticles with ordered intermetallic cores were prepared as an efficient and durable oxygen reduction reaction (ORR) electrocatalyst for polymer electrolyte membrane fuel cells (PEMFCs). $PdCu_2$ cores prepared using a chemical reduction method were thermally treated to produce ordered intermetallic structures. A Pt shell was then deposited via a galvanic displacement process. The effect of the galvanic displacement conditions on the properties and structure of the obtained core–shell nanoparticles was investigated by varying the solution pH and anion concentration. Acidic conditions and low $Cl^-$ concentrations were found to provide a uniform Pt layer with a hollow core, while maintaining the ordered intermetallic core structure. These hollow $PdCu_2$@Pt core@shell nanoparticles showed high activity and stability for ORR electrocatalysis in PEMFCs.

## 1. Introduction

Efficient electrocatalysis of the oxygen reduction reaction (ORR) is crucial as sluggish reactions result in heavy consumption of Pt-based electrocatalysts, which is considered a major obstacle for widespread utilization of polymer electrolyte membrane fuel cells (PEMFCs). As ORR electrocatalysis occurs on Pt surfaces, strategies to enhance ORR activity while reducing Pt consumption are straightforward: increase the turnover frequency of surface Pt atoms and maximize the fraction of surface Pt atoms. To enhance the turnover frequency of surface Pt atoms, alloying with transition metals, such as Ni, Co, Y, and Sc, has been investigated [1–4]. The enhanced turnover frequency of Pt alloys with transition metals (by 3–7 times) is often explained by the weaker bond strength of the reaction intermediate ($OH_{ad}$) [3]. Further, it has been suggested that the fraction of surface Pt atoms could be maximized by depositing a few layers of Pt atoms on foreign nanoparticles to achieve "core@shell" structures [5–7]. In particular, carefully selected cores were reported to enhance the turnover frequency as well as the surface fraction of Pt atoms [5,7]. Pd and Pd alloy cores enhance the turnover frequency of surface Pt atoms by 2.5–5 times, probably because of lattice contraction in the Pt layers [8–15]. As contraction of the Pt crystal lattice lowers the d-band center of Pt atoms, the bond strength of $OH_{ad}$ decreases and, thereby, the ORR activity increases [8].

Several approaches have been introduced to form surface Pt layers, including galvanic displacement of Cu with Pt [8–14], chemical reduction of Pt, and spontaneous deposition of Pt. Galvanic displacement of Cu with Pt has been widely utilized to produce Pt layers because this process allows easy manipulation of surface structure and composition [11,13,16]. As the standard reduction potential of Cu (0.337 V) is more negative than that of Pt (0.735 V), $PtCl_6^{2-}$ is expected to replace Cu atoms. Furthermore, if Cu atoms are present in the nanoparticles as well as on the surface of the nanoparticles, continuous replacement of Cu with Pt has been reported to generate porous cores and Pt-rich surfaces [11,16].

Among the various possible architectures, we are interested in Pt-decorated Pd–Cu alloys ($Pd_xCu_y$@Pt), as Pt lattice contraction by $Pd_xCu_y$ cores should enhance the turnover frequency of Pt atoms and surface Pt layers should be easily formed by galvanic replacement of Cu in the core particles with Pt [9–11,13,16]. If the core nanoparticles do not contain Cu atoms, an additional process to make sacrificial Cu layers, e.g., electrodeposition, is required for the galvanic displacement process [8,12,14]. Despite numerous studies on $Pd_xCu_y$@Pd core@shell nanoparticles for ORR electrocatalysis [9–11,13,16], there has been little investigation of the effect of chemical environment on the

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https://doi.org/10.1016/j.apcatb.2017.11.052
Received 16 May 2017; Received in revised form 4 September 2017; Accepted 20 November 2017

structure and electrochemical properties of the obtained $Pd_xCu_y$@Pt nanoparticles. In particular, to the best of our knowledge, although ordered intermetallic structures are beneficial for high durability [17–19], the ORR activity and stability of $Pd_xCu_y$@Pt nanoparticles with ordered intermetallic $Pd_xCu_y$ cores has not been reported.

In this study, we developed highly efficient and durable hollow $PdCu_2$@Pt core@shell electrocatalysts with ordered intermetallic cores. As $PdCu_2$ cores provide a unique ordered intermetallic structure, both high stability and high activity were expected. The effect of galvanic displacement conditions, such as pH and $Cl^-$ concentration, on the structure and electrochemical properties of $PdCu_2$@Pt nanoparticles were examined.

## 2. Experimental

### 2.1. Preparation of electrocatalysts

As the core material, carbon-supported $PdCu_2$ nanoparticles ($PdCu_2$) were prepared via the chemical reduction of $Pd(NO_3)_2$ (Kojima Chemicals) and $Cu(NO_3)_2$ (Shinyo Pure Chemicals) in a mixture of deionized water (18.3 MΩ cm) and carbon support (Vulcan XC72, Cabot), followed by heat treatment at 500 °C under a mixture of hydrogen and nitrogen gases (10/90, v/v) for 2 h. The weight composition of metal nanoparticles in the core material was 30%. A sodium borohydride (Sigma Aldrich) solution (0.21 mM) was utilized as the reducing agent. To obtain core@shell electrocatalysts, $PdCu_2$/C was dispersed in deionized water and 10 mL of Pt precursor ($H_2PtCl_6 \cdot xH_2O$, Kojima Chemicals) solution was introduced to the mixture under an inert ($N_2$) atmosphere. The atomic ratio of Pd and Pt was adjusted to 2. The mixture was stirred for 1 h and then filtered and washed with deionized water to isolate the black precipitate. The precipitate was then dried in a convection oven at 100 °C for approximately 12 h ($PdCu_2$@Pt-H). To investigate the effect of the galvanic displacement conditions on the structure and electrochemical properties of the obtained $PdCu_2$@Pt electrocatalysts, $PdCu_2$-Pt-K and $PdCu_2$-Pt-K-HCl samples were prepared using the same procedure as for $PdCu_2$@Pt-H by replacing the $H_2PtCl_6 \cdot xH_2O$ solution with a $K_2PtCl_6$ (Sigma Aldrich) solution and a $K_2PtCl_6$ in 0.05 M HCl (Sigma Aldrich) solution, respectively (Scheme. 1).

### 2.2. Physicochemical analysis

Transmission electron microscopy (TEM) images, scanning transmission electron microscopy (STEM) images, and energy dispersive spectroscopy (EDS) line profiles were obtained using a JEOL-2010 microscope (JEOL). The X-ray diffraction (XRD) patterns of the electrocatalysts were recorded using an X'pert Powder diffractometer (PANanalytical). The atomic compositions of the electrocatalysts were determined using an ICPS-7510 inductively coupled plasma (ICP) emission spectrometer (Shimadzu). X-ray photoelectron spectroscopy (XPS) analysis was carried out using a K-Alpha ESCA system (Thermo Scientific).

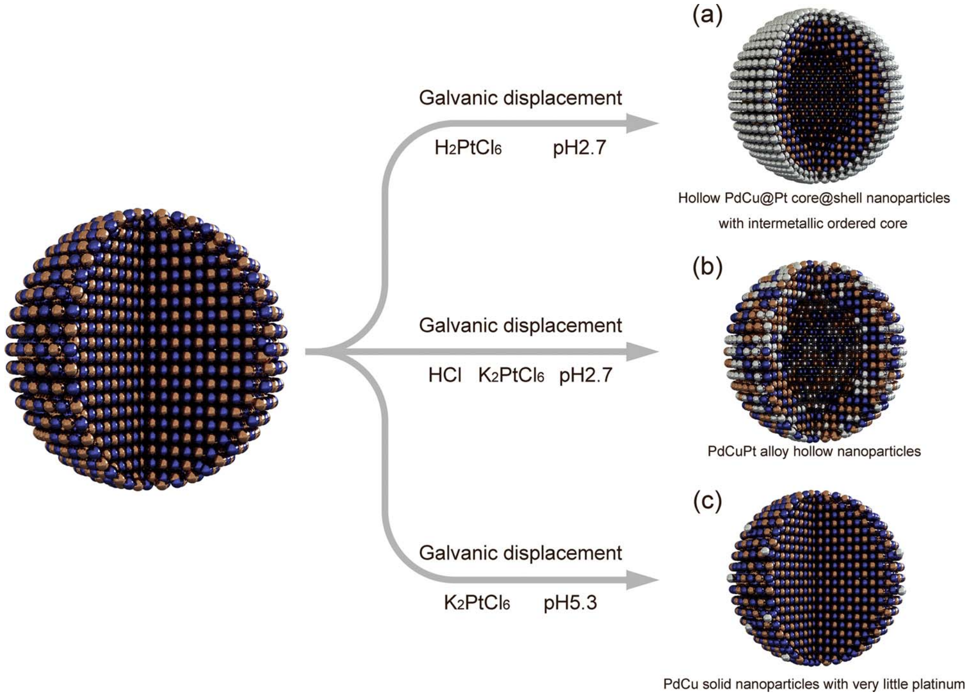
### 2.3. Electrochemical analysis

Electrochemical analysis of the electrocatalysts was conducted using a conventional three-electrode setup with a CHI700C electrochemical analyzer (CH Instruments). An electrocatalyst-coated rotating ring disk electrode (RRDE) with a glassy carbon disk (0.2475 $cm^2$) and Pt ring electrode (Pine Instruments) was utilized as the working electrode. To prepare the working electrode, a mixture of electrocatalyst, Nafion solution, and isopropanol was dropped onto the RRDE and then dried under an air atmosphere. A Ag/AgCl reference electrode (BASi) and a Pt wire served as the reference and counter electrodes, respectively. ORR polarization curves were recorded in $O_2$-saturated 0.1 M $HClO_4$ at a rotating speed of 1600 rpm. To evaluate the stability of the electrocatalysts, ORR polarization curves were obtained after potential cycling between 0.6 and 1.0 V for 10,000 cycles at a scan rate of 50 mV in Ar-saturated 0.1 M $HClO_4$. Cyclic voltammograms of the electrocatalysts were recorded in Ar-saturated 0.1 M $HClO_4$ at a scan rate of 20 mV $s^{-1}$.

## 3. Results and discussion

### 3.1. Effect of galvanic displacement conditions on the morphology and crystalline structure of the electrocatalysts

Fig. 1 shows TEM and STEM images and EDS line scan profiles of the $PdCu_2$ cores and the $PdCu_2$@Pt-H, $PdCu_2$-Pt-K, and $PdCu_2$-Pt-K-HCl electrocatalysts. The $PdCu_2$ cores are spherical nanoparticles with



**Scheme 1.** Schematic illustration of the structures of (a) $PdCu_2$@Pt-H, (b) $PdCu_2$-Pt-K-HCl, and (c) $PdCu_2$-Pt-K electrocatalysts.