



Short communication

Preparation and electrocatalytic activity of palladium–platinum core–shell nanoalloys protected by a perfluorinated sulfonic acid ionomer

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ARTICLE INFO

Article history:

Received 3 March 2011

Received in revised form 11 April 2011

Accepted 21 April 2011

Available online 30 April 2011

Keywords:

Oxygen reduction reaction

Fuel cells

Nanoparticles

Electrocatalysis

Nafion

Core–shell structure

ABSTRACT

Palladium–platinum nanoalloys with a core–shell and nano-network structure were successfully synthesized by a hydrogen sacrificial protective method in an aqueous solution directly using a perfluorinated sulfonic acid (PFSA) ionomer as a protecting agent. The structure, local composition and electrocatalytic activity for the oxygen reduction reaction of the Pd/Pt/PFSA nanoalloys were investigated by transmission electron microscopy (TEM), aberration corrected scanning transmission electron microscopy (Cs-STEM), energy-dispersive X-ray spectrometry (EDS) and voltammetry. The core–shell structure was completed without contaminating reducing agents, organic solvents, useless protecting agents and a mediator. The Pd/Pt/PFSA core–shell nanoalloys realized a high electrochemical surface area and better electrocatalytic mass-activity for the oxygen reduction reaction than the Pt/PFSA nanoparticles.

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1. Introduction

The fact that the size and shape as well as dispersibility of metal nanoparticles can be controlled in an aqueous phase by making use of a water soluble protecting agent, such as poly(N-vinyl-2-pyrrolidone) (PVP), surfactants, polyelectrolyte, and ionic liquid [1–6], due to their specific chemical and physical properties has attracted significant attention. Controlling the structure and composition of bi-/multi-metallic nanoalloys were also established by preparation methods, such as the simultaneous and successive reduction with protecting agents in the solution. The structure-controlled platinum-bimetallic nanoparticles showed a better catalytic activity than that of simple alloys in a homogeneous phase [7,8]. Protecting agents, however, sometimes deactivate the catalytic/electrocatalytic reactions or inhibit the diffusion of reactants and products on the nanoparticle surface due to their strong interaction with the surface [9]. Thus, to realize a high electrocatalytic activity, additional procedures are required to remove the protecting agents before applying the nanoparticles to the catalyst without re-aggregation of the nanoparticles. Recently, we achieved the direct use of a perfluorinated sulfonic acid ionomer (PFSA) as the protecting agent for synthesizing platinum nanoparticles in an aqueous solution. The PFSA-protected Pt nanoparticles formed

nano-wires and a nano-network. Its electrocatalytic activity for the oxygen reduction reaction (ORR) was better than that of conventional carbon supported platinum catalysts [10].

Recently, Adzic's group established a remarkable synthesis method for the galvanic displacement of underpotentially deposited (UPD) Cu adatoms on substrate metal surfaces using a platinum monolayer (ML) [11]. They reported that the platinum monolayer deposited on a palladium core catalyst showed an excellent electrocatalytic activity for the ORR and high durability for potential modulation during fuel cell operations [12,13]. Their procedure, however, requires precise potential control and contains contaminating mediators.

In this study, we successfully tried to synthesize palladium–platinum core–shell nanoalloys covered with PFSA (Pd/Pt/PFSA) in an aqueous solution by the hydrogen sacrificial protective method without electrochemical procedures and contaminating mediators, such as copper. The core–shell nanoalloys fully covered with PFSA and homogeneously dispersed in the aqueous solution should increase the utilization of Pt. In addition, we prepared the Pd/Pt/PFSA nanoalloys with a nano-network structure in order to improve the gas diffusion and electric conductivity in the catalyst layer. The structure, local composition and electrocatalytic activity for the ORR of the Pd/Pt/PFSA nanoalloys were investigated by transmission electron microscopy (TEM), aberration corrected scanning transmission electron microscopy (Cs-STEM), energy-dispersive X-ray spectrometry (EDS) and voltammetry.

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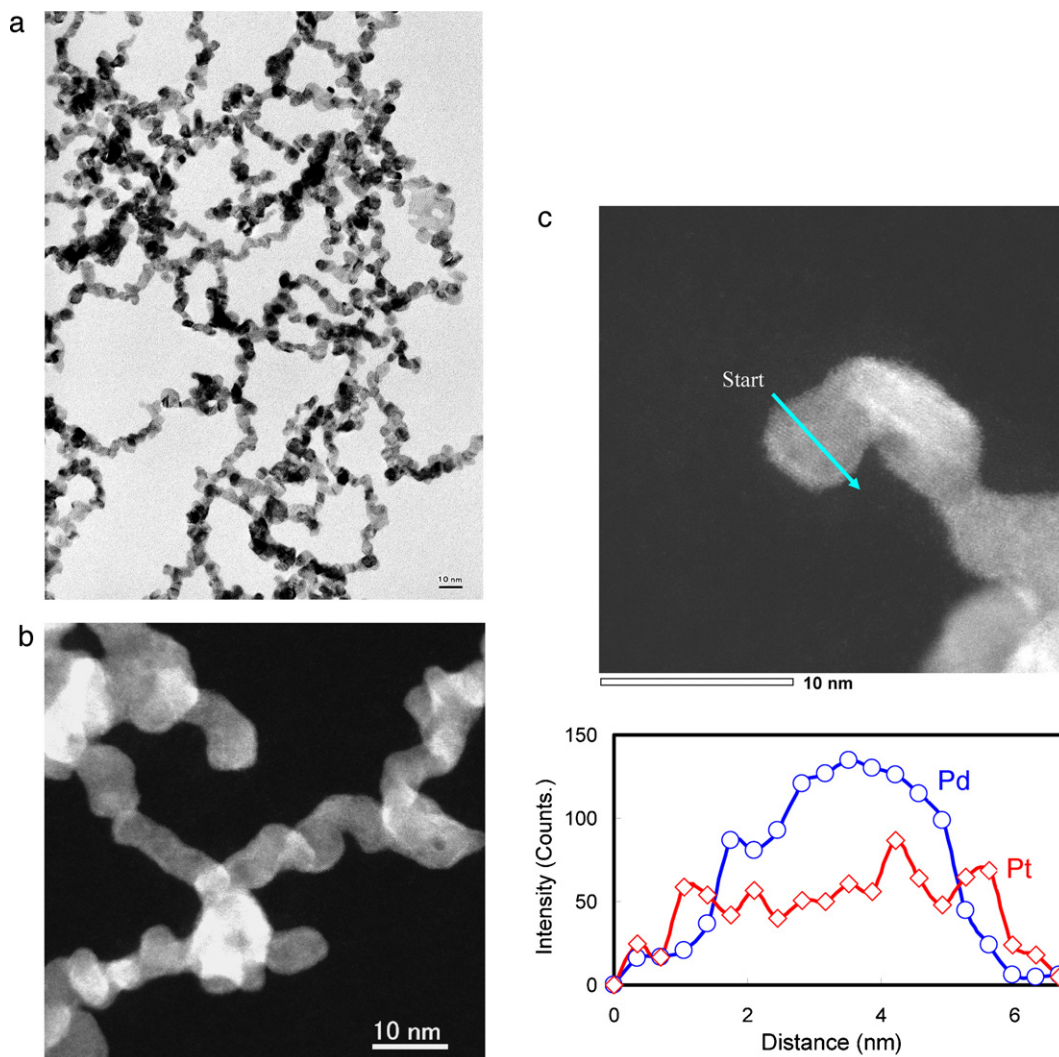


Fig. 1. (a) TEM and (b) HAADF images of the Pd/Pt/PFSA nanoalloys forming the nano-network. (c) EDS analysis of the Pd/Pt/PFSA nanoalloys along a line in the magnified image.

2. Experimental

The Pd/Pt/PFSA nanoalloys were synthesized from palladium(II) sulfate, hydrogen hexachloroplatinate(IV) hexahydrate (Wako Pure Chemical Industries) and a Nafion® DE1020CS PFSA dispersion (DuPont Fuel Cells) by successive reduction. A fixed volume of PFSA ($R=0.05$) was mixed with deoxidized Milli-Q water and palladium(II) sulfate in the dark. R denotes the molar ratio of the monomer unit of PFSA to palladium. After reduction of the palladium ions by flowing hydrogen for 2 h, the produced PFSA protected palladium (Pd/PFSA) nanoparticles were purified several times by ultrafiltration using an ultrafilter (Advantec, Q0100 076E) and Milli-Q water under argon at a pressure of $1.05\text{--}1.20\text{ kg cm}^{-2}$. Hydrogen was then absorbed into the palladium nanoparticles to act as a reductant [14] by bubbling into the Pd/PFSA dispersion, followed by purging the hydrogen in the solution by bubbling nitrogen to prevent individual production of the platinum nanoparticles in the solution. The deoxidized platinum solution was slowly dropped into the Pd/PFSA dispersion in the dark at 0°C and stirred for 12 h. The produced dispersion was purified again until no chloride ions were detected in the filtered solution. Finally, the dispersion was concentrated to a $0.02\text{--}0.05\text{ wt.}\%$ metal content for the electrochemical measurements.

The electrochemical measurements were carried out using a rotating disk electrode (RDE) in an argon or oxygen saturated 0.1 mol L^{-1} perchloric acid solution. A conventional three-electrode cell was equipped with a reversible hydrogen electrode (RHE) and platinum foil as the reference and counter electrodes, respectively. The sample electrode was prepared by direct dropping of $3.92\text{ }\mu\text{g}$ platinum in the Pd/Pt/PFSA nanoalloys onto a rotating electrode surface (0.196 cm^2) made of glassy carbon then dried under a nitrogen flow. The actual platinum content in the colloidal solution was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). TEM and Cs-STEM/EDS measurements were carried out using a JEM 2010F and JEM 2100F, respectively.

3. Results and discussion

3.1. Pd/PFSA nanoparticles

In order to form the Pd/Pt/PFSA nanoalloys, which have a core-shell structure, and achieve a high electrocatalytic activity, by the successive reduction, we first synthesized the mono-dispersed core palladium nanoparticles with average diameters of ca. 5 nm by bubbling gaseous hydrogen as a reductant into the aqueous solution. As the sulfate anion could adsorb on the palladium

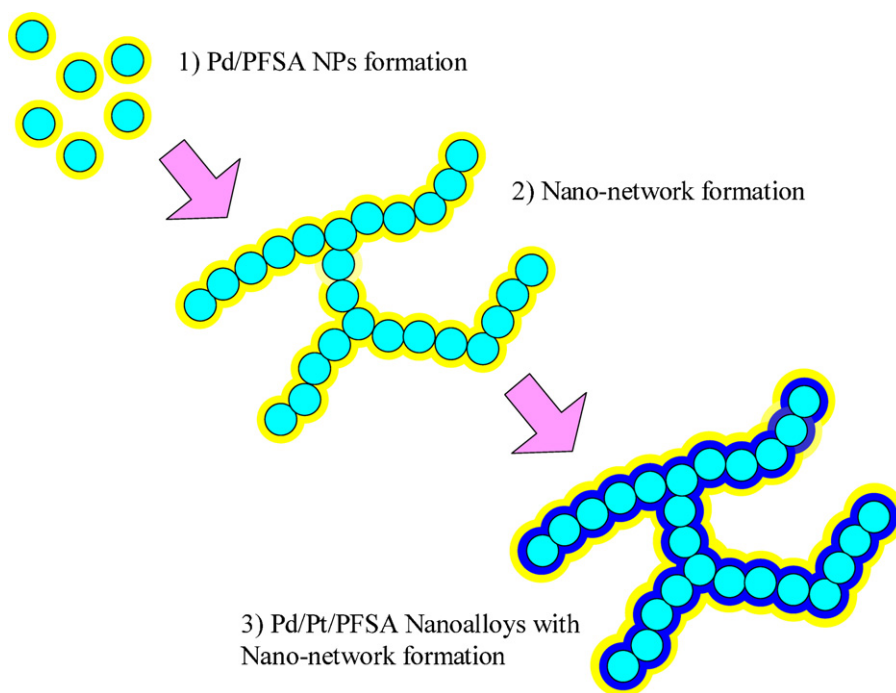


Fig. 2. A schematic view of the Pd/Pt/PFSA nanoalloy formation with the nano-network structure during the successive reduction procedure.

surface the same as on the platinum surface [15], the PFSA polymer should cover the palladium nanoparticles in the same manner as the platinum nanoparticles [10,16]. After purifying the Pd/PFSA core nanoparticles using an ultrafilter and Milli-Q water, nano-wire and nano-network formation was observed the same as the Pt/PFSA nanoparticles. Recently, Wang et al. reported that palladium nanoparticles stabilized by sodium citrate formed a similar nano-network structure [17].

3.2. Reduction of platinum in Pd/PFSA dispersion

The reduction of platinum ions by the hydrogen sacrificial protective method with the Pd/PFSA dispersion was confirmed by ultraviolet and visible spectroscopies (UV-vis) before and after the reduction. A large absorption peak and a small shoulder at 260 nm and 380 nm, assigned to the d-d transition and ligand-to-metal charge-transfer transition of $[\text{PtCl}_6]^{2-}$ [18] completely disappeared and a broad tailing absorption was observed after 12 h of stirring.

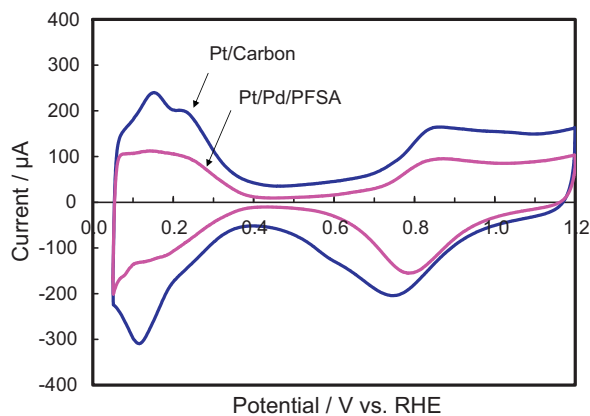


Fig. 3. Cyclic voltammograms of the Pd/Pt/PFSA nanoalloys and Pt/carbon catalyst observed in the argon saturated 0.1 mol L^{-1} perchloric acid solution. Sweep rate: 50 mV s^{-1} . Pt loading is $3.92 \mu\text{g}$ on GC disk.

This indicates that $[\text{PtCl}_6]^{2-}$ was completely reduced to platinum metal by the hydrogen sacrificial protective method in the presence of a Pd/PFSA dispersion. The dark dispersion of the nanoalloys is quite stable against aggregation for several months.

3.3. Characterization and nano-network formation

The structures of the Pd/Pt/PFSA nanoalloys were characterized by TEM and STEM. Fig. 1a shows a TEM image of the nanoalloys after platinum deposition. The nanoalloys, the particle size of which was almost uniform, formed nano-wires and a nano-network. The mean diameter of the nano-wires was $5.2 \pm 1.6 \text{ nm}$. The diameter of the particles became slightly larger than that of the Pd/PFSA cores due to platinum deposition on the surface.

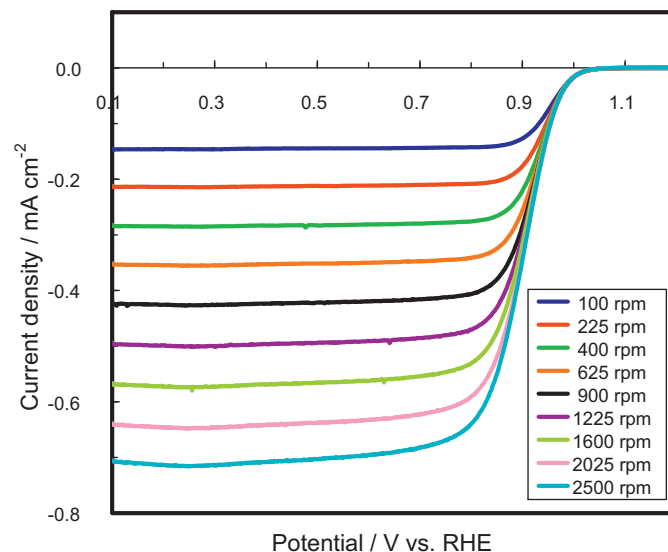


Fig. 4. Anodic linear sweep voltammograms of the Pd/Pt/PFSA nanoalloys measured in the oxygen saturated 0.1 mol L^{-1} perchloric acid solution. Sweep rate: 10 mV s^{-1} .

A high angle annular dark field (HAADF) measurement and a line analysis of the nanoalloys by EDS were carried out (Fig. 1b and c) to analyze the local composition of the nanoalloys forming the nano-network. The intensity of the HAADF image reflects the Z^2 (Z : atomic number) of the elements, so that a distribution of elements can be observed as an actual image with atomic resolution. In Fig. 1b and c, the bright areas are located on the rim of the nanoparticles in a manner similar to previous reports [12], indicating that platinum ($Z=78$) has deposited on the surface of the palladium ($Z=46$) nanoparticles. An EDS analysis along the line in Fig. 1c clearly illustrates the localization of the platinum on the surface of the nanoparticles. Platinum nanoparticles independently deposited of the palladium nanoparticles were not observed in the HAADF images and by EDS analysis over a wide area. STEM measurements clearly showed that nano-wires and the nano-network structure with a palladium–platinum core–shell structure were synthesized in the aqueous solution. Fig. 2 is a schematic view of the Pd/Pt/PFSA nanoalloys with the nano-network structure during the successive reduction procedure.

The metal compositions of the Pd/Pt/PFSA nanoparticles were confirmed by ICP-AES. The atomic ratio of platinum/(platinum+palladium) was 0.37. When considering the mean particle size in the TEM image, the distribution of the monolayer surface atoms in the nanoparticle with a 5.2 nm diameter is ca.0.15–0.2 [19], and the atomic ratio of platinum was in excess over the monolayer deposition. Since a 3-dimensional growth of platinum nanoparticles on the palladium core was not observed, platinum should be deposited on the palladium cores to form bilayers.

3.4. Electrocatalytic activity

Fig. 3 shows cyclic voltammograms (CVs) of the Pd/Pt/PFSA nanoalloys and a commercially available carbon supported 50 wt.% Pt electrocatalyst (Pt/C, mean particle size: ca. 2.5 nm) measured in an argon saturated 0.1 mol L⁻¹ perchloric acid solution. The electrochemical surface area (ECSA) of the Pd/Pt/PFSA nanoalloys calculated by the hydrogen desorption charge was 58.4 m²g-Pt⁻¹. This value is much higher than that of the Pt/PFSA nanoparticles (32.1 m²g-Pt⁻¹; Ref. [10]) and close to that of the Pt/C (68.3 m²g-Pt⁻¹). The higher ECSA of the Pd/Pt/PFSA nanoalloys with 5.2 nm diameter indicates that geometric effects of the core–shell structure, i.e., platinum, was more efficiently used at the surface than the Pt/PFSA nanoparticles. Voltammograms in the hydrogen adsorption/desorption region of the platinum–palladium alloy nanoparticles in a sulfuric acid solution were reported to change based on its ratio of palladium to platinum [20]. The voltammogram of the Pd/Pt/PFSA nanoalloys was different from those of the palladium–platinum alloys and the Pt/PFSA nanoparticles, similar to that of the platinum monolayer on palladium nanoparticles [10,21]. It supports the results of the EDS and HAADF measurements that a platinum shell was formed on the surface of a palladium nanoparticles. The oxidation and reduction peaks in the positive potential region of the Pd/Pt/PFSA nanoalloys were shifted in a positive direction by 12 and 40 mV, respectively, compared to those of the Pt/C catalyst. These features suggest that the stability and the electrocatalytic activity for the ORR of the Pd/Pt/PFSA nanoalloys should be improved when compared to the Pt/C catalyst [11–13].

Fig. 4 shows the anodic linear sweep voltammograms of the Pd/Pt/PFSA nanoalloys in the oxygen-saturated 0.1 mol L⁻¹ perchloric acid solution at various rotation speeds. Each oxygen reduction current is minus the blank current observed in the argon

saturated solution. The half-wave potential at 900 rpm is 921 mV, which is superior by 15 mV to that of the Pt/PFSA nanoparticles [10]. The kinetic current (I_k) of the Pd/Pt/PFSA analyzed by the Koutecky–Levich plot was 1.33 mA at 0.9 V. The mass activity (MA: 0.34 A mg-Pt⁻¹) and specific surface activity (SSA: 0.58 mA cm⁻²) at 0.9 V of the Pd/Pt/PFSA were 1.7 and 0.94 times those of the Pt/PFSA nanoparticles, and 2.0 and 2.3 times those of Pt/C, respectively. The mass activity of Pt/C increases in proportion to the Pt surface area [22,23]. These results show that the higher ECSA and MA of the Pd/Pt/PFSA nanoalloys compared to the Pt/PFSA nanoparticles were due to the geometric effects of the core–shell structure, and the small SSA of the Pt/C should be due to its small particle size. Such oxygen species on the surface that inhibit the ORR could be more easily produced on the small particles than on the large particles [19].

More detail information about the uniformity and the electronic structure of the platinum shell, and the fuel cell test of the Pd/Pt/PFSA nanoalloys is under investigation by X-ray measurements and MEA configuration.

4. Conclusions

Palladium–platinum core–shell nanoalloys with a nano-wire and nano-network structure were successfully synthesized by the hydrogen sacrificial protective method in an aqueous solution directly using the PFSA ionomer as a protecting agent. The core–shell structure was completed without contaminating reducing agents, organic solvents, useless protecting agents and a mediator. The Pd/Pt/PFSA nanoalloys realized a high electrochemical surface area and better electrocatalytic mass-activity for the oxygen reduction reaction than the Pt/PFSA nanoparticles and the Pt/carbon catalyst. This synthesis method is very important and valuable to scale up and form the actual catalyst layer without additional dispersing procedures.

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