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# Pt-Pd nanodendrites as oxygen reduction catalyst in polymer-electrolyte-membrane fuel cell

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## ABSTRACT

Platinum-palladium (Pt-Pd) bimetallic alloys have shown prospect as electrocatalyst for the oxygen reduction reaction (ORR) in the cathode of polymer-electrolyte-membrane (PEM) fuel cells. This article reports a facile solvothermal synthesis of Pt-Pd bimetallic nanodendrites (Pt-Pd NDs). The characterization with a variety of spectroscopic techniques indicates that the Pt-Pd NDs possess a three-dimensional (3-D) porous structure consisting of interconnected branches of highly alloyed Pt-Pd nanorods (NR). The measurements using rotating disk electrode in electrolyte solution show that the catalyst of Pt-Pd NDs supported on carbon (Pt-Pd NDs/C) possesses a Pt mass activity for ORR that is more than 3 times higher than that of the state-of-the-art Pt/C catalyst, as well as the significantly improved stability due to the branched porous structure. The measurements using membrane-electrode-assembly (MEA) in a single PEM fuel cell indicate the 3-D interconnected dendrite structures make the Pt-Pd NDs/C catalyst significantly advantageous over the nanoparticle Pt/C catalyst in reducing the mass transport and ohmic polarization which would become significant at high current density in MEA.

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## Introduction

Polymer electrolyte membrane (PEM) fuel cells have attracted significant attention because of the high energy conversion efficiency and low carbon emission [1]. Highly active and durable electrocatalyst for the oxygen reduction reaction (ORR) is among the key challenges in the commercialization of the PEM fuel cells. As well as the high cost and limited supply, the activity and stability of the current Pt catalysts remain some distance away from that required for the large scale application of PEM fuel cells. An effective approach to improve the activity of cathode electrocatalysts is to partially substitute Pt with a secondary metal.

The bimetallic nanostructures not only inherit the properties of Pt, but also usually show a superior performance when compared with monometallic Pt, owing to the strain and ligand effects of the secondary elements that downshift of the d-band center of Pt and weaken the Pt-O interaction accordingly [2–4]. Recent reports have shown that Pt-Pd bimetallic alloys exhibit exciting activity for ORR [5–7]. Since Pt and Pd share the same face-centered cubic (fcc) structure, together with good miscibility and a minor lattice mismatch of 0.77% [7], it is feasible to optimize the performance of Pt-Pd nanostructures by simply adjusting the molar ratio of Pt to Pd [8,9].

Not only the composition, but also the shape and structure of bimetallic Pt nanocatalysts are generally considered critical

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in determining the catalytic properties. To date, Pt-based nanostructures with the unique 3-D dendritic structures have gained sustained research interest due to their higher catalytic performance than 0-D Pt nanoparticles, which typically stems from the porous structure, a large specific surface area, many active catalytic spots, excellent electrical connectivity and high index exposed facets, better ability of resistance to aggregation and so on [10–17]. For example, in Xia's work, Pt-Pd bimetallic nanodendrites synthesized through a seed-mediated method showed excellent electrocatalytic activity compared to carbon supported Pt and Pt-black catalysts for O<sub>2</sub> reduction reaction (ORR) [18]. In addition, Y. Huang et al. used the wet-chemical method for the preparation of highly porous Pt<sub>3</sub>Ni nanocrystals, which shows the outstanding catalytic activity due to their attractive structural features such as porosity, high surface area, interconnected nanostructure and excellent electrical connectivity [19]. However, these investigations all focus only on the pure material research, and the real applications of Pt-Pd bimetallic catalysts in practical PEM fuel cells still remains as a challenge. Currently, PEM fuel cells continue to face severe performance and durability challenges associated with their components and materials [20].

It is well known that the formation of a continuous and interconnected transport pathway for fast transport of protons, electrons and oxygen in cathode catalyst layers is critical for excellent fuel cell performance [21]. For effective triple phase boundary (TPB) formation in catalyst layers, different catalyst layer architectures, such as carbon nanotubes (CNT) [22] and 3D-ordered porous materials [23], have been successfully applied. The design of these catalyst layer is mainly focused on building ordered structures containing pores that allow easy access of oxygen to the Pt nanoparticles, thus promoting the enhancement of fuel cell performance, particularly under high-current conditions. In this respect, conventional Pt/C catalysts are unsuitable for making perfect catalyst layer structures because of the aggregation of Pt nanoparticles, leading to poor single-cell stability and performance [24]. In order to overcome the limitations of mass transport, extensive effort has recently been devoted to increasing their intrinsic catalytic activity by introducing alloy materials and modifying the morphology of the catalysts, such as 3-D nanostructures, which facilitate the efficient transfer of the catalyst activity to a real fuel cell. From the above, developing a simple method to construct highly branched 3D Pt-M nanostructures is of high significance for the application of PEM fuel cells.

Herein, we developed a facile seedless solvothermal method for the preparation of highly porous Pt-Pd nanodendrites (NDs) with uniform shape and controllable size. As well as taking advantage of the enhanced activity and stability of the Pt-Pd alloy catalyst, the present study aims at enhancing the ORR performance of Pt-Pd alloy in PEM fuel cells by facilitating the mass and electron transport through the 3-D interconnected dendrite structures. The work demonstrates that the interconnected 3D Pt-Pd nanocrystals are indeed promising electrocatalysts with enhanced catalytic activity, improved durability and fuel cell performance for practical applications.

## Experimental section

### Chemicals and commercial materials

Pt(acac)<sub>2</sub> (acac = acetylacetonate), Pd(acac)<sub>2</sub>, oleylamine (OAm, >70%), 1-octadecene (ODE), hexane, ethanol, acetic acid (99%), Cetyltrimethylammonium hydrogensulfate (CTAS) and Nafion solution (5%, Dupont D520) were all purchased from Sigma Aldrich. Carbon-supported Pt nanoparticles (Pt/C, 20 wt % Pt), which served as the reference catalyst, was obtained from Johnson-Mathew (JM).

### Synthesis of Pt-Pd nanodendrites

In a typical synthesis of highly-branched Pt-Pd nanodendrites (Pt-Pd NDs), 22.5 mg Pt(acac)<sub>2</sub>, 5.82 mg Pd(acac)<sub>2</sub> and 10 mg CTAS were added into the solution of 10 mL ODE and 1 mL OAm in a small baker, which the CTAS was used as surfactant and size controlling agents. The solution was kept at 60 °C under magnetic stirring for 20 min to let Pt(acac)<sub>2</sub> and Pd(acac)<sub>2</sub> dissolve, then the resultant homogeneous and transparent solution was transferred into a 50 mL Teflon-lined autoclave. The autoclave was maintained at 170 °C for 6 h. After cooling down to room temperature, the black products were collected by addition of ethanol (30 mL) and centrifugation at 11000 rpm for 10 min, and then washed for at least three times with ethanol. The final black precipitate was re-dispersed into 25 mL hexane for further use.

### Preparation of carbon-supported Pt-Pd NDs

First, ~14.7 mg XC-72 carbon black was added into the hexane solution containing the synthesized Pt-Pd nanocrystallites under ultrasonic stirring. The resulted suspension was then magnetically stirred for overnight to allow deposition of the nanocrystallites on carbon. The product was separated from solvent by centrifugation and was then dispersed in 30 mL acetic acid and kept at 70 °C for 10 h to remove the organic residuals on the nanocrystallites. The resultant solid product was separated from the acetic acid by centrifugation and washed with ethanol and deionized water for several times. The total metal (Pt + Pd) loadings were ~20 wt % as determined by the ICP-AES. Supporting the Pt-Pd NDs on high-surface-area carbon was to prevent their aggregation in the structural and electrocatalytic characterizations. In this study, only the TEM observation was conducted using unsupported Pt-Pd NDs.

### Materials characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer using Cu K $\alpha$  radiation source operating at 40 kV and 30 mA. The XRD profiles were recorded at scanning rate of 4° per min. The morphologies and crystal structures of the Pt-Pd nanocrystallites were obtained using transmission electron microscopy (TEM), high-resolution TEM (HRTEM) at JEM-2100 microscope operated at an accelerating voltage of 200 kV. X-ray photoelectron

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