



The chemical functionalized platinum nanodendrites: The effect of chemical molecular weight on electrocatalytic property



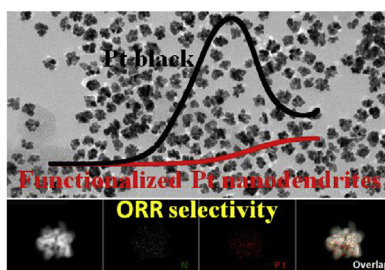
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HIGHLIGHTS

- Polyallylamine functionalized Pt nanodendrites (Pt-NDs@PAA) were synthesized.
- The molecular weight of PAA affected the electrochemical property of Pt-NDs.
- Pt-NDs@PAA showed the improved activity for oxygen reduction reaction.
- PAA functionalization imparted Pt-NDs with selectivity for oxygen reduction reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface chemical functionalization of noble metal nanocrystals is a promising strategy for improving the catalytic/electrocatalytic activity and selectivity of noble metal nanocrystals. In this work, we successfully synthesize the polyallylamine (PAA) with different molecular weight functionalized Pt nanodendrites (Pt-NDs) using a facile hydrothermal reduction method. The morphology and surface composition are investigated by transmission electron microscopy, element map, and thermogravimetric analysis. Furthermore, we detailedly investigate the effect of the molecular weight of PAA on the electrochemical property of the functionalized Pt-NDs. Electrochemical measurements show only low molecular weight PAA functionalized Pt-NDs allow electrolytes to access freely the Pt sites. Meanwhile, the low molecular weight PAA functionalized Pt-NDs show the excellent selectivity and activity for the oxygen reduction reaction in the presence of methanol.

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1. Introduction

Direct methanol fuel cells (DMFCs) are highly attractive portable power devices for the direct conversion of chemical energy into electrical energy, owing to low operating temperature, ease of handling, low cost of methanol, and high energy density, *etc* [1–8].

At now, the low selectivity of Pt electrocatalysts for the oxygen reduction reaction (ORR) is one of the main obstacles that hindering the commercialization of DMFCs due to methanol crossover problem [9]. Although Pd electrocatalysts have high methanol tolerance and presentable ORR activity, they suffer from the low durability in acidic media due to the Pd dissolution [10–12]. So, the considerable efforts still focus on developing methanol-tolerant Pt-based cathodic electrocatalysts [10–23].

Besides the alloying strategy that restraining the methanol adsorption on Pt sites by means of the second element dilution

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mechanism [18–20], the another promising physical block strategy has emerged recently, in which porous shell materials (such as Ru [21] and carbon frameworks [22]) on Pt@porous-materials core–shell nanocomposites effectively block the accessibility of methanol with larger molecular size than oxygen molecule on Pt sites by controlling the pore size of shell materials. As a result, these Pt@porous-materials core–shell nanocomposites exhibit the excellent selectivity for the ORR in the presence of methanol.

In this work, we use polyallylamine (PAA, Scheme 1) with different molecular weight as reaction precursor to synthesize the PAA-functionalized Pt nanodendrites (Pt-NDs@PAA) through a facile hydrothermal reduction method. The molecular weight of PAA remarkably affects the compactness of PAA shell layers on Pt nanodendrites (Pt-NDs) surface. Thus, the molecular weight of PAA has a significant impact on electrocatalytic performance of Pt-NDs@PAA for the ORR. The work provides an effective strategy and crucial information for the design and optimization of methanol-tolerant Pt cathodic electrocatalysts.

2. Experimental

2.1. Reagents and chemicals

Both polyallylamine (PAA, Scheme 1) with weight-average molecular weight 5000 and 15 000 were supplied from Nitto Boseki Co., Ltd (Tokyo, Japan). Other reagents were of analytical reagent grade and were used as received.

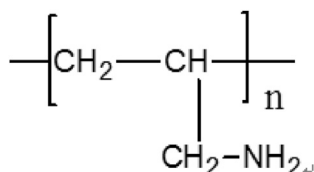
2.2. Preparation of PAA functionalized Pt-NDs (Pt-NDs@PAA)

In a typical synthesis, 1 mL of 0.025 M K_2PtCl_4 , 0.6 mL of 0.50 M PAA (molarity of PAA given with respect to the repeating unit), and 0.5 mL of acetaldehyde solution (40%) were added into 7.0 mL of water with vigorous stirring. Then, the mixture solution (pH 3.0) was heated at 140 °C for 6 h in Teflon-lined stainless-steel autoclave. After reaction, the products were collected by centrifugation, washing, and then drying. When low molecular weight PAA ($M_w \approx 5000$) and high molecular weight PAA ($M_w \approx 150,000$) were used as reaction precursors, the resultant products were named as Pt-NDs@PAA-5000 and Pt-NDs@PAA-150000, respectively.

Unless otherwise specified, Pt-NDs@PAA-5000 and Pt-NDs@PAA-150000 were directly used for the physical characterization and electrochemical measurements.

2.3. Apparatus

Morphology, size, structure, surface composition, and chemical state of samples were characterized by transmission electron microscopy (TEM, JEM-2100F), X-ray powder diffraction (XRD, DX-2700), transmission electron microscopy (TEM, JEM-2100F), X-ray photoelectron spectroscopy (XPS, AXIS ULTRA), and thermogravimetric analysis (TGA, TA Q600SDT). Electrochemical experiments were performed using CHI 660 D electrochemical analyzer at 30 ± 1 °C in a conventional three-electrode cell, including a Pt wire



Scheme 1. The molecular structure of PAA.

counter electrode, a saturated calomel reference electrode, and a catalyst modified glassy carbon work electrode. Potentials in this study were given relative to the reversible hydrogen electrode (RHE). Rotating disk electrode (RDE) measurements were performed on a RDE710 Gamry's rotating disk electrode. The working electrode was prepared according to the procedure reported previously with slight modification [24]. Typically, the catalyst ink was obtained by mixing 8 mg of catalyst and 4 mL of isopropanol/Nafion® solution (20% isopropanol and 0.02% Nafion®) in ultrasonic condition for 60 min. Then, 10 μL of catalyst ink was dispersed on the glassy carbon electrode surface and dried at room temperature. The loadings of Pt metal on the electrode was ca. $101.9 \mu\text{g cm}^{-2}$.

3. Results and discussion

3.1. Physical characterization of Pt-NDs@PAA

In a typical synthesis, two kinds of Pt-NDs@PAA were obtained by reducing K_2PtCl_4 with acetaldehyde in the presence of low molecular weight PAA ($M_w \approx 5000$) or high molecular weight PAA ($M_w \approx 150,000$) at 140 °C for 6 h, which were named as Pt-NDs@PAA-5000 and Pt-NDs@PAA-150000, respectively (see Experimental section for details). Fig. 1A-a shows TEM image of Pt-NDs@PAA-5000. The dendritic-like Pt nanostructures with 25 nm size are the dominant products, indicating the high-yield synthesis of Pt-NDs. Fig. 1A-b shows high-resolution TEM (HRTEM) image of Pt-NDs@PAA-5000. As observed, an individual Pt-NDs@PAA-5000 is consisted of small Pt grains with a diameter of 5–7 nm. Fig. 1A-c shows magnified HRTEM images recorded from regions marked by square in (b) and corresponding fast Fourier transform (FFT) diffraction pattern. The inter-atomic lattice fringe distance is ca. 0.227 nm, which is well consistent with lattice spacing of (111) facets in face-centered cubic (fcc) Pt crystal. The FFT diffraction pattern exhibits a regularly and discretely dotted pattern with six-fold symmetry, confirming Pt-NDs@PAA-5000 are enclosed by (111) facets. Fig. 1A-d shows high-angle annular dark-field scanning TEM (HAADF-STEM) image and corresponding elemental maps patterns of Pt-NDs@PAA-5000. HAADF-STEM image clearly shows Pt-NDs@PAA-5000 are actually interconnected porous nanostructures, confirming their dendritic nature. The corresponding elemental maps show the existence of N element. Meanwhile, map patterns of N and Pt elements are almost same, confirming the successful functionalization of Pt-NDs by PAA-5000 due to strong Pt–N interaction [25]. Under same experimental conditions, PAA-150000 functionalized Pt-NDs@PAA-150000 with 26 nm size and dominant (111) facets are obtained by using high molecular weight PAA ($M_w \approx 150,000$) as reaction precursor (Fig. 1B). PAA-150000 has bigger molecular volume than PAA-5000, which more may efficiently prevent the aggregation of primary Pt crystal nucleus and consequently generate Pt-NDs with the smaller Pt grains. As shown in Fig. 1B-b, the size of primary Pt grains in Pt-NDs@PAA-150000 is about 3–5 nm, which is smaller than that in Pt-NDs@PAA-5000.

Fig. 2A shows the XRD patterns of Pt-NDs@PAA-5000 and Pt-NDs@PAA-150000. For both Pt-NDs, the four strong diffraction peaks at Bragg angles of 40.1°, 46.6°, 67.9° and 80.9° correspond to the (111), (200), (220) and (311) facets of fcc Pt, respectively. Using Scherrer's equation, the average particle size of primary Pt grains is calculated to be 5.8 nm and 4.1 nm for Pt-NDs@PAA-5000 and Pt-NDs@PAA-150000, which is consistent with the HRTEM results. Fig. 2B shows XPS spectra of Pt-NDs@PAA-5000 and Pt-NDs@PAA-150000 in Pt 4f region. According to splitting-peak fitting curves, the percentage of metallic Pt is calculated to be 82.2% and 86.4% for Pt-NDs@PAA-5000 and Pt-NDs@PAA-150000, demonstrating the complete reduction of K_2PtCl_4 precursor by acetaldehyde.

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