



Short communication

Platinum–titanium intermetallic nanoparticle catalysts for oxygen reduction reaction with enhanced activity and durability



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ABSTRACT

A facile method to prepare Pt–Ti intermetallic nanoparticles supported on carbon was developed. Starting from a commercial Pt/C catalyst, TiO₂ layers were formed on the Pt/C then thermal annealing under a reducing condition successfully produced intermetallic Pt–Ti nanoparticles with an average size of 4.2 nm. The intermetallic Pt–Ti/C showed enhanced activity and durability for oxygen reduction reaction due to the change in electronic structure and less aggregation.

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1. Introduction

The oxygen reduction reaction (ORR) is an important reaction in many energy devices such as fuel cells [1] and lithium–air batteries [2]. Pt minimization has received much attention because of the high cost and scarcity of Pt [3]. Various approaches to controlling the nanostructures of Pt-based catalysts have been extensively studied, e.g., for a core-shell structure [4,5], shape-controlled nanoparticles [6,7], size-controlled nanoparticles [8,9], and alloys with other transition metals [10–12]. In particular, such alloys may have modified electronic structures compared to bare Pt with enhanced ORR activity and durability [13].

Unlike random disordered alloy structures, intermetallic structures are fully ordered with definite compositions and crystalline structure [14–16]. The intermetallic compounds are known to have significantly different catalytic properties resulting from the change in electronic structure [17,18] or geometric surface [18–20]. In previous researches, intermetallic face-centered tetragonal (fct) PtFeCo nanoparticles have exhibited higher catalytic activity and durability during ORR than disordered face-centered cubic (fcc) PtFeCo nanoparticles [21]. The intermetallic Pt₃Co [14], PtFe@Pt core-shell [22], fct-FePt [23], and Pt₃Cr [24] catalysts have also shown high ORR performances.

Intermetallic Pt–Ti catalysts have been synthesized by reducing Pt precursors and Ti precursors dissolved in solution at the same time [25,26]. It is known that the Pt–Ti intermetallic structures have high corrosion resistance in chemical environments and there is a strong

Lewis acid and base interaction between Pt and Ti with electron transfer from Ti to Pt [27]. During the synthesis of the intermetallic structures, a thermal annealing process at high temperatures above 600 °C is generally required [25,28]. But, the nanoparticles become easily agglomerated during the annealing process. Studies using carbon coating [29] or using a KCl matrix [25] have been reported to alleviate the aggregation of the nanoparticles. However, the catalytic active sites can be blocked by the thick coating materials or the intermetallic nanoparticles can become agglomerated during the harsh catalytic reaction after the removal of the KCl matrix.

Here, we report a facile synthesis of 4.2 nm-sized intermetallic Pt–Ti nanoparticle catalysts with enhanced activity and durability for ORR. Commercial Pt/C was used as the starting materials, TiO₂ layers were formed on the surface of the Pt/C, then the intermetallic Pt–Ti nanoparticles were formed by thermal annealing under H₂ flow. Ti atoms can inter-diffuse into the Pt lattice; moreover, a TiO₂ layer can protect the nanoparticles from being aggregated. The intermetallic structures were investigated by electron microscopy, X-ray diffraction, and X-ray absorption measurements, and their electrocatalytic properties were tested.

2. Experimental section

2.1. Synthesis of Pt–Ti intermetallic nanoparticles supported on carbon

Commercial Pt/C 20 mg (20 wt%, Johnson Matthey) was mixed with 120 μl of deionized water and 43.2 μl of benzyl alcohol (anhydrous, 99.8%, Sigma–Aldrich) in 5 ml of anhydrous ethanol (≤0.005% water,

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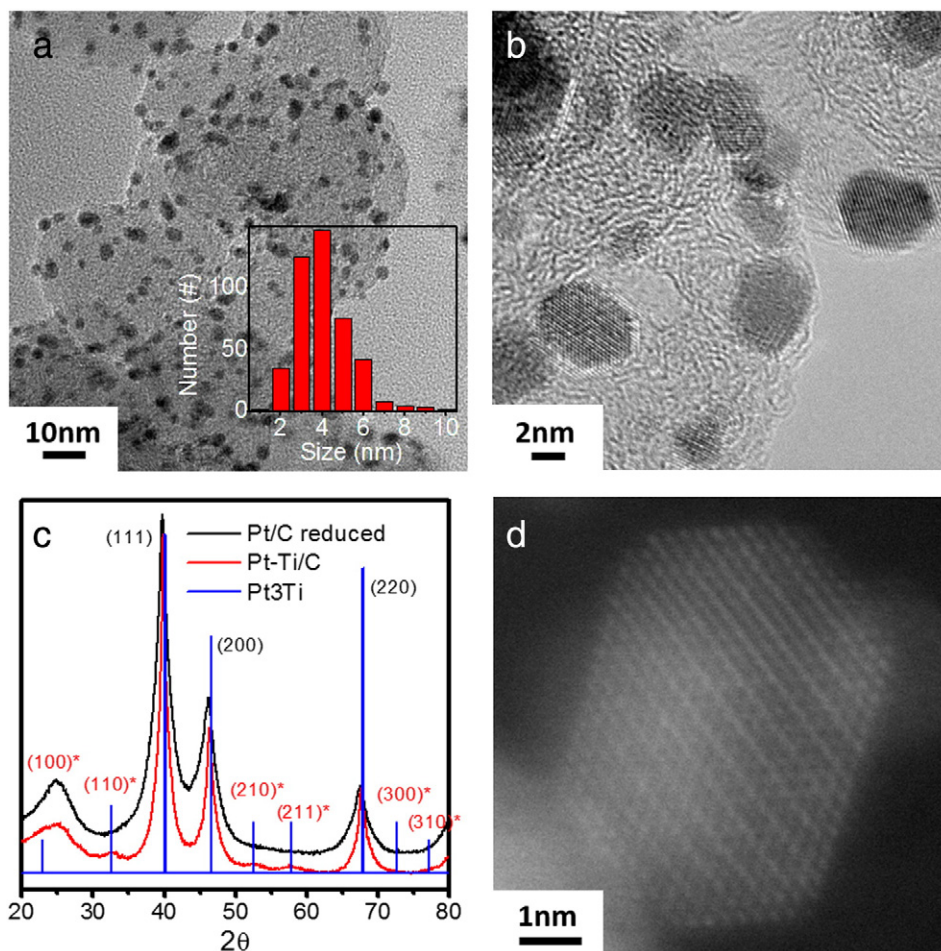


Fig. 1. (a) TEM image of the Pt-Ti intermetallic nanoparticles supported on the carbon prepared with 10 vol% H_2 flow. The inset shows a histogram for estimating the size distribution of the Pt-Ti nanoparticles. (b) High-resolution TEM image. (c) XRD pattern for the Pt/C and the intermetallic Pt-Ti/C; the Pt/C was reduced at 200 °C for 2 h under a 10 vol% H_2 flow to remove any oxide formed at the Pt surface. *Peaks observed only for the intermetallic structure. (d) STEM image showing the intermetallic structure clearly.

Sigma-Aldrich). Titanium(IV) butoxide (97%, Sigma Adrich) 54.4 μ l dissolved in 5 ml of ethanol was put into the Pt/C solution. The solution was stirred for 1 h. All processes were conducted in an ice bath. The resultants were washed three times by centrifugation using anhydrous ethanol and dried in a vacuum oven at 50 °C overnight. The Pt-TiO_x/C composites were heated at 210 °C for 2 h under N_2 flow. Then the temperature was raised to 700 °C and maintained for 4 h under 10 vol% H_2 flow (with balance N_2). The catalysts were cooled down, washed by centrifugation using anhydrous ethanol, and dried in a vacuum oven at 50 °C.

2.2. Characterization

The metal contents in the catalysts were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES 720, Agilent). The catalysts were observed by transmission electron microscopy (TEM, Tecnai TF30 ST, FEI) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM, Titan cubed G2 60–300, FEI) equipped with a Cs-corrector. All TEM analyses were operated at 200 kV. The crystalline structure of the catalysts was observed by

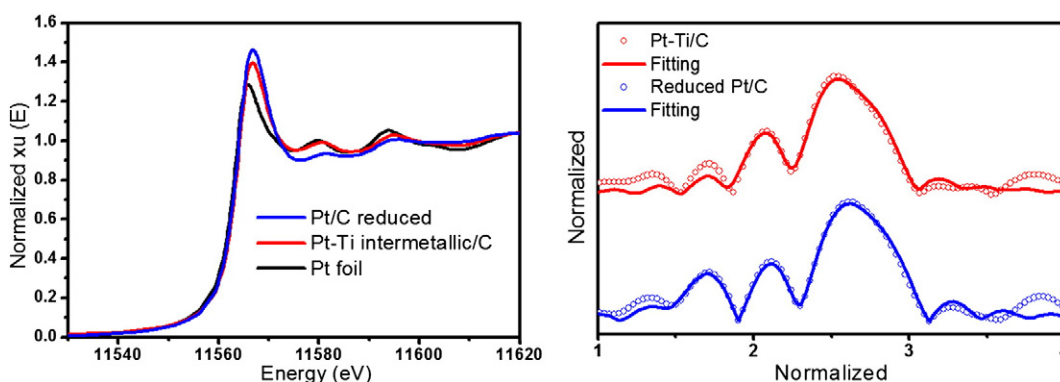


Fig. 2. (a) XANES and (b) EXAFS fitting results on Pt L₃-edges for the reduced Pt/C and the intermetallic Pt-Ti/C.

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