# Synthesis of Ordered Intermetallic $PtBi_2$ Nanoparticles for Methanol-Tolerant Catalyst in Oxygen Electroreduction

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Ordered intermetallic phase $PtBi_2$ nanoparticles with an average particle size of 4.1 ± 1.7 nm were synthesized at ambient conditions in an aqueous solution by co-reducing $H_2PtCl_6$ and $Bi(NO_3)_3$ with $NaBH_4$ in the presence of polyvinylpyrrolidone (PVP) as a capping agent. The produced $PtBi_2$ nanoparticle catalyst, which has some distinguishable properties from Pt or Pt-based disordered catalysts, displays a strong electrocatalytic activity toward oxygen reduction with a methanol-tolerant property. The methods, such as powder X-ray diffraction (XRD), transmission electron micrograph (TEM), selected area electron diffraction (SAED), energy-dispersed X-ray spectroscopy (EDS), and cyclic voltammetry, were employed for catalyst structure and activity characterization.

## Introduction

Electrocatalysis plays a vital role in some emerging clear-energy technologies such as fuel cells, especially the proton-exchange membrane fuel cells (PEMFCs), which include direct methanol fuel cells (DMFCs).[1] The activity and selectivity of a monometallic electrocatalyst can be greatly improved if the second metal is added into the material to form a bimetallic electrocatalyst. A typical example is the PtRu bimetallic catalyst for anode reaction in DMFCs. The addition of Ru into the Pt catalyst can significantly increase the catalytic activity compared with a Pt monometallic catalyst.

Great efforts have been made toward the development of bimetallic nanoparticle catalysts with some disordered structures, such as a core−shell bimetal, a partially segregated alloy, or a pure alloy.[2] In order to improve the activity, some approaches have been explored at high temperature to transform disordered alloys into ordered intermetallic compounds.[3] Recently, bulk ordered intermetallic compounds such as PtBi and PtPb have emerged as a new kind of electrocatalyst. Compared to a pure Pt catalyst, these intermetallic catalysts display some different properties in terms of catalytic activity.[4] In general, ordered intermetallic compounds have predictable, structural, geometric, and electronic effects that are not offered by bimetal alloys. However, the preparation of intermetallic compounds with the nanoparticle size at a mild ambient environment faces some challenges. Normally, a successful process for intermetallic compound synthesis is often carried out at some aggressive conditions, such as melting and long-time annealing at high temperatures. Recently, Sra et al. reported a novel approach to preparing ordered AuCu and $AuCu_3$ intermetallic nanocrystals from Au and Cu monometallic nanoparticle precursors at low temperature.[5] Xie et al. reported the synthesis of some nanosized $NiSb_2$ and $CoSb_3$ intermetallic compounds by a solvothermal route.[6] Further treatments such as annealing and high-energy ball milling are necessary for the particle to be uniform. Howard et al. reported a one-pot synthetic route to preparing chemically ordered PtFe nanoparticles without annealing treatment.[7] The synthesis of PtBi intermetallic nanoparticles was reported

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by DoSalvo's research group, in which a polyol process was successfully employed and the produced particle size was at a nano level.[8] The synthesized PtBi nanoparticle catalyst showed remarkable electrocatalytic activity toward formic acid oxidation.

In the efforts to synthesize effective catalysts for fuel cells, an innovative synthesis route has been developed, resulting in some new catalysts that have the remarkable property of methanol tolerance. It is well-known that a cathode platinum catalyst has no inertness for methanol oxidation in a DMFC. In a DMFC, methanol crosses through the membrane from the anode to the cathode and then reacts with the cathode Pt catalyst. This reaction leads to a drop in cathode potential and then an unwanted drop in cell voltage. There are few works in which Pt-based catalysts show remarkable selectivity to $O_2$ reduction and inertness to methanol oxidation.[9] In this paper, $PtBi_2$, one of the new catalysts, has been synthesized in the form of nanoparticles by co-reducing $H_2PtCl_6$ and $Bi(NO_3)_3$ with $NaBH_4$ in the presence of polyvinylpyrrolidone (PVP) as a capping agent. The influence of the experimental conditions on the synthesis process and final products is also discussed. The characterization of the products was performed using XRD, TEM, SAED, EDS, and cyclic voltammetry. The prepared nanoparticles of the $PtBi_2$ intermetallic catalyst exhibited different properties with Pt and other disordered Pt-based alloys in terms of methanol tolerance of the electrocatalytic oxygen reduction in the presence of concentrated methanol. This methanol-tolerance property suggests that the $PtBi_2$ compound can be employed as an effective DMFC cathode catalyst.

## Experimental Section

**Chemical Preparation.** The Beijing Chemical Reagent Center supplied bismuth nitrate ($Bi(NO_3)_3$), hexachloroplatinic (IV) acid ($H_2PtCl_6$), sodium borate ($NaBH_4$), polyvinylpyrrolidone (PVP), tetrahydrofuran, and other chemical reagents of analytical grade, which were used as received. Vulcan XC-72 carbon with an average particle size diameter of 30 nm was purchased from E-TEK. The $H_2PtCl_6$ and $Bi(NO_3)_3$ salts were dissolved in a 2.0 M HCl solution with a 1:2 initial metal atomic concentration ratio (Pt:Bi). In this 2.0 M HCl acidic solution, the hydrolysis of $Bi^{3+}$ can be avoided. Double distilled water and tetrahydrofuran were used to wash the products. The purpose of using tetrahydrofuran was to remove residual PVP on the catalyst particle surfaces. In order to prevent the metal from being oxidized by dissolved $O_2$, we bubbled the nitrogen through the solution during the whole synthesis process.

**Synthesis Procedure.** Two hundred milliliters of 2.0 M HCl was degassed with nitrogen for 2 h before adding the reactants. Next, 0.058 mmol $H_2PtCl_6$, 0.116 mmol $Bi(NO_3)_3$, and 0.1 g of PVP were dissolved together in this aqueous solution confined in a three-neck flask under constant magnetic stirring and nitrogen bubbling. $NaBH_4$ (0.05 g) was then added into the solution, immediately turning the solution a deep black color. After that, 0.1 g of Vulcan XC-72 carbon was added into the solution and the mixture was continually stirred for 12 h. The final products were collected by a centrifugation process, and then washed successively by tetrahydrofuran and water. As identified below, the produced catalyst has a formula of $PtBi_2$ with particle sizes at the nanometer level. Because of the addition of Vulcan XC-72 carbon to form supported catalyst, the catalyst should be expressed as $PtBi_2/C$. The Pt load is about 6.3 wt %, 1:2 Pt:Bi, which was tested by ICP-AES.

**Characterization.** Cyclic voltammetry measurements were conducted in 0.5 M $H_2SO_4$ and 0.5 M $H_2SO_4$ + 5.0 M $CH_3OH$ solutions. At the same time, the oxygen reduction and methanol oxidation catalytic activities were measured with a three-electrode electrochemical cell. A suspension of $PtBi_2/C$ for the electrode surface coating was prepared by adding $PtBi_2/C$ into double-distilled water, which was then sonicated for 30 min. A glass-carbon disk electrode with a diameter of 4 mm was employed for the catalyst coating preparation. Before coating, the electrode was polished successively with 1.0, 0.3, and 0.05 $\mu$m alumina until a shiny, mirrorlike surface was obtained. The polished electrode was then ultrasonicated for 10 min in a beaker containing double-distilled water, followed by a water-rinsing step to produce a clean electrode surface on which the $PtBi_2/C$ was coated by depositing 20 $\mu$L of a $PtBi_2/C$ (about 0.0775 mg) water suspension with 0.02% Nafion solution. After the water evaporation, the catalyst particles were firmly attached on electrode surface. A $Hg_2SO_4/Hg$ electrode and a platinum foil were used as the reference and auxiliary electrodes, respectively. The oxygen reduction and methanol oxidation on the $PtBi_2/C$-coated electrode were examined in a solution containing 5.0 M methanol and 0.5 M sulfuric acid at a potential scan rate of 20 mV $s^{-1}$. An EG&G model 273A potentiostat controlled by M270 software was used for cyclic voltammetry. For particle characterization, an XRD method was used for data collection performed by a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation. High-resolution transmission electron microscopy (HRETM) images, EDS analysis, and electron diffraction data were collected on a JEOL JEM-2010.

All experiments were conducted at room temperature and ambient pressure.

## Results and Discussion

The TEM images of $PtBi_2$ nanoparticles are shown in images a and b of Figure 1. A uniform dispersion of the nanoparticles can be observed. The EDX spectrum analysis confirmed that the atomic ratio of Pt:Bi was about 1:2. Therefore, the compound has a chemical formula of $PtBi_2$. The TEM analysis for 200 particles selected randomly indicates that their average diameter is around 4.1 ± 1.7 nm. In Figure 1c, the electron diffraction pattern indicates that the $PtBi_2$ nanoparticle is a single, chemically ordered $PtBi_2$ phase rather than a simple mixture of two monometallic nanoparticles or a disordered Pt alloy. The HRTEM image of a single particle is shown in Figure 2, where the clear lattice fringes can be observed. Crystal lattices with interplanar spacings of 0.276 and 0.194 nm are fairly close to those of the $PtBi_2$ planes of (211) and (222), which are 0.273 and 0.193 nm, respectively. This further confirms that the observed nanoparticle in Figure 2 is in the chemically ordered $PtBi_2$ phase. The structure of $PtBi_2/C$ was also investigated by powder X-ray diffraction, as shown in Figure 3. The first reflection corresponds to the (002) plane of the carbon support. The reflections at $2\theta = 32.7, 46.9, 54.8, 68.6$, and 78.1°, corresponds to the 211, 222, 400, 422, and 521 planes,

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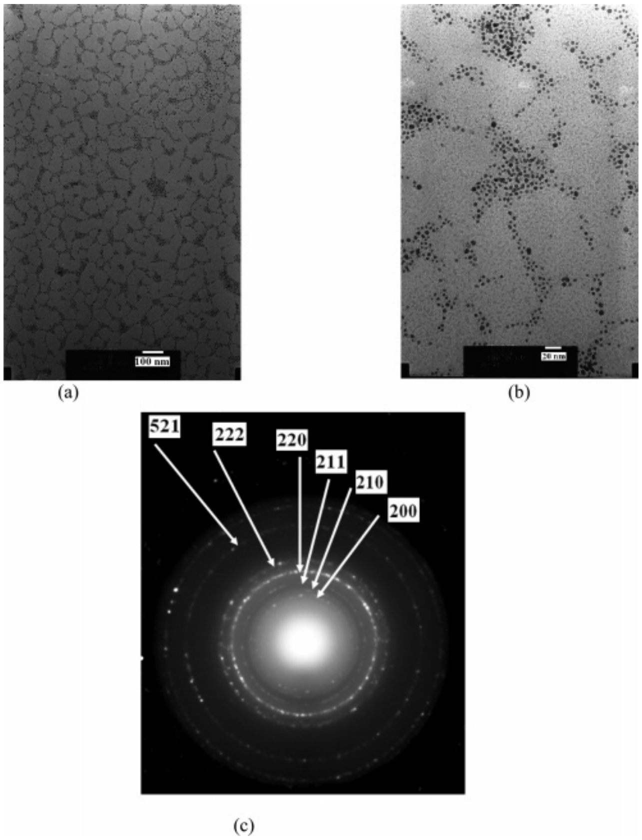

(a) (b)

(c)

**Figure 1.** (a, b) TEM micrographs of $PtBi_2$ bimetallic nanoparticles; (c) corresponding electron diffraction pattern.

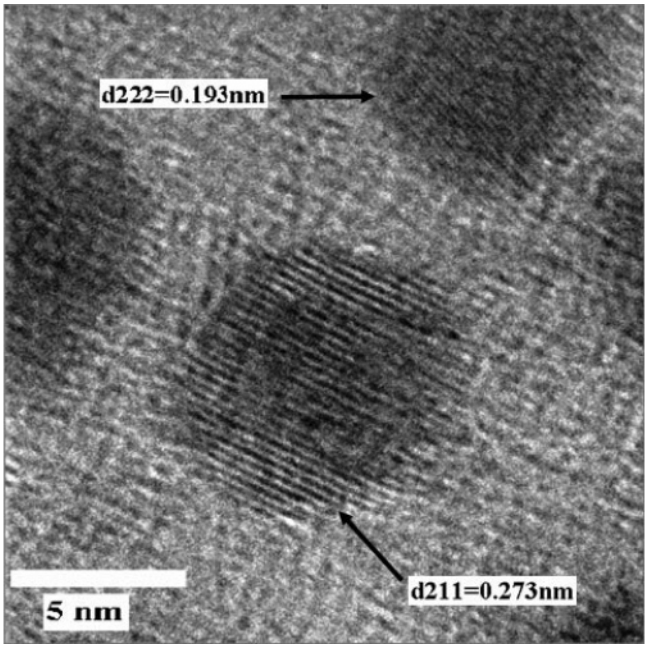

**Figure 2.** HRTEM image of the $PtBi_2$ nanoparticle with (211) and (222) faces.

respectively, for a chemically ordered $PtBi_2$ crystal structure. The reflections of the impurities such as $Pt_3O_4$ and $Bi_2O_3$ can also be identified from the spectrum, which might be from the side reaction. The most important conclusion is that the chemically ordered $PtBi_2$ with an intermetallic phase can be synthesized even in an aqueous solution under ambient conditions.

To confirm the results, the Pt and Bi initial metal atomic ratio was changed from 1:2 to 1:1 and 3:1, respectively. The SAED and XRD patterns at these two different atomic ratios gave almost the same pattern as $PtBi_2$, suggesting that the main product under such reaction conditions is the ordered intermetallic $PtBi_2$ phase regardless of the initial metal atomic ratios. The presence of a capping agent is critical to the successful synthesis of an ordered intermetallic $PtBi_2$ compound. Experiments using Pt and Bi with initial atomic ratios of 1:2 and 1:3 were carried out without a capping agent. The product was an amorphous structure rather than an ordered intermetallic structure, indicating the necessity of a capping agent.

To evaluate the electrochemical reaction of the $PtBi_2/C$ catalyst, we made a comparison with polycrystalline Pt first; Figure 4 showed the typical cyclic voltammogram curves of polycrystalline Pt in the electrolytes of 0.5 M $H_2SO_4$ (Figure 4, solid line) and 0.5 M $H_2SO_4$ + 1.0 M $CH_3OH$ (Figure 4, dashed line). We can see the oxygen reduction reaction occurs at the polycrystalline Pt smoothly in the acid electrolyte without methanol. However, we cannot see the oxygen reduction peak in the presence of methanol because of the simultaneous methanol oxidation reaction that occurred at the polycrystalline Pt. The steady-state surface cyclic voltammogram of the coated $PtBi_2/C$ catalyst, shown in Figure 5 (solid), displays a redox wave near 0 mV (vs $Hg_2SO_4/Hg$) after $N_2$ was bubbled through the solution for 1 h. This redox process is believed to be the surface electrochemical oxidation and reduction of $Pt/PtO_x$ ($1 < x < 2$). More detailed work is underway to confirm this assignment. After the oxygen was introduced into the solution, a strong oxygen reduction wave starting at ~100 mV can be observed (Figure 5b), demonstrating that $PtBi_2$ has catalytic activity toward oxygen reduction. In order to test the methanol tolerance of this catalyst, we added 5.0 M methanol to the solution. The obtained cyclic voltammogram is shown in Figure 5c together with that recorded in the absence of methanol (Figure 5b). Such cyclic voltammogram curves did not change with the increase in cyclic times; it is obvious that no methanol oxidation could be observed. This result clearly indicates that the $PtBi_2$ catalyst has an electrochemical resistance to methanol oxidation, and the stable cyclic voltammogram curve shows that the methanol tolerant property of $PtBi_2/C$ did not change with time. The experiments with pure Pt and other Pt-based catalysts, such as PtRu, PtFe, and PtNi showed that these catalysts have no such property for methanol tolerance, which is consistent with the results reported in the literature.[9] As mentioned in the Introduction, one of the major challenges in DMFC is the methanol crossover from the anode to cathode, causing the depletion of oxygen surface concentration, poisoning of the cathode catalyst, and a reduction in fuel efficiency. Therefore, it is highly desirable to use a cathode catalyst that has no catalytic activity toward methanol oxidation.[10] It is believed that this $PtBi_2$ catalyst could be a feasible cathode catalyst

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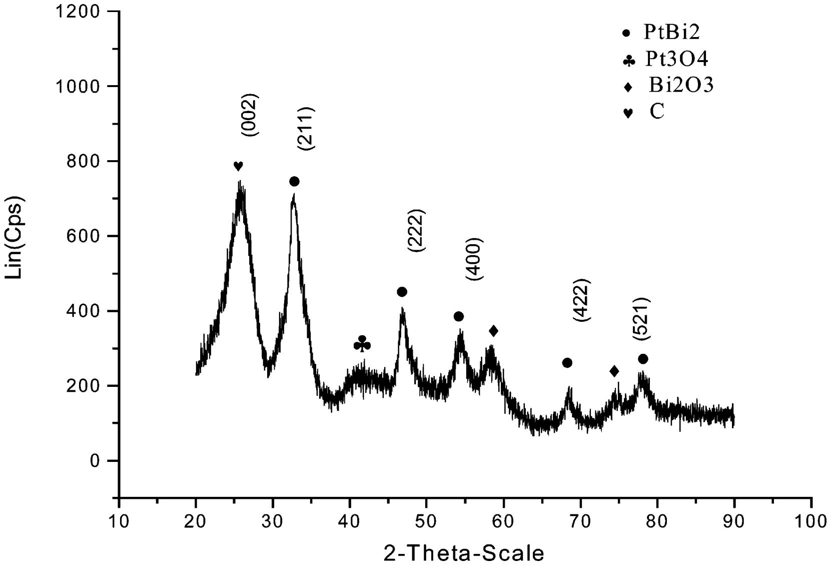

**Figure 3.** XRD pattern of PtBi$_2$/C.

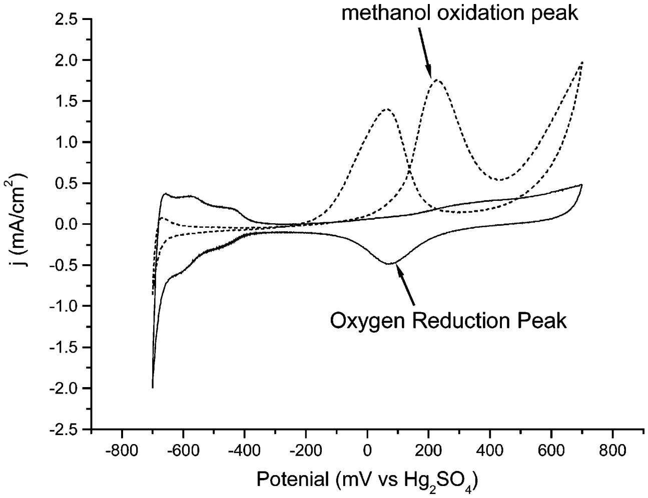

**Figure 4.** The CV curve of polycrystalline Pt in 0.5 M $H_2SO_4$ (solid line) and in 0.5 M $H_2SO_4$ + 1.0 M $CH_3OH$ (dashed line).

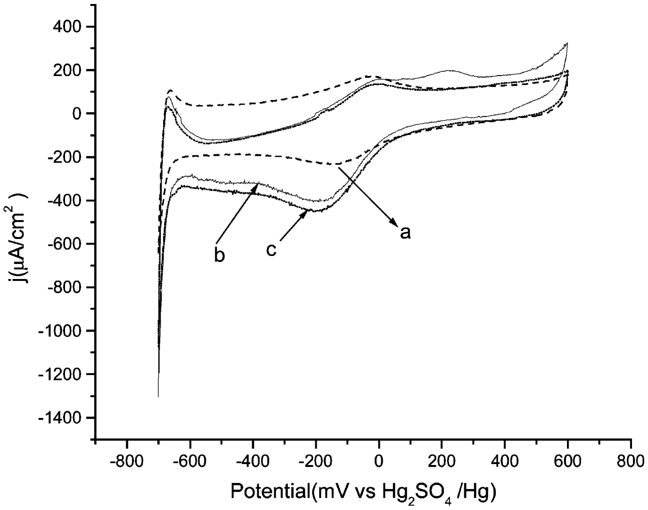

**Figure 5.** Cyclic voltammograms of a PtBi$_2$/C-coated glass carbon electrode in (a) a 0.5 M $H_2SO_4$ solution saturated by $N_2$, (b) a 0.5 M $H_2SO_4$ solution saturated by $O_2$, and (c) a 0.5 M $H_2SO_4$ + 5.0 M methanol solution saturated by $O_2$. Potential scan rate: 20 mV $s^{-1}$.

for DMFCs to eliminate the negative effect of the methanol crossover. The mechanism for methanol tolerance of the PtBi$_2$/C catalyst is not clear at this stage. One of the possible explanations is that the formation of the PtBi$_2$ phase may result in a charge redistribution, which in turn may lead to difficulties in the formation of oxygen-containing species from water dissociation. This is one of the key steps for methanol oxidation. Another fact is that the Pt−Pt distance in PtBi$_2$ is larger than that in other Pt-based catalysts, which may prohibit the formation of oxygen-containing species. More work is underway toward fundamental understanding and mechanism exploration.

## Conclusions

The ordered intermetallic PtBi$_2$ nanoparticle catalyst was synthesized successfully at ambient conditions in an aqueous solution. Several sophisticated instrumental methods were employed for the catalyst structure and component analysis. The prepared PtBi$_2$/C exhibited a property for methanol tolerance in electrocatalytic oxygen reduction, suggesting that this catalyst could be employed as a DMFC cathode catalyst to reduce the negative impact for the methanol crossover.

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