Intermetallic PtBi Nanoplates Boost Oxygen Reduction Catalysis with Superior Tolerance over Chemical Fuels

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The crossover issue of small-molecule organic fuels usually makes the Pt-based nanocatalysts exhibit low efficiency, and poor tolerance and durability under the practical fuel cell operating conditions. Here, a new approach to prepare a class of intermetallic hexagonal PtBi nanoplates with superior tolerance over chemical fuels for boosting oxygen reduction catalysis is reported. The time-dependent morphology studies reveal that the well-defined hexagonal PtBi nanoplates are transformed from a new reaction immediate (triangular/truncated triangular bismuth oxides nanoplates). Different from conventional Pt-based catalysts, the hexagonal PtBi nanoplates exhibit much improved tolerance over CH₃OH, HCOOH, and CO. X-ray photoelectron spectroscopy results reveal that the charge displacement resulting from Pt–Bi bonding is the main factor in enhancing the tolerance. The PtBi nanoplates also exhibit much higher ORR activity than all the reported PtBi nanoparticles. Considering their exceptional antipoisoning ability and high activity, these hexagonal nanoplates show great potential in the development of commercial fuel cells.

1. Introduction

Oxygen reduction reaction (ORR) is of critical importance for polymer electrolyte membrane fuel cells and lithium air batteries.¹⁻² Pt alloys have been regarded as the most efficient electrocatalytic system for ORR.³⁻⁵ This has stimulated the researchers to devote their great efforts to engineering Pt alloys for boosting ORR activity by precisely tuning composition, shape, electronic structure, surface strain and defects, etc.⁶⁻¹² However, due to the crossover of small-molecule organic fuels from the anode to the cathode through the polymer membranes, the reported Pt-based catalysts usually exhibit low efficiency and poor durability under long-term fuel cell operating conditions, which severely limit their commercial applications.²,¹³,¹⁴ To this end, the creation of stable Pt-based nanocatalysts that possess exceptional tolerance to small-molecule organic fuels is highly desirable for the future fuel cells. The ordered intermetallic PtBi nanoparticles exhibit high tolerance to methanol (CH₃OH) and CO poisoning, but still show the very limited activity and stability due to the their nonuniform alloy and aggregation behavior during the catalytic process.¹⁵⁻¹⁷ A combination of the ordered intermetallic nanostructure with 2D structure might be a unique system for not only enhancing catalytic activity but also improving the tolerance and durability of ORR, however, achieving such target is still a great challenge.
Here, we demonstrate a new strategy for making intermetallic PtBi nanoplates with uniform hexagonal morphology to achieve more efficient ORR catalysis with high tolerance over the chemical fuels, and high activity and durability. The PtBi nanoplates were synthesized by using platinum(II) acetylacetonate (Pt(acac)$_2$) and bismuth(III) acetate (BiAc$_3$) as precursors, phloroglucinol and CO as reducing agent, polyvinylpyrrolidone (PVP) as capping agent, and $N,N$-dimethylformamide (DMF) as solvent. The prepared PtBi nanoplates exhibit excellent stability and promising tolerance over the CH$_3$OH, formic acid (HCOOH), and CO poisonings compared with the commercial Pt/C in ORR, as well as show the much improved ORR activity to PtBi nanoparticle, suggesting a new class of stable ORR electrocatalyst for future fuel cell applications.

2. Results and Discussion

In a typical preparation of PtBi nanoplates, Pt(acac)$_2$, BiAc$_3$, phloroglucinol, and PVP were mixed together with DMF in a glass pressure vessel and subjected to ultrasoundication for 0.5 h. After filling with CO to 1 bar, the vessel was heated from room temperature to 160 °C and kept at 160 °C for 2 h under magnetic stirring. The solution was washed with a mixture of ethanol and acetone and further centrifuged for several times. Electron microscopes, energy dispersive X-ray spectroscopy (EDX), and powder X-ray diffraction (PXRD) were carried out to characterize the structure and composition of the products. The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) (Figure 1a,b) and transmission electron microscope (TEM) (Figure S1, Supporting Information) images clearly show that the as-made PtBi nanocrystals have the hexagonal plate-like morphology with the size of around 100 nm. The thickness of PtBi nanoplates is determined to be about 18 nm by TEM images of PtBi nanoplates supported on the carbon nanotube (Figure S2, Supporting Information). The molar ratio of Pt to Bi in the nanoplates was determined to be Pt: Bi = 48.6: 51.4, revealed by EDX (Figure 1c), being in good agreement with the result from inductively coupled plasma atomic emission spectroscopy (ICP-AES, Pt: Bi = 49.2: 50.8).

PXRD was conducted to determine the phase of the PtBi nanoplates, displaying the intermetallic phase. Furthermore, no characteristic peaks related to metallic Pt, Bi, bismuth oxides or hydroxides are observed (Figure 1d), indicating the formation of pure PtBi alloys. The crystalline nature of the PtBi nanoplates was further characterized by high-resolution TEM (HRTEM) (Figure 1e). An interplanar spacing of 0.37 nm is clearly observed, assigned to the (100) plane of PtBi. The chemical states of Pt and Bi in the PtBi nanoplates were examined by X-ray photoelectron spectroscopy (XPS) (Figure S3, Supporting Information). The peak ratio of Pt(0) to Pt(II) in the PtBi nanoplates is 2.4, indicating that most of Pt is in the metallic state. Notably, there is a large proportion of Bi(III) on the surface of the PtBi nanoplates, attributed to the relative weak antioxidant capacity of Bi. The elemental distribution of PtBi nanoplates was investigated by line-scan analysis and STEM-EDX elemental mapping analysis, where the Pt and Bi were uniformly distributed throughout the whole PtBi nanoplate (Figure 1f,g).
To reveal the growth mechanism of the PtBi nanoplates, the PtBi nanoplate intermediates were collected at different reaction times. Figure 2 shows TEM images, PXRD patterns, and Pt/Bi atomic ratios of all the intermediates. At the initial stage, small dispersive triangular/truncated triangular nanoplates with the lateral size of around 50 nm were found (Figure 2a). After the reaction was proceeded to 45 min, the truncated triangular plates began to stick each other (Figure 2b). The majority of the intermediates obtained at the early period are bismuth oxides (Bi$_2$O$_3$), as determined by PXRD and EDX (Figure S4 (Supporting Information) and Figure 2h). When the reaction time was increased to 60 min, the hexagonal shape nanoplates grew up with the dominated PtBi phase (Figure 2c,g). After 90 min, the uniform hexagonal plates were obtained with the PtBi phase (Figure 2d,g). Further extension of the reaction time to 105 min or even 120 min did not result in any obvious morphological changes with the preserved PtBi phase, confirmed by the XRD patterns (Figure 2e–g). The compositional evolution from triangular/truncated triangular nanoplates to hexagonal of PtBi nanoplates was also verified by EDX, where the content of Pt constantly increased during the growth process, being consistent with the PXRD result (Figure 2h).

Here, this transformation from triangular/truncated triangular nanoplates to hexagonal PtBi nanoplates is a very interesting phenomenon. Theoretically, the reduction of Pt$^{4+}$ ions is easier than Bi$^{3+}$ under the same condition because the standard reduction potentials of Pt and Bi are +1.3 and +0.31 V, respectively.[24] While in the present synthesis, the triangular/truncated triangular bismuth oxides were first formed. According to the previous reports, CO acted as a key reducing and/or shape controlling agent due to its preferential absorption on Pt (100),[25–28] favoring the formation of Pt nanocubes or other Pt-based nanostructures when further introducing the second metal. Therefore, we believe that the preformation of bismuth oxides was largely credited to the strong binging of CO to Pt. That is why there are only ill-defined nanoplates could be observed in the absence of CO (Figure S5, Supporting Information). It is worth noting that only irregular nanoplates could be observed when phloroglucinol was absent with keeping other...
conditions be the same (Figure S6, Supporting Information), suggesting that the use of phloroglucinol as the coreducing agent is also critical for the successful synthesis of PtBi nanoplates because phenyl organic molecules can absorb on metal, oxides, and carbon materials.[29–31] For the combined adsorption effect of phloroglucinol and CO, the triangular/truncated triangular bismuth oxides grow up in a certain direction and transfer Pt and Bi into intermetallic phases during the growth process, finally leading to the formation of hexagonal nanoplates. Therefore, for the preparation of well-defined hexagonal PtBi nanoplates, proper amounts of precursor, reducing agent, as well as capping agent are necessary (Figures S7–S9, Supporting Information).

To demonstrate the excellent methanol tolerance of the obtained PtBi nanoplates, we first loaded the nanoplates on a carbon black (Vulcan XC72R carbon, C) by sonication and washed with acetic acid for two times. This procedure makes the PtBi nanoplates uniformly deposit on the carbon support (Figure S10, Supporting Information). Figure S11 (Supporting Information) shows the typical cyclic voltammogram (CV) curves of PtBi nanoparticles, PtBi nanoplates (Figure S12, Supporting Information), and the commercial Pt/C in N2-purged 0.1 M HClO4 at a sweep rate of 50 mV s⁻¹.

The obvious Pt-H oxidation/Pt-H adsorption regions are observed in the CV of commercial Pt/C, while none of them are shown in that of the PtBi nanoplates and PtBi nanoparticles.

The ORR tests of the PtBi nanoplates, PtBi nanoparticles, and the commercial Pt/C were performed in different O2-saturated 0.1 M HClO4 solutions containing 0, 0.1, and 0.5 M CH3OH at the rotation rate of 1600 rpm. To further compare the ORR performances between PtBi nanoplates, PtBi nanoparticles, and the commercial Pt/C, the mass loading of Pt was fixed at 2.0 µg for all the catalysts through ICP-AES. A comparison of ORR polarization curves of the commercial Pt/C, PtBi nanoparticles, and PtBi nanoplates is shown in Figure 3a–c. It is obvious that the onset potential and the oxygen reduction current density of the commercial Pt/C substantially decreased even in the presence of 0.1 M CH3OH. By contrast, the current density of PtBi nanoplates was largely maintained even in the presence of high-concentration CH3OH (0.5 M). The half-wave potential of PtBi nanoplates was kept at 0.84 V and with increasing the concentration of CH3OH from 0.1 to 0.5 M whereas under the same condition, that of the Pt/C decreased from 0.85 V to 0.61 V, which clearly indicates that the intermetallic PtBi nanoparticles have excellent CH3OH tolerance. Significantly, the PtBi nanoplates also show much higher ORR activity than the PtBi nanoparticle. As shown in Figure 3d, the mass activity of PtBi nanoplates is 1.04 A mgPt⁻¹, 4.7-fold higher than that of PtBi nanoparticles (0.22 A mgPt⁻¹) at 0.85 V versus reversible hydrogen electrode (RHE), and also much higher than recently reported PtBi nanomaterials.[15]

To verify the ORR catalytic pathway, the rotating-disk voltammetry experiments were carried out at different rotating speeds, as displayed in Figure 3e. These polarization curves show a typical larger current at a higher rotation speed, mainly due to the increased O2 diffusion on the electrode surface at the high speed.[32,33] The kinetic parameters were calculated by the Koutecky–Levich plots obtained from polarization curves at different potentials (Figure 3f). The corresponding Koutecky–Levich plots at various potentials are approximately linearity and near parallelism, suggesting the first-order reaction kinetic with respect to the concentration of dissolved oxygen and similar electron transfer number for ORR at different potentials.

Figure 3. ORR polarization curves of a) the commercial Pt/C, b) PtBi nanoparticles, and c) PtBi nanoplates. The insets of panels (a)–(c) show the half-wave potentials of a) the commercial Pt/C, b) PtBi nanoparticles, and c) PtBi nanoplates in the presence of CH3OH with different concentrations. d) The comparison of half-wave potential and mass activity of the commercial Pt/C, PtBi nanoparticles, and PtBi nanoplates (NA: no activity). e) ORR polarization curves of PtBi nanoplates at different rotation rates. f) Koutecky–Levich plots of PtBi nanoplates at different potentials.
HCOOH, and d) CO into three different O₂-saturated 0.1 M HClO₄ solutions, respectively. As shown in Figure 4b, after adding CH₃OH to the O₂-saturated electrolyte at 200 s, the PtBi nanoplates and PtBi nanoparticles showed stable current response whereas 80% of the current responses of the commercial Pt/C were lost. To further verify the antipoisoning ability of PtBi-based nanomaterials, the ORR measurements of PtBi nanoparticles, PtBi nanoparticles, and the commercial Pt/C in the presences of small molecules were also performed. After injecting HCOOH to the O₂-saturated electrolyte at 200 s, the Pt/C lost around 90% of the initial current instantaneously whereas the current loss of PtBi nanoparticles and PtBi nanoparticles was nearly negligible (Figure 4c). CO was also introduced into O₂-saturated electrolyte at 200 s. As shown in Figure 4d, the commercial Pt/C lost nearly 70% of the initial current but PtBi nanoparticles and PtBi nanoparticles showed a little decay during the initial 100 s after the introduction of CO, probably owing to the temporary decrease of O₂ concentration and adsorption of CO on the surface of PtBi nanoplates and PtBi nanoparticles. It is worth noting that the activity of PtBi nanoparticles and PtBi nanoparticles can self-recover within a short period of time (~5 min). We can conclude that the PtBi nanoplates possess excellent antipoisoning ability and catalytic selectivity, and also much higher ORR activity than PtBi nanoparticles, making them be the best Pt-based catalysts without any poison for fuel cell applications.

In order to obtain a deeper understanding of their tolerance abilities for CO, the CO stripping experiments were also carried out (Figure 5). A sharp peak was detected on the commercial Pt/C, ascribed to the oxidation of absorbed CO. However, the CO oxidation peaks on intermetallic PtBi nanoparticles and PtBi nanoparticles were dramatically restricted after exposure to CO. The voltammetric profiles were essentially unchanged, suggesting that the PtBi nanoparticles and PtBi nanoparticles own the excellent tolerance capability for CO.

The improved CO tolerance of the intermetallic PtBi nanoplates is probably attributed to the increased Pt–Pt distance induced by the addition of Bi. The Pt–Pt distance in ordered intermetallic PtBi is about 4.32 Å, largely distinct from 2.77 Å in pure Pt, owing to the formation of Pt–Bi bonding in the special NiAs type hexagonal structure, as reported in the approximate molecular orbital calculations.[35,36] This unique bonding structure can mitigate CO poisoning by reducing bridge sites and eliminating adsorption sites.[37] The XPS results also give several evidences about Pt–Bi bonding that the characteristic signals of Pt and Bi in PtBi nanoplates are greatly different from those in the pure Pt and Bi. As shown in Figure S3 (Supporting Information), the Pt 4f spectrum presents two distinct features at 74.1 eV (Pt 4f₇/₂) and 70.9 eV (Pt 4f₅/₂), slightly shifted to the lower locations compared with pure Pt (Pt 4f₇/₂ (74.5 eV) and Pt 4f₅/₂ (71.2 eV)).[38] Meanwhile, the Bi 4f region reveals that the peaks located at 164.1 eV and 162.0 eV correspond to the Bi 4f₇/₂ and Bi 4f₅/₂, respectively.

4.07 based on the slopes of Koutecky–Levich plots in the potential range from 0.45 to 0.65 V, suggesting that the ORR of PtBi nanoplates is dominated by a four-electron oxygen reduction process, similar to the commercial Pt/C. The durability of PtBi nanoplates, PtBi nanoparticles, and the commercial Pt/C toward ORR was then evaluated through the chronoamperometric (CA) measurement. As shown in Figure 4a, after 10 000 s CA test, the PtBi nanoplates still retained 87% of the initial current, whereas there was a nearly 20% and 55% current loss for PtBi nanoparticles and the commercial Pt/C, respectively, indicating PtBi nanoplates have much better stability than PtBi nanoparticles and the commercial Pt/C. The catalysts after the durability tests were also characterized by TEM and EDX. The morphology and composition of PtBi nanoplates were largely maintained (Figure S13, Supporting Information) while an aggregation and obvious aggregation were observed for PtBi nanoparticles (Figure S14, Supporting Information) and the commercial Pt/C (Figure S15, Supporting Information) under the identical condition, respectively.

The catalytic selectivity for the cathode reaction against the fuel oxidation is an important parameter for an efficient ORR electrocatalyst for fuel cell applications. In many cases, the small-molecule organic fuels (i.e., CH₃OH and HCOOH) could cross over from anode to cathode through the polymer electrolyte membrane, which may seriously compromise the whole cell performance.[33,34] Therefore, both PtBi nanoplates, PtBi nanoparticles, and the commercial Pt/C were subjected to test the antipoisoning ability in the presence of 0.5 M CH₃OH. As shown in Figure 4a, the PtBi nanoplates, PtBi nanoparticles, and the commercial Pt/C displayed a nearly negligible decay of current (≈5 min). We can conclude that the PtBi nanoplates possess excellent antipoisoning ability and catalytic selectivity, and also much higher ORR activity than PtBi nanoparticles, making them be the best Pt-based catalysts without any poison for fuel cell applications.
3. Conclusion

In summary, we demonstrate the first example on using colloidal chemistry method for creating the intermetallic PtBi nanoplates with regular hexagonal shape for achieving more efficient ORR catalysis with superior tolerance over the chemical fuels. The time-dependent morphology studies reveal that the synthetic evolution process of PtBi nanoplates was from triangular/truncated triangular bismuth oxides nanoplates to well-defined hexagonal nanoplates. The as-made intermetallic PtBi nanoplates exhibit excellent tolerance over the CH$_3$OH, HCOOH, and CO relative to the commercial Pt/C, which is of great importance to address the durability issue of the fuel cells. XPS studies reveal that the charge displacement resulting from Pt–Bi bonding probably contributed to the greatly enhanced tolerance. Moreover, the PtBi nanoplates also exhibited much enhanced electrocatalytic activity for ORR compared with PtBi nanoparticles due to its unique 2D nanostructure. The present work opens an exciting avenue to make a new class of high-performance ORR electrocatalyst with high stability and tolerance for future fuel cell applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bismuth, nanoplates, oxygen reduction reaction, platinum, tolerance

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Figure 5. CO stripping voltammetries of a) the commercial Pt/C, b) PtBi nanoparticles, and c) PtBi nanoplates recorded in 0.1 M HClO$_4$ solution at a scan rate of 5 mV s$^{-1}$ with (the first cycle) and without (the second cycle) a CO adsorbed adlayer. CO was dosed for 20 min before each measurement.

158.6 eV from Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ are slightly higher than the characteristic signals of Bi–Bi band (Bi 4f$_{5/2}$ (162.9 eV) and Bi 4f$_{7/2}$ (157.6 eV)), contributing to the charge displacement resulting from Pt–Bi bonding.$^{[39,40]}$
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