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Gram-Scale Synthesis of Carbon-Supported Sub-5 nm PtNi Nanocrystals for Efficient Oxygen Reduction

Minli Wang¹,², Xu Chen¹, Wenwen Xu¹, Zhongfeng Wang¹,², Peilei He¹,²,* and Zhiyi Lu¹,²,*

¹ Key Laboratory of Advanced Fuel Cells and Electrolyzers Technology of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China; wangminli@nimte.ac.cn (M.W.); chenxu@nimte.ac.cn (X.C.); xuwenwen@nimte.ac.cn (W.X.);
wangzhongfeng@nimte.ac.cn (Z.W.)
² College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China
* Correspondence: hepeilei@nimte.ac.cn (P.H.); luzhiyi@nimte.ac.cn (Z.L.)

Abstract: The preparation of a high performance and durability with low-platinum (Pt) loading oxygen reduction catalysts remains a challenge for the practical application of fuel cells. Alloying Pt with a transition metal can greatly improve the activity and durability for oxygen reduction reaction (ORR). In this work, we present a one-pot wet-chemical strategy to controllably synthesize carbon supported sub-5 nm PtNi nanocrystals with a ~3% Pt loading. The as-prepared PtNi/C-200 catalyst with a Pt/Ni atomic ratio of 2:3 shows a high oxygen reduction activity of 0.66 A mg⁻¹ Pt and outstanding durability over 10,000 potential cycles in 0.1 M KOH in a half-cell condition. The PtNi/C-200 catalyst exhibits the highest ORR activity, with an onset potential (E_onset) of 0.98 V and a half-wave potential (E_1/2) of 0.84 V. The mass activity and specific activity are 3.89 times and 9.16 times those of 5% commercial Pt/C. More importantly, this strategy can be applied to the gram-scale synthesis of high-efficiency electrocatalysts. As a result, this effective synthesis strategy has a significant meaning in practical applications of full cells.

Keywords: oxygen reduction; platinum alloy; sub-5 nm nanocrystals; electrocatalyst; gram-scale synthesis

1. Introduction

As a renewable energy source, fuel cells have been studied and developed by many researchers in recent years due to their high-energy density, environmental friendly attribute, and high efficiency [1–3]. For the electrodes of the fuel cells, catalysts play a crucial role in the efficiency of energy conversion, especially the sluggish kinetics of ORR at the cathode [4]. Platinum (Pt) as the cathode catalyst is generally considered as the most desirable and promising electrocatalyst to promote the ORR [5–8]. Nevertheless, to realize the large-scale commercial implementation of Pt catalysts in fuel cells, the following challenges need to be addressed: the low durability of catalysts, the high cost of Pt, and the sluggish kinetics of the ORR [9].

Recently, different strategies have been explored to reduce the platinum usage without compromising the ORR activity. First, engineering the structure of the Pt nanocrystals could tune the Pt coordination environment and exposed catalytic surface [10–12]. Nonetheless, some of the obtained catalysts are still suffering from a high cost and poor durability [13–15]. Second, alloying Pt with a less expensive 3d transition metal (Ni, Co, Cu, etc.) is a feasible method to improve the ORR intrinsic activity [16–20]. For example, Tian et al. reported that 1D bunched PtNi alloy nanocages with a Pt-skin structure displayed a high activity and durability for ORR [21]. Third, nonmetal element doping has been adopted to tune the electronic structure of Pt and Pd, such as boron, phosphorus, and sulfur [22–25]. However, the promoting effect of nonmetal doping is much lower than that of pure Pt or Pt-based alloy catalysts [26]. Nowadays, the strategies for improving the performance of the Pt
catalyst mainly focus on Pt alloying with transition metals. However, some reported Pt alloy catalysts have too large a particle size and a low Pt utilization, which are not suitable for fuel cell applications [27,28]. Meanwhile, it is still difficult to achieve the large-scale synthesis of Pt alloy catalysts due to the harsh experimental conditions in the preparation of the alloy structure [29]. As a result, the gram-scale synthesis of Pt alloy electrocatalysts with a smaller size is highly desirable to realize the commercial viability of fuel cells.

In this work, we present a facile and gram-scale synthesis of sub-5 nm PtNi alloy nanoparticles on carbon carriers (PtNi/C) via a one-pot wet-chemical approach. The formation of the PtNi alloy induced the Pt lattice contraction and lowered the d-band center of Pt, leading to a weaker adsorption of oxygen species. Benefiting from the PtNi alloy structure, the obtained PtNi/C shows excellent ORR activity, with a mass activity of 0.66 A mg\textsuperscript{pt}\textsuperscript{−1} and a specific activity of 2.13 mA cm\textsuperscript{−2} at the potential of 0.9 V vs. the reversible hydrogen electrode (RHE) in 0.1 M KOH, which are three times and nine times higher than those of 5% commercial Pt/C. The PtNi/C also shows a superior stability, with only a 5 mV negative shift after 10,000 potential cycles. This work may inspire new ideas for the gram-scale synthesis of a low-Pt electrocatalyst for the future practical application of fuel cells.

2. Materials and Methods

2.1. Chemicals and Reagents

Platinum(II) acetylacetonate (Pt(acac)\textsubscript{2}, 97%, Aladdin, Shanghai, China), nickel(II) acetylacetonate (Ni(acac)\textsubscript{2}, 95%, Aladdin, Shanghai, China), polyvinyl pyrrolidone (PVP, average MW = 8000, Aladdin, Shanghai, China), benzoic acid (C\textsubscript{6}H\textsubscript{5}COOH, ≥99.5%, Aladdin, Shanghai, China), carbon black (Vulcan XC-72, Cabot, Boston, MA, USA), benzyl alcohol (C\textsubscript{7}H\textsubscript{8}O, Aldrich, St. Louis, MO, USA), acetone (CH\textsubscript{3}COCH\textsubscript{3}, Sinopharm Chemical ReagentCo., Ltd., Shanghai, China.), ethanol (95%, Sinopharm Chemical ReagentCo., Ltd., Shanghai, China).

2.2. Electrocatalysts Synthesis

Synthesis of the PtNi/C catalysts. The PtNi/C-200 catalysts were prepared by a one-pot method. A total of 8 mg Pt(acac)\textsubscript{2}, 10.28 mg Ni(acac)\textsubscript{2}, 90 mg carbon black, 50 mg benzoic acid, 80 mg PVP, and 5 mL benzyl alcohol were added to a flask with magnetic stirring and heated to 200 °C in an oil bath with a ramp of 5 °C min\textsuperscript{−1}. The temperature was held at 200 °C for 12 h. Then, the flask was naturally cooled down to room temperature. The products were collected by centrifugation and washed with an ethanol/acetone mixture three times. Finally, the products were vacuum dried for 12 h. PtNi/C-150, PtNi/C-170, and PtNi/C-190 catalysts were synthesized by adjusting the reaction temperature to 150 °C, 170 °C, and 190 °C. PtNi/C-3:1, PtNi/C-2:1, PtNi/C-1:1, and PtNi/C-1:3 catalysts were synthesized by adjusting the amounts of nickel(II) acetylacetonate (Ni(acac)\textsubscript{2}) to 1.74, 2.61, 5.20, and 15.68 mg. For the synthesis of the PtNi nanocrystals, the procedures were the same as for the PtNi/C catalysts, except that carbon black was not added.

Gram-scale synthesis of PtNi/C catalysts. The G-PtNi/C-200 catalysts were prepared by a one-pot method. A total of 96 mg Pt(acac)\textsubscript{2}, 123.36 mg Ni(acac)\textsubscript{2}, 1080 mg carbon black, 600 mg benzoic acid, 960 mg PVP, and 60 mL benzyl alcohol were added to a flask with magnetic stirring and heated to 200 °C in an oil bath with a ramp of 5 °C min\textsuperscript{−1}. The temperature was held at 200 °C for 12 h. Then, the flask was naturally cooled down to room temperature. The products were collected by centrifugation and washed with an ethanol/acetone mixture three times. Finally, the products were vacuum dried for 12 h.

2.3. Material Characterization

X-ray diffraction (XRD, D8 DISCOVER, Brukerb, Salbrucken, Germany) patterns were collected using Cu K\textalpha radiation. Transmission electron microscopy (TEM, Talos F200x, ThemoFisher, Waltham, MA, USA) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Talos F200x, ThemoFisher, Waltham, MA, USA) were
used to characterize the PtNi/C catalysts. Energy dispersive X-ray spectroscopy (EDS, Talos F200x, ThermoFisher, Waltham, MA, USA) was used to analyze the composites of PtNi/C catalysts. The valence states of the elements on the PtNi/C catalysts were determined by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, Kratos, Manchester, England). Inductively coupled plasma optical emission spectrometry (ICP-OES, SPECTRO ARCOII, Kleve, Germany) was used to analyze the composition of the catalysts.

2.4. Electrochemical Characterization

The electrocatalytic activity and stability for the oxygen reduction reaction (ORR) were evaluated by an electrochemical workstation (CHI 760E, Shanghai ChenHua Instrument, Shanghai, China) with a classic three-electrode system. A glassy-carbon rotating disk electrode (RDE, Pine Research Instrumentation, Durham, NC, USA, diameter: 5 mm, area: 0.1963 cm²), a graphite rod, and a saturated calomel electrode were used as the working electrode, counter electrode, and reference electrode, respectively. The catalyst inks were prepared by dispersing 10 mg of the catalyst powder in 950 µL isopropanol containing 50 µL of 5 wt% Nafion solution under sonication for 30 min. A total of 5 µL of the ink was dropped onto the glassy carbon rotating disk electrode and dried in air. The Pt loading amounts of all PtNi/C catalysts on the glassy carbon rotating disk electrode were 7.64 µgPt cm⁻². For comparison, the commercial Pt/C catalyst (5 wt.%, Alfa Aesar, Shanghai, China) and the commercial Pt/C catalyst (20 wt.%, TANAKA, Tokyo, Japan) were used as benchmark catalysts with Pt loading with 12.73 µgPt cm⁻² and 50.94 µgPt cm⁻². Cyclic voltammograms (CV) were performed at the range of 0 to 1 V (vs. RHE) at a scan rate of 50 mV s⁻¹ in a 0.5 M H₂SO₄ N₂-saturated solution to measure electrochemically active surface area (ECSA). Alkaline electrochemical properties were tested in 0.1 M KOH. Linear sweep voltammograms (LSV) were conducted between 0 and 1 V (vs. RHE) at a scan rate of 10 mV s⁻¹ in 0.1 M KOH with saturated oxygen. The accelerated durability testing (ADT) was performed at room temperature by applying cyclic potential sweeps between 0.6 and 1.1 V vs. RHE at 200 mV s⁻¹ for 10,000 cycles.

3. Results

3.1. Characterization of PtNi/C Nanostructures

Firstly, PtNi alloy nanocrystals with a particle size of approximately 5 nm were synthesized using Pt(acac)₂ and Ni(acac)₂ (initial ratio 1:2) as precursors in which polyvinylpyrrolidone (PVP) acted as capping agents (Figure S1). In order to further reduce the Pt loading and enhance the mass transfer capacity, the carbon-supported PtNi alloy could be obtained by introducing a carbon carrier (Vulcan XC-72) into this system. As illustrated in Figure 1, PtNi/C was synthesized by a one-pot wet-chemical method (detailed experiments can be seen in the Section 2).

![Figure 1. Schematic illustration of the formation of PtNi/C.](image-url)
PtNi/C could be synthesized at 150, 170, 190, and 200 °C to obtain the PtNi/C-T samples (T = 150, 170, 190, and 200). As shown in Figure 2, the crystal structure of the as-synthesized PtNi/C was further explored by X-ray diffraction (XRD). The diffraction peak between 20° and 30° is consistent with the Vulcan XC-72 [30] (Figure S2). Compared with the standard Pt, all of the characteristic peaks shift to a higher angle due to the Pt lattice contraction after alloying with Ni. The lattice contraction of Pt is profitable to the adsorption and dissociation of the oxygen molecule, which could result in the improvement of the ORR performance [31]. It is clearly observed that characteristic peaks become stronger and narrower as the reaction temperature increases from 150 °C to 200 °C. As the temperature increases to 200 °C, the crystallinity of the PtNi alloy is much higher, verified by the sharp characteristic peaks in the XRD patterns. These control experiments reveal that the reaction temperature contributes significantly to the structural evolution of PtNi/C-T.

To further determine the structure of the PtNi/C, the as-synthesized PtNi/C-200 was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 3a,b, spherical nanoparticles with uniform particle size are carbon carriers. The high-resolution TEM (HRTEM) image (Figure 3c) shows that the lattice spacing is 0.216 nm, coinciding with the face-centered-cubic phase of the PtNi(111) plane. The lattice spacing of PtNi is contracted compared with Pt (Figure S3). The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image (Figure 3d) indicates that PtNi alloy nanoparticles are uniformly distributed on the carbon carrier. According to the size histogram in Figure 3e, more than 97% of the nanoparticles are smaller than 5 nm, and the nanoparticles in the range of 3–4 nm are predominant. The energy disperse spectroscopy (EDS) elemental mapping exhibits an even distribution of Pt and Ni elements throughout the particles, further indicating the formation of the PtNi alloy structure (Figure 3f). Furthermore, this synthesis protocol can also be realized for a 12-fold scale up, which can produce over 1 g of catalyst at one time (Figure 1). According to the XRD pattern, the product was consistent with those samples synthesized in small batches (Figure S4). Therefore, the present synthetic method allows for the synthesis of PtNi/C in a milligram-to-gram scale.

Figure 2. XRD patterns of PtNi/C at different reaction temperatures.
Then, inductively coupled plasma optical-emission spectrometry (ICP-OES) was used to determine the contents of Pt and Ni. The ICP-OES results indicate that the loading for Pt and Ni in the PtNi/C-200 are 3.04% and 1.29%, respectively (Table S1). The calculation results show that the atomic ratio of Pt to Ni is 2:3. The surface composition and electronic structure of the PtNi/C were investigated by X-ray photoelectron spectroscopy (XPS). As shown in Figure 4a, two major peaks at 71.3 eV and 74.7 eV are assigned to metallic Pt 4f\textsubscript{7/2} and Pt 4f\textsubscript{5/2}. The two peaks at 72.2 eV and 76.1 eV are assigned to the oxidation state of Pt. The Ni 2p XPS spectrum (Figure 4b) indicates that the surface Ni is dominated by an oxidation state, which is consistent with the previous study [32]. The peaks at 852.8 eV and 870 eV also show that a portion of the surface Ni is in a metallic Ni(0) state. The binding energy of PtNi/C-200 at Pt 4f\textsubscript{7/2} shows a positive shift relative to pure Pt (71.0 eV), which could be ascribed to the electron transfer from Ni to Pt, suggesting the downshift of the d-band center [26].
3.2. ORR Performance of PtNi/C

The electrocatalytic performance of PtNi/C for ORR was evaluated by the rotating disk electrode (RDE) in an O₂-saturated 0.1 M KOH solution at room temperature. In the beginning, we investigated the polarization curves of PtNi/C-T synthesized at different temperatures. As shown in Figure S5, the PtNi/C-200 exhibits the highest half-wave potential in alkaline electrolytes, suggesting that alloy nanoparticles with high-crystallinity contributed to a higher ORR activity. To explore the effect of the Pt/Ni atomic ratio on the ORR performance, the PtNi/C with various initial ratios were synthesized at 200 °C, designated as PtNi/C-3:1, PtNi/C-2:1, PtNi/C-1:1, PtNi/C-1:2, and PtNi/C-1:3, respectively (Figure S6). The metal content of these samples was evaluated by ICP-OES (Table S1). Among these samples, PtNi/C-1:2 exhibits the best oxygen reduction performance (Figure S7). The typical cyclic voltammetry (CV) curves of PtNiC-200 catalysts are shown in Figure S8. The considerable difference in onset and half-wave potential between these catalysts indicates that ORR activity is also determined by the metal contents of alloy nanoparticles. In addition, carbon carriers also have a great impact on the ORR performance of alloys [33]. Therefore, different carbon carriers (Ketjen Black and Vulcan XC-72) have also been adopted to synthesize carbon-supported sub-5 nm PtNi nanocrystals. Figure S9 shows the ORR polarization curves of PtNi/C with different carbon carriers. The polarization curves indicate that the Vulcan XC-72 supported PtNi nanoparticles have the best oxygen reduction performance. Therefore, the PtNi/C mentioned in the following paper is the sample synthesized at 200 °C, using Vulcan XC-72 as a carbon carrier with an initial Pt/Ni ratio of 1:2.

Figure 5a shows the ORR polarization curves of PtNi/C, 5%, and 20% commercial Pt/C. The half-wave potential of PtNi/C with a Pt loading of 3.04% exhibits a 60 mV positive shift compared with the 5% commercial Pt/C. The ORR performance has no attenuation after amplification (Figure S10). Therefore, the existence of Ni has improved the electrocatalytic activity of PtNi/C. The main reason is that the contraction of Pt lattice spacing is more conducive to weakening the binding between O/OH and Pt sites [34], and the strong electronic interaction between Pt and Ni atoms results in the downshift of the d center of the alloyed Pt, thus improving the electrochemical performance [35]. Furthermore, the fast ORR kinetics of the PtNi/C could be indicated by its lowest Tafel slope (77.08 mv dec⁻¹) among all of these catalysts (Figure 5b). In order to further investigate the reaction kinetics of PtNi/C, Figure 5c shows the ORR polarization curves at different rotation rates and Koutecky–Levich (K-L) plots [36]. The number of transferred electrons of PtNi/C is approximately four according to the K-L plots. This indicates that PtNi/C tends to be a four-electron oxygen reduction pathway in 0.1 M KOH.

To evaluate the intrinsic activity of different catalysts, the mass activity and specific activity were calculated by normalizing over the Pt mass and electrochemically active surface areas (ECSA) at 0.9 V vs. RHE [37]. The PtNi/C demonstrates a superior mass activity of 0.66 A mg⁻¹, which is much greater than that of 5% Pt/C (0.17 A mg⁻¹) and 20% Pt/C (0.22 A mg⁻¹). The ECSA of the catalysts measured by underpotentially deposited hydrogen [38] is shown in Figure S11. The ECSA of PtNi/C, commercial Pt/C-5%, and commercial Pt/C-20% electrocatalysts are determined to be 31.05 m² g⁻¹, 79.24 m² g⁻¹, and 54.76 m² g⁻¹, respectively. Meanwhile, the specific activity of PtNi/C reached 2.13 mA cm⁻², which is almost a tenfold higher activity than that of 5% Pt/C (0.23 mA cm⁻²). Obviously, the PtNi/C exhibits a higher mass activity and specific activity than the commercial Pt/C.
Furthermore, the electrochemical impedance spectroscopy (EIS) was employed to study the electrode kinetics during ORR processes, and the application of a Randles-type model was used as the equivalent circuit. Figure 5e shows the Nyquist plots of both bimetallic PtNi/C and Pt/C, featuring a depressed semi-circle shape. The smaller diameter of the semi-circle PtNi/C verifies that the PtNi/C would possess a lower charge transfer resistance $R_{CT}$ (25.79 Ω) and also enhanced ORR kinetics relative to the reference Pt/C (38.13 Ω), as listed in Table S2 and Figure S12.

In order to determine the ORR durability of the catalysts, we measured the ORR performance of different catalysts before and after 10,000 cycles of accelerated durability tests (ADTs). As shown in Figure 5f, PtNi/C exhibited an impressive durability, with only a 5 mV negative shift in the half-wave potential after 10,000 potential cycles in the alkaline electrolyte, which is much better than the 5% commercial Pt/C (Figure S13). A comparison of the electrochemical performance of PtNi/C and recently reported Pt-based electrocatalysts in the alkaline solutions is listed in Table S3. These findings demonstrate that the PtNi/C exhibits a greater long-term catalytic durability.

4. Conclusions

In conclusion, we report a facile method for the gram-scale synthesis of sub-5 nm PtNi nanocrystals on Vulcan XC-72 via a one-pot method to achieve a highly efficient and stable catalyst for ORR. As a result, with a much lower platinum loading of 3.04%, the obtained PtNi/C-200 exhibits an extraordinary ORR activity and outstanding durability over 10,000 potential cycles in 0.1 M KOH. Particularly, the specific activity and mass
activity of the PtNi/C are 9.16 and 3.89 times those of the 5% commercial Pt/C. The superior ORR performance of the PtNi/C originated from the exposure of PtNi(111) facets and Pt lattice contraction due to the incorporation of Ni atoms into the Pt lattice. This study provides a simple strategy for the future development of the gram-scale synthesis of Pt-based electrocatalysts, which might be conducive to the future practical application of low-Pt catalysts in fuel cells.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/met12071078/s1, Figure S1: TEM images of PtNi nanocrystals; Figure S2: XRD patterns of PtNi nanocrystals and Vulcan XC-72; Figure S3: HRTEM image of the initial Pt/C; Figure S4: XRD patterns of G-PtNi/C-200 nanocrystals; Figure S5: The ORR polarization curves of PtNi/C-150, PtNi/C-170, PtNi/C-190, and PtNi/C-200 catalysts were conducted in 0.1 M KOH with saturated oxygen; Figure S6: XRD patterns of PtNi/C-3: 1, PtNi/C-2: 1, PtNi/C-1: 1, PtNi/C-1: 2, and PtNi/C-1: 3 nanocrystals; Figure S7: The ORR polarization curves of Ni/XC-72, Pt/XC-72, PtNi/C-3: 1, PtNi/C-2: 1, PtNi/C-1: 1, PtNi/C-1: 2, and PtNi/C-1: 3 catalysts were conducted in 0.1 M KOH with saturated oxygen; Figure S8: The CV curves of PtNiC-200 catalysts; Figure S9: The ORR polarization curves of PtNi/Ketjen Black and PtNi/XC-72 catalysts were conducted in 0.1 M KOH with saturated oxygen; Figure S10: The ORR polarization curves of G-PtNi/C-200, PtNi/C-200 in O2-saturated 0.1 M KOH; Figure S11: ECSA of commercial Pt/C and PtNi/C-200 at 0.9 V (vs. RHE); Figure S12: Nyquist plots of PtNi/C-200 and commercial Pt/C; Figure S13: Long-term stability of commercial Pt/C (5 wt.% catalyst; Table S1: ICP-OES results for various PtNi/C samples; Table S2: Fitting data of EIS results of commercial PtNi/C-200 in 0.1 M KOH; Table S3: Comparison of the alkaline ORR activity of different Pt-based catalysts. References [39–46] are cited in Supplementary Materials.

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