Research Article

A Platinum Monolayer Core-Shell Catalyst with a Ternary Alloy Nanoparticle Core and Enhanced Stability for the Oxygen Reduction Reaction

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We synthesize a platinum monolayer core-shell catalyst with a ternary alloy nanoparticle core of Pd, Ir, and Ni. A Pt monolayer is deposited on carbon-supported PdIrNi nanoparticles using an underpotential deposition method, in which a copper monolayer is applied to the ternary nanoparticles; this is followed by the galvanic displacement of Cu with Pt to generate a Pt monolayer on the surface of the core. The core-shell Pd₁Ir₁Ni₂@Pt/C catalyst exhibits excellent oxygen reduction reaction activity, yielding a mass activity significantly higher than that of Pt monolayer catalysts containing PdIr or PdNi nanoparticles as cores and four times higher than that of a commercial Pt/C electrocatalyst. In 0.1 M HClO₄, the half-wave potential reaches 0.91 V, about 30 mV higher than that of Pt/C. We verify the structure and composition of the carbon-supported PdIrNi nanoparticles using X-ray powder diffraction, X-ray photoelectron spectroscopy, thermogravimetry, transmission electron microscopy, and energy dispersive X-ray spectrometry, and we perform a stability test that confirms the excellent stability of our core-shell catalyst. We suggest that the porous structure resulting from the dissolution of Ni in the alloy nanoparticles may be the main reason for the catalyst's enhanced performance.

1. Introduction

Although proton exchange membrane fuel cells (PEMFCs) are recognized as a promising form of technology to meet the global energy crisis and address various associated environmental problems, many technical and economic challenges prevent their large-scale commercialization, one of which is the high cost of platinum [1]. Despite the fact that numerous efforts have been paid to search for substitute materials for platinum, such as Pd [2], Ir [3], Ag [4], Au [5], Fe- and N-doped carbon catalyst [6], and carbon nanotube/Fe₃C nanoparticle [7], a platinum-based catalyst is still the best choice for oxygen reduction in an acidic environment. In recent years, the emergence of core-shell catalysts [8–12], especially those with a Pt monolayer [13–20], has brought PEMFC commercialization closer to becoming a reality, because the mass activity of Pt in a core-shell catalyst can be enhanced by several times. However,

most current core-shell catalysts still use precious metals (such as Pd [21, 22]) as the cores, and this makes it difficult to reduce the cost of catalysts effectively. To address this problem, some studies have introduced nonprecious metals into the alloy nanoparticles, yielding cores such as PdCo, PdNi, and PdFe [23–25]. However, catalyst stability has remained a problem. Kuttiyiel et al. reported that an electrocatalyst's stability could be significantly enhanced by adding a negligible amount of Au to the PdNi nanoparticle core [25]. Knupp et al. found that the stability of a Pd@Pt/C catalyst could be improved by adding iridium to the Pd core [26].

In this study, we prepared a Pt monolayer core-shell catalyst with a ternary PdIrNi alloy nanoparticle as the core using an underpotential deposition (UPD) method. As expected, this catalyst exhibited superior oxygen reduction reaction (ORR) activity to a commercial Pt/C catalyst as well as enhanced stability.

2. Experimental

2.1. Preparation of Carbon-Supported PdIrNi Nanoparticles. The carbon-supported ternary alloy nanoparticles were prepared as follows. Palladium chloride, iridium chloride, and nickel chloride in an atomic ratio of 1:1:2 were added to deionized water to obtain a solution. Next, sodium citrate was added as a complexing agent using a metal/citrate molar ratio of 1:5, after which carbon black XC-72R was added to the solution under strong stirring. After the mixture was purged with high-purity N_2 for 15 minutes, excess $NaBH_4$ solution (10 wt%) was slowly added, using ultrasonication and under the protection of nitrogen. After reaction with ultrasonication for one hour, the mixture was filtered and washed with deionized water three to five times and then dried overnight in a vacuum oven at 50°C. For comparison, binary nanoparticles of PdNi, IrNi, and PdIr were prepared using the same procedures. The metal content in each of the samples was 20 wt%.

2.2. Synthesis of Core-Shell Catalyst on Glassy Carbon Electrode by UPD. The Pt monolayer core-shell catalyst PdIrNi@Pt/C was prepared on a glassy carbon electrode using a UPD method. First, 5.0 mg carbon-supported ternary PdIrNi alloy nanoparticles were dispersed in 1 mL Nafion ethanol solution (0.1 wt%) via ultrasonication for 30 minutes to make a uniform suspension. Then, 5 μ L of the suspension was pipetted onto a glassy carbon disk electrode (5 mm diameter) and dried in air. Next, a Cu monolayer was deposited on the surface of the PdIrNi nanoparticles in a 0.05 M H_2SO_4 + 0.05 M $CuSO_4$ solution by holding the deposition potential at about 0.37 V for one minute, under the protection of high-purity nitrogen. Finally, the electrode was transferred into a solution of 1 mM K_2PtCl_4 + 0.05 M H_2SO_4 for 10 minutes in a nitrogen atmosphere, in which the Cu monolayer was galvanically replaced by Pt to form a Pt monolayer. The theoretical Pt content in the catalyst was calculated from the UPD charge of Cu, and the real content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

This prepared electrode bearing the core-shell structured catalyst was used for the subsequent electrochemical performance measurements without further treatment.

2.3. Measurement of the Catalysts' Electrochemical Performance. The electrochemical performance of the catalysts was measured by cyclic voltammetry (CV) on an electrochemical workstation (Ivium, Netherlands) using a three-electrode electrochemical cell. An Ag/AgCl/KCl (3 M) leak-free reference electrode and a Pt wire were used as the reference and counter electrodes, respectively. ORR and hydrogen underpotential deposition (HUPD) measurements were performed in 0.1 M $HClO_4$ solution saturated with oxygen and nitrogen at room temperature.

2.4. Catalyst Characterization. X-ray powder diffraction (XRD) patterns were obtained with a TD-3500 powder diffractometer (Tongda, China) using filtered Cu-K α

radiation operating at 40 kV and 30 mA. Scanning transmission electron microscope (STEM) images were recorded on a JEOL JEM 2100F operated at 200 kV. Thermogravimetric (TG) analyses were performed on a Q600 SDT analyzer (TA Inc., USA) in a pure nitrogen flow (100 mL min⁻¹) at a heating rate of 10°C min⁻¹ from room temperature to 950°C. X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra DLD X-ray photoelectron spectrometer (Kratos, England) employing a monochromated Al-K α X-ray source ($h\nu = 1486.6$ eV). ICP-AES (Leema PROFILE, America) was used to analyze the contents of trace metal elements.

3. Results and Discussion

3.1. Characterization. The structures of the as-prepared catalysts were characterized by XRD (Figure 1). The first peak, located at about 23.2°, refers to the Vulcan XC72 carbon support. The diffraction peaks at the 2θ values of 42.5° for the PdIrNi/C catalysts readily correspond to the (111) crystal planes of the face-centered cubic crystalline structure. As shown in Figure 1(a), the (111) diffraction peak of Pd₁Ir₁Ni₂@Pt/C has shrunk sharply and shifted negatively slightly (about 0.8°) compared to that of Pd₁Ir₁Ni₂/C; we suggest this is due to the dissolution of Ni from the alloy nanoparticles during the UPD process, and the results of the ICP-AES analysis confirm this explanation.

It should be pointed out that no diffraction peaks corresponding to Pt could be observed in the XRD pattern of Pd₁Ir₁Ni₂@Pt/C, perhaps because the Pt monolayer could not generate diffractions.

It is interesting that no diffraction peaks of Ni and Ir could be observed for the Pd₁Ir₁Ni₂/C sample, even though the Ni and Ir contents were up to 50 at % and 25 at %, respectively. There may be two reasons: (1) the Ni atoms entered the Pd lattice to form a complete alloy; (2) Ni formed an X-ray amorphous phase that will not be observed in the diffractogram. Figure 1(b) shows the XRD patterns of the PdIrNi/C catalysts with a Pd/Ir ratio of 1 and various Pd/Ni ratios. The lattice parameters of Pd₁Ir₁/C, Pd₂Ir₂Ni₁/C, Pd₁Ir₁Ni₂/C, and Pd₁Ir₁Ni₈/C were 3.873, 3.783, 3.688, and 3.681 Å calculated from the (111) diffraction plane by Jade software. The atomic radii of Pd, Ir, and Ni atoms are 1.37, 1.36, and 1.25 Å, respectively. When more Ni atoms entered into the Pd lattice, it can result in the decrease of the lattice parameter and the Pd–Pd interatomic distance because the radius of the Ni atom was smaller than that of the Pd atom [27]. Clearly, the (111) diffraction peak for the catalysts shifted positively as the Ni content increased, and the lattice parameters decreased obviously with the increase of the content of nickel.

Figure 2 presents TEM images of the Pd₁Ir₁/C, Pd₁Ir₁@Pt/C, Pd₁Ir₁Ni₂/C, and Pd₁Ir₁Ni₂@Pt/C catalysts. It can be observed that all of the nanoparticles were well dispersed on the carbon support without apparent aggregation either before or after the Pt deposition. The Pd₁Ir₁/C and Pd₁Ir₁Ni₂/C nanoparticles exhibited a rather narrow size distribution, in the range of 1–3.5 and 1.25–2.5 nm, with average diameters of about 2.2 and 1.7 nm, respectively, which are in agreement with the particle results predicted by XRD. On the basis of the high-resolution

FIGURE 1: (a) XRD patterns of the $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ and $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ catalysts. (b) XRD patterns of PdIrNi/C catalysts with different atomic ratios.

TEM (HRTEM) shown in Figures 2(b) and 2(f), there was a decrease of the lattice distance for $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ (0.22 nm) compared to that of $\text{Pd}_1\text{Ir}_1/\text{C}$ (0.225 nm), which can be explained by the addition of Ni. XRD measurements also demonstrated that lattice contraction occurred, as the (111) diffraction peak of $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ showed a slight positive shift compared to that of $\text{Pd}_1\text{Ir}_1/\text{C}$. The smaller size and better dispersion observed for $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ in comparison to $\text{Pd}_1\text{Ir}_1/\text{C}$ can be attributed to the addition of Ni to the alloy.

After the deposition of Pt, the $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ and $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ catalysts showed average diameters of ~ 2.85 and ~ 2.30 nm, respectively (see the size distributions provided in Figures 2(c) and 2(g)). The diameters of both nanoparticles increased by ca. 0.6 nm, indicating that the thickness of the Pt shell layer was ca. 0.3 nm, corresponding to a monolayer of Pt atoms. These results confirm the core-shell structure of $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ and $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$. To obtain a better distribution of Pd, Ir, Ni, and Pt in $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, we employed high-angle annular dark field (HAADF) imaging and conducted a line-profile analysis using STEM/energy dispersive spectroscopy (EDS). As shown in Figures 2(i) and 2(j), the profile analysis revealed a lower intensity of Pt at the center than at the PdIrNi edges, suggesting the formation of a core (PdIrNi)/shell (Pt) structure. The lattice distances were found to be 0.217 nm for $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ and 0.215 nm for $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ (Figures 2(d) and 2(h)), compared to 0.225 and 0.22 nm for $\text{Pd}_1\text{Ir}_1/\text{C}$ and $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$, respectively. The decrease of interplanar spacing was caused by the force between the core and the Pt shell.

The elements on the surfaces of the $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$, $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, and Pt/C catalysts were characterized by XPS. Figures 3(a) and 3(b) show the XPS survey spectra, and Figures 3(c)–3(h) show the Pd 3d, Ir 4f, and Pt 4f XPS spectra of $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$, $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, and Pt/C . The binding energy was calibrated by means of the C 1s

TABLE 1: Results of fitting the XPS spectra; values given in percentage of total intensity.

Sample	Concentration (%)						
	Pd 3d	Ir 4f	Ni 2p	Pt 4f	C 1s	O 1s	F 1s
$\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$	1.92	1.8	2	—	82.02	12.25	—
$\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$	0.48	0.46	—	0.37	54.58	9.04	34.42

peak energy of 284.56 eV. The results, given as percentages of total intensity, are presented in Table 1. It can be seen that $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ showed a decrease in Pd 3d and Ir 4f concentrations compared to $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$, even though the Pd/Ir ratio was almost unchanged. Ni was not detected in the $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ nanoparticles for two main reasons: first, most of the Ni nanoparticles leached out from the $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$; second, the strong F Auger (833.0 eV) covered the peak of the Ni nanoparticles. The best fits of the Pd (0) 3d spectra (Figure 3(a)) were obtained using two doublets (Pd $3d_{5/2}$ and $3d_{3/2}$) with a fixed doublet separation (DS = 5.2 eV). This method revealed that the binding energy of Pd (0) 3d (336.5 and 341.7 eV) in $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ experienced a positive shift of 0.3 eV compared with that of $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ (336.19 and 341.35 eV), and the binding energy of Ir (0) 4f (61.58 and 62.79 eV) in $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ underwent a positive shift of 0.2 eV compared with that of $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ (61.39 and 62.6 eV). What is more, a clear negative shift of ca. 0.3 eV in the binding energy of Pt 4f for $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ catalyst with respect to the 20% JM-Pt/C catalyst can be observed. These observations further confirmed the electron interactions involving the alloy core and Pt atoms within the $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ catalyst. The negative shift of the Pt 4f binding energy implied that the Pt nanoparticles can get electrons from the alloy core, leading to a weakened interaction between intermediate oxide species and Pt atoms that the ORR was improved [28].

FIGURE 2: Continued.

FIGURE 2: TEM images and the corresponding particle core size histograms (inset) of $\text{Pd}_1\text{Ir}_1/\text{C}$ (a), $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ (c), $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ (e), and $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ (g); the HRTEM images of $\text{Pd}_1\text{Ir}_1/\text{C}$ (b), $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ (d), $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ (f), and $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ (h); HAADF images of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ (i) and EDS analysis of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ (j).

3.2. Oxygen Reduction Reaction. Figure 4(a) shows the CV curves for $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$, $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, $\text{Pd}_1\text{Ir}_1/\text{C}$, and $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ in deaerated 0.05 M H_2SO_4 at a scan rate of 50 mV s^{-1} . $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ and $\text{Pd}_1\text{Ir}_1/\text{C}$ clearly exhibited almost the same CV curves, apart from the slight positive shift in the position of the metal oxide reduction peak in $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$; both had almost the same hydrogen reduction and oxidation peaks. Conversely, it is interesting that, in the case of $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ and $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ exhibited obviously larger hydrogen reduction and oxidation peaks than $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, and the reduction peaks of the surface metal oxide shifted from ca. 0.7 V to ca. 0.8 V, clearly confirming that Pt was covering the core nanoparticles. It is important that the electrochemical surface area (ECSA) of $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ ($147.7 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$) was higher than that of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ ($114.5 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$); however, the mass activity of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ was higher than that of $\text{PdIr}@\text{Pt}/\text{C}$, as we will discuss later. As shown in Figure 4(b), the deposition reduction peak and oxidation peak related to the Cu UPD can be observed on the $\text{Pd}_1\text{Ir}_1/\text{C}$ and $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ clearly. It is found that the peak area of $\text{Pd}_1\text{Ir}_1/\text{C}$ was higher than that of $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$. The theoretical Pt contents in $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ and $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ catalysts by calculating from the UPD charge of Cu were $6.31 \mu\text{g cm}^{-2}$ and $5.21 \mu\text{g cm}^{-2}$, respectively.

Figure 5 shows the ORR polarization curves of $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$, $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, $\text{IrNi}@\text{Pt}/\text{C}$, $\text{PdNi}@\text{Pt}/\text{C}$, and 20% JM-Pt/C at 1600 rpm in oxygen-saturated 0.1 M HClO_4 solution. The $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ exhibited the best ORR activity, even superior to that of commercial 20% JM-Pt/C. The Pt loading of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ was 5.24 nmol ($5.22 \mu\text{g cm}^{-2}$), and the PdIr loading was 24 nmol ($18.29 \mu\text{g cm}^{-2}$). The electrocatalyst's considerable activity was indicated by the high onset potential of O_2 reduction (0.9–1.05 V) as well as by the high half-wave potential

(885 mV at a rotation rate of 1600 rpm). The mass activity of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ was 1.5 times that of $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$ and over four times that of commercial 20% JM-Pt/C. Based on these results, we can conclude that (1) the high mass activity of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ may be strong evidence for the formation of a core-shell structured catalyst and (2) the addition of Ni may have played an important role in performance enhancement.

To further understand this excellent mass activity enhancement and the role of Ni, we measured the real composition of all the catalysts, as shown in Table 2. For $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ and $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$, the actual Pt contents were close to their theoretical contents: the deviations were $\sim 3.5\%$ for $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ and $\sim 13.7\%$ for $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$. For all of the samples containing Ni, we found that the Ni was almost totally removed during the scanning and UPD steps; for $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, the Ni residue was only $0.05 \mu\text{g cm}^{-2}$ catalyst, which was just 0.05% of the Ni in the $\text{Pd}_1\text{Ir}_1\text{Ni}_2/\text{C}$ sample, indicating 99.5% of the Ni had been removed during the UPD process [29]. Clearly, $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ contained less deposited Pt than $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$, and the UPD step removed the Ni, so why did $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ exhibit higher mass activity than $\text{Pd}_1\text{Ir}_1@\text{Pt}/\text{C}$? Since the lower Pt loading of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ indicates that Ni was not replaced with Pt, we suggest that the porous structure created by the dissolution of Ni may be the reason for the enhanced mass activity of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$.

Figure 6 shows the ORR polarization curves of the catalysts containing various amounts of Ni and of 20% JM-Pt/C at 1600 rpm in oxygen-saturated 0.1 M HClO_4 . These results confirm that $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ exhibited the best ORR performance, implying that higher or lower Ni content may not be beneficial.

Figure 7(a) shows the rotating disk electrode (RDE) measurements for the ORR on $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ in

FIGURE 3: Continued.

FIGURE 3: (a) XPS survey spectrum and corresponding high-resolution spectrum of (c) Pd 3d and (e) Ir 4f for Pd₁Ir₁Ni₂/C; (b) survey spectrum and corresponding high-resolution spectrum of (d) Pd 3d, (f) Ir 4f, and (g) Pt 4f for Pd₁Ir₁Ni₂@Pt/C; (h) Pt 4f in 20% JM-Pt/C.

FIGURE 4: (a) The cyclic voltammetry curves for Pd₁Ir₁/C, Pd₁Ir₁@Pt/C, Pd₁Ir₁Ni₂/C, and Pd₁Ir₁Ni₂@Pt/C, recorded in deaerated 0.05 M H₂SO₄ at a scan rate of 50 mV s⁻¹. (b) CV curves from Pd₁Ir₁/C and Pd₁Ir₁Ni₂/C in deaerated 0.05 M H₂SO₄ + 0.05 M CuSO₄ solution with a scan rate of 10 mV s⁻¹.

TABLE 2: Pt and Ni content determined by ICP-AES.

Sample	Actual Ni content (wt%)	Theoretical Pt content (wt%)	Actual Pt content (wt%)
Pd ₁ Ir ₁ Ni ₂ /C	5.06	—	—
Pd ₁ Ir ₁ Ni ₂ /C after 20 cycles	0.05	—	—
Pd ₁ Ir ₁ Ni ₂ @Pt/C	0.05	4.16	4.02
Pd ₂ Ir ₂ Ni ₁ /C	1.52	—	—
Pd ₂ Ir ₂ Ni ₁ /C after 20 cycles	0.33	—	—
Pd ₂ Ir ₂ Ni ₁ @Pt/C	0.31	5.98	4.57
Pd ₁ Ir ₁ @Pt/C	—	4.72	5.47

FIGURE 5: ORR polarization curves of PdNi@Pt/C, IrNi@Pt/C, Pd₁Ir₁@Pt/C, Pd₁Ir₁Ni₂@Pt/C, and 20% JM-Pt/C, each in 0.1 M HClO₄.

FIGURE 6: ORR polarization curves of the core-shell catalysts with various amounts of Ni added to the core and of 20% Pt/C, in 0.1 M HClO₄ solution.

oxygen-saturated 0.1 M HClO₄ at different rotation speeds (400–2500 rpm). The Koutecky-Levich plots obtained from Figure 7(a) with the inverse current density ($1/j$) as a function of the inverse of the square root of the rotation rate ($\omega^{1/2}$) are presented in Figure 7(b). Using the average slopes of the Koutecky-Levich plots and the equation $B = 0.62nFAD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}$ ($D_{O_2} = 1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 1.009 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, $C_{O_2} = 1.26 \times 10^{-3} \text{ mol L}^{-1}$, F is the Faraday constant, and A is the geometric area of the electrode) [30], we calculated that the electron transfer number, n , was 4.12, indicating that the ORR on Pd₁Ir₁Ni₂@Pt/C predominantly followed the four-electron exchange pathway. Moreover, the linearity and parallelism of the plots shown in Figure 7(b) are signs of first-order kinetics with respect to molecular oxygen [31]. The Tafel plot obtained from the kinetic current, j_k , is shown in the inset of

Figure 7(b). The plot is linear, with a slope of $\sim -68 \text{ mV dec}^{-1}$ above 0.80 V.

Figures 7(c) and 7(d) show the ORR curves at various rotation speeds on Ir₁Ni₂@Pt/C, and the K–L plots derived from the curves at various potentials. From the slopes of the K–L plots, the calculated electron transfer number is 4.30, revealing that the ORR on Ir₁Ni₂@Pt/C also followed the four-electron transfer pathway.

The values of the Tafel slopes of Ir₁Ni₂@Pt/C were about -70.2 and $-93.1 \text{ mV dec}^{-1}$, which differ from the slope of -68 mV dec^{-1} obtained for Pd₁Ir₁Ni₂@Pt/C [32]. The latter's lower Tafel slope may be attributed to the addition of Pd.

3.3. Stability. The Pd₁Ir₁Ni₂@Pt/C core-shell structured catalyst exhibited excellent stability, as shown in Figure 8(a). After 10,000 CV cycles in nitrogen-saturated 0.05 mol L^{-1}

FIGURE 7: ((a), (c)) Polarization curves of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ and $\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$, obtained with a rotating disk electrode for the ORR in 0.1 M HClO_4 solution. ((b), (d)) Koutecky-Levich plots at different potentials using the data obtained from $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ and $\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ (Figures 7(a) and 7(c)).

H_2SO_4 solution, the ECSA decay was only 9.4%, compared to 28.1% for commercial Pt/C . Furthermore, after 10,000 ORR scans, the ORR performance of $\text{Pd}_1\text{Ir}_1\text{Ni}_2@\text{Pt}/\text{C}$ was almost unchanged, whilst for commercial Pt/C and home-prepared $\text{Pd}@\text{Pt}$ catalyst the decay was 34.7% and 39.2%, respectively, indicating the outstanding stability of our core-shell structured catalyst with a Pt monolayer around a ternary alloy core.

4. Conclusions

A high-performance, highly stable core-shell structured catalyst with a Pt monolayer shell and a ternary alloy nanoparticle core has been successfully prepared via a UPD method, and the catalyst has been characterized using XRD, TEM, and XPS. The catalyst exhibited very high ORR activity and excellent stability. We found that the Ni added to the alloy played an important role in significantly enhancing the

ORR performance, and we suggest that the formation of a porous structure—caused by the dissolution of Ni in the alloy nanoparticles, which left only residual Ni nanoparticles—may be the main reason for the catalyst's enhanced performance. After 10,000 ORR scans, the half-wave potential was almost unchanged, indicating this catalyst's outstanding stability.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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FIGURE 8: (a) CV curves of Pd₁Ir₁Ni₂@Pt/C and 20% JM-Pt/C at initial scanning and after 10,000 scans in deaerated 0.05 M H₂SO₄ at a scan rate of 50 mV s⁻¹. (b) ORR curves of Pd₁Ir₁Ni₂@Pt/C, Pd@Pt/C, and 20% JM-Pt/C at initial scanning and after 10,000 scans.

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