Research Article

Ultrathin PtRu Nanowires as Efficient and Stable Electrocatalyst for Liquid Fuel Oxidation Reactions

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Direct liquid fuel cells (DLFCs) are promising clean energy conversion devices for their high energy density, low environmental pollution, and convenient transportation and storage. However, the commercialization of DLFCs is still limited by the lack of highly active and stable catalysts for the anodic oxidation of liquid fuels. Herein, a new class of ultrathin PtRu nanowires (NWs) with a diameter of 1.1 nm was synthesized via a colloidal chemistry strategy. The as-made ultrathin PtRu NWs can not only expose large active sites but also enhance the kinetics of methanol oxidation reaction, which was confirmed by the in situ Fourier transform infrared (FTIR) spectroscopy. Consequently, ultrathin PtRu NWs exhibit greatly boosted activity and stability for methanol and ethanol oxidation reactions in an alkaline medium.

1. Introduction

The development of environment-friendly and sustainable energy technologies is critical for the comprehensive transformation of energy structure from fossil fuels to renewable energy sources in the future [1–8]. Direct liquid fuel cells (DLFCs) technology provides a promising strategy to convert chemical energy into electric power [9]. Because the alcohol oxidation reaction is the basic anode reaction in DLFCs, developing highly efficient and stable electrocatalysts for alcohol oxidation reaction is the key to realize the commercialization of fuel cells [10]. Platinum-based nanomaterials have received intensive research interests due to their superior catalytic nature in alcohol oxidation reaction. Pt-based alloy electrocatalysts have extraordinary activities in terms of oxidation of alcohol fuels (methanol, ethanol, etc.) since various effects, such as crystal facets and ligand effects, are at play [11–14]. According to the research on poisoning resistance by Pt-based catalysts in anode reaction, PtRu bimetallic catalysts are recognized as the best-performing anti-CO-poisoning electrocatalysts to date [15, 16]. The introduction of oxophilic metal, Ru, can provide oxidation species and oxidize the CO adsorbed on the neighboring Pt sites at a low potential [17–20].

Generally, the activity of catalyst can be enhanced by increasing either the intrinsic activity or the number of active sites of catalyst [21–25]. Specifically, ultrathin Pt-based alloy nanowires (NWs) have exceptional surface area, flexibility, and abundant active facets. Therefore, they show favorable prospect for the above mentioned electrocatalytic reactions. In addition, introducing another element into the catalyst can effectively increase the number of active sites. Many reports have shown that PtRu nanocrystals exhibit a huge promise for excellent methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR) electrocatalytic activity [26–33]. Therefore, Ru can be introduced into Pt for its excellent properties in anode reaction of DLFCs. However, the large lattice mismatch between Pt and Ru leads to the difficulty in synthesizing uniform PtRu nanocrystals. Therefore, the design and synthesis of uniform PtRu nanocrystals with outstanding performance in alcohol oxidation reaction are of great significance.

Herein, we report a facile strategy to construct ultrathin PtRu nanowires (NWs), which combine the advantages of ligand effect and one-dimensional structure. The combined features make the ultrathin PtRu NWs more active and stable than commercial Pt/C for both MOR and EOR. The
ultrathin PtRu nanowires exhibit activities for the MOR (1.55 A mg\(^{-1}\)PtRu) and EOR (1.49 A mg\(^{-1}\)PtRu) which are 3.7 times and 3.6 times higher than those of commercial Pt/C (0.42 A mg\(^{-1}\)Pt for the MOR and 0.41 A mg\(^{-1}\)Pt for the EOR). The ultrathin PtRu NWs also exhibit higher stability than commercial Pt/C, making the catalyst a promising electrocatalyst for practical fuel cells. Furthermore, the ultrathin PtRu NWs/C show good stability for alcohol oxidation reactions with negligible activity decay over the durability tests.

2. Materials and Methods

2.1. Chemicals. Platinum (II) acetylacetonate (Pt(acac)\(_2\), 97%), tungsten hexacarbonyl (W(CO)\(_6\), 97%), glucose, cetyltrimethylammonium bromide (CTAB, >99%), dodecyltrimethylammonium bromide (DTAB), and stearyltrimethylammonium bromide (CTAB, >99%) were purchased from Sigma-Aldrich. Commercial Pt/C catalyst (20 wt% loading of Pt on carbon black), ruthenium (III) acetylacetonate (Ru(acac)\(_3\), 97%), and Nafion solution (5 wt%) were purchased from Alfa Aesar. Isopropanol, ethanol, and cyclohexane were supplied by the Beijing Tongguang Fine Chemicals Company. All chemicals were used without further purification.

2.2. Synthesis of Pt-Ru Nanowires and Pt Nanowires. In a typical synthesis of PtRu NWs, 10.0 mg Pt(acac)\(_2\), 50 mg Ru(acac)\(_3\), 40 mg W(CO)\(_6\), and 90.0 mg CTAB were dissolved in 50 mL of OAm, followed by sonication for 1 h to generate a homogeneous solution. Before the solution was cooled down to room temperature, the formed solution was kept at 220 °C for 5 h. The product was precipitated by centrifugation and washed five times with an ethanol/cyclohexane mixture. The preparation of Pt NWs follows the same procedure except the absence of Ru(acac)\(_3\).

2.3. Synthesis of Pt-Ru Nanowires/C and Pt Nanowires/C. The as-synthesized PtRu nanowires, 10 mL of cyclohexane, and commercial carbon supports (Ketjenblack-300J) (10 mg) were mixed together and sonicated for 2 h. The catalyst was collected by centrifugation and further washed with cyclohexane/ethanol (5/1 v/v) twice and subsequently washed with acetic acid stirred for 12 h at 75 °C to remove residual surfactants around the surface of nanocrystals. The final products were collected by centrifugation, washed with cyclohexane/ethanol (5/1 v/v) twice and dried under ambient conditions to obtain the PtRu NWs/C for further use. The Pt NWs/C were fabricated by the same procedure except the absence of Ru(acac)\(_3\).

2.4. Characterization. Low-magnification TEM and TEM-EDS were conducted on a FEI Tecnai-G2T20 at 200 kV. PXRD was collected using an X-ray diffractometer equipped with a Cu radiation source (\(\lambda = 0.15406 \text{ nm}\)). Elemental compositions of catalysts were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, Leeman Prodigy 7). XPS tests were carried out prior to the electrocatalysis with Thermo Scientific Escalab 250Xi. All binding energies were calibrated to C 1 s adventitious carbon at 284.8 eV.

2.5. Electrochemical Measurements. A three-electrode system was used to conduct the electrochemical measurements: saturated calomel electrode as reference electrode, Pt wire as counter electrode, and glassy carbon electrode (GCE) as working electrode (diameter 5 mm, area 0.196 cm\(^2\)). Typically, 1.0 mg of the as-synthesized PtRu NWs was dispersed in 5 mL of hexane, and 8.0 mg of commercial carbon supports (Ketjenblack-300J) was dispersed in 15 mL ethanol, followed by sonication for 1 h. These carbon-supported catalysts were then collected by centrifugation and redispersed in 10 mL of acetic acid, followed by heating at 70 °C for 12 h to remove the residual OAm. Shortly afterwards, the catalyst was washed, dried, and redispersed in a mixture of deionized water, isopropanol, and Nafion (v/v/v = 6/4/0.05). Next, 10.0 \(\mu\)L of the mixture (the concentration of the catalysts was 1.0 mg mL\(^{-1}\)) was pipetted onto GCE and dried under ambient conditions. The MOR measurements were conducted in 0.1 M KOH+0.5 M CH\(_3\)OH aqueous solution at a sweep rate of 50 mV s\(^{-1}\). The accelerated durability tests (ADTs) were performed at room temperature in 0.1 M KOH +0.5 M CH\(_3\)OH solution by sweeping cyclic potential cycles between 0.0 and 1.1 V (versus RHE) at a scan rate of 50 mV s\(^{-1}\) for 300 cycles. The electrochemical measurements of EOR follow the same protocol as the MOR except for the electrolyte. The ECSA was estimated by measuring the charge associated with \(H_{\text{upd}}\) adsorption (\(Q_{\text{H}}\)) between −0.2 and 0.1 V vs. SCE, ECSA = \(Q_{\text{H}}/(Q_{\text{H}}m)\). The \(Q_{\text{H}}\) value was assumed to be 210 \(\mu\)C cm\(^{-2}\) for the adsorbed monolayer of hydrogen on Pt surface. The \(H_{\text{upd}}\) adsorption charge (\(Q_{\text{H}}\)) could be determined by \(Q_{\text{H}} = 0.5Q\), where \(Q\) was the charge in the \(H_{\text{upd}}\) adsorption/desorption area obtained after double-layer correction.

3. Results and Discussion

The ultrathin PtRu NWs were synthesized via a colloidal chemistry approach by using platinum acetylacetonate (Pt(acac)\(_2\)) and ruthenium acetylacetonate (Ru(acac)\(_3\)) as the metal precursors, tungsten hexacarbonyl (W(CO)\(_6\)) and (1-hexadecyl) cetyltrimethylammonium bromide (CTAB) as the structure-directing agents, and oleylamine as the solvent. The mixture was then heated to 220°C for 5 h in an oil bath. The obtained black product was collected by centrifugation and washed with cyclohexane and ethanol for several times after it was cooled to room temperature. The morphologies and micro-structures of the PtRu NWs were observed by transmission electron microscopy (TEM). The ultrathin PtRu NWs were uniformly dispersed with the diameter of around 1.1 nm and an average length of 55 nm (Figures 1(a) and 1(b) and S1). The high-resolution TEM (HRTEM) image (Figure 1(c)) reveals that the ultrathin PtRu NWs have interplanar spacing of 0.23 nm, corresponding the (111) facets of the ultrathin PtRu NWs. The corresponding fast Fourier transform (FFT) pattern further confirms the presence of (111) facets of ultrathin PtRu NWs. The powder XRD patterns (Figure 1(d)) of the NWs display the typical face-centered cubic structure, which is associated with the alloyed PtRu nanomaterials. The PtRu...
atomic ratio is about 87/13 measured by EDX (Figure 1(e)), being in accordance with the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) results. The high-resolution X-ray photoelectron spectroscopy (XPS) of Pt 4f and Ru 3p shows the binding energies of 75.1 and 71.8 eV, assigned to the metallic Pt 4f\(^{5/2}\) and Pt 4f\(^{7/2}\) (Figure 1(f) and Table S1), and the binding energies of 485.7 and 463.6 eV, assigned to the metallic Ru 3p\(^{1/2}\) and Ru 3p\(^{3/2}\) (Figure 1(g)). Obviously, the majority of Pt and Ru atoms are in metallic states.

To understand the formation process of the ultrathin PtRu NWs, a series of intermediate products with different reaction times were investigated by TEM. At the initial state, PtRu nanoparticles with a size of 0.9 nm were formed (Figures 2(a) and 2(b)). When the reaction time reached 10 min, the nanoparticles grew into nanorods with a length of 14 nm and a diameter of 0.9 nm (Figure 2(c) and S2). The nanorods then gradually morphed into nanowires. After five hours of reaction, all nanoparticles and nanorods grew into ultrathin NWs (Figures 2(d)–2(g)). In addition, a set of control experiments were conducted to investigate the surfactants effect in the formation of the ultrathin PtRu NWs (Figure S3). We found that only nanoparticles were obtained without CTAB. When W(CO)\(_6\) was replaced by glucose, nanoflowers formed instead of NWs. Therefore, the W(CO)\(_6\) and CTAB played a crucial role in the formation of ultrathin PtRu NWs. Moreover, changing the alkyl chains of surfactants had no significant effect on the diameter of NWs, but the amount of surfactant and reducing agents can unidirectionally affect the diameter of nanowires (Figure S4-S6). These results reveal that the micelle concentration of surfactants and the powerful reductant affect the diameter of PtRu nanowires.

The as-made ultrathin PtRu NWs/C was explored as an electrocatalyst for monohydric alcohol oxidation reaction in alkaline medium. Before the electrochemical evaluation, the PtRu nanowires were loaded on commercial carbon support by sonication (Figure S7). Then, the catalyst was pretreated by applying consecutive cyclic potential cycles until the cyclic voltammogram (CV) curves became stable. For the MOR performance, CV curves (Figure 3(a)) were tested in N\(_2\)-saturated 0.1 M KOH solution containing 0.5 M methanol at a sweep rate of 50 mV s\(^{-1}\). The oxidation current densities of methanol are normalized over the noble metal loading.
amount determined by ICP-AES and electrochemically active surface areas (ECSA) to get the mass activity and specific activity, respectively. In order to study the relationship between size and electrochemical activity, we synthesized PtRu NWs with various diameters (1.1 nm, 1.4 nm, 1.6 nm, and 1.9 nm) (Figure S5&S6). The test results revealed that the electrochemical activity decreases with the increase of diameter and PtRu NWs with diameter of 1.1 nm exhibited best electrocatalytic performance (Figure S8). In order to explore the contribution of Ru to the electrochemical activity of PtRu nanowires, we compared the activity of PtRu nanowires and Pt nanowires. The mass activity of PtRu nanowires is 3.4 times that of Pt nanowires (Figure S9), indicating that the introduction of Ru into Pt NWs contributes to the increased MOR activity. And the mass activity of the ultrathin PtRu NWs/C for MOR is calculated to be 1.55 A mg$^{-1}$ Pt+Ru, which is 3.7 times higher than that of commercial Pt/C (0.42 A mg$^{-1}$ Pt). Additionally, the specific activity of the ultrathin PtRu NWs/C is 3.86 mA cm$^{-2}$, higher than that of Pt/C (1.16 mA cm$^{-2}$) (Figure 3(b)).

The operation durability is another critical parameter for the performance evaluation of electrocatalysts. In this work, the long-term stability of the ultrathin PtRu NWs/C was examined by the chronoamperometric (CA) measurements in 0.1 M KOH solution containing 0.5 M methanol performed at 0.8 V vs. RHE for 5000 s. A slightly slow decay of current density was observed for the ultrathin PtRu NWs/C. After 5000 s, the performance of the ultrathin PtRu NWs/C (0.53 A mg$^{-1}$ Pt+Ru) was much higher than that of commercial Pt/C (0.047 A mg$^{-1}$ Pt) (Figure 3(c)). The
Figure 3: Electrocatalytic performance of the ultrathin PtRu NWs and commercial Pt/C catalyst. (a) CVs of the ultrathin PtRu NWs/C and commercial Pt/C for MOR. MOR measurements were conducted in 0.1 M KOH+0.5 M CH₃OH solution at a sweep rate of 50 mV s⁻¹. (b) Mass activity and specific activity of as-prepared ultrathin PtRu NWs/C and commercial Pt/C for MOR in 0.1 M KOH+0.5 M CH₃OH solution at a sweep rate of 50 mV s⁻¹. (c) I-t curves recorded at 0.8 V vs. RHE.

Figure 4: In situ FTIR spectra of different catalysts. In situ FTIR spectra recorded from 0.10 to 1.20 V vs. RHE during MOR on commercial Pt/C (a) and on ultrathin PtRu NWs/C (b). Note that (c) and (d) were enlarged graph taken from (a) and (b).
ultrathin PtRu NWs/C outperforms most of these noble metal catalysts reported in alkaline medium (Table S2). Furthermore, after 300 cycles, a retention rate of 73% was obtained for the ultrathin PtRu NWs/C, much higher than that of commercial Pt/C (42%) (Figure S10).

In order to gain insightful understanding of the enhanced MOR performance on the ultrathin PtRu NWs/C, we employed in situ FTIR spectroscopy on different catalysts (Figures 4(a) and 4(b)). The upward band at 1100 cm\(^{-1}\) can be attributed to the C-O stretching vibration of methanol, indicating the consumption of methanol in oxidation. Distinct downward peaks at 1560 and 1380 cm\(^{-1}\) can be assigned to the produced formate ion (HCOO\(^-\)) and CO\(_3^{2-}\) (which can be assigned to carbonate), corresponding to the asymmetric and symmetric stretching band of O-C-O. The methanol oxidation in PtRu NWs/C occurs at a more negative potential than commercial Pt/C, revealing its accelerated reaction kinetics. In addition, the adsorption strength of the band at 1560 and 1380 cm\(^{-1}\) are obviously higher than that on commercial Pt/C (Figures 4(c) and 4(d)), indicating more intermediates in the electrolyte. Moreover, a peak at 2343 cm\(^{-1}\) belonging to CO\(_2\) (O-C-O asymmetric stretching) is observed. The CO\(_2\) is the final product of methanol oxidation, reflecting the complete oxidation of methanol. The final product CO\(_2\) is dissolved into the solution to produce carbonic acid, which reacts with the alkali in the solution to produce carbonate. The much lower potential at which CO\(_2\) appears in the FTIR spectra of PtRu NWs/C than that of commercial Pt/C manifests easier complete oxidation of methanol on the ultrathin PtRu NWs/C. It can be concluded that the ultrathin PtRu NWs/C can more effectively convert methanol to CO\(_2\).

We further studied the EOR performances of these catalysts. The ethanol oxidation performance of the ultrathin PtRu NWs/C was then evaluated in the N\(_2\)-saturated 0.1 M KOH solution containing 0.5 M ethanol (Figure 5(a)). The current density of the ultrathin PtRu NWs/C is 1.49 A mg\(^{-1}\) which is 3.6 times higher than that of commercial Pt/C (0.41 A mg\(^{-1}\)). Regarding the specific activity, the as-prepared ultrathin PtRu NWs/C (3.78 mA cm\(^{-2}\)) is much higher than commercial Pt/C (1.10 mA cm\(^{-2}\)) (Figure 5(b)). In addition, the PtRu NWs/C also has enhanced stability (Figure 5(c) and S11). The EOR activity of ultrathin PtRu NWs/C is among the best in most reported noble metal-based catalysts in alkaline medium (Table S3). These results collectively demonstrate that ultrathin PtRu NWs/C possess enhanced electrocatalytic activity toward electrode-oxidation reaction of various liquid alcohols.

4. Conclusion

To summarize, we have successfully synthesized ultrathin PtRu NWs with a diameter of 1.1 nm by co-reduction of the metal precursors in the presence of W(CO)\(_6\) and CTAB. The structure guiding effect of different surfactants and formation mechanism were systematically studied through control experiments and time-dependent study. ICP-AES, EDX, XPS, and XRD results revealed that binary PtRu NWs have fcc structure, and the atomic ratio is about 87/13. The as-prepared ultrathin PtRu NWs/C shows the ultrahigh mass activity toward MOR and EOR. The in situ FTIR results revealed that the ultrathin PtRu NWs/C can facilitate the kinetics of methanol oxidation reaction. The enhanced electrocatalytic properties of ultrathin PtRu NWs/C can be attributed to the ultrathin one-dimensional structure and the introduced Ru element. Overall, the ultrathin PtRu NWs/C not only mitigates the poisoning problem of the reaction intermediates toward MOR, but also demonstrates a general strategy to boost electrocatalytic performance of other liquid alcohols.

Data Availability

All data presented in the paper and the supporting information are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no competing interests.
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