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Pt Monolayers on Electrodeposited Nanoparticles of Different Compositions for Ammonia Electro-Oxidation

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Abstract: Pt monolayers (Pt_{ML}) supported on nanoparticles with different compositions (i.e., Ru, Rh, Pd, Ir, and Au) were synthesized by the surface-limited redox replacement of underpotentially deposited Cu monolayers on nanoparticle supports. Nanoparticle supports with different compositions were directly deposited on the conducting substrate by a clean and one-step electrodeposition method with controlled deposition potential and time. The whole synthesis process of the electrode was free of surfactants, binders, capping agents and reductants, and without an additional coating process of electrocatalysts. The results show that the specific activity (SA) of Pt_{ML} electrocatalysts depended strongly on the composition of the nanoparticle support. For example, the Pt_{ML} supported on the Au nanoparticle exhibited 8.3 times higher SA than that supported on the Ru and Pd nanoparticles. The change in the SA of the Pt_{ML} supported on different nanoparticles was related to the substrate-induced strain in the Pt_{ML} resulting from the lattice mismatch between the Pt_{ML} and the nanoparticle support. As the strain in the Pt_{ML} changed from the tensile strain to the compressive strain, the SA of the Pt_{ML} electrocatalysts decreased remarkably.

Keywords: Pt monolayer nanoparticles; electrocatalysts; ammonia oxidation; electrodeposition

1. Introduction

Growing concern in energy and environmental issues has stimulated considerable research on the electro-oxidation of ammonia, since it addresses both clean energy supply and removal of pollutants [1–6]. Ammonia is a carbon-free chemical energy carrier, which has a high capacity of hydrogen storage (17.7 wt.%) and high energy density (3000 Wh kg^{−1}) [1,7]. On the other hand, ammonia is an environmental pollutant and a toxic gas. Therefore, the electro-oxidation of ammonia has important applications in direct fuel cells [8–10], hydrogen production [1,11,12], ammonia decomposition in wastewaters [8,13] and electrochemical sensors for detecting ammonia [14]. Since ammonia electro-oxidation is a sluggish reaction, electrocatalysts are required to catalyze the oxidation of ammonia to N₂. Among various investigated electrocatalysts, Pt has been acknowledged as the most effective single-component electrocatalyst for ammonia electro-oxidation [15,16]. However, it is a limited resource and has high cost which been the main obstacles for wide usage of Pt [17–20], strongly limiting the large-scale applications of ammonia electro-oxidation technologies. Therefore,

great efforts have been paid to the development of Pt-based electrocatalysts with a high activity for ammonia electro-oxidation and simultaneously low Pt loading.

Developing Pt_{ML} catalysts is one of the most promising strategies because of its unique advantages, such as an extremely high utilization degree of Pt atoms and tunable activity through the electronic and structural effects between the Pt_{ML} and the substrate [15–18]. Adzic's group successfully developed a class of electrocatalysts consisting of a Pt_{ML} on different metals (e.g., Au, Pd, Rh, Ir, and Ru) [15,19,20], alloys (e.g., PdCo [21], PdFe [22], PdAu [23], IrNi [24], and AuNiFe [25]). Pt_{ML} electrocatalysts can be synthesized by deposition of a Cu monolayer on the substrate through underpotential deposition (UPD), followed by a surface-limited replacement reaction between Pt ions and Cu monolayer [26,27]. It has been well demonstrated that a Cu monolayer can be replaced by a Pt_{ML} [26]. Due to the high Pt utilization, the mass activity of these Pt_{ML} electrocatalysts could be more than an order of magnitude higher than traditional all-Pt electrocatalysts [15,18,27]. Since the catalytic activity of the Pt_{ML} electrocatalysts is strongly dependent on the interaction between the Pt_{ML} and the supporting substrate [18,19,28,29], it is of great interest to investigate the effect of the supporting substrate on the catalytic activity of electrocatalysts. Such studies are important for further enhancing the electrocatalytic activity of Pt_{ML} electrocatalysts by rationally selecting or designing substrate materials. To date, a number of characteristics of substrate materials, such as composition [19,30,31], crystalline orientation [20,21,28,31] and particle size [17,21], have been studied as Pt_{ML} electrocatalysts for oxygen reduction reactions and methanol electro-oxidation. However, there has so far been very limited work on Pt_{ML} electrocatalysts for ammonia electro-oxidation [18,32]. Previous work from our group synthesized the Pt_{ML} on an Au substrate (bulk Au electrode [32] or Au particles [18]) for ammonia electro-oxidation. These Pt_{ML} electrocatalysts exhibited several times, to a more than 10-fold increase, in the mass activity compared with the all-Pt electrocatalysts for ammonia electro-oxidation. It has also been found that the surface morphology of substrate material greatly influences the SA of Pt_{ML} electrocatalysts [18]. Nevertheless, the effect of the composition of the substrate on the catalytic activity of Pt_{ML} nanoparticles for ammonia electro-oxidation has remained unclear.

The purpose of the present work is to illustrate whether and how the composition of the substrate material would have an influence on the activity of the surface Pt_{ML} nanoparticles. For practical electrocatalytic applications, it is required to support Pt_{ML} on high surface area nanoparticles. Therefore, we investigated the activity of the Pt_{ML} on nanoparticles with various compositions including Ru, Rh, Pd, Ir and Au. A clean, facile and one-step electrodeposition method was proposed to synthesize nanoparticles with different compositions as the supporting core, synthesized directly on the surface of conducting substrate. Pt_{ML} was synthesized on the surface of these nanoparticles by a well-established method, consisting of Cu UPD on nanoparticles and subsequently the galvanic replacement of Pt [15,33]. The entire synthesis process was free of any surfactants, binders, capping agents and reductants, ensuring an extremely clean surface of electrocatalysts. In addition, the electrocatalysts were synthesized directly on the conducting substrate surface, avoiding the transfer process of the electrocatalysts. This greatly decreases the uncertainty resulting from the synthesis procedures, allowing the truly comparison of the impact of the composition of the supporting core on the electrocatalytic activity of the supported Pt_{ML}. Furthermore, the relationship between the composition of the nanoparticle core of Pt_{ML} electrocatalysts and the electrocatalytic activity for the ammonia oxidation was investigated by cyclic voltammetry (CV). To the best of our knowledge, this is the first time to report the synthesis of Pt_{ML} electrocatalysts with nanoparticle core of different compositions by the electrochemical method as well as the compositional effect of the core materials on the activity of Pt_{ML} electrocatalysts for electro-oxidation of ammonia. Interestingly, this study shows that the composition of the nanoparticle core had a great influence on the intrinsic activity of Pt_{ML} electrocatalysts.

2. Results and Discussion

Figure 1a–e shows the SEM images of electrodeposited Ru, Rh, Pd, Ir, and Au nanoparticles, respectively. It can be seen that all these deposited nanoparticles were randomly distributed over the surface of the glassy carbon electrode (GCE). Due to the different nature of these five metals, it is very difficult to obtain different kinds of nanoparticles with exactly the same particle size. As mentioned in the experimental part, preliminary work has tried various electrodeposition parameters including potentials and times, and finally found the optimal conditions to synthesize these five kinds of nanoparticles with a similar particle size. The particle size distribution histograms in insets of Figure 1 show that the average particle sizes for electrodeposited Ru, Rh, Pd, Ir, and Au nanoparticles were 34.2 ± 7.9 nm, 15.2 ± 3.2 nm, 18.8 ± 1.7 nm, 24.2 ± 2.9 nm, 21.4 ± 5.1 nm, respectively. It was also noticed that much larger overpotential (i.e., more negative deposition potential) was required for the electrodeposition of Ru and Ir compared to other metals. Similar results have also been reported by previous studies for the electrodeposition of Ru [34] and Ir [35], due to the slow kinetics for their deposition. For example, Le Vot et al. [35] reported that the deposition of Ir on GCE required a large overpotential for the reduction of Ir^{3+} ions in 1.0 mM $\text{IrCl}_3 + 0.5$ M H_2SO_4 solution. In their work, the lowest deposition potential was -0.6 V (vs. Ag/AgCl). The Ir deposits electrodeposited at this potential were characterized by large aggregates at several micrometers in size, indicating that the deposition process was very slow, and Ir tended to be deposited on previously formed Ir deposits than on the carbon substrate [35]. However, in the present work, Ir nanoparticles with good dispersion and small particle size of 24.2 ± 2.9 nm could be obtained at a further decreasing deposition potential of -0.7 V (vs. reversible hydrogen electrode (RHE)) in 5 mM $\text{IrCl}_3 + 0.05$ M H_2SO_4 solution (Figure 1d). Such well-dispersed Ir nanoparticles are beneficial for increasing the effective surface area.

Figure 1. Scanning electron microscopy (SEM) images of (a) Ru, (b) Rh, (c) Pd, (d) Ir, and (e) Au nanoparticles electrodeposited on the GCE, respectively. Insets of SEM images show the corresponding particle size distribution histogram.

Figure 2a–e shows the cyclic voltammetry (CV) curves of pure Ru, Rh, Pd, Ir, and Au nanoparticles electrodeposited on the GCE in 0.5 M H₂SO₄ solution at a scan rate of 0.05 V s^{−1}. Rh, Ir and Pd nanoparticles showed characteristic hydrogen adsorption and desorption (0.05 to 0.2 V (vs. RHE)) peaks while no such hydrogen adsorption/desorption peaks could be observed for Au and Ru nanoparticles. All these CV curves exhibited very similar features compared to previously reported nanoparticles synthesized by a water-in-oil microemulsion method [36].

Figure 2. CVs measured on pure (a) Ru, (b) Rh, (c) Pd, (d) Ir, and (e) Au nanoparticles electrodeposited on the GCE in 0.5 M H₂SO₄ solution at 0.05 V s^{−1}, respectively.

Figure 3a–e shows CVs measured on pure Ru, Rh, Pd, Ir, and Au nanoparticles electrodeposited on the GCE in 0.1 M ammonia + 1 M KOH aqueous solution at 0.05 V s^{−1}. Only for Ir nanoparticles did the CV curve exhibited an anodic current peak at 0.59 V (vs. RHE) (Figure 3d). Such an oxidation current peak has been extensively reported on pure Ir and also Pt electrodes and is ascribed to the electro-oxidation of ammonia to N₂ [12,13,37]. Previous work performed CV measurements in the absence of ammonia and found that a such characteristic current peak did not appear [13,37,38]. For 4d transition metals (i.e., Ru, Rh and Pd), all CV plots showed no anodic oxidation current peak related with the ammonia electro-oxidation from 0.4 to 0.7 V (vs. RHE). This is in good agreement with previous results reported by de Vooy et al. [13] and Vidal-Iglesias et al. [36]. Based on differential electrochemical mass spectroscopy (DEMS) measurements, de Vooy et al. [13] found the dehydrogenation of ammonia occurred at significantly lower potentials on Ru, Rh and Pd than that on Pt and Ir, resulting in the surface poisoning by adsorbed nitrogen atoms (N_{ads}) at much lower potentials on Ru, Rh and Pd. As a result, Ru, Rh and Pd were inactive towards the ammonia electro-oxidation to N₂ [13]. It was also observed that the peak height at 0.2 V (vs. RHE) for Rh nanoparticles (Figure 3b) is remarkably higher compared to other metals. This agrees well with previous studies reported by Cooper et al. [39], which attributed such peak to the OH[−] adsorption by Rh.

Figure 3. CVs of the ammonia electro-oxidation on pure (a) Ru, (b) Rh, (c) Pd, (d) Ir, and (e) Au nanoparticles electrodeposited on the GCE in aqueous solution containing 1 M KOH + 0.1 M ammonia at 0.05 V s^{-1} , respectively.

Figure 4a–e shows anodic stripping voltammograms of Cu UPD adlayer on synthesized Ru, Rh, Pd, Ir and Au nanoparticles on the GCE, respectively. All these curves showed typical Cu UPD stripping peaks. The amount and the corresponding surface area of the UPD Cu layer could be estimated from the stripping charge of the UPD Cu, as calculated by integrating the area covered by the Cu stripping current peak after subtracting the background [33,40,41]. To achieve the formation of Pt_{ML} on those metal nanoparticles, the GCE was immersed into 5 mM K_2PtCl_4 and 0.05 M H_2SO_4 solution for the galvanic replacement of the surface Cu monolayer by Pt ions. Assuming that the Faraday efficiency of the replacement reaction between the UPD Cu and Pt ions is 100%, the amount and the corresponding surface area of the formed Pt can be calculated based on the amount of UPD Cu monolayer. The corresponding surface area of Pt can also be measured by the stripping charge of Cu UPD monolayer, assuming $480 \mu\text{C cm}^{-2}$ for Pt_{ML} [19,42]. The calculated data of the Cu stripping charge, Cu amount, Pt amount and Pt surface area are summarized in Table 1.

Figure 4. Anodic stripping voltammograms after Cu UPD on electrodeposited (a) Ru, (b) Rh, (c) Pd, (d) Ir and (e) Au nanoparticles on the GCE, respectively.

Table 1. Calculated values of the Cu stripping charge, Cu amount, Pt amount and Pt surface area.

Composition of Nanoparticle Supports	Cu Stripping Charge (μC)	Cu Amount (μg)	Pt Amount (μg)	Pt Surface Area ($\text{cm}^2 \mu\text{g}^{-1}$)
Ru	70.45	0.023	0.071	0.147
Rh	50.48	0.017	0.051	0.105
Pd	60.98	0.020	0.062	0.127
Ir	54.68	0.018	0.055	0.114
Au	43.98	0.015	0.044	0.092

Figure 5a–e shows the transmission electron microscopy (TEM) images of Pt_{ML} nanoparticles with Ru, Rh, Pd, Ir, and Au cores, respectively. As a result of TEM sample synthesis, which is required to strip nanoparticles from GCE and then to transfer them to the Cu grid, it is unavoidable to result in the agglomeration of nanoparticles. Therefore, it could be seen that Pt_{ML} nanoparticles with different composition cores were not dispersed uniformly, showing some extent of agglomeration (Figure 5) compared to freshly electrodeposited core nanoparticles (Figure 1). Nevertheless, it is clear that the overall structure of a single Pt_{ML} nanoparticle with different composition cores consisted of the smaller, interconnected nanoparticles, suggesting a large surface area. Obviously, the Pt_{ML} nanoparticles with different composition cores observed in SEM images (Figure 1) were composed of interconnected smaller nanoparticles. The insets of Figure 5 show the corresponding small nanoparticle size distribution histograms. It could be seen that the average nanoparticle sizes of the small Pt_{ML} nanoparticles with Ru, Rh, Pd, Ir, and Au cores were approximately 4.1 nm, 5.0 nm, 2.6 nm, 4.9 nm and 4.4 nm respectively (the insets of Figure 5), and all of which had narrow nanoparticle size distribution.

Figure 5. TEM images of Pt_{ML} particles with (a) Ru, (b) Rh, (c) Pd, (d) Ir, and (e) Au cores electrodeposited on the GCE, respectively. Insets of TEM images show the corresponding particle size distribution histogram.

Figure 6a–e shows CVs measured on Pt_{ML} nanoparticles with different core compositions in 0.5 M H₂SO₄ solution at a scan rate of 0.05 V s^{−1}. Compared to Figure 2, a significant change in the electrochemical behavior could be observed after applying a Pt_{ML} on nanoparticles. All CV profiles had typical voltammetric characteristics of Pt in H₂SO₄ aqueous solution, showing characteristic potential regions including the hydrogen adsorption/desorption region from 0.05 to 0.3 V(vs. RHE) and the double-layer region from 0.3 to 0.85 V(vs. RHE) [43]. It has been extensively reported that the hydrogen desorption profile on pure polycrystalline Pt is characterized by two well-separated anodic peaks [5,36,44,45]. However, Pt_{ML} nanoparticles showed only one relatively broad anodic peak in the hydrogen desorption region. Similar results have also been widely reported by previous studies, which is attributed to the interaction between the Pt_{ML} and the substrate [32,46–49]. The above results provide clear evidence of the formation of the Pt_{ML} on these nanoparticles. Generally, the electrochemically active surface area of pure Pt can be estimated from the CV based on the charge related with the hydrogen desorption [50–53]. However, in the case of Pt_{ML} nanoparticles, the hydrogen desorption profile would be affected due to the interaction between underlying core particles and the Pt_{ML}, therefore it is possibly not accurate to calculate the effective surface area of Pt. Therefore, previous studies, including the present work, used the amount of Cu monolayer to estimate the Pt surface area assuming the complete replacement of Cu by Pt (Table 1).

Figure 6. CVs measured on (a) Pt_{ML}/Ru nanoparticles, (b) Pt_{ML}/Rh nanoparticles, (c) Pt_{ML}/Pd nanoparticles, (d) Pt_{ML}/Ir nanoparticles, and (e) Pt_{ML}/Au nanoparticles on the GCE in 0.5 M H₂SO₄ solution, respectively.

To investigate the electrocatalytic activity for the electro-oxidation of ammonia, Figure 7a shows the CVs measured on five different Pt_{ML} covered nanoparticles in 0.1 M ammonia + 1 M KOH. In order to reveal the SA, the current was normalized by the effective electrochemical surface area. Compared to observed CVs on bare nanoparticles (Figure 3), applying a Pt_{ML} on these nanoparticles resulted in an obvious change of CV curves. All five CV curves showed a current peak around 0.7 V (vs. RHE) on the positive sweep, which is a typical feature of ammonia electro-oxidation on Pt as previously discussed. This again confirms the successful deposition of Pt on various nanoparticles by the replacement of UPD Cu. It is worth noticing that the SA of Pt_{ML} covered nanoparticles strongly depends on the composition of core nanoparticles, which can be clearly seen in Figure 7b. The SA for electro-oxidation of ammonia decreases in the following order: Pt_{ML}/Au nanoparticles > Pt_{ML}/Ir nanoparticles $\approx$ Pt_{ML}/Rh nanoparticles > Pt_{ML}/Ru Nanoparticles $\approx$ Pt_{ML}/Pd nanoparticles. Pt_{ML} supported on Au nanoparticles showed the highest SA, which was about 8.3 times higher than that on Ru and Pd nanoparticles. In addition, compared to other Pt-based catalysts reported in previous work, the obtained Pt_{ML}/Au nanoparticles exhibited relatively high SA for electrooxidation ammonia and Pt surface area among the various catalysts (Table 2). As a typical representative, as-prepared Pt_{ML}/Au nanoparticles are provided in Figure 7c since it exhibited highest SA among the obtained catalysts. The high-resolution transmission electron microscopy (HRTEM) image showed the clear lattice fringes indicating a high crystallinity of the Pt_{ML}/Au nanoparticles, and it also revealed that the Pt_{ML}/Au nanoparticles were composed of multiple crystalline domains, suggesting a polycrystalline structure. The widely accepted mechanism of ammonia electro-oxidation on Pt was proposed by Gerischer and Mauzer [54], involving dehydrogenation of NH_{3,ads} to NH_{x,ads} (x = 1 or 2) intermediates and N_{ads}. The partially dehydrogenated NH_{2,ads} species are key precursors to promote the formation of N₂H₄ that is then dehydrogenated quickly to N₂ [54]. This mechanism has been later confirmed by

experimental methods [55,56] and density functional theory calculations [57], supporting that NH_2 species are active intermediates, and therefore a Pt surface with a higher binding energy of NH_2 intermediates has higher activity for ammonia electro-oxidation. Previous studies found that due to the lattice mismatch between the Pt_{ML} and the substrate, different level of tensile or compressive strain is exerted on the Pt_{ML} depending on the substrate material [19]. For example, Au exerts a tensile strain on Pt_{ML} (over 4%) while other metals such as Pd, Ru and Rh exert on it a compressive strain (about $-2 \sim -4\%$) [19]. This affects the binding abilities of the Pt_{ML} and thus changes the surface activity. In consistence with theoretical calculations [58,59], Li et al. [19] demonstrated that the tensile surface strain in the Pt_{ML} (e.g., Pt_{ML} supported on Au) tends to upshift the weighted center of the d-band (ε_d) in energy and thus increases the binding of CO and OH. This contributes to a significant enhancement in the activity of the Pt_{ML} on Au towards electrocatalytic oxidation of methanol and ethanol [19]. On the contrary, Pt_{ML} on other substrates (i.e., Ru, Rh, Ir and Pd) is under compressive strain, resulting in decreased activity for the electro-oxidation of methanol and ethanol [19]. It is interesting to note that the substrate-induced surface strain effect on activity was also been found in the present work. For example, the Pt_{ML} supported on electrodeposited Au nanoparticles showed significantly higher SA compared to that supported on electrodeposited Pd and Ru nanoparticles. Similarly, the tensile surface strain in the Pt_{ML} induced by the substrate Au is expected to increase the binding of the Pt_{ML} for active intermediates such as NH_2 to activate ammonia electro-oxidation and thus improves the SA. On the contrary, Pd and Ru nanoparticles exert a compressive strain on the Pt_{ML} [19] and therefore they have an opposite effect compared to Pt_{ML} on Au, exhibiting low specific activities among all investigated Pt_{ML} nanoparticles. However, it was noticed that Pt_{ML} on electrodeposited Rh and Ir nanoparticles had remarkably higher activity than those on Pd and Ru nanoparticles despite of the compressive strain exerted by Rh or Ir on Pt, which is different with that reported by previous studies [19]. This was due to the positive synergistic effect between Pt and Rh or Ir. Cooper et al. [39] pointed out that the presence of Rh along with Pt will increase active sites on the Pt surface for ammonia electro-oxidation. The synergic effect of Ir to Pt has also been reported by previous studies, which was attributed to the ability of Ir to dehydrogenate ammonia molecules at lower potentials [36,60,61]. Our results agree well with these studies [36,39,60].

Figure 7. (a) CVs of the ammonia electro-oxidation on Pt_{ML} supported on Ru nanoparticles, Rh nanoparticles, Pd nanoparticles, Ir nanoparticles, and Au nanoparticles on the GCE in aqueous solution containing 1 M KOH + 0.1 M ammonia at 0.05 V s^{-1} , respectively. (b) Comparison of the SA of Pt_{ML} supported on Ru nanoparticles, Rh nanoparticles, Pd nanoparticles, Ir nanoparticles, and Au nanoparticles on the GCE. (c) HRTEM image of as-prepared Pt_{ML} /Au nanoparticles.

Table 2. Comparison of SA for ammonia electro-oxidation and Pt surface area of as-prepared electrocatalysts with previous work.

Electrocatalyst Type	Test Protocol ^[a]	Pt Surface Area ^[b] (cm ² μg ^{−1})	SA ^[c] [mA cm ^{−2}]	Reference
Pt _{ML} /Au nanoparticles	0.1 M NH ₃ and 1 M KOH aqueous solution, scan rate 10 mV s ^{−1}	0.092	0.29	this work
Pt _{0.8} Ru _{0.2} alloy	1 M NH ₃ and 1 M KOH aqueous solution, scan rate 10 mV s ^{−1}	-	0.21	[62]
Pt _{0.8} Ni _{0.2} alloy	1 M NH ₃ and 1 M KOH aqueous solution, scan rate 10 mV s ^{−1}	-	0.12	[62]
Polycrystalline Pt	1 mM NH ₃ and 0.1 M NaOH aqueous solution, scan rate 10 mV s ^{−1}	-	0.12	[63]
Pt ₈₀ Ru ₂₀ nanoparticles	0.1 M NH ₃ and 0.2 M NaOH aqueous solution, scan rate 10 mV s ^{−1}	-	0.05	[36]
Pt ₇₅ Rh ₂₅ nanoparticles	0.1 M NH ₃ and 0.2 M NaOH aqueous solution, scan rate 10 mV s ^{−1}	-	0.15	[36]
Pt ₈₀ Pd ₂₀ nanoparticles	0.1 M NH ₃ and 0.2 M NaOH aqueous solution, scan rate 10 mV s ^{−1}	-	0.11	[36]
Polycrystalline Pt electrode	1 mM NH ₃ and 0.1 M NaOH scan rate 50 mV s ^{−1}	-	0.25	[64]
Pt thin films with preferential (100) orientation	0.1 M NH ₃ and 0.2 M NaOH aqueous solution, scan rate 1 mV s ^{−1}	-	0.212	[65]
Flower-like Pt particles	-	0.031	-	[66]
Flower-like Pt particles on single-walled carbon nanotubes	-	0.067	-	[67]
Pt nanoparticles on GC electrode electrodeposited for 2 min	-	0.017	-	[68]
Pt nanoparticles on GC electrode electrodeposited for 15 min	-	0.012	-	[68]

^[a] CV was performed at room temperature. ^[b] Pt surface area is the effective electrochemical surface area of Pt normalized by the Pt amount. ^[c] SA was calculated by the peak oxidation current density normalized by the effective electrochemical surface area of Pt.

3. Experimental Section

3.1. Reagents

RuCl₃, RhCl₃, PdCl₂, IrCl₃, HAuCl₄·3H₂O, K₂PtCl₄, CuSO₄, H₂SO₄, and (NH₄)₂SO₄ were obtained from Beijing Chemicals (Beijing, China). All reagents employed were of analytical grade and used directly without further purification. All the aqueous solutions used in this work were prepared with ultrapure water (Milli-Q Millipore, > 18.2 MΩ cm).

3.2. Electrode Synthesis and Characterization

All electrochemical syntheses and characterizations were performed on a three-electrode setup. A glassy carbon electrode (GCE, 5 mm in diameter) served as the working electrode, a Pt plate (1 × 1 cm²) electrode and a mercury sulfate electrode (MSE) served as counter and reference electrodes respectively. For the convenience of comparison, the potential measured by MSE was referred to reversible hydrogen electrode (vs. RHE). Prior to the electrodeposition, the GCE was first polished and then ultrasonically cleaned in ultrapure water for 3 min. Through controlling the deposition potential under potentiostatic conditions, nanoparticles with different compositions were synthesized on the surface of GCE. Some preliminary experiments had been carried out to find out the optimal

electrodeposition potentials and times, and the following conditions were employed to synthesize nanoparticles. Ru nanoparticles were synthesized on the GCE at -0.8 V (vs. RHE) for 8 s in 5 mM $\text{RuCl}_3 + 0.05$ M H_2SO_4 solution. Rh nanoparticles were synthesized on the GCE at -0.05 V (vs. RHE) for 0.2 s in 5 mM $\text{RhCl}_3 + 0.05$ M H_2SO_4 solution. Pd nanoparticles were synthesized on the GCE at 0 V (vs. RHE) for 0.2 s in 5 mM $\text{PdCl}_2 + 0.05$ M H_2SO_4 solution. Ir nanoparticles were synthesized on the GCE at -0.7 V (vs. RHE) for 800 s in 5 mM $\text{IrCl}_3 + 0.05$ M H_2SO_4 solution. Au nanoparticles were synthesized on the GCE at 0 V (vs. RHE) for 0.2 s in 5 mM $\text{HAuCl}_4 + 0.05$ M H_2SO_4 solution. The synthesis of Pt_{ML} on electrodeposited nanoparticles was achieved by a well-established method, as described as follows. After the synthesis of core nanoparticles on the GCE, the modified GCE, rinsed thoroughly with ultrapure water, was transferred into 0.05 M $\text{H}_2\text{SO}_4 + 0.05$ M CuSO_4 aqueous solution for the subsequent Cu UPD. The modified GCE was initially kept at 0.8 V (vs. RHE) for 20 s to make sure there is no Cu on the surface [18,33]. The electrode potential was subsequently swept at 0.4 V s^{-1} to the Cu UPD potential of 0.36 V (vs. RHE) and held at this potential for 60 s [18,33]. When the Cu UPD was finished, the corresponding GCE, rinsed thoroughly with ultrapure water, was immediately transferred into solution containing 5 mM K_2PtCl_4 and 0.05 M H_2SO_4 under the protection of high-purity Ar (99.999%) atmosphere to achieve the replacement of Cu with Pt^{2+} ions for 20 min. After the replacement reaction, the Pt_{ML} covered nanoparticles on the GCE were rinsed thoroughly with ultrapure water and dried in a nitrogen stream. The amount of the deposited Cu monolayer by UPD could be measured by the anodic stripping technique. For anodic stripping tests, the electrode potential was kept at 0.36 V (vs. RHE) for 60 s to complete the Cu UPD, and then swept back to 0.8 V (vs. RHE) at 0.4 V s^{-1} to strip off the Cu layer [33].

The particle size and dispersion degree of the Pt_{ML} decorated nanoparticles were determined by scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan) and transmission scanning electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan). For the TEM measurements, the electrodeposited nanoparticles were gently scraped and dispersed in ethanol on surface of GCE, and then the nanoparticle dispersions were transferred onto a Cu grid, which was directly conducted on surface of GCE.

3.3. Electrochemical Tests

Electrochemical tests were also carried out on the electrochemical workstation (IviumStat, Eindhoven, Netherland). Electrodeposited pure nanoparticles, or Pt_{ML} covered nanoparticles, on the GCE served as the working electrode. A Pt plate ($1 \times 1 \text{ cm}^2$) served as the counter electrode. A CV technique was used to investigate the electrochemical performance of nanoparticles with different compositions before and after the coverage of the Pt_{ML} . For the CVs tested in 0.5 M H_2SO_4 aqueous solution, an MSE was used as the reference electrode with a scan rate of 0.05 V s^{-1} . The electro-oxidation of ammonia was conducted in aqueous solution containing 1 M KOH + 0.1 M ammonia by CV at 0.01 V s^{-1} , and a Hg/HgO (filled with 1 M KOH) served as the reference electrode in this case. All the electrochemical measurements were performed in testing solutions saturated with argon gas (99.999%). All the measured potentials by the reference electrode were referred to as the RHE for the convenience of comparison. All experiments were carried out at controlled temperature of 25 ± 1 °C.

4. Conclusions

The effect of the composition of nanoparticle supports on the electrocatalytic activity of Pt_{ML} electrocatalysts for ammonia oxidation was investigated. A clean electrochemical approach free of binders, surfactants, capping agents and reductants was proposed to synthesis nanoparticle supports with various compositions including Ru, Rh, Pd, Ir and Au. Pt_{ML} supported on different nanoparticles were obtained by the Cu UPD and subsequent replacement of Pt ions. The SA of the Pt_{ML} electrocatalysts was significantly dependent on the composition of nanoparticle supports, which decreased in the following order: $\text{Pt}_{\text{ML}}/\text{Au}$ nanoparticles > $\text{Pt}_{\text{ML}}/\text{Ir}$ nanoparticles $\approx$ $\text{Pt}_{\text{ML}}/\text{Rh}$

nanoparticles > Pt_{ML}/Ru Nanoparticles $\approx$ Pt_{ML}/Pd nanoparticles. The SA of the Pt_{ML} supported on Au nanoparticles was about 8.3 times higher than that of the Pt_{ML} supported on Ru Nanoparticles and Pd Nanoparticles. This trend was generally related to the change of the surface strain in the Pt_{ML} exerted by the nanoparticle support. As the surface strain in the Pt_{ML} exerted by the nanoparticle support changed from a tensile strain to a compressive strain, the SA of Pt_{ML} electrocatalysts decreased. Therefore, the highest SA was observed for the Pt_{ML} supported on the Au nanoparticles, where the Pt_{ML} was under a tensile strain. On the contrary, for Ru, Rh and Pd nanoparticle supports that exerted on the Pt_{ML} a tensile strain had much lower specific activities.

Author Contributions: J.L. and B.L. contributed equally to this work, that is, they performed the synthesis, electrochemical characterizations of the catalysts and wrote the draft. X.C. and J.Z. carried out structural characterizations with SEM and TEM. Y.W. and Y.D. contributed to the data analysis. W.H. supervised the project. C.Z. supervised the project, designed the experiments and revised manuscript.

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