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Synthesis and Activation of PtRu Alloyed Nanoparticles with Controlled Size and Composition

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FCC PtRu nanoparticles with narrow size distribution were prepared by polyalcohol reduction of platinum acetylacetonate and ruthenium acetylacetonate in diphenyl ether, using oleylamine as the capping agent. The particle size ranged from 3.5 to 6.5 nm and was controlled by varying the amount of capping agent added in the synthesis. Adjusting the stoichiometric ratio of introduced Pt and Ru precursors yielded particles with different compositions. A simple fractionation was employed to narrow the size distribution of particles and nearly monodispersed particles were obtained. To activate the catalytic activity of the particles, oleylamine bound to the particle surface was removed through repeated washing of the as-prepared particles with ethanol and tetramethylammonium hydroxide (TMAOH) aqueous solution. The washed particles could be well redispersed and electrostatically stabilized in TMAOH aqueous solution and uniformly loaded on a Vulcan XC-72 carbon support. A cyclic voltammetry (CV) study revealed that the carbon-supported, cleaned PtRu nanoparticles exhibit considerably higher electrocatalytic activity for methanol oxidation compared with the as-prepared particles that have oleylamine ligands.

Introduction

Recent revival of interest in alternative fuels for automobiles has led to renewed interest in basic research on electrode nanocatalysts. Pt/C remains the catalyst of choice for either the anode or the cathode. However, Pt is not active enough to make fuel cell technology economically viable. For example, a problem with Pt catalyst on the anode is that trace CO binds tightly to the Pt surface, blocking active sites, thereby decreasing the catalytic activity. The CO may be a trace impurity in the hydrogen fuel made by reforming the methanol. CO also may be a byproduct of methanol oxidation reaction (MOR) on the anode of direct methanol fuel cells (DMFCs). Recently, there has been excitement about PtRu bimetallic catalysts in which the PtRu nanoparticles exhibit a high tolerance to the poison of CO. The unusual catalytic activity of PtRu was always interpreted by the “bifunctional mechanism”, in which the Pt provides sites for the dehydration of methanol and Ru provides sites for the oxidation of CO adsorbed on the Pt sites.[1,2]

Many studies have demonstrated that the catalytic activity of nanoparticles is strongly dependent on the particle size, shape, and composition,[3−6] so a synthetic method that can allow for a good control over these parameters is needed. In the last several years, many approaches for PtRu nanoparticle preparation have been reported, including conventional wet impregnation,[7,8] chemical reduction or thermal decomposition of 1:1 Pt/Ru bimetallic molecular precursors,[9,10] and colloidal methods.[11−13] The wet impregnation approach has the advantage of simplicity over other synthetic methods, but controlling the particle size, composition, and shape is still a big challenge. The synthetic approach based on Pt/Ru bimetallic molecular precursors gives a better way to control the particle composition, but synthesis of the molecular precursors is complicated and time consuming. However, in the colloidal methods based on capping agents, the size, composition, shape, even the dispersion of particles can be easily controlled.

Sun et al. reported a new method for preparing monodisperse FePt nanoparticles.[14] In this method, particles were synthesized by polyalcohol reduction of organometallic precursors and decomposition of metal carbonyls in high-

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boiling-point solvents with the presence of capping agents, which was employed to control the particle size and shape. Moreover, the capping agents play a crucial role in stabilizing the particles in solvent and making the particles well-dispersed and completely separated from each other. It would be very exciting if this method, with some modifications, can be applied to the synthesis of PtRu nanoparticles; however, the capping agent bound to the surface of as-prepared particles can also block the active surface sites of particles. Thus, removing the capping agents from the particle surface is a key step in activating the catalytic activity of particles. Generally, the capping agent is removed by high-temperature thermal treatments in inert atmospheres, in which capping agents decompose under high temperature. However, this kind of treatment may cause the aggregation of particles; the surface area will be lost and, consequently, the catalytic activity will be degraded.[15] Burning the capping agents off the particle surface in oxidizing atmospheres gives another possible route for removing capping agents at relatively lower temperatures (150−300 °C), but the oxidation and change of surface composition become a big concern for this treatment. Therefore, the activation of as-prepared PtRu nanoparticles requires a nonthermal treatment that does not lead to the aggregation of particles.

In this paper, we report a simple synthetic approach to obtaining high-activity PtRu nanoparticles with controlled sizes and compositions. PtRu nanoparticles were prepared by polyalcohol reduction of platinum acetylacetonate and ruthenium acetylacetonate in diphenyl ether with the presence of oleylamine. The sizes and compositions of particles were tuned by adjusting the amounts of oleyamine and the stoichiometric ratio of Pt and Ru precursors introduced in synthesis. A nonthermal treatment was then successfully developed to remove the oleylamine bound to the particle surface. Finally, in a comparison with as-prepared ones, the electrocatalytic activity of activated PtRu particles supported on carbon was studied using cyclic voltammetry (CV).

Experimental Section

Materials. Platinum acetylacetonate ($Pt(acac)_2$, 97%), ruthenium acetylacetonate ($Ru(acac)_3$, 97%), 1,2-hexadecanediol ($C_{16}H_{34}O_2$, 90%), oleylamine ($C_{18}H_{37}N$, 70%), and Nafion (5 wt %) were purchased from Aldrich. Diphenyl ether ($C_{12}H_{10}O$, 70%) was purchased from Acros. Other chemicals including ethanol, methanol (HPLC grade), acetone, hexane, and sulfuric acid were purchased from Fisher Chemicals. Vulcan XC-72 carbon powder was a gift from Cabot Inc. All the chemicals were used without further purification. Deionized water was used to prepare aqueous solutions.

Synthesis of PtRu Nanoparticles. Taking the synthesis of 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles as an example, 101.4 mg (∼0.25 mmol) of platinum acetylacetonate, 102.7 mg (∼0.25 mmol) of ruthenium acetylacetonate, 574.3 mg (∼2.0 mmol) of hexadecanediol, and 20.0 mL of diphenyl ether were added in a three-necked round-bottom flask equipped with magnetic stirring and a reflux condenser. The mixture was heated to 110 °C to dissolve the precursors in diphenyl ether under a N_2 atmosphere. The resulting solution was held at this temperature for 2 min, during which 1.36 mL oleylamine, used as a capping agent, was dropwise injected into the mixture via a microsyringe. The brown solution was then continuously heated to reflux and finally gave a black dispersion after 1 h of reflux. The particle dispersion was then allowed to cool at room temperature, and the particles were subsequently precipitated by adding 30 mL of ethanol in the dispersion. The yellow-brown supernatant of the mixture was discarded, and the black particle dispersion precipitated at the bottom of the tube was transferred to a centrifugation tube containing 5 mL of ethanol, followed by sonication for 5 min. The particles were finally isolated by centrifugation. To remove the excessive oleylamine bound to the particle surface, we redispersed the precipitated particles in hexane; they were then washed with ethanol, isolated by centrifugation, and finally dispersed in hexane. Particles of 4.0, 4.5, and 6.5 nm diameter were prepared by the same procedures except different amounts of oleylamine (0.68, 0.34, and 0.17 mL) were introduced. $Pt_{76}Ru_{24}$ and $Pt_{25}Ru_{75}$ particles (3.5 nm) were also prepared the same way, except 3:1 and 1:3 molar ratios of platinum acetylacetonate and ruthenium acetylacetonate were added in synthesis.

Narrowing the Particle Size Distribution. The size distribution of as-prepared PtRu nanoparticles could be further narrowed through a simple size selection method. In a typical size selection process, about 4 mL of ethanol was added to 6 mL of as-prepared PtRu nanoparticle dispersion described above. The extra oleylamine bound to the particle surface was dissolved in ethanol, and the color of the dispersion turned from deep black to brown because of the nonpolarity of particle surface. The mixture was then centrifuged at 2000 rpm for 5 min. Larger particles were easier to precipitate than the small-size particles because of their mass difference. As a result, after centrifugation, the small-size particles were still floating in the dispersion and were collected for use. With the repetition of this process, nearly monodispersed PtRu nanoparticles with different sizes were obtained.

Catalytic Activation of As-Prepared PtRu Nanoparticles. Two kinds of treatments were tried to remove the capping agent. One is a nonthermal treatment, which was achieved by repeated washing of the particles with ethanol and 0.1 wt % tetramethylammonium hydroxide (TMAOH) aqueous solution. The washing procedures are as follows: Briefly, 5 mL of ethanol was added into 3 mL of as-prepared 3.5 nm $Pt_{50}Ru_{50}$ particle dispersion, followed by sonication for 10 min. The particles were then isolated by centrifugation, and the supernatant was discarded. Hexane (3 mL) was added to redisperse the precipitated particles. This ethanol-washing process was performed three times. As for the TMAOH-washing procedures, 10 mL of 0.1 wt % TMAOH solution was added in the centrifugation tube with precipitated PtRu nanoparticles at the bottom. The precipitated particles were then redispersed in TMAOH aqueous solution by sonicating the sample for 5 h. The dispersed particles were precipitated by centrifugation, and the supernatant was removed. The TMAOH-washing process was also conducted three times. Finally, the washed particles could be well-dispersed in 0.05 wt % TMAOH aqueous solution. The other method used for removing oleylamine on the particle surface is heat-treating the particles in a tube furnace at 350 or 400 °C for 2 h under an Ar/H_2 atmosphere (5% of H_2). Oleylamine was removed because of its thermal decomposition at high temperature.

Characterization of Particles. The particle size and shape were characterized by a Hitachi 8000-200 kV transmission electron microscope(TEM). High-resolution TEM image of particles were obtained on a FEI TECNAI S20 microscope. TEM samples were prepared by diluting the particle dispersion with hexane or deionized water, and several drops of diluted dispersion were then placed onto a carbon-coated copper TEM grid (400-mesh from SPI). The X-ray diffraction (XRD) ($\theta-2\theta$ scan) data of particles were

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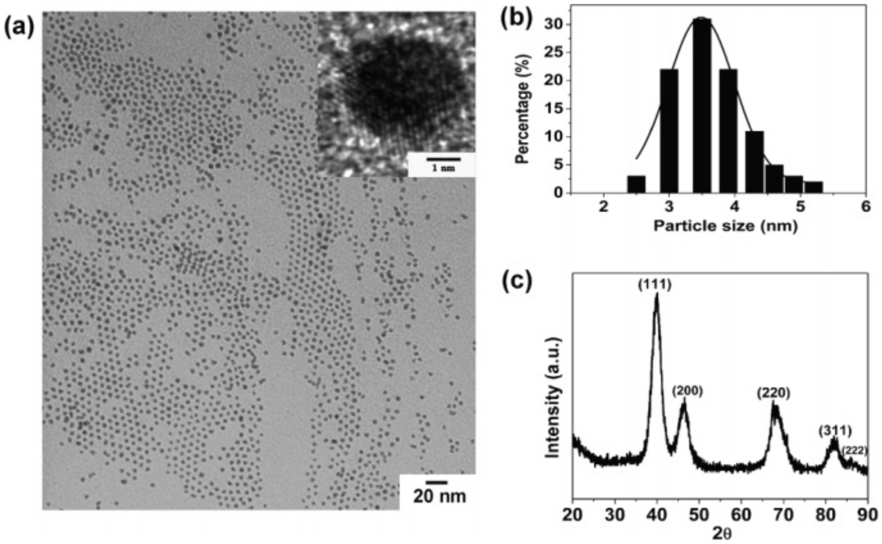

Figure 1. (a) TEM image (the inserted image is the high-resolution TEM image of one as-prepared particle), (b) size distribution, and (c) X-ray diffraction pattern of as-prepared 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles.

collected on a Rigaku model D/MAX-2BX thin film diffractometer, using Cu Kα radiation ($\lambda = 1.5406$ Å). The particle films were made by placing several drops of particle dispersion on p-type silicon substrates with native oxides on their surface. Particle compositions were determined with energy-dispersive X-ray analysis on a scanning electron microscope (Philips XL30). X-ray photoelectric spectroscopy (XPS) spectra were collected on a Kratos AXIS 165 Multitechnique Electron Spectrometer. Mg Kα (1486.6 eV) was used as X-ray source, and the binding energy of samples was referenced to the C1s peak (285.0 eV). The samples for XPS characterization were prepared by depositing several drops of PtRu particle dispersion on silicon substrates followed by evaporation of the solvents. Fourier transform infrared (FT-IR) analysis of particle dispersion was performed on a FT-IR spectrometer (Bio-RAD, FTS-40), which was used to determine if the oleylamine had been removed from the particle surface after washing. The samples were prepared by casting the particle dispersion on a ZnSe lens (25 mm diameter, 2 mm thick), followed by evaporation of the solvents.

Loading PtRu Nanoparticles on a Vulcan XC-72 Carbon Support. To prepare carbon-supported $Pt_{50}Ru_{50}$ catalyst with 20% loading, we mixed 2 mL (5 mg/mL) of $Pt_{50}Ru_{50}$ particles dispersed in TMAOH solution with 40 mg of Vulcan XC-72 carbon powder. The mixture was sonicated for 24 h to make the particles uniformly deposited on the carbon support. The catalyst powder then was filtered and washed with water, followed by drying at 50 °C under an air atmosphere. The dried catalyst powder was finally mixed with deionized water and 0.88 g of Nafion (5wt %) to give 1 mg/mL catalyst slurry. The carbon-supported as-prepared $Pt_{50}Ru_{50}$ catalyst slurry was prepared in a similar way.

Cyclic Voltammetry Study. 4 μL catalyst slurry was pipetted on the polished glassy carbon (GC) electrode (3 mm diameter) by a micropipette, and the catalyst ink was dried in a vacuum at 60 °C for 1 h. The GC electrode with a dried catalyst layer on its surface was used as a working electrode, and Pt wire and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrolyte was 2.0 M CH_3OH in 1.0 M H_2SO_4 and was bubbled with N_2 for 30 min before analysis.

Results and Discussion

Figure 1a shows a representative TEM image of as-prepared $Pt_{50}Ru_{50}$ nanoparticles. The size distribution curve (Figure 1b) shows that the average size of particles is about 3.5 nm, which is consistent with the size estimated from the Scherrer equation on the basis of the (111) peak shown in Figure 1c, and the particles display a narrow size distribution (~1 nm standard deviation). The inserted high-resolution TEM image suggests the particles have a good crystal phase. The XRD pattern of particles indicates that the particles possess a face-centered cubic (FCC) structure. The particle composition was varied by simply varying the stoichiometric ratio of Pt and Ru precursors introduced in the synthesis. Figure 2 shows the XRD patterns of 3.5 nm PtRu nanoparticles with different compositions. All patterns displayed a FCC phase similar to that of pure Pt particles. However, shifts to higher values of 2θ were observed for both the (111) peak and (200) peak with increasing ruthenium content. For example, the (111) peak shifted from 39.6 to 39.8 and 40.2° when the ruthenium content increased from 25 to 50 and 75%, which suggests that the as-prepared PtRu particles are alloyed nanoparticles, instead of a physical mixture of Pt and Ru nanoparticles. In the alloyed PtRu nanoparticles, the Ru atoms substitute the Pt atoms in the Pt FCC lattice, shrinking the lattice size. Figure 3 shows the TEM images of as-prepared $Pt_{76}Ru_{24}$, $Pt_{25}Ru_{75}$ nanoparticles, and the average size of particles is about 3.5 nm.

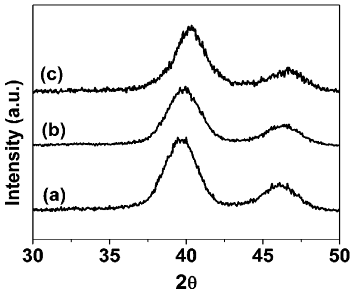

Figure 2. XRD patterns of PtRu nanoparticles with different compositions: (a) $Pt_{76}Ru_{24}$, (b) $Pt_{50}Ru_{50}$, and (c) $Pt_{25}Ru_{75}$.

Another desirable feature associated with this synthetic approach is that the particle size can be controlled by simply varying the amount of capping agent introduced in the synthetic procedures. Figure 4 shows the XRD patterns of

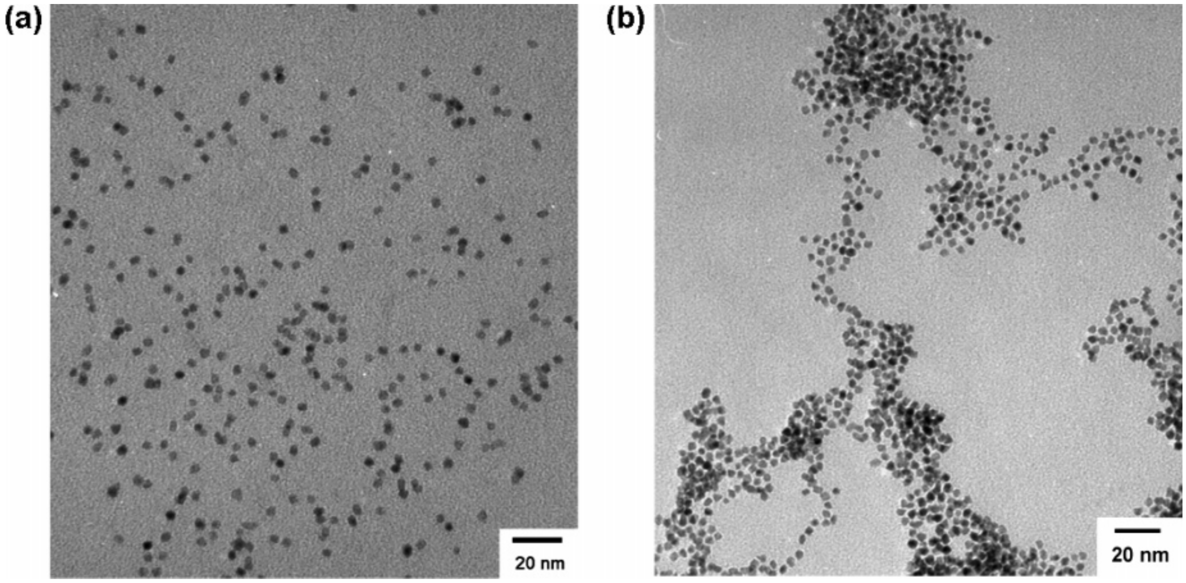

Figure 3. TEM images of 3.5 nm as-prepared particles with different compositions: (a) $Pt_{76}Ru_{24}$ and (b) $Pt_{25}Ru_{75}$.

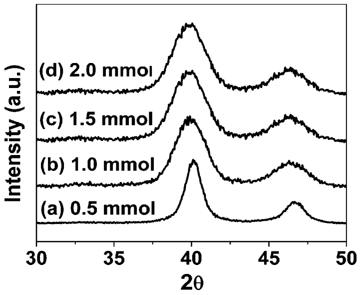

Figure 4. XRD patterns of PtRu nanoparticles synthesized using different amounts of oleylamine: (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 mmol.

synthesized $Pt_{50}Ru_{50}$ nanoparticles, using different amounts of oleylamine. The particle sizes were tuned to 3.5, 4, 4.5, and 6.5 nm, respectively, when 2.0, 1.5, 1.0, and 0.5 mmol oleylamine was added into 20 mL of diphenyl ether under the same experimental conditions. Particle sizes were estimated on the basis of TEM analysis and Scherrer analysis of Gaussian fitted (111) peaks. These results suggest particle growth can be effectively inhibited by high-concentration oleylamine, which is covalently bound to the particle surface, and particle size can be controlled by adjusting the amount of oleylamine.

It was also interesting to find that the size distribution of as-prepared PtRu nanoparticles could be further narrowed through a simple size-selection method. Figure 5a shows the TEM image of 3.5 nm nearly monodispersed $Pt_{50}Ru_{50}$ nanoparticles after one size-selection procedure described above, using the 3.5 nm as-prepared $Pt_{50}Ru_{50}$ nanoparticles shown in Figure 1a as original materials. Figure 5b indicates that the particles after size selection have a very narrow size distribution.

XPS was used to identify the oxidation states of as-prepared PtRu particles. Figure 6a shows the survey scan of as-prepared 3.5 nm $Pt_{50}Ru_{50}$ particles, and the signal of Pt and Ru was clearly observed. Ru 3p was then used to analyze the oxidation states of Ru on the particle surface, because of the overlapping between the zero-valence Ru peak and the C 1s peak. As shown in Figure 6b, the acquired Ru $3p_{5/2}$ peak could be fit into two distinct peaks. The two peaks centered at 461.3 and 462.9 eV were associated with Ru(0) and RuO_2, respectively.[16] Thus, a certain amount of ruthenium oxide was present on the as-prepared particle surface.

Removing the oleylamine bound to the particle surface is a key step for particle activation. It was interesting to find

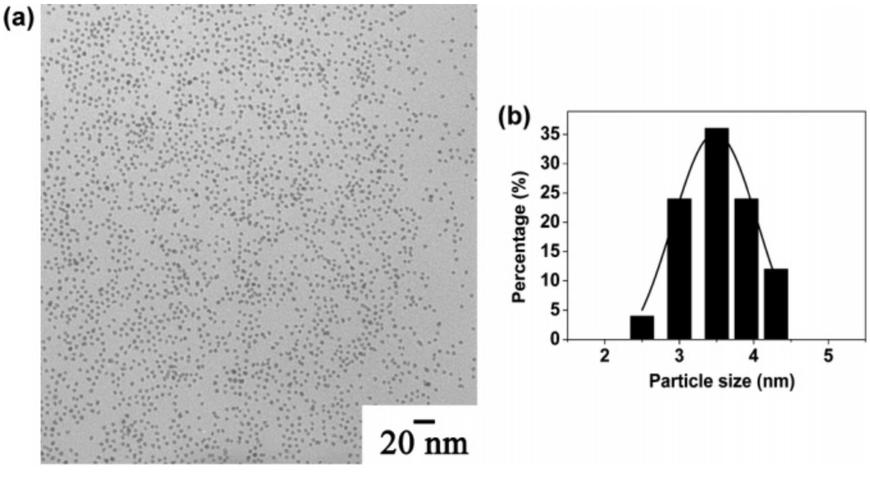

Figure 5. (a) TEM image and (b) size distribution of 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles obtained after one size selection procedure.

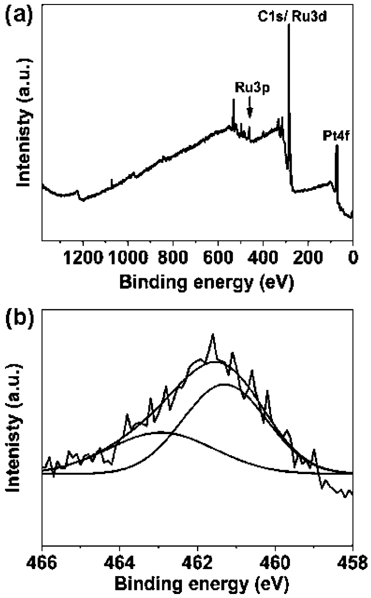

Figure 6. XPS spectra of as-prepared 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles: (a) survey scan and (b) high-resolution scan of Ru $3p_{5/2}$ line.

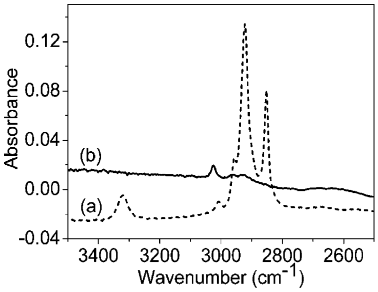

Figure 7. FT-IR spectra of 3.5 nm $Pt_{50}Ru_{50}$ particle dispersion: (a) as-prepared and (b) after repeated washing procedures.

that oleylamine could be removed from the particle surface by repeatedly washing the particles with ethanol and TMAOH aqueous solution. Figure 7b shows the FT-IR spectrum of particle dispersion after washing, compared with that of as-prepared particle dispersion (Figure 7a). It can be seen that the absorption peaks associated with NH (~3300 cm^{-1}) and C−H stretch (~2922 and ~2852 cm^{-1}) almost disappeared for the particles after the washing processes, which suggests most of oleylamine bound to the particle surface has been removed after these washing procedures. The washed particles could finally be well-dispersed in 0.05 wt % TMAOH aqueous solutions (Figure 8). We think that the particles were possibly stabilized in aqueous TMAOH solution through the electrostatic interactions between the hydroxide ions adsorbed on RuO_2 and the positively charged tetramethylammonium counterions in solution. It should be mentioned that a similar washing procedure has been used to remove the oleylamine and oleic acid bound to surface of FePt nanoparticles.[17] It was proposed that FePt nanoparticles were stabilized by electrostatic interactions between the hydroxide ions adsorbed on the iron oxides presented on the particle surface and the tetramethylammonium counterions. To further prove this mechanism on PtRu particle stabilization, we used the same procedure to wash and disperse pure Pt nanoparticles capped with oleylamine; it was observed that the Pt nanoparticles could not be well-dispersed in TMAOH solution, even after being sonicated for a longer time. Moreover, 3.5 nm $Pt_{25}Ru_{75}$ nanoparticles were found to show a much better dispersibility in TMAOH aqueous solution than both $Pt_{76}Ru_{24}$ and $Pt_{50}Ru_{50}$ particles with the same size. Thus, the content of Ru in the particles is a crucial factor for particle stabilization; however, more work is needed to completely understand the details of the stabilization mechanism.

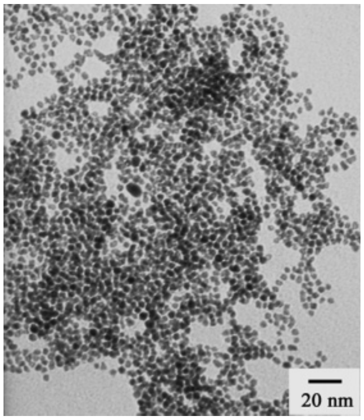

Figure 8. TEM image of 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles dispersed in 0.05 wt % TMAOH aqueous solution.

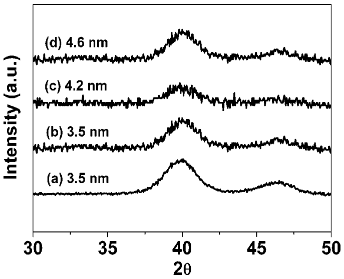

Figure 9. XRD patterns of PtRu nanoparticles: (a) as-prepared, (b) after washing with ethanol and TMAOH aqueous solution, (c) after the heat treatment in Ar/H_2 at 350 °C for 2 h, and (d) after the heat treatment in Ar/H_2 at 400 °C for 2 h.

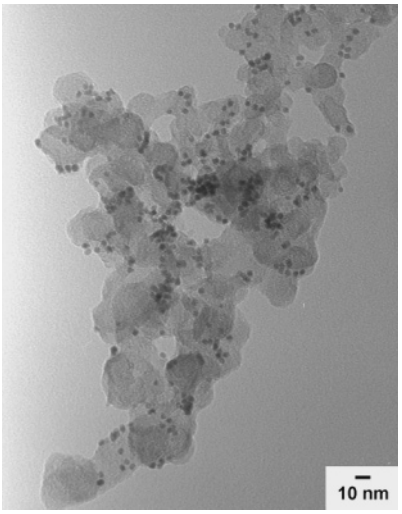

Figure 10. TEM image of 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles supported on a Vulcan XC-72 carbon powder with 20% loading.

Figure 9 shows the XRD patterns of $Pt_{50}Ru_{50}$ nanoparticles after different treatments. The particles washed by ethanol

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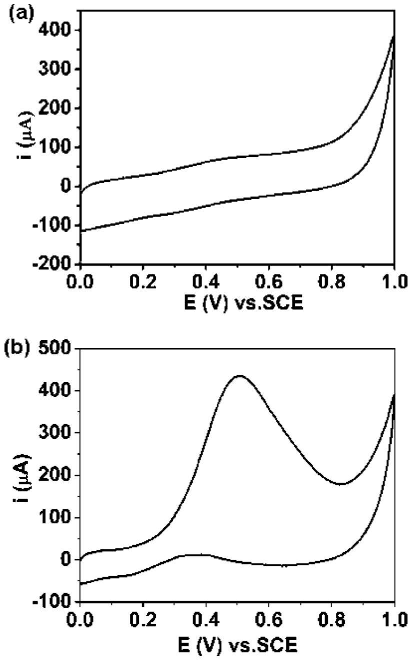

Figure 11. Cyclic voltammetry curves of 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles supported on a Vulcan XC-72: (a) as-prepared and (b) washed with ethanol and TMAOH solution. Both curves were obtained in 2.0 M CH_3OH + 1.0 M H_2SO_4 at a scanning rate of 20 mV/s.

and TMAOH solution still retained their initial size (Figure 9b), which demonstrated the appealing feature associated with this nonthermal treatment. On the other hand, the particle size was observed to increase from 3.5 to 4.2 and 4.6 nm, respectively, after the carbon-supported 3.5 nm as-prepared $Pt_{50}Ru_{50}$ particles were heat-treated at 350 °C (Figure 9c) and 400 °C (Figure 9d) for 2 h under an Ar/H_2 atmosphere. The particles after heat treatments aggregated because of the decomposition of oleylamine. The particle size was estimated on the basis of Scherrer analysis of Gaussian fitted (111) peaks.

To prepare electrode catalysts, we loaded the washed particles onto Vulcan XC-72 carbon by the physical deposition method. Figure 10 shows the TEM image of 3.5 nm $Pt_{50}Ru_{50}$ nanoparticles supported on carbon powder. As shown in the image, the particles were well-deposited on the carbon powder. Cyclic voltammetry was then employed to evaluate the electrocatalytic activity of particles. Figure 11 shows the CV of carbon supported 3.5 nm as-prepared $Pt_{50}Ru_{50}$ nanoparticles (Figure 11a) and activated $Pt_{50}Ru_{50}$ nanoparticles (Figure 11b). It can be seen that the as-prepared PtRu nanoparticles have no catalytic activity for methanol oxidation, which is mainly attributed to two reasons. One is that oleylamine blocks the active surface sites of PtRu nanoparticles, and the other is that methanol molecules cannot access the particle surface, because of the hydrophobic nature of particle surface. In a contrast, PtRu nanoparticles washed with ethanol and TMAOH displayed much higher activity for methanol oxidation. It should also be pointed out that its forward anodic peak negatively shifted approximately 200 mV compared with that of pure Pt nanoparticles. Moreover, the ratio of forward anodic peak current to the reverse anodic peak current associated with PtRu particles is much higher than that of pure Pt nanoparticles, which suggests most of the methanol has been electrochemically oxidized to CO_2 on washed $Pt_{50}Ru_{50}$ catalysts, instead of generating partially oxidized intermediates.[11]

Conclusions

This work has demonstrated the capability of the capping-agent-based polyalcohol reduction method for preparing alloyed PtRu nanoparticles with controlled sizes and compositions. Oleylamine bound to the surface of as-prepared particles was removed through a nonthermal treatment, without causing the sintering of particles. The cleaned PtRu particles supported on carbon show much better catalytic activity for methanol oxidation compared with as-prepared ones. The study of the dependence of particle electrocatalytic activity on particle size and composition is still underway.

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