

Synthesis of Pt–Ru–Mo ternary metal nanoparticles by microemulsions, their characterization and electrocatalytic properties

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Syntheses of nanoparticles with controlled size and composition are of great interest because nanoparticles possess unique physical and chemical properties [1, 2]. Considerable effort has been devoted to develop electrocatalyst of the nanoscale metallic alloy for the methanol fuel cells. The Pt–Ru binary metallic catalyst has been accepted as the best electrocatalyst for methanol oxidation in direct methanol fuel cells (DMFC). However, the efficiency of the DMFC operating on Pt–Ru alloy catalysts is still insufficient for practical application. Many investigations have been made to improve the performance of the Pt–Ru binary catalyst with the incorporation of a third metal, such as PtRuOs [3], PtRuSn [4], PtRuW [5]. Early investigations revealed that Mo has an excellent promoting effect for CO and methanol oxidation [6, 7]. However, the above studies focused mainly on conventional preparations resulting in the difficulties of controlling chemical composition and particle size limiting their application. The application of ternary metal nanoparticles can significantly enhance the catalytic activity toward methanol oxidation.

Preparation of nanoparticles using microemulsion provides a convenient control of size and composition. The bimetallic nanoparticles such as Pt/Co [8] and Pt/Ru [9] have been prepared using the microemulsion technique used in our previous investigation and it showed a higher catalytic performance for methanol oxidation. The synthesis of ternary metal nanoparticles is much more difficult than that of bimetallic nanoparticles because of the control of optimal composition. It should be possible to synthesize ternary metal nanoparticles following a similar bimetallic pathway. Despite its importance for the electrocatalysis of fuel cell reactions, ternary Pt–Ru–Mo nanoparticles prepared by the w/o microemulsion have not been reported.

In this communication, we report the synthesis of Pt–Ru–Mo ternary metal nanoparticles using a water-in-oil reverse microemulsion of water/Triton X-100/propanol-2/cyclohexane. The preparation of Pt–Ru–Mo nanoparticles was by a two-emulsion technique. The microemulsion system used in this study consisted of Triton X-100 as a surfactant, propanol-2

as a cosurfactant, cyclohexane as the continuous oil phase and either Pt–Ru–Mo precursor solution or hydrazine solution (as reducing agent) as the dispersed aqueous phase. The aqueous phases in the two-microemulsion systems have the same volume fraction but with different composition (typical atomic composition: Pt:Ru:Mo = 4.5:4.5:1) as indicated in Table I. The two stable microemulsions were then mixed with a stirrer. Pt–Ru–Mo nanoparticles were formed upon contact between the precursor containing droplets and the hydrazine containing droplets.

Fig. 1 shows a typical TEM image of Pt–Ru–Mo nanoparticles (Fig. 1a) and the electron diffraction pattern (Fig. 1b) obtained from a selected area of Fig. 1a. The particles were monodispersive and the bright rings with some bright spots are due to the presence of polycrystals and some degree of crystallinity. Histograms of particle diameters constructed indicate an average diameter of 2.4 ± 0.7 nm with a narrow size distribution as shown in Fig. 1c. X-ray diffraction (XRD) results are displayed in Fig. 2 for 2θ angle values of $10\text{--}90^\circ$. For comparison, the XRD patterns of the pure Pt and bimetal Pt–Ru fcc structure are also shown in Fig. 2. The diffraction peaks in the Pt–Ru–Mo catalyst of curve (a) matches the $\langle 111 \rangle$, $\langle 200 \rangle$, and $\langle 311 \rangle$ characteristics of a platinum fcc structure slightly shifted to higher 2θ values. There were also no observable lines in the XRD spectra corresponding to those of pure ruthenium and molybdenum. The shift in 2θ in curve (a) corresponds to a decrease in the lattice constant compared to pure platinum fcc structure due to the incorporation of Ru and Mo atoms [10]. It is evidence of the presence of a well-mixed Pt–Ru–Mo alloy.

Energy dispersive X-ray analyses (EDX) are also conducted by focusing the electron beam on several different selected regions on each sample (each region area $1 \mu\text{m} \times 1 \mu\text{m}$) of the unsupported Pt–Ru–Mo nanoparticles. An EDX spectrum of Pt–Ru–Mo nanoparticles is shown in Fig. 3. The average composition of the sample was in atom ratio of Pt:Ru:Mo = 0.45:0.45:0.1. The compositions of Pt–Ru–Mo nanoparticles in different regions are in close agreement and with no significant deviations.

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TABLE I Compositions of the microemulsion system used for the synthesis of Pt–Ru–Mo nanoparticles

	Micro Emulsion I	Micro Emulsion II	Volume (ml)	Vol%
Aqueous phase	9 mM H ₂ PtCl ₆ + 9 mM RuCl ₃ + 2 mM MoCl ₅	2 M hydrazine	3	15
Surfactant	Triton X-100	Triton X-100	2	10
Cosurfactant	Propanol-2	Propanol-2	8	40
Oil phase	Cyclohexane	Cyclohexane	7	35

Composition control is an attractive feature for preparing mixed metal nanoparticles using microemulsion reduction technique. The reduction reaction occurs in a confined reaction zone within the microemulsions. The ultimate nanoparticles should follow the metal composition in the precursor solution, without losing control of particle size. Optimization of composition and size of mixed metal at the nanometer level is the main subject of electrocatalysis for fuel cell applications. We performed preparations of several

TABLE II The EDX results of Pt–Ru–Mo nanoparticles and the corresponding compositions of precursors

Initial atomic composition Pt:Ru:Mo	Structure of nanoparticles	Atomic composition in nanoparticle Pt:Ru:Mo
0.45:0.45:0.1	fcc	0.452:0.444:0.104
0.6:0.3:0.1	fcc	0.58:0.32:0.10
0.6:0.33:0.07	fcc	0.604:0.328:0.068
0.58:0.35:0.07	fcc	0.582:0.346:0.0728

Pt–Ru–Mo nanoparticles by changing the initial composition of the precursor solution. The characterization results in Table II showed that the composition of ternary nanoparticles closely followed the initial metal salt solution. The control of particle size is another advantage for nanoparticle preparation in microemulsion system. The molar ratio (ω) of water to surfactant is one of size-determining key parameters. Fig. 4 showed the relationship of Pt–Ru–Mo nanoparticle size and the molar ratio (ω) of water to surfactant. Experimental results indicated that particle size could be controlled by the preparation conditions.

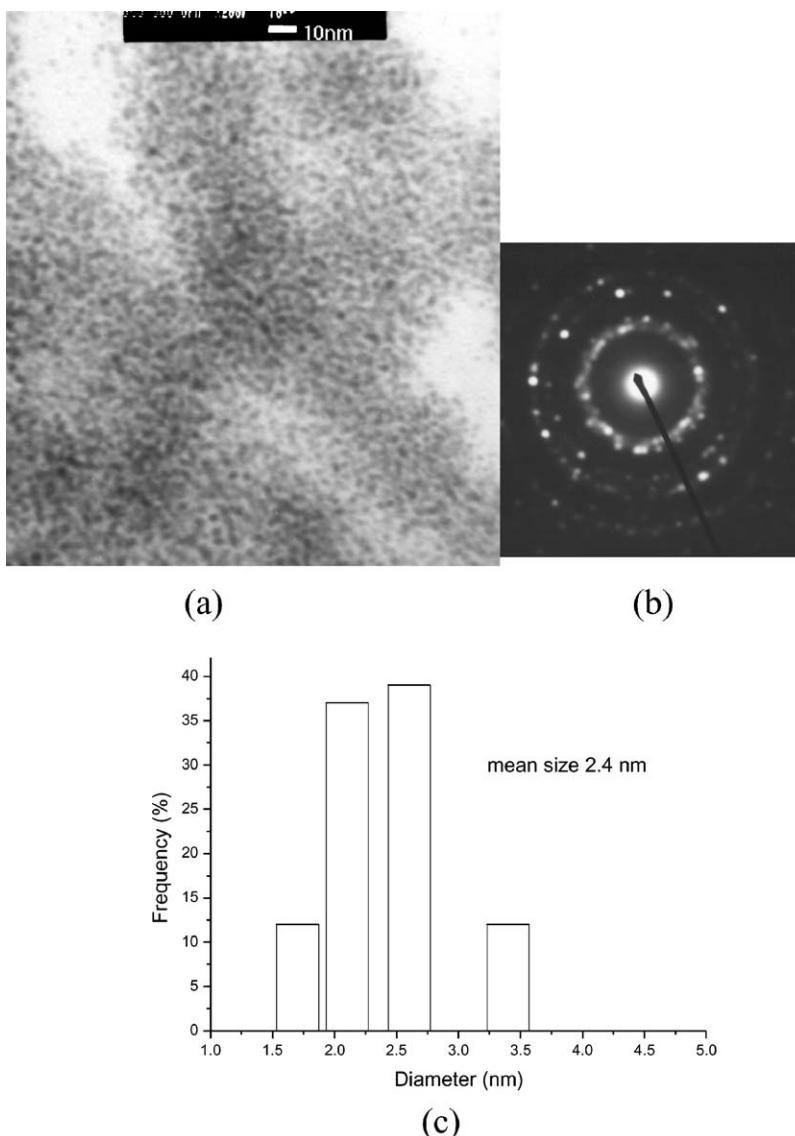


Figure 1 (a) Transmission electron microscope (TEM) of Pt–Ru–Mo nanoparticles prepared by the w/o microemulsion method. (b) Electron diffraction pattern of a region of the same sample as Fig. 1a. (c) Pt–Ru–Mo nanoparticle size distribution histogram.

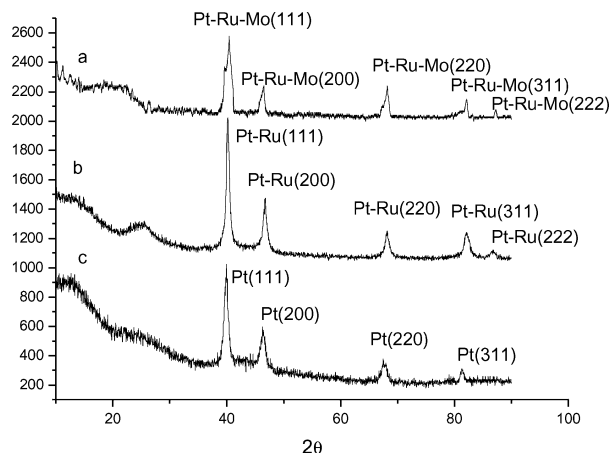


Figure 2 X-ray diffraction patterns of metallic nanoparticles supported on carbon: (a) Pt–Ru–Mo nanoparticles/Vulcan 72 carbon, (b) Pt–Ru nanoparticles/Vulcan 72 carbon, and (c) Pt nanoparticles/Vulcan 72 carbon.

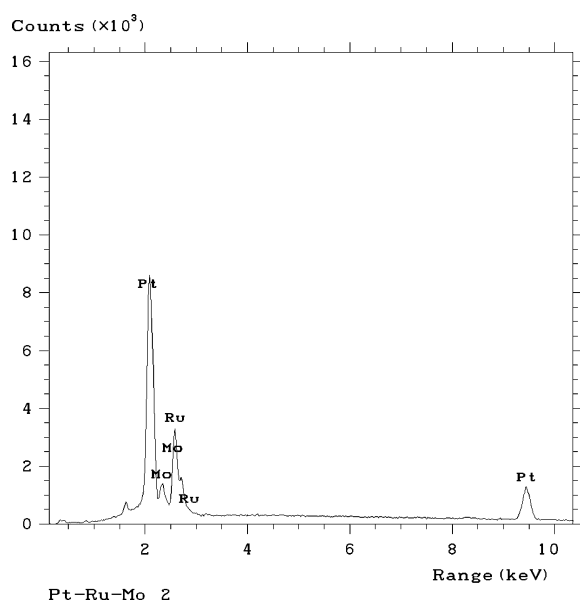


Figure 3 Broad area EDX spectra of the unsupported Pt–Ru–Mo nanoparticles.

Fig. 5 shows the step current (chronopotentiometry) results for the room temperature oxidation of methanol on the Pt–Ru–Mo nanoparticles/carbon electrode (atomic composition in nanoparticle Pt:Ru:Mo = 0.45:0.45:0.1), Pt–Ru nanoparticle/carbon electrode (atomic composition in nanoparticle Pt:Ru = 1:1), and pure Pt nanoparticle/carbon electrode prepared by microemulsion with the same Pt loadings. The Pt–Ru–Mo nanoparticles/carbon electrode gave higher activity and longer stability than that of Pt–Ru and pure Pt nanoparticles/carbon electrode. These results demonstrate that the catalytic performance of Pt–Ru bimetal catalyst for methanol oxidation can be further improved by the addition of molybdenum. The Pt–Ru–Mo ternary catalyst shows the improving catalytic activity compared to that of Pt–Ru and potential for direct methanol fuel cell applications because of the combination of Ru and Mo leading to a promising synergistic effect [11–13].

In conclusion, the synthesis of Pt–Ru–Mo nanoparticles has been achieved through microemulsions of

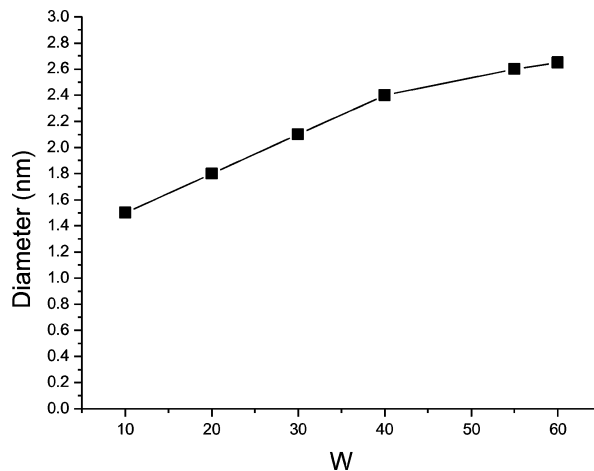


Figure 4 Effect of molar ratio of water to surfactant (ω) on the mean diameter of Pt–Ru–Mo nanoparticles.

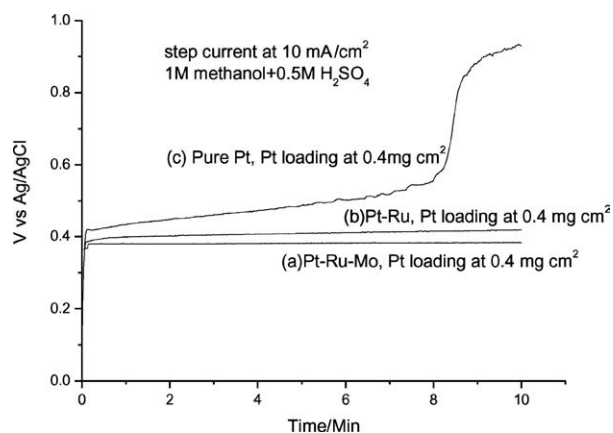


Figure 5 Chronopotentiometry of methanol oxidation at 10 mA/cm^2 in 1 M methanol + 0.5 M H_2SO_4 at room temperature. Different electrodes with the same Pt loading: (a) Pt–Ru–Mo nanoparticles carbon electrode (atomic composition in nanoparticles Pt:Ru:Mo = 0.45:0.45:0.1) and (b) Pt–Ru nanoparticles carbon electrode carbon (atomic composition in nanoparticle Pt:Ru = 1:1); (c) Pt nanoparticles carbon electrode.

water/Triton X-100/propanol-2/cyclohexane (w/o). The composition and particle size of ternary Pt–Ru–Mo nanoparticles can be controlled by adjusting the initial salt metal solution and the preparation conditions. Pt–Ru–Mo ternary metallic nanoparticles showed an enhanced catalytic activity towards methanol oxidation compared with that of Pt–Ru bimetallic nanoparticles.

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