

Preparation of a carbon supported Pt catalyst using an improved organic sol method and its electrocatalytic activity for methanol oxidation

Yawen Tang^a, Lingling Zhang^a, Yanen Wang^a, Yiming Zhou^a, Ying Gao^b,
Changpeng Liu^c, Wei Xing^c, Tianhong Lu^{a,c,*}

^a College of Chemistry and Environmental Science, Nanjing Normal University, Nanjing 210097, PR China

^b Department of Chemistry, College of Physical and Chemistry, Harbin Normal University, Harbin 150080, PR China

^c Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

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Abstract

The organic sol method for preparing ultrafine transition metal colloid particles reported for the first time by Bonnemann et al. [H. Bonnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Joußen, B. Korall, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 1312] has been improved in this paper. The improved organic sol method uses SnCl₂ as the reductant and methanol as the organic solvent. Thus, this method is very simple and inexpensive. It was found that the average size of the Pt particles in the Pt/C catalysts can be controlled by adjusting the evaporating temperature of the solvent. Therefore, the Pt/C catalysts prepared by the same method are suitable for evaluating the size effect of the Pt particles on electrocatalytic performance for methanol oxidation. The results of the X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed that when the evaporating temperatures of the solvent are 65, 60, 50, 40, and 30 °C, the average sizes of the Pt particles in the Pt/C catalysts prepared are: 2.2, 3.2, 3.8, 4.3, and 4.8 nm, respectively. The X-ray photoelectron spectroscopic (XPS) results demonstrated that the small Pt particles are easily oxidized and the decomposition/adsorption of methanol cannot proceed on the surfaces of Pt oxides. Thus, the Pt/C catalyst with small Pt particles has a low electrocatalytic activity for methanol oxidation. The Pt/C catalyst with a large average size of the Pt particles also possesses a small electrochemically active surface area. Therefore, only the Pt/C catalyst with a middle average size of Pt particles, such as 3.8 nm exhibited optimal electrocatalytic performance for methanol oxidation. Because the Pt/C catalysts with the different particle sizes were prepared with the same method, the size effect on the electrocatalytic performance of the catalysts could be reliably investigated.

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Keywords: Direct methanol fuel cell; Pt/C catalyst; Improved organic sol method; Methanol oxidation

1. Introduction

The direct methanol fuel cell (DMFC) has good potential applications as the power sources for transportation and portable devices [1–6]. However, the DMFC still has some problems. One of them is the low electrocatalytic activity of the Pt catalyst usually used for the methanol oxidation. Thus, a study of the increase in electrocatalytic performance for the Pt catalyst is important [7]. This has involved the variation of both the catalyst preparation method and the catalyst composition [8]. Many composite catalysts, such as Pt-Sn [9], Pt-WO₃ [10,11],

Pt-Ru-WO₃ [12], Pt-heteropoly acids [13], Pt-macrocyclic co-catalysts [14] and Pt-Ru [15–19] have been investigated. Also, many catalyst preparation methods, such as the general chemical reduction method, organic sol method [8], electrochemical deposition method [20], vapor deposition method [21,22], thermal decomposition method [23], co-impregnation method [24,25], spray pyrolysis method [26], ionic liquid method [27], solid phase reduction method [28], etc., have been reported.

In 1991, Bonnemann et al. [8] firstly reported the organic sol method for preparing colloidal transition metal catalysts, such as Pt, Ru, Pd, Os, Ir, Cr, Mn, and Ni catalysts using NR₄BEt₃H (R = octyl, hexyl, decyl) as the reductant. Thereafter, using this method, some groups prepared different carbon supported catalysts. For example, Frelink et al. [29] prepared the Pt/C catalyst with ca. 2.10 nm Pt particle size. Schmitt et al. synthesized the

* Corresponding author. Tel.: +86 25 83598031; fax: +86 25 83243286.
E-mail address: tianhonglu@263.net (T. Lu).

Pt-Ru/C [30–32] and Pd-Au/C [33] catalysts. The colloidal Pt-Ru, Pt-Ru-Sn, Pt-Ru-Mo, and Pt-Ru-W catalysts with 1.7 nm particle size were prepared by Gotz and Wendt [34]. However, this organic sol method has some disadvantages. Especially, the raw materials, such as $\text{NR}_4\text{BEt}_3\text{H}$ (R = octyl, hexyl, decyl) are expensive and the procedure is very complicated. Therefore, this method is only suitable for the research work in the laboratory.

It has been reported that the size of the Pt particles in the Pt/C catalyst could affect the electrocatalytic activity of the Pt/C catalysts for the methanol oxidation [35–39]. Therefore, the preparation of the Pt/C catalyst with an optimal average size of the Pt particles and a narrow size distribution of the Pt particles is important. In order to know what average size of the Pt particles is optimal for methanol oxidation, some groups [35–38] have studied the effects of size of the Pt particles in the Pt/C catalyst on electrocatalytic activity for the methanol oxidation. However, the results were very different. Using the Pt/C catalysts prepared with different methods, Attwood et al. [35] found that the best average size of the Pt particles in the Pt/C catalyst for methanol oxidation is about 3 nm. Frelink et al. [36] indicated that the electrocatalytic activity of the Pt/C catalysts for the methanol oxidation decreases with decreasing the Pt particles size in the range 4.5–1.2 nm. Takasu et al. [37] came to a similar conclusion using a Pt catalyst supported on glassy carbon electrodes with the Pt particle sizes from 7 to 2 nm. Watanabe et al. [38] reported that no Pt particle size effect was observed when the Pt/C catalysts with the different sizes of Pt particles on different carbon supporters were prepared by the same method. These contradictory results may be due to the difference in the preparation methods and supports for the Pt/C catalyst. Obviously, many factors, such as the average particle size, the relative crystallinity, the surface groups, the surface morphology and the Pt–C interface of the Pt/C catalysts can affect the electrocatalytic activity of the Pt/C catalysts [40–44]. Therefore, when the Pt/C catalysts are prepared with the different methods or using different carbon supports, many factors can influence the electrocatalytic activity of the Pt/C catalysts, leading to the different conclusions.

In this paper, the organic sol method for preparing the transition metal colloid particles, reported for the first time by Bonnemann et al. [8], was improved. A Pt/C catalyst with a small average size of the Pt particles was prepared with the simple improved organic sol method using inexpensive SnCl_2 as the reductant in methanol. It was found that the average size of Pt particles in the Pt/C catalyst can be controlled by adjusting the evaporating temperature of the methanol. Therefore, the Pt/C catalysts prepared by this method are suitable for evaluating the size effects of the Pt particles on the electrocatalytic performance for methanol oxidation.

2. Experimental

2.1. Preparation and characterization of the catalysts

The preparation procedure for the Pt/C catalysts is as follows. After 5.0 mL 41.2 mM SnCl_2 in methanol was added to 2.67 mL

38.6 mM H_2PtCl_6 in methanol at the room temperature with sonication, a Pt sol was obtained. Then, 80 mg of Vulcan XC-72 carbon black (from the Cabot Co.) was mixed with the Pt sol and the mixture was dried in a N_2 atmosphere at a controlled temperature until the methanol was completely evaporated. The Pt/C catalyst obtained was washed with 6 M NaOH solution to eliminate SnCl_2 and SnCl_4 . Finally, it was washed with water until no Cl^- was detected in the effluent. After drying at 90°C in vacuum, a Pt/C catalyst with 20 wt% Pt was obtained. The measurements of the energy dispersion spectroscopy (EDS) and XRD indicated that there was no Sn in the Pt/C catalyst.

In order to check if H_2PtCl_6 can be completely reduced with SnCl_2 , the reaction of H_2PtCl_6 and SnCl_2 was traced by in situ UV–vis absorption spectroscopy using a Perkin-Elmer UV-2200 UV–vis recording spectrophotometer. The scan range was 200–500 nm and the scan rate was 0.2 nm s^{-1} . 0.240 mL 41.2 mM SnCl_2 in methanol was dropwise added into 2.47 mL of 2.0 mM H_2PtCl_6 in methanol. The measurement of the UV–vis absorption spectra of H_2PtCl_6 was carried out after every addition of 10 μL SnCl_2 solution.

XRD patterns of the catalysts were obtained with a Japanese Rigaku D/max-rC X-ray diffractometer using $\text{Cu K}\alpha$ radiation. The TEM measurements were carried out with a JEM-2010 instrument with a point resolution of 0.14 nm. XPS measurements were performed with an Escalab Mark II spectrometer (VG Scientific Ltd., England) using $\text{Mg K}\alpha$ radiation with a mean energy of 1253.6 eV. The binding energy was calibrated with respect to C_{1s} at 284.6 eV with $\pm 0.2\text{ eV}$ accuracy. The experimental data were curve-fitted with Gaussian peaks after subtracting a linear background. The surface concentrations of the different species were estimated from the integrated area under the respective Gaussian peaks.

2.2. Electrode preparation and electrochemical measurements

The Pt/C catalyst electrode was prepared using the method reported by Schmidt et al. [45]. Firstly, a glassy carbon electrode (4 mm in diameter) was successively polished with the slurry of 0.5 and 0.03 μm alumina. Then, it was sonicated and washed with triply distilled water. 6.6 mg Pt/C catalyst and 3.3 mL water were mixed ultrasonically. 8.8 μL ink of the Pt/C catalyst obtained was transferred onto the freshly polished glassy carbon electrode. After water was evaporated at 60°C in a N_2 atmosphere, 4.4 μL 5 wt% Nafion solution (Aldrich Co.) was sprayed onto the Pt/C catalyst layer. Finally, the electrode was dried at 60°C in a N_2 atmosphere. Pt loading was $28.0\text{ }\mu\text{g cm}^{-2}$ and Nafion film thickness was about 0.1 μm .

Electrochemical measurements were performed using a CHI 600 Potentiostat/Galvanostat and a conventional three-electrode electrochemical cell. The counter electrode was a Pt foil. A saturated calomel electrode (SCE) was used as the reference electrode and all potentials were quoted with respect to SCE. The Pt/C catalyst electrode prepared was used as the working electrode. The electrolyte solution was the 0.5 M HClO_4 or 0.5 M HClO_4 + 0.5 M CH_3OH solution. Oxygen was purged from the solution by bubbling with N_2 for 30 min prior to each

electrochemical measurement. All the electrochemical experiments were performed at $30 \pm 1^\circ\text{C}$.

3. Results and discussion

3.1. Characterization of Pt/C catalysts

Fig. 1 shows the UV–vis absorption spectra of 2.47 mL 2.0 mM H_2PtCl_6 in methanol measured after every addition of 10 μL 41.2 mM SnCl_2 in methanol. It can be observed from Fig. 1 that the characteristic absorption peak of H_2PtCl_6 is located at 263 nm. The absorbance of this peak decreases on adding SnCl_2 . After all the SnCl_2 solution is added, this peak disappears. This shows that H_2PtCl_6 can be completely reduced with SnCl_2 , forming the Pt sol. It was found that the Pt sol obtained was stable for months at room temperature, indicating the Pt particles in the sol are small.

Methanol is a very good solvent to H_2PtCl_6 . Yang et al. prepared Pt-Cr/C [46] and Pt-Ni/C [47] in methanol as a solvent through the carbonyl route. Methanol was also used as a reducing agent for H_2PtCl_6 reduction. Duff et al. [48] and Teranishi et al. [49] prepared a PVP-protected Pt particles using methanol as both the reductant and the solvent. However, in this system, the absorbance of the absorption peak of H_2PtCl_6 is not decreased before adding SnCl_2 , indicating that methanol is not a reductant for the H_2PtCl_6 reduction in this method.

The XRD patterns of the Pt/C catalysts prepared at the different evaporating temperatures of methanol are shown in Fig. 2. The characteristic diffraction peaks of the Pt [1 1 1], [2 0 0], [2 2 0], and [3 1 1] crystal faces are clearly observed at the 2θ values of ca. 39.8° , 46.6° , 67.8° , and 81.1° , respectively, in the XRD patterns for all the Pt/C catalysts. The average size and relative crystallinity of the Pt particles in the Pt/C catalyst can be calculated with the method reported in the literature [50,51]. When the evaporating temperatures of methanol are 65, 60, 50,

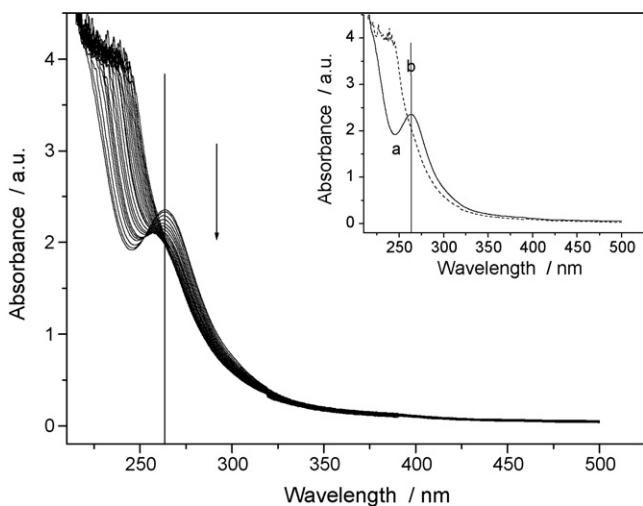


Fig. 1. The UV–vis absorption spectra of 2.47 mL 2.0 mM H_2PtCl_6 in methanol measured after every addition of 10 μL 41.2 mM SnCl_2 in methanol. Inset: the UV–vis absorption spectra of 2.47 mL 2.0 mM H_2PtCl_6 in methanol (a) before and (b) after adding 0.240 mL 41.2 mM SnCl_2 in methanol.

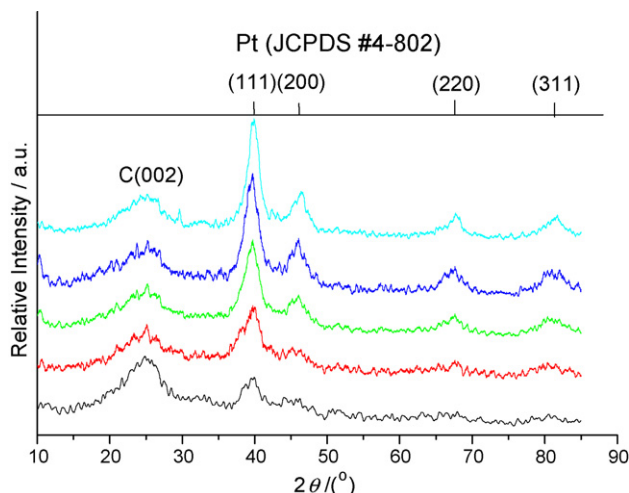


Fig. 2. The XRD patterns of the Pt/C catalysts prepared at the evaporating temperatures of methanol: (a) 65°C , (b) 60°C , (c) 50°C , (d) 40°C , and (e) 30°C .

40, and 30°C , the corresponding average sizes of the Pt particles in the Pt/C catalysts are 2.10, 3.18, 3.73, 4.17, and 4.80 nm, respectively, and the relative crystallinities are 0.61, 1.56, 2.32, 2.86, and 3.30, respectively (Fig. 3). It can be clearly observed from Fig. 3 that the average sizes and relative crystallinity of the Pt particles in the Pt/C catalysts gradually decrease with increasing the evaporating temperature of methanol.

Fig. 4 shows the TEM images of the Pt/C catalysts and the corresponding histograms of the Pt particle size distribution. The average sizes of the Pt particles in the Pt/C catalysts obtained from TEM images in Fig. 4 are 2.2, 3.2, 3.8, 4.3, and 4.8 nm, respectively, for the evaporating temperatures of methanol of 65, 60, 50, 40, and 30°C . This is in the good agreement with the XRD data. In addition, it can be seen from Fig. 4 that the size distribution of the Pt particles in the Pt/C catalysts is narrow.

Fig. 5 shows the Pt4f XPS spectra of the Pt/C catalysts with different average sizes of the Pt particles. In each XPS spectrum, two overlapping peaks at about 71 and 75 eV can be observed and belong to the $\text{Pt}4f_{7/2}$ and $\text{Pt}4f_{5/2}$ peaks, respectively. In order to compare the contents of Pt with different valences, each $\text{Pt}4f_{7/2}$

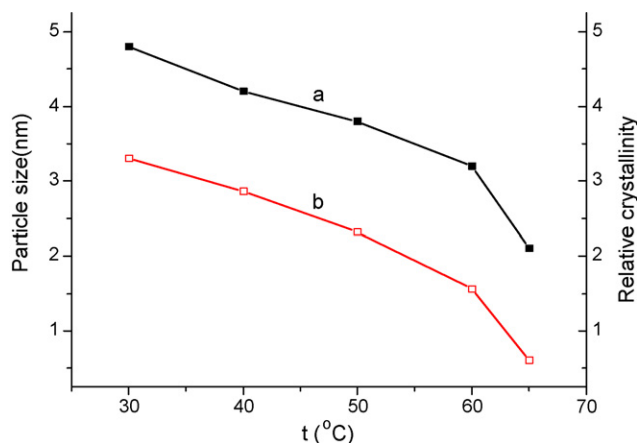


Fig. 3. The evaporating temperature of methanol vs. (a) the average size and (b) the relative crystallinity of the Pt particles in the Pt/C catalysts.

peak should be deconvoluted into three overlapping curves at 71.2, 72.2, and 73.7 eV. They belong to Pt⁰, Pt^{II} and Pt^{IV}, respectively [43]. The contents of Pt with different valences in the different Pt/C catalysts are listed in Table 1. It can be observed

from Table 1 that the Pt⁰ content increases and the contents of Pt^{II} and Pt^{IV} decrease with increasing the average size of the Pt particles, illustrating that the Pt particles with small average size are easily oxidized [52,53].

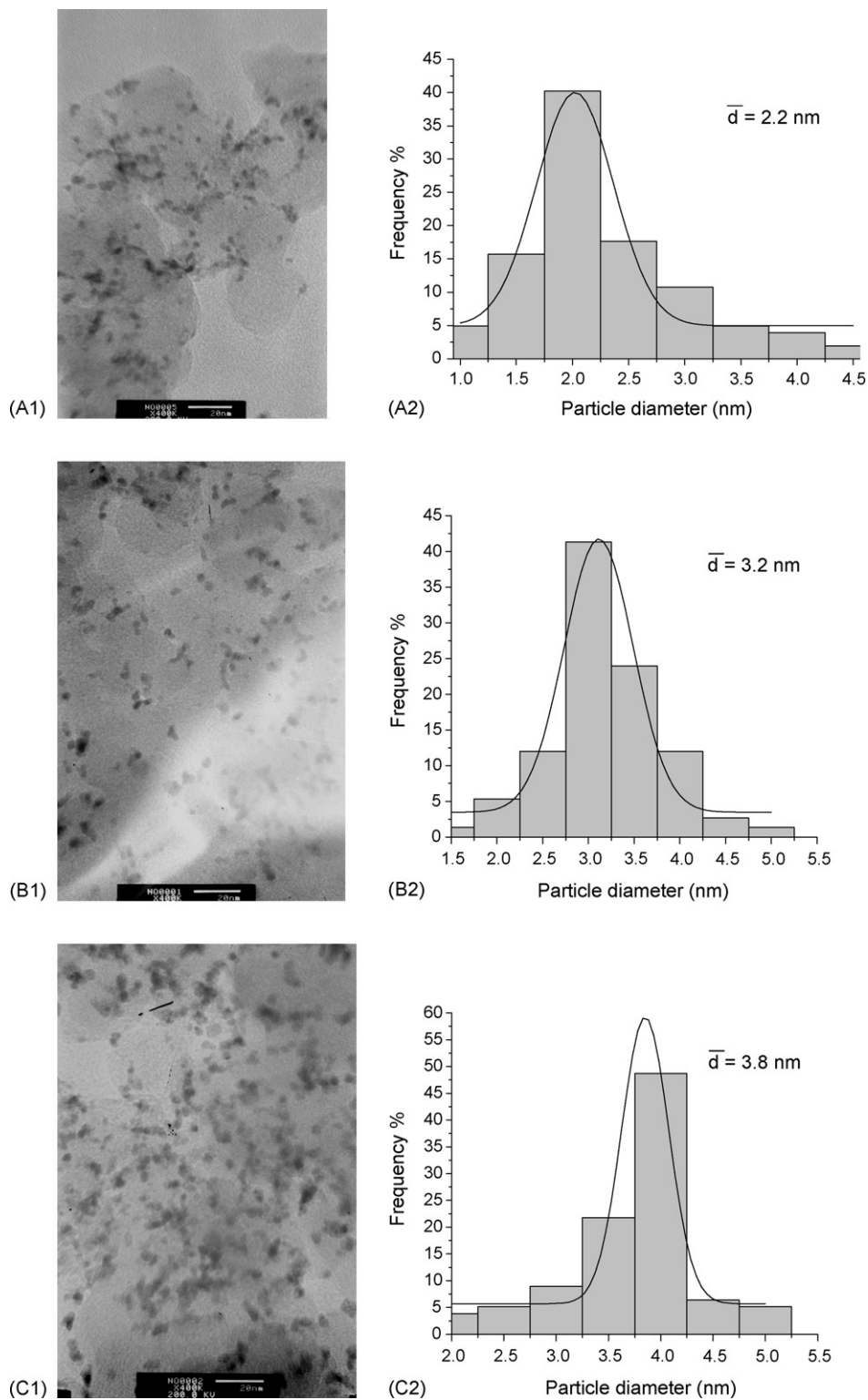


Fig. 4. The TEM images of the Pt/C catalysts with the average sizes of the Pt particles: (A1) 2.2 nm, (B1) 3.2 nm, (C1) 3.8 nm, (D1) 4.3 nm, and (E1) 4.8 nm and the histograms of the Pt particle size distribution of the Pt/C catalysts with the average sizes of the Pt particles: (A2) 2.2 nm, (B2) 3.2 nm, (C2) 3.8 nm, (D2) 4.3 nm, and (E2) 4.8 nm.

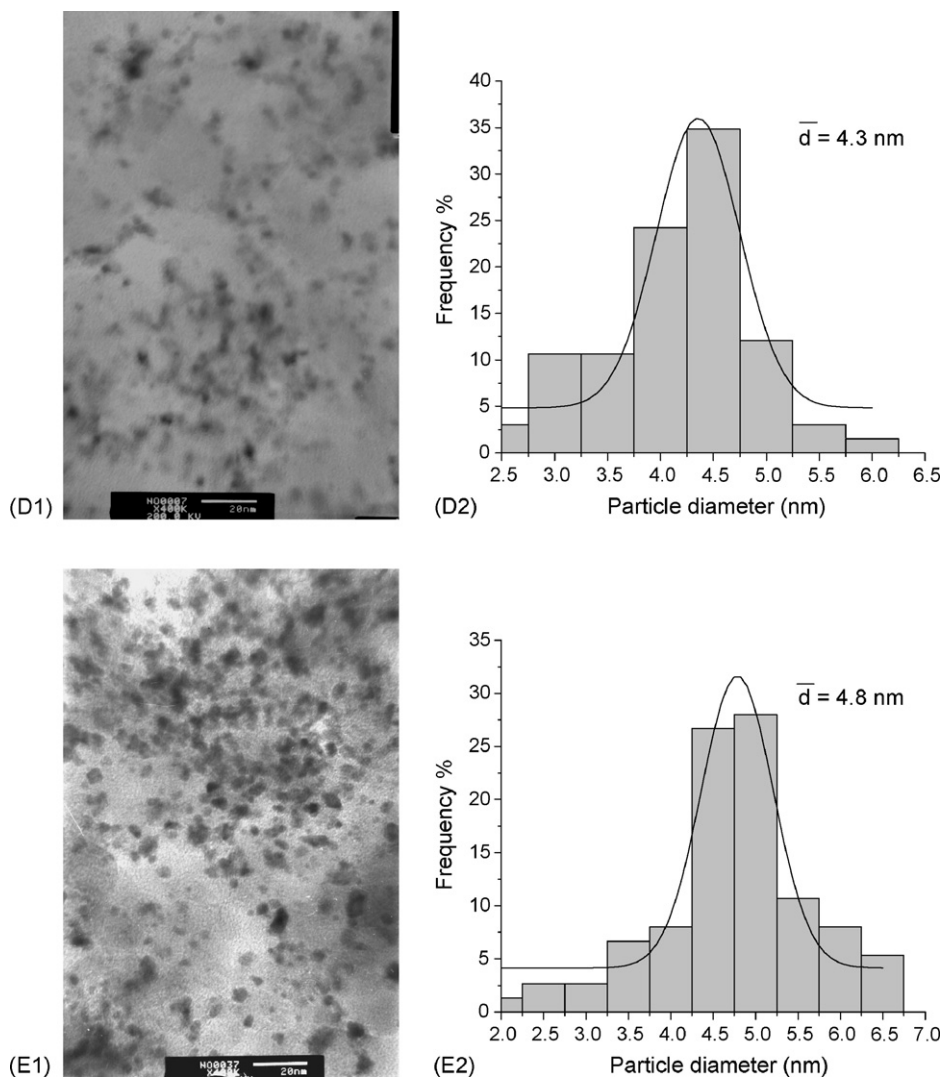


Fig. 4. (Continued).

Table 1

Binding energies and relative intensities of the Pt particles with the different average sizes in the Pt/C catalysts

Pt particle size (nm)	Species	Binding energy of Pt 4f _{7/2} (eV)	Relative intensity (%)
2.2	Pt ⁰	71.2	63.6
	Pt ^{II}	72.3	25.7
	Pt ^{IV}	73.7	10.7
3.2	Pt ⁰	71.3	67.6
	Pt ^{II}	72.5	23.3
	Pt ^{IV}	73.8	9.1
3.8	Pt ⁰	71.2	70.0
	Pt ^{II}	72.3	21.5
	Pt ^{IV}	73.7	8.5
4.3	Pt ⁰	71.2	70.8
	Pt ^{II}	72.2	20.4
	Pt ^{IV}	73.6	8.8
4.8	Pt ⁰	71.2	73.6
	Pt ^{II}	72.5	19.2
	Pt ^{IV}	73.7	7.2

3.2. Electrochemical measurements

Fig. 6 shows the cyclic voltammograms of the Pt/C catalyst electrodes with different average sizes of the Pt particles in a 0.5 M HClO₄ solution. No well-defined hydrogen adsorption/desorption peaks are observed from Fig. 5, suggesting that the Pt particles in the Pt/C catalyst prepared are highly uniform and dispersed [46]. The coulombic charge for the hydrogen desorption obtained from Fig. 6 can be used to calculate the electrochemical active surface (EAS) of the different Pt/C catalysts [54–56]. The EAS of the Pt/C catalysts with 2.2, 3.2, 3.8, 4.3, and 4.8 nm average sizes of the Pt particles are 13.54, 20.83, 20.57, 16.45, and 11.49 m² g⁻¹ Pt, respectively. Thus, the Pt/C catalyst with 3.2 and 3.8 nm average sizes of the Pt particles shows a large EAS. Usually, it is considered that the Pt/C catalyst with a small average size of the Pt particles should possess the largest EAS. However, the XPS measurements indicated that Pt is easily oxidized when the Pt particles are small. The oxidized Pt cannot adsorb hydrogen [57,58] so that EAS of the Pt/C catalyst with 2.2 nm average size of the Pt particles is not the largest among all the Pt/C catalysts.

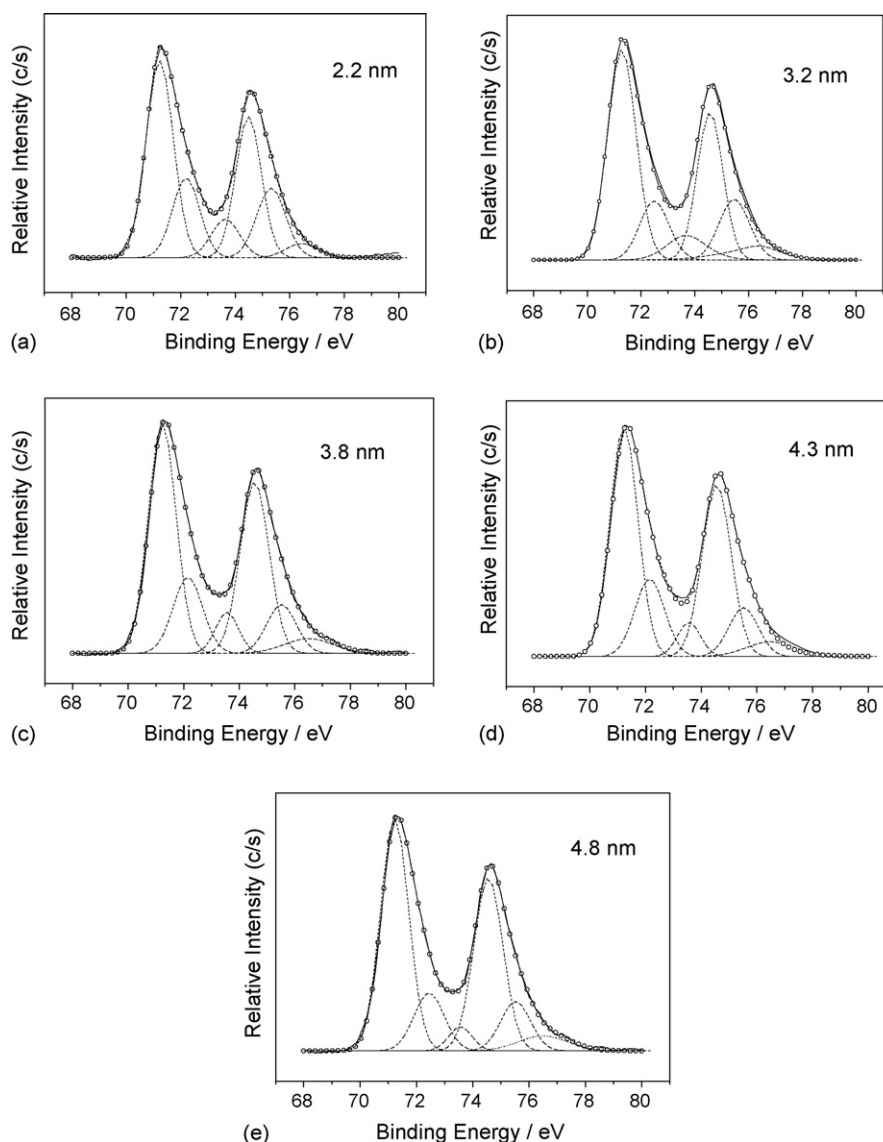


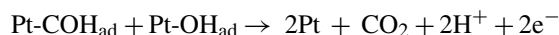
Fig. 5. The Pt4f XPS spectra of the Pt/C catalysts with the average sizes of the Pt particles: (a) 2.2 nm, (b) 3.2 nm, (c) 3.8 nm, (d) 4.3 nm, and (e) 4.8 nm.

Fig. 7 shows the linear sweep voltammograms of the Pt/C catalyst electrodes with different average sizes of the Pt particles in the 0.5 M CH₃OH + 0.5 M HClO₄ solution. It can be seen in Fig. 7 that the oxidation peaks of methanol at all the Pt/C catalyst electrodes are located at ca. 0.62 V. However, the peak current densities for methanol oxidation are: 5.11, 8.45, 10.23, 9.07, and 7.69 mA cm⁻² for 2.2, 3.2, 3.8, 4.3, and 4.8 nm average sizes of the Pt particles, respectively. Fig. 8 shows the relationship between the mass activity of the Pt/C catalysts and the average size of the Pt particles in the Pt/C catalysts. It can be observed from Fig. 8 that the mass activity increases with decrease in the average size of the Pt particles up to 3.8 nm and then decreases with further decrease in the Pt particle size. The above results illustrate that the electrocatalytic activity of the Pt/C catalyst with a 3.8 nm average size of the Pt particles is highest among the five Pt/C catalysts.

Fig. 9 shows the chronoamperometric curves for 0.5 M CH₃OH in a 0.5 M HClO₄ solution for the Pt/C catalysts with

different average sizes of Pt particles for 700 s at a fixed potential of 0.6 V. It can be observed from Fig. 9 that the current densities at the Pt/C catalyst electrodes with: 2.1, 3.2, 3.8, 4.3, and 4.8 nm average sizes of the Pt particles at 700 s are: 0.40, 0.99, 2.20, 1.54, and 0.69 mA cm⁻², respectively. The results demonstrate that the electrocatalytic stability of the Pt/C catalyst with a 3.8 nm average size of the Pt particles for the methanol oxidation is also the best among the Pt/C catalysts.

The reason for above results can be explained as follows. Generally, it is accepted that the rate-limiting step in the methanol oxidation is the oxidation of Pt-CO_{ad}, an adsorbed intermediate of the methanol oxidation [56,57,59,60]. H₂O can be dissociated and adsorbed on Pt, forming Pt-OH_{ad}. Pt-OH_{ad} can promote the oxidation of Pt-CO_{ad}:



Apparently, the rate of this reaction depends on the proportion and coverage of -CO_{ad} and -OH_{ad}. There are more oxygen-

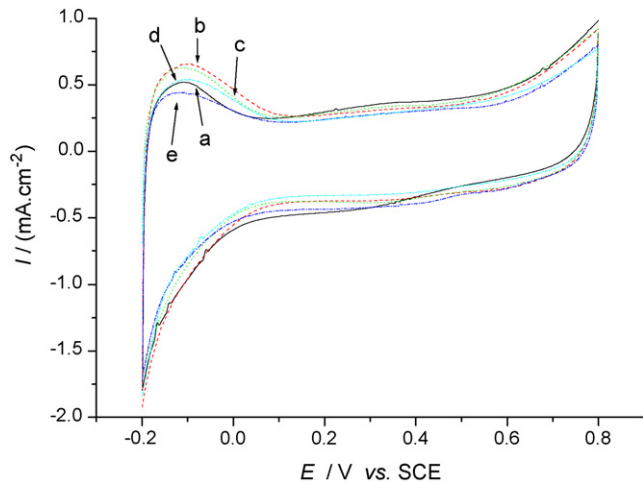


Fig. 6. The cyclic voltammograms of the Pt/C catalysts with average sizes of the Pt particles: (a) 2.2 nm, (b) 3.2 nm, (c) 3.8 nm, (4) 4.3 nm, and (5) 4.8 nm in the 0.5 M HClO₄ solution at the scan rate of 50 mV/s.

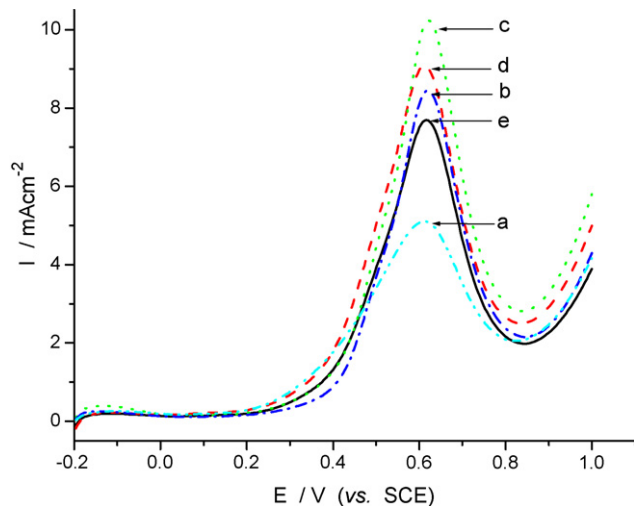


Fig. 7. The linear sweeping voltammograms of 0.5 M CH₃OH in the 0.5 M HClO₄ solution at the Pt/C catalysts with average sizes of the Pt particles: (a) 2.2 nm, (b) 3.2 nm, (c) 3.8 nm, (d) 4.3 nm, and (e) 4.8 nm. Scan rate: 50 mV s⁻¹.

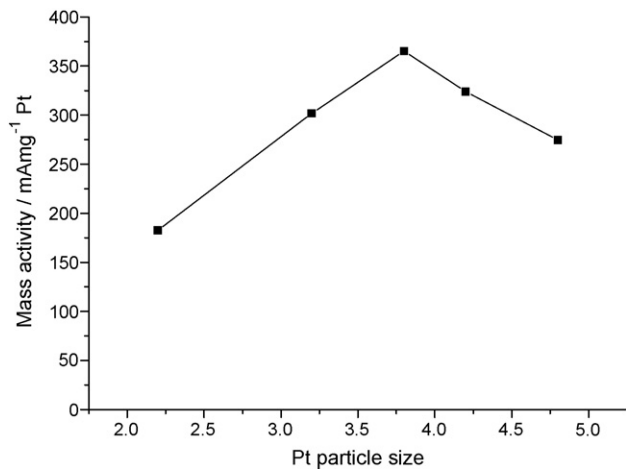


Fig. 8. The relationship curve between the mass activity of the Pt/C catalyst for the methanol oxidation and the average size of the Pt particles in the Pt/C catalyst.

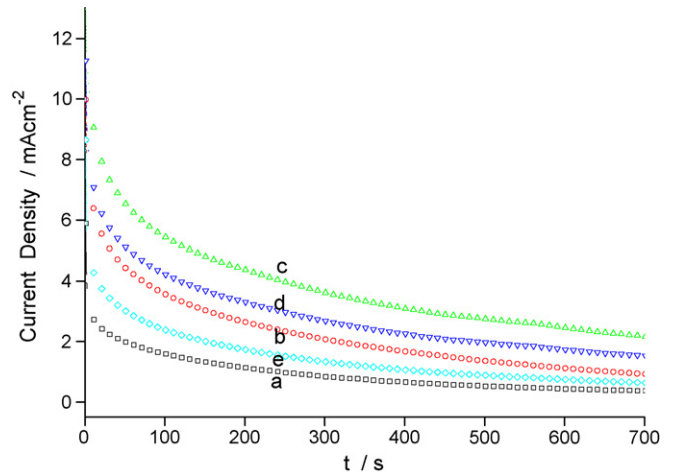


Fig. 9. The chronoamperometric curves of 0.5 M CH₃OH in 0.5 M HClO₄ solution at the Pt/C catalysts with average sizes of the Pt particles: (a) 2.2 nm, (b) 3.2 nm, (c) 3.8 nm, (4) 4.3 nm, and (5) 4.8 nm for 700 s. Fixed potential: 0.6 V.

containing groups on the surface of the small Pt particles because Pt is easily oxidized when the Pt particles are small [52,53]. The oxygen-containing groups on the surface of the Pt particles would restrain the decomposition/adsorption of methanol in the low potential region, i.e. the formation of -COH_{ad} . Thus, the electrocatalytic activity of the Pt/C catalyst with small Pt particles for methanol oxidation is low. On the contrary, total coverage of COH_{ad} and OH_{ad} is also small when the average size of the Pt particles is too large due to the small electrochemically active surface area as mentioned above. Thus, when the average size of the Pt particles in the Pt/C catalyst is too large, such as 4.8 nm, its electrocatalytic activity is also low. Therefore, the best electrocatalytic activity of the Pt/C catalyst for the methanol oxidation is obtained when the average size of the Pt particles in the Pt/C catalyst would be in the middle, e.g. about 3.8 nm.

4. Conclusions

In summary, the organic sol method for preparing ultrafine transition metal colloid particles reported for the first time by Bonnemant et al. [8], was improved. The improved organic sol method used SnCl₂ as the reductant and methanol as the organic solvent. Thus, this method is simple and inexpensive. In addition, it was found that the average size of the Pt particles in the Pt/C catalyst could be controlled by controlling the evaporation temperature of the methanol. The size effect of the Pt particles in the Pt/C catalyst on electrocatalytic activity of the Pt/C catalyst for methanol oxidation can be accurately investigated because the Pt/C catalysts with the different average size of the Pt particles were prepared using the same method. The XPS results demonstrated that the small Pt particles are easily oxidized so that the decomposition/adsorption of methanol on the surfaces of the Pt oxides could not occur. Thus, the Pt/C catalyst with small Pt particles shows low electrocatalytic activity for methanol oxidation. Because the Pt/C catalyst with a large average size of the Pt particles possesses a low specific surface area, the small

electrochemically surface area, its electrocatalytic activity for methanol oxidation is also low. Therefore, only the Pt/C catalyst with a medium average size of the Pt particle sizes, such as about 3.8 nm, shows high electrocatalytic activity for methanol oxidation.

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