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Fuel cells, particularly direct methanol fuel cells (DMFCs), have great potential as mobile power sources. It has been extensively reported that the DMFC performance strongly depends on the electrode catalyst, and many research groups have focused on the preparation of high efficiency cathode catalysts using all types of metal nanoparticle and support. However, most of these methods are either time-consuming with multiple-steps or there is low loading of the nanocatalyst dispersed on the supports. In this study, platinum nanoparticles of uniform diameter (approximately 4.3 nm) were efficiently dispersed on multi-walled carbon nanotubes (MWCNTs) by the temperature-controlled, microwave-assisted polyol method with the addition of sodium dodecyl sulfate (SDS) and [poly(vinyl pyrrolidone)] (PVP). The addition of SDS and PVP in chloroplatinic acid/ethylene glycol (EG) solution can cause the efficient and homogeneous dispersion of the catalyst particles on MWCNTs, enhance the adsorption of platinum particles, and reduce the residue of platinum particles. Moreover, temperature was determined to be the most important factor affecting the reduction of Pt in the process, and large amounts of Pt particles were characterized when the temperature ranged from 140 to 160 °C. The results indicate that the optimum temperature ranges from 140 to 160 °C, and that the loading amount of Pt/CNTs can reach more than 50 wt % in only 90 s of processing time. The significant improvements in dispersion and loading are due to the ability of SDS, to wrap the PVP-stabilized Pt nanoparticles around the surface of the carbon nanotubes. The characterization analyses were conducted by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), and thermal gravimetric analysis (TGA). [DOI: 10.1143/JJAP.47.2324]

KEYWORDS: carbon nanotubes, DMFC, catalyst, polyol process

1. Introduction

In recent years, owing to various environmental protection issues, the greenhouse effect, and the energy crisis, fuel cells have become the subject of great interest. With the world-wide interest in fuel cells are expected to meet energy needs with less environmental impact, greater efficiency and lower cost compared with traditional fossil fuels. Fuel cells have been proposed as a major energy source in the future because of their potential applications in electric vehicles and portable power sources.[1–4]

There are many factors that affect the efficiencies of the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC), but the Pt/C catalyst is one of the effective factors for the transformation of hydrogen or methanol to water.[5,6] It is well known that the catalytic activity of the Pt/C catalyst is strongly related to the particle size of Pt, the degree of particle size distribution, and the dispersion of Pt on the carbon support.[7] Therefore, the Pt catalyst with a suitable size, narrow size distribution, and high dispersion should have a high electrocatalytic activity for fuel cell application. As a result, considerable attention has been paid to the synthesis and characterization of catalyst nanoparticles.[8–10] Wet impregnation, the simplest method used for synthesizing Pt nanoparticles on a support as an electrocatalyst, requires the impregnation of the support (usually carbon black) with a platinum precursor, which is then heated at more than 300 °C in hydrogen atmosphere. However, the control of the particle size and size distribution by this method is rather limited.[11] Hence, there are continuing efforts to investigate alternative methods of synthesizing highly dispersed supported Pt particles with size control and uniform size, such as using microemulsions,[12] supercritical fluid,[13] sonochemistry,[14,15] polyol process,[16,17] and sputtering method.[18] All these methods generate colloids and clusters on the nanoscale with greater uniformity. However, these methods are either time-consuming, complex with multiple-steps, or there is low loading of Pt nanoparticles dispersed on supports.

Recently, several research teams have reported the synthesis of a metal catalyst by using microwave-assisted heating polyol process.[19,20] The reactant mixture of Pt or other metal precursor, support materials, ethylene glycol, and different types of additive in a beaker was placed in the center of a household microwave oven and heated for 5 s with irradiation on and 60 s with irradiation off for six cycles (so-called "intermittent microwave heating", IMH), or heated only for 30–60 s. These studies showed that the microwave-synthesized metal nanoparticles were very uniform in size and well dispersed on the support material. The process indeed has advantages in terms of simplisity, short reaction time, and high energy efficiency. However, the most important key factor for the chemical reaction is still unknown; that is, the actual reaction temperature of a metal precursor to precipitate as metallic nanoparticles in a household microwave oven is difficult to control or record during experiments. Moreover, the loading amount and the dispersion density of Pt particles on the support are still lower than those obtained by convention methods (<20 wt % compared with about 40–60 wt % by conventional methods). In this work, a temperature-controlled microwave heating system was used to demonstrate the effect of temperature on the polyol process. The effects of additives, reaction time, and other parameters on particle size, size distribution, loading amount and dispersion were also investigated under the temperature controlled micro-

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wave heating process to obtain highly dense Pt clusters on CNTs.

2. Experimental Procedure

Commercial raw multi-walled carbon nanotubes (MWCNTs) with diameters ranging from 40–60 nm were used in this study. The raw CNTs were first purified by microwave-assisted purification as described in our previous works to eliminate metal catalysts.[21,22] Chloroplatinic acid (H_2PtCl_6) dissolved in 30 mL of ethylene glycol (EG) and the purified MWCNTs sample were put in a 100 mL Teflon microwave closed vessel. The poly(vinyl pyrrolidone) (PVP) and sodium dodecyl sulfate (SDS) were mixed in the solution at the weight ratio of PVP : SDS : Pt = 1 : 1 : 1, and deionized water was also added into the solution at the volume ratio of water : EG = 1 : 9. The prepared mixture was ultrasonically treated for 10 min and then put into the temperature-controlled microwave heating system (Milestone, 2.45 GHz). The microwave power was set at 250 W. The temperature of the microwave vessels was controlled using the ATC-400CE Milestone temperature control system. A thermocouple was installed in a standard Milestone reference vessel to detect the temperature.

The microwave solution temperature was increased to the setting temperature within 90 s, and polyol reactions were carried out isothermally at different setting temperatures at various program-controlled durations. The experimental conditions are summarized in Table I.

After the microwave polyol procedure, the suspension was filtered using a 0.1 μm poly(tetrafluoroethylene) (PTFE) membrane in deionized water. After rinsing with alcohol and de-ionized (DI) water and vacuum drying for 8 h, the products were obtained.

The morphology of the Pt catalysts dispersed on MWCNTs was characterized by FEI Nova 200 scanning electron microscopy (SEM). The size and distribution of the Pt nanoparticles dispersed on CNTs were analyzed by JEOL JSM-2010 high-resolution transmission electron microscopy (HRTEM). X-ray diffraction (XRD) analysis was carried out on a Shimadzu XRD-6000 diffractometer system with Cu Kα radiation ($\lambda = 1.54$ Å) to calculate the mean particle size of the Pt particles. X-ray photoelectron spectroscopy (XPS; VG Scientific Microlab 310F) analysis was carried out using an Al Kα (1486.6 eV) X-ray source to analyze the compositions and chemical boinding change. The loading amount of Pt on CNTs was estimated by thermogravimetric analysis (TGA; Q500 Thermogravimetric Analyzer) with a rate t of 20 °C/min from 30 to 800 °C at the air flow rate of 60 sccm.

Table I. Summary of experiment conditions.

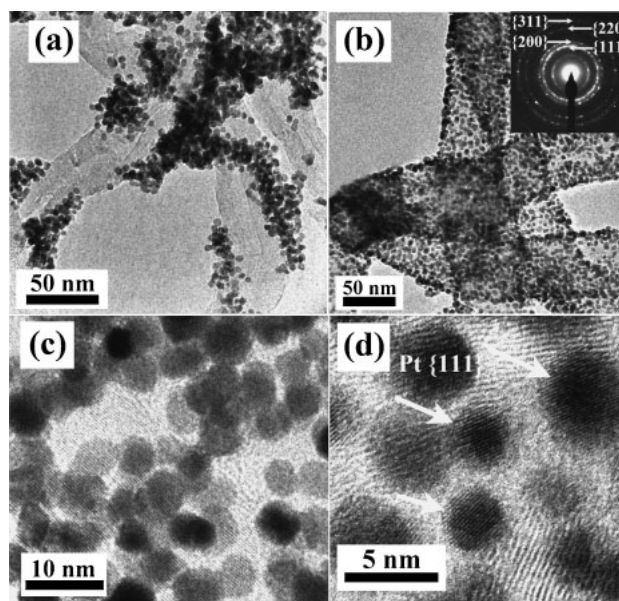|	
Carbon nanotubes	MWCNTs, 40–60 nm in diameter
Platinum precursor	H_2PtCl_6, 3.5×10^{-3} M
Stabilizer	Poly(vinyl pyrrolidone) (PVP), $M_W = 8000$
Surfactant	Sodium dodecyl sulfate (SDS)
Temperature (°C)	140
Reaction time (s)	90
Solvent	Ethylene glycol (EG)
Microwave power (W)	250
Microwave frequency (GHz)	2.45

Fig. 1. Effect of additives on synthesis of Pt/CNT electrode catalyst: (a) only PVP was added, (b) both PVP and SDS were added, (c) uniform particle size, (d) lattice fringes of Pt catalyst.

3. Results and Discussion

3.1 Effect of additives on dispersion of Pt particle on CNTs

Figure 1 shows TEM images of the dispersion of Pt clusters on CNTs under different experiment conditions for the reduction of the Pt particle from chloroplatinic acid by the microwave polyol procedure. The effects of changing the additives were investigated at a power of 250 W and 140 °C reaction temperature.

Figure 1(a) shows that Pt particles are about 4–5 nm when only 20 mg of PVP was added to the solution. However, the Pt particles are clustered and not well dispersed on the carbon nanotubes. There is no Pt particle supported on some CNT surfaces, as indicated by the arrow in Fig. 1(a). PVP can effectively reduce the particle size and even control the particle shape but the dispersion of the Pt particles on the CNTs is not uniform. This conclusion is the same as that of other researchers.[23] The reason is that the hydrophobicity of the CNTs makes it difficult for the Pt particles to highly disperse on the CNTs. Some researchers have found that the functionalization of the surface of CNTs can improve the dispersion of Pt on supports.[23] However, most synthesis methods require a long treatment time for the loading of Pt on CNTs. A very long treatment time will waste more energy and damage the structure of the CNTs, resulting in low mechanical strength which is needed in fuel cell cycle operation.

Figure 1(b) shows a TEM image of Pt particles prepared by adding 20 mg of SDS and PVP. It is clear that Pt nanoparticles of uniform sizes are nearly monodispersed on the surface of the CNTs and have similar particle sizes of approximately 4–5 nm as estimated from this TEM image. Also shown in the inset of Fig. 1(b) are rings in the corresponding selected area diffraction (SAD) pattern, which indicate that the Pt nanoparticles are polycrystalline and randomly oriented. Figure 1(c) shows a higher magnification HRTEM image of the Pt/CNT electrode catalyst. It is clear
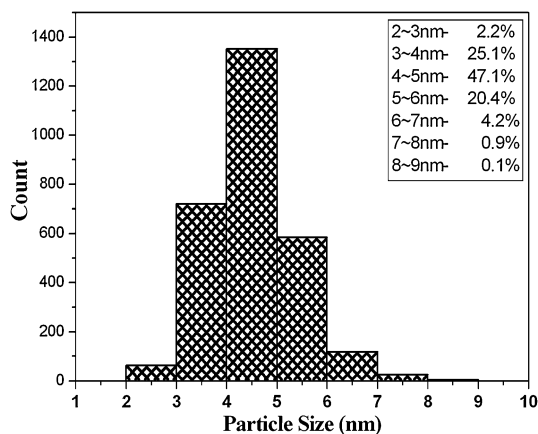
Fig. 2.　Particle size distribution of Pt nanoparticles.

that the nanoparticles are spherical in shape and uniform in size, and the size of the Pt nanoclusters is about $4-5$ nm. As indicated by the arrow in Fig. 1(d), a clear lattice fringe of the Pt cluster can be observed. It should be noted that this arrow indicates the {111} planes of this Pt nanoparticle.

Figure 2 shows the histogram of the Pt particle size distribution obtained from the enlarged HRTEM images of the well-dispersed Pt particles on the CNTs. The total sampling amount is 2868 particles. This diagram shows the narrow size distribution of the Pt clusters supported on the CNTs in which about 47% of the particles have diameters ranging from 4 to 5 nm, and only a few particles are larger than 6 or smaller than 3 nm. The average particle size is 4.3 nm as determined by statistical analysis.

3.2　Effect of temperature on reduction rate of Pt particle from chloroplatinic acid

Figure 3 shows TEM images of the Pt particles synthesized at different reaction temperatures by the microwave polyol method. Twenty milligrams of PVP and 20 mg of SDS were added to the synthesis solution. The reaction temperatures were 80, 100, 120, 140, 160, and 180 °C.

In Fig. 3(a), there is no Pt particle loading on the CNTs at the low reaction temperature of 80 °C, and at 100 °C only rare Pt nanoparticles can be found, as shown in Fig. 3(b). Figures 3(c)–3(e) show that the Pt particles are densely loaded on the CNTs when the synthesis temperatures increase. In Fig. 3(f), some lumps of Pt particles are occasionally observed, and the high temperature might have caused the aggregation or coarsening of the Pt clusters. Thus, higher temperatures cause the increase in the loading amounts of Pt particles but aggregate and broaden the particle size.

Figure 4 shows the Pt loading amounts at different reaction temperatures as determined by TGA analysis. Clearly, the loading amount is low at the low treatment temperature of 80 °C, and increases with increasing temperature to 140 °C where the largest loading amount of 54.64 wt % is achieved. When the temperature keeps increasing to 180 °C, the loading amount slightly decreases to 51.12 wt %, and this might be because some nanoparticles aggregates together or becomes coarse, and then peel off form the surface of the CNTs. The TGA analysis results are consistent with the SEM analysis results obtained, as shown in Fig. 3.
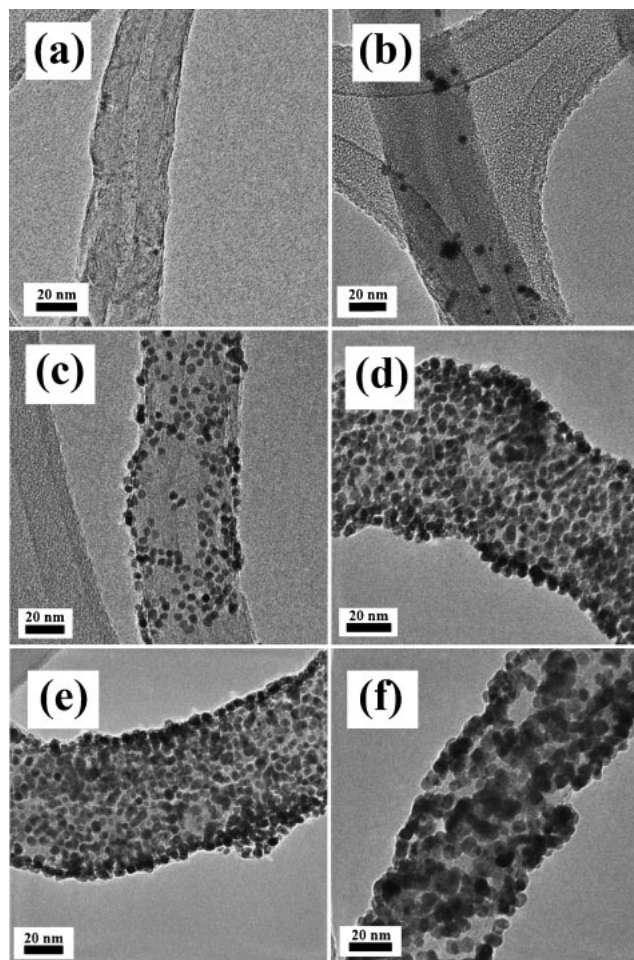

Fig. 3.　Synthesis of Pt nanoparticles on CNTs at different temperatures: (a) 80, (b) 100, (c) 120, (d) 140, (e) 160, and (f) 180 °C.
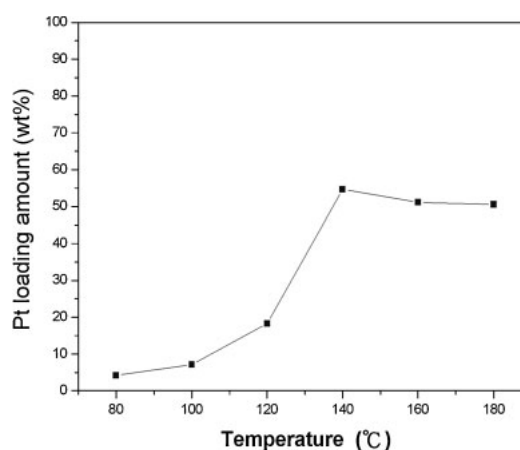

Fig. 4.　Loading amount of Pt clusters on CNTs at different reaction temperatures.

Thus, the reduction rate of the Pt particle from chloroplatinic acid and the loading amounts of the Pt particle can be controlled using the synthesis temperature. The reaction temperature is outstanding and seems to be the key factor that affects the loading amount of Pt particles on supports.

Figure 5 shows the XRD diffraction spectra of the samples under different treatment temperatures for the synthesis of Pt particles on the CNTs. The major diffraction
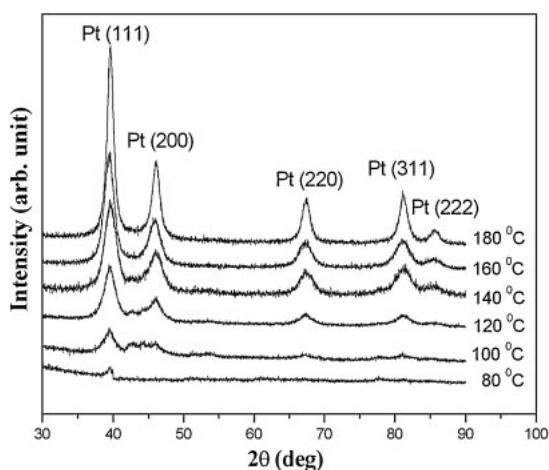
Fig. 5. XRD spectra of Pt/CNT catalysts synthesized at different temperatures.

Fig. 6. Chemical state analysis of Pt nanoparticles by XPS spectrum.

peaks at $2\theta = 39.6, 46.1, 67.4, 81.2$, and $85.6°$ correspond to the reflection planes of (111), (200), (220), (311), and (222), respectively, which are consistent with the face-centered cubic structure of Pt. It can be observed that there is only a weak Pt signal found in the sample synthesized at $80°C$ at 2θ of $39.6°$, which agrees with the results of the TEM analysis, as shown in Fig. 3(a). Moreover, by increasing the temperature, the Pt signals become stronger in the sample synthesized at 100 and $120°C$. When the temperatures keep increasing above $140°C$, the Pt peaks become much stronger in the samples of 140, 160, and $180°C$.

The mean Pt nanoparticle size can be calculated using the Scherrer equation[24] on the basis of the Pt(111) peak illustrated in Fig. 5.

$$D = \frac{0.9\lambda_{K\alpha}}{B_{2\theta}\cos\theta}$$

Here, D is the mean particle size of the Pt catalyst, $\lambda_{K\alpha}$ is the wavelength of the incident X-ray $(1.54\,\text{Å})$, 2θ is the Bragg diffraction angle for peak position, and $B_{2\theta}$ is the full width at half maximum (FWHM). The average particle size of Pt is about $4.3–4.5\,\text{nm}$ in all the samples of $100–160°C$ shown in Figs. 3(b)–3(e), but is $7.6\,\text{nm}$ for the sample synthesis at $180°C$. These results totally agree with the TEM analysis result, as shown in Fig. 3, and indicate that temperature might be a key factor for controlling the amount of Pt particles dispersed on the CNT, but a high temperature could result in the coarsening of Pt particle size.

3.3 Effect of process time on loading amounts of Pt particle

The TGA analyses of Pt loading amounts in different synthesis time ranges from 1.5 to 90 min at $140°C$ show that the loading amount reaches $52.1\,\text{wt}\%$ as soon as the temperature reaches $140°C$, and the dispersion of Pt on the CNTs is highly uniform. As the reaction time increases, the loading amount of Pt on the CNTs slightly increases. The loading amount rises to $60\,\text{wt}\%$ after 90 min of reaction time. However, the disadvantages of long treatments are in terms of time and energy consumption. Thus, the optimum reaction time is 1.5 min, within which the loading amounts of Pt particles approach $53.2\,\text{wt}\%$.
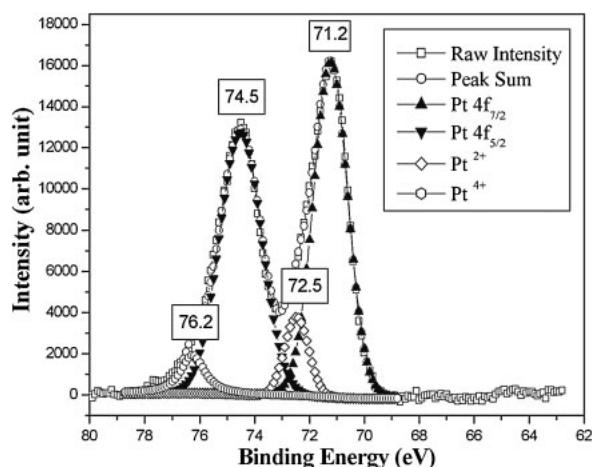
3.4 XPS analyses of chemical state

Figure 6 shows the XPS spectrum of the Pt 4f peak of the microwave-polyol-synthesized Pt particles on MWCNTs. The Pt 4f peak consisted of two pairs of signals and the most intense peaks ($4f_{7/2}$ at $71.2\,\text{eV}$ and $4f_{5/2}$ at $74.5\,\text{eV}$) can be assigned to metallic Pt. A weak peak that appeared at $72.5\,\text{eV}$ could be regarded as the chemical state of Pt^{2+} in $Pt(OH)_2$, and the other peak at $76.0\,\text{eV}$ might be attributable to halides. Compared with the results reported by Chen et al.,[25] they synthesized Pt on CNTs by microwave heating without the addition of PVP as protector. Their XPS results showed intense Pt oxidation state of PtO in their products. However, there was no oxide found in our experiments, only a weak peak attributable to halides. This result indicates that the surface protection of Pt particles during synthesis is required to prevent nanoparticles oxidation.

Many methods of synthesizing Pt particles on all types of carbon support have been reported. Guo et al.[26] reported a method of preparing $20\,\text{wt}\%$ Pt/C electrocatalysts by the reduction of chloroplatinic acid with sodium borohydric and using citric acid as a stabilizing agent in an ammonium hydroxide solution. Although the temperature of this method was sufficiently low at $50°C$, the total stirring time reached 13 h and the Pt particles were not only clearly clustered together on carbon black but also partially oxidized during synthesis. Liu et al.[12] studied the synthesis of the PtRu/C catalyst from microemulsions and emulsions. This method could be carried out at room temperature but required a long reaction time of 24 h, and the particle size distribution widely ranged from 1 to 8 nm with a mean size of 4.3 nm, and that ranging from 4 to 14 nm with mean size of 9.2 nm. Lin et al.[13] reported the synthesis of the PtRu/CNT nanocomposite in supercritical fluid for DMFC application. The total reaction time was shortened to 75 min; however, the reaction temperature was increased to $200°C$ and the high pressure required to maintain the supercritical fluid may cause safety problems. Moreover, this method results in a relative low loading amount of metal nanoparticles at $6.4\,\text{wt}\%$ compared with our results $(>50\,\text{wt}\%)$ and the aggregation of particles on CNTs still appeared in their TEM analysis. Kim et al.[23] proposed a method for the high dispersion of Pt particles on CNTs by the surface thiolation of CNTs and wet impregnation. In this method, MWCNTs

were first treated for 12 h with 3 M HCl at 70 °C, then stirred in concentrated HNO_3 for 15 min to prepare carboxylated MWCNTs, and chlorinated by refluxing for 12 h with $SOCl_2$ at 70 °C. After the remaining thionyl chloride was evaporated, the thiolated MWCNTs were obtained by reacting with $NH_2C_6H_4SH$ in dehydrated toluene for 24 h at 70 °C. Needless to say, this method was too complicated and required more than 48 h to pretreat the CNTs. The dispersion of Pt on the CNTs reported in this method was, moreover, lower than that of our results based on both TEM analyses. Shao *et al.*[27] studied the preparation of Pt on MWCNTs by the *in situ* ion exchange method for oxygen reduction. The MWCNTs were first immersed in a Pt precursor for 48 h, then in ultrapure water, and then stirred for 48 h to remove the non-ion-exchanged precursor. The ion-exchanged Pt ions were then reduced to Pt nanoparticles in H_2 at 190 °C. Although this method was simple without requiring more equipment, the total treatment time was so long at more than 96 h, and both the dispersion density and loading amount (25 wt %) of Pt particles were lower than those obtained in this study.

Aside from the conventional methods discussed previously, there are many researchers who have devoted their efforts on the microwave-assisted heating method to synthesize Pt nanoparticles on all types of support.[28–37] The size and size distribution of Pt nanoparticles have been reported to be well controlled, but the dispersion density and loading amount on CNTs are still low (<20 wt %) compared with those obtained by conventional methods. And, most of their reports did not discuss the effect of temperature on Pt loading amount in the microwave heating methods; only the reaction time were recorded.

In our studies, the high loading and dispersion of Pt nanoparticles with a suitable and uniform size distribution on MWCNTs have been successfully investigated by the addition of SDS. Although it has been reported that sputtered Pt nanoparticles could also have such high dispersion on CNTs, the disadvantage is that only several layers of CNTs on the top surface can be sputtered on.[18]

Chemical methods do not have such restrictions and can be used to disperse nanoparticles on CNTs at any direction; however, it has never been reported that chemical methods can result in the same high dispersion of Pt on CNTs as the sputter method and the method used in this work. This work shows that the addition of SDS in solution maximizes the advantages of both physical and chemical methods to realize highly dispersed Pt particles on each CNT at any direction. These results showed a successful way of synthesizing a Pt catalyst having a suitable and uniform size distribution with high dispersion on CNTs by the microwave-assisted heating method with the addition of SDS.

The mechanism explaining the role of SDS in the Pt particle distribution and loading amount can be considered as two parts. First, it is well known that PVP in the solution can be adsorbed on the surface of the Pt cluster to affect the growth of particle size or the shape of particles; that is, during the process, a layer of PVP covers the Pt particles. Second, SDS is known to have the ability to wrap the PVP monolayer around single-walled carbon nanotubes (SWNTs) to form a fluorescent coating of CNTs without covalent modification by chemical treatment that could change the favorable properties of the tubes.[38] This denotes that SDS has an excellent ability to attach PVP on the CNTs. Based on these two points, Pt nanoparticles have PVP covering them in solution and SDS could wrap PVP around CNTs. It is considered that the added SDS in this work could improve the dispersion and loading of Pt on tubes by binding the Pt-covering PVP and tubes together.

4. Conclusions

Pt nanoparticles on CNTs were prepared by rapid and uniform microwave heating, which provided a more homogeneous temperature gradient for the quick nucleation and growth of Pt particles. The effects of temperature and time on the synthesis of Pt by the microwave-assisted methods were clarified by carefully controlling them individually, and the results showed that temperature is indeed the more effective parameter than reaction time, and this is first reported in this work. A Pt/CNT electrocatalyst with a suitable narrow distribution size and highly dispersed Pt nanoparticles was synthesized by a one-step microwave-assisted polyol method by adding an appropriable amount SDS to the synthesis solution. It was found that the SDS in the solution could be used as a good agent for ping many PVP-adsorbed Pt nanoparticles around MWCNTs side by side without particle agglomeration, and the loading of Pt on CNTs could exceed 50 wt %, which is higher than the 20 wt % or lower obtained by conventional methods or other microwave methods without the addition of SDS. The synthesis method proposed in this paper is simple and fast and may have great potential for preparing other high-loading-supported metal and alloy systems.

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