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Microwave polyol synthesis of Pt/C catalysts with size-controlled Pt particles for methanol electrocatalytic oxidation

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Abstract Pt/C catalysts with different mean size of Pt particles were prepared by a microwave-assisted polyol process and characterized by TEM and XRD. The effects of the synthesis solution pH on Pt particles size and distribution, and their activity for methanol electrooxidation were investigated. Pt nanoparticles were small and uniform with mean size of 2.7 nm under the pH of 9.5. Pt/C catalyst showed high activity for methanol electrooxidation.

Introduction

Direct oxidation methanol fuel cell (DMFC) has been a subject of intense study because of its numerous advantages [1, 2]. The excellent catalytic activity of platinum with respect to methanol oxidation at low temperatures makes this metal electrocatalyst ideal for use as an anode in DMFCs. As is well known, catalytic activity strongly depends on the size and size distribution of the metal particles, and their dispersion on supports [3]. Many studies on Pt or Pt-based alloys nanocatalysts have focused on the control of particle size and their effects on catalytic activity [4–10]. However, different preparation methods and different carbon supports were used, so the metal-support interaction could also have been changed [11]. Moreover, high temperature, complicated apparatus, complex process control, and special conditions are required for these approaches. Therefore, it is of great significance to find a fast, simple and energy efficient approach to control the size of Pt nanocatalysts.

The polyol process has been proven to be a simple and effective method for the synthesis of metal colloidal particles. In this method, ethylene glycol (EG) is commonly used as solvent for the metal salts, reducing agent, and growth medium for the metal particles. This polyol process has successfully been used to synthesize Pt/C nanocatalysts [12]. Conductive heating is often used in the conventional polyol process. However, microwave heating may be a better synthesis option in view of its uniformity, speed, energy efficiency and implementation simplicity. As a new promising method, the microwave heating has received considerable attention for nanosized materials synthesis [13–15]. The microwave in combination with the polyol process has been used to synthesize polymer stabilized noble metal colloids, such as Pt, Ru, Ag and Pd [16–19]. Pt and Ru nanoparticles supported on carbon have also been prepared by modified microwave polyol process [19, 20], and the Pt/XC-72 carbon and Pt/carbon nanotubes prepared as such showed very good electrocatalytic properties for methanol electrooxidation [21, 22].

It was reported that the polyol solution pH is a very important fact that influences noble metal particle size in the polyol process for preparing metal particles [16]. In order to investigate the effects of the synthesis solution pH on the size and distribution of Pt nanoparticles, herein the Pt/C were prepared by microwave heating of EG solution of hexachloroplatinic acid with different pH. The effects of the synthesis solution pH on the size and size distribution of Pt particles and the activity of Pt/C catalysts for methanol electrooxidation were discussed.

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Experiments

Preparation and characterization of Pt/Vulcan XC-72 carbon catalysts

Pt/C catalysts were prepared by microwave polyol process. Briefly, 2.0 ml of 0.05 M aqueous H_2PtCl_6 solution and 50 ml of EG were put into a 100 ml beaker. The synthesis solution pH was adjusted by adding 0.8 M aqueous KOH solution. The pH was estimated by close pH test paper. Then 80 mg of Vulcan XC-72 carbon was added into the above solution and ultrasonically dispersed in the solution. The beaker was placed in the center of a microwave oven (National NN-MX200WF, 2450 MHz, 800 W) and heated for 60 s at 800 W. The resulting suspension was filtered and the residue was washed with acetone and deionized water. The solid products were dried at 100 °C for 12 h in a vacuum oven.

The products were characterized by TEM on a JEOL-200CX transmission electron microscope operating at 200 kV, and XRD on a Thermo X'Tra X-ray diffractometer with monochromatized Cu K_α radiation. The mass percentages of Pt in Pt/C catalysts were analyzed by energy dispersion X-ray (EDX) on JEOL JSM-5600 LV scan electron microscopy.

Electrochemical measurements.

Cyclic voltammetry of methanol electrooxidation was performed in a three-electrode cell on CHI 660 B potentiostat/galvanostat at room temperature. Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrolyte was an aqueous solution 2 mol/l CH_3OH+1 mol/l H_2SO_4. The working electrode was a thin layer of Nafion-impregnated catalyst cast on a vitreous carbon disk with 4 mm diameter held in a Teflon cylinder. The catalyst layer was obtained in the following way: a slurry was first prepared by sonicating 1 h a mixture of 500 mg of deionized water, 10 mg of Pt/C catalyst and 200 mg of Nafion solution (Aldrich, 5 w/o Nafion); then 2.0 μl of the slurry was pipetted and spread on the vitreous carbon disk; the electrode was finally dried at 80 °C for 10 min. All electrolyte solutions were deaerated by high purity nitrogen for 30 min prior to electrochemical measurement.

Results and discussion

Repeated EDX measurements showed that the mass fraction of Pt in Pt/C catalysts prepared by microwave assisted polyol process ranged from 19.3% to 20.1%, which agreed with the ratio of Pt: carbon support in the starting materials. Figure 1 shows a typical EDX spectrum for Pt/C catalyst. Figure 2 shows the XRD patterns of Pt/C catalysts prepared in EG solution with different pH values by microwave heating. It can be seen that Pt nanoparticles supported on XC-72 carbon form a face-centered cubic (fcc) structure and have major peaks at $2\theta = 39.7°$ (111), 46.2° (200), 67.5° (220), which is consistent with the standard card (JCPDS No. 04-0802). The peak at $2\theta = 25°$ is attributed to XC-72 carbon (002). The above facts indicate that platinum (IV) has been reduced to Pt (0), the Pt nanoparticles were adsorbed on XC-72 carbon. Figure 2 also shows that the FWHM of XRD peaks attributed to Pt nanoparticles increase with the increase of the synthesis solution pH, indicating that Pt particle become smaller with the increase of the pH.

TEM images and the Pt particles size distribution histograms of Pt/C catalysts synthesized by microwave heating polyol process are shown in Fig. 3. The mean particle size and size distributions were obtained by measuring about 150–200 randomly chosen particles in the TEM images. As shown in TEM images of Fig. 3, Pt nanoparticles show a uniform and high dispersion of Pt particles on the carbon surface, except a slight particle agglomeration of Pt/C prepared from the synthesis solution of pH = 3.4. Figure 3 clearly shows that the Pt particle size become smaller and uniform with the increase of the synthesis solution pH. In addition, the particle size distribution becomes narrow, and the standard deviation decreases with the increase of the pH. It indicates that the uniformity of Pt nanoparticles is improved with the increase of the synthesis solution pH. Figure 4 shows the variation of the mean size of Pt particles of the microwave-synthesized Pt/C catalysts by varying the synthesis solution pH. Figure 4 clearly shows that the mean size decreases form 5.5 ± 0.3 nm to 2.7 ± 0.3 nm with the increase of the synthesis solution pH from 3.4 to 9.5. The above facts demonstrate that the synthesis solution pH is an important factor that influences the Pt particle size and size distribution in microwave

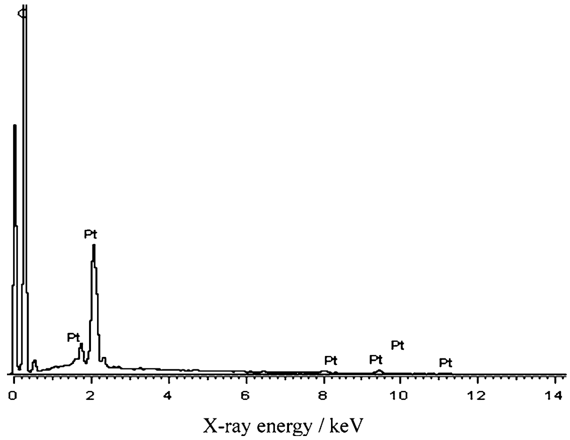


Fig. 1 A typical EDX spectrum of microwave-prepared Pt/XC-72 catalyst from EG solution

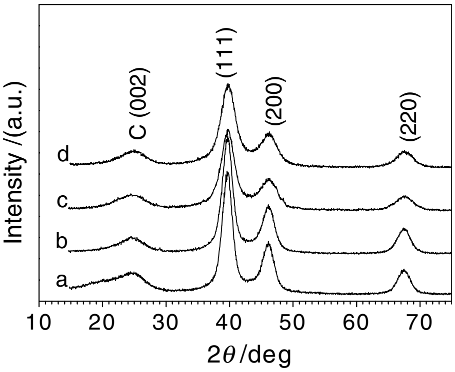


Fig. 2 XRD patterns of microwave-prepared Pt/XC-72 from EG solution with different pH (a: pH = 3.4; b: pH = 5.5; c: pH = 7.3 and d: pH = 9.5)

polyol process for preparing Pt/C catalysts. Therefore, Pt particle size and size distribution could be controlled by varying the synthesis solution pH.

The general mechanism for the synthesis of metal nanoparticles by microwave polyol process is as follows: polyol can be rapidly heating by microwave radiation due to its high dielectric constant. The temperature of the synthesis solution was tested by a thermocouple to be above 170–180 °C at the end of the microwave heating. The polyol decomposes to generate reducing species for the reduction of the metal ions to metallic particles at high temperatures [18, 19]. The fast and uniform microwave heating leads to rapid reduction of the metal ions and formation of metallic nuclei, thus greatly facilitates small and uniform particle formation. On the other hand, there are a large number of functional groups such as carboxyl and carbonyl group on the surface of Vulcan XC-72 carbon. Platinum ions in the EG solution would interact with and attach to these surface functional groups on carbon by a coordination reaction or an ion-exchange reaction, thus functioning as a nucleation precursor that finally reduced to produce Pt nanoparticles supported on carbon surface [23].

In our experiments, we observed that the synthesis solution pH greatly influenced the Pt particle size and size distribution. The effect of pH on the particle size has also been reported in polyol process for synthesis of noble metal colloidal particles by other researchers [17, 24]. But in such a liquid phase process, noble metal particles have a strong tendency to agglomerate during their formation. Polymers, especially poly-vinylpyrrolidone (PVP) were employed as a steric stabilizer in microwave polyol process to avoid particles agglomeration [25, 26]. But in previous works, it was found that PVP stabilizer would restrain Pt nanoparticles from supporting on carbon materials due to PVP's strong adsorption on Pt particles. Recently, Yang et al. [27] reported synthesis of small and uniform Pt nanopartilces by microwave polyol process. They observed that the reduction of metal ions was equally complete even if no adding NaOH, but the metal colloids so obtained were unstable, and precipitates would appear several minutes later. They put forward a modified reaction mechanism as following equations:

$$\mathrm{CH_2OHCH_2OH = CH_3CHO + H_2O}$$

$$\begin{aligned}\mathrm{2CH_3CHO + PtCl_6^{2-} + 6OH^-} &= \mathrm{2CH_3COO^-} \\ &\quad \mathrm{+ Pt + 6Cl^- + 4H_2O}\end{aligned}$$

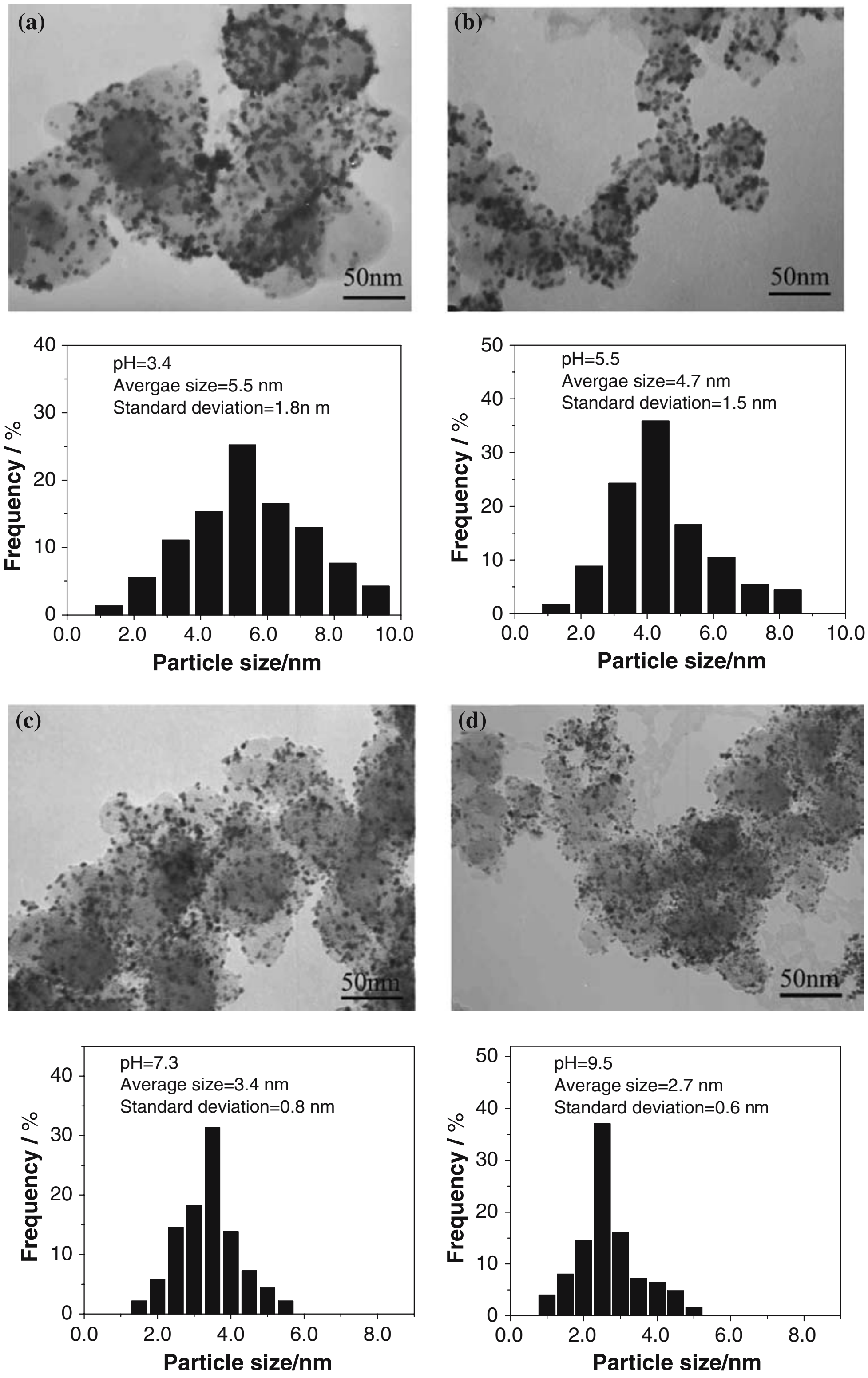
Acetate is believed to act as a good stabilizer for the metal colloids. It was also reported that acetate was used as a stabilizer for preparing noble metal nanoparticles in polyol solution [27, 28]. The stabilizing mechanism is explained by forming chelate-type complexes via its carboxyl groups. But such interaction between Pt particles and acidic form (acetate acid) is smaller. Acetate acid is believed to be a poor stabilizer for noble metal nanoparticles. The pH of the synthesis solution is thus expected to greatly influence the stability and size of the metal particles. Therefore, Pt particles would become smaller and more uniform when the synthesis solution pH increases. So Pt particle size can be selected by adjusting the synthesis solution pH. The synthesis method reported in this work may offer the opportunity to control metal particle size.

Figure 5 shows the cyclic voltammograms of methanol electrooxidation over Pt/C catalysts prepared in EG solution with different pH by microwave polyol process in 2 M CH_3OH/1 M H_2SO_4 electrolyte. The electrooxidation of methanol began at 0.30–0.35 V versus SCE as shown in Fig. 5. The current peaks at about 0.70 V versus SCE in the forward scan are attributed to methanol electrooxidation. When the synthesis solution pH increases from 3.4 to 9.5, the current peaks increase, which indicates that the activity of Pt/C catalyst for methanol electrooxidation increases by increasing the synthesis solution pH from 3.4 to 9.5. It is well known that the size and distribution of metal catalyst particles is one of the important factors that greatly influence its catalytic activity. The smaller and more metal particles exhibit commonly the higher catalytic activity. As shown in Fig. 3, when the synthesis pH increases from 3.4 to 9.5, Pt particles become smaller and more uniform, the mean size decreases from 5.5 to 2.7 nm. The activity of Pt/C catalyst for methanol electrooxidation is thus improved with the increase of the synthesis solution pH.

Conclusions

A simple and effective method for preparing Pt/C catalysts with size-selected Pt particle size was presented. In

Fig. 3 TEM images of microwave-synthesized Pt/XC-72 and size distribution of Pt nanoparticles (a: pH = 3.4; b: pH = 5.5; c: pH = 7.3 and d: pH = 9.5)



this method, Pt particles with different mean sizes supported on XC-72 carbon were prepared by microwave polyol process. When the EG solution pH increases from 3.4 to 9.5, Pt particles become smaller and uniform, and the mean particle size decreases from 5.5 to 2.7 nm. Therefore, the activity of Pt/C for methanol electrooxidation is improved with the increase of the synthesis solution pH.

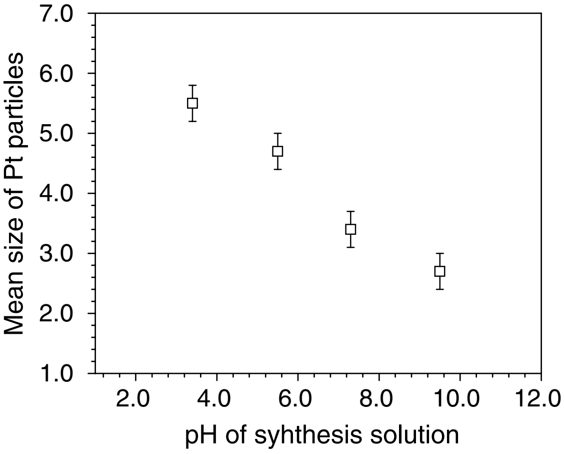


Fig. 4 Variation of mean size of Pt particles of the microwave-synthesized Pt/C catalysts by varying the synthesis solution pH

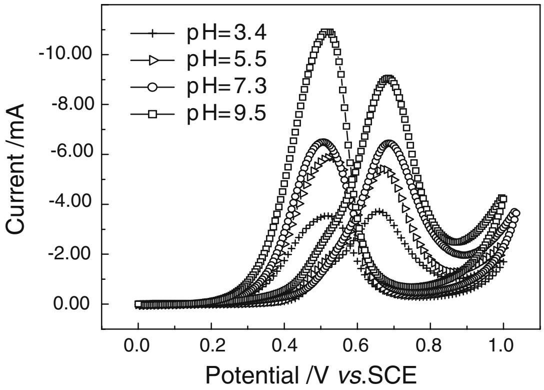


Fig. 5 Cyclic voltammograms of methanol electrooxidation over the microwave synthesized Pt/XC-72 catalysts in 2M CH_3OH/1 M H_2SO_4 at a scan rate of 20 mV/s at room temperature

The effects of the synthesis solution pH on Pt particle size and distribution can be explained as follows: EG is oxidized to acetate [27], which is believed to be a good stabilizer [28], but acetate acid is a poor stabilizer. In the EG solution with the higher pH (7.4 and 9.5) acetate acts as a good stabilizer, result in the formation of Pt particles with the small and uniform size, but under lower pH (3.4 and 5.5), acetate acid acts as a poor stabilizer, result in the formation of Pt particles with large size and broad distribution.

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