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Pd/C Catalysts Synthesized by Microwave Assisted Polyol Method for Methanol Electro-Oxidation

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Pd/C (20 wt%) catalysts are synthesized using microwave-assisted polyol method and employed for methanol electro-oxidation. A narrow size distribution and uniformly dispersted Pd nanoparticles were achieved by adjusting the solution pH, addition of stabilizer KBr, microwave heating time and solvents. The structure, morphology and electrocatalytic activities of the catalysts are characterized with XRD, TEM and cyclic voltammetry(CV). The results show that the optimum addition of KBr (0.12 M) and NaOH (0.05 M) are respectively 4 mL and 5 mL, the proper heating time is 2 min. Solvents were found to be key factor for influence the performance of catalyst. The sample prepared in 10 vol % ethylene glycol and 90 vol % glycerol mixture under the optimal condition shows the best catalytic activity with its anodic peak current density reaching to 785 A/g Pd in deoxygenated 0.1 M KOH + 1 M CH_3OH mixed solution.

Keywords: microwave assisted polyol method, methanol electro-oxidation, nano palladium, catalysts,

1. INTRODUCTION

Direct methanol fuel cells(DMFCs) is attracting widespread interest over the past few years due to its high energy efficiency, easy transportation and storage of the fuel, and low pollution for environment [1]. It is considered as one of the promising power source for portable electronic devices and electric vehicles [2]. However, it is difficult for commercialization of DMFCs [3] owing to slow anode kinetics, the poisoning of anode catalyst, and methanol crossover [4]. Therefore, the study on the anode catalyst is still worth making. How to choose the right materials and the appropriate preparation method to improve the activity and stability of the anode catalysts is the most urgent problem to be solved [5].

The most serious reason to decrease catalytic activity is that the catalyst is often influenced by strongly chemisorbed carbonaceous intermediates [6]. It is widely known that Pt and Pt-based alloys are the most promising anode catalysts used in DMFC, but Pt has limitations for large scale applications because of its limited abundance, high cost and terrible CO tolerance [7]. However, Pd is more widespread in the earth crust than Pt [8], replacing Pt by Pd would decrease the cost of the electrodes. In addition, it is stable in an alkaline environment and shows better CO tolerance comparing to Pt catalysts [9,10]. These properties have lead to consider Pd as a possible catalyst for the reactions in which CO appears as a poisoning intermediate, such as in the methanol or in the ethanol [11].

Preparation method of electrode catalysts plays a crucial role in improving catalytic activity [12]. For this reason, researchers attempt various approaches to prepare catalysts, such as chemical reduction [13,14,15], pulsed laser deposition [16], catalytic Chemical Vapor Deposition (cCVD) [17], electrodeposition [18], reverse microemulsion method [19], immersion method etc. Within which the microwave assisted polyol process, as a convenient, fast, effective method， attracted a lot of attention [20, 21]. Many factors influence the effect of microwave assisted polyol method, such as pH, heating time [22], stabilizer. But up to now, the effect of solvents has been rarely reported.

In this study, we used the microwave assisted polyol method to synthesize the Pd nonoparticles supported on carbon black (Pd/C) catalysts for methanol oxidation in DMFCs. A series of catalysts were synthesized in order to optimize the preparation conditions such as the addition of NaOH and KBr, microwave heating time and solvents. The influence of Pd deposition conditions and size distribution of Pd nanoparticales were discussed. Furthermore, the catalytic activities of obtained catalysts were studied.

2.EXPERIMENTAL

Synthesis of catalysts— Pd/C catalysts with the Pd loading of 20 wt% were prepared by microwave-assisted polyol process in polyol solution with $PdCl_2$ as a precursor salt. In brief, Vulcan XC-72 Carbon Black treated by 4.0 M HNO_3 (with the aim to increase the hydrophilic functional groups) were firstly impregnated with 1 mL of 0.0565 M $PdCl_2$, then 4 mL 0.12 M KBr was added, after ultrasonic treatment for 1 h, 5 mL 0.05 M NaOH was added drop by drop under magnetic stirring, $PdCl_2$, KBr and NaOH were all dissolved in glycerol or other solvents. The beaker containing the solution was put into a household microwave oven and then heated for 2 min at 800 W. Finally, the samples were filtered, washed with distilled water and ethanol, dried in an oven at 60 ℃ over night. Table 1 shows the preparation conditions of different samples.

Characterization of catalysts—The morphology of Pd/C catalysts is investigated using a JEM 2100 transmission electron microscope (TEM, JEOL). The X-ray diffraction patterns were recorded on Rint D/max2000 wide angle goniometer (Rigaku Co. Ltd.) using Cu target, Kα radiation with a scanning range (2 theta) from 20° to 90° at 40 kV/40 mA, divergence slit = 1°.

Table 1. The preparation conditions of the samples

Sample	NaOH (mL)	KBr (mL)	Heating time(min)	solvent	Impregnation
A1	5	4	2	glycerol	With
A2	5	4	2	glycerol	Without
B1	0	4	2	glycerol	With
B2	1	4	2	glycerol	With
B3	2	4	2	glycerol	With
B4	3	4	2	glycerol	With
B5	4	4	2	glycerol	With
B6	6	4	2	glycerol	With
B7	7	4	2	glycerol	With
C1	5	0	2	glycerol	With
C2	5	1	2	glycerol	With
C3	5	2	2	glycerol	With
C4	5	3	2	glycerol	With
C5	5	5	2	glycerol	With
C6	5	6	2	glycerol	With
D1	5	4	0.5	glycerol	With
D2	5	4	1	glycerol	With
D3	5	4	3	glycerol	With
E1	5	4	2	ethylene glycol	With
E2	5	4	2	propylene glycol	With
E3	5	4	2	butanediol	With
F1	5	4	2	10 vol % EG +90vol% glycerol	With
F2	5	4	2	20vol% EG +80vol% glycerol	With
F4	5	4	2	40vol% EG +60vol% glycerol	With
F6	5	4	2	60vol% EG +40vol% glycerol	With

Electrode preparation and electrochemical measurement— All electrochemical measurements are performed in a conventional three-electrode cell at room temperature (25℃) using an CHI 1100A electrochemical workstation (Shanghai, China). The fabrication of the working electrode is given below: 5 µL of catalyst ink, prepared by mixing 2.0 mg of Pd/C catalyst with 1 mL 0.2 wt% Nafion ethanol solution (DuPont Corp., U.S.A.), is placed on a polished glassy carbon working electrode (Φ4) with a microsyringe. A sheet of Pt and a saturated calomel electrode (SCE) are used as counter and reference electrodes, respectively. Before electrochemical measurements, the electrolytes are deaerated by bubbling with high-purity nitrogen for 30 min.

3. RESULTS AND DISCUSSIONS

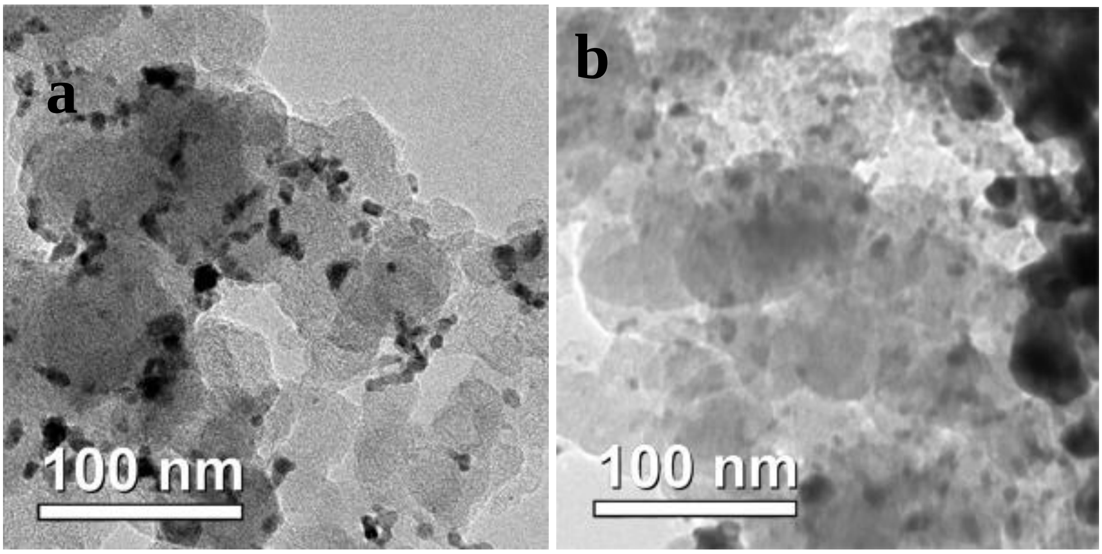

Figure 1. TEM pictures of (a) sample A1 prepared with impregnation progress and (b) sample A2 prepared without impregnation.

3.1 Effect of the sequence of adding materials

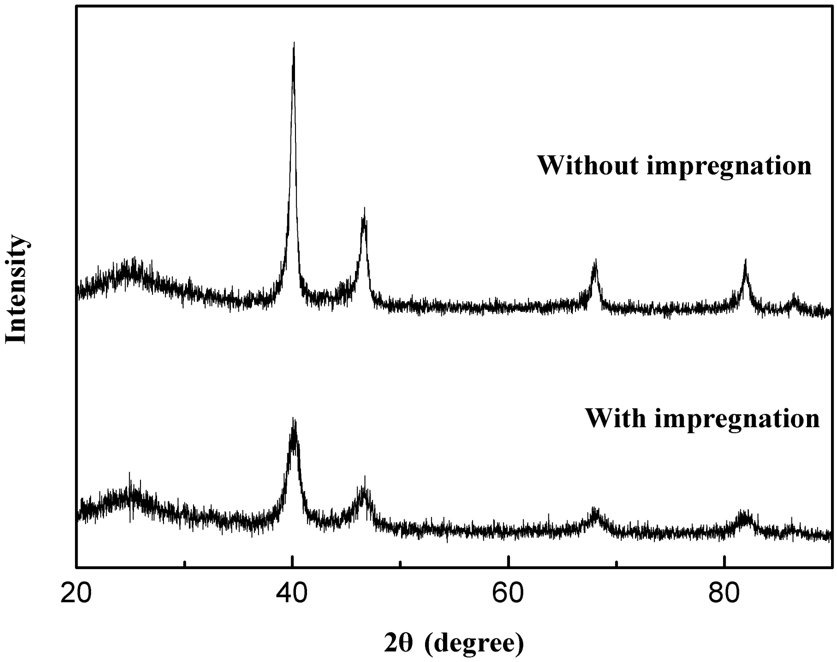

Figure 2. X-ray diffraction patterns of A1(with impregnation) and A2(without impregnation).

For Sample A1, Carbon Blacks were impregnated in $PdCl_2$ solution for a while and then ultrasound was used after adding the KBr solution, after that, adding NaOH solution dropwise while stirring. For Sample A2, all solutions were mixed before adding Carbon Blacks, then the supports were dispersed in the solution by ultrasound and stirring. After that, microwave was introduced to heat the solution. From the TEM images in Fig 1a and 1b, it can be seen that the Pd nanoparticles of Sample A1 are uniform and well dispersed on the carbon support. The Pd particles of A2 agglomerate seriously.

XRD patterns of A1 and A2 catalysts are showed in Figure 2, which reveals that the peaks of the sample prepared without impregnation is much narrower than that prepared with impregnation. This implies that the particles of A2 are much larger than those of A1. The result is also demonstrated by TEM images. To sum up， the impregnation process is a very important progress for the preparation of highly dispersed Pd/C catalyst. The possible process during which Pd nanoparticles grow on carbon black under our preparation conditions is described as follows: in the process of A1, concentrated $PdCl_2$ solution attached to the surface of the carbon black easier, when adding NaOH solution dropwise with magnetic stirring, Pd^{2+} ions reacted with OH^- ions to form precipitation and deposited on the surface of the carbon supports. This is not only makes for the nucleation process of Pd^{2+}, but also makes Pd nanoparticles more even and better dispersive. For comparison, the as-prepared sample (A2) synthesized under the condition that carbon supports were added after the addition of NaOH, it is seen from TEM image that the Pd nanoparticles agglomerate seriously, because the solution is too sticky for $Pd^{2+}$to diffuse to the surface of the supports before Pd^{2+} and NaOH form precipitation and agglomerate . The mean particle size of A2 calculated from the XRD patterns by Debye-Scherrer formula [23] is 8.80 nm, which is much larger than that of A1, 3.99 nm.

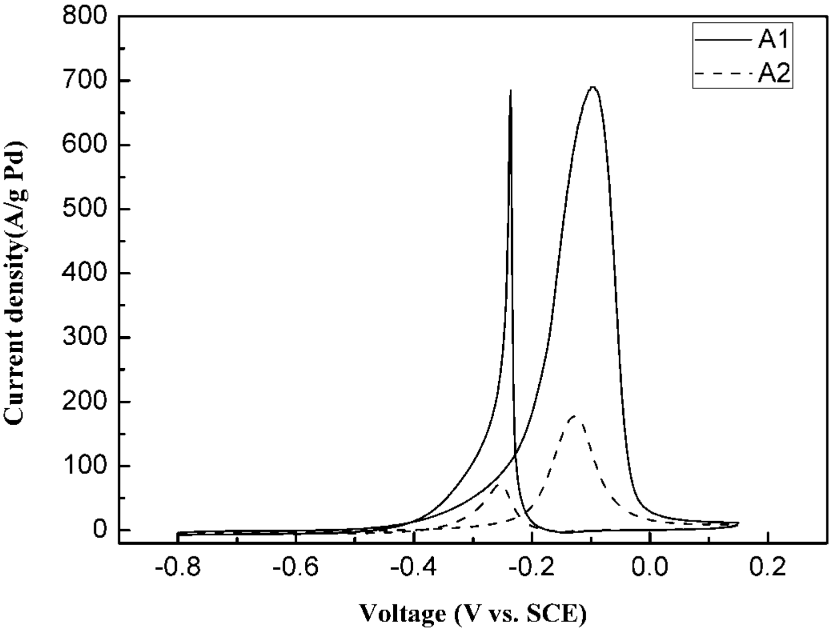

Figure 3. Cyclic voltammograms on Pd/C catalysts prepared with(A1) and without impregnation(A2) at a scan rate of 20 mV/s in deoxygenated 0.1 M KOH + 1 M CH_3OH solutions (The 40th cycle)

Fig. 3 displays the cyclic voltammograms (CVs) of A1 and A2 at a scan rate of 20 mV/s in the deoxygenated 0.1 M KOH and 1 M CH_3OH mixed solution. It indicates that the peak current densities of A1 and A2 are respectively 690 and 177 A/g Pd at the 40th cycle, showing that the catalytic activity of A1 is much higher than that of A2. This is related to the mean size and the dispersion of the Pd nanoparticles. A1 has smaller particles and better dispersion compared to A2, the specific surface area of A1 is much larger than that of A2. Furthermore, seriously sedimentation occurred during the preparation process of A2. Therefore, A1 has better catalytic activity than A2.

3.2 Effect of pH on the performance of Pd/C catalyst

pH is a very important factor for catalyst preparation. Different catalysts preparation methods reported in literatures have different optimum pH[22]. In this study, it is difficult to directly measure the solution pH for the exciting large amount of TG with high viscosity, so, a series of the Pd/C catalysts are synthesized by adjusting the addition of NaOH. The samples prepared with the addition of NaOH solution from 0 mL to 7mL is named B1, B2, B3, B4, B5, A1, B6, B7, The average particle sizes calculated from their XRD patterns (Fig.4) of the samples mentioned above is 10.70, 10.00, 9.80, 7.80, 4.36, 3.99, 2.82, and 2.62 nm, respectively. The mean particle size decreases with the increase of the addition amount of NaOH solution. This is also demonstrated by the TEM images.

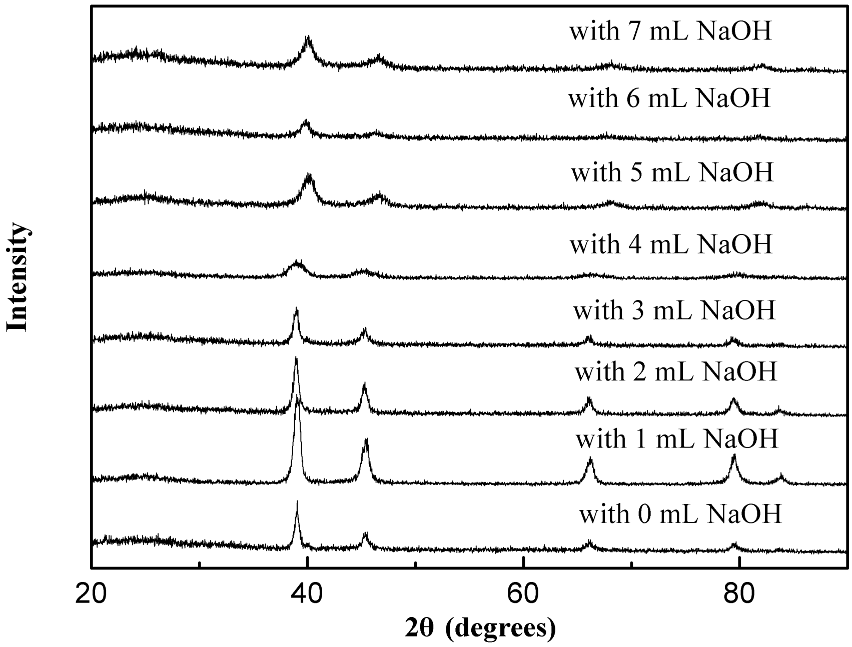

Figure 4. X-ray diffraction patterns of different addition of 0.05 M NaOH solution

One possible reason is that Pd^{2+} react with OH^- in the solution to form deposition, which favors the nucleation of Pd nanoparticles. Another possible reason is that some acetate-like ions exist in the glycerol solution at a high pH value [22]. These ions as a stabilizer restrain the growth of Pd nanoparticles, possibly forming chelate-type complexes via its carboxyl groups [24]. However, they can barely be observed in the acidic solution.

It can be found from TEM image of A2 that the particles agglomerate seriously, indicating that deposition formed after adding 5 mL NaOH. It is obvious that the Pd nanoparticles become smaller and more dispersive with the increase of NaOH addition, meaning that the ions like acetate increase with the addition of NaOH. They serve as stabilizer and control the growth of Pd nanoparticles, thus control the particle size.

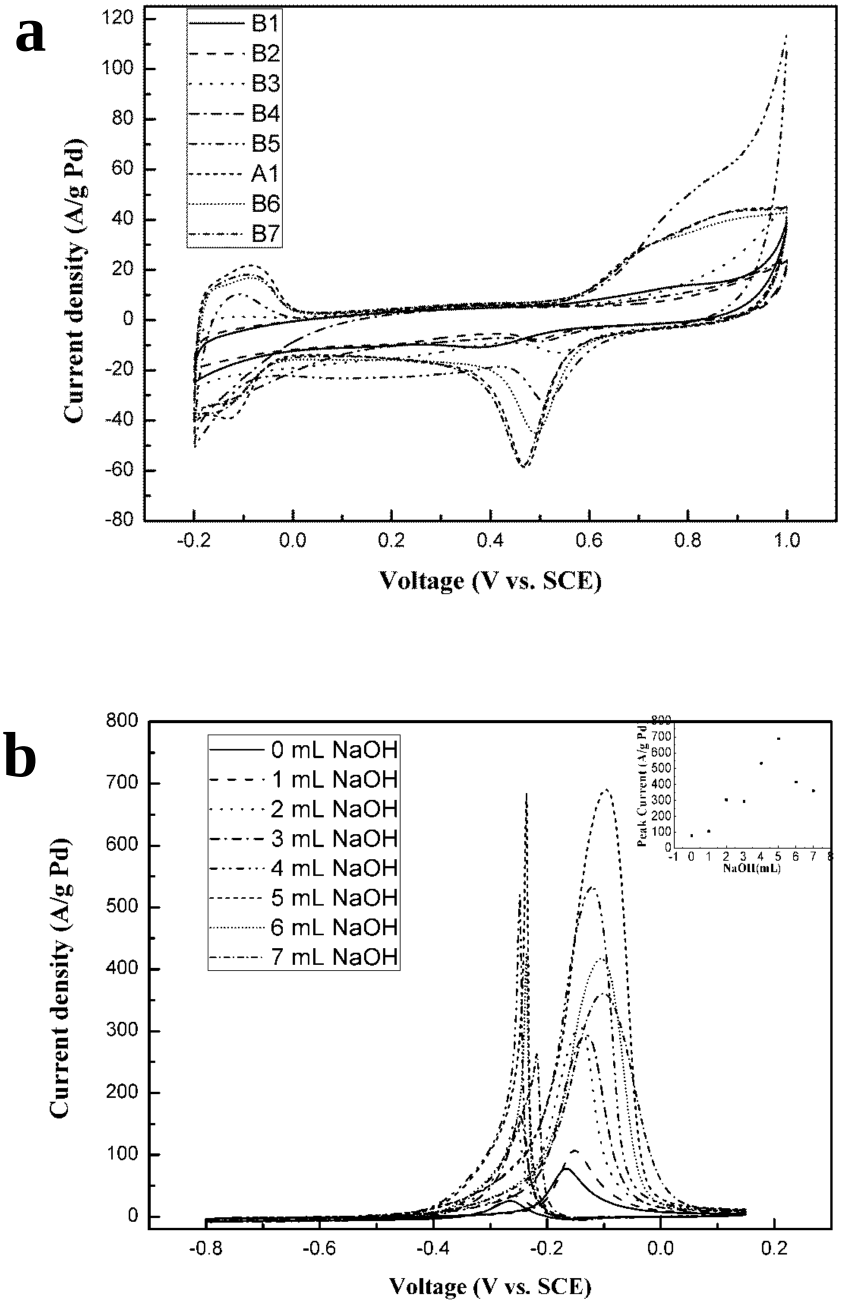

Figure 5. Cyclic voltammograms on Pd/C catalysts prepared with different addition of NaOH in an N_2-saturated solution of 0.5mol·L^{-1} H_2SO_4 at 25 ^oC. Scanning rate:0.05V·s^{-1} (a), at a scan rate of 20 mV/s in deoxygenated 0.1 M KOH + 1 M CH_3OH solutions (b)

According to the CVs in Fig. 5, the EAS increases with the increasing addition of NaOH from 0 to 5mL, and then decreases with the addition of NaOH increasing from 5mL to 7mL. The hightest peak current obtained by sample A1 with the addition of 5 mL NaOH has reached to 137 A/g Pd, which is a very attractive result for Pd/C catalyst. The sample with addition of 5 mL NaOH can exhibit larger electrochemically active surface area, which can offer more active sites for adsorption of methanol and shows the highest activity. It also can be seen from Fig 5 that the catalytic activity decreased with the increasing addition of NaOH from 5mL to 7mL. It is found that the metal nanoparticles size plays an important role in effecting the catalytic activity [27]. So the optimum addition of NaOH is 5 mL corresponding to the solution pH of 8.

3.3. Effect of the addition of KBr on the performance of Pd/C catalyst

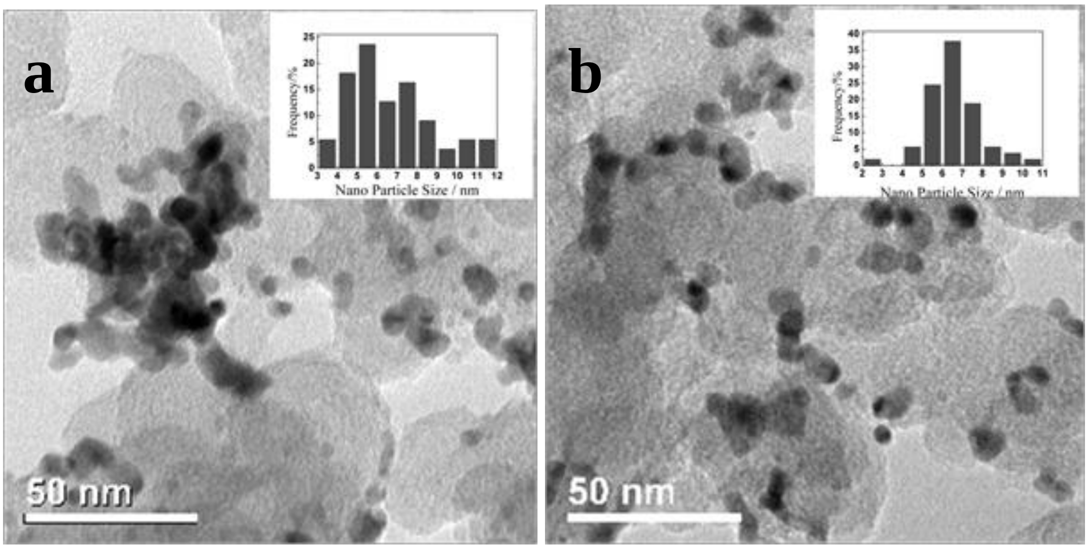

Figure 6. TEM pictures of (a) sample C1 prepared without the addition of KBr solution(0.12 M) and (b) sample C4 prepared with the addition of 3 mL KBr solution.

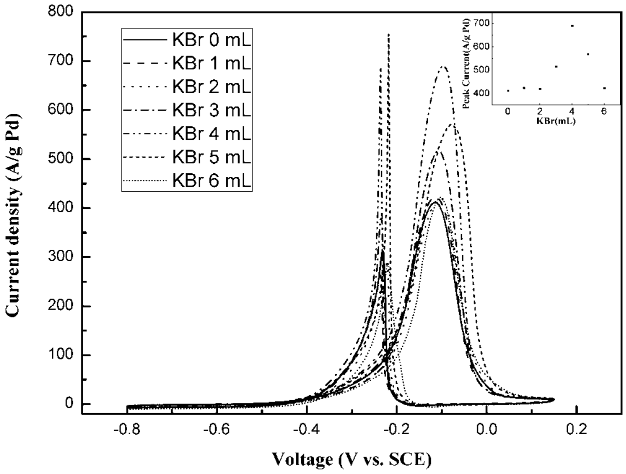

Figure 7. Cyclic voltammograms on Pd/C catalysts prepared with different addition of KBr at a scan rate of 20 mV/s in deoxygenated 0.1 M KOH + 1 M CH_3OH solutions

Polymer stabilizer can be used in the synthesis of NP catalyst to prevent the agglomeration of the NPs. It influences the growth rate and reduction of NPs, but these affects depend on the solvent, temperature, and the stabilizer itself [25].

As a stabilizer, KBr used in the experiments is better than PVP and CTAB, etc. It can be washed more easily and it is more environmentally friendly. It can be seen from Fig 6 that when the addition of KBr is high enough, Pd nanoparticles' agglomeration is relieved, and the nanoparticles dispersion becomes more uniform, which indicates that Br^- can adsorb on the surface of Pd particles, and control the growth of Pd. The XRD patterns of samples with different KBr addition have no obvious difference.

It is found from CV results in Fig. 7 that the peak current density increase with increasing addition of KBr. Especially, when the addition of KBr reaches to 3 mL, the catalytic activity increases remarkably. Sample A1 (the addition of KBr is 4 mL) with a peak current density 132A/g Pd shows the best catalytic activity. It is obvious that the catalytic activity decreased immediately when the addition of KBr increased from to 4 mL to and 6mL.

In the previous researcher's work, they found that it was difficult for Pt nanoparticles to support on carbon materials with PVP stabilizer due to PVP's strong adsorbing on Pt particles. On the contrary, carbon supports could interrupt noble metal particles agglomeration in the absence of PVP stabilizer, due to the particles' anchorage on carbon materials [26]. KBr can control the size and shape of particles without restraining Pd nanoparticles support on carbon materials. So KBr is more suitable for this preparation method than PVP. Based on the above results, the addition of 4 mL KBr was chosen as the appropriate value in this experiment.

3.4. Effect of microwave heating time on the performance of Pd/C catalyst

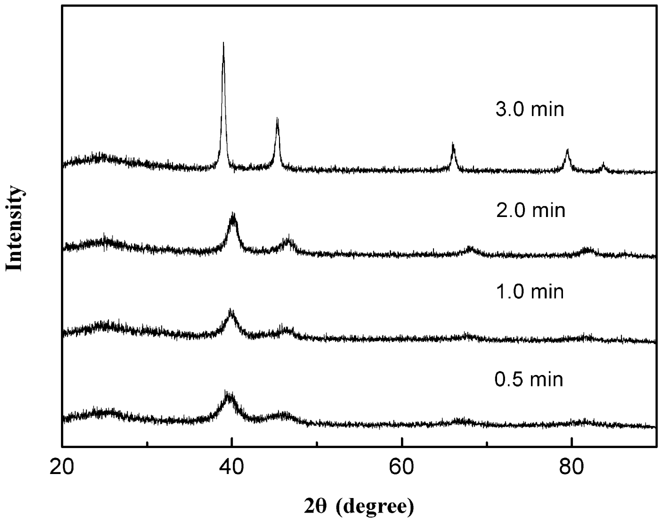

Figure 8. XRD patterns of the Pd/C catalysts prepared for different microwave heating time

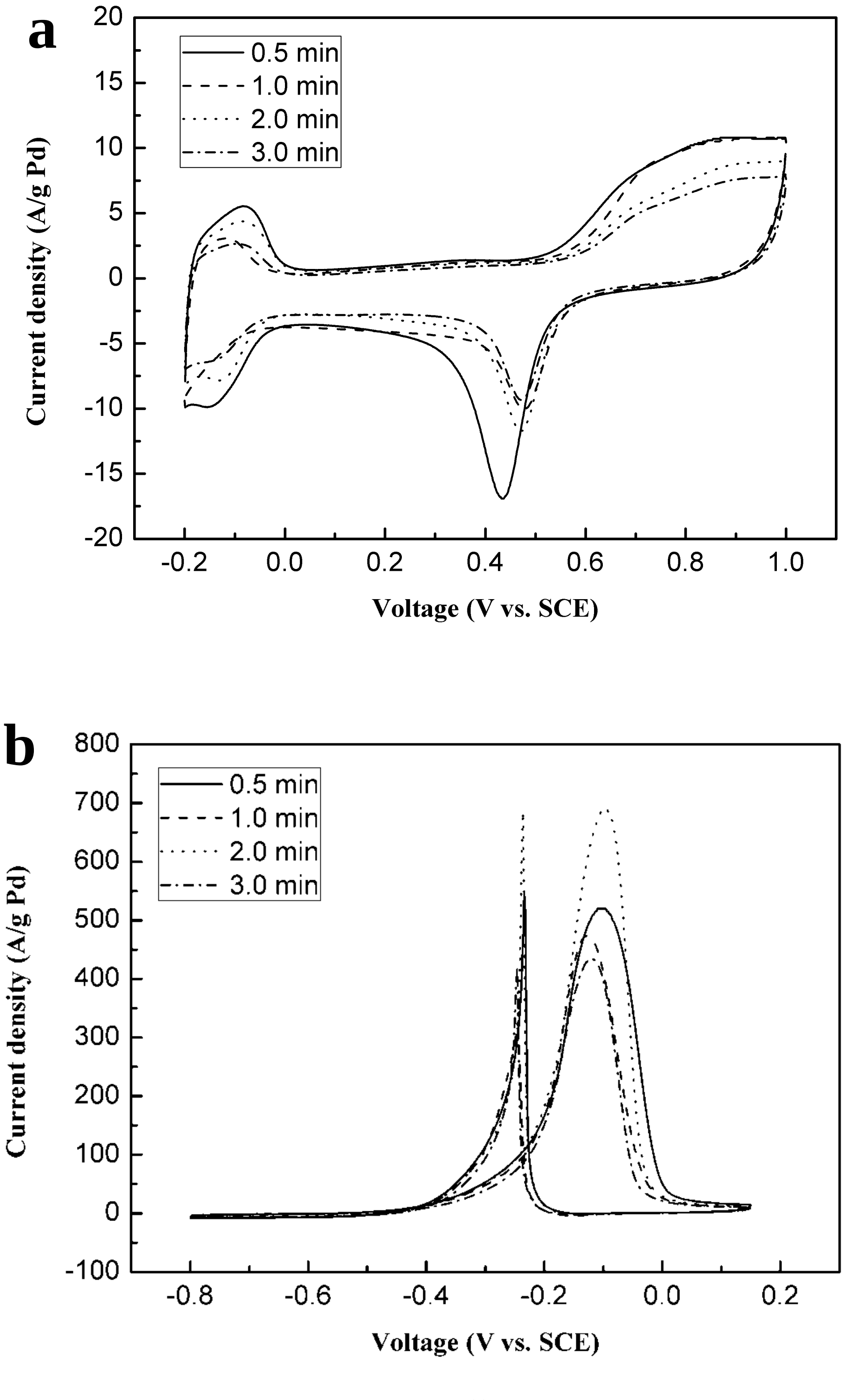

Figure 9. Cyclic voltammograms on Pd/C with different heating time in an N_2-saturated solution of 0.5 mol·L^{-1} H_2SO_4 at 25 ℃. Scanning rate:0.05 V·s^{-1}(a) , at a scan rate of 20 mV/s in deoxygenated 0.1 M KOH + 1 M CH_3OH solutions (b)

Microwave heating time has large influence on the particle characteristic [22]. It is calculated from XRD patterns (see Fig. 8) that the mean particle size of D1, D2, A1 and D3 is 2.37, 3.75, 3.99, 10.30 nm, respectively. The particle size increased with the heating time going on. The result is also demonstrated by TEM images. CVs in Fig.9b reveal that the sample with a heating time of 2min shows the best catalytic activity.

The nuclei are forming at the beginning of the heating process. Then the Pd nanoparticles grow with the temperature rising. When the temperature is at a higher level, the Pd nanoparticles will begin to agglomerate.

Particle size is considered to be an important parameter affecting the catalytic activity [27]. Appropriate size means better catalytic activity. It is reported that PtRu particles with about 3.0 nm displayed best catalytic activity for methanol electrooxidation [28]. When the particles are too small, crystallinity is not suitable for methanol to adsorb to the surface of Pd. If the particles are too large, electrochemical active surface will decrease.

Sample D1 (with heating time of 0.5 min) has the smallest particles size and the highest specific surface area comparing to other samples(seen in Fig 9a), but its catalytic activity is not the most excellent. This is related to its low crystallinity and some active sites being not suitable for methanol adsorption and oxidation. A1 (with heating time of 2 min) has high crystallinity, most suitable particle size (3.99 nm), good Pd dispersion, and shows the best catalytic activity among the samples. The nanoparticles of D3 (with heating time of 3 min) are too large and begin to agglomerate because of the overhigh temperature.

3.5 Effect of solvents on the performance of Pd/C catalyst

Solvent is an important influence factor for preparing catalyst. Different microstructures of the synthesized products can be obtained using the solvent with different compositions [29].

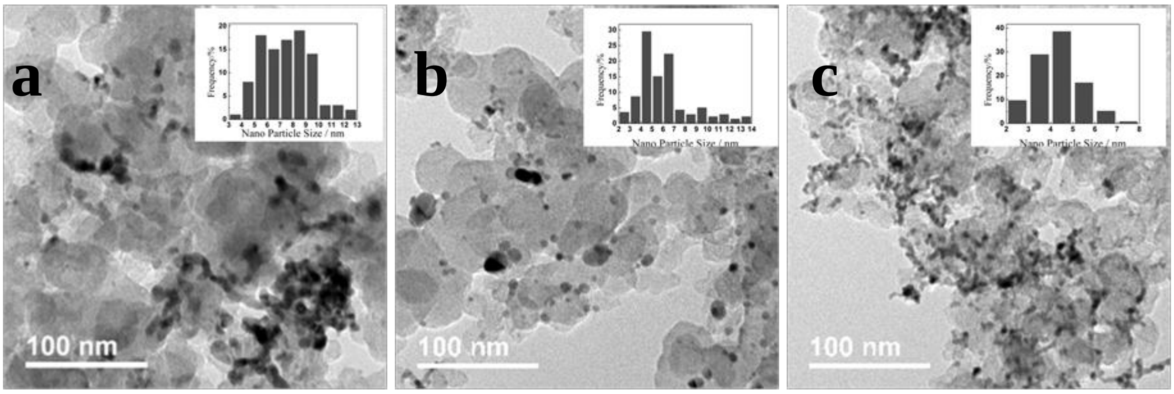

Figure 10. TEM pictures of Pd/C catalysts prepared with different solvent(a-c represents sample E1, E2, E3, respectively, the solvent of which is ethylene glycol, propylene glycol, butanediol)

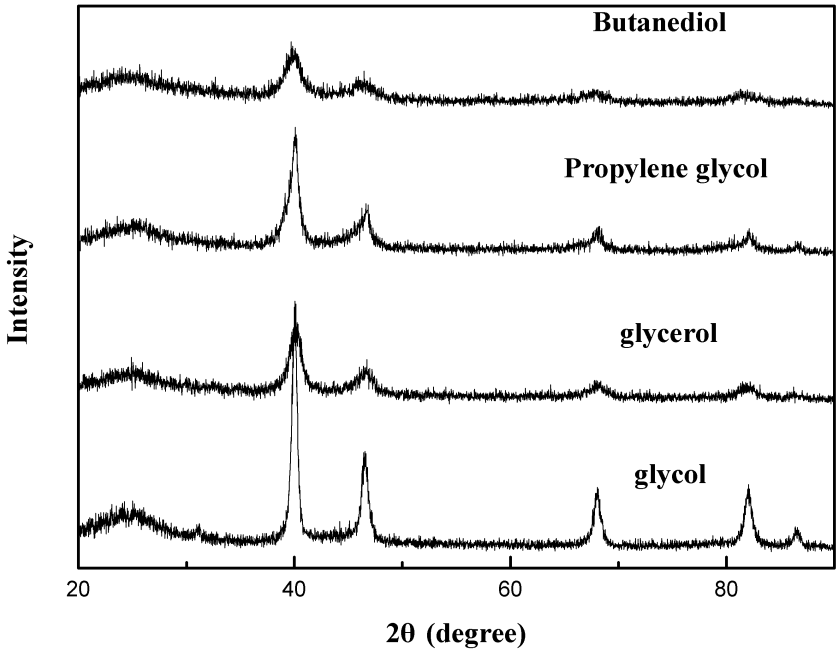

Figure 11. XRD patterns of the Pd/C catalysts prepared with different solvents

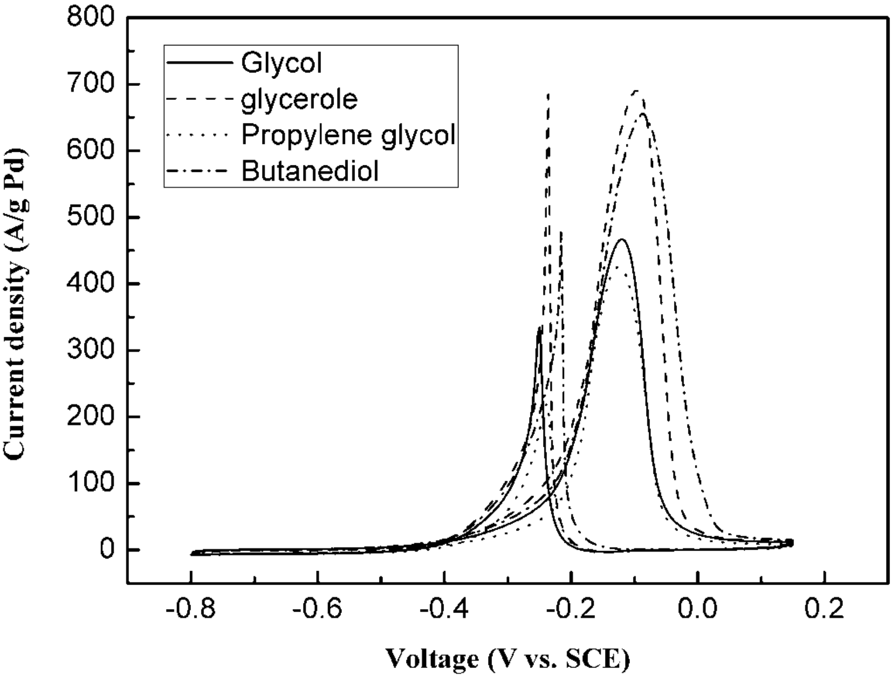

Figure 12. Cyclic voltammograms on Pd/C prepared with different solvent at a scan rate of 20 mV/s in deoxygenated 0.1 M KOH + 1 M CH_3OH solutions

Particles with the desired characteristics can be prepared with the technique by controlling the parameters, such as the solution pH, reaction temperature, reaction time, solute concentration and the types of solvent depending on the particular application [30]. Moreover, the solvent in a solvothermal process could be used as shape-controller of nanoparticles, the solvent physico-chemical properties such as polarity, viscosity, boiling point and softness will immensely influence the solubility and transport behavior of the precursors [31].

In this work, some different solvents were used to synthesize Pd/C catalysts. The TEM images of the samples are showed in Fig. 10, it can be seen that the particles of the samples prepared with propylene glycol and butanediol are more dispersive and uniform than that prepared with ethylene glycol. XRD patterns in Fig. 11 demonstrate that the samples have different mean particle size. The samples prepared with glycerin and butanediol have samller particle size than the other two. It is also seen from Fig. 12 that the catalyst activity of the samples prepared with glycerin and butanediol are better than the other two. And the sample prepared with glycerin shows the best catalyst activity.

Solvent's viscosity and boiling point play an important role in effecting the catalytic activity. High viscosity can restrain the diffusion of the precursor into the surface and micropore of the activated carbon, and high boiling point ensures that the temperature can meet the needs of the reduction process. Glycerin and butylglycol have high viscosity and boiling point, but glycerin has more hydroxyl and stronger reducibility, so the catalytic activity of Pd/C prepared with glycerin is higher than that prepared with butylglycol. Glycol is the most common solvent used in the microwave assisted polyol process, but the sample prepared with glycol shows the weakest catalytic activity among the four.

On the other hand, high viscosity means that it is difficult to mix the support and the precursor uniformly. Therefore, impregnation is adopted in this work.

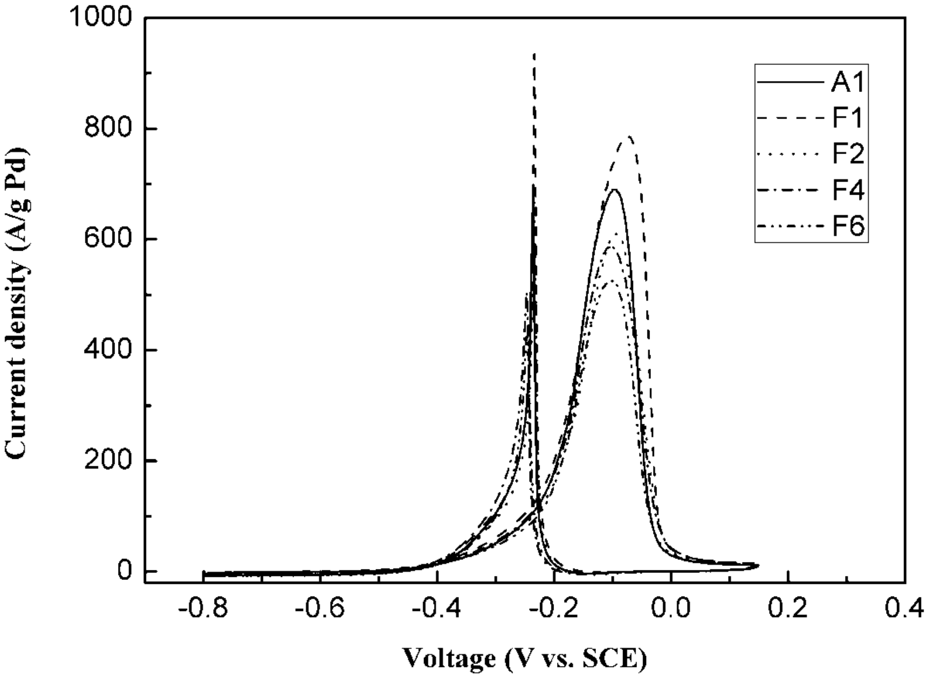

Figure 13. Cyclic voltammograms on Pd/C prepared with different ratio of EG and glycerol at a scan rate of 20 mV/s in deoxygenated 0.1 M KOH + 1 M CH_3OH solutions

Furthermore, we discussed the effect of solvent mixture on the activity of the samples, Fig.13 shows Cyclic voltammograms on Pd/C prepared with different ratio of EG and glycerol at a scan rate of 20 mV/s in deoxygenated 0.1 M KOH and 1 M CH_3OH solutions. For F2, F4 and F6, the catalytic activity decreased with the increase of EG content, which demonstrated that glycerol was a better solvent for preparing Pd/C by Microwave assisted polyol process than EG. It is important to note that F1 shows the best catalytic activity, even better than that of A1. It was demonstrated that impregnation plays the key role in the preparation progress. Ethylene glycol could infiltrate into the micropore and attach to the surface of activate carbon more easily, and make Pd nanoparticles more dispersive. 90% glycerol ensures the viscosity and the reaction temperature. It can be seen from Fig.14 that the nanoparticles of F1 have a better distribution than A1 and suitable size due to ethylene glycol's low viscosity.

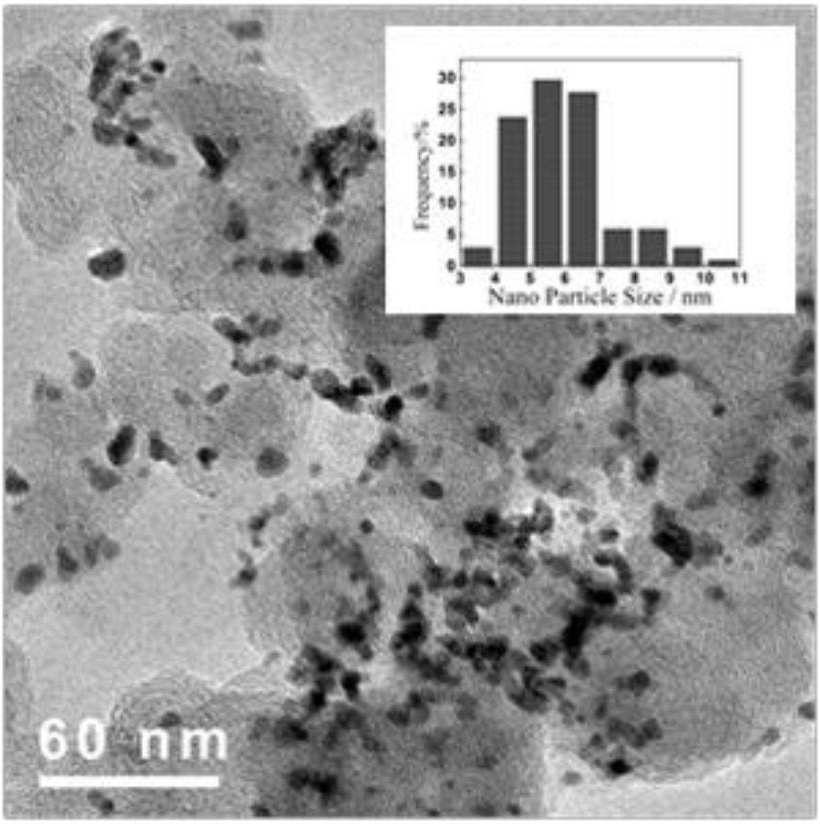

Figure 14. TEM image of F1

4. CONCLUSIONS

Pd/C catalysts are prepared by impregnated microwave assisted polyol process.

A narrow size distribution and uniformly dispersted Pd nanoparticles were achieved. The structure, morphology and electrocatalytic activities of the catalysts are characterized with XRD, TEM and cyclic voltammetry(CV). The results show that the optimum addition of KBr (0.12 M) and NaOH (0.05 M) are respectively 4 mL and 5 mL, the heating time is 2 min. The sample F1 prepared in 10 vol

% ethylene glycol and 90 vol % glycerol mixture under the optimal condition shows the best catalytic activity with its anodic peak current density reaching to 785 A/g Pd in deoxygenated 0.1 M KOH + 1 M CH_3OH mixed solution.

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