

Optimization Growth of Platinum and Palladium Nanoparticles on Stainless Steel 316L and Activated Carbon Pellet Substrates

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Abstract. In this study, an optimization growth of platinum (PtNs) and palladium (PdNs) nanoparticles has successfully grown on stainless steel 316L and activated carbon pellet as substrates. PtNs and PdNs were grown on the substrates by wet chemical method. The effect of concentration of ascorbic acid and multi-growth step had shown the significantly in density and particle size distribution on the both substrates. The morphology and the structure of PtNs and PdNs were characterized by a field-emission scanning electron microscope (FESEM), X-ray diffraction (XRD), respectively. Homogenous particles size and high density of PtNs and PdNs on the substrates were also successfully grown with current method.

Keywords: Platinum nanoparticles, Palladium nanoparticles, wet chemical, multi growth.

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INTRODUCTION

Metal nanoparticles have attracted a considerable attention during the last decade due to their catalyst properties. Among them, platinum, palladium and gold are very promising metals with potential application in order to increase quality of current collector and carbon electrode of supercapacitor [1,2].

To this stage, limited techniques are available for direct growth of both metallic nanoparticles directly on the substrate surface [3,4]. Owing to their potential catalytic properties in application particularly in supercapacitor device [5-6], to develop a versatile technique that can control the size and density of nanoparticles on the surface is highly required.

Here, we demonstrate a simple method to grow high density platinum and palladium nanoparticles on stainless steel current collector via a seed-mediated-multi-steps growth process in an aqueous solution phase. The typical results showed that the nanoparticles of platinum and palladium of size ranging from 10 to 30 nm were effectively grown on the surface. They were found to cover the entirety of the substrate surface. In this study, the characteristic of nanoparticles growth on a carbon pellet electrode was also studied. The procedure and the mechanism of the growth process will be discussed.

EXPERIMENTAL

Preparation of Substrates

Activated carbon pellets were prepared from rubber wood sawdust (RWSD). Firstly, the RWSD was pre-carbonized at a low temperature (about 280°C), then it was ball-milled for about 36 hours and finally it was sieved with particle size of less than 53 micron. The powder of self-adhesive carbon grains were converted into green monoliths using a mold of 20 mm in diameter and 8 tons of compressive force. The next step is the samples were carbonized at 600°C under N₂ atmosphere. These carbon pellets were then activated by using CO₂ gas at 800°C with a heating rate of 10°C per minute for an activation time of 1 hour. The result of activated carbon pellets were polished to the desired thickness then washed with distilled water [7]. The stainless steel 316L substrates were prepared by washing them with acetone and ethanol for 10 minutes using an ultrasonic bath.

Growth of Nanoparticles

The growth of platinum nanoparticles was carried out by adopting the method developed by Oyama etc



[4,8] with several modifications. In typical procedure, the growth of platinum nanoparticles was realized by simply soaking the substrates in the platinum nanoparticle growth solution for a certain growth period. The growth solution was prepared by mixing 1 mL of a solution of K_2PtCl_4 (platinum source) with a variety of concentrations (0.05M, 0.07M, 0.09M, 0.1M and 0.13M) into a solution that contains 20 mL of cetyltrimethylammonium bromide- $C_{19}H_{42}NBr$ (CTAB), a capping agent that can control the particle size and 1 mL of a solution of ascorbic acid (AA). In this study, the concentration of CTAB was varied from 0.5 to 1.3 M, meanwhile the AA was from 0.2 to 0.5 M. Standard solution for platinum nanoparticle growth here was contained 0.5 mL of 0.01M K_2PtCl_4 , 20 mL of 0.1 M CTAB and 0.1 mL of 0.1 M ascorbic acid. The substrates were soaked into the nanoparticle growth solution in two times of growth process (multigrowth) for 4 different duration times of growths (2 hours + 2 hours, 3 hours + 3 hours, 4 hours + 4 hours and 5 hours + 5 hours) in each process.

Meanwhile, the growth of palladium nanoparticles was carried out by modifying the original method reported in [8]. It was carried out by firstly put the substrates in to a Poly-L-Lysine (PLL) 5% solution to positively charge the surface, then soaked into a seed solution (containing negatively charged spherical palladium nanoseed with diameter of 3 to 4 nm [4]), which was prepared by mixing 0.5 mL of 0.01 M solution of K_2PdCl_6 , 0.5 mL of 0.01 M solution of trisodium citrate, 20 mL of DI water and 0.5 mL of 0.1 M solution of $NaBH_4$ for 30 minutes. The seed-mediating process was taken in 3 times, under the same condition. After putting the substrates in the seed solution, the substrate was then soaked into a palladium growth solution, which was prepared by adding 0.1 mL of ascorbic acid (a reduction agent) into a solution that contains 0.5 mL of K_2PdCl_4 and 20 mL of CTAB solution. In this work, 5 different concentrations of K_2PdCl_4 , namely 0.1, 0.2, 0.3, 0.4 and 0.5M, were used). Meanwhile, CTAB was varied in five variations, namely 0.05, 0.1, 0.15, 0.2 and 0.25). Standard solution for palladium nanoparticle growth here was contained 0.5 mL of 0.01M K_2PdCl_4 , 20 mL of 0.1 M CTAB and 0.1 mL of 0.1 M ascorbic acid.

Characterizations

The structure of the samples was investigated by X-Ray Diffraction, using a diffractometer of Bruker AXD D8 advance that employed $CuK\alpha$ radiation with a 2θ range from 0° to 60° . The morphology and elemental composition of the samples were studied

using a field-emission scanning electron microscope (FESEM) integrated with the instrument that can measure the size particle, and energy dispersive X-ray analysis (EDAX) instruments (Supra PV 55).

RESULTS AND DISCUSSION

Platinum Nanoparticles

A comparison of SEM images of the platinum nanoparticles with different concentrations of ascorbic acid solution grown on stainless steel is shown in Figure 1. It is clearly shown that in the sample of 0.2M of ascorbic acid solution, the particles were distributed uniformly on the surface and therefore has a highest density compared to the other samples.

Unlike in the sample of 0.2 M, the samples of 0.3 M, 0.4 M and 0.5 M concentration of AA still have quite a lot of porous. In term of nanoparticle size (diameter), which was measured using the FESEM image analysis software here, the sample of 0.2M AA also shows highest homogeneity compared to the others, which the size of particles is in the range of 20.1 – 23.44 nm.

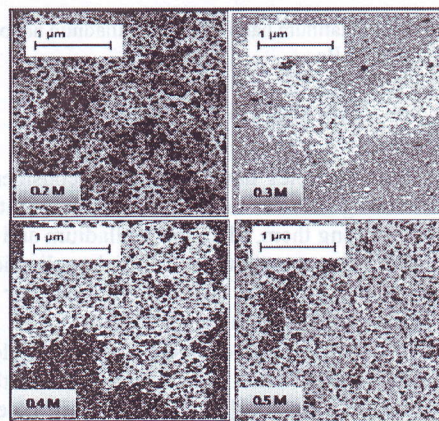


FIGURE 1. SEM images of platinum nanoparticles with different concentrations of AA with other components, K_2PtCl_4 and CTAB, were fixed at 0.01 M and 0.1 M, respectively (standard solution). Growth time is 2 h.

The effect of concentration of platinum precursor (K_2PtCl_4) in the growth solution on the nanoparticle growth characteristic was evaluated. It showed that the sample with 1 mL concentration was the best among the others (see Figure 2). The particles appear to be distributed evenly throughout the surface of substrate. The size of nanoparticles was measured in the range of 23.4 – 26.8 nm. Growth time dependent is shown in Figure 3. Much more homogeneous and denser particles were found in the sample with 5 hours of multigrowth process. It is due to an effectively

formation of new nanoparticles of platinum on the surface when being subjected to a consecutive growth process.

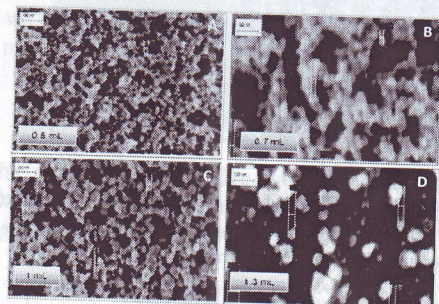


FIGURE 2. FESEM image of platinum nanoparticles growth on the substrate surface prepared using for different concentration of K_2PtCl_4 . A) 0.5, B) 0.7, C) 1.0 and 1.3 mL of 0.01 M. Other reagents were unchanged (see standard solution) except AA, 0.2 M was used. Growth time is 2 h.

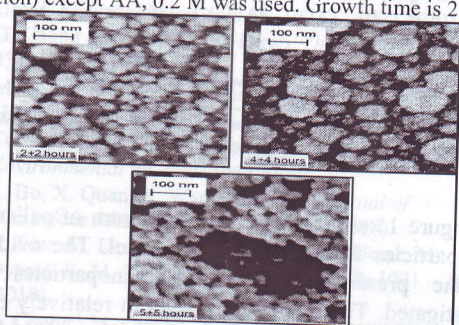


FIGURE 3. Platinum nanoparticles with different duration time of multigrowth process. The growth solution used was the optimum condition (Figure 2), namely 1 mL of 0.01 M K_2PtCl_4 , 0.1 mL of 0.2 M AA and 20 mL of 0.1 M CTAB.

Figure 4 shows SEM images of spherical platinum nanoparticles formed on activated carbon pellet with 0.2 M of AA, 1 mL of 0.01 M K_2PtCl_4 and 20 mL of 0.1 M CTAB solution and 5+5 hours multigrowth. The nanoparticles distributed uniformly throughout the surface, which the sizes ranging from 24.6 nm to 26.8 nm. This condition might probably be demanded in electrochemical applications as the unique catalytic properties of nanoparticles of platinum. Typical application of this nanostructured platinum modified current collector in supercapacitor application has been presented in our recent publication [9].

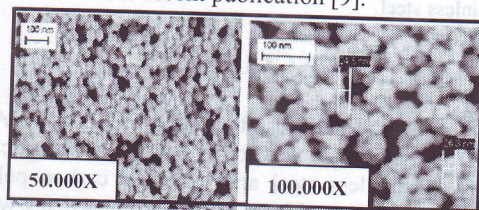


FIGURE 4. Spherical platinum nanoparticles grown on activated carbon pellet prepared using the optimum growth solution.

Figure 5 demonstrates the EDAX result for the platinum nanoparticles formed on the activated carbon pellet. The EDAX peaks corresponding to platinum nanoparticles are clearly observed on the surface, confirming that the present approach has successfully grown nanoparticles of platinum of the substrate surface.

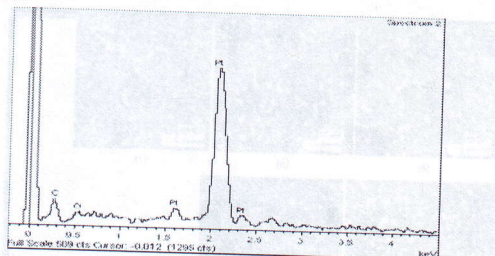


FIGURE 5. EDAX result for platinum particles grown on activated carbon pellet prepared using the optimum growth solution.

X-ray diffractogram of the platinum nanoparticles on carbon pellet surface samples with 2θ ranging from 20° to 80° was investigated in Figure 6. The diffraction peaks in relative broad form observed at $2\theta=40.163^\circ$ and 46.761° . According to the standard platinum diffraction pattern (JCPDS File no. 4-0802), the peaks can be attributed to (111) and (200) planes. This results further confirm the presence of platinum nanoparticles on the carbon pellet substrate in crystalline form [10].

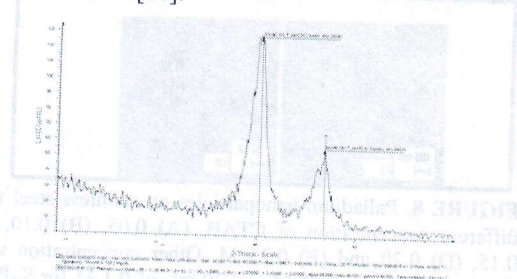


FIGURE 6. XRD diffractogram of platinum nanoparticles form on activated carbon pellet.

Palladium Nanoparticles

Figure 7 demonstrates comparative SEM images of the palladium particles with 5 different concentrations of ascorbic acid grown on stainless steel. The figure clearly shows that the palladium nanoparticles appear to be distributed throughout the surface. Among 5 samples, the sample of 0.3 M AA is the best, the particles were distributed uniformly on the surface and therefore has a highest density compared to the others.

The effect of concentration of CTAB solution was evaluated by using the optimum, AA concentration as shown in Figure 7. The results are shown in Figure 8.

It shows that the palladium nanoparticles grow and distribute on the substrates with high density and a narrow variety of particle size. The 0.1 M CTAB sample in general is much better than the others. Unlike in the 4 other samples, the palladium particles spread in every part of the surface.

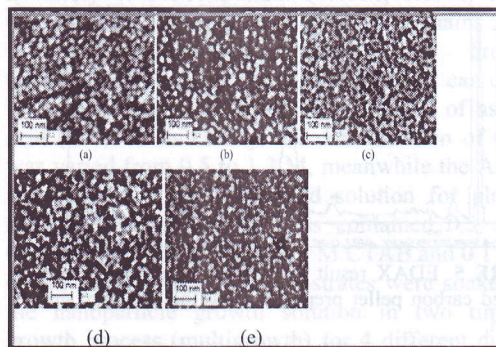


FIGURE 7. SEM images of Palladium nanoparticles on stainless steel with different concentration of ascorbic acid, (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4 and (e) 0.5 M. Other reagents were fixed at 0.5 mL of 0.01 M K_2PtCl_4 , 20 mL of 0.1 M CTAB. The growth time is 4 h.

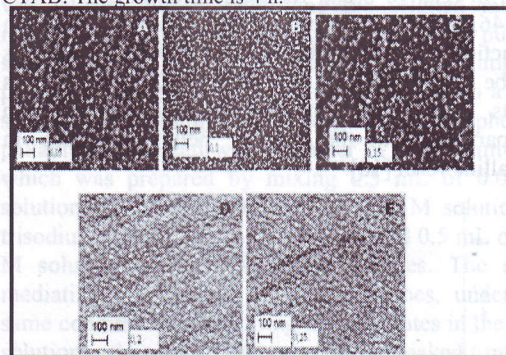


FIGURE 8. Palladium nanoparticles on stainless steel with different concentration of CTAB, (A) 0.05, (B) 0.10, (C) 0.15, (D) 0.20 and (E) 0.25 M. Other concentration were fixed at 0.5 mL of 0.01 M and 20 mL of 0.1 M for K_2PtCl_4 and CTAB, respectively. Meanwhile the AA was fixed at 0.5 mL of 0.3 M. The growth time is 4 h.

The best sample of palladium nanoparticles grown on stainless steel and on activated carbon pellet were shown in Figure 9 (a) and (b), respectively. The samples were prepared using the optimum growth solution as indicated in the FESEM results shown in Figure 8. As can be seen, the particles have spherical shape, with very high density and uniform in size (16.7 nm – 24.6 nm).

The EDAX result of palladium nanoparticles grown on stainless steel is shown in Figure 10. The EDAX peaks corresponding to palladium nanoparticles are clearly observed on the surface.

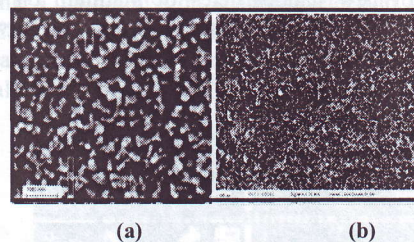


FIGURE 9. Optimum samples of Palladium nanoparticles grown on (a) stainless steel and (b) activated carbon pellet prepared using the optimum growth solution for 4 h.

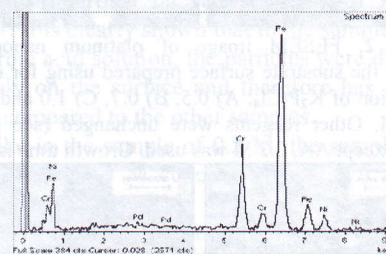


FIGURE 10. EDAX result for palladium particles grown on stainless steel

Figure 11 shows X-ray diffractogram of palladium nanoparticles formed in stainless steel. The evidence of the present of palladium nanoparticles was investigated. The diffraction peaks in relatively broad form were observed at $2\theta = 40.225^\circ$ and 46.713° . Refer to the standard XRD pattern for palladium as shown in JCPDS File No. 87-0638, the peaks can be associated to (111) and (200) planes of fcc palladium nanocrystals. These results further confirm the successful formation of palladium nanoparticles on the surface prepared using the present method.

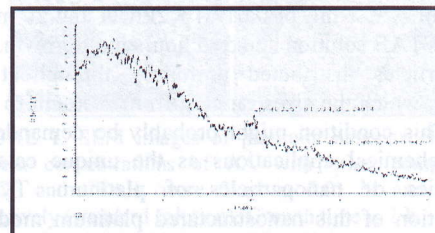


FIGURE 11. X-ray diffractogram of palladium nanoparticles on stainless steel.

CONCLUSIONS

Based on the data resulted using FESEM, EDAX and XRD methods, it was found that the nanoparticles grown on stainless steel and activated carbon pellet have spherical form. The platinum nanoparticles with highly density, uniform and size of 24.6 nm – 26.8 nm in diameter was obtained using multigrwth technique with 0.2 M of AA, 1 mL of 0.01 M K_2PtCl_4 solution

and 5+5 hours multigrowth time. Whereas, 0.3 M of AA and 0.1 mL of 0.1 M CTAB were chosen in order to obtain palladium particles grown on the substrates with very high density and uniform in size (16.7 nm – 24.6 nm).

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