Int. J. Electrochem. Sci., 8 **(2013)** 8662 - 8668

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Synthesis of Au@Pt Core-Shell Nanoparticles with High Electro-catalytic Activity of Methanol Oxidation by Photochemical Seeding Growth

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Received: 30 April 2013 / *Accepted:* 18 May 2013 / *Published:* 1 June 2013

Au@Pt core-shell nanoparticles were synthesized by photochemical seeding growth method in PEG-acetone system, in which the thickness of Pt shell could be controlled by changing the molar ratio of Au seed to Pt(IV). The morphology and size of synthesized nanoparticles were characterized by using UV-Vis, TEM, HR-TEM and XPS. These also proved their core-shell structure. The electrochemical tests indicated that the Au@Pt core-shell structure nanoparticles were active and stable in the reaction of methanol catalytic oxidation. When the molar ratio of Au to Pt was 1:1, the activity of composite nanoparticles was the highest, which was 304.8% higher than that of Pt/C. Electro-catalytic activity of the Au@Pt core-shell nanoparticles is little affected by temperature.

Keywords: Core-Shell Structure; Photochemical; Electro-catalytic Activity; Methanol Oxidation

1. INTRODUCTION

New green energy technology is one of hot topics in modern scientific research, while fuel cell technology is highly concerned as the fourth generation of energy technology [1,2]. Direct Methanol Fuel Cell (DMFC) is one type of fuel cells with priority to develop, whose anode catalysts Pt/C and PtRu/C are mainly employed as. Due to the lack of Pt resources, the high price of its catalytic materials and easily getting CO poisoning, the fuel cells are limited to large-scale of development and application. Recent research showed that Au-Pt bimetallic catalyst, especially Au@Pt core-shell nano-catalysts (including fully coated and modified like strawberry shape), had a promising application on reducing Pt amount in electro-catalyst, reducing CO poisoning in Pt catalyst and so on [3-5]. With respect to the synthetic methods of Au@Pt core-shell nanoparticles, there were many reports about underpotential deposition method and chemical reduction method [4-11]. However, it is still a challenging task that how to economically conveniently quickly synthesize Au@Pt core-shell nanoparticles with the controlled size and shell thickness.

This work reported one new method for synthesis of Au@Pt core-shell nanoparticles based on photochemistry. In PEG (polyethylene-glycol)-acetone system, Au nanopaticles were obtained by ultraviolet radiation of Au(III) at 254 nm, which was used as the seed, followed by Pt deposition on Au seed through the reduction of Pt(IV) under ultraviolet radiation. It was showed from characterization of UV-Vis 、TEM 、HR-TEM and XPS that core-shell nanoparticles with uniform size and monodispersity were obtained, while the thickness of its Pt shell could be efficiently adjusted by changing the molar ratio of Au seed to Pt(IV). The average diameter was in the range of 4.4-7.3 nm. The electrochemical tests indicated that the as-prepared Au@Pt nanoparticles had high activity in the reaction of methanol catalytic oxidation (MOR). Also, briefly discussion was taken on mechanism of high activity.

2. EXPERIMENTAL SECTION

2.1. Preparation of products

All the reagents were analytical pure (AR) and water was ultrapure. In 50 mL volumetric flask, 4 mL PEG-400, 1 mL acetone and 1.22×10^{-5} mol $HAuCl_4$ were added and then water was used to get the constant volume. After being mixed well, the solution was transferred into one quartz container and then exposed 4 cm away under UV light. UV-Vis spectra were recorded with time until the spectral curve was the same as the previous one, which indicated that the reduction was finished with Au nanoparticles with the size of about 4.1 nm. The Au nanoparticle colloid as seed was added into mixed solution of H_2PtCl_6, PEG-400 and acetone with the above same concentration (the total volume was 50 mL, the molar ratio of Au to Pt was respectively 4:1, 1:1 or 1:4, and kept the total molar amount of metals as 1.22×10^{-5} mol). After mixing, the solution was exposed to UV light according to the above condition until the reaction was finished.

2.2. Characterization

Images of single or composite nanoparticles were taken by transmission electron microscopy (TEM). The images of the sample which was prepared by dropping several drips of colloidal solution on formvar stabilized with carbon support film copper grid and dried at room temperature, were taken on H-800 TEM operated at an voltage of 200 kV. By using lacey support film grid, HR-TEM measurements were made on Tecnai G^2 F20 field emission transmission electron microscopy operated at an voltage of 200 kV. At the same time, XPS was also employed on the sample. According to the method from reference [11], the obtained nanoparticles were loaded on XC-72 carbon black (20% capacity by weight) for electro-chemical measurements. In the electro-chemical measurement, three electrode system was adopted with Pt as counter electrode and SCE as reference electrode, whose electrolyte was 0.5 mol·L^{-1} KOH + 2.0 mol·L^{-1} CH_3OH and temperature was 30~60 ℃. Before the measurement, high purity of N_2 was bubbled into the electrolyte to remove the dissolved O_2 and then cyclic voltammograms (CVs) were recorded in the atmosphere of N_2. The measurement conditions: potential range -0.6~0.8 V, potential scan rate 50 mV·s^{-1}, time-current curve (I-t) at -0.3 V.

3. RESULTS AND DISCUSSION

3.1. Characterization of Au@Pt nanoparticles

In the selected solution system, surface plasmon resonance (SPR) absorption spectra of obtained colloidal solution were shown in Figure 1. In the spectra of Au-Pt particles, the characteristic absorption peak of Au at near 520 nm obviously decreased along with the concentration of Pt increasing. When Au:Pt= 1:4, it was almost the same with the single Pt particles, which demonstrated transition feature from Au to Pt. In the process of synthesizing composite nanoparticles, it was predicted that the surface of Au atoms was gradually coated by Pt atoms along with decreasing Au:Pt in molar then to form Au-Pt core-shell nano structure. As the concentration of Pt element was low, the characteristic absorption of Au hadn't fully disappeared in the SRP absorption spectra of composite particles, which stated that Pt shell was still thin or the coating of Pt on Au seed was not completed. This was basically the same with reference [6,7].

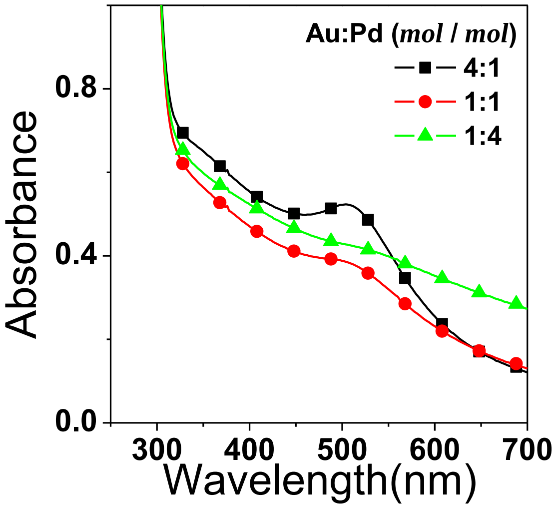

Figure 1. UV-Vis spectra of Au-Pt bimetallic colloidal solution

TEM/HR-TEM images of Au@Pt particles were given by Figure 2. It could be seen that particles with uniform size and good dispersion were obtained and the average diameter above that of Au seed (4.1 nm) increased as the amount of Pt increased, which was respectively 4.4, 5.2 and 7.3 nm with Au:Pt=4:1, 1:1 and 1:4. This indicated that Pt shell grew gradually. In figure 2b, the inset was

HR-TEM images of particles when Au:Pt=1:1, in which the lattic fringes of spherical particles were apparent. But due to similar lattice constants of Au and Pt, these two atoms with high activity mutually spread and permeated to form solid solution on the surface in the nano scale. Therefore, it was hard to observe the clear metallic phase interfaces even by high resolution TEM images.

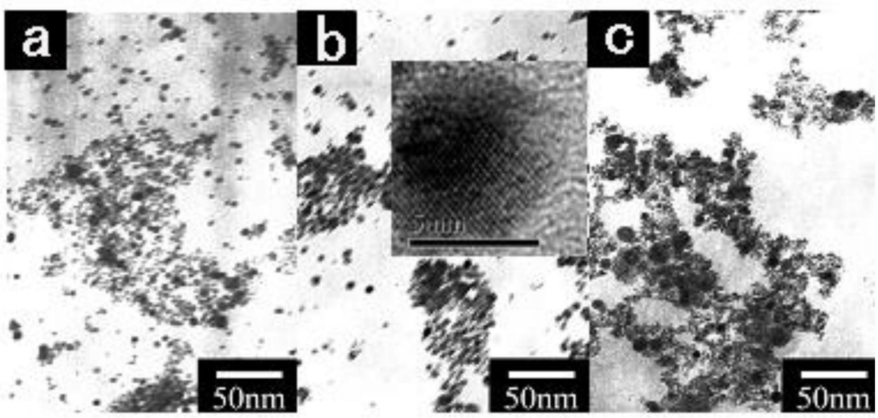

Figure 2. TEM and HR-TEM images of Au core@Pt shell particles： Au:Pt =4:1 (a), 1:1 (b), 1:4(c)

According to the model of Au@Pt composite particles, the detected depth for the surface should be in the range of 0.5~1 nm by XPS in the condition of the experiment. Based on XPS results (Table 1), the molar ratio of Au:Pt in the surface structure of obtained nanoparticles was far less than that in the preparation solution. Apparently Pt atoms occupied a large portion of near-surface structure of composite particles, which showed that formed particles had core-shell structure. As Au:Pt=1:4, the peak of Au 4f spectrum had completely disappeared. This indicated that coated Pt shell was integrated to form certain thickness, which also satisfied the characterized results from UV-vis absorption spectra.

Table 1. Results of the XPS analysis of Au@Pt particles

Au:Pt of Au@Pt	4:1	1:1	1:4
The near-surface composition of Au@Pt particles	62.2:37.8	28.7:71.3	0:1
Pt $4f_{7/2}$ Binding Energy (eV)	71.35	71.41	71.85
ΔE (Binding Energy, eV)	-0.51	-0.45	-0.01
Note: Pt nanoparticles Pt $4f_{7/2}$ E= 71.86 eV			

Figure 3 was the Au 4f and Pt 4f spectra of Au@Pt composite nanoparticles from XPS. In Figure 3, it was known that Au was in simple substance phase when the binding energy (BE) of Au $4f_{7/2}$ was about 84 eV; and Pt was in simple substance phase when the BE of Pt $4f_{7/2}$ was about 71 eV [12]. In Table 1, the BE of Pt $4f_{7/2}$ in the Au@Pt composite particles with different ratios was present and increased as the ratio of Au decreased, whose value was less than 71.86 eV that was the BE of single Pt nanoparticles. This indicated the Pt shell gaining d-electrons from the Au core, which fit the phenomenon the reference [11] reported. The phenomenon became not obvious when Pt shell was thick (Au:Pt= 1:4).

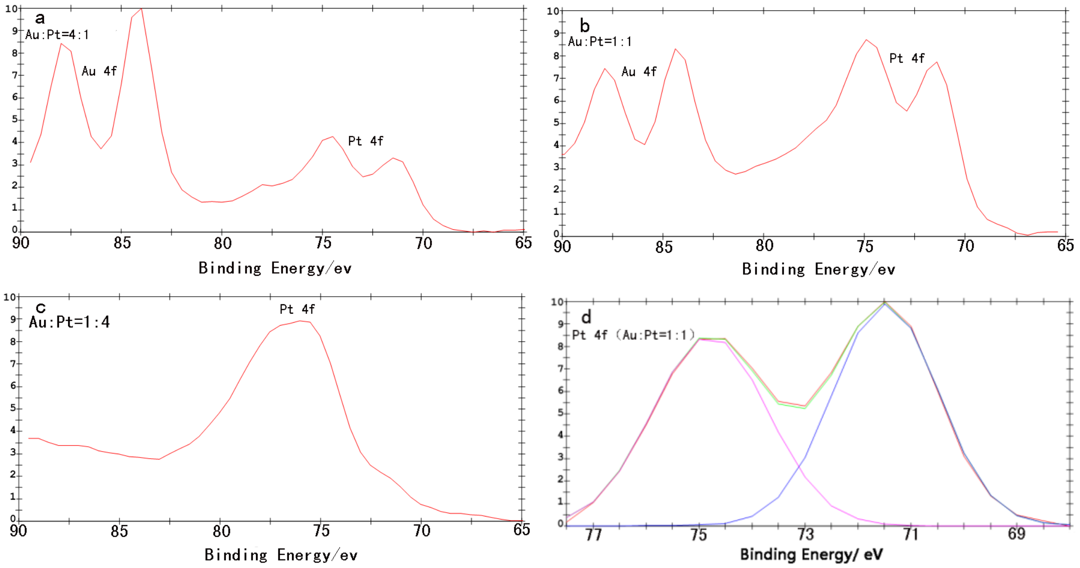

Figure 3. XPS spectra of Au 4f and Pt 4f of Au core@Pt shell nanoparticles： Au:Pt =4:1 (a), 1:1 (b), 1:4(c), Pt 4f of Au:Pt=1:1(d)

3.2. MOR activity of Au@Pt core-shell nanoparticle electrocatalyst

Figure 4a showed CVs of methanol catalytic oxidation at the condition of putting prepared Au@Pt/C electrode into basic solution at experiment temperature (30℃). Accordingly in the same figure, electro-catalytic features of methanol oxidation were given by using the electrode made by commercial catalyst 20% Pt/C (JM), whose data was recorded into Table 2. Based on the data analysis, it was showed that peak current density of Au@Pt/C in terms of the total amount of Pt and Au was apparently above that of Pt/C, however, Au had been widely considered to be no activity for MOR. The value was highest when Au:Pt=1:1, which was 304.8% higher than that of Pt/C and made catalytic effect of Pt increase by 709.7%. The electrochemical measurement results indicated that core-shell structure could not only improve the using efficiency of Pt but also dramatically promote the electro-catalytic activity of Pt shell from Au core, while the promotion might be derived from the Pt shell gaining d-electrons from the Au core, which might change d-electrons orbit cavity of Pt.

It must be noted that the peak current of Au@Pt/C (Au:Pt=1:1) changed respectively by 18.0% and 33.3% at 45 ℃ and 60 ℃ compared with 30 ℃, apparently lower than 76.8% and 117.1% of Pt/C, while other samples had the similar situations. This indicated that temperature had little effect on the electro-catalytic activity of Au@Pt core-shell nanoparticles. Figure 4b showed CVs of Au@Pt/C（Au:Pt=1:1）at different temperature.

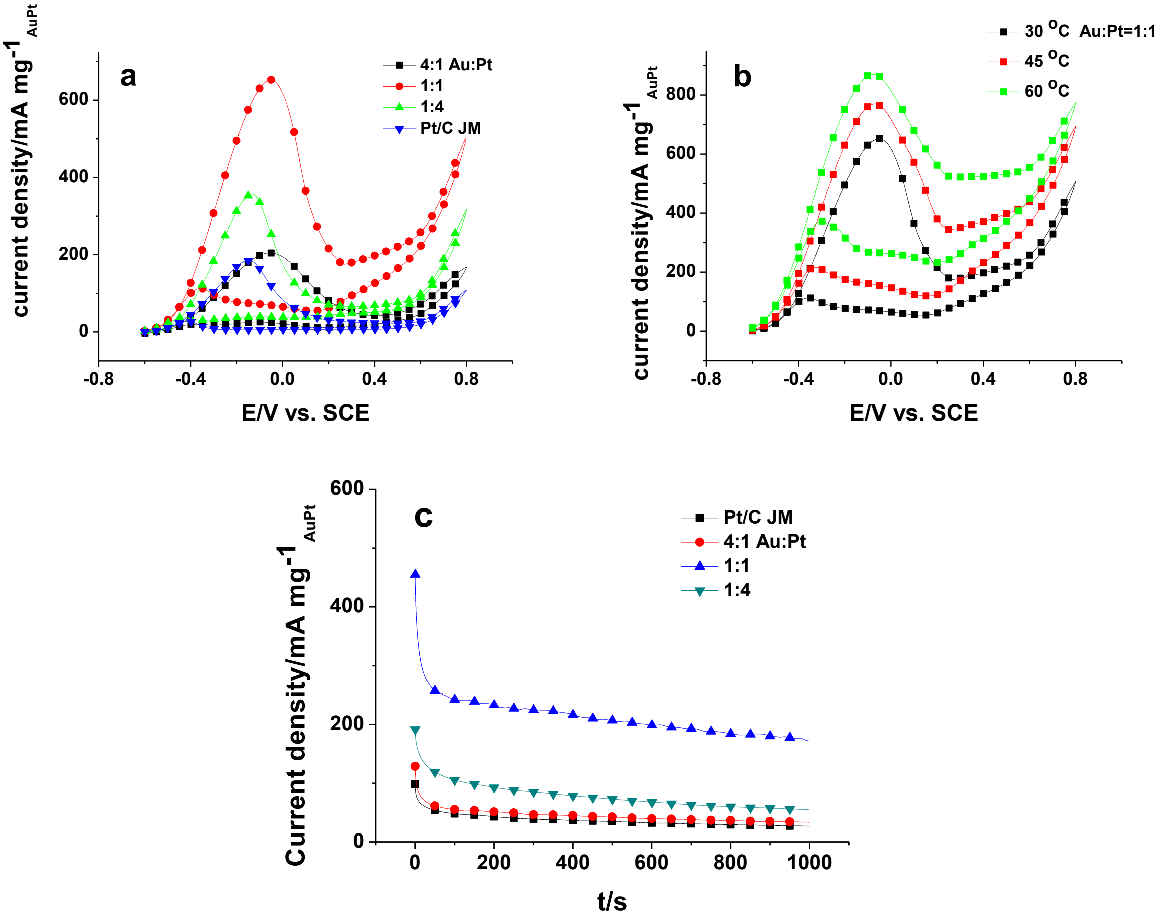

Figure 4. CV (a), (b) and I-t (c) of Au@Pt/C in 0.5 mol·L^{-1} KOH + 2.0 mol·L^{-1} CH$_3$OH solution

Table 2. Results of the electrochemical tests of Au@Pt/C and Pt/C

Test temperature	Peak current density of CV (Am·mg^{-1}AuPt)			
	Pt/C	Au@Pt/C (the molar ratio of Au to Pt)		
		4:1	1:1	1:4
30 ℃	161.2	204.5	652.5	357.5
45 ℃	285.0	204.7	770.0	605.0
60℃	350.0	225.5	870.0	740.0

Regarding I-t curves in figure 4c, the current values of Au@Pt/C electrode synthesized at different ratios of Au to Pt were all higher than that of Pt/C at constant potential, the order of whose activity was agreed with the results of CV curves in figure 4a. Accordingly, it was the optimum for synthesizing Au@Pt/C catalyst when Au:Pt=1:1, furthermore the catalytic current was stable as time changed.

4. CONCLUSIONS

In this experiment, Au@Pt composite nanoparticles were synthesized by Au seed growth method under ultraviolet radiation at 254 nm in PEG-acetone system. Through varying the molar ratio of Au seed to Pt(IV), the Pt shell thickness of composite particles could be efficiently adjusted, whose average diameter was in the range of 4.4-7.3 nm. The particles were proved to be core-shell structure by characterazation of UV-vis absorbed spectrum, TEM, HR-TEM and XPS, while it was found that the Pt shell gaining d-electrons from the Au core. The analysis of CV and I-t showed the synthesized Au@Pt core-shell nanoparticles had better activity and similar stability for methanol electro-catalytic oxidation compared with commercial Pt/C catalyst at the same loaded amount. The activity was the highest when Au:Pt=1:1, which was 304.8% higher than that of Pt/C. The result indicated that the Au@Pt core-shell nanoparticles synthesized from the experiment had potential application value in the area of anode catalyst for DMFC.

ACKNOWLEDGEMENTS
The authors are grateful for the support of the National Natural Science Foundation of China under grant nos. 51164017 and 20863003.

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