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Short Communication

Synthesis of Pt-Au/C Composite Catalysts with Different Au Compositions and Their Electrocatalytic Properties for Methanol Oxidation

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Carbon-supported Pt-Au/C composite nanoparticles (NPs) catalysts with different composition were synthesized by a two steps loading method including adsorption of Au colloid and reduction of H_2PtCl_6 precursor on carbon black. The effect of Au NPs composition on the electrocatalytic activity of Pt-Au/C composite catalysts was investigated by cyclic voltammetry in a 1 M H_2SO_4 and 1 M CH_3OH aqueous solution. 30Pt-10Au/C composite catalyst showed the highest mass-specific current density. The enhanced electrocatalytic activity of Pt-Au/C catalyst is due to high Pt utilization for methanol oxidation reaction and catalytic effect of Au NPs.

Keywords: platinum, gold, composite catalyst, DMFC, cyclic voltammetry

1. INTRODUCTION

The direct methanol fuel cell (DMFC) is a promising energy source for mobile and portable applications due to the advantages of methanol over hydrogen, such as its higher solubility in liquid electrolytes, availability at lower cost, easier handling, transfer and storage. In addition, methanol has a high energy density. However, DMFC electrocatalysts are based on Pt-group metals, and their high cost, poor activity and poisoning by CO-like intermediate species at anode still remain the drawbacks to the widespread use of these energy conversion system [1-5]. To overcome the CO poisoning problem at anode, Pt-Ru catalysts on carbon support have been developed for methanol oxidation reaction (MOR). The catalysts show a bi-functional catalytic mechanism in which Pt provides the main site for the dehydrogenation of methanol and Ru provides the sites for hydroxide (OH) and for oxidizing CO-like species to CO_2 [6-11].

It was well known that Gold nanoparticles show excellent catalytic activity for CO oxidation [12-14]. Therefore, an examination of nanoscale Pt-Au bimetallic materials might provide a solution for the CO poisoning problem at anode [15-19]. A recent study prepared Pt-Au nanoparticle (NPs) with core-shell like structure, and showed that the mass activity for methanol oxidation was approximately 1.5 times larger than that of the Pt catalyst due to the bi-functional catalytic effect [20]. On the other hand, Pt-Au alloy nanoparticles were synthesized to enhance the electrocatalytic activity. Xu et al. synthesized carbon-supported Pt-Au alloy NPs with different compositions, and reported that the catalyst with 47 at% Au exhibited 1.5 times higher peak power density in single cell test than that of conventional Pt/C catalyst [21]. Park et al. have reported that Au NPs improved the catalytic activity of Pt NPs on Pt-modified Au NPs (core-shell like structure) having lower Pt compositions than that of Pt [22]. To the best of our knowledge, simple mixed type of Pt and Au NPs loaded carbon black (Pt-Au/C) composite catalyst was very less reported and the loading composition of Pt and Au NPs depending upon total metallic catalyst loading was not be optimized.

In this present paper, simple mixed type of Pt-Au/C composite catalyst was synthesized by a two steps loading method including adsorption of Au colloid and reduction of H_2PtCl_6 precursor on carbon black, and the composition of Pt and Au NPs for Pt-Au/C composite catalysts with total metallic catalyst loading of 30 and 40 wt% was optimized. The electrocatalytic activity of the prepared Pt-Au/C composite catalysts was investigated by cyclic voltammetry and compared with that of carbon-supported Pt NPs.

2. EXPERIMENTAL

2.1. Synthesis of Au colloid

Au NPs with particle size of 5-8 nm were prepared by the chemical reduction of $HAuCl_4$ precursor. The synthesizing method was as follows. A 189 ml aqueous solution containing 0.25 mM $HAuCl_4 \cdot 4H_2O$ (SHOWA Chemicals Co.) and 5 ml of a 0.25 mM tri-sodium citrate (SHOWA Chemicals Co.) solution was prepared in a conical flask. Subsequently, 6 ml of a freshly prepared 0.1 M $NaBH_4$ (SHOWA Chemicals Co.) solution was added to the solution, and stirred for 5 min. The color of the solution changed immediately from yellow to red after adding the $NaBH_4$, indicating particle formation [23]. The appropriate amount of this Au colloid was used for preparing Pt-Au/C catalysts with different Au compositions.

2.2. Synthesis of Au/C composite powder

Au/C composite powder with various content of Au NPs were synthesized as follows; first, carbon black (Vulcan XC-72R, 0.03g) was added to 40 ml DI water, and then the suspension was added to an adequate amount of Au colloids. During the stirring period of 24 hours, Au NPs were spontaneously supported on the surface of the carbon black particle. After supporting Au NPs on the surface of the carbon black particles, the red color of the solvent changed to transparent. This implies that all of the Au NPs were completely adsorbed on carbon black. The aqueous Au/C composite NPs were filtered and dried at 70^{o}C to get powder state sample.

2.3. Synthesis of Pt-Au/C composite catalyst

Table 1. Added amounts of Pt precursor and Au colloid for preparing Pt/C and Pt-Au/C catalysts with different compositions.

Sample Name	Added amount of Au colloid (weight of Au NPs in colloid)	Added amount of H_2PtCl_6 solution (weight of Pt in Pt precursor)
30Pt/C	-	100 mL of 0.663 mM solution (0.013 g)
20Pt-10Au/C	100mL (0.005 g)	62 mL of 0.663 mM solution (0.008 g)
15Pt-15Au/C	130mL (0.0065 g)	50 mL of 0.663 mM solution (0.0065 g)
40Pt/C	-	100 mL of 1.025 mM solution (0.02 g)
30Pt-10Au/C	100 mL (0.005 g)	75.5 mL of 1.025 mM solution (0.015 g)
25Pt-15Au/C	150 mL (0.0075 g)	64 mL of 1.025 mM solution (0.0125 g)
20Pt-20Au/C	200 mL (0.01 g)	50 mL of 1.025 mM solution (0.01 g)

The added amount of carbon black in 40 mL DI water was 0.03 g for each sample.

Pt-Au/C composite catalysts were prepared from Au/C composite powder by reduction reaction of Pt precursor, $H_2PtCl_6 \cdot 5.8H_2O$ (Kojima Chemicals Co.) aqueous solution. Methanol was added as reducing agent. The mixed solution was boiled to boiling point for 15 min, and then cooled to room temperature. The aqueous Pt-Au/C composite NPs were filtered, and dried at 70^{o}C to obtain powder samples. Table 1 shows the volumes of Pt precursor and Au colloid solutions applied for synthesizing Pt-Au/C catalysts with different compositions. 30 wt% and 40 wt% loaded Pt/C (30Pt/C and 40Pt/C) catalysts were also prepared for comparison with Pt-Au/C catalysts in electrocatalytic activity. For 30Pt/C catalyst, 33.3 and 50 wt% of Pt NPs were replaced with Au NPs, respectively. On the other hand, for 40Pt/C catalyst, 25, 37.5 and 50 wt% of Pt NPs were replaced with Au NPs, respectively.

2.4. Physical characterization

The crystalline structure and size of the synthesized Pt-Au/C composite NPs catalysts were characterized by X-ray diffraction (XRD, RIGAKU, D-MAX 2500, Cu K_α= 1.5405 Å). The morphology of the Au and Pt NPs on the carbon black support was examined by transmission electron microscopy (TEM, JEOL, JEM-2010).

2.5. Electrochemical measurement

Cyclic voltammetry (CV) was performed in conventional three-electrode electrochemical cells at room temperature. The catalyst inks were prepared with 20 mg of 40Pt/C (or 30Pt-10Au/C) catalyst powder, 1ml of DI water, 50 μl of a 5 wt% Nafion solution and 1 ml of ethanol. The mixture was dispersed ultrasonically for 90 min. One drop (40 μl) of the ink was placed on a carbon electrode (6 mm in diameter) with a micropipette, and the electrode was then dried at 60°C for 10 min. A solution of 1M CH_3OH and 1M H_2SO_4 was prepared as the electrolyte and CV was conducted at potentials between - 0.02 V and 1.2 V with a 50 mVs^{-1} scan rate. The potentials were given with respect to the reference electrode (Ag/AgCl saturated NaCl). The CV curves were generally obtained after 50 cycle scans for stable current-potential behavior.

3. RESULTS AND DISCUSSION

3.1. Characterization of synthesized catalysts

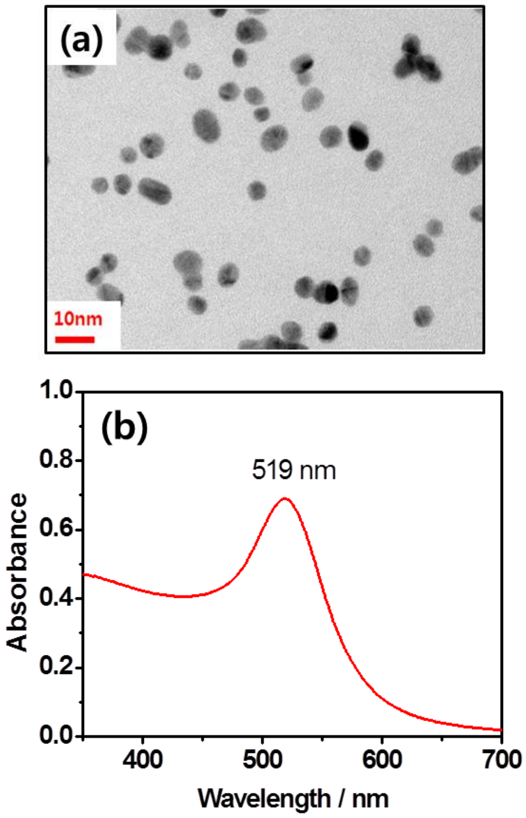


Figure 1. (a) TEM image and (b) UV-visible spectrum of Au colloid.

Au colloid was synthesized by chemical method for loading on carbon black before preparing Pt-Au composite NPs. The TEM image and UV-visible spectrum of the synthesized Au colloid was shown in Fig. 1. The TEM image reveals the formation of well dispersed uniform spherical Au NPs with particle size of 5-8 nm. The UV-visible spectrum shows a sharp surface plasmon resonance peak of Au NPs at 519 nm, and it indicates also that the Au colloid is very uniform and well dispersed [20, 23]. For preparing Au/C composite powder, the suspension of carbon black was added to the Au colloids. During the stirring for 24 hours, all of Au NPs in the colloid was spontaneously supported on the surface of the carbon black particle. After that, Pt NPs was loaded on Au/C composite powder through reduction of Pt ions from H_2PtCl_6 aqueous solution.

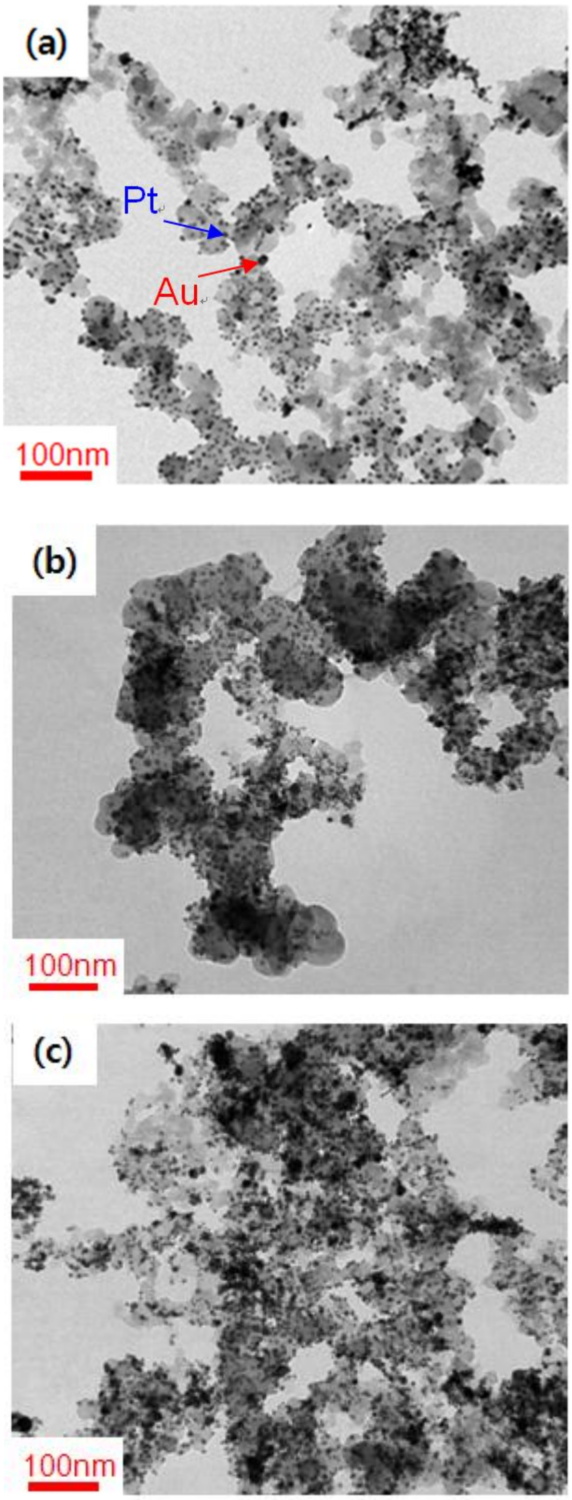


Figure 2. TEM images of Pt-Au/C composite catalysts with different compositions: (a) 30Pt-10Au/C, (b) 25Pt-15Au/C, and (c) 20Pt-20Au/C.

The morphological and structural properties of synthesized Pt-Au/C composite NPs catalysts with different compositions were examined. Fig. 2 shows TEM images of Pt-Au/C catalysts with different compositions. Fig. 2 (a) shows a TEM image of 30Pt-10Au/C composite catalyst. The particle size of Pt loaded on carbon black is 3-4 nm, and the Pt NPs (smaller black particles) are quite uniform. The particle size of Au is 5-8 nm, and Au NPs (bigger black particles) are well dispersed on carbon black. Fig. 2 (b) and (c) show TEM images of 25Pt-15Au/C and 20Pt-20Au/C catalysts, respectively. From these TEM images, it is found that the number of Au NPs increase as the composition of Au in Pt-Au/C catalyst increases, and Pt and Au NPs are deposited independently on the surface of carbon black in every sample.

The X-ray diffraction patterns of various compositions of 40Pt/C and Pt-Au/C composite NPs catalysts with different compositions of Au NPs are presented in Fig. 3. The peak intensity of Au NPs (111) plane increased sharply as the composition of Au NPs became larger, while the peak intensity of Pt NPs decreased.

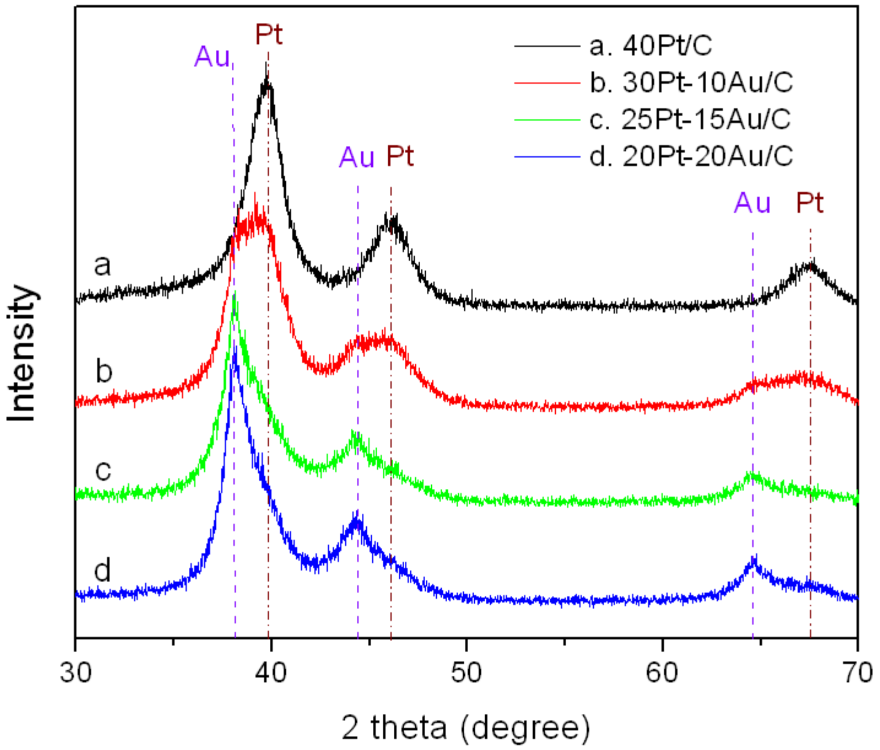


Figure 3. XRD patterns of Pt-Au/C composite catalysts with different compositions: (a) 30Pt-10Au/C, (b) 25Pt-15Au/C, and (c) 20Pt-20Au/C.

3.2. Catalytic activity of methanol oxidation reaction

Cyclic voltammetry (CV) was performed to evaluate the activity of Pt-Au/C composite NPs catalysts with different compositions. Fig. 4 shows cyclic voltammograms of the 30Pt/C, 20Pt-10Au/C and 15Pt-15Au/C composite catalysts. The mass-specific peak current density of 30Pt/C catalyst is 195 A/g. On the other hand, the mass-specific peak current densities of 20Pt-10Au/C and 15Pt-15Au/C catalysts show 211.3 and 138.8 A/g, respectively. The mass-specific peak current density of 20Pt-10Au/C is similar to that of 30Pt/C.

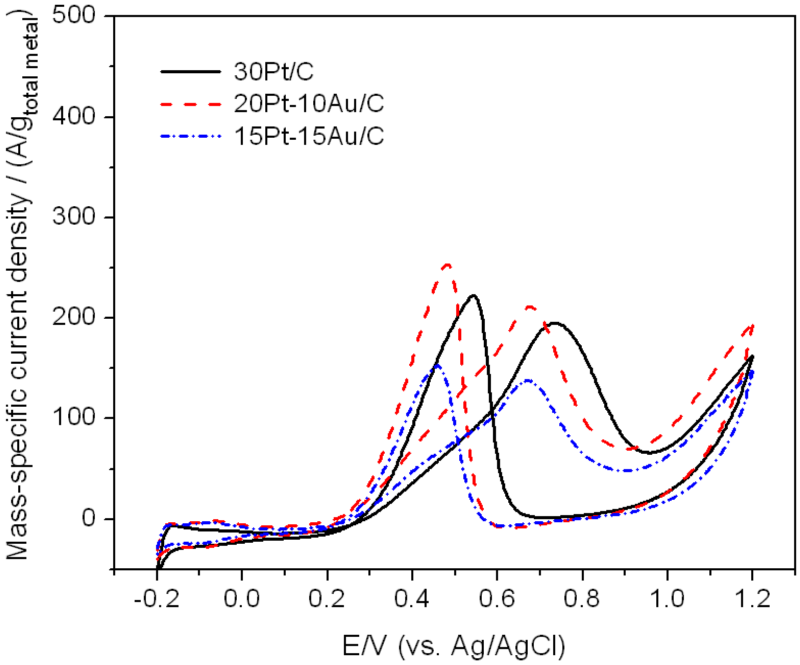
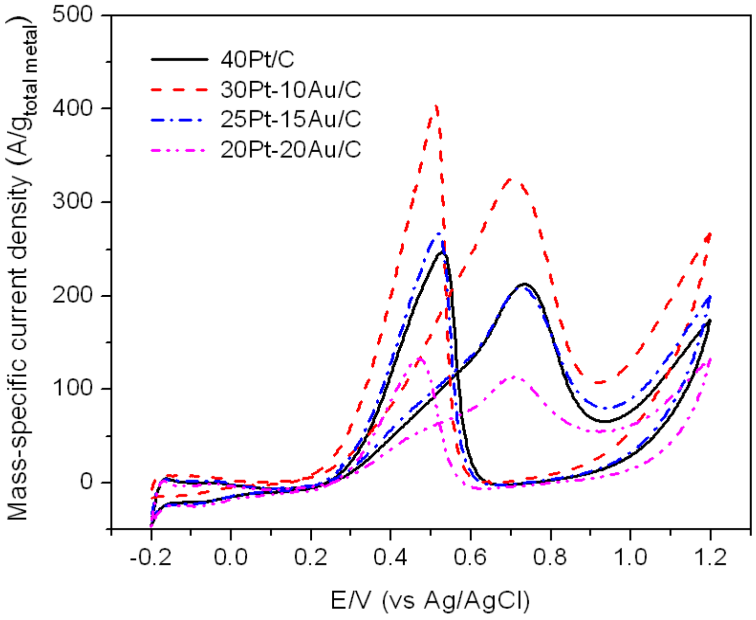
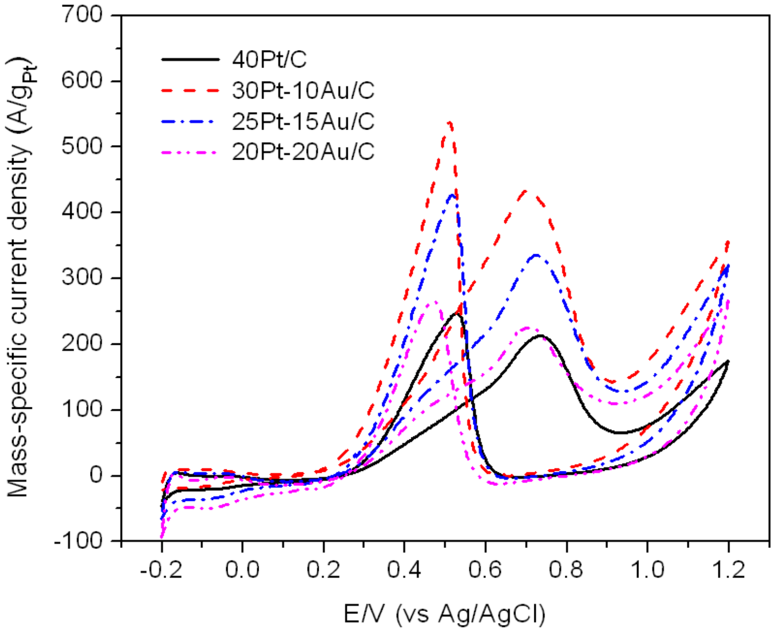


Figure 4. Cyclic voltammograms of the 30Pt/C and Pt-Au/C composite catalysts with different compositions (Scan rate: 50mVs^{-1}, electrolyte: 1M H_2SO_4 and 1M CH_3OH).

Fig. 5 (a) shows the cyclic voltammograms of 40Pt/C, 30Pt-10Au/C, 25Pt-15Au/C and 20Pt-20Au/C composite catalysts on the base of total metallic catalyst loading. The mass-specific peak current density of 40Pt/C catalyst is 212.8 A/g, while the mass-specific peak current densities of 30Pt-10Au/C, 25Pt-15Au/C and 20Pt-20Au/C catalysts show 325.1, 209.3 and 113.8 A/g respectively. The highest mass-specific peak current density showed at 30Pt-10Au/C, and the current density of 25Pt-15Au/C is almost the same as that of 40Pt/C. Fig. 5 (b) shows Pt-specific current density vs potential plot for Fig. 5 (a).



(a)



(b)

Figure 5. Cyclic voltammograms of 40Pt/C and Pt-Au/C composite catalysts with different compositions (Scan rate: 50mVs^{-1}, electrolyte: 1M H_2SO_4 and 1M CH_3OH): (a) total metal-specific current density vs potential plot, and (b) Pt-specific current density vs potential plot.

In Pt-specific current density, the Pt-Au/C catalyst shows, on the whole, a greater increase than 40Pt/C. The 30Pt-10Au/C catalyst shows about 2 times higher peak current density than 40Pt/C catalyst. This result indicates that Au NPs can improve the catalytic activity of Pt NPs for methanol oxidation by the oxidation of CO-like species into CO_2 on the basis of bi-functional catalytic mechanism [24, 25]. The enhanced electrocatalytic activities of Pt-Au/C catalyst might be due to the catalytic effect of Au NPs and the high Pt utilization for methanol oxidation reaction [22].

4. CONCLUSION

Pt-Au/C composite NPs catalysts with different compositions, of which the total metallic catalyst loading is 30 and 40 wt%, were synthesized by the two step loading method including adsorption of Au colloid and reduction of H_2PtCl_6 precursor on carbon black. The Pt NPs were replaced with Au NPs until the loading of Au NPs became 50 wt% for both the different metallic catalyst loading samples. For 30 wt% total metallic catalyst loading samples, 20Pt-10Au/C composite catalyst showed the highest mass-specific current density. On the other hand, for 40 wt% total metallic catalyst loading samples, 30Pt-10Au/C composite catalyst showed the highest mass-specific current density. The mass-specific current density of 25Pt-15Au/C catalyst was similar to that of 40Pt/C. This result indicates that Au NPs can improve the catalytic activity of Pt NPs for methanol oxidation, and the enhanced electrocatalytic activities of Pt-Au/C catalyst might be due to the catalytic effect of Au NPs and the high Pt utilization for methanol oxidation reaction.

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References

1. E. A. Franceschini, M. M. Bruno, F. A. Viva, F. J. Williams, M. Jobbagy and H. R. Corti, *Electrochim. Acta* 71 (2012) 173
2. M. Zhiani, B. Rezaei and J. Jalili, *Int. J. Hydrogen Energy* 35 (2010) 9298
3. Y. Huang, T. Wang, M. Ji, J. Yang, C. Zhu and D. Sun, *Mater. Lett*. 128 (2014) 93
4. T. R. Ralph and M. P. Hogarth, *Platinum Metals Rev*. 46 (2002) 117
5. W. Chen, G. Sun and Z. Liang , *J. Power Source* 160 (2006) 933
6. O. Sahin and H. Kivrak, *Int. J. Hydrogen Energy* 38 (2013) 901
7. O. Guillen-Villafuerte, R. Guil-Lopez, E. Nieto, G. Garcia, J. L. Rodriguez, E. Pastor and J. L. G. Fierro, *Int. J. Hydrogen Energy* 37 (2012) 7171
8. K. Yao, Y. Chen, C. Chao, W. Wang, S. Lien, H. Shih, T. Chen and Ko. Weng, *Thin Solid Films* 518 (2010) 7225
9. P. L. Antonucci, A. S. Arico and P. Creti, *Sol. Stat. Ionics* 125 (1999) 431
10. C. He, H. R. Kunz and J. M. Fenton, *J. Electrochem. Soc*. 150 (2003) A1017
11. W. Xu, T. Lu and C. Liu, *J. Phys. Chem*. 109 (2005) 14325
12. M. Haruta, *Catal. Today* 52 (1997) 153
13. M. Haruta and M. Date, *Appl. Catal*. A 222 (2001) 427
14. M. Valden, X. Lai and D.W. Goodman, *Science* 281 (1998) 1647
15. D. Cameron, R. Holliday and D. Thompson, *J. Power Sources* 118 (2003) 298
16. E. E. Switzwe, A. K. Datye and P. Atanassov, *Top. Catal*. 46 (2007) 334
17. C. Coutanceau, A. F. Rakotondrainibe and A. Lima, *J. Appl. Electrochem*. 34 (2004) 61
18. Z. He, J. Chen and D. Liu, *Diamond Relat. Mater*. 13 (2004) 1764
19. K. S. Lee, I. S. Park and H. Y. Park, *J. Electrochem. Soc*. 156 (2009) B1150
20. N. Kristian and X.Wang, *Electrochem. Comm*. 10 (2008) 21
21. J. B. Xu, T. S. Zhao, W. W. Yang and S. Y. Shen, *Int. J. Hydrogen Energy* 35 (2010) 8699
22. I. S. Park, K. S. Lee, J. H. Choi, H. Y. Park and Y. E. Sung, *J. Phys. Chem*. C 111 (2007) 19126
23. N. R. Jana, L. Gearheart and C. J. Murphy, *Langmuir* 17 (2001) 6782
24. A. K. Tripathi, V. S. Kamble and N. M. Gupta, *J. Catal.* 187 (1999) 332
25. H. Liu, A. I. Kozlov and A. P. Kozlova, *J. Catal.* 185 (1999) 252