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# Methanol electro-oxidation on carbon-supported and Pt-modified Au nanoparticles

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## Abstract

Methanol electro-oxidation on Pt-modified Au nanoparticles was studied in aqueous 0.5 M $H_2SO_4$/1 M $CH_3OH$. The Pt-modified Au nanoparticles showed lower values than pure Pt nanoparticles in area-specific current densities. The activity also decreased with lower amounts of Pt on the Pt-modified Au nanoparticles. This result indicates that the intrinsic activities of the Pt-modified Au nanoparticles were lower than that of Pt/C. This phenomenon may be due to the strengthened Pt–CO bonding or the weakened ensemble effect in the methanol electro-oxidation. However, in the Pt-specific current densities, the Pt-modified Au nanoparticles showed higher values than pure Pt nanoparticles. This enhanced electrocatalytic activity could be attributed to more reaction-favorable surface structures of Pt-modified Au nanoparticles, which most likely lead a high level of Pt utilization for the electro-oxidation reaction.

*Keywords:* Direct methanol fuel cell; Successive chemical reduction process; Pt-modified Au nanoparticles; Methanol electro-oxidation

## 1. Introduction

Methanol electro-oxidation has been an important topic because of its role in direct methanol fuel cells (DMFCs). There are certain advantages to be found in the use of methanol as fuel, namely its high energy density and its liquid state at room temperature [1–3].

Research so far indicates that methanol electro-oxidation is dependent on the surface geometry of Pt electrocatalysts, and the oxidation of reactive intermediate CO to $CO_2$ has been identified as the rate-determining step (rds) during the decomposition of methanol [4,5]. The adsorption of methanol on Pt initiates at a potential as low as 0.2 V with the standard hydrogen electrode (SHE), and a strongly adsorbed intermediate blocks the surface from further methanol adsorption. Binary Pt-based electrocatalysts with a second metal have been discovered to circumvent this problem. The requirements for the second metal are as follows: it must have a greater ability to form surface oxygen species compared to Pt (the bi-functional effect) [6] and must have a lower d-band electron density than Pt (the ligand effect) [7]. An additional useful feature of the second metal would be an ability to suppress the formation of poisonous species adsorbed on more than one surface active site (the ensemble effect) [8].

Nowadays, Pt-modified Au electrodes have been attracting much attention due to their high activity and stability in methanol electro-oxidation [9–13]. Zeng et al. reported that the CO-stripping peak of core–shell Au–Pt nanoparticles was found at a potential more negative than that of pure Pt nanoparticles. It indicates that the interface between the Pt shell and the Au core was effective for the removal of CO adsorbed on Pt. In the area-normalized current densities, the core–shell Au–Pt nanoparticles showed a higher value than pure Pt nanoparticles [9]. In a report by Du et al., spontaneously deposited Pt on an Au substrate showed that the CO peak positions at potentials more positive than that of Pt surface alone; furthermore, the peak positions were dependent on the level of Pt coverage on the Au substrate. The Pt–CO bond was also found to be stronger on the Pt deposited on Au compared to that on pure Pt surface. They also explained that Pt-covered Au surfaces were inactive for methanol electro-oxidation at low Pt coverage. This result could be a direct experimental evidence for the ensemble effect of Pt on methanol electro-oxidation [10]. Clearly, a more thorough investigation of the enhancement effect of Au on the intrinsic activity of methanol electro-oxidation is necessary.

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In this work, Pt-modified Au nanoparticles were used as electrocatalysts for methanol electro-oxidation. The surface structures and electrocatalytic activities of these nanoparticles were investigated and compared with those of carbon-supported Pt nanoparticles.

## 2. Experimental

### 2.1. Preparation of Pt-modified Au nanoparticles

All aqueous solutions were prepared with deionized (DI) water further purified with a Mili-Q system (Millipore water, 18.2 MΩ cm). The following chemicals were obtained from Aldrich: $HAuCl_4 \cdot 3H_2O$, $H_2PtCl_6 \cdot xH_2O$, sodium citrate tribasic dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), $NaBH_4$ and L-ascorbic acid ($C_6H_8O_6$). All chemicals were of analytical grade and were used as received.

The procedural details for preparing the carbon-supported Au and Pt-modified Au nanoparticles were presented in our previous reports [13,14]. The carbon-supported 30 wt.% Au nanoparticles (Au/C) were prepared as follows: first, Au colloid nanoparticles were prepared by stirring $HAuCl_4 \cdot 3H_2O$ into 800 ml of DI water, followed by the addition of aqueous sodium citrate 1 min later. After one additional minute, $NaBH_4$/sodium citrate solution was added quickly with vigorous stirring [15]. The solution was stirred for 30 min, and then carbon black (Vulcan XC-72R) was added. During the 48 h stirring period, gold colloid particles were supported spontaneously on the carbon particles. After supporting Au nanoparticles on the carbon particles, the solution lost its color and turned clear. The resultant solution was then purified by precipitation and decantation.

The Pt-modified Au nanoparticles (Pt–Au/C) were prepared using a successive chemical reduction process whose procedures were as follows: first, a solution of a Pt precursor was added to 400 ml of the Au/C dispersed solutions. Next, a solution of ascorbic acid was added [16,17]. After stirring for 20 h, the resultant solution was filtered, washed and dried in a vacuum oven at 70 °C. Two types of Pt-modified Au nanoparticles with different amounts of Pt were prepared and designated SN[0.25] and SN[0.75], as shown in Table 1. The characteristics of all the prepared nanoparticles were also compared with those of the carbon-supported 40 wt.% Pt nanoparticles (Johnson-Matthey, Pt/C in Table 1).

### 2.2. Characterization

High-resolution transmission electron micrographs (HR-TEM) were obtained on a JEOL 2010 operated at 200 kV. The samples were prepared by dispersing a small amount of the nanoparticles (in powder form) in ethanol by ultrasonic treatment. Then, a drop of the dispersion was taken by a pipette and put on a carbon-coated copper grid and dried in air at 70 °C.

Cyclic voltammogram was obtained in a conventional three-electrode electrochemical cell using a glassy carbon electrode (6 mm diameter) as a working electrode, Pt wire as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode [18–25]. Electrochemical measurements were all recorded and reported with a normal hydrogen electrode (NHE). The glassy carbon (GC) electrode was polished with 1, 0.3, 0.05 μm $Al_2O_3$ slurry and washed ultrasonically with DI water before use. The ink slurry was prepared by mixing carbon-supported nanoparticles, DI water, a 5 wt.% Nafion® solution (Aldrich Chem. Co) as a binding material, and 2-propanol. Two hundred microlitres of DI water, 572 μl of Nafion® solution, and 8 ml of 2-propanol per 0.1 g of electrocatalysts were mixed and then stirred until ink slurry was homogeneous. A constant amount of ink slurry was dropped on the GC electrode with a micropipette, and the GC electrode was then dried in a vacuum oven. Electrochemical experiments were performed with an Autolab general purpose electrochemical system (Eco Chemie).

The experimental procedure for electrochemical reactions was as follows: a 0.5 M $H_2SO_4$ solution was purged with nitrogen gas for 30 min prior to electrochemical measurements. Subsequently, five consecutive scans were performed in the potential range of 0.05–1.2 V versus NHE with a scan rate of 20 mV $s^{-1}$. For the measurement of methanol electro-oxidation, a solution of 0.5 M $H_2SO_4$/1 M $CH_3OH$ was purged with nitrogen gas prior to measuring. Cyclic voltammetry was conducted in the potential between 0.05 and 1.2 V versus NHE at a scan rate of 20 mV $s^{-1}$.

## 3. Results and discussion

### 3.1. Preparation of Pt-modified Au nanoparticles

Pt-modified Au nanoparticles prepared as described were characterized by HR-TEM. The images of SN[0.75] electrocatalyst are shown in Fig. 1a and b. The images show the spherical and uniform nanoparticles (~5 nm in diameter) to be highly dispersed on the carbon particles. This is consistent with nature of the Au nanoparticles which are also uniform (~4 nm in diameter) and highly dispersed [13,14].

In our previous work, the experimental diameters of the Pt-modified Au nanoparticles corresponded closely to the theoretically calculated ones, and the exposed Au surface area decreased as the amount of Pt increased [13]. For the

Table 1
Description of Pt–Au/C and Pt/C electrocatalysts

| Sample | Description | Assumed Pt:Au atomic ratio | Metal loading (wt.%) |
|---|---|---|---|
| 3N[0.25] | Pt-modified Au nanoparticles (Pt–Au/C) | 0.25:1.0 | 34.82 |
| SN[0.7S] | Pt-modified Au nanoparticles (Pt–Au/C) | 0.75:1.0 | 42.76 |
| Pt/C | 40 wt.% Pt | | 40 |

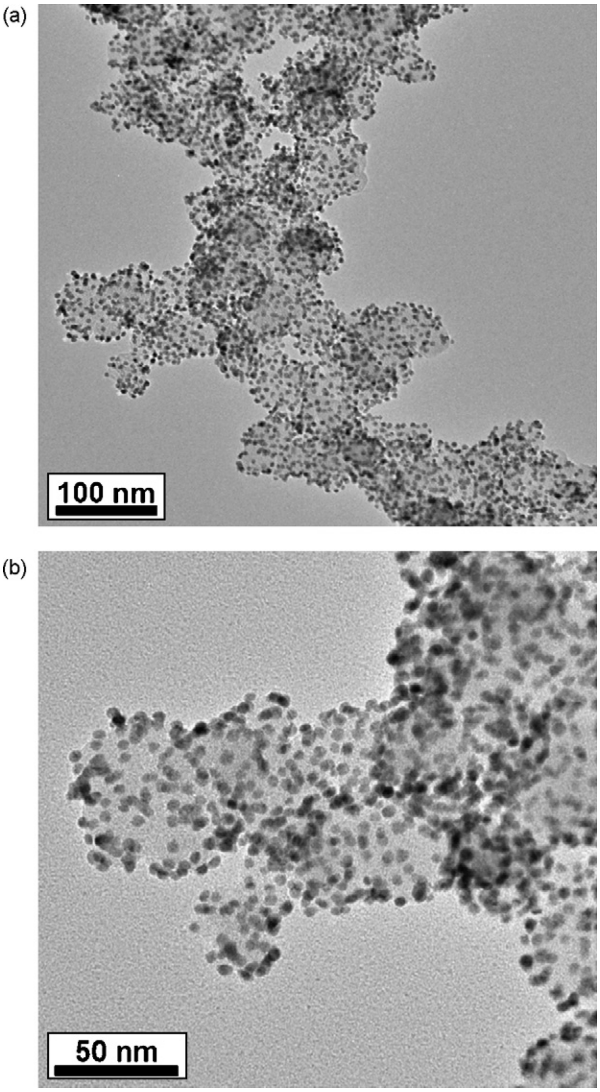

Fig. 1. HR-TEM images of Pt-modified Au nanoparticles: (a) TEM image and (b) magnified image of SN[0.75] electrocatalyst.

identification of deposited Pt on the Au surface, core–shell Au–Pt nanoparticles (~20 nm in diameter) were also prepared using an ascorbic acid reduction method. HR-TEM analysis showed clearly that the shell of these nanoparticles consisted of a 2D-structured Pt [14]. Therefore, in the Pt-modified Au nanoparticles, it could be concluded that the Pt selectively deposited on the Au surface of the carbon-supported Au nanoparticles and might exist as a 2D atomic structure with a high degree of roughness.

Surface characteristics of nanoparticles are very important because the surface structure has a great effect on the catalytic reactions. Fig. 2 shows the cyclic voltammogram in 0.5 M $H_2SO_4$ solution at room temperature. The currents were normalized by the corresponding active areas. From the CO-stripping analysis, the metal-specific areas of SN[0.25], SN[0.75], and Pt/C were 321.2, 317.8, and 327.5 $cm^2 mg^{-1}$, respectively [14]. The Pt-modified Au nanoparticles and Pt nanoparticles show well-defined profiles in the hydrogen and oxygen adsorption–desorption regions. In the oxygen reduction region, the reduction peak potentials of SN[0.25], SN[0.75], and Pt/C were 0.73, 0.74, and 0.75, respectively. This result demonstrates that oxygen containing species bind more strongly to the Pt on the Pt-modified Au nanoparticles than to the Pt on the pure Pt nanoparticles. The bonding on the Pt-modified Au nanoparticles becomes stronger as the amount of Pt decreases [10,26]. In our previous study, all CO oxidation

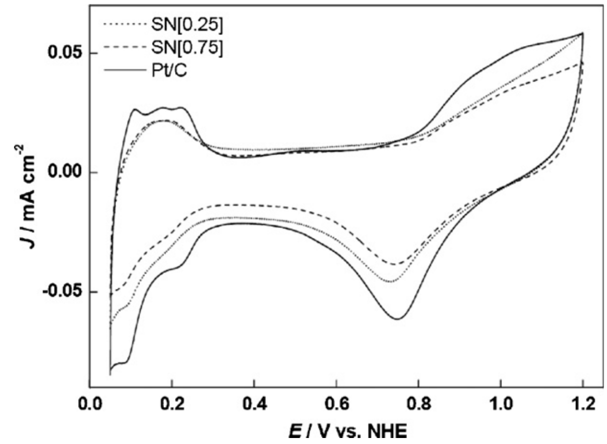

Fig. 2. Cyclic voltammogram of the Pt–Au/C and Pt/C electrocatalysts. Current densities vs. potentials were measured in 0.5 M $H_2SO_4$ solution at room temperature.

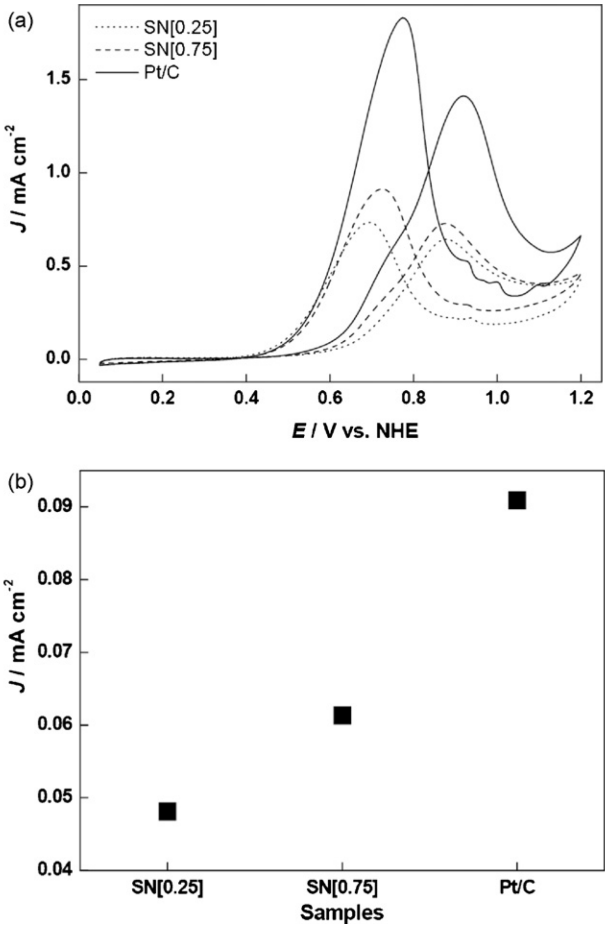

Fig. 3. Cyclic voltammetric analysis of Pt–Au/C and Pt/C electrocatalysts for methanol electro-oxidation: (a) area-specific current densities and (b) area-specific current densities at 0.6 V vs. NHE.

Table 2
Electrocatalytic activities of Pt–Au/C and Pt/C electrocatalysts

| Sample | Area-specific current density (J/mA $cm^2$ at 0.6 V vs. NHE) | Metal-specific current density (J/A $g_{metal}^{-1}$ at 0.6 V vs. NHE) | Pt-specific current density (J/A $g_{Pt}^{-1}$ at 0.6 V vs. NHE) |
|---|---|---|---|
| SN[0.25] | 0.0481 | 15.26 | 78.09 |
| SN[0.75] | 0.0613 | 17.52 | 41.18 |
| Pt/C | 0.0909 | 29.97 | 29.97 |

peaks ($E_{CO}$) of Pt-modified Au nanoparticles appeared in the more positive potential region than that of Pt/C. This also indicates that the Pt-modified Au nanoparticles show more enhanced Pt–CO bonding than pure Pt nanoparticles [10,27]. This enhanced binding is most likely due to the effects of Au nanoparticle, since the CO oxidation peak positions were dependent on the Pt coverage.

### 3.2. Electrocatalytic activities of Pt-modified Au nanoparticles for methanol electro-oxidation

The electrocatalytic activities of Pt-modified Au nanoparticles were measured by cyclic voltammetry in 0.5 M $H_2SO_4$/1 M $CH_3OH$ solution. The reported current was normalized by the corresponding active areas. As shown in Fig. 3a, the Pt-modified Au nanoparticles show a similar voltammogram to that of Pt/C. Fig. 3b shows the area-specific current densities at 0.6 V, which are also listed in Table 2. The Pt-modified Au nanoparticles showed lower current densities than Pt/C, indicating lower intrinsic electrochemical activities than Pt/C. This result is likely due to the strengthened Pt–CO bonding or the weakened ensemble effect.

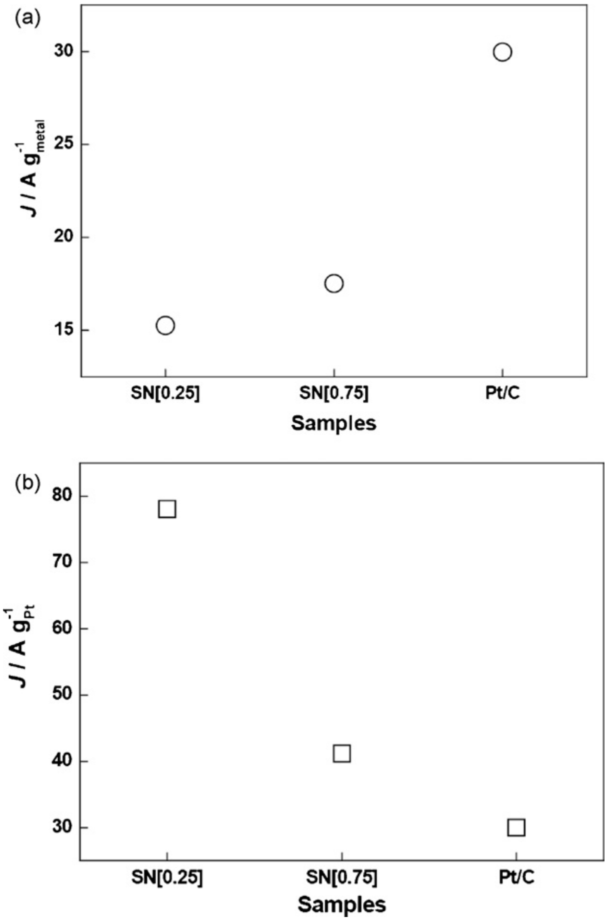

Fig. 4. Mass-specific current densities: (a) metal-specific current densities (A $g_{metal}^{-1}$) at 0.6 V vs. NHE and (b) Pt-specific current densities (A $g_{metal}^{-1}$) at 0.6 V vs. NHE. Current densities vs. potential plots were measured in 0.5 M $H_2SO_4$/1 M $CH_3OH$ solution at room temperature.

The Pt-modified Au nanoparticles have efficient structures for the surface reaction. A comparison of the mass-specific current densities is required to confirm the contribution of these efficient structures in the activities of methanol electro-oxidation. The mass-specific current density is dependent on the intrinsic activity of the active site and the dispersion of active elements. In our previous work, the $S_M$ (metal-specific area) values of Pt-modified Au nanoparticles were similar to that of Pt/C, while their $S_P$ (Pt-specific area) values increased rapidly as the amount of deposited Pt decreased [14]. Fig. 4a and b shows the metal- and Pt-specific current densities of the Pt-modified Au nanoparticles and Pt/C, respectively (also listed in Table 2). Fig. 4a shows the lower current densities of the Pt-modified Au nanoparticles compared to Pt/C. This is most likely due to the low intrinsic activities of the Pt-modified Au nanoparticles, since their metal-specific areas were similar to that of Pt/C. Fig. 4b shows greater increases in the Pt-specific current densities in the Pt-modified Au nanoparticles than in Pt/C. A possible explanation for this phenomenon is that there is a higher level of Pt utilization for the methanol electro-oxidation reaction on the Pt-modified Au nanoparticles.

## 4. Conclusion

Pt-modified Au nanoparticles were prepared by a successive chemical reduction process. The spherical and uniform Pt-modified Au nanoparticles (<5 nm in diameter) were highly dispersed on the carbon particles. In methanol electro-oxidation, the Pt-modified Au nanoparticles showed lower intrinsic electrocatalytic activities than the pure Pt nanoparticles. Those intrinsic activities also decreased with lower amounts of deposited Pt. This result may be due to the strengthened Pt–CO bonding or the weakened ensemble effect in the methanol electro-oxidation. However, improved Pt-specific current densities were obtained in the Pt-modified Au nanoparticles compared to pure Pt nanoparticles. These increased electrocatalytic activities might be attributed to the more reaction-effective surface structures of Pt-modified Au nanoparticles, possibly leading to a higher Pt utilization for methanol electro-oxidation reaction. The newly developed Pt-modified Au nanoparticles may serve as efficient electrocatalysts for oxygen reduction in DMFC because of their high tolerance for methanol electro-oxidation. Further investigation into the properties of the Pt-modified Au nanoparticles is well warranted by this study.

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